CRANFIELD UNIVERSITY

Paul Barton

Enhancing separation of fats, oils and greases (FOGs) from catering establishment wastewater

School of Applied Sciences

PhD

Supervisors: Dr Raffaella Villa and Professor Bruce Jefferson

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

ABSTRACT

Removal of fats, oils and greases (FOG) from commercial food premises prior to discharge of wash waters into the sewer is critical in restricting blockage events. The FOG droplets that form are commonly removed in passive gravity separators. Enhanced separation through design modification, would allow a reduction in size required to achieve target removal. The aim of the project was to determine the feasibility of enhancing removal of FOGs in gravity separation devices and or in post treatment units. The thesis work examined the effect characteristics of oil droplet size and density had on FOG removal with a view to increasing droplet rise rates and hence separation.

Examination of kitchen wastewater from a number of restaurants established that droplet sizes were typically in the mechanically emulsified oil size range, often with high zeta potential indicating electrostatic stabilisation of suspensions.

Oil removal rates were examined using different oils typical of food preparations in laboratory scale experiments. Under a fixed energy input the different oils produced different droplet size distributions such that very different separation efficiencies were observed. The removal rates obtained allowed the prediction of oil removal from a sample in a given time when the median droplet size and density of the oil were known. For effective understanding of separator design and testing, droplet densities and sizes must be adequately measured and replicated. In addition, the light fuel oil used in the certification test produced very unstable suspensions, easily separable in the standard testing conditions, proving it a poor surrogate test material.

Pre-formed droplets of sunflower oil were treated in a vertically aligned reaction chamber with an ultrasonic transducer fitted at the base. FOG removal, measured as HEM removal, was monitored as a function of power input, frequency, reactor size and residence time, the incoming flow entered counter currently to the ultrasonic wave propagation. The ultrasound treatment procedure removed 80% of oil from a suspension of droplets in the mechanically emulsified oil size range during the course of a 54 minute continuous experiment compared to 20-30% removal in the case of an equivalent separated without ultrasonic enhancement. The enhanced separation was found to be dependent on the power input and the reactor size. Application of ultrasound energy in modified grease separators to remove short-circuiting droplets would allow a reduction in overall size of units through reduced residence time requirement.

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To my fellow students I would like to express my appreciation for your friendship and good humour over the years.

Finally I would like to dedicate this thesis to my parents Roy and Connie.

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ABBREVIATIONS AND NOTATION

Notation

A	Hamaker constant (10^{-20} J)
D	Impeller diameter (m)
d	Particle diameter (m)
d_{50}	Mean volume drop diameter (m)
E/τ	Applied power per residence time (kWh m^{-3} min^{-1})
G	Velocity gradient (s^{-1})
h_{crit}	Critical film thickness before rupture for coalescence to occur (m)
N	Impeller speed (rps)
n	Slope of log-log plot V_s v Ø
P	Power (W)
q	Flow rate (L min^{-1})
R	Droplet radius (m)
t_c	Contact time required for film drainage to critical thickness (h_{crit}) (s)
t_{int}	Droplet interaction time (s)
t_{stir}	Time stirred (s)
V	Volume of vessel (m^3)
V_s	Velocity of particles in suspension (m s^{-1})
V_{Stokes}	Stokes velocity (m s^{-1})

Greek Symbols

ε	Turbulence dissipation rate (m^{2} s^{-3})
$\bar{\mu}$	Viscosity of liquid-liquid mixture (Pa·s)
$\bar{\rho}$	Bulk density of liquid-liquid mixture (kg m^{-3})
$\dot{\gamma}$	Shear rate (s^{-1})
$\varnothing$	Disperse phase volume fraction (kg m^{-3})
$\varnothing_a$	Acoustic contrast factor
$\Delta\rho$	Density difference ($\rho_p - \rho_c$) (g ml^{-1})
η	Kolmogorov microscale of turbulence (m)
μ_c	Viscosity of continuous phase (Pa·s)
μ_d	Viscosity of disperse phase (Pa·s)
v	Particle velocity (m s^{-1})
v_c	Kinematic viscosity of continuous phase, μ_c/ρ_c (m^{2} s^{-1})
ρ	Particle density (kg m^{-3})
ρ_c	Density of continuous phase (kg m^{-3})
σ	Interfacial tension (N m^{-1})
τ	Residence time (min)

Dimensionless Groups

Ca	Capillary number,
p	Viscosity ratio between phases μ_d/μ_c
P_0	Impeller power number, $P/\rho_c N^3 D^5$

P_{coa}	Probability of coalescence between droplets (coalescence frequency)
P_{coll}	Probability of collision between droplets
Re	Reynolds number for stirred vessel (impeller)
Re_p	Particle Reynolds number

Abbreviations

APHA	American Public Health Association
API	American petroleum institute
BDD	Bromododecane
BOD	Biochemical oxygen demand
CCD	Charge-coupled device
CE1 – CE4	Catering establishments 1 to 4
CFD	Computational fluid dynamics
CMC	Critical micelle concentration
COD	Chemical oxygen demand
d_{50}	Median volume diameter
FOG	Fat oil grease
HEM	Hexane extractable material
HPLC	High performance liquid chromatography
MTBE	Methyl tert butyl ether
NTU	Nephelometric turbidity units

PSD	Particle size distribution
PTFE	Polytetrafluoroethylene
rpm	Revolutions per minute
SDS	Sodium dodecyl sulphate
SPE	Solid phase extraction
STS	Susceptibility to oil separation
SVS	Standard volumetric solution
THF	Tetrahydrofuran
TSS	Total suspended solids
US EPA	United States Environmental Protection Agency
v/v	Volume to volume

Measurement notation

°C	Degrees centigrade
g L^{-1}	Gram(s) per litre
kg	Kilogram
kWh m^{-3}	Kilowatt hours per cubic metre
m	Metre
M	Molar (g L^{-1})
m^3	Cubic metre
mg	Milligram
mg L^{-1}	Milligrams per litre

MHz	Megahertz
ml	Millilitres
mm	Millimetre
mM	Millimolar (g L^{-1})
mV	Millivolts
R^2	Coefficient of determination for a linear regression
s	Second
x *g*	Relative centrifugal force
µg	Micrograms
µm	Micrometer (micron)

Chemical notation

$CH_2Cl_3F_3$	1.1.2-trichloro-1.2.2-trifluoroethane
HCl	Hydrochloric acid
Na_2SO_4	Sodium sulphate
NaCl	Sodium chloride
$NaHCO_3$	Sodium hydrogen carbonate

1 Introduction

1.1 Project background

Fats, oils and greases (FOGs) from commercial food preparation premises are implicated in 75% of the estimated 200,000 sewer blockages in the UK every year, with the related cost of unblocking the sewers running to millions of pounds per annum (Water UK). Blocked sewers, or drains leading to them, can cause flooding of premises with associated health risks and costs for clean-up. Sewage overflow can also enter and pollute streams and rivers which may lead to eutrophication with consequent adverse impact on aquatic wildlife (Smith *et al.,* 1998). If high levels of FOGs enter wastewater treatment works (WwTWs) they can interfere with gas exchange between the air and water reducing the oxygen levels in the water and decreasing or stopping microbial activity in the biological treatment process. FOGs could also interfere with floc formation and hinder the removal of organics resulting in untreated material passing through the WwTWs and discharging into watercourses (Chipasa and Medrzycka, 2006).

To mitigate FOG entering the sewer there are a number of management strategies available using biological, physical and/or chemical methods.

Biological methods: (or bioaugmentation) is the most common FOG management system in the UK. The method is based on the addition of exogenous lipolytic microorganisms, either into a small trap or directly into the drain (Fairley, 2010).

Physical methods: are the simplest and cheapest technologies for FOG removal. The gravity grease interceptor or separator prevents grease and food solids from entering the sewer system by separating them in the first of its two chambers where the lighter density FOGs will rise to the top and the heavier food solids will sink to the bottom. A schematic of a gravity separator is shown in Figure 1. This kind of separator relies on its size to provide sufficient residence time for different density materials to separate out under gravity.

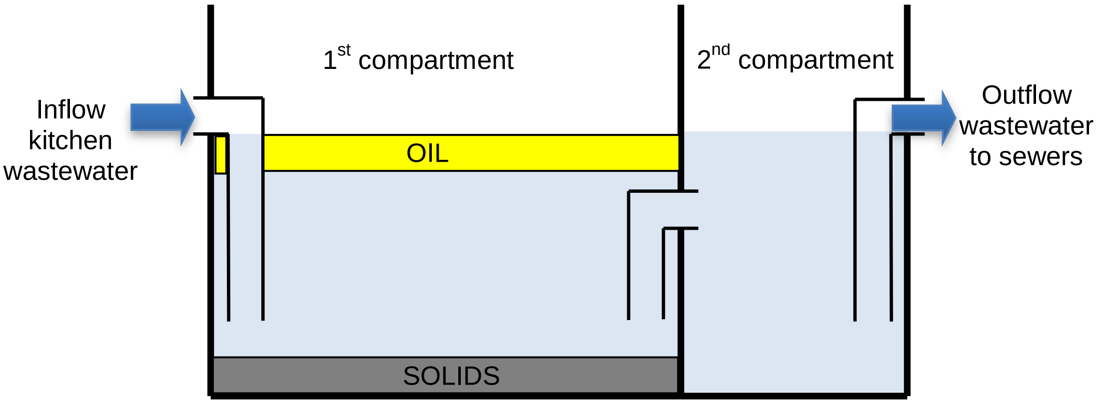

Figure 1: *Schematic of a conventional grease separator*

Table 1: *Summary of physico-chemical separation technologies (Italtraco, 2000; Bande, 2008)*

Separation processes	Particle size removed	Advantages	Disadvantages
Gravity separation	150 µm	Economical and simple	Limited efficiency
Centrifugation	100 µm	Simple operation	High operational costs/Poor separation
Plates (inclined /corrugated	45-60 µm	Simple operation	Large areas required /Clogging
Air flotation	35-50 µm	High solid content	Coagulant problem in the sludge /Costly chemicals
Filtration	25-30 µm	High solid content	Requires backwash /Power required
Chemical coagulation	15-20 µm	High solid content	Costly chemicals /Sludge disposal problem
Ultrafiltration	<5 µm	Soluble oil removal	Low flux /Membrane fouling
Electrocoagulation /Electrofiltration	<5 µm	Removes soluble oils/High efficiency/Low cost	Replacement of electrode

Chemical methods: the technology relies on the addition of chemicals to break the oil/water emulsion and increase oil particle coagulation to facilitate physical separation. Chemical coagulation is most commonly achieved by addition of acids or cations, which destabilise the emulsion by neutralizing the droplets charge (Rubio *et al.*, 2002).

Coagulation can also be achieved by introducing air or energy into the system for example through air flotation and electrocoagulation. Where time is restricted, a number of physical-chemical technologies can be employed to facilitate the oil/water/solid separation such as centrifugation or filtration and treatments including a combination of chemical or electrical processes. A summary of these technologies is reported in Table 1. A more comprehensive review of enhanced oil/water separation technologies in gravity separators is presented in Frising *et al.* (2006) and summarised in Table 2.

Energy input using ultrasound has also been used as a means to separate particles, with separation achieved by generating a standing wave in small reaction chambers (Pangu and Feke, 2004). An alternative ultrasound treatment to separation by standing wave, acoustic streaming, was reported by Wakeman and Bailey (2000) who suggested that in industrial situations particle fractionation into standing wave pressure nodes could encounter problems with high flow rates disrupting separation and larger solids blocking collection channels. They found acoustic streaming was effective in removing calcite particles from water. Research into the use of ultrasound as a means to separate oil from water has been reported in very few scientific papers (Nii *et al.,* 2009). To address this one of the objectives of this thesis was to investigate the possibility of using acoustic streaming to improve coagulation of oil droplets and enhance their removal from water.

Table 2: *Physico-chemical separation technologies for oil in water emulsions*

Technology	**Ceramic microfiltration membrane**	**Polyethersulfone ultrafiltration membranes**	**Coagulation/ coalescence on clay particles**	**Electrochemical coagulation**	**Electro-hydrodynamic flows**	**Stirring/shear flow coalescence**	**Dissolved air flotation and flocculation**
Disperse phase volume (mg L^{-1})	Up to 1000 mg L^{-1}		1000 mg L^{-1}		1000 mg L^{-1}	5000 to 20000 mg L^{-1}	1630 mg L^{-1}
Droplet size (µm) range		Up to 30 µm	Up to 50 µm		2 µm	2.1 to 2.4 mm	
Removal	> 92.4% oil measured as TOC	100%	90% photomicrograph droplet count	99% measured as turbidity	Coalescence achieved	Related shear and disperse phase concentration to droplet size formed	Up to 99% measured as turbidity
Flow rates	Up to 1.68 m s^{-1}	Up to 83 L m^{-2} h^{-1}	Batch	Up to 320 L min^{-1}	Batch		Batch
Authors	Hua *et al*. (2007)	Chen *et al.* (2009)	Tansel and Sevimoglu (2006)	Yang (2007)	Vigo and Ristenpart (2010)	Ross *et al.* (1978)	Al-Shamrani *et al.* (2002)

1.2 Aim and objectives

The aim of the project was to determine the feasibility of enhancing removal of fats, oils and greases (FOGs) in gravity separation devices and or in post treatment units.

The aim of this project has been achieved through a series of objectives as follows:

1. A review on the FOG coalescence process, its quantification and its improvement through the application of ultrasound.
2. Characterisation of input FOGs from different catering establishment sources including particle size, particle charge and their quantification.
3. Characterisation of in water suspensions of oils with different density including particle size, particle charge and their separation behaviour.
4. Laboratory testing of FOG separation improvements through design modification.
5. Laboratory testing of FOG separation improvements through energy input using ultrasound.
6. Design proposal of a smaller ultrasound-based gravity separator.

1.3 Thesis plan

The thesis will be presented as a series of chapters with chapters 2 to 6 formatted as papers for publication. All the papers were written by the primary author Paul Barton and edited by Dr Raffaella Villa and Professor Bruce Jefferson (supervisors). Initial objectives were devised by supervisors, all subsequent development and experimental work, with the exception of work on surfactants, was planned, designed and performed by Paul Barton. Surfactant experiments were conducted by Paula Pizzardini supervised by Paul Barton.

Chapter 1: presents an introduction to gravity grease separators role in FOG management systems and provides an overview of the range of technologies used to separate oil from water and the particle sizes removed.

Chapter 2: provides a review of characterisation, quantification and physical treatment techniques for oil in water emulsions. Grease separators work on the principle defined by Stokes Law that immiscible phases will separate out under gravity where the characteristics of phase density difference and particle size determine the rate of separation. The second chapter reviews the development of techniques to measure the rates of separation this includes the effects of polydispersity and concentration, which may interfere with or hinder separation rates, with consequent corrections to Stokes velocity. Under conditions in a passive gravity separator the main characteristic variable, identified in the Stokes equation, is droplet size. To better understand how treatments might increase droplet size, the process of coagulation was reviewed with respect to the application of either stirring or ultrasound, the two treatment techniques used in this project.

Chapter 3: covers the FOG laden wastewater characterisation in order to elucidate the range of droplet sizes and electrical charges present in washing up water and from within a grease separator; to bench mark separation performance. Oil quantification techniques are compared to identify the most suitable for monitoring changes in FOG content.

Chapter 4: aims to provide an understanding of performances of grease traps and parameters influencing phase separation. This chapter covers the work aimed at developing a bench scale simulation of the basic phase separation process that occurs in a gravity grease separator. Measurement of oil removal from a separating funnel for a range of prepared oil in water suspensions of pre-determined median droplet size at incremental residence times showed the phase separation rate. This was repeated for a range of different density oils which were then multiplied by the square of their median droplet size and plotted against corresponding oil removal at different residence times. The slopes produced allowed prediction of oil removal for a given residence time if median droplet size and density of a sample are known.

Chapter 5: looks at the impact of agitation and surfactants on the removal of FOGs in passive gravity separators. A jar test was used to investigate the effect of transitional to turbulent fluid flow on oil droplets in suspension. Energy is transferred from a stirring impeller into the suspension as bulk flow and turbulent shear within the impeller zone. Any changes in median droplet size would indicate either droplet coalescence or breakup which could then be linked to input energy. The influence of surfactant type on droplet characteristics and removal was also examined to determine how they might influence droplet formation and removal.

Chapter 6: covers the impact of ultrasonic pre-treatment on removal of fats oils and greases in passive gravity separators. This chapter investigates the effect ultrasound treatment parameters of frequency and power input have on droplet size distributions and oil removal in a reaction vessel. Parameters in the reaction vessel were varied to compare oil removal for different bed volumes and residence times to optimise conditions in terms of power input.

Chapter 7: this section draws together the findings from the experimental data to suggest a treatment unit that could be incorporated into existing grease separator design.

Chapter 8: presents the overall conclusions of the thesis work and future development of the results.

The work is summarised in Figure 2.

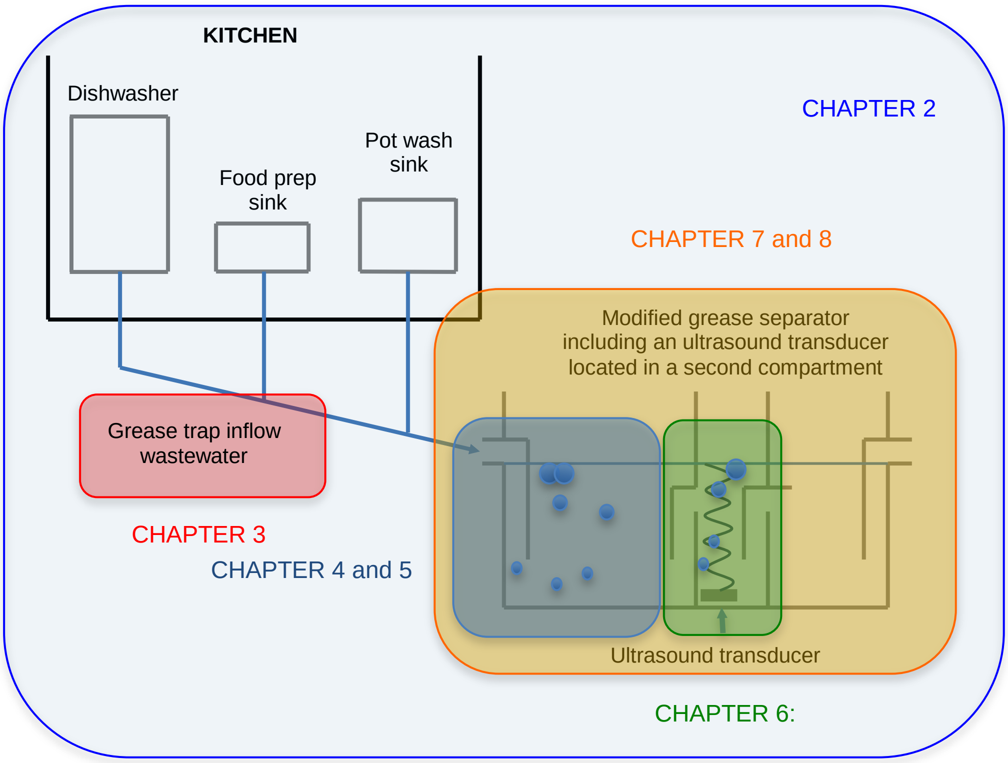

Figure 2: *Schematic of work reported in this thesis*

Table 3: *Summary of thesis plan*

Chapter	Paper	Objectives addressed	Chapter title
2	1	1	Oil in water emulsions: a review of quantification, characterisation and separation improvement using ultrasound.
3	2	2	Catering establishment wastewater characterisation.
4	3	3	Understanding performance of grease traps: parameters influencing phase separation.
5	4	3 and 4	Impact of agitation and surfactants on the removal of fats, oils and greases in passive gravity separators
6	5	5	The impact of ultrasonic pre-treatment on removal of fats, oils and greases in passive gravity separators.
7		1-5	Overall implications for enhancing fats, oils and grease separation

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2 Oil in water emulsions: a review of quantification, characterisation and separation improvement using ultrasound

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Abstract

Measurement techniques for FOG quantification and droplet sizing form part of the objective for improving gravity separation processes. However the precision and repeatability of oil quantitation using standard methods has been identified as problematic with low recoveries and large variations between replicate samples. FOG extraction into solvent was identified as the issue with solvents not being able to break down emulsions. Therefore techniques that aid emulsion breakdown for example solid phase extraction or surrogate methods such as turbidity measurements that do not rely on oil extraction were examined.

Approaches to enhancing FOG separation have been focussed on separator design modifications to reduce turbulent flow thereby reducing droplet breakup, short circuiting and scouring of separated layers. Literature reporting the effect of stirring on hydrocarbon oil droplet coalescence suggests that droplets in the mechanically emulsified oil range can be coalesced in turbulent conditions but surfactant stabilised droplets will need alternative treatments.

The use of ultrasound standing waves as a treatment to aggregate or coalesce particles has been widely investigated with one report identifying ultrasound travelling waves or acoustic streaming as a novel technique to separate particles (calcite). Acoustic streaming to separate oil from water is the treatment technique investigated in this project.

2.1 Introduction

The fat, oil and grease (FOG) content of waste water from commercial kitchens and catering establishments is relatively high, with concentrations ranging from 80 to over a 1000 mg L^{-1}. In addition, lipids represent a significant portion of the organic fractions of domestic wastewater (Chapter 3). The term ‘fat, oil and grease’ describes a heterogeneous group of chemicals comprising mainly tri-, di- and mono-glycerides (glycerol and fatty acids), sterols, non-volatile hydrocarbons, waxes and other complex lipids.

The efficacy of the physical separation of FOG from water, using gravity removal units depends upon several factors, one of which is droplet size. The size of the droplets provides an indication as to the nature of the emulsion undergoing the separation process. Droplets bigger than 150 µm are able to separate out under gravity and are classified as free oil (American Petroleum Institute publication 421, 1990). Droplets between 20 and 150 µm are defined as mechanically emulsified micro-emulsion with separation times of hours, and chemically emulsified micro-emulsion with droplets size between 1 and 20 µm have separation times of days (Bande *et al.,* 2008). Wastewater from catering establishments contains detergents which employ surfactants to help enhance the emulsification of oil droplets and the formation of difficult-to-separate sub-20 µm droplets. Effective gravity separation relies on the disruption of these emulsions and is influenced by three physical characteristics: droplet size, surfactant concentration and oil viscosity. The process of de-emulsification consists of two stages: an initial coagulation step followed by a coalescence step. In this second step the coagulated droplets join together to form bigger droplets. This is an irreversible process where the emulsions are disrupted, providing improved oil/water separation yields. The quantification and characterisation of catering establishment wastewater emulsions is an important stage in the improvement of the separation process in gravity traps.

The first part of this paper reviews current available methods for the characterisation and quantification of oil-in-water emulsions and the quantification of FOG in wastewater samples. The paper then covers coalescence improvement via design modification and the use of ultrasound.

2.1.1 FOG and emulsion quantification

FOGs are insoluble in water and soluble in solvents such as hydrocarbons, chlorinated fluorocarbons and alcohols. These solvents are therefore often used for their extraction and quantification. FOG quantification usually involves complex and time-consuming methods. Standard methods for the quantification of FOG in wastewater are based on gravimetric, infrared or chromatographic techniques these methods all require an initial liquid–liquid extraction step. Solid phase extraction represents an alternative to liquid-liquid extraction, which helps reduce extraction time, emulsion formation and the amount of solvent involved in the extraction. There are question marks over the suitability of the current standard methods employed to quantify oil in water with evidence that predicted oil removal does not match measured oil removal (Lopez-Vazquez and Fall, 2004; DuCoste *et al.,* 2008). The next paragraphs will provide an overview of the standard methods used for the quantification of FOG and emulsions in wastewater.

2.1.1.1 Solvent-based extraction methods – Standard methods

In the UK there is a standard method (BS EN 1825-1:2004) for analysis of effluent samples from grease separators, which is based on a liquid-liquid extraction with an organic solvent, 1.1.2-trichloro-1.2.2-trifluoroethane ($C_2Cl_3F_3$) in a separating funnel. However the Montreal Protocol has phased out supply of $C_2Cl_3F_3$, because it is implicated in depletion of ozone in the upper atmosphere, so a replacement solvent carbon tetrachloride (C_2Cl_4) is suggested as an alternative. Extracted FOG is then quantified by infrared spectroscopy. A second quantification method, gas chromatography, is included in BS 1825-1 however for this technique the FOG needs to be extracted into petroleum ether. As BS 1825-1 is based on measurements of hydrocarbons it does not take account of the need to trans-esterify non-volatile triglycerides to convert them into volatile fatty acid methyl esters (FAMEs) before they can be run on a gas chromatograph. However a method for esterifying triglycerides, by use of trimethylsulphonium hydroxide, is detailed in BS EN ISO 12966-3:2009 (2010).

2.1.1.2 Quantification using infrared spectroscopy

According to BS 1825-1 to measure oil FOG content a calibration curve needs to be produced from measurement of the extinction coefficients of known concentrations of a fuel oil (diesel) at 3.38 µm (CH_3 absorption band) and 3.42 µm (CH_2 absorption band). There is no explanation of how this measurement corresponds with triglyceride concentration so presumably a calibration curve needs to be constructed by measuring extinction coefficients for known concentrations of an animal or vegetable oil. A further issue is that the fatty acid composition of different fats and oils will not be the same so CH_2 and CH_3 ratios will vary producing different absorption values.

2.1.1.3 Quantification using gas chromatography

Quantity of oil in a sample is determined by integrating the total peak area in a chromatogram produced from an experimental run and comparing it with peak values obtained from a calibration curve constructed from specified concentrations of two reference standards, n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$). The samples are spiked with known volumes of the reference standards as internal standards prior to chromatographic runs to demonstrate recovery. It is not clear if chromatographic conditions optimised for hydrocarbon separation will have same discrimination/sensitivity for FAMEs and not using reference FAMEs as calibration standards is not comparing like with like.

2.1.1.4 Alternative extraction and quantification methods

US EPA method 1664 Revision A. (US EPA /R-98-002, 1999) allows for modification of the procedure provided results obtained can be demonstrated to meet performance criteria and there is equivalency with the original method. Specifically if, “after shaking, an emulsion is present after standing for 10 minutes the laboratory should complete phase separation by using an emulsion breaking technique”. Depending on sample type suggestions for breaking emulsions include: solid phase extraction, centrifugation, stirring, ultrasonic bath, addition of NaCl, solvent phase separation papers, filtration through glass wool and continuous liquid-liquid extraction.

US EPA 1664 is similar to BS 1825-1 in that it is employs a liquid-liquid extraction in a separating funnel and differs from BS 1825-1 since 1999 by replacing

$CH_2Cl_3F_3$ as an extraction solvent with n-hexane. Recognising different solvents potentially extract different components the US EPA 1664 A revision; suggests referring to extracted material in terms of the solvent used for extraction. So FOGs extracted by n-hexane become hexane extractable material or HEM. Quantification is by gravimetric determination the extraction solvent being recovered by distillation and HEM residue weighed.

The American Public Health Association (APHA) Standard Methods for the Analysis of Water and Wastewater (Cleseri *et al.,* 1998) Method 5520 B is based on US EPA 1664 (and referred to as a partition-gravimetric analysis) has replaced $CH_2Cl_3F_3$ with a solvent system of hexane and methyl tert butyl ether (MTBE) for extraction of lipids and hydrocarbons.

In response to variable results for analyses of oil in water samples returned from independent laboratories Ducoste *et al.* (2008) replaced the separating funnel and manual shaking specified in US EPA 1664 (A) with a measuring cylinder and magnetic stirrer to extract oil from FOG suspensions and quantified the extracted oil on a portable infrared meter.

2.1.1.5 Solid phase extraction (SPE)

The solid phase extraction technique involves passing a sample through a plastic cartridge containing a hydrophobic matrix that will retain the non-aqueous components of the sample allowing the water to pass through. Retained oils can then be eluted from the cartridge with appropriate solvents, into a pre-weighed flask, the solvent is then dried off and the residue in the flask weighed. Manufacturers claim that the matrix in SPE cartridges helps to break down emulsions thereby increasing their extraction efficiency.

A report by Daghbouche *et al.* (1997) compared liquid-liquid with SPE extractions, using carbon tetrachloride (CCl_4) as solvent. Extractions were then measured gravimetrically and by Fourier transform infra-red (FTIR) spectroscopy. These techniques were compared to another technique, microwave assisted extraction into CCl_4 with FTIR measurement. The extractions were performed on spiked clean and waste water samples using selected oils, but poor recoveries were found for liquid-liquid and SPE methods whereas the microwave extraction method showed good recoveries. By contrast Raisglid and Burke, (2000) were able to demonstrate extraction of hexadecane and stearic acid using a bespoke

SPE cartridge (matrix mix of ISOLUTE C18 and silica material) and eluting with a solvent system of 1:1 v/v hexane and tetrahydrofuran (THF is water miscible) conformed with US EPA 1664 (A). (Hexadecane forms a hydrophobic attachment to silanol groups in the C18 material; stearic acid forms hydrophobic and polar interactions with the C18). Addition of individual solvents would allow fractionation of oil mixtures with hexane disrupting the hydrophobic association between oils and matrix releasing the hydrocarbon (hexadecane), the more polar THF disrupts both hydrophobic and polar associations of stearic acid so that it is eluted from the matrix, a mixed solvent system will elute both types of oil together.

Satisfactory SPE-gravimetric techniques have also been used by Wells *et al.* (1995) and Lau and Stenstrom (1997) to extract oils from water samples the authors also pointing out that SPE reduces extraction time and solvent consumption.

2.2 Characterisation techniques

2.2.1 Characterising droplet rise rates

The process by which the oil droplets (disperse phase) rise through water (continuous phase) is generically called creaming and the rate of separation is generally determined from the Stokes equation which predicts the terminal velocity of a particle in a fluid under the influence of gravity mediated by its size and phase density difference (equation 1):

$$V_t = \frac{(\rho_p - \rho_f) g d^2}{18\mu} \tag{1}$$

Where V_t is the terminal velocity, ρ_p and ρ_f are the density of the particle and fluid respectively, g is gravitational force, d is diameter of the particle and μ is the dynamic viscosity of the continuous phase

Stokes equation has some limitations in predicting creaming rates as it describes motion of an individual solid spherical particle moving through a fluid and does not take into account potential reductions of droplet velocity caused by particle-particle interactions that are likely in multi-particle suspensions.

In his theory of sedimentation Kynch, (1952) suggested that the equation describing Brownian motion on particle interactions defined by Einstein and Smoluchowski (equation 2) worked for suspensions with low concentrations but that for more concentrated suspensions other interactions would influence particle velocity.

$$V_t = V_{Stokes}(1 - 2.5\emptyset) \tag{2}$$

Where V_{Stokes} is the terminal velocity calculated from equation (1), and Ø is the disperse phase concentration (g L^{-1}).

Kynch introduces the concept of hindered velocity when, as particles approach the bottom of their container, a zone will build up where the particles become concentrated by accretion, the more concentrated suspension serves to slow velocity of the particles. Where particles are more closely associated (concentration density is large) Kynch proposes that the particles move as one "whatever their size owing to the close packing."

A refinement of the Einstein-Smoluchowski equation was developed by Richardson and Zaki (1997), who correlated sedimentation rate measurements for a range of monodispersed suspensions of different concentrations:

$$V_{RZ} = V_{Stokes}(1 - \emptyset)^n \tag{3}$$

Where V_{RZ} is the Richardson-Zaki corrected particle velocity, V_{Stokes} is the terminal velocity calculated from equation (1) and Ø is the disperse phase concentration (kg m^{-3}) and the exponent n is a factor related to the particle Reynolds number (eqn. 4).

$$Re_p = \frac{\rho V d}{\mu} \tag{4}$$

Where ρ is the particle density (kg.m^{-3}), V is the particle velocity (m.s^{-1}), d is the particle diameter (m) and μ *is the* viscosity of the continuous phase (kg^{-1} m^{-1} s^{-1}).

For suspensions of particles with a low Reynolds number > 0.1 the value for *n* was found to be 4.65 such that the particle velocity followed the Stokes prediction. For suspensions of particles with high particle Reynolds number < 500 the value of *n* was found to be 2.45 and the particle velocity is determined by Newton's law (Rhodes, 1999) (equation 5):

$$V_t = 1.74\left(\frac{d\left(\rho_p - \rho_f\right)}{\rho_f}\right)^{\frac{1}{2}} \tag{5}$$

The intermediate range 0.1 < Re_p > 500 covers the transition from Stokes (laminar flow conditions) to Newtonian (turbulent flow conditions), formulas to predict velocities of particles in the intermediate or transitional region have been proposed by Khan and Richardson (1989) and Rowe (1987).

Batchelor and Wen (1982) investigated particle motion in a bidisperse system using a suspension composed of two particle sizes with different densities. Where particles are the same size and density the Stokes velocity correction factor was calculated to be:

$$V_t = V_{Stokes}(1 - 6.55\emptyset) \tag{6}$$

Where two particles of the same size but different densities were compared the correction factor becomes:

$$V_t = V_{Stokes}(1 - 2.6\emptyset) \tag{7}$$

Comparing two particles of different sizes which have the same density the velocity correction factor becomes:

$$V_t = V_{Stokes}(1 - 5.6\emptyset) \tag{8}$$

Berres *et al.* (2005) found that small variations in particle size and density had little effect on overall sedimentation rates.

A report by Kumar *et al*. (2000) demonstrated that for dilute polydisperse suspensions (Ø = 0.2%) oil separation followed the Stokes equation prediction. Whilst in more concentrated polydisperse suspensions (Ø = 2.6%) droplets greater than 20 μm separated out according to Stokes with smaller droplets separating out faster than Stokes, the suggestion was that larger droplets were dragging the smaller droplets with them. In dilute systems, such as catering wastewater, where particle size of concern ranges between 20 and 150 µm and particle Re < 0.1, Stokes law is expected to apply.

The American Petroleum Institute (API publication 421, 1990) when defining characteristics that need to be considered when sizing separators describe a separation measurement technique ‘susceptibility to separation test’ using a 6 litre glass separating funnel. Oil in water suspensions are allowed to separate for 30 minutes with the remaining oil classified as not susceptible to separation.

Pal (1994) reviewed a selection of methods used to characterise the oil and water content of emulsions. He divides them into two categories (Table 1).

Table 1: *Methods used to characterise oil in water emulsions adapted from Pal (1994)*

Destructive	Non-destructive
Titration and other chemical methods	Electrical
Total Organic Carbon (TOC) analysis	Microwave
Centrifugation	Radiation scattering
Distillation	Spectroscopic
Flash vaporisation	Ultrasonic
Solvent extraction	Density
Differential Scanning Calorimetry	Viscosity

Techniques for characterising emulsions were also reviewed by McClements (2007) who stated that: “there are currently no standardised experimental protocols for characterising emulsion stability”. The review includes examples of methodologies based on the techniques in Table 1.

2.2.2 Turbidity

Turbidity can be used to measure the oil content of dilute, 0 to 5000 mg L^{-1} oil in water suspensions (Pal, 1994). Turbidity measurements are based on the principle that particles in a suspension will absorb or reflect an incident light beam and the resultant back scattering, or reduction in light transmission can then be measured by a detector in the instrument.

The correlation of known concentrations (between 100 and 1000 mg L^{-1}) of motor oil in prepared emulsions with their turbidity readings was used by Yang (2007) when assessing the effect of various treatments on oil removal from wastewater. The report demonstrated that whilst surfactant stabilised emulsions followed the Beer-Lambert Law, which predicts a linear relationship between concentration and absorbance, in surfactant free oil in water emulsions there was a decrease in the ratio between oil content and turbidity as the oil content increased.

Measurements in a turbidimeter are snapshots of the emulsion in a measuring cell, in a dynamic system for example, where droplets are moving at different rates, the droplet concentration will vary over the height of the sample. Recognising this an instrument called a TurbiScan© is available that, scans up and down the height of the measuring cell producing a plot of the backscattering and transmittance at different heights giving a picture of any creaming, coalescence, flocculation or sedimentation taking place in the sample. This technique was used by Frising *et al*. (2006) who demonstrated that if the vertical part of the backscattering curve moved over time and the horizontal part remained stationary the suspension was separating out by sedimentation whilst if the horizontal part of the backscattering curve migrates with time and the vertical part remains static then separation is primarily through coalescence. This technique has also been used by Juliano *et al.* (2011) when looking at enhanced creaming of milk fat globules by application of ultrasound and by Abismaïl *et al.* (1999) when comparing stability of emulsions produced by a rotor stator mixer or by application of ultrasound.

2.2.3 Absorption measurement

Measuring free fat in emulsions Palanuwech *et al.* (2003) used a known quantity of a lipophilic dye, Oil red O, to colour non-emulsified lipid that was then separated out from emulsions using a centrifugation step. A portion of this dyed oil was measured in a spectrophotometer at 517 nm the absorption then compared to a calibration curve of known dye dilutions in oil to obtain an oil concentration. This technique could lend itself to measurement of lipids in field samples where turbidity methods do not distinguish oil droplets from other non-lipid particles.

2.2.4 Droplet size distribution changes

For particle sizing in liquid suspensions a number of instruments are available typically based on one of two techniques; electro-zone sensing (Coulter counter type) and laser diffraction spectroscopy, alternatively image capture and analysis is also used.

2.2.5 Electro-zone sensing

The electro-zone sensing technique is based on a measuring chamber divided into two compartments connected by one or more micro-channels filled with an electrolyte solution; each of the two compartments has an electrode connected to a meter to complete an electrical circuit. Measurements are made as the sample suspension is drawn from one chamber into the other, via the micro-channels, where droplets in the suspension displace a volume of electrolyte proportional to their size. The displaced electrolyte causes a small change in the impedance of the solution which is measured by the instrument and over time a picture of the suspension droplet size distribution can be built up.

2.2.6 Laser diffraction spectroscopy

The principle of the technique involves a sample being passed through a laser beam in the instrument and the incident light is scattered by particles in the sample, the pattern of scattering is related to particle size with larger particles scattering light at narrower angles with greater intensity and smaller particles scattering light at wider angles with lower intensity. Detectors capture the light scattering patterns and these are integrated using software based on a mathematical model, usually the “Mie theory” (McClements, 2007) and reported as a table or plot of particle concentration against particle size.

2.2.7 Image analysis with the use of photomicrography

This technique involves capturing images of the sample suspension with a CCD camera attached to an optical microscope and using image capture software to size particles in the photographs. The data is then collated to give a particle size distribution. Disadvantages in the use of microscopy identified by McClements (2007) include the amount of time required to analyse sufficient numbers of particles to acquire statistically reliable data and the element of subjectivity where a bias exists towards larger particles during the initial focussing stage and where smaller particles are often out of focus and discarded from measurement so results become skewed.

2.2.8 Measurement of separation in flow through systems

An experimental procedure to estimate the effect of concentration on creaming and settling velocities of particles in polydisperse suspensions under flow conditions has been designed by Kumar *et al.* (2000). They reported two experimental arrangements, one looking at creaming and one looking at sedimentation, using columns with an inlet and outlet ports. Suspensions were pumped though the columns and samples were taken from the inlet and an outlet port with hindered velocity determined from the change in particle size distributions between the two sampling points.

They found the creaming rate for oil in water suspensions with particle size distributions ranging from 7 to 27 µm in diameter and with disperse phase concentrations of 0.2 % were very similar to those predicted by the Stokes equation. In experimental runs with a more concentrated oil suspension (2.6 %) it was found that creaming velocities of droplets with a particle diameter greater than 20 µm matched Stokes prediction. However the smaller particles appeared to move at a similar rate to the larger particles, i.e. greater than predicted by Stokes law, the authors suggested this was due to larger particles dragging smaller particles with them thereby equalising out the overall creaming rate.

2.3 Additional measurement techniques outside scope of this project

2.3.1 Computational Fluid Dynamics (CFD)

To better understand how fluid flow in grease separators affects FOG removal Ducoste *et al.* (2008) used CFD simulations to model and compare motion and fate of 80 and 150 µm droplets. Also examined, were how different inlet, baffle and outlet arrangements in the separator affected fluid flow and how that impacted on the different separated phases. CFD analysis was also used by Ciofalo *et al.* (1996) when looking at discrepancies between models for vortexing in closed and open unbaffled stirred tanks.

2.3.2 Photometric and video

Particle or droplet motion and interactions have been observed using photometric or video image capture and analysis, (Spicer *et al.*, 1996; Nandi *et al.*, 2006) light probes, (Park and Blair, 1975; Colaloglou and Tavlarides, 1977) laser light diffraction, (Polat *et al.,* 1999; Angle *et al.*, 2006), and particle image velocimetry (Bouyer *et al.*, 2005; Coufort *et al.*, 2005)

2.4 Physical treatment techniques

2.4.1 Enhancing separation through design improvement

One approach to improving phase separation has been to reduce turbulent flow in separators by changing their design parameters. Andresen *et al.* (2000) compared four inlets with a standard inlet design by a supplier (Kvaerner Process Systems) one low shear and one high shear, one feeding into a low exit liquid diffuser, relative to level of liquid in separator, and one into a high exit liquid diffuser after the inlet. Having used an oil continuous system they saw very little difference in water droplet size produced by the different inlets and suggested that difference in shear between the different inlet configurations was insufficient to alter average drop size.

Investigating removal of oil in wastewater from vehicle service facilities Lopez-Vazquez and Fall (2004) optimised design configurations of a small 10 litre separator using a fractional factorial statistical technique (Plackett-Burman 16 run 6 factor at 2 levels) to evaluate oil removal efficiency.

The method involved comparing two variables of six factors: internal dimensions of separator area (length and depth), position of baffles (horizontal and penetration into liquid), and the type of inlet weir (rectangular and V-notch), type of outlet weir (rectangular or two circular tubes), residence time and overflow rate. They found type of inlet weir, length and depth of water, and penetration of baffle were the factors that affected hydrodynamic and removal efficiency of the separator. Lopez-Vazquez and Fall (2004) suggested that relative errors of – 27.0 to + 44.2 % between predicted and measured oil concentrations meant that model was not sufficiently precise to predict optimum configurations rather than ascribing analytical accuracy as the reason for the poor repeatability. They stated that the Plackett-Burman technique was a good way of optimising design of small gravity separators but the work they had done did not explain specific mechanisms by which one particular configuration worked better than another. Hence results presented do not provide generic information or criteria for separator design.

A more comprehensive examination of separator performance was conducted by DuCoste *et al.* (2008), who acquired field data for three different size separators with two compartments and three different inlet configurations; a standard straight-pipe inlet tee, a specially designed distributive inlet tee and one with no inlet tee. Measuring depth of separated FOG material and settled solids in the different separators the principal findings were that separators with the distributive inlet tee had greatest accumulation of FOG and solids in the separator compartments. This was attributed to the slower inlet velocity induced by the larger cross-sectional flow area of the distributive tee which allows time for upward migration of oil drops or settling of solids. The faster inlet flow rates of the other tee configurations potentially leading to short circuiting of influent through the separator compartments.

The field observations were followed up with bench scale experimental measurements of FOG removal using a selection of inlet and outlet configurations with different internal baffle arrangements. They found that a standard two chamber configuration with one hour residence time achieved 90 % FOG removal, for the same arrangement with a 20 minute residence time removal was 78 %, however without a baffle FOG removal after 20 minutes residence time was 86 %.

The most efficient oil removal configuration was achieved with a distributive inlet tee and baffle with 87 % removal after 20 minutes residence time, although this was only marginally better than the standard configuration without a baffle which achieved 86 % removal. The distributive tee arrangement and standard set up were scaled up to pilot scale and removal efficiency was compared. At pilot scale oil removal was increased from 50 % in the standard arrangement to 66 % using the distributive tee and baffle arrangement. The difference in oil removal efficiency between pilot and bench scale oil removal was attributed to the different impeller and reactor configurations, producing different spatial distributions of turbulence resulting in different droplet size distributions in the dispersions.

The study also investigated effect of residence times and found that tripling residence time only increased separation by 10 % (also noted that studies on refinery separators found no advantage in increased residence times beyond a certain point).

2.4.2 Stirring as a method to enhance aggregation in liquid-liquid suspensions

Low energy input in the form of slow rotations of cylinders or stirrers will produce a laminar flow where there is an absence of the turbulent eddies that can cause breakup of deformable droplets and conditions are thought to be conducive to particle aggregation and or coalescence.

Application of rapid stirring will introduce a high energy input into the suspension which is dissipated as vortices or 3 dimensional eddies the size of which determine the size of the droplets formed. Conversely eddies can cause droplets to come into contact with each other potentially resulting in aggregation or coalescence (Hemrajani and Tatterson, 2004).

Park and Blair, (1975) investigated droplet behaviour in agitated liquid-liquid dispersions using high-speed cine-photography to film what happened to droplets during stirring. They observed that droplet breakup occurred predominantly within a short distance of the impeller zone, as did the highest rates of coalescence. Outside the impeller zone collisions between droplets resulting in coalescence was less than 10 %. They noted that there was only binary coalescence and rate of coalescence did not appear to be affected by droplet size.

Shear conditions produced during mixing are defined by the impeller Reynolds number $Re = \rho N D^2 / \mu$. When the Reynolds number in a mixing system is < 10, laminar flow conditions exist, whilst > 10^4 fully turbulent conditions occur, between these two regimes transitional flows take place (Hemrajani and Tatterson, 2004).

2.4.3 Ultrasound as a method to enhance aggregation in liquid-liquid suspensions

Sound travels through a medium as sinusoidal waves (sound waves) and are defined in terms of their wavelength (m) and its reciprocal frequency (cycles s^{-1} or hertz (Hz)) i.e. short wavelengths will have a high frequency. In liquids sound travels as alternating waves of high pressure (compaction) and low pressure (rarefaction). Ultrasound is defined as sound waves that have a frequency higher than that which is audible to humans; above about 20 kHz.

Six ultrasound treatment parameters are identified with corresponding particle removals (Table 2):

Table 2: *Particle removal for treatment parameters of ultrasound frequency, applied power, disperse phase, separation mechanism, size of reaction chamber, and flow rate.*

Frequency	Power	Disperse phase	Standing wave	Size of reaction chamber	Flow rate	Removal	Authors
0.35, 0.725, 1.4 MHz (625 kHz)	16 W, 25 W	0.1 to 100 µm, Al_2O_3 (aq suspensions), also olive oil emulsion in olive oil	Yes	314 ml	10 ml min^{-1}	Up to 97.5% for Al_2O_3 demonstrated movement of emulsion droplets to nodal plane.	Tolt & Feke (1993)
250 kHz	0.0142 - 0.0162 Jm^{-3}	Polystyrene particles 100 & 170 µm	Yes	10 ml	Feed 3.2 or 5.6 ml min^{-1}. Carrier 17.8 or 31.4 ml min^{-1}	Objective: fractionation	Johnson & Feke (1995)
20 – 800 kHz	3.2 W cm^{-1}	Cavitation bubbles	Liquid air interface acts as reflector	1357 ml	Batch	Bubble behaviour	Laborde *et al.* (1998)
2.1 - 2.4 MHz	30 W L^{-1}	Polystyrene particles 10.2 µm	Yes	16 ml	Batch	Droplet trajectories	Woodside & Piret (1998)
3 MHz	Up to 2. 2 W cm^{-2}	14 µm glass spheres	No	6 litres	Batch	Streaming velocities	Frenkel *et al.* (2001)
680 kHz	6.3W to 25.8W & 47.2W	Vegetable oil droplets 1 – 10 µm	Yes	48 ml	35 ml min^{-1}	80% on polyester mesh	Pangu & Feke (2004)
40 kHz	0.14 W cm^{-1} to 21.7 W cm^{-1}	Wash water including surfactants	Standing wave generated	Not specified	Batch	100%	Stack *et al.* (2005)

Frequency	Power	Disperse phase	Standing wave	Size of reaction chamber	Flow rate	Removal	Authors
0.525 MHz & 1.69 MHz (2 MHz)	90 J m^{-3}	0.1 % oil in water & o/w + surfactant 24 to 193 µm	Yes	28.9 ml	–	Droplet trajectory and coalescence demonstrated	Pangu & Feke (2007)
1, 1.5, 2.25 MHz	36 V	Motor oil 5 to 25 % by volume	Yes	45 ml	Batch	Demonstrated oil accumulation	Garcia-Lopez & Sinha (2008)
420 kHz or 2 MHz	2 W, 12 W, 30 W, 45 W	2 – 6 µm canola oil in water	Yes	0.44 ml	Batch	Demonstrated oil removal as drop in absorbance	Nii *et al.* (2009)
525 kHz & 1.69 MHz	19.7 J.m^{-3} & 56 J m^{-3}	Vegetable oil in water	Yes	40 ml	Batch	Demonstrated droplet size increases	Pangu & Feke (2009)
400 kHz & 1.6 MHz	Power input 400 kHz = 2.45 W cm^{-2} & 2.2 W cm^{-2} for 1.6 MHz dissipated power = 1.8 W cm^{-2} & 18 W cm^{-2} E_{ac} of 10-25 J m^{-3}	Milk fat d[4,3] = 9.3 µm and 2.7 µm	Yes	7 ml	Batch	Up to 100 % in 2 transducer set up	Juliano *et al.* (2011)

Frequency	Acoustic pressure	Disperse phase	Standing wave	Size of reaction chamber	Flow rate	Removal	Authors
(0.5 MHz) 1.02 MHz & 3.14 MHz	65 V pk-pk (Po = 0.4 MPa)	10 µm polystyrene microspheres	Yes	24.5 ml	Batch	Demonstrated movement of particles to nodal planes	Whitworth & Coakley (1991)
3 MHz	525 kPa	96 µm polystyrene particles	Yes	4.4 ml	Batch	Demonstrated movement of particles along nodal planes	Gould *et al.* (1992)
20 kHz	up to 200 kPa	Cavitation bubbles	Yes	250 ml			Luther *et al*. (2001)

Research into the use of ultrasound as a means to separate oil from water has been reported in very few scientific papers (Nii *et al.,* 2009). Amongst those reported Stack *et al.* (2005), who were investigating parameters that maximised phase separation, demonstrated ultrasound treatment alone was not sufficient to overcome the electrostatic and steric barriers to grease coagulation. Another quantification technique used by Pangu and Feke (2004) was to compare the differences in droplet size distribution between samples of feed and effluent taken from an ultrasound reaction chamber from which changes in oil volume before and after treatment could be calculated. More recently Juliano *et al.* (2011) achieved separation of milk fat in a Turbiscan measuring tube using ultrasound frequencies of 0.4 and 1.6 MHz. where separation and collection of dyed milk fat droplets was demonstrated photographically. Removal of the droplets was achieved by turning the ultrasound off and allowing the droplets to rise under gravity the resultant reductions in turbidity measured by the instrument confirming removal.

The use of ultrasound as a means to separate phases in liquids has mainly focussed on creating a standing wave producing pressure nodes and anti-nodes where particles or droplets can be concentrated or collected (Figure 1). Ultrasound standing waves are generated in reaction chambers, containing a fluid, by use of piezoelectric transducers with a reflector on the opposite side of the device. The geometry of these chambers needs to be defined in order to create the standing wave (Hill and Harris, 2007) and will differ according to whether fluid is particle free or not with particle concentration then also becoming a factor.

The mechanism that drives droplet motion in a standing wave is the formation of pressure nodes (minimum pressure area) and anti-nodes (maximum pressure area) where droplets are pushed towards the pressure nodal plane by the primary axial acoustic force (F_{Ax}). At the nodal plane primary transverse acoustic force (F_{Tr}) and secondary acoustic forces (F_B) will act to aggregate the droplets within the nodal plane (Hill and Harris, 2007).

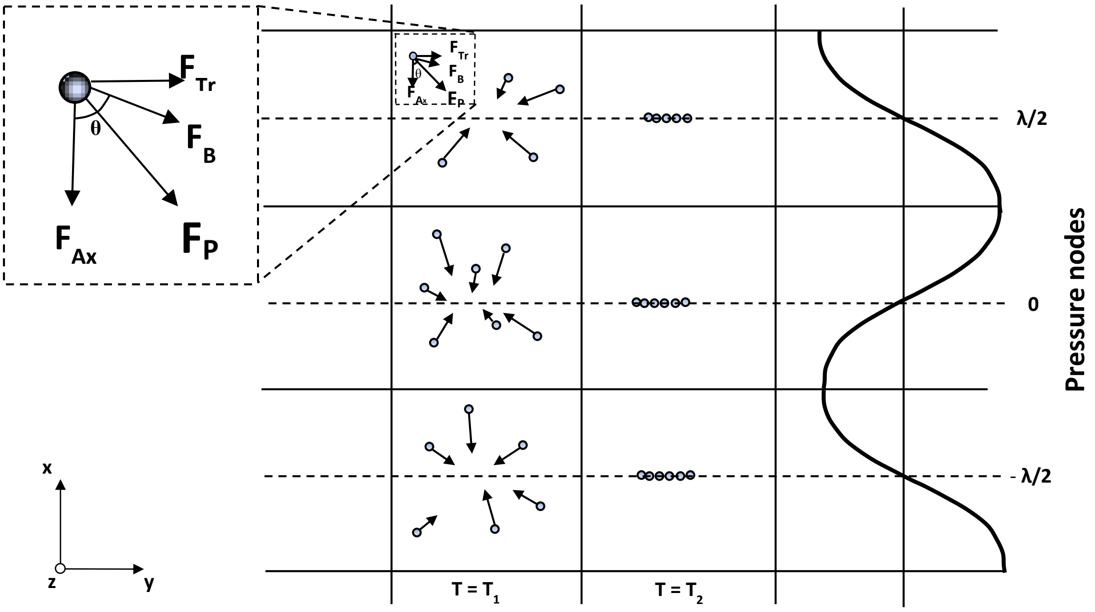

Figure 1: *Primary acoustic force* F_P *comprises an axial component* F_{Ax} *and a transverse component* F_{Tr}*. The secondary acoustic, Bjerknes force,* F_B *represents the inter-particle force. Time* T_1 *is when acoustic forces have just started to act on the droplets with time* T_2 *the point at which steady state has been achieved. The pressure nodes occur at ½ λ intervals. Adapted from* Laurell *et al.* (2007).

Ultrasound applied to a suspension of oil droplets (compressible spheres) will produce a primary axial acoustic force, on the droplets, in a direction parallel to that of wave propagation (Pangu and Feke, 2007). The primary radiation force is expressed as:

$$F_p = 4\pi r^3 k E_{ac} \emptyset_a sin\left(\frac{4\pi x}{\lambda}\right) \qquad (9)$$

Where F_P is the acoustic radiation force, r is radius of droplet/sphere (m) k is wave number $\left({}^{2\pi}/_{\lambda}\right)$ of the applied ultrasound (m), E_{ac} the average acoustic energy density (J m^{-3}), $Ø_a$ the acoustic contrast factor, and x the distance from a nodal point of the standing wave.

The acoustic contrast factor is determined from:

$$\phi_a = \frac{5\rho_f - 2\rho_p}{2\rho_f - \rho_p} - \frac{\beta_c}{\beta_p} \qquad (10)$$

Where ρ_f and ρ_p, are the density and β_f and β_p, are the compressibility of the continuous phase and the disperse phase respectively.

Droplet compressibility β is related to the speed of sound c by $\beta = {}^{1}/_{\rho c^2}$. Droplets will reflect a portion of the sound waves with the resultant scattered energy giving rise to secondary acoustic (Bjerknes) forces (F_B) (Pangu and Feke, 2004) and are calculated from:

$$F_B = \frac{k^2 E_{ac}}{2\pi}\left(1 - \frac{\beta_p}{\beta_f}\right)^2 \frac{V_1 V_2}{y^2} \qquad (11)$$

Where V_1 and V_2 are the volumes of the interacting droplets and y is the distance between the centres of the interacting droplets.

For two adjacent droplets with the same compressibility β_p the secondary acoustic force is attractive (Pangu and Feke, 2007) and as the acoustic pressure pushes droplets together combined with van der Waals forces the likelihood of coalescence increases.

As acoustic force applied to a reaction chamber is increased coalescence rate might also be expected to increase, however so does probability of acoustic cavitation and acoustic streaming (Pangu and Feke, 2009). Acoustic cavitation occurs when micro-bubbles are formed and then collapse releasing energy as a result of rapid compression and decompression in the liquid caused by acoustic waves. Measurements of energy required to induce cavitation and/or streaming in water at megahertz frequencies were made by Gould *et al.* (1992). They found that in general, the higher the frequency used the higher the energy density one can apply without inducing the onset of cavitation. Their studies indicate that an energy density of up to 100 J m^{-3} (2.78 x 10^{-5} kWh) does not induce cavitation in water at frequencies of 1.02 and 3.14 MHz. Also for a phase density difference ($\Delta\rho$) of 0.1 g cm^{-3} with an acoustic contrast factor ($Ø_a$) of -10 (values representative of water in oil emulsions), the minimum energy density required to induce droplet collection in a nodal plane at 2 MHz was 0.38 J m^{-3}, which was well below the cavitation threshold.

Ultrasound reaction chambers used in experimental research on breaking edible oil emulsions have usually been small rectangular devices ranging in volume from 0.4 cm^3 used by Nii *et al.* (2009) to 100 ml used by Pangu and Feke (2004; 2007: 2009). Earlier work by Tolt and Feke, (1993) used a 2.5 x 25 cm (123 ml) glass cylinder with a transducer at one end and a reflector plate at the other to produce a standing wave at frequencies of between 620 and 635 kHz with applied power of 25 W to separate and remove aluminium oxide particles. A further test to evaluate the collection strength of the system was performed using a water in olive oil emulsion fed into an olive oil continuous phase. The experiment also demonstrated coalescence of water droplets. Particle removal was achieved by introducing a cyclic ‘sawtooth’ frequency change of approximately 8 kHz, and applying an automatic sweep mode in the signal generator, to create a gradual displacement of the standing wave, which carried the particles in the pressure nodes towards an outlet port in the reaction cylinder.

2.5 Conclusions

Oil in water emulsions, especially those that are electrostatically stabilised, are not fully extracted by solvents alone. Treatments to break down the emulsion are required for total oils and greases to be measured. Alternatively surrogate measurements such as turbidity could be used.

The key characteristics determining FOG removal are droplet size and the density difference between the disperse phase oils and the continuous waste water phase. The rise rate and hence removal of oil droplets in a dilute suspension typical of kitchen wash water is defined by Stokes Law.

Energy applied to oil in water suspensions has two impacts on droplet size: the creation of non-isotropic flows in turbulent conditions will increase collision rates and provide inertial energy to overcome barrier forces between droplets. Increased collision rates are balanced by faster droplet velocities which increase interface formed between collided droplets thereby increasing drainage time required to facilitate coalescence thereby reducing coalescence efficiency. Smaller droplets will tend to act as solid objects and rebound off of each other.

The use of ultrasound to remove particles from water has been identified as a viable treatment process in small resonant chambers but there is little research on removal of oil from water in larger vessels.

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3 Catering establishment wastewater characterisation

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Abstract

Current grease separator sizing in UK is determined either from an empirical formula or a performance test using a light fuel oil as defined in the relevant European-British standards (BS EN 1825 pt 1 & 2). These standards assume FOG (lipid) behaviour and separation in these separators will be the same as mineral oil. According to the American Petroleum Institute free oil droplets (> 150 µm in diameter) would separate out under gravity whilst droplets smaller than 20 µm in diameter would require more time or additional measures to facilitate separation.

There is very little published data on the evaluation of removal efficiency in working grease separators. To address this, physico-chemical measurements were used to characterise the wastewater from a number of catering establishments. Catering wastewater the washing-up water samples (separator influent) and samples from the first and second compartments of a grease separator (separator effluent) were used for this characterisation. A key issue in wastewater characterisation is the variability in results for known concentrations of total oil and grease. Four extraction techniques were used to quantify the oil fraction of oil-in-water suspensions and their results compared.

Particle size measurements in samples from the catering wastewater and first compartment of the separator showed that droplet median volume diameter (d_{50}) typically fell within the mechanically emulsified oil range (20 - 150 µm). Droplet d_{50} measurements in the grease separator second compartment were in the chemically emulsified or soluble oil range (1 to 20 µm). Zeta potential measurements for influent samples were variable (up to - 60 mV) whilst those from within the separator were lower (below - 30 mV) indicating potential for suspension breakdown/destabilisation.

3.1 Introduction

Commercial enterprises discharging wastewater to a drainage system will incur a Trade Effluent Charge by the local utility company to cover the costs of maintaining the drainage system and the treatment at a wastewater treatment works. Utility companies also set consent levels for discharges to the drainage system which normally include flow rate, temperature, total suspended solids (TSS), chemical oxygen demand (COD) and may also include biochemical oxygen demand (BOD) and FOGs. Catering establishments producing a wastewater with a high FOG content will need to meet discharge consent levels and these levels can often be achieved with a grease separator device. A gravity grease separator is usually composed of two chambers, the capacity of which depends on several factors such as kitchen type, effluent flow, retention time of the trap and operating hours of the restaurant (EN BS 1825 pt 1 & 2). The American Petroleum Institute (API 421, 1990), defining characteristics that would influence oil interceptor design calculations, determined that free oil droplets (> 150 µm in diameter) would separate out under gravity whilst droplets smaller than 20 µm would require additional measures to facilitate separation (API 421, 1990). API 421 does not however specify what happens to the intermediate oil droplet fraction. Rayan (1986) established that a gravity separator will only be able to remove oil droplets bigger than 50 µm in diameter, whereas Sokolowich *et al*. (1992) determined that fine oil-water dispersions with oil droplets smaller than 10 µm in diameter will not separate out in conventional gravity systems. A more detailed classification of emulsions present in oily wastewater was provided by Bande *et al.* (2008) who defined particle size, emulsion stability and separation time under gravity for the range between 1 and 150 µm. Emulsions with droplets between 20 and 150 µm were defined as mechanically emulsified micro-emulsions with moderate stability and separation times of hours. Emulsions between 1 and 20 µm were defined as chemically emulsified micro-emulsions with strong stability and separation times of days (Bande *et al.,* 2008). Catering establishments' wastewater contains detergents, and therefore anionic or cationic surfactants, which help and enhance the emulsification of the oil droplets and the formation of these sub 20 µm droplets. Small oil droplets in catering wastewater can also be formed as a consequence of acidic or alkaline cleaners used at high temperatures for oven cleaning. It is therefore pivotal when trying to improve gravity separators to understand the composition of the wastewater to be treated and in particular the size of the particles involved in the separation process. There is very little published data on the characteristics of kitchen wastewater entering or leaving the separation systems. Most publications limit their characterisation to COD, BOD, TSS and FOG content and focus instead on the influence of restaurant type (Converse *et al.*, 1984; Stoll and Gupta, 1997; Lesikar *et al.*, 2006) or effect kitchen and water management has on these characteristics (DuCoste *et al.*, 2008; Nakajima *et al*., 1999). No information is available on the physical characteristics of catering wastewater in term of particle size or density, which are the main factors involved in the separation. This lack of information has also been reported by Kommalapati (2001) who identified the need for data from real high strength wastewater for the design of novel treatment systems.

An additional key issue in the characterisation of wastewater, recognised by DuCoste *et al.* (2008), is the variability in results for known concentrations of total oil and grease when analysed using the standard US EPA 1664 (A) method (1999). Their variation in results was of the order of 40 %. In the UK the standard method for measuring oil in the grease separator, detailed in BS 1825-1 is based on the same extraction technique and stipulates the use of 1.1.2-trichloro-1.2.2-trifluoroethane, as the primary extraction solvent for oil and grease. For this project alternative solvents were considered with n-hexane chosen as the replacement as per US EPA 1664 revision A and the extracted material defined as hexane extracted material (HEM). In addition four different extraction procedures including: liquid/liquid extraction (LLE), solid-phase extraction (SPE), stirred extraction and centrifugation were compared.

The aim of the work described in this chapter was to improve our understanding of the physicochemical properties of catering wastewater in order to be able to improve separator design. Samples were taken over 2 periods of one week each from four catering establishments on the Cranfield University campus and characterised. In addition, the four extraction techniques were used to remove oil from oil-in-water suspensions and their results compared.

3.2 Materials and methods

3.2.1 Sampling methodology

The sampling campaign consisted of taking wastewater grab samples from 4 catering facilities on site with the following characteristics:

CE1 – Cafeteria (45 seats), has 3 sinks with a total capacity of 81.3 litres that are emptied once per day. A Hobart dishwasher typically washes 20 loads per day using 2.5 litres water per load with a total discharged to drain = 131.3 litres per day.

CE 2 – Restaurant mixed cuisine (90 seats), has 2 sinks (a pot-wash and a food preparation sink) and a dishwasher.

CE 3 – Dining Hall (146 seats), has 7 sinks (3 pot-wash and 4 food preparation sinks) and a dishwasher.

CE 4 – Dining Hall (110 seats), has 5 sinks (2 pot-wash and 3 food preparation sinks) and a dishwasher.

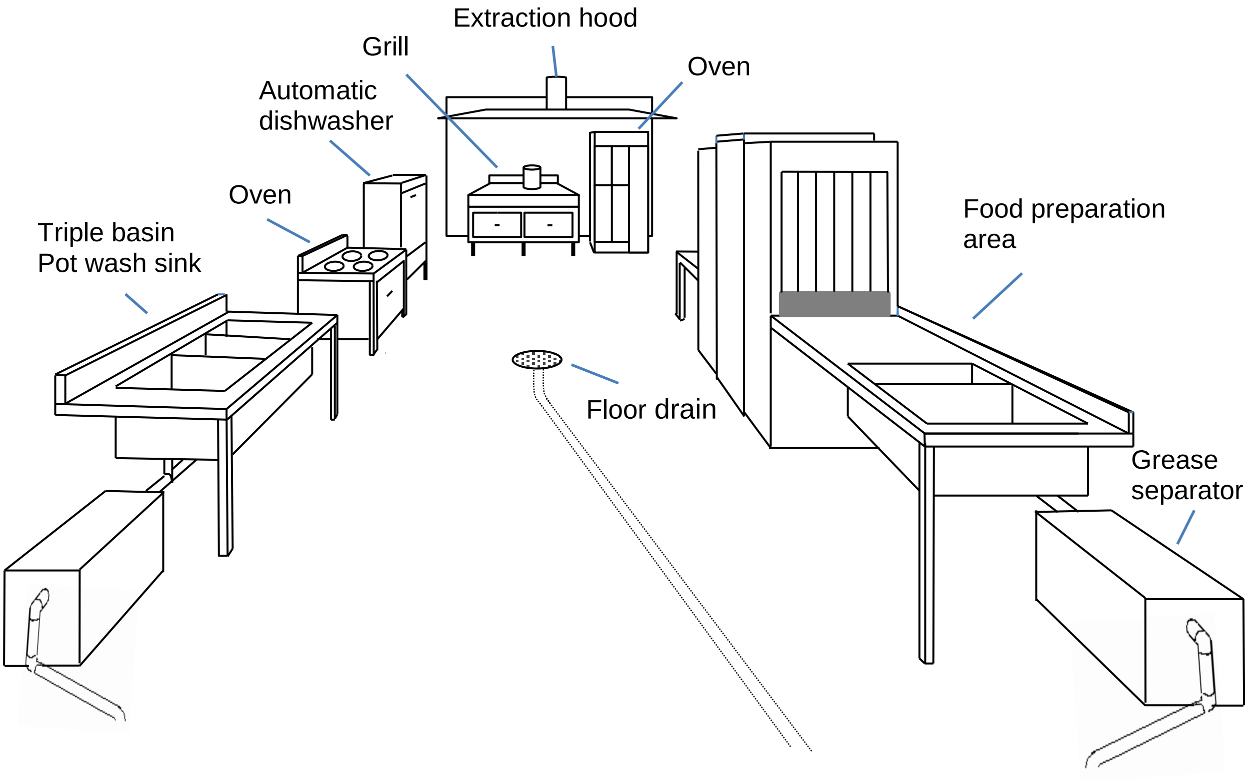


Figure 1: *Potential points of FOG production and accumulation in a typical catering establishment kitchen*

All the samples represent water entering the grease trap or sewers.

The sampling schedule aimed at capturing effluents from a restaurant at its peak time after the lunchtime service. Each restaurant was sampled on two occasions for 5 consecutive days, to capture variations during a typical week, for a total of 40 samples. The data reported in the chapter corresponds to the first week for which there is matching FOG quantification.

Samples taken from the two chambers of the cafeteria (CE1) gravity separator over 5 consecutive days were analysed in the same way as the wastewater samples.

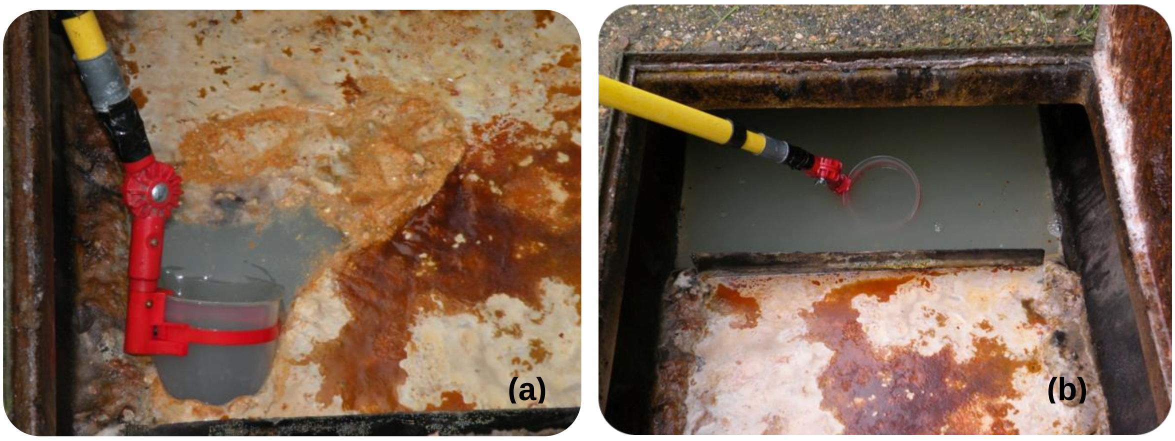


Figure 2: *CE1 gravity grease separator, sampling compartments 1 (a) and 2 (b).*

3.2.2 Characterisation of wastewater samples

The wastewater samples from the four catering establishments, along with samples taken from the grease separator of CE 1, were analysed for BOD (BOD, BS EN 1899-1:1998), TSS (TSS, BS EN 872:2005), COD (Orion COD test kits, VWR, Leicestershire, UK) and FOG content (US EPA 1664 A and SPE cartridges, (Isolute O&G, Kinesis, Cambridgeshire, UK)).

The samples were also measured for pH (Jenway model 3510, Fisher, UK), turbidity (Turbidimeter Hach 2100N Camlab, UK), zeta potential (Zetasizer model 3000 HAS, Instruments, Malvern, UK) and particle size distribution (Mastersizer 2000, Malvern Instruments, UK).

3.2.3 Extraction and quantification of FOGs

Solvents used for FOG extraction were n-hexane (HPLC grade, Fisher Scientific, Loughborough, UK) and tetrahydrofuran (AnalaR grade, Fisher, UK). Adjustments to pH were made with hydrochloric acid, (5 M standard volumetric solution, Fisher, UK). FOG analogues used in experiments were commercially available sunflower oil and salad cream (Cranfield, UK.).

Oil in water suspension samples for recovery measurements were prepared by transferring aliquots of sunflower oil or salad cream by means of a tared plastic syringe (10 ml Discardit, Fisher, UK) weighed on an analytical balance (Adams Balances model PW 254, Adam Equipment, Milton Keynes, UK) directly into a separating funnel containing deionised water. The syringe was reweighed to determine amount of oil added to separating funnel. The oil in water mixture was manually shaken for two minutes and then adjusted to below pH 2 by addition of 5 M hydrochloric acid.

The four methods used for the extraction and quantification were as follows:

3.2.3.1 Liquid-liquid extraction and gravimetric quantification

The liquid-liquid extraction into n-hexane followed by a gravimetric determination based on US EPA 1664 A. Samples were collected in a tared glass bottle (500 ml, Duran, Fisher, UK) adjusted to below pH 2 with hydrochloric acid (5 M standard volumetric solution, Fisher, UK) and transferred to a 1 litre glass separating funnel (Fisher, UK). Three x 10 ml portions of n-hexane, (HPLC grade Fisher, UK) were used to rinse the bottles containing the sample and the washings combined into a separating funnel. Further 20 ml aliquots of n-hexane were added to the funnel; the separating funnel was then manually shaken for 2 minutes and allowed to stand for 30 minutes. After phase separation the aqueous portion was drained into the original glass sample bottle and the separated hexane portion filtered through a glass funnel containing approximately 10 g of anhydrous sodium sulphate, (GPR, Fisher, UK) into a pre-weighed 250 ml round bottom flask, (Quickfit©, Fisher, UK). The extracted aqueous portion in the sample bottle underwent two more n-hexane extractions as described previously. The filtered solvent rinses were all combined in the round bottom flask and the hexane was dried off in a rotary evaporator (Heidolph Laborota 4000) connected

Figure 3: *Liquid-liquid extraction*

to a vacuum pump (RE200, Patterson Scientific, Cambridge, UK). After solvent removal the flasks were placed in a drying oven (Genlab, Widnes, UK) overnight at 45 °C, before being transferred into a desiccator to cool, the flasks were then weighed on an analytical balance (model PW 254, Adam Equipment, MK, UK).

3.2.3.2 Solid phase extraction and gravimetric quantification

The solid phase extraction into n-hexane followed by a gravimetric quantification is an adaptation of the US EPA Method 1664 as amended by Raisglid and Burke (2000). Solid phase extraction cartridges (Isolute O&G 3g/70ml Kinesis Cambridgeshire, UK) were placed on an extraction manifold (VacElut 20, Agilent, Cheshire, UK) attached to a vacuum pump (KNF model NO35.1.2.AN18, Witney, UK) The cartridges were pre-conditioned with 10 ml methanol (HPLC grade, Fisher, UK) at a flow rate of 10 ml min^{-1} and equilibrated with 10 ml of acidified deionised water (adjusted to pH 2 with 5 M hydrochloric acid) at 10 ml min^{-1}. Sample from pre-weighed 500 ml Duran bottles was poured into the SPE cartridge and eluted at 10 ml min^{-1} with flow rate gradually increased to between 50 and 100 ml min^{-1}. In instances where the particulate loading of a sample caused blockages, evidenced by greatly reduced flow rate, sample elution was discontinued and the remaining sample weighed to determine amount of sample eluted. Where the entire sample was eluted the sample bottle was rinsed twice, initially with 20 ml of acidified deionised water and then with 10 ml acetone (HPLC grade, Fisher, UK) and 40 ml acidified deionised water. Both rinses were added, separately, to the SPE cartridge. The acetone rinse step was repeated until bottle washings appeared clear. The SPE cartridge was dried on the vacuum manifold for approximately 30 minutes, (or when cartridge was no longer cold to the touch). The retained lipids were eluted from the SPE cartridge by addition of 4 ml 1:1 v/v n-hexane : tetrahydrofuran (AnalaR grade, Fisher, UK) which was

Figure 4: *Solid-phase extraction*

allowed to soak for 2 minutes before being eluted into a pre-weighed 100 ml round bottom flask in the vacuum manifold. The elution step was repeated, after which the round bottom flask was removed from the vacuum manifold and attached to a rotary evaporator to dry off the solvent. After solvent removal the round bottom flask was placed in a drying oven at 45 °C overnight. The following day the flask was transferred to a desiccator and allowed to cool before weighing on an analytical balance.

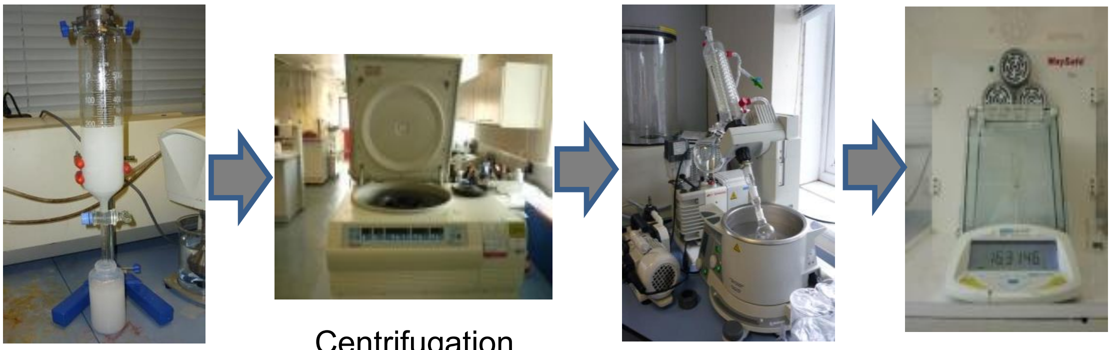
3.2.3.3 Liquid-liquid extraction in cylinder and infrared quantification

The liquid-liquid extraction into n-hexane followed by infrared quantification is based on US EPA Method 1664 as amended by DuCoste *et al.* (2008). Aliquots of sunflower oil were transferred using a tared plastic syringe into deionised water in a measuring cylinder (500 ml glass Pyrex, Fisher, UK) and the volume recorded. The suspension was adjusted to below pH 2 with 5 M hydrochloric acid then 50 ml ofn-hexane (HPLC grade, Fisher, UK) was added to the measuring cylinder from a bottle top dispenser (Brand Dispensette 5 – 50 ml, Fisher, UK). The measuring cylinder was placed on a magnetic stirrer (model CB161, Stuart, Fisher, UK) and a magnetic stirring bar added. The stirrer was turned on for two minutes to expedite solvent extraction after which the phases were allowed to separate for two minutes. The hexane layer was removed using a variable volume pipettor (Finnpipette 2 - 10 ml, Fisher, UK) and dispensed through a glass filter funnel containing approximately 10 g of anhydrous Na_2SO_4 (GLR grade, Fisher, UK). The filtered hexane was collected in a 50 ml volumetric flask (Fisher, UK) and made up to the mark. Quantification of oil content was determined on a portable infrared meter (IR) (OMD Cranfield University, Cranfield, UK). Sample measurements were made from 0.5 ml aliquots of the hexane extracted material, transferred from the volumetric flask, via a variable volume pipettor (Finnpipette, 10 – 1000 µl, Fisher, UK) to the measuring chamber of the I.R. meter. The hexane was allowed to evaporate off, resultant oil content was displayed on a personal digital assistant device (PDA) (Hewlett Packard iPAQ, Bracknell, UK) and reading recorded. A five point calibration curve was constructed from measurements of sunflower oil in hexane ranging from 50 mg L^{-1} to 1000 mg L^{-1} and results stored within software on a the PDA.

Figure 5: *Portable infrared meter (Cranfield University – Cranfield, UK)*

3.2.3.4 Liquid/liquid extraction in bottle and gravimetric quantification

The fourth procedure was a partition-gravimetric method replacing the separating funnel and manual shaking step with a PTFE centrifuge bottle and centrifugation; a technique developed in house during the course of this project.



Sample collection + hexane addition

Centrifugation

Solvent evaporation

HEM-gravimetric analysis

Figure 6: *Cranfield modified liquid-liquid extraction and gravimetric analysis with centrifugation step.*

Oil in water suspension samples of approximately 200 ml were collected in pre-weighed centrifuge bottles (250 ml, PTFE, Fisher, UK) and weighed on a top pan balance (GF2000 A & D, Balances, Camlab, Cambridge, UK). The samples were acidified to below pH 2 with additions of hydrochloric acid (5 M Standard Volumetric Solution, Fisher, UK). Pairs of PTFE centrifuge bottles containing the acidified samples were adjusted to the same weight with deionised water prior to addition of 50 ml n-hexane (HPLC grade, Fisher, UK) using an adjustable bottle top dispenser (Brand Dispensette 5 – 50 ml, Fisher, UK). After closure the centrifuge bottles were manually shaken for approximately two minutes to replicate US EPA 1664 procedure for liquid-liquid extraction. The paired PTFE centrifuge bottles were placed in a centrifuge (Sorvall Legend RT+, DJB Labs, Newport Pagnall, UK) and spun at 4000 x *g* for ten minutes. On completion of centrifugation 3 x 10 ml aliquots of the hexane layer were transferred using a variable pipettor (Finnpipette 2 – 10 ml, Fisher, UK) from the centrifuge bottle into a pre-weighed 100 ml round bottom flask. The flask was then attached to a rotary evaporator (Heidolph Laborota 4000 connected to a RE202 vacuum pump, Patterson, UK) and the hexane dried off. After solvent removal the flask was removed from the rotary evaporator and placed in a drying oven (model N75C, Genlab, Widnes, UK), set at 45 °C and dried overnight. The following day flasks were transferred to a desiccator, allowed to cool and weighed on an analytical balance.

Calculation for HEM removal:

Oil in suspension (g):

$$\frac{A}{500} \times B = C$$

Where A is weight of oil from syringe, B is the weight of collected suspension and C is the disperse phase concentration (g).

Residual oil in round bottom flask (g) x $^{5}\!/_{3}$ = D

HEM removed (%):

$$\frac{C - D}{C} \times 100$$

3.3 Results and discussion

3.3.1 Extraction and quantification of FOGs

Grab samples from a catering establishment grease trap were taken over a 5 day period and analysed for oil content using standard LLE-gravimetric and SPE-gravimetric methods. Results using the LLE-gravimetric method ranged between 138 and 1042 mg L^{-1} HEM over the 5 day sampling period, measurements ranged between 118 and 1485 mg L^{-1} HEM for the SPE-gravimetric technique. The results of the extractions over the 5 days are reported in Figure 7.

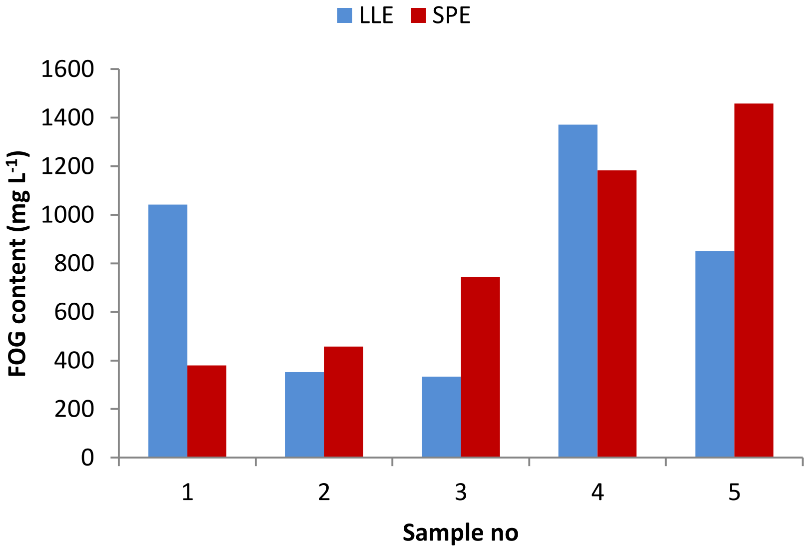


Figure 7: *Comparison of two FOG extraction methods (standard LLE-gravimetric and SPE-gravimetric) using catering wastewater from a grease trap over 5 days*

Comparisons of HEM extraction results from the two techniques, on samples taken at the same time, showed little similarity. This was probably due to sample heterogeneity and problems with blockages of the stopcock in the separating funnel or fouling of the solid phase matrix by particulate matter in the samples. The SPE method, including careful addition of sample to pre-empt blockages, provided a higher concentration of sample and therefore potentially higher recovery. To ascertain these hypotheses a comparison of LLE and SPE was performed using a catering wastewater analogue with a known content of FOG.

3.3.2 FOGs extraction from catering wastewater analogue

The same standard extraction techniques (LLE and SPE with gravimetric analysis) were utilised with synthetic catering wastewater prepared using salad cream suspensions in water. For comparison purposes fat content values (Table 1) were calculated from the oil content in the nutritional information declaration on the label of the salad cream. In addition, the proteins and carbohydrates contained in the salad cream simulated the other constituents of the catering wastewater. The average oil recovery using the LLE-gravimetric technique was 66.1 % ranging between 61.3 and 70.8 %. Using the solid phase extraction technique oil recovery was higher averaging 70.1 % and ranging between 63.4 and 78.2 %.

Table 1: *Comparison of two FOG extraction methods using salad cream in water suspensions.*

Extraction and quantification technique	Sample no	Actual value (calculated from label data) (mg L^{-1})	Value measured (mg L^{-1})	Recovery by difference (%)
Liquid/liquid extraction and gravimetric quantification	1	262	161.0	61.3
	2	259	184.2	70.8
	3	285	189.0	66.2
Solid phase extraction and gravimetric quantification	1	292	201.6	68.7
	2	246	192.4	78.2
	3	262	166.5	63.4

Comparisons of the two standard extraction methods showed higher recovery with SPE (average 70.1%) than with LLE (average 66.1%). One of the advantages of solid phase extraction is that the column aids emulsion breakdown. The reduced oil recovery with both techniques can be explained in terms of hexane extractable material. A portion of the oil is not extracted by this solvent because it is bound to either carbohydrate or protein or a combination of the two, such that it is shielded from the hexane and not solubilised. Solvents alone will not extract oils that are surfactant-stabilised (chemically emulsified oil and dissolved oil) or are combined with other compounds so current extraction techniques for measuring oil in water will only measure free* (clean) or mechanically emulsified oil. The HEM is a measure of the free* (clean) oil in the suspension; in contrast to the total oil in the suspension which comprise in addition the bound and occluded lipids not extracted by the n-hexane. This bound lipid could potentially be released by boiling the sample in a dilute acid as is used for example in dairy analysis, and detailed in BS ISO 8262-3: 2005 (2005) followed by, after suitable drying, a solvent extraction and gravimetric quantitation to determine total oil.

*Free oil in this instance refers to extractable oil not associated with any other material that may shield it from exposure to solvents as opposed to size of oil droplet defined in API 421 and Bande *et al*.(2008) used elsewhere in this thesis.

3.3.3 FOGs extraction from oil in water suspensions

A modification of the standard BS 1825-1 method was developed at Cranfield and compared to the standard LLE and SPE methods and the modified method reported by Ducoste *et al.* (2008), using a simple oil in water suspension.

Two samples extracted with the modified method had an additional sodium sulphate drying step (results not shown). The comparative results of the different extraction methods for oil measurements are reported in Table 2.

Table 2: *Comparison of four different extraction methods using oil in water suspensions*

Extraction and quantification technique	**Sample**	**Actual values (mg L^{-1})**	**Value measured (mg L^{-1})**	**Recovery (by difference) (%)**
Liquid/liquid extraction and gravimetric quantification	1	284.3	209.7	73.8
	2	368.0	278.7	75.7
	3	186.2	145.0	77.9
Solid phase extraction and gravimetric quantification	1	1343	1218	90.7
	2	1468	1356	92.4
	3	1148	1043	91.1
Liquid/liquid extraction modified by Ducoste *et al.* (2008) and IR quantification	1	892.2	681.8	76.4
Liquid/liquid extraction with centrifugation and gravimetric quantification	1	685.7	701.5	102.3
	2	665.2	658.4	99.0
	3	705.8	707.3	100.2
	4	832.3	820.7	98.6

The average oil recovery using the partition-gravimetric technique was 75.3% with a standard deviation of ± 2.1 % (table 1) which is an improvement on the 65.3 % ± 5.0 % and 61.6 % ± 4.6 % recoveries reported by DuCoste *et al.* (2008). The average oil recovery achieved using the solid phase extraction technique was 91.4 % ± 1.0 % which showed an improvement in recovery performance that was also more repeatable compared to the partition-gravimetric method. The extraction technique adopted by DuCoste *et al.* (2008) with subsequent infra-red meter quantification produced an oil recovery of 76.4 % which did not provide any efficiency improvement over the other techniques. The four samples treated with the modified LLE with centrifugation had oil recoveries between 98.6 and 102.3 % whilst the samples that were passed through the drying agent had recoveries of 81.0 and 85.6 % respectively. This would suggest that a significant oil loss occurred during the filtration through the drying agent. It was also noted that after the sample was shaken for 2 minutes, as per standard method, the sample aqueous layer remained slightly turbid suggesting that small oil droplets remained in suspension. After centrifugation the aqueous layer was clear. The variations in recovery values for the four samples were likely to be linked to pipetting errors.

Standard liquid-liquid extraction techniques were found to produce both low recovery and variable results even with clean samples.

Similarly to the synthetic wastewater samples, better recovery values were obtained with the solid phase extraction technique than with the liquid-liquid one. Liquid-liquid extractions that included centrifugation and excluded drying with anhydrous sodium sulphate, enabled complete oil removal from oil in water suspensions and proved to be the best extraction method for it. However, the presence of surfactants or organic matter in these systems interfere with solvent extraction either preventing solvation or by coextracting.

3.3.4 FOGs extraction from oil in water suspensions with surfactants

Oil-in-water suspensions in presence of surfactants (5 g L^{-1} of oil and 0.5 g L^{-1} of sodium dodecyl sulphate (SDS)) were used to evaluate the recovery efficiencies of the newly developed LLE with centrifugation.

Table 3: *LLE with centrifugation using oil/water/surfactant suspensions.*

Extraction and quantification technique	Sample	Actual values (mg L^{-1})	Value measured (mg L^{-1})	Recovery (%)
Liquid/liquid extraction with centrifugation and gravimetric quantification	1	5003	2447	49
	2	5064	3209	63
	3	5363	2514	47

As reported for synthetic and real wastewater, the comparison of the two standard extraction methods showed better recovery with solid phase extraction than with liquid-liquid extraction. However, recovery values of the new method were very low (47 - 63 %) when surfactant was introduced into the system. Extractions to meet effluent consent should be based on a more robust method involving an acid digestion step as per BS ISO 8262-3: 2005, to release the organic matter bound oil in order to determine TOGs.

3.3.5 Turbidity measurement for FOGs quantification

Turbidity measurements were used to provide a simple and rapid monitoring alternative to Soxhlet or SPE extraction for routinely quantifying FOGs in oil/water emulsions in the presence of surfactants. This surrogate method relies on the existence of a correlation between turbidity and HEM. Suspensions of oil, detergent and water, with oil concentrations ranging from 600 to 5000 mg L^{-1} and surfactant concentration of 500 mg L^{-1} (SDS, Tween 80, and commercial washing-up liquid), were used to build correlation curves between HEM and turbidity. The values showed linear correlations, even in presence of surfactants (Figure 8). FOG concentration of samples from CE1 catering wastewater was quantified using the SPE method and compared to concentrations calculated from turbidity readings from the same sample (Figure 9).

Both oil and oil-surfactants in water suspensions showed a linear correlation between oil content and turbidity (Figure 8). The commercial detergent curve was used to calculate the concentrations using the turbidity readings. Turbidity measurements of CE 1 samples ranged from 171 to 419 nephelometric turbidity units (NTUs) with a mean of 254 ± 96 NTU based on one standard deviation.

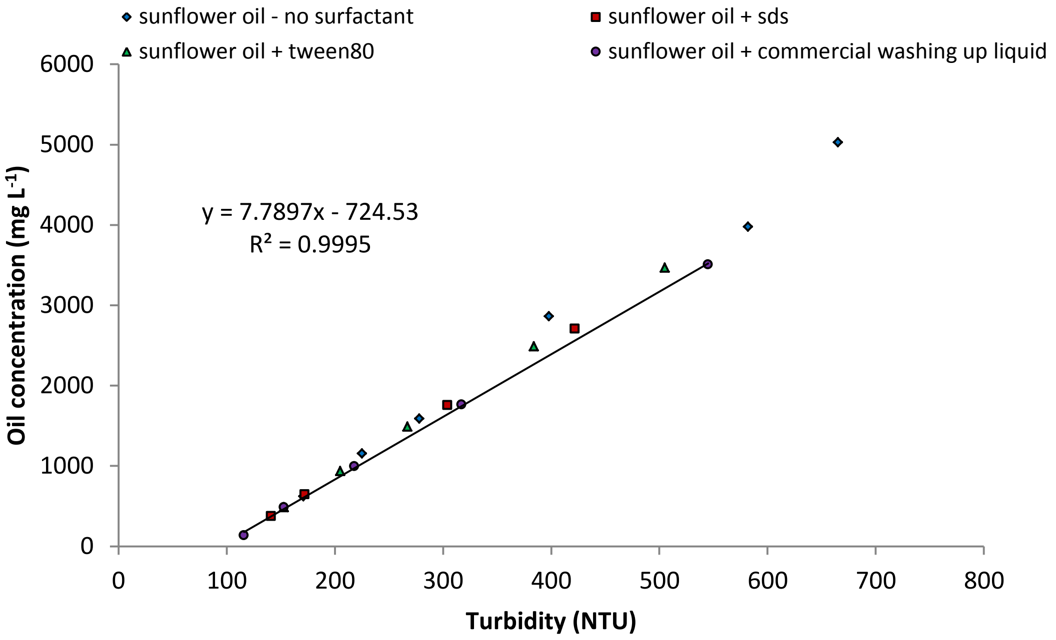


Figure 8: *Correlation between FOGs concentration in suspensions of oil-water-surfactants and turbidity.*

When comparing FOG content measured by the SPE method with corresponding calculated values from turbidity measurements (Figure 9) the data follow a similar trend except for the sample taken on day 4, where a high turbidity value of 419 NTUs corresponded to a low FOG content of 118 mg L^{-1} by SPE. The low FOG recovery with the SPE method was due to fouling of solid phase by a high solids loading as indicated by the high turbidity. A similar low FOG content (138 mg L^{-1}) was observed on day 4 with the partition-gravimetric technique. To address this problem future work could look at mitigating fouling by settling or pre-filtering samples to remove coarse particulates before extraction or turbidity reading.

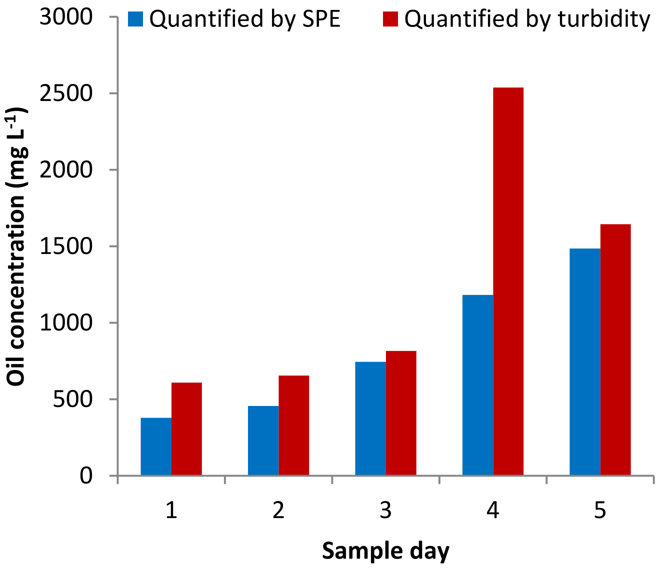


Figure 9: *Comparison of FOG values for the CE1-cafeteria wastewater obtained using SPE-gravimetric method with turbidity readings.*

These results demonstrate that turbidity measurements of surfactant stabilised emulsions could be a useful and cheap alternative for routinely measured oil content changes under experimental conditions for synthetic wastewaters.

3.3.6 Catering wastewater characterisation: BOD, TSS and FOG content

Samples from the 4 catering establishments and from the 2 compartments of the CE1 grease trap were taken over 5 days and measurements of pH, total suspended solids (TSS), biochemical oxygen demand (BOD), Fats oil and grease (FOG), median particle size distribution (d_{50}) and zeta potential were recorded (Table 4).

Table 4: *Catering wastewater characterisation of four on-campus restaurants.*

	pH	TSS ($mg\ L^{-1}$)	BOD ($mg\ L^{-1}$)	FOG ($mg\ L^{-1}$)	Particle size d_{50} (μm)	Zeta potential (mV)	Turbidity (NTU)
CE 1 - Cafeteria	6.0 - 8.0	200 - 1000	150 - 3250	118 - 1485	48 - 56	6 - 64	171 - 419
CE 2 - Restaurant mixed cuisine	7.1 - 7.8	200 - 900	2000 - 2100	97	9 - 123	19 - 59	21 - 159
CE 3 - Dining Hall	6.8 - 7.5	27 - 880	500 - 750	71	23 - 274	14 - 48	8 - 166
CE 4 - Dining Hall	5.5 - 7.5	30 - 380	150 - 600	5 - 15	31 - 138	24 - 64	4 - 68
CE 1 – Grease separator compartment 1	4.1 - 4.6	1.5×10^5	8000	4200 – 4600	60 - 100	10 - 30	
CE 1 – Grease separator compartment 2	4.1 - 4.8	400 - 700	2100 - 2300	150 – 300	4 - 10	20 - 30	

A fall in pH from between 6 and 8 for washing up water to between 4.1 and 4.8 in the grease trap is in line with results reported by DuCoste *et al.* (2008) who suggested microbial activity was responsible for drop in pH values (mechanism is hydrolysis of triglycerides to release free fatty acids thereby lowering pH). Total suspended solids of 200 to 1000 mg L^{-1} were measured in samples taken from the sink with values, in the first compartment of the grease trap, of 1.5×10^{-5} mg L^{-1} and between 400 and 700 mg L^{-1} in the second compartment. The high concentration of suspended solids in the first compartment of the grease trap, relative to the second chamber, shows that the device is achieving its purpose of reducing the amount of food particles that would otherwise enter the sewer. This is further evidenced by the decrease in FOGs, from between 4200 and 4300 mg L^{-1} in the first compartment to below 300 mg L^{-1} in the second compartment with a similar reduction in biochemical oxygen demand (BOD) from 8000 to less than 2300 mg L^{-1}. The relatively high BOD values suggest that there is high soluble organic matter present in the grease trap wastewater. The measurements of particle size distributions in the two compartments (Figure 10) similarly demonstrates removal of food particles with a reduction in d_{50} from between 60 and 100 μm to less than 10 μm because the larger particles will have separated out under gravity through sedimentation or creaming. This fraction, classified as chemically emulsified, will take days to separate by gravity only.

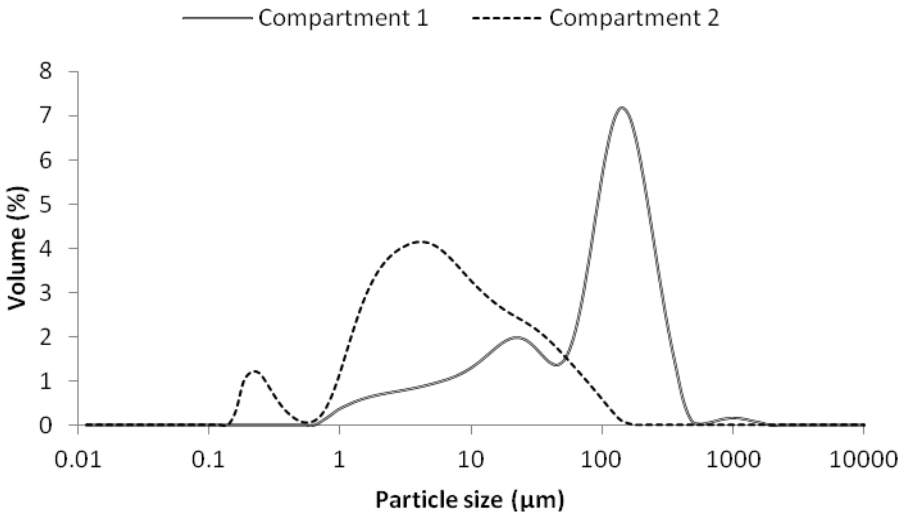


Figure 10: *Comparison of particle size distributions in the 2 grease trap compartments of CE1.*

Zeta potential measurements in both compartments of the separator remain below - 30 mV which is in the region of potential emulsion instability i.e. electrostatic repulsion is reduced so particles are more likely to aggregate and increase possibility of free lipids coalescing.

The characterisation values were compared to the data found in literature which are summarised in Table 5. The data showed a large variation in results obtained for each of the parameters measured. Chen *et al*. (2000) analysed different types of restaurants and obtained BOD and FOG values ranging from 13 to 1320 mg L^{-1} and from 53 to 1970 mg L^{-1} respectively, similar to the values obtained in this study. Values reported by Stoll and Gupta (1997) showed higher BOD and FOG intervals, ranging from 3300 to 9200 mg L^{-1} and from 200 to 3200 mg L^{-1} respectively. This is probably due to the type of cuisine and the kitchen management of the restaurants analysed.

The values obtained from the second chamber of the grease separator are comparable to the results reported by Converse *et al*. (1984) who characterised effluent post-separator from 11 commercial facilities. The values measured ranged from 101 to 880 mg L^{-1} for BOD, from 44 to 372 mg L^{-1} for TSS, and from 24 to 144 mg L^{-1} for FOGs. These same characteristics were used by Garza *et al.* (2005) to identify those management practices and cuisine types that had most effect on wastewater characteristics. The parameters identified as being statistically significant in affecting grease separator effluent were: cuisine type, the presence of self-service salad bars and the number of seats in the establishment. This data confirms the high variability of the values obtained for the influent wastewater across the different studies. DuCoste *et al.* (2008) identified other variables, such grease separator cleaning cycles that were not assessed, which may also cause variation in the measured parameters and as a consequence suggest incorrect conclusions may have been drawn. In their report DuCoste *et al.* (2008) carried out a more extensive examination of wastewater characteristics, including measurements of the flow rates into 23 in-situ grease separators over a 24 hour period and observed that flow rates were highly intermittent with peak flows occurring when food preparation and cleaning procedures were taking place. As sizing of grease separators is largely based on maximum flow rate into them it was noted that during the 24 hour sampling period 75 % of flow was a third of the maximum flow rate resulting in long average residence times exceeding 2 hours. This implies that most of the separators, able to meet the required removal, are oversize and separation is achieved as a consequence of long residence time (more than 2 hours). When analysing the data from Table 6 flow rate and particle size, which are critical in the gravity separation process, are very rarely monitored. There is therefore potential for grease separator size reduction provided the separation efficiency at peak flow could be improved through design or application of a pre and/or post treatment procedure.

Table 5: *Wastewater grease separator influent and effluent characterisation*

Grease separator INFLUENT	**No of Seats**	**pH**	**TSS ($mg\ L^{-1}$)**	**BOD ($mg\ L^{-1}$)**	**COD ($mg\ L^{-1}$)**	**FOG ($mg\ L^{-1}$)**	**Particle Size d_{50} (μm)**	**Zeta potential (- mV)**	**Turbidity (NTU)**	**Flow rate**	**References**
Chinese restaurant	–	–	13 - 246	58 - 1430	292 - 3390	120 - 172	–	–	–		Chen *et al.* (2000)
Western restaurant	–	–	152 - 545	489 - 1410	912 - 3500	53 - 2100	–	–	–		
Fast-Food	–	–	68 - 345	405 - 2240	980 - 4240	158 - 799	–	–	–		
Dining Hall	–	–	124 - 1320	545 - 1630	900 - 3250	415 -1970	–	–	–		
Cafeteria/Bistro	–	–	359 - 567	451 - 704	1500 - 1760	140 - 410	–	–	–		
Thai and Japanese restaurant	150	6.7	1380	7400	21300	200 - 1850	–	–	–	54 (L/meal)	Stoll and Gupta (1997)
Western restaurant	300	7	1100	9200	20900	580 - 3200	–	–	–	27 (L/meal)	
Thai and western	140	7.3	2160	6000	20900	730	–	–	–	2.5 (L/meal)	
Asian Cafateria	200	7.1	2400	3330	8100	1110	–	–	–	16 (L/meal)	
Average from 11 commercial facilities	–	–	44 - 372	101 - 880	–	24 - 144	–	–	–	–	Siegrist *et al.* (1985)
Fast food restaurant	–	–	–	–	1970 - 2400	312 - 836	–	–	–	–	Chan (2010)
Cafeteria (CE1)	–	4.4 - 6.9	200 - 1000	150 - 3250	–	256 - 1183	48 - 56	6 - 34	171 - 419		Present study (average of 5 sampes)
Restaurant - mixed cuisine (CE 2)		7.1 - 7.8	200 - 900	2000 - 2100	–	97	9 - 123	19 - 59	21 - 159	–	
Dining Hall (CE 3-4)		6.8 - 7.5	27 - 880	150 - 600	–	5 - 71	23 - 274	14 - 64	3 - 166	–	
Restaurant, hotel, stores in Japan		5 - 8.1	2 - 2800	3 - 1600	4 - 410	0 - 3800	–	–	–	–	Nakajima *et al.* (1999)

Grease separator EFFLUENT	**No of Seats**	**pH**	**TSS (mg L^{-1})**	**BOD (mg L^{-1})**	**COD (mg L^{-1})**	**FOG (mg L^{-1})**	**Particle Size d_{50} (µm)**	**Zeta potential (- mV)**	**Turbidity (NTU)**	**Flow rate**	**References**
Wastewater in grease separator											
Compartment 1	–	4.1 - 4.6	1.5 x 10^5	8000	–	4200 - 4600	60 - 100	–	–	–	Present study (average of 5 sampes)
Compartment 2	–	4.1 - 4.6	400 - 700	2100 - 2300	–	150 - 300	4 - 10	–	–	–	
Restaurant wastewater after trap											
Average domestic after septic tank	–	6.6 - 7.4	88	140	356	38	–	–	–		Harkin (1979)
Dining hall	–	5.5 - 6.2	–	–	–	66 - 1380	–	–	–		WERF (2008)
Restaurant	70 - 160	5.5 - 7.1	65 - 372	261 - 880	586 - 1667	40 - 144	–	–	–	28 - 49 (L/seat)	Converse (1996)
Restaurant/Motel	160	6.5 - 7.1	66	171	381	45	–	–	–	–	
Restaurant/Golf club	100	6.0 - 7.4	44 - 121	101 - 333	227 - 620	33 - 46	–	–	–	31 (L/seat)	
Bar/Grill	40	6.0 - 7.0	79	179	449	49	–	–	–	42 (L/seat)	
Fast food restaurant	–	–	–	–	15 - 82	450 - 1250	–	–	–	–	Chan (2010)
Cafeteria (CE1)	–	4.1 - 4.6	400 - 700	2100 - 2300	–	150 - 300	4 - 10	–	–	–	Present study
Restaurant, hotel, stores in Japan	–	3.7 - 8.2	0 - 120	1 - 120	4 - 130	0 - 13	–	–	–	–	Nakajima *et al.* (1999)
Average results for samples from 28 restaurants	–	–	664	1523	–	197	–	–	–	96 (L/seat)	Lesikar *et al.* (2006)

3.3.7 Catering wastewater characterisation: zeta potential

The zeta potential of wastewater samples collected at the 4 catering establishments was monitored for 2 periods of 5 days each. The results of the first week are reported in Figure 11. The values across all the samples ranged between - 5.8 and - 68.2 mV. Samples taken from CE1 ranged from - 5.8 to - 34.1 mV which contained both the lowest value and narrowest range of zeta potential measured. CE2 sample measurements ranged from - 19.9 to - 57.9 mV, with those from CE3 ranging between – 16.3 and - 46.6 mV. Measurements of CE 4 samples ranged from – 24.9 to – 68.2 mV which included both the highest value and widest range of zeta potential.

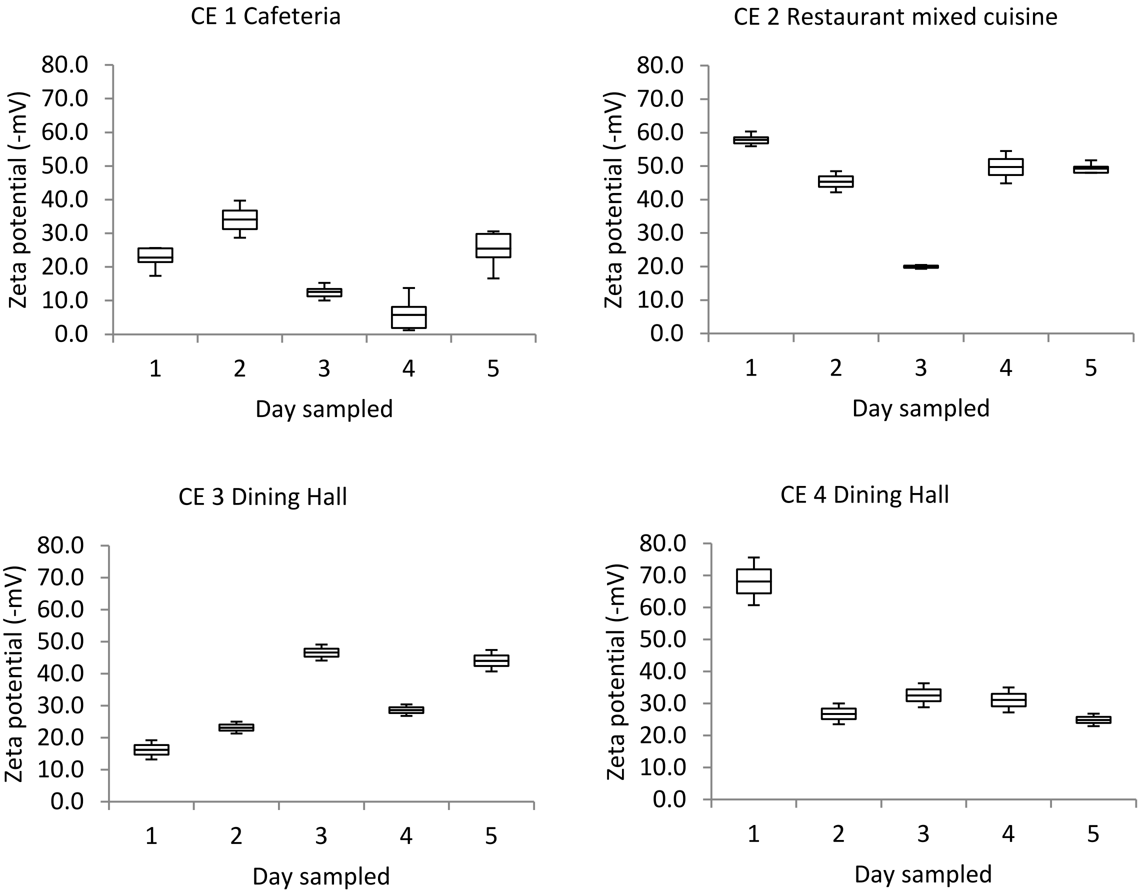


Figure 11: *Zeta potential measurements of wastewater from four on-campus catering establishments.*

It is conventionally accepted that suspensions with a zeta potential in excess of ± 25 - 30 mV are electrostatically stabilised where charge repulsion between particles prevents their aggregation or coalescence. As commercial washing up detergents used for dishwashing contain anionic surfactants, combined with dishwasher salts and hard water locally the zeta potential of any samples would be expected to have an increase in their negative charge. The charge naturally associated with oil in water suspensions was measured, for two widely used vegetable oils, to be of the order of - 53 mV for sunflower oil and - 44 mV for olive oil. In a buffered solution (10 mM Na_2SO_4, 1 mM NaCl) the zeta potential increased to - 86 mV for the sunflower oil and - 82 mV for the olive oil suspensions. The addition of sodium dodecyl sulphate,(SDS) an anionic surfactant, to the sunflower oil suspension increased the zeta potential to - 111 mV. The overall zeta potentials of the washing up water were all significantly lower than this and measurements could reflect the absence of either oil droplets or detergent in some of the samples or the presence of other food proximates that have positive charge associated with them. This was demonstrated in samples taken from CE 4 on days one and two where low turbidity readings of 3 and 6 NTUs, indicated there were no fine food particles suspended in the samples, but had zeta potentials of - 64 mV on day one and - 26 mV on day two which would imply that there was more detergent in the day one sample. The CE 1 samples were taken from the pot wash sink, where utensils used in production of fried food were washed in hot water using a commercial washing up liquid (CRG994 Country Range, Burnley, UK). All the samples had a zeta potential of less than - 35 mV over the five day sampling period and it was noticeable that these samples also have the highest average turbidity, (254 NTU) and lowest average zeta potential, (- 20 mV). This suggests that other ingredients in the washing up water have a positive charge associated with them or they have a buffering action, which reduces the overall charge. Lower zeta potential is associated with lower emulsion stability making more likely the process of aggregation and/or coalescence.

3.3.8 Catering wastewater characterisation: particle size distribution

The particle size distribution of wastewater samples collected at the four catering establishments was monitored for 2 periods of 5 days each. The results of the first week are reported in Figure 12. For samples taken from CE 1 droplet median particle size (d_{50}) ranged from 48 to 56 µm, which was the narrowest range of values, measured over the week. The CE 2 samples had values ranging from 17 to 204 µm that included the lowest d_{50} value measured. Samples from CE3 d_{50} ranged from 23 to 274 µm which included widest range and highest median particle size measured during the week. The CE 4 samples had median particle sizes ranging from 58 to 138 µm.

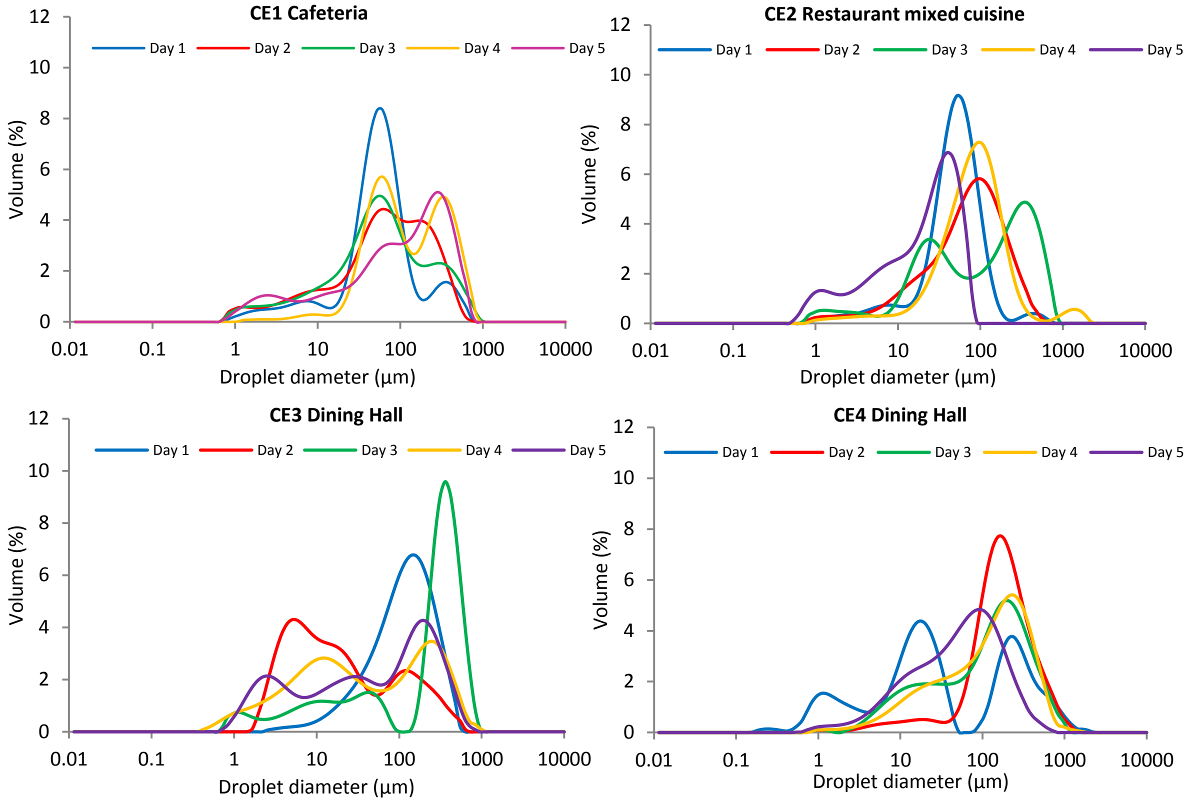


Figure 12: *Median particle size distribution (d_{50}) measurements for on-campus catering establishments*

Due to the heterogeneity of the samples we might expect the d_{50} values to be very variable however measurements made over the 5 day sampling period were relatively similar and fell between 48 and 124 µm with the exception of the samples from the CE 2 and CE 4 taken on day 2 and CE 3 on day 3. Unless food particles are the same density as the water we might expect larger particles to separate out under the influence of gravity leaving a range of particles below a certain size as being representative of a typical washing up water suspension.

API 421 states that "conventional oil-water separators remove only free oil; stable emulsions and dissolved oil require additional treatment". It does not, however, specify what happens to the intermediate oil droplet fraction. Table 6 summarises the different types of emulsion found in catering wastewater.

With the exception of three samples, the d_{50} of all our measurements fell between 20 and 150 µm, according to the classification reported in Table 6, these measurements correspond to the droplet size distribution fraction of mechanically-emulsified oil, as defined by Bande *et al.* (2008).

Table 6: *Classification of oil in water emulsions according to their droplets size.*

Droplets Size (µm)	Emulsion type	Emulsion Stability	Separation Time
≥150	Free oil - Low miscibility with water, rapidly rises to the surfaces	Macro emulsion Weak	≤10 minutes
20-150	Dispersed or mechanically emulsified oil – Produced by the water flow and stabilised by electrical charges	Micro-emulsion Moderate	Hours
1-20	Chemically emulsified oil - Miscible with water, stabilized by surfactants.	Micro-emulsion Strong	Days
≤1 (colloidal)	Dissolved oil - water is translucent and transparent. Removal by filtration, gravity settling is impossible.	Very Strong	Weeks

Modified from Bande et al. (2008) and API (1990)

3.3.9 Catering wastewater characterisation: FOG concentration

For illustrative purposes the FOG concentration values from the SPE analysis of day 4 and the particle size distribution reported in Figure 11 were used to quantify the different fractions defined above for the four catering establishments. FOG concentrations for the four establishments on day 4 were: 257 mg L^{-1} for CE1, 71 mg L^{-1} for CE2, 97 mg L^{-1} for CE3 and 5 mg L^{-1} for CE4. The results are reported in Figure 12.

The fraction of free-oil is not present in samples from CE1 and CE2 and only less than 20% of the particles in the suspensions fall in the range below 20 µm and therefore into the “inseparable by gravity” category. The sample of CE4 was very clear and the presence of particle size above 20 µm (Figure 12) was probably due to the free surfactant (air bubble inclusion).

The particles found in the catering wastewater are therefore potentially separable in a matter of hours. The average residence time in gravity separators calculated by

Ducoste *et al.* (2008) across 23 catering establishment over a 24 hour period, was approximately 2 hours. This would allow the majority of such separation to happen. The measurement of the droplet size of the oil-water emulsion is an important parameter defining the stability and the rheology of the emulsion. The measurement and prediction of droplet sizes in the catering wastewater system is fundamental in assessing and improving gravity separator performance. If improvements to the separation are required, it is important to acknowledge this information by allowing longer retention times, preventing mechanical emulsion formation or facilitating mechanically emulsified FOGs coalescence.

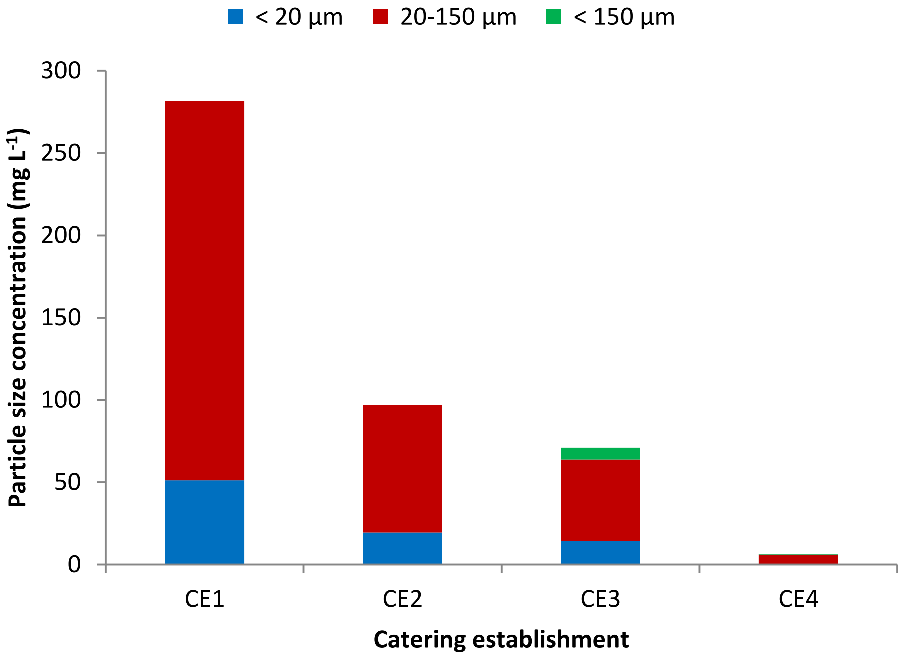


Figure 13: *Quantification of the fractions of emulsified (d < 20 µm), mechanically emulsified or dispersed (d = 20 to 150 µm) and free oil (d > 150µm) from four different catering establishments.*

The zeta potential and the particle size measurements of all the samples from the 4 catering establishments collected over the 2 weeks sampling campaign were plotted against each other and are presented in Figure 14. An Anova single factor analysis resulted in an F value of 190 and an F crit value of 4 when F > F crit the null hypothesis is rejected such that there is a difference between measurements.

The wastewater samples collected from the catering establishments had pH ranging between 4.4 and 7.8 and zeta potential values between - 6 and - 64 mV. The particle size measurements of the catering wastewater indicate that the majority of the oil droplets are included into the mechanically emulsified range between 20 and 150 µm diameter.

Very few samples fall into the “gravity inseparable” zone (zeta potential > ±30 mV and particle size < 20 µm). This suggests that possible improvements in gravitational separation can still be achieved by, for example, decreasing zeta potential to aid increasing particle size, the main aim of this thesis work.

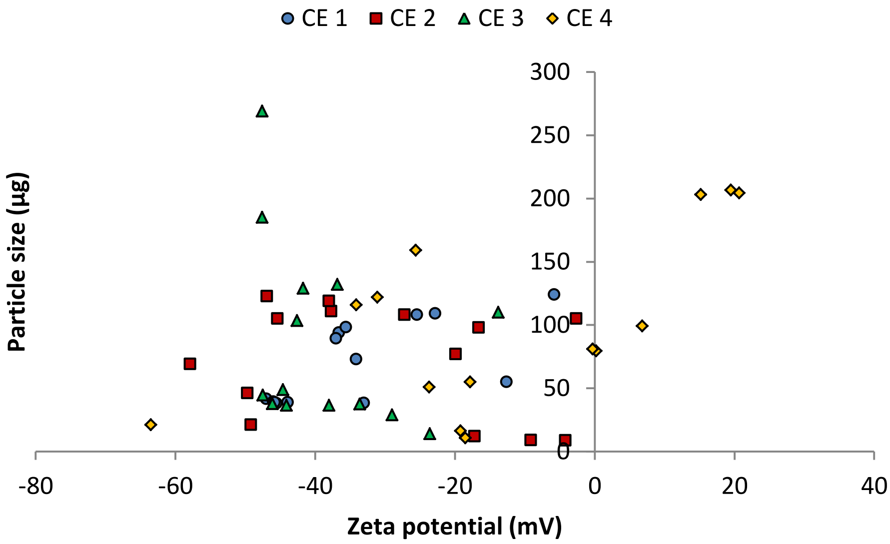


Figure 14: *Particle size and zeta potential measurements of four Cranfield University catering establishments over 2 weeks sampling campaign.*

3.4 Conclusions

Over the sampling period there is substantial variability in measured characteristics both between catering establishments and between samples collected at the same establishment. When characterising or monitoring oil content in catering wastewater it is important to select the most suitable method. Solvent-based extractions (SPE and LLE) will only extract the “free” (clean) lipid fraction, rather than total FOG, from catering wastewater samples. Comparison of the two extraction methods showed better recovery with SPE than with LLE as the SPE column aids emulsion breakdown. Thus, although it does not extract all FOGs, solvent based SPE is probably still a suitable method for routine monitoring purposes designed to detect relative changes. Turbidity measurements of surfactant-stabilised emulsions provide comparable results to SPE-based extraction and could be a useful and cheap alternative for routine in-house measurement of oil content changes in laboratory scale defined wastewater treatment systems.

Assessment of discharge consent compliance, on the other hand, requires that TOGs in the suspension are determined, making both solvent based methods inappropriate. Such assessments, therefore, need an acid digestion step to release the ‘bound’ oil as typically used, for example, in dairy analysis.

Zeta potential measurements in many of the samples was greater than – 30 mV and, unless a chemical coagulant is added to the system, suggest that significant coagulation will be unlikely to occur.

Whilst there was variation in median particle size distribution (d_{50}) in kitchen wastewater samples from different establishments and between daily samples, they were mostly below the minimum free oil value of 150 µm and within the mechanically emulsified/dispersed oil droplet size range of 20 to 150 µm produced by washing/cleaning operations and stabilised by electrical charges. These micro-emulsions generally have moderate stability and should separate by gravity in a matter of hours.

It is essential to monitor these parameters when trying to improve the design of wastewater treatment systems serving the restaurant industry.

The initial evaluation of the data suggests that improvements can be achieved by simple design change, allowing longer retention times or preventing mechanical emulsion formation. In addition, simple pre-treatments to facilitate mechanically emulsified FOG coalescence could be added to the design, potentially allowing for the development of smaller separation tanks.

3.5 References

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4 Understanding performance of grease traps: parameters influencing phase separation

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Abstract

Removal of fats, oils and greases (FOGs) from commercial food premises prior to discharge of wash waters into the sewer is critical in restricting blockage events. The FOG droplets that form are commonly removed in passive gravity separators which have been tested against a standard based on light fuel oil (diesel). The current study aims to investigate the impact of density and droplet size on the removal in passive separators to better understand treatment efficacy and discuss appropriate testing procedures to mimic real situations. To achieve this a series of oils were dispersed in water and removed in a batch separator. The droplet size formed under a fixed energy input was different for each oil such that very different separation efficiencies were observed. Elucidation of the potential factors revealed that separation could be effectively defined through application of the parameters included in Stokes law. The overall implications of the work are that for effective understanding of separator design and testing droplet densities and sizes must be adequately measured and replicated.

4.1 Introduction

Fats, oils and greases (FOGs) from commercial food preparation premises are implicated in 50% of the estimated 25,000 sewer blockages in the UK every year with an associated remediation cost of £15 - 50 million (Williams *et al.*, 2012). FOG management strategies often include the installation of a grease trap/interceptor/separator in the drain between the kitchen or food processing area and the sewer to reduce the FOG concentration entering the sewer as a consequence of washing operations. Grease separators fall into three main categories: passive gravity separators, mechanically assisted separators (skimmers) and biological treatment/separators. This paper is focussed on passive grease separators that work on the principle that immiscible liquids with different densities will separate out under gravity in quiescent flow conditions.

The British standard BS EN 1825-1:2004, prescribes methods to assess the separation performance of passive grease separators, whilst the sizing of separators in BS EN 1825-2:2002 is determined by a set of empirical data based on flow rates into the unit. The maximum flow rates are multiplied by factors for the density difference between phases, influent temperature and use of cleaning agents, to produce a nominal size (NS). Additional volume, based on NS, is included to accommodate a grease separation zone (NS x 240 litres), accumulated sediment (NS x 100 litres) and FOG (NS x 40 litres) so an NS 2 separator would be a minimum of 760 litres in volume (0.76 m^3). Direct measurement of flow into grease separators can alternatively be estimated from type of catering equipment or type of establishment discharging into the separator. There is also provision for a special calculation that can be used for individual cases and this dispensation in the regulations for determining flow rates has allowed grease separator suppliers to expand the sizing methodology to take account of other variables to calculate NS, for example the number of seats in a restaurant and hours of kitchen operation (ACO Building Drainage, 2006). Ultimately, current design practice is to size separators for a residence time of 4 minutes at peak flow although a recent study has suggested that over a 24 hour period the actual flow is less than a third of the peak for 75 % of the time resulting in a daily average residence time of 2 hours (DuCoste *et al*., 2008).

However for all the emphasis on sizing methodology there is a paucity of published scientific data related to the performance efficiency of the separators in the field or to confirm the scientific basis of the sizing (DuCoste *et al*., 2008). For instance, data on grease separator effluent published by Lesikar *et al.* (2006) identified external factors influencing effluent characteristics but there was no data of the corresponding influent for assessing the separator performance. More recently Ducoste *et al*. (2008) produced data from examination of in-situ grease separators demonstrating that under quiescent conditions typical food waste solids sediment out efficiently. They also measured total oil and grease of the separator influent and effluent over 2 days but the results were insufficient to calculate removal efficiency.

Earlier work on grease separator design published by the American Petroleum Institute (API Publication 421, 1990) looking at removing mineral oils from refinery waste water identify oil droplets in three major forms; free, emulsified and dissolved. Free oil is defined as droplets with a diameter greater than 150 µm that will rise due to buoyant forces under quiescent flow conditions Emulsified oil is defined as droplets with a diameter between 1 and 20 µm where inter-particle forces overcome buoyancy force preventing gravity separation and requires some additional treatment to effect its removal. Dissolved oil is identified as droplets with sub 1 µm diameter which again needs additional treatment (possibly biological) to remove.

Theoretical consideration of the problem indicates that the rise rate of droplets and hence removal is influenced by the droplet size, density and droplet concentration. In dilute cases with relatively small sized droplets the motion of the droplets in quiescent fluids can be considered in terms of an individual droplet and is described by Stokes law:

$$v_t = \frac{\Delta\rho g d^2}{18\mu} \tag{1}$$

where v_t is the terminal rise velocity, $\Delta\rho$ is the density difference between the droplet and water, d is the droplet diameter and µ is viscosity of water. The applicability of Stokes law is defined through calculation of the particle Reynolds number that must be less than 1 equivalent to particle sizes typically over several 100 µm:

$$Re_p = \frac{\rho v d}{\mu} \tag{2}$$

where ρ = particle density (kg^{-1} m^{-3}), v = particle velocity (m s^{-1}), d = particle diameter (m) and μ = dynamic viscosity of the continuous phase (kg^{-1} m^{-1} s^{-1}). As the droplet concentration increases the rise velocity is hindered (reduced) due to the influence of the neighbouring droplets. The impact on mono dispersed particles is most commonly accounted for through the use of the Richardson and Zaki equation (1997):

$$V_s = V_{stokes}(1 - \varnothing^n) \tag{3}$$

Where V_s = velocity of particles in suspension (m s^{-1}), $\varnothing$ = volume fraction of particles and n = slope of the log plot of velocity of the suspension (V_s) versus log plot of the particle volume fraction ($\varnothing$). Critical concentration beyond which hindered rise can be expected is around a minimum of 1% by mass (1000 mg L^{-1}) (Holdich, 2002). Typical FOG characteristics (Chapter 3) equate to particle Reynolds numbers below 0.1 and concentrations of less than 1% and hence Stokes law is expected to apply. This has been confirmed by investigations into the creaming velocity of polydispersed paraffin oil in water with a particle size ranging between 7 to 27 µm and a concentration of 0.2% (Kumar *et al.*, 2000). In experimental runs with a more concentrated suspension (2.6 %) Stokes law was still seen to apply but the smaller droplets moved at a similar rate to the larger droplets, a rate greater than predicted by Stokes through the larger droplets dragging the smaller ones along with them.

Application and inclusion of the interaction of particles is not always considered in the design and testing of FOG separators due in part to the paucity of available data on incoming FOG characteristics. In addition performance testing of separators is commonly conducted with a light fuel oil that is added in an uncontrolled way making judgement about the droplet size difficult. Overall there remains uncertainty as to the suitability of a light fuel oil as a surrogate for FOG when assessing the efficacy of separators (Forty, 2005). The current study aims to address this by investigating the impact of changes in the oil type, droplet size and density on the separation of FOG in passive separators. The work included the assessment of the batch separating characteristics of ten oils to provide coverage of the likely properties to be encountered. The work assessed the role of changes in droplet size on separation efficiency and consequences for FOG separation design and testing.

4.2 Materials and methods

4.2.1 Materials

Samples of commercially available sunflower oil, (Costcutter, Cranfield, UK), olive oil, (J. Sainsbury, Bedford, UK), celery seed oil (d-limonene: 1-methyl-4-(1-methylethenyl)-cyclohexane), star anise oil (anethole: 1-methoxy-4-(1-propenyl) benzene), cinnamon oil (cinnamaldehyde: 3-phenylprop-2-enal), fish oil, octanoic acid (Sigma, Dorset, UK) and oleic acid (Fisher, Loughborough, UK) were used in these experiments.

4.2.2 Sample preparation

Oil in water suspensions were prepared by adding, via a tared 10 ml syringe, weighed portions of oil to approximately 490 ml of buffered deionised water (1 mM $NaHSO_4$, 0.1 mM NaCl adjusted to pH 7 with 5 M HCl) in a 500 ml graduated cylindrical separating funnel. The total volume in the separating funnel was then made up to 500 ml with buffered deionised water and dispersed at 3000-10000 rpm for one minute with a high speed mixer (IKA Ultra-Turrax T25 with a S25N 18G dispersing head, Fisher Scientific, UK). All samples were made to a concentration of 0.5 % based on preliminary trials to establish appropriate operating ranges for the analytical equipment

4.2.3 Oil characteristics

Oil density was measured in a 5 ml pycnometer (Fisher Scientific, UK) and viscosities determined using a ‘Cup and bob’ viscometer (Brookfield model DV-E, Harlow, UK). Static interfacial tension between oils and water was measured using a du Knoy ring tensiometer (Kruss K6, Bristol, UK). Zeta potential was measured using a Zetasizer 2000HSA (Malvern instruments, UK).

4.2.4 Particle size distribution measurement

Droplet size distribution was measured by transferring the oil in water dispersion into a 1 litre glass beaker. The suspensions were pumped at (60 ml min^{-1}) by peristaltic pump, (model 505S Watson Marlow, Falmouth, UK), through a laser diffraction particle sizer (Mastersizer, Malvern Instruments, UK) and the particle size distribution measured at 1 minute intervals for 10 minutes.

4.2.5 Separation trials

Oil droplet separation was assessed in a batch separation device (Figure 1) based on an adaptation of the method used to assess the susceptibility to separation (STS) of oil droplets in the API publication 421 appendix B (1990) and as suggested in a critical review by McClements (2007). Batches of oil in water suspensions were prepared in 500 ml separating funnels with each allowed to stand for a residence time (τ) between 0.15 and 120 minutes before sample aliquots were taken by draining the lower 200 ml of the suspension into pre-weighed centrifuge bottles. A sample was also taken immediately after sample preparation ($\tau = 0$) to remove losses due to oil adhering to the preparation equipment.

Figure 1: *Batch separation simulation*

4.2.6 Oil quantification: Control experiment for oil recovery

Into a series of 250 ml PTFE centrifuge bottles, containing approximately 200 ml of deionised water, recorded portions of sunflower oil between 665.2 mg and 932.3 mg were added via a tared syringe. The samples were then treated as described in the following hexane extractable material (HEM) measurement technique. HEM from two of the six samples was passed through anhydrous sodium sulphate (Na_2SO_4), as recommended in US EPA Method 1664 (US EPA /R-98-002, 1999) to remove any water that may be included in the sample.

4.2.7 Hexane extractable material (HEM) measurement

The oil content, referred to henceforth as HEM of samples, was quantified according to a partition-gravimetric method adapted from US EPA Method 1664. Each of the samples collected in a 250 ml PTFE centrifuge bottle was adjusted to approximately pH 2.0 by the addition of a predetermined volume of acid, (5M hydrochloric SVS, Fisher, UK). Paired centrifuge bottles containing the pH amended samples were adjusted to the same weight with deionised water prior to addition of 50 ml n-hexane, (HPLC grade, Fisher, Loughborough, UK) via a bottle top dispenser, (Brand Dispensette III Fisher, UK). After closure the centrifuge bottles were manually shaken for 2 minutes, to replicate standard method US EPA 1664 for liquid-liquid extraction, before centrifugation at 4,000 x g in a centrifuge (Sorvall Legend RT+, DJB labs, Newport Pagnall, UK) for 10 minutes. Following centrifugation 3 x 10 ml aliquots of the hexane layer were transferred using a variable 10 ml pipettor, (Finnpipette Fisher, UK), from the centrifuge bottle into a pre-weighed 100 ml round bottom flask which was then attached to a rotary evaporator (Heidolph Laborota 4,000) connected to a vacuum pump (RE202 Patterson Scientific, Cambridge, UK) and the solvent dried off under vacuum at 45°C. The flasks were placed in a drying oven (Genlab N75C, Widnes, UK), set at 45°C and dried overnight before transferring to a desiccator to cool. The flasks were weighed on an analytical balance (Adam Balances PW 254, Adam Equipment, Milton Keynes, UK) and HEM residue calculated by difference.

4.3 Results and discussion

4.3.1 Impact of oil type on droplet properties and HEM removal

The density of the different oils under investigation ranged between 0.89 and 1.04 g ml^{-1} which compares to 0.85-0.94 g ml^{-1} for animal fat, 0.91 g ml^{-1} for butter, 0.9 g ml^{-1} for cooking oil and 0.84 g ml^{-1} for diesel oil (Table 1). Variation was also seen in terms of the viscosity and interfacial tension of the bulk oils and the zeta potential of the formed droplet. The former results from differences in the size and structure of the molecules contained within each oil and the respective inter molecular and interfacial bonding energies. For instance olive oil, sunflower oil and fish oil are made up of larger aliphatic triglyceride molecules compared to celery seed, star anise and cinnamon oils which are essential or volatile oils that are primarily composed of relatively small short chain aromatic molecules. The practical consequence is that for a fixed energy input (i.e. rpm) the different oils generate different droplet sizes (Figure 2). To illustrate, the median droplet size varied between 7 µm for cinnamon oil and 32 µm for sunflower oil and this correlates approximately to the interfacial tension for each oil. Overall the oils composed of the larger aliphatic triglyceride molecules tended to have the higher viscosity, interfacial tension and droplet size.

Analysis of the size distributions (Figure 2) in terms of the API definitions of FOG indicated that all the oil existed in droplets of less than 150 µm in diameter The implication is that in all cases the oil does not exist as free oil indicating that additional treatment will be required to aid removal in traditional separators according to the current treatment guides (API, 421; DuCoste *et al.*, 2008). The percentage of the droplets defined as chemically emulsified (1 - 20 µm) varied between the oils with some grouping based on the type of molecules the oil contains. For instance, 7 %, 10 %, 97 % and 100 % of the droplets were sized below 20 µm for the star anise oil, oleic acid, celery seed oil and cinnamon oil respectively which are mainly comprised of small short chain aromatic molecules. In contrast only 20 %, 34 % and 35 % of the droplets were below 20 µm for the sunflower oil, fish oil and olive oil respectively that are made up of the larger aliphatic triglyceride molecules. In comparison diesel oil was comprised of 80 % sub 20 µm droplets indicating that it is a poor surrogate of the types of droplets formed by triglyceride oils under the controlled testing environments utilised in the current study.

The stability of the droplets was confirmed by zeta potential measurements that varied between -53.5 and -106 mV as a median value. These levels are known to generate sufficient electrostatic repulsion to inhibit aggregation (coalescence) (Henderson *et al.,* 2006) and so can be assumed to remain discrete during the subsequent separation experiments

Table 1: *Physical characteristics of oils and fatty acids*

Oil/acid type	**Density (g ml^{-1})**	**Viscosity (mPa s)**	**Interfacial tension (mN m^{-1})**	**Zeta potential (mV)**	**Median particle size (d_{50})* (μm)**	**HEM removal after 10 minutes (%)**
Celery seed	0.89	2.47	39.0	- 88.2	12	8.6
Oleic‡	0.89	32.4	40.5	- 106.0	20	32.5
Octanoic‡	0.91	5.74	34.8	- 81.4	9	2.5
Olive	0.91	77.0	54.2	- 81.9	30	56.1
Sunflower	0.92	56.6	49.0	- 86.0	32	41.5
Fish	0.93	45.5	51.9	- 66.9	29	33.3
Star anise	0.98	2.82	54.9	- 53.5	21	3.9
Cinnamon	1.04	8.85	36.8	- 58.0	7	2.0
Diesel	0.84	< 5^	51.2	-	14	70.7

*dispersion for 2 minutes at 10,000 rpm; ‡ acids; ^Forty (2005).

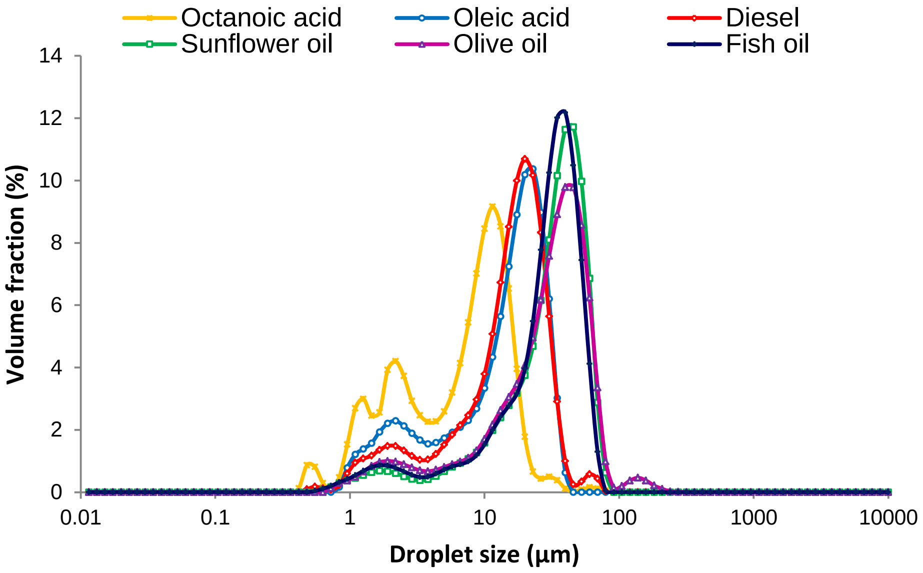

Figure 2: *Particle size distributions for different oils and fatty acids when dispersed at 10,000 rpm for 1 minute.*

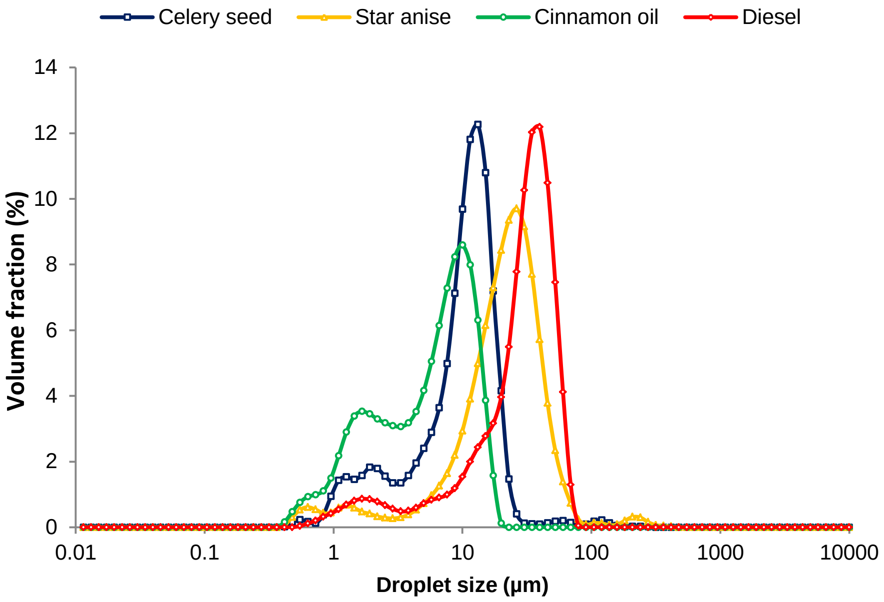

Figure 3: *Particle size distributions for different aromatic oils and diesel when dispersed at 10,000 rpm for 1 minute.*

HEM removal over time followed a similar pattern for most of the tested oils where removal remained low for the initial 2-10 minutes of separation followed by a rapid increase in removal (Figure 4). To illustrate, in the case of diesel oil, removal remained below 50% for the first two minutes after which HEM removal increased to 73%, 90% and 93% after 10, 20 and 120 minutes respectively. A different pattern was observed for sunflower oil, olive oil and fish oil where removal increased steadily over the duration of the experiment. Removal after 10 minutes ranged between 2 and 56% with the highest values recorded for olive oil (56%) and sunflower oil (42%). In comparison, after 120 minutes oil removed had increased to between 12 and 95% with removal exceeding 90% with four of the oils tested indicating a clear impact of oil type on the removal profile obtained.

The implication is that changes in the properties of oil droplets will influence the achievable removal in existing separators and will alter the required size for new installations. To illustrate, to achieve 60% removal approximate separation times of 10.5, 15, 22, 30 and 60 minutes are required for olive oil, sunflower oil, fish oil, oleic acid and celery seed oil respectively. In contrast, 60% removal was not achieved within 120 minutes in the case of star anise oil, octanoic acid and cinnamon oil. The data also indicates that diesel oil over predicts removal compared to oil types commonly used in kitchens. For instance 70% of the diesel had been removed after 10 minutes of separation, which increased to 90% after 20 minutes. Further, 60% removal occurred after around 4 minutes, the standard design residence time at peak flow.

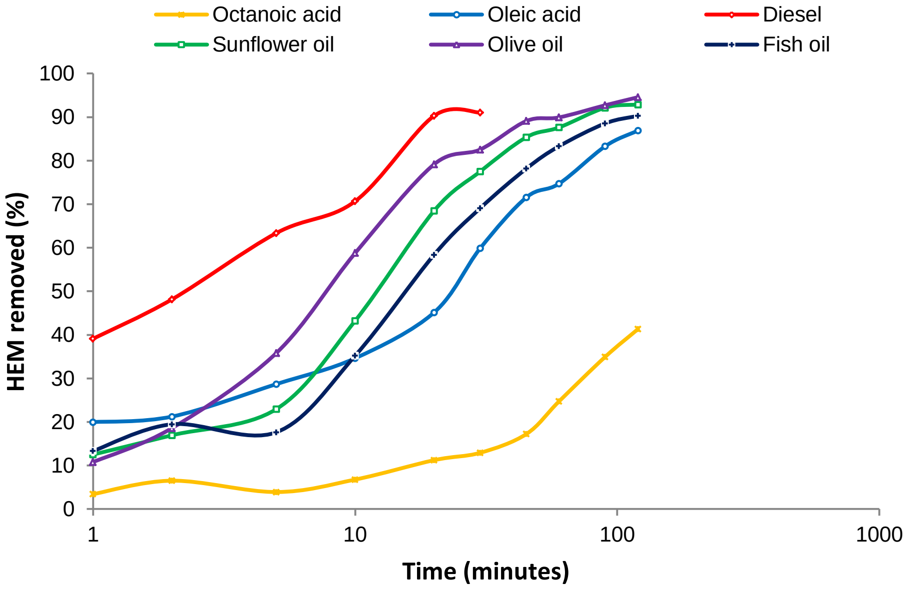

Figure 4: *HEM removal for different oil and fatty acid suspensions when prepared at 10,000 rpm for 1 minute.*

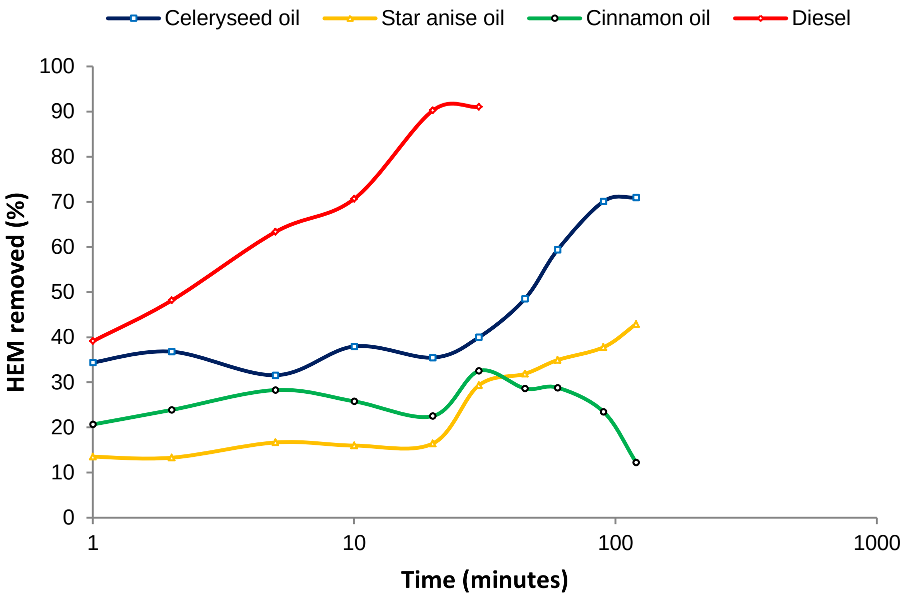

Figure 5: *HEM removal for different aromatic oils and diesel suspensions when prepared at 10,000 rpm for 1 minute*

4.3.2 Influence of density on HEM removal

To further elucidate the impact of the different oil properties a series of separation experiments were conducted on oils whose droplet size had been normalised to 32 µm (sunflower case) through changes in the dispersion energy input (mixing speed of the stirrer) (Figure 6). In all cases a decrease in shear rate resulted in an increase in the median droplet size demonstrating the levels of agitation associated with the initial droplet formation are likely to have a significant influence on overall separator performance. The change in median droplet size was not consistent based on the droplet size formed at 10,000 rpm with any of the physical properties of the oil indicating the relationships are complex and is not easily predicted but did show that diesel oil followed an observably different pattern to the triglyceride oils used in the current investigation.

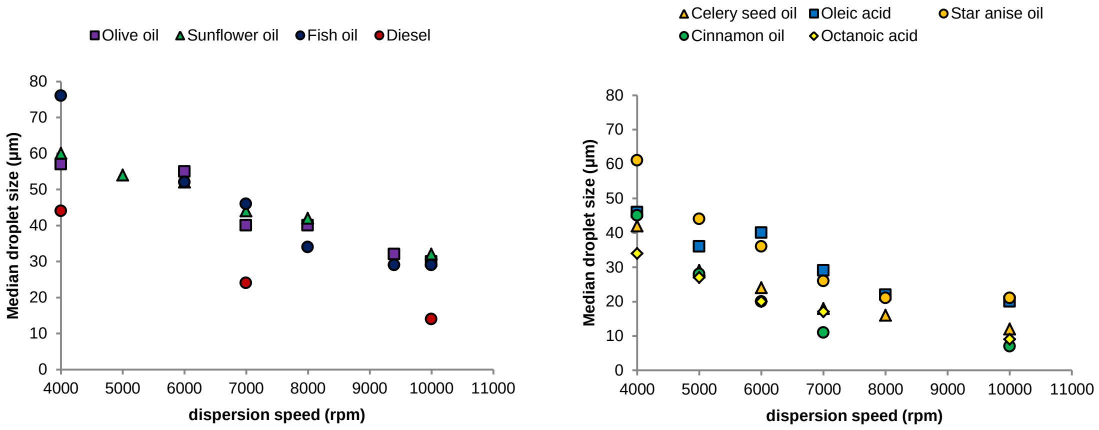

Figure 6: *change in median droplet size for each oil as a function of dispersion energy input.*

The removal of oil droplets normalised to a size of 32 µm decreased as the density of the oil increased. To illustrate, HEM removal after 10 minutes of separation decreased from 59% for an oil with a density of 0.89 g ml^{-1} (celery seed oil) to 4.3% for an oil with a density of 0.98 g ml^{-1} (star anise oil) (Figure 7). Cinnamon oil recorded a slight negative removal consistent with its density being greater than water (1.04 g ml^{-1}) but within the error of the measurement. Differences were also observed in removal levels between the free fatty acids and triglycerides of the same density. For example, celery seed oil and oleic acid both have a density of 0.89 g ml^{-1} with corresponding removal rates of 59 and 44 % after 10 minutes of separation. Similarly, HEM removal after 10 minutes of separation for olive oil and octanoic acid was 75 and 40% respectively although both have a density of 0.91 g ml^{-1}. Free fatty acids will be produced during the cooking process and from bio-dosing so will influence overall FOG separation rates.

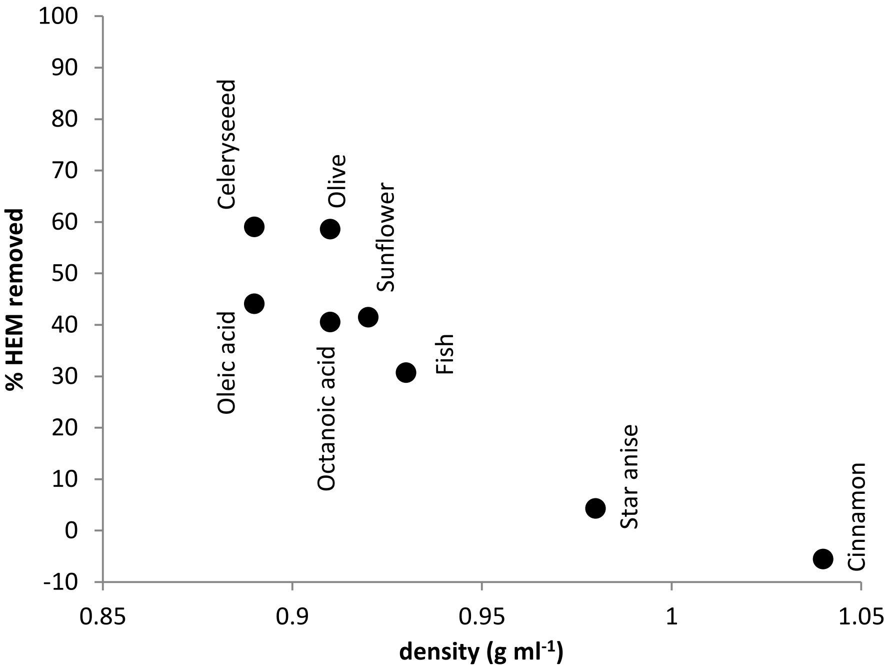

Figure 7: *Impact of density on HEM removal for 32 μm sized droplets after 10 minutes of separation*

4.3.3 Influence of droplet size and temperature on HEM removal

Sunflower oil suspensions with a median droplet size (d_{50}) of 32 µm, 44 µm and 60 µm were sampled and measured for HEM at separation times between 0 and 120 minutes (Figure 8). HEM removal rates increased with droplet size such that for median droplet sizes of 32, 44 and 60 µm the respective separation rates were 4.3, 7.8 and 9.8 % min^{-1}. The consequence is a significant reduction in the required separation time for any level of removal. To illustrate, to achieve a 90 % removal of HEM approximate separation times of 3, 30 and 61 minutes are required for the 32, 44 and 60 µm droplets respectively. Supporting findings have been reported by DuCoste *et al*. (2008) based on a computational fluid dynamic study of flows through a grease interceptor. HEM removal efficiency rose from 47 % for 80 µm oil droplets to 89 % for 150 µm droplets although this was explained in terms of changes in flow pattern resulting from differences in droplet size with 150 µm droplets creating a larger up force, because of their greater buoyancy and separating out, with 80 µm droplets being short-circuited through the separator.

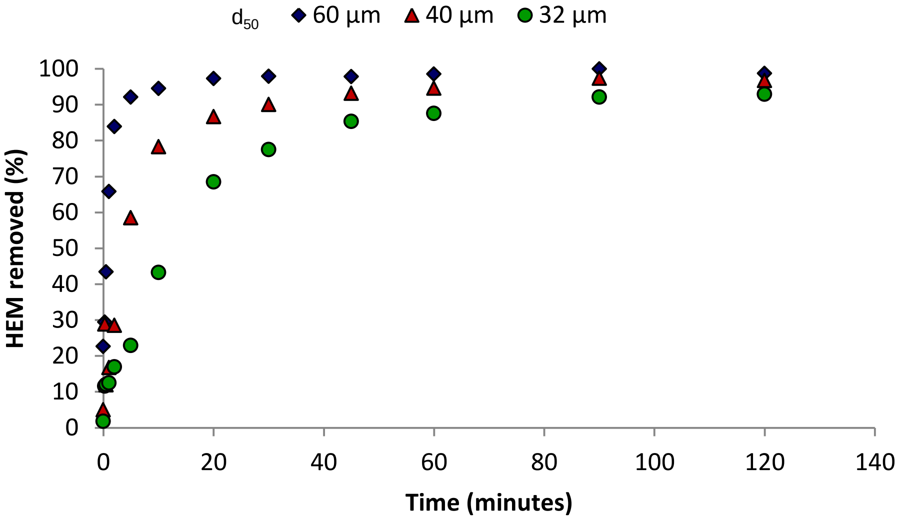

Figure 8: *Effect of d_{50} on HEM removal rates for a 0.5% v/v sunflower oil dispersion in water*

There was little observable difference for the removal of a 32 µm sunflower droplet as a function of temperature between 20 and 60°C (Figure 9). In all cases maximum HEM removal occurred between 1 and 30 minutes separation time corresponding to removal rates of 2.6 % min^{-1} at 20°C, 2.4 % min^{-1} at 40°C and 2.1 % min^{-1} at 60°C demonstrating a slight decrease in removal rate as temperature increases. The slight change in removal rate reflects the impact of temperature on the density and viscosity of both the surrounding water and the oil droplet. Improvements related to changes in viscosity are associated with changes to the droplets interfacial mobility. Decreasing viscosity increases interfacial mobility that reduces drag and hence the droplet rise rate will increase (Chesters, 1991). However, the experimental data demonstrates a decreasing removal rate with temperature indicating viscosity is not the main factor. Further, comparison across the oils normalised to a fixed size revealed no relationship between HEM removal and viscosity suggesting that at best it is a secondary factor influencing FOG separation.

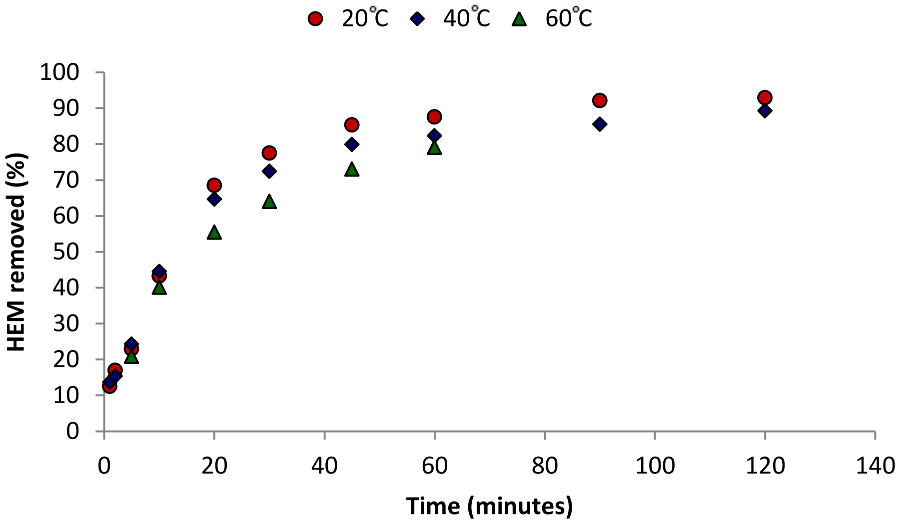

Figure 9: *Impact of temperature on HEM removal for a sunflower oil in water suspension with a* d_{50} *of 32 µm.*

4.3.4 Overall influence of oil character on HEM removal

The above experimental findings have demonstrated that the size and the density of oil droplets influence the performance of physical separation units. Although there remains a significant paucity of data concerning the characterisation and concentration of FOG going into separators (Chapter 3) the available data suggests median droplet sizes are likely to be less than 150 µm and volume concentrations less than 0.5 %. Under such conditions the particle Reynolds number is less than 0.1 and no hindrance of particle motion should occur such that Stokes law is a valid description of a droplet's motion. Accordingly the terminal rise velocity of the droplets measured in Figure 8 would be 2.7, 5.0 and 9.0 µm min^{-1} for the 32, 44 and 60 µm droplets respectively. Comparison between the two indicates a causal relationship such that Stokes parameters (d^2 and $\Delta\rho$) provide a meaningful pair of characteristics to measure when defining treatability of FOG in physical separators (Figure 10). To illustrate, all the data obtained during the separation trials of the different oils has been combined and compared to the HEM removal achieved after 10 minutes of separation time demonstrating the significance of knowing these parameters when designing FOG separators.

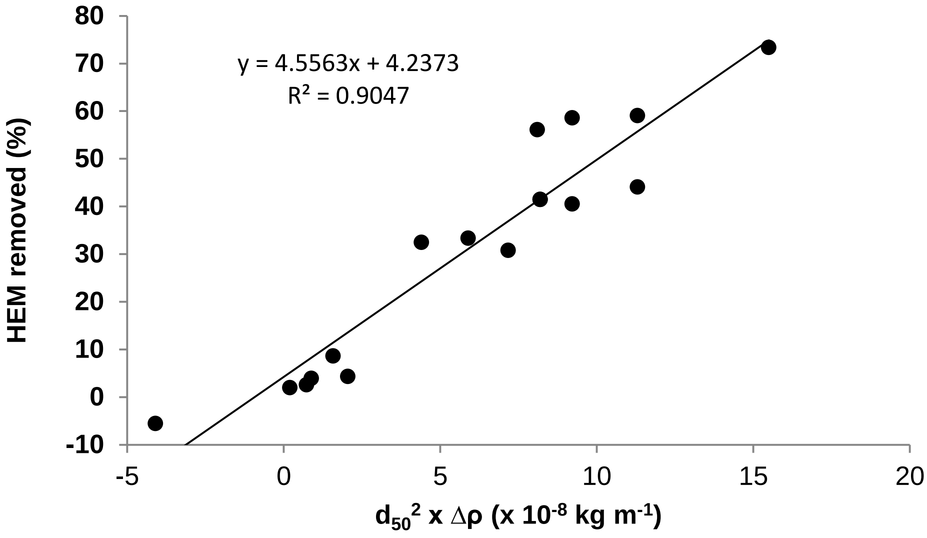

Figure 10: *Relationship between droplet size and density with oil removed after 10 minutes residence time.*

The scatter around the linear fit corresponds to variation in the droplet size for each oil (size distribution), rather than being mono-dispersed, leading to a range of rise velocities.

Similar plots of d^2 and $\Delta\rho$ against HEM removal were repeated for different residence times the resultant gradients (m from $y = mx + c$) were plotted (Figure 11) demonstrating a stabilisation in the gradient of the HEM curve for separation times of 20 minutes or greater. The implication is that if droplet size and density of the target FOG is known then a rationale design of a FOG separator can be derived for any given level of removal. Given that in most cases ρ of the oil is fixed then the data clearly identifies the importance of droplet size in the efficacy of physical separators. Increasing droplet size prior to the separator will make a significant difference in the removal achieved in any given separator. The work presented here suggests that the increase in droplet size does not need to be substantial such that target droplet sizes over 50 µm are sufficient. If droplet size can be reliably increased then smaller separators can be effectively used enhancing the application of the technology.

The work also enables consideration of the current testing procedure that uses a light fuel oil (diesel) as its target droplet. Diesel has a specific gravity of 0.84 such that the expected removal of a 34 µm droplet would be around 90% in 10 minutes. In comparison a similar sized sunflower oil droplet would only achieve 47% removal suggesting that the use of a low density oil results in an over prediction of separator efficiency. In the comparative studies presented currently, diesel oil forms a smaller droplet than the other oils and that removal was shown to be significantly enhanced compared to the other oils. Consequently the use of diesel over predicts separator efficiency and suggests caution should be applied when using it as a surrogate. The work has also shown that different oils form different sized droplets under a set energy input such that further development of the testing procedure should ensure it matches both the size and density of the droplets commonly found in FOG to provide a more robust basis for standardised testing.

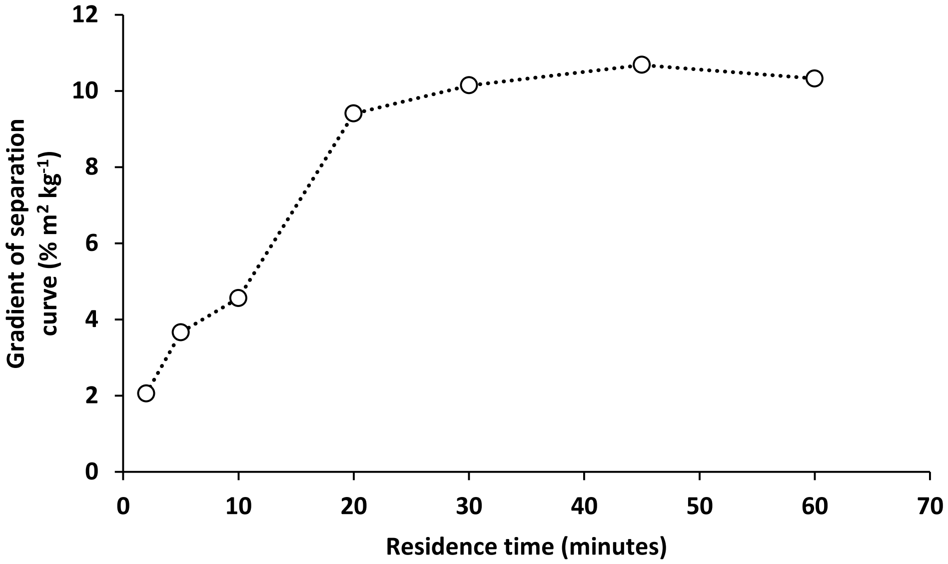

Figure 11: *Variation in gradient of separation curve (m) as determined in Figure 10 as a function of incremental residence times.*

4.4 Conclusions

The efficacy of passive grease separators can be understood through knowledge of the size of the formed oil droplets to be removed consistent with Stokes law. This includes droplets in the mechanically emulsified/dispersed size range (20 to 150 µm) where relatively small increases in droplet size will have a significant impact on the overall removal. Based on the current trials effective removal should occur within 10 minutes once the droplet size exceeds 44 µm. The size of the formed droplet under any given energy input is dependent on the type of oil such that variation in the likely droplet sizes formed in practice should be expected. The implications of the findings suggest that appropriate testing of separators requires the size and density of typical FOG to be matched and that the use of diesel oil is a poor surrogate for efficacy testing. This suggests that further work is required to appropriately characterise FOG from real sites to understand what the likely sizes encountered in practice are and what influences them so that an appropriate test fluid can be developed.

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5 Impact of agitation and surfactants on the removal of fats, oils and greases in passive gravity separators.

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Abstract

Washing operations in commercial food preparation premises produce discharge waters high in fats, oils and greases as well as general debris and surfactants. Protection of the receiving sewer is normally accomplished by inclusion of a passive gravity separator to remove FOG droplets due to their natural buoyancy. A paucity of data on the characteristics of FOG mean that understanding surrounding coalescence or break up of the formed FOG droplets is limited. The current study addresses this, in part, by assessing the impact of agitation and surfactant on the droplet size in relation to both initial formation and subsequent mixing. The level of agitation and surfactants was shown to impact on the initial size of droplets formed but did not significantly influence downstream coalescence or breakup. Neither occurred to any significant level suggesting source control of the initial droplet size is critical in increasing separator performance.

5.1 Introduction

Washing operations in catering and food preparation premises are known to generate wash waters relatively high in fats, oils and greases as well as other debris and surfactants (Chapter 3). Discharge of such wash water into the sewer has been implicated in 50% of all sewer blockages such that it is common practice to include some form of treatment between the washing operation outlet and the sewer inlet. One of the most common approaches is to use passive gravity separators that remove FOG in the form of droplets due to their natural buoyancy. Consequently, the size of the formed droplets is of critical importance in the effectiveness of the separator (Chapter 4). Unfortunately, extremely limited data exists on the characteristics of FOG such that understanding the role of surfactants in terms of the initial generation of the FOG droplets and any subsequent coalescence is unknown restricting technology development and innovation.

As design for individual sites will always remain highly variable understanding the potential for coalescence/breakage is of critical importance to avoid unnecessary poor performance due to uninformed installation choices providing excessive turbulence to the flow. Coalescence/breakage is dependent on the hydrodynamic and physical conditions that the pre-existing droplets are exposed to. Classical visualisation of the mechanism includes a combination of droplet collision followed by drainage of the film between the two approaching droplets (Figure 1).

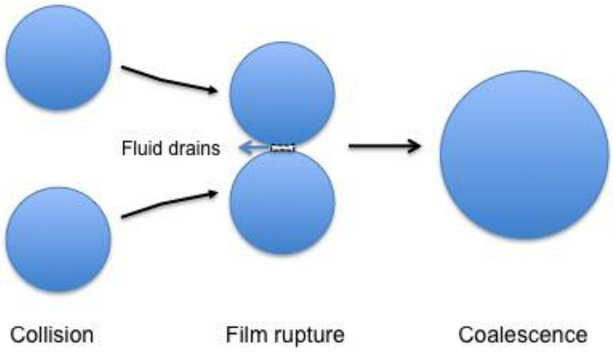


Figure 1: *Visualisation of coalescence*

Collisions do not always lead to coalescence because there will be a film of the continuous phase between droplets keeping them apart (Leng and Calabrese, 2004). For coalescence to take place the film between the droplets needs to drain sufficiently for it to rupture thereby allowing contact between the droplets. To predict whether droplets will coalesce Chesters (1991) proposes that film rupture (i.e. coalescence) will occur if the contact time (t_c) required for film drainage is less than the droplet interaction time (t_{int}). Droplet interaction time will be determined by velocity gradients (*G*) in the continuous phase with higher *G* reducing droplet interaction time since higher flow rates will tend to carry droplets apart more rapidly.

Previous studies have identified a number of factors that influence the probability of coalescence related to the size and type of the droplets involved. For instance, in relation to size two factors influence coalescence, as droplet size decreases, so does the contact area between droplets and this speeds up drainage (t_c) (Park and Blair, 1975) but increases the momentum required to force the droplets together (Coulaloglou and Tavlarides, 1977). In the case of sub mm sized droplets, as typically found in FOG (Chapter 3), the former dominates and so coalescence is enhanced as the size is decreased. Further, Kumar *et al.* (1993) observed that coalescence efficiency between droplets of different sizes was better than between same size droplets indicating that coalescence will be enhanced in polydispersed systems.

The other major factor is the mobility of the interface as oil droplets are known to be deformable such that the interfacial area increases as the velocity force increases. Scheele and Leng (1971) showed for coalescence to happen droplets need to deform, prior to contact, into an elliptical shape so that collision can occur between the narrowest points of the ellipsoids minimising contact area. Consequently, Chesters (1991) asserts that coalescence is more likely with gentle collisions where a smaller interfacial area is produced. More recently, Yeung *et al.* (2003) reported that glancing contact was more effective than head on collision for coalescence and related this to incomplete coverage of surfactant over the entire droplet surface providing opportunities for bridging and patchwork attractions commonly described during the use of polymer for aggregation (Fabrizi *et al.*, 2010).

The probability of collision can be considered as a hydrodynamic issue as the scale of interactions beyond which film rupture is important is thought to be no more than 50 nm (Hunter, 2000). The process is normally studied in vessels with moving impeller blades where the localised shear rates can be defined (Bridgeman *et al.*, 2008). The imparted kinetic energy forms trailing edge vortices creating turbulent flows in the liquid. The vortices created introduce shear flows that will impact on any droplets that are caught up in them. In the case of oil droplets, which can be considered as hydrophobic deformable particles, when they are smaller than the size of a vortex they will not experience deforming shear forces but the fluid flow will have sufficient energy to carry them into contact or collision with other droplets (Fabrizi *et al.*, 2010). Conversely where droplets are larger than the size of the vortex they will experience shear forces that may deform them to the point where they are broken up into daughter droplets (Kresta and Brodkey, 2004). Earlier observational experiments on droplet behaviour by Park and Blair (1975), using high speed cinematography in a stirred vessel arrangement, established for their set up that virtually all droplet break up occurred within ⅙th of the impeller diameter. They noted coalescence rate was directly proportional to turbulence level i.e. highest coalescence rates occurred closest to impeller but outside the impeller region coalescence was very inefficient with at best only 10% of collisions resulting in coalescence. They also stated that drop size did not appear to affect coalescence rate.

The amount of energy distributed into the suspension as a function of mixing can be estimated in terms of the average velocity gradient (*G*) expressed in reciprocal seconds (s^{-1}) and derived from the equation developed by Camp and Stein (1943):

$$G = \sqrt{\frac{P}{\bar{\mu}V}} \tag{1}$$

Where *P* the power applied to a unit volume *V* of liquid with a dynamic viscosity $\bar{\mu}$ (Pa s) can be related to the dissipation rate ε ($m^2\ s^{-3}$) of the kinetic energy in a stirred vessel of fluid density *ρ* and volume *V*.

$$\varepsilon = \frac{P}{\rho V} \tag{2}$$

The local rate of dissipation of turbulent energy per unit mass ε can be used to estimate ultimate size of eddies or vortices produced under a given set of stirring conditions using the Kolmogorov length scale η (µm) and will determine whether droplets will be subjected to shear stress.

$$\eta = \left(\frac{\nu^3}{\varepsilon}\right)^{0.25} \tag{3}$$

Where ν is the kinematic viscosity of the fluid.

As shear forces have the potential to cause both coalescence or droplet break up the process optimisation target for phase separation is a shear rate that minimises break up and maximises coalescence/aggregation. The current investigation aims to enhance understanding in this area in relation to FOG separation and in particular understand the role of surfactants on the possibility of coalescence or breakage in FOG systems.

5.2 Materials and methods

5.2.1 Materials

Samples of commercially available sunflower oil, olive oil and washing up liquid were purchase from local supermarkets (Costcutter, Cranfield, UK; J. Sainsbury, Bedford, UK). All other chemicals were laboratory grade including celery seed oil (Sigma, Dorset, UK) and oleic acid (Fisher, Loughborough, UK), Cetyltrimethylammonium bromide (CTAB), polysorbate (Tween80), (VWR, Lutterworth, UK) and sodium dodecyl sulphate (SDS), (Fisher Scientific, UK).

5.2.2 Suspension preparation

Oil in water dispersions were prepared by adding, via a tared 10 ml syringe, (Discardit, Fisher Scientific, UK), weighed portions of sunflower oil (Costcutter, Cranfield, UK) to approximately 490 ml of buffered deionised water (1 mM $NaHCO_3$, 0.1 mM NaCl adjusted to pH 7 with 5 M HCl) in a 500 ml glass cylindrical separating funnel (Fisher, UK). The total volume in the separating funnel was then made up to 500 ml with buffered deionised water. An IKA Ultraturrax model T25 high speed mixer (S25N 18G with a rotor-stator dispersing head Fisher Scientific, UK) was used to produce a monomodal polydisperse suspension whose volume median diameter (d_{50}) was determined by speed (rpm) of mixer. Median particle size (d_{50}) produced by range of mixer speeds between 4,000 and 10,000 rpm was determined earlier (Chapter 4). When required;

surfactants were added either during initial make up (dispersion experiments) or after the droplets had been preformed (coalescence experiments).

5.2.3 Oil quantification photomicrography and other measurements

Estimation of oil content in suspension was made by determining area of droplets in photomicrographs, calibrated against a graticule, taken using an optical microscope GXM L3030 with a CCD camera (QImaging) and image analysis software (ImagePro plus) (GX Optical, Suffolk, UK). Turbidity was measured on a turbidimeter (Hach 2100N, Camlab, UK) and zeta potential on a ZetaSizer 2000HSA (Malvern Instruments, UK)

5.2.4 Stirring and particle size distribution measurement.

Two 500 ml oil in water suspensions prepared as previously described were transferred to a 1 litre beaker that was placed in a 2 place Jar tester (Phipps and Bird). A flat 2 blade impeller (25 x 75 mm) was used to stir the suspension and the particle size distribution was measured in a laser diffraction spectrometer (Mastersizer 2000, Malvern Instruments, UK) Sampling flow rate (litres per minute) was controlled using a peristaltic pump (Watson Marlow model 505S, Falmouth, UK).

5.3 Results and discussion

5.3.1 Theoretical considerations of coalescence

In stirred liquid-liquid dispersions, there are a range of hydrodynamic and physical forces influencing fluid motion and droplet behaviour which need to be considered when describing coalescence (Coulaloglou and Tavlarides, 1977; Chesters, 1991). The basic premise is that the probability of coalescence is dependent on the frequency of droplet collisions and the likelihood of droplets coalescing upon collision, i.e. the coalescence efficiency. One such approach originally developed by Chesters, (1991) and later refined by Janssen and Meijer, (1995) predicts the probability of coalescence P_{coa} between droplets during liquid–liquid mixing:

$$P_{coa} = \exp\left(-\frac{\pi}{8\dot{\gamma}\emptyset t_{stir}} - \frac{\sqrt{3}}{4}\frac{R}{h_{crit}}\,pCa^{3/2}\right) \tag{4}$$

Where $\dot{\gamma}$ = shear rate (s^{-1}), $\emptyset =$ disperse phase volume fraction (kg m^{-3}), t_{stir} = time stirred (s), R = droplet radius (m) and h_{crit} = critical film thickness at which rupture and thus coalescence occurs (m):

$$h_{crit} \sim \left(\frac{AR}{8\pi\sigma}\right)^{1/3} \tag{5}$$

Where A is the Hamaker constant representing the van der Waals attraction between two interacting bodies (typically 10^{-20} Joules), σ is the interfacial tension (N m^{-1}) and p is the viscosity ratio between the two phases:

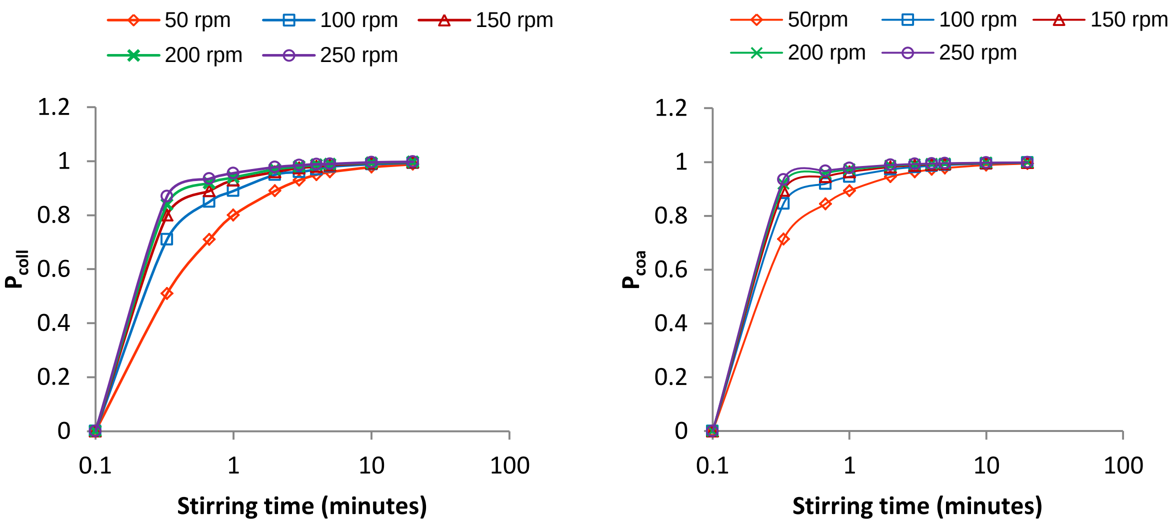
$$p = \frac{\mu_d}{\mu_c} \tag{6}$$

Where μ_d = dynamic viscosity of disperse phase (Pa s), μ_c = dynamic viscosity of continuous phase (Pa s) and Ca = capillary number which is the ratio of viscous force to surface tension across an interface:

$$Ca = \frac{\mu_c\dot{\gamma}R}{\sigma} \tag{7}$$

The first term in the equation $\left(\frac{\pi}{8\dot{\gamma}\emptyset t_{stir}}\right)$ describes the collision efficiency as a consequence of agitation and so the relative importance of the collision efficiency in the coalescence process can be discerned separately.

Analysis of the theoretical predictions based on the setup used in the current investigation indicates that the probability of collision between droplets increases as a function of both stirring speed and time. To illustrate, collision efficiency increased from 51% after 30 seconds to 93% after 3 minutes at a speed of 50 rpm (Figure 2a). In comparison, at a speed of 200 rpm the respective collision efficiencies were 84% and 95%.



(a) (b)

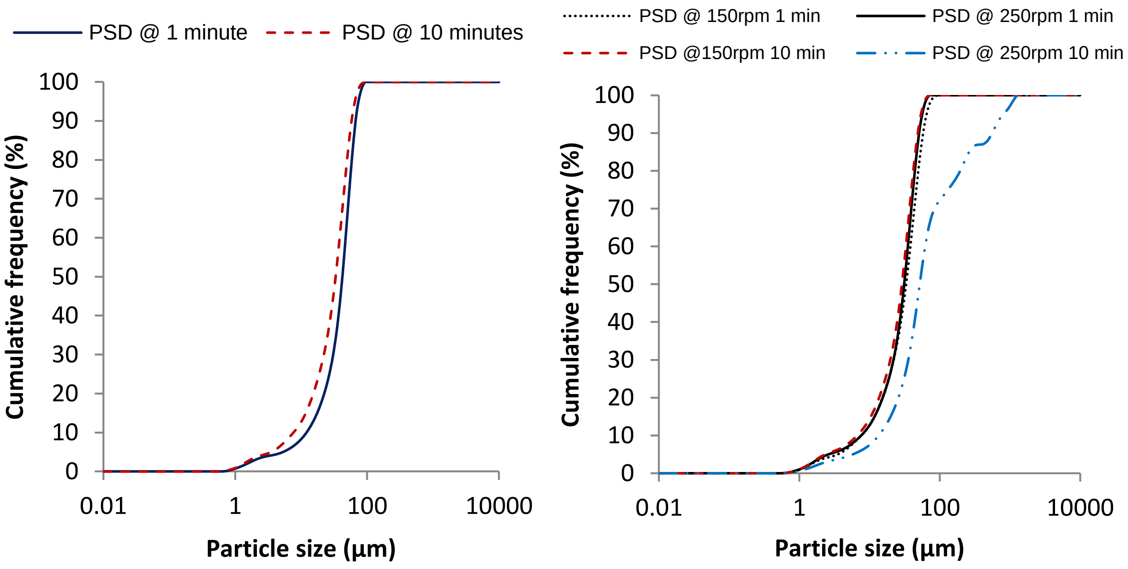
Figure 2: *Theoretical prediction of (a) collision and (b) coalescence in the experimental set up*

Comparison to the overall prediction of coalescence reveals that collision is likely to be the rate limiting factor. The above analysis considers the drainage of the films between droplets to be related to the interfacial tension and the van der Waals attraction forces only. In reality other forces are known to exist such as electrostatic repulsion, steric forces and hydrophobic interaction forces. Further, surfactants are known to hinder coalescence by immobilising the interface slowing down the drainage rate ultimately overcoming the film rupture process that is driven by the van der Waals forces across the approaching films (Hunter, 2000). Consequently if experimental observations of coalescence are reduced, compared to the predictions, then the impact of the other forces can be considered dominant in the overall process.

5.3.2 Impact of agitation on the size of pre formed droplets

The median particle size (d_{50}) of an unstirred oil in water suspension decreased from 42 to 38 µm during a 10 minute period (Figure 3a). The reduction in size is a consequence of larger droplets separating out under the influence of gravity and indicates any increase in size observed during the agitation experiments is likely to be due to coalescence. Once stirring was introduced into the system the median droplet size remained almost unchanged at 42 µm during the course of each 10 minute experimental run for each of the incremental stirring speeds up to

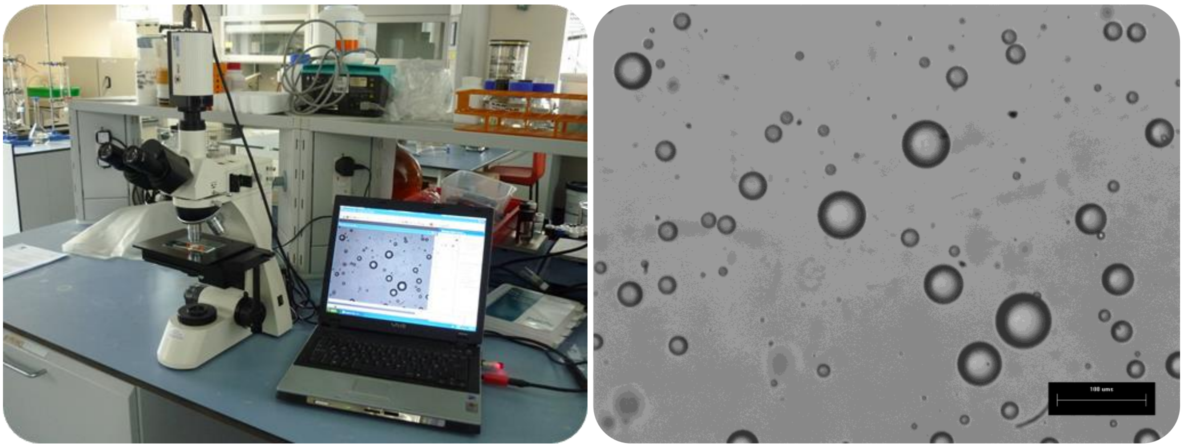
200 rpm (Figure 2). This observation would indicate that stirring has not increased droplet size and removal of larger droplets was similar to that observed in the non-stirred experimental run. However it is not possible to say definitively that there has been droplet removal using particle sizing alone as a measure because there may have been some droplet breakup resulting in a reduction in median particle size distribution.



(a) (b)

Figure 3: *Change in droplet size in (a) the absence of agitation and (b) varying levels of agitation.*

When the sample dispersion was stirred at 250 rpm the particle size distribution became polymodal with some larger droplet sizes being measured (Figure 3b). As the set-up is an open non-baffled container the stirring produced a vortex that increased in depth as stirring speed was increased and air became entrained into the dispersion via the vortex. Subsequent visual observation of the spectrometer measuring cell showed air bubbles had adhered to the glass wall of the measuring cell which could have interfered with the particle size measurement. To confirm; the droplet size distribution was measured through image analysis of photo-micrographs so that any bubbles could be excluded (Figure 4).



(a) (b)

Figure 4: *Image capture equipment set up (a) and example of photomicrograph (b)*

The particle size distribution, determined from image analysis, showed that there was little change in oil droplet particle size distribution during 20 minutes of stirring at 250 rpm and when compared to particle size distribution in the laser diffraction spectrometer confirmed result had been skewed by inclusion of air bubbles (Figure 5).

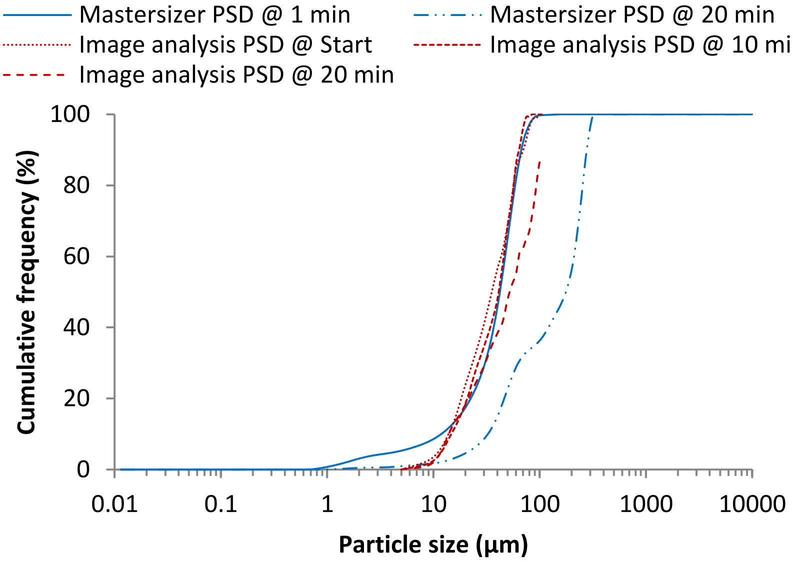


Figure 5: *Impact of agitation on droplet size*

To determine if any removal had taken place the oil content was estimated by measuring the change in droplet area observed in a series of photo-micrographs compared to an initial reading before stirring commenced (Figure 6). If droplet area decreased it would indicate coalescence and removal was occurring. The droplet area initially measured was 4.8 ± 0.1 %, and after 10 minutes of stirring at 250 rpm was 3.7 ± 0.5 % and after 20 minutes stirring was 4.9 ± 0.3 %. Statistical analysis determines that *F* is less than *F crit* so null hypothesis stands; there is no difference between measurements.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
start	12	57.12	4.76	2.566109
10 min	14	52.34	3.738571	5.122613
20 min	13	63.35	4.873077	2.30784

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	10.55191	2	5.275955	1.550292	0.22602	3.259446
Within Groups	122.5152	36	3.403201			
Total	133.0672	38				

Analysis of the mixing system was conducted in relation to the Kolmogorov length scale (η) that decreased from 189 µm at 50 rpm to 59 µm at 250 rpm. In all cases the eddy size is larger than the median droplet size and so the droplets are able to sit within turbulent eddies without experiencing the differential shear that occurs at the boundary of the eddy such that limited breakup of droplets would be expected. Energy dissipation in jar mixing is known to be more varied than described by global G with the maximum shear rates identified in close proximity to the impellor tip (Baldyga and Bourne, 1992; Bridgeman *et al.,* 2008). However, no substantial breakup or coalescence was observed in the current study indicating that the droplets were sufficiently stabilised within the system.

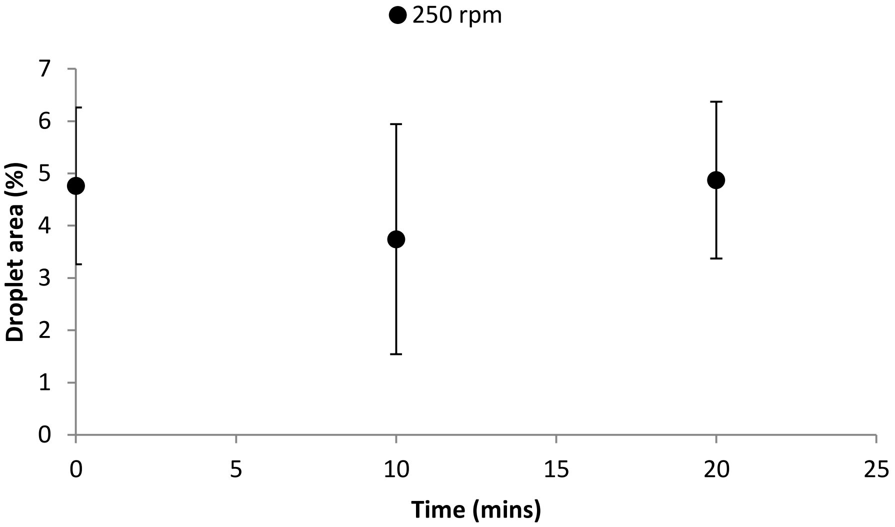


Figure 6: *Impact of agitation on droplet area for sunflower oil droplets*

5.3.3 Impact of surfactants on droplet characteristics and removal

Addition of surfactants to preformed sunflower oil droplets altered their zeta potential in a way that was consistent with the main charged groups within each surfactant type (Figure 7). For instance, CTAB, a cationic surfactant reversed the sign of the charge at a dose of approximately 2%, beyond which the droplets became progressively positively charged; exceeding 65 mV at a dose of 3% and 148 mV at a dose of 30%. In comparison, SDS, an anionic surfactant did not alter the zeta potential significantly as they remained between -75 and -95 mV. The commercial washing up liquid followed a similar pattern as expected given that it contains anionic surfactant such that subsequent experiments were performed using SDS to enable better dose control.

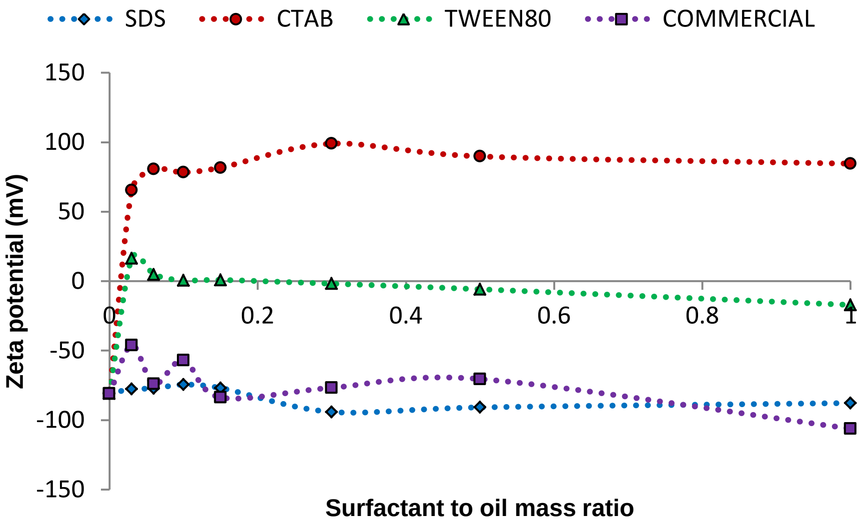


Figure 7: *Impact of surfactants on the zeta potential of sunflower oil droplets*

The impact of surfactants was assessed in terms of both the initial formation and the subsequent coalescence of oil droplets. In the case of the initial dispersion stage surfactant oil solutions were prepared and then dispersed at 10,000 rpm for 2 minutes (Figure 8). The median droplet size increased with all the surfactant doses used up to 20%. For example, addition of SDS increased the median droplet size from 32 µm when no surfactant was added to 37.7, 44.5 and 48.4 µm when the surfactant oil mass ratio was 0.03, 0.06 and 0.1 respectively. Further addition of SDS reduced the droplet size such that once the mass ratio of surfactant to oil had reached 0.5 the mean droplet size had become 38.5 µm. Droplet size reduction was observed in the case of CTAB addition and occurred once the mass ratio exceeded 0.2. No reported data exists on actual surfactant–oil mass ratios in operating FOG systems but measurements of the size distributions indicates median sizes that vary between 23 and 274 µm (Chapter 3) suggesting other components or operating practices influence the size of formed droplets. Importantly, the Tween80 surfactant reduced the zeta potential of the droplets to near neutral charge (-5.8mV to +4.8mV for dose ratios of 6-50%) and this did not influence the median droplet size significantly. The implications are that electrostatic repulsion is not the dominant factor influencing droplet stability as such levels are known to aid aggregation in particle and organic systems (Henderson *et al.,* 2006).

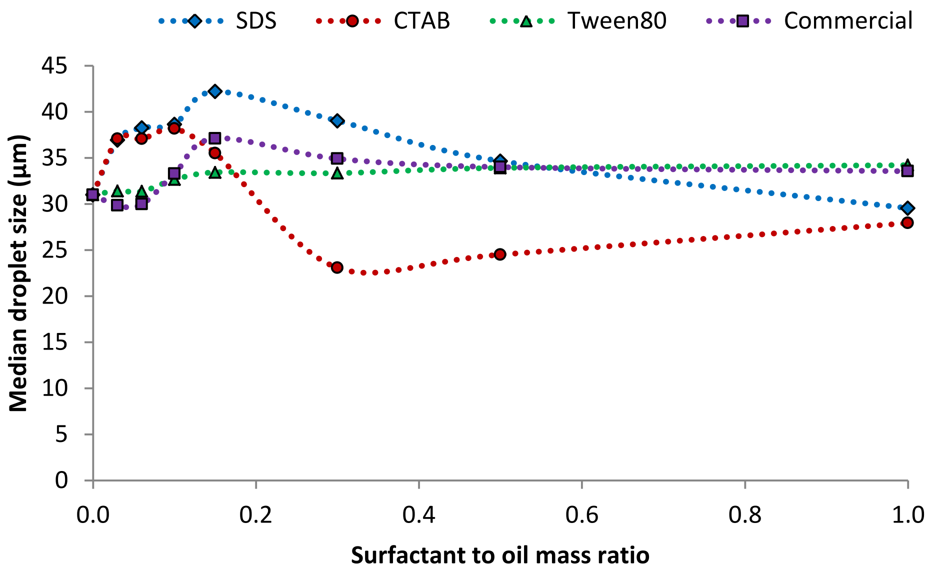


Figure 8: *Impact of surfactant to oil ratio on the median droplet size for different surfactants during dispersion of sunflower oil*

The addition of SDS altered the median droplet size that formed for the four oils tested across the range of surfactant to oil ratios trialled (Figure 9). The initial dispersion speed was fixed for each oil so that in the absence of surfactant a median droplet size of 32 µm was formed. Consequently, dispersion speeds of 10000 rpm, 9800 rpm, 5200 rpm and 6500 rpm were required for sunflower oil, olive oil, celery seed oil and oleic acid respectively. Previous investigation into the influence of oil type on droplet formation has identified a link between size and interfacial tension (Chapter 4) that is related to the type of molecules contained within any specific oil. Addition of SDS altered the median droplet size in two distinct ways (Figure 9). In the case of sunflower oil and olive oil, addition of SDS increased the median droplet size for all mass ratios to a maximum value of 41-42 µm. In contrast, the median droplet size decreased in the case of celery seed oil and oleic acid with a minimum value of 16 and 10 µm respectively. The exact mechanism for these changes have not been investigated in this study but are likely to relate to the differences in the types of molecules contained within the oils. Sunflower oil and olive oil are mainly comprised of relatively large aliphatic triglyceride molecules that tend to have a higher interfacial tension and viscosity, compared to celery seed oil and oleic acid which are relatively smaller molecules.

Overall, the results indicate that changes in oil type can have a significant impact on the influence of surfactants on the system in terms of the formed droplet sizes.

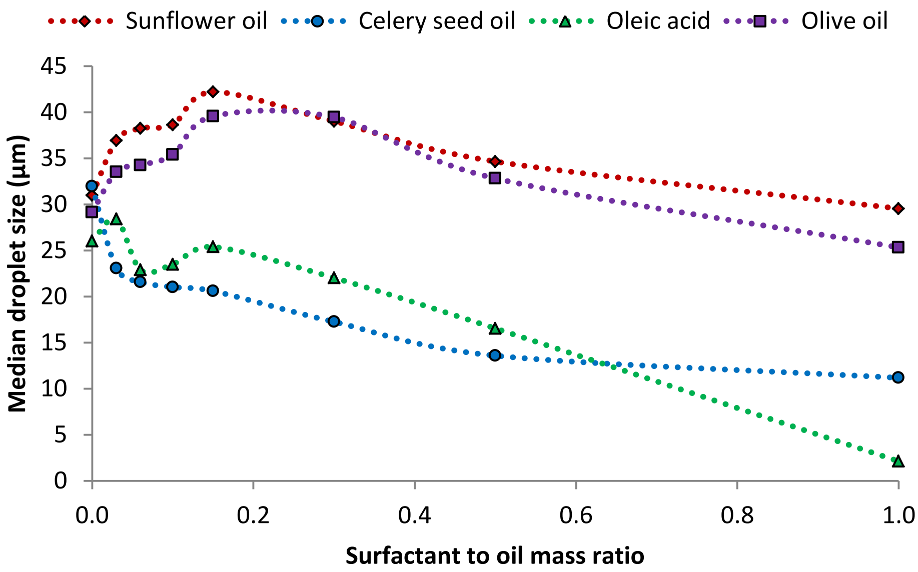


Figure 9: *Impact of surfactant oil ratio on the median droplet size for different oils dispersed with SDS*

The impact of SDS addition on preformed droplets was analysed in terms photo-micrographic droplet volume measurement due to bubble entrainment into the particle sizing equipment. Experimental runs at a stirring speed of 250 rpm compared surfactant additions of 0.01%, 0.1% and 0.2% sampled at the start of and after stirring for periods of 10 minutes and 20 minutes (Figure 10). The critical micelle concentration (CMC) of SDS was found to be 0.2% and dispersions containing this level of SDS had an oil droplet volume ranging between 3.7% and 5.8% which when compared to oil an droplet volume of between 3.1% and 4.9% measured when no surfactant was added showed an increase in oil volume compared to the surfactant free system. In contrast addition of sub-critical micelle concentrations of SDS caused a decrease in oil droplet volume, ranging between 3.2 and 4.5% at 0.01% SDS, and between 2.5 and 3.0% at 0.1% SDS.

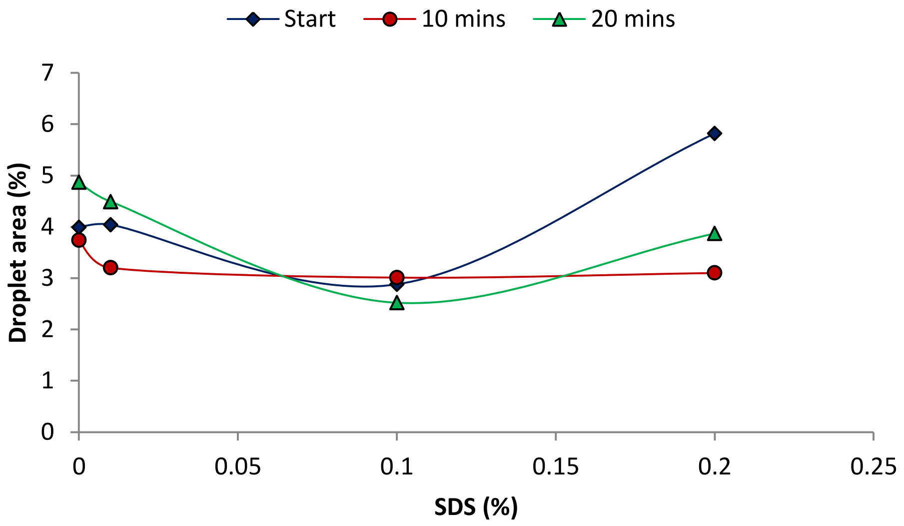


Figure 10: *Impact of SDS on sunflower oil droplets in terms of droplet area*

Initial investigations into the impact of surfactants on FOG removal in passive gravity separators suggested greatly enhanced separation (data not shown). However, further investigation revealed that surfactants interfere with the standard methods for measuring FOG (see Chapter 3 for methods). As the system only contained oil and surfactant a proxy measure was utilised based on turbidity as this had been validated for clean systems such as those under investigation here (Chapter 3, Figure 8). Separation was conducted in a separating funnel (see Chapter 4 for details) based on a sunflower oil droplet with and without surfactant. Inclusion of either SDS or the commercial washing up liquid resulted in a lower final turbidity indicating enhanced separation. To illustrate; the turbidity of the dispersion without surfactant decreased from 652 NTU after 5 minutes to 241 NTU after 60 minutes, equivalent to a reduction in turbidity of 63%. Comparative reductions of 70% and 66% for the commercial washing up liquid and SDS respectively confirm the slight improvement in FOG removal when surfactants are present (Figure 11).

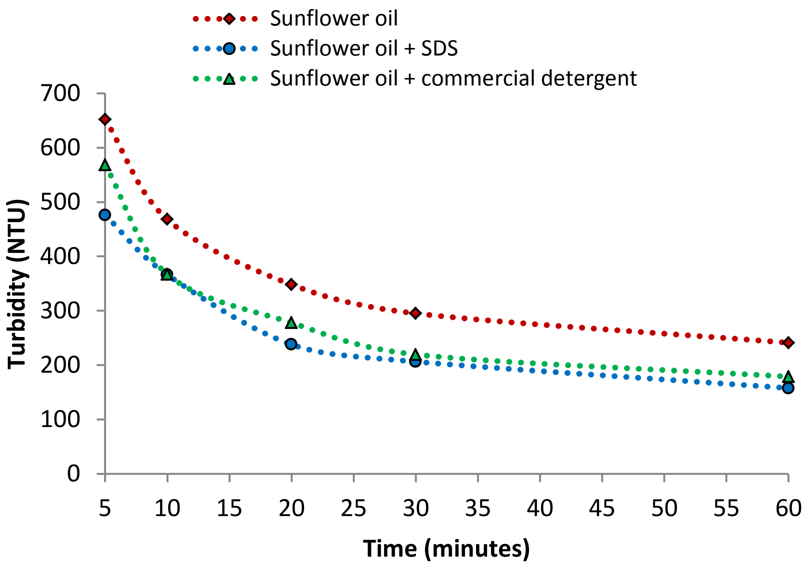


Figure 11: *Impact of SDS and a commercial detergent on overall turbidity*

5.3.4 FOG removal with a batch separator

The results obtained in this study indicated that only minor alterations to the droplet size can be expected once they are formed such that enhancement in removal is more likely to be achieved through innovation in the design of the passive separator. Current separators are single unit devices containing baffles to manage flow and have been shown to be effective as long as sufficient time is available for separation (Chapter 4). Removal of the separated oil is conducted infrequently such that re-entrainment is also possible. Consideration of these two features indicates that a sequenced batch separator may provide benefit whereby a chamber is filled and then rested to allow sufficient time for separation before being drained and refilled. The concept was tested with a batch separating vessel (Figure 12) operated on a sequenced cycle based on either fill and draw or draw and fill (Figure 13) to establish which generated the greater degree of re-entrainment.

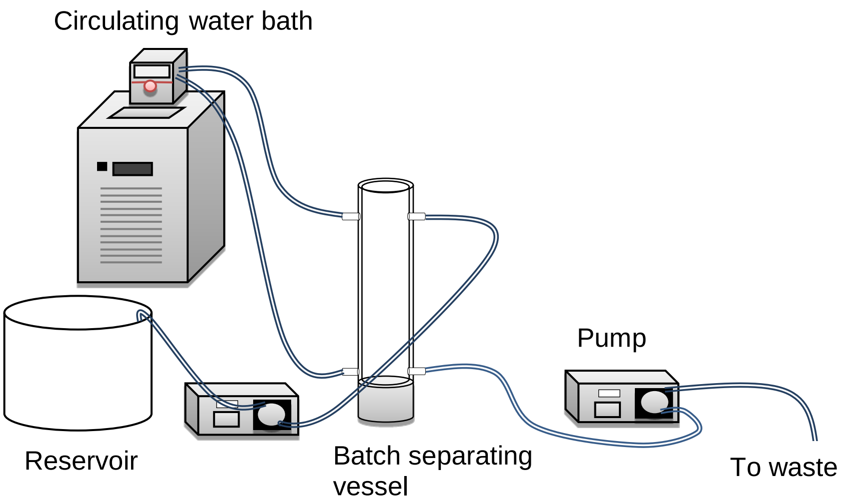


Figure 12: *Schematic of batch reactor set up*

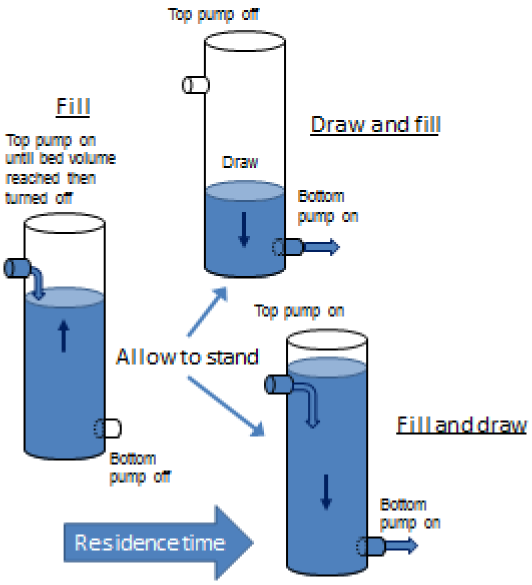


Figure 13: *Schematic of batch reactor draw & fill and fill & draw techniques*

The tests used a preformed sunflower oil droplet at a volume concentration of 0.7% and a median droplet size of 40 µm. The total reactive bed volume was 1.2 L with the feed and draw cycles operated at a flow rate of 600 ml min^{-1} in a downward feed flow direction. Flow into and out of chamber stopped when required volume (1.2 L) was added and then three 200 ml samples were collected after a residence time of 30 minutes and analysed to give an average

HEM removal from each batch. HEM removal was measured at five consecutive 30 minute residence times and then at one residence time of 1 hour.

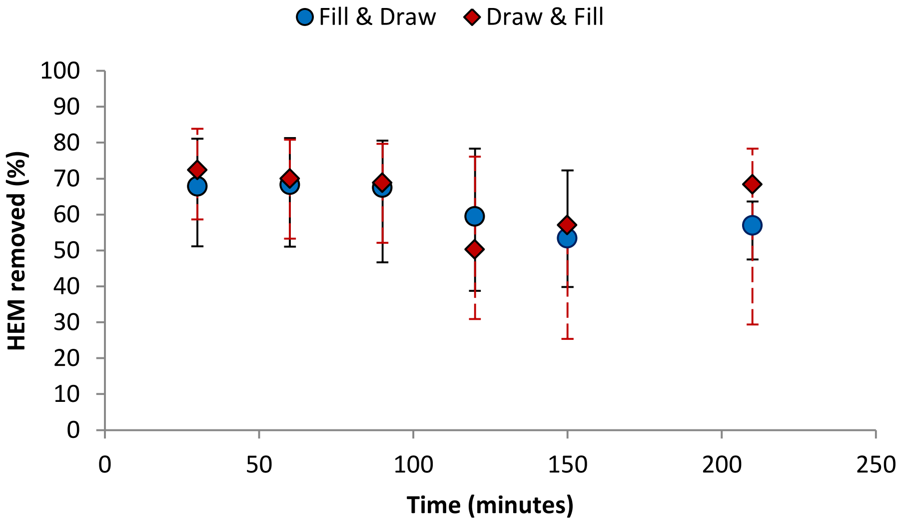


Figure 14: *Comparison of oil removal from a batch separator operated either as fill & draw or draw & fill.*

A gradual decline in efficiency from 68 to 56 % for the average HEM removal was observed in the case of the fill and draw sequence (Figure 14). This compared to a reduction of 72 to 44 % in the case of the draw then fill sequence indicating that the former was a more effective operating sequence. HEM removal after the final 60 minute residence time remained at 56 % for the fill and draw sequence and improved to 59 % for the draw then fill sequence. Whilst there was a gradual decrease in HEM removal over successive separations with 30 minute residence times decline in performance was greatest in the draw then fill system. This would indicate that the more concentrated HEM accumulating near top of the chamber is being collected whilst with the fill and draw system some of the fresh suspension is diluting the more concentrated disperse phase volume. Both systems showed an improvement in HEM removal as a consequence of longer residence time measured at the end of the experimental run.

5.4 Conclusions

The results presented in the paper indicate that coalescence or break up of preformed oil droplet appears unlikely during the transport of wash waters from sinks to the FOG separator. Consequently, the key feature appears to be the initial levels of turbulence encountered when the droplets are formed and this wants to be minimised to increase the average droplet size that will enhance removal in passive gravity separators. Surfactants are also shown to have a significant impact that can alter the size of the formed droplets. Whilst both features are currently poorly characterised in real situations the work presented in this paper indicates the benefits of reduced shear environments during washing operations. Future work is required to better characterise flows and turbulence encountered during the formation of FOG droplets and in particular the comparison of hand washing compared to automatic dishwashers and this should help shape future technology requirements.

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6 The impact of ultrasonic pre-treatment on removal of fats oils and greases in passive gravity separators

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Abstract

Ultrasonically enhanced separation of oil droplets in a gravity separator was investigated as a possible method for improving fats, oils and grease removal from commercial food preparation premises prior to discharge of washing up water into the sewer. Pre formed droplets of sunflower oil were treated in a vertically aligned reaction chamber with an ultrasonic transducer fitted to the bottom. FOG removal, measured as HEM removal, was monitored as a function of power input (0-100W), residence time (0.63-2.5 minutes), reactor size (0.5-1.85 litres) and frequency (582-1144 kHz) the incoming flow entered counter currently to the ultrasonic wave propagation. Enhanced separation was observed due to the application of ultrasound with the power input and the reactor size identified as the critical variables. Trials with an optimised setup demonstrated sustained HEM removal above 80% during the course of a 54 minute continuous experiment compared to 20-30% removal in the case of an equivalent separated without ultrasonic enhancement.

6.1 Introduction

The removal of fats, oils and greases (FOGs) from commercial food preparation premises is a critical component in the effective management of sewer catchments as FOG has been implicated in 50% of all sewer blockages (Williams *et al*., 2012). One of the most common amelioration methods is to include a passive gravity separator between the washing up stations and the drain. These devices take advantage of the natural buoyancy of FOG droplets and hence performance is related to the size and density of the formed droplets (Chapter 4). Enhancement of FOG removal through assisted separation has not been reported but is used in other fields for the collection of high purity products by exploitation of electro-kinetic, acoustic, magnetic and centrifugal forces (Wakeman and Smythe, 2000). Concerns over processing time and prohibitive pressure, electrical or magnetic field requirements limit most developments to the use of acoustic waves. Suspensions of fine particles or droplets respond to acoustic field as long as a non-zero acoustic contrast exists between the particle and the surrounding fluid. The associated acoustic radiation forces that act upon particles can be many orders of magnitude greater than their weight enabling rapid separation (Wakeman and Bailey, 2000).

Most studies to date have used the creation of a resonant standing wave to concentrate particles at pressure nodes that are then either allowed to separate out by gravity (Nii *et al.,* 2009; Juliano *et al.,* 2011), are transported to outlets by frequency sweeping (Tolt and Feke, 1993) or are collected within a porous medium (Pangu and Feke, 2004). For instance ultrasonically enhanced separation of aluminium particles in water and water droplets in oil has been demonstrated (Tolt and Feke, 1993) although this has not been shown for removal of oil droplets in water. The majority of studies to date have been based on batch treatments in small reaction chambers (sonochemical reactors) ranging between 0.44 ml and 250 ml in size to study movement and aggregation of the particles making translation to FOG separators difficult.

An alternative approach is to apply ultrasound by means of a travelling or progressive wave that creates a number of possible mechanisms that can enhance separation of dispersed particles and droplets. The resultant pressure waves will produce a flow in the dispersion through a mechanism called acoustic streaming (Leighton, 1978; Whitworth and Coakley, 1992) and has been demonstrated to lift particles to the surface of membranes (Qi and Breterton, 1995) or used to concentrate fine particles in a continuous separator (Wakeman and Bailey, 2000). For instance, application of 20 kHz ultrasound at a power density of 10 W cm^{-2} resulted in the generation of a particle velocity of up to 12 m s^{-1} for a 1 μm calcite particle (Wakeman and Bailey, 2000). In addition at sufficient power inputs the rarefaction or decompression phase of the wave cycle causes the creation of micro bubble in the process known as cavitation (Gould *et al.,* 1992) that can aid separation through an enhanced flotation mechanism.

The concept behind the current study is that ultrasonic waves can enhance oil droplet separation as the pressure waves would be expected to push buoyant particles upwards thereby increasing their rise rate. The efficacy of the approach was tested in both batch and flow through systems utilising an upright reaction chamber with a transducer at the base operating in a counter current direction to the flow. Experiments were performed to ascertain the impact on droplet size and removal of a preformed sunflower oil droplet suspension at a realistic FOG concentration for application into passive gravity FOG separators.

6.2 Materials and Methods

6.2.1 Materials

Sunflower oil was purchased from a local supermarket (Costcutter, Cranfield, UK) with sodium bicarbonate, sodium chloride, 5 M hydrochloric acid, n-hexane (HPLC grade) all purchased from Fisher Scientific, UK.

6.2.2 Sample preparation

Oil in water suspensions (Ø ~ 0.7%) were prepared by transferring weighed portions of sunflower oil via a tared 10 ml syringe into approximately 490 ml buffered deionised water (1 mM $NaHCO_3$, 0.1 mM NaCl, pH 7) into 500 ml graduated cylindrical separating funnels. The volume was made up to 500 ml with buffered deionised water. The oil was dispersed using a high speed mixer set at a pre-determined speed (rpm) to produce the required median droplet diameter (d_{50}). For batch treatments oil in water suspensions were transferred directly to the ultrasound apparatus prior to treatment. For flow through treatments 25 L reservoirs of oil in water suspensions were prepared and stirred continuously with an overhead laboratory mixer at 300 rpm to keep droplets in suspension. Oil in water suspensions for the reservoir were produced by adding increased amounts ~ 35 g of sunflower oil to five 500 ml separating funnels prior to mixing.

6.2.3 Ultrasonic pre-treatment

The ultrasound reaction chamber comprised a double walled cylindrical glass reaction vessel coupled at the base to a multi-frequency transducer controlled by a frequency generator and power amplifier (Figure 1) (Meinhardt Ultraschalltechnik, Leipzig, Germany). The unit was able to operate at three frequencies 0.58, 0.86 and 1.15 MHz with power inputs between 0 and 100 W. Temperature control during treatments was by circulating water through outer walls of the reaction vessel by means of a refrigerated circulating bath (Grant, T 100 R, Cambridge, UK).

In the batch experiments, pre prepared samples were transferred into the reactor vessel and circulated around a loop containing the particle sizing equipment. In the flow through experiments the suspension flow rate was controlled by two pumps, one feeding the suspension from the reservoir to the top inlet of the reactor and the second drawing treated suspension from the bottom outlet. This setup was used as it was found to provide the most effective means of controlling a constant reactor size during the tests. The application of ultrasound was quantified through the ratio of the applied energy and the residence time referred to as the power density (E/τ):

$$\frac{E}{\tau} = \frac{Power\ (kW) \big/ flow\ rate\ (m^3 h^{-1})}{residence\ time\ (min^{-1})} = kWh\, m^{-3}\, min^{-1} \tag{1}$$

The units of power density have not been compressed to help elucidate the different factors influencing removal.

6.2.4 HEM removal measurements

Samples of suspensions were collected in 250 ml centrifuge bottles (PTFE, Fisher UK) to measure oil content by hexane extraction and then adjusted to pH 2. Then 50 ml n-hexane (HPLC grade, Fisher UK) was added followed by manual shaking for 2 minutes and centrifugation at 4000 x *g* for 10 minutes (Sorvall Legend RT+, DJB labs, UK). Subsequently 3 x 10 ml aliquots of the hexane layer were transferred into pre-weighed 100 ml round bottom flasks and the solvent removed in a rotary evaporator (Heidolph Laborota 4000) under vacuum at 45°C. The flasks were placed in a drying oven (Genlab N75C, Widnes, UK), set at 45°C and dried overnight before transferring to a desiccator to cool. The flasks were weighed on an analytical balance, (Adam Balances PW 254, Adam Equipment, Milton Keynes, UK) and HEM residue calculated by difference. Particle size distribution measurements were made using a laser diffraction spectrometer (Mastersizer 2000, Malvern Instruments, Malvern, UK).

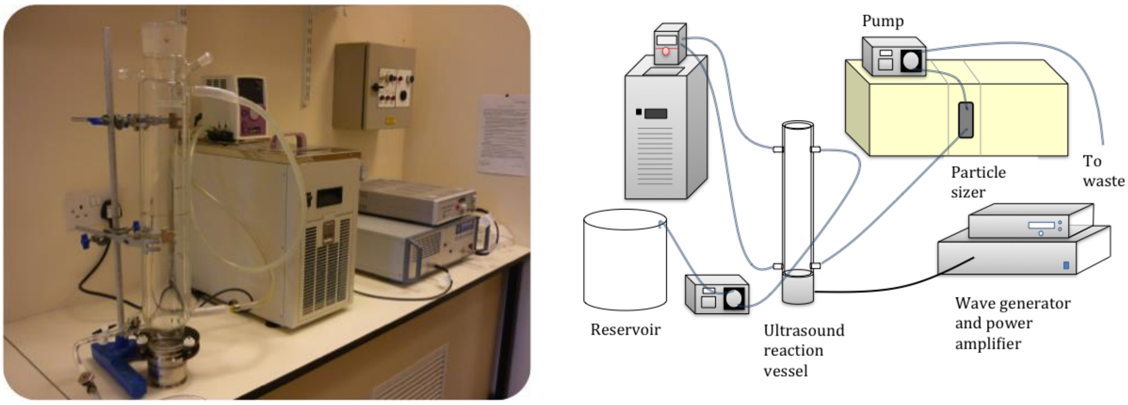

Figure 1: *Ultrasonic device connected to a water bath and schematic of set up*

6.3 Results and discussion

6.3.1 Impact of ultrasonic frequency and applied power on droplet size and HEM removal in a closed loop system.

The size of the oil droplets measured in the bulk liquid remained at 40 ± 4 µm throughout the closed loop experiments when ultrasound was applied at a power of 20 W and a frequency of 582 kHz (Figure 2). An increase in power to 40 W resulted in a decrease in the median droplet size from 42 to 18 µm over the course of the 20 minute experiment with the majority of the change occurring within the first 11 minutes. Application of larger applied power levels resulted in smaller residual median droplet sizes culminating at 8 µm when a power of 100 W was used. The change in droplet size was greatest at higher power inputs such that after 8 minutes of ultrasound treatment the median droplet size had stabilised to a d_{50} of 14 µm at 60 W, 11 µm at 80 W and 9 µm at 100 W. This corresponds to a rate of change of 1.4 µm min^{-1} at 40 W input compared to 5.4 µm min^{-1} at 100 W, the increasing power input speeding up the separation process.

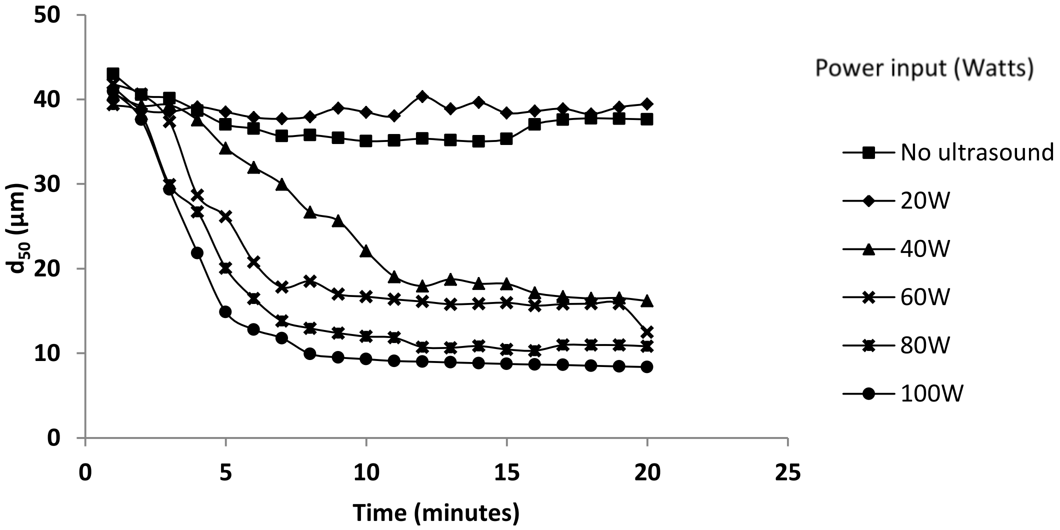

Figure 2: *Median particle size d_{50} resulting from different applied power using ultrasound frequency at 582 kHz.*

The transducer used in the ultrasound reactor vessel could be operated at one of three fixed frequencies; 582 kHz, 862 kHz or 1144 kHz. Experimental runs were performed using a power input of 100 W for each of the frequencies (Figure 3). No change in median droplet size occurred without the application of ultrasound such that d_{50} of the droplets remained at 40 ± 4 µm. By contrast application of ultrasound resulted in a decrease in the median particle size of the oil droplets for all three frequencies tested after 2 minutes. A difference in response was seen in relation to the ultimate level of change observed with use of ultrasound at a frequency of 1144 kHz resulting in a decrease in the median droplet size from 42 to 20 µm. In comparison, similar changes were observed in the case of application of ultrasound at 862 and 582 kHz resulting in a decrease in the median droplet size from 42 to 8 µm. The initial rate of the decrease in droplet size was greatest during first 5 minutes of treatment with the lower frequencies producing a faster rate of decrease: 582 kHz = 5.4 µm min^{-1}, 862 kHz = 5.2 µm min^{-1}, relative to a 3.0 µm min^{-1} decrease at 1144 kHz.

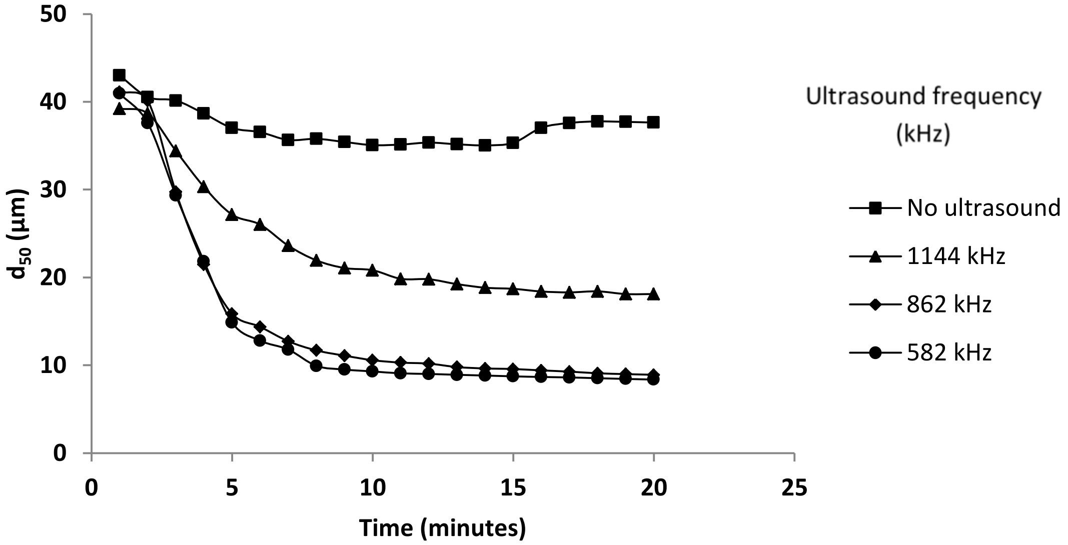

Figure 3: *Median particle size d_{50} produced by application of different ultrasound frequencies at 100W applied power.*

6.3.2 Impact of frequency and power density on HEM removal in a flow through system

The incremental reduction in d_{50} with increasing power input indicated that increasingly smaller droplets were being removed in agreement with the observation by Nii *et al*. (2009) who, although not measuring PSD directly, determined that as acoustic force increases “smaller droplets would be collected and flocculated”. The observed decrease in droplet size observed during the application of ultrasonic waves can be explained as a consequence of either larger droplets being removed by sound pressure waves leaving smaller droplets in suspension or breakup of larger droplets by sonication. Elucidation of the principal mechanism was achieved through measuring the change in FOG content during a flow through experiment (Figure 4). An increase in power density (equivalent to increased power and application time in the batch experiment) for each of the different frequencies showed a commensurate rise in HEM removal with oil removal increasing from 39 to 83 % at 582 kHz, from 30 to 67 % at 862 kHz and from 26 to 67 % at 1144 kHz. Consequently, the decrease in observed droplet size was due to enhanced removal of oil droplets rather than just breakup of the larger droplets.

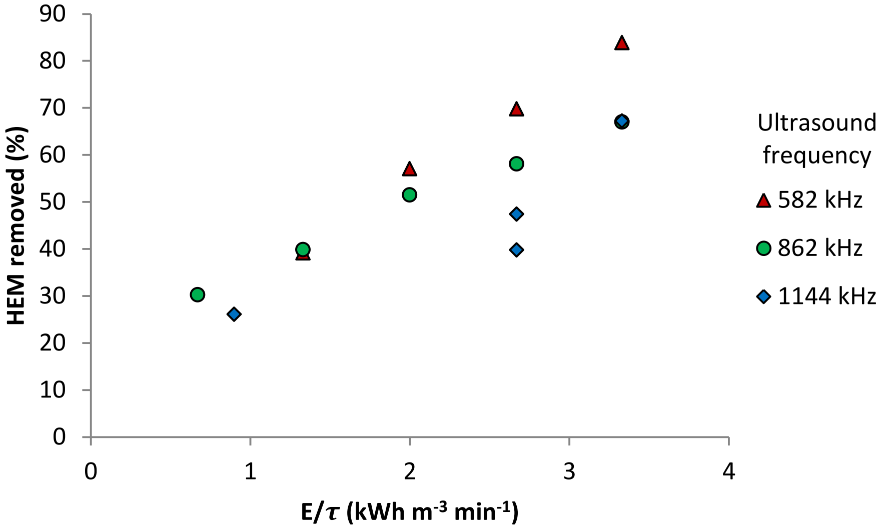

Figure 4: *Impact of power density (E/τ) on HEM removal in a flow through system operated at different ultrasonic frequencies and a bed volume of 0.5 L.*

The impact of power density was seen to be most significant at a frequency of 582 kHz where removal increased from 26 % with a power density of 0.5 kWh m^{-3} min^{-1} to 84 % when treated with ultrasound at a power density of 3.3 kWh m^{-3} min^{-1}. Application of the ultrasound at 862 and 1144 kHz resulted in a smaller change in HEM removed as a function of power density indicating that the efficacy of ultrasound is maximised when applied at lower frequencies (Figure 4). Lower frequencies are associated with longer wavelengths generating greater separation between the nodal planes and enhanced cavitation compared to higher frequencies (Gould *et al.,* 1992). No concentration of the droplets could be observed at pressure nodes suggesting the separation was due to other mechanisms. The rapid compression and decompression of the liquid dispersion causes dissolved gases to vaporise generating micro-bubbles that may either collapse releasing energy or coalesce with other micro-bubbles to form more stable bubbles enhancing buoyancy and hence removal (Laborde *et al.,* 1998; Luther *et al.,* 2001). In addition the collapse of micro-bubbles during cavitation is known to generate free radicals that have the potential to alter the charge associated with oil droplets reducing their electrostatic repulsion which will encourage aggregation or coalescence (Gogate and Kabadi, 2009). Formation of bubbles was observed in the ultrasound reaction chamber at 582 kHz with energy inputs > 40 W suggesting that enhanced separation through bubble attachment was partially responsible for the enhanced removal (Figure 5).

Direct visual observation of the bubble formation in the reaction vessel indicated that insufficient bubbles were produced to account for the observed removal. Consequently, the main mechanism appears related to the acoustic field adding an additional separation force which enhances the rise velocity of the droplets. As the volume fraction of the droplets in the water was low the distance between droplets can be assumed to be large thereby negating the influence of inter-particle forces. In such cases any enhancement in rise velocity will be as a direct result of the action of the ultrasonic force on the droplets. Discussion of the mechanism by which the velocity is imparted relate to acoustic streaming, that is a time independent flow of fluid induced by the acoustic field which generates a velocity in the axial direction of the transducer (Qi and Brereton, 1995; Wakeman and Bailey, 2000). Previous experiments on 1 µm calcite particles have demonstrated that the impacts are maximised at lower frequencies and more dilute systems (Wakeman and Bailey, 2000). For instance, Wakeman and Bailey (2000) measured a maximum acoustically developed particle velocity of 12 m s^{-1} at the transducer surface that decreased to 1-2 m s^{-1} at a distance of 0.09 m from the surface of the transducer. Estimation of the exposed ultrasonically derived force in the axial flow direction was between 1-2 x 10^{-7} N making it considerably larger than the associated gravity force indicating the ultrasonic force is the dominant action close to the surface of the transducer.

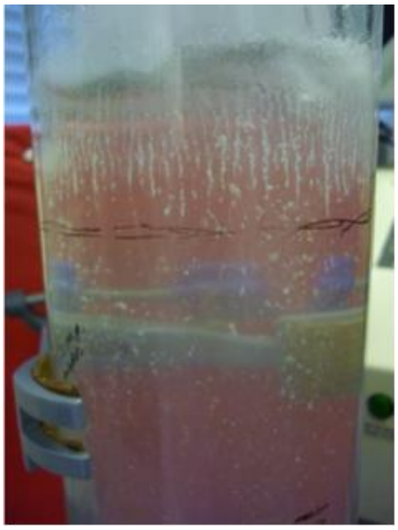

Figure 5: *Photograph of bubble formation during ultrasound treatment*

6.3.3 Impact of power density, residence time and reactor size on HEM removal in a flow through system

The impact of residence time on the efficacy of HEM removal was seen to be negligible between 1 and 2.3 minutes across the full range of power densities tested (Figure 6). For instance, at a residence time of 1 minute and power densities between 0.36 and 0.9 kWh m^{-3} min^{-1}, HEM removal increased from 22 to 77.5 %, compared to 21 to 83 % and 20 to 82 % for residence times of 1.5 and 2.3 minutes respectively. Reduced removal was seen in the case of the 1 minute residence time at power densities of 0.54 and 0.72 kWh m^{-3} min^{-1} suggesting that a minimum residence time of 90 seconds may be required to ensure stable removal for lower power densities. The observed decrease in disperse phase removal efficiency with increased flow rate (residence time) is not in agreement with Pangu and Feke (2004) who, although they compared only two flow rates and were looking to collect oil droplets within a porous media aided by ultrasound, found that separation performance was sensitive to residence times. Rather than measuring oil content directly Pangu and Feke (2004) quantified the volume fraction of oil from the droplet size distribution so a reduction in number of larger droplets corresponded to oil removal. Using a much smaller reactor with a volume of 40 cm^3 and lower flow rates they found oil collected within the media was reduced from 75 % at a flow rate of 35 ml min^{-1} to 27 % at a flow rate of 70 ml min^{-1} and made the observation that relatively higher flow rates washed larger droplets out of the porous media into the effluent that was then measured. Oil removal efficiency therefore had more to do with droplet short-circuiting than residence time.

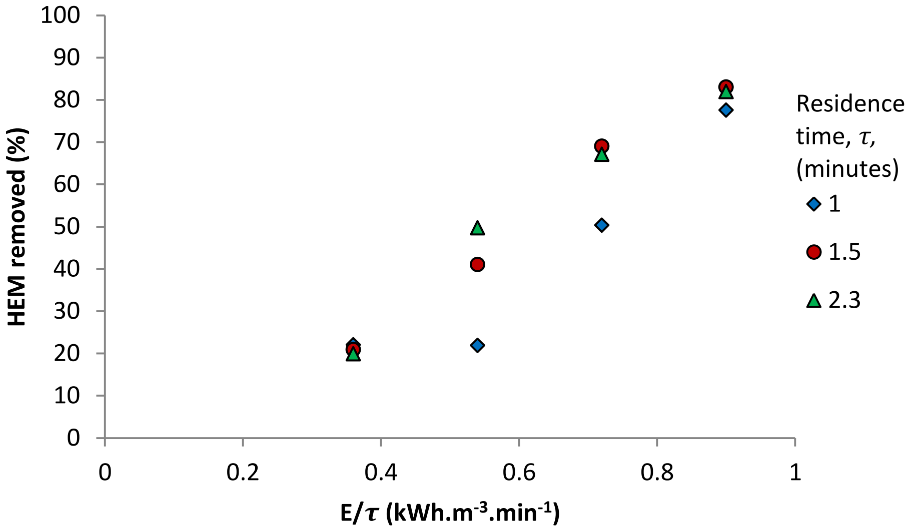

Figure 6: *Impact of residence times and power density on HEM removal in a reaction chamber with a bed volume of 1.85 litres, (ultrasound treatment frequency 582 kHz).*

To further elucidate the importance of the different factors contained within the power density term on the stability of HEM removal performance the system was monitored for 8 bed volumes across a range of power densities, residence times and reactor volumes (Figure 7). Volumetric flow rates (q) between 0.2 and 1.85 L min^{-1} and power inputs of either 40 or 100 W were used to produce a selection of power densities E/τ (Figure 7) all operated at an ultrasound frequency of 582 kHz.

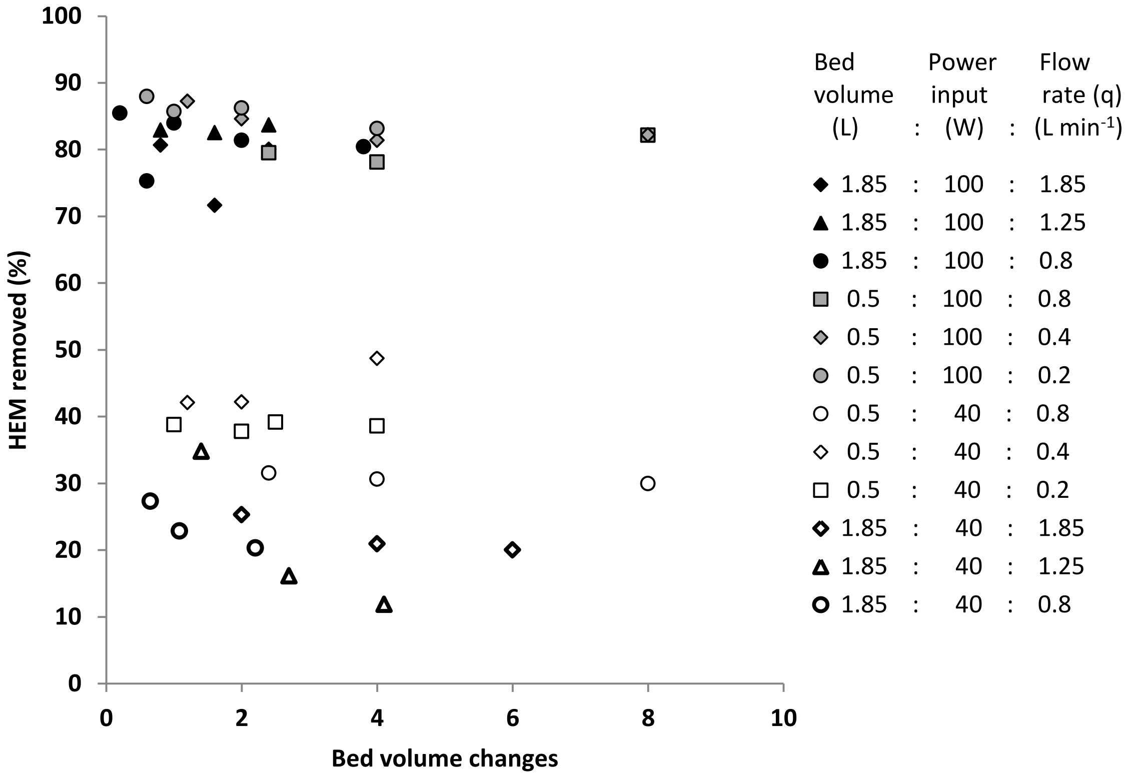

Figure 7: *Comparison of the effect bed volume changes had on HEM removal for different volumetric flow rates with an ultrasound treatment of 582 kHz at 100 W and 40 W applied power.*

Overall oil removal remained above 70 % when operating with a power input of 100 W for all reactor volumes and residence times tested. To illustrate, removal ranged between 71.3 % (q = 1.85 L min^{-1}, 1.6 bed volume changes) and 88.0 % (q = 0.2 L min^{-1}, 0.6 bed volume changes) with a standard deviation of 3.8 %. No obvious trend in increase or decrease of HEM removal was discerned in relation to the number of bed volume treated at different flow rates. In contrast, at a power input of 40 W the overall HEM removal was reduced and varied between 11.9 % (q = 1.25 L min^{-1}, 4.1 bed volumes) and 48.7 % (q = 0.4 L min^{-1}, 4.1 bed volumes) with a standard deviation of 10.2 % indicating much greater variability than observed when a power input of 100 W was applied. Comparison of the other variables indicated that, when applying low power inputs, greater removal was achieved with the smaller reactor volume (0.5 L) at between 20.3 and 48.7 % compared to the larger reactor volume (1.85 L) where removal varied between 11.9 and 34.8 % (Figure 7). The decrease in removal observed in the larger bed volume for successive changes corresponded to the number of treatment cycles consistent with a fraction of the previously separated oil re-dispersing into the bulk fluid as successive batches of fresh feed are added.

Comparison of the different variables revealed that, across the ranges tested, residence time and reactor size are not critical in defining removal when high power inputs (100W) are used. In contrast at lower power inputs (40W) residence time appears to become important when smaller reactor sizes are used. To illustrate, HEM removal increased from 29% at a residence time of 0.63 minutes to 44 % at a residence time of 1.25 minutes (Figure 8).

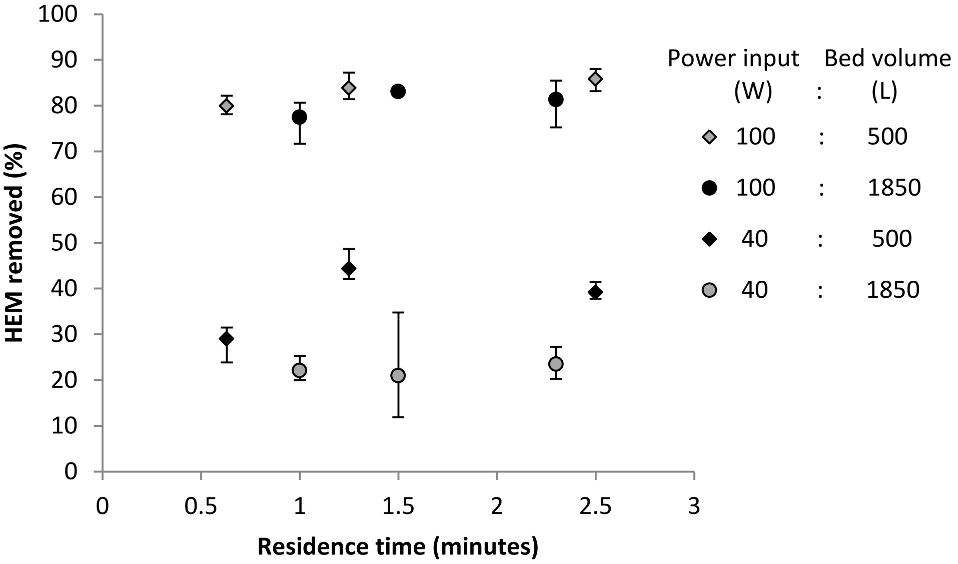

Figure 8: *Comparison of the effect bed volume had on HEM removal for different residence times (τ) with an ultrasound treatment of 582 kHz at 100W and 40W applied power.*

To further investigate the role of reactor size on HEM removal a series of trials were performed at a fixed residence time of 2 minutes to ensure that all the fluid experienced the impact of ultrasound for the same length of time (Figure 9). The level of HEM removal increased with power density with greater than 70% removal observed once a sufficient power density was applied. The efficacy of the process improved with increasing reactor size such that lower power densities were required to achieve the same HEM removal as the reactor increased in size. For example, to achieve 30% removal the required power density decreased from 1.1 kWh m^{-3} min^{-1} for a reactor size of 0.3 litres to 0.4 kWh m^{-3} min^{-1} in the case of a 1.85 litre reactor. To remove larger quantities of HEM the difference in power density was significantly greater. For instance, in order to achieve 75 % HEM removal the difference in power density between the 0.3 and 1.85 litre reactors was 2.5 kWh m^{-3} min^{-1} compared to 0.5 kWh m^{-3} min^{-1} (Figure 10). Removal efficiency levels off with bed volumes greater than 1 litre.

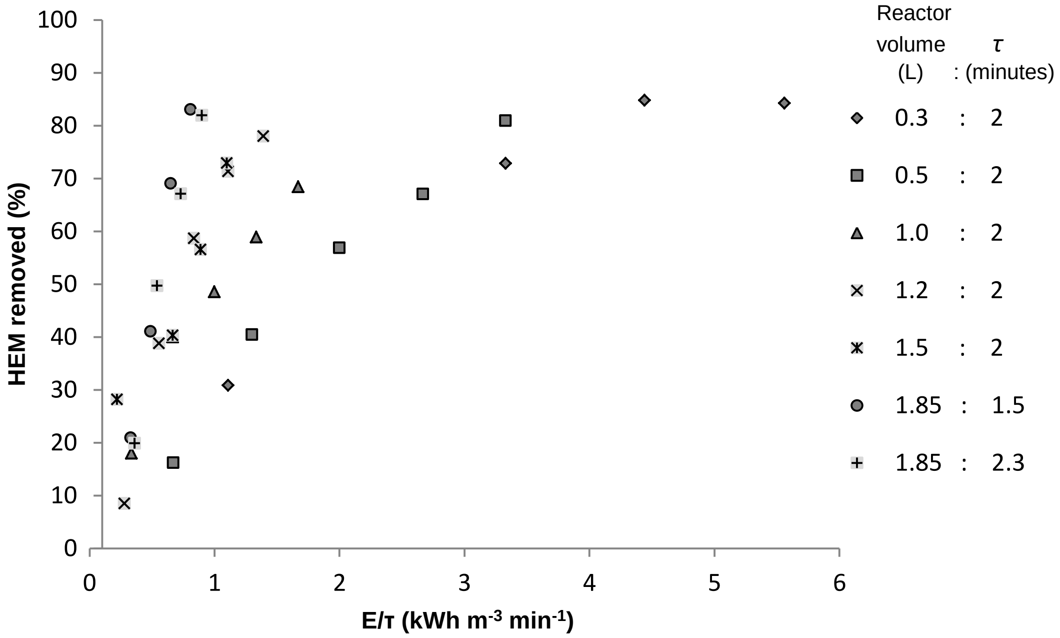

Figure 9: *Comparison of HEM removal rates for different bed volumes with an ultrasound treatment of 100W at 582 kHz*

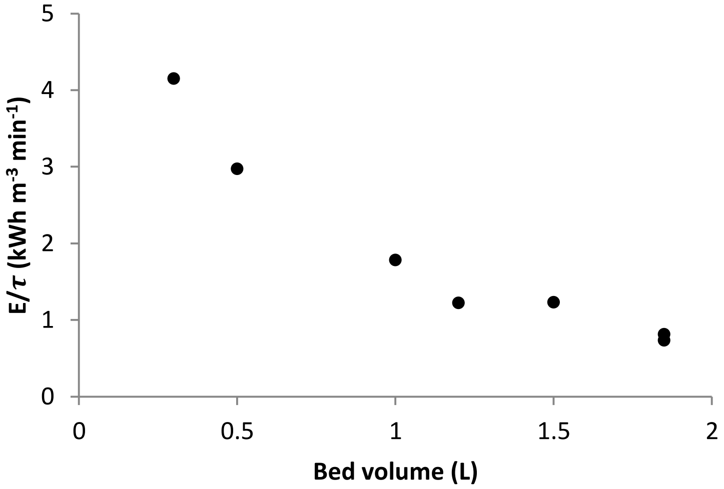

Figure 10: *Applied power required to achieve 75% HEM removal for different reactor bed volumes*

6.3.4 Stability of removal under optimised conditions

The parameters examined thus far have shown HEM removal rates are affected by ultrasound frequency, power input and bed volume. The optimal conditions to enhance removal of a disperse phase of 0.7 % were determined to be a bed volume of 1.85 litres with a frequency of 582 kHz at 100 W applied power. To confirm the impact of ultrasound the optimum conditions were used against a comparative control (no ultrasound) in a continuous run of 54 minutes treatment operating at a flow rate of 0.465 L min^{-1} (Figure 11). In the case of the of the control the median droplet size (d_{50}) decreased from 38 to 33 µm over 54 minutes indicating the relative stability of the droplet suspension in continuous flow conditions. HEM removal decreased from 73 to 29 % in the first 5 minutes consistent with the impact of the reactor initially containing clean water and hence diluting the incoming feed. The stability in removal beyond 15 minutes which remained at around 20 – 30 % is similar to those observed when ultrasound was applied at low power inputs suggesting it was having no real impact. In contrast, when ultrasound was applied the d_{50} reduced to 14 µm within 2 minutes and remained between 12 and 16 µm during the course of the experimental run. Over the same time period oil removal decreased from 93 to 80 %. Oil removal started as soon as ultrasound was applied and remained stable during the course of the run indicating the efficacy of the approach. The slight decrease in HEM removal during the course of the run is consistent with slight re-entrainment of separated oil droplets as the fresh feed passes through the oil layer. The separated oil was not withdrawn during the trial such that the captured layer increased in volume as the experiment continued.

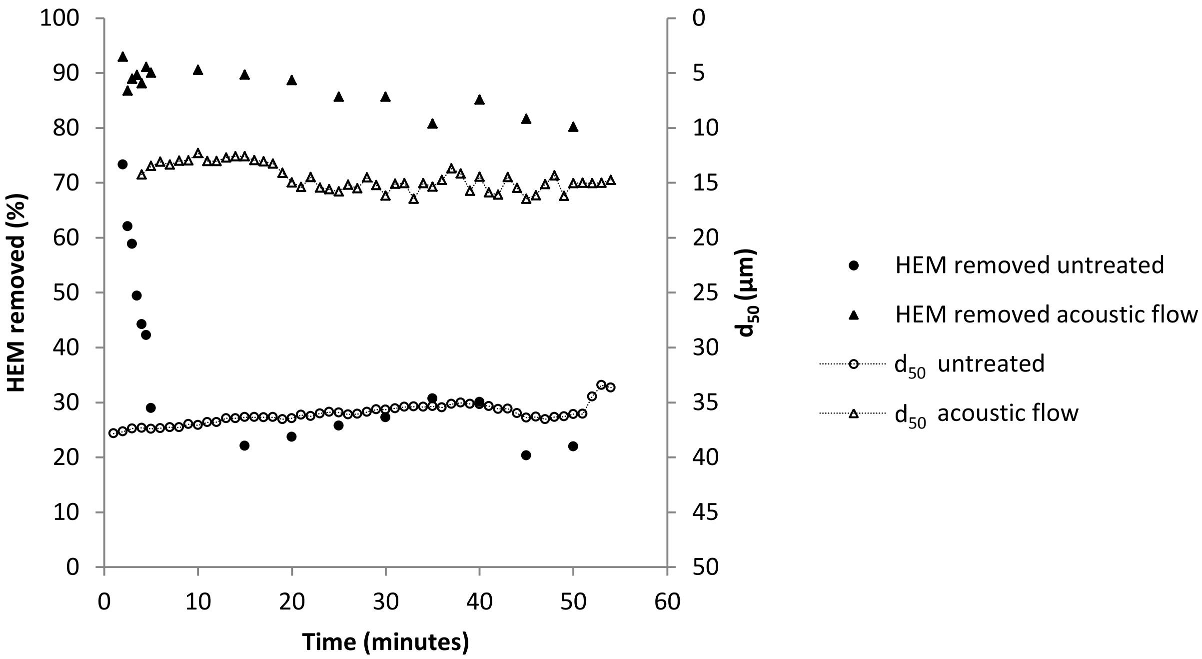

Figure 11: *Effect of ultrasound treatment on HEM removal and PSD.*

6.4 Conclusions

Passive gravity separation of FOG can be enhanced through the use of ultrasound energy input. The efficacy of ultrasound is maximised at lower frequency and can be explained by a combination of acoustic streaming with micro bubble formation. The result is a removal of smaller droplet sizes in any given residence time compared to cases when no ultrasound is applied. Comparison of the different variables associated with application of ultrasound indicates that the power input and reactor size are the critical variables. Overall a relationship exists between the required power density applied and the level of removal achieved for any given reactor size enabling the specification of an ultrasonic enhancement unit to be designed for any separator.

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7 Overall implications for enhancing FOG separation

The key observations within this thesis with respect to enhancing FOG separation in grease separators were:

1) Current standard methods for FOG determination produce low and variable recoveries thereby overestimating removal. This variability can lead to incorrect assumptions about the effect separator design changes have on removal efficiency.
2) The standard material used in grease separator FOG removal tests is a mineral oil which was found to separate out more rapidly than the more typical triglyceride oils found in kitchen wastewater which again can lead to an overestimation of removal efficiency.
3) Separation efficiency is determined by a buoyancy factor linked to droplet size and density. So it is important to know the sizes and variations in droplets that are likely to occur.
4) The droplet sizes found in samples of kitchen washing up water taken from different establishments was found to vary between kitchens and from day to day and were found to be in the mechanically and chemically emulsified oil size ranges which means they require extended residence times for their removal.
5) As droplet size changes occur during their initial formation due to energy input and surfactant concentrations then differences between wastewater from manual washing and dishwashers can be expected to produce different characteristics of droplet size and zeta potential.
6) Mechanically and chemically emulsified oil droplets do not break up or coalesce under turbulent conditions so understanding initial formation is key. Future investigations should examine the variations between manual and automatic washing operations and look into reducing turbulence in dishwashers to see if larger droplets are formed.
7) Application of acoustic energy in the form of ultrasound waves can be used to enhance FOG removal with power input and frequency determining removal efficiency. Optimising treatment parameters will allow estimation of how much improvement can be expected.

The above findings suggest that current standard methods for FOG quantitation do not produce accurate or repeatable results even for clean oil in water systems. As a consequence grease separator removal efficiency cannot be accurately evaluated as low recoveries lead to overestimation of separation performance. Variable results mean that incorrect conclusions can be drawn about the effect design changes or treatment has on removal efficiency.

To address this alternative FOG measurement techniques needed to be evaluated for model and wastewater samples. It was found that solid phase extraction cartridges were marginally better than standard liquid-liquid extraction when extracting a wastewater analogue (dilute salad cream) although recoveries were low at 70 and 66 % respectively. Turbidity measurements, as a proxy for FOG content, showed good correlation with solid phase extraction of wastewater and were shown to correlate well with surfactant stabilised oil in water suspensions (Chapter 3). Quantification of clean oil in water suspensions was accurate and repeatable when replacing the standard extraction method of shaking solvent and sample in a separating funnel by centrifugation of sample and solvent in a centrifuge bottle during the extraction step (recoveries of 100 ± 2 % achieved). This makes the technique ideal for evaluating separation performance of treatments or the impact changes in separator design parameters have at bench or pilot scale. The centrifugation-solvent extraction method was not suitable for surfactant stabilised model systems showing poor oil recovery as a result of surfactants shielding oil droplets from the solvent and also potentially co-extracting into the solvent. Field sample FOGs which have a mixture of foodstuffs, oils and cleaning agents can be estimated by proxy using turbidity measurements and confirmed using solid phase extraction.

Kitchen grease separator certification measurements are based on standards for mineral oil separators and use a light fuel oil (diesel) as the test material. Diesel, an aliphatic hydrocarbon, was found to have different physical characteristics to the more usual triglycerides found in kitchen wastewater FOGs (Chapter 4). Oil in water suspensions produced at 10,000 rpm for diesel and sunflower oil produced median droplet sizes (d_{50}) of 14 and 32 µm and HEM removal of 63 and 23 % respectively after 5 minutes residence time. Consequently, under the same mixing conditions, light fuel oil will overestimate triglyceride removal performance of separators.

To better reflect the separation performance of grease separator designs it will be necessary to use a more appropriate type of oil (mix of triglycerides and free fatty acids) with a defined droplet size distribution for consistent measurement.

A range of oil in water suspensions of known d_{50} and known oil specific gravity were prepared and the oil content measured after incremental residence times. The oil droplet variables of diameter and density difference ($d^2 \times \Delta\rho$ from the Stokes equation) were plotted against actual oil removed to produce curves for different residence times. The slopes ($y = mx + b$) of these curves can then be used to predict oil removal rates in field samples for example in CE 2 with the smallest median droplet size suspension of 9 µm with a density of 0.92 kg m^{-3} the oil removal will be 7.2 % after a 10 minute residence time. The average median droplet size of the four catering establishments sampled over a week was 52, 88, 105 and 95 µm respectively and the method predicts that oil droplets with diameters greater than 50 µm and density of 0.92 g ml^{-1} will completely separate out with a residence time of 10 minutes. The method will enable design of separators or treatments to be tailored to achieve a particular droplet size that will separate out in a target residence time.

Variations in energy input (mixing rpm) and surfactant concentration were found to produce different size droplets which reflect potential differences in waste water such as that from manual washing and that from dishwashers. As mechanically emulsified oil size range droplets and smaller were found not to coalesce or breakup under turbulent flow conditions their initial formation will be key in determining their separation rate in a grease separator. By minimising the energy input, for example reducing turbulence in dishwashers to potentially increase the droplet size produced, would improve oil removal rates in grease separators.

A number of studies have investigated particle removal from suspension using standing waves produced by ultrasound in reaction chambers. For oil in water suspensions the idea is to use the difference in acoustic energy attenuation between oil and water to push oil droplets towards pressure nodes where droplets will aggregate and potentially coalesce. The ultrasound can then be turned off and the aggregated/coalesced droplets with concomitant increased size are allowed to separate out. However this has only been demonstrated in very small reaction chambers and no data has been presented showing quantified removal rates in larger scale systems. Work in this thesis demonstrated that an alternative to ultrasound standing wave removal, namely acoustic streaming, could also be used to enhance oil removal rates. Measurements of oil removal from suspension were made in a vertical cylindrical chamber made of glass with a 3 frequency transducer located at the base. Oil suspensions were passed through the reaction chamber in the opposite direction to the acoustic energy. A scaled up version of this system could be accommodated in a grease separator (Figure 1). It is suggested that a traditional design grease separator could accommodate a submersible ultrasound transducer (Figure 2) in a second compartment to polish flow entering from the first compartment of the grease separator. When high influent flow rates are detected the ultrasound transducer can be triggered to turn on and apply acoustic energy to remove any short circuiting droplets.

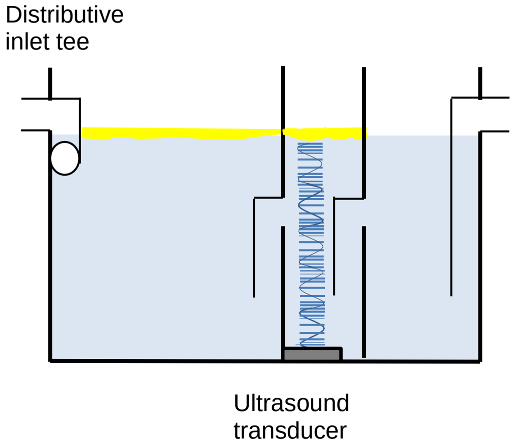

Figure 1: *Grease and ultrasound transducer located in a second chamber that is activated when high flow rate is detected*

Figure 2: *Example of a submersible ultrasonic transducer*

Measurements of ultrasound treatment showed that the lower frequencies of 582 and 862 kHz reduced droplet size d_{50} of sunflower oil suspensions from 32 µm to 8 µm. Increases in rate of droplet size reduction were seen when applied power was increased. In flow through experiments a frequency of 582 kHz at applied power of 100 W was used for ultrasound treatments. It was found that the largest bed volume of 1.85 litres produced the most energy efficient oil removal with applied energy of 0.9 kWh m^{-3} min^{-1} removing more than 80% of oil during 54 minutes of treatment

8 Conclusions and future work

The work presented in this thesis aimed at improving the performances of a gravity grease separator and reducing its size, through design modification of the system and/or input of external energy. Separation efficiency of passive grease separators is related to the physical-chemical characteristics of the droplets to be removed, as predicted by Stokes Law. These characteristics should be used to define removal efficiencies of edible oils when sizing gravity separators or assessing removal technologies. The literature review underlined the limited amount of publications related to the physical-chemical characterisation of FOG from catering establishments entering the sewers or the separation systems. Most of the available data for FOG removal efficiency is limited to bench or pilot scale investigations assessing design modifications or treatments with no physical measurement of droplet size.

FOG droplet size and zeta potential in samples of kitchen wastewater were found to vary between catering establishments and from day to day operation. However, median droplet sizes produced during washing/cleaning operations in the kitchens are stabilised by the presence of surfactants and fell typically in the mechanically emulsified oil range. Experimental results suggest that these stabilised pre-formed droplets are unlikely to coalesce during transport from kitchen sinks to the FOG separator and can be considered the input material of the separator.

Droplets in the mechanically emulsified range (20 to 150 µm) given sufficient residence time will separate out in a gravity separator, with small increases in droplet size having a significant impact on removal rate. Experimental data produced during the project show that removal of oil droplets down to 44 µm should occur within 10 minutes. High zeta potentials (± 30 mV) were found in most of the samples suggesting that coalescence assisted separation by gravity is unlikely to occur. The outcome of the work identified droplet size and zeta potential, in addition to removal efficiencies, as the key parameters that will need to be monitored when trying to enhance separation in catering establishment wastewater treatment systems.

Current separators are single unit devices containing baffles to manage flow and have been shown to be effective as long as sufficient time is available for separation. Removal of the separated oil is conducted infrequently such that re-entrainment is also possible. Improved separation could be achieved through design modifications to increase residence time or by reducing mechanical emulsion formation. Consideration of these two features indicates that a sequenced batch separator may provide benefit whereby a chamber is filled and then rested to allow sufficient time for separation before being drained and refilled.

Additionally treatments to coalesce mechanically emulsified FOGs, for example through the use of ultrasound energy input, could be incorporated into the design with the potential of allowing the development of smaller separators. Separation of FOG in passive gravity separators can be enhanced by application of ultrasound energy. Comparisons of the different variables in ultrasound treatment show that power input and reactor size are the critical variables for removal for any given residence time. There is a relationship between power density applied and the amount of FOG removed in any given reactor size which enables the specification of an ultrasonic enhancement unit to be designed for any separator.

Compliance with discharge consents requires determination of total oils and greases (TOGs) in separators wastewater. Current recommended extraction techniques are liquid-liquid and solid phase extraction. These techniques are unsuitable for the quantification of total oils and greases in kitchen wastewater, rich in emulsifying substances, which will need an acid digestion step, as used in dairy fat extraction techniques, that can be used to release the ‘bound’ oils.

Conventional solvent extractions extract only ‘free’ (clean) oil rather than all FOGs and result in poor recovery and repeatability, especially in surfactant stabilised suspensions such as catering wastewater. Alternative quantification methods such as solid phase extraction where column matrix aids emulsion destabilisation show better recovery. Whilst not extracting all FOGs, SPE could be used to monitor relative changes in FOG content. Turbidity measurements were found to be comparable with SPE measurements of surfactant stabilised suspensions so could be a rapid and cheap alternative for routine monitoring of oil content changes in laboratory or pilot scale trials using synthetic wastewaters.

Finally, our work demonstrated that oil suspensions prepared with different oils produced very different droplet sizes for any given energy input. These droplets, similar to the one measured in catering grease separators, were significantly different from the droplet size produced by the light fuel oil used for testing separators systems efficiency. The presence of free fatty acids will also impact on FOG separation rates. Our recommendation is that, for certification purposes to better represent separation in grease separators, a more representative oil and fatty acid with similar dispersion characteristics and density to food lipids should be used.

The work carried out for this thesis added to existing knowledge by showing kitchen wastewater particle size distribution was in the mechanically emulsified range (d = 20 – 150 μm) and electrically stabilised (ζ = >± 30 mV).
Also demonstrated that given sufficient residence time mechanically emulsified oil down to a median droplet size of 50 μm would separate out under gravity and that current certification standard material overestimates removal efficiency of food oils.
Studies showed mechanically emulsified oil droplets remained the same size under turbulent flow conditions and size was determined during kitchen cleaning processes.
A novel approach to sizing grease separators was developed by linking the Stokes Law parameters of d^2 and $\Delta\rho$ for different food oils to their removal rates at incremental residence times such that the residence time required to remove oil to a target droplet size could be predicted.
A novel treatment process for separation of food oil suspensions from water using ultrasound acoustic streaming showed that removal of mechanically emulsified oil could be enhanced by over 80 %.

8.1 Future work

8.1.1 Research work

If separators are to be sized according to droplet characteristics as described by Stokes it will require a more detailed knowledge of the kitchen wastewater to be treated. Recognising the impracticalities involved in characterising each and every catering establishment, in terms of time and expense, sampling from a range of representative cuisine types should be carried out over the course of a year to establish a reference library for use in future sizing or design of separator units

The effect on FOG separation rates by the ratio of triglycerides to free fatty acids needs to be investigated as the ratio can be changed by biological and chemical processes over time. The rate of free fatty acid creation may have other implications such as contribution to ‘fatberg’ formation.

Sizing criteria can be further refined by sampling FOG rich wastewater from the different sources of FOG production and accumulation in kitchens (grills, ovens, pot wash sinks and preparation areas) to identify those sources where particle size needs to be increased. To determine if cleaning processes can be modified to increase droplet size surfactant free pre-rinses should be compared with surfactant containing washes. Similarly a comparison between the droplet sizes produced by hand-washing and automatic dishwashers should be performed to establish potential for droplet size increase through design modification of automatic dishwashers.

Flow paths within a separator should be determined using tracers to characterise areas of turbulence and short-circuiting within the unit the effect design modifications have on turbulence reduction and short circuiting can then be evaluated.

Ultrasound frequency was observed to affect FOG removal performance with the lowest frequency produced by the ultrasound transducer generating the greatest FOG removal. Application of lower ultrasound frequencies should be investigated to optimise the procedure with a view to reducing the power requirement for treatment.

8.1.2 Industrial/commercial investigation

Currently separators are sized to remove a target amount of oil under maximum influent flow rate. We know that most of the time separators operate at less than maximum flow rate so arguably have redundant capacity. It has been established that given sufficient residence time mechanically emulsified oil droplets will separate out. Therefore comparing the removal performance of a NS separator (maximum flow rate) with that of a separator sized on a residence time determined either by droplet characteristics associated with cuisine type or removal of a target droplet size, should be undertaken. Selection of a more appropriate standard material to represent catering wastewater FOGs is required.

Reducing the size of conventionally designed separators will decrease residence time such that at maximum inlet flow rates smaller droplets might be expected to short-circuit the first compartment. Control of residence time, thereby FOG removal, could be achieved by designing a fill and draw batch reactor system using solenoid valves to regulate residence time in a series of reaction chambers.

Application of ultrasound energy has been shown to rapidly remove oil droplets from suspension and could be used as a tertiary treatment for short-circuiting in a conventional separator design. By locating an ultrasound transducer in the base of a second chamber to be activated when high flow is detected short-circuited droplets can be removed from suspension.