CRANFIELD UNIVERSITY

KALU SAMUEL UKANWA

APPROACHES TO MAXIMISE THE UTILISATION OF RESIDUES FROM THERMAL CONVERSION OF OIL PALM WASTE

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Energy and Power

DOCTOR OF PHILOSOPHY
(PhD)

Academic Year: 2017 - 2020

Supervisor: Dr Kumar Patchigolla
Associate Supervisor: Dr Ruben Sakrabani

December 2020

CRANFIELD UNIVERSITY

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Energy and Power

DOCTOR OF PHILOSOPHY
(PhD)

Academic Year 2017 - 2020

KALU SAMUEL UKANWA

Approaches to maximise the utilisation of residues from thermal conversion of oil palm waste

Supervisor: Dr Kumar Patchigolla
Associate Supervisor: Dr Ruben Sakrabani
December 2020

This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

ABSTRACT

Palm oil processing generates enormous volume of waste, which can be used as a feedstock in thermal processing. Subsequently, these can be valuable in the production of activated carbon (AC) and soil amelioration. The production of AC often results in secondary contamination through activating agents. This prompts the necessity for a non-toxic activating agent for high quality production of high adsorptive AC. Therefore this research aims to assess and determine the optimum route for efficient utilisation of biowaste from thermal conversion process of palm oil residues in producing activated carbon and soil amelioration by evaluating the impact of the selected utilisation techniques.

In the production process, energy demand and process duration have influence on the efficiency of AC; therefore, an appropriate design configurations and parameter selection are required to achieve an anticipated yield. AC was produced by microwave and conventional techniques through pyrolysis. The feedstock was also used in combustion and the thermal residues were applied in agricultural soil and crop yield relative to application rate was assessed on Habanero chili pepper. Therefore, the requisite to quantify the processes, which include appropriate assessment of the technology and economic performance. The accomplishment of the project overall aim was dependent on the design of a microwave system for efficient biomass pyrolysis. The process also evaluated the microwave interaction with reactors implemented to produce AC from mixed oil palm waste, using Trona ore as an activating agent. The AC was analysed to determine the effectiveness of Trona ore for activation using Fourier infrared spectrometry, Brunauer-Emmett-Teller (BET) analyser and scanning electron microscope. The oil palm waste ash was applied to the soil. The optimum outcome of the microwave assisted technique for combine palm waste (CPW) was obtained at 600 W, BET surface area (S_{BET}) is 980 m^2/g compared to 920 m^2/g from a conventional technique; total volume (V_{total}) 0.865 cm^3/g; mean pore diameter 2.2 nm and AC yield is 42%. Therefore, this study additionally identifies the need for an even distribution of electromagnetic waves within the reactor during activation to ensure uniformity of AC. It also proposes that the design of a composite reactor for an industrial production of AC is necessary to enable heterogeneous waste stream of the process. For ash application, the physiological development and crop yield were measured. The combine maximum yield for both sites were 49 t/ha/first season and 71.8 t/ha/second season, occurred at 8 t/ha treatment plot against the control plot with 1.3 t/ha/first season and 0.7 t/ha/second season. The interaction between oil palm waste ash and soil, improved agronomic efficiency of Habanero chilli pepper by 66-69% and Scoville value by 3.52%. These utilisation routes (AC production and ash to soil) were further integrated for economic and technological benefits using Aspen plus Economy. The processes have 16-17% return on investment for the 8-9 year payback period. This study therefore concluded that thermal residues of oil palm waste are useful in the production of high quality AC and also has rich effect on agricultural soil.

Keywords:

Activated carbon, adsorption, porous material, kinetic model, economic assessment, soil amelioration

ACKNOWLEDGEMENTS

Throughout the period of this research, many people provided help and I can never thank everyone by name. My supervisors, Doctors Kumar Patchigolla and Ruben Sakrabani; were great source of inspiration and guidance. They supported this study, coached me passionately to achieve this academic dream and also encouraged me during my emotional crisis. Their scientific experiences were shared, which gave meaning to my research approach. I thank Professor Bernard Anthony for his assistance. My review panel brought the best out of me, Professors Phil Longhurst, Ewan McAdam and Fiona Charnley. I appreciate the effort of my senior colleagues who were always challenging and discussing my work, Drs Jonathon Gillard, Hisham, Adeola, Reward, Igwemezie and many others. I doubt, if I could go this far without the daily support of my lovely wife Anurika and gorgeous daughter Chiziterem Mary Ukanwa, her constant play made the study period fun. They saw me through good and bad times especially during the COVID-19 crisis that forced me to work from home.

A reserved honour to my late father, Sir Ukanwa Kalu, who laid the foundation; unfortunately, could not live to see me become a doctor and greatest thanks is to my family members: my mother, Mary Ukanwa; sisters, Ngozi and Onyinyechi; brother, Pharmacist Igwe; uncles, Engineer Ogbaegbe Kalu and Monsieur Martin Uko. Truly, they have been my strength, never frown at my absence from home, always been there for me, praying and wishing me success.

I would want to extend my gratitude to the head of department Agricultural and Bioresources Engineering of FUTO for the provision of experimental site and facilities. Professors Chinweze, Egwuonwu, Okereke, Asoegwu, Mr Veratius Anyanwu and Ekebuisi Moses Chukwu were always there to supervise the field activities; I say thank you.

I am also grateful to my colleagues at Easyfront services Ltd, UK. I must not forget the former president of Federal Republic of Nigeria, Dr Goodluck Ebele Jonathan; he saw the little giant in me and called me to contribute to the growth of our nation through this research scholarship and senior appointment. I am also indebted to PTDF for the support and funding of this research.

Finally, my greatest adoration to the almighty God, whose grace brought strength through spiritual meditation.

TABLE OF CONTENTS

ABSTRACT i
ACKNOWLEDGEMENTS iii
LIST OF FIGURES ix
LIST OF TABLES xii
LIST OF EQUATIONS xiv
LIST OF ABBREVIATIONS xvi
1 INTRODUCTION 1
  1.1 Overview of the research 1
  1.2 Research background 1
    1.2.1 Oil palm waste as a renewable carbon source in energy and activated carbon: prospects and challenges in Nigeria 1
    1.2.2 Oil palm processing waste 6
    1.2.3 Oil palm waste characteristics 8
    1.2.4 Oil palm waste utilisation potentials 9
    1.2.5 Biomass energy overview in Nigeria 15
    1.2.6 Research Inference 17
  1.3 Research question, aim and objectives 18
    1.3.1 Research questions, scientific challenges and gaps 18
    1.3.2 Aim 20
    1.3.3 Objectives 20
  1.4 References 22
2 BIOMASS ASH APPLICATION IN AGRICULTURE: A SHORT REVIEW 37
  2.1 Introduction 37
  2.2 Mineral composition of biomass ash relative to the influence on soil properties and plant growth 41
  2.3 Mechanism of soil-ash balance, relationship and chemical alteration 46
  2.4 Ash from heterogeneous waste stream for soil amelioration 48
  2.5 The response coefficient of different ash types to crop yield 51
  2.6 Palm waste thermal residual ash, its potency as fertilizer and application rate 52
  2.7 The challenges of biomass ash application to the soil 53
  2.8 Conclusion 57
  2.9 References 58
3 A REVIEW OF CHEMICALS TO PRODUCE ACTIVATED CARBON FROM AGRICULTURAL WASTE BIOMASS 75
  3.1 Introduction 75
  3.2 Fuel characterisation for AC production 79
  3.3 Modes of activation 85
    3.3.1 Chemical activation 86

3.3.2 A comparison of activation by microwave and the conventional process ... 89
3.4 Activating agent effect ... 91
3.4.1 The effects of activating agent on renewable and non-renewable precursors ... 91
3.4.2 Acidic treatment of agricultural residues ... 94
3.4.3 Base treatment of agricultural residues ... 95
3.4.4 Salts treatment of agricultural residues ... 96
3.5 Characterisation of AC ... 106
3.5.1 Surface chemistry mechanism and morphology ... 106
3.5.2 Adsorption and kinetic mechanism ... 107
3.6 Production process challenges ... 117
3.6.1 Washing and milling ... 117
3.6.2 Microwave power and radiation duration ... 119
3.6.3 Activation interaction and temperature ... 120
3.6.4 Tar deposition ... 121
3.6.5 Equipment selection and mode ... 122
3.6.6 Dielectric properties ... 123
3.7 Scale of microwave for use in preparing AC ... 124
3.8 Conclusion ... 125
3.9 References ... 127
4 MICROWAVE THERMAL PROCESS AND MATERIAL INTERACTIONS RELATIVE TO REACTORS FOR THE PRODUCTION OF ACTIVATED CARBON ... 155
4.1 Introduction ... 155
4.2 Materials and methods ... 159
4.3 Results and discussion ... 162
4.3.1 Electrodynamic properties of biomass interaction under microwave ... 162
4.3.2 Percentage gas, liquid and char yield for conventional and microwave processes ... 164
4.3.3 Synthesis variations with different reactors ... 168
4.3.4 Effect of activating agents ... 169
4.3.5 Microwave energy and reactor efficiency: techniques for improvement ... 171
4.3.6 Potential energy within the bond and bond stretching interactions ... 172
4.4 Conclusion ... 175
4.5 References ... 176
5 PREPARATION AND CHARACTERISATION OF ACTIVATED CARBON FROM PALM MIXED WASTE TREATED WITH TRONA ORE ... 181
5.1 Introduction ... 181
5.2 Materials and Methods ... 185

5.2.1 Materials 185
5.2.2 Production of activated carbon 189
5.2.3 Characterisation of Trona ore activated carbon (ToAC) 190
5.3 Results and discussion 190
5.3.1 Thermogravimetric analyses of OPW 190
5.3.2 Elemental analysis of the combine palm waste activated carbon 195
5.3.3 AC morphology and surface chemistry mechanism 196
5.3.4 Effect of process parameters and modes of production on AC characteristics 199
5.3.5 Overview of the process and resultant challenges in the use of microwave 202
5.3.6 The effectiveness of Trona ore 202
5.4 Conclusion 204
5.5 References 205
6 OIL PALM WASTE THERMAL RESIDUE IMPROVES SOIL FERTILITY AND QUALITY OF HABANERO CHILLI PEPPER (*Capsicum chinense jacq.*) PRODUCE IN SOUTHERN NIGERIA 215
6.1 Introduction 215
6.2 Material and methods 218
6.2.1 Experimental sites 218
6.2.2 Weather condition 219
6.2.3 Preparation of oil palm waste ash 219
6.2.4 Soil laboratory analysis 220
6.2.5 Nursery Preparation 221
6.2.6 Soil experimental design, layout and treatments 221
6.2.7 Transplanting and Irrigation 222
6.2.8 Field plant analysis 222
6.2.9 Statistical analyses 224
6.3 Results and discussion 224
6.3.1 Soil and ash analyses 224
6.3.2 Weather and optimum planting period 229
6.3.3 Nursery development 230
6.3.4 Effect of the ash on the soil temperature and on soil fertility 233
6.3.5 Influence of PWA on crop development and yield 234
6.3.6 Comparison of HCP characteristics in site A and B 241
6.3.7 Stomata and weather relationship on the development of HCP 242
6.3.8 Post-harvest soil nutrient depletion and fertility coefficient 242
6.4 Conclusion 244
6.5 References 246
7 ENERGY AND ECONOMIC ASSESSMENT OF COMBINED PALM WASTE THERMAL RESIDUE UTILISATION TO PRODUCE ACTIVATED CARBON AND SOIL AMENDMENT 251

  7.1 Introduction 251
  7.5 References 276
8 PROJECT INTEGRATED DISCUSSION 283
  8.1 Integrated discussion 283
9 CONCLUSIONS AND RECOMMENDATIONS 290
  9.1 Conclusions 290
  9.2 Recommendations 294
APPENDICES 297
  Appendix A Preparation and activation of AC from CPW 297
  Appendix B Weather report 301
  Appendix C Plant analysis 304
  Appendix D Economic assessment 308
  Appendix E Arsenic adsorption 309

LIST OF FIGURES

Figure 1-1 World oil and fat production (USDA, 2017; Mundi, 2018) 4

Figure 1-2 African palm oil producers (USDA, 2017; Mundi, 2018) 5

Figure 1-3 Mechanical operation of palm oil and Palm kernel oil process 6

Figure 1-4 Percentage of processing palm oil waste 7

Figure 1-5 (a) OPW generation in processing mill (b) Palm biowaste applications 10

Figure 2-1 Mechanism of biomass ash formation in a thermal system 37

Figure 2-2 Variation of different feedstock relative to temperature and ash production 39

Figure 2-3 Soil-ash chemical interactions for plant growth 47

Figure 3-1 A structural model of lignocellulosic components of biomass 81

Figure 3-2 Activation temperature’s effect on activate carbon’s (AC) pore development and morphology A: biomass structure; B: partially developed char structure; C: well-defined porous AC structure 85

Figure 3-3 Examples of conventional and microwave heating effects 90

Figure 3-4 The interactions between layers and NaOH 96

Figure 3-5 S_{BET} and total pore volume ranges of some activating agents on agricultural waste 99

Figure 3-6 Hammer milling process for biomass 118

Figure 4-1. Microwave interaction with water and ionic conduction (Leonelli and Mason, 2010) 156

Figure 4-2 ASPEN PLUS flow chat for pyrolysis 161

Figure 4-3 Thermal decomposition profile of combined palm waste 165

Figure 4-4 (a) Percentage gas, liquid and char yield for conventional process (b) Percentage yield for microwave process relative to simulated yield 167

Figure 4-5 SEM images of AC products from different process parameters and reactors 170

Figure 4-6 (A). Bond stretching interaction in microwave; (B). Heat transfer direction relative to the biomass sample in the microwave (Salema *et al.*, 2013) 173

Figure 4-7. Overall reactor response to microwave power and heating rate .. 175

Figure 5-1. Microwave experimental setup for AC production 189

Figure 5-2 DTA/TGA of OPW and variation of the samples impregnated with Trona ore 192

Figure 5-3. (a) Microwave heating time relative to moisture content and temperature variation (b) Mass flow relationship relative to the influence of temperature change on the composition of syngas 194

Figure 5-4. SEM analysis of the AC produced from Trona 197

Figure 5-5. FTIR of OPW from different processing methods and activation conditions (b) raw feedstock (b) Trona ore activated AC 198

Figure 5-6. Mechanism of Trona during activation process 203

Figure 6-1 Experimental and analytical processes for palm waste ash application for growing chili pepper 218

Figure 6-2 Nursery development and survival rate 231

Figure 6-3 Average Morphological parameters and Phenological parameters site A on first and second seasons 237

Figure 6-4 Average Morphological parameters and Phenological parameters site B on first and second seasons 238

Figure 6-5 Soil mean characteristics for 8 tonnes/ha plot (THP) from pre-season to post harvest 243

Figure 7-1 Mass and energy relativity for the OPW thermal process 256

Figure 7-2 Thermal combined processes of pyrolysis, gasification and combustion 258

Figure 7-3 Mass flow relationship relative to the influence of temperature change on the composition of syngas. 262

Figure 7-4 (a) Operating and (b) Capital cost for combined thermal processes. 265

Figure 7-5 The relationships between flow rate, temperature and syngas produced in gasification. 269

Figure 7-6 Percentage production cost of HCP in this study 271

Figure 8-1 Overall project structure 283

Figure A-1 Yield from CPW relative to temperature 297

Figure A-2 Microwave setup and process equipment for AC production 298

Figure A-3 FTIR of all the samples 299

Figure A-4 Proposed design for large scale AC production system 300

Figure B-1 Weather report for site A 301

Figure B-2 Weather report for site B 302

Figure B-3 Combined weather report relative to planting and transplanting ... 303

Figure C-1 Treatment and application rate 304

Figure C-2 Nursery response in two weeks 305

Figure C-3 Nursery survival rate 306

Figure C-4 Fruit characteristics 307

Figure E-1 Journal paper prepared for publication 309

Figure E-2 FTIR illustration of activated carbon used in adsorption 310

Figure E-3 Adsorption isotherms simulations for As (V) adsorption by AC at initial concentrations of 10–100 mg/L at 25 °C 312

Figure E-4 Adsorbent dosage relationship with adsorption capacity for MTA-5 314

Figure E-5 Removal of arsenic at diverse pH for 25 ^{o}C, adsorbent dosage, 10 mg/L; initial concentration, 20 mg/L 315

Figure E-6 Final pH after arsenic adsorption at various initial pH 316

LIST OF TABLES

Table 1-1 Palm oil processing unit operations 8

Table 1-2 Recent works on the optimisation process OPW for AC 14

Table 2-1 Nutrients available in biomass ash and their overall impact on soil and plant 43

Table 3-1 Analytical characterisation and composition of agricultural waste biomass 82

Table 3-2 An overview of the three modes for the chemical activation process 87

Table 3-3 Comparison of the differences between various processing parameters for microwave and conventional activation methods 90

Table 3-4 The effects of activating chemical on the precursors 100

Table 3-5 Adsorption capacities and parameters of chemically-activated agricultural wastes based on activating agent 110

Table 3-6 Adsorption isotherm models descriptions and challenges 114

Table 3-7 Relationship between penetration depth of biomass and various microwave frequencies (Oyejobi *et al.*, 2012; Abubakar, Salema and Ani, 2013; Okahisa *et al.*, 2018) 123

Table 4-1. The relative permittivity of Combine Palm Waste AC at different frequencies for each reactor 163

Table 4-2 Pore structure relative to reactor type 169

Table 5-1 Biochemical analysis of individual palm waste biomass 186

Table 5-2. Elemental analysis of combine palm waste activated carbon based on different production processes 196

Table 5-3. Yield and pore structural parameters 199

Table 6-1 Properties of soil for site A and B; chemical analysis and EDX of palm waste ash 226

Table 6-2 The mean Physiological changes in HCP with the application of OPWA. 235

Table 7-1 Chemical and biochemical properties of CPW 255

Table 7-2 Cost parameter for a thermal process plant 263

Table 7-3 Economic analysis of thermal processes and investment summary 264

Table 7-4 Percentage process input and yield 268

Table D-1 Process yield 308

Table E-1 The characteristics of CPW and the comparison of porosity structure of the AC for arsenic adsorption 311

Table E-2 The characteristics of CPW and the comparison of porosity structure of the AC for arsenic adsorption 313

LIST OF EQUATIONS

(3-1) ... 78

(3-2) ... 108

(3-3) ... 109

(3-4) ... 118

(4-1) ... 160

(4-2) ... 161

(4-3) ... 161

(4-4) ... 161

(4-5) ... 161

(4-6) ... 173

(5-1) ... 187

(5-2) ... 187

(5-3) ... 187

(5-4) ... 187

(5-5) ... 187

(5-6) ... 187

(5-7) ... 188

(5-8) ... 188

(5-9) ... 188

(5-10) ... 188

(5-11) ... 188

(5-12) ... 188

(5-13) ... 203

(5-14) ... 203

(5-15) ... 203

(5-16) ... 203

(6-1) ... 222

(6-2) ... 222

(6-3)........ 223
(6-4)........ 223
(6-5)........ 223
(6-6)........ 223
(6-7)........ 223
(6-8)........ 240
(6-9)........ 240
(6-10)........ 240
(6-11)........ 240
(7-1)........ 256
(7-2)........ 256
(7-3)........ 256
(7-4)........ 257
(7-5)........ 257
(7-6)........ 257
(7-7)........ 259
(7-8)........ 259
(7-9)........ 259
(7-10)........ 259
(7-11)........ 259
(7-12)........ 259
(7-13)........ 260
(7-14)........ 260
(7-15)........ 260
(7-16)........ 260

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
A-ROI	Annualised return on investment
ASPEN	Advanced system for processing Engineering
BG	Bagasse
BR-B	Borosilicate Pyrex glass reactor
CEC	Cation exchange capacity
CFn	Annual cash flows
CIC	Capital investment cost
CR	Concentration ratio
CPW	Combine palm waste
DAEM	Distributed activation energy model
DM	Dry mass
Dp	Pore diameter
DTA	Differential thermal analysis
EC	Electrical conductivity
EFB	Empty fruit bunch
EFBAC	Empty fruit bunch activated carbon
FC	Fixed carbon
FFB	Fresh fruit bunch
FTIR	Fourier transform infrared spectrometry
GDP	Gross domestic product
GM	Gross margin
GMO	Genetic modified organism
HCP	Habanero chili pepper
HHV	Higher heating value
IR	Impregnation ratio
LAI	Leaf area index
LHV	Lower heating value
LRWC	Leaf relative water content
MB	Methyl blue

MF	Mesocarp fibre
MW	Microwave
NPV	Net present value
OPPW	Oil palm processing waste
OPWA	Oil palm waste ash
PAEK	Polyaryletherketone
PBA	Palm based ash
PEEK	Polyetheretherketone
PFW	Plant fresh weight
PKS	Palm kernel shell
PR-C	Porcelain (ceramic) reactor
PTFE	Polytetrafluoroethylene
RCBD	Randomised complete block design
RGR	Relative growth rate
S_{BET}	Brunner Emma Teller surface area
SEM	Scanning electron microscope
SW	Swollen weight
TC	Total cost
TFC	Total fixed cost
TGA	Thermogravimetric analysis
THP	Tonnes per hectare plot
ToAC	Trona ore activated carbon
TR	Total revenue
TVC	Total variable cost
USDA	United states department of agriculture
V	Volume
V_{meso}	Mesopore volume
V_{micro}	Micropore volume
V_{total}	Total volume
W	Watt

1 INTRODUCTION

1.1 Overview of the research

This chapter is intended to govern the principal background of this project. It illustrates the synopsis of the primary feedstock and the wastes sources. The underlined factors such as: palm wastes value, technologies and routes related to the utilisation are considered. The current utilisation status conveyed the need for appropriate measures and imperative parameters for utilisation. This phase also outlined the fundamental challenges relative to the scope of this study with focus on oil palm. The aim is spawned from the challenges identified and objectives were set based on previous and ongoing studies in biomass revaluation and utilisation. They were established to answer scientific, technological, social and economic questions.

1.2 Research background

1.2.1 Oil palm waste as a renewable carbon source in energy and activated carbon: prospects and challenges in Nigeria

1.2.1.1 Agricultural waste in Nigeria

Global food predicament, energy demand, environmental pollution and climate change are persistent challenges to mankind especially in developing countries; therefore, appropriate attention is required for mitigation(Kong *et al.*, 2014). The enormous increase in solid waste generation with one of the major sources emanating from agriculture, through direct production and processing has created global environmental challenges (Bello, Norshafiq and Kabbashi, 2016). It is one of the major environmental problems yet to be addressed in developing countries (Ojo, 2014; Giwa *et al.*, 2017), which has entreated a mandate for control measures owing to the adverse effects (Hoornweg and Bhada-Tata, 2012).

Agricultural wastes from parts of fruits which are considered inconsequential are generated both during production and processing. The economic value of these waste products is assumed to be low and they can pose a threat to food production and general agricultural development, especially if mismanaged (Obi, Ugwuishiwu and Nwakaire, 2016). Waste classification are based on its characteristics, mode of production and health effect and further classified as hazardous and non-hazardous. A study by Vaish (2016) estimated global municipal solid waste generation to be at 4 billion tonnes annually and agricultural waste have a large share of about 50%. Agricultural wastes include waste from livestock, tree shavings, harvested products and waste from several levels of food processing.(Idris *et al.*, 2015). About 90 Million tonnes of palm waste are produced globally (Ng *et al.*, 2012). Further processing of these wastes can be the solution to mitigate pollution and improve reuse (Izah, Ohimain and Angaye, 2016). Developing countries have a low rating in management of agricultural waste from these activities. Hence, this results in littering of the road sides, dumping in rivers, drainages and communal dump sites (Akindutire and Alebiosu, 2014), unlike developed countries where waste management is a lucrative venture as the waste could be used in several expedient ways (Izah, Ohimain and Angaye, 2016). Recycling technology, renewable energy and soil amendment have also benefitted immensely from wastes. Studies on the utilisation of agricultural wastes in developing countries are links to creativity with tendencies to also generate employment, promote alternative energy generation, and provide solution to certain agricultural and industrial needs.

Oil palm waste (OPW), these include the palm fronds, trunks and processing wastes are considered major contributor to agricultural wastes in developing countries where they are produced and Nigeria generates millions of tonnes of oil palm processing waste (OPPW) which are mostly underutilised (Izah and Ohimain, 2015). Nigeria with a population of approximately 150-200 Million as estimated in the year 2010 and an annual growth rate of 2.5% (WIPO, 2012), also ranked as one of the most populated of the developing countries; although the last official census 0f 2006 stated 140 million. Agricultural land accounts for approximately 745,000 sq.km of the total land area of 911,000 sq.km for the country with about 40% of the agricultural land arable, 11% forest zone and 3% active cropped area. More than 60% of the people are involved in direct and indirect agricultural production. About 70% of farmers practice small scale or subsistence farming defined as < 0.05 sq.km per person. Nigerian agriculture contributes about 40% to the non-oil GDP with palm plantation being one of the major cash crops in the South of Nigeria (Simonyan and Fasina, 2013; Bank, 2016). Nigeria palm oil average demand is 8M_tonnes/year against the supply of 4.5M_tonnes/year (Federal Ministry of Agriculture Nigeria, 2016), which will continue to increase (Embrandiri, Singh, *et al.*, 2012; Kurnia *et al.*, 2016).

1.2.1.2 Oil palm

Oil palm (*Elaeis guineensis jacq*.), belongs to palmaceae family and to the genus Elaeis. It is a perennial monocot flowering plant in the order Arecales, which has three major species, E. guineensis which is dominant, E. oleifera (Abdullah *et al.*, 2012) and E.odora which is an infrequent specie in Africa (Henson, 2012; Godswill *et al.*, 2016). Oil palm is a unique monoecious plant, which seasonally produces unisexual male and female flowers in an alternating cycle in cross-fertilisation mode of reproduction (Godswill *et al.*, 2016). The fruitlet weight is about 10 g, bunch weight 30 kg and 5-8% weight of kernel per fruit (Yusoff, 2015) It grows in wild and semi-wild but in the last century, it is cultivated majorly in areas with lots of sunshine, adequate rainfall, deep and permeable soil (Sapey and Adusei-Fosu, 2012). It produces oil fit for human consumption principally derived from oil palm fruits (Pande, Akor and Lai, 2012). Oil palm is native to West Africa, many Asian countries adopted the oil palm and developed it into a high economic agriculture, it generates high revenues to the local farmers and provides raw materials for several domestic and industrial uses (Teoh, 2010). Palm oil, has become one of the household products and foremost seed oil products in the world (Figure 1-1), used widely in food processing and manufacture of cosmetics, industrial chemicals and biodiesel.

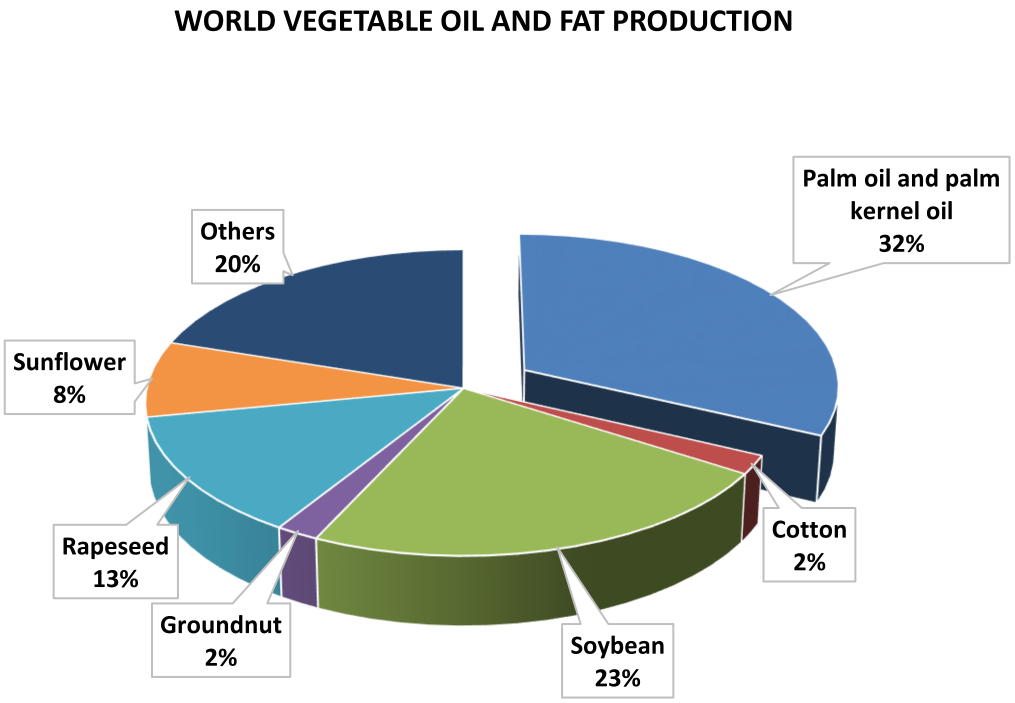
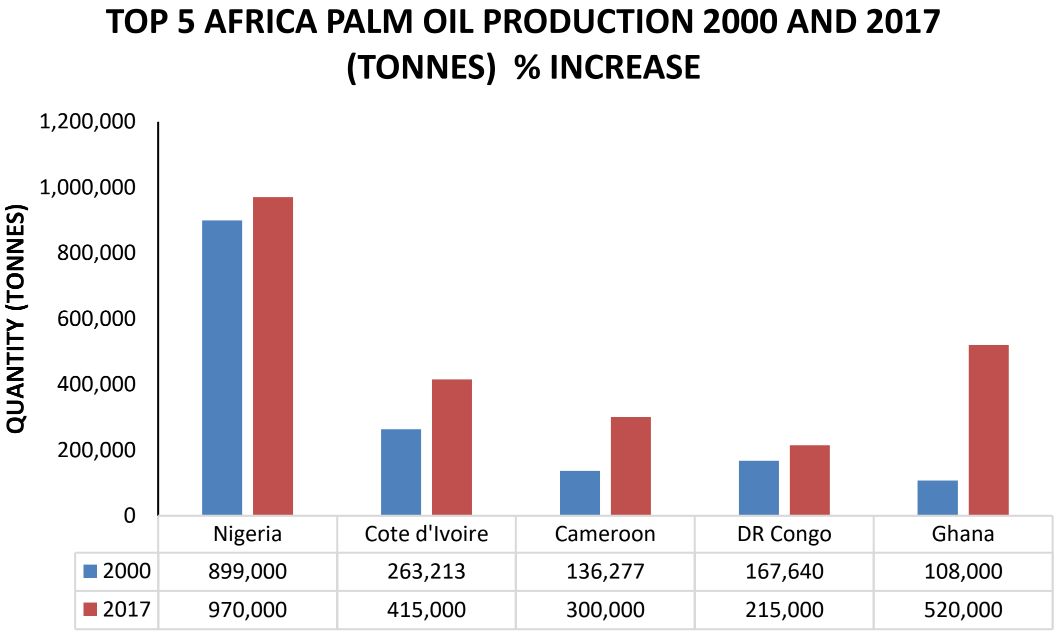


Figure 1-1 World oil and fat production (USDA, 2017; Mundi, 2018)

Oil palm in a favourable environmental condition, produces fruit bunches which ripen throughout the year. In the production year, there are high and low periods which are also comparative to yield (Henson, 2012; Obahiagbon, 2012; Mba, Dumont and Ngadi, 2015). Palm oil is the major source of palmitic acid, which is nutritional and medically useful as a source of vitamin A. It is abundant in West Africa, majorly in Nigeria, Cameroon, Ghana and central Africa, Nigeria is the leading producer of palm oil, Figure 1-2 (USDA, 2017; Mundi, 2018). Oil palm is a common and most abundant cash crop in the east and south of Nigeria for centuries only recently has it been eclipsed by the crude oil boom as the major source of income (Soh, 1965; Ofosu-budu, 2013). The palm oil industry generates employment (Garcia-Nunez *et al.*, 2016). The increasing demand for palm oil, which is the 32% of global fats and oil production, is because, its variety of application and low production cost. It is wholly GMO free and have multiple usage (Darby, 2014; Mancini *et al.*, 2015)



	Nigeria	Cote d'Ivoire	Cameroon	DR Congo	Ghana
🟦 2000	899,000	263,213	136,277	167,640	108,000
🟥 2017	970,000	415,000	300,000	215,000	520,000

Figure 1-2 African palm oil producers (USDA, 2017; Mundi, 2018)

Palm wastes are organic, rich in macro minerals and could be useful in both energy production and soil improvement. Due to poor recycling and waste management facilities in developing countries, palm wastes are littered on dump sites and could pollute the rivers, resulting in weed invasion and other direct health related issues (Sabiiti, 2011). As the world population increases with advancement in industrialisation, the volume of waste generated and the demand for food will continue to increase and waste control system will become more critical (Terefe, Gashaw and Warkineh, 2015). This therefore, has direct impact on the level of waste from palm oil production. The utilisation of OPW could be implemented at several stages of production and processing. Sometimes, the designated utilisation process is influenced by the waste composition and most agricultural wastes could fit in all the processes. Anyaoha *et al* (2018) suggested that co-utilization is appropriate as a robust measure for efficient utilization of palm waste. Various potential applications are studied with focus on energy production and AC. There are also several researches related to these applications; however, the case studies of Nigeria are limited and this study addresses two aspects of utilisation. The technologies are at an initial stage in

Nigeria. Hence, the necessity to address some of the key challenges affecting the utilisation and outline how to overcome them.

1.2.2 Oil palm processing waste

In Nigeria, oil palm is struggling to meet the high demand; attracting many investors. This is the reason for diversification of palm oil in the production of several other products. Palm oil production requires interlinked process to produce palm oil and kernel oil. Figure 1-3 outlines the process from receipt of fresh fruit bunch (FFB) to storage of palm oil. Each of the processes requires a specific equipment to process efficiently. In an industrial large scale, it is designed to run as a unit operation with automated processes at some stage. However, each of the stages generates waste materials.

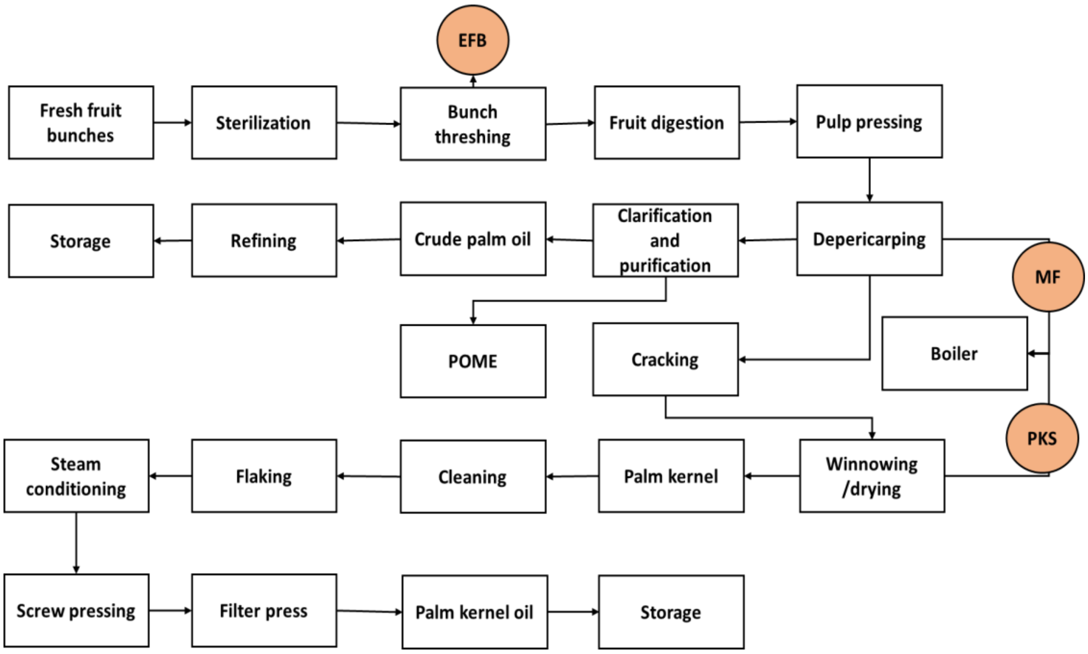


Figure 1-3 Mechanical operation of palm oil and Palm kernel oil process

Most Nigerian palm oil production setup are traditional and non-mechanised process. Therefore, development is geared towards building a unit mechanised process that requires less human input in the operation, however, both methods still produce high volume of waste. Nigeria falls within the developing scale therefore; technological advancement and modern agricultural progress are very slow but, the multiple application potentials of oil palm require proper attention to uphold and compete with other nations in promoting food security. One of the major effects of traditional or low technological methods is oil loss during processing and production. In Nigeria and Ghana, 60% of palm oil production is done through traditional methods (Mokhtar *et al.*, 2012; Obibuzor, Okogbenin and Abigor, 2012). In Nigeria, unregistered farms are mostly unaccounted for and many vegetable oils produced do not get to the market, it is estimated that 40% of palm oil produced is for domestic consumption. Hence, the high waste generation in rural areas.

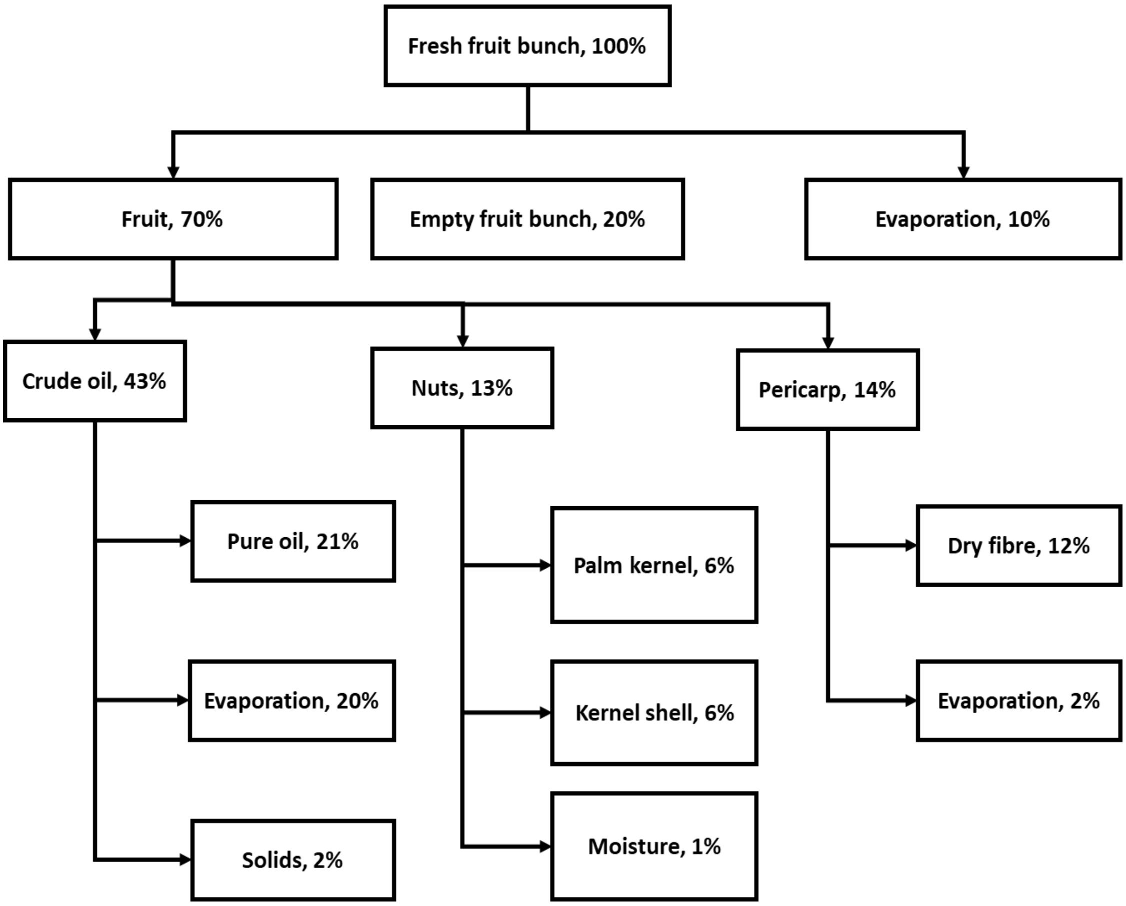


Figure 1-4 Percentage of processing palm oil waste

Considering the amount of biomass generated in the processing of palm oil and other agricultural waste, it prompts concern of where the waste should go (Lorestani and Zinatizadeh, 2006). Palm Kernel Shell (PKS), Palm Kernel Cake (PKC), mesocarp fibre (MF) and empty Fruit Bunch (EFB) account for about 44% percent dry weight. The production process is highlighted in Table 1-1. The percentage waste in Figure 1-4 indicates high waste production and could be ideal and useful in cushioning bioenergy demand (Lorestani and Zinatizadeh, 2006; Sharma *et al.*, 2017).

Table 1-1 Palm oil processing unit operations

Operation	Purpose (Poku and Nations, 2002; Panapanaan *et al.*, 2009)	Equipment
Bunch threshing	Removal of fruits from the spikelets	Rotating drum, with rotary beater
Sterilisation	To use wet-heat treatment, destroys oil-splitting enzymes, solidifies protein, breaks down gums and resins, makes detachment easy, slow down rancidity	High pressure steam steriliser
Fruit digestion	Rupture cells	Digester/oil press
Mash/Pulp pressing	To release palm oil from the digested fruit	Spindle screw press Hydraulic press
Oil purification/clarification	Remove water soluble gums and resins through heat	Clarifier Oil filter
Fibre-nut separation	To extricate de-oiled fibre from nuts	Nut separator
Subsequent pressing	To recover residual oil Compacting the fibre	Spindle screw press Hydraulic press
Nut drying	To dry nuts for cracking	Drying conveyor
Nut cracking	Separating the kernel from the shell	Palm nut cracker

1.2.3 Oil palm waste characteristics

OPW have a defined proportion of H_2, 5-6% found in cellulose, hemicelluloses and lignin by weight (Hossain, Jewaratnam and Ganesan, 2016; Sukiran, Abnisa, Wan Daud, Abu Bakar and Soh Kheang Loh, 2017). Several studies also investigated that OPW could also be used to produce cellulosic ethanol (Piarpuzán, Quintero and Cardona, 2011; Ofori-Boateng and Lee, 2014).

The characteristics of biomass influence the physical and chemical properties of the products. Hence, Abnisa *et al.* (2013) studied bio-oil and biochar produced from different residues of OPW, the yield was 16.58-43.50 wt. % while biochar yielded average range of 28.63-36.75 wt. %. The energy density differs depending on the type of OPW.

1.2.4 Oil palm waste utilisation potentials

Oil palm produces 90% waste biomass by weight and several agroindustry are advancing in the use these biomass materials. Several aspects of technology such as pyrolysis, enzymatic digestion composting, briquetting have improved the value of OPW (Prasertsan and Sajjakulnukit, 2006; Chiew and Shimada, 2013). The processing wastes are more reliable for further thermal conversion but residual wastes such as trunk and fronds are not always available and could be difficult to transport from the farm to the utilisation destination.

Palm oil processing waste produces about 0.3M_tonnes of empty fruit bunches, 0.3M_tonnes of PKS, 0.7M_tonnes of POME, and 0.4M_tonnes of MF in Nigeria (Anyanwu *et al.*, 2013), this can generate significant quantities of energy. The total production of FFB industrially is estimated to be about 6M_tonnes annually of which 10% is oil (Gourichon H., 2013b). Palm wastes could be used in diverse ways as outlined in Figure 1-5.

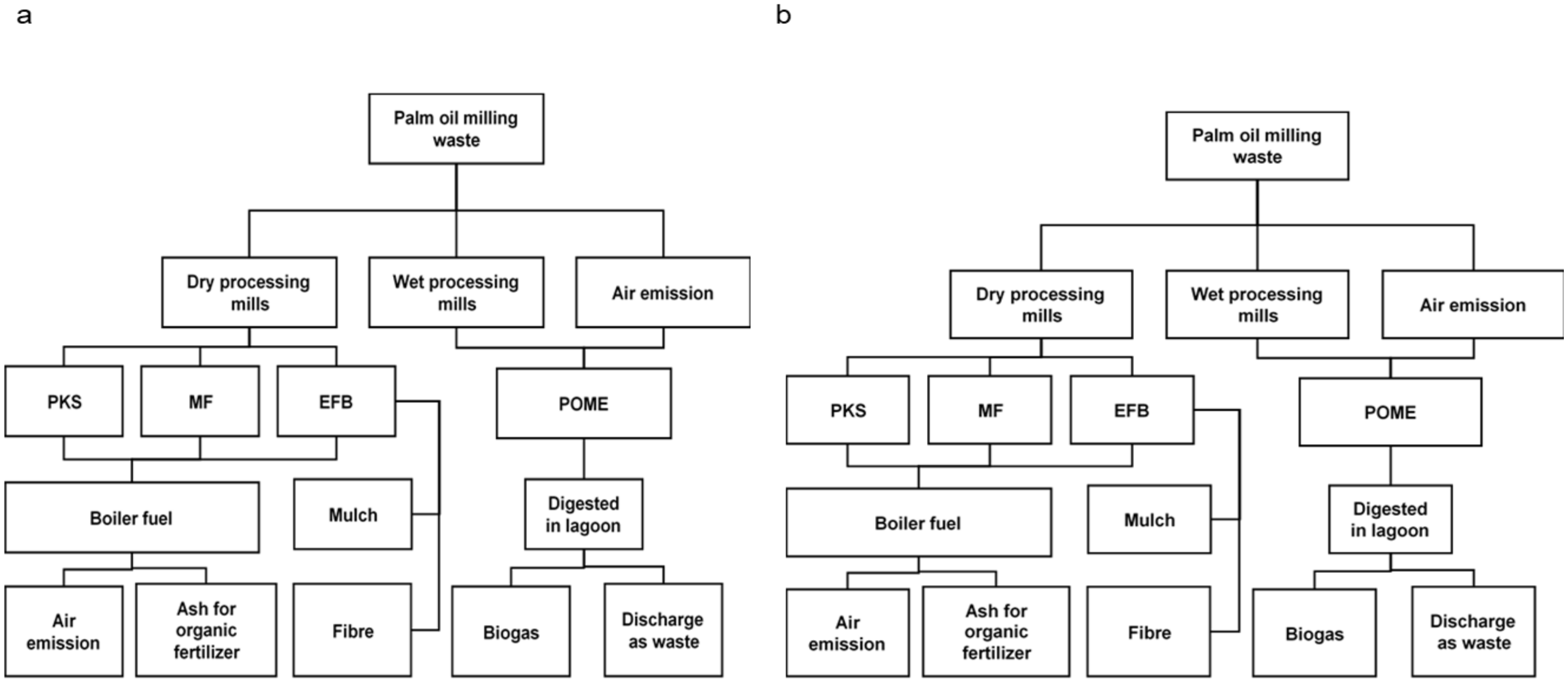


Figure 1-5 (a) OPW generation in processing mill (b) Palm biowaste applications

1.2.4.1 Oil palm waste thermal products

Due to the high energy content and availability, OPW is gaining attention as a renewable resource for power generation and could contribute to mitigation of greenhouse gases (Ng *et al.*, 2012). OPW has economic impact on energy at low or no cost for power generation (Aghamohammadi *et al.*, 2016). It reduces air and water pollution thereby reducing health hazards and a good strategy to the increasing energy demand. Begum (2013), studies show that 30 tonnes of FFB/hr could generate 20-35 MW of power (Nasution, Herawan and Rivani, 2014; Aziz and Kurniawan, 2016). OPW gasification and POME digestion are being studied to obtain a wider efficiency in utilising palm waste in energy (Aziz *et al.*, 2017). Mixture of MF and PKS have been proven effective as fuel for steam production in low pressure boilers (Aghamohammadi *et al.*, 2016; Nasrin *et al.*, 2017) and can also be used in fast or slow pyrolysis or solvolysis to produce bio-oil. Chang (2014) highlighted the difference in production methods and the properties of bio-oil produced compared to petroleum fuel oil and show that the HHV of bio-oil from palm waste is more than half that of petroleum.

Abnisa et al (2013) compared the use of trunks of oil palm, coconut palm, rubber wood and poplar. Yusoff (2006) established that both palm oil and its waste have high potential in energy. Therefore, estimated the calorific value at about, 44 GJ/tonnes for the oil, 20.46 GJ/dry tonnes for MF and 22.88 GJ/dry tonne for PKS. EFB has a very high heating value more than frond and trunk which is value to be 15.5 GJ/tonne (3702 kcal/ kg) (Anyanwu *et al.*, 2013). In every 1 MT of palm waste biomass 80- 200 Gwh of energy can be generated (Ismaiel, Aroua and Yusoff, 2013).

Pre-treatment of palm biomass is one way to increase the usability and storage properties, this is because palm biomass, has high moisture content, hygroscopic, low calorific value and highly fibrous. For example, torrecfaction at a temperature of 200-300 ^{o}C in the absence of oxygen with retention time of about 10-60 minutes, produces a biomass of very low moisture content, high calorific value which is easy to pelletize, easy to grind and hydrophobic (Sukiran, Abnisa, Wan Daud, Abu Bakar and Soh Kheang Loh, 2017). This process can yield about

75% char, 20% gas and up to 5% liquid containing organics and lipids (Sukiran, Abnisa, Wan Daud, Abu Bakar and Soh Kheang Loh, 2017). Oil palm frond has unique characteristics in terms of biodiesel production and succinic acid production (Panapanaan, 2009; Anyanwu *et al.*, 2013).

1.2.4.2 Activated carbon

Biomass has been relevant in energy production to mankind since pre-civilization era, it has a wide range of application from energy generation, soil treatment and production of industrial materials such as AC. The high demand for AC is because of its relevance in, waste treatment, pharmaceutical, desalination, gas storage, water purification and other domestic and industrial applications (Eltom *et al.*, 2012; Nabais *et al.*, 2013). Carbon from coal and biomass have been in use for many centuries, it is one of the major multi-applicable adsorbents with high efficiency, low production cost and less complex production technology (Rashidi and Yusup, 2017a). The source of precursor and activation process could be vital to the quality of AC produced and environmental and economic concerns favour production from wastes (Selvaraju and Bakar, 2017). The abundance of OPW and the resultant quality of AC produced from them make it an interesting area for further development, particularly the economic advantage, good pore structure and effective adsorption capacity (Rashidi and Yusup, 2017a). There have been several studies directed towards enhancing the usefulness and effectiveness of waste in AC production. The use of OPW in the production of AC was considered to promote the green agenda, safer activated carbon and support waste management initiative.

Kong et al (Kong *et al.*, 2014) highlighted the effect of different pyrolysis conditions of the palm biomass slow pyrolysis of EFB at temperature of about 300 ^{o}C produces char (Abdullah *et al.*, 2017) while the mixture of PKS, EFB and MF in thermogravimetric analyser produces gas at 700 ^{o}C and at higher temperature gas production increases (Yang *et al.*, 2007; Zhai *et al.*, 2015) at the heating rate typically below -173 ^{o}C. Fast pyrolysis of PKS in a fixed bed pyrolyser yields high percent of bio-oil, gas and char at temperature between 500-900 ^{o}C at the heating rate above 725 ^{o}C (Razuan *et al.*, 2011; Mabrouki *et al.*, 2015). The physical and chemical activation processes have both advantages and disadvantages in between them (Hernández-Montoya, García-Servin and Bueno-López, 2012). For physical activation, there are some basic advantages such as; minimal impurities, less corrosive process, washing may not be necessary, cheaper method of activation. However, it has some disadvantages such as; high activation temperature and poorly defined porous structure. For chemical activation, there are fundamental advantages over physical activation such as; AC could be produced in one step, shorter activation time, lower temperature, Better control of textural properties, high yield, high surface area of the ACs, well-developed pores, narrow micro pore size distributions, reduction of mineral content matter. Some disadvantages include; high corrosion to the system, inorganic impurities, high energy in washing and overall expensive process.

This experimental research are used relative to the mass balance to validate the adsorption efficiency. (Mekonnen, Yitbarek and Soreta, 2015; Mohammad and Ahmed, 2017; Puccini *et al.*, 2017). Though AC has a wide application ranging from industrial to pharmaceutics, it is identified by González-García (2017) that it is mostly used in metallic adsorption. But, recent researches showed that its application in capacitors and sensors are gaining global scientific acknowledgements. AC percentage uses are 59.95% metals, 8.47% for dyes, 7.41% for sensors, 6.77% for catalysts, 5.82% for CO_2, 1.48% for capacitors and the others go for different adsorption and pharmaceuticals (González-García, 2018). There are two major methods of producing AC in commercial processing and key limitations such as activation time, concentration of activation agents, impregnation ratio and other parameters identified and listed in Table 1-2.This further identifies the methods of heating (Şentorun-Shalaby *et al.*, 2006; Li, Zheng and Li, 2010; Abbas and Ahmed, 2016). In chemical mode, converting biomass to AC, several other activation agents can be used instead of acid and base which can offer safer options.

Table 1-2 Recent works on the optimisation process OPW for AC

Mode of activation	Palm biomass part	Method of heating	Major findings, Key gaps and limitations	Reference
Chemical	PKS	Microwave	Irradiation time, concentration of chemical activators, impregnation ratio, Microwave power, activation time, impregnation ratio, size No comparative study with other activating agents Comparison of the conventional and microwave method There was no adsorption analysis Limited trials with several activating agents	(Hoseinzadeh Hesas, Arami-Niya, *et al.*, 2013a; Kundu, Gupta, *et al.*, 2015; Kundu, Sen Gupta, *et al.*, 2015)
Physical	PKS, Fibre	Furnace	Types of raw precursors, particle size, temperature, heating rate, holding time, gas flow rate	(Rashidi *et al.*, 2012a)
	EFB	Furnace	Activation temperature, Time	(Kadir, 2014).
Physio-chemical	PKS	Furnace	Physical activation temperature and time, impregnation ratio	(Arami-Niya *et al.*, 2012)
	Frond	Furnace	Temperature, activation time, impregnation ratio	(Salman, 2014)

1.2.5 Biomass energy overview in Nigeria

1.2.5.1 Nigeria bioenergy advancement

Biomass resources in Nigeria has the potential to fulfil and support the energy demand in Nigeria through conversion of agricultural waste into biofuel and bio-oil. About 80% of Nigerian primary energy is derived from petroleum (Akorede *et al.*, 2017) and the huge biomass resource is yet to be harnessed, due to poor policy structure and loopholes in generic policy implementation. Therefore, if adopted policies are implemented, it can generate about 47.97 MT of oil equivalent annually (Simonyan and Fasina, 2013).

The vision 20:20 agenda of Nigeria with the target of annual increase of power generation by 4.3 GW (Nigeria, 2014), has not yielded the expected result. This is attributed to the ineffective use of biomass resources in energy resources. The nation with a huge promise to use effective biomass conversion technologies are stringing together more formidable policies to meet the target (Diji, 2013). According to (Aliyu, Modu and Tan, 2017) Nigeria bio power is expected to grow from 40 MW to 400 MW in 2025 if policies and development agenda are strictly followed. Low technical skills and poor infrastructure are the reasons for poor awareness (Aliyu, Dada and Adam, 2015). Effort to establish biogas as kerosene alternative, will decrease CO_2 by more than 65,000 tonnes annually. The environmental challenge of greenhouse gas effect has triggered a renewed approach to ensure a steady growth in biogas production with a long-term target (Akinbami *et al.*, 2001).

There are several bioenergy projects in Nigeria targeted at meeting the present challenges and helping to reduce waste and landfill activities. Biomass to gas project established to control waste in Lagos, Ekiti biofuel industries operated by Global Biofuels, Sugarcane biofuel in many locations in the North of Nigeria, and many others in a developing stage (Nwofe, 2014).

1.2.5.2 The conceptual challenges of bioenergy advancement

There are several other challenges slowing the pace of Nigeria biofuels development. Therefore, these issues should be identified and evaluated before integrating them for power. Several studies revealed that the abundance of fossil fuel is the highest income generator in Nigeria. The government greatly depend on the wealth of fossil fuel with little attention on renewable resources for power generation (Giwa *et al.*, 2017). Adoption of energy crops for bioenergy requires huge land resource, however the use of agricultural waste has intervened in the cultivation of energy crops or establishing biofuel process plant for biofuels production. Due to cultural and traditional customs, the decision for leasing land or purchase is ideal. The fertility profile of an area can also influence the scheme. The rate of unemployment is one of the social factors that is severe in Nigeria. Therefore, the biomass into biofuels would generate employment for the youths.

Relative to agricultural waste for biofuel production, the location of the process plant could be a major concern, due to the difficulty in gathering and transporting to the process plant. The technology for biofuel process is expensive in in large scale, however, government should initiate a support fund and policies to encourage investors and support biofuel production scheme (Akinbami *et al.*, 2001). Improving business environment, establishing a direct link between the economy, agriculture and waste management can reset the utilisation agenda.

The poor utilisation of OPPW requires an explicit approach to harvest its prospects. Agricultural waste revaluation in developing countries with emphasis on Nigeria deserve more efficient conditions and approach in the production of AC from palm wastes. Wildlife is endangered but in certain areas in Africa where there is no orang-utan, it is not considered to be danger to other wildlife. Researches on how it affects biodiversity in Africa require further investigation (Zuma, 2013). The relevance of ash application on soils in locations with palm waste abundance could be a link between chemical and organic fertilizer.

Although, biomass thermal residue revaluation in agriculture is a long existed technology which has undergone several levels of development in controlled and field trials using different crops. However, requires further investigation to evaluate the actual influence on soil chemical behaviours. Several countries have different rating for ash production and utilisation, while some countries do not have proper documentation and standard data. The role of biosolids which is a product of pyrolysis and fly ash in soil improvement has been studied and tested in several soils (Ahmaruzzaman, 2010). It is considered to also increase soil carbon sequestration and crop yield (Lim *et al.*, 2017).

Ash application improves soil texture, reduces bulk density of soil, improves water holding capacity, optimises pH value, increases soil buffering capacity, improves soil aeration, percolation and water retention in the treated zone, reduces crust formation, provides micro and macro nutrients (Kishor P., Ghosh A. K. and Kumar D., 2010; Kumar *et al.*, 2017a). Ashes improve physiochemical properties of soil, enhance soil texture, reduce toxicity, stabilise economic and environmental burden on chemical fertilizers (Kishor P., Ghosh A. K. and Kumar D., 2010). Due to the bioaccumulation of toxic heavy metals and their critical level in plant and human health. There is scarcity of field based evidence in developing countries, using fly ash and bottom ash in the same experimental field. Exploring new amendments in field studies with fly ash co-application with bottom ash for growing crops could have a significant impact on the yield. (Kishor P., Ghosh A. K. and Kumar D., 2010; Shaheen, Hooda and Tsadilas, 2014a; Mupambwa, Dube and Mnkeni, 2015; Yao *et al.*, 2015).

1.2.6 Research Inference

Palm oil as the most consumed vegetable oil, is a useful source of oil and fat in the world and one of the major economy drivers that encourages technology advancement in Nigeria and other developing countries. It contributes greatly to national economy and reduces unemployment. Nigeria as the 5th most palm oil producing countries therefore generates more than 10 million tonnes of palm waste annually. The poor utilisation of OPW contributes significantly to reduce environmental pollution. Several opportunities for efficient utilisation are hindered by poor agricultural waste policies, low technology in processing and poor awareness of stakeholders. There are various utilisation techniques and routes in the production of biofuel, biodiesel, power generation, AC, briquettes and organic manure. If optimally utilised, can improve Nigeria bioenergy level, promote technology advancement, boost economy and reduce pollution due to waste. The products from the waste could also contribute to improving Nigerian energy demand and AC will be useful in water treatment and other chemical related activities.

Palm waste utilisation in Nigeria and other developing countries is poor despite high production and consumption, efficient utilisation of its waste can reduce water and air pollution. Due to palm waste varieties of application and abundance it could help in improving energy production, create jobs and boost the local and international economy. The plantation is considered safe when it does not threaten wildlife.

Government agricultural policies in Nigeria should be tailored to boosting every aspect of palm production and processing. More than 80% of palm oil are produced through traditional process method, therefore modern machinery and expertise should be encouraged through investors and government. Agricultural waste policies should also be implemented to enable a bridge to the energy gap in Nigeria, thereby meeting the renewable energy goal by utilising palm waste in several outlined applications. Palm oil and its waste are capable of boosting employment thereby reduce crime and poverty rate in Nigeria therefore should be integrated in agricultural investment scheme. More efficient and less complex process machinery should be produced in smaller units and be made affordable to local farmers for biofuels and AC production. There should be a common front for stakeholders in governing policy for proper integration of all stakeholders. More studies should be directed to considering the environmental impact for optimum utilisation route.

1.3 Research question, aim and objectives

1.3.1 Research questions, scientific challenges and gaps

The poor utilisation of waste in the developing countries has resulted health challenges and environmental pollution (Efe, 2013; Vaish *et al.*, 2016), there is a search for efficient approach. There is no formidable policy, appropriate status of utilisation approach and model (Abila, 2014; Malico *et al.*, 2019); therefore, all sectors should be integrated. The impact of poor utilisation of waste requires immediate attention (Lee and Nikraz, 2015). There are prospects of utilisation of waste in AC and agriculture (Anyanwu *et al.*, 2013; Event and London, 2015) and these are also applicable to palm waste. Based on these narratives, there is a need for further investigation on how appropriate palm waste can be utilised in AC production and agriculture. To satisfy the investigation, critical reviews on the area that require attention are highlighted.

There is a global safety requirement for safety of AC and also an improved hydrophilicity (Alaei Shahmirzadi *et al.*, 2018) and this is critically influenced by the choice of an activating agent (Olorundare *et al.*, 2014). Trial with trona ore (Nnorom, I.C; Ebo O and Igwe, J.C; Nwoko, 2013; Jo, No and An, 2016) is necessary due to the chemical behaviour of trona and the safety. Setup for the advancement toward industrial scale production and further study on reactor behaviour in the microwave (Dąbrowska, Chudoba, Wojnarowicz, *et al.*, 2018). Improving a microwave setup that can meet large-scale processing target (Nakamura *et al.*, 2010; Zaini and Kamaruddin, 2013). In order to produce an AC with well-developed pores through microwave, there are reported basic challenges which requires experimental investigations.

Microwave reactor evaluation for AC production are have been identified in several studies as the critical aspect of the research that should be studied (Yuen and Hameed, 2009; Asomaning *et al.*, 2018; Dąbrowska, Chudoba, Wojnarowicz, *et al.*, 2018; Falciglia *et al.*, 2018). They are parameters that influence AC characteristics. These are linked to the prerequisite study for an efficient production of AC. The characterisation of produced AC is a technique to study the application efficiency and measuring the efficiency of palm waste-based AC for arsenic adsorption (Gallegos-Garcia, Ramírez-Muñiz and Song, 2012) is required to evaluate the new process. There should be an underlined basic boundary parameter that are favourable for arsenic adsorption (Mekonnen, Yitbarek and Soreta, 2015) which is relative to production techniques. This prompts the expansion of the characterisation beyond SEM and FTIR but application for adsorption of arsenic and other pollutants.

Oil palm waste ash (OPWA) as a thermal process residue has been applied in several projects for soil amelioration, however not in a combined form of three individual wastes. This study is necessary as to know how to utilise it and understand the potency of OPWA in growing pepper and evaluating the yield (Shi *et al.*, 2017). Soil behaviour and temperature changes due to the application of OPWA (Munachiso, 2017) and this is an aspect of the study that is relevant to understand the soil interaction. Determination of formative yield pattern of chili (Das *et al.*, 2016) when ash is applied, is necessary. Evaluating the influence of OPWA on the physiological characteristics of the crop is also a technique to acquire a comprehensive representation of the importance (Saletnik *et al.*, 2018). The evaluation of AC production and ash application as an alternative to fertilizer has not been done in any project. Hence, the need for economic assessment of a combined process of OPWA as soil fertilizer and AC

Investment criteria for and policy requirements in these processes have been identified as a precipitate for an advancement in bioenergy (Ladanai and Vinterbäck, 2009; Malico *et al.*, 2019). To effectively address the outlined challenges, five level connective objectives are set for stage by stage assessment of the laboratory and field experiments.

1.3.2 Aim

The purpose of this research is to assess and determine the optimum route for efficient utilisation of biowaste from thermal conversion process of palm oil residues in producing activated carbon and soil amelioration; evaluate the impact of the selected utilisation techniques.

1.3.3 Objectives

1. Critique wastes generated in palm oil processing, its prospects and utilisation challenges in Nigeria. This considers the utilisation opportunities relative to government policies on waste.

2. Evaluate the effectiveness of different approaches in producing AC from OPW through safe activation. Determine the various challenges of producing AC from OPW through microwave and microwave interactions during activation processes.

3. Characterise the activated carbon produced from a novel activating agent (Trona ore) using Scanning electron microscope, Fourier transform infrared spectrometry and adsorption of heavy metals (although, not within the scope of the research).

4. Determine the physiochemical effects of palm waste ash as fertilizer to grow pepper in two Nigeria soils. Consider the pre-planting conditions and seasonal evaluation of the yield relative to the quantity of palm waste ash.

5. Assessment of technology and economic valuation of the CPW thermal processes in AC production and OPWA application for soil amelioration using Aspen plus economy for simulation.

1.4 References

Abbas, A. F. and Ahmed, M. J. (2016) ‘Mesoporous activated carbon from date stones (Phoenix dactylifera L.) by one-step microwave assisted K_2CO_3 pyrolysis’, *Journal of Water Process Engineering*, 9, pp. 201–207. doi: 10.1016/j.jwpe.2016.01.004.

Abdullah, M. O., Madon, M., Low, E. T. L., Ithnin, M. and Singh, R. (2012) ‘3 – Oil Palm Genomics’, *Palm Oil*, (6), pp. 59–86. doi: 10.1016/B978-0-9818936-9-3.50006-X.

Abdullah, Rahmawati Sianipar, R. N., Ariyani, D. and Nata, I. F. (2017) ‘Conversion of palm oil sludge to biodiesel using alum and KOH as catalysts’, *Sustainable Environment Research*, 27(6), pp. 291–295. doi: 10.1016/j.serj.2017.07.002.

Abila, N. (2014) ‘Managing municipal wastes for energy generation in Nigeria’, *Renewable and Sustainable Energy Reviews*, 37, pp. 182–190. doi: 10.1016/j.rser.2014.05.019.

Abnisa, F., Arami-Niya, A., Wan Daud, W. M. A., Sahu, J. N. and Noor, I. M. (2013) ‘Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis’, *Energy Conversion and Management*. Elsevier Ltd, 76, pp. 1073–1082. doi: 10.1016/j.enconman.2013.08.038.

Aghamohammadi, N., Reginald, S. S., Shamiri, A., Zinatizadeh, A. A., Wong, L. P. and Sulaiman, N. M. B. N. (2016) ‘An investigation of sustainable power generation from oil palm biomass: A case study in Sarawak’, *Sustainability (Switzerland)*, 8(5), pp. 1–19. doi: 10.3390/su8050416.

Ahmaruzzaman, M. (2010) ‘A review on the utilization of fly ash’, *Progress in Energy and Combustion Science*, 36(3), pp. 327–363. doi: 10.1016/j.pecs.2009.11.003.

Akinbami, J.-F. ., Ilori, M. ., Oyebisi, T. ., Akinwumi, I. . and Adeoti, O. (2001) ‘Biogas energy use in Nigeria: current status, future prospects and policy implications’, *Renewable and Sustainable Energy Reviews*, 5(1), pp. 97–112. doi: 10.1016/S1364-0321(00)00005-8.

Akindutire, I. O. and Alebiosu, E. O. (2014) ‘Environmental Risk-Factors of Indiscriminate Refuse Disposal in Ekiti State, Nigeria’, *IOSR Journal of Research & Method in Education (IOSRJRME)*, 4(5), pp. 54–59. doi: 10.9790/7388-04525459.

Akorede, M. F., Ibrahim, O., Amuda, S. A., Otuoze, A. O., Olufeagba, B. J., Of, D. E., Ngineering, C. O. E., Lorin, U. N. O. F. I. and Lorin, I. (2017) ‘Current Status and Outlook of Renewable Energy Development in Nigeria’, *Nigerian Journal of Technology*, 36(1), pp. 196–212. doi: 10.4314/njt.361.1230.

Alaei Shahmirzadi, M. A., Hosseini, S. S., Luo, J. and Ortiz, I. (2018) ‘Significance, evolution and recent advances in adsorption technology, materials and processes for desalination, water softening and salt removal’, *Journal of Environmental Management*, 215, pp. 324–344. doi: 10.1016/j.jenvman.2018.03.040.

Aliyu, A. K., Modu, B. and Tan, C. W. (2017) ‘A review of renewable energy development in Africa: A focus in South Africa, Egypt and Nigeria’, *Renewable and Sustainable Energy Reviews*, (June), pp. 1–17. doi: 10.1016/j.rser.2017.06.055.

Aliyu, A. S., Dada, J. O. and Adam, I. K. (2015) ‘Current status and future prospects of renewable energy in Nigeria’, *Renewable and Sustainable Energy Reviews*, 48, pp. 336–346. doi: 10.1016/j.rser.2015.03.098.

Anyanwu, C. N., Ibeto, C. N., Eze, I. S. and Ezeoha, S. L. (2013) ‘Present and prospective energy use potentials of selected agricultural wastes in Nigeria’, *Journal of Renewable and Sustainable Energy*, 5(3). doi: 10.1063/1.4808046.

Anyaoha, K. E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Critical evaluation of oil palm fresh fruit bunch solid wastes as soil amendments : Prospects and challenges’, *Resources, Conservation & Recycling*, 136(January), pp. 399–409. doi: 10.1016/j.resconrec.2018.04.022.

Arami-Niya, A., Wan Daud, W. M. A., S. Mjalli, F., Abnisa, F. and Shafeeyan, M. S. (2012) ‘Production of microporous palm shell based activated carbon for methane adsorption: Modeling and optimization using response surface methodology’, *Chemical Engineering Research and Design*, 90(6), pp. 776–784. doi: 10.1016/j.cherd.2011.10.001.

Asomaning, J., Haupt, S., Chae, M. and Bressler, D. C. (2018) ‘Recent developments in microwave-assisted thermal conversion of biomass for fuels and chemicals’, *Renewable and Sustainable Energy Reviews*, 92(March), pp. 642–657. doi: 10.1016/j.rser.2018.04.084.

Aziz, M. and Kurniawan, T. (2016) ‘Enhanced utilization of palm oil mill wastes for power generation’, 52, pp. 1–2. doi: 10.3303/CET1652122.

Aziz, M., Kurniawan, T., Oda, T. and Kashiwagi, T. (2017) ‘Advanced power generation using biomass wastes from palm oil mills’, *Applied Thermal Engineering*, 114, pp. 1378–1386. doi: 10.1016/j.applthermaleng.2016.11.031.

Bank, W. (2016) *World Development Indicators*. Washington, DC. doi: 10.1596/978–1-4648–0683–4.

Begum, S., Kumaran, P. and Jayakumar, M. (2013) ‘Use of Oil Palm Waste as a Renewable Energy Source and Its Impact on Reduction of Air Pollution in Context of Malaysia’, *IOP Conference Series: Earth and Environmental Science*, 16, p. 012026. doi: 10.1088/1755-1315/16/1/012026.

Bello, I. A., Norshafiq, M. and Kabbashi, N. A. (2016) ‘Solid Waste Management in Africa : A Review’, *International Journal of Waste Resources*, 6(2), pp. 4–7. doi: 10.4172/2252-5211.1000216.

Chang, S. H. (2014) ‘An overview of empty fruit bunch from oil palm as feedstock for bio-oil production’, *Biomass and Bioenergy*, 62, pp. 174–181. doi: 10.1016/j.biombioe.2014.01.002.

Chiew, Y. L. and Shimada, S. (2013) ‘Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer -

A case study of Malaysia', *Biomass and Bioenergy*. Elsevier Ltd, 51, pp. 109–124. doi: 10.1016/j.biombioe.2013.01.012.

Dąbrowska, S., Chudoba, T., Wojnarowicz, J. and Łojkowski, W. (2018) 'Current Trends in the Development of Microwave Reactors for the Synthesis of Nanomaterials in Laboratories and Industries: A Review', *Crystals*, 8(10), p. 379. doi: 10.3390/cryst8100379.

Darby, S. (2014) *Palm Oil Facts & Figures*, *SimeDarby plantation*. Available at: www.simedarbyplantation.com (Accessed: 16 July 2017).

Das, S., Teja, K. C., Duary, B., Kumar, P. and Sundar, S. (2016) 'Impact of nutrient management , soil type and location on the accumulation of capsaicin in Capsicum chinense (Jacq .): One of the hottest chili in the world', *Scientia Horticulturae*, 213, pp. 354–366. doi: 10.1016/j.scienta.2016.10.041.

Diji, C. J. (2013) 'Electricity Production From Biomass in Nigeria : Options , Prospects and Challenges', *International Journal of Engineering and Applied Sciences*, 3(4), pp. 84–98. doi: 10.4028/www.scientific.net/AMR.824.444.

Efe, S. I. (2013) 'Waste Disposal Problems and Management in Ughelli, Nigeria', *Journal of Environmental Protection*, 4(April), pp. 4–11. doi: 10.4236/jep.2013.44A002.

Eltom, A. E., Fournier Lessa, M. P., Da Silva, M. J. and Da Rocha, J. C. (2012) 'Production & characterization of activated carbon membranes', *Journal of Materials Research and Technology*, 1(2), pp. 80–83. doi: 10.1016/S2238-7854(12)70015-7.

Embrandiri, A., Singh, R. P., Ibrahim, H. M. and Ramli, A. A. (2012) 'Land application of biomass residue generated from palm oil processing: Its potential benefits and threats', *Environmentalist*, 32(1), pp. 111–117. doi: 10.1007/s10669-011-9367-0.

Event, E. and London, L. (2015) 'Agricultural Waste as Source of Energy & Income : Making Agriculture More Rewarding'.

Falciglia, P. P., Roccaro, P., Bonanno, L., De Guidi, G., Vagliasindi, F. G. A. and Romano, S. (2018) ‘A review on the microwave heating as a sustainable technique for environmental remediation/detoxification applications’, *Renewable and Sustainable Energy Reviews*, 95(July), pp. 147–170. doi: 10.1016/j.rser.2018.07.031.

Federal Ministry of Agriculture Nigeria (2016) ‘The agriculture promotion policy’, p. 59. doi: http://fmard.gov.ng/wp-content/uploads/2016/03/2016-Nigeria-Agric-Sector-Policy-Roadmap_June-15-2016_Final.pdf.

Gallegos-Garcia, M., Ramírez-Muñiz, K. and Song, S. (2012) ‘Arsenic removal from water by adsorption using iron oxide minerals as adsorbents: A review’, *Mineral Processing and Extractive Metallurgy Review*, 33(5), pp. 301–315. doi: 10.1080/08827508.2011.584219.

Garcia-Nunez, J. A., Ramirez-Contreras, N. E., Rodriguez, D. T., Silva-Lora, E., Frear, C. S., Stockle, C. and Garcia-Perez, M. (2016) ‘Evolution of palm oil mills into bio-refineries: Literature review on current and potential uses of residual biomass and effluents’, *Resources, Conservation and Recycling*, 110, pp. 99–114. doi: 10.1016/j.resconrec.2016.03.022.

Giwa, A., Alabi, A., Yusuf, A. and Olukan, T. (2017) ‘A comprehensive review on biomass and solar energy for sustainable energy generation in Nigeria’, *Renewable and Sustainable Energy Reviews*, 69(September 2015), pp. 620–641. doi: 10.1016/j.rser.2016.11.160.

Godswill, N.-N., Frank, N.-E. G., Walter, A.-N., Edson, M.-Y. J., Kingsley, T.-M., Arondel, V., Martin, B. J. and Emmanuel, Y. (2016) ‘Chapter 10 – Oil Palm’, in *Breeding Oilseed Crops for Sustainable Production*. doi: 10.1016/B978-0-12-801309-0.00010-0.

González-García, P. (2017) ‘Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications’, *Renewable and Sustainable Energy Reviews*, (xxxx), pp. 1–22. doi: 10.1016/j.rser.2017.04.117.

González-García, P. (2018) ‘Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications’, *Renewable and Sustainable Energy Reviews*, 82(August 2017), pp. 1393–1414. doi: 10.1016/j.rser.2017.04.117.

Gourichon H. (2013) ‘Analysis of incentives and disincentives for sorghum in Nigeria. Technical notes series, MAFAP, FAO,Rome’, (July).

Henson, I. E. (2012) ‘Ripening, Harvesting, and Transport of Oil Palm Bunches’, *Palm Oil: Production, Processing, Characterization, and Uses*, pp. 137–162. doi: 10.1016/B978-0-9818936-9-3.50008-3.

Hernández-Montoya, V., García-Servin, J. and Bueno-López, J. I. (2012) *Thermal Treatments and Activation Procedures Used in the Preparation of Activated Carbons*, *Lignocellulosic Precursors Used in the Synthesis of Activated Carbon - Characterization Techniques and Applications in the Wastewater Treatment*. Edited by D. V. H. Montoya. InTech, Mexico. doi: 10.5772/39365.

Hoornweg, D. and Bhada-Tata, P. (2012) ‘A Global Review of Solid Waste Management’, *World Bank Urban Development Series Knowledge Papers*, pp. 1–116. Available at: https://openknowledge.worldbank.org/handle/10986/17388.

Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2013) ‘Preparation of granular activated carbon from oil palm shell by microwave-induced chemical activation: Optimisation using surface response methodology’, *Chemical Engineering Research and Design*, 91(12), pp. 2447–2456. doi: 10.1016/j.cherd.2013.06.004.

Hossain, M. A., Jewaratnam, J. and Ganesan, P. (2016) ‘Prospect of hydrogen production from oil palm biomass by thermochemical process – A review’, *International Journal of Hydrogen Energy*, 41(38), pp. 16637–16655. doi: 10.1016/j.ijhydene.2016.07.104.

Idris, J., Shirai, Y., Anduo, Y., Ali, A. A. M., Othman, M. R., Ibrahim, I., Husen, R. and Hassan, M. A. (2015) ‘Improved yield and higher heating value of biochar from oil palm biomass at low retention time under self-sustained carbonization’, *Journal of Cleaner Production*, 104(May 2015), pp. 475–479. doi: 10.1016/j.jclepro.2015.05.023.

Ismaiel, A. A., Aroua, M. K. and Yusoff, R. (2013) ‘Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the removal of mercury from contaminated water’, *Chemical Engineering Journal*. Elsevier B.V., 225, pp. 306–314. doi: 10.1016/j.cej.2013.03.082.

Izah, S. C. and Ohimain, E. I. (2015) ‘Comparison of Traditional and Semi-mechanized Palm Oil Processing Approaches in Nigeria ; Implications on Biodiesel Production’, 3(2), pp. 82–87.

Izah, S. C., Ohimain, E. I. and Angaye, T. C. N. (2016) ‘Potential Thermal Energy from Palm Oil Processing Solid Wastes in Nigeria : Mills Consumption and Surplus Quantification’, 01(01), pp. 39–45.

Jo, O., No, O. and An, O. (2016) ‘Comparative Evaluation of the Effects of Palm Bunch Ash and Trona on the Liver of Albino Rats’, 27, pp. 21–27.

Kadir, S. A. S. A. (2014) ‘Preparation of Activated Carbon from Oil Palm Empty Fruit Bunch (EFB) by Steam Activation Using Response Surface Methodology’, *International Journal of Materials Science and Applications*, 3(5), p. 159. doi: 10.11648/j.ijmsa.20140305.15.

Kishor P., Ghosh A. K. and Kumar D. (2010) ‘Use of Flyash in Agriculture: A way to improve soil Fertility and its Productivity’, *Asian Journal of Agricultural Research*, 4(1), pp. 1–14.

Kong, S. H., Loh, S. K., Bachmann, R. T., Rahim, S. A. and Salimon, J. (2014) ‘Biochar from oil palm biomass: A review of its potential and challenges’, *Renewable and Sustainable Energy Reviews*, 39, pp. 729–739. doi: 10.1016/j.rser.2014.07.107.

Kumar, K., Kumar, S., Gupta, M. and Garg, H. C. (2017) ‘Characteristics of Fly Ash in Relation of Soil Amendment’, *Materials Today: Proceedings*, 4(2), pp. 527–532. doi: 10.1016/j.matpr.2017.01.053.

Kundu, A., Sen Gupta, B., Hashim, M. A. and Redzwan, G. (2015) ‘Taguchi optimization approach for production of activated carbon from phosphoric acid impregnated palm kernel shell by microwave heating’, *Journal of Cleaner Production*, 105, pp. 420–427. doi: 10.1016/j.jclepro.2014.06.093.

Kundu, A., Gupta, B. Sen, Hashim, M. a., Sahu, J. N., Mujawar, M. and Redzwan, G. (2015) ‘Optimisation of the process variables in production of activated carbon by microwave heating’, *RSC Adv.*, 5(45), pp. 35899–35908. doi: 10.1039/C4RA16900J.

Kurnia, J. C., Jangam, S. V., Akthar, S., Sasmito, A. P. and Mujumdar, A. S. (2016) ‘Advances in biofuel production from oil palm and palm oil processing wastes: A review’, *Biofuel Research Journal-Brj*, 3(1), pp. 332–346. doi: 10.18331/BRJ2016.3.1.3.

Ladanai, S. and Vinterbäck, J. (2009) ‘Global Potential of Sustainable Biomass for Energy’, *SLU, Institutionen för energi och teknik Swedish University of Agricultural Sciences Department of Energy and Technology*, p. 32. doi: ISSN 1654-9406.

Lee, A. . and Nikraz, H. (2015) ‘BOD: COD Ratio as an Indicator for River Pollution’, *International Proceedings of Chemical, Biological and Environmental Engineering,* 51(26), pp. 139–142. doi: 10.7763/IPCBEE.

Li, K., Zheng, Z. and Li, Y. (2010) ‘Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H3PO4 activation’, *Journal of Hazardous Materials*, 181(1–3), pp. 440–447. doi: 10.1016/j.jhazmat.2010.05.030.

Lim, S. S., Choi, W. J., Chang, S. X., Arshad, M. A., Yoon, K. S. and Kim, H. Y. (2017) ‘Soil carbon changes in paddy fields amended with fly ash’, *Agriculture, Ecosystems and Environment*, 245(June 2016), pp. 11–21. doi: 10.1016/j.agee.2017.03.027.

Lorestani, A. and Zinatizadeh, A. (2006) ‘Biological Treatment of Palm Oil Mill Effluent (Pome) Using an Up-Flow Anaerobic Sludge Fixed Film (Uasff)

Bioreactor', *PhD Thesis*, (December), p. 53. doi: 10.1017/CBO9781107415324.004.

Mabrouki, J., Abbassi, M. A., Guedri, K., Omri, A. and Jeguirim, M. (2015) 'Simulation of biofuel production via fast pyrolysis of palm oil residues', *Fuel*. Elsevier Ltd, 159, pp. 819–827. doi: 10.1016/j.fuel.2015.07.043.

Malico, I., Nepomuceno Pereira, R., Gonçalves, A. C. and Sousa, A. M. O. (2019) 'Current status and future perspectives for energy production from solid biomass in the European industry', *Renewable and Sustainable Energy Reviews*, 112(May), pp. 960–977. doi: 10.1016/j.rser.2019.06.022.

Mancini, A., Imperlini, E., Nigro, E., Montagnese, C., Daniele, A., Orrù, S. and Buono, P. (2015) 'Biological and nutritional properties of palm oil and palmitic acid: Effects on health', *Molecules*, 20(9), pp. 17339–17361. doi: 10.3390/molecules200917339.

Mba, O. I., Dumont, M.-J. and Ngadi, M. (2015) 'Palm oil: Processing, characterization and utilization in the food industry – A review', *Food Bioscience*, 10, pp. 26–41. doi: 10.1016/j.fbio.2015.01.003.

Mekonnen, E., Yitbarek, M. and Soreta, T. R. (2015) 'Kinetic and Thermodynamic Studies of the Adsorption of Cr (VI) onto Some Selected Local Adsorbents', *South African Journal of Chemistry*, 68, pp. 45–52. doi: 10.17159/0379-4350/2015/v68a7.

Mohammad, S. G. and Ahmed, S. M. (2017) 'Preparation of environmentally friendly activated carbon for removal of pesticide from aqueous media', *International Journal of Industrial Chemistry*, 8(2), pp. 121–132. doi: 10.1007/s40090-017-0115-2.

Mokhtar, A., Hassan, K., Aziz, A. A. and May, C. Y. (2012) 'Oil Palm Biomass for Various Wood-based Products', *Palm Oil: Production, Processing, Characterization, and Uses*, pp. 625–652. doi: 10.1016/B978-0-9818936-9-3.50024-1.

Munachiso, O. (2017) ‘Palm kernel shell ash as a soil stabilizing agent and its optimum calcine temperature’, *International Journal of Advanced Research and Publications*, 1(4), pp. 191–193.

Mundi, I. (2018) *Palm Oil Production by Country*, *Website*. Available at: http (Accessed: 25 October 2018).

Mupambwa, H. A., Dube, E. and Mnkeni, P. N. S. (2015) ‘Fly ash composting to improve fertiliser value - A review’, *South African Journal of Science*, 111(7–8), pp. 1–6. doi: 10.17159/sajs.2015/20140103.

Nabais, J. M. V., Laginhas, C., Carrott, M. M. L. R., Carrott, P. J. M., Amorós, J. E. C. and Gisbert, A. V. N. (2013) ‘Surface and porous characterisation of activated carbons made from a novel biomass precursor, the esparto grass’, *Applied Surface Science*, 265, pp. 919–924. doi: 10.1016/j.apsusc.2012.11.164.

Nakamura, T., Nagahata, R., Kunii, K., Soga, H., Sugimoto, S. and Takeuchi, K. (2010) ‘Large-scale polycondensation of lactic acid using microwave batch reactors’, *Organic Process Research and Development*, 14(4), pp. 781–786. doi: 10.1021/op900325e.

Nasrin, A. B. ., VijayiA, S. ., LOoh, S. K. ., Astimar, A. A. and Lim, W. . S. (2017) ‘Quality Compliance and Environmental Impact Assessment of Commercial Empty Fruit Bunch (Efb) Pellet Fuel in Malaysia’, *Journal of Oil Palm Research*, 29(DECEMBER), pp. 570–578.

Nasution, M. A., Herawan, T. and Rivani, M. (2014) ‘Analysis of palm biomass as electricity from palm oil mills in north sumatera’, *Energy Procedia*. Elsevier B.V., 47, pp. 166–172. doi: 10.1016/j.egypro.2014.01.210.

Ng, W. P. Q., Lam, H. L., Ng, F. Y., Kamal, M. and Lim, J. H. E. (2012) ‘Waste-to-wealth: Green potential from palm biomass in Malaysia’, *Journal of Cleaner Production*, 34(September 2011), pp. 57–65. doi: 10.1016/j.jclepro.2012.04.004.

Nigeria, M. of P. F. R. of (2014) *National Renewable Energy and Energy Energy and Energy efficiency Policy*.

Nnorom, I.C; Ebo O, N. K. and Igwe, J.C; Nwoko, C. (2013) ‘ABSU Journal of Environment, Science and Technology, Vol. 2:275 - 289, 2012 www.absujest.org’, 2(1989), pp. 275–289.

Nwofe, P. (2014) ‘Utilization of solar and biomass energy: A panacea to energy sustainability in a developing economy’, (September). Available at: www.factfish.com.

Obahiagbon, F. I. (2012) ‘A Review: Aspects of the African Oil Palm (Elaeis guineesis jacq.) and the Implications of its Bioactives in Human Health’, *American Journal of Biochemistry and Molecular Biology*, 3(2), pp. 106–119. doi: 10.3923/ajbmb.2012.106.119.

Obi, F. O., Ugwuishiwu, B. O. and Nwakaire, J. N. (2016) ‘Agricultural Waste Concept, Generation, Utilization and Management’, *Nigerian Journal of Technology*, 35(4), pp. 957–964. doi: 10.4314/njt.v35i4.34.

Obibuzor, J. U., Okogbenin, E. A. and Abigor, R. D. (2012) ‘Oil Recovery from Palm Fruits and Palm Kernel’, *Palm Oil: Production, Processing, Characterization, and Uses*, pp. 299–328. doi: 10.1016/B978-0-9818936-9-3.50014-9.

Ofori-Boateng, C. and Lee, K. T. (2014) ‘An oil palm-based biorefinery concept for cellulosic ethanol and phytochemicals production: Sustainability evaluation using exergetic life cycle assessment’, *Applied Thermal Engineering*. Elsevier Ltd, 62(1), pp. 90–104. doi: 10.1016/j.applthermaleng.2013.09.022.

Ofosu-budu, K. (2013) ‘Oil palm industry growth in Africa ’:

Ojo, O. M. (2014) ‘Solid Waste Management in Obantoko Area of Abeokuta , Nigeria’, 5(2), pp. 111–115.

Olorundare, O. F., Msagati, T. A. M., Krause, R. W. M., Okonkwo, J. O. and Mamba, B. B. (2014) ‘Activated carbon from lignocellulosic waste residues: Effect of activating agent on porosity characteristics and use as adsorbents for organic species’, *Water, Air, and Soil Pollution*, 225(3). doi: 10.1007/s11270-014-1876-2.

Panapanaan, V., Helin, T., Marjukka, K., Soukka, R., Heinimö, J. and Linnanen, L. (2009) *Sustainability of Palm Oil Production and Opportunities for Finnish Technology and Know-How Transfer*, *Production*. Available at: www.doria.fi/lutpub.

Pande, G., Akor, C. C. and Lai, O. (2012) ‘19 – Food Uses of Palm Oil and Its Components’, *Palm Oil*, pp. 561–586. doi: 10.1016/B978-0-9818936-9-3.50022-8.

Piarpuzán, D., Quintero, J. A. and Cardona, C. A. (2011) ‘Empty fruit bunches from oil palm as a potential raw material for fuel ethanol production’, *Biomass and Bioenergy*, 35(3), pp. 1130–1137. doi: 10.1016/j.biombioe.2010.11.038.

Poku, K. and Nations, F. and A. O. of the U. (2002) *Small-scale palm oil processing in Africa*. FAO agricultural services bulletin, 1010-1365 ; 148.

Prasertsan, S. and Sajjakulnukit, B. (2006) ‘Biomass and biogas energy in Thailand: Potential, opportunity and barriers’, *Renewable Energy*, 31(5), pp. 599–610. doi: 10.1016/j.renene.2005.08.005.

Puccini, M., Stefanelli, E., Hiltz, M. and Seggiani, M. (2017) ‘Activated Carbon from Hydrochar Produced by Hydrothermal Carbonization of Wastes’, *Chemical Engineering Transactions*, 57, pp. 169–174. doi: 10.3303/CET1757029.

Rashidi, N. A. and Yusup, S. (2017) ‘A review on recent technological advancement in the activated carbon production from oil palm wastes’, *Chemical Engineering Journal*, 314, pp. 277–290. doi: 10.1016/j.cej.2016.11.059.

Rashidi, N. A., Yusup, S., Ahmad, M. M., Mohamed, N. M. and Hameed, B. H. (2012) ‘Activated Carbon from the Renewable Agricultural Residues Using Single Step Physical Activation: A Preliminary Analysis’, *APCBEE Procedia*, 3, pp. 84–92. doi: 10.1016/j.apcbee.2012.06.051.

Razuan, R., Finney, K. N., Chen, Q., Sharifi, V. N. and Swithenbank, J. (2011) ‘Pelletised fuel production from palm kernel cake’, *Fuel Processing Technology*, 92(3), pp. 609–615. doi: 10.1016/j.fuproc.2010.11.018.

Sabiiti, E. (2011) ‘Utilising Agricultural Waste to Enhance Food Security and Conserve the Environment’, *African Journal of Food, Agriculture, Nutrition and Development*, 11(6), pp. 1–9. Available at: http://www.ajfand.net/Volume11/No6/ShortCommunication-EllySabiiti.pdf.

Saletnik, B., Zagula, G., Bajcar, M., Czernicka, M. and Puchalski, C. (2018) ‘Biochar and biomass ash as a soil ameliorant: The effect on selected soil properties and yield of giant miscanthus (Miscanthus x giganteus)’, *Energies*, 11(10). doi: 10.3390/en11102535.

Salman, J. M. (2014) ‘Optimization of preparation conditions for activated carbon from palm oil fronds using response surface methodology on removal of pesticides from aqueous solution’, *Arabian Journal of Chemistry*, 7(1), pp. 101–108. doi: 10.1016/j.arabjc.2013.05.033.

Sapey, E. and Adusei-Fosu, K. (2012) ‘Collection of Oil Palm (Elaeis guineensis Jacq.) Germplasm in the Northern Regions of Ghana’, *Asian Journal of …*, 4(5), pp. 325–328. Available at: http://maxwellsci.com/print/ajas/v4-325-328.pdf.

Selvaraju, G. and Bakar, N. K. A. (2017) ‘Production of a new industrially viable green-activated carbon from Artocarpus integer fruit processing waste and evaluation of its chemical, morphological and adsorption properties’, *Journal of Cleaner Production*, 141, pp. 989–999. doi: 10.1016/j.jclepro.2016.09.056.

Şentorun-Shalaby, Ç., Uçak-Astarlioğlu, M. G., Artok, L. and Sarici, Ç. (2006) ‘Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones’, *Microporous and Mesoporous Materials*, 88(1–3), pp. 126–134. doi: 10.1016/j.micromeso.2005.09.003.

Shaheen, S. M., Hooda, P. S. and Tsadilas, C. D. (2014) ‘Opportunities and challenges in the use of coal fly ash for soil improvements - A review’, *Journal of Environmental Management*, 145, pp. 249–267. doi: 10.1016/j.jenvman.2014.07.005.

Sharma, B., Sarkar, A., Singh, P. and Singh, R. P. (2017) ‘Agricultural utilization of biosolids: A review on potential effects on soil and plant grown’, *Waste Management*, 64, pp. 117–132. doi: 10.1016/j.wasman.2017.03.002.

Shi, R. yong, Li, J. yu, Ni, N., Mehmood, K., Xu, R. kou and Qian, W. (2017) ‘Effects of biomass ash, bone meal, and alkaline slag applied alone and combined on soil acidity and wheat growth’, *Journal of Soils and Sediments*, 17(8), pp. 2116–2126. doi: 10.1007/s11368-017-1673-9.

Simonyan, K. J. and Fasina, O. (2013) ‘Biomass resources and bioenergy potentials in Nigeria’, *African Journal of Agricultural Research*, 8(40), pp. 4975–4989. doi: 10.5897/AJAR2013.6726.

Soh, C. A. (1965) ‘Breeding and Genetics of the Oil Palm’, *The University of Nottingham Malaysia Campus, School of Bioscience, Jalan Broga, 43500 Semenyih, Selangor, Malaysia*, pp. 31–58. doi: 10.1016/B978-0-9818936-9-3.50005-8.

Sukiran, M. A., Abnisa, F., Wan Daud, W. M. A., Abu Bakar, N. and Loh, S. K. (2017) ‘A review of torrefaction of oil palm solid wastes for biofuel production’, *Energy Conversion and Management*, 149, pp. 101–120. doi: 10.1016/j.enconman.2017.07.011.

Teoh, C. H. (2010) ‘Key Sustainability Issues in the Palm Oil Sector’, *World Bank Group*.

Terefe, H., Gashaw, T. and Warkineh, B. (2015) ‘Evolution of waste management industries : from passive to proactive in’, 2(3), pp. 84–90.

USDA (2017) *Oilseeds: World markets and trade*, *United Staes Department of Agriculture*.

Vaish, B., Srivastava, V., Singh, P., Singh, A., Singh, P. K. and Singh, R. P. (2016) ‘Exploring untapped energy potential of urban solid waste’, *Energy, Ecology and Environment*, 1(5), pp. 323–342. doi: 10.1007/s40974-016-0023-x.

WIPO (2012) *World Intellectual Property Indicators*, *WIPO Economics and Statistics Series*. doi: 10.1016/0172-2190(79)90016-4.

Yang, H., Yan, R., Chen, H., Lee, D. H. and Zheng, C. (2007) ‘Characteristics of hemicellulose, cellulose and lignin pyrolysis’, *Fuel*, 86(12–13), pp. 1781–1788. doi: 10.1016/j.fuel.2006.12.013.

Yao, Z. T., Ji, X. S., Sarker, P. K., Tang, J. H., Ge, L. Q., Xia, M. S. and Xi, Y. Q. (2015) ‘A comprehensive review on the applications of coal fly ash’, *Earth-Science Reviews*, 141, pp. 105–121. doi: 10.1016/j.earscirev.2014.11.016.

Yuen, F. K. and Hameed, B. H. (2009) ‘Recent developments in the preparation and regeneration of activated carbons by microwaves’, *Advances in Colloid and Interface Science*, 149(1–2), pp. 19–27. doi: 10.1016/j.cis.2008.12.005.

Yusoff, M. S. A. (2015) ‘Food Applications of Palm Oil’. Available at: http://www.mpoc.org.my/upload/P5-Food-Applications-in-Palm-Oil.pdf.

Yusoff, S. (2006) ‘Renewable energy from palm oil - Innovation on effective utilization of waste’, *Journal of Cleaner Production*, 14(1), pp. 87–93. doi: 10.1016/j.jclepro.2004.07.005.

Zaini, M. A. A. and Kamaruddin, M. J. (2013) ‘Critical issues in microwave-assisted activated carbon preparation’, *Journal of Analytical and Applied Pyrolysis*, 101, pp. 238–241. doi: 10.1016/j.jaap.2013.02.003.

Zhai, N., Mao, C., Feng, Y., Zhang, T., Xing, Z., Wang, Y., Zou, S., Yin, D., Han, X., Ren, G. and Yang, G. (2015) ‘Current status and future potential of energy derived from chinese agricultural land: A review’, *BioMed Research International*. Hindawi Publishing Corporation, 2015. doi: 10.1155/2015/824965.

Zuma, N. D. (2013) *African agriculture, transformation and outlook*, *NEPAD Transforming Africa*.

2 BIOMASS ASH APPLICATION IN AGRICULTURE: A SHORT REVIEW

2.1 Introduction

The challenges of global warming caused by fossil fuel combustion has resulted in the advancement of bioenergy production and the desire to replace fossil fuel will continue to rise, and influence the use of other renewable options for human and environmental safety (Elum and Momodu, 2017). Biomass are useful in several ways such as energy, composting and construction. The use of biomass in energy through thermal processes generate high volume of different classes of ash, such as unburnt carbon materials, bottom and fly ashes.

The large-scale incineration and gasification have provoked some consequences and challenges, these problems are the environmental concern of waste management and disposal techniques (Vassilev and Vassileva, 2019)**.** The ash produced from these processes must be appropriately managed to circumvent deleterious impact on the environment (Fernández-Delgado *et al.*, 2019). These ashes can be processed into useful energy products such as briquettes for electricity and heat (Lohri *et al.*, 2015). Some studies argued that biomass ash is safer in the landfill (Brännvall and Kumpiene, 2016). However, the long-time effect and cost of handling could be a discouraging factor (James *et al.*, 2012). Therefore, Tosti et al. (2019) recommended that due to the differences in ash contents, the reuse can be according to need.

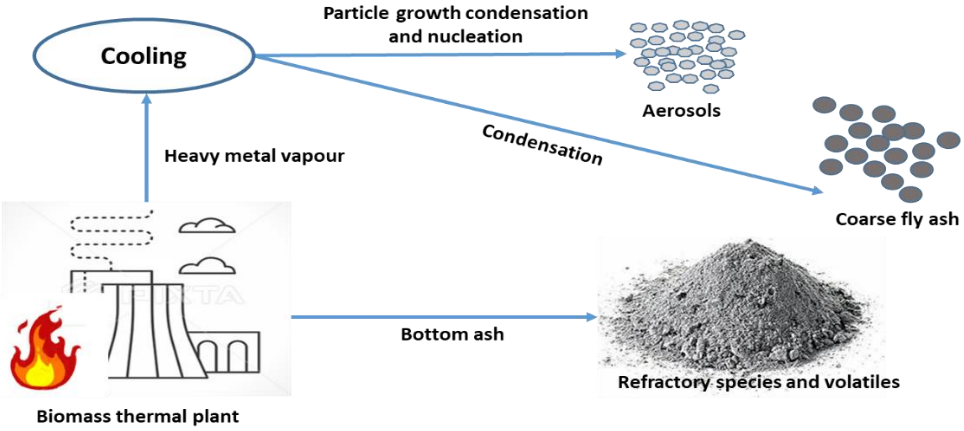


Figure 2-1 Mechanism of biomass ash formation in a thermal system

Thermal residues vary according to the temperature of the process system, configurations and feedstock. Biomass thermal process bottom ash is the heavy portion obtained from the base of the combustion chamber while fly ash is light residues obtained from flue gas cleaning techniques as described in Figure 2-1**.** All classes of biomass ash consist of macronutrients and micronutrients which are useful for growing plant (Z. Chen *et al.*, 2015). These essential nutrients decrease soil acidity and nourish agricultural soil for enhanced crop yield (Shi *et al.*, 2017). Different parts of plant produce different kinds of wastes that are of different physical classes and properties. When used in a thermal process could be singly or in a combined form (Ukanwa *et al.*, 2020). These can result in a complex biosolids waste. The three major biosolids that could be obtained from the thermal process are biochar, bottom ash and fly ashes.

Techniques and the cost of disposal are the major challenges and currently, most ashes go to the landfill (Kronenberger and Groß, 2018). The general difficulty of waste disposal had prompted the development of technique for utilisation and revaluation of these wastes. Fly ashes from coal are also applicable in agriculture and has been reported in several literatures as being useful in plant growth and soil amendment. However, the resultant effect differs as coal contains less available minerals (Michalik and Wilczynska-Michalik, 2012; Kleinhans *et al.*, 2018) Coal ash can contaminate the soil (Yao *et al.*, 2015) while biomass ash has not been marked for toxic influence in the soil (de Jong *et al.*, 2017)**.**

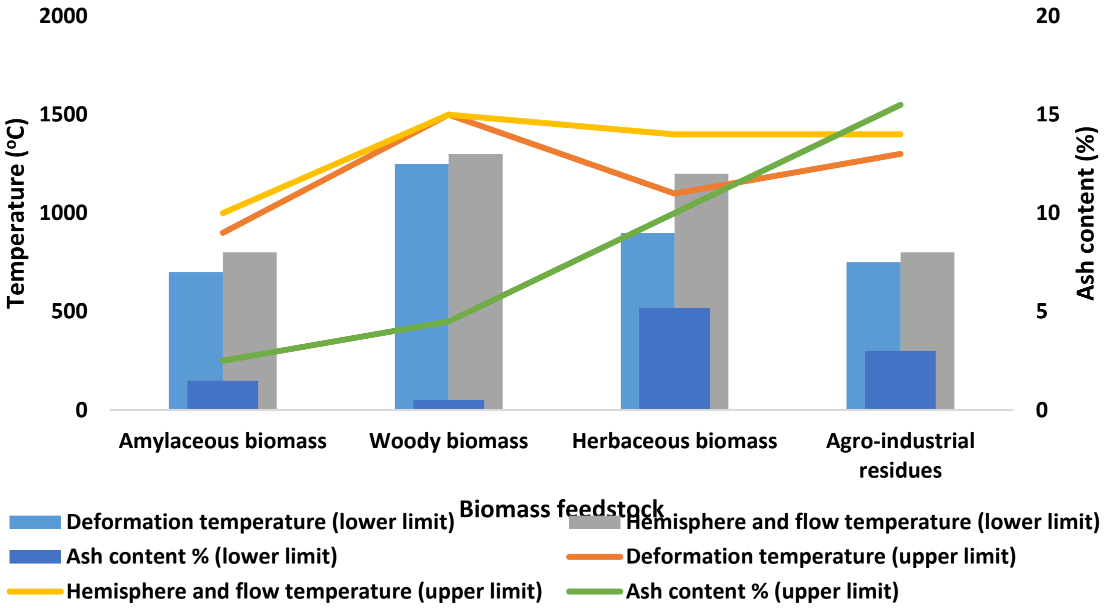


Figure 2-2 Variation of different feedstock relative to temperature and ash production

Variations of biomass ash from different kinds of biomass and their thermal behaviour have direct influence on the ash content and mineralisation potency. This is illustrated in Figure 2-2, from the data obtained from a study by Wirth et al. (2016). Indeed, there are reports on the effectiveness of biomass ash on crops (Yu *et al.*, 2019)**.** Although, the non-uniformity of ash could be a challenge in terms of the determination of application rate and predicting the mineral content. The mineral contents of biomass ash differ from fly ash. Although, coal ash has high content of mineral; however it is only available to crops in low quantity (Kumar *et al.*, 2017b). However, the potential of biomass ash application is widely supported and, these are based on individual biomasses for specific crops. Yu et al. (2019) considered this utilisation technique as efficient but argued the extent of its sustainability and suggested a wider study into the longer-term benefit, instead of immediate yield efficiency. Few literatures tried to compare individual biomasses based on the production techniques. Adekayode and Olojugba (2010) reviewed the benefits of biomass ash over chemical fertilizers; and more importantly in a combined form. The application need of soil is required to determine the type of mineral required and the appropriate ash rate (Shaheen, Hooda and Tsadilas, 2014b)**.** The use of coal ash can inhibit the respiration of soil microbes and enzyme activities which, can result in deleterious influence on the soil conditions (Nayak *et al.*, 2015).

The use of biomass ash based on waste generation and thermal process of a particular area is important as it addresses environmental challenge. It is also a recycling technique; although using this technique when it is not appropriate such as overdose application, could pose danger to the soil. Therefore, consideration for diversification would be an effective approach to achieving a more efficient utilisation target. The cost of waste is a factor due to its implication on the prices of products. It could be complex to tag a value to ash but, the process could have a relative impact on the utilisation chain. Available data show that energy from biomass contributes to 59,2 EJ/yr or 10.3% to the global prime energy supply (Giwa *et al.*, 2017)**.** Lauri et al. (2014) made this assumption and projected it to be 18% by 2050**.** An electricity output of about 1.5 MWh/ton of biomass, which results in 483 TWh of an electric production. Therefore, considering 3-15% ash production means that around 10 Million tonnes of ashes can be produced from biomass electricity projects (James *et al.*, 2012). The primary goal of biomass ash application is the re-introduction of basic nutrients that are lost due to harvesting. Although this may have counter influence on the soil chemical properties and a sharp increase in nutrient concentration and sudden pH change may be unworthy**.** Fernández-Delgado et al (2019) suggested that care must be taken to minimise risk.

The already existing field trials in agriculture confirmed the availability of vital nutrients as the factor for its soil fertility in Thailand, Italy (Carcasci, Mussato and Neri, 2017), USA (Headlee and Hall, 2015) and Nigeria (Ajala, Awodun and Oladele, 2017).

The biochemical and physiological influences of the ash; on soil and crops require further techniques of study (Karltun *et al.*, 2008). Therefore, Wilczyńska-Michalik et al (2018) suggested the use of ash from multiple sources, because of nutrient variety make-up. Coal fly as was combined with biomass fly ash for soil amelioration and the result showed an improved fertility (Vamvuka and Kakaras, 2011; Yeboah *et al.*, 2014). In the study by Brod et al (2012), bottom ash was mixed with fly ash and the resultant influence produced an increased crop yield of 15%. The possibility of heterogeneous waste ash was tried in some studies (Grau *et al.*, 2015; Silva *et al.*, 2017; Tripathi *et al.*, 2019). Basically, they reported an improved effect on soil and crop. However, did not discuss the soil mechanism interaction. Therefore, the necessity to further evaluate the relative influence of ashes from heterogeneous waste. Hence, this study aims is to evaluate the potentials, quantification rate of application and the soil response relative to yield. Furthermore, the impact of application of ashes from heterogeneous waste stream, and this requires comprehensive evaluation to fulfil an optimal integration of heterogeneous wastes.

2.2 Mineral composition of biomass ash relative to the influence on soil properties and plant growth

Several literatures show that biomass ash contain micro and macro nutrients and some reported the suitability to the soil. Some studies explored the leaching of biomass ash by serial extractions, set leaching tests and percolation tests (Supancic *et al.*, 2014; Liu *et al.*, 2020). Fernández-Delgado et al. (2019) confirmed the deficiency of C and N which are emitted and eliminated as gaseous oxides in the thermal process. The acid neutralising effect of the ash is attributable to the presence of carbonates and hydroxides (Fernández-Delgado *et al.*, 2019). The ash may contain heavy metals, although they are essential nutrients; however, these heavy metals could form insoluble soil organic matter (Fernández-Delgado *et al.*, 2019)**.** Biomass ash also contains traces metalloids and does not depend on the parent feedstock (Freire, Lopes and Tarelho, 2015; Nikravan, Ramezanianpour and Maknoon, 2020).

The degree of solubility of biomass ash depends on various chemical and physical dynamics such as the type of biomass feedstock, particle sizes and variation between mineral elements (Quirantes *et al.*, 2016). Oxides and hydroxides of potassium dissolves faster than that of calcium and magnesium (Emmanuel-Ikpeme, 2014). In acidic soils there is always a phosphorous adsorption challenge due to complex formation with Al and Fe (Quirantes *et al.*, 2016). In this case the increase in microbial activity can influence the mineralisation and plant available N. Table 2-1 outlines nutrients and relative influence on soil and plant. It also compares the nutrient availability of fly and bottom ashes.

Table 2-1 Nutrients available in biomass ash and their overall impact on soil and plant

Nutrients and major elements	Biomass bottom ash (Füzesi, Heil and Kovács, 2015; Tosti *et al.*, 2019)	Biomass fly ash (Fernández-Delgado *et al.*, 2019; Tosti *et al.*, 2019)	Influence of ash on soil properties and plant growth	Reference
pH	10.3-12.2	10.3-12.7	Influence on soil bacteria, nutrient leaching, nutrient availability and soil structure. Increase in pH enhances biodegradation, nitrification and denitrification.	(Neina, 2019)
Electrical Conductivity (EC) (mS/cm)	7-12	6.7-19.1	Correlate with particle size and texture of the soil Increase in EC improves water holding capacity It can also result in the balance of soil porosity and temperature	(Spekreijse *et al.*, 2020)
Macronutrients (g/kg)				
Al	14-40	3.6-26	Limits plant growth when in excess Enhances phosphorous efficiency	(Rob *et al.*, 2020)
Ca	79-300	100-280	Maintains chemical balance of the soil Lack of calcium results in root diseases	(White and Broadley, 2003)
Cu	0.06-0.2	0.1-1.1	Promotes enzymatic activities in plant Vital for seed production Cu toxicity is difficult to correct	(Sonmez *et al.*, 2006)
Fe	4.6-26	2.8-59	Components of many vital enzymes Promotes synthesis of chlorophyll	(Ribeiro *et al.*, 2017)

N	0.2-0.4	1.6-4.9	Increases microbial activities	(Moragues-Saitua, Arias-González and Gartzia-Bengoetxea, 2017)
K	35-73	40-160	Maintain water balance Increase plant tolerance to disease Increase root growth	(Saraswat and Chaudhary, 2015)
Mg	16-44	19-50	Enhances crop tolerance to stress Increase crop yield Mg is mobile in the soil	(Brueck and Senbayram, 2009)
P	7.2-22	4.3-22.9	Increases crop yield It reacts rapidly in the soil for good germination It has rapid impact on crop development	(Ryan *et al.*, 2013)
S	0.1-2.5	4.2-25	Influences rate of germination Essential for Nitrogen-fixing nodules on legumes Formation of chlorophyll	(Klikocka *et al.*, 2020)
Micronutrients (mg/kg)				
Mn	3470-19400	1300-30300	A co-factor for number of enzymes Improves plant productivity	(Nayak *et al.*, 2015)
Na	4800-12000	3100-12000	High content decreases crop production Reduces water intake Imposes osmotic stress	(Pugliese *et al.*, 2014)
Si	120000-250000	11000-124000	Influence on endogenous phytohormone Good for fibre crops	(Luyckx *et al.*, 2017)
Zn	65-950	370-40000	Helps to overcome stunted growth Chloroplast development	(Sharma *et al.*, 2013)

Heavy metals with environmental concern (mg/kg)				
As	1.4-3.2	1.5-24	Causes disruption of plant metabolism Causes low crop productivity	(Jackson and Punshon, 2015)
Ba	8802-2200	684-4300	Decreases in leaf area Results in reduced yield	(Francisco *et al.*, 2011)
Cd	0.1-5.7	0.1-34	Alteration of the minerals uptake Reduces the population of soil microbes	(Mahajan and Kaushal, 2018)
Co	4.2-11	5.8-13	Disturbs soil homeostatic Diffuses chlorosis of young leaves	(Chatterjee and Chatterjee, 2003)
Cr	25-320	26.5-290	Causes alteration in a germination process	(Tosti *et al.*, 2019)
Hg	0.02-0.1	1.7	Disturbance in cellular structure	(Luo and Tu, 2018)
Mo	1-5.8	1.5-16	Yellowing or browning of plants	(Liu *et al.*, 2019)
Ni	20-200	19-74	It is concentration sensitive Reduces seed germination Causes chlorosis and necrosis	(Hassan *et al.*, 2019)
Pb	4-80	10.7-470	Toxic to living organisms Inhibits biological function Causes biochemical dysfunction of plants	(Fahr *et al.*, 2013)
Se	0.1-16.7	0.24-24	Induces oxidative stress in the soil and plants	(Gupta and Gupta, 2017)
Sn	0.3-16	1.2-22	Its oxides resist weathering	(Müller *et al.*, 2015)
Sr	466-710	578-2100	Decreases growth rate in some plants and shortens roots system	(Chu *et al.*, 2015)

2.3 Mechanism of soil-ash balance, relationship and chemical alteration

Biomass ash for soil improvement should have some basic qualities and minimum suitability for intended application. Ash application is most suitable when there is a specific need or deficiency in the soil that the ash possesses. The amount of micro and macronutrients are essential determinant. The ecological behaviour is an indicator of how responsive and reactive the ash could be to the soil, which is also relative to the leaching behaviour.

As soil response ability differs, these considerations are vital to the application and weather is a unique factor that determines soil response to fertilizer application. Flooding and rate of run-off can also have a direct impact on how the soil interact with the ash, retaining ability and mineral dissolution. Soil physical and chemical status such as existing structure, past amendments, history and soil basic minerals are primary to application rate evaluation.

Otunyo and Chukuigwe (2018) examined the use of palm bunch ash for the pH balance of poor laterite soil. Anyaoha et al. (2018) did similar investigation for cassava but, in acidic soil. Some studies focused on the liming ability of ash; this is important as the pH plays vital role in soil nutrient absorption. The reason for appropriate application rate is due the ability of ash to rapidly change the soil pH. The primary cause of alkalinity due to ash application is CaO, when hydrolysed results in $Ca(OH)_2$ (Rousk *et al.*, 2010). The use of these ashes was reported to have improved the concentration of ammonifying microorganisms by 15%, the total and nitrifying microorganisms reduced (Ozolincius *et al.*, 2018)**.** When biomass fly ash was mixed with soil, the hydraulic conductivity was reduced by 65.4% (Daud *et al.*, 2016). Wójcik et al. (2020) relatively reported a reduction in the number of bacteria by 83–89% in a controlled laboratory setup and by 40–53% on a field scale.

The soil pH relationship in the biogeochemical process is proportional to the principle of biodegradation of organic pollutants and rhizosphere processes; these are reliant on the influence of the soil pH relative to external application.

Dissolution of organic matter and heavy metals are also contingent on the ions and charges of the components of the soil; hence, the nitrification and denitrification. The microbial ecophysiological indicators point towards the control of soil enzyme activities and ammonia volatilisation (Neina, 2019).

The effectiveness of biomass ash to transform soil pH has direct effect on ecophysiological indicators based on environmental and metabolic quotient. A decrease in microbial community at the initial phase of application makes C more available to plant. This influences the plant size, yield correction of sulphur and boron deficiency in the soil due to ash application is due to the ion exchange and the low Nitrogen in the ash (Neina, 2019).

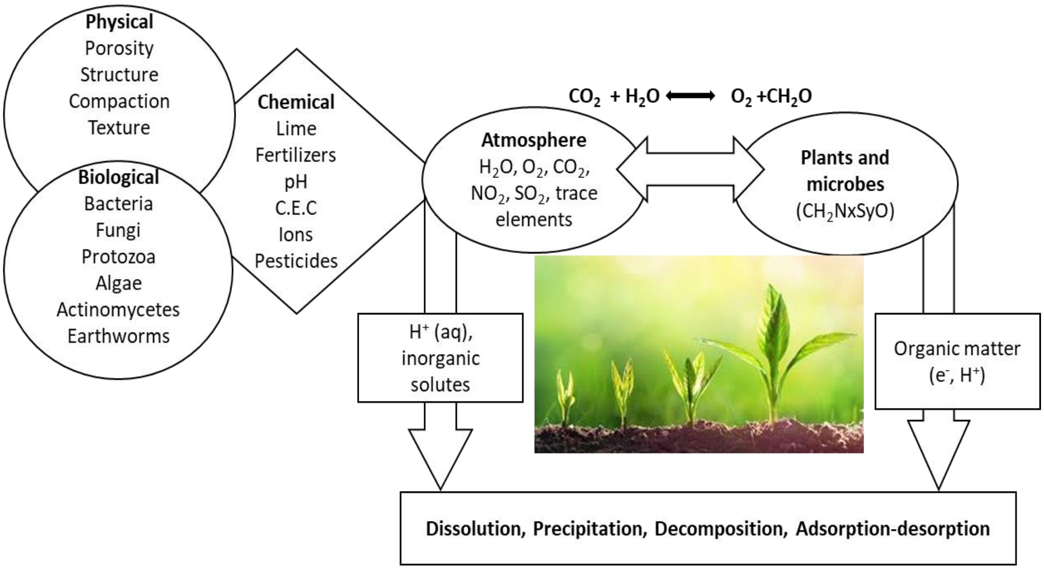


Figure 2-3 Soil-ash chemical interactions for plant growth

The soil chemical changes are vital in predicting the effect of fertilizer application. In studies reported by some literatures, they confirmed nutrient supply as the focus of ash addition (Schiemenz and Eichler-Löbermann, 2010; Headlee and Hall, 2015). Beyond addition of nutrients are soil chemical behaviour and response to applied nutrients as illustrated in the nutrient cycle in Figure 2-3; therefore, soil history and previous cropping system could influence the rate of reaction with ash (Maltas *et al.*, 2013).

The consideration of application rate relative to metalloids toxicity was reported by (Nayak *et al.*, 2015; Sharma *et al.*, 2017). These also result in the accumulation of heavy metals due to biomass ash application (Yu *et al.*, 2019). The concern for long term effect of ash application to soil was verified based on a 5-year investigation which showed that an increase in the number of leaves per plant of the leave. Although has not been studied in several plant and soils (Karltun *et al.*, 2008)**.**

Embrandiri et al. (2012) investigated the trend of soil properties with different application rate. At 10% application, there was no significant variations in pH and C: N ratio. With the subsequent increase in the application rate, electrical conductivity was increased by 20% and C: N ratio increased by 50% and stated this as the major difference between ash and biochar; the pyrolysis temperature which also influences the solubility of the residues. Although, the physiochemical properties show that biochar has higher carbon content (Aziz *et al.*, 2015)**.** The percentage carbon content of biochar is about 60% greater than ash and Nitrogen content is about 65% greater. Biomass ash has higher content of P, K, Mg and Ca and the pH range of biochar is within the nuetral line but pH of biomass ash is >12. (Zapałowska *et al.*, 2017; Saletnik *et al.*, 2018)**.** A positive impact on bacteria could increase N mineralization rates (Vestergård *et al.*, 2018) increasing the potential for inorganic N, which would enhance the fertilizer value of ash. The evaluation of the concentration range of biomass ash and lime shows ash to be higher than lime except for magnesium. However, biomass ash contains more heavy metals than lime (Risse, 2013). The Fe, Mg and heavy metal content of coal fly ash is higher than biomass fly ash. Al, Ca, K and P of biomass fly and bottom ashes are greater than coal fly ash (Shaheen, Hooda and Tsadilas, 2014b)**.** The solubility and availability of nutrients is low for P but high for potassium; therefore, follows the order K > Mg > Ca > P (Mandre, 2006).

2.4 Ash from heterogeneous waste stream for soil amelioration

Biomass thermal process can take multiple biomass feedstock, this however has several processing and residual impacts on the system. When more than a single biomass waste is used, the process plant should be fitted to accommodate the variations in process parameters. The demand for fuel and energy has stimulated biomass-to-fuel conversion processes and this exploits conservation of energy in the products. (Sorek *et al.*, 2014). Because, biomass ashes are richer than coal ashes in minerals, differential thermal analysis and objective overview of application techniques should be explored for an optimised process. Some studies evaluated the potentials of individual ashes and their effectiveness when combined. An ideal assessment from the point of application of heterogeneous biomass feedstock for thermal processes is necessary until the final stage of utilisation of the ashes for growing crops (Vamvuka and Kakaras, 2011). The process effect of heterogeneous waste is relative to the difference in moisture content and product characteristics shows that when multiple biomass materials are processed, there are changes in the rate different stages and forms of combustion (Tarelho *et al.*, 2015).

The design of power plants for heterogeneous waste process should be to accommodate different forms of biomass from feeder to combustion chamber. The mixed or multi-fuel design, the trial plants by CleanTech could take about twenty-five mixed fuels (Zając *et al.*, 2018). Mixed biomass generates more ashes and is well supported for soil amendment due to the rich qualities (Zając *et al.*, 2018; Liu *et al.*, 2020). The energy requirement for thermal processes could be classified based on the moisture content and particle sizes, the higher the energy requirements and process duration. The case design must account for the properties of the biomass mix and the combustion characteristics. Wattana et al. (2017) suggested that heterogeneous biomass could be more efficient both for process management and product quality. The co-mixture with coal which is considered environmentally friendly although could reduce the calorific value by 8% if biomass is 30% (Sasongko *et al.*, 2017). Residual target and yield of the thermal processes using heterogeneous waste can change the operation parameters, thereby influencing the target and resultant yield. This can result in the production of ashes with deposits of partially burnt carbon. The importance of heterogeneous biomass was emphasized by Zhao et al.(2013); however, reported that less temperature is required to get same result. Although this retained the mineral content of individual biomasses. There was no property change but could be further investigated with varies quantities (Bartlett, Venter and Marx, 2018).

Additional consideration with ashes and the potentials of nutrient intensity of mixed waste for soil application must possess a level of minerals and a minimum quantity of heavy metals. The mixture of ashes from different biomass material could improve the soil requirements and demands. Using the ash properties such as physical, chemical, leaching behaviour and mineralogy, confirm that so many properties affect the properties and qualities of ash and focus should be more on the impact of economic and environmental benefits of ash utilisation (Nikravan, Ramezanianpour and Maknoon, 2020) and the qualities for mixed biomass could satisfy soil application (Biedermann and Obernberger, 2005). Ash co-application with biochar resulted in increased yield of 8-68% compared to control plot and this could be linked to the absorption rate of ash mineral content to the soil (Saletnik *et al.*, 2018). Some biomass materials produce ash rich in a particular mineral; therefore, the mixture of ashes from different sources or heterogeneous waste stream could result in the availability of different classes of nutrients for plant and crop use. When nutrients are supplied in adequate measures, there is direct influence on the crop yield. The mixture can summarily, influence the soil structure thereby being an alternative option to chemical fertilizers. Crop needs could also be fulfilled when there are wide range of nutrient availability and therefore influence crop growth and harvest yield (International and Journal, 2016).

The environmental influence and biomass plant feedstock requirements for mixed waste is profitable. Though, agricultural waste is commonly used in thermal process and made of different forms, it could be more efficient to utilise in a multiple streams to minimise wastage. Li et al. (2016) suggested that the mixed waste could also reduce cost, make the entire process energy efficient and improve biomass supply systems. There could be perceived challenges, due the fact that ashes contain low presence of heavy metals; therefore, the possibilities of have unburnt carbon and exposure results in the accumulation. Zając et al. (2018) argued that the quantity of heavy metals is safe enough to be used in soil; however, the application rate can play a vital role in controlling the effect on both soil and crops. The risk is considered higher in biochar than in ash (Liu *et al.*, 2020). The actual identified challenges of the heterogeneous biomass technique are the non-uniform characteristics of the ashes and could cause disparity on its effect on common field (Mierzwa-Hersztek *et al.*, 2019) and to overcome this, the ash could be mixed with water prior to application to obtain a uniform solution throughout the field. This would address the differences in particle sizes (Kenney *et al.*, 2013).

2.5 The response coefficient of different ash types to crop yield

The co-application of coal fly and bottom ashes in the soil preserves soil carbon. This influenced the grain yield and individual grain weight (Lim *et al.*, 2017). When coal ash is combined with NPK, the growth and yield of wheat was increased (Tripathi *et al.*, 2019) and 10 tonnes/ha of coal ash increased paddy yield by 15% (Saraswat and Chaudhary, 2015). Assenting to Mittra et al. (2005),10 tonnes/ha of FA when combined with other fertilizers results in greater yield more than when chemical fertilizers alone. This addition of FA promotes root development due to soil textural vicissitudes, better water-holding capacity and more developed pore space (Ukwattage, Ranjith and Bouazza, 2013). The use of biomass bottom and FA for field experiments were done on an acidic sandy loam using biomass ash at the rate of 2.4 kg/plot. The resultant effects show on the growth indices and chlorophyll content for maize (Ajala, Awodun and Oladele, 2017).

When biomass ashes are applied to the soil, the response is more effective on acidic soils because carbonates, bicarbonates, sulphates, P, K, B, Ca, Mg, Mn, and Zn, increase at a good rate (Vassilev *et al.*, 2013). NPK co-mixed biomass ashes also have quick responses. According to an experiment in Omoku and Umudike in Nigeria where the effects of PWA was evaluated in comparison with NPK, 2.5 tonnes/ha biomass ash resulted in highest mean root yield and tuber yield of sweet cassava; higher than single NPK application by 83% (Ojeniyi *et al.*, 2009). Biochar mixed with FA resulted in 8–68% over the two years of research when compared with the control plots, at the application rate of 1.5 tonnes/ha (Saletnik *et al.*, 2018). Ashes from heterogeneous waste from the combination of fly and bottom ashes in some conventional and non-research applications are considered to have a balanced nutrient factor and could possess high soil nutrient coefficient (Maresca, Hyks and Astrup, 2017). Variations of heterogeneous biomass ash is indicative on the individual biomass ashes and the individual properties summed up (Toscano and Corinaldesi, 2010; Wirth *et al.*, 2016). However, during the thermal process, the agglomeration index, ash fusibility index and slag viscosity index could impact on the physical properties of the ash, thereby influencing the mineral dissolution index (ToxicoWatch *et al.*, 2016). Kleinhans et al. (2018) further illustrated how soil properties and fertility are improved by ash addition. The presence of oxygen in the soil at a higher temperature gradient reacts with the sulphates and carbonates, water molecules also causes dissolution of soluble mineral compounds; therefore, causing a release of nutrients to the plant, improve soil aeration. Moisture plays significant role when ash is applied to the soil.

2.6 Palm waste thermal residual ash, its potency as fertilizer and application rate

About 4 million tonnes of palm waste ash is generated annually (Ooi *et al.*, 2014). Saletnik et al. (2018) observed a 20% increase in germination rate with 15 g per 200 g of soil and attributed to potassium content. Conversely, there are few reports on nursery preparation using fly ash. Several application rates had been reported to have given different yields. Although, these depend on the type of soil, crops and the soil response to the application rate range. In some studies, the ash was mixed with biochar or other soil fertility enhancer. The yield range of 8-68% was reported by (Saletnik *et al.*, 2018) at an application rate of 1.5 tonnes/ha (Ribeiro *et al.*, 2017)**.** Using an application rate as low as 7.5 mg/ha and recorded an improvement in soil pH (Ribeiro *et al.*, 2017)**.** High chlorophyll and carotenoid content were reported by (Khan and Khan, 1996). When ash was applied on tomatoes, with a yield of 60-70% increment. Brod et al (2012) reported an improved plant growth due to the application of ash. The study also compared the application with lime, higher physiological influence was got from the application of biomass ash. The response of different crops to fertilizer application differs; tubers requires well loosed loamy and pH of 5-5.5. Legumes requires sandy and silty soil and a pH of 6-6.5. Vegetables requires highly organic soil with soil pH of 6-7 and well-balanced trace nutrients. Every area has some particular types of crops they produce, their waste centres on those particular crops. This also affect the feedstock of the biomass thermal system available in that area.

Oil palm thermal residues have been used in agriculture and they possess an appropriate amount of nutrients capable of influencing the chemical and physical behaviour of the soil. A study by Adjei-Nsiah and Obeng (2013) shows that the application of palm-based ash (PBA) promotes vegetative growth. In the same study, the crop yield of pepper and other vegetables were increased by up to 83%. These are due to the liming effect and nutrient supplement. The macro nutrients were made adequate by 2 tonnes per hectare application.

In a study with thirteen treatments and three replications, the mixture of PBA and poultry manure increased the physical characteristics of mango seedlings by 27%. The treatment proved to be effective at 8 tonnes/ha (Moyin-Jesu and Adeofun, 2008). Ooi et al. (2014) suggested that particle size of the ash is a factor to extent of their impact. This was supported by a study in Ishiagu, Nigeria, where the impact of PBA was beyond soil fertility but effective in the control of soybean Meloidogyne incognita infections with tendency to suppress root-knot nematode (Ogwulumba and Ogbuka, 2016). There is a further study which shows that PBA improves soil chemical properties and nutrient level from 0.27 - 0.37% N, 0.22 – 0.37% P and 1.14% K at 2.5 tonnes/ha application rate for growing cassava (Ojeniyi *et al.*, 2009). It widely suggested that PBA are most effective in acidic soil due to their ability to transform the soil acidity within a short period (Otunyo and Chukuigwe, 2018). The effectiveness of PBA although not effectively tried with several crops and in many locations; however, could be an alternative to chemical fertilizer and also a waste utilisation technique.

2.7 The challenges of biomass ash application to the soil

The utilisation of biomass ash looks promising in agriculture. However, the potential risk is due to the content of heavy metals (Kalembkiewicz, Galas and Sitarz-Palczak, 2018) and worth consideration. Although, it is reported to have influenced the mycorrhizal community and the risk quotient is still classified as low (Cruz-Paredes *et al.*, 2017). The few negative influences of biomass ash application to the soil was reported by (Freire, Lopes and Tarelho, 2015). The study described biomass ash application to the soil as ineffective in the growth of certain crops. However, failed to report the application rate. García-Sánchez et al (2015) highlighted some of the long-term effect relative to the type of soil the project worked on. Other reported effects were based on individual crops. In rice produce, heavy metals from the soil have been enlisted as one of the major challenges. Therefore, Cruz-Paredes et al (2017) advised on the precautions for using biomass ash as a substitute to chemical fertilizers.

Further studies on the negative impact of ash, could result in investigation into the adsorption limits by plants and how dissolution in water before application could minimise the concentration of certain heavy metals. This can also provide more opportunities for studying the efficiencies in a combined form with other organic fertilizers and regulation of ratios of the nutrients that pose threats to particular crops. The greatest concern of biomass ash is the incidence of heavy metals which are in traces. Cd incorporates into the biological system of plants and bio accumulates to create challenges due to its ability to replace Zn in metabolic processes and cause DNA damage. Cd in high concentration in the soil could also result in apoptosis inhibition (Sharma *et al.*, 2013). The accumulation of heavy metals can be exported to the ecosystem with indirect effect on human and the ecosystem.

The economics of biomass waste availability is key to evaluation of how the application of ash can improve yield and relatively reduce cost of production. The cost of fertilizer and how this impact on the price of goods. Babalola et al.(2012) studied the economic impact of fertilizer relative to cost and substituting chemical fertilizers with biomass ash would reduce the product cost by more than 10%. Locations of availability and relativity of access to fertilizer affects the logistics in the supply chain if ash is considered a choice. Gathering, storage and transportation in the fertilizer supply chain is most engaging factor; therefore, a process model up to the field of application can be modelled using the available data from projects and locations. Evaluating location of thermal plants and crop processing mills could be measured for each location relative to the type of crop grown in that area. It is reported that the insufficiency of biomass ash as a chemical fertilizer substitute (Okmanis, Petaja and Lupik¸is, 2017). Vassilev and Vassileva (2019) also expressed concern on how non-steady application and interchange with chemical fertilizer can result in unbalance of soil chemical relationship. However, did not consider that as a major threat to crop production.

Potential negative effects on the environment and humans are due to heavy metals, of which percentage compositions depend on the type of feedstock, process techniques and thermal process temperature. The toxicity to the soil also depends on the application rate therefore, appropriate analysis of the ash, crop and soil are required to get the right balance for crop growth. The tolerance of biomass ash as a fertilizer is not reported yet. The intermittent and continuous application could be evaluated to determine the long-term chemical influence on the environment. However, most studies argued that the amount of heavy metals in the biomass ash is not enough to create soil challenges because, ash reacts with water and slows down the solubility of heavy metals (Freire, Lopes and Tarelho, 2015). Contamination of feedstock can result in the contamination of ash (Johansson and Van Bavel, 2003). Huotari et al. (2015) recounted that the upsurge in fungi-bacteria ratio due to ash addition could result in the reduction in the activities of fungal feeding pathway.

The government policy on waste utilisation plays a major role in controlling the level of production and utilisation. Policies should be tailored to promote the agenda of utilisation of biomass ash in agriculture. One of the major agricultural waste generates in high volume of which waste is effective in the production of biofuels and biodiesel is palm waste. Palm waste has about 5 different types of processing waste. These wastes can be used in individually or in a combined form in a thermal process plant. The resultant ashes have been investigated in several studies as one of the best biomass ashes for soil amelioration due to its low content of heavy metals and sufficient soil nutritional contents (Brod, Haraldsen and Breland, 2012).

Other technical and non-technical challenges of ash application to the soil; non-uniformity of biomass ashes cause difficulty in mineral determination as different portions are not same. The influence of partially burnt carbon materials in the ash is also a major factor in the non-uniformity of ash components (James *et al.*, 2012). There are different compositions of ash produced by same process and this is due to the use of different kinds of biomass in the thermal process (Garba, 2015). The policies affect the use of organic materials for growing crops in different countries. In some countries, biomass ash is classified as biomass, in some they are chemical waste while in Africa, there is no policy on disposal and reuse. Thermal process companies follow their individual waste policies and regulations on biomass ash disposal. Although, these could also be affected by the size of production, feedstock and reuse agenda (Burgess *et al.*, 2012).

Framework on agricultural policies also determine the soil requirement, type of crops and the techniques of applications. Local policies on utilisation of chemical fertilizers are important in the implementation of ash addition. Insufficient study data and low rate of advancement in the application of non-chemical fertilizers have affected the use of biomass ash. However, (Rhebergen *et al.*, 2016) suggested soil differences as the major reason for inappropriate us of ash. Cultural practices and weather influence on soil behaviours could impact on the decision to use ash. Furthermore, the uncertainty on long term effect could result in fear of the unknown. Location of thermal plants to application sites could cause a high operating cost thereby discourage the use in large-scale. The insufficient volume of ash in some area could be a discouraging factor. The transport and storage of the ash could be complex. The appropriate application techniques could discourage non-experienced farmers.

There are few technical regulations and standards for fly ash used in engineering BS EN 450-1: 2012. The regulations for the use of ash as fertilizer are based on heavy metals content and does not have a legal undertone. However, some countries ensure a standard practice to ensure the biomass feedstock is not contaminated. There are limits for maximum load of heavy metal application. Lack of supply chains for ash utilization and difficult to trace some origins of ashes and this requirement could impact on the cost. The challenge of quality variance between different plants and the degradation in quality over time. Also, different boilers and process parameters affect the quality of ash produced. There is limitation of knowledge and awareness for the use of ash in agriculture. Therefore, there is no global market price and recognition.

2.8 Conclusion

The utilisation of biomass ash in agriculture is effective, when applied rightly. This has been experimented in several projects. It is yet be adopted as an appropriate substitute to chemical fertilizers. The outcome of most field trials show that, it has ability to influence the soil nutrient thereby improve yield. Due to a balanced concentration of micro and macro minerals, ash has a significant effect on the crop development and yield. Although, in most cases, it is co-applied with other fertilizers; however, it can be applied independently. The issue of variability of heterogeneous feedstock and resultant ashes could improve waste management techniques; therefore, contribute to overall process efficiency. Biomass ash has the ability to reduce soil acidity and enhance nutrient transport. Right application rate, right crop and appropriate season are influential on the effectiveness. To avoid altering the chemical balance of the soil, moderate quantity should be applied and gradually increased with time. Ash applications to acidic soil can be done safely to stimulate microbial activity and nutrient transport. Adequate policy framework should be established in line with waste utilisation policies for the application of ash in agriculture especially in developing countries.

2.9 References

Adekayode, F. and Olojugba, M. (2010) *The utilization of wood ash as manure to reduce the use of mineral fertilizer for improved performance of maize (Zea mays L.) as measured in the chlorophyll content and grain yeild*, *Journal of Soil Science and …*. Available at: http://www.academicjournals.org/journal/JSSEM/article-full-text-pdf/523F8BE9571 (Accessed: 15 February 2019).

Adjei-Nsiah, S. and Obeng, C. B. (2013) *Effect of Palm Bunch Ash Application on Soil and Plant Nutrient Composition and Growth and Yield of Garden Eggs, Pepper and Okra*, *International Journal of Plant and Soil Science*. Available at: http://www.journalijpss.com/index.php/IJPSS/article/view/1890 (Accessed: 18 September 2018).

Ajala, R., Awodun, M. and Oladele, S. (2017) 'Effects of Wood Ash Biomass Application on Growth Indices and Chlorophyll Content of Maize and Lima bean Intercrop', *Turkish Journal of Agriculture - Food Science and Technology*, 5(6), pp. 614–621. doi: https://doi.org/10.24925/turjaf.v5i6.614-621.1093.

Anyaoha, K. E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) 'Evaluating oil palm fresh fruit bunch processing in Nigeria', *Waste Management and Research*, 36(3), pp. 236–246. doi: 10.1177/0734242X17751848.

Aziz, N. S. binti A., Nor, M. A. bin M., Manaf, S. F. binti A. and Hamzah, F. (2015) 'Suitability of Biochar Produced from Biomass Waste as Soil Amendment', *Procedia - Social and Behavioral Sciences*. Elsevier B.V., 195, pp. 2457–2465. doi: 10.1016/j.sbspro.2015.06.288.

Babalola, O. O., Ilori, M. O. and Adegbite, S. A. (2012) *Engineering Economic Analysis of Organic Fertilizer Production in Nigeria*, *International Journal of Engineering Research & Technology*. Available at: https://www.ijert.org/research/engineering-economic-analysis-of-organic-fertilizer-production-in-nigeria-IJERTV1IS9220.pdf (Accessed: 24 January 2019).

Bartlett, D., Venter, R. and Marx, S. (2018) ‘Effect of Biomass Feedstock Composition on Biochar Properties Produced Through Hydrothermal Liquefaction’, pp. 271–276. doi: 10.17758/eares4.eap1118263.

Biedermann, F. and Obernberger, I. (2005) *Ash-related Problems during Biomass Combustion and Possibilities for a Sustainable Ash Utilisation Friedrich Biedermann*, *Proceeddings of the Internacional Conference “World Renewable Energy Congress” (WREC)*. Available at: https://www.bios-bioenergy.at/uploads/media/Paper-Biedermann-AshRelated-2005-10-11.pdf (Accessed: 17 March 2020).

Brännvall, E. and Kumpiene, J. (2016) ‘Fly ash in landfill top covers – a review’, *Environ. Sci.: Processes Impacts*, 18(1), pp. 11–21. doi: 10.1039/C5EM00419E.

Brod, E., Haraldsen, T. K. and Breland, T. A. (2012) *Fertilization effects of organic waste resources and bottom wood ash: Results from a pot experiment*, *Agricultural and Food Science*. Available at: https://journal.fi/afs/article/view/5159/5782 (Accessed: 27 November 2019).

Brueck, H. and Senbayram, M. (2009) ‘Low nitrogen supply decreases water-use efficiency of oriental tobacco’, *Journal of Plant Nutrition and Soil Science*, 172(2), pp. 216–223. doi: 10.1002/jpln.200800097.

Burgess, P. J., Rivas Casado, M., Gavu, J., Mead, A., Cockerill, T., Lord, R., Van Der Horst, D. and Howard, D. C. (2012) ‘A framework for reviewing the trade-offs between, renewable energy, food, feed and wood production at a local level’, *Renewable and Sustainable Energy Reviews*, 16(1), pp. 129–142. doi: 10.1016/j.rser.2011.07.142.

Carcasci, C., Mussato, L. and Neri, M. (2017) ‘Biomass residues revaluation with energy production in a nursery company’, *Ecological Engineering*, 106, pp. 496–506. doi: 10.1016/j.ecoleng.2017.05.006.

Chatterjee, J. and Chatterjee, C. (2003) ‘Management of phytotoxicity of cobalt in tomato by chemical measures’, *Plant Science*, 164(5), pp. 793–801. doi: 10.1016/S0168-9452(03)00066-9.

Chen, Z., Hu, M., Zhu, X., Guo, D., Liu, S., Hu, Z., Xiao, B., Wang, J. and Laghari, M. (2015) ‘Characteristics and kinetic study on pyrolysis of five lignocellulosic biomass via thermogravimetric analysis’, *Bioresource Technology*. Elsevier Ltd, 192, pp. 441–450. doi: 10.1016/j.biortech.2015.05.062.

Chu, Q., Watanabe, T., Sha, Z., Osaki, M. and Shinano, T. (2015) ‘Interactions between Cs, Sr, and other nutrients and trace element accumulation in amaranthus shoot in response to variety effect’, *Journal of Agricultural and Food Chemistry*, 63(8), pp. 2355–2363. doi: 10.1021/jf5058777.

Cruz-Paredes, C., López-García, Á., Rubæk, G. H., Hovmand, M. F., Sørensen, P. and Kjøller, R. (2017) ‘Risk assessment of replacing conventional P fertilizers with biomass ash: Residual effects on plant yield, nutrition, cadmium accumulation and mycorrhizal status’, *Science of the Total Environment*, 575, pp. 1168–1176. doi: 10.1016/j.scitotenv.2016.09.194.

Daud, N., Norsyahariati, N., Muhammed, A. S. and Yaacob, W. Z. (2016) ‘Attenuation capacity of soil mixed with palm oil fuel ash (POFA) liner for treating leachate’, *Jurnal Teknologi*, 6(March), pp. 99–103. doi: 10.11113/jt.v78.9646.

Elum, Z. A. and Momodu, A. S. (2017) ‘Climate change mitigation and renewable energy for sustainable development in Nigeria: A discourse approach’, *Renewable and Sustainable Energy Reviews*, 76(February), pp. 72–80. doi: 10.1016/j.rser.2017.03.040.

Embrandiri, A., Rupani, P. F., Quaik, S., Ibrahim, M. H. and Rajeev, P. (2012) *Environmental Sustainability in the Palm Oil Industry ; Palm Waste as Nutrient Supplement and Effects on Plant Growth Characteristics*, *2012 International Conference on Environmental, Biomedical and Biotechnology*. Available at: http://www.ipcbee.com/vol41/010-ICEBB2012-H00011.pdf (Accessed: 22 March 2018).

Emmanuel-Ikpeme, C. (2014) ‘Comparative Evaluation of the Nutritional, Phytochemical and Microbiological Quality of Three Pepper Varieties’, *Journal of Food and Nutrition Sciences*, 2(3), p. 74. doi: 10.11648/j.jfns.20140203.15.

Fahr, M., Laplaze, L., Bendaou, N., Hocher, V., El Mzibri, M., Bogusz, D. and Smouni, A. (2013) 'Effect of lead on root growth', *Frontiers in Plant Science*, 4(JUN), pp. 1–7. doi: 10.3389/fpls.2013.00175.

Fernández-Delgado, J. M., Fabiani, G., Mazzier, T., Schönegger, D., Pietramellara, G., Gómez-Brandón, M. and Insam, H. (2019) 'Reclamation of Acid Soils with Biomass Ashes from Pyrolytic Wood Liquefaction', *Waste and Biomass Valorization*. Springer Netherlands, (0123456789). doi: 10.1007/s12649-019-00789-5.

Francisco, A. M., Nogueirol, R. C., Melo, L. C. A., Adriana, G. A. and da Fabiana, R. (2011) 'Effect of barium on growth and macronutrient nutrition in Tanzania guineagrass grown in nutrient solution', *Communications in Soil Science and Plant Analysis*, 42(13), pp. 1510–1521. doi: 10.1080/00103624.2011.581725.

Freire, M., Lopes, H. and Tarelho, L. A. C. (2015) 'Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F', *Waste Management*, 46, pp. 304–315. doi: 10.1016/j.wasman.2015.08.036.

Füzesi, I., Heil, B. and Kovács, G. (2015) 'Effects of wood ash on the chemical properties of soil and crop vitality in small plot experiments', *Acta Silvatica et Lignaria Hungarica*, 11(1), pp. 55–64. doi: 10.1515/aslh-2015-0004.

Garba, B. (2015) *Overview of Biomass Energy Resources, technologies and programmes in Nigeria*. Abuja, Nigera. Available at: http://cgpl.iisc.ernet.in/site/Portals/0/Publications/Presentations/EGM/10_Nigeria-egm.pdf (Accessed: 18 November 2019).

García-Sánchez, M., Siles, J. A., Cajthaml, T., García-Romera, I., Tlustoš, P. and Száková, J. (2015) 'Effect of digestate and fly ash applications on soil functional properties and microbial communities', *European Journal of Soil Biology*, 71, pp. 1–12. doi: 10.1016/j.ejsobi.2015.08.004.

Giwa, A., Alabi, A., Yusuf, A. and Olukan, T. (2017) 'A comprehensive review on biomass and solar energy for sustainable energy generation in Nigeria', *Renewable and Sustainable Energy Reviews*, 69(November 2016), pp. 620–641. doi: 10.1016/j.rser.2016.11.160.

Grau, F., Choo, H., Hu, J. W. and Jung, J. (2015) ‘Engineering behavior and characteristics of wood ash and sugarcane bagasse ash’, *Materials*, 8(10), pp. 6962–6977. doi: 10.3390/ma8105353.

Gupta, M. and Gupta, S. (2017) ‘An overview of selenium uptake, metabolism, and toxicity in plants’, *Frontiers in Plant Science*, 7(January), pp. 1–14. doi: 10.3389/fpls.2016.02074.

Hassan, M. U., Chattha, M. U., Khan, I., Chattha, M. B., Aamer, M., Nawaz, M., Ali, A., Khan, M. A. U. and Khan, T. A. (2019) ‘Nickel toxicity in plants: Reasons, toxic effects, tolerance mechanisms, and remediation possibilities—a review’, *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, 26(13), pp. 12673–12688. doi: 10.1007/s11356-019-04892-x.

Headlee, W. L. and Hall, R. B. (2015) ‘Biomass Fly Ash as Foliar Fertilizer for Hybrid Aspen Trees: Nutrient Uptake, Growth Response, and Compatibility with Nitrogen Fertilizer’, *Journal of Plant Nutrition*, 38(4), pp. 647–662. doi: 10.1080/01904167.2014.936615.

Huotari, N., Tillman-Sutela, E., Moilanen, M. and Laiho, R. (2015) ‘Recycling of ash - For the good of the environment?’, *Forest Ecology and Management*. Elsevier B.V., 348, pp. 226–240. doi: 10.1016/j.foreco.2015.03.008.

International, A. N. and Journal, Q. (2016) ‘Influence of biochar and biomass ash applied as soil amendment on germination rate of Virginia mallow seeds (Sida hermaphrodita R .) Bogdan Saletnik , Marcin Bajcar , Grzegorz Zaguła , Maria Czernicka , Czesław Puchalski Department of Bioenergy Technolog’, 5(3), pp. 71–76.

Jackson, B. P. and Punshon, T. (2015) ‘Recent Advances in the Measurement of Arsenic, Cadmium, and Mercury in Rice and Other Foods’, *Current environmental health reports*, 2(1), pp. 15–24. doi: 10.1007/s40572-014-0035-7.

James, A. K., Thring, R. W., Helle, S. and Ghuman, H. S. (2012) 'Ash management review-applications of biomass bottom ash', *Energies*, 5(10), pp. 3856–3873. doi: 10.3390/en5103856.

Johansson, I. and Van Bavel, B. (2003) 'Polycyclic aromatic hydrocarbons in weathered bottom ash from incineration of municipal solid waste', *Chemosphere*, 53(2), pp. 123–128. doi: 10.1016/S0045-6535(03)00299-6.

de Jong, J., Akselsson, C., Egnell, G., Löfgren, S. and Olsson, B. A. (2017) 'Realizing the energy potential of forest biomass in Sweden – How much is environmentally sustainable?', *Forest Ecology and Management*. The Authors, 383, pp. 3–16. doi: 10.1016/j.foreco.2016.06.028.

Kalembkiewicz, J., Galas, D. and Sitarz-Palczak, E. (2018) 'The physicochemical properties and composition of biomass ash and evaluating directions of its applications', *Polish Journal of Environmental Studies*, 27(6), pp. 2593–2604. doi: 10.15244/pjoes/80870.

Karltun, E., Saarsalmi, A., Ingerslev, M., Mandre, M., Andersson, S., Gaitnieks, T. and State, L. (2008) 'Wood ash recycling – possibilities', in Röser, D., Asikainen, A., Raulund-Rasmussen, K., Stupak, I. (Eds. . (ed.) *Sustainable Use of Forest Biomass for Energy: A Synthesis with Focus on the Baltic and Nordic Region*, pp. 79–108.

Kenney, K. L., Smith, W. A., Gresham, G. L. and Westover, T. L. (2013) 'Understanding biomass feedstock variability', *Biofuels*, 4(1), pp. 111–127. doi: 10.4155/bfs.12.83.

Khan, M. R. and Khan, M. W. (1996) 'The Effect of Fly Ash on Plant Growth and Yield', *Science*, 92(2), pp. 105–111. doi: 0269-7491(95)00098-4.

Kleinhans, U., Wieland, C., Frandsen, F. J. and Spliethoff, H. (2018) 'Ash formation and deposition in coal and biomass fired combustion systems: Progress and challenges in the field of ash particle sticking and rebound behavior', *Progress in Energy and Combustion Science*. Elsevier Ltd, 68, pp. 65–168. doi: 10.1016/j.pecs.2018.02.001.

Klikocka, H., Podlesna, A., Podlesny, J., Narolski, B., Haneklaus, S., Bloem, E. and Schnug, E. (2020) ‘Improvement of the content and uptake of micronutrients in spring rye grain DM through nitrogen and sulfur supplementation’, *Agronomy*, 10(1), pp. 1–11. doi: 10.3390/agronomy10010035.

Kronenberger, D. and Groß, B. (2018) ‘Chemical and Physical Analysis of Different Ash Fractions from Small Biomass Boilers’, *Chemical Engineering and Technology*, 41(11), pp. 2159–2167. doi: 10.1002/ceat.201800095.

Kumar, K., Kumar, S., Gupta, M. and Garg, H. C. (2017) ‘Characteristics of Fly Ash in Relation of Soil Amendment’, *Materials Today: Proceedings*. Elsevier Ltd, 4(2), pp. 527–532. doi: 10.1016/j.matpr.2017.01.053.

Lauri, P., Havlík, P., Kindermann, G., Forsell, N., Böttcher, H. and Obersteiner, M. (2014) ‘Woody biomass energy potential in 2050’, *Energy Policy*, 66(March), pp. 19–31. doi: 10.1016/j.enpol.2013.11.033.

Li, C., Aston, J. E., Lacey, J. A., Thompson, V. S. and Thompson, D. N. (2016) ‘Impact of feedstock quality and variation on biochemical and thermochemical conversion’, *Renewable and Sustainable Energy Reviews*, 65, pp. 525–536. doi: 10.1016/j.rser.2016.06.063.

Lim, S. S., Choi, W. J., Chang, S. X., Arshad, M. A., Yoon, K. S. and Kim, H. Y. (2017) ‘Soil carbon changes in paddy fields amended with fly ash’, *Agriculture, Ecosystems and Environment*, 245(June 2016), pp. 11–21. doi: 10.1016/j.agee.2017.03.027.

Liu, C., Hu, C., Tan, Q., Sun, X., Wu, S. and Zhao, X. (2019) ‘Co-application of molybdenum and zinc increases grain yield and photosynthetic efficiency of wheat leaves’, *Plant, Soil and Environment*, 65(10), pp. 508–515. doi: 10.17221/508/2019-PSE.

Liu, Z., Wang, L. ao, Xiao, H., Guo, X., Urbanovich, O., Nagorskaya, L. and Li, X. (2020) ‘A review on control factors of pyrolysis technology for plants containing heavy metals’, *Ecotoxicology and Environmental Safety*. Elsevier Inc., 191(January). doi: 10.1016/j.ecoenv.2020.110181.

Lohri, C. R., Faraji, A., Ephata, E., Rajabu, H. M. and Zurbrügg, C. (2015) ‘Urban biowaste for solid fuel production: Waste suitability assessment and experimental carbonization in Dar es Salaam, Tanzania’, *Waste Management and Research*, 33(2), pp. 175–182. doi: 10.1177/0734242X14564644.

Luo, Y. and Tu, C. (2018) ‘Twenty years of research and development on soil pollution and remediation in China’, *Twenty Years of Research and Development on Soil Pollution and Remediation in China*, (41771343), pp. 1–818. doi: 10.1007/978-981-10-6029-8.

Luyckx, M., Hausman, J. F., Lutts, S. and Guerriero, G. (2017) ‘Impact of silicon in plant biomass production: Focus on bast fibres, hypotheses, and perspectives’, *Plants*, 6(3). doi: 10.3390/plants6030037.

Mahajan, P. and Kaushal, J. (2018) ‘Role of Phytoremediation in Reducing Cadmium Toxicity in Soil and Water’, *Journal of Toxicology*, 2018. doi: 10.1155/2018/4864365.

Maltas, A., Charles, R., Jeangros, B. and Sinaj, S. (2013) ‘Effect of organic fertilizers and reduced-tillage on soil properties, crop nitrogen response and crop yield: Results of a 12-year experiment in Changins, Switzerland’, *Soil and Tillage Research*, 126, pp. 11–18. doi: 10.1016/j.still.2012.07.012.

Mandre, M. (2006) ‘Influence of wood ash on soil chemical composition and biochemical parameters of young Scots pine’, *Proceedings of the Estonian Academy of Sciences: Biology, Ecology*, 55(2), pp. 91–107. doi: 0269-7491(95)00098-4.

Maresca, A., Hyks, J. and Astrup, T. F. (2017) ‘Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties’, *Waste Management*, 70, pp. 127–138. doi: 10.1016/j.wasman.2017.09.008.

Michalik, M. and Wilczynska-Michalik, W. (2012) ‘Mineral and chemical composition of biomass ash’, *European Mineralogical Conference*, 1(July 2014), pp. 2012–423. doi: 10.13140/2.1.4298.5603.

Mierzwa-Hersztek, M., Gondek, K., Jewiarz, M. and Dziedzic, K. (2019) ‘Assessment of energy parameters of biomass and biochars, leachability of heavy metals and phytotoxicity of their ashes’, *Journal of Material Cycles and Waste Management*. Springer Japan, 21(4), pp. 786–800. doi: 10.1007/s10163-019-00832-6.

Mittra, B. N., Karmakar, S., Swain, D. K. and Ghosh, B. C. (2005) ‘Fly ash - A potential source of soil amendment and a component of integrated plant nutrient supply system’, *Fuel*, 84(11), pp. 1447–1451. doi: 10.1016/j.fuel.2004.10.019.

Moragues-Saitua, L., Arias-González, A. and Gartzia-Bengoetxea, N. (2017) ‘Effects of biochar and wood ash on soil hydraulic properties: A field experiment involving contrasting temperate soils’, *Geoderma*, 305(September 2016), pp. 144–152. doi: 10.1016/j.geoderma.2017.05.041.

Moyin-Jesu, E. I. and Adeofun, C. O. (2008) ‘Comparative evaluation of different organic fertilizers on the soil fertility, leaf mineral composition and growth of bitter kola seedlings’, *Emirates Journal of Food and Agriculture*, 20(1), pp. 31–45. doi: 10.9755/ejfa.v12i1.5179.

Müller, F. L., Cyster, L. F., Raitt, L. M. and Aalbers, J. (2015) ‘The effects of tin (Sn) additions on the growth of spinach plants’, *Phyton*, 84(2), pp. 461–465. doi: 0031 9457 (2015) 84: 461-465.

Nayak, A. K., Raja, R., Rao, K. S., Shukla, A. K., Mohanty, S., Shahid, M., Tripathi, R., Panda, B. B., Bhattacharyya, P., Kumar, A., Lal, B., Sethi, S. K., Puri, C., Nayak, D. and Swain, C. K. (2015) ‘Effect of fly ash application on soil microbial response and heavy metal accumulation in soil and rice plant’, *Ecotoxicology and Environmental Safety*. Elsevier, 114, pp. 257–262. doi: 10.1016/j.ecoenv.2014.03.033.

Neina, D. (2019) ‘The Role of Soil pH in Plant Nutrition and Soil Remediation’, *Applied and Environmental Soil Science*, 2019(3). doi: 10.1155/2019/5794869.

Nikravan, M., Ramezanianpour, A. A. and Maknoon, R. (2020) ‘Study on physiochemical properties and leaching behavior of residual ash fractions from a municipal solid waste incinerator (MSWI) plant', *Journal of Environmental Management*. Elsevier Ltd, 260(January). doi: 10.1016/j.jenvman.2019.110042.

Ogwulumba, S. I. and Ogbuka, A. D. (2016) 'Efficacy of Oil Palm Bunch Ash in Controlling Meloidogyne Incognita on Soybean (Glycine Max)', 05(02). doi: Int. J. Phytopathol. 05 (02) 2016. 55-60.

Ojeniyi, S. O., Ezekiel, P. O., Asawalam, D. O., Awo, A. O., Odedina, S. A. and Odedina, J. N. (2009) 'Root growth and NPK status of cassava as influenced by oil palm bunch ash', *African Journal of Biotechnology*, 8(18), pp. 4407–4412. doi: 10.5897/AJB2009.000-9418.

Okmanis, M., Petaja, G. and Lupik¸is, A. (2017) 'Productivity of mechanized wood ash application in forest', *Research for Rural Development*, 1, pp. 62–68. doi: 10.22616/rrd.23.2017.009.

Ooi, Z. X., Ismail, H., Bakar, A. A. and Teoh, Y. P. (2014) 'A review on recycling ash derived from Elaeis guineensis by-product', *BioResources*, 9(4), pp. 7926–7940. doi: 10.15376/biores.9.4.7926-7940.

Otunyo, A. W. and Chukuigwe, C. C. (2018) 'Investigation of the impact of palm bunch ash on the stabilization of poor lateritic soil', *Nigerian Journal of Technology*, 37(3), p. 600. doi: 10.4314/njt.v37i3.6.

Ozolincius, R., Armolaitis, K., Raguotis, A., Varnagiryte, I. and Zenkovaite, J. (2018) 'Influence of wood ash recycling on chemical and biological condition of forest Arenosols', *Journal of Forest Science*, 52(Special Issue), pp. 79–86. doi: 10.17221/10164-jfs.

Pugliese, S., Jones, T., Preston, M. D., Hazlett, P., Tran, H. and Basiliko, N. (2014) 'Wood ash as a forest soil amendment: The role of boiler and soil type on soil property response', *Canadian Journal of Soil Science*, 94(5), pp. 621–634. doi: 10.4141/cjss-2014-037.

Quirantes, M., Calvo, F., Romero, E. and Nogales, R. (2016) 'Soil-nutrient availability affected by different biomass-ash applications', *Journal of Soil*

Science and Plant Nutrition, 16(1), pp. 159–163. doi: 10.4067/S0718-95162016005000012.

Rhebergen, T., Fairhurst, T., Zingore, S., Fisher, M., Oberthür, T. and Whitbread, A. (2016) ‘Climate, soil and land-use based land suitability evaluation for oil palm production in Ghana’, *European Journal of Agronomy*, 81, pp. 1–14. doi: 10.1016/j.eja.2016.08.004.

Ribeiro, J. P., Vicente, E. D., Gomes, A. P., Nunes, M. I., Alves, C. and Tarelho, L. A. C. (2017) ‘Effect of industrial and domestic ash from biomass combustion, and spent coffee grounds, on soil fertility and plant growth: experiments at field conditions’, *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, 24(18), pp. 15270–15277. doi: 10.1007/s11356-017-9134-y.

Risse, M. (2013) *Best Management Practices for Wood Ash Used as an Agricultural Soil Amendment*, *UGA Cooperative Extension Bulletin 1142*. Available at: https://secure.caes.uga.edu/extension/publications/files/pdf/B1142_3.PDF (Accessed: 24 February 2020).

Rob, M. M., Hossen, K., Iwasaki, A., Suenaga, K. and Kato-Noguchi, H. (2020) ‘Phytotoxic activity and identification of phytotoxic substances from Schumannianthus dichotomus’, *Plants*, 9(1), pp. 1–12. doi: 10.3390/plants9010102.

Rousk, J., Bååth, E., Brookes, P. C., Lauber, C. L., Lozupone, C., Caporaso, J. G., Knight, R. and Fierer, N. (2010) ‘Soil bacterial and fungal communities across a pH gradient in an arable soil’, *ISME Journal*, 4(10), pp. 1340–1351. doi: 10.1038/ismej.2010.58.

Ryan, J., Ibrikci, H., Rashid, A. and Sommer, R. (2013) ‘Phosphorus in Low-Input Dryland Agriculture: The Perspective from Syria’, *Communications in Soil Science and Plant Analysis*, 44(16), pp. 2378–2392. doi: 10.1080/00103624.2013.794825.

Saletnik, B., Zagula, G., Bajcar, M., Czernicka, M. and Puchalski, C. (2018) ‘Biochar and biomass ash as a soil ameliorant: The effect on selected soil properties and yield of giant miscanthus (Miscanthus x giganteus)’, *Energies*, 11(10). doi: 10.3390/en11102535.

Saraswat, P. K. and Chaudhary, K. (2015) *Effect of Fly Ash (FA) to improving soil quality and increase the efficiency of crop productivity*, *European Journal of Biotechnology and Bioscience*. Available at: https://www.semanticscholar.org/paper/Effect-of-Fly-Ash-(FA)-to-improving-soil-quality-of-Saraswat-Chaudhary/b9f674536a51b432b436be76eb808b9dae6ad6c5 (Accessed: 3 August 2019).

Sasongko, D., Wulandari, W., Rubani, I. S. and Rusydiansyah, R. (2017) ‘Effects of biomass type, blend composition, and co-pyrolysis temperature on hybrid coal quality’, *AIP Conference Proceedings*, 1805(January). doi: 10.1063/1.4974430.

Schiemenz, K. and Eichler-Löbermann, B. (2010) ‘Biomass ashes and their phosphorus fertilizing effect on different crops’, *Nutrient Cycling in Agroecosystems*, 87(3), pp. 471–482. doi: 10.1007/s10705-010-9353-9.

Shaheen, S. M., Hooda, P. S. and Tsadilas, C. D. (2014) ‘Opportunities and challenges in the use of coal fly ash for soil improvements - A review’, *Journal of Environmental Management*. Elsevier Ltd, 145, pp. 249–267. doi: 10.1016/j.jenvman.2014.07.005.

Sharma, A., Patni, B., Shankhdhar, D. and Shankhdhar, S. C. (2013) ‘Zinc - An Indispensable Micronutrient’, *Physiology and Molecular Biology of Plants*, 19(1), pp. 11–20. doi: 10.1007/s12298-012-0139-1.

Sharma, B., Sarkar, A., Singh, P. and Singh, R. P. (2017) ‘Agricultural utilization of biosolids: A review on potential effects on soil and plant grown’, *Waste Management*, 64, pp. 117–132. doi: 10.1016/j.wasman.2017.03.002.

Shi, R. yong, Li, J. yu, Ni, N., Mehmood, K., Xu, R. kou and Qian, W. (2017) ‘Effects of biomass ash, bone meal, and alkaline slag applied alone and combined on soil acidity and wheat growth', *Journal of Soils and Sediments*, 17(8), pp. 2116–2126. doi: 10.1007/s11368-017-1673-9.

Silva, R. V., de Brito, J., Lynn, C. J. and Dhir, R. K. (2017) 'Use of municipal solid waste incineration bottom ashes in alkali-activated materials, ceramics and granular applications: A review', *Waste Management*. doi: 10.1016/j.wasman.2017.06.043.

Sonmez, S., Kaplan, M., Sonmez, N. K., Kaya, H. and Uz, I. (2006) 'High level of copper application to soil and leaves reduce the growth and yield of tomato plants', *Scientia Agricola*, 63(3), pp. 213–218. doi: 10.1590/S0103-90162006000300001.

Sorek, N., Yeats, T. H., Szemenyei, H., Youngs, H. and Somerville, C. R. (2014) 'The implications of lignocellulosic biomass chemical composition for the production of advanced biofuels', *BioScience*, 64(3), pp. 192–201. doi: 10.1093/biosci/bit037.

Spekreijse, J., Vis, M., Reumerman, P., Pfau, S. and Lammens, T. (2020) *Renewable residential heating with fast pyrolysis bio-oil*, *Residue 2 Heat*. Available at: https://cordis.europa.eu/project/id/654650 (Accessed: 12 June 2020).

Supancic, K., Obernberger, I., Kienzl, N. and Arich, A. (2014) 'Conversion and leaching characteristics of biomass ashes during outdoor storage - Results of laboratory tests', *Biomass and Bioenergy*. Elsevier Ltd, 61, pp. 211–226. doi: 10.1016/j.biombioe.2013.12.014.

Tarelho, L. A. C., Teixeira, E. R., Silva, D. F. R., Modolo, R. C. E., Labrincha, J. A. and Rocha, F. (2015) 'Characteristics of distinct ash flows in a biomass thermal power plant with bubbling fluidised bed combustor', *Energy*. Elsevier Ltd, 90, pp. 387–402. doi: 10.1016/j.energy.2015.07.036.

Toscano, G. and Corinaldesi, F. (2010) 'Ash Fusibility Characteristics of Some Biomass Feedstocks and Examination of the Effects of Inorganic Additives', *Journal of Agricultural Engineering*, 41(2), p. 13. doi: 10.4081/jae.2010.2.13.

Tosti, L., van Zomeren, A., Pels, J. R., Dijkstra, J. J. and Comans, R. N. J. (2019) 'Assessment of biomass ash applications in soil and cement mortars', *Chemosphere*, 223(2019), pp. 425–437. doi: 10.1016/j.chemosphere.2019.02.045.

ToxicoWatch, Wirth, X., Yeboah, N. N. N., Burns, S. E., Williams, C. L., Westover, T. L., Emerson, R. M., Tumuluru, J. S., Li, C., Mittra, B. N., Karmakar, S., Swain, D. K., Ghosh, B. C., Pintana, P. and Tippayawong, N. (2016) 'Predicting ash deposit tendency in thermal utilization of biomass', *Engineering Journal*, 20(5), pp. 15–24. doi: 10.4186/ej.2016.20.5.15.

Tripathi, N., Hills, C. D., Singh, R. S. and Atkinson, C. J. (2019) 'Biomass waste utilisation in low-carbon products: harnessing a major potential resource', *npj Climate and Atmospheric Science*. Springer US, 2(1). doi: 10.1038/s41612-019-0093-5.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R. and Anthony, E. (2020) 'Preparation and Characterisation of Activated Carbon from Palm Mixed Waste Treated with Trona Ore', *Molecules*, 25(21), p. 5028. doi: 10.3390/molecules25215028.

Ukwattage, N. L., Ranjith, P. G. and Bouazza, M. (2013) 'The use of coal combustion fly ash as a soil amendment in agricultural lands (with comments on its potential to improve food security and sequester carbon)', *Fuel*, 109, pp. 400–408. doi: 10.1016/j.fuel.2013.02.016.

Vamvuka, D. and Kakaras, E. (2011) 'Ash properties and environmental impact of various biomass and coal fuels and their blends', *Fuel Processing Technology*. Elsevier B.V., 92(3), pp. 570–581. doi: 10.1016/j.fuproc.2010.11.013.

Vassilev, S. V., Baxter, D., Andersen, L. K. and Vassileva, C. G. (2013) 'An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification', *Fuel*. Elsevier Ltd, 105, pp. 40–76. doi: 10.1016/j.fuel.2012.09.041.

Vassilev, S. V. and Vassileva, C. G. (2019) ‘Water-Soluble Fractions of Biomass and Biomass Ash and Their Significance for Biofuel Application’, *Energy and Fuels*, 33(4), pp. 2763–2777. doi: 10.1021/acs.energyfuels.9b00081.

Vestergård, M., Bang-Andreasen, T., Buss, S. M., Cruz-Paredes, C., Bentzon-Tilia, S., Ekelund, F., Kjøller, R., Hindborg Mortensen, L. and Rønn, R. (2018) ‘The relative importance of the bacterial pathway and soil inorganic nitrogen increase across an extreme wood-ash application gradient’, *GCB Bioenergy*, 10(5), pp. 320–334. doi: 10.1111/gcbb.12494.

Wattana, W., Phetklung, S., Jakaew, W., Chumuthai, S., Sriam, P. and Chanurai, N. (2017) ‘Characterization of Mixed Biomass Pellet Made from Oil Palm and Para-rubber Tree Residues’, *Energy Procedia*. Elsevier B.V., 138, pp. 1128–1133. doi: 10.1016/j.egypro.2017.10.218.

White, P. J. and Broadley, M. R. (2003) ‘Calcium in plants’, *Annals of Botany*, 92(4), pp. 487–511. doi: 10.1093/aob/mcg164.

Wilczyńska-Michalik, W., Gasek, R., Michalik, M., Dańko, J. and Plaskota, T. (2018) ‘Mineralogy, chemical composition and leachability of ash from biomass combustion and biomass-coal co-combustion’, *Mineralogia*, 49(1–4), pp. 67–97. doi: 10.2478/mipo-2018-0008.

Wirth, X., Yeboah, N. N. N., Burns, S. E., Møller, H., Huber, F., Blasenbauer, D., Aschenbrenner, P., Fellner, J., Toscano, G., Corinaldesi, F., Kamble, M. G., Deokar, S. K., Mandavgane, S. A., Williams, C. L., Westover, T. L., Emerson, R. M., Tumuluru, J. S., Li, C., Pintana, P., Tippayawong, N., Farzad, S., Mandegari, M. A., Görgens, J. F., Wang, L., Skjevrak, G., Hustad, J. E., Skreiberg, Ø., Zając, G., Szyszlak-Bargłowicz, J., Gołębiowski, W., Szczepanik, M., Bogush, A. A., Dabu, C. I., Tikhova, V. D., Campos, L. C., Stegemann, J. A., Anoshin, G. N., Lira-Zúñiga, S., Sáez-Navarrete, C., Rodríguez-Córdova, L., Herrera-Zeppelin, L., Herrera-Urbina, R., Ruíz, A. A. B., Kitamura, H., Dahlan, A. V., Tian, Y., Shimaoka, T., Yamamoto, T., Takahashi, F., Maschowski, C., Kruspan, P., Garra, P., Talib Arif, A., Trouvé, G., Gieré, R., Wang, Q., Endo, T., Apar, P., Gui, L., Chen, Q., Mitsumura, N., Qian, Q., Niida, H., Animesh, S., Sekiguchi, K., Williams, C. L., Westover, T. L., Emerson, R. M., Tumuluru, J. S., Li, C. and ToxicoWatch (2016) ‘Sources of Biomass Feedstock Variability and the Potential Impact on Biofuels Production’, *Bioenergy Research*. Elsevier Ltd, 9(1), pp. 1–14. doi: 10.1007/s12155-015-9694-y.

Wójcik, M., Stachowicz, F. and Masłoń, A. (2020) ‘The Use of Wood Biomass Ash in Sewage Sludge Treatment in Terms of Its Agricultural Utilization’, *Waste and Biomass Valorization*, 11(2), pp. 753–768. doi: 10.1007/s12649-018-0518-0.

Yao, Z. T., Ji, X. S., Sarker, P. K., Tang, J. H., Ge, L. Q., Xia, M. S. and Xi, Y. Q. (2015) ‘A comprehensive review on the applications of coal fly ash’, *Earth-Science Reviews*, 141, pp. 105–121. doi: 10.1016/j.earscirev.2014.11.016.

Yeboah, N. N. N., Shearer, C. R., Burns, S. E. and Kurtis, K. E. (2014) ‘Characterization of biomass and high carbon content coal ash for productive reuse applications’, *Fuel*. Elsevier Ltd, 116(X), pp. 438–447. doi: 10.1016/j.fuel.2013.08.030.

Yu, C. L., Deng, Q., Jian, S., Li, J., Dzantor, E. K. and Hui, D. (2019) ‘Effects of fly ash application on plant biomass and element accumulations: a meta-analysis’, *Environmental Pollution*. Elsevier Ltd, 250, pp. 137–142. doi: 10.1016/j.envpol.2019.04.013.

Zając, G., Szyszlak-Bargłowicz, J., Gołębiowski, W. and Szczepanik, M. (2018) ‘Chemical characteristics of biomass ashes’, *Energies*, 11(11), pp. 1–15. doi: 10.3390/en11112885.

Zapałowska, A., Puchalski, C., Hury, G. and Makarewicz, A. (2017) ‘Influence of fertilization with the use of biomass ash and sewage sludge on the chemical composition of Jerusalem artichoke used for energy-related purposes’, *Journal of Ecological Engineering*, 18(5), pp. 235–245. doi: 10.12911/22998993/76214.

Zhao, L., Cao, X., Mašek, O. and Zimmerman, A. (2013) ‘Heterogeneity of biochar properties as a function of feedstock sources and production temperatures’, *Journal of Hazardous Materials*, 256–257, pp. 1–9. doi: 10.1016/j.jhazmat.2013.04.015.

3 A REVIEW OF CHEMICALS TO PRODUCE ACTIVATED CARBON FROM AGRICULTURAL WASTE BIOMASS

Kalu Samuel Ukanwa[1], Kumar Patchigolla[1]*, Ruben Sakrabani[2], Edward Anthony[1] and Sachin Mandavgane[3]

1 Centre for Thermal Energy and Materials, School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK.

2 Cranfield Soil and Agrifood Institute, Cranfield University, Cranfield MK43 0AL, UK.

3 Chemical Engineering Department, Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur 440010, Maharashtra, India.

Received: 11 October 2019; Accepted: 1 November 2019; Published: 6 November 2019

DOI: 10.3390/su11226204

Statement of contribution of joint authorship

The concept development, data collection and preparation of the original manuscript was done by Kalu Samuel Ukanwa. Kumar Patchigolla suggested the feedstock in focus and jointly provided supervision with Ruben Sakrabani. Sachin Mandavgane provided advice on the graphical representation of the data. Edward Anthony modified and edited the manuscript.

3.1 Introduction

Activated carbon (AC), is a carbonaceous solid derived from coal or biomass via thermal or thermochemical processes. ACs are typified by their well-developed pore morphology, remarkably high surface area, electron-conducting amphoteric tendencies and high adsorptive capacity (Pezoti *et al.*, 2016). AC is used widely in various applications beyond adsorption to treat various industrial effluents. Currently, the global market for AC is worth several billion dollars annually (Arena, Lee and Clift, 2016).

AC offers one of the best means for dealing with water and air pollution issues, which pose major health risks (Lu *et al.*, 2018). Such problems arise from effluent discharges from a wide array of industries, including the textile, brewing, chemical and food processing ones, and are due to inappropriate disposal of domestic and industrial wastes, and thermal processes, such as coal combustion (Rashidi *et al.*, 2012b). Advances in water treatment processes are dependent on the removal of impurities, heavy metals in particular (Teh *et al.*, 2016). Generally, the use of AC is one of the most acceptable means of waste water treatment, because of the wide range of production methods and target system applications for adsorbates (Bhatnagar *et al.*, 2013). Most often, the application of the adsorbate determines the production method and activating agent (Hadi *et al.*, 2015). AC is also useful as a battery component, such as in the production of capacitors (Ling *et al.*, 2013). AC can also be useful for treating the inhalation of poisonous gases and in cosmetic applications, like teeth whitening (Zhenchao *et al.*, 2015). Finally, ACs are also effective for drug overdose, hemoperfusion, removal of endogenous and exogenous toxins in uraemia and in the dressing of suppurating wounds to decrease odour (Pavlenko *et al.*, 2017).

AC can be synthesized from feedstock, such as petroleum residue, coal (in particular lignite), agricultural residues, wood and a range of biomass materials. Crop residue production is ubiquitous where agriculture is practiced and its production is more than 3107 Mt/a for 17 varieties of cereals and 25 varieties of legumes, and 3758 Mt/a for 27 food crops at the commercial level (Bentsen, Felby and Thorsen, 2014). Based on data from 227 countries, global production of agricultural residues for cereals was estimated to be about 3.7×10^{12} t/a (Bentsen, Felby and Thorsen, 2014). Waste management and disposal costs could be reduced by utilizing such materials in AC production (Nabais *et al.*, 2013). The abundance of agricultural waste generated globally remains a significant environmental issue (Liu, Zhang and Zhong, 2016) and AC production offers the prospect of using it as a renewable carbon source to produce highly porous AC. Another option is biochar production from agricultural waste, which is produced at much lower temperatures (250–500 ˚C) and typically has an average Brunauer–Emmett–Teller surface area ($S_{BET)}$ of 200 m^2/g, while for AC, S_{BET} typically exceeds 700 m^2/g.

According to global AC data, the market was estimated at $2007 million in 2012 and is expected to reach $5305 million by 2020. Here, the compound annual growth rate was estimated to be about 13.3% from 2014 to 2020 (Research, 2014). The chemical characteristics of AC are defined by the surface groups and chemical bonding of heteroatoms. The surface functional groups influence characteristics such as polarisation intensity, hydrophobicity, acidity and adsorption properties. The optimum activation temperature is also subject to various factors, such as physiochemical traits of the biomass, oxygen content, electrical and catalytic properties and the pollutant targeted (Chand Bansal and Goyal, 2005).

There are several methods of producing AC. However, the use of microwaves for AC production is attracting more research interest due to its numerous advantages compared to conventional heating techniques. These advantages include: uniform volumetric heating, internal heating, higher, selective heating, good regulation of the process and indirect contact with the heat source (Xiao *et al.*, 2012). Microwaves specifically function with electromagnetic radiation, within the frequency scope of 300 MHz to 300 GHz (Kim, Lee and Lee, 2014). Domestic and industrial microwave units sometimes operate in the same frequency range; however, most are designed for 2.45 GHz frequency, which is equivalent to 122 mm and 1.02×10^{-5} eV for wavelength and energy respectively (Kumar *et al.*, 2001). The fundamental physics of microwaves' applications with respect to material treatment or AC production are dependent on the compounds adsorbed and the carbon matrix (Menéndes *et al.*, 1999). Maxwell equations derived from appropriate boundary conditions can be used to describe the microwave process (Namazi, Allen and Jia, 2015).

$$\mathrm{P} = \left[\left(\sigma + \omega\epsilon''\right)\mathrm{E}^2 + \omega\mu''\,\mathrm{H}^2\right]. \quad \textbf{(3-1)}$$

The power density available for adsorption P is given in Equation **(3-1**), and is measured in W/m^3. Here, E represents the electric field vector; the vector H is the magnetic field; and б and µ are: electro conductivity and magnetic permeability, respectively. The dielectric factor and angular velocity are denoted with ϵ'' and ω, respectively. Microwave processes can control the heating and materials being heated internally and uniformly, and rapidly with high efficiency to pyrolyse large particles (Klinger *et al.*, 2018).

This study reviews agricultural waste as an AC precursor regarding its activation conditions and chemical activating agents, with a substantial emphasis on the characteristic properties of AC (Lahti *et al.*, 2017) and adsorption application targets (Danish and Ahmad, 2018a). While there are reviews on this subject (Martí-Rosselló, Li and Leo, 2016; González-García, 2017) none to date have considered the pre-processing challenges of parent materials, and only provide limited insight into kinetic and adsorption parameters and the important issue of scale-up.

This review attempts to evaluate multiple activating agent effects and make generic comparisons and assessments of multiple agricultural wastes, while outlining current process challenges. In particular, this study considers the effectiveness of some of the chemical activating agents used for AC production under various production conditions and also looks at the effects on the product characteristics, of surface functional groups and of overall adsorption efficiency for several applications. Comparative analyses of production methods are also examined to suggest more appropriate pathways. Finally, this review also concentrates on the behaviour and chemical properties of precursors relative to several treatments, production conditions, comparative analyses of modes of production and their challenges.

3.2 Fuel characterisation for AC production

Agricultural waste can be thermally and chemically treated to generate a wide range of valuable products, such as biofuels, bio-oils, bio-gases and bio-solids (Martí-Rosselló, Li and Leo, 2016). It can also be considered an energy storage medium (Aziz *et al.*, 2017). For such wastes, it is essential to allow for the wide variation in chemical contents. The proximate, ultimate and lignocellulose contents of such materials through biochemical analysis are shown in Table 3-1. The three main structural components: hemicelluloses, cellulose and lignin (Ben-Iwo, Manovic and Longhurst, 2016) are produced in varying amounts depending on whether they are produced by thermochemical (Uemura *et al.*, 2011) or biochemical conversion processes, and this affects the properties of the AC.

Agricultural waste is abundant, renewable and available at low cost (Rashidi and Yusup, 2017a). Its use is potentially environmentally friendly (Hidayu and Muda, 2017). However, there are some caveats; Abbas and Ahmed (2016) showed that leaves are not good for AC, due to their low carbon content, high volume to weight ratio and ash content. Research has also shown that in chemical activation, the activating agent digests amorphous lignin better than it does the biomass cellulose, so it is important to understand the characteristics of any material used (Chen, 2014).

Lignocellulosic biomass contains 10%–30% lignin, and materials such as coir, have about 45% lignin. Lignin is a natural insoluble polymer, and contains aldehydic and carbonyl groups, which make it highly polarised (Chowdhury *et al.*, 2013). Typically, during carbonisation and activation, the initial volatiles removed come from cellulose and hemicellulose (Sharma *et al.*, 2017). Several lignocellulosic materials possess special characteristics for AC production (Kelechi E Anyaoha *et al.*, 2018) and there are also several simple and low-cost methods for obtaining AC from biomass, using acids, bases and salts (Shamsuddin, Yusoff and Sulaiman, 2016). The cross-linking between the lignocellulosic components determines the suitability of biomass material for AC, and the morphology of the cells is also a determinant (Kongsomart, Li and Takarada, 2015). The energy requirement is subject to the characteristic properties of the feedstock. The structure of biomass materials, the physiognomies and the chemical behaviour of each component affect the reactivity and have potential involvement in processing AC (Chen, 2014).

Cellulose and hemicellulose are similar, with the main difference being the number of saccharide units, the latter having fewer saccharide units than the former (Danish and Ahmad, 2018a). Cellulose has a straight chain structure and is classified as an insoluble polysaccharide made up of monomers of beta-1,4-glycosidic bonds between glucose. By contrast, hemicellulose is a cross-linked polymer with some sugars which play vital roles in AC production, such as glucose, mannose, galacturonic acid, xylose, arabinose, O-methyl-glucuronic acid and galactose, which are all are soluble in water.

The thermal decomposition of hemicellulose takes place above 200 °C, after which cellulose’s decomposition follows; more specifically, in the temperature range of 250–400 °C with the release of CO and CO_2 from the glycopyranose rings (Danish and Ahmad, 2018a). Lignin is hydrophobic and inhibits water penetration, unlike polysaccharide polymers. The molecular relationship expressed in Figure 1 (Kan, Strezov and Evans, 2016), are of ether and β-1,4-Glycosidic bonds. Therefore, these linkages must be broken thermally or chemically to establish a reactive activated carbon.

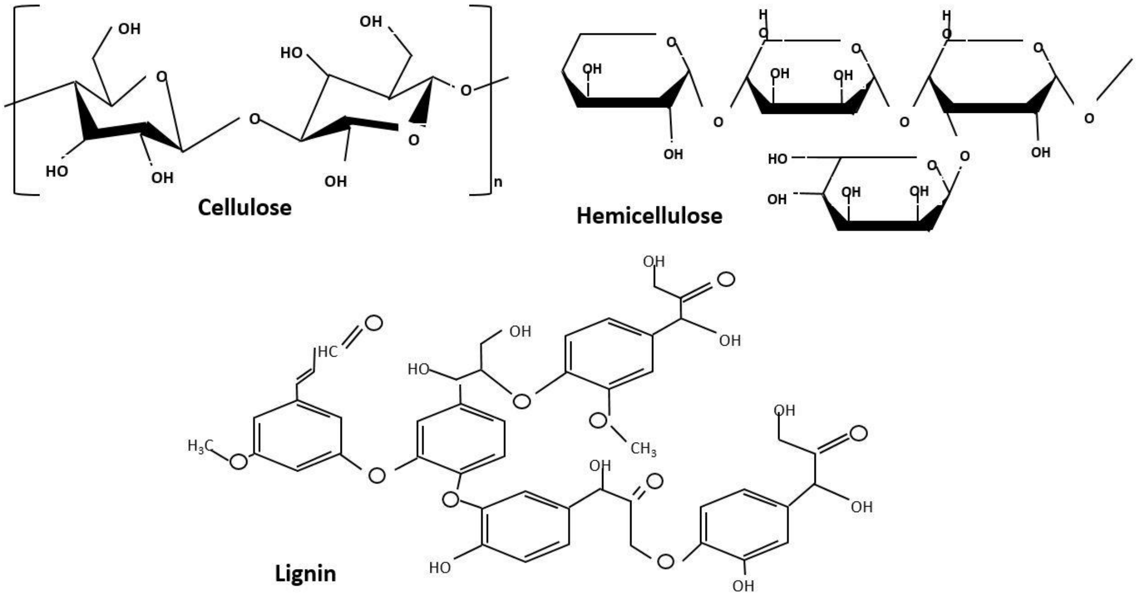


Figure 3-1 A structural model of lignocellulosic components of biomass

Table 3-1 Analytical characterisation and composition of agricultural waste biomass

Agricultural waste	Proximate analysis (% w/w)			Ultimate analysis (% w/w)					Lignocellulosic composition (% w/w)			Reference
	Moisture	Ash	Volatiles	C	H	N	S	O	Cellulose	Hemicellulose	Lignin	
Almond stone	11.05	0.76	77.32	48.76	7.52	0.48	0.56	43.68	21.70	27.70	36.10	(Sun *et al.*, 2017)
Bamboo	15.30	1.76	70.12	34.40	4.61	0.22	0.07	-	26	15	21	(Hirunpraditkoon *et al.*, 2011)
Banana peel	11.56	9.28	88.02	35.65	6.19	1.60	20.75	45.94	-	-	-	(Kabenge *et al.*, 2018)
Cassava peel	14	4.50	59.40	59.31	9.78	2.06	0.11	28.74	37.90	23.90	7.50	(Daud *et al.*, 2013)
Coconut shell	8.21	0.80	77.82	49.62	7.31	0.22	0.10	42.75	14.00	32.00	46.0	(Mohd Iqbaldin *et al.*, 2013)
Cotton stalks	6.00	6.30	70.50	43.60	5.80	0.80	0.00	49.80	80-95	5-20	-	(Abdolali *et al.*, 2015)
Durian shell	11.27	4.84	-	39.30	5.90	1.00	0.06	53.74	60.45	13.09	15.45	(Rashidi *et al.*, 2012b)
Grape stalk	8.86	3.15	96.80	34.40	0.438	1.11	0.087	63.96	-	-	-	(Pangavhane and Tare, 2012)
EFB	15.01	4.48	82.98	43.89	5.33	0.52	0.10	54.32	42.00	18.90	11.70	(Onochie *et al.*, 2017)
Oil Palm MF	11.10	7.90	84.03	42.20	5.21	2.21	0.14	42.34	42	22	14	(Onochie *et al.*, 2017)

PKS	7.96	1.10	72.47	50.01	6.90	1.90	0.03	41	20.80	22.70	50.70	(Rashidi *et al.*, 2012b)
Olive stone	10.40	1.40	74.40	44.80	6.00	0.10	0.01	49.09	30.80	17.10	32.60	(Plaza *et al.*, 2014)
Orange peel	-	2.15	77.93	40.28	6.12	1.08	0.06	52.46	-	-	-	(Zhou, 2017)
Peanut shell	7.98	12.80	79.10	41.52	7.43	2.12	0.60	27.96	-	-	-	(Braz and Crnkovic, 2014)
Rice husk	6.34	16.70	67.50	36.52	4.82	0.86	-	41.10	30.42	28.03	36.02	(Huang *et al.*, 2016)
Sugarcane BG	8.61	4.05	86.02	47.30	6.20	0.27	-	44.15	42.16	36.00	19.30	(Huang *et al.*, 2016)
Walnut shell	8.73	1.27	77.42	49.30	5.82	44.49	0	-	40.10	20.70	18.20	(Plaza *et al.*, 2014)
Waste tea	5.80	4.29	-	52.72	6.34	2.61	0.18	38.15	17.50	41.30	41.20	(Gurten *et al.*, 2012)
C: carbon, H: hydrogen, N: nitrogen, S: sulphur, O: oxygen, EFB: empty fruit bunch, MF: mesocarp fibre, PKS: palm kernel shell, BG: bagasse												

3.3 Modes of activation

The preparation of AC typically involves two major steps: pyrolysis or carbonisation of the precursor, and activation. Carbonisation produces a stable structure, with an elementary and partially-developed pore structure (Osman, Shamsuddin and Uemura, 2016), which must be enlarged properly by physical or chemical activation. The development stages are illustrated in Figure 2. In addition, physicochemical activation is also a potential form of activation (Xiao *et al.*, 2012). Figure 3-2 illustrates the pore development of empty fruit bunch (EFB) AC, represented with A, B and C, following thermal treatment at 350, 500 and 600 °C, respectively (Claoston *et al.*, 2014). The pore development is better defined with increased temperature, and modification and treatment methods for raw biomass are discussed by Pathak et al. (2015).

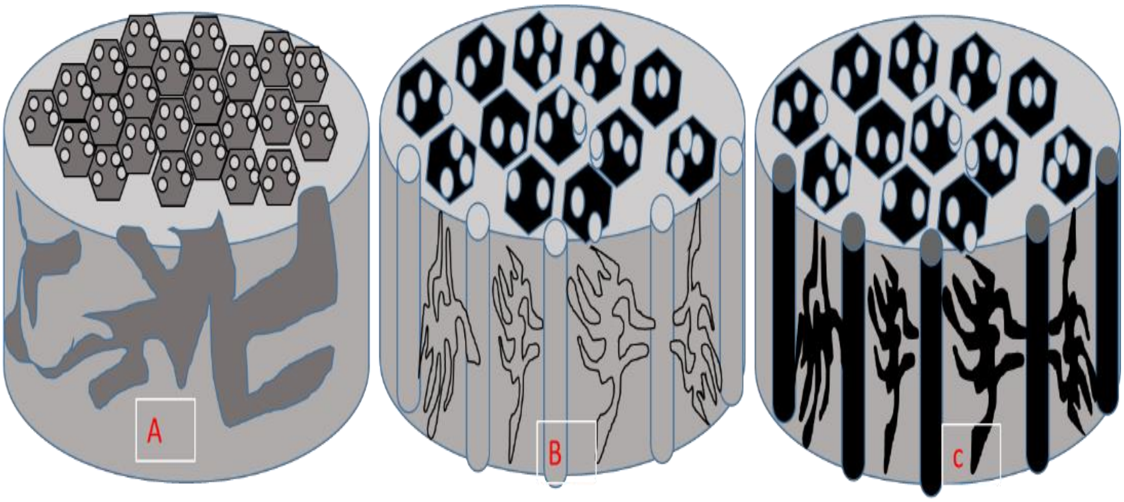


Figure 3-2 Activation temperature's effect on activate carbon's (AC) pore development and morphology A: biomass structure; B: partially developed char structure; C: well-defined porous AC structure

Physical activation occurs over the dual stages of carbonisation of the precursor in a reactor with a steady flow of an inert gas, and then over a successive activation process of the char product with CO_2. Steam, air or their mixtures or other fluid activating agents at 800–1100 °C are also used (Calvo-Muñoz *et al.*, 2016). However, excessive temperatures of, say, 1200 °C and above, lead to low carbon yields, collapse of the pore structures and ash generation (Olorundare *et* *al.*, 2014), while devolatilising processes encourage pore formation and further enlarge any micropores created (Girgis, Soliman and Fathy, 2011). Physical activation is environmentally safe, but the speed and the temperature requirements are problematic. Appropriate activation temperature and duration are important to ensure adequate porous development and the creation of functional groups.

The physicochemical activation process involves both physical and chemical methods (Arami-Niya *et al.*, 2012), where the raw precursor or char is permeated with an activating agent; then, heated in a chamber with an oxidant flow (Ooi *et al.*, 2017). This method is often employed when the activating agent used in activation is unable to be effectively removed through washing, and might otherwise lead to pore clogging (Chowdhury *et al.*, 2013). This process is expensive due to the elevated temperature requirements, and the need for a two-step process, extended process time and a generally low-percentage AC yield (Ooi *et al.*, 2017). There are various modifications and treatments, including acidic treatment, basic treatment, impregnation and microwave process treatment. Other routes include: ozone, plasma treatments and biological modification—which is a developing technology and will not be discussed here further (Bhatnagar *et al.*, 2013). Although conventional heating is still an effective method of AC production, there are basic challenges that affect the process, such as the high cost of the heating, extended heating duration and thermal energy flow from the outer layer to the core of a biomass material. Chemical treatment of agricultural waste and other biomass materials can also improve the overall efficiency of AC and provide opportunities for target applicability due to the potential to use several activating agents for the process (Wahi *et al.*, 2017). Chemical activation processes are summarised in Table 3-2 with the key advantages and disadvantages presented.

3.3.1 Chemical activation

A series of pre-activation steps is required to achieve an adequate and quick production process. Biomass materials must be free from soil and any other impurities by washing with deionized water, and then dried at a temperature between 65 and105°C (Ooi *et al.*, 2017). The biomass selected often undergoes milling to reduce the particle size (Farma *et al.*, 2017), enabling uniform and quick carbonisation by lowering the thermal gradient. The biomass physical properties influence the milling process. The chemical activation process can be achieved in several ways, as outlined below:

The chemical activation method is accomplished by the infusion, mixing and permeation of a solution, usually a dehydrating chemical with the ability to induce and accelerate material decomposition by pyrolysis, while inhibiting the creation of semi-solid volatile substances before activation. Activating agents, such as bases; acids; and salts, such as K_2CO_3 and $ZnCl_2$ are impregnated into the biomass by mixing and stirring (Ahmida *et al.*, 2015). Although this is a single-step technique, in some cases, the precursor may first be carbonised to produce char (Xin-hui *et al.*, 2011; Hoseinzadeh Hesas, Arami-Niya, *et al.*, 2013a) The impregnated char is then heated in the presence of nitrogen (Moreno-Castilla, 2016). The temperature requirement used in chemical activation range of 400–800 °C, which is lower than the average temperature for the physical activation process (Xin-hui *et al.*, 2011) and is applicable to lignocellulosic materials. Here, the raw precursor can be mixed and permeated with an activating agent directly before carbonisation (Hernández-Montoya, García-Servin and Bueno-López, 2012). Typically, the biomass material is added to the activating agent at an optimised ratio, and mixed, before undergoing thermal treatment. Each activating agent performs differently with different precursors, dependent on its structure and the activation conditions. It is also possible to use a two-step activation process by impregnating biochar with activating agent and then subjecting it to a second heat process, under the conditions outlined in Table 3-2 (Hoseinzadeh Hesas, Arami-Niya, *et al.*, 2013a).

Table 3-2 An overview of the three modes for the chemical activation process

	One-step conventional	Two-step conventional	Microwave process
Temperature or power requirements	400–1200 °C	400–800 °C then 400–1200 °C	300–1000 W
Heating duration	1-3 h	3-6 h	5-30 min

Average yield	30-50%	30-40%	>40%
Risk of system corrosion	High	High	Low
Product efficiency	Low	High	High
Flow process	Continuous feed in and out	Batch	Batch

3.3.1.1 Chemical activation

The one-step process system for AC production requires impregnation before heat treatment under a controlled environment, and this is known as direct activation. A wide thermal range between the hot exterior and the interior risks encourages significant combustion of the biomass. The microwave system can be used for this process and will shorten the process time compared to a two-step process (Liu *et al.*, 2016).

3.3.1.2 Two-step activation process

Two-step process systems for AC production involve carbonisation and then activation (Bachrun *et al.*, 2016). This process enhances the carbon content and forms a char with an initial porosity. It requires an extended time and consumes more energy. It can also be used for non-uniform particles so that a milling stage is not required in pre-processing. This process is common for microwave activation, but in the production of large quantities of AC, the transfer and reloading lead to loss of materials and increase production cost. Oginni et. al (Oginni *et al.*, 2019) reported that the two-step process does not result in more effective AC.

3.3.1.3 Microwave activation process

The high energy requirement and time involved in conventional heating can make the activation process expensive (Oghbaei and Mirzaee, 2010), making microwave heating attractive (Yao *et al.*, 2015). Some biomass types are good microwave absorbers, and hence, are interesting for possible use at the commercial scale (Gan *et al.*, 2015). Microwave-induced pyrolysis is more efficient, especially when a material with higher microwave absorbance is mixed with metal oxides (Domínguez *et al.*, 2007). Microwave pyrolysis reduces selfgasification during the activation process, unlike conventional pyrolysis, due to the high heating levels that are involved in conventional approaches (Fidalgo *et al.*, 2014).

Compared to conventional heating methods, the microwave method of activation has additional benefits, including uniform volumetric heating, regulation of the heating process, a high heating rate and ensuring that the biomass has indirect contact with the heat source. Thus, the microwave AC production technique has been suggested as a prospective method to replace the conventional thermal process (Xiao *et al.*, 2012). In some cases, the activation process is planned according to the availability of resources and the heat source. Activation duration, though, depends on the type of precursor but can be affected strongly by the particle size and heat distribution mechanism. Carbon yield depends on the overall management of the sample, its temperature, its washing and handling techniques.

3.3.2 A comparison of activation by microwave and the conventional process

Microwave-assisted activation produces AC with wider micropores and mesopores than the conventional products. The pore size, surface area and adsorption efficiency in both conventional and microwave activation processes are affected by activation temperature, dwell time, heating rate, type of activating agent, activation agent-feedstock ratio, particle size, inert gas flow rate, microwave power and weight of sample (Nomanbhay and Ong, 2017).

Figure 3-3 shows that heat flows from the external regions in conventional heating and from the interior for microwave heating (Gadkari, Fidalgo and Gu, 2017). This is the distinguishing factor between conventional and microwave heating. Direction of heat flow relative to the activation environment influences the molecular movement, volatile discharge and heat distribution. Conventional heating exhibits an extended temperature gradient, while thermal energy flows from the surface to the central portion of the biomass. However, it can be minimised by slow heating. An isothermal holding system may also be employed (Puziy *et al.*, 2005). A thermal gradient results in the obstruction of the passage for volatiles through the pores, leading to the development of partial or undefined pores (Puziy *et al.*, 2005; Braz and Crnkovic, 2014).

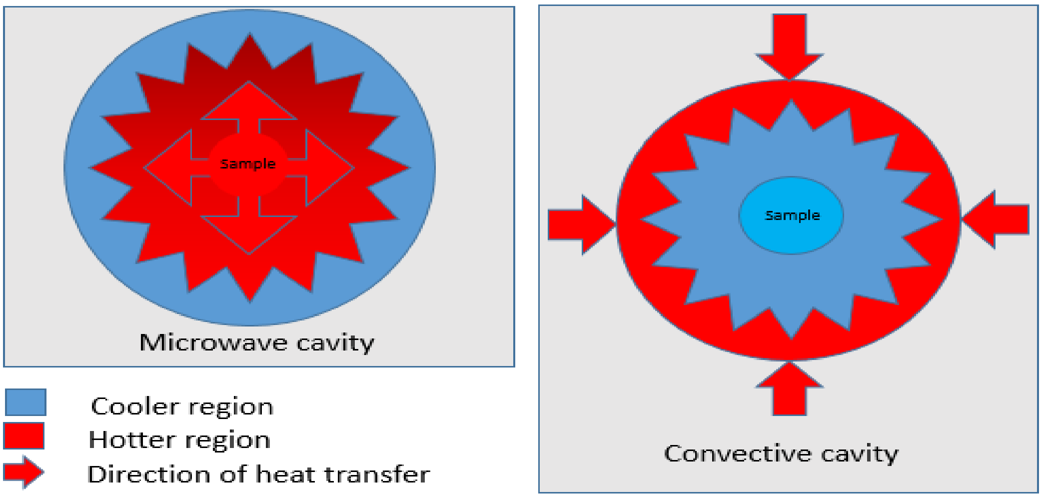


Figure 3-3 Examples of conventional and microwave heating effects

Microwave AC is characterised by wider micropores and mesopores than conventional activated AC, but it comes with process challenges (Puziy *et al.*, 2005). Xin-hui et al*.* (2011) studied activation approaches for AC production from Jatropha hulls with steam as the activation agent, and showed the carbon yields for microwave and conventional methods were 16.6% and 13.3%, respectively. With CO_2 as an activating agent, the yield for conventional method was 18%, and it was 36.6% for the corresponding microwave method. Foo and Hameed (2011d) compared EFBAC produced through a conventional furnace and microwave and reported S_{BET} and V_{total} values of 255.77 m^2/g and 0.14 cm^3/g, and 807.54 m^2/g and 0.45 cm^3/g, respectively. A general overview of the two approaches is shown in Table 3-3 (Fidalgo *et al.*, 2014; Kopac, Kırca and Toprak, 2017).

Table 3-3 Comparison of the differences between various processing parameters for microwave and conventional activation methods

Framework	Microwave activation	Conventional activation	Observation
Treatment time	Shorter process time	Several hours and days	Shorter time reduces process risks

Heating process	Internal and volumetric heating	Surface heating Non-uniform heating	Thermal gradient is eliminated by microwave heating
Mode of heat transfer	Energetic coupling Coupling at molecular level	Conduction and convection Superficial and wall heating	Uniform heating is easily achieved on coupling at molecular level
Gas/Energy consumption	Due to short treatment time, it is low	High	Microwave process saves energy
Equipment size	Small	Large	Developing a large size microwave is expensive and complex
Preparation conditions	300- 700 W 5-15 min	400-1200 °C 1-3 h	Same for both except when two-step activation process is required
AC characteristics	Higher surface area	High surface area	Choice may depend on application and process requirements
Complexity	High	Low	Conventional equipment is easy to build. Equipment repair is easier with conventional approaches

3.4 Activating agent effect

3.4.1 The effects of activating agent on renewable and non-renewable precursors

Activating agents play major roles in the activation process, and the various compounds used react differently depending on the biomass type and the temperatures employed.

Several non-renewable precursors (petroleum tar pitch and coal) have been used for AC production. When coke is impregnated with KOH, the porosity decreases as the ratio varies from 4:1 to 2:1, and the results obtained are in the following ranges: S_{BET}, 1800–1200 m^2/g; V_{micro} 0.71–0.48 cm^3/g; and mean pore size, 1.12–0.76 nm (Kopac, Kırca and Toprak, 2017). AC from bituminous coal can be produced by chemical activation with KOH and Borax decahydrate, but the resulting AC produced has an irregular pore structure.

Similarly, paracetamol, phenol and salicylic acid can used for coal-based ACs (Kopac, Kırca and Toprak, 2017), while nitric acid is used for the activation of pitch, resulting in an AC with a S_{BET} of 1401 m^2/g and an adsorption capacity of 3.51 mol/kg, and is employed for the adsorption of CO_2 (Danish *et al.*, 2014). The microwave process for coal, produced an AC with a 1048 mg/g adsorption capacity for methyl blue (MB) and values of 1770 m^2/g and 0.99 cm^3/g, for S_{BET} and V_{total}, respectively, under production conditions of a 1:3 impregnation ratio for 12 min at 700 W (Köseoǂlu and Akmil-Başar, 2015).

Gao et al. (Gao *et al.*, 2016) showed tar residues permeated with H_3PO_4 were activated at 850 °C, resulting in the following: adsorption capacity, V_{total} and V_{micro} values of 793 mg/g, 0.286 cm^3/g and 0.255 cm^3/g, respectively. In addition, the mixture of coal and carbon monolith for AC production had a S_{BET} of 1044 m^2/g (Franca *et al.*, 2010).

The reactivity of chemical activating agents on biomass materials under high thermal conditions creates an intermolecular reaction that gives rise to efficient AC production. Surface textural analysis shows that the increase in the ratio of activating agents is proportional to the efficiency until the optimal range is reached, and this creates AC with higher pore volume on activation. There are clear morphological differences depending on the activating agent; thus, the K_2CO_3-impregnated sample forms columnar and hexagonal shapes. Köseoǂlu and Akmil-Başa, showed that $ZnCl_2$-impregnated AC forms an asymmetrical and irregular surface morphology (Köseoǂlu and Akmil-Başar, 2015), and they found that K_2CO_3 produced AC with a higher S_{BET} and a well-defined porosity; however, the implication of such studies is not clear, as results are strongly dependent on technical activation conditions and impregnation parameters.

Microwave treatment has the potential to eliminate some volatiles, starch molecules and saturated and acidic oxygen-linking functional groups; therefore, making the AC basic; thus, promoting reactivity (Huang *et al.*, 2011). The type of bonding on the carbon layer is influenced by type of feedstock, microwave power, impregnation ratio and radiation time. Other variables, such as inert gas flow rate, can influence AC characteristics. These have a substantial impact on the adsorption capacity and other applications of AC (Hoseinzadeh Hesas, Wan Daud, *et al.*, 2013).

The adsorption capacity is attributable to the effectiveness and reactivity of ions and ionic exchange in the carbon structure. The increase in charge density is proportional to the adsorption capacity (Franca *et al.*, 2010). At certain ranges of microwave power, pores can be blocked by deposits formed from volatile substances (Foo and Hameed, 2012e). Raw materials, precursor particle size, activation process and mode of heat treatment also influence the surface chemical and functional groups of ACs (Szymański *et al.*, 2002). Foo and Hameed (Foo and Hameed, 2011b) identified the removal of loosely-bound atoms and switching with heteroatoms, which are naturally basic, within the molecular layers. For the microwave activation process, the power requirement is critical due to possible collapse of the pore structure beyond the optimum heat requirement (Somorjai and Li, 2011).

Activating agents possess great capacity in the microwave activation process. Biomass materials, due to poor dielectric properties, heat quickly with higher thermal penetration when impregnated with chemical agents (Wang, Tan and Liang, 2009). For example, AC prepared from orange peel when all processing parameters are constant, showed substantial changes. However, any activation effect is insignificant, and minimal adsorption occurs at microwave power below 200 W. A study by Foo and Hameed (Foo and Hameed, 2012g) showed that adsorption capacity increases directly proportionally to the increase in microwave power.

Deng et al. (Deng, Zhang, *et al.*, 2010) explored the influence of microwave power on coconut shell-based AC. Therein, K_2CO_3 and KOH were used for impregnation and the resulting adsorption capacity was similar at same microwave power (Foo and Hameed, 2013). In some cases, impregnation ratio influences AC properties and is used in the optimum range of 0.5–2 wt.% (Foo and Hameed, 2011e). A further challenge in AC production is incomplete activation, which results in poor adsorption caused by partial elimination of the acidic functional groups, and the dominance of saturated molecule and incomplete removal of volatiles (Huang *et al.*, 2011). Fourier-transform infrared spectroscopy (FTIR) evaluation shows the presence of individual bonds and clearly defines the difference between carbonisation and activation. It can also be used to determine the optimum range of activation at different parameters. The peaks are indicative of the reactive sites and functional groups responsible for adsorption (Hoseinzadeh Hesas *et al.*, 2015).

3.4.2 Acidic treatment of agricultural residues

The sensitivity of cellulose linkage to acidic hydrolysis is due to the presence of glycoside bonds and it varies relative to type of acid, the concentration and the reactive temperature within the amorphous region. It is homogenous with strong acids and heterogeneous with weak acids. The kinetics of the hydrolysis reaction are also governed by decrystallisation of microcrystalline cellulose. Hydrolysation, which results in the elimination of xylan, helps in the separation of complex structures. Most acids are able to transform crystalline cellulose to amorphous, while HCl can remove lignin to enable symmetric pore creation. The cell walls of plants, where cellulose and hemicellulose have polymeric bonds, are easily broken by acids, and that results in delignification.

Introducing nitric acid into AC production was successful in improving the physical properties of AC. HNO_3 successfully removed some contaminants attached to the surface of AC, such as Fe, Si, K and Al. The surface of AC pores was clearly seen to have unbroken cavities when treated (Allwar, Hartati and Fatimah, 2017) and showed an improved hydrophilic character (Bhatnagar *et al.*, 2013) Comparing HCl and HNO_3 under the same conditions for palm kernel shell (PKS) activation produced: S_{BET} values of 164.2 and 325.4 m^2/g; V_{total} values 0.10 and 0.19 cm^3/g; and pore diameters 9.50 and 8.00 nm, respectively. H_3PO_4 is corrosive to both metals and tissues, undergoing rapid polymerisation with epoxides and polymerisable compounds, but it can separate lignin and cellulose from lignocellulose (Qin, Clarke and Li, 2014). H_3PO_4 breaks down cellulose and hemicellulose polymers in biomass to form monomeric sugars. It can also react directly with lignin under any conditions, and cellulose dissolves in it. H_3PO_4 has been used extensively in the activation of AC, whose adsorption isotherm indicates multilayer filling, with significant mesopore formation. H_3PO_4, used for AC production from olive stone, has a good S_{BET} of about 1218 m^2/g and a good pore volume of 0.6 cm^3/g (Yakout and Sharaf El-Deen, 2016). Örkün et al*.* (2012) studied the impact of concentration variations of H_3PO_4 on some precursors and considered it effective for the development of pores and producing a significant improvement of the morphology, surface chemistry and size distribution. A significant contribution to microporosity and mesoporosity was observed for grape seed activation in the 1:1 to 3:1 ratio range, especially in the pore size arrangement.

3.4.3 Base treatment of agricultural residues

Alkaline can cause the degradation of glucose and cause the branching of carbohydrates, such as 4-O-methylglucuronic acid. They are reactive to lignin and the solvation of ether linkages and hydroxyl groups. This is useful in AC production due to delignification. The dissolution of lignin causes the removal of xylan. The use of KOH results in the breakage of longer fibres and exfoliation (Lee, An and Kim, 2014). Improved porosity as a result of activation with KOH can be attributed to potassium interaction and the stretching of carbon layers. KOH is more effective at creating micropores due to the evidence of an interaction between layers, while NaOH is extremely active for disordered carbon materials; however, both activating agents require temperature above 800 °C. Figure 3-4 shows how NaOH' interacts with biomass to breakdown the long chains.

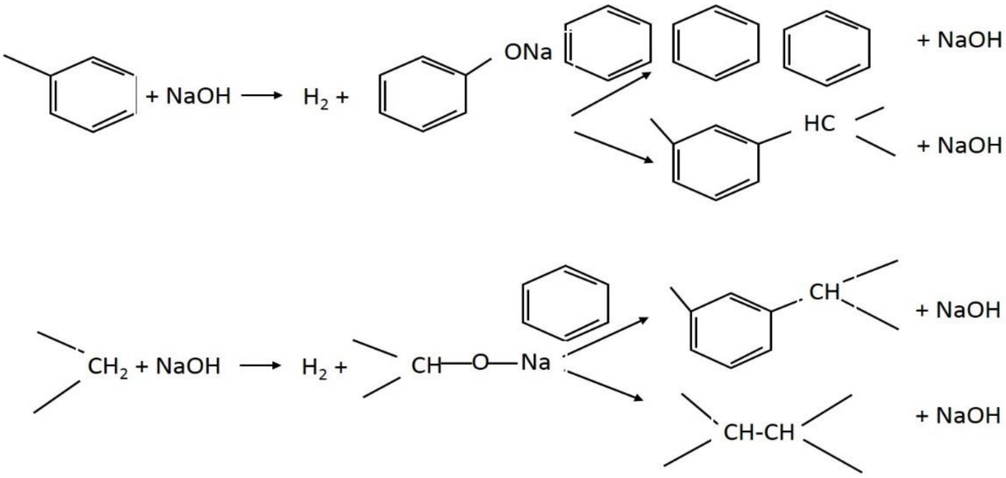


Figure 3-4 The interactions between layers and NaOH

The use of KOH, in the temperature range of 230–650 °C, results in a high char yield. The oxidation of biomass with KOH creates oxygen-containing surface functional groups, which may not develop properly at temperatures below 600 °C (Ello *et al.*, 2013). KOH is highly-effective in biomass; sugar cane activated by KOH has an S_{BET} of 2300 m^2/g with high methyl blue adsorption (Wu and Tseng, 2008). During the KOH activation process, surface species, such as alkaloids, as well as molecular species like K_2CO_3 and K_2O, are formed (Ello *et al.*, 2013). NaOH impregnation of corncob resulted in high S_{BET} between 2318 and 2474 m^2/g. When using the optimum ratio of 1:2 to 1:1, the mesopore volumes of the AC were increased from 21% to 58% (Tseng, 2006). AC perpared from date palm showed competitive characteristics of 1282.49 m^2/g, 0.66 cm^3/g and 20.73 nm—S_{BET}, V_{total} and average pore diameter, respectively. The adsorption was determined to be lowest at pH 3 (104.88 mg/g), increasing to 106.4 mg/g at pH 7. AC properties vary indirectly with temperature, and a maximum of 612.1 mg/g at 30 °C for relative adsorption capacity was observed with the AC from guava seed, which showed an effectiveness for amoxicillin adsorption with a S_{BET} of 2573 m^2/g and an average pore diameter of 1.96 nm (Pezoti *et al.*, 2016).

3.4.4 Salts treatment of agricultural residues

The hydrolysis of hemicelluloses is strongly affected by temperature and pH; a near neutral pH lowers the activation process; however, ethers and carbon-carbon bonds are relatively stable. Some salts can catalyse the ether linkages in the lignin. At a high temperature, some salts undergo the Leidenfrost effect, causing steam explosion; thus, liberating soluble phenolics in the liquid form. The hydrophilicity of lignin is increased due the bond breakages at that stage. The increase in the reaction time or temperature results in the degradation of oligomers and monomers. That could also influence degradation to produce glycoaldehyde dimer, D-fructose, 1,3-dihydroxyacetone dimer, anhydroglucose, 5-HMF and furfural. Salt can also act as a catalyst to influence the gasification rate of cellulose at the low temperature of about 400 °C.

$ZnCl_2$ is commonly used as an activating agent in AC production, especially with biomass to obtain a high-reactivity and high-surface-area AC (Liu, Huang and Zhao, 2016). $ZnCl_2$ as an activating agent acts as a dehydrating agent when impregnated in biomass, resulting in hydrolysis reactions because of intermolecular exchange and molecular migration which would cause structural alteration due to weight loss and discharge of volatiles. Hydrocarbon and oxygenated organic compounds are not affected by $ZnCl_2$, thereby providing the AC with a skeleton with developed pores. Şahin et al. (2015) studied AC preparation from Elaeagnus angustifolia seeds using $ZnCl_2$ at 500 °C, a 1:1.5 impregnation ratio for 48 h and activation for a 1 h duration, resulting in an S_{BET} of 1836 m^2/g. Potato peel biomass was studied for AC production with H_3PO_4, KOH and $ZnCl_2$. The activation was done at 400 °C, resulting in: S_{BET} 1642 and 1489 m^2/g, and V_{total} 0.96 and 0.93 cm^3/g, for KOH and $ZnCl_2$, respectively (Arampatzidou and Deliyanni, 2016). K_2CO_3 has been proven effective for several agricultural waste precursors. For sisal, for example, the resultant AC had an S_{BET} of 1038 m^2/g, V_{total} of 0.49 cm^3/g and was confirmed to be effective and appropriate for the purification of solutions contaminated by ibuprofen and paracetamol from the liquid phase. Studies on bamboo and pinewood showed a higher S_{BET} when impregnated with K_2CO_3 with microwave activation than for any other method. Foo and Hameed (2012e) compared K_2CO_3 and KOH for pineapple peel for 6 minutes in a microwave; the results showed ACs with S_{BET} values of 680 and 1006 m^2/g, respectively. Furthermore, comparison using grapeseed as the precursor, activated at 800 °C with K_2CO_3 and KOH, yielded

ACs with S_{BET} values of 1238 m^2/g and 1222 m^2/g, respectively. The average pore diameter of both remained the same, at 1.7 nm (Okman *et al.*, 2014).

$FeCl_2$ and $FeCl_3$ as activating agents can boost the intermolecular interactions between activating agent and biomass precursor. There are limited investigations on the use of $FeCl_2$ and $FeCl_3$ for biomass AC production (Fu *et al.*, 2017). At the temperature range of 400–1000 °C, $FeCl_3$ as an activating agent proved itself effective on Tara gum with a resultant S_{BET} of 1680 m^2/g and a V_{total} of 1 cm^3/g (Lee and Ahmad Zaini, 2016). Under the same conditions for Arundo donax Linn activation, results were: S_{BET} 760 and 927 m^2/g; V_{total} 0.466 and 0.509 cm^3/g; and average pore diameters (nm) 2.451 and 2.11, for $FeCl_2$ and $FeCl_3$, respectively (Fu *et al.*, 2014). Another comparative study with $ZnCl_2$, $FeCl_3$ and $MgCl_2$ for waste coffee biomass resulted in S_{BET} values of 123, 977 and 846 m^2/g, respectively (Rufford *et al.*, 2010b). The comparative study of AC synthesis from coffee ground waste with $ZnCl_2$ and $FeCl_3$ resulted in S_{BET} values of 977 and 846 m^2/g, respectively. Further study with the same precursor using $MgCl_2$ gave a value of 123 m^2/g (Rufford *et al.*, 2010b), and the same trend was observed for the date stone (Ahmed, 2011). $MgCl_2$ also proved to be effective in activation of Tara gum with S_{BET} of 1680 m^2/g (Bedia *et al.*, 2018). Figure 5 and Table 4 clearly show the disparity of different activating agents compared alongside the production methods. However, this comparative table shows that most activating agents under optimum production conditions have different effects on different precursors.

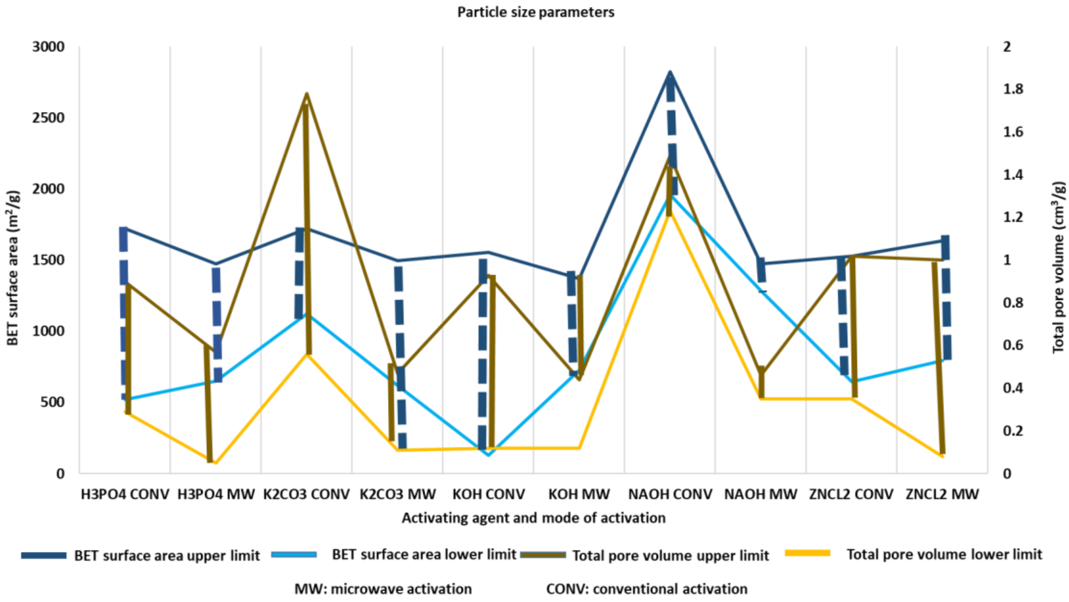


Figure 3-5 S_{BET} and total pore volume ranges of some activating agents on agricultural waste

The fact that primary characteristics of AC depend on the pyrolytic conditions and activating agents, mean that the hydrogen and oxygen contents decrease with increases in carbonisation and activation temperature. The aromaticity of carbon and morphology increases as the hydrogen/carbon ratio decreases. The relationship between temperature and surface area is not linear due to other factors that contribute to the characteristics of AC. The impregnation time and activating agent are additional determinants of these characteristics because of their direct influence on the pore sizes, and thus, release of volatiles. However, an extended impregnation period can result in the gasification of pore walls. Therefore, the burn-off as a factor should be adequately considered. Figure 3-5 and Table 3-4 show that acids, bases and $ZnCl_2$ are more effective for activation (Deng *et al.*, 2009; Rufford *et al.*, 2010a; Hoseinzadeh Hesas, Arami-Niya, *et al.*, 2013b; Fu *et al.*, 2014; Ahmed, 2016).

Table 3-4 The effects of activating chemical on the precursors

Precursor	Time (hr)	T(°C)/ MW(W)	I.R	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	D_p (nm)	Yield (%)	Reference
Result of H_3PO_4 activation of conventional process										
Cotton stalk	2	500	1.5	1720	0.890		0.710			(Nahil and Williams, 2012)
Peach stones	2	500	0.4	1393	0.689	0.055	0.634	0.99	41.8	(Khedr *et al.*, 2014)
Bamboo	1	600	1.5	1335	0.625	0.140	0.485	1.87		(Liu *et al.*, 2010)
Maize tassel	1	500	1.4	1263	1.592					(Olorundare *et al.*, 2014)
Palm kernel shell	0.5	425	2	1109	0.903			3.20		(Lim, Srinivasakannan and Balasubramanian, 2010)
Durian shell	0.4	500		1021	0.350		0.210		63	(Jun *et al.*, 2010)
Cotton cake	1.5	450	2	584	0.298	0.075	0.223	2.04	29.8	(Ibrahim *et al.*, 2014)

Rice straw	2	450	1	522	0.550	0.370	0.180	4.21	51.9	(Basta *et al.*, 2009)
Result of H_3PO_4 activation of microwave process										
Palm shell	0.28	800	2	1473						(Kundu, Gupta, *et al.*, 2015)
Lotus stalk	0.25	700	2	1434	0.307	1.030	1.337			(Huang *et al.*, 2011)
Bamboo	0.5	350	1	1432	0.503	0.193	0.696		48	(Liu *et al.*, 2010)
Waste tea	0.5	350	3	1157	0.573	0.256	0.829	35		(Yagmur, Ozmak and Aktas, 2008)
Cotton stalk	8	400	0.5	652	0.057	0.419	0.476	2.92		(Girgis *et al.*, 2009)
Result of K_2CO_3 activation of conventional process										
Waste tea		900	1	1722	0.583	0.039	0.554	2.0	22.7	(Gurten *et al.*, 2012)
Rice husk	1.5	1000	1.5	1713	1.785	1.070	0.715	4.16		(Foo and Hameed, 2011e)
Mangosteen shell	2	900	1	1123	0.560	0.110	0.450	1.98	20.7	(Foo and Hameed, 2012c)
Result of K_2CO_3 activation of microwave process										

Wood saw dust	0.1	600	1.3	1496	0.470	0.394	0.864	2.30	80.0	(Foo and Hameed, 2012d)
Rice husk	0.11	600	1.3	1165	0.330	0.450	0.780	2.68		(Foo and Hameed, 2011e)
Orange peel	0.1	600	1.3	1104	0.247	0.368	0.615	2.22	80.9	(Foo and Hameed, 2012g)
Pineapple peel	0.1	600	0.8	680	0.280	0.170	0.450	2.59		(Foo and Hameed, 2012e)
Cotton stalk	0.13	660	0.8	621	0.110	0.270	0.380	2.43		(Deng, Li, *et al.*, 2010)
Result of KOH activation of conventional process										
Rice straw	1	800	4	1554	0.930	0.340	0.500	1.14	13.5	(Basta *et al.*, 2009)
Bamboo	3	800	2	1533	0.491					(Hirunpraditkoon *et al.*, 2011)
Cocoa pod husk	1	800	1	490	0.240			2	13.5	(Cruz *et al.*, 2012)
PKS	0.75	800	1	127	0.120		0.110		43.4	(Abechi *et al.*, 2013)
Result of KOH activation of microwave process										

Empty FB	0.11	600	1	1372	0.440	0.320	0.760	2.20	73.7	(Foo and Hameed, 2011d)
Mesocarp Fibre	0.1	600	0.8	1223	0.420	0.300	0.720	2.35	32.0	(Foo and Hameed, 2011a)
Pineapple peel	0.1	600	0.8	1006	0.280	0.310	0.590	23.44		(Foo and Hameed, 2012e)
Palm Shell	0.16	600	0.6	895			0.491	2.19		(Abechi *et al.*, 2013)
Rice husk	0.11	600	1.3	752	0.260	0.380	0.640	3.41		(Foo and Hameed, 2011e)
Coconut husk	0.11	600	1.3	752	0.260	0.380	0.640	3.41		(Foo and Hameed, 2012b)
Cotton stalk	0.16	680	0.6	729	0.120	0.260	0.380	2.08		(Deng, Li, *et al.*, 2010)
Result of NaOH activation of conventional process										
Coconut shell	1.5	700	3	2825	1.498	0.355	1.143	2.27	18.8	(Cazetta *et al.*, 2011)
Rice husk	0.05	850	2	1958	1.230	0.573	0.550	1.25		(Youssef *et al.*, 2015)
Result of NaOH activation of microwave process										

Durian shell	0.1	600	1.5	1475	0.467	0.374	0.841	2.28	80.0	(Foo and Hameed, 2012a)
Langsat bunch	0.1	600	1.3	1293	0.449	0.303	0752	2.32	81.3	(Foo and Hameed, 2012h)
Jackfruit peel	0.11	600	1.5	1286	0.356	0.408	0.764	2.37	80.8	(Foo and Hameed, 2012f)
Result of $ZnCl_2$ activation of conventional process										
Tea seed shell	1	500	1	1530	0.783	0.184	0.599	2.05	44.1	(Gao *et al.*, 2013)
Oceania palm	2	600	4.5	1483	1.022	0.456	0.494	2.76	40.0	(Dural *et al.*, 2011)
Waste apricot	1	500	1	1060	0.790	0.640	0.150	2.98		(Köseołlu and Akmil-Başar, 2015)
Date stone	1.2	500	2	1045	0.641	0.129	0.512	2.45	40.4	(Theydan and Ahmed, 2012)
Rice husk				927	0.560			0.80		(Boonpoke *et al.*, 2013)
Palm Shell		900		926	0.480		0.470	2.05		(Arami-Niya, Daud and Mjalli, 2010)

Wood apple shell			2	794	0.470					(Bhadusha and Ananthabaskaran, 2011)
Hazelnut shell				647	0.350			34.0		(Özçimen and Ersoy-Meriçboyu, 2009)
Result of $ZnCl_2$ activation of microwave process										
Peanut shell	0.3	600	1.4	1634						(He *et al.*, 2013)
Rice husk	0.3	600	1.4	1527			2.070	5.99		(He *et al.*, 2013)
Cotton stalk	0.15	560	1.6	794	0.083	0.547	0.630	3.20	37.5	(Deng *et al.*, 2009)
IR: impregnation ratio, V_{total}: total volume, V_{meso}: mesopore volume, V_{micro}: micropore volume, D_p: pore diameter, nm: nanometre, FB: fruit bunch										

3.5 Characterisation of AC

3.5.1 Surface chemistry mechanism and morphology

AC porosity, pore volume, size, surface area and other structural characteristics are relative to adsorption capacity. FTIR analysis identifies the functional groups and chemical on the edges and planes of ACs, which are very important in AC characterisation and in prediction of adsorption performance. The surface chemistry and functional groups of AC are reliant on the precursor, activating agent, activation process and conditions. Franca et al., (2010) identified oxygen, nitrogen and hydrogen, as important atoms on the surface of AC, because of their ability to bond with other elements (Pezoti *et al.*, 2016).

In surface chemistry analysis, metal ions are bound by electrostatic forces into the permeable networks at acidic pH, as most effective adsorptions occur below pH 7. This is because of the strong role of the oxygenated acidic surfaces. Some adsorption at higher pH is assisted by chelating and complex formation (González-García, 2018). Carboxyl groups also contribute to heavy metal adsorption by biomass adsorbents while phenolic groups are associated with the formation of complexes with heavy metal pollutants (Shafeeyan *et al.*, 2010), and these could be direct determinants of the effectiveness of AC. While FTIR analysis provides important information, monoatomic species do not possess infrared spectra and this makes complex mixtures difficult to analyse (Coates, 2000).

A comparison of the FTIR spectra of bamboo feedstock, traditional and conventionally activated AC and microwave-assisted activated AC (Liu *et al.*, 2010) shows the effect of the H_3PO_4-induced microwave activation of bamboo's spectral pattern and shows that thermal activation with a furnace and microwave have distinctive differences. Pathak and Mandavgane examined the FTIR frequencies and the resultant effects of activation with citric acid on banana peels, showing that there are major differences dependent on the method of activation and the activating agent (2015).

Huang et al. (2011) demonstrated that H_3PO_4 breaks bonds and dissociates aliphatic and aromatic molecules, especially in biomasses, encouraging the removal of many volatile substrates, and initiating partial aromatisation and carbonisation for a defined AC. A study investigating pineapple peel impregnated with KOH activation showed FTIR spectra of the AC as major peaks within these ranges: 3230, 2360, 2040, 1420, 1050 and 830 cm^{-1}, indicating the location of N–H and C≡C, which are highly unstable; C=C—moderately unstable; and C–N, C–O and N–O functionalities, respectively, which indicates AC's capacity to permit attachment (Foo and Hameed, 2012e). KOH and K_2CO_3-induced AC were both enhanced in relation to its char and developed better when activated by microwave irradiation (Foo and Hameed, 2011e). The same activation process when used on a cotton stalk as a precursor showed identical absorbance bands. However, there was substantial variance in the spectra of $ZnCl_2$-activated AC. Sharp bands of 1630 and 1600 cm^{-1} are distinctive and are absent in KOH and K_2CO_3 ACs (Deng, Li, *et al.*, 2010). The surface chemistry of NaOH-induced AC from pomelo skin was observed to have an FTIR spectrum within 3413 and 3247 cm^{-1} correlated to the amine groups, and the band at 2980 cm^{-1} indicated the presence of an alkane group (Foo and Hameed, 2011b). For PKS, AC was produced through microwave and conventional methods with $ZnCl_2$; the O–H stretching vibration receded, validating the effectiveness of the two processes. The significant effect and reduction of hydrogen bonding spectral bands show that the $ZnCl_2$ typically dehydrates the sample from the point of impregnation.

3.5.2 Adsorption and kinetic mechanism

Pyrolysis takes place under inert conditions; this causes the release of volatile substances that form tar at elevated temperatures, depending on the type and quantity of material. Current kinetic models are inadequate for biomass pyrolysis, specifically in terms of the prediction of pyrolysis rate. Molecular modelling can potentially identify the pathways for cellulose and lignin to production of biofuels and AC. Models presume that kinetic constraints, such as the frequency factor and activation energy, are interdependent and contingent on both conversion mechanism and the extent of heating. Kinetic models presume a series of decompositions, for nth order reactions. By contrast, the distributed activation energy model (DAEM) describes the pyrolysis reaction itself, and postulates that many decomposition, nth order reactions occur simultaneously, with distributed activation energies (Dhaundiyal and Singh, 2017). There are also double exponential terms which can be used to describe the distributed activation energy model for isothermal pyrolysis. In order to find the accurate approximation, an asymptotic methodology is implemented (Dhaundiyal and Singh, 2017). The amount of tar depends on the temperature and duration of carbonisation. Feed rate also affects tar deposition, due to prevention of the escape of volatiles. Furthermore, the type of activating agent is also critical in determining the rate of tar transformation into gas.

Adsorption can be classified as physisorption or chemisorption. Physisorption uses van der Waals forces, whose effects rapidly decrease with increasing temperature (Al-Anber, 2011), while chemisorption results in the formation of chemical bonds between the adsorbate and adsorbent (Kong *et al.*, 2014). Several factors and variables influence adsorption processes of pollutants with AC. Consequently, AC adsorbs through van der Waals, hydrogen bonding and electrostatic charge (Maneerung *et al.*, 2016). The functional groups of the adsorbent are primarily relative to the production process. Skouteris et al., (2015) showed that, in some types of adsorption processes, such as in liquid-phase, the adsorption efficiency and potency of AC are strongly dependent on the physical structure of the AC, the pore assemblage and the functional groups with respect to the parent materials, and also showed that molecular weight and polarity of adsorbent are influential. Other secondary properties of the solutions that are potentially important include the adsorption thermodynamics, pH, molecular diffusion, concentration of adsorbate and ionic energy (Demiral *et al.*, 2014).

Adsorption capacity is generally determined by the percentage of the pollutant removed, calculated as in Equations **(3-2**) and **(3-3**) (Mohammad and Ahmed, 2017):

$$q_t = (\frac{C_0 - C_t}{m})\, V \,, \qquad \textbf{(3-2)}$$

$$R = \left(\frac{C_0 - C_t}{C_0}\right) 100\% , \tag{3-3}$$

where, q_t (mg/g) symbolises the adsorption capacity, C_0 represents, initial pollutant concentration at start time and C_t (mg/cm^3) represents pollutant concentration at time (t). V (cm^3) denotes the volume of the adsorption medium and m (g), the adsorbent weight.

The adsorption performances of ACs derived from agricultural wastes are shown in Table 3-5. Unfortunately, the literature usually provides insufficient information on the adsorption parameters. However, AC activated by H_3PO_4 is very effective in the removal of contaminants and adsorption, taking place at 25–30 °C. Adsorption occurs mostly in the pH range of 4–7. Salt activators have a wide range of pH for adsorption, which also depends on concentration of the solution.

Table 3-5 Adsorption capacities and parameters of chemically-activated agricultural wastes based on activating agent

Adsorbent	Activator	Activation Temp /MW power (W)	IR	Adsorbate	S_{BET} m^2/g	Adsorption capacity (mg/g)	CR	Contact time (min)	Contact Temp °C	Contact pH	Reference
Durian shell	H_3PO_4	500 °C	1:0.30	Toluene	1404	874		2 h	25		(Tham *et al.*, 2011)
Waste tea	H_3PO_4			MB	1398	288.34					(Gokce and Aktas, 2014)
Sugarcane bagasse	H_3PO_4	500 °C	3:1	Pb	320	170.90	6	30 min	25	4	(Huang *et al.*, 2014)
Cotton stalk	H_3PO_4	500 °C	3:2	Pb(II)	1570	119			25	4.4	(Li, Zheng and Li, 2010)
Olive stone	H_3PO_4	600 °C	1:1.5	Cd	1565	24.83				5	(Obregón-Valencia and Sun-Kou, 2014)
Coconut husk	KOH	700 °C		MB	1356	418.15					(Foo and Hameed, 2012b)
Banana peel	KOH	800 °C		MB	2086	385.12			60	6	(Liu *et al.*, 2014)

EFB (char)	KOH	360 W	1:0.75	MB	807	344.80	50			4	(Foo and Hameed, 2011d)
Date stone	KOH	600 W	1:1.75	MB	856	316.10					(Foo and Hameed, 2011c)
Coconut shell	KOH	700 °C	1.5:1	Benzene	478	212.77			30		(Mohammed *et al.*, 2015)
Orange peel	NaOH			Reactive Blue 19		166.60	100	24 h	30	4	(Ahmed, Khalil and El-nabarawy, 2012)
Coconut shell	KOH	800 °C	1:2	Pb	1135	151.52	4			5	(Song *et al.*, 2014)
Peanut shell	KOH			Cr(VI)	96	16.26	40	7 h	25	4	(AL-Othman, Ali and Naushad, 2012)
Tea seed shell	$ZnCl_2$	500 °C	1:1	MB	1531	342.70				6.3	(Gao *et al.*, 2013)
Pineapple waste	$ZnCl_2$	500 °C	1:1	MB	915	288.34		12 h			(García *et al.*, 2017)

Corn cob	K_2CO_3	600 W	1:0.75	MB	765	275.32					(Elsayed and Zalat, 2015)
Cotton stalk	$ZnCl_2$	560 W	1:1.6	MB		193.50	4	2 h		7	(Deng *et al.*, 2009)
Pistachio nut shell	$ZnCl_2$			Hg	1492	24.78		100 min	25	6	(Aghajani, Zand-Monfraed and Bahmani-Androod, 2014)
Hazelnut shell	$ZnCl_2$	700 °C		Pb	1067	13.05	200	10 min		5.7	(Imamoglu and Tekir, 2008)
Olive stone	$ZnCl_2$	650 °C		Cd	790	1.85	50	90 min	25	9	(Kula *et al.*, 2008)
IR: impregnation ratio, CR: concentration range, MW: Microwave, W: watt, MB: methyl blue											

Adsorption isotherms are series of measurements relative to adsorbed and non-adsorbed amounts in a single process. The gas and solute adsorptions are functions of pressure and are dependent on chemical structure. Isotherm models are necessary for AC when a batch system for wastewater treatment is designed. This evaluates the suitability of the adsorption system, also showing the system to be endothermic or exothermic (Oginni *et al.*, 2019). The thermodynamic assumptions provide a guide to the adsorption mechanism, adsorbent affinity and the fundamental approaches. The models are illustrated in Table 3-6 and consider several assumptions and parameters for plotting adsorption isotherms.

Table 3-6 Adsorption isotherm models descriptions and challenges

Isotherm (Ayawei, Ebelegi and Wankasi, 2017)	Nonlinear form (Ayawei, Ebelegi and Wankasi, 2017)	Linear form	Plot	Nomenclature	Description/Assumptions
Langmuir	$q_e = \frac{Q_0 bc_e}{1 + bc_e}$	$\frac{q_e}{C_e} = bQ_0 - bq_e$	$\frac{q_e}{C_e} vs\ q_e$	q_e=equilibrium sorption capacity for metal C_e=equilibrium solute concentration in solution b=Langmuir constant	-The simplest isotherm -Assumes that adsorption is limited to monolayer -There is insignificant interaction and change in the sorption process -The model is identical to energy being adsorbed
Freundlich	$q_e = K_f\ C_e^{1/n}$	$logq_e = logK_F + \frac{1}{n}\ logC_e$	$logq_e\ vs\ logC_e$	K_F= equilibrium constant for relative adsorption n =adsorption constant indicative of intensity	-Relative to multi-layer adsorption -widely applied in organic compounds and highly interactive substance

Sip’s isotherm	$q_e = \frac{K_s C_e^{\beta}\ s}{1+\ a_s\ C_e^{p}\ s}$	$\beta In(C_e) = -In\left(\frac{K_s}{q_e}\right) + In(a_s)$	$In\left(\frac{K_s}{q_e}\right) vs\ In(C_e)$	β = Sip’s constant	-combination of Langmuir and Freundlich -It is governed by pH, temperature and concentration changes
Temkin	$q_e = \frac{RT}{bT} InA_T C_e$	$q_e = \frac{RT}{b_T} InA_T + (\frac{RT}{b_T}) InC_e$	$q_e\ vs\ InC_e$	A_T and b_T =Tempkin constants	-Takes care of adsorbate-adsorbent interaction -Used for predicting the gas-phase equilibrium
Khan	$q_e = \frac{q_s b_k C_e}{(1+b_k C_e)a_k}$			b_k and a_k are model constant and model exponent	-General adsorption model for adsorbate from pure dilute equation solutions
Redlich-Peterson	$q_e = \frac{K_g C_e}{1+a_g C_e^{\beta}}$	$In\left(K_R \frac{C_e}{q_e} - 1\right) = gIn(C_e) + In(a_R)$	$In\left(K_R \frac{C_e}{q_e}\right) vs\ In(C_e)$	KR, aR, and β = Redlich–Peterson parameters. β takes values between 0 and 1. For β=1 the model can be correlated to the Langmuir form	- It is anti-ideal monolayer adsorption -Has a linear relative dependence on concentration of solution

Radke-Prausnitz	$q_e = \frac{a_{gp} r_g C_e^{\beta g}}{a_{gp} + r_g C_e^{\beta_e - 1}}$			The outlook of surface diffusion Relative role of pore volume. aR and rR = model constants	-Preferred in most systems at low adsorbate concentration Good for wide range of adsorbate concentration
Frenkel-Halsey-Hill	$In\left(\frac{C_e}{C_s}\right) = -\frac{\alpha}{RT}(\frac{q_s}{q_e^d})^r$			Where d, α and r = sign of the interlayer spacing (m),	
Toth	$Q_e = Q_{max} \frac{b_T C_e}{[1 + (b_1 C_e)^{1/\eta\tau}]^{\eta\tau}}$			bT and nT = constants. if nT=1, Toth isotherm can be transformed to Langmuir isotherm equation	-Reduces error in experimental data -Predicts equilibrium data -Applicable in the modelling of several multilayer and heterogeneous adsorption systems
Dubinin-Radushkevich	$q_e = (q_e) \exp(-k_d \varepsilon^2)$	$In(q_e) = In(q_s) - K_{ad} \varepsilon^2$	$In(q_e) vs\ \varepsilon^2$	k_d = isotherm constant. ε = RT ln(1+1/C_e) ,R, T and Ce = gas constant Ce Temperature (K)	

3.6 Production process challenges

3.6.1 Washing and milling

Some biomass wastes, such as oil palm residue (OPR), have a high percentage of tramp material, including soil, while oil palm processing waste (OPW) does not, and instead has a high oil content. Hence, the need for washing can vary significantly. A high water requirement raises the production cost and hot water may be required to remove the oil attached to the biomass precursor. If the oil is not properly removed, it produces copious amounts of smoke during carbonisation, and if the temperature is not high enough (say below 400 °C), it forms tars within the biomass material, preventing the escape of volatiles, thereby resulting in improper development of pore structure, which requires a high inert gas flow rate to effectively displace volatile materials.

OPW is produced mostly in the form of large particles and lumps; therefore, size reduction is crucial for utilisation in AC production. This is done by milling figure 6 (Gil, Luciano and Arauzo, 2015), a high-energy operation (Kelechi E. Anyaoha *et al.*, 2018). Particle size is one of the crucial determinants in the thermochemical route; physical condition of biomass notwithstanding, the method influences activation rate and other production parameters (Gil and Arauzo, 2014). There is also difficulty in milling mesocarp fibre (MF) and EFB, rather than palm kernel shell (PKS), due to low brittleness. Conventional hammer mills typically have a 250 mm diameter rotor at a rated power of about 20 kW (Vigneault, C., Rothwell, T.M., Bourgeois, 1992), but there may be a need to use swinging hammers operating at high velocity (Liu, Wang and Wolcott, 2016). Biomass waste can be crushed when dry, sieved and graded into different uniform sizes of less than 2 mm using a milling machine (Deng, Li, *et al.*, 2010), to achieve uniform distribution of heat. The mechanical properties of different parts of OPW vary and it is important to minimise dust production. To minimise loss of biomass, a dust collector is installed, which aids in throughput flow and overcomes air flow resistance (Bitra *et al.*, 2009). Pre-treatments, such as drying and sieving, occasionally play a role in determining energy consumption. Establishing uniformity of particle sizes is largely contingent on their moisture content and other physical properties. Brittleness, hardness and elasticity also affect the energy requirements in milling. Phillip et al. (2017), studied the mechanical and physical influence of PKS, and showed that the aggregate crushing value is 5.3% and that of the flakiness index is 63.2%, indicating that PKS milling behaviour is acceptable.

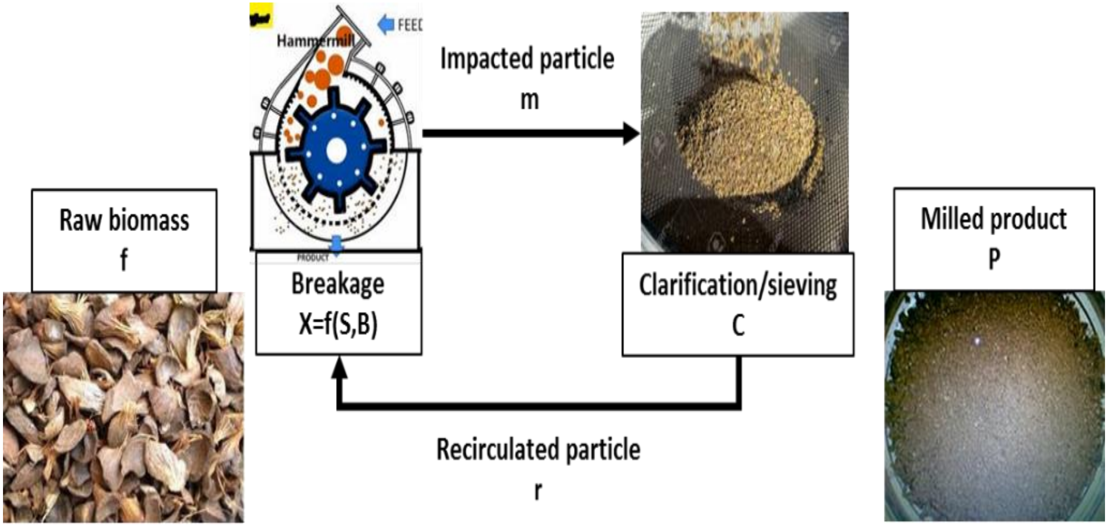


Figure 3-6 Hammer milling process for biomass

The efficiency of a hammer milling operation is determined by the nature of the biomass, and thus, milling tendencies vary widely. Several physical and mechanical properties are important, e.g., material breakage, as the fracture reaction is contingent on impact frequency, energy, moisture content and biomass properties (Gil, Luciano and Arauzo, 2015). Vogel and Peukert (2003) expressed the phenomenon of breakage as in Equation **(3-4)**:

$$S = 1 - exp\{-f_{mat} xk(W_{m,kin} - W_{m,min})\}. \qquad \textbf{(3-4)}$$

X represents the initial particle size, and k and $W_{m,ki}$ are the impact frequency and specific kinetic energy of the impact, respectively. $W_{m,min}$ is the threshold energy. The material properties in terms of its resistance and minimum specific energy are relevant to determine fracture and breakage factor which define the milling rate (Vogel and Peukert, 2004). The energy requirement increases with reducing particle size (Naimi *et al.*, 2013). However, it should be noted that the physical properties influence feeder design, biomass flow rate and reactor performance

(Dai, Cui and Grace, 2012). For each batch of AC production, the biomass should be of uniform particle size. Higher density also translates to lower tensile strain. The energy requirement for the milling process contributes to about 15%–30% of the overall energy requirement for AC production (Naimi *et al.*, 2013).

3.6.2 Microwave power and radiation duration

The energy requirement is dependent on the type of reactor and the effect of power is relative to the duration of the process. The reaction temperature is maintained after the heating stage, as power remains constant. Evaluating the influence of microwave power on yield, time is a primary factor. Hoseinzadeh Hesas et al. (Hoseinzadeh Hesas *et al.*, 2015) assessed the influence time of the microwave radiation relative to the surface consistency of AC, in order to optimise power output to achieve the appropriate heating rate and process temperature. High radiation power of above 1000 W for an extended time may result in total carbonisation with the adverse effect of reducing surface area and porosity (Josip *et al.*, 2016). For activation, the power range of 100–200 W is inadequate to create complete release of volatile substances, thereby resulting in improper development of pores with negligible influence on the adsorption capacity. At about 300–1000 W, the adsorption efficiency increases and pore development is better defined. However, with a higher thermal radiation there is greater loss in weight beyond the optimum range and collapse of the pore structures; thus, there needs to be a balance between activation duration and microwave power.

Microwave radiation duration is another important factor and strongly affects the resulting characteristics of the activated material. Thus, using the microwave heating method for a period of 5 min, the S_{BET} initially increases to a maximum value of 2996 m^2/g at 20 min, and then hardly changed with the increase in the activation duration for the char of Mesocarbon microbeads (Ji *et al.*, 2007).

Adsorption can be improved by an increase in radiation time. For example, with pineapple as a precursor, a 4 min radiation time difference increased adsorption from 206 to 283 mg/g, which then decreased after 6 min as carbon yield decreased. Further increase in process time beyond the optimum always leads to the formation of hotspots and collapse of pore structures (Foo and Hameed, 2012e). A typical duration is 5–20 min for char, but if raw biomass is impregnated with activation agent, an appropriate time will be about 15 min. Moisture content could also create imbalance in the prediction table for process duration.

3.6.3 Activation interaction and temperature

The inter-molecular interaction within the biomass precursor under an electromagnetic field involves the release of an enormous amount of energy relative to the quantity of material being processed. The process outcome is dependent on the dielectric factors of the precursor (Thostenson and Chou, 1999). Reaction during activation is highly influenced by the type of activating agent. Each biomass material reacts differently to different activating agents and the products differ. Palm kernel shell (PKS) and other oil palm wastes (OPW) were used in biochar production by microwave process, at different radiation levels. The biochar yields were 38, 35 and 33 wt.%, for 500, 600, 700 W respectively. Typically, more volatiles are released as microwave power is increased. In conventional systems, the major carbon losses occur during milling, sieving and washing. The losses during carbonisation can be minimised by the right choice of carbonisation temperature range. Mushtaq et al. (2014) have explored the effects of sample variability, particle size, moisture content, type of activating agent and inert gas flow rate on the pyrolysis and activating process and concluded that each type of biomass must be individually characterised.

The external surface temperature can be measured with infrared pyrometer; however, not during the actual processing itself. Another challenge of microwave radiation is the generation of hot spots because of the non-vegetative impurities in the precursor [79,94]. The thermal energy and temperature value of the sample core can be up to 500 °C higher than the external temperature (Hoseinzadeh Hesas *et al.*, 2015). Nonetheless, microwave power of 450 W is considered to be the lowest possible power required to cause significant changes in the in the biomass's structure for production of an efficient AC; below that, AC cannot be effectively produced (Huang *et al.*, 2011). In order to reduce AC process time, a novel method of impregnating OPW char with CuO receptors resulted in the rapid increase of sample thermal energy, although its use resulted in the generation of widely varying pore structures (Nüchter *et al.*, 2004).

Unfortunately, due to limited choices of measuring technique, sample temperature measurement was often ignored in previous works on microwave-assisted reactions (Nüchter *et al.*, 2004). There are three options for the measurement of temperature in microwaves operation: shielded thermocouples; IR-sensors, which measure infrared radiation as passive sensors; and a fibre optics sensor, which measures temperature up to 400 °C using an external transducer based on the wavelength modulation principle. Shielded thermocouple measurement is a cost-effective option (Ji *et al.*, 2007). However, it is inappropriate in the presence of non-polar solvents. In AC production occurring above 300 °C, thermocouples are not recommended (Nüchter *et al.*, 2004). The temperature of the sample during MW treatment can also be measured by using an infrared pyrometer (Ji *et al.*, 2007). In general, there is difficulty in ensuring good temperature regulation, though the use of a water jacket is possible (Waheed Ul Hasan and Ani, 2014). However, such an approach will not work for any large-scale process, given the thermal inertia inherent in such a system. A built-in-sensor on the reactor and further research on the appropriate reactor material could help to overcome such challenges.

3.6.4 Tar deposition

The constituents and characteristics of tars depend on the type of fuel and thermal process. The formation of tar is common; however, at a high temperature, primary tars vapours can be cracked. This situation can be influenced by reactor. The primary tars contain substances such as dimethoxy phenol, trimethoxybenzene and hydroxy methoxy benzoic acid, and these can be transformed into xylene phenol and toluene. There are tertiary tars also contain materials such as benzene, naphthalene, acenaphthylene, phenalene and pyrene. The presence of tar compounds such as 1-methylnaphthalene, which has a boiling point of 244.8 °C, are problematic, as they can emit acrid smoke during decomposition.

The presence of tar in a thermal process creates complex problems, especially in the utilisation downstream. During AC production, AC can re-adsorb it. Tar can be removed by decomposition or adsorption by activated carbon. In the process of AC production, tar causes reduction in the performance of AC (Phuphuakrat, Namioka and Yoshikawa, 2010). Phenol and cresol available in biomass can be degraded by microbial agents such as yeast (Alexieva *et al.*, 2008) in tar removal.

A study by Abu El-Rub et al., (2008) showed that tar can be removed by thermal cracking and a catalytic processes. It is necessary to address the influence of tars due to their carcinogenic character, ability to form coke and plugging which could disrupt the system. However, some catalysts can also affect the characteristics of AC. Finally, the use of alkali–metal–base for the removal of tar can also result in particle agglomeration at a high temperature.

3.6.5 Equipment selection and mode

The laboratory scale microwave typically only produces small quantities of material and 10–20 g of AC is typical. Pyrex glass reactors and Teflon reactors generally perform well in the laboratory but may not be suitable for scaling up. Ceramic/solid sintering materials also seem suitable for microwave processing but require further study. Evaluating AC production by means of laboratory-scale microwave systems is inexpensive, but cannot provide appropriate understanding of the molecular interactions and transformational kinetics in AC production at scale (Liew *et al.*, 2017a), and there is an urgent need for results from appropriately sized equipment.

There are advantages related to using a concentrated stream of energy when utilising unimode microwave radiation. However, most practical systems will use multimode radiation in a thermochemical process (Nüchter *et al.*, 2004). Multimode is relatively cheap and can be designed to deal with large sample sizes. However, unimode is better in terms of controllability (Leonelli and Veronesi, 2015). The energy release of unimode radiation depends on reactor material, size, waveguide channel, the properties precursor and other contents of the sample. Generally, these devices have magnetrons directed through a waveguide and an electromagnetic field (Nüchter *et al.*, 2004). Operation is also influenced by the mixing of biomass and activating agents, the cooling method, control heating rate, the seal and microwave leakage rate. To overcome these technical challenges and reduce overall process time, a continuous process should be used, since it eliminates wastage during transfer and mechanical washing, and ensures uniform production, as most operations are automated.

3.6.6 Dielectric properties

The dielectric properties of any material are primary factors in the transformation of electromagnetic energy into heat for AC production. Most biomass has poor microwave absorbing properties (Salema *et al.*, 2013). Abubakar et al. (2013) explored the influence of dielectric properties of OPW and several studies have explored the dielectric properties of agricultural waste and other biomass materials.

The relative dielectric constant, dielectric loss factor (ε_r) and tangent loss for OPW and corresponding biochar, at varying frequencies (0.2–10 GHz) and at ambient conditions (room temperature of about 25 °C) are given in Table 3-7, for a range of materials. The dielectric constant for most materials decreases with increasing frequency (Salema *et al.*, 2013), while the loss factor varies in the opposite direction. Most biomass materials are only weak absorbers. The average loss tangent of biomass feedstock is less than 0.1. The addition of activating agents improves the microwave absorbability (Chang *et al.*, 2017). In some biomass materials, absorbability increases rapidly at elevated temperatures and this can result in process challenges due to thermal runaway (Bykov, Rybakov and Semenov, 2001). The poor understanding of the relative influence of electromagnetic energy on combined and mixed biomass on the microwave heating remains a challenge in obtaining homogeneous products (Namazi, Allen and Jia, 2015). High moisture content in a material can affect its dielectric properties and result in a high microwave treatment efficiency (Chang *et al.*, 2017).

Table 3-7 Relationship between penetration depth of biomass and various microwave frequencies (Oyejobi *et al.*, 2012; Abubakar, Salema and Ani, 2013; Okahisa *et al.*, 2018)

Material	Frequency (GHz)	Penetration depth (cm)	Permittivity (ε'_r)	Tangent loss (Tanδ)
PKS	0.9-5.8	5.5-36	2.7	0.13
MF	2.5-5.8	10.2-24.8	2.0	0.08
EFB	-	-	6.4	0.3
Water	2.54	1-4	-	-
Paper	2.54	20-60	-	-
Wood	2.54	8-350	2.3	0.11
Natural Rubber	2.54	15-350	2.1	0.003

During carbonisation and activation, the delivery of products helps to release volatiles. When the volatile products are not desired, the issue of how to exhaust them arises in the design setup. In most laboratory tests and analyses of microwave-induced activation, modified domestic systems are used for the work, so are not relevant for industrial applications. There are also a few issues with the use of stirrers in microwave systems. Small particles are capable of elutriating with any vapour generated, especially at higher stirring speeds, affecting the carbon yield; therefore, a stirrer should not be installed close to the volatiles delivery line and size should be designed to reduce arcing which is seen as flashes or sparks (Salema and Ani, 2012).

3.7 Scale of microwave for use in preparing AC

The technique of the microwave method to produce AC depends first and foremost on the scale of potential units. In 2010, Leonelli and Mason published an article claiming that microwave and ultrasonic processing have good prospects for industry, but the focus was primarily on the food industry (Leonelli and Mason, 2010). Progress in the food area seems to have continued, with microwaves being used in particular for lower-temperature applications, such as drying, although interestingly, even for this type of application, there are issues with the formation of hot spots (Guo *et al.*, 2017). Generally, what has been offered is still relatively small, with levels of 6 L/h being suggested as adequate (Morschhäuser *et al.*, 2012). However, there does seem to be some recent progress and a current paper suggested that microwave units were available able to process flow rates of up to 750 kg/h for drying (Petri *et al.*, 2019). There is also at least one company offering a microwave reactor with a capacity of 7 m^3, which seems to be sufficient for this type of application (World, 2013). Interestingly, a recent patent for AC preparation from nuts, gave the technology a technological readiness level of 5 (Bridge, 2019). Thus, it is clear that, at least to date, there are no full-scale demonstrations of microwave technology producing AC at an industrial scale, and it is there that future research is essential if this technology is to be meaningfully used to make commercial quantities of AC in the near future (Beims, Simonato and Wiggers, 2019).

3.8 Conclusion

The choice of activating agent for the thermochemical production of high-grade activated carbon (AC) from agricultural residues and wastes, such as feedstock, requires innovative methods. Overcoming energy losses, and using the best techniques to minimise secondary contamination and improve adsorptivity, are critical. Here, we review the importance and influence of activating agents on agricultural waste: how they react and compare conventional and microwave processes. In particular, adsorbent pore characteristics, surface chemistry interactions and production modes were compared with traditional methods. It was concluded that there are no best activating agents; rather, each agent reacts uniquely with a precursor, and the optimum choice depends on the target adsorbent. Natural chemicals can also be as effective as inorganic activating agents, and offer the advantages that they are usually safe, and readily available. The use of a microwave, as an innovative pyrolysis approach, can enhance the activation process within a duration of 1–4 h and temperature of 500–1200 °C, after which the yield and efficiency decline rapidly due to molecular breakdown. This study also examines the biomass milling process requirements; the influence of the dielectric properties, along with the effect of washing; and experimental setup challenges. The microwave setup system, biomass feed rate, product delivery, inert gas flow rate, reactor design and recovery lines are all important factors in the microwave activation process, and contribute to the overall efficiency of AC preparation. However, a major issue is a lack of large-scale industrial demonstration units for microwave technology.

The chemical activation approach for AC production is widely applied because of its ability to produce AC with a wide range of activating agents under a myriad of processing conditions. The choice of activating agent is contingent on the adsorption target and precursor. Each activating agent has a unique impact on the characteristics and applications of the resultant AC. However, due to the challenges of AC production from biomass, there is a need to develop techniques to achieve industrial-scale production of AC. Microwave systems accelerate the activation process. Bases, acids and $ZnCl_2$ are generally considered to be particularly effective. Unfortunately, natural chemicals are rarely used for activation despite their potential to reduce secondary contamination which arises when materials like $ZnCl_2$ and inorganic acids are used, due to the difficulty of effectively removing them by washing. It is clear that microwave treatment is potentially better than conventional approaches, especially in terms of energy saving and process duration; however, to date there are no commercial application of such technology. Despite the existence of larger and larger microwave systems, there remains an urgent need to demonstrate this technology at a commercial or near-commercial scale

3.9 References

Abbas, A. F. and Ahmed, M. J. (2016) ‘Mesoporous activated carbon from date stones (Phoenix dactylifera L.) by one-step microwave assisted K_2CO_3 pyrolysis’, *Journal of Water Process Engineering*, 9, pp. 201–207. doi: 10.1016/j.jwpe.2016.01.004.

Abdolali, A., Ngo, H. H., Guo, W., Zhou, J. L., Du, B., Wei, Q., Wang, X. C. and Nguyen, P. D. (2015) ‘Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies’, *Bioresource Technology*, 193, pp. 477–487. doi: 10.1016/j.biortech.2015.06.123.

Abechi, S. E., Gimba, C. E., Uzairu, A. and Dallatu, Y. A. (2013) ‘Preparation and Characterization of Activated Carbon from Palm Kernel Shell by Chemical Activation’, *Research Journal of Chemical Sciences*, 3(7), pp. 54–61. doi: 10.1088/1757-899X/226/1/012156.

Abu El-Rub, Z., Bramer, E. A. and Brem, G. (2008) ‘Experimental comparison of biomass chars with other catalysts for tar reduction’, *Fuel*, 87(10–11), pp. 2243–2252. doi: 10.1016/j.fuel.2008.01.004.

Abubakar, Z., Salema, A. A. and Ani, F. N. (2013) ‘A new technique to pyrolyse biomass in a microwave system: Effect of stirrer speed’, *Bioresource Technology*, 128, pp. 578–585. doi: 10.1016/j.biortech.2012.10.084.

Aghajani, Z., Zand-Monfraed, M.-R. and Bahmani-Androod, S. (2014) ‘Removal of lead (II) and mercury (II) from aqueous solutions and waste water using pistachio soft shell as agricultural by- products’, 5(3), pp. 170–176.

Ahmed, M. J. (2011) ‘Preparation of Activated Carbons from Date Stones by Chemical Activation Method Using Fecl3 and Zncl2 as Activating Agents’, *Journal of Engineering*, 17(4), pp. 1007–1022.

Ahmed, M. J. (2016) ‘Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments: Review’, *Process Safety and Environmental Protection*. Institution of Chemical Engineers, 102, pp. 168–182. doi: 10.1016/j.psep.2016.03.010.

Ahmed, S. A. S., Khalil, L. B. and El-nabarawy, T. (2012) ‘Removal of Reactive Blue 19 dye from Aqueous Solution Using Natural and Modified Orange Peel’, 13(4), pp. 212–220.

Ahmida, K., Darmoon, M., Al-tohami, F., Erhayem, M. and Zidan, M. (2015) ‘Effect of Physical and Chemical Preparation on Characteristics of Activated Carbon from Agriculture Solid Waste and their Potential Application’, *International Conference on Chemical, Civil and Environmental engineering (CCEE-2015) ,Istanbul,Turkey*, pp. 83–87.

Al-Anber, M. A. (2011) ‘Thermodynamics Approach in the Adsorption of Heavy Metals’, in *Thermodynamics - Interaction Studies - Solids, Liquids and Gases*. London, UK, pp. 737–764. doi: 10.5772/21326.

AL-Othman, Z. A., Ali, R. and Naushad, M. (2012) ‘Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies’, *Chemical Engineering Journal*, 184, pp. 238–247. doi: 10.1016/j.cej.2012.01.048.

Alexieva, Z., Gerginova, M., Manasiev, J., Zlateva, P., Shivarova, N. and Krastanov, A. (2008) ‘Phenol and cresol mixture degradation by the yeast Trichosporon cutaneum’, *Journal of Industrial Microbiology and Biotechnology*, 35(11), pp. 1297–1301. doi: 10.1007/s10295-008-0410-1.

Allwar, A., Hartati, R. and Fatimah, I. (2017) ‘Effect of nitric acid treatment on activated carbon derived from oil palm shell’, in *International Conference on Chemistry, Chemical Process and Engineering*. Mumbai, India: American Institute of Physics. doi: 10.1063/1.4978202.

Anyaoha, Kelechi E, Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Critical evaluation of oil palm fresh fruit bunch solid wastes as soil amendments : Prospects and challenges’, *Resources, Conservation & Recycling*, 136(January), pp. 399–409. doi: 10.1016/j.resconrec.2018.04.022.

Anyaoha, Kelechi E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Evaluating oil palm fresh fruit bunch processing in Nigeria’, *Waste Management and Research*, 36(3), pp. 236–246. doi: 10.1177/0734242X17751848.

Arami-Niya, A., Daud, W. M. A. W. and Mjalli, F. S. (2010) ‘Using granular activated carbon prepared from oil palm shell by ZnCl 2 and physical activation for methane adsorption’, *Journal of Analytical and Applied Pyrolysis*, 89(2), pp. 197–203. doi: 10.1016/j.jaap.2010.08.006.

Arami-Niya, A., Wan Daud, W. M. A., S. Mjalli, F., Abnisa, F. and Shafeeyan, M. S. (2012) ‘Production of microporous palm shell based activated carbon for methane adsorption: Modeling and optimization using response surface methodology’, *Chemical Engineering Research and Design*, 90(6), pp. 776–784. doi: 10.1016/j.cherd.2011.10.001.

Arampatzidou, A. C. and Deliyanni, E. A. (2016) ‘Comparison of activation media and pyrolysis temperature for activated carbons development by pyrolysis of potato peels for effective adsorption of endocrine disruptor bisphenol-A’, *Journal of Colloid and Interface Science*, 466, pp. 101–112. doi: 10.1016/j.jcis.2015.12.003.

Arena, N., Lee, J. and Clift, R. (2016) ‘Life Cycle Assessment of activated carbon production from coconut shells’, *Journal of Cleaner Production*, 125, pp. 68–77. doi: 10.1016/j.jclepro.2016.03.073.

Ayawei, N., Ebelegi, A. N. and Wankasi, D. (2017) ‘Modelling and Interpretation of Adsorption Isotherms’, *Journal of chemistry*, 2017(September). doi: 10.1155/2017/3039817.

Aziz, M., Kurniawan, T., Oda, T. and Kashiwagi, T. (2017) ‘Advanced power generation using biomass wastes from palm oil mills’, *Applied Thermal Engineering*, 114, pp. 1378–1386. doi: 10.1016/j.applthermaleng.2016.11.031.

Bachrun, S., AyuRizka, N., Annisa, S. and Arif, H. (2016) ‘Preparation and characterization of activated carbon from sugarcane bagasse by physical activation with CO $_2$ gas', *IOP Conference Series: Materials Science and Engineering*, 105, p. 012027. doi: 10.1088/1757-899X/105/1/012027.

Basta, A. H., Fierro, V., El-Saied, H. and Celzard, A. . (2009) '2-Steps KOH activation of rice straw: An efficient method for preparing high-performance activated carbons', *Bioresource Technology*, 100(17), pp. 3941–3947. doi: 10.1016/j.biortech.2009.02.028.

Bedia, J., Belver, C., Ponce, S., Rodriguez, J. and Rodriguez, J. J. (2018) 'Adsorption of antipyrine by activated carbons from FeCl3-activation of Tara gum', *Chemical Engineering Journal*, 333(August 2017), pp. 58–65. doi: 10.1016/j.cej.2017.09.161.

Beims, R. F., Simonato, C. L. and Wiggers, V. R. (2019) 'Technology readiness level assessment of pyrolysis of trygliceride biomass to fuels and chemicals', *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 112(March), pp. 521–529. doi: 10.1016/j.rser.2019.06.017.

Ben-Iwo, J., Manovic, V. and Longhurst, P. (2016) 'Biomass resources and biofuels potential for the production of transportation fuels in Nigeria', *Renewable and Sustainable Energy Reviews*, 63, pp. 172–192. doi: 10.1016/j.rser.2016.05.050.

Bentsen, N. S., Felby, C. and Thorsen, B. J. (2014) 'Agricultural residue production and potentials for energy and materials services', *Progress in Energy and Combustion Science*, 40(1), pp. 59–73. doi: 10.1016/j.pecs.2013.09.003.

Bhadusha, N. and Ananthabaskaran, T. (2011) 'Adsorptive Removal of Methylene Blue onto ZnCl 2 Activated Carbon from Wood Apple Outer Shell : Kinetics and Equilibrium Studies', *Journal of chemistry*, 8(4), pp. 1696–1707.

Bhatnagar, A., Hogland, W., Marques, M. and Sillanpää, M. (2013) 'An overview of the modification methods of activated carbon for its water treatment applications', *Chemical Engineering Journal*, 219, pp. 499–511. doi: 10.1016/j.cej.2012.12.038.

Bitra, V. S. P., Womac, A. R., Chevanan, N., Miu, P. I., Igathinathane, C., Sokhansanj, S. and Smith, D. R. (2009) ‘Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions’, *Powder Technology*, 193(1), pp. 32–45. doi: 10.1016/j.powtec.2009.02.010.

Boonpoke, A., Chiarakorn, S., Laosiripojana, N., Towprayoon, S. and Chidthaisong, A. (2013) ‘Synthesis of activated carbon and MCM-41 from bagasse and rice husk and their carbon dioxide adsorption capacity’, *Journal of Sustainable & Environment*, 2, pp. 77–81.

Braz, C. E. and Crnkovic, P. M. (2014) ‘Physical – Chemical Characterization of Biomass Samples for Application in Pyrolysis Process’, *Chemical Engineering Transactions VOL. 37*, 37, pp. 523–528. doi: 10.3303/cet1437088.

Bridge, I. (2019) *Department of Science and Technology, South Africa*, *Activated carbon*. Available at: https://www.innovationbridge.info/ibportal/?q=content/activated-carbon (Accessed: 16 September 2019).

Bykov, Y. V., Rybakov, K. I. and Semenov, V. E. (2001) ‘High-temperature microwave processing of materials’, *Journal of Physics D: Applied Physics*, 34(13). doi: 10.1088/0022-3727/34/13/201.

Calvo-Muñoz, E. M., García-Mateos, F. J., Rosas, J. M., Rodríguez-Mirasol, J. and Cordero, T. (2016) ‘Biomass Waste Carbon Materials as adsorbents for CO_2 Capture under Post-Combustion Conditions’, *Frontiers in Materials*, 3(May), pp. 1–14. doi: 10.3389/fmats.2016.00023.

Cazetta, A. L., Vargas, A. M. M., Nogami, E. M., Kunita, M. H., Guilherme, M. R., Martins, A. C., Silva, T. L., Moraes, J. C. G. and Almeida, V. C. (2011) ‘NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption’, *Chemical Engineering Journal*, 174(1), pp. 117–125. doi: 10.1016/j.cej.2011.08.058.

Chand Bansal, R. and Goyal, M. (2005) *Activated Carbon Adsorption*, *Activated Carbon Adsorption*. Boca Raton, USA: CRC Press. doi: 10.1201/9781420028812.

Chang, J. S. L., Chan, Y. S., Law, M. C. and Leo, C. P. (2017) ‘Comparative microstructure study of oil palm fruit bunch fibre, mesocarp and kernels after microwave pre-treatment’, *IOP Conference Series: Materials Science and Engineering*, 217(1). doi: 10.1088/1757-899X/217/1/012026.

Chen, H. (2014) ‘Biotechnology of lignocellulose: Theory and practice’, in *Biotechnology of Lignocellulose: Theory and Practice*. Springer,:Berlin, Germany, pp. 1–511. doi: 10.1007/978-94-007-6898-7.

Chowdhury, Z. Z., Hamid, S. B. A., Das, R., Hasan, Md. Rakibul; Sharifuddin, M. Z., Khalid, K. and Uddin, M. N. (2013) ‘Preparation of Carbonaceous Adsorbents from Lignocellulosic Biomass and Their Use in Removal of Contaminants from Aqueous Solution’, *BioResources*, 8, pp. 6523–6555.

Claoston, N., Samsuri, A. W., Ahmad Husni, M. H. and Mohd Amran, M. S. (2014) ‘Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars’, *Waste Management and Research*, 32(4), pp. 331–339. doi: 10.1177/0734242X14525822.

Coates, J. (2000) ‘Interpretation of Infrared Spectra , A Practical Approach Interpretation of Infrared Spectra , A Practical Approach’, *Encyclopedia of Analytical Chemistry*, pp. 10815–10837. doi: DOI: 10.1002/9780470027318.

Cruz, G., Pirilä, M., Huuhtanen, M., Carrión, L., Alvarenga, E. and Keiski, R. L. (2012) ‘Production of Activated Carbon from Cocoa (Theobroma cacao) Pod Husk’, *Journal of Civil & Environmental Engineering*, 02(02). doi: 10.4172/2165-784X.1000109.

Dai, J., Cui, H. and Grace, J. R. (2012) ‘Biomass feeding for thermochemical reactors’, *Progress in Energy and Combustion Science*, 38(5), pp. 716–736. doi: 10.1016/j.pecs.2012.04.002.

Danish, M. and Ahmad, T. (2018) ‘A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application’, *Renewable and Sustainable Energy Reviews*, 87(April 2017), pp. 1–21. doi: 10.1016/j.rser.2018.02.003.

Danish, M., Hashim, R., Ibrahim, M. N. M. and Sulaiman, O. (2014) ‘Optimized preparation for large surface area activated carbon from date (Phoenix dactylifera L.) stone biomass’, *Biomass and Bioenergy*, 61(February), pp. 167–178. doi: 10.1016/j.biombioe.2013.12.008.

Daud, Z., Kassim, A. S. M., Aripin, A. M., Awang, H. and Hatta, M. Z. M. (2013) ‘Chemical Composition and Morphological of Cocoa Pod Husks and Cassava Peels for Pulp and Paper Production’, *Australian Journal of Basic and Applied Sciences*, 7(9), pp. 406–411.

Demiral, H., Baykul, E., Gezer, M. D., Erkoç, S., Engin, A. and Baykul, M. C. (2014) ‘Preparation and Characterization of Activated Carbon from Chestnut Shell and its Adsorption Characteristics for Lead’, *Separation Science and Technology (Philadelphia)*, 49(17), pp. 2711–2720. doi: 10.1080/01496395.2014.942742.

Deng, H., Li, G., Yang, H., Tang, Jiping and Tang, Jiangyun (2010) ‘Preparation of activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation’, *Chemical Engineering Journal*, 163(3), pp. 373–381. doi: 10.1016/j.cej.2010.08.019.

Deng, H., Yang, L., Tao, G. and Dai, J. (2009) ‘Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation-Application in methylene blue adsorption from aqueous solution’, *Journal of Hazardous Materials*, 166(2–3), pp. 1514–1521. doi: 10.1016/j.jhazmat.2008.12.080.

Deng, H., Zhang, G., Xu, X., Tao, G. and Dai, J. (2010) ‘Optimization of preparation of activated carbon from cotton stalk by microwave assisted phosphoric acid-chemical activation’, *Journal of Hazardous Materials*, 182(1–3), pp. 217–224. doi: 10.1016/j.jhazmat.2010.06.018.

Dhaundiyal, A. and Singh, S. B. (2017) 'Study of Distributed Activation Energy Model Using Various Probability Distribution Functions for the Isothermal Pyrolysis Problem', *Rudarsko-geološko-naftni zbornik*, 32(4), pp. 1–14. doi: 10.17794/rgn.2017.4.1.

Domínguez, A., Menéndez, J. A., Fernández, Y., Pis, J. J., Nabais, J. M. V., Carrott, P. J. M. and Carrott, M. M. L. R. (2007) 'Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas', *Journal of Analytical and Applied Pyrolysis*, 79(1-2 SPEC. ISS.), pp. 128–135. doi: 10.1016/j.jaap.2006.08.003.

Dural, M. U., Cavas, L., Papageorgiou, S. K. and Katsaros, F. K. (2011) 'Methylene blue adsorption on activated carbon prepared from Posidonia oceanica (L.) dead leaves: Kinetics and equilibrium studies', *Chemical Engineering Journal*, 168(1), pp. 77–85. doi: 10.1016/j.cej.2010.12.038.

Ello, A. S., De Souza, L. K. C., Trokourey, A. and Jaroniec, M. (2013) 'Development of microporous carbons for CO2 capture by KOH activation of African palm shells', *Journal of CO_2 Utilization*, 2, pp. 35–38. doi: 10.1016/j.jcou.2013.07.003.

Elsayed, M. A. and Zalat, O. A. (2015) 'Factor Affecting Microwave Assisted Preparation of Activated Carbon from Local Raw Materials', *International Letters of Chemistry, Physics and Astronomy*, 47, pp. 15–23. doi: 10.18052/www.scipress.com/ILCPA.47.15.

Farma, R., Fatjrin, D., Awitdrus and Deraman, M. (2017) 'Physical properties of activated carbon from fibers of oil palm empty fruit bunches by microwave assisted potassium hydroxide activation', *AIP Conference Proceedings*, 1801. doi: 10.1063/1.4973090.

Fidalgo, B., Williams, H. M., Dawson, E. A. and Parkes, G. M. B. (2014) 'Conventional and microwave-heated oxygen pulsing techniques on metal-doped activated carbons', *Journal of Porous Materials*, 21(1), pp. 81–89. doi: 10.1007/s10934-013-9750-y.

Foo, K. Y. and Hameed, B. H. (2011a) ‘Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption’, *Chemical Engineering Journal*, 166(2), pp. 792–795. doi: 10.1016/j.cej.2010.11.019.

Foo, K. Y. and Hameed, B. H. (2011b) ‘Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes’, *Chemical Engineering Journal*, 173(2), pp. 385–390. doi: 10.1016/j.cej.2011.07.073.

Foo, K. Y. and Hameed, B. H. (2011c) ‘Preparation of activated carbon from date stones by microwave induced chemical activation: Application for methylene blue adsorption’, *Chemical Engineering Journal*, 170(1), pp. 338–341. doi: 10.1016/j.cej.2011.02.068.

Foo, K. Y. and Hameed, B. H. (2011d) ‘Preparation of oil palm (Elaeis) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue’, *Desalination*, 275(1–3), pp. 302–305. doi: 10.1016/j.desal.2011.03.024.

Foo, K. Y. and Hameed, B. H. (2011e) ‘Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K_2CO_3 activation’, *Bioresource Technology*, 102(20), pp. 9814–9817. doi: 10.1016/j.biortech.2011.07.102.

Foo, K. Y. and Hameed, B. H. (2012a) ‘A cost effective method for regeneration of durian shell and jackfruit peel activated carbons by microwave irradiation’, *Chemical Engineering Journal*, 193–194, pp. 404–409. doi: 10.1016/j.cej.2012.04.055.

Foo, K. Y. and Hameed, B. H. (2012b) ‘Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance’, *Chemical Engineering Journal*, 184, pp. 57–65. doi: 10.1016/j.cej.2011.12.084.

Foo, K. Y. and Hameed, B. H. (2012c) ‘Factors affecting the carbon yield and adsorption capability of the mangosteen peel activated carbon prepared by microwave assisted K_2CO_3 activation', *Chemical Engineering Journal*, 180, pp. 66–74. doi: 10.1016/j.cej.2011.11.002.

Foo, K. Y. and Hameed, B. H. (2012d) 'Mesoporous activated carbon from wood sawdust by K_2CO_3 activation using microwave heating', *Bioresource Technology*, 111, pp. 425–432. doi: 10.1016/j.biortech.2012.01.141.

Foo, K. Y. and Hameed, B. H. (2012e) 'Porous structure and adsorptive properties of pineapple peel based activated carbons prepared via microwave assisted KOH and K_2CO_3 activation', *Microporous and Mesoporous Materials*, 148(1), pp. 191–195. doi: 10.1016/j.micromeso.2011.08.005.

Foo, K. Y. and Hameed, B. H. (2012f) 'Potential of jackfruit peel as precursor for activated carbon prepared by microwave induced NaOH activation', *Bioresource Technology*, 112, pp. 143–150. doi: 10.1016/j.biortech.2012.01.178.

Foo, K. Y. and Hameed, B. H. (2012g) 'Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K_2CO_3 activation', *Bioresource Technology*, 104, pp. 679–686. doi: 10.1016/j.biortech.2011.10.005.

Foo, K. Y. and Hameed, B. H. (2012h) 'Preparation of activated carbon by microwave heating of langsat (Lansium domesticum) empty fruit bunch waste', *Bioresource Technology*, 116, pp. 522–525. doi: 10.1016/j.biortech.2012.03.123.

Foo, K. Y. and Hameed, B. H. (2013) 'Utilization of oil palm biodiesel solid residue as renewable sources for preparation of granular activated carbon by microwave induced KOH activation', *Bioresource Technology*, 130, pp. 696–702. doi: 10.1016/j.biortech.2012.11.146.

Franca, A. S., Oliveira, L. S., Nunes, A. A. and Alves, C. C. O. (2010) 'Microwave assisted thermal treatment of defective coffee beans press cake for the production of adsorbents', *Bioresource Technology*, 101(3), pp. 1068–1074. doi: 10.1016/j.biortech.2009.08.102.

Fu, K., Yue, Q., Gao, B., Sun, Y., Wang, Y., Li, Q., Zhao, P. and Chen, S. (2014) 'Physicochemical and adsorptive properties of activated carbons from Arundo donax Linn utilizing different iron salts as activating agents', *Journal of the Taiwan Institute of Chemical Engineers*. Taiwan Institute of Chemical Engineers, 45(6), pp. 3007–3015. doi: 10.1016/j.jtice.2014.08.026.

Fu, K., Yue, Q., Gao, B., Wang, Y. and Li, Q. (2017) 'Activated carbon from tomato stem by chemical activation with FeCl2', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 529(February), pp. 842–849. doi: 10.1016/j.colsurfa.2017.06.064.

Gadkari, S., Fidalgo, B. and Gu, S. (2017) 'Numerical investigation of microwave-assisted pyrolysis of lignin', *Fuel Processing Technology*. The Authors, 156, pp. 473–484. doi: 10.1016/j.fuproc.2016.10.012.

Gan, C., Liu, Y., Tan, X., Wang, S., Zeng, G., Zheng, B., Li, T., Jiang, Z. and Liu, W. (2015) 'Effect of porous zinc-biochar nanocomposites on Cr(VI) adsorption from aqueous solution', *RSC Advances*. Royal Society of Chemistry, 5(44), pp. 35107–35115. doi: 10.1039/c5ra04416b.

Gao, J., Qin, Y., Zhou, T., Cao, D., Xu, P., Hochstetter, D. and Wang, Y. (2013) 'Adsorption of methylene blue onto activated carbon produced from tea (Camellia sinensis L.) seed shells: kinetics, equilibrium, and thermodynamics studies', *Journal of Zhejiang University SCIENCE B*, 14(7), pp. 650–658. doi: 10.1631/jzus.B12a0225.

Gao, L., Dong, F. Q., Dai, Q. W., Zhong, G. Q., Halik, U. and Lee, D. J. (2016) 'Coal tar residues based activated carbon: Preparation and characterization', *Journal of the Taiwan Institute of Chemical Engineers*. Elsevier B.V., 63, pp. 166–169. doi: 10.1016/j.jtice.2016.02.029.

García, J. R., Sedran, U., Zaini, M. A. A. and Zakaria, Z. A. (2017) 'Preparation, characterization, and dye removal study of activated carbon prepared from palm kernel shell', *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, pp. 1–10. doi: 10.1007/s11356-017-8975-8.

Gil, M. and Arauzo, I. (2014) ‘Hammer mill operating and biomass physical conditions effects on particle size distribution of solid pulverized biofuels’, *Fuel Processing Technology*, 127, pp. 80–87. doi: 10.1016/j.fuproc.2014.06.016.

Gil, M., Luciano, E. and Arauzo, I. (2015) ‘Population balance model for biomass milling’, *Powder Technology*, 276, pp. 34–44. doi: 10.1016/j.powtec.2015.01.060.

Girgis, B. S., Smith, E., Louis, M. M. and El-Hendawy, A. N. A. (2009) ‘Pilot production of activated carbon from cotton stalks using H3PO4’, *Journal of Analytical and Applied Pyrolysis*, 86(1), pp. 180–184. doi: 10.1016/j.jaap.2009.06.002.

Girgis, B. S., Soliman, A. M. and Fathy, N. A. (2011) ‘Development of micro-mesoporous carbons from several seed hulls under varying conditions of activation’, *Microporous and Mesoporous Materials*, 142(2–3), pp. 518–525. doi: 10.1016/j.micromeso.2010.12.044.

Gokce, Y. and Aktas, Z. (2014) ‘Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol’, *Applied Surface Science*, 313, pp. 352–359. doi: 10.1016/j.apsusc.2014.05.214.

González-García, P. (2017) ‘Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications’, *Renewable and Sustainable Energy Reviews*, (xxxx), pp. 1–22. doi: 10.1016/j.rser.2017.04.117.

González-García, P. (2018) ‘Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications’, *Renewable and Sustainable Energy Reviews*, 82(August 2017), pp. 1393–1414. doi: 10.1016/j.rser.2017.04.117.

Guo, Q., Sun, D. W., Cheng, J. H. and Han, Z. (2017) ‘Microwave processing techniques and their recent applications in the food industry’, *Trends in Food Science and Technology*, 67, pp. 236–247. doi: 10.1016/j.tifs.2017.07.007.

Gurten, I. I., Ozmak, M., Yagmur, E. and Aktas, Z. (2012) ‘Preparation and characterisation of activated carbon from waste tea using K2CO3’, *Biomass and Bioenergy*, 37, pp. 73–81. doi: 10.1016/j.biombioe.2011.12.030.

Hadi, P., Xu, M., Ning, C., Sze Ki Lin, C. and McKay, G. (2015) ‘A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment’, *Chemical Engineering Journal*. Elsevier B.V., 260, pp. 895–906. doi: 10.1016/j.cej.2014.08.088.

He, X., Ling, P., Qiu, J., Yu, M., Zhang, X., Yu, C. and Zheng, M. (2013) ‘Efficient preparation of biomass-based mesoporous carbons for supercapacitors with both high energy density and high power density’, *Journal of Power Sources*, 240, pp. 109–113. doi: 10.1016/j.jpowsour.2013.03.174.

Hernández-Montoya, V., García-Servin, J. and Bueno-López, J. I. (2012) *Thermal Treatments and Activation Procedures Used in the Preparation of Activated Carbons*, *Lignocellulosic Precursors Used in the Synthesis of Activated Carbon - Characterization Techniques and Applications in the Wastewater Treatment*. Edited by D. V. H. Montoya. InTech, Mexico. doi: 10.5772/39365.

Hidayu, A. R. and Muda, N. (2017) ‘Preparation and Characterization of Activated Carbon from Palm Kernel Shell’, *IOP Conference Series: Materials Science and Engineering*, 226, p. 012156. doi: 10.1088/1757-899X/226/1/012156.

Hirunpraditkoon, S., Tunthong, N., Ruangchai, A. and Nuithitikul, K. (2011) ‘Adsorption Capacities of Activated Carbons Prepared from Bamboo by KOH Activation’, *World Academy of Science, Engineering and Technology*, 5(6), pp. 591–595.

Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2013a) ‘Preparation of granular activated carbon from oil palm shell by microwave-induced chemical activation: Optimisation using surface response methodology’, *Chemical Engineering Research and Design*, 91(12), pp. 2447–2456. doi: 10.1016/j.cherd.2013.06.004.

Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2013b) ‘Preparation of granular activated carbon from oil palm shell by microwave-induced chemical activation: Optimisation using surface response methodology’, *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 91(12), pp. 2447–2456. doi: 10.1016/j.cherd.2013.06.004.

Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2015) ‘Microwave-assisted production of activated carbons from oil palm shell in the presence of CO_2 or N_2 for CO_2 adsorption’, *Journal of Industrial and Engineering Chemistry*, 24, pp. 196–205. doi: 10.1016/j.jiec.2014.09.029.

Hoseinzadeh Hesas, R., Wan Daud, W. M. A., Sahu, J. N. and Arami-Niya, A. (2013) ‘The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review’, *Journal of Analytical and Applied Pyrolysis*, 100, pp. 1–11. doi: 10.1016/j.jaap.2012.12.019.

Huang, L., Sun, Y., Wang, W., Yue, Q. and Yang, T. (2011) ‘Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC)’, *Chemical Engineering Journal*, 171(3), pp. 1446–1453. doi: 10.1016/j.cej.2011.05.041.

Huang, Y. F., Chiueh, P. Te, Kuan, W. H. and Lo, S. L. (2016) ‘Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics’, *Energy*, 100, pp. 137–144. doi: 10.1016/j.energy.2016.01.088.

Huang, Y., Li, S., Lin, H. and Chen, J. (2014) ‘Fabrication and characterization of mesoporous activated carbon from Lemna minor using one-step H3PO4 activation for Pb(II) removal’, *Applied Surface Science*, 317, pp. 422–431. doi: 10.1016/j.apsusc.2014.08.152.

Ibrahim, T., Moctar, B. L., Tomkouani, K., Gbandi, D., Victor, D. K. and Phinthè, N. (2014) ‘Kinetics of the Adsorption of Anionic and Cationic Dyes in Aqueous Solution by Low-Cost Activated Carbons Prepared from Sea Cake and Cotton Cake’, 4(1), pp. 38–57.

Imamoglu, M. and Tekir, O. (2008) ‘Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks’, *Desalination*, 228(1–3), pp. 108–113. doi: 10.1016/j.desal.2007.08.011.

Ji, Y., Li, T., Zhu, L., Wang, X. and Lin, Q. (2007) ‘Preparation of activated carbons by microwave heating KOH activation’, *Applied Surface Science*, 254(2), pp. 506–512. doi: 10.1016/j.apsusc.2007.06.034.

Josip, Ć., Matoši, M., Crnek, V., Stuli, V. and Mijatovi, I. (2016) ‘Adsorption Characteristics of Different Adsorbents and Iron (III) Salt for Removing As (V) from Water’, 54(2), pp. 250–255. doi: 10.17113/ftb.54.02.16.4064.

Jun, T. Y., Arumugam, S. D., Latip, N. H. A. and Latif, A. M. A. P. A. (2010) ‘Effect of Activation Temperature and Heating Duration on Physical Characteristics of Activated Carbon Prepared from Agriculture Waste’, *EnvironmentAsia*, 7(1), pp. 104–111. doi: 10.14456/ea.2010.32.

Kabenge, I., Omulo, G., Banadda, N., Seay, J., Zziwa, A. and Kiggundu, N. (2018) ‘Characterization of Banana Peels Wastes as Potential Slow Pyrolysis Feedstock’, *Ccsenet.Org*, 11(2), pp. 14–24. doi: 10.5539/jsd.v11n2p14.

Kan, T., Strezov, V. and Evans, T. J. (2016) ‘Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters’, *Renewable and Sustainable Energy Reviews*, 57, pp. 126–1140. doi: 10.1016/j.rser.2015.12.185.

Khedr, S., Shouman, M., Fathy, N. and Attia, A. (2014) ‘Effect of Physical and Chemical Activation on the Removal of Hexavalent Chromium Ions Using Palm Tree Branches’, *ISRN Environmental Chemistry*, 2014(6), pp. 1–10.

Kim, T., Lee, J. and Lee, K.-H. (2014) ‘Microwave heating of carbon-based solid materials’, *Carbon letters*, 15(1), pp. 15–24. doi: 10.5714/CL.2014.15.1.015.

Klinger, J. L., Westover, T. L., Emerson, R. M., Williams, C. L., Hernandez, S., Monson, G. D. and Ryan, J. C. (2018) ‘Effect of biomass type, heating rate, and sample size on microwave-enhanced fast pyrolysis product yields and qualities’, *Applied Energy*, 228(June), pp. 535–545. doi: 10.1016/j.apenergy.2018.06.107.

Kong, S. H., Loh, S. K., Bachmann, R. T., Rahim, S. A. and Salimon, J. (2014) ‘Biochar from oil palm biomass: A review of its potential and challenges’, *Renewable and Sustainable Energy Reviews*, 39, pp. 729–739. doi: 10.1016/j.rser.2014.07.107.

Kongsomart, B., Li, L. and Takarada, T. (2015) ‘Preparation of Activated Carbons From Teak Sawdust Using Chicken Dropping Compost and Empty Fruit Bunch’, *International Journal of Biomass & Renewables*, 4(2), pp. 1–7.

Kopac, T., Kırca, Y. and Toprak, A. (2017) ‘Synthesis and characterization of KOH/boron modified activated carbons from coal and their hydrogen sorption characteristics’, *International Journal of Hydrogen Energy*, 42(37), pp. 23606–23616. doi: 10.1016/j.ijhydene.2017.01.195.

Köseoʇlu, E. and Akmil-Başar, C. (2015) ‘Preparation, structural evaluation and adsorptive properties of activated carbon from agricultural waste biomass’, *Advanced Powder Technology*, 26(3), pp. 811–818. doi: 10.1016/j.apt.2015.02.006.

Kula, I., Uğurlu, M., Karaoğlu, H. and Çelik, A. (2008) ‘Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by $ZnCl_2$ activation’, *Bioresource Technology*, 99(3), pp. 492–501. doi: 10.1016/j.biortech.2007.01.015.

Kumar, S. B., Mathew, K. T., Raveendranath, U. and Augustine, P. (2001) ‘Dielectric properties of certain biological materials at microwave frequencies’, *J Microw Power Electromagn Energy*, 36(2), pp. 67–75. doi: 10.1080/08327823.2001.11688450.

Kundu, A., Gupta, B. Sen, Hashim, M. a., Sahu, J. N., Mujawar, M. and Redzwan, G. (2015) ‘Optimisation of the process variables in production of activated carbon by microwave heating’, *RSC Adv.*, 5(45), pp. 35899–35908. doi: 10.1039/C4RA16900J.

Lahti, R., Bergna, D., Romar, H., Tuuttila, T., Hu, T. and Lassi, U. (2017) ‘Physico-chemical properties and use of waste biomass-derived activated carbons’, *Chemical Engineering Transactions*, 57, pp. 43–48. doi: 10.3303/CET1757008.

Lee, H.-M., An, K.-H. and Kim, B.-J. (2014) ‘Effects of carbonization temperature on pore development in polyacrylonitrile-based activated carbon nanofibers’, *Carbon letters*, 15(2), pp. 146–150. doi: 10.5714/CL.2014.15.2.146.

Lee, L. Z. and Ahmad Zaini, M. A. (2016) ‘Metal chloride salts in the preparation of activated carbon and their hazardous outlook’, *Desalination and Water Treatment*, 57(34), pp. 16078–16085. doi: 10.1080/19443994.2015.1077348.

Leonelli, C. and Mason, T. J. (2010) ‘Microwave and ultrasonic processing: Now a realistic option for industry’, *Chemical Engineering and Processing: Process Intensification*, 49(9), pp. 885–900. doi: 10.1016/j.cep.2010.05.006.

Leonelli, C. and Veronesi, P. (2015) ‘Production of Biofuels and Chemicals with Microwave’, in *Biofuels and Biorefineries*. Springer: Berlin Germany, pp. 17–39. doi: 10.1007/978-94-017-9612-5.

Li, K., Zheng, Z. and Li, Y. (2010) ‘Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H_3PO_4 activation’, *Journal of Hazardous Materials*, 181(1–3), pp. 440–447. doi: 10.1016/j.jhazmat.2010.05.030.

Liew, R. K., Nam, W. L., Chong, M. Y., Phang, X. Y., Su, M. H., Yek, P. N. Y., Ma, N. L., Cheng, C. K., Chong, C. T. and Lam, S. S. (2017) ‘Oil palm waste: An abundant and promising feedstock for microwave pyrolysis conversion into good quality biochar with potential multi-applications’, *Process Safety and Environmental Protection*. Institution of Chemical Engineers, pp. 1–13. doi: 10.1016/j.psep.2017.10.005.

Lim, W. C., Srinivasakannan, C. and Balasubramanian, N. (2010) ‘Activation of palm shells by phosphoric acid impregnation for high yielding activated carbon’, *Journal of Analytical and Applied Pyrolysis*, 88(2), pp. 181–186. doi: 10.1016/j.jaap.2010.04.004.

Ling, P., He, X., Zhao, N., Yu, M., Zhang, X., Zheng, M. and Zhu, T. (2013) ‘Facile preparation of porous carbons from rice husk by microwave heating for supercapacitors’, *ICMREE 2013 - Proceedings: 2013 International Conference on Materials for Renewable Energy and Environment*, 2, pp. 524–528. doi: 10.1109/ICMREE.2013.6893726.

Liu, J., Deng, Y., Li, X. and Wang, L. (2016) ‘Promising Nitrogen-Rich Porous Carbons Derived from One-Step Calcium Chloride Activation of Biomass-Based Waste for High Performance Supercapacitors’, *ACS Sustainable Chemistry and Engineering*, 4(1), pp. 177–187. doi: 10.1021/acssuschemeng.5b00926.

Liu, L., Zhang, X. and Zhong, T. (2016) ‘Pollution and health risk assessment of heavy metals in urban soil in China’, *Human and Ecological Risk Assessment: An International Journal*, 22(2), pp. 424–434. doi: 10.1080/10807039.2015.1078226.

Liu, Q. S., Zheng, T., Wang, P. and Guo, L. (2010) ‘Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation’, *Industrial Crops and Products*, 31(2), pp. 233–238. doi: 10.1016/j.indcrop.2009.10.011.

Liu, R. L., Liu, Y., Zhou, X. Y., Zhang, Z. Q., Zhang, J. and Dang, F. Q. (2014) ‘Biomass-derived highly porous functional carbon fabricated by using a free-standing template for efficient removal of methylene blue’, *Bioresource Technology*, 154, pp. 138–147. doi: 10.1016/j.biortech.2013.12.034.

Liu, Y., Wang, J. and Wolcott, M. P. (2016) ‘Assessing the specific energy consumption and physical properties of comminuted Douglas-fir chips for bioconversion’, *Industrial Crops and Products*, 94, pp. 394–400. doi: 10.1016/j.indcrop.2016.08.054.

Liu, Z., Huang, Y. and Zhao, G. (2016) ‘Preparation and characterization of activated carbon fibers from liquefied wood by ZnCl2 activation’, *BioResources*, 11(2), pp. 3178–3190. doi: 10.15376/biores.11.2.3178-3190.

Lu, Y., Yuan, J., Lu, X., Su, C., Zhang, Y., Wang, C., Cao, X., Li, Q., Su, J., Ittekkot, V., Garbutt, R. A., Bush, S., Fletcher, S., Wagey, T., Kachur, A. and Sweijd, N. (2018) ‘Major threats of pollution and climate change to global coastal ecosystems and enhanced management for sustainability’, *Environmental Pollution*, 239, pp. 670–680. doi: 10.1016/j.envpol.2018.04.016.

Maneerung, T., Liew, J., Dai, Y., Kawi, S., Chong, C. and Wang, C. H. (2016) ‘Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies’, *Bioresource Technology*, 200, pp. 350–359. doi: 10.1016/j.biortech.2015.10.047.

Martí-Rosselló, T., Li, J. and Leo, L. (2016) ‘Kinetic models for biomass pyrolysis.’, *Arch Ind Biotechnol*, 1(4), pp. 4–7.

Menéndes, J. a., Menéndez, E. M., Parra, J. B. and Pis, J. J. (1999) ‘Thermal Treatment of active carbons: a comparison between microwave and electrical heating.pdf’, *Journal of Microwave Power and Electromagnetic Energy*, 34(3), pp. 137–143. doi: 10.1080/08327823.1999.11688398.

Mohammad, S. G. and Ahmed, S. M. (2017) ‘Preparation of environmentally friendly activated carbon for removal of pesticide from aqueous media’, *International Journal of Industrial Chemistry*, 8(2), pp. 121–132. doi: 10.1007/s40090-017-0115-2.

Mohammed, J., Nasri, N. S., Ahmad Zaini, M. A., Hamza, U. D. and Ani, F. N. (2015) ‘Adsorption of benzene and toluene onto KOH activated coconut shell based carbon treated with NH3’, *International Biodeterioration and Biodegradation*, 102, pp. 245–255. doi: 10.1016/j.ibiod.2015.02.012.

Mohd Iqbaldin, M. N., Khudzir, I., Mohd Azlan, M. I., Zaidi, A. G., Surani, B. and Zubri, Z. (2013) ‘Properties of coconut shell activated carbon’, *Journal of Tropical Forest Science*, 25(4), pp. 497–503. doi: 10.2307/23616990.

Moreno-Castilla (2016) ‘Chemical and physical activation of olive- mill waste water to produce activated carbons Chemical and physical activation of olive-mill waste water to produce activated carbons', 39(March), pp. 1415–1420. doi: 10.1016/S0008-6223(00)00268-2.

Morschhäuser, R., Krull, M., Kayser, C., Boberski, C., Bierbaum, R., Püschner, P. A., Glasnov, T. N. and Kappe, C. O. (2012) 'Microwave-assisted continuous flow synthesis on industrial scale', *Green Processing and Synthesis*, 1(3), pp. 281–290. doi: 10.1515/gps-2012-0032.

Mushtaq, F., Mat, R. and Ani, F. N. (2014) 'A review on microwave assisted pyrolysis of coal and biomass for fuel production', *Renewable and Sustainable Energy Reviews*, 39, pp. 555–574. doi: 10.1016/j.rser.2014.07.073.

Nabais, J. M. V., Laginhas, C., Carrott, M. M. L. R., Carrott, P. J. M., Amorós, J. E. C. and Gisbert, A. V. N. (2013) 'Surface and porous characterisation of activated carbons made from a novel biomass precursor, the esparto grass', *Applied Surface Science*, 265, pp. 919–924. doi: 10.1016/j.apsusc.2012.11.164.

Nahil, M. A. and Williams, P. T. (2012) 'Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks', *Biomass and Bioenergy*, 37, pp. 142–149. doi: 10.1016/j.biombioe.2011.12.019.

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C. J., Womac, A. R., Lau, A. K. and Melin, S. (2013) 'Development of Size Reduction Equations for Calculating Energy Input for Grinding Lignocellulosic Particles', *Food & Process Engineering Institute Division of ASABE in*, 29(1), pp. 93–100.

Namazi, A. B., Allen, D. G. and Jia, C. Q. (2015) 'Probing microwave heating of lignocellulosic biomasses', *Journal of Analytical and Applied Pyrolysis*, 112, pp. 121–128. doi: 10.1016/j.jaap.2015.02.009.

Nomanbhay, S. and Ong, M. Y. (2017) 'A Review of Microwave-Assisted Reactions for Biodiesel Production', *Bioengineering*, 4(2), p. 57. doi: 10.3390/bioengineering4020057.

Nüchter, M., Ondruschka, B., Bonrath, W. and Gum, A. (2004) 'Microwave assisted synthesis – a critical technology overview', *Green Chem.*, 6(3), pp. 128–141. doi: 10.1039/B310502D.

Obregón-Valencia, D. and Sun-Kou, M. D. R. (2014) ‘Comparative cadmium adsorption study on activated carbon prepared from aguaje (Mauritia flexuosa) and olive fruit stones (Olea europaea L.)’, *Journal of Environmental Chemical Engineering*, 2(4), pp. 2280–2288. doi: 10.1016/j.jece.2014.10.004.

Oghbaei, M. and Mirzaee, O. (2010) ‘Microwave versus conventional sintering: A review of fundamentals, advantages and applications’, *Journal of Alloys and Compounds*, 494(1–2), pp. 175–189. doi: 10.1016/j.jallcom.2010.01.068.

Oginni, O., Singh, K., Oporto, G., Dawson-Andoh, B., McDonald, L. and Sabolsky, E. (2019) ‘Influence of one-step and two-step KOH activation on activated carbon characteristics’, *Bioresource Technology Reports*. Elsevier, 7(April), p. 100266. doi: 10.1016/j.biteb.2019.100266.

Okahisa, Y., Furukawa, Y., Ishimoto, K., Narita, C., Intharapichai, K. and Ohara, H. (2018) ‘Comparison of cellulose nanofiber properties produced from different parts of the oil palm tree’, *Carbohydrate Polymers*, 198(March), pp. 313–319. doi: 10.1016/j.carbpol.2018.06.089.

Okman, I., Karagöz, S., Tay, T. and Erdem, M. (2014) ‘Activated carbons from grape seeds by chemical activation with potassium carbonate and potassium hydroxide’, *Applied Surface Science*, 293, pp. 138–142. doi: 10.1016/j.apsusc.2013.12.117.

Olorundare, O. F., Msagati, T. A. M., Krause, R. W. M., Okonkwo, J. O. and Mamba, B. B. (2014) ‘Activated carbon from lignocellulosic waste residues: Effect of activating agent on porosity characteristics and use as adsorbents for organic species’, *Water, Air, and Soil Pollution*, 225(3). doi: 10.1007/s11270-014-1876-2.

Onochie, U. P., Obanor, A. I., Aliu, S. A. and Ighodaro, O. O. (2017) ‘Proximate and Ultimate Analysis of Fuel Pellets From Oil Palm Residues’, *Nigerian Journal of Technology*, 36(3), pp. 987–990.

Ooi, C. H., Cheah, W. K., Sim, Y. L., Pung, S. Y. and Yeoh, F. Y. (2017) ‘Conversion and characterization of activated carbon fiber derived from palm empty fruit bunch waste and its kinetic study on urea adsorption’, *Journal of*

Environmental Management, 197, pp. 199–205. doi: 10.1016/j.jenvman.2017.03.083.

Örkün, Y., Karatepe, N. and Yavuz, R. (2012) ‘Influence of temperature and impregnation ratio of H3PO4 on the production of activated carbon from hazelnut shell’, *Acta Physica Polonica A*, 121(1), pp. 277–280.

Osman, N. B., Shamsuddin, N. and Uemura, Y. (2016) ‘Activated Carbon of Oil Palm Empty Fruit Bunch (EFB); Core and Shaggy’, *Procedia Engineering*, 148, pp. 758–764. doi: 10.1016/j.proeng.2016.06.610.

Oyejobi, D. O., Abdulkadir, T. S., Yusuf, I. T. and Badiru, M. J. (2012) ‘Effects of Palm Kernel Shells Sizes and Mix Ratios on Lightweight Concrete’, *Journal of Research Information in Civil Engineering*, 9(2). doi: 10.5281/zenodo.192493.

Özçimen, D. and Ersoy-Meriçboyu, A. (2009) ‘Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons’, *Journal of Hazardous Materials*, 168(2–3), pp. 1118–1125. doi: 10.1016/j.jhazmat.2009.02.148.

Pangavhane, D. R. and Tare, S. (2012) ‘Grape stalk briquettes as an alternative feedstock of biomass gasifiers’, *International Energy Journal*, 13(1), pp. 11–20. doi: 10.1109/ICUEPES.2011.6497722.

Pathak, P. D., Davgane, S. A. and Kulkarni, B. D. (2015) ‘Fruit peel waste as a novel low-cost bio adsorbent’, *Reviews in Chemical Engineering*, 31(4), pp. 361–381. doi: 10.1515/revce-2014-0041.

Pathak, P. D. and Mandavgane, S. A. (2015) ‘Preparation and characterization of raw and carbon from banana peel by microwave activation: Application in citric acid adsorption’, *Journal of Environmental Chemical Engineering*, 3(4), pp. 2435–2447. doi: 10.1016/j.jece.2015.08.023.

Pavlenko, D., Giasafaki, D., Charalambopoulou, G., Van Geffen, E., Gerritsen, K. G. F., Steriotis, T. and Stamatialis, D. (2017) ‘Carbon Adsorbents with Dual Porosity for Efficient Removal of Uremic Toxins and Cytokines from Human Plasma’, *Scientific Reports*, 7(1), pp. 1–7. doi: 10.1038/s41598-017-15116-y.

Petri, I., Martins, A. L., Duarte, C. R. and Ataíde, C. H. (2019) 'Development and performance of a continuous industrial microwave dryer for remediation of drill cuttings', *Journal of Petroleum Science and Engineering*, 176(January), pp. 362–368. doi: 10.1016/j.petrol.2019.01.075.

Pezoti, O., Cazetta, A. L., Bedin, K. C., Souza, L. S., Martins, A. C., Silva, T. L., Santos Júnior, O. O., Visentainer, J. V. and Almeida, V. C. (2016) 'NaOH-activated carbon of high surface area produced from guava seeds as a high-efficiency adsorbent for amoxicillin removal: Kinetic, isotherm and thermodynamic studies', *Chemical Engineering Journal*, 288, pp. 778–788. doi: 10.1016/j.cej.2015.12.042.

Philips, E. S., Mutuku, R. N. and Mwero, J. N. (2017) 'Effects of Palm Kernel Shell and Rice Husk Ash as Partial Replacements of Normal Weight Aggregate and Ordinary Portland Cement in Concrete', pp. 42–54.

Phuphuakrat, T., Namioka, T. and Yoshikawa, K. (2010) 'Tar removal from biomass pyrolysis gas in two-step function of decomposition and adsorption', *Applied Energy*. Elsevier Ltd, 87(7), pp. 2203–2211. doi: 10.1016/j.apenergy.2009.12.002.

Plaza, M. G., González, A. S., Pis, J. J., Rubiera, F. and Pevida, C. (2014) 'Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO_2 capture', *Applied Energy*, 114, pp. 551–562. doi: 10.1016/j.apenergy.2013.09.058.

Puziy, A. M., Poddubnaya, O. I., Martínez-Alonso, A., Suárez-García, F. and Tascón, J. M. D. (2005) 'Surface chemistry of phosphorus-containing carbons of lignocellulosic origin', *Carbon*, 43(14), pp. 2857–2868. doi: 10.1016/j.carbon.2005.06.014.

Qin, C., Clarke, K. and Li, K. (2014) 'Interactive forces between lignin and cellulase as determined by atomic force microscopy', *Biotechnology for Biofuels*, 7(1). doi: 10.1186/1754-6834-7-65.

Rashidi, N. A. and Yusup, S. (2017) ‘A review on recent technological advancement in the activated carbon production from oil palm wastes’, *Chemical Engineering Journal*, 314, pp. 277–290. doi: 10.1016/j.cej.2016.11.059.

Rashidi, N. A., Yusup, S., Ahmad, M. M., Mohamed, N. M. and Hameed, B. H. (2012) ‘Activated Carbon from the Renewable Agricultural Residues Using Single Step Physical Activation: A Preliminary Analysis’, *APCBEE Procedia*, 3, pp. 84–92. doi: 10.1016/j.apcbee.2012.06.051.

Research, G. V. (2014) *Activated Carbon Market Analysis and Segment Forecasts to 2020*. San Francisco, CA 94105, USA. Available at: https://www.grandviewresearch.com/press-release/global-activated-carbon-market (Accessed: 16 February 2019).

Rufford, T. E., Hulicova-Jurcakova, D., Zhu, Z. and Lu, G. Q. (2010a) ‘A comparative study of chemical treatment by $FeCl_3$, $MgCl_2$, and $ZnCl_2$ on microstructure, surface chemistry, and double-layer capacitance of carbons from waste biomass’, *Journal of Materials Research*, 25(8), pp. 1451–1459. doi: 10.1557/jmr.2010.0186.

Rufford, T. E., Hulicova-Jurcakova, D., Zhu, Z. and Lu, G. Q. (2010b) ‘A comparative study of chemical treatment by $FeCl_3$, $MgCl_2$, and $ZnCl_2$ on microstructure, surface chemistry, and double-layercapacitance of carbons from waste biomass’, *Journal of Materials Research*, 25(08), pp. 1451–1459. doi: 10.1557/JMR.2010.0186.

Şahin, Ö., Saka, C., Ceyhan, A. A. and Baytar, O. (2015) ‘Preparation of High Surface Area Activated Carbon from Elaeagnus angustifolia Seeds by Chemical Activation with $ZnCl_2$ in One-Step Treatment and its Iodine Adsorption’, *Separation Science and Technology (Philadelphia)*, 50(6), pp. 886–891. doi: 10.1080/01496395.2014.966204.

Salema, A. A. and Ani, F. N. (2012) ‘Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer’, *Journal of Analytical and Applied Pyrolysis*, 96, pp. 162–172. doi: 10.1016/j.jaap.2012.03.018.

Salema, A. A., Yeow, Y. K., Ishaque, K., Ani, F. N., Afzal, M. T. and Hassan, A. (2013) 'Dielectric properties and microwave heating of oil palm biomass and biochar', *Industrial Crops and Products*, 50, pp. 366–374. doi: 10.1016/j.indcrop.2013.08.007.

Shafeeyan, M. S., Daud, W. M. A. W., Houshmand, A. and Shamiri, A. (2010) 'A review on surface modification of activated carbon for carbon dioxide adsorption', *Journal of Analytical and Applied Pyrolysis*, 89(2), pp. 143–151. doi: 10.1016/j.jaap.2010.07.006.

Shamsuddin, M. S., Yusoff, N. R. N. and Sulaiman, M. A. (2016) 'Synthesis and Characterization of Activated Carbon Produced from Kenaf Core Fiber Using H_3PO_4 Activation', *Procedia Chemistry*, 19, pp. 558–565. doi: 10.1016/j.proche.2016.03.053.

Sharma, B., Sarkar, A., Singh, P. and Singh, R. P. (2017) 'Agricultural utilization of biosolids: A review on potential effects on soil and plant grown', *Waste Management*, 64, pp. 117–132. doi: 10.1016/j.wasman.2017.03.002.

Skouteris, G., Saroj, D., Melidis, P., Hai, F. I. and Ouki, S. (2015) 'The effect of activated carbon addition on membrane bioreactor processes for wastewater treatment and reclamation - A critical review', *Bioresource Technology*, 185, pp. 399–410. doi: 10.1016/j.biortech.2015.03.010.

Somorjai, G. A. and Li, Y. (2011) 'Impact of surface chemistry', *Proceedings of the National Academy of Sciences*, 108(3), pp. 917–924. doi: 10.1073/pnas.1006669107.

Song, C., Wu, S., Cheng, M., Tao, P., Shao, M. and Gao, G. (2014) 'Adsorption studies of coconut shell carbons prepared by KOH activation for removal of lead(ii) from aqueous solutions', *Sustainability (Switzerland)*, 6(1), pp. 86–98. doi: 10.3390/su6010086.

Sun, K., Leng, C. Y., Jiang, J. C., Bu, Q., Lin, G. F., Lu, X. C. and Zhu, G. Z. (2017) 'Microporous activated carbons from coconut shells produced by self-activation using the pyrolysis gases produced from them, that have an excellent electric double layer performance', *Xinxing Tan Cailiao/New Carbon Materials*. Institute of Coal Chemistry, Chinese Academy of Sciences, 32(5), pp. 451–459. doi: 10.1016/S1872-5805(17)60134-3.

Szymański, G. S., Karpiński, Z., Biniak, S. and Świątkowski, A. (2002) 'The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon', *Carbon*, 40(14), pp. 2627–2639. doi: 10.1016/S0008-6223(02)00188-4.

Teh, C. Y., Budiman, P. M., Shak, K. P. Y. and Wu, T. Y. (2016) 'Recent Advancement of Coagulation-Flocculation and Its Application in Wastewater Treatment', *Industrial and Engineering Chemistry Research*, 55(16), pp. 4363–4389. doi: 10.1021/acs.iecr.5b04703.

Tham, Y. J., Latif, P. A., Abdullah, A. M., Shamala-Devi, A. and Taufiq-Yap, Y. H. (2011) 'Performances of toluene removal by activated carbon derived from durian shell', *Bioresource Technology*, 102(2), pp. 724–728. doi: 10.1016/j.biortech.2010.08.068.

Theydan, S. K. and Ahmed, M. J. (2012) 'Optimization of preparation conditions for activated carbons from date stones using response surface methodology', *Powder Technology*, 224, pp. 101–108. doi: 10.1016/j.powtec.2012.02.037.

Thostenson, E. T. T. and Chou, T.-W. (1999) 'Microwave processing : fundamentals and applications', *Composites Part A: Applied Science and Manufacturing*, 30(9), pp. 1055–1071. doi: 10.1016/S1359-835X(99)00020-2.

Tseng, R. L. (2006) 'Mesopore control of high surface area NaOH-activated carbon', *Journal of Colloid and Interface Science*, 303(2), pp. 494–502. doi: 10.1016/j.jcis.2006.08.024.

Uemura, Y., Omar, W. N., Tsutsui, T. and Yusup, S. B. (2011) 'Torrefaction of oil palm wastes', *Fuel*, 90(8), pp. 2585–2591. doi: 10.1016/j.fuel.2011.03.021.

Vigneault, C., Rothwell, T.M., Bourgeois, G. (1992) 'Hammermill grinding rate and energy requirements for thin and conventional hammers', *Canadian Agricultural Engineering*, 34(2), pp. 203–207.

Vogel, L. and Peukert, W. (2003) 'Breakage behavior of different materials - construction of a mastercurve for the breakage probability', *Powder Technology*, 129, pp. 101–110.

Vogel, L. and Peukert, W. (2004) 'Determination of material properties relevant to grinding by practicable labscale milling tests', *International Journal of Mineral Processing*, 74(SUPPL.), pp. 329–338. doi: 10.1016/j.minpro.2004.07.018.

Waheed Ul Hasan, S. and Ani, F. N. (2014) 'Review of limiting issues in industrialization and scale-up of microwave-assisted activated carbon production', *Industrial and Engineering Chemistry Research*, 53(31), pp. 12185–12191. doi: 10.1021/ie501432q.

Wahi, R., Zuhaidi, N. F. Q. ain, Yusof, Y., Jamel, J., Kanakaraju, D. and Ngaini, Z. (2017) 'Chemically treated microwave-derived biochar: An overview', *Biomass and Bioenergy*. doi: 10.1016/j.biombioe.2017.08.007.

Wang, T., Tan, S. and Liang, C. (2009) 'Preparation and characterization of activated carbon from wood via microwave-induced $ZnCl_2$ activation', *Carbon*, 47(7), pp. 1880–1883. doi: 10.1016/j.carbon.2009.03.035.

World, C. (2013) *Largest Industrial Microwave System*, *Gardner Business Media, Inc*. Available at: https://www.compositesworld.com/products/large-industrial-microwave-system (Accessed: 1 June 2019).

Wu, F. C. and Tseng, R. L. (2008) 'High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution', *Journal of Hazardous Materials*, 152(3), pp. 1256–1267. doi: 10.1016/j.jhazmat.2007.07.109.

Xiao, H., Peng, H., Deng, S., Yang, X., Zhang, Y. and Li, Y. (2012) 'Preparation of activated carbon from edible fungi residue by microwave assisted K_2CO_3 activation-Application in reactive black 5 adsorption from aqueous solution', *Bioresource Technology*, 111, pp. 127–133. doi: 10.1016/j.biortech.2012.02.054.

Xin-hui, D., Srinivasakannan, C. ., Jin-hui, P., Li-bo, Z. and Zheng-yong, Z. (2011) 'Comparison of activated carbon prepared from Jatropha hull by conventional heating and microwave heating’, *Biomass and Bioenergy*, 35(9), pp. 3920–3926. doi: 10.1016/j.biombioe.2011.06.010.

Yagmur, E., Ozmak, M. and Aktas, Z. (2008) ‘A novel method for production of activated carbon from waste tea by chemical activation with microwave energy’, *Fuel*, 87(15–16), pp. 3278–3285. doi: 10.1016/j.fuel.2008.05.005.

Yakout, S. M. and Sharaf El-Deen, G. (2016) ‘Characterization of activated carbon prepared by phosphoric acid activation of olive stones’, *Arabian Journal of Chemistry*. King Saud University, 9, pp. S1155–S1162. doi: 10.1016/j.arabjc.2011.12.002.

Yao, Z. T., Ji, X. S., Sarker, P. K., Tang, J. H., Ge, L. Q., Xia, M. S. and Xi, Y. Q. (2015) ‘A comprehensive review on the applications of coal fly ash’, *Earth-Science Reviews*, 141, pp. 105–121. doi: 10.1016/j.earscirev.2014.11.016.

Youssef, A. M., Ahmed, A. I., Amin, M. I. and El-Banna, U. A. (2015) ‘Adsorption of lead by activated carbon developed from rice husk’, *Desalination and Water Treatment*, 54(6), pp. 1694–1707. doi: 10.1080/19443994.2014.896289.

Zhenchao, J., Yuting, Z., Jiuming, Y., Yedan, L., Yang, S., Jinyao, C. and Lishi, Z. (2015) ‘Safety assessment of dietary bamboo charcoal powder: A 90-day subchronic oral toxicity and mutagenicity studies’, *Food and Chemical Toxicology*, 75, pp. 50–57. doi: 10.1016/j.fct.2014.11.002.

Zhou, H. (2017) *Research Method*. 1st edn, *Combustible Solid Waste Thermochemical Conversion*. 1st edn. Springer, Singapore. doi: 10.1007/978-981-10-3827-3.

4 MICROWAVE THERMAL PROCESS AND MATERIAL INTERACTIONS RELATIVE TO REACTORS FOR THE PRODUCTION OF ACTIVATED CARBON

Kalu Samuel Ukanwa[1], Kumar Patchigolla[1],*, Ruben Sakrabani[2] and Edward Anthony[1]

1 Centre for Thermal Energy and Materials, School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK;

2 Cranfield Soil and Agrifood Institute, Cranfield University, Cranfield MK43 0AL, UK;

Statement of contribution of joint authorship

The novelty of this work, insight development, data collection, methodology, all laboratory experiments and analyses were done by Kalu Samuel Ukanwa. The manuscript was also prepared by Kalu Samuel Ukanwa. Kumar Patchigolla and Ruben Sakrabani provided advice and supervision.

4.1 Introduction

The use of microwave in thermal processes has attracted attention due to the breakthrough, high yield and quick duration (Leonelli and Mason, 2010). Although, there are challenges that affect the development such as the choice of reactor, temperature measurement and upgrade to industrial large-scale (K.S. Ukanwa *et al.*, 2019). The principle of magnetism and conductivity is an integral of microwave relative to the thermal process therefore, material properties are important to achieve an efficient thermal conversion process. The application of large-scale microwave in incineration, devulcanization and activated carbon (AC) regeneration have received adequate technological attention (Xin-hui *et al.*, 2012). However, not enough to revolutionise the process due to the challenges of material-reactor interaction. Therefore, understanding of the reactor behaviour during AC processing will encourage the production of highly efficient AC. The ability of materials in a microwave to achieve maximum absorption depend on type of reactor material, distance, direction and position of the reactor in the microwave system.

The material-reactor interaction is governed by the type of reactor materials(Dąbrowska, Chudoba, Leonelli, *et al.*, 2018). Conductors such as metals reflect microwave energy and do not heat up. Insulators are pellucid to microwave energy therefore cannot emit heat but allow the passage of microwave(Horikoshi *et al.*, 2018). This is useful in the design of reactors for microwave thermal process. Dielectric materials are microwave absorptive and can be processed thermally (Dąbrowska, Chudoba, Leonelli, *et al.*, 2018). The mechanism for absorption is relative to dipole rotation and ionic conduction. Internal heat is achieved through liquid structure dissipation, ion flow enhancement, 3-dimensional distortion, conformational changes and molecular rotation (Leonelli and Mason, 2010); this movement is illustrated in Figure 4-1.

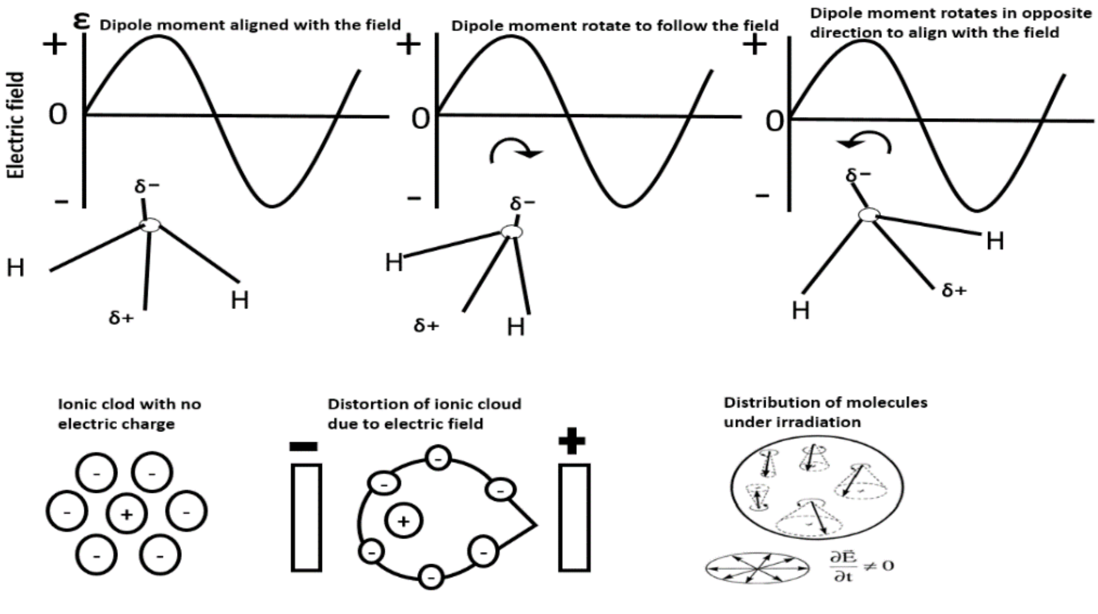


Figure 4-1. Microwave interaction with water and ionic conduction (Leonelli and Mason, 2010)

Microwave heating of solutions is influenced by the principle of dipolar polarisation and ionic conduction. Hence, solvents have permanent dipoles that rotates with a delay due to electric field and this molecular friction results in heating (Zhang, Su and Zhang, 2018). When ions exist, the intermolecular conduction promotes rapid temperature rise. Microwave processing of biomass and carbon-based solids have been widely applied in pyrolysis science because microwave has the ability to dissipate heat due to frictional damping relative to electromagnetic field. They possess a freely rotating dipole, interpreted by interfacial polarisation (Zhang, Su and Zhang, 2018). Due to the semiconducting characteristics of carbon-based materials the delocalised pi-electrons in the graphitic region promotes heating (Kim, Lee and Lee, 2014).

ACs are usually manufactured by pyrolysis of biomass (Thue *et al.*, 2016) and microwave is ideal for the process (Leite *et al.*, 2017). When microwave is used for activation process, several factors affect the efficiency of the product (K.S. Ukanwa *et al.*, 2019). The interaction of the material within the microwave distinguishes it from conventional technique (Namazi, Allen and Jia, 2015). For a chemical activation technique, chemical oxidation occurs at the surface to increase –OH and –COOH when inorganic acids are used as activating agents. This results in the increase in adsorption capacity and hydrophilicity. When the activating agent is alkali, reduction occurs and this improves the non-polarity of the AC. The impregnation of metals into the carbon materials results in process that is more efficient and produces AC with sensitive chemical surfaces (Zhang, Su and Zhang, 2018). This also improves the energy storage by increasing the magnetic properties. The direction of heat transfer in a microwave system differentiates it from conventional heating (Huang *et al.*, 2011). The typical overheating of the polar solvents on homogeneous and heterogeneous substances result in the effects observed on the material and reactor. Many researchers and industries have studied thermal and non-thermal microwave effects (Waheed Ul Hasan and Ani, 2014; Koyama *et al.*, 2018; Barham *et al.*, 2019). Therefore, the different behaviours of each catalyst, and the formation mode of hot spots, temperature irregularity, there are limited evidence of microwave effect on reactors for AC production. Priecel and Lopez-Sanchez (2019) argued the relationship between the non-thermal effect and enhanced diffusion of the substrate. However, could not clearly affirm the level of influence and the range at which such occur relative to the type of substrate. The parameters affecting the microwave thermal processes are classified based on load (feedstock morphology, penetration depth, application position), applicator (microwave mode and set-up accessories), heating mechanisms (electric and magnetic field heating), dielectric and magnetic properties (temperature, frequency or radiation and the chemical state of the material) (Loharkar, Ingle and Jhavar, 2019).

Few reactor challenges are reported in literatures (Sansaniwal, Rosen and Tyagi, 2017; Dhyani and Bhaskar, 2018; K.S. Ukanwa *et al.*, 2019). The scale of reactor is dependent on the type of process, material and heat capacity relative to isobaric thermal capacity. Menéndez et al. (2010) further studied several processes and evaluated the energy consumption, although with a sample quantity of less than 200 g. The challenges of reactors have discouraged the industrialisation of microwave pyrolysis process (Dhyani and Bhaskar, 2018; Nagahata and Takeuchi, 2019). Energy losses in the reactor can be minimised, the reactor material must be high temperature resistant and incapable of absorbing microwave. Resistance to thermal shock and chemical attack is important. The available reactors include: polytetrafluoroethylene (PTFE), with different commercial names such as Teflon, algoflon, hostaflon, fluon and chemloy (Soleimani *et al.*, 2012; Jiang and Bian, 2019; Priecel and Lopez-Sanchez, 2019). These fluoroplastics resins are resistant to corrosion chemical reaction and high temperature. Other reactors commonly used are pure and fused quartz glass, which are amorphous and transparent. They have low thermal expansion and thermal shock resistance. They do not react to chemicals and can withstand temperature of up to 1500 ^{o}C. It is fragile and affected by microwave especially during arcing. Polyetheretherketone (PEEK) and polyaryletherketone (PAEK) are the organic thermoplastic polymer with good chemical resistance (Littlefield and Bartolucci, 2018). Resistant to high temperature with good mechanical properties of 3.6-4 GPa and a tensile strength of 90–100 MPa. Other reactors are borosilicate glass with commercial names as Pyrex (Mandal and Sen, 2015). There is also insufficient study on the impact of microwave on several types of reactors. Although, the corrodibility of the reactor relative to activating agents were assessed by Ravindran and Jaiswal (2016); this however requires further investigation relative to other process techniques, product selection and material efficiencies (Nagahata and Takeuchi, 2019). Hence, this study focuses to evaluate the relationship between the biomass material and selected reactors. This study also assesses the suitability of those reactors for AC production, compared the material-reactor efficiencies, thermal response and possible application in industrial scale. The outcome of the analysis would help recommend suitable reactors for different condition of AC production, illustrate range of applicability, minimise the wastages and interpret material behaviour at different ranges during microwave thermal process.

4.2 Materials and methods

The procedure for verifying the efficiency of reactors is by applying them in the thermal process. The following reactors; Teflon (Polytetrafluoroethylene) reactor TR-A, Borosilicate Pyrex glass reactor BR-B, Porcelain (ceramic) reactor PR-C were provided for this experiment. These involved the reconstruction by microwave systems, UK. The system was modified from a domestic microwave Panasonic NN-SD27HS. It was fitted with vents and reconstructed to allow an efficient pyrolysis process and volatiles delivery. The modified microwave has a frequency capacity of 2.45 GHz, a maximum output power of 1000 W and approximate wavelength of 12.23 cm. The cooling unit is a condenser and liquid collector. All the reactors are assumed to be of the same size and shapes and Teflon pipes were used in the delivery of inert gas and volatiles.

Each of the reactors were used to produce AC from combined palm waste, obtained from Nigeria. For the activating agent, Trona ore ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) was used for chemical impregnation. These were impregnated into the sample and pyrolysed at different durations and microwave power. The individual ACs produced were tested with scanning electron microscope (SEM) to estimate the level of activation and the material chemical behaviour. The surface morphology AC is necessary as it contributes to the structure and pore network. AC structure was studied using SEM (Phillips XL30ESEM) to measure surface morphology. The S_{BET} and material structural porosity of the ACs were assessed with a surface area analyser (3P surface DX, Germany). The rate of carbonisation relative to each reactor were evaluated. There are few basic assumptions made throughout the experiments. All samples are biomass and considered as a homogenous material. The influence of mass transfer is ignored, as the heat capacity was not taken into account. The temperature field distribution is assumed at intervals relative to time. The dielectric constant and conductivity constant were obtained from the literature based on known biomass standard (Stachowicz *et al.*, 2014). The physical parameters for combined palm waste are; dielectric constant Ɛ’ is 2-6. The magnetic permeability Ur is 1. Material conductivity Q (S/m) is 0. Dielectric loss factor is 0.1-1.9, Tangent loss is 0.08-0.3 (Salema *et al.*, 2013). Thermal conductivity k is 0.68 W/mK, density p is 144-560 kg/m^3 and specific heat capacity Cp is 1.4-1.98 kJ/kgK (Bevan Nyakuma, Johari and Ahmad, 2013; Fono-Tamo and Koya, 2013). Anyaoha et. al. (2018) reported density of EFB, PKS, MF from Nigeria.

The magnetic permeability is dependent on magnetisation capacity of material, which is expressed as;

$$\mathrm{M'(t) = yMxH(w) - \alpha Mx\big(MxH(w)\big)} \qquad \textbf{(4-1)}$$

$M = X_0 H, M = (\mu_r - 1)H \; and \; M = \sum m_i$; Therefore, m_i and M′ are microscopic, atomic magnetic moments and precession velocity respectively. H(ω) is the microwave magnetic field and gyromagnetic ratio is γ. The damping constant is represented by α. Therefore, the increase in frequency results in the high losses. Therefore, damped precessions cause loss of microwave energy in the process system. The resultant effect is due to the magnetic permeability complex, which is frequency dependent. Applying Equation 1 (Salema *et al.*, 2013), vacuum with a relative permittivity of 1 and susceptibility of 0 gives 1.2566 μH/m.

The microwave direct impact on the reactor is governed by the same principle of materials and feedstock. However, this is evaluated based on a dual principle of microwave-reactor and reactor-material relationships. The wave pattern in a cylindrical cavity as and illustrated by the equation. For a transparent material, the electromagnetic penetration is infinite and zero in a reflective material. The attenuation (α) denoted by;

$$\alpha = \frac{2л}{\lambda}\sqrt{\frac{Ɛ_e\left(\sqrt{1+\tan^2 б}\right)-1}{2}} \tag{4-2}$$

The loss tangent (tan δ) is assumed to be less than 1, this implies that

$$\sqrt{1+\tan^2 б}-1 \approx \frac{\tan^2 б}{2} = \tan\delta = \frac{Ɛ''}{Ɛ'} \tag{4-3}$$

The loss factor ($Ɛ''$) is directly relative to the attenuation. It is inversely to the product of wavelength and the square root of the dielectric constant, hence Equation 2-4.

$$\alpha = \frac{лLf}{\lambda\sqrt{Ɛ'_r}} = \frac{лx\tan б\sqrt{Ɛ'_r}}{\lambda} \tag{4-4}$$

$$D_p = \frac{\lambda_0\sqrt{Ɛ'}}{2лƐ''} \tag{4-5}$$

Microwave pyrolysis was performed using a modified microwave and different reactors drilled on the upper face of the oven to transport the pyrolysis volatiles to the condensation system. The experiments were performed at 600 W microwave power with a continuous nitrogen flow of 0.5 L/min. The temperature changes were obtained at 1 minute intervals. The yields of char were calculated by measuring the mass of condensed vapours and the residual mass of the char left over in the reaction vessel.

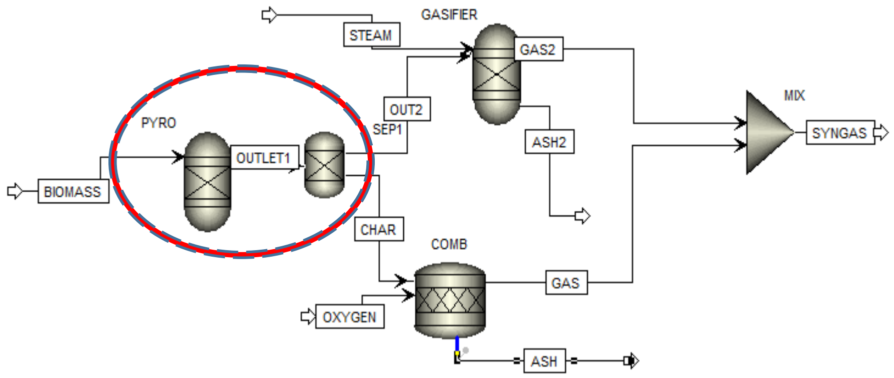


Figure 4-2 ASPEN PLUS flow chat for pyrolysis

Advanced System for Process Engineering (ASPEN) is used for computational modelling to simulate and optimize the process involved in microwave pyrolysis for the pyrolysis part of the thermal process (Figure 4-2).

4.3 Results and discussion

4.3.1 Electrodynamic properties of biomass interaction under microwave

The results of the material interaction and its behaviour relative to the types of microwave reactor are outlined based on permittivity and dielectric, these are related to electric dipole. Damp oscillation is observed at an average frequency due to the absorption of microwave; this motion is relative to energy loss. The incident microwaves decrease by 63% of absorbed wave in a penetration distance Dp. Penetration Depth of Microwaves principle supports that the heating efficiency reduces with large particles. To quantify heating efficiency, the penetration depth must be estimated which depends on the distance from the peripheral to the point where the capacity of the field capacity reduces by half relative to value at the surface. This could be measured by wave power density and also at a point where it decreases to e^{-1} (=0.368) of its value at the exterior, which is half of field permeation depth.

Activating agent has significant effect on the ε' in a temperature-dependent way, trona which is ionic causes ionic polarisation which enhances ε' with increased temperature. As the temperature increases permittivity increases in all the reactors. However, decreases after attaining maximum ε' due to strengthened disordered thermal fluctuations of molecules.

The increase and decrease of the ε' is contingent on the type of parent material, activating agent and the reactor interaction. The higher the reactor and material microwave absorptivity the decreased the value of tan δ. Increase in temperature basically reduces relaxation time due to reduced polarization. Frequency increase, the dipole alignment is affected which results in partial polarization that slows the relaxation time.

The AC produced show decrease in Dp. The porosity and high S_{BET} contribute to the low Dp. Dp relates with the effect of loss factor as a higher Dp is favourable for effective microwave heating. The moisture trapped in the pores of the AC is relative to the Dp. Water has a very low Dp which has insignificant dependence on frequency of the microwave. The more porous an AC material, the lower the Dp. Therefore, the amount of ion due to the activating agent, moisture content and carbon contributes to the dielectric properties and how effective the activation process would interact with the microwave system.

Table 4-1. The relative permittivity of Combine Palm Waste AC at different frequencies for each reactor

Reactor	Raw CPW: Ɛ‘=2.06 tan δ=0.010, Dp=36 cm at 2.45 GHz measured at 25 ^{o}C								
	0.915 GHz			2.45 GHz			5.8 GHz		
	Ɛ‘	tan δ	Dp (cm)	Ɛ‘	tan δ	Dp (cm)	Ɛ‘	tan δ	Dp (cm)
TR-A	1.97	0.065	51	1.8	0.075	32	1.74	0.045	31
BR-B	1.68	0.075	46.2	1.62	0.066	24.6	1.64	0.46	13.5
PR-C	1.58	0.072	48	1.56	0.072	30.5	1.52	0.60	9.2
Teflon (Polytetrafluoroethylene) reactor, TR-A; Borosilicate Pyrex glass reactor, BR-B; Porcelain (ceramic) reactor, PR-C, Dielectric constant (Ɛ‘), loss tangent (tan δ), penetration depth Dp (cm)									

This is due to the increase in frequency that subsequently results in the diminution of penetration depth. Therefore, low-loss materials experience comparatively high penetration depth. Non-polar materials and quartz glass can be transparent to microwave and minimal energy loss is experienced. Relatively, the microwave penetration depth is small and inhibits uniform heating. When sample dimension is equivalent to microwave depth, the efficiency of microwave heating is at optimum. There are factors that influence solution heating: Physical characteristics such as dielectric, heat capacity, viscosity, temperature and polarity. Ionic characteristics such as concentration, mobility, charge and size. Wavelength is also very important. Consequently, the microwave interaction is also observed to be influenced by magnetic properties, mass and molecular sizes. Other factors such as frequency, angle of incidence, dielectric constant, impedance and loss mechanism play enough role in the thermal interactions (Lo *et al.*, 2017).

The temperature of biomass materials with metallic activating agent cannot be raised rapidly because it gradually reflects the incident with minimised penetration depth of electromagnetic field. The resultant discharge of energy due to the eddy current results in arcing. Although, the principle of magnetic loss in the process is yet to be defined. The particle size could be a major factor in the case of impregnation with metallic substances. The higher the conductivity, the lower the penetration depth for a given frequency with implied influence of temperature variation relative to permittivity and dielectric loss factor (Sun, Wang and Yue, 2016). The electric field-material interaction is influenced by the material capacity to store electric energy and convert the stored energy into heat. Many heating mechanisms affect microwave process. The influence of magnetic energy and hysteresis loss and when closed current loop are formed due to eddy current and heat dissipation. The relationship between temperature and activation process for a conventional activation process is different from microwave due to the nature and direction of heat dissipation. It is also observed that the interaction depends on the heat conduction of the reactor under microwave.

4.3.2 Percentage gas, liquid and char yield for conventional and microwave processes

Biomass and char are defined in Aspen Plus as a nonconventional solid and can be evaluated relative to experimental data. In this procedure only carbon, hydrogen, and oxygen are considered in the ultimate compositions of biomass.

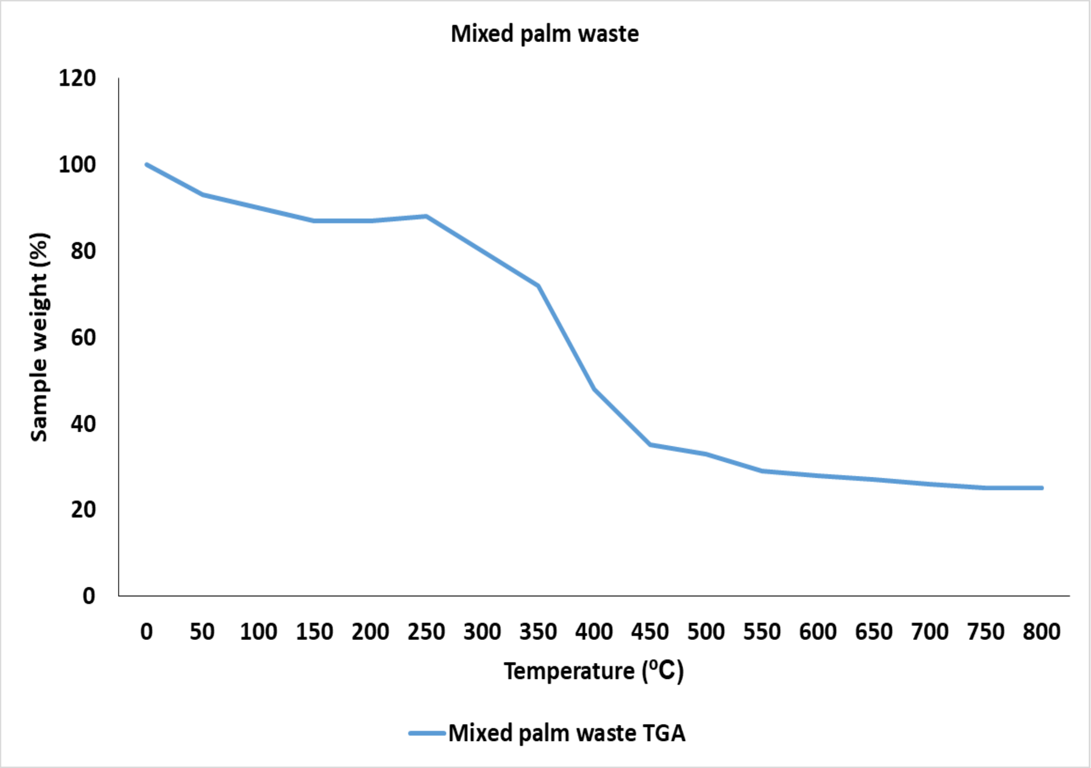
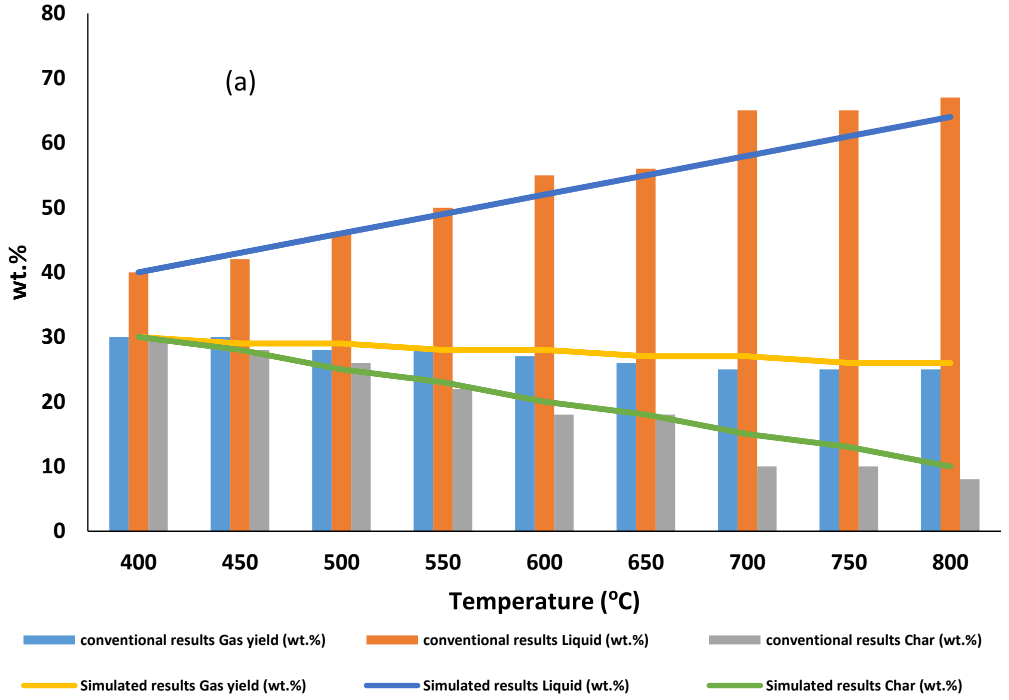


Figure 4-3 Thermal decomposition profile of combined palm waste

Thermal decomposition of palm waste identifies the temperature regions for thermal decomposition. Although this does not take into account the influence of reactor. Hence, to evaluate kinetic parameters such as activation energy, frequency factor and reaction order. The biomass thermal behaviour is required (Ukanwa *et al.*, 2020). Based on the decomposition profiles, hemicellulose was first to be decomposed at 250-300 °C, trailed by cellulose decomposition at 340-350 °C.

The increase in temperature upheld the hydrocarbon endothermic reaction yielding increased H_2 concentration and a significant decrease in the CH_4 concentration which resulted in the reduction of char yield. At higher temperatures the char yield reduces significantly in conventional activation process.

According to Figure 4-4, there is an increase in the percentage weight of liquid relative to the increase in temperature and same for simulated profile. However, the liquid produced is lower in simulated consideration. The difference in char yield between 400-800 ^{o}C is about 20%. For the microwave thermal process, gas yield is higher than liquid. The increase in gas yield is uniform with increase in microwave power. Char yield is higher in microwave process than in conventional technique.



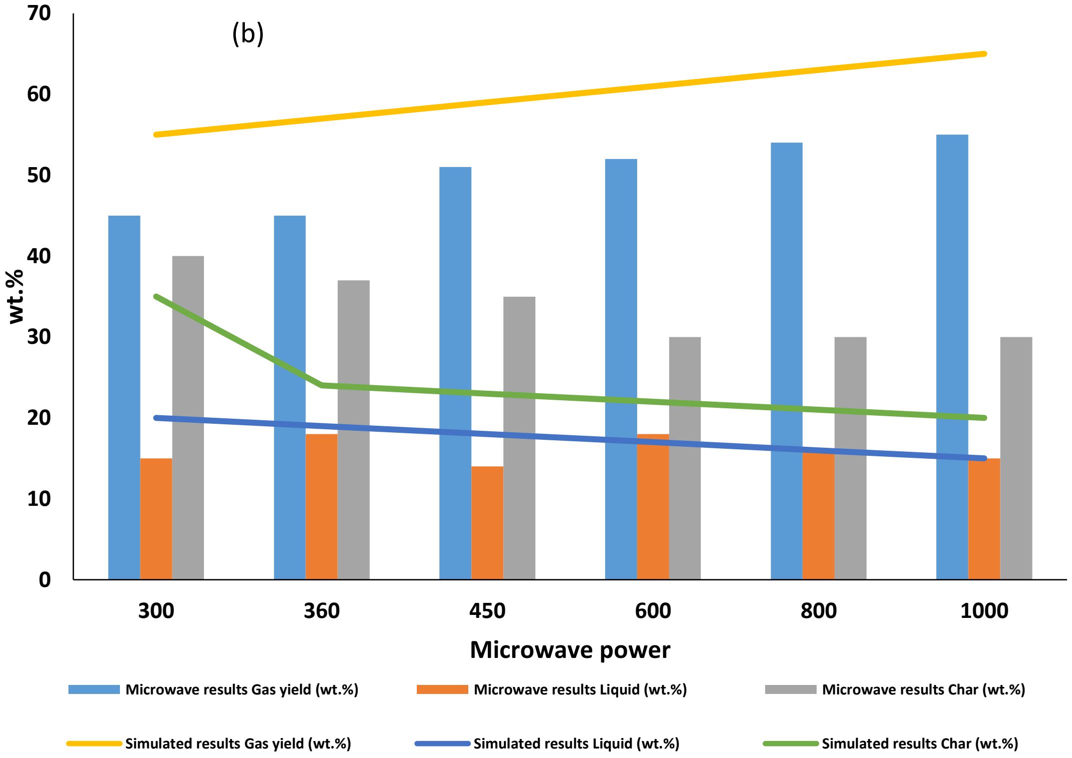


Figure 4-4 (a) Percentage gas, liquid and char yield for conventional process (b) Percentage yield for microwave process relative to simulated yield

4.3.3 Synthesis variations with different reactors

The microwave irradiation and its interaction with matter are characterized by absorption, transmission, and reflection. The size of the reactor vessel is very important for dielectric heating, since the microwave energy is absorbed by the specimen volume till a certain (penetration depth). The assumed boundary parameters of the synthesis and the microwave device are required in the process.

The reactor material does not take part in the reaction, can they strongly interact with the microwave field and cause bursts of burn. The impact of the nature of the substrate (homogenous or heterogeneous). The mixability of the feedstock before microwave reaction. The pressure build up and potential risk of explosion. If reaction cup in batch mode is hermetically closed in a high pressure vessel, it is necessary to leave an empty space in the reaction cup (about 20% of volume without precursor for thermal expansion), and the reactor must have safety valves.

Based on the temperature variations and products from different reactors. The content of the reactors has little or no influence on the behaviour and thermal impact effect on the reactor. The electrodynamic influence on the reactor and within the cavity is dependent on shape, position in the microwave and field power. The electrodynamic power can be evaluated relative to whether the reactor is closed or open. The pressure range, which depends on the inert gas supply, flow rate and outlet setting, can be evaluated. The challenges of closed reactor are the build-up of pressure and difficulty in the control of other parameters. The appropriate way to minimise this is to use only small quantity of sample of about 0.5 g. For AC production, the reactor is considered a partially open cavity due to the passage of inert gas in a controlled condition.

Figure 4-3 shows the temperature variation with time. This explains the reason activation occurs beyond 10 minutes. PR-C has the shortest time to attain a temperature required for activation.

4.3.4 Effect of activating agents

Different solvents interact differently during microwave thermal process. This is due to the polar and ionic properties. Ethanol and water are few solvents that interacts well with microwave. Non-polar solvents such as toluene and hexane are not suitable (Rana and Rana, 2014). The type of impregnated activating agent influences the absorption efficiency and the moisture content of the sample is a factor, which illustrates the conductivity and dipole orientation to the dielectric constant. This is because of nonlinear molecular geometry of water and its large dipole movement under an electric field. The moisture content of the matter causes dipole relaxation, that result in intense energy absorption. The magnetic field vector can initiate linear transfer of energy by resonance. The temperature range within the matter is reliant on the electromagnetic field distribution, thermal conductivity and heat capacity. The physical behaviour and unpredicted characteristics could be due to hot spots. However, desirable in AC production but not in sintering of ceramics.

The continuous generation of hotspots influences chemical reaction process and the product yield, which is due the molecular interaction at the bond. The confirmation of the influence of activating agent in microwave as a good microwave absorber indicates that it improves heating efficiency. AC has a large dielectric loss and low penetrating power (Sun, Wang and Yue, 2016). The quantum absorption of microwave can be predicted based on fundamental relationship.

Table 4-2 Pore structure relative to reactor type

Reactor	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	D_p (nm)	Yield (%)
TR-A	645	0.620	0.205	0.244	2.5	40
BR-B	980	0.865	0.256	0.380	3.3	42
PR-C	1100	0.742	0.282	0.318	4.6	38

Teflon (Polytetrafluoroethylene) reactor, TR-A; Borosilicate Pyrex glass reactor, BR-B; Porcelain (ceramic) reactor, PR-C; S_{BET}, BET surface area; V_{total}, total volume; V_{meso}, mesopore volume; V_{micro}, micropore volume; D_p, pore diameter.

The surface area of AC produced using TR-A is the least while PR-C is the highest. However, BR-B has the highest V_{total} and yield as shown in Table 4-2. The reason for PR-C low yield is due to heating from microwave energy and heating by conduction of the reactor as PR-C was also partly heated by the microwave. The yield efficiency of the three reactors could be evaluated based on the material interaction and rate of release of volatiles. Figure 4 shows that pore formation was well defined with BR-B and PR-C. The rate of activation was affected by the type of reactor. The response of the reactors to microwave radiation and transmissibility efficiency, which determines the energy efficiency on the sample. These influenced the pore development, rate of volatile displacement and tar accumulation. Figure 4-5 further illustrates the slower pore development in the AC produced with TR-C and the trapped tars at 20 minutes. It would take a longer duration to process AC with TR-A.

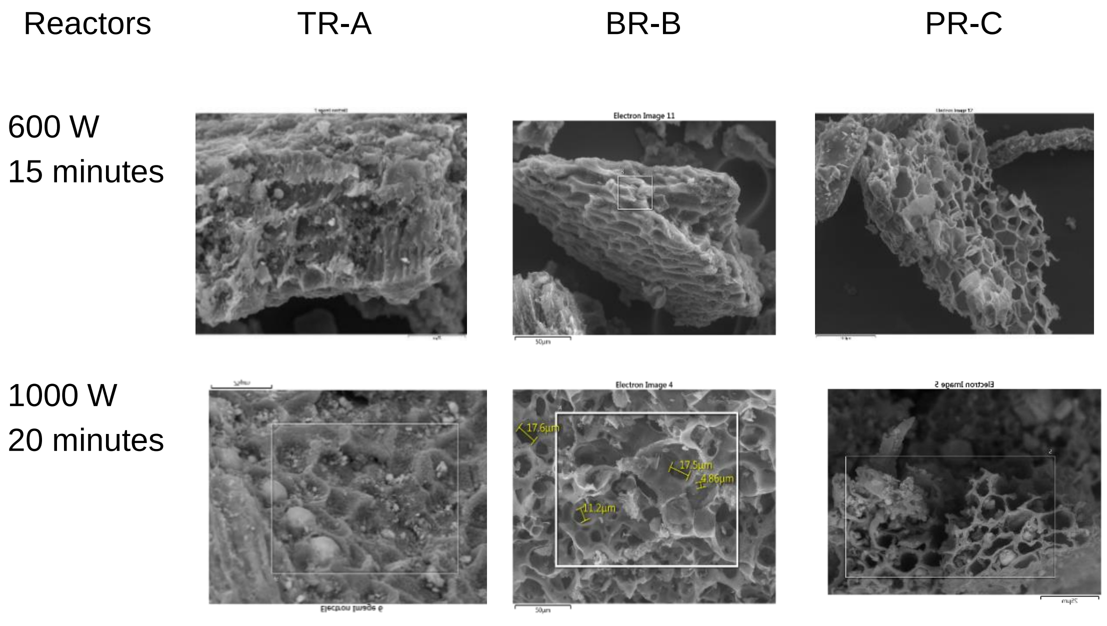


Figure 4-5 SEM images of AC products from different process parameters and reactors

4.3.5 Non-thermal interaction of different reactors with microwave radiation

Reaction rate varies according to microwave power. Dielectric heating is inadequate to define the localised heating effect and observed reaction rate. An increased rate of reaction is observed due to a rapid shift of the dipole and molecular agitation. The rotation of the dipole in the intermolecular bond under electromagnetic radiation is evaluated by the principle of the heating effect.

Product selectivity of microwave irradiation influences the high yield of products while the same reaction conventionally yields less percent of the desired product, this is applicable to the reactors in use. The degradation based on mechanical strength are not quantified. However, the reactors were examined for cracks and pattern of total carbonisation. One of the parameters for assessing microwave heating is penetration depth. A material perpendicular to the incident of microwave receives higher penetration, therefore the distance at which the microwave power is half is the penetration depth and it differs from material to material (Sun, Wang and Yue, 2016).

4.3.5 Microwave energy and reactor efficiency: techniques for improvement

The improvement of energy efficiency of a microwave system for thermal processing is still a major issue. To achieve an economic, industrial and commercial technology. Focus should be on achieving an appropriate reactor dimension with adequate penetration depth and microwave-matter interaction mechanism. There should be a defined guide on constructive interference of propagating waves. Surducan et al. (2013) tried the use of ceramic crucible and thermally insulating casket in order to treat poor wave adsorption material. Ceramic crucible can heat material by conduction, convection, and radiation. However, this overcome the benefit of microwave-matter interaction and selective heating characteristics.

The electric dipole moment is governed by the distance between the negative and positive charges in the molecule. They are related to dielectric constant of liquid water. This implies that dielectric is high for intermolecular processes and low for atomic and electronic polarisation. The rate of heating dissipation from an electromagnetic field based on the dielectric heating principle. The rate of heat dissipation is relative to microwave efficiency and dependent on the heat capacity and microwave-material relationship of reactor. The frequency–dependence of dielectric permittivity and intensity is determined to plot the variation of heat dissipation. The transitional process effect relative to temperature and pressure with conjunctive dependence on the dielectric constant. Using water as a case study, when temperature increases, the dielectric constant reduces and increases with increase in pressure. Microwave does not rely on the temperature gradient for heat transfer. The water dipole recurrently repositions in an oscillating electric field of electromagnetic radiation. In some cases, the movement is contingent on the electron mobility, frequency and viscosity.

The decrease in strength and hydrogen bonding occur as temperature increases. This results in the low static and optical dielectric permittivity. The movement of dipole becomes easier as water molecules oscillate thereby reducing friction and dielectric loss. Dissolved salt plays a role in the microwave process, because it reduces the relative permittivity and the average hydration number of materials. Salt is a better microwave absorber. The arrows showing the effect of increasing temperature. The above narrative of water is applicable to hydroxyl group and polysaccharides, the reason microwave use in biomass pyrolysis is appropriate. There is similarity in the behaviour with that of water.

4.3.6 Potential energy within the bond and bond stretching interactions

The external characteristics of any material is the outcome of changes occurred in the bond and molecular structure. To predict dielectric response, molecular simulation and interaction are evaluated. Different functions exist to describe the potential energy within a bond but the most common approximation is to represent the bond stretching potential U_b as a harmonic. Bond stretching, angle bending and dihedral torsion. The shape of this potential is shown in Figure 4-6 in which the lowest energy corresponds to a situation in which the bond has reached its equilibrium length. In many cases it is decided to constrain the bond length to a specific value. This is accomplished by applying an algorithm that ensures the distance between atoms stays at the desired value (Kochhar and Singh, 2011).

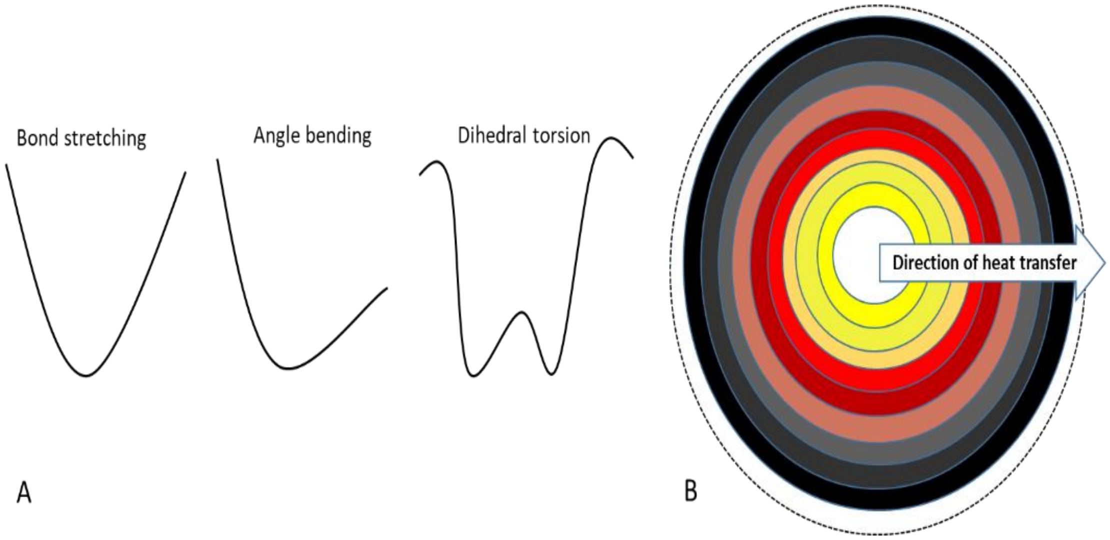


Figure 4-6 (A). Bond stretching interaction in microwave; (B). Heat transfer direction relative to the biomass sample in the microwave (Salema *et al.*, 2013)

In a similar manner to the bond stretching potential, angle bending in a molecule can be represented using a harmonic potential Ua:

$$U_a = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \qquad (4\text{-}6)$$

$k\theta$ is the spring constant of the system and θ is the equilibrium angle. This potential has a similar shape to the bond stretching potential as shown in Figure **4-6**. Although it is a less common feature, in some cases it may be interesting to constrain the angle to a specific value Dihedral torsion interaction. The last of the bonded interactions usually considered is the one corresponding to the internal torsion of the molecule. The potential relationship to the dihedral angle between four consecutive atoms in a molecule U_d can be described by Ryckaert-Bellemans function. As it can be seen in Equation (4-6), a more complex function is obtained in this case. Several low energy states are observed, corresponding to the most probable configurations of the molecule.

4.3.7 Hydrodynamic aspects of hotspots and polemic of microwave thermal influence

The heat transfer mechanism, convection is an important factor. Heat is transferred in a convectional reactor from the walls of the reactor to the sample and vice versa. Therefore, hydrodynamic instability is due to the thermal and density gradient due to fluid in motion. Microwave has a control on the spatial thermal profile of both the reactor and the material relative to heating rate. This is prepotent in the presence of moisture and ethanol at 50 ^{o}C and above up to 200 ^{o}C. This improves an intrinsic ability of the process to overcome thermal gradient within the reactor between the main feedstock and the evaporating materials. The boiling temperature of fluid in microwave is high compared to conventional heating conditions, due to the combined effect of molecular vibration and pressure difference and acknowledged as nucleation partial boiling temperature (Zhang and Hayward, 2006). In AC production, the addition of anti-bumping granules and stirring can reduce localised heating.

Moisture content decreases with increase in microwave heating time. The rapid initial temperature change between 50-60 ^{o}C is due to an increased molecular interaction of the material. The first 120 seconds is significant and could be used to predict the interaction in the long run. Figure 4-7 indicates that heating rate increases with the increase in microwave power.

Due to inverse heat transfer that makes heat to move from inside to outside, there is significant thermal effect and the heating of reactor is common. However, this could have a direct effect on the carbonising material. There are few pertinent issues, which considers the involvement of reactors in the process, the level of explosion relative to pressure and temperature for each reactor. This dynamic observation can be monitored by the linear plots illustrated in Figure 4-7.

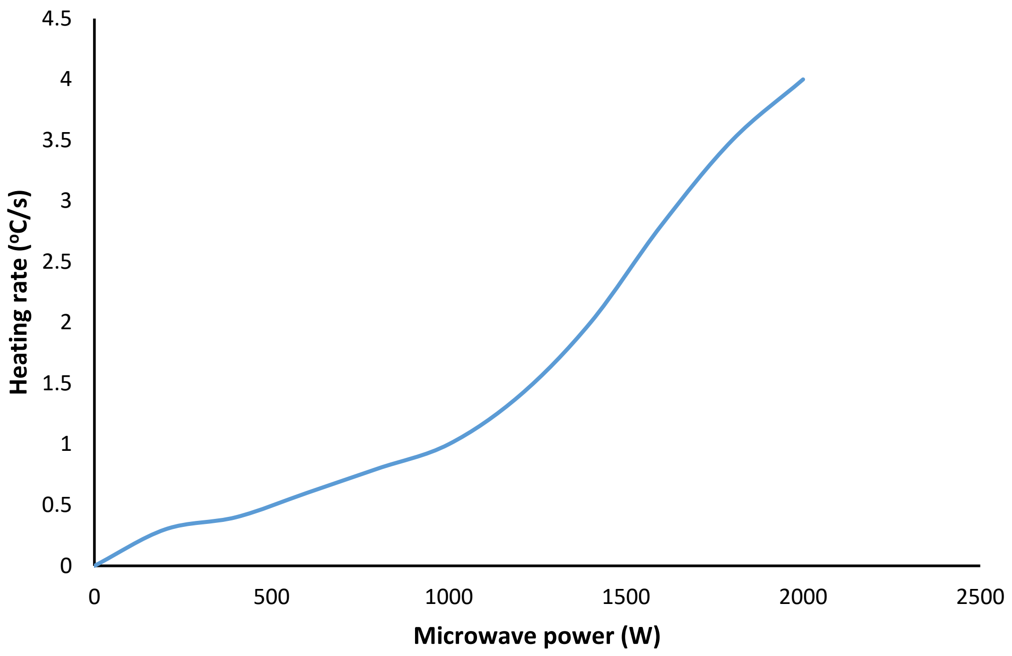


Figure 4-7. Overall reactor response to microwave power and heating rate

4.4 Conclusion

The influence of reactor in AC production is a relevant study and the relative impact of the microwave on the reactor and materials, promote optimising the process parameters. The evaluation involves thermal conductivity of the materials and reactors, processing conditions and dielectric properties. These encourage the upgrade of developmental processes to industrial scale. The emphasis on the design and electromagnetic field; would enable a consistent and reliable evaluation. Constitutive relationship principle was applied to assess the microwave-material interaction. The optimisation of these parameters improves yield and productivity. AC production requires a highly efficient reactor. Mixing the material with microwave absorber can be further verified to evaluate the influences on the AC and the impact on the production cost. Non-thermal specific activation of reactions by microwaves also requires further investigation. To overcome temperature measurement uncertainties, microwave with reproducible fields should be used for consistent variation. This technique overcomes slow heat transfer by thermal diffusivity. The trial with the addition of microwave absorber is the best approach to improve efficiency.

4.5 References

Anyaoha, K. E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Evaluating oil palm fresh fruit bunch processing in Nigeria’, *Waste Management and Research*, 36(3), pp. 236–246. doi: 10.1177/0734242X17751848.

Barham, J. P., Koyama, E., Norikane, Y., Ohneda, N. and Yoshimura, T. (2019) ‘Microwave Flow: A Perspective on Reactor and Microwave Configurations and the Emergence of Tunable Single-Mode Heating Toward Large-Scale Applications’, *Chemical Record*, 19(1), pp. 188–203. doi: 10.1002/tcr.201800104.

Bevan Nyakuma, B., Johari, A. and Ahmad, A. (2013) ‘Thermochemical analysis of palm oil wastes as fuel for biomass gasification’, *Jurnal Teknologi (Sciences and Engineering)*, 62(3), pp. 73–76. doi: 10.11113/jt.v62.1891.

Dąbrowska, S., Chudoba, T., Leonelli, C., Wojnarowicz, J. and Łojkowski, W. (2018) ‘Problems of Exploitations of Microwave Reactors for Nanoparticles Synthesis’, (October).

Dhyani, V. and Bhaskar, T. (2018) ‘A comprehensive review on the pyrolysis of lignocellulosic biomass’, *Renewable Energy*, 129, pp. 695–716. doi: 10.1016/j.renene.2017.04.035.

Fono-Tamo, R. S. and Koya, O. A. (2013) ‘Characterisation of Pulverised Palm Kernel Shell for Sustainable Waste Diversification’, *International Journal of Scientific & Engineering Research*, 4(4), pp. 2229–5518. doi: 2229-5518.

Horikoshi, S., Watanabe, T., Narita, A., Suzuki, Y. and Serpone, N. (2018) ‘The electromagnetic wave energy effect(s) in microwave-assisted organic syntheses (MAOS)’, *Scientific Reports*. Springer US, 8(1), pp. 1–10. doi: 10.1038/s41598-018-23465-5.

Huang, L., Sun, Y., Wang, W., Yue, Q. and Yang, T. (2011) ‘Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline

(OTC)’, *Chemical Engineering Journal*, 171(3), pp. 1446–1453. doi: 10.1016/j.cej.2011.05.041.

Jiang, P. and Bian, J. (2019) ‘Low dielectric loss BST/PTFE composites for microwave applications’, *International Journal of Applied Ceramic Technology*, 16(1), pp. 152–159. doi: 10.1111/ijac.13083.

Kim, T., Lee, J. and Lee, K.-H. (2014) ‘Microwave heating of carbon-based solid materials’, *Carbon letters*, 15(1), pp. 15–24. doi: 10.5714/CL.2014.15.1.015.

Kochhar, S. P. and Singh, A. P. (2011) ‘Developments in microwave processing of materials’, *Asian Journal of Chemistry*, 23(8), pp. 3307–3312.

Koyama, E., Ito, N., Sugiyama, J. ichi, Barham, J. P., Norikane, Y., Azumi, R., Ohneda, N., Ohno, Y., Yoshimura, T., Odajima, H. and Okamoto, T. (2018) ‘A continuous-flow resonator-type microwave reactor for high-efficiency organic synthesis and Claisen rearrangement as a model reaction’, *Journal of Flow Chemistry*. Journal of Flow Chemistry, 8(3–4), pp. 147–156. doi: 10.1007/s41981-018-0021-6.

Leite, A. J. B., Carmalin, S. A., Thue, P. S., dos Reis, G. S., Dias, S. L. P., Lima, E. C., Vaghetti, J. C. P., Pavan, F. A. and de Alencar, W. S. (2017) ‘Activated carbon from avocado seeds for the removal of phenolic compounds from aqueous solutions’, *Desalination and Water Treatment*, 71, p. 20540. doi: 10.5004/dwt.2017.20540.

Leonelli, C. and Mason, T. J. (2010) ‘Microwave and ultrasonic processing: Now a realistic option for industry’, *Chemical Engineering and Processing: Process Intensification*, 49(9), pp. 885–900. doi: 10.1016/j.cep.2010.05.006.

Littlefield, A. and Bartolucci, S. F. (2018) ‘Graphene-PEEK Composites as Microwave- activated High-temperature Adhesives’, in *Society of the Advancement of Material and Process Engineering*. North America, pp. 1–18.

Lo, S. L., Huang, Y. F., Chiueh, P. Te and Kuan, W. H. (2017) ‘Microwave Pyrolysis of Lignocellulosic Biomass’, *Energy Procedia*, 105(3), pp. 41–46. doi: 10.1016/j.egypro.2017.03.277.

Loharkar, P. K., Ingle, A. and Jhavar, S. (2019) ‘Parametric review of microwave-based materials processing and its applications’, *Journal of Materials Research and Technology*. Elsevier B.V., 8(3), pp. 3306–3326. doi: 10.1016/j.jmrt.2019.04.004.

Mandal, A. and Sen, R. (2015) ‘Microwave Absorption of Barium Borosilicate, Zinc Borate, Fe-Doped Alumino-Phosphate Glasses and Its Raw Materials’, *Technologies*, 3(2), pp. 111–125. doi: 10.3390/technologies3020111.

Menéndez, J. A., Arenillas, A., Fidalgo, B., Fernández, Y., Zubizarreta, L., Calvo, E. G. and Bermúdez, J. M. (2010) ‘Microwave heating processes involving carbon materials’, *Fuel Processing Technology*. Elsevier B.V., 91(1), pp. 1–8. doi: 10.1016/j.fuproc.2009.08.021.

Nagahata, R. and Takeuchi, K. (2019) ‘Encouragements for the Use of Microwaves in Industrial Chemistry’, *Chemical Record*, 19(1), pp. 51–64. doi: 10.1002/tcr.201800064.

Namazi, A. B., Allen, D. G. and Jia, C. Q. (2015) ‘Probing microwave heating of lignocellulosic biomasses’, *Journal of Analytical and Applied Pyrolysis*, 112, pp. 121–128. doi: 10.1016/j.jaap.2015.02.009.

Priecel, P. and Lopez-Sanchez, J. A. (2019) ‘Advantages and Limitations of Microwave Reactors: From Chemical Synthesis to the Catalytic Valorization of Biobased Chemicals’, *ACS Sustainable Chemistry and Engineering*. American Chemical Society, 7(1), pp. 3–21. doi: 10.1021/acssuschemeng.8b03286.

Rana, K. K. and Rana, S. (2014) ‘Microwave Reactors: A Brief Review on Its Fundamental Aspects and Applications’, *OALib*, 01(06), pp. 1–20. doi: 10.4236/oalib.1100686.

Ravindran, R. and Jaiswal, A. K. (2016) ‘A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: Challenges and opportunities’, *Bioresource Technology*. Elsevier Ltd, 199, pp. 92–102. doi: 10.1016/j.biortech.2015.07.106.

Salema, A. A., Yeow, Y. K., Ishaque, K., Ani, F. N., Afzal, M. T. and Hassan, A. (2013) ‘Dielectric properties and microwave heating of oil palm biomass and biochar’, *Industrial Crops and Products*, 50, pp. 366–374. doi: 10.1016/j.indcrop.2013.08.007.

Sansaniwal, S. K., Rosen, M. A. and Tyagi, S. K. (2017) ‘Global challenges in the sustainable development of biomass gasification: An overview’, *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 80(May), pp. 23–43. doi: 10.1016/j.rser.2017.05.215.

Soleimani, Hassan, Yahya, N., Soleimani, Hojjatollah and Sadrolhosseini, A. R. (2012) ‘Electromagnetic properties of polytetrafluoroethylene at microwave frequencies using finite element modeling waveguide adapter’, *AIP Conference Proceedings*, 1482(September), pp. 122–127. doi: 10.1063/1.4757450.

Stachowicz, M., Opyd, B., Granat, K. and Markuszewska, K. (2014) ‘Effect of electrical properties of materials on effectiveness of heating their systems in microwave field’, *Archives of Foundry Engineering*, 14(2), pp. 111–114. doi: 10.2478/afe-2014-0047.

Sun, J., Wang, W. and Yue, Q. (2016) ‘Review on microwave-matter interaction fundamentals and efficient microwave-associated heating strategies’, *Materials*, 9(4). doi: 10.3390/ma9040231.

Surducan, E., Neamtu, C., Surducan, V., Limare, A. and Di Giuseppe, E. (2013) ‘Microwaves heating in a specific experimental configuration’, *AIP Conference Proceedings*, 1565(November), pp. 161–163. doi: 10.1063/1.4833718.

Thue, P. S., Adebayo, M. A., Lima, E. C., Sieliechi, J. M., Machado, F. M., Dotto, G. L., Vaghetti, J. C. P. and Dias, S. L. P. (2016) ‘Preparation, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution’, *Journal of Molecular Liquids*. Elsevier B.V., 223, pp. 1067–1080. doi: 10.1016/j.molliq.2016.09.032.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R. and Anthony, E. (2020) ‘Preparation and Characterisation of Activated Carbon from Palm Mixed Waste Treated with Trona Ore’, *Molecules*, 25(21), p. 5028. doi: 10.3390/molecules25215028.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R., Anthony, E. and Mandavgane, S. (2019) ‘A review of chemicals to produce activated carbon from agricultural waste biomass’, *Sustainability (Switzerland)*, 11(22), pp. 1–35. doi: 10.3390/su11226204.

Waheed Ul Hasan, S. and Ani, F. N. (2014) ‘Review of limiting issues in industrialization and scale-up of microwave-assisted activated carbon production’, *Industrial and Engineering Chemistry Research*, 53(31), pp. 12185–12191. doi: 10.1021/ie501432q.

Xin-hui, D., Srinivasakannan, C., Qu, W. W., Xin, W., Jin-hui, P. and Li-bo, Z. (2012) ‘Regeneration of microwave assisted spent activated carbon: Process optimization, adsorption isotherms and kinetics’, *Chemical Engineering and Processing: Process Intensification*, 53, pp. 53–62. doi: 10.1016/j.cep.2011.12.011.

Zhang, X. and Hayward, D. O. (2006) ‘Applications of microwave dielectric heating in environment-related heterogeneous gas-phase catalytic systems’, *Inorganica Chimica Acta*, 359(11), pp. 3421–3433. doi: 10.1016/j.ica.2006.01.037.

Zhang, Z., Su, T. and Zhang, S. (2018) ‘Shape Effect on the Temperature Field during Microwave Heating Process’, *Journal of Food Quality*, 2018, pp. 1–24. doi: 10.1155/2018/9169875.

5 PREPARATION AND CHARACTERISATION OF ACTIVATED CARBON FROM PALM MIXED WASTE TREATED WITH TRONA ORE

molecules

Kalu Samuel Ukanwa[1], Kumar Patchigolla[1],*, Ruben Sakrabani[2] and Edward Anthony[1]

1 Centre for Thermal Energy and Materials, School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK;

2 Cranfield Soil and Agrifood Institute, Cranfield University, Cranfield MK43 0AL, UK;

Academic Editor: João Valente Nabais

Received: 2 October 2020; Accepted: 26 October 2020; Published: 29 October 2020

DOI: 10.3390/molecules25215028

Statement of contribution of joint authorship

The novelty of this work, concept development, data collection, methodology, all laboratory experiments and analyses were done by Kalu Samuel Ukanwa. The manuscript was also prepared by Kalu Samuel Ukanwa. Kumar Patchigolla and Ruben Sakrabani supervised the experiments, ensured they followed the approved standard operating procedures. Edward Anthony edited the manuscript.

5.1 Introduction

Environmental safety has become an increasing global concern in the last three decades. In developing countries, water pollution due to the presence of these heavy metals are threat to both flora and fauna and especially aquatic life (Okoroigwe *et al.*, 2013), plants (Suresh Kumar Reddy, Al Shoaibi and Srinivasakannan, 2012). Water contamination by heavy metals has become an increasing problem due to industrialization (H. Chen *et al.*, 2015). The use of pesticides, fungicides, and manufacture of paints, paper and welding activities can contaminate the environment due to heavy metals (Hou *et al.*, 2019). These heavy metals can be removed by treatment with activated carbon (AC). AC is a carbonaceous adsorbent with enhanced porosity and a very high surface area (Köseoǂlu and Akmil-Başar, 2015; Danish and Ahmad, 2018b) and can be produced using coal, agricultural residues and other waste biomass. Waste biomass is an important alternative to coal as a rich carbon source and the wastes associated with the production of the 76 million metric tonnes (MT) of palm oil are of particular importance as they represent about 20% of the total waste generated in the process line (Shahbandeh, 2020). With the addition of palm trunks, fronds and other residues, the annual global waste generation from oil palm is approximately 500 MT.

The use of residual biomass from the palm oil agro-industry has gained more attention in recent years since it can be converted, through technologies like cogeneration, composting, pelletizing, briquetting, pressing, pyrolysis and enzymatic digestion into value-added products (Chiew and Shimada, 2013). Palm biomass as a feedstock has economic contribution to power generation as it reduces operational cost (Aghamohammadi *et al.*, 2016); given the low-cost of palm waste. Pellets and briquettes from oil palm waste are also potential alternatives to traditional fossil fuels in boilers, furnaces and kilns and has a more widescale applicability in; domestic cooking, central heating systems, water purification (Unpinit *et al.*, 2015). Moreover, the ash derived from palm residue is also a useful supplementary cementitious material (Thomas, Kumar and Arel, 2017), as partial replacement for Portland cement and clinker waste for concrete (Ahmmad *et al.*, 2017). Nonetheless more high value uses are desirable and one of them is AC is because of its wide applicability in water treatment, pharmaceutical, desalination, gas storage by the porosity and other domestic and industrial uses (Nabais *et al.*, 2013; Rashidi and Yusup, 2017a).

Low-cost options for AC production, include cassava peel, rice husk, corn pods, bamboo, oil palm waste (OPW) (Hoseinzadeh Hesas, Wan Daud, *et al.*, 2013; Abioye and Ani, 2015). Others are, cotton residues (Nahil and Williams, 2012), stems of tobacco (Chen *et al.*, 2017), bamboo trees (Fujishige *et al.*, 2017), varieties of flower stalks (Huang *et al.*, 2011), coconut shell and coir which are also good precursors (Hidayu and Muda, 2016). However, OPW is among the lowest-cost feedstock with high carbon content of up to 50% and good characteristic potentials for AC production (Liew *et al.*, 2017a; Rashidi and Yusup, 2017b). They are the typical feedstock for gasification process, production of ACs, (Sethupathi *et al.*, 2015) and production of carbon fibre filaments (Hossain, Jewaratnam and Ganesan, 2016). OPW is currently an underutilised wastes in some developing countries, due to the high quantities generated in the process (Gourichon H., 2013a), its bulkiness, difficulty in transporting them from plantation to processing plants and assumed low value. The utilisation of OPW is poor, despite its use for heat generation in boiler unit of palm processing plant(Aziz and Kurniawan, 2016). However, it is good precursor for AC production (Ooi *et al.*, 2017) and the performance of OPW based AC has been demonstrated in several studies for the adsorption of heavy metals (Omoriyekomwan *et al.*, 2017; Khanday and Hameed, 2018), dyes (Foo and Hameed, 2011b), organic and inorganic pollutants (Ooi *et al.*, 2017). All of the OPW components typically contain about 5-6% hydrogen in the form of cellulose, hemicelluloses and lignin (Hossain, Jewaratnam and Ganesan, 2016). Lignin in particular, as an organic cross-linked polyphenolic polymer, is highly amorphous and contributes to the internal structure of AC (Loh, 2017).

Oil palm residues and oil palm processing waste are abundant in Asia and Africa as an agricultural waste and have many applications as low-cost adsorbent when processed into AC (Karri and Sahu, 2017). They can be processed into AC by conventional direct heating or by microwave-assisted pyrolysis method. Microwave systems are a recent development compared to conventional route and can create excellent pore structural development within a short process time (Foo and Hameed, 2012g). The non-uniform sizes and shapes of the material in palm oil biomass are the major disadvantages for its use over other biomass precursors and contributed to the high pre-production cost of AC (Kalu Samuel Ukanwa *et al.*, 2019). Studies are still being directed on the optimum and more eco-friendly modes to achieve efficient production (Bagheri *et al.*, 2015). OPW research has gained interest in South-East Asia and Africa, where it is abundantly available and could be utilised as adsorbent AC (Karri and Sahu, 2017). There are numerous ways of producing AC; but the two dominate methods are physical and chemical activation (Xiao *et al.*, 2012).

Unfortunately, chemical activating agents frequently associated with excessive costs and in some cases can be associated with secondary contamination. Some studies have considered the use of natural and organic chemicals to overcome the challenge

(Wang *et al.*, 2018). However, for chemical routes relatively inexpensive materials like $ZnCl_2$ are generally considered to be particularly effective but present a major difficulty due to the need for their effectively removal by washing (Kalu Samuel Ukanwa *et al.*, 2019). *Bergna et al.*(Bergna *et al.*, 2018) identified the difference between one and two-step activation. Consequently, in this study there are two kinds of two-step method used; conventional-conventional and conventional-microwave.

Trona ore ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is a crude soda ash commonly deposited on soil surfaces, and can be found in some parts of Nigeria, in combination with other compounds such as Na_2SO_4, $CaCO_3$, $CaSO_4$, with high trace of K_2CO_3 and about 14% insoluble substances (Biliaminu and Ibrahim, 2010). Some success with individual palm wastes has been recorded in activation through microwave method (Zainal *et al.*, 2017). This method improves the physiochemical properties of AC and yield (Yang *et al.*, 2010), It also reduces the preparation period and activates at uniform temperature (Xin-hui *et al.*, 2011).

Most AC production use inorganic activating agents; however, considering the health and environment impact of some of the activating agents (Lee and Ahmad Zaini, 2016), their cost and availability an alternative is necessary. Most AC produced are of a mono-precursor, however, this study investigated the preparation of AC from combined waste of palm kernel shell (PKS), mesocarp fibre (MF) and empty fruit bunch (EFB) using microwave system with the objective of demonstrating the viability of crude Trona ore, and evaluating the effects of irradiation power and impregnation ratio (IR).

The surface chemistry determination enable one to obtain estimate the efficiency for any given type of pollutant to be adsorbed. AC targeted for water treatment, should demonstrate both thermal stability and have wide pores. The surface area must be large for a fast adsorption rate. For gas adsorption, the AC must be explicitly gas compatible and have a high reactivity for the target pollutant. When energy storage is the primary focus, sufficient wettability and other characteristics mentioned are expected.

In recent years microwave has been suggested by several researchers as a technique to reduce time and energy when producing AC from biomass (Ahmed, 2016; Nomanbhay and Ong, 2017). This technique has been demonstrated in several studies, but has not reached commercial scale due to various challenges. These include design of suitable microwave reactors, and the poor dielectric properties of biomass and the poor understanding of the interaction mechanisms when using biomass which has hindered the large-scale development (Kalu Samuel Ukanwa *et al.*, 2019). Therefore, the use in AC production require appropriate design and material selection and optimisation of the parameters.

Hitherto, the use of Trona ore and combined palm waste for AC production has not been reported. Na_2CO_3 which is a parent compound of trona ore is a poor activating agent. However, because trona ore is a mixture of many salts in a balanced form as a homogenous compound, that would increase the activating power. The multi-interactive influence of the individual salt will enhance the elimination of volatiles and create and improve tar decomposition. The overall synthesis is based on the differential thermal effects, process duration and choice of precursors. This study aims to prepare AC using microwave and conventional method from combined palm waste at different temperature using Trona ore. It also evaluate the effectiveness of Trona ore in the elimination of alcohol, acids and aldehyde, with focus of increasing the hydrophilicity of the resultant AC. The optimum parameters and the capacity Trona ore as an activating agent which are examined using Fourier transform infrared spectrometry (FTIR), thermogravimetric analysis (TGA) and other techniques including scanning electron microscope (SEM). SEM is used to determine the ability of Trona ore to creating a comb-like morphology, while Brunauer, Emmett and Teller surface area (S_{BET}) for nitrogen adsorption and desorption determine the total volume and surface area of the resulting AC.

5.2 Materials and Methods

5.2.1 Materials

The feedstock was selected from a processing mill at the palm plantation site of Desai Impex Nigeria Ltd in Abia state, Nigeria. It was first ground into a particle sizes of about 0.5-2 mm using a hammer mill then it washed with warm water 60-80 ^oC to remove oil residues and finally rinsed with de-ionised water. The OPW samples were dried for five days and supplementary dried in an electric oven at 70 ^oC for 4 h, to eliminate surface moisture. Trona ore was obtained from Desai Impex Nigeria Ltd where it is used for cleaning oily vessels. De-ionised water was used throughout the experiment and chemicals were of analytical grade. For CPW, the individual wastes were 3:2:1 proportion by weight of EFB, MF and PKS proportion by weight respectively. This combination gave a more balanced and uniform blend for this study.

The analysis for individual palm wastes (Bevan Nyakuma, Johari and Ahmad, 2013; Chima and Nwabinye, 2017) are given in Table 5-1. This shows the differences between the individual feedstock. The high carbon content of the three individual waste qualifies them as appropriate feedstock for AC production.

Table 5-1 Biochemical analysis of individual palm waste biomass

		PKS	MF	EFB
Proximate analysis (%w/w)	Moisture	12	12.1	14.4
	Ash	1.5	4.8	4.4
	Volatiles	70.6	72.9	73.7
	Fixed carbon	15.9	10.5	7.5
Ultimate analysis (%w/w)	C	46	45.8	37.5
	H	5.1	6.3	5.0
	N	0.4	0.9	0.4
	S	0.02	0.2	0.1
	O*	35	29.5	38
Lignocellulosic composition**	Cellulose	20.8	33.9	38.3
	Hemicellulose	22.7	26.1	35.3
	Lignin	50.7	27.7	22.1
Thermal and energy properties	Organic content	94.2	92	95.7
	Inorganic content	5.8	8	4.3
	Combustion rate, C_R (X 10^{-8} kg/s) **	4	4.2	3.8
	Specific Heat, c, (J/kgK) **	3113	3231	2832

*Oxygen by difference include moisture and ash, ** (Bevan Nyakuma, Johari and Ahmad, 2013)

PKS: palm kernel shell, MF: Mesocarp fibre, EFB: Empty fruit bunch

The thermal processes were done under a controlled condition; the overall carbon conversion was evaluated. Carbon conversion efficiency η (%), the volume of volatile production is calculated based on equations () and (5-2) respectively.

$$\eta\ (\%) = \left(1 - \frac{\text{Carbon in residue}\ [\frac{\text{mol}}{\text{s}}]}{\text{Carbon in feedstock/fuel}\ [\frac{\text{mol}}{\text{s}}]}\right) * 100 \tag{5-1}$$

$$V_{gas}(cm^3) = \frac{W_{(0-f)} X x_c}{\sum x_t\ (\frac{MW_c}{V_{STP}}) * \eta} \tag{5-2}$$

Here, the volume of gas collected at the end of the process (m^3). The final weight is denoted by W_f and the initial weight of CPW sample is W_0. The post process weight is represented by $W_{(0\text{-}f)}$ (kg), η is the conversion efficiency of carbon which is the ratio of AC produced and biomass available. Xi is the product gas volume. V_{STP} is the volume of 1 mol of ideal gas at STP. x_c is the carbon content. MW is microwave radiation measured in power.

Brief descriptions of the scenarios for analysis, procedure were performed by simulation. Evaluation for mass, energy balances were outlined. Aspen plus V.10 under the academic license was used for pyrolysis. Activation process in relation to material and energy balances were simulated using the background equation (7-16) . Pyrolysis and activation conditions were formulated relative to the gases emissions were analysed and the macro thermogravimetric profile during the thermal decomposition, was recorded.

Mass balance of activation process is based on the summary by (Daoud *et al.*, 2019).

$$Mass_{(g)} = Char + gases + Water + Tars + condensable \tag{5-3}$$

For gases:

$$m_{gases} = \sum m_{gas,i} \tag{5-4}$$

$$V_{gas,i,t} = \sum_{0}^{tf} V_{gas,i,t} \tag{5-5}$$

$$\%\ Material\ yield = Y\%_{AC\ product} = \frac{m_{AC\ product}}{m_{biomass}} * 100 \tag{5-6}$$

Energy input based on solid material which is calculated based on Lower heat value dry basis (LHV_{dry}) (kJ/kg or kJ/Nm^3).

For energy input:

$$E_{i,biomass} = LHV_{biomass}\left(\frac{kJ}{kg}\right) * m_{biomass} \tag{5-7}$$

$$\begin{aligned} E_{i,process} = {} & m_{biomass}(kg) * C_{p\ wood(lower\ activation\ temp-20^oC)} * \Delta\theta \\ & + m_{AC}(kg) \\ & * C_{p,AC\ (higher\ activation\ temp-lower\ activation\ temperature)} \\ & * \Delta\theta \end{aligned} \tag{5-8}$$

The output energy (E $_{\text{output}}$ (kJ) is based on the quantification of AC, dried gas, condensable and activation gases. These are outline thus:

$$\mathrm{E_{0,AC}} = \mathrm{LHV_{AC}}\left(\frac{\mathrm{kJ}}{\mathrm{Nitrogen\ litre}}\right) * \mathrm{m_{AC}}\ (kg) \tag{5-9}$$

$$\mathrm{E_{0,dried\ gas}} = \sum \mathrm{E}_{\mathrm{gas,i}} \tag{5-10}$$

$$\mathrm{E_{gas,i}} = \mathrm{LHV_{gas,i}}\left(\frac{\mathrm{kJ}}{\mathrm{Nitrogen\ litre}}\right) * \mathrm{V_{cummulated\ gas,i}}\ (Nitrogen\ gas) \tag{5-11}$$

$$\mathrm{E_{0,activation\ gases}} = \mathrm{E_{0,dried\ gases}} + \mathrm{E_{0,condensable}} \tag{5-12}$$

The microwave construction and set-up were done by microwave systems, UK. The device is a modified system from a domestic microwave Panasonic NN-SD27HS. It was fitted with vents and reconstructed to allow an efficient pyrolysis process. Teflon tubes were used as delivery lines in all the processes as illustrated in Figure 5-1. For efficient delivery and management of the volatiles, Teflon pipes were constructed to support inert gas supply and volatile outlet. The outlet is affix to a condenser and a pressure regulator. The safety of the system depends on the management of material handling, pressure regulation and establishing a zero-microwave leakage. The production was done at 460, 600, 800 and 1000 W at different microwave time ranging from 10-20 minutes.

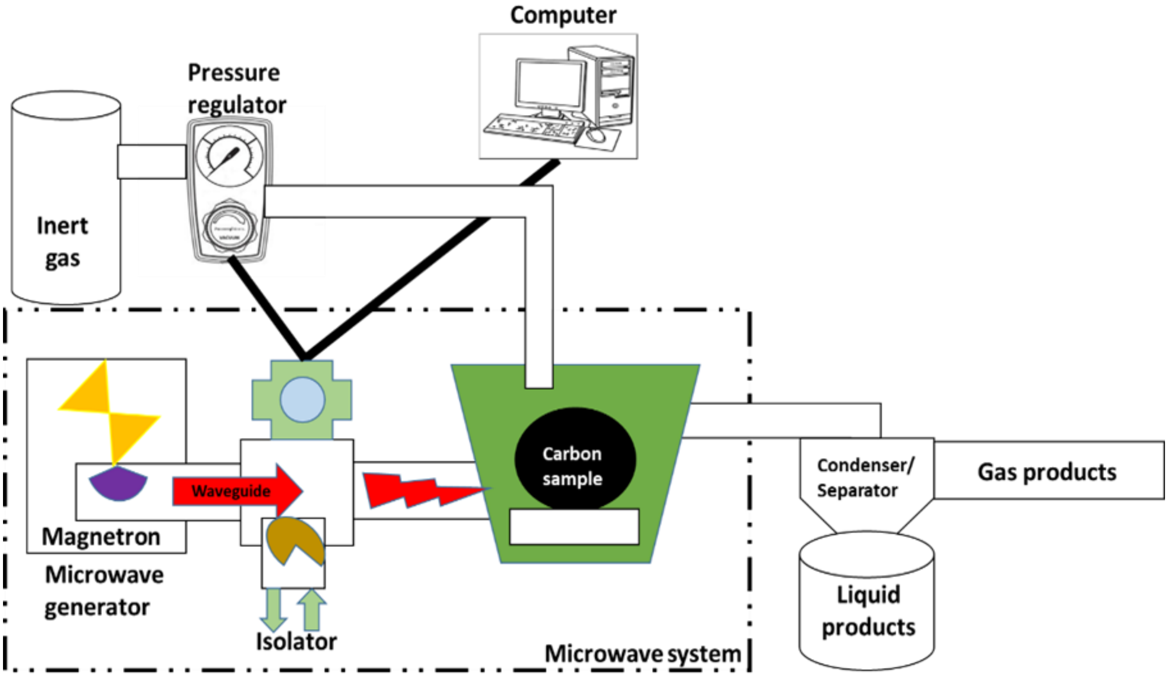


Figure 5-1. Microwave experimental setup for AC production

5.2.2 Production of activated carbon

The OPW ground was introduced into a beaker mixed with Trona ore dissolved in water, then stirred to form a solution, 1 g/ml. The samples were subject to an impregnation ratio of 0.5:1, 1:1, 1:2 and stored for 18 h in a fume cupboard. There is also a control sample without an activating agent. The sample was carbonised in an electric furnace at 500, 600, 800 °C for 1 and 2 h. Another set of samples was put in the microwave and power was varied between 450 and 1000 W. A 200 cm^3/min flow rate stream of pure nitrogen gas (99.9%) was used throughout the production process. After cooling in a desiccator, the samples were soaked and washed in de-ionised water until filtrate is reach a neutral pH. Filtered and dehydrated in the oven at 105 °C for 18 h to achieve a constant weight. The carbonised sample was ground with a 15 horsepower biomass hammer mills to an elemental size of 0-2 mm with standard sieve and kept in a desiccator for about 2 h to ensure no adsorption of moisture. The two-step process involves the production of biochar and further treatment of the biochar with activating agent to produce more efficient AC.

5.2.3 Characterisation of Trona ore activated carbon (ToAC)

The thermal properties and behaviour of OPW were evaluated before and after impregnation with Trona ore using thermogravimetric analyser (Perkin Elmer Pyris 1). The analyser was programmed for 4 h and the analysis of the behaviour was evaluated based on weight loss relative to time. ToAC structure was observed individually using SEM (Phillips XL30ESEM) magnified between 500-2500 times that of the original size. Surface texture relative to activation temperature and mode were studied. The resultant images were compared, the pore symmetry and sizes were determined. The S_{BET} and material structural porosity of the ToAC were evaluated for micropore, mesopore and macropore by N_2 adsorption/desorption isotherm using a surface area analyser (3P surface DX, Germany). This is based on the principle of relative pressure and adsorbed volume. Fourier transform infrared (FTIR) analysis of the AC was done to assess and identify organic, polymeric and inorganic compounds in the material. These techniques were also used for the surface chemical comparison, relationship using infrared emission and adsorption spectra. It determines the infrared adsorption bands, identify the molecular components and structures. These were analysed using OPUS software linked device (Bruker, VERTEX 70, Germany) (FTIR) in Cranfield University UK. The thermogravimetric analysis is used for macroscopic kinetic modelling by evaluating the temperature change relative to mass loss. Therefore, in this study all pyrolysis products are categorised as char, tar and gases.

5.3 Results and discussion

5.3.1 Thermogravimetric analyses of OPW

TGA results are shown in Figure 5-2, and shoe that evaporation of moisture occurs between 90–150 ^oC, and that below 150 °C there is only 10% weight loss with no significant devolatilization occurring until one reaches temperatures from 200^oC to 450 ^oC. After which decomposition of the lignocellulosic components in the OPW begins, resulting in the formation of condensable hydrocarbons (Lam *et al.*, 2016). At 450–900 ^oC char is formed, along with the partial formation of tar. CO, CO_2 or H_2, which are also produced.

Normally, every form of activation process starts at a minimum of 400 ^oC and the duration depends on the heating medium, quantity and type of material. The TGA for samples impregnated by Trona underwent thermal breakdown at 500 ^oC.

Trona appears to initiate depolymerisation of biomass as lignin interface with the CO_2 produced from the thermal breakdown of the activating agent. The cleavage of the numerous intermolecular bonds with hydrogen in cellulose is due to the release of water which causes the dissolution of lignin (Kan, Strezov and Evans, 2016). Further treatment at temperature beyond 400 ^oC yields phenolic monomers and materials like 4-ethylguaiacol. The crystalline structure of cellulose at high temperature retains its morphology in the presence of Na_2CO_3. Moreover, hydrophobic interaction is minimised by the concentration of Na_2CO_3 precipitates. When hemicellulose undergoes hydrolysis, the changes observed depend on temperature variation and pH (Wang *et al.*, 2017).

Lignin linkages can be catalysed by salt due to the presence of ether group. This could result in the release of CO^{2-}, Cl^- and other ions, which react with unstable monomers, liberating the soluble phenolic compounds. However, the breakage of the bonds results in the increase in the hydrophilicity. At temperature of above 400 ^oC, there is increase in the rate of reaction that promotes degradation of oligomers and monomers. The rate of gasification was influenced as salt acts as a catalyst to cause cellulose degradation at temperature of about 400 ^oC. The degradation further produces hydroxycarboxylic acids. The formation of glycolic and lactic acids, which are low molecular mass fragments, also increases at higher concentration and temperature.

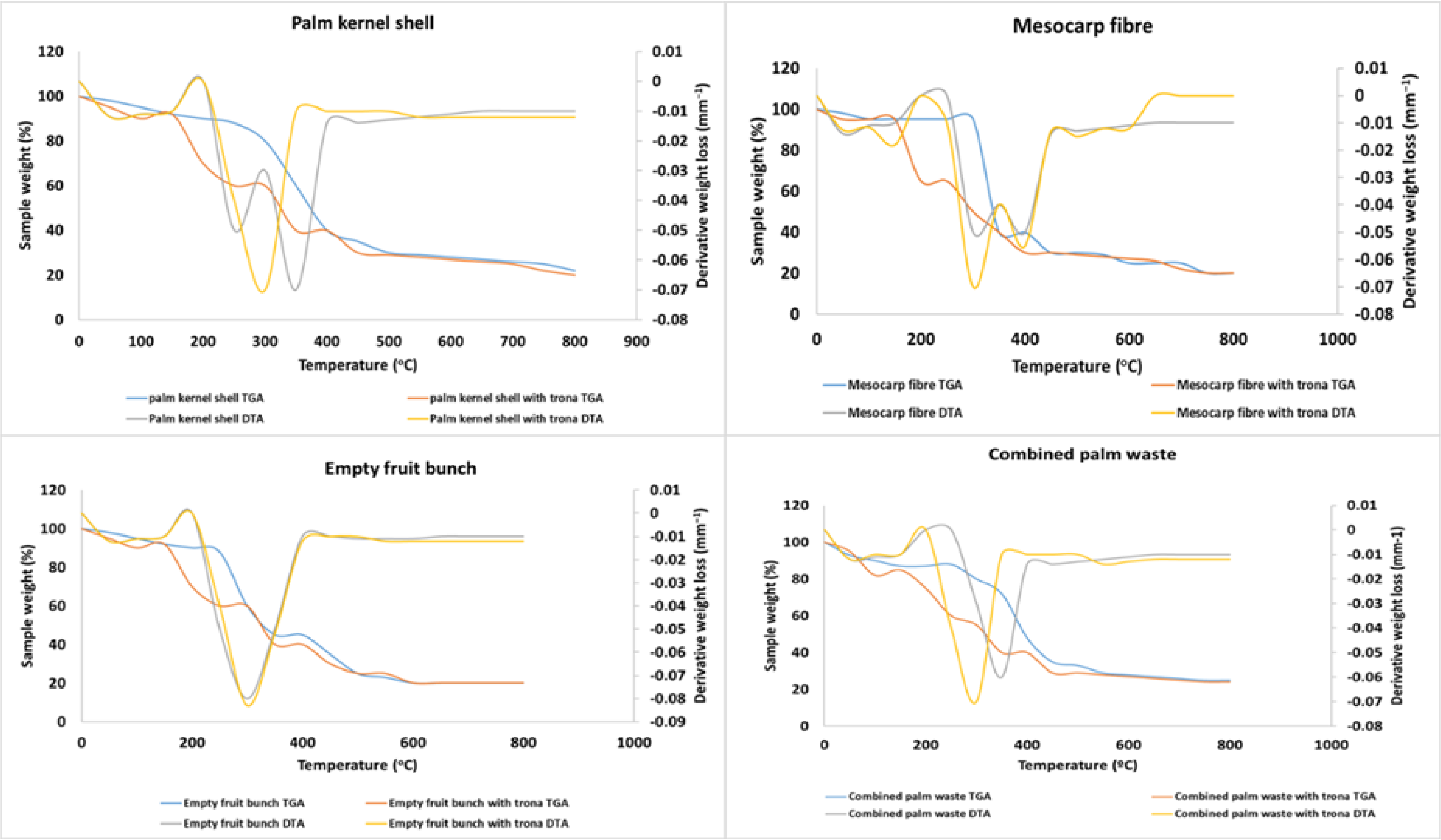


Figure 5-2 DTA/TGA of OPW and variation of the samples impregnated with Trona ore

The addition of Trona increases the carbon yield from 6% to 50% and reduces the temperature of maximum degradation rates as shown in Figure 5-2. This is because organic metal salts have an effective catalytic effect on char formation (Fu *et al.*, 2014). With only Na_2CO_3, there would be no devolatilisation at lower temperature but with other salts as impurities, devolatilisation can occur at 300 ^oC. In the DTA curve, the peak of the weight loss is significant at 450 ^oC. The moisture content is increase because of salt addition. When Trona is added to lignin, the weight loss behaviour slows and the degradation rate is relative to the concentration of Trona. Typically, K_2CO_3 suppresses the formation of char but with Trona, the rate of char formation is high. The temperature at 350 ^oC, and above causes decomposition of cellulose which results in a sharp weight loss.

The addition of activating agent, basically, increase in temperature relative to duration affects pore development, at 400-600 ^oC, the volatile displacement is low and tar formation which resulted to clogging of pores was obvious. The increase in process temperature to about 700 ^oC causes a rapid release of volatiles and widens the pores. High temperature for a long time could lead to low yield and pore structural collapse as observed in the two-step activation process. There is always a period in the process, after the peak of activation, where heat energy is being supplied but there is no change in surface chemistry and morphology. However, after this period, the yield begins to decrease as increasing amounts of ash are produced. As the heating duration increases the pores in the AC gradually begin to collapse.

The presence of moisture in the precursor is subjective to the dissolution rate of the gases emitted in the process. The moisture content is relative to the energy requirement for thermal decomposition for the conventional and microwave activation processes. Microwave has a control on the spatial thermal profile of both the reactor and the material relative to heating rate. This is prepotent in the presence of moisture at 50 ^oC and above at above 400^oC, this improves an intrinsic ability of the process to overcome thermal gradient within the reactor between the main feedstock and the evaporating materials. The boiling temperature of fluid in microwave is high compared to conventional heating conditions, due to the combined effect of molecular vibration and pressure difference and acknowledged as nucleation partial boiling temperature.

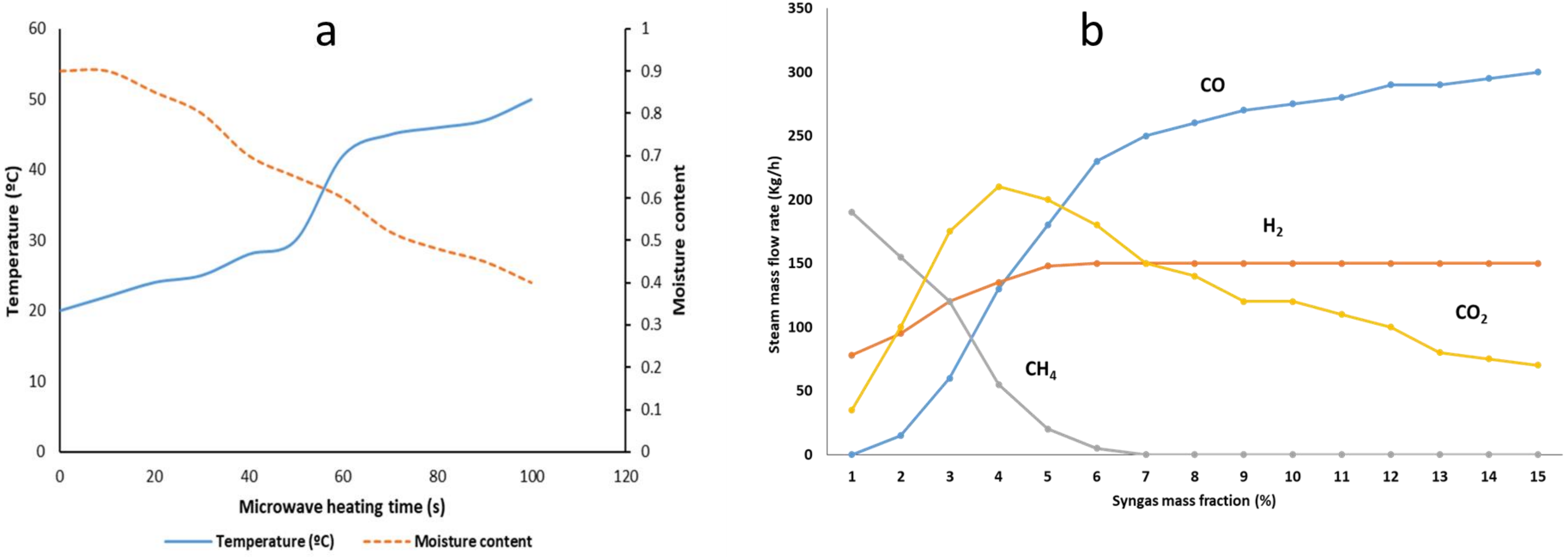


Figure 5-3. (a) Microwave heating time relative to moisture content and temperature variation (b) Mass flow relationship relative to the influence of temperature change on the composition of syngas

Figure 5-3, Moisture content decreases with increase in microwave heating time. The rapid temperature change between 50-60 ^{o}C is due to an increased molecular interaction of the material. The first 120 seconds is significant and could be used to predict the interaction in the long run. Figure 5-3, indicates that heating rate increases with the increase in microwave power. The energy and material balances quantify the process application and the input parameters. The results show the how the heat input parameter affects the yield relative to moisture content and gas yield for all the thermal processes. This is useful in the design of material requirement for a defined quantity of product.

5.3.2 Elemental analysis of the combine palm waste activated carbon

The elemental analyses of the CPW and their resultant AC are summarised in Table 5-2. The increased in temperature produced AC with oxygen containing functional group removed from carbon skeletal due to the release of volatiles. During the carbonisation and activation processes decarboxylation and aromatisation results in the breakage of unstable chemical bonds in the carbon matrix, this causes the release of volatiles which results in the high fixed carbon (FC), of which good precursor depends on.

During activation of CPW, FC content increased from 16.25 wt% to 73.56 wt% for single step conventional technique and 76.60 wt% for 2-step conventional technique. There is only 1.68 wt% difference between single step microwave technique and the combine approach of conventional and microwave. Therefore, single microwave technique produces almost the same result as a 2-step conventional process. Reduced volatile content in two-step conventional and microwave processes is due to an increased thermal energy which enabled the displacement of volatiles from the carbon matrix. Although conventional activated ACs have lower volatile content, the hydrogen-carbon ratio is higher than the conventional AC by 0.1-0.5 across this study. This might be due to high purity carbon as a result of microwave irradiation which produces uniform structural heating with low thermal gradient between the outer and inner parts of the biomass structure.

Sulphur content was thermally stable in both processes as there was no residual sulphur due to the use of trona which is non-acidic. There is an enrichment in carbon content and decline of hydrogen and oxygen after activation due to the removal of moisture. However, the presence of moisture in the precursor ensured the maintenance of uniform temperature profile during the activation process.

Table 5-2. Elemental analysis of combine palm waste activated carbon based on different production processes

Sample/ Process parameters	Proximate Analysis				Ultimate Analysis				
	Moisture	Volatile	FC	Ash	C	H	N	O	S
Raw CPW	4.05	74.50	16.25	5.20	44.60	6.35	0.80	48.10	0.15
CPW ℗ A: 800 °C-1 h	5.25	12.95	73.56	8.24	74.20	2.88	1.10	21.70	0.12
CPW ℗ B: 500°C-1 h + 800 °C-1 h	2.46	10.38	76.60	10.56	76.95	2.22	1.38	19.33	0.12
CPW ℗ C: 600 W-20 min	6.44	14.69	71.22	7.65	73.87	3.10	1.30	21.63	0.10
CPW ℗ D: 500 °C-1 h + 600 W-10 min	4.05	11.20	75.90	8.85	74.63	2.42	1.18	21.67	0.10
CPW: combine palm waste, ℗: Process									

5.3.3 AC morphology and surface chemistry mechanism

The surface morphology of raw PKS, MF, and EFB are illustrated in Figure 5-4. Activation with Trona ore after the evaporation of the volatiles clearly show the creation of well-developed pores. The SEM diagram indicates no major difference due to activation temperature but show clear variation with activation methods. The structure of samples activated by conventional methods look rough and uneven while the samples by microwave method appear smoother. The changes in Figure 5-4 show the difference in surface porosity prepared with each of the OPW. These cavities were created during the thermal process as starch and the organic materials are transformed into volatile and leaving carbon structure behind. The impregnation accompanied by thermal treatment resulted in degradation of the microstructure.

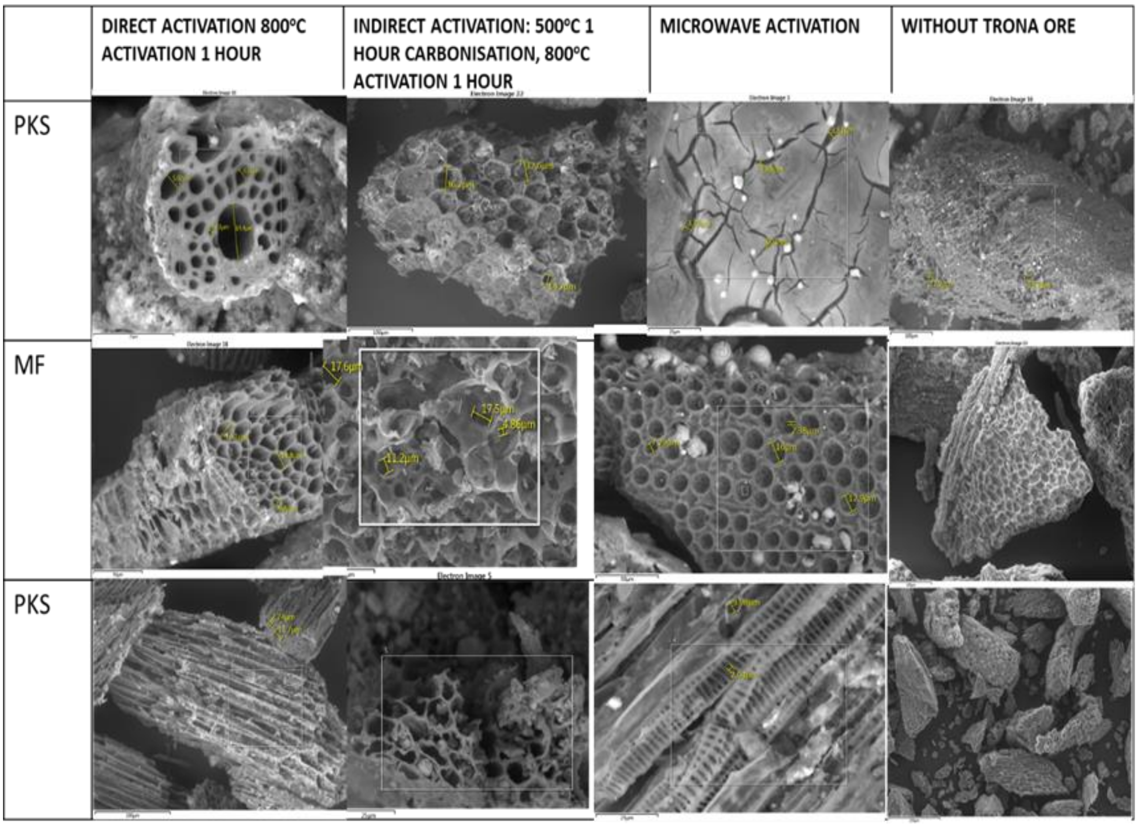


Figure 5-4. SEM analysis of the AC produced from Trona

The surface areas of all the samples were measured, and the attenuated total reflectance and absorbance and transmittance were analysed and for better representation, transmittance was used for the comparison. The feedstock for each of the CPW components were measured and the correspondent ACs.

For raw feedstock, spectra at 3000-3500 cm^{-1}, O-H stretching showing the presence of alcohol, phenol or carboxylic acid indicating a typical biomass formulation, which are eliminated by the activation process. At the range of 1700-1750 cm^{-1}, C=O stretching. The presence of aldehyde, ketone or carboxylic acid are the factors. Low temperature activation shows peak at 2800-3000 cm^{-1}, C-H stretching alkanes, this require additional heating and further release of volatiles and biomass tars. High temperature range of 800-1200 ^{o}C shows the C-O bending, reduced alcohol and ether. C-H bending signifies alkane and further eliminated by activating agent and longer duration of heating. Further increase in temperature and activation duration show C=O stretching representing alkenes and partial aromatic ring.

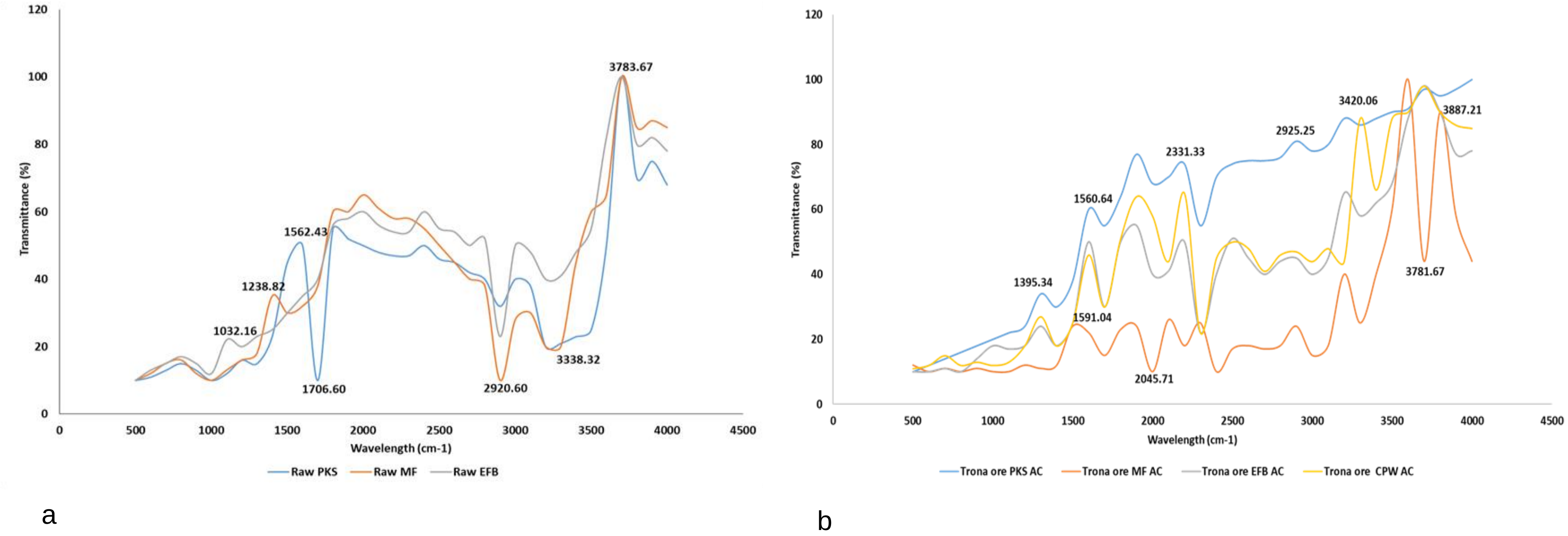


Figure 5-5. FTIR of OPW from different processing methods and activation conditions (b) raw feedstock (b) Trona ore activated AC

5.3.4 Effect of process parameters and modes of production on AC characteristics

The results presented in Table 5-3 show that, at 800 ^{o}C the S_{BET} are high with high pore volume. However, the yield reduces with increase in temperature. Here, the result indicates that pore volume is linearly proportional to S_{BET} and inversely proportional to pore diameter.

The effect of microwave power in AC production process is obvious as it influences duration of activation and carbon yield. Microwave power increases from 360 to 600 W increase the porosity and adsorption efficiency. S_{BET} and other parameters increases with increase in microwave power until the optimum range. In this analysis, the optimum microwave power range is 600 W. Beyond this range energy is wasted without corresponding increase in porosity. The relative pressure relationship with the volume adsorbed are considered and the relationship between different process methods are highlighted. AC activated using microwave had the highest S_{BET} for CPW. However, the pattern of adsorption remains the same.

Table 5-3. Yield and pore structural parameters

Sample	Process parameter	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	D_p (nm)	Yield (%)
PKS	℗ A: 800^{o}C-1 h	923	0.750	0.122	0.285	3.2	35
MF		1105	0.882	0.230	0.302	3.4	42
EFB		845	0.645	0.234	0.285	2.3	30
CPW		920	0.840	0.356	0.354	2.2	40
PKS	℗ B: 500^{o}C-1 h + 800^{o}C-1 h	650	0.745	0.108	0.230	2.8	30
MF		736	0.646	0.280	0.262	2.4	30
EFB		820	0.568	0.250	0.145	2.5	24
CPW		870	0.622	0.286	0.162	2.0	34
PKS	℗ C: 600W-20 min	1030	0.825	0.105	0.245	3.3	42
MF		1220	0.887	0.274	0.465	3.8	45
EFB		735	0.640	0.222	0.346	3.1	37

CPW		980	0.865	0.256	0.380	3.3	42
PKS	℗ D: 500^{o}C-1 h + 600W-10 min	670	0.542	0.089	0.200	3.1	37
MF		864	0.650	0.182	0.230	2.8	28
EFB		810	0.712	0.234	0.242	3.0	28
CPW		900	0.660	0.310	0.380	3.0	38
PKS: palm kernel shell, MF: Mesocarp fibre, EFB: Empty fruit bunch, CPW: combine palm waste, V: Volume, Dp: Pore diameter, ℗: Process							

One-step production are considered to be energy friendly more than the two-step process. In terms of yield the latter is lower. The low energy requirement of microwave technique is based on the activation duration and fast uniform heating. Possible breakdown of the pore structure is more common in the two-step process. Relative trapping of the activating agents in the pores are minimal with microwave heating. This is because microwave heats from the inside to the outer layer, which is opposite for conventional heating. Microwave saves energy and time; however, biomass is a poor microwave absorber and requires the right activating agent to improve dielectric properties. AC produced by microwave assisted process, has a more defined pore structure and this could be due to rapid escape of volatile from the inside.

Considering the surface chemical and stability of product, the analysis shows that activating agent effect on the biomass prior to activation is significant on the elimination of hydroxyl group, depolymerisation and degradation to simple sugar and subsequent reaction at the temperature above 600 ^{o}C. From Figure 5-5, there are indications of the differences in the production processes. For PKS samples, process C, has the highest S_{BET} and the highest yield. The highest micropore volume was observed in PKS process A while PKS process B was the lowest. For MF, process C has the highest S_{BET}, yield and micropore volume. For EFB, process A has the highest S_{BET} and micropore volume, process D has the highest total pore volume and process C with the highest yield. CPW sample has a different trend from the other individual feedstock. CPW process C has the highest S_{BET} and total pore volume. CPW process A has the highest mesopore volume while CPW process C and CPW process D has the same micropore volume. In relative comparison with other activating agents A study by Hussaro

(Hussaro, 2014) showed that at 700^oC activation temperature, PKS impregnated with Na_2CO_3 yielded an AC with S_{BET} of 725 m^2/g and V_{total} of 0.404 cm^3/g. The same technique with $ZnCl_2$ resulted in 533 m^2/g and Vtotal of 0.300 cm^3/g.

The particle size effect on the individual OPW is not a factor except for PKS. The process time for MF and EFB does not depend on the particle sizes. This is the case for both conventional and microwave methods. The optimum temperature for CPW is 800 ^oC for 1 h, but this depends on the combining ratio of the OPW. With the increase in the quantity of PKS the process time increases. For two step activation, the optimum range is 500 ^oC and 800 ^oC for an hour each. While the one-step process at 800 ^oC requires an hour. This result is based on batch process; however, in a continuous process there would likely be some differences. S_{BET} increases with production temperature, however, it’s also influenced by particle size before and after activation. Initial carbonisation temperature has direct influence on the displacement of volatiles and thereby affects tar deposition (Yakout and Sharaf El-Deen, 2016). The N_2 adsorption–desorption isotherms at of AC, at 400-800 ^oC temperature and activation mode suggests that the AC contain mostly micro pores, which is also shown by the absence of hysteresis.

Although the activation duration is affected by type of reactor, it also depends on other primary factors. In particular, the type of feedstock, affects the time needed to initiate carbonisation and ensure adequate release of volatiles which are; PKS>CPW>MF>EFB. For the microwave method, the time difference is insignificant rather relative to moisture content and microwave power determines the duration of activation (Kalu Samuel Ukanwa *et al.*, 2019). For the conventional production technique, temperature has significant impact in the carbonisation and activation duration. Particle sizes interestingly affect the duration of activation, and the finer the feedstock the shorter the activation duration. Particle size effects were clearly present for PKS, but not for MF and EFB.

5.3.5 Overview of the process and resultant challenges in the use of microwave

The primary efficiency of AC depends on the type of feedstock and production techniques. Tar deposition, which results in pore blockages, is one of the challenges of AC efficiency. Tar formation is common for all types of biomass pyrolysis but is minimised by the operating at a higher temperature that helps to remove primary tar vapours. This situation proves the relevance of activating agents which improve tar elimination and widen the AC pores. For OPW and related biomass materials, dimethoxy phenol, trimethoxybenzene and hydroxyl methoxyl benzoic acid can be eliminated at temperature above 250 ^oC. However, tertiary tars such as naphthalene, acenaphthylene, phenalene and pyrene can create a process challenge by being re-adsorbed by the AC (Kalu Samuel Ukanwa *et al.*, 2019), thereby lowering the efficiency (Phuphuakrat, Namioka and Yoshikawa, 2010). In microwave activation, the dielectric properties of the feedstock are critical for transforming electromagnetic energy into heat. One of the major challenges with most biomass materials including OPW, is their low microwave absorbing properties and they are weak absorbers with average loss tangent less than 0.1 (Salema *et al.*, 2013). Activating agent acts as an adjuvant to increase the microwave absorbability. Furthermore, the readiness of microwave technique is nearing commercial stage. However, the challenges of reactors and working out safety measures are expected to be achieved soon. This technique is currently being studied in various projects for largescale production and the ability to handle heterogeneous materials is being tested.

5.3.6 The effectiveness of Trona ore

Due to the release CO_2 from Trona due to thermal decomposition above 300 °C, contributes to the activation process. As temperature is further increases the CO_2 reacts with the char to produce CO; decreasing the carbon yield as shown below. Therefore, prolonged activation time is not necessary when Trona is used as an activating agent. Carbonisation temperature is very significant in AC production, in this study, only two temperatures were considered at 600 and 800 ^oC. Trona can cause degradation of glucose due to the presence of Na_2CO_3 and possibly other alkaline substances present. These cause the branching of carbohydrates. Trona causes solvation of ether linkages because of delignification, which is a factor for pore creation (Ukanwa et al., 2019). This further results in the dissolution of xylan, breakage of longer fibres, exfoliation and eventual removal of xylan as outlined in Figure 5-6 (Kim, Lee and Lee, 2014).

$$Na_2CO_3 + C \rightarrow -COONa + \ -CONa \tag{5-13}$$

$$-COONa + C \ \rightarrow \ -CONa + CO \tag{5-14}$$

$$-CNa + CO_3 \ \rightarrow \ -CONa + CO_2 \tag{5-15}$$

$$-CONa + CO_3 \ \rightarrow \ -COONa + CO \tag{5-16}$$

Therefore, the use of Na_2CO_3 as an activating agent has a significant effect on CO formation at temperature above 600 °C during alkali lignin gasification (Guo *et al.*, 2012). However, the behaviour is different in the absence of oxygen. The catalytic effect of Trona due to the presence of two major compound Na_2CO_3 and K_2CO_3, is effective in cellulose pyrolysis (Guo *et al.*, 2012).

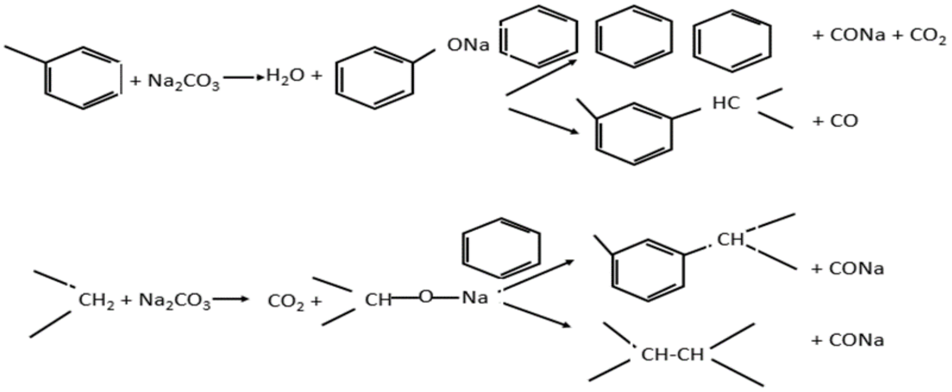


Figure 5-6. Mechanism of Trona during activation process

For conventional method, the effect of impregnation ratio is obvious. At 1:0.5 impregnation the pores are not well defined; however, this became more developed at 1:1. At 1:2, the structural walls appeared to be collapsed. For microwave activation method, the walls were intact and well defined for 1:0.5. S_{BET}, which is an important factor for adsorption depends on the particle size of the AC. The relativity of Trona ore AC with other activating agents are evaluated Figure 5-6. Pore sizes of AC activated by Trona ore in assessment with a physical activation process indicate good characteristics. Most AC are used for water purification; and should contain no trace of corrosive or toxic chemicals. Activation with Trona makes it easy to wash the AC, but still guarantees its safety in the case of improper washing.

For the efficiency of CPW, the individual OPW must be of the same particle sizes. For individual OPW, the process is less complex and gives a predictable outcome. However, the individual OPW has a few challenges such as poor carbon yield for MF and EFB, therefore complementing with PKS could increase the yield in a single process. The CPW at uniform particle size and appropriate is better than individual OPW, However, thorough mixing and stirring during impregnation are important for uniforms result. For CPW, the individual components must be properly mixed before impregnation and impregnation duration could increase.

5.4 Conclusion

Palm waste in a combined form can be an effective feedstock for the production of AC with Trona ore. The morphology of the AC produced were honeycomb-like, the total volume and surface area of the AC produced by this technique improved relative to the conventional approach. The AC yield was improved in this process and this confirms that direct activation process enables effective activating agent and biomass interaction for the release of volatiles with no obstruction of the pores.

The method of activation influenced the morphology, single-step activation with microwave has more unbroken pores while the two-step and conventional techniques produce ACs with broken and uneven pore linkages. The microwave activation method was better due to energy and time saving due to a reduced activation duration. The pore structures were enhanced by the increase in microwave power and temperature. The AC produced in this study has the potential to be used for heavy metal, dyes and other gases adsorption given their high surface area of about 1220 m^2/g, well defined pore structures.

5.5 References

Abioye, A. M. and Ani, F. N. (2015) ‘Recent development in the production of activated carbon electrodes from agricultural waste biomass for supercapacitors: A review’, *Renewable and Sustainable Energy Reviews*, 52, pp. 1282–1293. doi: 10.1016/j.rser.2015.07.129.

Aghamohammadi, N., Reginald, S. S., Shamiri, A., Zinatizadeh, A. A., Wong, L. P. and Sulaiman, N. M. B. N. (2016) ‘An investigation of sustainable power generation from oil palm biomass: A case study in Sarawak’, *Sustainability (Switzerland)*, 8(5), pp. 1–19. doi: 10.3390/su8050416.

Ahmed, M. J. (2016) ‘Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments: Review’, *Process Safety and Environmental Protection*. Institution of Chemical Engineers, 102, pp. 168–182. doi: 10.1016/j.psep.2016.03.010.

Ahmmad, R., Alengaram, U. J., Jumaat, M. Z., Sulong, N. H. R., Yusuf, M. O. and Rehman, M. A. (2017) ‘Feasibility study on the use of high volume palm oil clinker waste in environmental friendly lightweight concrete’, *Construction and Building Materials*, 135, pp. 94–103. doi: 10.1016/j.conbuildmat.2016.12.098.

Aziz, M. and Kurniawan, T. (2016) ‘Enhanced utilization of palm oil mill wastes for power generation’, 52, pp. 1–2. doi: 10.3303/CET1652122.

Bagheri, S., Julkapli, N. M., Bee, S. and Hamid, A. (2015) ‘Functionalized Activated Carbon Derived from Biomass for Photocatalysis Applications Perspective Functionalized Activated Carbon Derived from Biomass for Photocatalysis Applications Perspective’, *International Journal of Photoenergy*, 2015(JANUARY). doi: 10.1155/2015/218743.

Bergna, D., Varila, T., Romar, H. and Lassi, U. (2018) ‘Comparison of the Properties of Activated Carbons Produced in One-Stage and Two-Stage Processes’, *C*, 4(3), p. 41. doi: 10.3390/c4030041.

Bevan Nyakuma, B., Johari, A. and Ahmad, A. (2013) ‘Thermochemical analysis of palm oil wastes as fuel for biomass gasification’, *Jurnal Teknologi (Sciences and Engineering)*, 62(3), pp. 73–76. doi: 10.11113/jt.v62.1891.

Biliaminu, H. D. and Ibrahim, K. . O. (2010) *Non-Metallic Mineral Endownments in Nigeria*. Abuja, Nigeria: Nigeria : Raw Minerals Research and Development Council.

Chen, H., Teng, Y., Lu, S., Wang, Y. and Wang, J. (2015) ‘Science of the Total Environment Contamination features and health risk of soil heavy metals in China’, *Science of the Total Environment, The*, 512–513, pp. 143–153. doi: 10.1016/j.scitotenv.2015.01.025.

Chen, R., Li, L., Liu, Z., Lu, M., Wang, C., Li, H., Ma, W. and Wang, S. (2017) ‘Preparation and characterization of activated carbons from tobacco stem by chemical activation’, *Journal of the Air & Waste Management Association*, 67(6), pp. 713–724. doi: 10.1080/10962247.2017.1280560.

Chiew, Y. L. and Shimada, S. (2013) ‘Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer - A case study of Malaysia’, *Biomass and Bioenergy*, 51, pp. 109–124. doi: 10.1016/j.biombioe.2013.01.012.

Chima, I. K. and Nwabinye, M. V. (2017) ‘Economic Analysis of Household Waste Generation , Disposal and Management in Umuahia Metropolis , Abia’, *International Journal of Health Economics and Policy*, 2(2), pp. 47–56. doi: 10.11648/j.hep.20170202.12.

Danish, M. and Ahmad, T. (2018) ‘A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application’, *Renewable and Sustainable Energy Reviews*, 87(February), pp. 1–21. doi: 10.1016/j.rser.2018.02.003.

Daoud, M., Benturki, O., Fontana, S., Rogaume, Y. and Girods, P. (2019) ‘Energy and matter balance of process of activated carbon production from Algerian agricultural wastes: date palm rachis and jujube stones’, *Biomass Conversion* *and Biorefinery*. Biomass Conversion and Biorefinery. doi: 10.1007/s13399-019-00543-w.

Foo, K. Y. and Hameed, B. H. (2011) ‘Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes’, *Chemical Engineering Journal*, 173(2), pp. 385–390. doi: 10.1016/j.cej.2011.07.073.

Foo, K. Y. and Hameed, B. H. (2012) ‘Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K_2CO_3 activation’, *Bioresource Technology*, 104, pp. 679–686. doi: 10.1016/j.biortech.2011.10.005.

Fu, K., Yue, Q., Gao, B., Sun, Y., Wang, Y., Li, Q., Zhao, P. and Chen, S. (2014) ‘Physicochemical and adsorptive properties of activated carbons from Arundo donax Linn utilizing different iron salts as activating agents’, *Journal of the Taiwan Institute of Chemical Engineers*. Taiwan Institute of Chemical Engineers, 45(6), pp. 3007–3015. doi: 10.1016/j.jtice.2014.08.026.

Fujishige, M., Yoshida, I., Toya, Y., Banba, Y., Oshida, K. ichi, Tanaka, Y. suke, Dulyaseree, P., Wongwiriyapan, W. and Takeuchi, K. (2017) ‘Preparation of activated carbon from bamboo-cellulose fiber and its use for EDLC electrode material’, *Journal of Environmental Chemical Engineering*, 5(2), pp. 1801–1808. doi: 10.1016/j.jece.2017.03.011.

Gourichon H. (2013) ‘Analysis of incentives and disincentives for Palm oil in Nigeria. Technical notes series, MAFAP, FAO,Rome’, (July).

Guo, D., Wu, S., Liu, B., Yin, X. and Yang, Q. (2012) ‘Catalytic effects of NaOH and Na2CO3 additives on alkali lignin pyrolysis and gasification’, *Applied Energy*, 95, pp. 22–30. doi: 10.1016/j.apenergy.2012.01.042.

Hidayu, A. R. and Muda, N. (2016) ‘Preparation and Characterization of Impregnated Activated Carbon from Palm Kernel Shell and Coconut Shell for CO_2 Capture’, *Procedia Engineering*, 148, pp. 106–113. doi: 10.1016/j.proeng.2016.06.463.

Hoseinzadeh Hesas, R., Wan Daud, W. M. A., Sahu, J. N. and Arami-Niya, A. (2013) ‘The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review’, *Journal of Analytical and Applied Pyrolysis*, 100, pp. 1–11. doi: 10.1016/j.jaap.2012.12.019.

Hossain, M. A., Jewaratnam, J. and Ganesan, P. (2016) ‘Prospect of hydrogen production from oil palm biomass by thermochemical process – A review’, *International Journal of Hydrogen Energy*, 41(38), pp. 16637–16655. doi: 10.1016/j.ijhydene.2016.07.104.

Hou, S., Zheng, N., Tang, L., Ji, X., Li, Y. and Hua, X. (2019) ‘Pollution characteristics, sources, and health risk assessment of human exposure to Cu, Zn, Cd and Pb pollution in urban street dust across China between 2009 and 2018’, *Environment International*, 128(May), pp. 430–437. doi: 10.1016/j.envint.2019.04.046.

Huang, L., Sun, Y., Wang, W., Yue, Q. and Yang, T. (2011) ‘Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC)’, *Chemical Engineering Journal*, 171(3), pp. 1446–1453. doi: 10.1016/j.cej.2011.05.041.

Hussaro, K. (2014) ‘preparation of activated carbon from palm oil shell by chemical activation with Na2CO3 and zncl2 as imprenated agents for H2S adsorption’’, *American Journal of Environmental Sciences*, 10(4), pp. 336–346. doi: 10.3844/ajessp.2014.

Kan, T., Strezov, V. and Evans, T. J. (2016) ‘Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters’, *Renewable and Sustainable Energy Reviews*, 57, pp. 126–1140. doi: 10.1016/j.rser.2015.12.185.

Karri, R. R. and Sahu, J. N. (2017) ‘Modeling and optimization by particle swarm embedded neural network for adsorption of zinc (II) by palm kernel shell based activated carbon from aqueous environment.’, *Journal of environmental management*, 206, pp. 178–191. doi: 10.1016/j.jenvman.2017.10.026.

Khanday, W. A. and Hameed, B. H. (2018) ‘Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption’, *Fuel*, 215(April 2017), pp. 499–505. doi: 10.1016/j.fuel.2017.11.068.

Kim, T., Lee, J. and Lee, K.-H. (2014) ‘Microwave heating of carbon-based solid materials’, *Carbon letters*, 15(1), pp. 15–24. doi: 10.5714/CL.2014.15.1.015.

Köseoğlu, E. and Akmil-Başar, C. (2015) ‘Preparation, structural evaluation and adsorptive properties of activated carbon from agricultural waste biomass’, *Advanced Powder Technology*, 26(3), pp. 811–818. doi: 10.1016/j.apt.2015.02.006.

Lam, S. S., Wan Mahari, W. A., Cheng, C. K., Omar, R., Chong, C. T. and Chase, H. A. (2016) ‘Recovery of diesel-like fuel from waste palm oil by pyrolysis using a microwave heated bed of activated carbon’, *Energy*, 115, pp. 791–799. doi: 10.1016/j.energy.2016.09.076.

Lee, L. Z. and Ahmad Zaini, M. A. (2016) ‘Metal chloride salts in the preparation of activated carbon and their hazardous outlook’, *Desalination and Water Treatment*, 57(34), pp. 16078–16085. doi: 10.1080/19443994.2015.1077348.

Liew, R. K., Nam, W. L., Chong, M. Y., Phang, X. Y., Su, M. H., Yek, P. N. Y., Ma, N. L., Cheng, C. K., Chong, C. T. and Lam, S. S. (2017) ‘Oil palm waste: An abundant and promising feedstock for microwave pyrolysis conversion into good quality biochar with potential multi-applications’, *Process Safety and Environmental Protection*. Institution of Chemical Engineers, pp. 1–13. doi: 10.1016/j.psep.2017.10.005.

Loh, S. K. (2017) ‘The potential of the Malaysian oil palm biomass as a renewable energy source’, *Energy Conversion and Management*, 141, pp. 285–298. doi: 10.1016/j.enconman.2016.08.081.

Nabais, J. M. V., Laginhas, C., Carrott, M. M. L. R., Carrott, P. J. M., Amorós, J. E. C. and Gisbert, A. V. N. (2013) ‘Surface and porous characterisation of activated carbons made from a novel biomass precursor, the esparto grass’, *Applied Surface Science*, 265, pp. 919–924. doi: 10.1016/j.apsusc.2012.11.164.

Nahil, M. A. and Williams, P. T. (2012) ‘Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks’, *Biomass and Bioenergy*, 37, pp. 142–149. doi: 10.1016/j.biombioe.2011.12.019.

Nomanbhay, S. and Ong, M. Y. (2017) ‘A Review of Microwave-Assisted Reactions for Biodiesel Production’, *Bioengineering*, 4(2), p. 57. doi: 10.3390/bioengineering4020057.

Okoroigwe, E, C., Ofomatah, A, C., Oparaku, N, F., Unachukwu and G, O. (2013) ‘Production and evaluation of activated carbon from palm kernel shells (PKS) for economic and environmental sustainability’, *International Journal of Physical Sciences*, 8(19), pp. 1036–1041. doi: 10.5897/IJPS2013.3889.

Omoriyekomwan, J. E., Tahmasebi, A., Zhang, J. and Yu, J. (2017) ‘Formation of hollow carbon nanofibers on bio-char during microwave pyrolysis of palm kernel shell’, *Energy Conversion and Management*, 148, pp. 583–592. doi: 10.1016/j.enconman.2017.06.022.

Ooi, C. H., Cheah, W. K., Sim, Y. L., Pung, S. Y. and Yeoh, F. Y. (2017) ‘Conversion and characterization of activated carbon fiber derived from palm empty fruit bunch waste and its kinetic study on urea adsorption’, *Journal of Environmental Management*, 197, pp. 199–205. doi: 10.1016/j.jenvman.2017.03.083.

Phuphuakrat, T., Namioka, T. and Yoshikawa, K. (2010) ‘Tar removal from biomass pyrolysis gas in two-step function of decomposition and adsorption’, *Applied Energy*, 87(7), pp. 2203–2211. doi: 10.1016/j.apenergy.2009.12.002.

Rashidi, N. A. and Yusup, S. (2017a) ‘A review on recent technological advancement in the activated carbon production from oil palm wastes’, *Chemical Engineering Journal*, 314, pp. 277–290. doi: 10.1016/j.cej.2016.11.059.

Rashidi, N. A. and Yusup, S. (2017b) ‘Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption’, *Journal of Cleaner Production*, 168, pp. 474–486. doi: 10.1016/j.jclepro.2017.09.045.

Salema, A. A., Yeow, Y. K., Ishaque, K., Ani, F. N., Afzal, M. T. and Hassan, A. (2013) ‘Dielectric properties and microwave heating of oil palm biomass and biochar’, *Industrial Crops and Products*, 50, pp. 366–374. doi: 10.1016/j.indcrop.2013.08.007.

Sethupathi, S., Bashir, M. J., Akbar, Z. A. and Mohamed, A. R. (2015) ‘Biomass-based palm shell activated carbon and palm shell carbon molecular sieve as gas separation adsorbents’, *Waste Management and Research*, 33(4), pp. 303–312. doi: 10.1177/0734242X15576026.

Shahbandeh, M. (2020) *Palm oil: global production volume*, *US Department of Agriculture; USDA Foreign Agricultural Service*. Available at: https://www.statista.com/statistics/613471/palm-oil-production-volume-worldwide/ (Accessed: 8 April 2020).

Suresh Kumar Reddy, K., Al Shoaibi, A. and Srinivasakannan, C. (2012) ‘A comparison of microstructure and adsorption characteristics of activated carbons by CO_2 and H_3PO_4 activation from date palm pits’, *Xinxing Tan Cailiao/New Carbon Materials*. Institute of Coal Chemistry, Chinese Academy of Sciences, 27(5), pp. 344–351. doi: 10.1016/S1872-5805(12)60020-1.

Thomas, B. S., Kumar, S. and Arel, H. S. (2017) ‘Sustainable concrete containing palm oil fuel ash as a supplementary cementitious material – A review’, *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 80(July 2016), pp. 550–561. doi: 10.1016/j.rser.2017.05.128.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R., Anthony, E. and Mandavgane, S. (2019) ‘A review of chemicals to produce activated carbon from agricultural waste biomass’, *Sustainability (Switzerland)*, 11(22), pp. 1–35. doi: 10.3390/su11226204.

Unpinit, T., Poblarp, T., Sailoon, N., Wongwicha, P. and Thabuot, M. (2015) *Fuel Properties of Bio-Pellets Produced from Selected Materials under Various Compacting Pressure*, *Energy Procedia*. doi: 10.1016/j.egypro.2015.11.551.

Wang, L., Chen, Z., Wen, H., Cai, Z., He, C., Wang, Z. and Yan, W. (2018) ‘Microwave assisted modification of activated carbons by organic acid ammoniums activation for enhanced adsorption of acid red 18’, *Powder Technology*, 323, pp. 230–237. doi: 10.1016/j.powtec.2017.10.021.

Wang, S., Dai, G., Yang, H. and Luo, Z. (2017) ‘Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review’, *Progress in Energy and Combustion Science*, 62, pp. 33–86. doi: 10.1016/j.pecs.2017.05.004.

Xiao, H., Peng, H., Deng, S., Yang, X., Zhang, Y. and Li, Y. (2012) ‘Preparation of activated carbon from edible fungi residue by microwave assisted K2CO3 activation-Application in reactive black 5 adsorption from aqueous solution’, *Bioresource Technology*, 111, pp. 127–133. doi: 10.1016/j.biortech.2012.02.054.

Xin-hui, D., Srinivasakannan, C. ., Jin-hui, P., Li-bo, Z. and Zheng-yong, Z. (2011) ‘Comparison of activated carbon prepared from Jatropha hull by conventional heating and microwave heating’, *Biomass and Bioenergy*, 35(9), pp. 3920–3926. doi: 10.1016/j.biombioe.2011.06.010.

Yakout, S. M. and Sharaf El-Deen, G. (2016) ‘Characterization of activated carbon prepared by phosphoric acid activation of olive stones’, *Arabian Journal of Chemistry*. King Saud University, 9, pp. S1155–S1162. doi: 10.1016/j.arabjc.2011.12.002.

Yang, K., Peng, J., Srinivasakannan, C., Zhang, L., Xia, H. and Duan, X. (2010) ‘Preparation of high surface area activated carbon from coconut shells using microwave heating’, *Bioresource Technology*, 101(15), pp. 6163–6169. doi: 10.1016/j.biortech.2010.03.001.

Zainal, N. H., Aziz, A. A., Idris, J., Mamat, R., Hassan, M. A., Bahrin, E. K. and Abd-Aziz, S. (2017) ‘Microwave-assisted pre-carbonisation of palm kernel shell produced charcoal with high heating value and low gaseous emission’, *Journal of Cleaner Production*, 142(October 2016), pp. 2945–2949. doi: 10.1016/j.jclepro.2016.10.176.

6 OIL PALM WASTE THERMAL RESIDUE IMPROVES SOIL FERTILITY AND QUALITY OF HABANERO CHILLI PEPPER (*Capsicum chinense jacq.*) PRODUCE IN SOUTHERN NIGERIA

Kalu Samuel Ukanwa[1], Kumar Patchigolla[1]* and Ruben Sakrabani[2]

1 Centre for Thermal Energy and Materials, School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK;

2 Cranfield Soil and Agrifood Institute, Cranfield University, Cranfield MK43 0AL, UK;

Ready for submission

Statement of contribution of joint authorship

The project conception, development, data collection, methodology, laboratory experiments and analyses were done by Kalu Samuel Ukanwa. Kalu Samuel Ukanwa also premeditated the novelty, selected and prepared the sites for growing crops. The farm activities were done by Federal University of Technology, Owerri staff and remotely monitored by videos and photographs. The manuscript was prepared by Kalu Samuel Ukanwa. Kumar Patchigolla and Ruben Sakrabani supervised the experiments, ensured it followed the approved standard operating procedures. Ruben Sakrabani provided scope management and stage by stage editing of the manuscript.

6.1 Introduction

Improving soil fertility is a critical factor to increasing food production. To achieve this, adequate and appropriate soil amendments are required, which are at times expensive. Fertilizers are key to enhancing soil fertility, even though the production processes are energy intensive. Chemical fertilizers also have huge implications on greenhouse gas (GHG) emissions. The impact of global warming due to GHG emission has impelled concepts and strategies to implement renewable energy agenda in agriculture (Sansaniwal, Rosen and Tyagi, 2017). GHG from agricultural activities are increasing due to the use of inorganic fertilizers and other agro-chemicals. There is a need to use organic amendments that are sustainable and have low energy demand.

Most soils in southern Nigeria are acidic due to heavy rainfall and resultant leaching of nutrients (Jemo *et al.*, 2014). Nutrient depletion occurs due to a high weathering of soils and leaching; worsen with intercropping. Industrialisation in agriculture and inorganic chemical application to improve soil fertility have severe negative effects on the soil and crops; as well as on the environment, human and animal health (Savci, 2012). Although, commercial fertilizers promote crop yield, they increase the input cost and degrade the soil significantly with time. These negative effects can be minimised by organic fertilizer application. Compost is known to be effective in amending acidic soils. Generally, organic amendments improve soil mineral adsorption, organic carbon and nitrogen content; which can ameliorate the soil with long-time impact on yield (van Wesemael *et al.*, 2019). Biomass residues are effective for the safety of the environment through enhancement of microbial community and improve soil chemical properties. It can also improve the soil nutrient dynamic balance and overall nutrient adsorption.

In this study the focus is on biomass ash as a safe option of soil amendment as in Nigeria oil palm is one of the major crops and results in large generation of waste (Kelechi E Anyaoha *et al.*, 2018). Biomass ash is a by-product of thermal processes and in the presence of oxygen, undergoes complete combustion process (Kalu Samuel Ukanwa *et al.*, 2019). Oil palm residues and their processing wastes could be useful in composting and other thermochemical processes. The combination of different parts such as palm kernel shell (PKS), palm kernel cake, mesocarp fibre (MF) and empty fruit bunch (EFB), account for about 38% percent dry weight of Fresh Fruit Bunch (Lorestani and Zinatizadeh, 2006). They can be combined in a single thermal process and the resulting residue applied to the soil. Conventionally, biomass gasification process, bottom ashes are dense and abrasive due to the high content of minerals and a heterogeneous base. These have the capacity as carbon capture mitigation strategy in relation to energy sustainability (Moragues-Saitua, Arias-González and Gartzia-Bengoetxea, 2017). The oil palm waste ash (OPWA) and other biomass ashes produced in this process can also be applied as a fertilizer to support and ameliorate, soil fertility and structure, thereby reducing soil acidity especially for crops such as pepper, which do not survive in acidic environments. These can encourage carbon sequestration and also improve soil characteristics for higher crop yield, as well overcome the negative impacts of inorganic fertilizers.

There is a great value for chilli pepper due to high demand and market value of $2.13 per kg in Nigeria (Alawode and Abegunde, 2016). Commercial chilli pepper farming is not common in southern Nigeria, due to low yield. This is attributed to the climatic condition, soil status and poor research on the optimum period and condition for pepper growth (Ndaeyo *et al.*, 2017). There are varieties of chilli peppers in the Nigerian market, which differ from its pungency to sizes. These varieties include the short and spicy pepper, bird's eye pepper (*Capsicum frutescens*) also known as Atawere, the long and thin Cayenne pepper or red pepper (Capsicum annum), also known as Sombo. Tatase (*Capsicum annum L.*), a very mild with bright red colour. The very spicy species locally known as Atarodo or Ose Nsukka is Habanero chilli pepper (HCP), (*Capsicum chinense jacq.*) (Ndaeyo *et al.*, 2017), with Scoville heat level of 100000-350000. HCP has several colours in one plant, red, orange or yellow at different levels of maturity.

Nigeria is known for chilli food and high spice intake and growing seasons influence the commodity price. However, most of the chilli peppers consumed in southern Nigeria are grown in the North and most times, perish in transit unless they are dried (Olayemi *et al.*, 2011). These have resulted in increase in the market price of fresh pepper in southern Nigeria. The increase in domestic demand for chilli pepper has resulted in low export and competition from Brazil, Indonesia and India for European, Australia and USA markets. Despite the level of production, Nigeria still imports chilli pepper. The incorporation of OPWA into the soil could enhance germination. This can improve the soil ability to retain and release water, enhance root growth due to proper water infiltration. Improved soil fertility and good agronomy practice could encourage production capacity, especially in the Southern part of Nigeria. Dada and Ogunsesu (2016) did a field study in the south-west but, used compost extract and recorded an average yield of 7.8 tonnes/ha.

The low production is attributed to the low soil fertility, excessive cost of irrigation systems, and poor inorganic fertilizer influence on the soil (Ikeh et al., 2012). The productivity and yield of HCP, like every other crop, largely depend on factors such as; soil nutrients bioavailability, kinetics of nutrient uptake, weather conditions, nitrogen fixation, soil structure and characteristics.

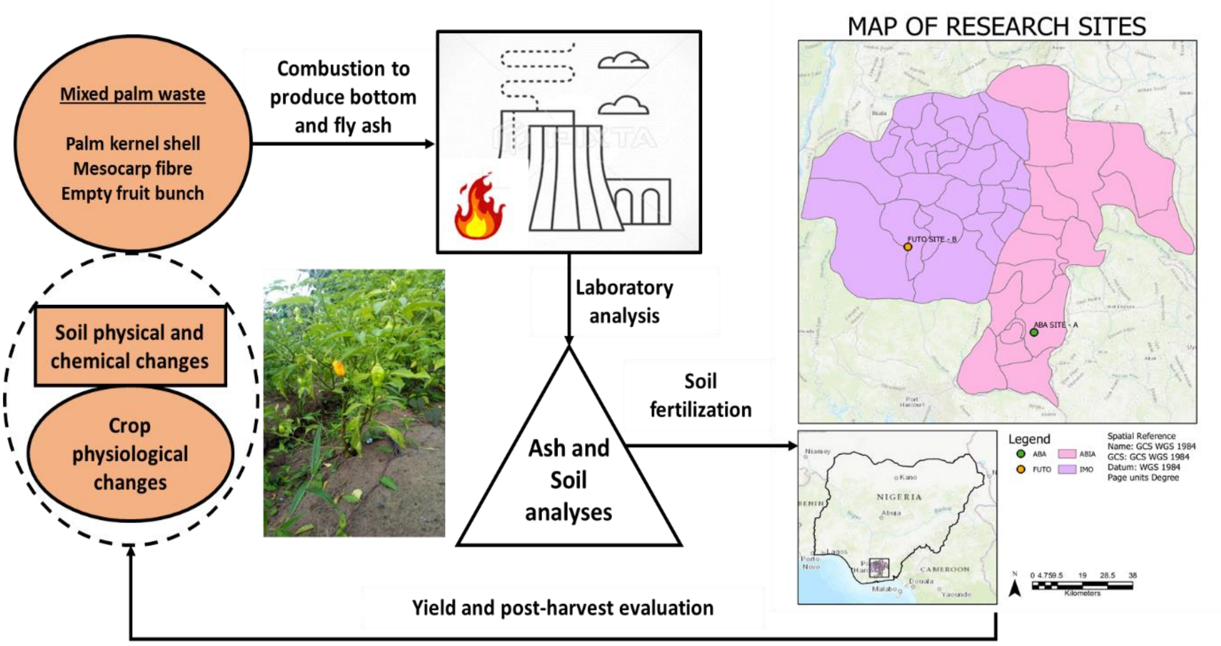


Figure 6-1 Experimental and analytical processes for palm waste ash application for growing chili pepper

The aim of this study is to utilise OPWA in a low fertile and acidic soils located in two different parts of southern Nigeria to evaluate the efficiency of OPWA as a fertiliser from organic sources to establish HCP. The field trials on other crops in Nigeria provided evidences of positive impact of biomass ash on the soil (Kelechi E. Anyaoha *et al.*, 2018). However, there is a knowledge gap on how the planting period affects HCP, the influence of OPWA relative to yield and morphological development. Hence, the hypotheses of this study is that amendment of soil with OPWA would improve retention of soil water, decrease soil acidity and improve macro nutrient availability thereby improving crop yield.

According to Figure 6-1, the thermal residue of mixed palm waste was applied in two different soils. The influence of OPWA was further evaluated by the physiological development of HCP, fruit morphology and a combined assessment of first and second seasons. This technique will address the challenge of oil palm waste utilisation and add value to palm waste thermal residues by incorporation in agriculture.

6.2 Material and methods

6.2.1 Experimental sites

This study was carried out and evaluated across two sites. Site A was located in a research site jointly owned by Desai Impex Nigeria Ltd (DINL) and Daksh BHL

International Ltd Aba, Abia state, Nigeria. It is located at latitude 5.1554°N and longitude 7.4571°E. Site B was a demonstration site of Federal University of Technology Owerri (FUTO), Imo state Nigeria, which is location at latitude 5.378 N and longitude 6.98675 E (Figure 6-1). Both sites (A and B) have 15 nursery beds of 3 m x 2 m each to demonstrate week-by-week response of the seedling, their survival rate and actual planting period.

Fifteen soil samples were collected from each site and analysed in Cranfield University soil laboratory, UK to obtain baseline information. The choice of both sites was for adequate comparative study based on different soils and weather. The number of trial beds were made according to the available size of land for the study and the choice amendment was determined based on known characteristics of Southern Nigeria soil**.**

6.2.2 Weather condition

Extreme weather especially temperature is unsuitable for pepper growth, this also has direct influence on the development and fruit yield of HCP. The climatic conditions of the two sites aren't the same; however, the weather conditions were obtained from the sites using Black Cobblestone Shape, PINGKO Weather Station Digital Temperature Monitor Outdoor Wireless Station Monitoring (pk-392, Shenzhen Vivistar Tech, China) and complemented by the weather report by Nigerian Meteorological Agency. The temperature was measured with Hanna Instruments HI7669/2W Temperature Probe and humidity by HSM50 Digital soil moisture meter (Hanna instruments, UK). Weather condition is vital in determining germination especially temperature and humidity. This is also important shortly after germination; it controls the survival at the tender stage. The germination temperature for chilli is within 25 to 35 °C beyond which could hinder germination.

6.2.3 Preparation of oil palm waste ash

Oil palm waste was collected in a processing mill in Aba, measured in 3:2:1 proportion by weight of PKS, MF and EFB. These were burnt completely into ash in the combustion unit of the boiler plant. The ash was preserved in an aluminium box and allowed to cool for two days. The ash was sieved with a 0.2 mm sieve afterwards to get a fine particle of the OPWA. Samples of the OPWA were collected for analysis and the chemical compositions were determined. The ash analyses were done with Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (Phillips XL30ESEM).

Further analysis of the chemical properties of the ashes were also performed with OPUS software controlled (Bruker, VERTEX 70, Germany), Fourier Transform Infrared Spectrometry (FTIR) in Cranfield University UK, other mineral determinations of OPWA were analysed in DINL laboratory. The Energy Dispersive X-Ray confirmed the available minerals in the ash with the potentials to release them to both the soil and directly to the plant. Each sample was allowed to cool in a desiccator. The residue later dissolved in 0.5 ml to 1.0 ml of water and add, while mixing, 21 ml of hydrochloric acid followed by 7 ml of nitric acid, Aqua regia technique was adopted. Flame emission capability double beam Atomic Absorption Spectrophotometer (AAS) (GBC Sens) was used for the determination of the major elements. The variation in the ash samples were due to some of them containing fine particles of unburnt carbon and because of this, 5 samples were analysed and the mean and standard deviation recorded.

The sites were cleared with cutlass, soil was collected using a W-shape sampling method (Peters and Laboski, 2013) and 15 samples were collected in each site, in February 2018 (dry season). Steel soil auger was used at the depth of 25-30 cm, air dried for about 2 days, crushed and sieved with 2 mm sieve. The 30 samples from the two sites were analysed in Cranfield University, UK. The choice of sampling method was directed to capture the actual representation of the entire fields of study. This is to determine the baseline initial fertility level.

6.2.4 Soil laboratory analysis

The soil particle size distribution was determined and classed into particle grades. This procedure applied to determine the particle size distribution in mineral soil material using scientific standard method for sieving and sedimentation (ISO, 2020).

Soil sample weighing 500 g was sieved through a set of sieves openings with four aggregate size classes (ASCs) are obtained. The results were calculated based on the percentage passage through the sieves. Soil organic matter of the pulverized dry soil was evaluated by loss on ignition method according to the standard procedure. Soil pH was measured in water with a pH probe. The ability of the soil to hold exchangeable cations was measured, using specification for topsoil at pH 7, which is applied and illustrated as soil cation exchange capacity (CEC). Inductively coupled plasma optical emission spectrometry (ICP-OES) was applied through quantitative analysis of ammonium acetate extracts of soil using concentrated HCl (37%) and HNO_3 (65%) analytical reagent grade acids. Electrical conductivity (EC) was measured in this study with Groline equipment (HI-98331, Hanna Instruments, UK).

6.2.5 Nursery Preparation

It is necessary to have a rich and fertile soil for nursery. However, for this study, the beds were prepared to study the nursery performance under natural conditions. Each nursery bed was about 4 m x 5 m, one bed per week. The seeds were obtained from the National Root Crops Research Institute Umudike, Nigeria. For both site A and B, it started from May week one to August week three in 2018. There was occasional shade over the nursery bed, although this is to allow natural atmospheric influence on the survival rate. This system was adopted to estimate the optimum nursery period for the soil when irrigation is not involved. Thinning was done 10 days after emergence and transplanting after 7 weeks at nursery.

6.2.6 Soil experimental design, layout and treatments

Randomized Complete Block Design (RCBD) were laid for the two sites that comprised of four treatments, one control and three replications. Each plot measured 3 x 2 m each, giving 15 plots for each site. The land was manually cleared and tilled with shovels and hoes. Various rates of the OPWA formed the treatments levels. The treatments were integrated into the soil twelve days prior to sowing as one full dose application (Mbah *et al.*, 2010). For the three weeks the beds were monitored and protected with thin plywood to avoid sweeping the ash out by wind or rain.

There are several application techniques, but the suitability is contingent on the state of the beds, type of plant, quantity of ash and experimental parameters. Ash was measured and applied, two weeks before transplanting, at the rate of 2 tonnes/ha, 4 tonnes/ha, 6 tonnes/ha and 8 tonnes/ha with no OPWA application on the control plot. This application was done evenly on the surface of the beds and covered thinly with soil from same bed. Date of ash application-Site B: 29 August 2018 and Site A, 6 October 2018. The beds were monitored for weeds, only few appeared before transplanting and were uprooted manually with minimum disturbance to the soil. Raised beds are very easy to maintain, free from encroaching weeds, which made pest control manageable. There was no rainfall on the day of ash application.

6.2.7 Transplanting and Irrigation

Seven weeks into the nursery and fourteen days after the ash was applied, the plants were ready for transplanting. The healthy plants were selected based on the physical features such as healthy leaves and deep roots. Trowel was used for the transplanting. Planting was done using inter-row spacing and intra row spacing of 30 cm respectively. Transplanting distance was 30 cm by 30 cm, number of plants per bed was 65-66 and the total number was 990. Date of transplanting for site A and B were 17 October 2018 and 9 September 2018 respectively. Inorganic chemicals were strictly avoided in this research to avoid interference with OPWA and also to minimise cost of production. The grasses were manually uprooted at the later stage, hoe was used for weeding. Hence, no pesticide was also applied. There was no irrigation, the nursery and the plant beds were rain fed. Rodents and birds were kept off by net fence and electronic scarecrow. The sites were established on flat ground to avoid bed erosion due to slope.

6.2.8 Field plant analysis

6.2.8.1 Morphological parameters and stomata measurement

The morphological analysis of plant parts may represent an efficient tool for the characterisation and description of their development.

$$\mathbf{Leaf\ area\ Index\ (LAI)} = \frac{\mathbf{Leaf\ area}}{\mathbf{Ground\ area}} \tag{6-1}$$

Leaf Area is the product of mean length, breadth and a leaf size constant k, where k is 0.75 (Ajala, Awodun and Oladele, 2017) Leaf area measurement was determined with a surface area meter. It is also necessary to evaluate leaf relative water content (LRWC) and other leaf-related analysis.

$$\mathbf{LRWC}\ (\%) = \left[\frac{(\mathbf{PFW}-\mathbf{DWL})}{(\mathbf{SW}-\mathbf{DWL})}\right]\mathbf{100} \tag{6-2}$$

PFW = Plant fresh weight of the plant, DWL = Dry weight of HCP leaf, SW = swollen weight of HCP leaf. The growth analyses were calculated based on these parameters, leaf area ratio. These are used to evaluate HCP relative growth rate (RGR).

The Equation 1 and 2 would enable the determination of physical variance and changes in growth. The physiological traits of habanero chilli pepper are factors of the indicative influence of yield and potential ability for yield. Dry mass (DM) and the relative growth rate (RGR) are the physical techniques of growth determination. The leaf physical features and characteristics can also be used to evaluate and determine the plant performance. The leaf parameters were measured according to Hunt et al. (2002). In each harvest 5 HCP plant were randomly picked for measurements. There are parameters defined and their relationship expressed by (Ballina-Gómez *et al.*, 2013).

$$\text{Relative growth rate} = \frac{\text{Change in height}(\mathrm{DM}_2 - \mathrm{DM}_1)}{\text{Change in time}(\mathrm{t}_2 - \mathrm{t}_1)} \tag{6-3}$$

$$\mathrm{LAR} = \mathrm{SLA} * \mathrm{LWR} = \frac{\mathrm{LA}}{\mathrm{DML}} * \frac{\mathrm{DML}}{\mathrm{DM}} \tag{6-4}$$

$$\mathrm{NAR} = \frac{\mathrm{RGR}}{\mathrm{LAR}} \tag{6-5}$$

SLA is the specific leaf area of an average HCP leaf in plant, while LWR is the weight ratio of leaf and LAR represents the area ratio of leaf. DM is the dry mass of an average HCP plant in a plot, t is the period from germination, LA is the total leaf area per plant and DML is total leaf dry mass per plant. These are analysed according to Equation 3-5.

Stomatal density was measured at the early stage of fruiting. The leaf is cut in two and immerse in MES/KOH buffer, preserved in a dark room for 2 hrs. One part of the peel is immersed in 4% formaldehyde solution. After 2-10 minutes of immersion, it is returned. This is later transferred to MES/KOH buffer. The remaining part of the peel is immersed in a solution without formaldehyde. The leaf peels were observed using epi-fluorescence microscope and returned to the preservation dishware. The dishware previously preserved in an illuminated room were transferred into a dark box in a dark room, whereas those from the dark box were transferred into an illuminated room for 60 minutes, were again analysed under microscope and evaluated according the Equation 6 and 7. The stomata number was evaluated for each of the plants and average were recorded.

$$\text{Average count} = \frac{\mathrm{N}_1 + \mathrm{N}_2 \ldots\ldots \mathrm{N}_{10}}{10} = \mathrm{M}_\mathrm{c} \tag{6-6}$$

$$\text{The density of stomata over } 1\mathrm{mm}^2 = \mathrm{M}_\mathrm{c} * \frac{1}{\mathrm{F}_\mathrm{v}} \text{ stomata number per mm}^2 \tag{6-7}$$

F_v is the field of view, Mc is the mean count and N number of counts per field view.

6.2.8.2 Capsaicin determination

HCP were wholly dried at 40 °C until all moisture is driven out. The water content was determined and recorded. High-performance liquid chromatography was used in analytical chemistry for its capacity to disperse and separate a mixture of chemical compounds. This enables the identification and quantification of the components of HCP mixture. This principle in capsaicin determination of HCP require extraction before the liquid chromatography analysis. All extractions were performed using ethanol and put on the sonicator for 45 minutes followed by more than 2 h of maceration. Determined by Column Ascentis Express RP-Amide with parameters expressed for capsaicin content determination of pepper as determined by calibration and calculated using Scoville organoleptic technique. This is expressed as, capsaicin per gram of HCP (Okunlola *et al.*, 2017).

6.2.9 Statistical analyses

The statistical analysis was performed using SPSS statistics and Microsoft Excel. Experimental and field data for this study were analysed using analysis variance (ANOVA). The ANOVA technique was used for statistical difference evaluation. Microsoft Excel was used for the graphical representation of the dataset. A combined design was used to test the influence of OPWA treatments relative to other outcomes, all factors of plant growth are necessary therefore were evaluated as single factors before equating them in the actual growth factor analysis. Regression methods were adopted to evaluate the variation that defines the trend in response and relationship between factors.

6.3 Results and discussion

6.3.1 Soil and ash analyses

The survival and optimum yield of pepper depends on several soil characteristics and should be within the optimum pH range of 5.6-6.8 (Starke Ayares, 2014). The average pH of all the samples in the two different sites were taken, the maximum and minimum values were also plotted. The results were represented in Table 6-1. This parameter is very important because the pH condition of the soil plays a role in activities of soil microorganisms and survival of plant.

Soil pH has direct influence on soil bacteria, nutrient leaching, and nutrient availability. Biodegradation, nitrification and denitrification are also affected. Due to the high acidity of soils of the two sites, low calcium had caused a decreased chemical balance which, could cause root diseases. The low potassium could cause a decreased water balance and plant tolerance to disease. The abundance of these minerals in the OPWA could results in improved crop germination and availability of potassium has influence on direct crop development. The high alkalinity of the ash and richness in minerals deficient in the soil can create a nutrient balance in the soil. The rate of OPWA dissolution in water improves the absorbability of the mineral by plant. The primary and secondary minerals in ash form simpler compounds at higher temperature and rainfall. The charges in in these oxides and hydroxides are influenced by the pH, the hydroxyl bond becomes weaker and this can influence the retention of cations, such as Mg, K and Ca and these are known as electrostatic cationic macronutrients (Fontes and Alleoni, 2006).

Table 6-1 Properties of soil for site A and B; chemical analysis and EDX of palm waste ash

	Soil		Chemical analyses of Palm waste ash analysis		Palm waste ash SEM/EDX (%)	
Variables	SITE A Mean ± SD	SITE B Mean ± SD	Parameters	Mean ± SD	Parameters	Mean ± SD
Total Phosphorus (mg/kg)	14.5±1.5	11.8±3	pH	11.85±0.26	Si	18.46±1.23
Available Phosphorus (mg/kg)	2.6±0.8	1.8±0.2	Organic Carbon	1.7±0.21	Al	1.3±0.33
Exchangeable Calcium (mg/kg)	1.8±1.2	1.5±0.2	Available Phosphorus (%)	0.194±0.07	K	20.42±2.18
Exchangeable Potassium (mg/kg)	0.12±0.5	0.1±0.3	Total P	0.28±0.02	Ca	13.44±1.63
Exchangeable Sodium (mg/kg)	0.09±0.02	0.12±0.4	Total N (%)	0.22±0.05	Na	0.072±0.049
Exchangeable Magnesium (mg/kg)	0.95±0.6	1.0±0.2	Total Potassium	25.6±3	Cl	0.42±0.29
Electrical Conductivity (dS/m)	0.25±0.15	0.18±1.4	Total Calcium	20.2±1.94	S	0.456±0.28
CEC (cmol/kg)	16.6±3	13.2±5	Total Magnesium	3.34±0.37	P	3.67±0.91
Base saturation (%)	80±2	72.6±4	Conductivity dS/m	18.8±1.2	Mg	2.05±0.63
C:N ratio	22.4±0.02: 1.4±0.01	16.6±0.003: 2.14±0.006	Ca^{2+} (mg/kg)	9.6±1.25	Fe	1.73±1.77
pH in H_2O	4.8±1.1	4.4±0.8	Mg^{2+} (mg/kg)	1.51±0.086		
Soil organic matter %	2.54±1.2	1.41±0.4	Na^+ (mg/kg)	0.56±0.066		
Bulk density (g/cm^3)	1.55±0.8	1.68±1.2	Total dissolved solid (mg/kg)	2239±146		
% coarse sand (0.6mm-2mm)	22.15±3	17±1	SiO_2, Silica Dioxide, %	34.6±4.079		

% medium sand (0.212mm-0.6mm)	60.8±3.4	63.5±2.8	Al_2O_3, Aluminium trioxide, %	10.7±0.75		
% fine sand (0.063mm-0.212mm)	14.52±2.5	15.94±4.3	Fe_2O_3, Iron Trioxide, %	1.4±0.49		
% Silt+Clay ≤ (0.002mm-0.063)	2.49±0.5	3.56±0.8	CaO, Calcium Oxide, %	6±0.30		
			MgO, Magnesium Oxide, %	3.62±0.27		
			SO_3, Sulphur Trioxide, %	0.55±0.2		
			P_2O_5, Phosphate Pentoxide, %	5.42±0.59		
			Mn_3O_4 Manganese oxide, %	0.41±0.16		
			Na_2O, Sodium Oxide, %	0.71±0.19		
			K_2O, Potassium Oxide, %	40±1.38		

6.3.2 Weather and optimum planting period

Weather condition is influential in the germination, growth and fruiting. The timing was based on known factors existing on the performance of chilli pepper. Pepper growth requires good soil moisture and moderate atmospheric condition. Both the planting and transplanting were targeted based on the peak of rainfall and low soil temperature. The purpose was to obtain the optimum period that does not require irrigation and where survival rate and yield could be high. This optimum period also with respect to the soil response to ash application. The atmospheric temperature and rainfall had a substantial impact on germination rate, survival of the nursery, growth and general development. This reflected on the decision of planting period which was based on those agronomic parameters. Figure 6-2 describes the week-by-week performance of the nursery, although the transplanting period for two sites were selected based on nursery survival rate and overall health of the nursery.

The optimum period for site A was August 2018 and site B July 2018. The transplant had a seven-day shock, struggled to adapt to the soils new condition. This first week of transplanting witnessed adequate rainfall and moderate temperature which aided survival. Germination was observed to be directly influenced by weather and soil moisture content. Germination rate and percentage germinated seeds were greatly enhanced by shading on a warmth day. At constant temperature below 21°C germination will be slow, therefore extreme temperatures are unhealthy for efficient germination. Therefore, February, March and July are the months for sowing the nursery and can have up to 38 °C. The days to flowering after transplant was shortened relative to the increase in OPWA. This was observed in both study sites. The shortest period was 46±4 and 47±7 days for site A and B respectively, as illustrated in Table 6-2. Plant survival was observed throughout the seasons. For the control plots, out of 65 plants transplanted, an average of 25 and 23 survived in control site A and B respectively. This shows the impact of OPWA in balancing nutrient efficiency of the soil. The application of OPWA also had a significant impact on the plant height. The maximum precipitation was in September 2018 at 400 mm and minimum was in December 2018 with temperature up to 32 ^{o}C.

6.3.3 Nursery development

Site A and B nursery planting happened on 24 August 2018 and 14 July 2018 respectively. Both nurseries were selected based on the result plotted in Figure 6-2. The major factors for the selection were the survival rate based on different planting weeks, the root depth, plant height and overall plant health.

Germination in the week of May was less than 20%, week 3 of June recorded about 70% against week 4 of June. First week of July which had about 260 mm rainfall and the lowest mean temperature of the year resulted in the highest germination rate of 90% in both sites. Evaluating the germination rate relative to the outlined characteristics in Figure 6-2, nursery plant height and number of leaves were highest in nurseries planted in July.

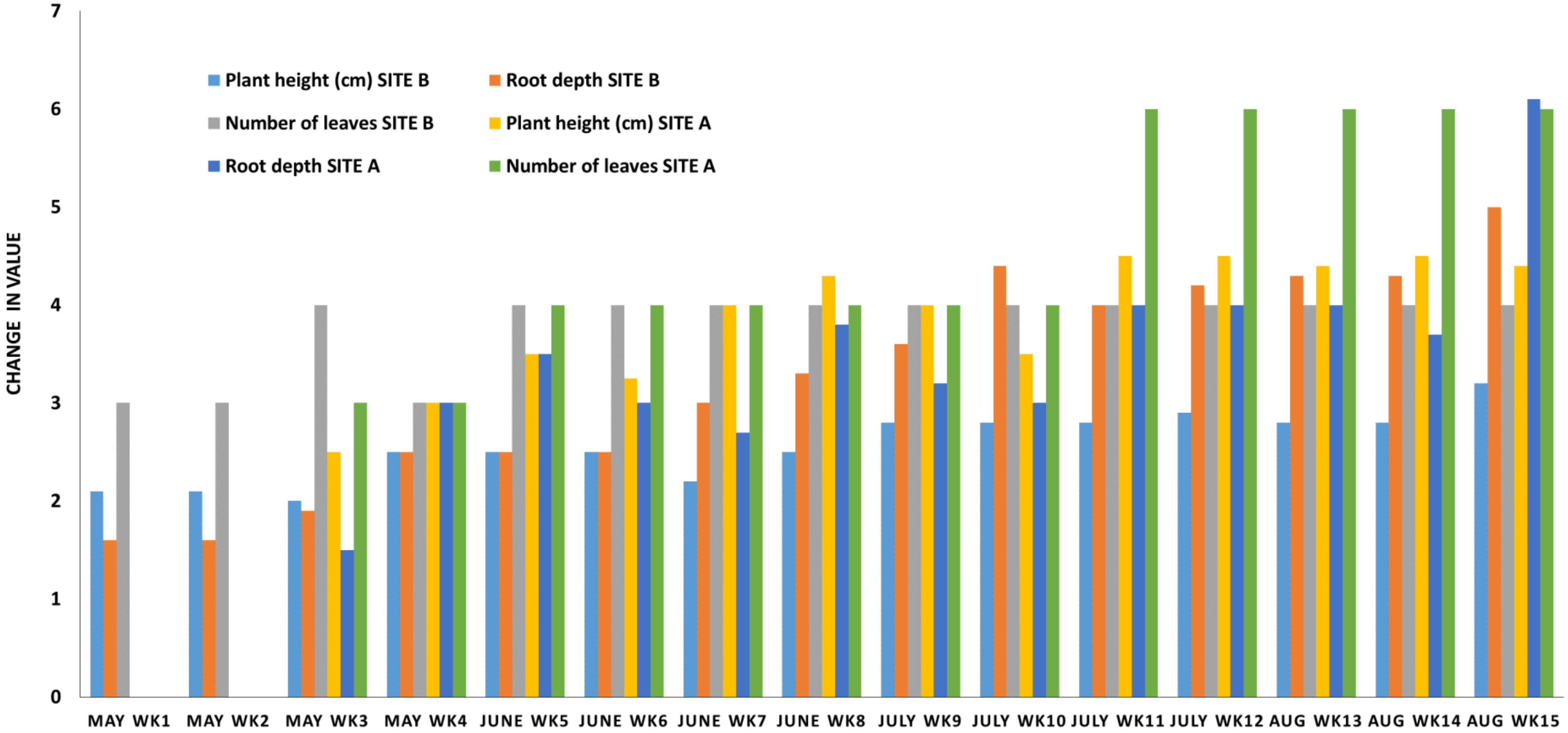


Figure 6-2 Nursery development and survival rate

6.3.4 Effect of the ash on the soil temperature and on soil fertility

Absorption of nutrients is affected by temperature as it influences diffusion and osmosis. However, an increase in temperature of the weather is relative to the absorption of soil mineral salts up to a certain peak range and beyond a certain temperature adsorption is impossible due to denaturation of proteins responsible for mineral adsorptions. The temperature of soil layer under different treatment of experimental plots were monitored and recorded in real-time, and the difference of soil temperature under different treatments was analysed. Soil temperature is of great significance in crop growth, development, water and salt movement in soil, soil carbon balance and so on. In this study, OPWA use resulted in the increase of the surface temperature of the soil. The increase in temperature lasted for the first few days which could be due to the increase in microbial activities, adsorptive capacity, soil nutrient transport and water retention.

Soils with high negative charges are assumed to be more fertile because of high cation retention (McKenzie et al. 2004). CEC influences nutrient sustainability and provides a cushion against soil acidification. Soils with a low clay fraction tend to have a lower CEC, which is indicative in this study. Soil leaching could be slowed by the addition of OPWA. As the soils were highly sandy, CEC was low signifying a poor water holding capacity and greater nitrogen and potassium leaching. The growth range as described in Figure 6-4 indicates that in site A, there is little or no noticeable change between 6 tonnes and 8 tonnes application while in site B, the influence on crop yield is linear from the minimum to the maximum application. The application of OPWA resulted to improved water holding capacity and increases relative to the quantity of OPWA applied. The evidence of improved fertility of the soil is more evident through the yield analysis. For an efficiency of any soil, adsorption, desorption, dissolution precipitation immobilisation and mineralisation must take place. Aeration primarily affects the availability of nutrients and the release of oxygen. The efficient air movement maintains aerobic respiration of soil microbes. Sandy soils generally have high hydraulic conductivity and low nutrient retaining ability, therefore the amendment with OPWA has the potential to improve that and are factorial indicators for assessing soil physical value and key to the storage and drive of water, air, and nutrients (Cullotta *et al.*, 2016). PWA application reduced the soil bulk density by 2.5% at 8 tonnes OPWA treatment rate.

Comparing biochar and OPWA using a field trial by Chen et al. (2018) shows that the finer the residue the more effective in the soil. Soil water content was relative to the increase in OPWA application rate and this results in the reduction of evaporation rate. The integration of OPWA increased the diffusion within the soil pores and creates room for water movement (Chen *et al.*, 2018). Soil water retention capacity is an important property as it is vital in the growth and yield of pepper. Relative to other fertilizers, which could boost saturated contents up to 15% more than control OPWA could hold beyond that, and up to 25% as illustrated in Table 6-2 the hydrophilic functional group of the OPWA and the pores helps to retain water. There are signs of stimulation of microflora due to OPWA application. OPWA also has the ability to adsorb and trap gases and nutrients and promotes the survival of bacteria and fungi. The interaction of OPWA with soil microorganisms could be complex; however, indicated positive interaction. OPWA application results in reduction for fertilizer need, and greenhouse gas emissions from fertilizer production. Converting agricultural waste by thermal process could also reduce the level of methane instigated by the regular decomposition of waste.

6.3.5 Influence of PWA on crop development and yield

Crop yield which represents the harvested production per unit of harvested area of pepper fruits was calculated per bed and treatments. The unit by which the yield of a crop is measured is tonnes per hectare. Each bed has an estimate of what its yield will be, called a potential yield. Different doses have ranges of impact. The yield in this study was compared with Habanero chilli pepper yield in other studies. In Yucatan project in Mexico, HCP was recorded to about 20 ton/ha (DeWitt, 2008). Arcos et al. (2012) studied different plots which was treated with different organic materials and compared with a control plot. The results show that HCP yielded 17.6 ton/ha on a plot treated with vermicomposting, 16 tonnes/ha on organic manure and 6 ton/ha for control plot. The physiological variation relative to OPWA application were illustrated in Table 6-2. This shows the variation in stomatal density, dry mass proportion and other growth features. During the harvest, the fruit features were measured and the variation in sizes and features were illustrated in Figure 6-4.

Table 6-2 The mean Physiological changes in HCP with the application of OPWA.

	Control		2 THP		4 THP		6 THP		8 THP	
	A	B	A	B	A	B	A	B	A	B
Density of stomata (number mm^{-2})	200±18	207±6	225±4	215±22	230±10	230±6	240±8	234±16	238±6	244±14
Days to flowering after transplanting	60±12	52±2	45±7	48±10	45±4	42±5	40±2	40±6	46±4	47±7
LWR (g/g)	0.34±0.2	0.32±0.1	0.45±0.08	0.4±0.1	0.47±0.2	0.47±0.2	0.44±0.1	0.48±0.2	0.5±0.2	0.48±0.2
LAR at fruiting (cm^2/g)	160±6	150±10	200±24	186±10	210±18	215±13	220±9	210±12	218±10	215±8
Specific leaf area (cm^2/g)	458±40	365±70	480±50	471±20	483±60	475±80	500±50	495±60	505±50	500±30
Leaf Area (cm^2)	1200±80	1100±100	1800±120	1400±80	1850±100	1600±150	1900±140	1600±100	1900±80	1850±40
Average root DMP (%)	10±2	12±2	6±1	8±2	10±2	9±3	6±1	6±2	6±2	7±2
Average stem DMP (%)	67±3	68±5	65±2	66±2	52±3	54±1	52±2	53±7	50±4	54±2

Average leaf DMP (%)	13±2	12±1	14±1	14±2	20±3	20±4	17±2	18±4	14±1	13±2
Average fruit DMP (%)	10±4	8±2	15±3	12±4	18±2	17±2	25±2	23±4	30±3	26±6
Number of surviving plants	25	13	35	20	60	45	65	52	65	55
Average plant height (cm)	72±15	78±8	120±18	105±12	125±10	100±20	125±8	125±16	135±5	125±12
Average plant canopy (cm)	55±8	50±10	60±6	50±12	75±7	68±4	78±8	68±12	94±8	70±6
LWR: Leaf Weight ratio, LAR: leaf area ratio, DMP: dry mass proportion, C: control, THP: tonnes/ha plot										

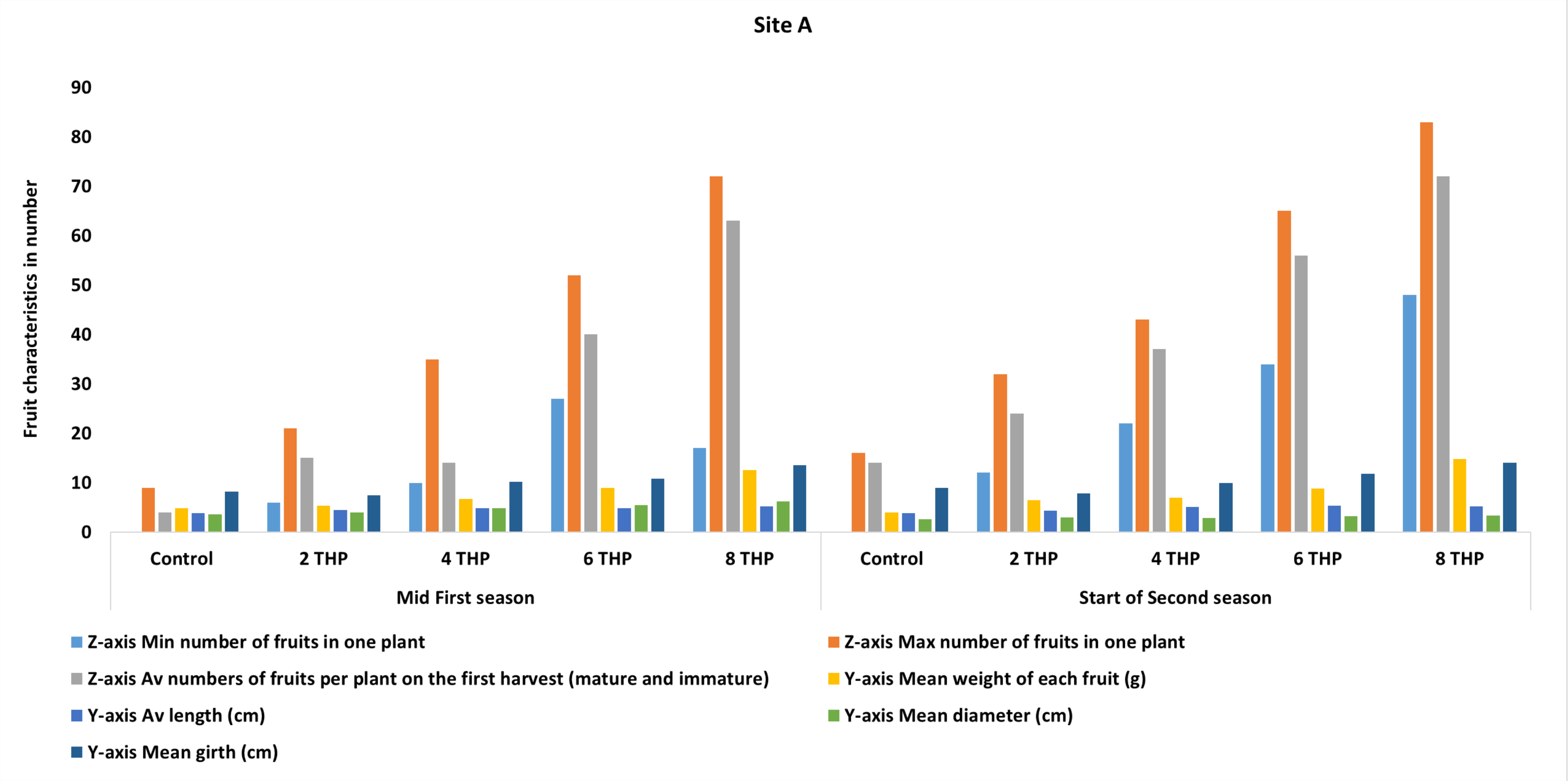


Figure 6-3 Average Morphological parameters and Phenological parameters site A on first and second seasons

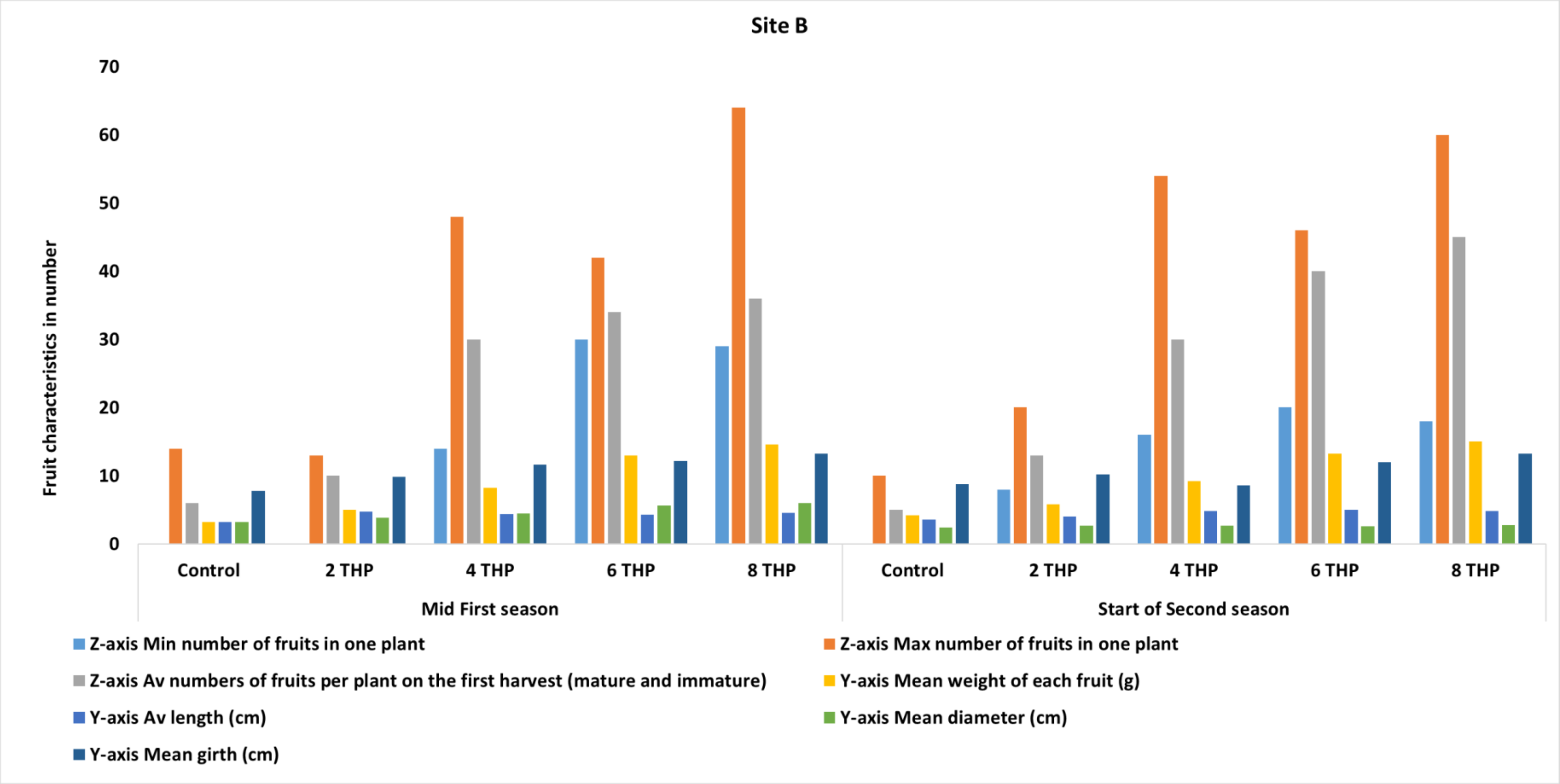


Figure 6-4 Average Morphological parameters and Phenological parameters site B on first and second seasons

Two seasons were expressed in Figure 6-4, relative to plant morphology and capsaicin value that were analysed on fresh and dry basis, presented the summary of yield for each season, the seasonal variations relative to OPWA application with reference to the control.

The result of elemental analysis show that the organic carbon of both sites are 0.20-0.27 wt.%, which indicates that the organic content of the soil is poor, therefore require amendment. The particle size distribution shows that both soils are very sandy, leading to inability to hold moisture and nutrients. The recommendation of ash for the amendment is for the three major effects of OPWA. The alkalinity of ash, the mineral content and the binding ability (Zalewska, Nogalska and Wierzbowska, 2018). The ash was expected to reduce the acidity of the soil at least to the optimum range, improve the structure of the soil and retain appropriate amount of water with the addition of exchangeable minerals to the soil.

The response of OPWA was evident through plant growth and crop yield. Figure 6-2 shows the variation in growth after two weeks of transplanting. The impact of the OPWA was not significantly felt on the plant growth difference during the first 14 days after transplantation. The application of OPWA was relative to the fruit yield. The bed with the highest OPWA had the highest yield. There was a response time of about three weeks because the first three weeks of transplantation in the control plot showed a higher growth rate that the other beds. Though the yield was influenced by ash application, it has no influence on the weight of the fruit and the size. The loss of leaves after transplant was high on the control plot and was minimum on the plot with highest ash application.

There was about 100% survival after transplant on the beds with ash and about 50% on control. After 20 days of transplanting, most plants under control treatment turned yellow and withered. The application of ash resulted to development of several branches, which in turn resulted to more fruits per plant. For site A at the time of first harvest, there was no fruit in the control plots. Both sites have few things in common. However, they responded differently to weather but in OPWA application, the responses were relative Comparing the overall yield with the study where inorganic fertilizer was applied at rate 0-38 ton/ha (Li *et al.*, 2017). It is assumed that, for efficient yield, the fertility of soil requires improvement. The comparative analysis also indicates that the application of OPWA resulted in increased yield. OPWA addition and crop productivity are relative;

however not uniform. Figure 6-4 shows the effect of OPWA on the agronomic properties of crop.

Relative to controls, OPWA increased the fruit yield of HCP by 70% due to more efficient mineral uptake and increase in soil enzymatic activities. Generic influences of OPWA on crop physiological response and yield are credited to the release and adsorption of essential soil from OPWA. The liming effect of OPWA contributes to its impact on the yield of HCP. The improvement of soil CEC high surface area of OPWA and advanced porosity increases the water holding capacity.

There are also physical evidences of microbial function, which contributes to the yield of Habanero pepper. According to Figure 6-4 the comparative study of the seasons between the control plot and the plot with the highest OPWA indicates the variation factor. There are significant changes in the physical parameters. The control plot depleted in the second season.

The relative growth difference in first season between control and 8 tonnes/ha, plot is: G_r

$$G_r = \frac{\text{Relative growth of Control}}{\sum_{\min}^{\max} \text{Plots}} * 100\% \tag{6-8}$$

Relative growth in first season for control is 25% and plot with 8 tonnes/ha, OPWA is 75%. For second season, control is 15.78% and plot with 8 tonnes/ha, OPWA is 84.22%. The comparison of control G_r for the first and second seasons were 57.14 and 42.86% respectively results in 14.28% negative difference. For the 8 tonnes/ha plot, G_r for the first and second seasons were 42.85 and 57.15% respectively results in 14.30% positive difference. Therefore, the agronomic efficiency is A_{eff}, evaluated as;

$$\%\text{Yield}_{\text{control}} = \frac{\text{yield}_{\text{control}}}{\text{yield}_{\text{control}}+\text{yield}_{\text{x}}} * 100 \tag{6-9}$$

$$\%\text{Yield}_{\text{x}} = \frac{\text{yield}_{\text{x}}}{\text{yield}_{\text{control}}+\text{yield}_{\text{x}}} * 100 \tag{6-10}$$

$$A_{\text{eff}} = \frac{(\%\text{yield}_{\text{x}}-\%\text{yield}_{\text{control}})G_r}{(\text{yield}_{\text{x}})\delta} \tag{6-11}$$

G_r is 0.14 and the growth impact factor which depends on the type of fertilizer relative to plant and response to changes evaluated from the growth difference, δ is estimated at 0.2. Therefore, the A_{eff} is 0.66-0.69 for both season one and two; also, for site A and B.

The relative yield analysis between site A and B, using Equation 8 above. Site A has 0.79, 1.04, 66.02 and 78.55 tonnes/ha for first season control, second season control, first season and second season 8 tonnes/ha respectively. Site B has 0.44, 1.62, 33 and 65.04 tonnes/ha for first season control, second season control, first season and second season 8 tonnes/ha respectively. The percentage difference between site A and B in the first season is 34.7% and 9.4% in season two. The combined yield difference shows that site A is higher than site B by 19.68% yield.

6.3.6 Comparison of HCP characteristics in site A and B

The active absorption and metabolic response of both sites are evaluated through the influence of the OPWA on the yield factors of the plant. Dry soil with low moisture content would cause shallow root, which may result to shed of leaves and flowers. This also affects the rate of fruit development in terms of quality and sizes. However, over irrigation multiplies *Phytophthora* and other root-rotting organisms, flower abortion, lack of oxygen and prevalent root diseases (Starke Ayares, 2014). The comparative of the two sites show that both controls have low survival rate, but site B had an overall better survival rate. The fruiting rate per plant was higher for site A, but higher per bed in site B. Comparing the beds with the highest ash application, the yield is higher for site B. The dry season encroached on site A and fruiting was delayed. However, required irrigation to survive the fruiting period. Bacterial spot is the most common and often the most serious disease affecting peppers in site A. Bacterial spot lesions can be observed on leaves and stems but not on fruits and occurs on all stages of plant growth. Site A had a better response to OPWA than site B, which could be as a result of planting period and being more fertile. Site A control and highest OPWA treatment yielded 0.79 and 66.2 tonnes/ha while site B had 1.62 and 32 tonnes/ha respectively.

The fruiting stage in site A, was not resilient to the dry weather and low soil moisture, therefore requires irrigation to survive the fruiting period. Site B does not require further irrigation for the initiation of second stage of fruiting.

Figure 6-4 shows the difference in the average length and diameter of the HCP fruits were insignificant. The changes were obvious in the weight of fruit, which is relative to plant sizes. The average girth of the fruits was proportional to the sizes of fruits. The average number of fruits per plant is influenced by the quantity of OPWA. The plot with highest number of fruits had the highest quantity of OPWA.

6.3.7 Stomata and weather relationship on the development of HCP

Stomata density and morphology play key roles in regulating water-use efficiency. HCP with high water requirement both through the root and the leaves depend on water availability for growth and fruiting. HCP in this study had poor development especially at nursery when rainfall was below 125 mm. This could impact on the crop throughout its lifetime. Therefore, stomata development is relative to drought tolerance (Bertolino, Caine and Gray, 2019). The application of OPWA does not have a direct impact on functions of stomata however; it promotes the density and cell multiplication. Stomatal distribution was observed to be an important trait of HCP for an improved yield (Sarwar, Karim and Rana, 2014). The important morphological features have direct influence on the yield due to the importance of cell density. The ribulose-1,5-bisphosphate carboxylase and oxygenase influences photosynthesis, cell expansion and tissue differentiation. Leaf characteristics are reliant on factors such as cell split, enlargement, development and the differential arrangement of tissues. Leaf venation and vascular pattern of HCP is useful in the distribution of nutrients and mobilizes photo-assimilated carbon to other parts. Flowering time is important in HCP growth; it is the transition from vegetative to reproductive growth. This period has influence on the optimal yield. HCP at some seasons has continuous flowering period and not all fruit develops at the same time. The transcription factors, phytohormone, enzymes and weather, influence the outcome of fruiting frequency and sizes.

6.3.8 Post-harvest soil nutrient depletion and fertility coefficient

Crops absorb nutrients from the soil as they grow. Nutrient depletion is not instant and the available could sustain the growing crops for a period of time. In the post-harvest evaluation, the soil nutrients were analysed at three stages before the end of the second season. At the end of the final harvest when the plant resilience dropped to zero, the soils were also analysed. The quantification of the soil-nutrient status were used to predict the application frequency and other related factors necessary to plan continual growing of HCP on the same plots. Soil fertility deterioration ensues when the amounts of nutrients absorbed by the crops exceed the quantities of nutrients being applied or available in the soil. In this state, the nutrient necessities of the crop are fulfilled from soil reserves until these reserves cannot satisfy crop needs. The consequences is observed in a reduction of plant development and yield.

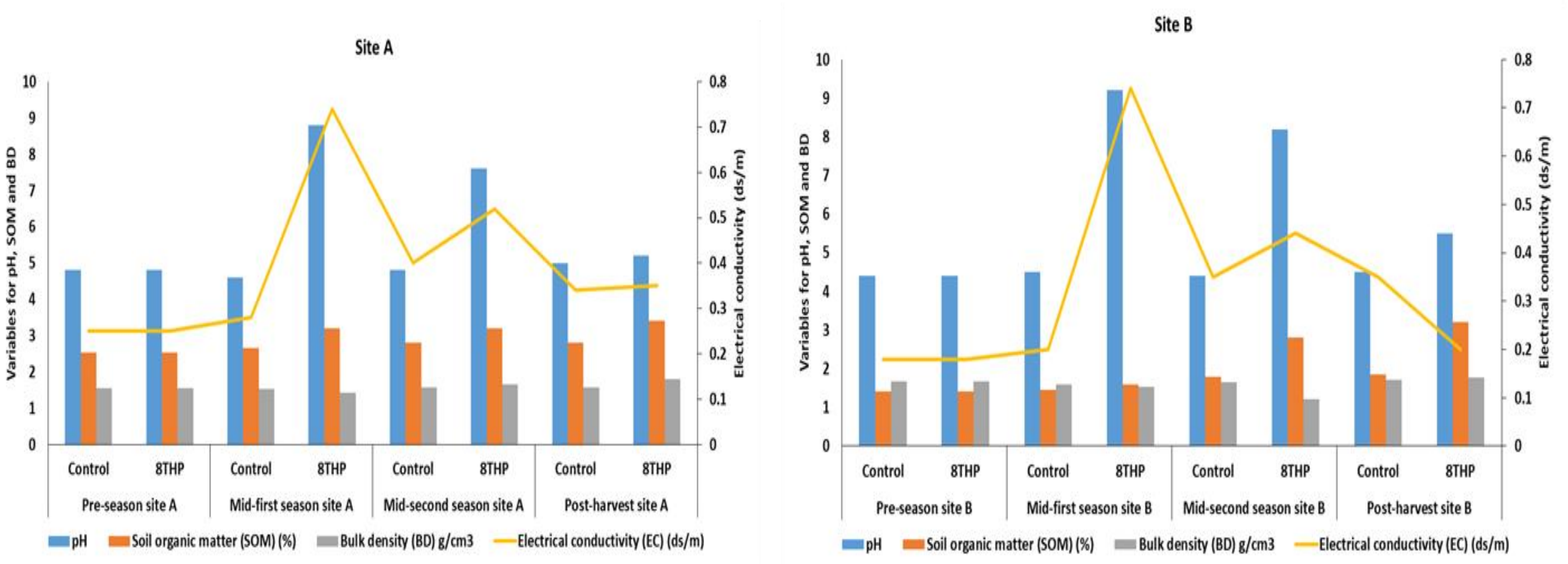


Figure 6-5 Soil mean characteristics for 8 tonnes/ha plot (THP) from pre-season to post harves

Soil as such lose fertility by growing crops and also due to depletion of vital inorganic salts from the soil by improper irrigation and acid rain water (quantity and quality of water). These nutrients are commonly removed by the crops but additional elements such as leaching and soil erosion can contribute to the diminishing of fertilities. The long term benefit can only be obtained if there is regular application; at least every season. Denitrification also losses nitrogen in gaseous form. The availability of water and harvest residues could impact on the soil post-harvest status. The gradual variation of soil characteristics were observed over 2-year period. According to

Figure 6-5, SOM was influenced by the application of OPWA and EC declined in the second season. This is due to top soil being washed by rain. The pH in both sites increased relative to OPWA application and was maintained across the season until post-harvest period. Bulk density was minimally affected throughout the season.

This study is the first time OPWA is used in a combined form for growing HCP pepper showing the relative influence on soil properties and plant growth as indicative of its potency as a fertilizer which further justified by the application in two different sites.

6.4 Conclusion

The optimum planting seasonal range of Habanero chilli pepper in southern Nigeria for nursery should be June to August or late February. Weather and planting period have a significant effect on the survival rate of both the nursery and the main plant and fruit yield having a combined yield for both sites as 1.26, 3.53, 11.02, 24.24, and 49.01 tonnes/ha/season relative to the order of treatments. Transplanting should be done at the peak of rainy season, which falls on mid-September. The minimum recommended application rate of OPWA for growing habanero pepper is 6 tonnes/ha. There was a linear increase in yield comparative to the rate of ash application and 25% relative growth. Capsaicin content difference was not significantly affected, as the variation was less than

4% between control and 8 THP. For the 8 tonnes/ha plot, G_r for the first and second seasons were 42.85 and 57.15% respectively results in 14.30% positive difference. The control plots showed lowest yield and the maximum yield was obtained from 8 THP.

This study has shown an innovation in the application of mixed palm waste ash to the soil and the resultant impact through the interaction with soil, by increasing agronomic efficiency of Habanero chilli pepper by 66-69% and Scoville value by 3.52%. For efficient output of pepper production in southeast Nigeria, soil acidity should be lowered. The planting period should not rely solely on the performance of the nursery. The variation between Control and OPWA treatments, witnessed significant growth rate, yield, morphological changes and the change in yield, which are relative to treatment rates. To reduce cost of production, irrigation can be avoided by planting and transplanting at the estimated periods.

6.5 References

Ajala, R., Awodun, M. and Oladele, S. (2017) ‘Effects of Wood Ash Biomass Application on Growth Indices and Chlorophyll Content of Maize and Lima bean Intercrop’, *Turkish Journal of Agriculture - Food Science and Technology*, 5(6), pp. 614–621. doi: https://doi.org/10.24925/turjaf.v5i6.614-621.1093.

Alawode, O. O. and Abegunde, V. O. (2016) *Economic Analysis of Pepper Marketing in Oyo State , Nigeria*, *Applied Tropical Agriculture*. Available at: https://www.futa.edu.ng/journal/home/downloadpdf/paper_3_1508325210 (Accessed: 15 September 2017).

Anyaoha, Kelechi E, Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Critical evaluation of oil palm fresh fruit bunch solid wastes as soil amendments : Prospects and challenges’, *Resources, Conservation & Recycling*, 136(January), pp. 399–409. doi: 10.1016/j.resconrec.2018.04.022.

Anyaoha, Kelechi E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Evaluating oil palm fresh fruit bunch processing in Nigeria’, *Waste Management and Research*, 36(3), pp. 236–246. doi: 10.1177/0734242X17751848.

Arcos, M. L., Edith, J., Matu, P., Mijangos, A., Tabasco, J. A. De and Tabasco, C. V. K. (2012) ‘Respuesta del chile habanero (’, *Revista Científica UDO Agrícola*, 12(2), pp. 307–312. doi: hdl.handle.net/1807/45626.

Ballina-Gómez, H., Latournerie-Moreno, L., Ruiz-Sánchez, E., Pérez-Gutiérrez, A. and Rosado-Lugo, G. (2013) ‘Morphological characterization of Capsicum annuum L. accessions from southern Mexico and their response to the Bemisia tabaci-Begomovirus complex’, *Chilean journal of agricultural research*, 73(4), pp. 329–338. doi: 10.4067/S0718-58392013000400001.

Bertolino, L. T., Caine, R. S. and Gray, J. E. (2019) ‘Impact of stomatal density and morphology on water-use efficiency in a changing world’, *Frontiers in Plant Science*, 10(March). doi: 10.3389/fpls.2019.00225.

Chen, C., Wang, R., Shang, J., Liu, K., Irshad, M. K., Hu, K. and Arthur, E. (2018) ‘Effect of biochar application on hydraulic properties of sandy soil under dry and wet conditions’, *Vadose Zone Journal*, 17(1). doi: 10.2136/vzj2018.05.0101.

Cullotta, S., Bagarello, V., Baiamonte, G., Gugliuzza, G., Iovino, M., La Mela Veca, D. S., Maetzke, F., Palmeri, V. and Sferlazza, S. (2016) ‘Comparing different methods to determine soil physical quality in a mediterranean forest and pasture land’, *Soil Science Society of America Journal*, 80(4), pp. 1038–1056. doi: 10.2136/sssaj2015.12.0447.

Dada, O. and Ogunsesu, Y. O. (2016) ‘Growth Analysis and Fruit Yield of Capsicum Chinense, Jackquin as Influenced by Compost Applied as Foliar Spray and Soil Augmentation in Ibadan, Southwestern Nigeria’, *Journal of Agriculture and Sustainability*, 9(1), pp. 83–103. doi: 9789676119926.

DeWitt, D. (2008) *The Habaneros of Yucatán*, *Fiery Foods and Barbecue*. Available at: http://www.fieryfoodscentral.com/2008/06/01/the-habaneros-of-yucatan/ (Accessed: 1 March 2019).

Fontes, M. P. F. and Alleoni, L. R. F. (2006) ‘Electrochemical attributes and availability of nutrients, toxic elements, and heavy metals in tropical soils’, *Scientia Agricola*, 63(6), pp. 589–608. doi: 10.1590/s0103-90162006000600014.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) ‘A modern tool for classical plant growth analysis’, *Annals of Botany*, 90(4), pp. 485–488. doi: 10.1093/aob/mcf214.

ISO (2020) *ISO - ISO 11277:2020 - Soil quality — Determination of particle size distribution in mineral soil material — Method by sieving and sedimentation*. Available at: https://www.iso.org/standard/69496.html (Accessed: 15 May 2020).

Jemo, M., Jayeoba, O. J., Alabi, T. and Montes, A. L. (2014) ‘Geostatistical mapping of soil fertility constraints for yam based cropping systems of North-central and Southeast Nigeria’, *Geoderma Regional*, 2–3(C), pp. 102–109. doi: 10.1016/j.geodrs.2014.10.001.

Li, S., Li, J., Li, G., Li, Y., Yuan, J. and Li, D. (2017) ‘Effect of Different Organic Fertilizers Application on Soil Organic Matter Properties’, *Compost Science and Utilization*. Taylor & Francis, 25(1), pp. S31–S36. doi: 10.1080/1065657X.2017.1344160.

Lorestani, A. and Zinatizadeh, A. (2006) ‘Biological Treatment of Palm Oil Mill Effluent (Pome) Using an Up-Flow Anaerobic Sludge Fixed Film (Uasff) Bioreactor’, *PhD Thesis*, (December), p. 53. doi: 10.1017/CBO9781107415324.004.

Mbah, C. N., Nwite, J. N., Njoku, C. and Nweke, I. A. (2010) ‘Response of maize (Zea mays L .) to different rates of wood-ash application in acid ultisol in Southeast Nigeria’, 5(7), pp. 580–583. doi: 10.5897/AJAR09.321.

Moragues-Saitua, L., Arias-González, A. and Gartzia-Bengoetxea, N. (2017) ‘Effects of biochar and wood ash on soil hydraulic properties: A field experiment involving contrasting temperate soils’, *Geoderma*, 305(September 2016), pp. 144–152. doi: 10.1016/j.geoderma.2017.05.041.

Ndaeyo, N. U., Utin, A. I., Ekpo, T. U. U. and Akpan, E. A. (2017) ‘Preliminary Evaluation of Growth and Yield Performances of Some Pepper (Capsicum Spp .) Varieties in an Ultisol’, *Nigerian Journal of Agriculture, Food and Environment*, 13(4), pp. 108–112.

Okunlola, G. O., Olatunji, O. A., Akinwale, R. O., Tariq, A. and Adelusi, A. A. (2017) ‘Physiological response of the three most cultivated pepper species (Capsicum spp.) in Africa to drought stress imposed at three stages of growth and development’, *Scientia Horticulturae*. Elsevier, 224(October 2016), pp. 198–205. doi: 10.1016/j.scienta.2017.06.020.

Olayemi, F., Adegbola, J., Bamishaiye, E. and Daura, A. (2011) ‘Assessment of post-harvest challenges of small scale farm holders of tomotoes, bell and hot pepper in some local government areas of Kano State, Nigeria’, *Bayero Journal of Pure and Applied Sciences*, 3(2). doi: 10.4314/bajopas.v3i2.63217.

Peters, J. B. and Laboski, C. A. M. (2013) ‘Sampling soils for testing’, *University of Wisconsin System Board of Regents and University of Wisconsin- Extension, Cooperative Extension*, p. 4. doi: (www.uwex. edu/ces/cty.

Sansaniwal, S. K., Rosen, M. A. and Tyagi, S. K. (2017) ‘Global challenges in the sustainable development of biomass gasification: An overview’, *Renewable and Sustainable Energy Reviews*, 80(May), pp. 23–43. doi: 10.1016/j.rser.2017.05.215.

Sarwar, A. G., Karim, M. A. and Rana, S. M. (2014) ‘Influence of stomatal characteristics on yield and yield attributes of rice’, *Journal of the Bangladesh Agricultural University*, 11(1), pp. 47–52. doi: 10.3329/jbau.v11i1.18207.

Savci, S. (2012) ‘Investigation of Effect of Chemical Fertilizers on Environment’, *APCBEE Procedia*, 1(January), pp. 287–292. doi: 10.1016/j.apcbee.2012.03.047.

Starke Ayares (2014) *Sweet & Hot Peppers Production Guideline*, *Starke Ayares report*. Available at: http://www.starkeayres.co.za/com_variety_docs/Sweet-&-Hot-Pepper-Production-Guideline-2014.pdf (Accessed: 15 September 2018).

Ukanwa, K. S., Patchigolla, K., Sakrabani, R., Anthony, E. and Mandavgane, S. (2019) ‘A review of chemicals to produce activated carbon from agricultural waste biomass’, *Sustainability (Switzerland)*, 11(22), pp. 1–35. doi: 10.3390/su11226204.

van Wesemael, B., Chartin, C., Wiesmeier, M., von Lützow, M., Hobley, E., Carnol, M., Krüger, I., Campion, M., Roisin, C., Hennart, S. and Kögel Knabner, I. (2019) ‘An indicator for organic matter dynamics in temperate agricultural soils’, *Agriculture Ecosystems & Environment*, 274(August 2018), pp. 62–75. doi: 10.1016/j.agee.2019.01.005.

Zalewska, M., Nogalska, A. and Wierzbowska, J. (2018) ‘Effect of basic cation saturation ratios in soil on yield of annual ryegrass (Lolium multiflorum L.)’, *Journal of Elementology*, 23(1), pp. 95–105. doi: 10.5601/jelem.2017.22.2.1360.

7 ENERGY AND ECONOMIC ASSESSMENT OF COMBINED PALM WASTE THERMAL RESIDUE UTILISATION TO PRODUCE ACTIVATED CARBON AND SOIL AMENDMENT

Kalu Samuel Ukanwa[1], Kumar Patchigolla[1]* and Ruben Sakrabani[2]

1 Centre for Thermal Energy and Materials, School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK;

2 Cranfield Soil and Agrifood Institute, Cranfield University, Cranfield MK43 0AL, UK;

Statement of contribution of joint authorship

The conceptualisation of this chapter was due to the requirement for economic outline of the project and to establish the feasibility of the technology flow to enable advancement. Data collection, experimental setup and simulation were performed by Kalu Samuel Ukanwa, ASPEN Economics design was advised by software experts in Cranfield University. Kumar Patchigolla and Ruben Sakrabani provided supervision.

7.1 Introduction

The enormous increase in solid waste generation with one of the major sources emanating from agriculture, through direct production and processing have created global environmental challenges (Bello, Norshafiq and Kabbashi, 2016). This is one of the major environmental problems yet to be addressed in developing countries (Giwa *et al.*, 2017a); although, adequate awareness has resulted in measures to mitigate the adverse effects (Hoornweg and Bhada-Tata, 2012). Oil Palm waste (OPW) is one of the solid wastes with major disposal challenges and can cause environmental pollution (Abdullah and Sulaim, 2013). Dumpsites are inappropriate for them due to greenhouse gas effect. The importance of environment and human health relative to waste management in the agricultural sector have stimulated waste utilisation attention in developing countries (Prusty, Patro and Basarkar, 2016).

Based on waste revaluation principles, OPW can be applied in several ways. Empty fruit bunch (EFB) is useful for the following; mulching, cooking fuel and soap production. Mesocarp fibre (MF) is widely used for heating, mulching and soil fertilisation. Palm oil mill effluent are used for pig alimentation and soil fertilisation. Palm kernel shell (PKS) is widely applied in energy, activated carbon and locally for heating (Kalu Samuel Ukanwa *et al.*, 2019). Gasification and pyrolysis are promising thermal technologies for converting OPW into energy and other valuable products for economic and environmental benefits (Liew *et al.*, 2017b). Typically, biomass gasification occurs in four stages namely; drying, pyrolysis, char gasification and combustion. The three major processes to generate either char or ash are combustion and gasification which are exothermic and pyrolysis which is endothermic. These processes are related; however, pyrolysis is the initial stage of both gasification and combustion and an independent thermal system and characterised by zero supply of oxygen or other oxidizing gases (Jahirul *et al.*, 2012).

The thermal conversion of carbonaceous feedstock into other useful products with a useable heating value is a good option (Kalu Samuel Ukanwa *et al.*, 2019). Therefore, thermal and thermochemical utilization of biomass is an environmentally friendly route to produce clean and sustainable products (Sukiran, Abnisa, Wan Daud, Abu Bakar and Soh Kheang. Loh, 2017). The gasification of biomass is very efficient, resulting in 20-97% conversion of feedstock into syngas (Hunpinyo *et al.*, 2013). This process can generate biosolids residues that are further processed into activated carbon (AC) or fertilizers. The production of AC for water purification as a safe and low-cost process; hence, the production and market values which are dependent on the direct and indirect factors that influence production. The use of fly and bottom ash from thermal conversion of the waste could be a substitute for chemical fertilizers for soil with high acidity and low fertility (Kumar *et al.*, 2017b). Although the primary benefits of NPK fertilizers are crop quality improvement and improved plant growth through soil enrichment. However, the potency and soil resilience begin to decline with time due to the application of these chemical nutrients (Manna *et al.*, 2007).

The heavy use of NPK and other chemical fertilizers has been reported for negative impact on the soil and the ecosystem (Savci, 2012). These adverse effects are observed in soil and crop health. In some cases, they are severe and could cause imbalance in the ecosystem. It is safe and eco-friendly to achieve sustainable farming with soil fertility balance using cost-effective and renewable resources readily available. For every metric tonne of chemical fertilizer, Nigeria spends above $500 of what organic fertilizer would cost (Babalola, Ilori and Adegbite, 2012). The use of biomass gasification bye-products could bridge the gap for quality, locally produced and environmentally friendly option. Nigeria fertilizer production and utilization status are low relative to population. Fertilizer importation status in Nigeria are: NPK 64%, NP compounds 19%, ammonium sulphate 5%, phosphate fertilizers 4%, urea 4% and other fertilizers 4% (Hellums, 2016). Though, there are several factors affecting the efficient production and distribution, which is the reason Nigeria consumes about 12-15 kg of nutrient per hectare against the global average usage of 100 kg/hectare (FEPSAN, 2014).

Due to the challenges of chemical fertilizer, farmers have shifted their focus to organic fertilizers. Chemical fertilizers are good; however, they pose some challenges and can also cause volatilisation of ammonia which results in relative acidification of land and water. Therefore, biomass ash as a fertilizer, is considered a sustainable option with minimal or no negative impact and no apparent unwanted effect to the soil and crop. It is a strategy to maintain the available Phosphorous (Cruz-Paredes *et al.*, 2017).

The analysis of oil palm waste ash (OPWA) showed that it contains 0.18%, 27.10-28.30%, 6.59-8.10%, 3.10-3.33% of available P, Total P, K, Ca and Mg 0.19%, respectively (Anyaoha et al., 2018). The influence of PWA on soil structure is also necessary in ultisol soils (Ikeh *et al.*, 2012). OPWA application rate could be flexible and application beyond average range has not been verified to have negative impact. OPW ash effect on the soil are improvement of water holding capacity, reduction of soil acidity, and increase in microbial activities of the soil. Effect on crop yield, has been proved in several researches, for the growing of cassava (Kelechi E. Anyaoha *et al.*, 2018) and pepper (Ikeh *et al.*, 2012).

OPW is also proven to be one of the raw materials for the production of highly adsorptive AC with well-defined pore structures and good surface area (Ooi *et al.*, 2017). Several OPW could be used individually for the AC production. These are effective in the adsorption of methyl blue, heavy metals and in the purification of fluid (García *et al.*, 2017). The availability of raw materials is a primary factor in the use of biomass for AC production. AC market and supply chain in Nigeria and Africa are growing at 7.5% annually, about 80% of AC used in Nigeria are imported while 70% used in Africa are imported (Research, 2014).

Environment and economics of OPW are required for fulfilment of zero-waste economy target in the palm industry (Khatun *et al.*, 2017). Due to the environmental need for OPW utilisation and the resultant benefits of the products, economic analysis is recommended to guide investment (Bevan Nyakuma, Johari and Ahmad, 2013). Some utilisation techniques are environmentally dangerous and economically poor (Vaish *et al.*, 2016) therefore, a combined approach to meet the biofuel target is considered a vital approach (Duku, Gu and Hagan, 2011). Further call for demonstrative projects in order to strengthen investment focus and develop a tool for waste utilisation policies in Africa (Aliyu, Dada and Adam, 2015); This is a primary drive for this study. Hence, this study further aims to economically, quantify the two utilisation approaches relative to, production, availability, need and market value. For the overall impact, commercialisation and the viability check of the process are necessary. The objectives of this study are to understand the economic relationship and value impact of OPW utilisation. This work leverages on the experimental data of a pilot plant and assumptions based on existing facilities.

In this study, the various setup mode for conversion of OPW into value-added products are used in evaluating thermal processes and economic resource conversion. The residues are quantified relative to syngas production and overall market value of the products. Hence, the economics of OPW for effective utilisation, which enables adequate estimation of production cost and optimisation of application route. The comparative study of the economic processes for PWA relative to soil amelioration and char for AC production were accessed. The choice of combined OPW for AC production and soil amendment require a technical and economic framework; for ideal development and optimum revaluation. A comprehensive sensitivity analysis was performed. The vital factors influential to the feasibility of the process systems were used to propose for cost-reduction techniques.

7.2 Materials and methods

The methodology of this study was modelled, simulated and outlined with a concept for determining the economic boundaries and optimised range of CPW utilisation. The scenarios for the analysis are dependent on the procedures applied for the simulation. The estimation for mass, energy and economic balances were outlined using Aspen plus V.10 (under the academic license) for pyrolysis, gasification and combustion.

Activation process; economic evaluation in relation to material and energy balances were simulated with Aspen Economy. Table 7-1 describes the combustion parameters and biochemical properties of OPW (Anyaoha et al., 2018; Bevan et al., 2013; Kong et al., 2014). The simulation and general analysis were performed with PKS, MF and EFB as an unconventional material; in a single and combined stream. Pyrolysis, gasification and combustion experiments were performed; focusing on AC production through pyrolysis, and fly ash production through combustion. The mass and energy balances are evaluated based on target and boundary conditions for each process.

Table 7-1 Chemical and biochemical properties of CPW

Proximate analysis (%w/w)	Moisture	4.05
	Ash	5.20
	Volatiles	74.50
	FC	16.25
Ultimate analysis (%w/w)	C	44.60
	H	6.35
	N	0.80
	S	0.15
	O	48.10
Lignocellulosic composition	Cellulose	30.8
	Hemicellulose	23.5
	Lignin	40.2
Thermal and energy properties	Organic content	91.8
	Inorganic content	8.2
	Combustion rate, C_R (10^{-8} kg/s)**	3.8-4.2
	Specific Heat, c, (J/kgK)**	2832-3231
*Oxygen by difference include moisture and ash, ** (Bevan Nyakuma, Johari and Ahmad, 2013), PKS: Palm kernel shell, Mesocarp fibre, EFB: Empty fruit bunch		

7.2.1 Mass and energy balance

In energy systems, material quantification is necessary and governed by mass conservation, which is relevant in the industries for control of yields and overall process. This is important in thermal conversion due to the energy and mass relations in determining the product and how temperature variation influences the process outcome; this is a cost-benefit determinant. The calculations contribute to the development of economic predictions. It estimates the mass and energy requirements for different variables. Formulating the mass of the feedstock equates with the sum of gaseous and solid products, waste products, stored products and losses. In Equation 1-3, M represents mass, E stands for energy, S represents store, P for product and L means losses (Jahirul *et al.*, 2012). R is the quantity received in the process, and mw is the mass of waste generated from a single process.

$$\mathrm{M_{store}} = \mathrm{M_{out}} - \mathrm{M_{in}} \tag{7-1}$$

$$\sum \mathrm{mR} = \sum \mathrm{mP} + \sum \mathrm{mw} + \sum \mathrm{ms} \tag{7-2}$$

$$\sum \mathrm{ER} = \sum \mathrm{EP} + \sum \mathrm{EL} + \sum \mathrm{Es} \tag{7-3}$$

Figure 7-1 shows the mass-energy relativity and resultant products. This also outlines the procedure for designing the thermal process model for biomass conversion. Figure 1b, a process flow illustrating the stages of OPW conversion. It shows the process stages defining the parameters for individual routes.

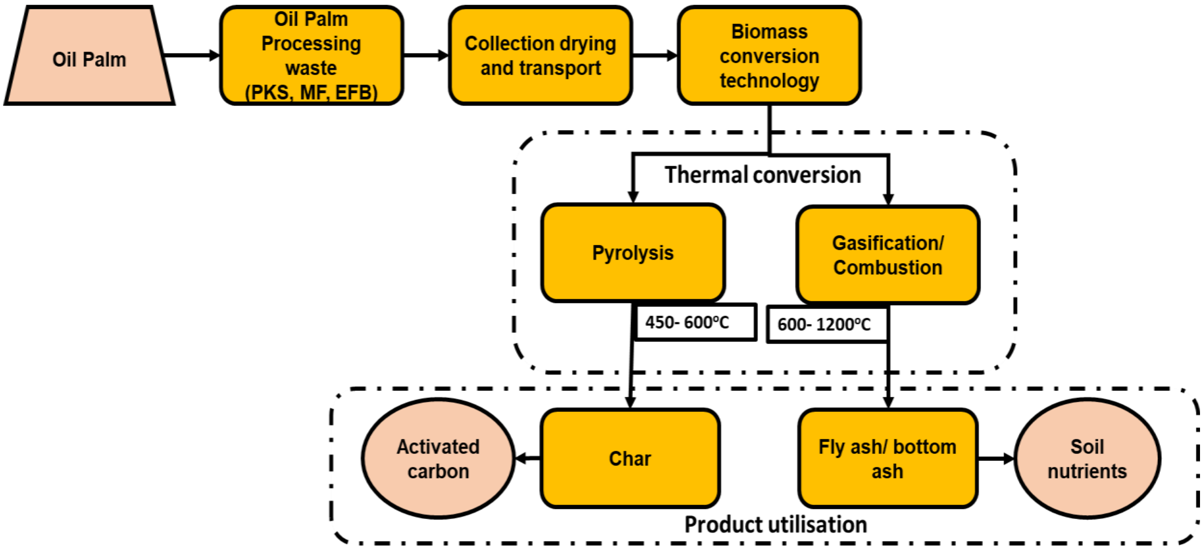


Figure 7-1 Mass and energy relativity for the OPW thermal process

This process described by (Jahirul *et al.*, 2012) considers heat energy based on the temperature and other energy inputs.

$$\Delta \mathrm{Q} = \mathrm{Q}_{\mathrm{out}} - \mathrm{Q}_{\mathrm{in}} \tag{7-4}$$

The heat calculation is based on enthalpy operation heat and heat loss. Using the pyrolytic assumptions;

$$\mathrm{E}_{\mathrm{thermal\ process}} = \mathrm{E}_{\mathrm{drying}} + \mathrm{E}_{\mathrm{target}} + \mathrm{E}_{\mathrm{reaction}} \tag{7-5}$$

The energy efficiency, which measures the performance of the system, is calculated thus:

$$\eta_{\mathrm{energy}} = \frac{\mathrm{E}_{\mathrm{product}}}{\mathrm{E}_{\mathrm{feedstock}} + \mathrm{E}_{\mathrm{pyrolysis}}} \tag{7-6}$$

Equation 4-6, is used to evaluate the energy requirement and predict dependent temperature requirement for each stream relative to proposed process target. In Equation 5, pre-process energy was considered. Hence, milling and drying consume energy and equated in the economic valuation in both simulation and conventional estimation.

7.2.2 Process modelling and simulation procedure for AC production

Numeric classification analyses derived from ten palm oil mills relative to mill capacity and quantity of waste generated in southern Nigeria with boundary consideration of EFB, MF and PKS. These companies produced yearly at average 800, 480, 250 tonnes respectively. A tonne of oil palm fresh fruit bunch yields, an average of 720 kg of fruits, 255 kg of EFB, and 50 kg of palm kernel cake, 60 kg for PKC, 115 kg of MF, 230 Litres of POME and 150 Litres of crude palm oil. An overview of the process line for AC and PWA are outlined in Figure 7-1. Some studies were carried out to determine the estimated pre-processing expenses. However, depends on GDP, location, access and the terrain for transportation of the residues.

Process simulation was used relative to flowsheet synthesis, which is application to all scenarios to generate energy and mass balance. The raw material properties, combining ratio was calculated and the design specification done in metric units. The three modes of simulation were combustion, combined state for gasification and pyrolysis and activation process. The sensitivity analysis was based on temperature, flow rate and several other factors and their variation effect on the output (Hunpinyo *et al.*, 2013).

Aspen plus (Figure *7-2*) was adopted for the simulation and sensitivity analysis while Microsoft excel and SPSS were used for mathematical calculations. The thermodynamic models selected defined the appropriate liquid and vapour phases and prediction by Peng-Robinson model was used. This process was structured based on the municipal solid waste pyrolysis and gasification study by Deng et al. (2019).

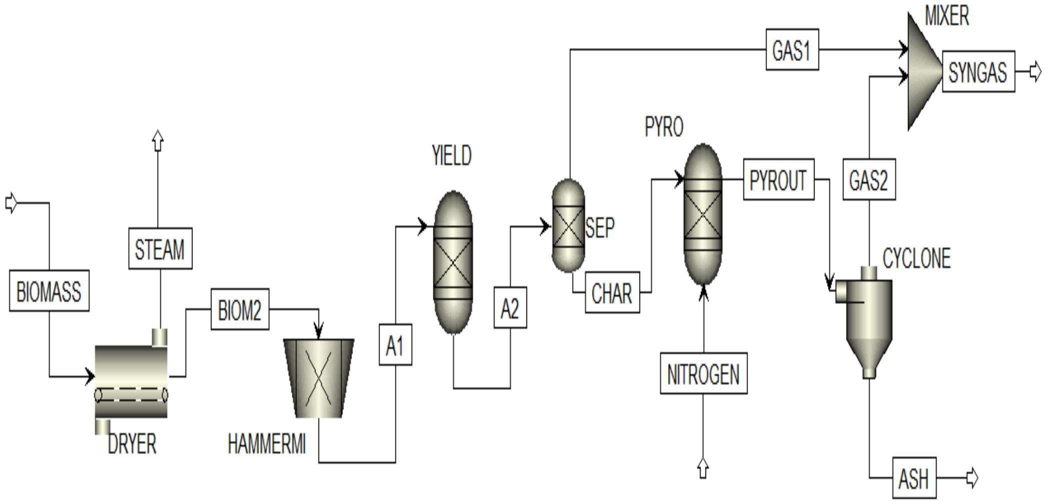


Figure 7-2 Thermal combined processes of pyrolysis, gasification and combustion

7.2.3 Thermal conversion and OPWA relative to chemical fertilizer

The economic analysis was executed using mathematical tools, combined with Aspen Economic Analyser. All financial estimation was in US dollar ($), modelled for a 20-year period at an annual interest rate of 10%- and 2.3%-income tax. The basic principles of biomass conversion technology are based on capacity and production context. The application of economic analysis of the process corresponds with the price/kg of chemical fertilizer in Nigeria N200-500 and £1-5 in international market. There are several ways of evaluating the cost and profit of agricultural crops, shown as Equation 7-9.

$$\mathrm{GM} = \mathrm{TR} - \mathrm{TVC} \tag{7-7}$$

$$\mathrm{NR} = \mathrm{TR} - \mathrm{TC} \tag{7-8}$$

$$\mathrm{TC} = \mathrm{TVC} + \mathrm{TFC} \tag{7-9}$$

Where: TR is the total revenue, GM is gross margin, and TVC is the total variable cost, which includes cost of labour, and raw material is represented by TVC. Net Returns that is based on total investment cost is denoted by NR. Total Fixed Cost which part of total cost (TC) is represented by TFC. TC is the Total Cost.

7.2.4 Economic assessment and sensitivity analysis

The tools for financial modelling are applicable to mass and energy. The conveyance within the system boundary using the process simulation tool are relevant and can be tested for several variables. For economic analysis relative to mass and energy relationship are the principal derivatives of economic assessment. The investment cost is relative to fixed capital investment on equipment and process cost. Other operating costs and annual cost are considered (Trippe *et al.*, 2011). These include the cost of equipment as described by (Jahirul *et al.*, 2012).

The calculation for obtaining Present Value (PV) and discount rate factor can be calculated using Equations (10) and (11), respectively.

$$\mathrm{PV} = \sum \frac{\mathrm{FV}}{(1+\mathrm{R})^{\mathrm{t}}} \tag{7-10}$$

$$\mathrm{F_R} = \frac{1}{(1+\mathrm{R})^{\mathrm{t}}} \tag{7-11}$$

These evaluations are based on discount rate, R=10% and the rate of cash outflows corresponds to the value of inflows for break-even discount rate. The percentage interest yield from the investment is the internal rate of return.

The cost evaluations are further outlined in Equation 12-16.

Total investment cost

$$C = Capital\ cost + Operational\ cost \tag{7-12}$$

Net present value

$$NPV = \sum_{n=1}^{T} \frac{CF_n}{(1+n)^n} - I_0 \qquad \textbf{(7-13)}$$

CF_n is the annual cash flows, I_0 is the initial total capital investment, T is the project life; i is discount rate.

Annualised Return on investment (A-ROI)

The challenges of the traditional return on investment metric is that it does not consider time periods. Hence, to overcome this issue an annualized ROI formula is used.

Where: No of years = (Ending date – Starting Date) / 365 **(7-14)**

Payback Period

Periodic cash flow is relative to a payback period of an investment

$$\text{Payback Period} = \frac{\text{Initial investment}}{\text{Net cash flow per period}} \qquad \textbf{(7-15)}$$

To find exactly when this occurs, the following formula can be used:

$$\text{Payback Period} = \frac{\text{Initial investment} - \text{Opening cummulative cash flow}}{\text{Closing cummulative cash flow} - \text{Opening cummulative cash flow}} \qquad \textbf{(7-16)}$$

The economic constraints and theories are based on parameters in literatures and known factors (Trippe *et al.*, 2011). They are formulated based on assumptions that reactions occur isothermally and at constant volume throughout the process. The pyrolysis and gasification process are performed in a stationary state. OPW are assumed spherical and uniform particle sizes. Tar formation is negligible and heat losses neglected. Equilibrium is established in all reaction and char is considered 100% carbon. The sensitivity analysis was hinged on three factors, temperature ranges as input variable, mass flow rate of the input gases and feedstock and output streams of syngas and biosolids. The relativities were equated to plot the optimum temperature and conditions for expected output.

7.3 Results and discussion

7.3.1 Mass, energy balance and thermal processes

During thermal process, the relationship between energy requirement and mass are determined based on the type of process plant, feedstock and target output. Mass and energy balances relative to input and output depend on the thermal decomposition in all the phases of conversion (Jaroenkhasemmeesuk and Tippayawong, 2015). Before and after thermochemical conversion, it is ideal to quantify and predict the yield using models of known parameters. These also help in evaluating biomass behaviour in the process. Based on parameters, such as temperature, a new system could be designed to process feedstock relative to the characteristics. Mass balance shows a dependable theoretical foundation for decision-making on investments and cost reduction. The temperature and waste relationship were illustrated by a thermogravimetric analysis (TGA) test.

Based on the design, the process capacity of 500 kg/hr could produce about 75 kg/hr of AC. The thermogravimetric analysis (TGA) is implemented to define the variations in the weight of a sample relative to temperature through the pyrolysis of PKS, MF and EFB. The DTG illustration shows that, mainly two and dominant peaks appearing at 280-300 °C for PKS and 340-360 °C for MF. EFB has a unique three peaks, however the combination of these three samples have little deviation from the individual components. The first peak indicates the thermal decomposition of hemicellulose and the second peak shows the cellulose decomposition which occurs at the same temperature despite the type of biomass. The curve due to the temperature above 400 °C designates the lignin decomposition section as validated by (Liew, Muda and Loh, 2016). This thermal behaviour emphasizes the heat requirement for the type of process for CPW and the reaction zones are defined and differentiated by the DTG.

Pyrolysis and gasification simulation with aspen plus are helpful in determining the fraction of syngas components and their relationship at different temperature phases. Gibbs reactor is based on the principle of controlling chemical and thermodynamic equilibrium of the processes. Sensitivity analysis for the product gas composition have been performed with respect to flow rate and reaction temperature. CO and CH_4 decreases whereas the concentration of CO_2 and H_2 increases with increasing steam flow rate.

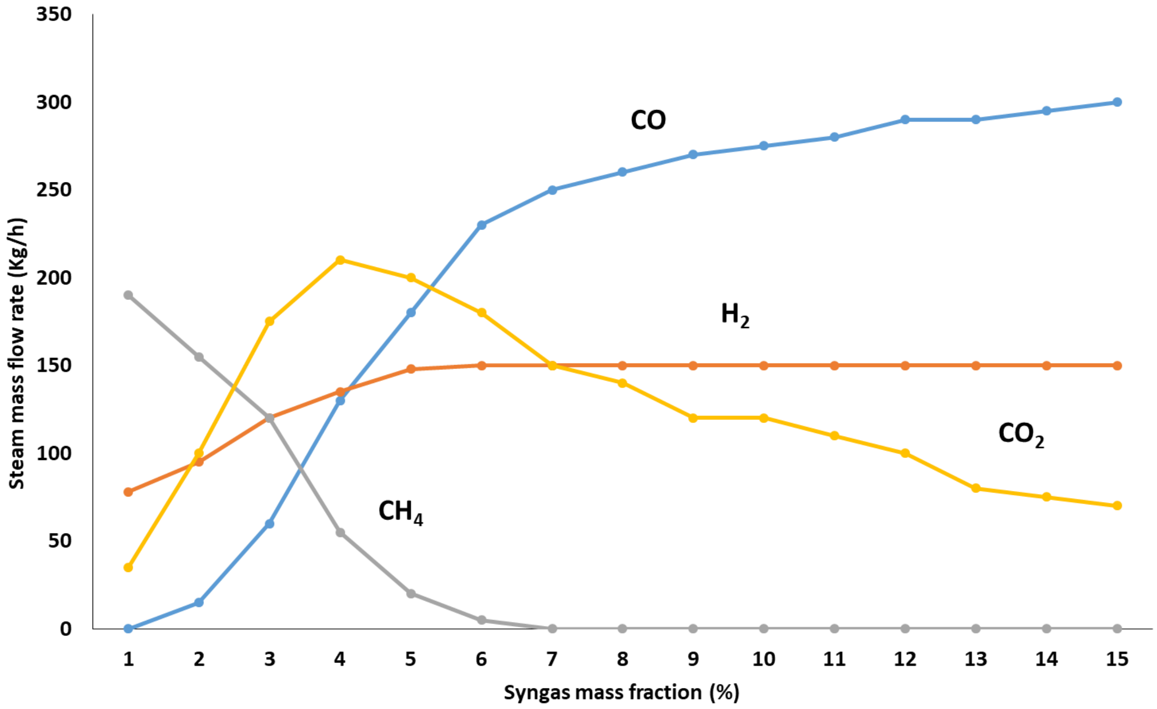


Figure 7-3 Mass flow relationship relative to the influence of temperature change on the composition of syngas.

The sensitivity analysis at difference temperature ranges as illustrated in Figure 7-3 shows the effect on syngas compositions and the variations in mass flow rate. The increase in gasification temperature increases mass flow rate of the output except for CH_4. At 800 ^{o}C and 120 kg/hr mass flow rate of feedstock, every product is at optimum. For AC production, only pyrolysis is used due to absence of oxygen in the system and high biosolids generation.

7.3.2 Economic analysis

Adopting a model developed by Porcu et al. (Porcu *et al.*, 2019), the economic and financial assumptions are based on cost and itemised indicators of production. The profit and investment output are predicted relative to the global market and gross domestic product of the location. These processes are the outline for AC production and the factors are determined based on proposed contracts and valuation by consulting company for Energy and construction firm.

Time period and economic assumptions, operating hours per year (7500), length of Start-up period (4 months), duration of construction phase (15 weeks), interest rate (10%), plant depreciation period (10 years) and project life (20 years). The four streams established in the simulation, show the variations at different thermal conditions. These variations have direct impact on the price of the output. The economic outcome of each process is directly influenced by capital, operational and product prices.

Table 7-2 Cost parameter for a thermal process plant

Parameter	Value ($)
Capital investment cost (CIC)	280, 400, 000
Annual labour cost	18, 500, 000
Annual repair and maintenance	5, 500, 000
Total cost of biomass per year	4, 800, 000
Depreciation	52, 080, 000 (20% of CIC)
Interest rate	2, 804, 000 (10% CIC)
Discount rate	2, 804, 000 (10% CIC)
Salvage value	2, 804, 000 (10% CIC)
Insurance and taxes	2, 804, 000 (10% CIC)
Total cost	372, 496, 000

Table 7-3 Economic analysis of thermal processes and investment summary

	S1	S2	S3	S4
Annual production sale of bio-products ($)	125, 000, 000	128, 450, 000	110, 300, 000	130,110, 000
Net present value of profit ($)	1, 062, 500, 000	1, 091, 825, 000	937, 550, 000	1, 105, 935, 000
Net present value of operation and maintenance cost ($)	297, 238, 489	297, 238, 489	297, 238, 489	297, 238, 489
Accumulated Net present value of all cost ($)	669, 734, 489	669, 734, 489	669, 734, 489	669, 734, 489
Net present value of the project ($)	1, 010, 420, 000	1, 039, 745, 000	885, 470, 000	1, 053, 855, 000
Benefit cost ratio	1.34	1.42	1.25	1.45
Payback period (years)	8.5	8.2	9.8	8
Internal rate of return (%)	16	17	14	17.2
S1: Pyrolysis, char production favoured, S2: Gasification, syngas production favoured, S3: Combustion, production of ash favoured, S4: Combined process				

Using expressive statistics and quantitative analytical techniques, the application of system models relative to the economic analyses with 2.5% income tax rate and 10% interest rate. The direct and indirect capital costs, were measured relative to estimated variables for maintenance cost, and other operational cost (Davis *et al.*, 2016).

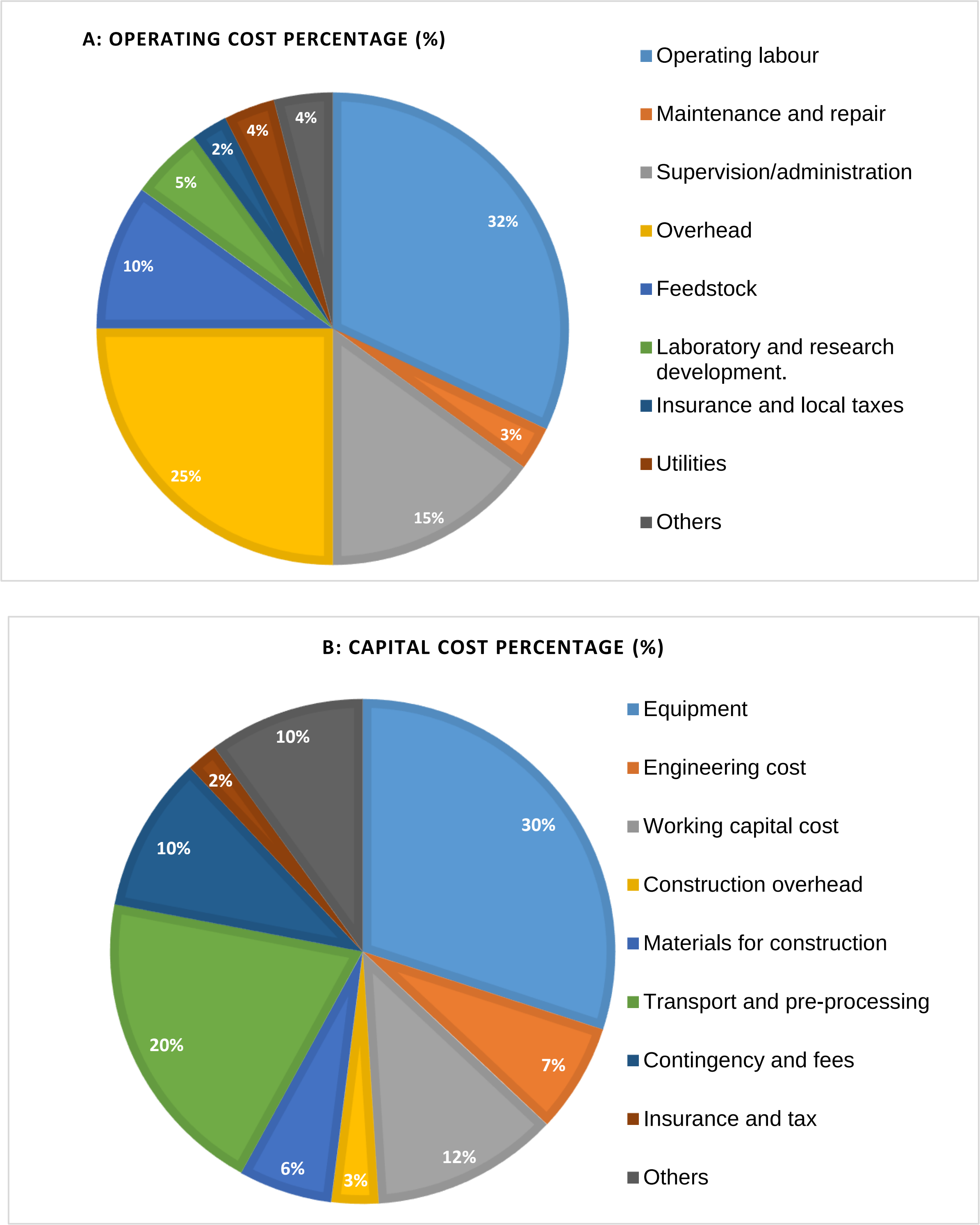


Figure 7-4 (a) Operating and (b) Capital cost for combined thermal processes.

The demand for energy in developing countries is increasing and the greenhouse gas emission is greatly influencing the utilisation of biomass. The biomass utilisation is more economical than coal. Economic investment on biomass gasification is lower than coal gasification system (Mirfendereski, 2008). Biomass energy can also contribute economically and generate wealth through different processing levels. Under same operational condition the economic performance of biofuel production and pyrolysis varies relative to energy requirements and equipment setup.

In pyrolysis the biomass only decomposes thermally, the resultant char is not further reacted with CO_2 and H_2O. This saves energy in the process and reduces process duration. While, gasification as a slow endothermic reaction which requires continuously thermal energy supply. Exothermic oxidation reaction is the technique for combustion process where there is complete decomposition of the biomass and could occur under atmospheric condition. Economic analysis was expressed to resolve and define the economic viability and optimised range for production of AC and application of PWA. An independent economic analysis was conducted for the selling price, and the influence of the price on economic status of the feedstock. The global activated carbon demand is expected to rise to 3,800 Kilo tonnes in 2021 at the economic value of $8 billion (Research, 2014).

The bio-oil production cost is dependent on the capacity of the processing plant and it is represented by the product sales with a relative payback period of 6.2 years. And for the pyrolysis process with primary target of generating biochar for AC production considers the price of AC by mass. The annual operating hour considered to be about 7500 could affect the profit if raised. The cost of biomass is based on the logistics and transport of the materials to the plant location. The handling capacity of the design is 1500 kg/hour and considered in the simulation. For the pyrolytic products about 10-120 kg/hour of biochar were produced. The capital cost has equipment as the highest percentage expenditure. Labour is the highest for operating cost and cost of input based on the process. The project payback period and profitability index are determined based on the product sales and overall cost of the process.

The total project capital cost includes all the equipment and engineering cost relative to the size of the project. Pre-processing facilities were units in the cost analysis. Transportation is a variable option as feedstock could be gotten from different locations, therefore could change in real-time analysis. Plant operating cost was calculated based on the factors influencing rate of production and continuous expenditure. Some key factors could have effect on this such as the country of plant location and the gross domestic products per capita of the country. The product sale could be realistic if the market is ready in such country. The profitability index is based on the sales relative to fixed and operating cost.

Using OPW for bio-oil and syngas production yield great economic results in the first few years likewise the use of biosolids for AC production. The use as a fertilizer alternative has lower economic impact. However, the environmental benefit and long-term influence is encouraging. The two processes have a relative balance in application despite the target output. This was analysed based on variable subsets and environmental and product benefit analysis setup. The factors are dependent on the economic analysis of this study and assumptive factors relative to energy projects.

Relative to the basic assumption there are factors responsible for how these utilisation techniques could affect the economic and environmental projections. The natural and climatic conditions, governmental policies and regulations and restrictions, energy content of the feedstock, OPW generation and quantification techniques were accounted for in the theoretical potential. Geographic potential is relative to land use and constraints of area availability which impact on the quantity of waste projected to generate. Sustainable potential is important factor due to the environment and dependence on recovery factor. Technical, economic and market potentials are valued for system sizing and performance, technology cost, energy demand, competition and investment capacity.

7.3.3 Sensitivity analysis for AC production

Sensitivity analysis operates on a principle of correlation, regression and subjective analysis. In order to perform the What-if analysis with the obtained data, the enlisted output parameters must be evaluated as illustrated in Table 7-4. This technique is based on analytical assumptions of the variation of dependent values and the resultant impact relative to independent variables. This quantifies single or multiple variables within the specific boundaries. However, changes could impact on the production cost and energy usage. The what-if principle helps in the conditional adjustment and optimisation of the process. In this study, the biochar yield is considered as AC yield.

Table 7-4 Percentage process input and yield

	% output/yield				
	Temperature (^oC)	Gas	Tar	Moisture	Biochar
Pyrolysis					
Scenario A1	400	60	9	8	23
Scenario A2	500	65	5	10	20
Scenario A3	600	70	5	10	15
Scenario A4	700	72	3	15	10
Scenario A5	800	75	1	16	8
Gasification					
Scenario B1	500	70	0	15	15
Scenario B2	600	75	0	12	13
Scenario B3	700	80	0	10	10
Scenario B4	800	88	0	7	5
Scenario B5	900	90	0	8	2

Temperature, pressure, biomass flow rate, N2/steam flow rate and O_2 flow rate are input factors. These were compared with literatures and experimental studies to validate the output. The syngas composition obtained through pyrolysis and gasification Figure 7-5 is varied at different temperatures and flow rates. The current prediction by Aspen plus was compared with experimental analyses in this study. Only four components are considered in the syngas stream, other possible gases were accounted for in the general analyses as being negligible.

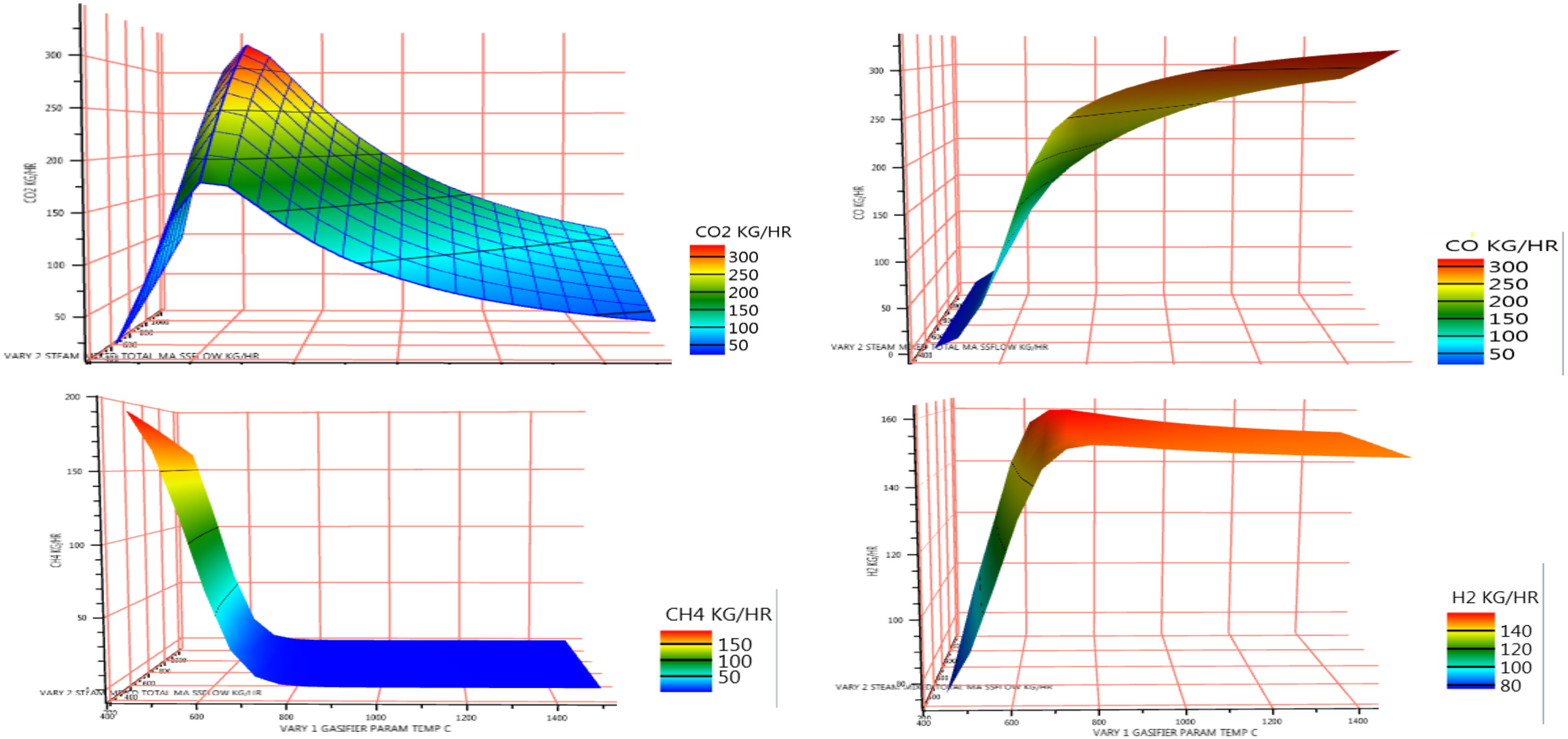


Figure 7-5 The relationships between flow rate, temperature and syngas produced in gasification.

7.3.4 Palm waste ash production cost and crop yield relative to profit

PWA as organic fertilizer is tested in several projects (Anyaoha et al., 2018) and there is a prominent indication of about 10% increase in yield in relation to mineral fertilizers (Dada and Ogunsesu, 2016). However, there are nutrient imbalance challenges with organic fertilizers (Alawode and Abegunde, 2016). The cost of fertilizer is one of the highest factors in production cost in agriculture, the total production cost is also affected hugely by pesticides and other chemicals. However, it is possible to grow crops without those. In practice, the cost of input of fertilizer affects the general yield of Habanero chili pepper (HCP) yield (Kletnikoski *et al.*, 2013). Relative to production cost, a field study by Mohammed et al. (2016) was compared with this study and the result of the production costs are outlined in Figure 7-6.

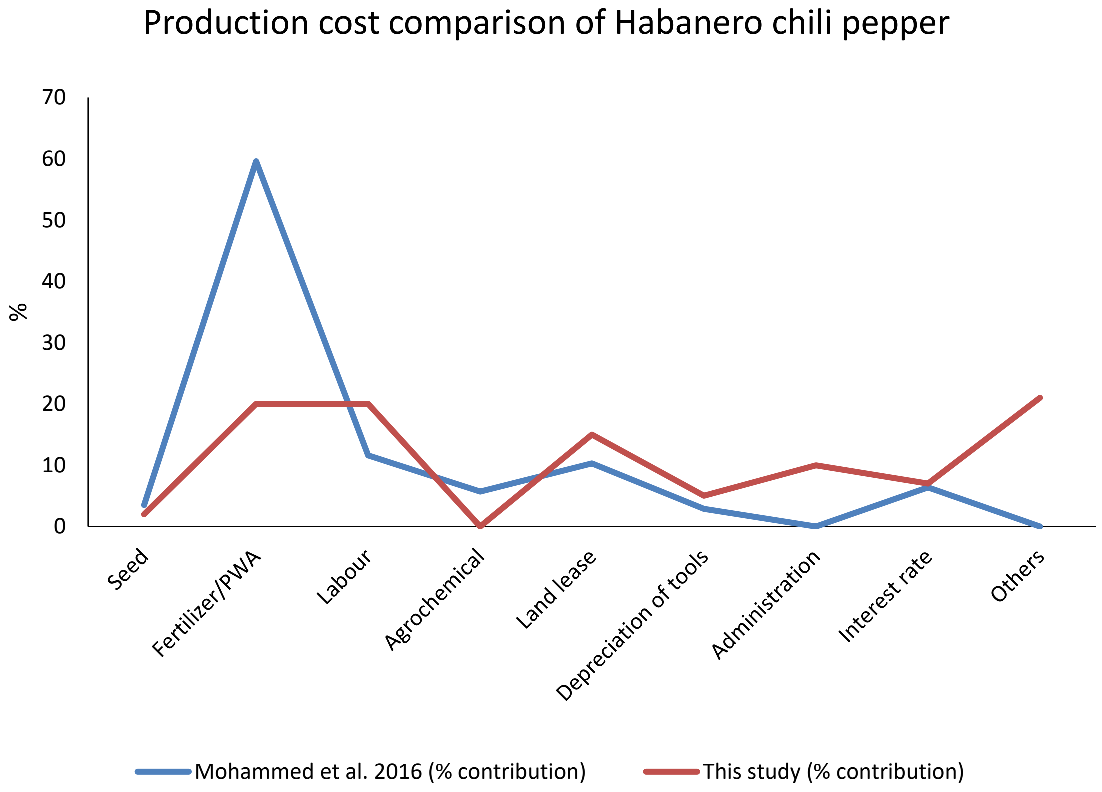


Figure 7-6 Percentage production cost of HCP in this study

7.3.5 Logistics, prospects of biomass utilisation and non-economic

OPW is free; however, the cost of gathering, transport and logistics could contribute to the overall cost of revaluation and utilisation project. This factor can be input in the cost analysis calculation and process quantification. The cost analysis of the two process show that energy equivalence is interrelated and depend on the size of the equipment, production capacity and output price range. Using Aspen economy analysis, non-economic valuations were non-inclusive in the analysis. Biomass energy complements other renewable energy systems, technological improvement in biomass setup helps improve agricultural and industrial revolutions. The focal points of biomass utilisation are low economic value, environmental impact and multiple application capabilities. This would create jobs for skilled and non-skilled workers (Simonyan and Fasina, 2013). The challenges of collections, pre-processing and drying varies and could be key factors in the overall analysis.

OPW is mostly in large particle sizes and lump form, therefore size reduction is crucial to utilize in AC production. This is done by milling, which requires high energy for operation. Particle size is one of the key factors in thermochemical process, physical conditions of OPW biomass notwithstanding the method influences activation rate and other production parameters (Gil and Arauzo, 2014). There is difficulty in milling MF and EFB rather than PKS due to low brittleness. OPW could be crushed when dry, sieved and graded into different uniform sizes of less than 2.0 mm using a milling machine (Deng, Li, *et al.*, 2010), to ensure uniform distribution of heat. The mechanical properties of different parts of OPW vary. This process requires energy and could result in material wastage in the form of dust and so minimise loss of biomass, a dust collector is installed, which aids in throughput flow and overcome air flow resistance (Bitra *et al.*, 2009). Pre-treatment such as drying and sieving also occasionally play a role in determining energy consumption. Establishing uniformity of particle sizes largely depends on the physical properties of biomass. Brittleness, hardness and elasticity; affects the energy requirement in milling. Phillip et al. (2017), studied the mechanical and physical influence of PKS, and showed that aggregate crushing value is 5.3% and flakiness index 63.2%, indicating that PKS has a good milling effect. The efficiency of hammer mill operation is factorised by the nature of the biomass. Due to the several types of OPW with varied sizes and shapes, their milling tendencies varies widely. There are several physical and mechanical properties. Material breakage as the fracture reaction is contingent on impact frequency, energy, moisture content and biomass properties (Gil, Luciano and Arauzo, 2015). The material properties in terms of its resistance and minimum specific energy are relevant to determine fracture and breakage factor which would defines the milling rate. The energy requirement increases with reducing particle size; however, it is also observed that physical properties influence feeder design, biomass flow rate and reactor performance (Dai, Cui and Grace, 2012).

7.3.6 Environmental analysis and process assessment

The reutilisation of PWA in soil amendment can be a good option for phosphorous and other key mineral input other than from finite sources; however, dumping of ashes in river can upset the balance of ecosystem and landfilling may result to environmental pollution due to its particle in the air. In the experimental study the yield due to PWA application equates the inorganic option of fertilizer. There are limited utilisation approaches for agricultural waste for many reasons. They are not economically exploited despite the large quantity produced. Managing these wastes for pollution and environmental health safety has being the principal goal. The use of biosolids has range of benefits which include carbon sequestration (Rodriguez et al., 2017).

The use of biomass thermal by-products could reduce loss of nutrients through leaching improve soil characteristics, reduce non-CO_2 greenhouse gas emission and remediate contaminated soils. The feasibility of breakeven cost of biochar production depends on location, biomass availability and technology (Arbestain et al., 2014).

Assessing the two-utilisation route of AC and PWA, few environmental factors are necessary for consideration. The impact can’t be directly quantified, however, impact in substituting chemical fertilizer and impact in avoiding pollution is trackable.

The increased soil carbon due to PWA addition to the soil contributes to the reduction of atmospheric carbon intensities. These play major role in minimising erosion and runoffs by binding the soil structure. The nitrate leaching experienced in sandy soil is greatly reduced by the application of PWA. The high natural gas-intensive due to Nitrogen fertilizer production is reduced. The application of fertilizer from organic sources reduces the application of pesticides and other agro-chemicals which could impact on the environment.

About 60% of the fertilizer are imported and Nigeria requires varieties of fertilizers to meet the growing demand. However, still a major importer of fertilizer. Crop yield has massive influence on the revenue and economy of every society. Agriculture contributes meaningfully to rural occupation and provides substantial non-oil foreign exchange incomes. Organic fertilizer comparative study with chemical fertilizer shows that it enhances soil structure, increase nutrient and water retention, increased the microbial activities of the soil. Excess application does not have harmful effect on crops and it prevents erosion. However, chemical fertilizers are harmful to crops and human, excess application destroys soil structure, leads to soil acidity and harmful to plants. State it. Organic fertilizer is 40% cheaper than other potassium fertilizer, 100% organic and eco-friendly, recommended for all kinds of plants, very effective for neutralising acidic soils.

7.4 Conclusion

The energy and economic analyses for the utilisation of OPW show that, AC production has higher technical and cost requirement than PWA utilisation. However, the application of PWA has relatively high environmental benefits because it can substitute chemical fertilizer. PWA is alternative to chemical fertilizer especially for the treatment of ultisol and acidic soils, this is most useful where the fertilizer market is not easily accessible. There is an estimated capital expenditure of $280, 400, 000 for biomass thermal processing plant and payback period was evaluated at 8.2-9.8 years. Therefore, AC market is a viable business; although, it has a high initial capital investment. The general efficiency of the two processes depends on requirements and demand. Advancing researches on multiple utility and compound wastes will further boost the annualised return on investment. Biomass thermal plant should be established in an area with good road network, available electricity and should be designed to take multiple processes simultaneously.

7.5 References

Abdullah, N. and Sulaim, F. (2013) ‘The Oil Palm Wastes in Malaysia’, *Biomass Now - Sustainable Growth and Use*. doi: 10.5772/55302.

Akorede, M. F., Ibrahim, O., Amuda, S. A., Otuoze, A. O., Olufeagba, B. J., Of, D. E., Ngineering, C. O. E., Lorin, U. N. O. F. I. and Lorin, I. (2017) ‘Current Status and Outlook of Renewable Energy Development in Nigeria’, *Nigerian Journal of Technology*, 36(1), pp. 196–212. doi: 10.4314/njt.361.1230.

Alawode, O. O. and Abegunde, V. O. (2016) *Economic Analysis of Pepper Marketing in Oyo State , Nigeria*, *Applied Tropical Agriculture*. Available at: https://www.futa.edu.ng/journal/home/downloadpdf/paper_3_1508325210 (Accessed: 15 September 2017).

Aliyu, A. S., Dada, J. O. and Adam, I. K. (2015) ‘Current status and future prospects of renewable energy in Nigeria’, *Renewable and Sustainable Energy Reviews*, 48, pp. 336–346. doi: 10.1016/j.rser.2015.03.098.

Anyaoha, Kelechi E, Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Critical evaluation of oil palm fresh fruit bunch solid wastes as soil amendments : Prospects and challenges’, *Resources, Conservation & Recycling*, 136(January), pp. 399–409. doi: 10.1016/j.resconrec.2018.04.022.

Anyaoha, Kelechi E., Sakrabani, R., Patchigolla, K. and Mouazen, A. M. (2018) ‘Evaluating oil palm fresh fruit bunch processing in Nigeria’, *Waste Management and Research*, 36(3), pp. 236–246. doi: 10.1177/0734242X17751848.

Babalola, O. O., Ilori, M. O. and Adegbite, S. A. (2012) *Engineering Economic Analysis of Organic Fertilizer Production in Nigeria*, *International Journal of Engineering Research & Technology*. Available at: https://www.ijert.org/research/engineering-economic-analysis-of-organic-fertilizer-production-in-nigeria-IJERTV1IS9220.pdf (Accessed: 24 January 2019).

Bello, I. A., Norshafiq, M. and Kabbashi, N. A. (2016) ‘Solid Waste Management in Africa : A Review’, *International Journal of Waste Resources*, 6(2), pp. 4–7. doi: 10.4172/2252-5211.1000216.

Bevan Nyakuma, B., Johari, A. and Ahmad, A. (2013) ‘Thermochemical analysis of palm oil wastes as fuel for biomass gasification’, *Jurnal Teknologi (Sciences and Engineering)*, 62(3), pp. 73–76. doi: 10.11113/jt.v62.1891.

Bitra, V. S. P., Womac, A. R., Chevanan, N., Miu, P. I., Igathinathane, C., Sokhansanj, S. and Smith, D. R. (2009) ‘Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions’, *Powder Technology*, 193(1), pp. 32–45. doi: 10.1016/j.powtec.2009.02.010.

Camps Arbestain, M., Saggar, S. and Leifeld, J. (2014) ‘Environmental benefits and risks of biochar application to soil’, *Agriculture, Ecosystems and Environment*, 191, pp. 1–4. doi: 10.1016/j.agee.2014.04.014.

Cruz-Paredes, C., López-García, Á., Rubæk, G. H., Hovmand, M. F., Sørensen, P. and Kjøller, R. (2017) ‘Risk assessment of replacing conventional P fertilizers with biomass ash: Residual effects on plant yield, nutrition, cadmium accumulation and mycorrhizal status’, *Science of the Total Environment*. Elsevier B.V., 575, pp. 1168–1176. doi: 10.1016/j.scitotenv.2016.09.194.

Dada, O. and Ogunsesu, Y. O. (2016) ‘Growth Analysis and Fruit Yield of Capsicum Chinense, Jackquin as Influenced by Compost Applied as Foliar Spray and Soil Augmentation in Ibadan, Southwestern Nigeria’, *Journal of Agriculture and Sustainability*, 9(1), pp. 83–103. doi: 9789676119926.

Dai, J., Cui, H. and Grace, J. R. (2012) ‘Biomass feeding for thermochemical reactors’, *Progress in Energy and Combustion Science*, 38(5), pp. 716–736. doi: 10.1016/j.pecs.2012.04.002.

Davis, R., Markham, J., Kinchin, C., Grundl, N., Tan, E. C. D. and Humbird, D. (2016) ‘Process Design and Economics for the Production of Algal Biomass: Algal Biomass Production in Open Pond Systems and Processing Through Dewatering for Downstream Conversion', *National Renewable Energy Laboratory*, (February), p. 128. doi: 10.2172/1239893.

Deng, H., Li, G., Yang, H., Tang, Jiping and Tang, Jiangyun (2010) 'Preparation of activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation', *Chemical Engineering Journal*, 163(3), pp. 373–381. doi: 10.1016/j.cej.2010.08.019.

Deng, N., Li, D., Zhang, Q., Zhang, A., Cai, R. and Zhang, B. (2019) 'Simulation analysis of municipal solid waste pyrolysis and gasification based on Aspen plus', *Frontiers in Energy*, 13(1), pp. 64–70. doi: 10.1007/s11708-017-0481-7.

Duku, M. H., Gu, S. and Hagan, E. Ben (2011) 'A comprehensive review of biomass resources and biofuels potential in Ghana', *Renewable and Sustainable Energy Reviews*, 15(1), pp. 404–415. doi: 10.1016/j.rser.2010.09.033.

FEPSAN, T. F. S. A. O. N. (FEPSAN) (2014) *A Study on Consumption and Fertilizer Use by Crops (FUBC) in Nigeria*. Accra, Ghana.

García, J. R., Sedran, U., Zaini, M. A. A. and Zakaria, Z. A. (2017) 'Preparation, characterization, and dye removal study of activated carbon prepared from palm kernel shell', *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, pp. 1–10. doi: 10.1007/s11356-017-8975-8.

Gil, M. and Arauzo, I. (2014) 'Hammer mill operating and biomass physical conditions effects on particle size distribution of solid pulverized biofuels', *Fuel Processing Technology*, 127, pp. 80–87. doi: 10.1016/j.fuproc.2014.06.016.

Gil, M., Luciano, E. and Arauzo, I. (2015) 'Population balance model for biomass milling', *Powder Technology*, 276, pp. 34–44. doi: 10.1016/j.powtec.2015.01.060.

Giwa, A., Alabi, A., Yusuf, A. and Olukan, T. (2017) 'A comprehensive review on biomass and solar energy for sustainable energy generation in Nigeria', *Renewable and Sustainable Energy Reviews*, 69(September 2015), pp. 620–641. doi: 10.1016/j.rser.2016.11.160.

Hellums, D. T. (2016) *Fertilizer Subsidy Policies in Selected Countries*, *IFDC*. International Fertilizer Development Center, USA. Available at: www.ifdc.org (Accessed: 1 June 2019).

Hoornweg, D. and Bhada-Tata, P. (2012) ‘A Global Review of Solid Waste Management’, *World Bank Urban Development Series Knowledge Papers*, pp. 1–116. Available at: https://openknowledge.worldbank.org/handle/10986/17388.

Hunpinyo, P., Narataruksa, P., Tungkamani, S., Pana-Suppamassadu, K. and Chollacoop, N. (2013) ‘Evaluation of techno-economic feasibility biomass-to-energy by using ASPEN Plus®: A case study of Thailand’, *Energy Procedia*. Elsevier B.V., 42, pp. 640–649. doi: 10.1016/j.egypro.2013.11.066.

Ikeh, A. O., Ndaeyo, N. U., Uduak, I. G., Iwo, G. A., Ugbe, L. A., Udoh, E. I. and Effiong, G. S. (2012) *Growth And Yield Responses of Pepper (Capsicum frutescens L .) to Varied Poultry Manure Rates in Uyo , Southeastern Nigeria*, *ARPN Journal of Agricultural and Biological Science*. Available at: www.arpnjournals.com (Accessed: 18 November 2018).

Jahirul, M. I., Rasul, M. G., Chowdhury, A. A. and Ashwath, N. (2012) ‘Biofuels production through biomass pyrolysis- A technological review’, *Energies*, 5(12), pp. 4952–5001. doi: 10.3390/en5124952.

Khatun, R., Reza, M. I. H., Moniruzzaman, M. and Yaakob, Z. (2017) ‘Sustainable oil palm industry: The possibilities’, *Renewable and Sustainable Energy Reviews*, 76(December 2016), pp. 608–619. doi: 10.1016/j.rser.2017.03.077.

Kletnikoski, P., Sofijanova, E., Jovanov, D. and Dimovska, V. (2013) ‘Comparative Cost Analyses of Pepper Production under Conventional and Integrated Crop Management Methods: The Case of Strumica Region in Republic Of Macedonia.’, *Scientific Works*, Volume LX(Icm), pp. 1375–1379.

Kumar, K., Kumar, S., Gupta, M. and Garg, H. C. (2017) ‘Characteristics of Fly Ash in Relation of Soil Amendment’, *Materials Today: Proceedings*, 4(2), pp. 527–532. doi: 10.1016/j.matpr.2017.01.053.

Liew, R. K., Nam, W. L., Chong, M. Y., Phang, X. Y., Su, M. H., Yek, P. N. Y., Ma, N. L., Cheng, C. K., Chong, C. T. and Lam, S. S. (2017) ‘Oil palm waste: An abundant and promising feedstock for microwave pyrolysis conversion into good quality biochar with potential multi-applications’, *Process Safety and Environmental Protection*, pp. 1–13. doi: 10.1016/j.psep.2017.10.005.

Manna, M. C., Swarup, A., Wanjari, R. H., Mishra, B. and Shahi, D. K. (2007) ‘Long-term fertilization, manure and liming effects on soil organic matter and crop yields’, *Soil and Tillage Research*, 94(2), pp. 397–409. doi: 10.1016/j.still.2006.08.013.

Mirfendereski, Y. (2008) ‘Techno-Economic Assessment of Carbon Capture and Sequestration Technologies in the Fossil Fuel-based Power Sector of the Global Energy-Economy System’, *Arbeit*, (May). Available at: http://www.pik-potsdam.de/members/edenh/theses/master_yasaman.

Mohammed, B., Abdulsalam, Z. and Ahmed, B. (2016) ‘Profitability in Chilli Pepper Production in Kaduna State, Nigeria’, *British Journal of Applied Science & Technology*, 12(3), pp. 1–9. doi: 10.9734/bjast/2016/20300.

Ooi, C. H., Cheah, W. K., Sim, Y. L., Pung, S. Y. and Yeoh, F. Y. (2017) ‘Conversion and characterization of activated carbon fiber derived from palm empty fruit bunch waste and its kinetic study on urea adsorption’, *Journal of Environmental Management*, 197, pp. 199–205. doi: 10.1016/j.jenvman.2017.03.083.

Philips, E. S., Mutuku, R. N. and Mwero, J. N. (2017) ‘Effects of Palm Kernel Shell and Rice Husk Ash as Partial Replacements of Normal Weight Aggregate and Ordinary Portland Cement in Concrete’, pp. 42–54.

Porcu, A., Sollai, S., Marotto, D., Mureddu, M., Ferrara, F. and Pettinau, A. (2019) ‘Techno-Economic Analysis of a Small-Scale Biomass-to-Energy BFB Gasification-Based System’, *Energies*, 12(3), p. 494. doi: 10.3390/en12030494.

Prusty, J. K., Patro, S. K. and Basarkar, S. S. (2016) ‘Concrete using agro-waste as fine aggregate for sustainable built environment – A review’, *International*

Journal of Sustainable Built Environment, 5(2), pp. 312–333. doi: 10.1016/j.ijsbe.2016.06.003.

Research, G. V. (2014) *Activated Carbon Market Analysis and Segment Forecasts to 2020*. San Francisco, CA 94105, USA. Available at: https://www.grandviewresearch.com/press-release/global-activated-carbon-market (Accessed: 16 February 2019).

Rodriguez Correa, C., Otto, T. and Kruse, A. (2017) ‘Influence of the biomass components on the pore formation of activated carbon’, *Biomass and Bioenergy*, 97, pp. 53–64. doi: 10.1016/j.biombioe.2016.12.017.

Savci, S. (2012) ‘Investigation of Effect of Chemical Fertilizers on Environment’, *APCBEE Procedia*, 1(January), pp. 287–292. doi: 10.1016/j.apcbee.2012.03.047.

Sethupathi, S., Bashir, M. J., Akbar, Z. A. and Mohamed, A. R. (2015) ‘Biomass-based palm shell activated carbon and palm shell carbon molecular sieve as gas separation adsorbents’, *Waste Management and Research*, 33(4), pp. 303–312. doi: 10.1177/0734242X15576026.

Simonyan, K. J. and Fasina, O. (2013) ‘Biomass resources and bioenergy potentials in Nigeria’, *African Journal of Agricultural Research*, 8(40), pp. 4975–4989. doi: 10.5897/AJAR2013.6726.

Sukiran, M. A., Abnisa, F., Wan Daud, W. M. A., Abu Bakar, N. and Loh, S. K. (2017) ‘A review of torrefaction of oil palm solid wastes for biofuel production’, *Energy Conversion and Management*, 149, pp. 101–120. doi: 10.1016/j.enconman.2017.07.011.

Trippe, F., Fröhling, M., Schultmann, F., Stahl, R. and Henrich, E. (2011) ‘Techno-economic assessment of gasification as a process step within biomass-to-liquid (BtL) fuel and chemicals production’, *Fuel Processing Technology*, 92(11), pp. 2169–2184. doi: 10.1016/j.fuproc.2011.06.026.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R. and Anthony, E. (2020) ‘Preparation and Characterisation of Activated Carbon from Palm Mixed Waste Treated with Trona Ore’, *Molecules*, 25(21), p. 5028. doi: 10.3390/molecules25215028.

Ukanwa, K. S., Patchigolla, K., Sakrabani, R., Anthony, E. and Mandavgane, S. (2019) ‘A review of chemicals to produce activated carbon from agricultural waste biomass’, *Sustainability (Switzerland)*, 11(22), pp. 1–35. doi: 10.3390/su11226204.

Vaish, B., Srivastava, V., Singh, P., Singh, A., Singh, P. K. and Singh, R. P. (2016) ‘Exploring untapped energy potential of urban solid waste’, *Energy, Ecology and Environment*, 1(5), pp. 323–342. doi: 10.1007/s40974-016-0023-x.

8 PROJECT INTEGRATED DISCUSSION

8.1 Integrated discussion

This PhD project incorporates the utilisation of mixed oil palm waste (OPW) in its raw form, from milling to various forms due to different thermal processes. This is applied in the production of activated carbon (AC) and characterisation using scanning electron microscope (SEM) and Fourier transform infrared spectrometry (FTIR). This study also evaluates the application of residues to the soil. The research is structured to assess and determine the requisite functions using optimum route for efficient utilisation of residues from thermal conversion process of OPW. The two logical utilisation routes were implemented in the production of AC and ash use for soil amelioration. The project procedures were organised based on literature review, and existing scientific trials. Laboratory and field experiments as highlighted throughout the thesis and structured in chapters as illustrated in Figure 8-1.

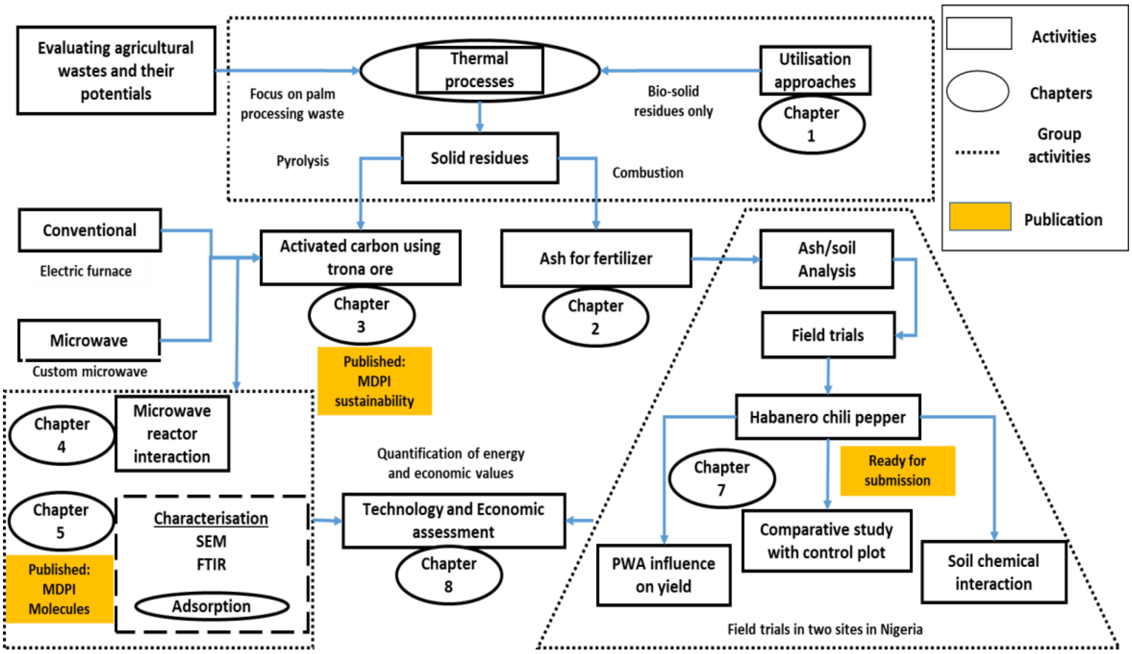


Figure 8-1 Overall project structure

All the biomass raw materials were obtained from the same source in Nigeria, the chemicals were of analytical grades and field and laboratory experiments followed Cranfield University, UK approved standard operating procedures. The basic raw material consists of palm kernel shell, mesocarp fibre and empty fruit bunch, from oil palm.

The exploring of palm waste opportunities and utilisation route were satisfied through the objective of reviewing and evaluation of the studies already undertaken in this field.

The review of the palm waste challenges and potential applications offered an insight on the economic, technological and environmental importance. Comparison of activating agents show that different activating agents behaves differently and the conventional route challenges could be overcome by the use of microwave system. Process routes were compared and the individual pros and cons show that microwave saves time and energy.

Due to the scientific fissure in the production of AC and the stage of AC production using microwave, the evaluation of different approaches and their effectiveness became necessary.

A flexible microwave system was designed and fabricated for pyrolysis to handle different kinds of biomass materials. The AC production techniques were considered based on the need for eliminating tar and create well-developed pores; minimise secondary contamination by the use of environmental friendly activating agent.

The parameter evaluation of AC production was done by microwave system designed in this study. This entails a good delivery system and process control for an activation process. The microwave technique saves energy, cost and time in comparison to traditional systems. Trona ore was selected with anticipation of being effective in the elimination of alcohol from biomass and this can contribute to its effectiveness as a catalyst for biofuel production. The effect of Trona ore in hydrophilicity indicates the effectiveness for a heterogeneous waste stream AC and more effective than individual feedstock. This study suggests that microwave process reactor has a great influence on the thermal process rate, tar deposition and conversion.

The use of trona ore in AC production as an activating agent has been assessed therefore evaluating different approaches by characterisation is justified.

The morphology and surface chemicals of the AC relative to activation temperature and modes were examined. The resultant images were compared, the pore symmetry and sizes were determined. The S_{BET} and material structural porosity of the trona ore AC were evaluated for micropore, mesopore and macropore by N_2 adsorption/desorption isotherm. This is centred on the principle of relative pressure and adsorbed volume. FTIR analyses of the AC were done to define the active ions and forms of bonding which is relevant to the adsorption efficiency of the AC. These techniques were also used for the surface chemical comparison, relationship using infrared emission and adsorption spectra. It determines the infrared adsorption bands, identifies the molecular components and structures.

Another important hypothesis of this study is application of the ash produced from the mixed feedstock combustion process to the soil as an alternative to chemical fertilizer were evaluated as an utilisation technique.

The site locations were selected based on literature reports of low fertility of the sites and the readiness for commercial agriculture. Soil and OPWA were analysed to assess the mineral potency of the OPWA and the fertility index of the sites for growing Habanero chili pepper (HCP). The determination of physical variance and changes in growth; the physiological traits of HCP are factors of the indicative influence of yield and potential ability for yield. The relative growth rate are the physical techniques evaluated for growth determination of HCP. The leaf physical features and other characteristics were used to evaluate and determine the plant performance.

Heterogeneous waste ash for soil amelioration with an average of 8 tonnes/hectare for growing pepper and the capacity to improve the resultant economic gain by 25%. Biomass ash used for soil improvement regulated the soil temperature, influenced the microbial activities and enhanced the structural state of the soil. The soil pH was hugely influenced by the addition and was raised from pH 4 to above neutral mark. Crop yield and soil chemical variation relative to application were affected.

The application of OPWA consequently improves yield. Results showed that the interaction between OPWA and soil improved agronomic efficiency by 66-69%. Crop yield in relation to the control indicated that OPWA is effective for soil improvement, nutrient delivery and exchange for improved pepper production by more than 20%, which led to the conclusion that OPWA is effective for growing pepper and improves soil fertility, but effect on soil aggregation is yet to be verified.

In order to fulfil the obligation for the assessment of economic profile of the processes and justify the energy and economic requirements, the pyrolysis and combustion processes which produced AC and OPWA respectively were evaluated based on energy and material balances featured for technology and economic assessment of the project; modelled with Aspen plus economy.

The sensitivity analysis of the processes were based on temperature, flow rate and their variation effects on the respective output. The thermodynamic models selected defined the appropriate liquid and vapour phases.

Based on the outcome of different systematic process analyses, comparative studies and validations, research inference were determined. Output determination and predictive formulations were outlined. Waste utilisation regulations should include secondary waste and utilisation techniques should implement multidimensional techniques. Composite and heterogeneous waste stream are effective in AC production and efficient utilisation in thermal processing could support waste management approaches. Composite feedstock for AC production are understood from this research to be a technique to integrate multiple waste streams in a single stream thermal process. Producing char for AC, OPWA and syngas are relative in the economic evaluation. The general efficiency of the two processes depends on requirements and demand. There is a high capital cost of establishing a thermal process plant and the equation of waste impact on the environment and utilisation was valued to be about 20%

better on the investment scale of the two processes. Waste management needs could be achieved through adequate and efficient utilisation of available resources.

Overview of project contribution to knowledge, technological and economic impact

The principle of agricultural waste utilisation is an integrated aspect of global environmental pollution regulations, enshrined in the control of greenhouse gas effect. The high waste generation and inadequate utilisation of the waste have reawaken innovations, which expanded the horizon of waste integration. The secondary waste (residues from waste thermal processes) integration was applied in this project and that could stretch the limit of waste utilisation. The scientific breakthrough in this project are grouped based on relative applications and assumptions relative to the objectives, answer research questions and fulfil the project aim.

- Waste utilisation technologies could influence pollution control. The setup techniques in this study would promote the design of an efficient waste revaluation in energy.

✓ The utilisation challenges of oil palm waste were addressed in this research, possible routes suggested.

✓ Multiple utilisation strategy was identified as means of integrating both the primary and secondary wastes from oil palm.

✓ The use of OPW secondary waste as a chemical fertiliser alternative is proven on pepper production and capable of boosting pepper production at low cost.

✓ The review also evaluated different works done in the field, compared and assessed the level of the advancement of the technology.

- The challenges expressed by microwave thermal processes were addressed by the laboratory scale design and reactor evaluation to overcome the challenge of tar deposition. These results were achieved to fulfil the gap of evaluating the effectiveness of different process routes.

- ✓ The scientific influence is in the establishment of reactor behaviour in producing AC
- ✓ Building a microwave thermal process facility with multiple output (biochar, bio oil, biofuels and ash) could increase profit. The same project responsible for the supply of bio-oil and biofuels with low-cost feedstock, could be efficiently managed to produce activated carbon.
- ✓ In scaling up, this research identified activating agent as a key component to regulating arcing and ensuring quick activation.
- This research suggested the design of a reactor with composite material to overcome heating by conduction on the wave path. Defining the material interactions during activation which would aid in the design of appropriate machines for efficient AC production. The activation trial and characterisation of effectiveness of Trona ore is one of the missing link for low-cost and safe activating agent. To fulfil the gap of the characterisation of the AC produced by microwave using trona ore.
- ✓ The scientific impact of this process is establishing the triple bond in the AC produced using trona ore
- ✓ Identifying the temperature range at which activation process is efficient using a combined palm waste
- The impact of OPW AC in adsorption have a positive economic influence in the production process.
- ✓ The validation of effectiveness of the feedstock indicates a cost reduction due to low cost raw material
- ✓ AC with the ability to adsorb wide range of impurities and heavy metals
- ✓ Indicating a high effectiveness of the production process adopted in this research.

- ✓ Approves of the production technique adopted and resolved the suitability of trona ore in activation process.
- ✓ Predictive tools and process parameters relative to production of AC opened up by the technical evaluation of reactor interactions and could influence other related technologies such as biofuel and bio-oil productions. The challenges of high soil acidity against growing pepper, is resolved through the influence of biomass residue for amelioration.
- The determination of yield efficiency and appropriate period of plantation is a tool to predict the outcome of related crops and fulfill the hypothesis of evaluating the effective of OPWA for growing pepper.
- ✓ The field experiment established a planting response relative to weather
- ✓ The yield factors show the effectiveness of mixed palm waste ash in growing pepper.
- ✓ The impact of reduction of soil acidity and quick absorption of the nutrient prove OPWA as a cost effective alternative to chemical fertiliser.
- ✓ AC production with a low-cost activating agent helps in reducing the production cost. Optimisation of thermal process relative to production method shows that microwave system saves time and energy 10-20 min against 1-2 h of conventional method.
- The economic aspect of thermal processes for the production of AC can be influenced by appropriate integration of an optimised route.
- ✓ Less chemical fertilizer could save about 30% of the production cost by applying ash coming from biomass thermal residues.
- ✓ The tool has the ability to predict AC yield based on quantitative value.

Biomass ash is a low cost and environmental friendly option of soil nutrient, it saves investment cost and boosts agricultural output.

.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

This PhD project focuses on revaluation of solid residue from oil palm waste (OPW) in a mixed form. The utilisation of OPW is instigated based on the disposal challenges and other negative effects of these residues. The selection of OPW residue for the production of activated carbon and in soil amelioration, justifies an approach for an efficient waste management. To advance this principle, this study was planned to evaluate the efficient route for utilising these wastes and contribute to developing the technology in waste revaluation. The principal challenges in the processes were evaluated based on the resultant impact of the output, relative to technology advancement and economic gain. Therefore, the objective contingency with the research and results reflect the expert decisions for quality AC products, soil amelioration resulting in efficient waste utilisation and advance researches.

The first objective, **critique wastes generated in palm oil processing, its prospects and utilisation challenges in Nigeria. This considers the utilisation opportunities relative to government policies on waste**. This reflects of utilisation opportunities relative to government policies on waste, which is based on general overview of the current waste utilisation status. Therefore, in this project some of the waste management challenges in the developing countries were appraised. Most developing countries are yet to have a waste regulation policies that incorporate agricultural waste management. This is due to low technology advancement, waste utilisation policies in agricultural sector has not gained a wide spread influence. Several routes of application are available although with low commercial status. The relative challenges of the OPW and their potential applicability can boost the economy, provide employment and deliver opportunities for technology advancement. Oil palm thermal residue can be managed efficiently by recycling in the soil as a carbon source.

The subsequent objective with synopsis to, **evaluate the effectiveness of different approaches in producing AC from OPW through safe activation. Determine the various challenges of producing AC from OPW through microwave and microwave interactions during activation processes**. This is based on the various challenges of producing AC from OPW using microwave technique resulted in microwave interactions consideration during activation processes. These challenges were subjected to review of projects and studies by other researchers relative to OPW and other biomass materials. It was observed that microwave reactor interaction is unique and has the same principle with drying of biomass but due to the low dielectric property of OPW, reactor selection is important. The incident microwaves decrease by 63% of absorbed wave in a penetration distance Dp. Penetration Depth of Microwaves principle supports that the heating efficiency reduces with large particles. Scale of the microwave technique of AC production is in a developing stage and would require advance development to handle mixed biomass materials. During activation of CPW, the FC content increased from 16.25 wt% to 73.56 wt% for the single step conventional technique and to 76.60 wt% for a 2-step conventional technique, demonstrating the superiority of the two-step process. Comparative study of conventional and microwave show the later to be quicker and saves energy, 10-20 min against 1-2 h of conventional method. Environmental health and safety of different approaches were considered. The evaluation of how several chemicals impact on the AC products show that trona ore is efficient in the activation process. The conclusion also precipitated the design of a microwave system for AC production with adjustable parameters and capacity for efficient removal of volatiles.

There subsequent approach obliged to **Characterise the activated carbon produced from a novel activating agent (Trona ore) using Scanning electron microscope, Fourier transform infrared spectrometry and adsorption of heavy metals (although, not within the scope of the research.** The results show that morphology of the AC produced were honeycomb-like, the total volume and surface area of the AC produced by this technique improved relative to the conventional approach. The AC yield was improved in this process and this confirms that direct activation process enables effective activating agent and biomass interaction for the release of volatiles with no obstruction of the pores. The optimum results for the conventional production technique at 800 ^oC yielded, S_{BET} 920 m^2/g V_{total} 0.840 cm^3/g, mean pore diameter 2.2 nm and AC yield 40%. The optimum outcome of the microwave assisted technique for CPW was obtained at 600 W, S_{BET} is 980 m^2/g; V_{total} 0.865 cm^3/g; mean pore diameter 2.2 nm and AC yield is 42%. The microwave technology approach to AC production is efficient for heterogeneous waste which is a low-cost option and results in AC with capacity to adsorb metal(oid)s. The method of activation influenced the morphology, single-step activation with microwave has unbroken pores while the two-step and conventional techniques have ACs with broken and uneven pore linkages. The process was more favourable for microwave activation method due to energy and time saving due to a reduced activation duration. The pore structures were enhanced by the increase in microwave power from 460-600 W and temperature from 500-800 ^oC and beyond 100 ^oC, the changes were not significant. The AC produced in this study has the potential to be used for heavy metal, dyes and other gases adsorption due to high surface area of about 1220 m^2/g, defined pore structures and the presence of double and triple bonds on the surface of the materials. The characterisation further revealed that trona ore is effective compared to other activating agents such as K_2CO_3, and Na_2CO_3.

The cycle of utilisation was extended by the use of OPW thermal residue to apply in the soil. This was done to **determine the physiochemical effects of palm waste ash as fertilizer to grow pepper in two Nigeria soils. Consider the pre-planting conditions and seasonal evaluation of the yield relative to the quantity of palm waste ash.** The pre-planting conditions and seasonal evaluation were assessed and the crop yield relative to the quantity of PWA per plot in two seasons. This study has shown an innovation in the application of mixed palm waste ash to the soil and the resultant impact through the interaction with soil, by increasing agronomic efficiency of Habanero chilli pepper by 66-69% and Scoville value by 3.52%. Site A had a better response to OPWA than site B, which could be as a result of planting period and being more fertile. Site A control and highest OPWA treatment yielded 0.79 and 66.2 tonnes/ha while site B had

1.62 and 32 tonnes/ha respectively. The fruiting stage in site A, was not resilient to the dry weather and low soil moisture, therefore requires irrigation to survive the fruiting period. Site B does not require further irrigation for the initiation of second stage of fruiting. For efficient output of pepper production in southeast Nigeria, soil acidity should be lowered from pH (4.4-4.8) to at least pH 7.5. The planting period should not rely solely on the performance of the nursery. The variation between Control and OPWA treatments, witnessed significant growth rate, yield, morphological changes and the change in yield, which are relative to treatment rates.

Finally, the two utilisation techniques were considered. The **assessment of technology and economic valuation of the CPW thermal processes in AC production and OPWA application for soil amelioration using Aspen plus economy for simulation** were appraised. The production of AC and the application of OPWA to the soil were jointly evaluated and used as a summary framework. This is achieved by the assessment of technology and economic valuation of the CPW thermal processes in AC production and OPWA application for soil amelioration using Aspen plus economy for simulation. OPWA is realised as an alternative to chemical fertilizer especially for the treatment of ultisol and acidic soils. This is most useful where the fertilizer market is not easily accessible. There is an estimated capital expenditure of $280, 400, 000 for biomass thermal plant and conversion process. Annual production sale of bio-products is estimated at ($) 110, 300, 000-130,110, 000, Net present value of profit at ($) 937, 550, 000-1, 105, 935, 000, Net present value of operation and maintenance cost ($) 297, 238, 489 and Accumulated Net present value of all cost ($) 669, 734, 489. The Net present value of the project ($) 885, 470, 000-1, 053, 855, 000, the Benefit cost ratio, 1.25-1.4, Payback period, 8.2-9.8 and Internal rate of return (%) 14-17.2 years. Therefore, commercial attention is more on AC which has a viable market value and a reliable business; although, it has a high initial capital investment. The general efficiency of the two processes depends on requirements and demand and economic relevance of the project is dependent on the multiple application of the waste for different purposes. Dual stream economic prediction shows that waste management can play a vital role in pollution control and add value to the economy. The relevance of these utilisation approaches are well demonstrated in this study. Hence, the necessity to widen the factor of OPW utilisation to ensure efficient waste revaluation for economic and environmental benefits. Some areas of this study require further analysis and advance assessment, which will ensure continuous advancement of the project. They are identified and outlined in the below recommendation section.

9.2 Recommendations

Focus on the overview of this study and the stage of utilisation of agricultural waste biomass; ideas and projections are required to advancing studies in this area. The technical challenges in the procedures could help enhance other aspects of thermal processes, encourage the commercialisation of the AC production using microwave and promote studies on production of syngas and facility management. These recommendations could also help in formulating policies, developing models and structures for overall scientific improvement. The research recommendations and opportunities are outlined here:

- There is a need to develop an adequate agricultural waste agenda in developing countries and formulate a regulation for agricultural waste utilisation techniques.

- Use of other environment friendly activating agents for the production of activated carbon and its applicability for separation science sector.

- The design of a composite reactor for an industrial production of AC is necessary to enable heterogeneous waste stream of the process.

- Biological activating agents should be tried for both conventional and microwave methods.

- The importance of water jackets for the microwave reactors should be examined and the relevance could help improve the microwave-reactor interactions.

- The impact of biomass ash on the microbial activities and their effect on crop physiological response can be studied further.

- The long-term impact of biomass ash on soil and crop is necessary in order to avoid post-harvest shock.
- Design and develop a computer software program that predicts the soil chemical changes relative to ash application.
- Design a tool for predicting crop yield production with and without fertilizer application.
- The economics of AC production and ash application can also be compared base on environmental value.

APPENDICES

Appendix A Preparation and activation of AC from CPW

A.1 Process yield

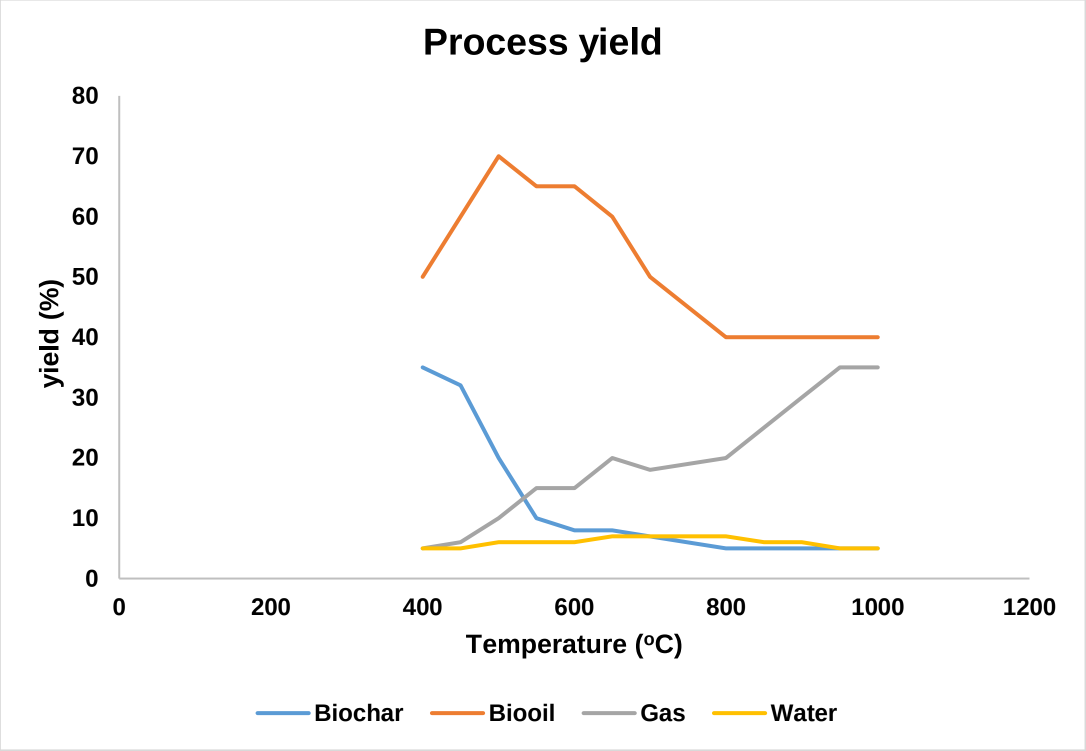


Figure A-1 Yield from CPW relative to temperature

A.2 AC production

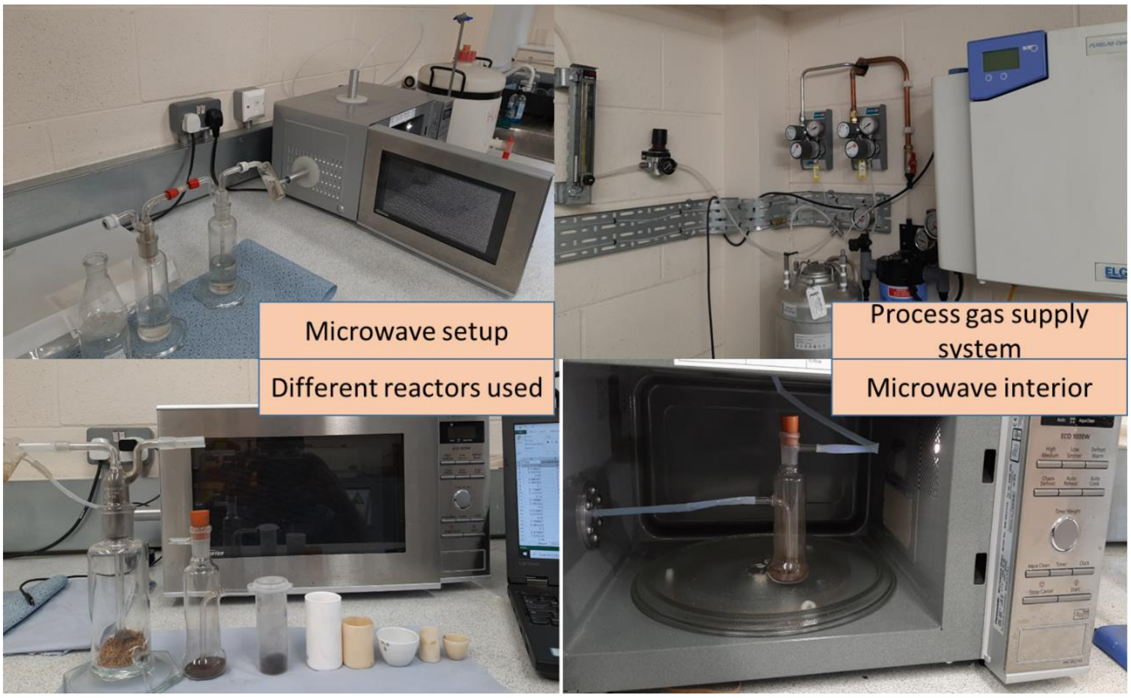


Figure A-2 Microwave setup and process equipment for AC production

A.3 Characterisation by FTIR

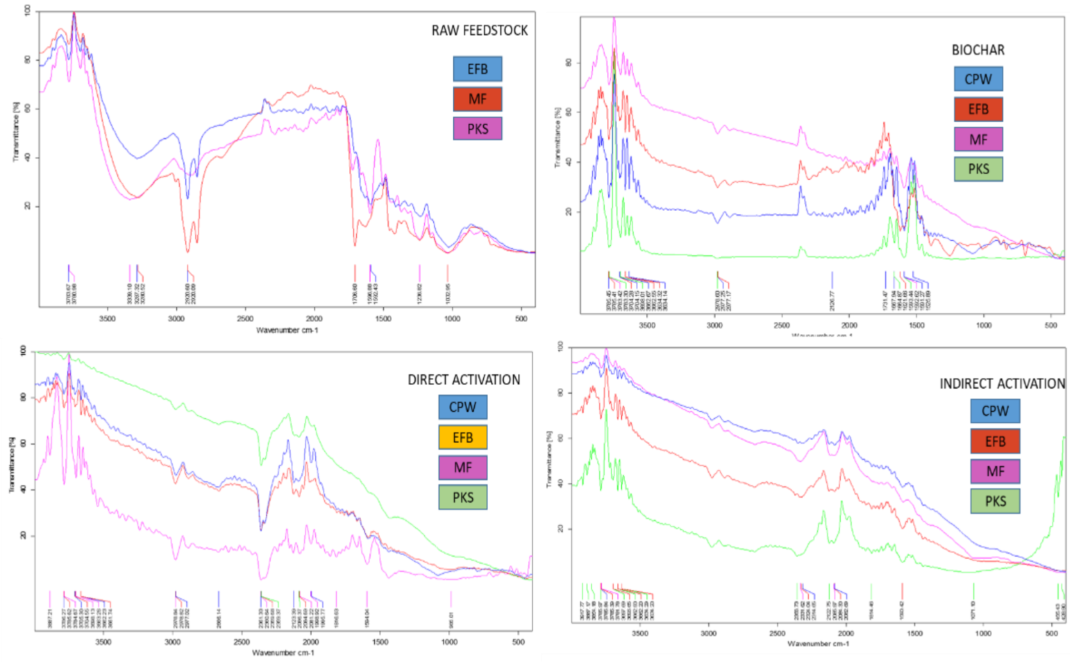


Figure A-3 FTIR of all the samples

A.4 Proposed design for large-scale microwave AC production system

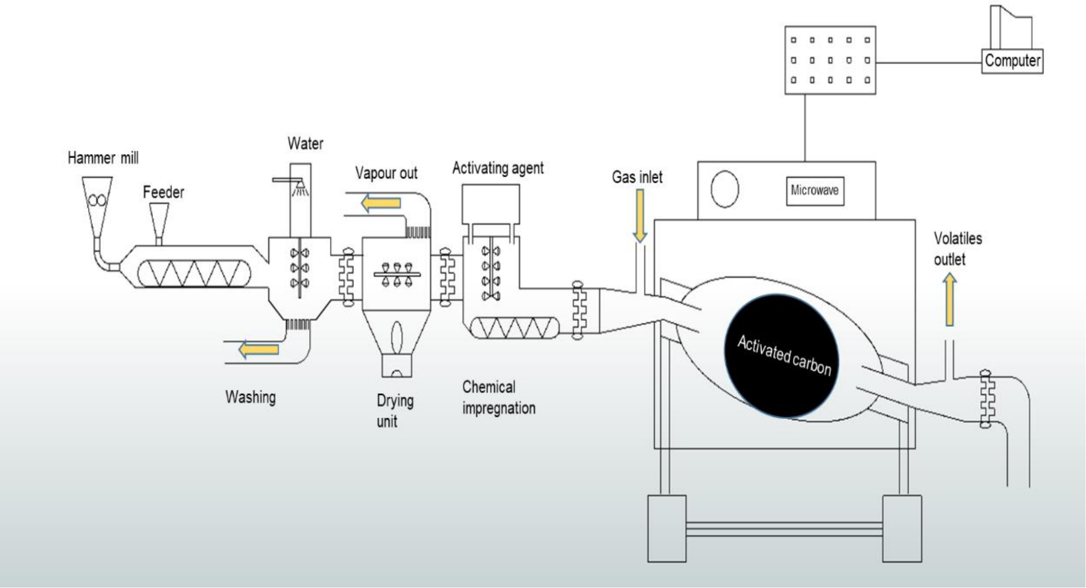


Figure A-4 Proposed design for large scale AC production system

Appendix B Weather report

B.1 Weather report

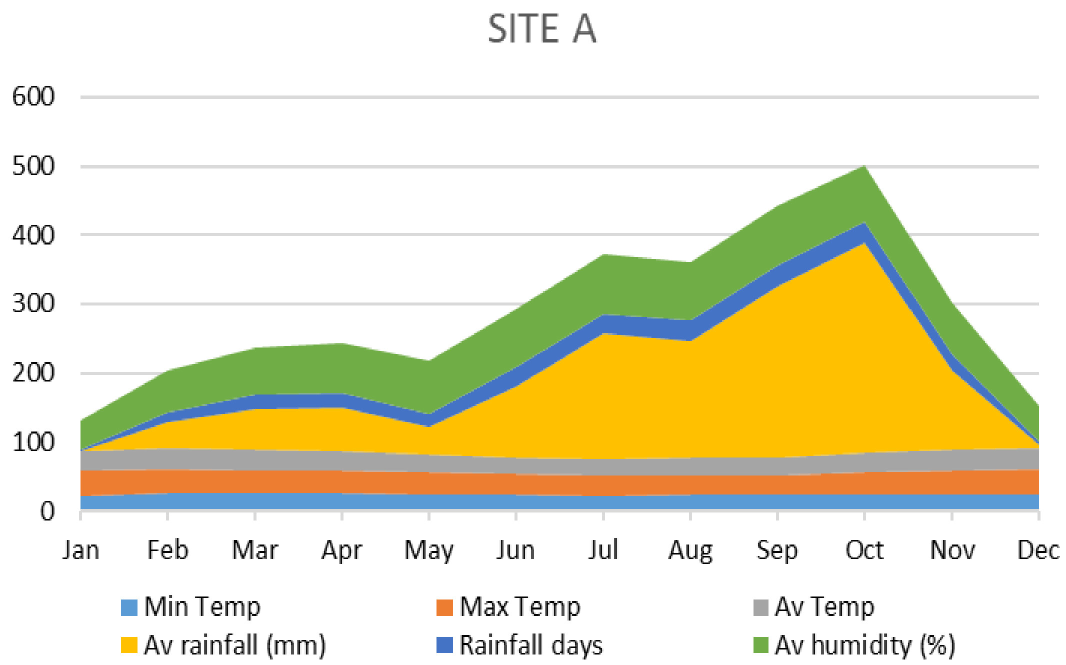


Figure B-1 Weather report for site A

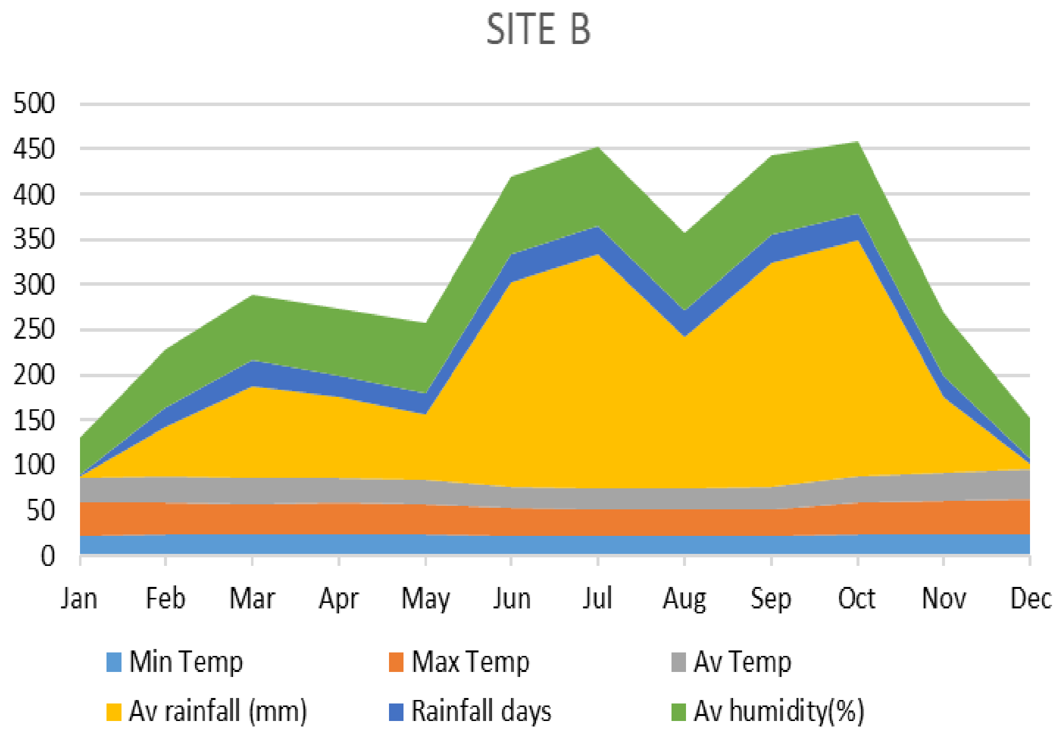


Figure B-2 Weather report for site B

Influence of weather

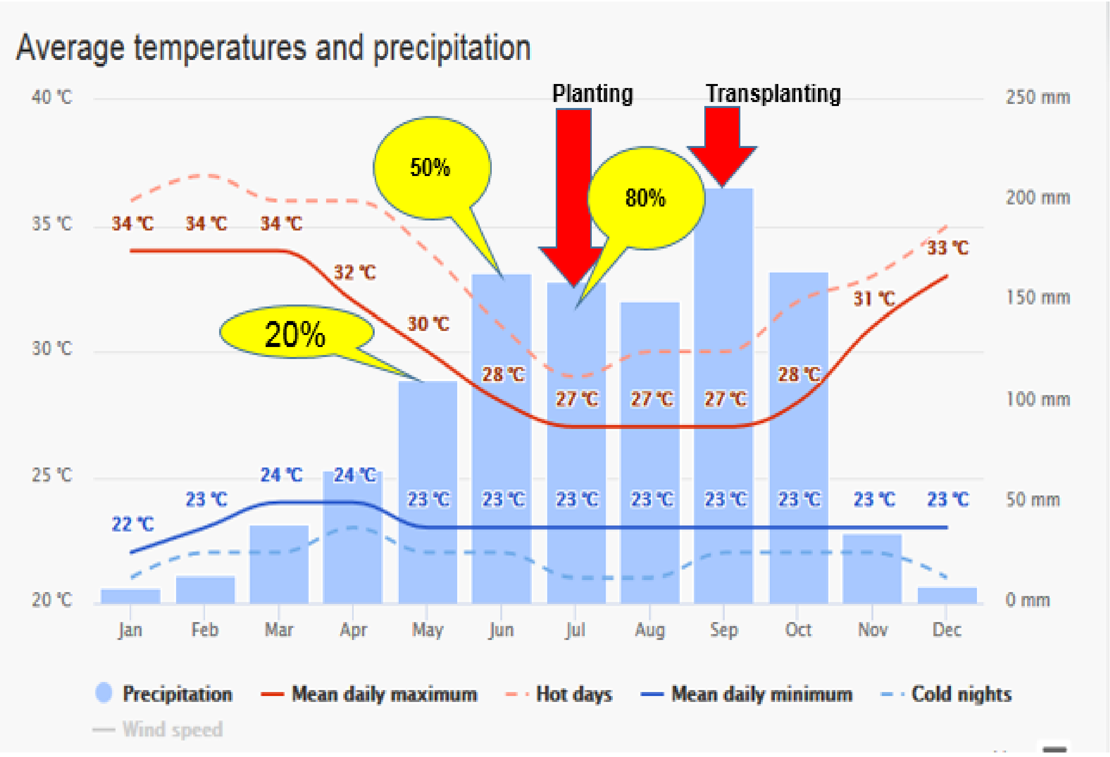
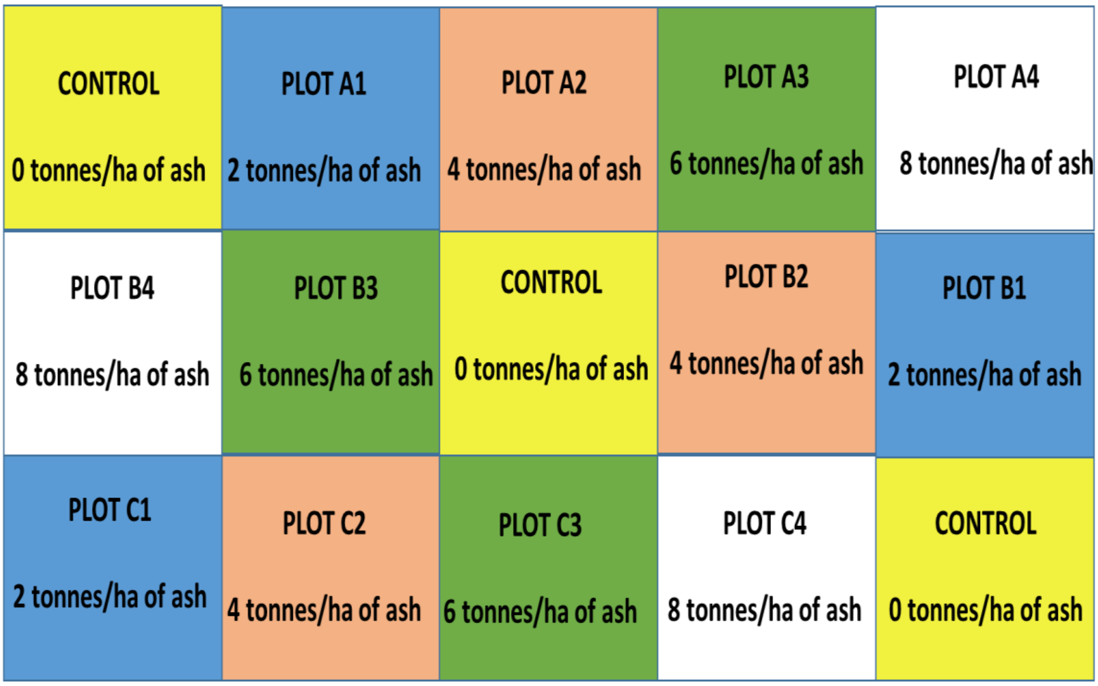


Figure B-3 Combined weather report relative to planting and transplanting

Appendix C Plant analysis

C.1 Field and treatment setup



CONTROL 0 tonnes/ha of ash	PLOT A1 2 tonnes/ha of ash	PLOT A2 4 tonnes/ha of ash	PLOT A3 6 tonnes/ha of ash	PLOT A4 8 tonnes/ha of ash
PLOT B4 8 tonnes/ha of ash	PLOT B3 6 tonnes/ha of ash	CONTROL 0 tonnes/ha of ash	PLOT B2 4 tonnes/ha of ash	PLOT B1 2 tonnes/ha of ash
PLOT C1 2 tonnes/ha of ash	PLOT C2 4 tonnes/ha of ash	PLOT C3 6 tonnes/ha of ash	PLOT C4 8 tonnes/ha of ash	CONTROL 0 tonnes/ha of ash

Figure C-1 Treatment and application rate

C.2 Field and treatment setup

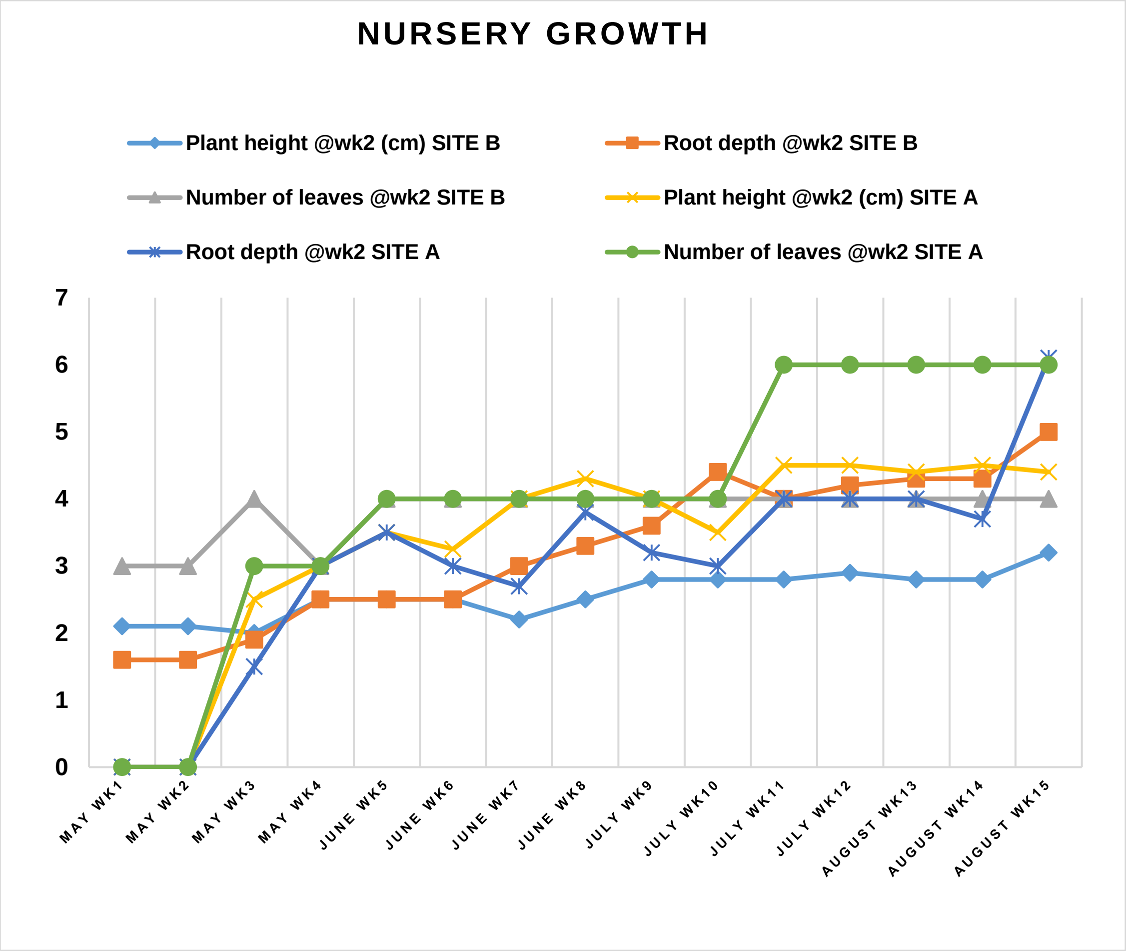


Figure C-2 Nursery response in two weeks

C.3 Field and treatment setup

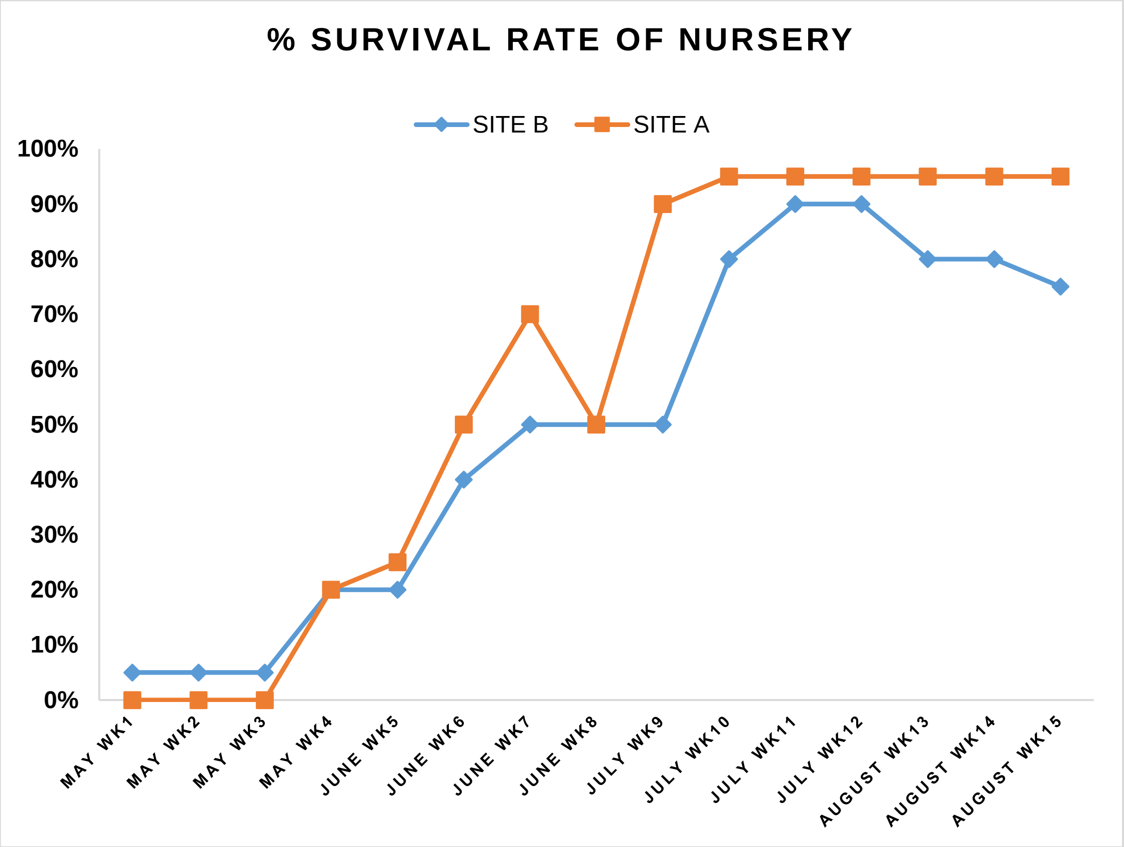


Figure C-3 Nursery survival rate

C.4 HCP fruit analysis

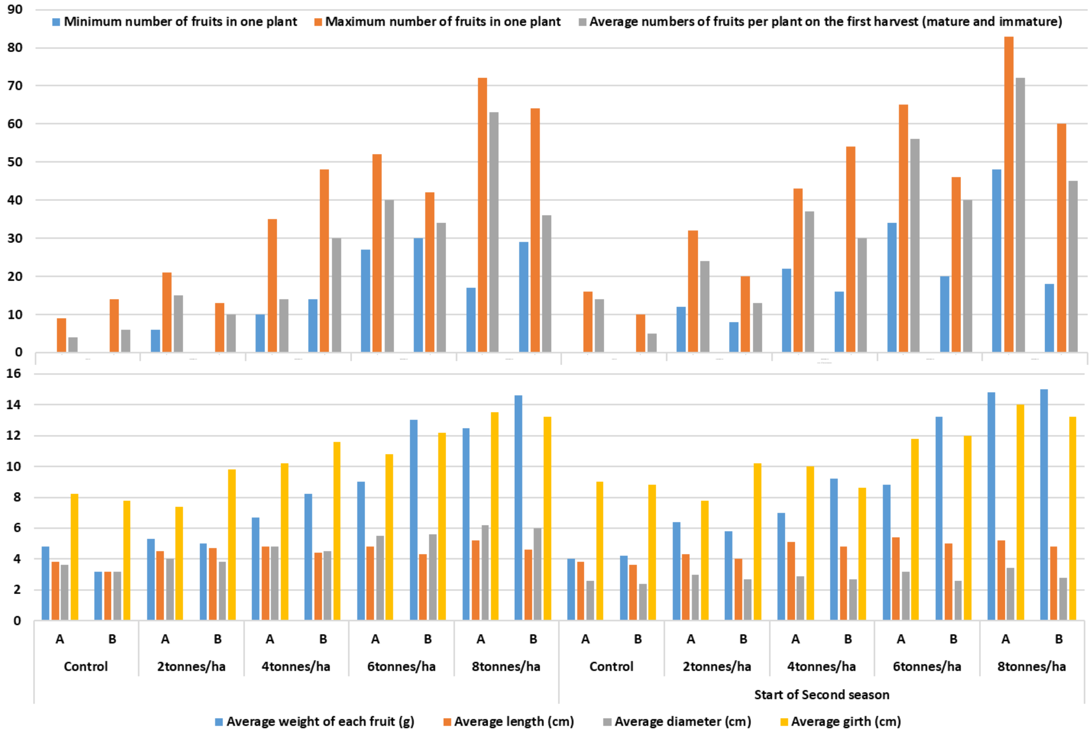


Figure C-4 Fruit characteristics

Appendix D Economic assessment

D.1 Process yield under different conditions

Table D-1 Process yield

	% output/yield Temperature (^oC)	Gas	Tar	Moisture	Biochar
Pyrolysis					
Scenario A1	400	60	9	8	23
Scenario A2	500	65	5	10	20
Scenario A3	600	70	5	10	15
Scenario A4	700	72	3	15	10
Scenario A5	800	75	1	16	8
Gasification					
Scenario B1	500	70	0	15	15
Scenario B2	600	75	0	12	13
Scenario B3	700	80	0	10	10
Scenario B4	800	88	0	7	5
Scenario B5	900	90	0	8	2

Appendix E Arsenic adsorption

E.1 Arsenic Removal from Aqueous Medium by Combined Palm Waste Activated Carbon and Modified Biochar Prepared by Microwave

Waste and Biomass Valorization (Springer-2.8)

Arsenic Removal from Aqueous Medium by Combined Palm Waste Activated Carbon and Modified Biochar Prepared by Microwave

Ukanwa, Kalu Samuel[a]; Patchigolla, Kumar[a*]; Sakrabani, Ruben[b]; Emenike, Chidozie PraiseGod[d]

a. Centre for Thermal Energy Systems and Materials, School of Water, Energy and Environment, Cranfield University, MK43 0AL, United Kingdom
b. Cranfield Soil and Agrifood Institute, Cranfield University, MK43 0AL, United Kingdom
c. Department of Civil Engineering, Covenant University, Ota, Ogun State, Nigeria
* Corresponding author: r.sakrabani@cranfield.ac.uk

Abstract

The use of combined palm waste in activated carbon (AC) production is an efficient waste utilisation approach, especially for the adsorption of dyes and metal(oid)s from wastewater. Arsenic contamination is highly toxic, and the adsorption is considered an effective removal technique. In this study, Trona ore and ammonium citrate were used as activating agents. These contributed to the production of safer AC products. ACs were produced by microwave, characterised with Fourier Transform Infrared Spectrometry (FTIR), scanning electron microscope and adsorption process. The analysis show the following for direct microwave activation with Trona ore (MT-2); S_{BET}, 980 m^2/g; V_{total}, 0.865 cm^2/g and for biochar modification with ammonium citrate (MTA-5) S_{BET}, 1055 m^2/g; V_{total}, 0.785 cm^2/g. For Arsenic adsorption, the capacities are, 4.28, 4.70 mg/g respectively for AC (MTA-5) and modified biochar respectively (CTA-6). The outcome indicated that the parameters for getting an optimum adsorption were established at pH 6-7, absorbent dosage of 1 g/L at contact time of 25 minutes. The initial absorbate concentration of 250 µg/L at the temperature of 26 °C. The FTIR were compared and it shows that AC has a greater presence of triple bond, hydroxyl and with numerous active sites appropriate for adsorption than modified biochar. Furthermore, the indication of resilient bond linking As (V) and chemical functional groups of adsorbent surface shown by the pseudo-second-order kinetics model; which, correlates by adsorption. Trona ore is an effective activating agent for oil palm waste and the resultant AC is effective in arsenic adsorption.

Keywords: activated carbon, adsorption, ammonium citrate, arsenic, oil palm waste, trona ore

Figure E-1 Journal paper prepared for publication

E.2 FTIR for trona ore activated carbon

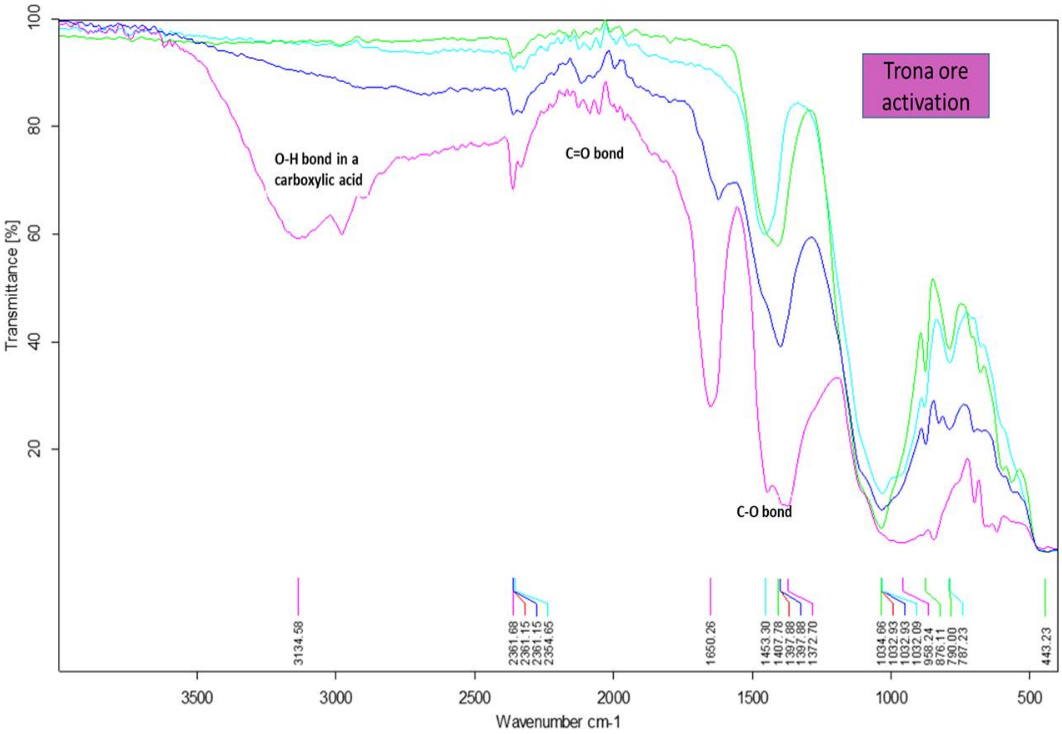


Figure E-2 FTIR illustration of activated carbon used in adsorption

E.3 Characterisation of activated carbon produced under different conditions

Table E-1 The characteristics of CPW and the comparison of porosity structure of the AC for arsenic adsorption

Activation mode	Activation time	Activating agent	BET surface area (m^2/g)	V_{micro}	V_{meso}	Total pore volume (cm^3/g)	Adsorption capacity (mg/g)
Conventional (CT-1)	1 hr	Trona ore	920	0.354	0.356	0.840	2.65
Microwave (MT-2)	20 min	Trona ore	980	0.380	0.256	0.865	4.28
Conventional/Microwave (CMT-3)	20 min	Trona ore	900	0.380	0.310	0.660	1.66
2-stepConventional (2CT-4)	1 hr	Trona ore	870	0.162	0.286	0.622	1.44
Microwave (MTA-5)	20 min	Trona ore/ Ammonium citrate	1055	0.350	0.374	0.785	4.70
Conventional (CTA-6)	1 hr	Trona ore/ Ammonium citrate	955	0.215	0.280	0.750	2.12

E.4 Adsorption kinetics and isotherm models

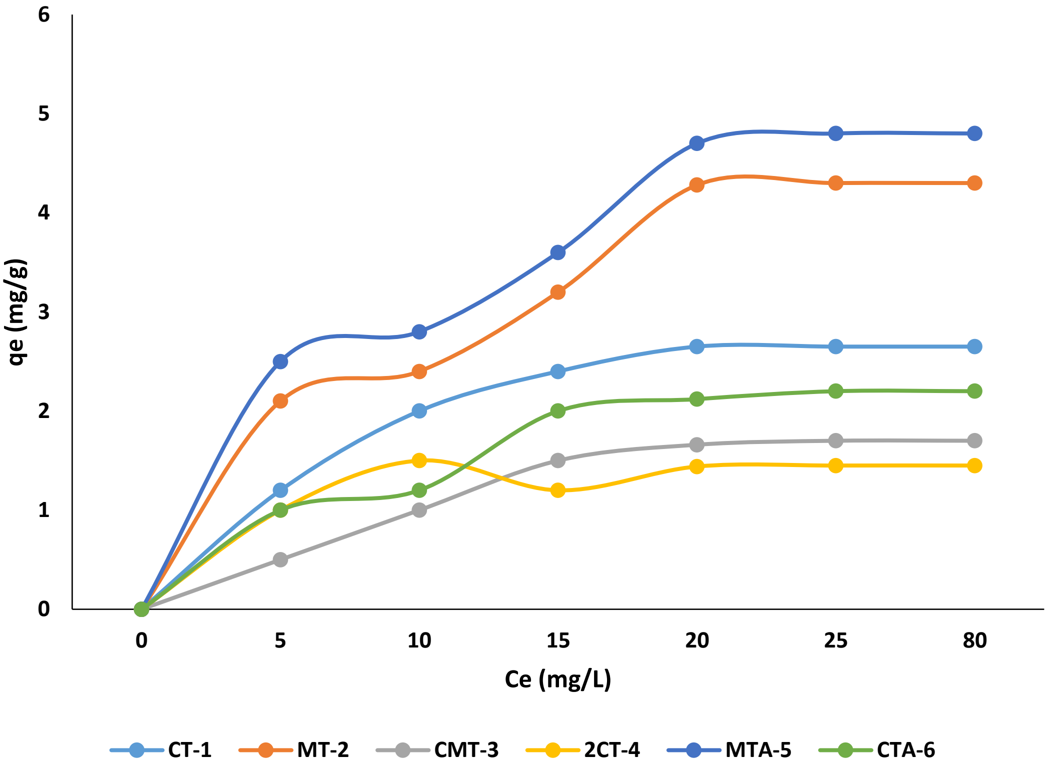


Figure E-3 Adsorption isotherms simulations for As (V) adsorption by AC at initial concentrations of 10–100 mg/L at 25 °C

Table E-2 The characteristics of CPW and the comparison of porosity structure of the AC for arsenic adsorption

Isotherm	Parameters	Arsenic concentration (mg/L)			
		6	30	65	100
Pseudo first order	K1	0.014	0.015	0.004	0.004
	R2	0.75	0.88	0.98	0.91
	q_{cal}	1.14	1.90	14.2	52.40
Pseudo second order	K2	0.06	0.04	0.01	0.012
	R2	0.999	0.999	1.000	0.999
	qe	9.4	17.1	25.5	28.50
Intra-particle	K_{diff}	0.320	0.635	1.055	1.285
	R2	0.902	0.875	0.865	0.858
	C	5.08	8.83	8.38	5.28

E.5 The effect of adsorbent dosage

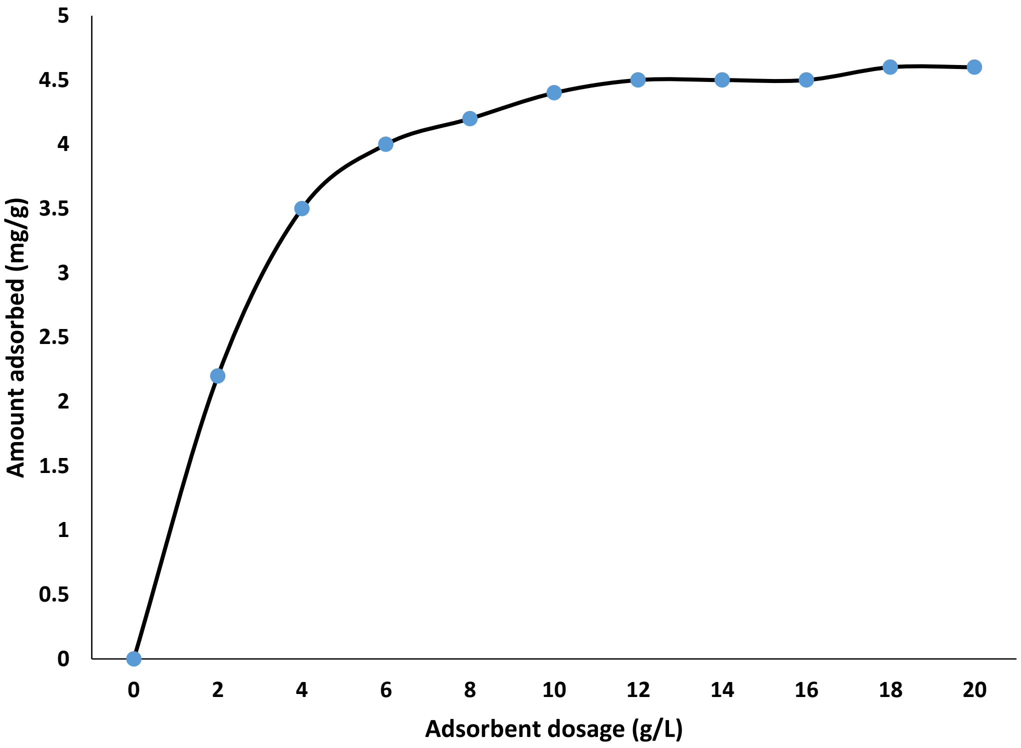


Figure E-4 Adsorbent dosage relationship with adsorption capacity for MTA-5

E.6 The effect of solution pH

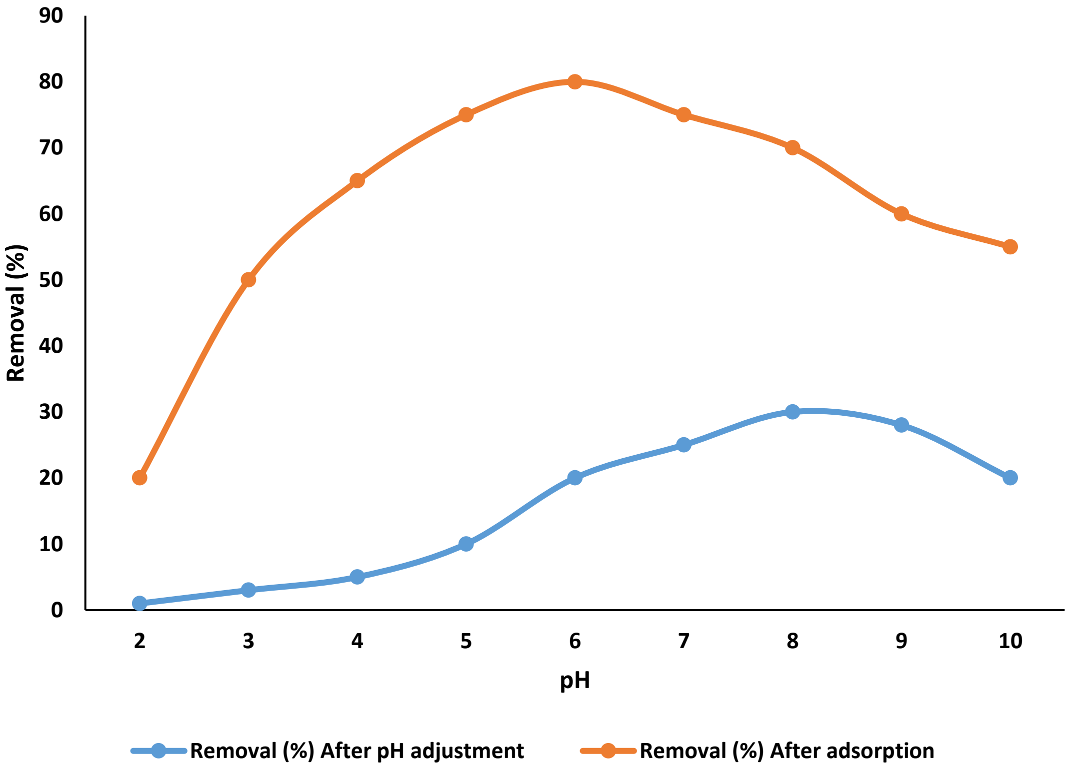


Figure E-5 Removal of arsenic at diverse pH for 25 ^{o}C, adsorbent dosage, 10 mg/L; initial concentration, 20 mg/L

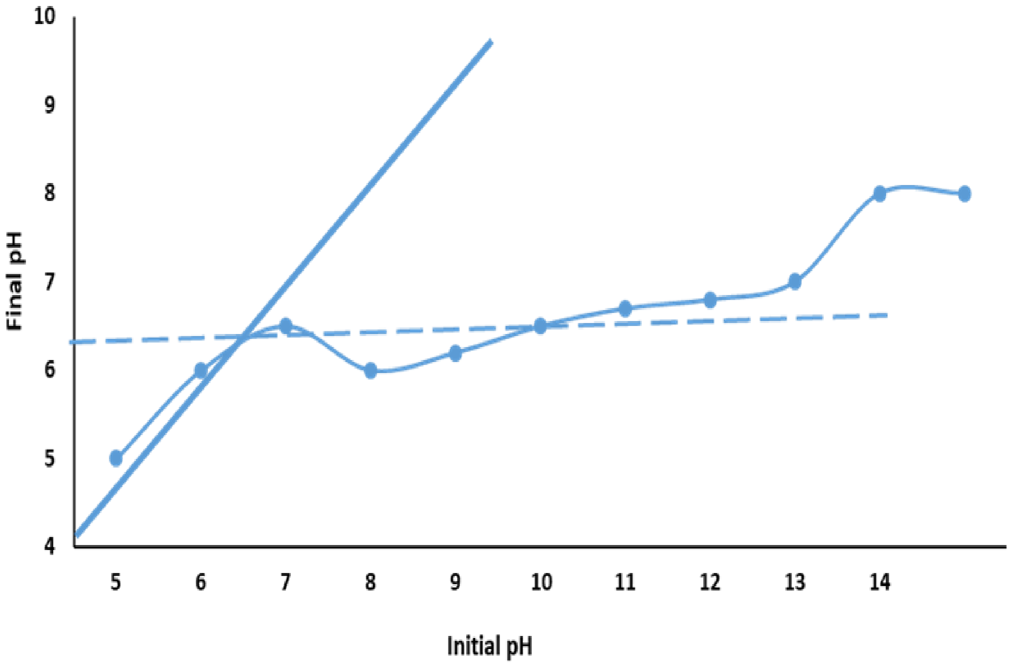


Figure E-6 Final pH after arsenic adsorption at various initial pH

This study evaluates the adsorption parameters of CPWAC for As (V) ions removal. The outcomes validated that the adsorption efficiency is hugely reliant on pH of the solution. Additionally, the isotherm study established the positive adsorption of As (V) process, agreeing to Langmuir adsorption isotherms. The kinetic of adsorption can be designated by pseudo-second-order model and intraparticle diffusion model as a model of transmission. The intended thermodynamic factors supported the exothermic and spontaneous status of the As (V) adsorption process using OPWAC. Oil palm waste can be utilised efficiently in AC production. The results of the current study show that the use of Trona ore for AC production is efficient and modification with Ammonium citrate improves adsorption efficiency for the removal of As (V) from wastewater. There is an increase in the percentage removal of arsenic by 4.8 % with direct activated

AC and biochar modified AC respectively. This is due to the higher S_{BET} of MTA-5 with 1055 m^2/g than MT-2 with 980 m^2/g. The adsorption capacity is relatively reliant on the pH of the solution and the kinetic of the sorption is interpreted by pseudo-second-order model. There is non-linearity all the parameters influence the adsorption and must be in equilibrium for optimum adsorption of arsenic in the medium. The variation in in Fourier transform infrared spectrometry illustrates the existence of triple bonds and hydrophilicity of the produced AC from both techniques.