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# Integrating life cycle assessment and characterisation techniques: A case study of biodiesel production utilising waste *Prunus Armeniaca* Seeds *(PAS)* and a novel catalyst

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## Abstract

*Prunus Armeniaca* seed oil was utilised as a waste biomass feedstock in biodiesel production via a novel catalytic system ($SrO-La_2O_3$) based on different stoichiometric ratios. The catalysts have been characterised and followed by a parametric analysis to optimise catalyst results. The catalyst with a stoichiometric ratio of Sr: La-8 (Sr-La-C) using parametric analysis showed an optimum yield of methyl esters is 97.28 % at 65 ℃, reaction time 75 minutes, catalyst loading 3 wt.% and methanol to oil molar ratio of 9. The optimum catalyst was tested using various oil feedstocks such as waste cooking oil, sunflower oil, PAS oil, date seed oil and animal fat. The life cycle assessment was performed to evaluate the environmental impacts of biodiesel production utilising waste PAS, with 1000 kg of biodiesel produced as a functional unit. The recorded results showed the cumulative abiotic depletion of fossil resources over the entire biodiesel production process as 22920 MJ, global warming potential as 1150 kg $CO_2$ equivalent, acidification potential as 4.89 kg $SO_2$ equivalent and eutrophication potential as 0.2 kg $PO_4^{3-}$ equivalent. Furthermore, the energy ratio (measured as output energy divided by input energy) for the entire production process was 1.97. These results demonstrated that biodiesel obtained from the valorisation of waste PAS provides a suitable alternative to fossil fuels.

***Keywords:*** $SrO-La_2O_3$, synergistic effect, *Prunus Armeniaca* seed oil, Waste biomass seed, Circular economy, Life cycle assessment

## Highlights

- Valorisation of sustainable waste *Prunus Armeniaca* Seeds (PAS) into biodiesel fuel.
- The synthesised catalysts showed a synergistic effect and formation of La-O-Sr.
- Parametric study showed optimum biodiesel yield of 97.28 %.
- Net energy ratio for PAS biodiesel production using SrO-$La_2O_3$ catalyst was 1.97.
- LCA showed global warming potential of PAS biodiesel as 25.4 g $CO_2$ eq/MJ.

## 1.0 Introduction

Modernisation based on industrial growth can lead to a better economic position in any location in which it is constituted. (Kleiman et al., 2021; Rezania et al., 2019). However, industrial growth causes a rise in the energy and transportation demands which are heavily dependent on fossil-based fuels (Andreo-Martínez et al., 2020). As a result, fossil-based fuel reserves are declining. Moreover, excess consumption of fossil-based fuels either for energy generation or transportation causes greenhouse gas (GHG) emissions causing climate change (Kan et al., 2020). Nevertheless, both concerns related to the consumption of fossil-based fuels can be addressed by introducing alternative environment-friendly fuel sources (Erdiwansyah et al., 2019), (Hernández and Martín, 2017).

One such alternative can be biodiesel derived from waste biomass (Al-Muhtaseb et al., 2021). Using waste biomass for biodiesel production is also in line with the circular economy approach. The circular economy principles in which materials are reduced, recirculated, reused, recycled and recovered are being adopted in many regions (such as in the European Union and China) (2020). Moreover, biodiesel is being promoted as one low-carbon alternative to fossil fuels as it could help reduce GHG emissions from transport. However, there are also concerns that its wider deployment could lead to unintended environmental consequences and increased costs. For example, there are concerns related to increasing biodiesel production, such as upward pressure on food prices, GHG emissions increase through the direct and indirect land-use change from production of biodiesel feedstocks, and the risks of soil and water degradation resources and ecosystems (Ali and Fadhil, 2013; Fadhil and Saeed, 2016). The use of first-generation feedstocks, such as corn, has become a particularly contentious issue, largely owing to the scarcity of land for food production and concerns over diverting agricultural land into fuel production. Some of these issues have been addressed by using second-generation feedstocks; however, the economic viability of some second-generation biodiesels remains disputable in the current economic context, largely because of the low oil prices.

In this study, Prunus Armeniaca seeds shells were used for production of second genereation biodiesel. *Prunus Armeniaca* is an edible fruit grown in colder regions and originates from the Asian region, and has abundant production (4.1 MT/year) (Kalia et al., 2017). *Prunus Armeniaca* belongs to the Rosaceae family and is thought to be polymorphic compared to other grown fruits

. Seeds of *Prunus Armeniaca* are a by-product of this fruit and are abundantly available. These can be utilised for second-generation biodiesel production. Utlising PAS for biofuel production can help overcome waste management issues.

Recently, research on biodiesel production focused on using catalysts to enhance production, minimise energy requirement, and reduce the processes' environmental impacts (Fadhil et al., 2020a; Fadhil et al., 2020b). The transition of catalysis systems from homogeneous to heterogeneous phase for biodiesel production via transesterification is one of the major breakthroughs to tackle the cost of biodiesel. The reusability and effectiveness of a heterogeneous catalyst make it suitable for biodiesel production in terms of product quality and cost(Mardhiah et al., 2017). Several heterogeneous catalysts are being used for biodiesel production, which includes alkaline earth metal oxides (MgO, CaO, SrO and BaO)(Al-Muhtaseb et al., 2020; Al-Muhtaseb et al., 2021; Chen et al., 2017; Jamil et al., 2021; Wan Omar and Amin, 2011), transition metals ($MnO_2$, $ZrO_2$, MoO and $Fe_2O_3$), carbon (Banerjee et al., 2019; Jamil et al., 2018; Jamil et al.), $La_2O_3$, $Al_2O_3$, SiO and CeO (Du et al., 2018; Du et al., 2019; Lin et al., 2020; Marinković et al., 2017; Yan et al., 2016).

Although several combinations of metallic oxides and active metals have been evaluated for biodiesel production, more recently, there has been a focus on catalysts that can reduce biodiesel production costs by reducing the intensive processing conditions (Fadhil et al., 2019). Yup et al. studied the combination of $La_2O_3$ with calcium oxide as a catalyst and reported relatively high biodiesel yield. Despite this catalyst being not reusable in the repeated experimental runs, it tends to deactivate rapidly by leaching CaO (Taufiq-Yap et al., 2014), tending to decrease the biodiesel yield. Jamil et al. studied the activity of several alkaline earth metal oxides with carbon as a catalyst for biodiesel production and found that SrO-Carbon is the most suitable catalyst with intensive processing conditions (Jamil et al., 2021).

When heterogeneous catalysts are being used for biodiesel production, different process dynamics were faced, which includes higher temperatures (65-150 ℃), more reaction time (2-4 hours), higher oil to methanol ratio (6-20) and catalyst loading (1-6 wt.%) (Nehdi et al., 2015; Rashid et al., 2014). Therefore, the current research is specifically focused on examining suitable combinations of different oxides as catalysts that can offer high biodiesel yield, along with processing conditions similar to homogeneous catalyst systems for biodiesel production. Keeping this fact in mind, a new combination of metallic oxides (SrO with $La_2O_3$) was experimented with, which is highly suitable and stable due to high activity towards biodiesel production. Furthermore, the environmental impacts of converting waste *Prunus Armeniaca* seed to biodiesel using SrO-$La_2O_3$ as a heterogeneous catalyst was evaluated using life cycle assessment (LCA). It is a comprehensive tool that measures the environmental impacts of production processes to assist in robust decision-making for sustainable development (Al-Mawali et al., 2021; Banerjee et al., 2019; Bolaji et al., 2021; Brigljević et al., 2019; Niero and Kalbar, 2019; Schmidt Rivera et al., 2020). It is imperative to evaluate and substantiate environmental impacts using LCA, because circular economy approaches may not necessarily be environmentally sustainable. The current research work is novel of its kind, as combination of metallic oxides (SrO with $La_2O_3$) was not used before specially of biodiesel production from Prunus Armeniaca seeds oil according to authors knowledge. Moreover, determination of environmental impacts of converting waste *Prunus Armeniaca* seed to biodiesel was evaluated using life cycle assessment (LCA).

## 2.0 Materials and Methodology

### 2.1 Materials

*Prunus Armeniaca* seeds shells (PAS) (5kg) were collected from Muscat-Oman and washed thoroughly with water to remove any fruit remaining and sun-dried for a week. The dried PAS were crushed and ground prior to extraction. Soxhlet apparatus was used to extract oil from powdered biomass by applying the official extraction method Am 2-93 (Jamil et al., 2016). The extracted oil from PAS was collected and stored in an airtight container in the laboratory until processed further. The oil yield obtained by extraction was 18.7 wt.%. The chemicals used for the catalytic systems synthesis, including n-Hexane, lanthanum nitrate hexahydrate, strontium nitrate, potassium carbonate, potassium hydroxide, were reagent grade and purchased from Sigma-Aldrich.

### 2.2 Catalyst Synthesis and characterisation

The co-precipitation technique was adopted to synthesise the required series of catalysts (Jamil et al., 2018). The series of catalysts just vary in the stoichiometric ratio of strontium to lanthanum in the metallic oxide framework. Firstly, in 100 ml of deionised water, both precursor materials (lanthanum nitrate hexahydrate and strontium nitrate) were added. Then, with the help of basic potassium hydroxide (1 M) solution, carbonate (0.25 M) was added to maintain the pH of the solution to 10 with continuous stirring. After the uniform mixing of solution for three hours, when its pH was maintained at 10 the mixture was then allowed to rest for overnight, and the solution beaker was covered with aluminium foil to avoid any kind of contamination. The precipitated solution was filtered and washed thoroughly with distilled water till it was neutralised. The filtered material was dried in an oven at 110 ℃ for 12 hours, and after drying, the material was calcined in a muffle furnace at 600 ℃ with a heating rate of 3 ℃/min for five hours.

The mixed metallic oxide is referred to as Sr-La-X, where X represents the stoichiometric ratio of both elements. The stoichiometric ratio of strontium to lanthanum was as Sr: La-4, Sr: La-6, Sr: La-8 and Sr: La-10, while catalyst samples were named as Sr-La-A, Sr-La-B, Sr-La-C and Sr-La-D, respectively. Prior to applying the synthesised catalyst for biodiesel production through transesterification of PAS oil, they were characterised using analytical techniques, including x-ray diffraction for phase analysis, x-ray photoelectron spectroscopy (XPS: Scienta Omicron, Germany) for surface analysis, high-resolution transmission electron microscopy (HRTEM) for morphology and energy dispersive x-ray for elemental analysis by using (JOEL JEM-2100, Japan) PANalytical, Xpert PRO machine, USA, Brunauer–Emmett–Teller (BET) for physicochemical properties was done by using ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA and carbon dioxide temperature-programmed desorption ($CO_2$-TPD) was carried out by using Thermo Finnigan TPDRO 1100, the USA for measuring basicity.

### 2.3 Methyl esters production and characterisation

Methyl esters were produced in a closed container (2 L), including a magnetic stirrer, temperature sensor, and condenser for continuous reactant refluxing. The reaction vessel was placed in the heating mantle to obtain the uniform temperature and obtain the desired reaction temperature. All the experiments (performed thrice to prove the accuracy) were conducted within the ranges defined for all independent variables (catalysts loading (wt%) from 1 to 5; methanol to oil ratio from 3 to 15; reaction time (min) from 30 to 90; and reaction temperature (ºC): 50 to 70).

PAS oil was poured into the reaction vessel and heated to the desired temperature prior to adding methanol and a catalyst. Methanol was mixed with a synthesised catalyst and added to a closed reaction vessel. The reaction mixture was subjected to continuous stirring and heating until the desired temperature was achieved for desired time. The reaction mixture was then allowed to cool down to room temperature. With the help of a centrifuge, a heterogeneous catalyst was separated from the reaction mixture and then poured into a separating funnel. The separating funnel reaction mixture was allowed to stay for 24 hours, and after that, two different distinct layers could be observed. The upper layer (methyl esters) and the bottom (bio-glycerol) were separated. Methyl esters were thoroughly washed with warm water to remove impurities and further analysis. The yield of methyl esters was calculated by equation 1

$$Yield = \frac{wt.of\ methyl\ esters}{wt.of\ oil} \times 100\% \qquad \text{(Eq. 1)}$$

The biodiesel composition was determined using gas chromatography-mass spectroscopy GC-MS which used the DB-Wax column in the Perkin Elmer machine. Standard procedures were followed to evaluate the fuel properties (American Society for Testing and Materials ASTM 6751, European EN 14214).

## 2.4 Life cycle assessment

The goal of using LCA was to evaluate the environmental performance of biodiesel utilising PAS oil, following ISO 14040: 2006 and ISO14044:2006 standards . SimaPro v9 software and Ecoinvent database were used for conducting LCA in the present study. This study used the cradle-to-gate attributional approach and did not include environmental impacts due to infrastructure processes associated with equipment production. The functional unit was 1000 kg of biodiesel produced using waste PAS. The production processes considered for LCA included: waste PAS transportation, oil extraction, preparation and reuse of catalyst, and transesterification.

## 3.0 Results and discussion

### 3.1 Detailed analysis of synthesised catalyst

X-ray diffraction analysis showed the different phases of the synthesised material (SrO-$La_2O_3$) by co-precipitation technique (Figure 1A). All samples of synthesised catalyst showed sharp diffraction lines in the XRD pattern, which depicts that parent $La_2O_3$ and all its modified forms with SrO are crystalline in nature. It has been reported earlier that crystalline phase catalyst shows better activity towards the reaction involving reactants with large oxygenated hydrocarbon chains (Al-Mawali et al., 2021; Lin et al., 2020). The XRD patterns showed that parent $La_2O_3$ has the definite diffraction lines at 2θ value of 26.2, 29.3, 40.1 and 46.2° (JCPDS 73-2141 library), demonstrating the purity of the material. Meanwhile, when parent $La_2O_3$ is modified with SrO, some additional diffraction lines were observed in the XRD pattern depicting the inclusion of active material into the parent material without changing its phase, and this can be attributed to the fact that active material SrO particles are immersed in pores of the parent material.

Moreover, some SrO species remained on the surface as well. The diffraction lines value at 22.1, 23.6, 34.5, 49.8 and 63.2° in SrO-$La_2O_3$ catalysts proved that active material is deposited to the parent support material. Therefore, according to XRD analysis, $La_2O_3$ is successfully modified with active material SrO without changing the phase of parent material.

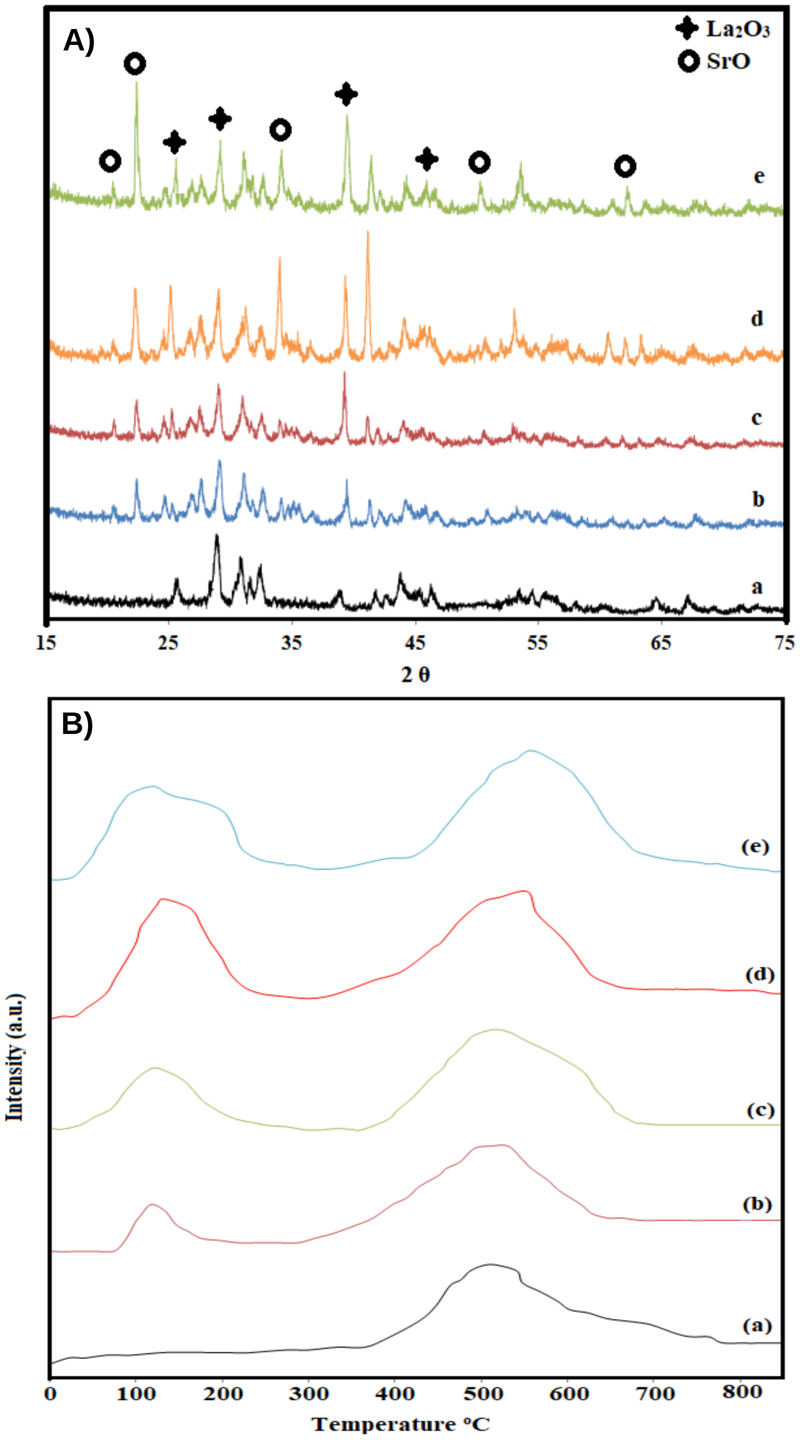


**Figure 1:** A) XRD diffractograms B) $CO_2$-TPD results for synthesised catalysts: (a) parent $La_2O_3$, (b) modified form of $La_2O_3$ with SrO with atomic ratio 4, (c) modified form of $La_2O_3$ with SrO with atomic ratio 6, (d) modified form of $La_2O_3$ with SrO with atomic ratio 8 and (e) modified form of $La_2O_3$ with SrO with atomic ratio 10.

The internal morphology of the synthesised catalyst performed using TEM highlighted better pore channels for reactants along products to transport (Figure 2). Moreover, during the elemental mapping, it was observed that both materials (SrO and $La_2O_3$) are well dispersed throughout the sample image. The uniform distribution of elements depicts that all the elements will be well exposed to reactants when used in the reaction. The exposure of all active elements to reactants will result in higher catalytic activity, and thus, higher yield of desired products.

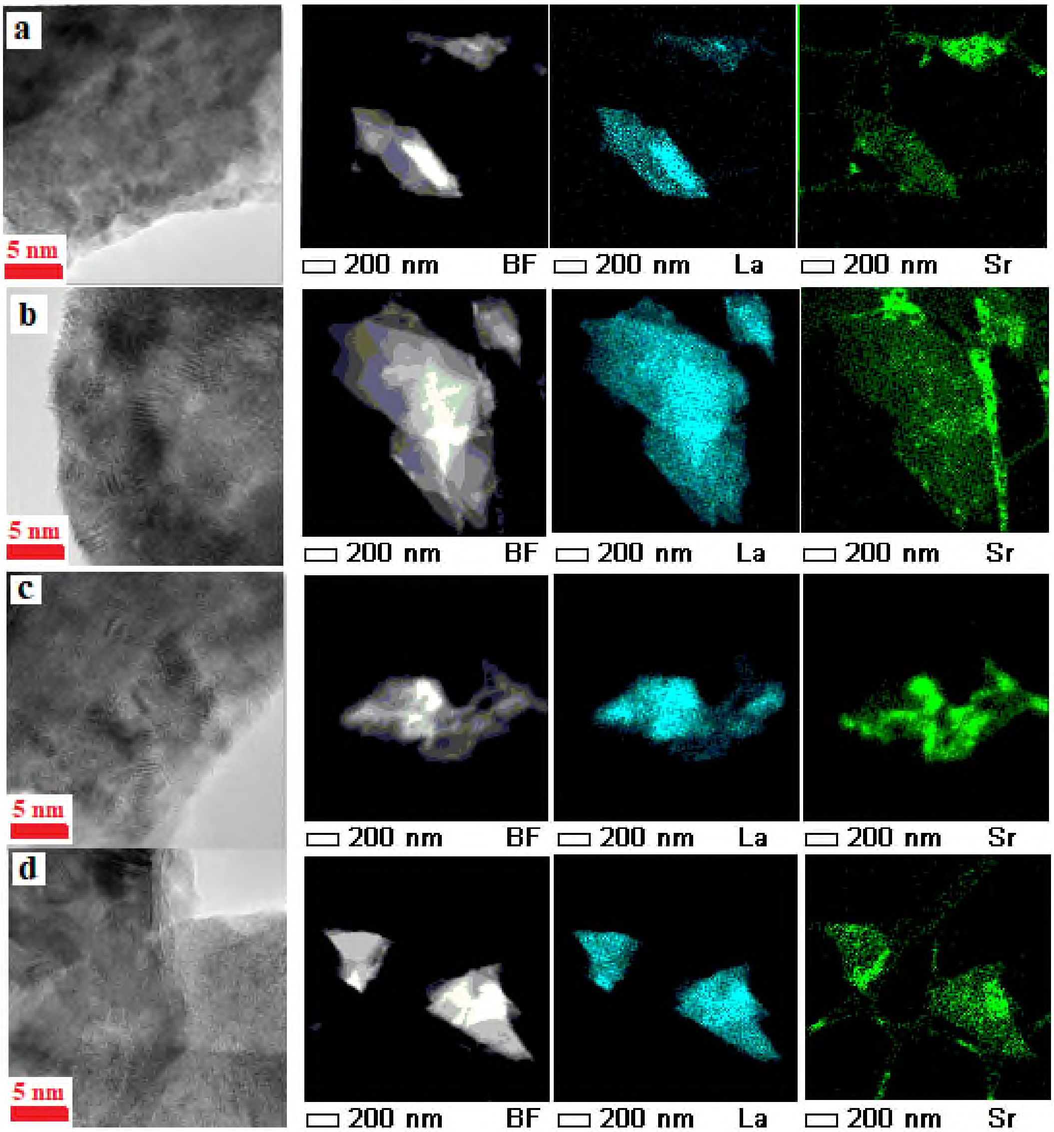


**Figure 2:** Images obtained by TEM for synthesised catalysts; (a) modified form of $La_2O_3$ with SrO with atomic ratio 4, (b) modified form of $La_2O_3$ with SrO with atomic ratio 6, (c) modified form of $La_2O_3$ with SrO with atomic ratio 8 and (d) modified form of $La_2O_3$ with SrO with atomic ratio 10.

The target application of synthesised catalyst was for methyl ester production through transesterification of PAS oil. Moreover, transesterification is usually supported by a basic catalyst, and the synthesised catalysts have metallic oxides that offer basic active sites in excess amount to take part in reaction (Teo et al., 2014). Therefore, $CO_2$-TPD was used for qualitative and quantitative analysis of the catalyst in terms of basic sites. The pattern referring to $La_2O_3$ shows that it possesses strong basic sites in a temperature range of 370-750 °C (Figure 1B). Typically, strong basic sites are due to the presence of anions or hydroxyl groups which shows the response against temperature when $CO_2$ is desorbed at higher temperatures. Moreover, when parent $La_2O_3$ is modified with SrO, the material showed two peaks in a pattern that depicts that by adding SrO in structure, weak basic sites are added, which appear to be within a temperature range of 80-220 °C. It can be noticed that when the amount of SrO is increased in the synthesised catalyst, the peak representing the weak basic sites broadens, which shows the addition of more basic sites into the catalyst.

The quantitative analysis of basic sites for synthesised catalysts is shown in Table S1, which are linked to the patterns in Figure 1B; e.g., for parent $La_2O_3$, there are only strong basic sites with a minimal amount of weak basic sites. When the other sample results were analysed, the quantity of weak basic sites increased and almost became equivalent for catalyst Sr-La-C. However, when the amount of SrO is increased further, the distribution is reshuffled, and weak basic sites decrease. The decrease in weak basic sites can be attributed to the fact that when SrO is increased, it tends to occupy the pores of catalyst, which let the less exposure of active to $CO_2$ to be adsorbed and then desorbed. So, this tends to decrease the amount of weak basic sites, and hence the chemical reaction will also be affected. Table S1 shows that the synthesised catalysts possess active sites that are basic in nature of both strengths depending on their composition, making them highly suitable for transesterification.

BET analysis was performed for all catalyst samples (Table S2). The surface area of any catalytic materials depicts the area of material that is to be exposed to the reactants. Moreover, pore diameter determines the ease with which the reactant material can enter the catalyst channels. The active sites within the pore channel will also be exposed to reactants, enhancing the product yield. It can be noticed that parent $La_2O_3$ possess a suitable surface area; however, it started to decrease upon the addition of SrO, which tends to fill the pores and forms a strong bond with parent material.

Moreover, regarding the pore diameter of the catalyst, it decreased as well upon the addition of SrO; however, it is still higher than 5.8 nm for all samples. It has been reported that the particle size of triglyceride is 5.8 nm, and all organic oils, including PAS oil, contains triglycerides in excess; thus, these triglycerides transform into methyl esters in the presence of catalyst and methanol (Tan et al., 2015; Wan Omar and Amin, 2011). Based on BET analysis, all synthesised catalysts can offer suitable pore channels to support the transesterification reaction to transform triglycerides to methyl esters by reacting with methanol. The BET results are in line with TEM analysis, in which elemental mapping depicted uniform distribution of active sites throughout the catalyst.

XPS analysis was carried out to understand the surface property of the synthesised catalysts. Figure 3a shows the survey spectra of synthesised catalysts, namely Sr-La-A, Sr-La-B, Sr-La-C and Sr-La-D. Apart from the typical elements such as oxygen (O), carbon (C), strontium (Sr) and lanthanum (La), no other contaminations were detected. Figure 3b shows the high-resolution O *1s* peaks for the synthesised catalysts. When the increasing stoichiometric ratio of strontium to lanthanum, O *1s* peak shifted to higher binding energy (Indicated with arrow). This could affirm the interaction or bond formation between La-O-Sr. Figures 3c and 4d show the core level high-resolution La *3d* and Sr *3d* peaks for the synthesised catalysts. Both peaks (La *3d* and Sr *3d*) were observed to be shifted to higher binding energy while increasing Sr content.

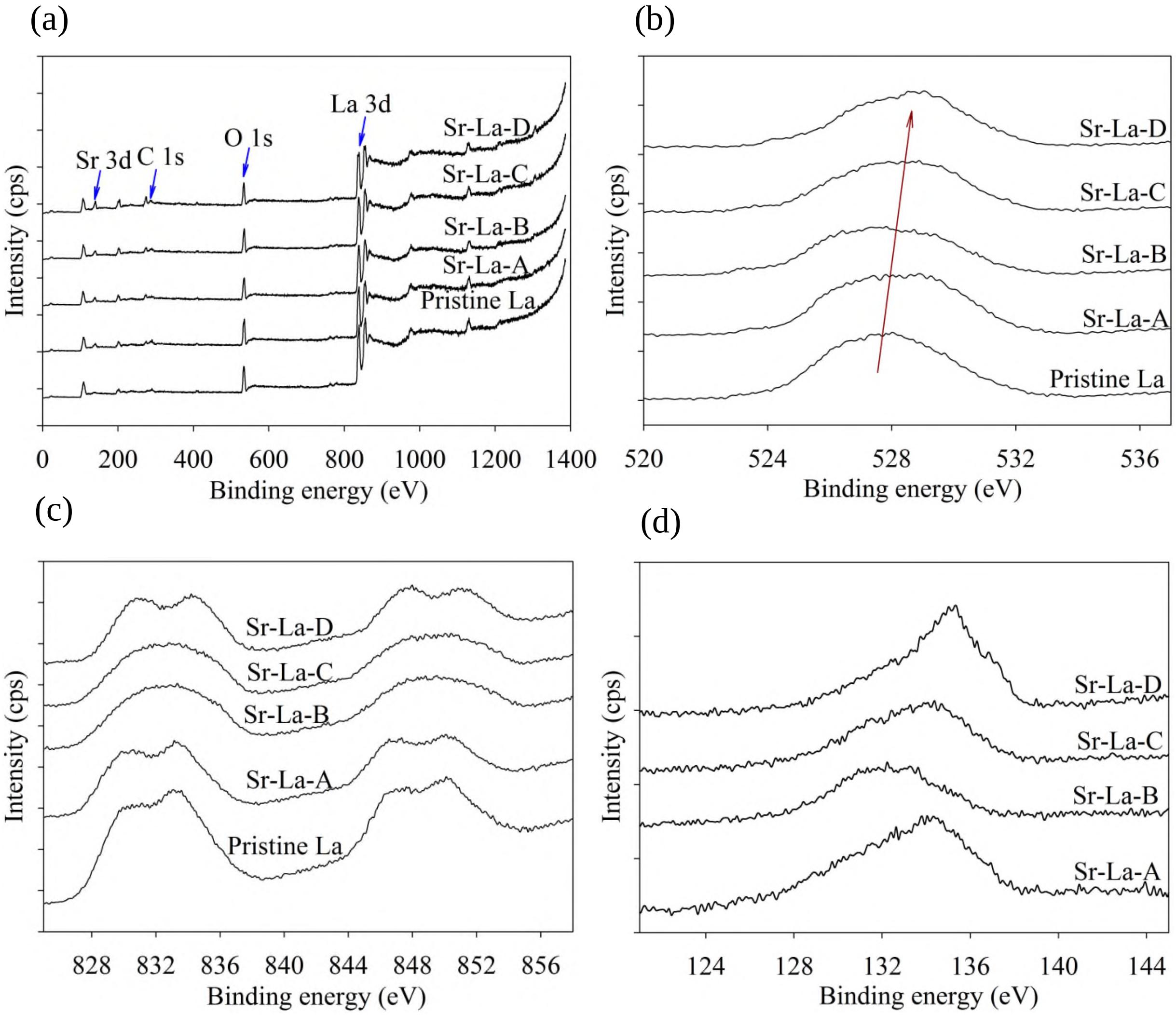


**Figure 3:** (a) XPS survey spectra (b) High-resolution O *1s* peaks (c) High-resolution La *3d* peaks (d) High-resolution Sr *3d* peaks for synthesised catalysts (Pristine La, Sr-La-A, Sr-La-B, Sr-La-C and Sr-La-D).

The surface composition of synthesised catalysts estimated from XPS survey spectra (Sr-La-A: O (75.9%), C (7.8%), La (13.6%), Sr (2.7%); Sr-La-B: O (74%), C (7%), La (14.6%), Sr (4.4%); Sr-La-C: O (69.9%), C (10.6%), La (14.6%), Sr (4.9%); and Sr-La-D: O (65.1%), C (12.2%), La (14.2%), Sr (8.5%)). It is worth noting that XPS is a surface-sensitive technique whereby the reported values were only reflected from the catalyst surface (0-10 nm range). Therefore, some deviation of atomic % concentration can be seen compared with the stoichiometric ratio of strontium to lanthanum. Moreover, the catalyst surface could be mainly covered with SrO (Sr concentration in Table S4) rather than $La_2O_3$, decreasing surface oxygen content while strontium content increases. This could be because of the difference in oxidation state between Sr (2+) and La (3+), where several oxygen occupied by Sr is less than La.

### 3.2 Optimising metallic oxides combination in catalysts

Four different types of catalysts with varying ratios of Sr and La were tested for the production of methyl esters by transesterification reaction, as shown in Figure 4A. It can be noticed that initially, when the ratio was kept at Sr-La-A, the biodiesel was quite low (59.89 wt. %). This observation of catalyst activity can be related to the presence of active sites in the catalyst as reported earlier in $CO_2$-TPD analysis as shown in Table S2 and Figure 1B that the concentration of active sites which are basic in nature is low; thus, this leads to offer a low yield of product methyl ester. However, when the atomic ratio of Sr to La increases, the biodiesel yield increases, and maximum yield is achieved when it is 8 (Sr: La-C). Therefore, the higher yield of methyl ester at a higher atomic ratio of Sr to La can be due to the presence of a higher quantity of basic active sites, as shown in Figure 4A as well.

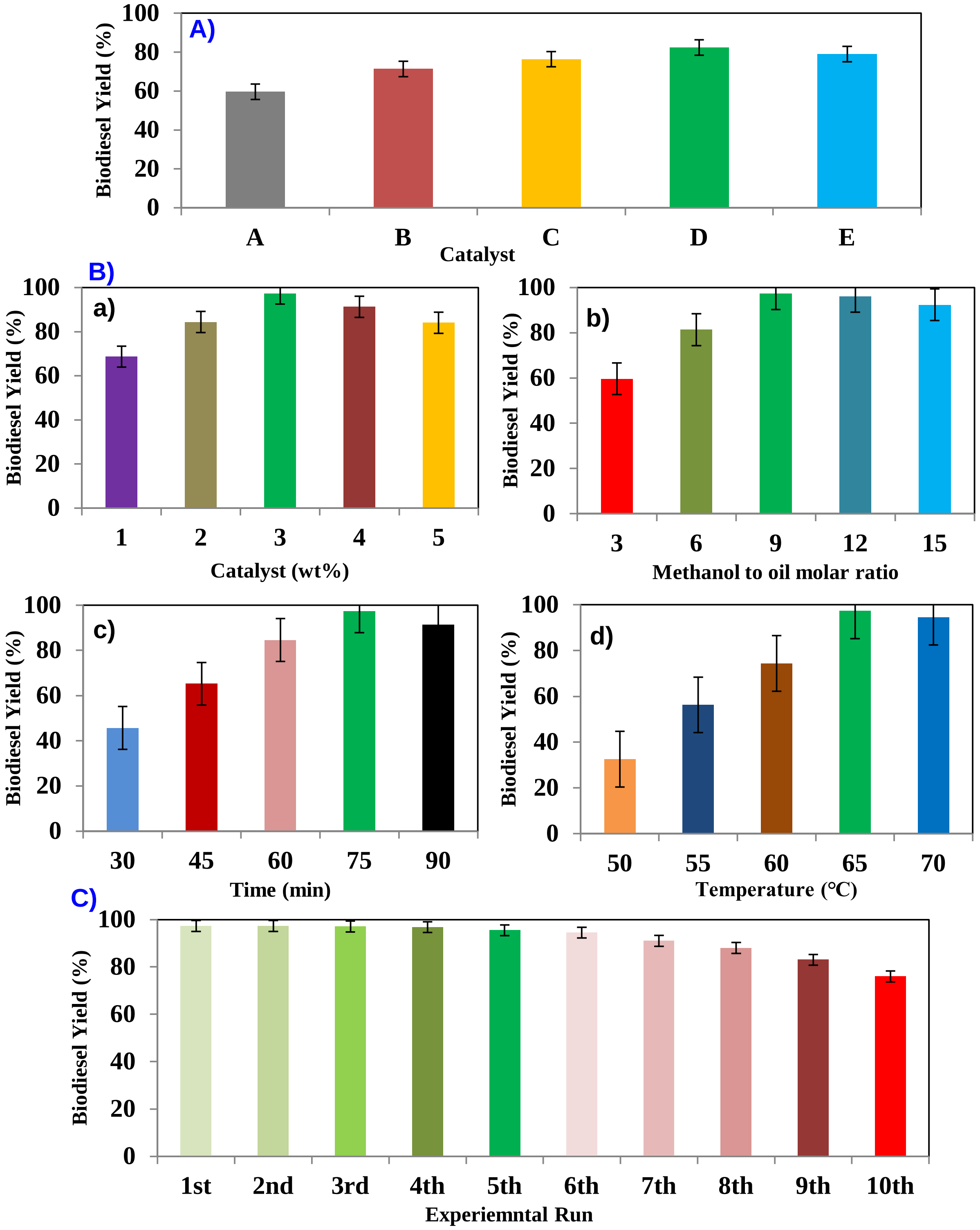


**Figure 4:** A) Biodiesel yield (%) for catalysts with varying concentrations of Sr and La. B) parametric study for:(a) catalyst loading, (b) methanol to PAS oil molar ratio, (c) reaction time and (d) reaction temperature. C) Evaluation of Sr: La-C catalyst reusability to produce biodiesel from PAS oil by transesterification.

Furthermore, when the ratio is changed and increased beyond 8 wt.%, the methyl ester yield decreases. Thus, even though the increase in the quantity of basic sites will increase the methyl ester yield, it can be related to the fact that transesterification becomes more favourable in the presence of weak basic sites than strong basic sites. Moreover, it has been reported that strong basic sites need intensive processing conditions; however, in current research work, the active catalyst gave an exceptionally higher number of weak basic sites; therefore, maximum yield was obtained at moderate operating conditions. Thus, the combination of metallic oxides Sr: La-C was used further to optimise methyl ester production.

Methyl esters production through transesterification is monitored by variation in four independent variables: temperature, time, catalyst loading, and methanol to oil molar ratios in response to methyl ester yield through parametric studies. Parametric study of the current process can be visualised in Figure 4B, in which the yield of methyl esters is given with reference to all process variables. Figure 4B(a) effect of catalyst on the methyl ester yield is given, and the parabolic trend is obtained within the defined range of catalyst loading. Initially, when catalyst loading was 1 wt.%, the methyl ester yield was quite low, which can be attributed to the fact that less catalyst is present in the reaction vessel, leading to fewer active sites available for reaction. Adding more catalysts to the reaction vessel, the yield started increasing and reached the maximum of 97% with 3 wt.% of catalyst in the reaction vessel. Increasing the amount of catalyst in the reaction vessel lets more active sites participate in the yield product's reaction. Despite this fact, it can be noticed that when the catalyst amount is increased beyond the 3 wt.%, the trend becomes parabolic, which means that the yield of methyl esters starts decreasing. This can be attributed to the fact that: (1) increasing the heterogeneous catalyst in the reaction vessel can cause the mass transfer limitation for reactants and products, leading to a reduction in the product (methyl ester), and (2) a higher amount of catalyst caused difficulty in agitation (Shan et al., 2018; Yan et al., 2016). Therefore, (3 wt.%) of catalyst was considered as optimum catalyst content.

Transesterification involves two reactants, methanol, and oil, which react in the presence of a catalyst to give methyl esters. So, based on the stoichiometric calculation, three moles of methanol is required for one mole of oil to give methyl ester and glycerol. As methanol is a limiting reactant, it will help the reaction proceed forward due to the reversible nature of the reaction if used in the excess amount. Thus, the methanol to oil molar ratio started from 3, as shown in and observed that yield of product methyl esters is very low (Figure 4B (b)). However, an increasing trend was observed when the ratio is increased beyond three and observed that the maximum yield of methyl esters was obtained at methanol to oil ratio of 9. When the methanol to oil molar ratio increased further, the product methyl ester yield started decreasing and ending up the parabolic shape of product yield within the defined range (3-15) of methanol to oil molar ratio. The product methyl ester yield decline at a higher ratio can be due to the phase separation issue of product and by-product, thus tending to decrease the methyl ester yield.

Residence time for transesterification reaction leads to the formation of methyl esters (biodiesel) depending on the type of catalyst. Typically, when heterogeneous catalysts are used, reactants need more time to interact with the active sites on the surface and within the pores of the catalyst. As in current research work, a heterogeneous catalyst is used; thus, reaction time is monitored to get optimum value (Figure 4B(c). When the reaction time was kept for 30 minutes, the methyl ester yield was quite low (42.21 %), indicating that the time for reactants was not enough to get the desired product. However, upon increasing the residence time, the yield of methyl esters started increasing and got up to the maximum (97%) when the reaction time was kept at 75 minutes. This shows that reactants got enough time to react when the residence time was increased, thus providing a higher biodiesel yield. However, when the time was increased beyond 75 minutes, the methyl ester yield declined due to difficulty in a downstream process.

Temperature variation demonstrated a parabolic-shaped trend against the methyl ester yield (Figure 4B(d). Initially, when the temperature is kept low at 50 °C and methanol and oil are allowed to react in the presence of a synthesised catalyst, the yield of methyl ester product was low, which is due to lower reaction temperature than the desired reactant molecules required to react and transform to methyl esters. However, by increasing the reaction temperature, the methyl ester yield increased and reached a maximum of 97.28 % at 65 °C.

However, at a temperature near the boiling point of methanol, the methyl group becomes unstable and rapidly dissociate from the parent molecule yielding methyl ester. However, when the temperature was increased beyond 65 °C, the yield of methyl esters started decreasing, which might be due to a decrease in the availability of methanol in reaction media. Thus, the optimum temperature was 65 °C which showed the maximum yield of methyl esters.

The parametric study demonstrated that the optimum yield of methyl esters was 97.28 % when process temperature was 65 °C, reaction time 75 minutes, catalyst loading 3 wt.% and methanol to oil molar ratio of 9. Furthermore, this study revealed that the synthesised catalyst is highly active, and importantly, the processing conditions such as temperature, time, and catalyst loading are not that intensive as reported earlier by researchers while using heterogeneous catalysts. Thus, the currently synthesised catalyst process can be economically feasible for biodiesel production from waste biomass when conducting the economic evaluation in future work.

### 3.4 Fuel properties of biodiesel

To assess the commercial suitability of producing methyl esters (biodiesel) from PAS, the oil content was analysed (Supplementary Material: Table S3) and potentially used as source oil for biodiesel production. In the presence of saturated components, biodiesel offers poor low-temperature properties, as it can probably solidify when used as fuel in colder regions. The biodiesel produced from PAS oil shows quite suitable low-temperature properties, such as the cloud point was 1.2 ℃, pour point -3.58 ℃, and cold filter plugging point was -2.47 ℃. Cloud point is the temperature when the assistance is observed on top of a liquid surface which might be due to saturated components, and pour point is the minimum temperature that biodiesel after that which biodiesel ceases for five seconds and does not flow.

The density of biodiesel was observed as 898 kg/m$^3$ (EN14214 limit is 860-900 kg/m$^3$). The fuel density is linked to the intermolecular spacing; i.e., if the density is higher, it means that the quantity of biodiesel will increase for a similar volume of biodiesel with low density. Moreover, highly dense biodiesel can also cause difficulty in atomisation in the engine, affecting combustion and ultimately affecting engine efficiency. The energy density of product biodiesel was measured as calorific value and 45.28 MJ/kg, which is in close range to diesel (45.59 MJ/kg). It shows that PAS based biodiesel is suitable for commercial application based on energy density value.

The kinematic viscosity of biodiesel was measured as 3.2 mm$^2$/s at 40 °C and was within the ranges defined by ASTM 6751 (1.9-6.0 mm$^2$/s) and EN14214 (3.5-5.0 mm$^2$/s). Kinematic viscosity indicates interlayer resistance, e.g. if the viscosity of biodiesel is higher and not within the range defined by standards, then it becomes difficult for the biodiesel to be injected for combustion, leading to poor efficiency of the engine.

Biodiesel acid value was observed as 0.17 mg KOH/g (ASTM6751 and EN14214 set the maximum as 0.5 mg KOH/g). Biodiesel acid value is used to determine the acidic content in the product. For instance, a higher acid value reflects a higher number of free fatty acids, which can cause storage problems as it will be corrosive and problematic for transportation.

The product biodiesel was also tested to measure its Cetane number, which was 72 and satisfied the standard value given by ASTM6751 (47 min) and EN14214 (51 min). Cetane number is also known to be the anti-knocking property of producing biodiesel. Moreover, the Cetane number of fuel directly affects fuel efficiency as biodiesel with lower Cetane number can cause the delay in the ignition in the engine; thus, a higher Cetane number of biodiesel is preferred.

One of the main properties of biodiesel to be determined is a flash point directly related to its storage and transportation, as it is the maximum temperature that fuel can sustain without being ignited. So, it is the main parameter to be part of the standard operating procedure of fuel; thus, the measured value of flash point of producing biodiesel is 168 ℃, and it satisfies the standard value given by ASTM6751 (93℃ minimum) and EN14214 (120℃ minimum).

One of the many reasons to claim biodiesel as environment-friendly fuel is that it does not emit SOx, which was observed as 0.011 mg/kg, which satisfies the standard value given by ASTM6751 (15 mg/kg maximum) and EN14214 (10 mg/kg maximum). Therefore, it is safe for the environment when combusted in an engine.

### 3.5 Catalyst evaluation for methyl ester production using different oils

The activity and feasibility of synthesised catalyst were evaluated via transesterification reaction for oils obtained from several feedstocks such as waste cooking oil, sunflower oil, PAS oil, date seed oil and animal fat. It can be noticed that the sunflower oil (which contains a minimum quantity of FFAs) gave a maximum yield of biodiesel in the presence of a synthesised catalyst compared to other nonedible oils

Moreover, the performance of the catalyst was quite suitable based on biodiesel production (Supplementary Material: Figure S1), oils, regardless of their source, gave biodiesel yield about >90%. Thus, ensuring that catalyst is not selective for certain oil feedstock and can be used for all organic oils, either edible or nonedible for biodiesel production. When biodiesel is produced on a large scale for energy generation and transportation purposes, raw bio-oil is used based on its availability; in order to keep various biomass feedstock usable within the process throughout the year, these kinds of catalysts are preferred for commercialisation.

### 3.6 Reusability

Methyl esters production through methanolysis in the presence of a synthesised catalyst (SrO-$La_2O_3$) was tested for regenerated catalyst (Figure 4C). Furthermore, to show the feasibility of the commercial application, a reusability study was conducted for SrO-$La_2O_3$, and it remained highly active till the sixth repeated experimental run for methyl ester production. Organic matter, either non-reacted reactants or products that remained with catalyst, can easily be removed by thorough washing with methanol followed by heat treatment. Moreover, post-treatment high activity of the synthesised catalyst for methanolysis shows the affinity of methanol towards the product methyl ester and bio-glycerol, which showed that when an excess amount of methanol after a certain limit was used in the reaction, the decrement in methyl esters yield was observed which was just due to difficulty in a downstream process.

Furthermore, when the catalyst was regenerated for a seventh onward experimental run, a rapid decrease in methyl ester yield was observed until the tenth experimental run. The decrease in the yield of methyl esters can be attributed to a reduction in the active sites of catalyst sites, which was also recorded in EDS analysis of catalyst performed after each experimental run and found that after the seventh run, the Sr wt.% showed a rapid reduction (Table S4). Moreover, as reported in parametric analysis, excess catalysts caused a reduction in biodiesel yield. This was also observed here as the Sr component is reduced due to leaching into the reaction mixture, which can cause the side reaction of soap formation to occur by joining with diglyceride intermediate, thus reducing the methyl ester production.

### 3.7 Life cycle assessment

Herein, we have analysed SrO-$La_2O_3$ catalyst, which was then utilised to produce biodiesel using PAS oil. Further to this, LCA was used to evaluate the environmental impacts of the overall production chain. The system boundary consisted of (i) Waste PAS transportation, (ii) Oil extraction, (iii) Preparation and reuse of SrO-$La_2O_3$ catalyst, and (iv) Transesterification of PAS oil to produce biodiesel (Figure 5).

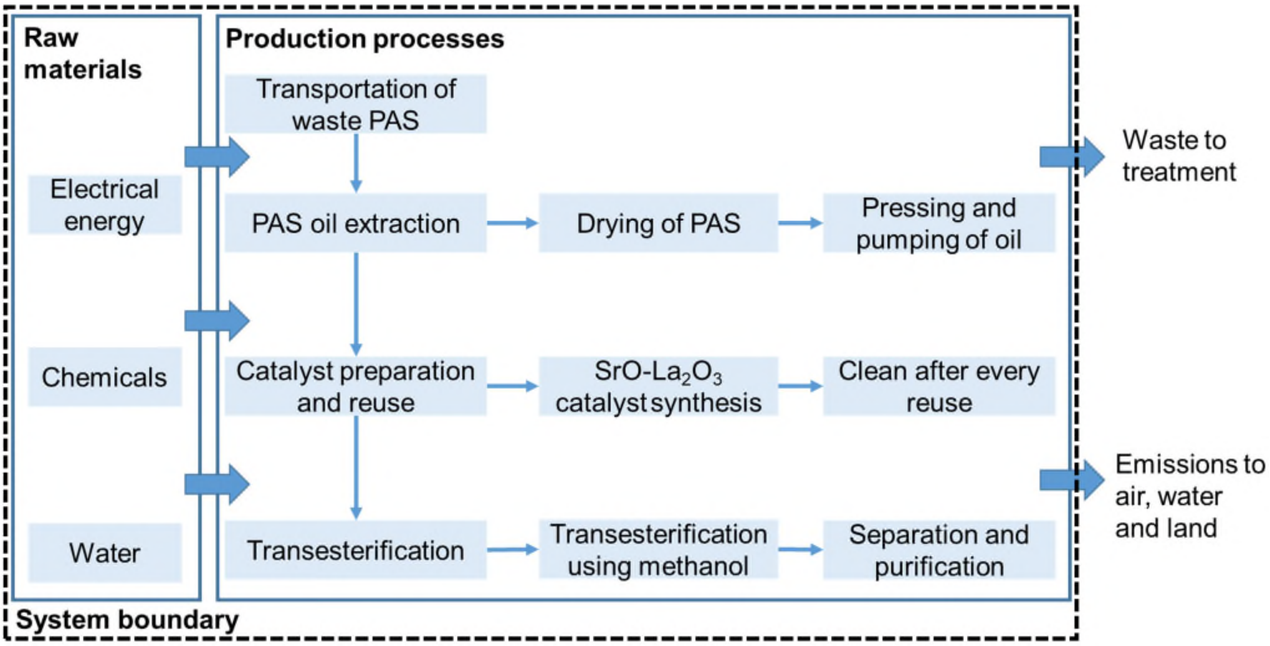


**Figure 5:** System boundary of conversion of waste *Prunus Armeniaca* seeds (PAS) to biodiesel.

### 3.7.1 Inventory analysis

The LCA conducted in the present study had a cradle-to-gate attributional approach. The production of PAS was not included in the system boundary as it is a waste-derived feedstock. Moreover, a distance of 200 km from farms to oil extraction unit was considered for waste PAS.

The PAS oil extraction in the present study used soxhlet extraction (Section 2.1). However, a large scale commercial production of PAS oil would likely include pressing and pumping of oil, for which electrical energy requirements were sourced from Fridrihsone et al. (Fridrihsone et al., 2020). Therefore, for efficiency of 19% during oil extraction, 5681 kg of waste PAS needs to be transported to produce 1028 kg of PAS oil (with 5% moisture weight loss during drying of waste PAS).

This study also considered catalyst preparation and reuse as a subset in the system boundary. For the production of 1000 kg of biodiesel, considering catalyst loading of 3 wt% (Section 3.3) and use of the catalyst for a total of seven runs (Section 3.6), it can be calculated that 5.8 kg of SrO-$La_2O_3$ will be utilised. It was assumed that 50 mL of deionised water was used for the dissolution of 2 g of precursor materials. Though in this study, the precursor materials used to produce catalysts were lanthanum nitrate hexahydrate and strontium nitrate, there was no literature identified for the production of these chemical reagents. However, Ecoinvent document reported environmental impacts of $La_2O_3$ production (Althaus, 2007).

Moreover, the study by Nuss et al. (Nuss and Eckelman, 2014) recorded impacts due to metallic production of Sr and reported $SrCO_3$ as an intermediate product. Therefore, environmental impacts due to $SrCO_3$ from Nuss et al. (Nuss and Eckelman, 2014) and $HNO_3$ from the Ecoinvent database can provide a conservative (worst-case) scenario estimate for strontium nitrate production (with 100% efficiency of chemical reactions). Moreover, no catalyst consumption during transesterification was considered in this study. Additionally, the consumption of 1 L of methanol for cleaning 1 kg of catalyst was considered.

Location of catalyst production and biodiesel production units was considered to be within close vicinity to each other; therefore, no transportation was accounted for between the two units. The highest yield of 97.28% was observed at a methanol to oil molar ratio of 9 (Section 3.3). Therefore, 1028 kg of PAS oil and 327.1 kg of methanol lead to 1000 kg of biodiesel production, considering no losses due to separation. The electrical energy required for carrying out transesterification to produce 1000 kg of biodiesel was sourced from Mohammadi et al.(Mohammadi Ashnani et al., 2014), and the electrical energy required for centrifuge (used only for separation) was considered negligible and not accounted for. It was assumed that 1 $m^3$ of warm water is required for the purification of 1000 kg of biodiesel mixture (Table 1). Wastewater generated during the purification process was assumed to be 90% of the input water quantities, considering evaporation losses (Photaworn et al., 2017). The calorific value of biodiesel obtained was 45.28 MJ/kg; thus, the total output energy of 45280 MJ can be estimated from the entire production chain (Section 3.4).

**Table 1:** Life cycle inventory of biodiesel production (1000 kg) using waste *Prunus Armeniaca* seeds (PAS).

| Inventory item | Unit | Input | Output | Reference |
|---|---|---|---|---|
| **Waste PAS transportation** | | | | |
| **Diesel** | kg | | | |
| **Transportation**[a] | tkm | | 1136.2 | Based on calculation (tonne*km) |
| **PAS oil extraction** | | | | |
| **PAS** | kg | 5680.8 | | Oil extraction details (Section 2.1) |
| **PAS powder** | kg | | 5410.3 | |
| **Electrical energy**[b] **for pressing oil** | kwh | 169.7 | | |
| **Electrical energy for pumping oil** | kwh | 0.8 | | |
| **Solid cake** | kg | | 4274.2 | |
| **Loss** | kg | | 108.2 | |
| **PAS oil** | | | 1028.0 | |
| **Catalyst preparation and reuse** | | | | |
| **Strontium nitrate** | kg | 2.86 | | Catalyst preparation process (Section 2.2) |
| **Lanthanum nitrate hexahydrate** | kg | 5.84 | | |
| **Deionised water** | L | 34.9 | | |
| **Electrical energy required for drying** | kwh | 4.6 | | Instrument operating conditions |
| **Electrical energy required for calcination** | kwh | 9.1 | | Instrument operating conditions |
| **Catalyst** | kg | | 5.8 | |
| **Catalyst reuse - 6 runs**[c] | kg | | 34.8 | Catalyst reuse (Section 3.6) |
| **Methanol** | L | 40.7 | | |
| **Wastewater** | L | | 36.6 | (Chung et al., 2019) |
| **Electrical energy required for drying** | kwh | 4.6 | | |
| **Transesterification** | | | | |
| **PAS oil** | kg | 1028.0 | | Transesterification reactions (Section 2.3) |
| **Methanol** | kg | 327.1 | | |
| **Electrical energy for transesterification** | kWh | 32.0 | | (Mohammadi Ashnani et al., 2014) |
| **Water** | L | 1000.0 | | |
| **Biodiesel**[d] | kg | | 1000.0 | |
| **Wastewater** | L | 900.0 | | |

[a] Transportation: Transport, freight, lorry 3.5-7.5 metric ton, EURO6 (RER)

[b] Electricity mix, AC, consumption mix at consumer, 1kV-60 kV EU-27 S (SimaPro v9 databases)

[c] Total consecutive use of catalyst was considered for seven runs (reuse for six runs).

[d] Biodiesel calorific value: 45.28 MJ/kg (biodiesel characterisation, Section 3.4)

### 3.7.2 Environmental impact assessment

This study evaluated environmental impacts in the midpoint indicator categories using the CML-IA baseline v3.06 method (Table 2). Midpoint assessment is problem-oriented and stops at the midpoint of the cause-effect chain (Navarro and Zhao, 2014). The treatment of waste products was not included in the system boundary (shown in Figure 5).

**Table 2:** Potential environmental impacts of 1000 kg of biodiesel production using waste *Prunus Armeniaca* seeds (PAS).

| Impact category | Unit | PAS transportation | Oil extraction | Catalyst preparation and reuse[a] | Transesterification | Total |
|---|---|---|---|---|---|---|
| **Abiotic depletion (fossil fuels)** | MJ | 6490.86 | 981.13 | 2750.25 | 12698.25 | 22920.5 |
| **Global warming (100 years)** | kg $CO_2$ eq | 460.14 | 95.70 | 148.71 | 445.59 | 1150.1 |
| **Acidification** | kg $SO_2$ eq | 0.74 | 0.71 | 1.26 | 2.18 | 4.9 |
| **Eutrophication** | kg $PO_4^{3-}$ eq | 0.09 | 0.02 | 0.05 | 0.03 | 0.2 |

[a] Catalyst was used for a total of seven runs.
The values represented as total are rounded up.

Oil extraction caused least environmental impacts in impact categories, which can be attributed to the fact that only electrical energy was used in this production process. Furthermore, as waste-derived feedstock were used in the present study, there was no environmental impact due to the production of PAS, such as land-use change, fertiliser production and fertiliser input to soil.

Focusing on energy demand, the highest impact was reported during the transesterification reaction (12698 MJ). This is due to the use of electrical energy and methanol during the process, which combined formed 55% of the energy demand for the entire production process. Moreover, the net energy ratio calculated by dividing output energy (1000 kg of biodiesel corresponds to 45280 MJ) by cumulative energy demand (22920.5) was observed as 1.97.

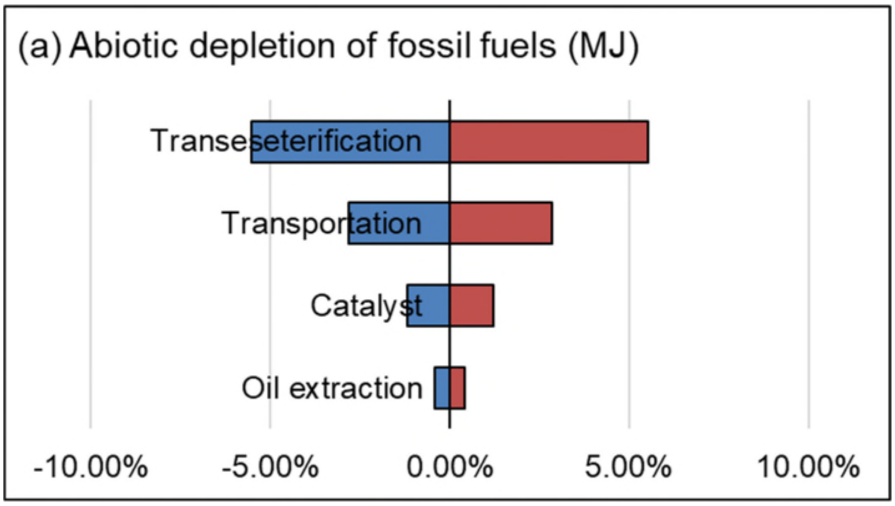
Global warming potential, which was calculated in the present study for a period of 100 years, was reported to be highest during waste PAS transportation (460 kg $CO_2$ equivalent, kg $CO_2$ eq) and transesterification (446 kg $CO_2$ eq). This is because of the use of fossil fuels and associated $CO_2$ emissions during these processes of the production chain.

Acidification potential is caused due to decrease in pH of rainwater and streams due to air pollutants such as $SO_2$ (Kim and Chae, 2016). Acidification increases the mobilisation and leaching behaviour of heavy metals in soil and exerts adverse impacts on aquatic and terrestrial animals and plants by disturbing the food web (Munawer, 2018). The transesterification stage showed the highest acidification potential (2.18 kg $SO_2$ eq), which could be due to the use of methanol and electrical energy. The second highest acidification was observed during the catalyst preparation and reuse stage (1.26 kg $SO_2$ eq), which can be attributed to the use of rare earth oxides for catalyst production. The mining process of rare earth oxides can include the disposal of sulfidic tailings and/or emissions of toxic or acidifying pollutants to air, soil, and water.

The waste PAS transportation recorded a eutrophication potential of 0.09 kg $PO_4^{3-}$ eq as road transportation can result in nitrogen oxides emissions. Additionally, as shown in Table 8**,** it was recorded that global warming potential was 1150 kg $CO_2$ eq, eutrophication potential was 0.2 kg $PO_4^{3-}$ eq and acidification potential was 4.9 kg $SO_2$ eq for the entire biodiesel production chain.

### 3.7.3 Sensitivity analysis

LCA studies are simplified models of the real-world system and thus are inherently sensitive to the input data used. Therefore, sensitivity analysis was performed to understand the environmentally burdensome processes in the entire biodiesel production chain. For a 10% increase in inputs required for transesterification, it was recorded that the cumulative abiotic depletion of fossil fuels increased by 5%. Furthermore, abiotic depletion of fossil fuels is most highly dependent upon transesterification (Tornado plots in Supplementary Material: Figure 6). In addition to this, the global warming potential increased by 4% by increase in road transportation inputs by 10%. As expected, the depletion of fossil fuels is closely related to global warming potential. To reduce impacts in these categories, attention should be paid to reducing distance (during waste PAS transportation) and electrical energy requirements (during transesterification reaction).



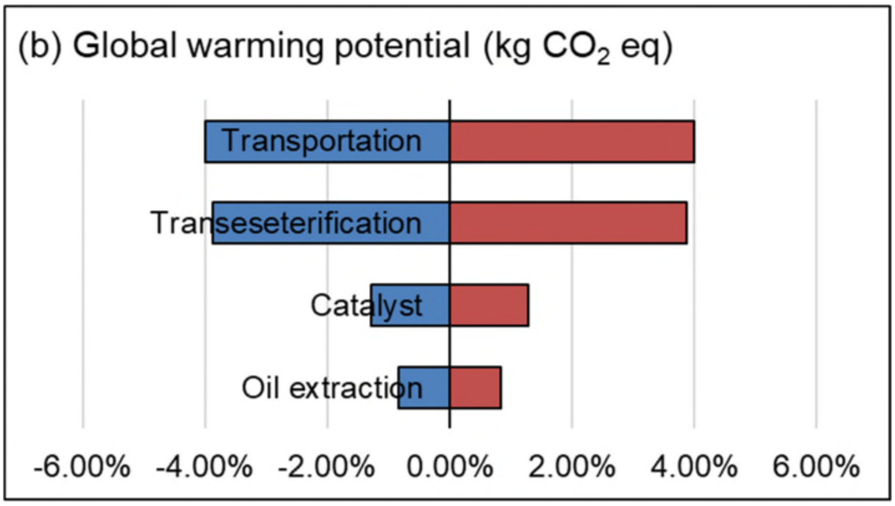


**Figure 6:** Percentage of variation of the potential environmental impacts due to a ±10% change in input parameters. For example, if the quantities required for all the parameters increase by 10% during transesterification, it can result in an increase in global warming potential by 3.9%. (Transportation: Waste PAS transportation, Catalyst: catalyst preparation and reuse, by considering use for a total of seven runs).

### 3.8 Implications

The net energy ratio (computed as output energy divided by input energy) for waste PAS oil to biodiesel production was observed as 1.97. Net energy ratio greater than 1 shows that the catalytic conversion of waste PAS oil to biodiesel resulted in net energy production. Moreover, the global warming potential was 1.150 kg $CO_2$ eq/kg of biodiesel produced. Global warming potential per

MJ of energy produced was 25.4 g $CO_2$ eq/MJ, which is in close range to second-generation biofuel produced using *Jatropha* (≈ 20-50 g $CO_2$ eq/MJ), *Camelina* (≈ 25-53 g $CO_2$ eq/MJ), used cooking oil/tallow (≈ 10-23 g $CO_2$ eq/MJ) (Jeswani et al. 2020)(Jeswani et al., 2020). This research contributes to United Nations Sustainable Development Goals (SDG) by providing a pathway to cleaner energy options (SDG 7) which is also aligned to SDG 13 to combat climate change and SDG 12 on Sustainable Production and Development. Going forward, it is imperative that the innovations applying circular economy approaches not only entail production and chemical processes but also assess life cycle environmental impacts.

## Conclusion

Herein, *Prunus Armeniaca* seed oil was utilised as a waste biomass feedstock over a novel catalytic system ($SrO-La_2O_3$) with different stoichiometric ratios as Sr: La-4 (Sr-La-A), Sr: La-6 (Sr-La-B), Sr: La-8 (Sr-La-C) and Sr: La-10 (Sr-La-D). The synthesised catalysts were characterised by several techniques (XRD, BET, TEM, EDX, TPD and XPS) to evaluate their suitability, performance, and reusability for biodiesel production reaction. The optimum catalyst in this study was Sr: La-8 (Sr-La-C) due to its enhanced surface morphology. Parametric analysis showed an optimum biodiesel yield of 97.28 % at a reaction temperature of 65 °C, the residence time of 75 minutes, catalyst loading of 3 wt.% and methanol to oil molar ratio of 9. The American Society for Testing and Materials (ASTM) and EU Standards were used to examine the quality of the produced biodiesel and showed that it satisfied all standards mentioned.

The optimum catalyst was also tested for biodiesel production for various oil feedstocks such as waste cooking oil, sunflower oil, PAS oil, date seed oil, and animal fat. It showed that it is not selective to specific oil feedstock. It also showed stable methyl ester production for a sixth repeated experimental run.

A life cycle assessment was conducted to evaluate the environmental impacts of the production of 1000 kg of biodiesel (functional unit). The recorded results in midpoint indicator categories showed the cumulative abiotic depletion of fossil resources over the entire production chain as 22920 MJ, acidification potential as 4.89 kg $SO_2$ equivalent and eutrophication potential as 0.2 kg $PO_4^{3-}$ equivalent. Transesterification resulted in the highest damage in the majority of impact categories. This was also recorded in a sensitivity analysis. Moreover, the net energy ratio was calculated as 1.97, and the global warming potential was 1.150 kg $CO_2$ equivalent/kg of biodiesel produced. These results demonstrated that biodiesel obtained from the valorisation of waste PAS provides a suitable alternative to fossil fuels.

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### Disclaimer

The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

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