

Rapid Screening of an Acid-catalysed Triglyceride Transesterification using Design of Experiments in a continuous Mesoscale Oscillatory Baffled Reactor

Luma Sh. Al-Saadi^{1a}, Alexandra Alegría², Valentine C. Eze¹, Adam P. Harvey¹

¹School of Engineering, Newcastle University, NE1 7RU, UK

²Department of Chemical Engineering, University of Salamanca, Spain.

Abstract

A mesoscale oscillatory baffled reactor (“meso-OBR”) was used as a continuous screening platform to rapidly investigate the operating conditions for acid-catalysed production of fatty acid methyl ester (FAME) from triglyceride feedstock. The acid catalyst used was 4-dodecylbenzenesulphonic acid (DBSA), and the triglyceride feedstock was rapeseed oil (RSO). The parameter space was explored using a Design of Experiments (DoE) methodology. The variables screened were the oscillatory mixing intensity (the oscillatory Reynolds number: Re_o), methanol-to-RSO molar ratio, catalyst-to-oil molar ratio and residence time (τ). The meso-OBR attained steady states rapidly (within 1.1 – 1.5 residence times) indicating rapid start-up/changeover time, thereby minimising waste. The oscillatory mixing intensity required was low, at $Re_o \geq 83$, making the energy consumption relatively low. Over 98% conversion of RSO to FAME was found to be achievable at 60°C, a methanol-to-oil molar ratio of 6.5:1, a catalyst-to-oil molar ratio of 0.48:1 and residence time of 120min. This molar ratio is significantly lower than that used for conventional acid catalysis (typically >9:1). Furthermore, the screening by DoE has led to identification of sets of conditions for high conversion at significantly lower

^a Corresponding author: Luma Sh. Al-Saadi
Email: lumashihab201@gmail.com

temperatures than previously reported. Significantly, the temperatures are now below the ambient pressure boiling point of the methanol.

Keywords: Acid catalysis, rapid biodiesel process, FAME, 4-dodecylbenzenesulfonic acid (DBSA), continuous mode, mesoscale oscillatory baffled reactors, response surface.

1 Introduction

Biodiesel is a mixture of fatty acid methyl esters (FAME), produced (usually) by the reaction of triglycerides such as vegetable oil (e.g. rapeseed oil) with alcohol (usually methanol), usually in the presence of a catalyst. The triglyceride transesterification occurs via three consecutive stepwise reversible reactions [1-3], summarised in the overall reaction shown in

Figure 1, below:

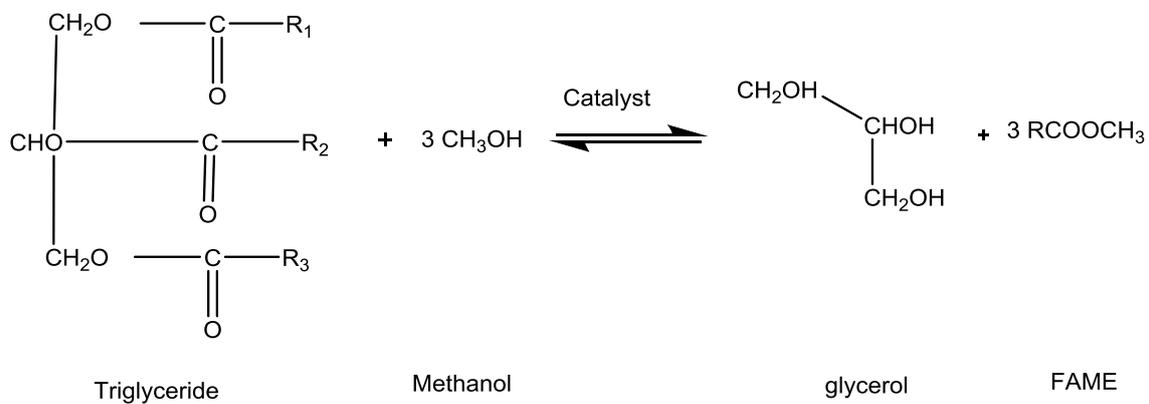


Figure 1: triglyceride transesterification

The main advantages of biodiesel are that it emits less unburned hydrocarbons, aromatic hydrocarbons, carbon monoxide and sulphur species than “petrodiesel”; by 90%, 75%, 47% and 20%, respectively. It also biodegrades faster than petro-diesel [4, 5], and is significantly less toxic. Biodiesel is costlier to produce than petrodiesel due to the high price of feedstocks (vegetable oil) and operating cost [4]. Non-edible oils (used cooking oil) can be used to reduce

the feedstock cost, but the processing costs are higher due to the presence of water and free fatty acids (FFAs). The transesterification of oils and fats can be catalysed using base catalysts [6-9], acid catalysts [10-12], or biocatalysts [13-15]. Supercritical fluid processing, which requires no catalyst, has also been investigated for biodiesel production [16-18]. However, the supercritical process for biodiesel production is not economical because of the high pressure (~8 MPa) and temperature (~ 350°C) requirements [16], which increases the capital cost of the process substantially. The use of biocatalysts (enzymes) is also not cost-effective for industrial application due to the high cost of biocatalysts, the low reaction rates, and enzyme deactivation [15]. Therefore, biocatalysts and supercritical methanol processes are not commonly used, and most developments in biodiesel production catalysts, and all commercial production, have used acid and/or base catalysts.

The most commonly used catalysts for conventional biodiesel production are base catalysts, mainly the hydroxides and methoxides of sodium and potassium, especially sodium methoxide which is used in more than 60% of the commercial biodiesel plants [9]. These base catalysts have high reaction rates which are typically 4000 times faster than that of acid catalysts at moderate temperatures [19]. The higher rates of the base alkaline catalysts make them preferable to the acid catalysts. However, base catalysts are not suitable for catalysis of “low quality” triglyceride feedstocks, which contain FFAs $\geq 0.5\text{wt}\%$ and water $\geq 0.3\text{wt}\%$ [12, 20]. These levels of FFA and water lead to excessive degrees of saponification of triglycerides and FAME [21], causing emulsification and consequent difficulties in the product separation [22]. Conventional processes for biodiesel production from feedstocks containing FFA $\geq 0.5\text{wt}\%$ FFA and water $\geq 0.3\text{wt}\%$ are one-step acid-catalysed transesterification, or a two-step process involving acid-catalysed FFA esterification followed by base-catalysed transesterification. A recent study, indicated that a one-step process with high biodiesel yield could be achieved using homogeneous base-catalysed transesterification, by using short reaction times and high (18:1)

methanol-to-waste cooking oil molar ratio even at 5.5wt% FFA and 3wt% water contents [23]. However, an efficient and rapid acid-catalysed transesterification process is desirable to allow commercial biodiesel producers the flexibility in utilisation of refined edible and non-edible vegetable oils, as well as low grade triglyceride feedstock containing higher FFA: some triglyceride feedstocks, such as “trap grease”, can contain as much as 57 wt% FFA [24]. Cost-effective processing of such FFA feedstocks would require an intensified acid-catalysed process that converts both FFA and triglyceride to FAME in one step, by simultaneous catalysis of the triglyceride transesterification (Figure 1) and FFA esterification (Figure 2).

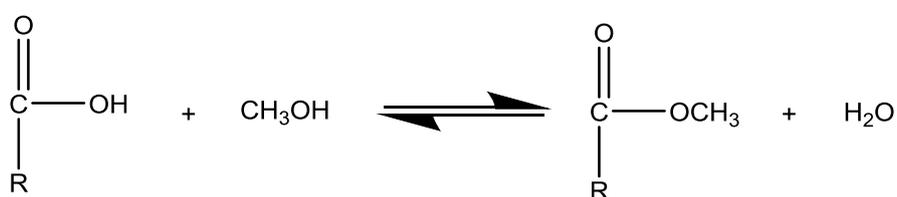


Figure 2: Acid-catalysed esterification of FFA

A number of studies have been performed to develop acid catalysts suitable for biodiesel production, especially from low quality triglyceride feedstocks, in order to overcome the problems associated with use of base catalysis in such systems. The acid catalysts that have been investigated for this application are sulphuric acid, phosphoric acid, hydrochloric acid and organic sulphonic acids [25-32]. The most widely used, among these acid catalysts, is H₂SO₄ because of its higher activity, low price and availability [33, 34]. The main disadvantages of acid catalysis of triglyceride transesterification are the requirements for high temperatures, high methanol molar ratios, and long reaction times. For instance, it has been reported that 19h was required to achieve 99% FAME yield in methanolysis of soybean oil at 9:1 of methanol-to-oil molar ratio and 120°C using H₂SO₄ catalyst [35]. Another study reports 99% FAME yield after 4h in a transesterification of waste frying oil at 70°C, 169–190kPa pressure and 245:1 methanol-to-oil molar ratio using 3.8:1 H₂SO₄ to oil molar ratio [26]. A recent study using 2wt% cucurbituril-protected Cs_{2.5}H_{0.5}PW₁₂O₄₀ as a catalyst achieved a

significantly lower reaction time of 150min in a transesterification of waste cooking oil at 70°C and 11:1 methanol-to-oil molar ratio, for 95.1% FAME conversion [36]. Apart from lower reaction rates, acid-catalysed transesterification also requires corrosion-resistant vessels to withstand the mineral acids [35, 37], which leads to a substantial increase in the capital and operating costs of acid-catalysed biodiesel process. The problems of long reaction times and equipment corrosion associated with catalysis of triglyceride transesterification using mineral acids (H₂SO₄) could be solved through the use of strong, but less corrosive acids, such as organosulphonic acids. One of the organosulphonic acids identified for this application is a 4-dodecylbenzene sulphonic acid (DBSA), which was used to achieve ≥96% FAME after 3 - 6h in transesterification of at 6:1 to 9:1 methanol-to-oil molar ratio and reaction temperature of 70 - 80°C, using a batch reactor [31]. The use of lower methanol molar ratio with the DBSA catalyst was attributed to an increased solubilisation of the methanol and oil phases due to the molecular architecture of the catalyst. The DBSA has a sulphonic acid group (-SO₃H) attached to an aromatic ring linked to an alkyl chain (see *Figure 3*).

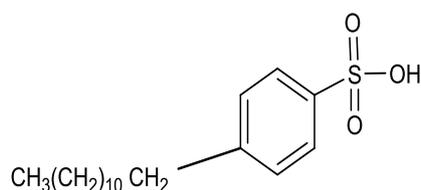


Figure 3: 4-dodecylbenzene sulfonic acid (DBSA) structure.

The sulphonic acid group on the DBSA is hydrophilic, which makes it soluble in methanol, while the aromatic ring linked to an alkyl chain confers hydrophobicity, which increases its solubility in oil. Therefore, the DBSA aids transition of the initially two-phase liquid-liquid (oil-methanol) reaction to a one-phase reaction. It would be expected therefore that use of DBSA in catalysis of triglyceride transesterification would lead to increased reaction rates due to the enhanced mass transfer between the oil and methanol phases. Also, use of continuous

reactors would enhance the biodiesel production and increase the efficiency of the process [38]. Therefore, to rapidly investigate the scope for reaction rate enhancements due to the use of DBSA, a small scale plug flow reactor with good mixing is required. One such reactor is the oscillatory baffled reactor (OBR).

Oscillatory baffled reactors are advantageous for systems with multiphase (liquid) mixing, requiring plug flow, to investigate reaction parameter spaces, whilst incurring low capital and running costs. Numerous studies have shown that OBRs are effective in multi-phase fluid mixing, enhancement of heat and mass transport, and particle suspension [39-47]. The OBR achieves effective multiphase mixing and plug flow behaviour through oscillating the reaction fluid through the orifices of equally spaced baffles [44]. Generally, the meso-OBR's niche application lies in screening reactions that have long residence times, using reactors of greatly reduced length-to-diameter ratio. This is due to the decoupling of the net fluid flow in the OBR from the oscillatory flow, which allows for independent control of the mixing intensity and residence time of the reaction [43].

This study investigates continuous processes for DBSA-catalysed transesterification of triglyceride feedstock using a mesoscale oscillatory baffled reactor (meso-OBR). The meso-OBR is a millilitre scale OBR platform used for process screening at minimised raw materials requirements, and reduced waste generation. The meso-OBR was used to screen various operating parameters (effects of mixing intensity, feed molar ratio, and catalyst requirement), to develop an optimised rapid biodiesel process that utilises the DBSA as a catalyst at moderate reaction conditions.

2 Materials and Methods

2.1 Materials

The chemicals used in the experiments were anhydrous methanol (99.8%), 4-dodecylbenzenesulfonic acid ($\geq 95\%$), hydrochloric acid (37%), heptane (99.5%), and methyl heptadecanoate (99%). These chemicals were purchased from Sigma-Aldrich, UK. The rapeseed oil was supplied from Henry Colbeck Limited, and had 0.05 wt. % of water and 1.5 wt. % of free fatty acids contents.

2.2 Experimental procedure

The meso-OBR system consisted of two connected glass tubes containing “integrally baffled” reactors (total length 1420mm), with a glass outer heating jacket, as shown in *Figure 4(a)*. Each meso-OBR had 8mm outer diameter, 5mm inner diameter and periodic constrictions of 2.5mm diameter along the length of the tube at 7.5mm spacing (*Figure 4(a)*). The reactors were connected via Swagelok fittings to four Confluent continuous syringe pumps (Eurodyne Ltd). One of these pumps was used to provide the oscillations at 2Hz - 6Hz frequency and 2mm - 8mm amplitude, and the other three to provide the net flows of rapeseed oil, methanol and catalyst solution. The DBSA catalyst was initially diluted in methanol to reduce its viscosity. The syringe pump used for oscillation was connected to the base of the reactor, and the fluid mixing inside the reactor provided by adjusting the speed of the piston movement (frequency) and the oscillation amplitude (centre-to-peak) of the pump [48, 49]. These syringe pumps were controlled via a PC interface via “Sapphire commander” software, and the pumps were initialised, and set at the required mixing intensity (amplitude and frequency) and reactants net flow rates prior to each experiment.

The reaction temperature was maintained by the circulation of heated water through the jacket of the meso-OBR using a temperature-controlled water bath (Ecoline, LUADA E100). The

reactants were pumped into the reactor from reservoirs heated at 60°C in the constant-temperature water bath, and the reactor was operated at atmospheric pressure for all the experiments. The experimental set-up is shown in *Figure 4(b)*.

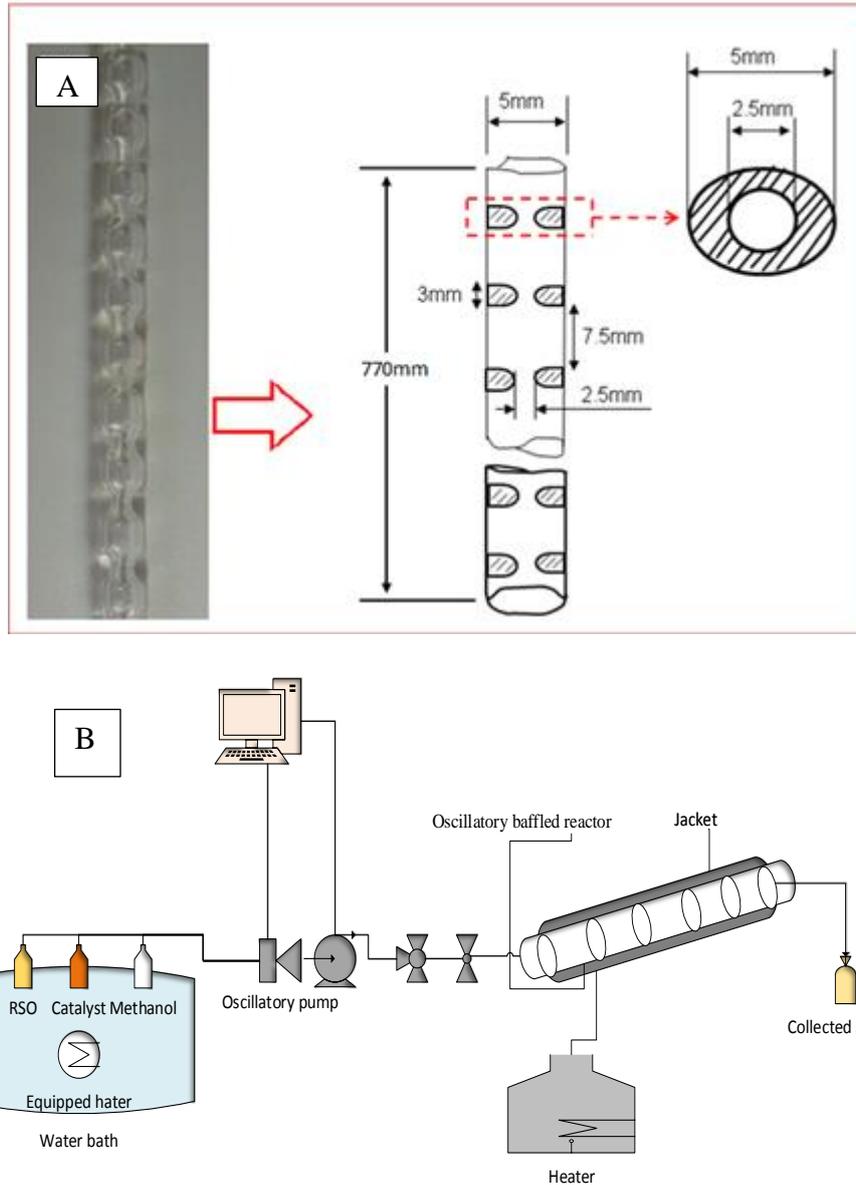


Figure 4: (a) Integrally baffled meso-OBR ; (b) experimental set-up.

The effect of oscillation conditions was investigated at 1mm - 8mm amplitude and 2Hz – 7Hz, corresponding to oscillatory mixing intensity (Re_o) in the range of $10 < Re_o < 166$ with Strouhal

numbers (St) of 0.05-0.4. Mixing intensity was investigated to ensure that the meso-OBR was operated in the mixing-independent region. The operating parameters investigated were: 30 - 120min residence time (corresponding to net flow Reynolds numbers (Re_n) of 0.16 - 0.65), methanol-to-RSO molar ratios of 3 - 10, and DBSA-to-RSO molar ratios of 0.03:1 to 0.48:1, which correspond to DBSA catalyst concentration of 0.031-0.499 mol/L of RSO. The Re_n and Re_o were calculated as shown in Equation 1 and Equation 2 respectively, and the ratio between the Re_n and Re_o is called velocity ratio (Equation 3).

$$Re_n = \frac{\rho UD}{\mu} \quad \text{Equation 1}$$

$$Re_o = \frac{\omega x_o \rho D}{\mu} = \frac{2\pi f_o x_o \rho D}{\mu} \quad \text{Equation 2}$$

$$\text{Velocity ratio } (\psi) = \frac{Re_n}{Re_o} \quad \text{Equation 3}$$

Where:

ρ : density of the fluid (kg.m^{-3});

U: superficial net flow velocity (m.s^{-1})

ω : angular oscillation frequency (rad.s^{-1});

μ : dynamic viscosity of the fluid (Pa.s).

D: internal diameter of the tube (m);

f_o : oscillatory frequency (Hz)

x_o : centre-to-peak amplitude of oscillation (m)

2.3 Design of experiments

A mixing study was performed to find the mass transfer independent region for RSO transesterification in the meso-OBR for the DBSA catalyst. This mixing condition was then used in the parametric studies, and the design of experiments methodology was used to investigate the effects of the mixing conditions. The response variable studied was the FAME yield, and the factors investigated were catalyst-to-oil molar ratio, methanol-to-oil molar ratio and residence time. In order to gather sufficient information, a wide range of catalyst-to-oil molar ratio (0.03:1 to 0.48:1, which correspond to DBSA catalyst concentration of 0.031-0.499

mol/L of RSO), methanol-to-oil molar ratio in the range of 3:1 to 10:1 and 30 - 120min residence time were studied (see Table 1). The coded values were calculated based on (Equation 4 -Equation 6), by assigning (-1) the lowest values, (1) the highest values while (0) is the middle values. The experiments were planned as a Box-Behnken design, with 12 experiments plus 3 experiments in the central point of the design.

$$\text{Coded value} = \frac{(\text{real value}) - (\text{central value})}{0.5 \text{ range}} \quad \text{Equation 4}$$

$$\text{Central value} = \frac{\text{low value} + \text{high value}}{2} \quad \text{Equation 5}$$

$$\text{Range} = (\text{high value}) - (\text{low value}) \quad \text{Equation 6}$$

2.4 DBSA Catalyst Recovery

Proof-of-concept for a DBSA recovery process was developed. The catalyst was recovered by passing the reaction product over a packed bed of basic ion-exchange resin (Amberlyst™ A26OH) (Figure 5).

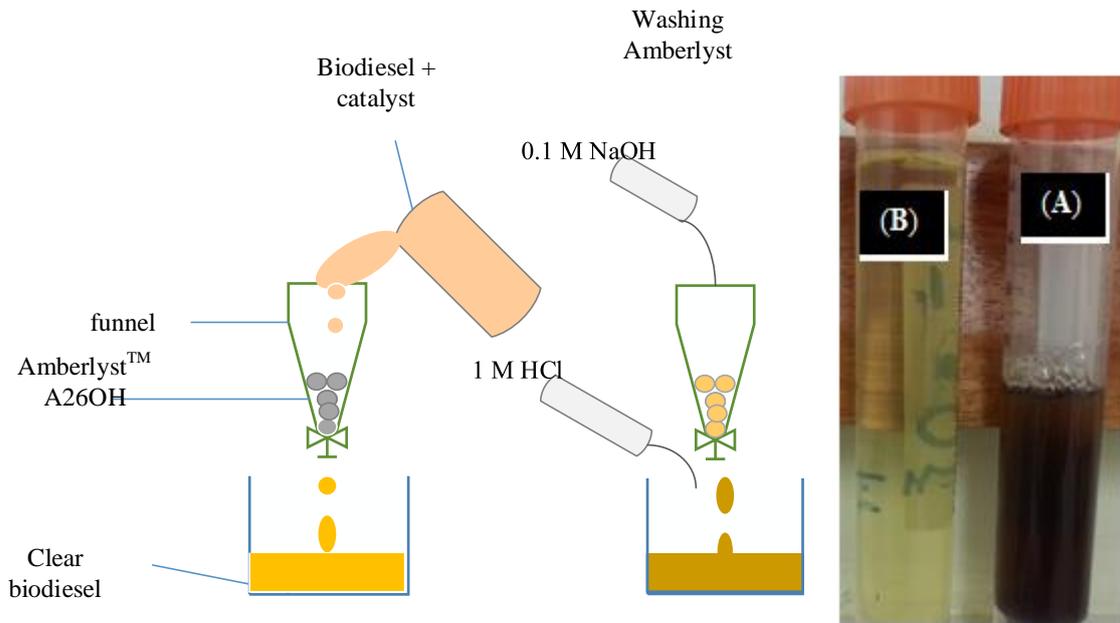


Figure 5: DBSA catalyst recovery process – (A) Before DBSA catalyst separations and (B) after DBSA catalyst separations

The Amberlyst resin was conditioned by washing 3 times in methanol and drying at 60°C for 2h, followed by soaking in anhydrous methanol for at least 3h to swell the resins and expose the porous network containing the OH⁻ active sites. Then, 50mL of reaction product from the DBSA-catalysed RSO transesterification was vigorously mixed with 20g of AmberlystTM A260H resin in a separating funnel for about 30min at room temperature (~25 °C). The liquid phase was collected through a 160µm wire mesh screen by opening the valve at the base of the separating funnel.

The AmberlystTM A260H residue in the separating funnel was washed 3 times with 25mL of methanol. This was followed by washing the Amberlyst resin with 50mL of 0.1M NaOH solution to regenerate the OH⁻ of the ion-exchange resin. The filtrate from this step contained the sodium salt of the DBSA. The regenerated Amberlyst resin was washed 5 times with 25mL of distilled water and 3 times with 25 mL of methanol, and then dried at 60°C for 2h. To recover the DBSA catalyst, the filtrate containing sodium salt of the catalyst was evaporated to near dryness, and then treated with 25mL of 1M HCl to regenerate the DBSA. This was followed by extracting the DBSA twice with equal volumes (25mL) of diethyl ether, and drying the extracted DBSA at 40°C and reduced pressure (20mbar) for 2h. The recovered DBSA was reused for catalysis of RSO transesterification at 0.03 of catalyst to oil molar ratio, 3:1 of methanol-to-oil molar ratio and 60 °C. Sulphur content analysis was carried out on the fresh and recovered DBSA catalyst.

2.5 Analysis of the samples

1mL samples were collected at various time intervals, depending on the residence time, and quenched using calcium carbonate to neutralise the DBSA. 1mL of tetrahydrofuran (THF) was added to each sample to homogenise it, and about 50 -70 mg of the homogenised samples were weighed into 2mL vials and mixed with 1mL of 10mg/mL solution of methyl heptadecanoate

(C₁₇) in heptane. The prepared samples were analysed for FAME contents using 5890 series Hewlett Packard gas chromatograph (GC), using the methyl heptadecanoate as an internal standard according to the British standards [50]. The conversions of the RSO to FAME were calculated as shown in Equation 7.

$$X_{FAME} = \frac{[FAME]_t}{3 * [RSO]_0} \quad \text{Equation 7}$$

Where:

- X_{FAME}: Yield of RSO to FAME
 [FAME]_t: Concentration of FAME in the samples at time, t (mol/L)
 [RSO]₀: Initial concentration of RSO (mol/L)

3 Results and Discussion

3.1 Mixing Study

Figure 6 shows the effects of varying oscillatory mixing intensity on the RSO transesterification for reactions at a residence time of 120min ($Re_n = 0.126$) reaction temperature of 60°C, 10:1 of methanol to RSO molar ratio, 0.249 mol/L of catalyst concentration to rapeseed oil and mixing intensities in the range of $10 \leq Re_o \leq 166$ (at $0.05 \leq St \leq 0.2$). It is clear from *Figure 6(a)* that the FAME yields and the “quality” of steady states improved with mixing intensity (Re_o) up to $Re_o > 83$. Above this value, mixing had a negligible effect on the FAME yield. At Re_o s of 10, 36 and 62 (*Fig 6(b)*) no clear steady state was achieved, as the FAME yields fluctuated in the range of 73–99 %. This shows that the levels of bulk mixing inside the reactor at these mixing conditions were not sufficient.

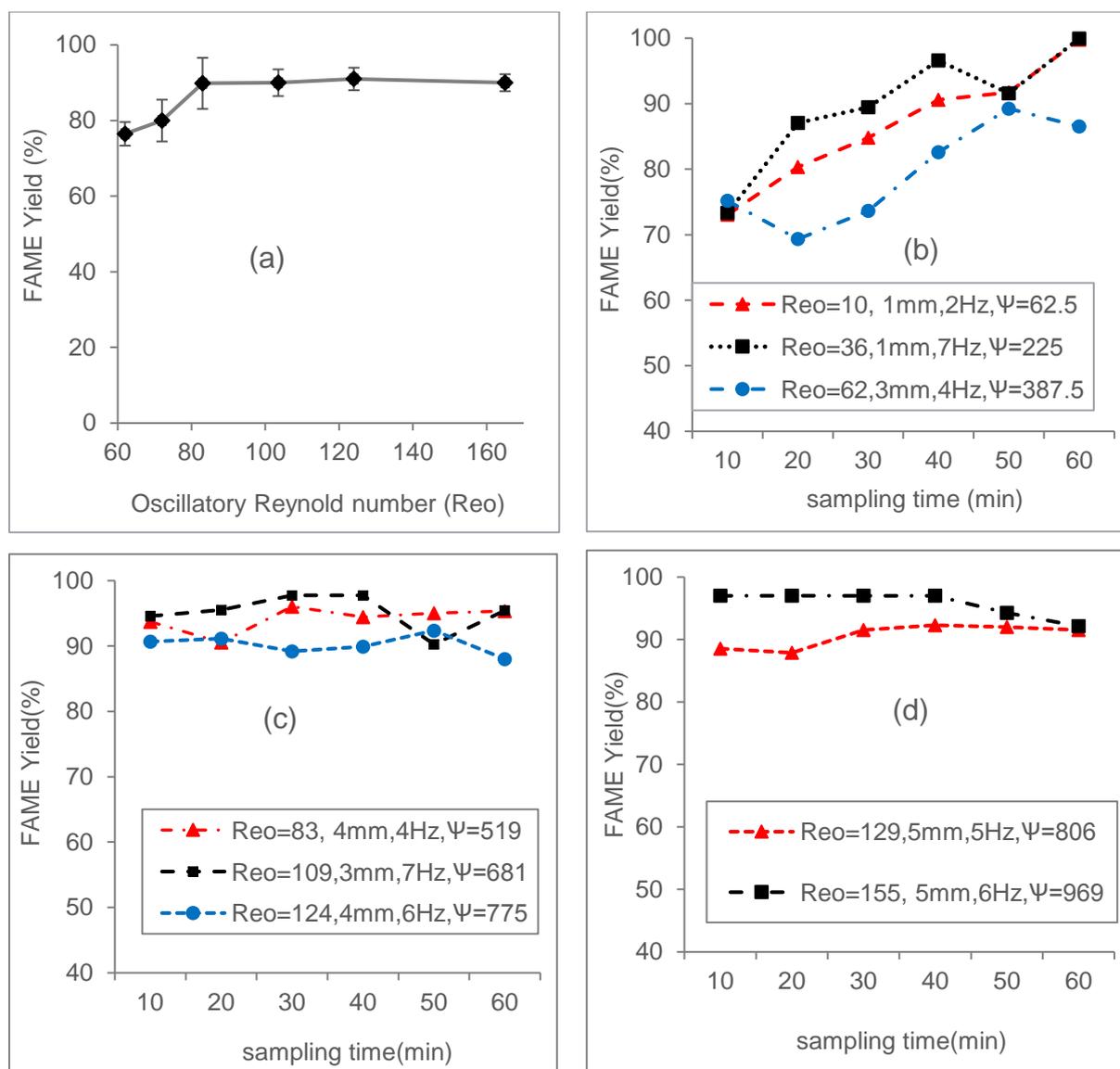


Figure 6. The influence of oscillatory mixing on stability of FAME Yields using the integral baffled reactor at 0.25 mol/L catalyst concentration, methanol to RSO molar ratio of 10:1 and residence time of 120min, (a) average steady state FAME Yields at various mixing intensities, (b) region of low oscillatory mixing ($0 < Re_o < 83$), (c) region of intermediate oscillatory mixing ($62 < Re_o < 129$), and (d) region of high oscillatory mixing ($124 < Re_o \leq 155$).

The intermediate $Re_{o,s}$ of 83, 109 and 124, resulted in average FAME yields of $94.2 \pm 1.95\%$, $95.2 \pm 2.7\%$ and $90.2 \pm 1.5\%$ respectively, as shown in *Figure 6(c)*. At these conditions, steady states were established after 130min running time, corresponding to 1.08τ . The results in *Figure 6(c)* clearly demonstrate that Re_o of 83 or more is required to establish steady state operation at these reaction conditions. Further increases in the mixing intensity, $Re_o = 129-155$ (corresponding to amplitudes of 5-6mm and 5-6 Hz) did not improve the FAME yield (*Figure*

6 (d)), indicating that the reaction had become mixing independent at $Re_o \geq 83$. The FAME yields from *Figure 6(d)* were 91.5% at Re_o of 129 and 92.13% at Re_o of 155.

The results in *Figure 6* demonstrate that the use of DBSA catalyst for steady state biodiesel production in the integrally baffled reactor requires lower oscillatory mixing ($Re_o \geq 83$), than the $Re_o > 107$ reported for base catalysis of RSO transesterification when non-surfactant base catalysts were used [51]. This was attributed to the surfactant properties of the DBSA catalyst, which enhances mass transfer between the RSO and methanol phases. In practice this would mean that the power consumption for mixing was reduced, and the reactor design could be more compact (i.e. a lower L/D ratio) [52].

3.2 Design of experiments (DoE) study

Table 1 shows the results of the DOE screening of the parameters affecting the RSO conversion to FAME with fixed oscillatory mixing intensity at $Re_o = 124$ (4mm amplitude and 6Hz frequency) and reaction temperature of 60°C. The variable parameters were DBSA catalyst to RSO molar ratios in the range of 0.03:1 - 0.48:1 corresponding to 0.031 - 0.499 mol DBSA per L of RSO, methanol to RSO molar ratios in the range of 3:1 - 10:1 and residence times of 30min – 120min.

Table 1: experimental design (factors level and value of response)

Methanol/oil molar ratio	Catalyst/oil molar ratio	Residence time (min)	FAME yield (%)
3	0.255	30	44
6.5	0.48	30	70.3
10	0.255	120	93.3
3	0.255	120	60
10	0.255	30	49
3	0.03	75	34
10	0.03	30	12.6
6.5	0.48	120	98.7
10	0.48	75	97
6.5	0.255	75	84
6.5	0.03	30	25.4
6.5	0.255	75	85.5
6.5	0.255	75	85
3	0.48	30	63
6.5	0.03	120	47

A response surface method, stepwise procedure using full quartic model was the most suitable fitting for the data. The fitted line plot indicating the agreement between the experimental and predicted FAME is shown in Figure 7. The p- values of all parameters (Table 2) were below 0.05, indicating that the effect of all variables on the biodiesel yield was significant [53]. The model was also validated experimentally, and the results confirms its validity within the studied range of parameters.

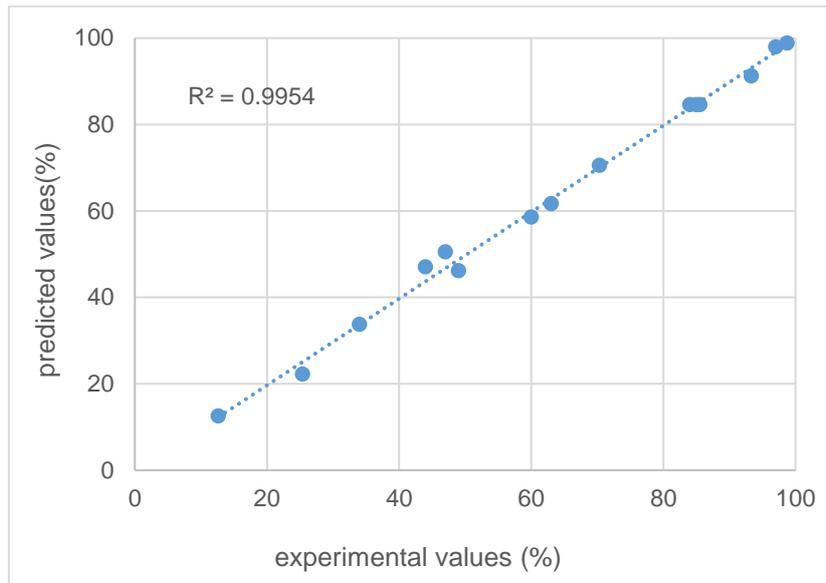


Figure 7: Fitted line plot between the predicted values and experimental values of FAME yield

Table 2 Estimated regression coefficient, T and P value of Box-Behnken design.

term	effect	Coef	SE Coef	T-Value	P-Value	VIF
	Constant		84.61	1.37	61.56	0
M	15.917	7.959	0.924	8.61	0	1.1
C	48.308	24.154	0.924	26.14	0	1.1
term	28.238	14.119	0.821	17.19	0	1.06
M*M	-18.55	-9.27	1.34	-6.94	0	1.08
T*T	-29.18	-14.59	1.42	-10.26	0	1.09
M*T	16.77	8.38	1.11	7.53	0	1.2

The empirical model of the response surface is as follows:

$$\text{FAME Yield (\%)} = -39.84 + 8.12 M + 203.0 C + 1.049 T - 0.757 M^2 - 187.6 C^2 - 0.007206 T^2 + 0.05324 M.T \quad \text{Equation 8}$$

Where: T: is the residence time (min), C: is the catalyst to oil molar ratio, M: is the methanol-to-oil molar ratio. Equation 8 is represented in the contour plots in Figure 8:

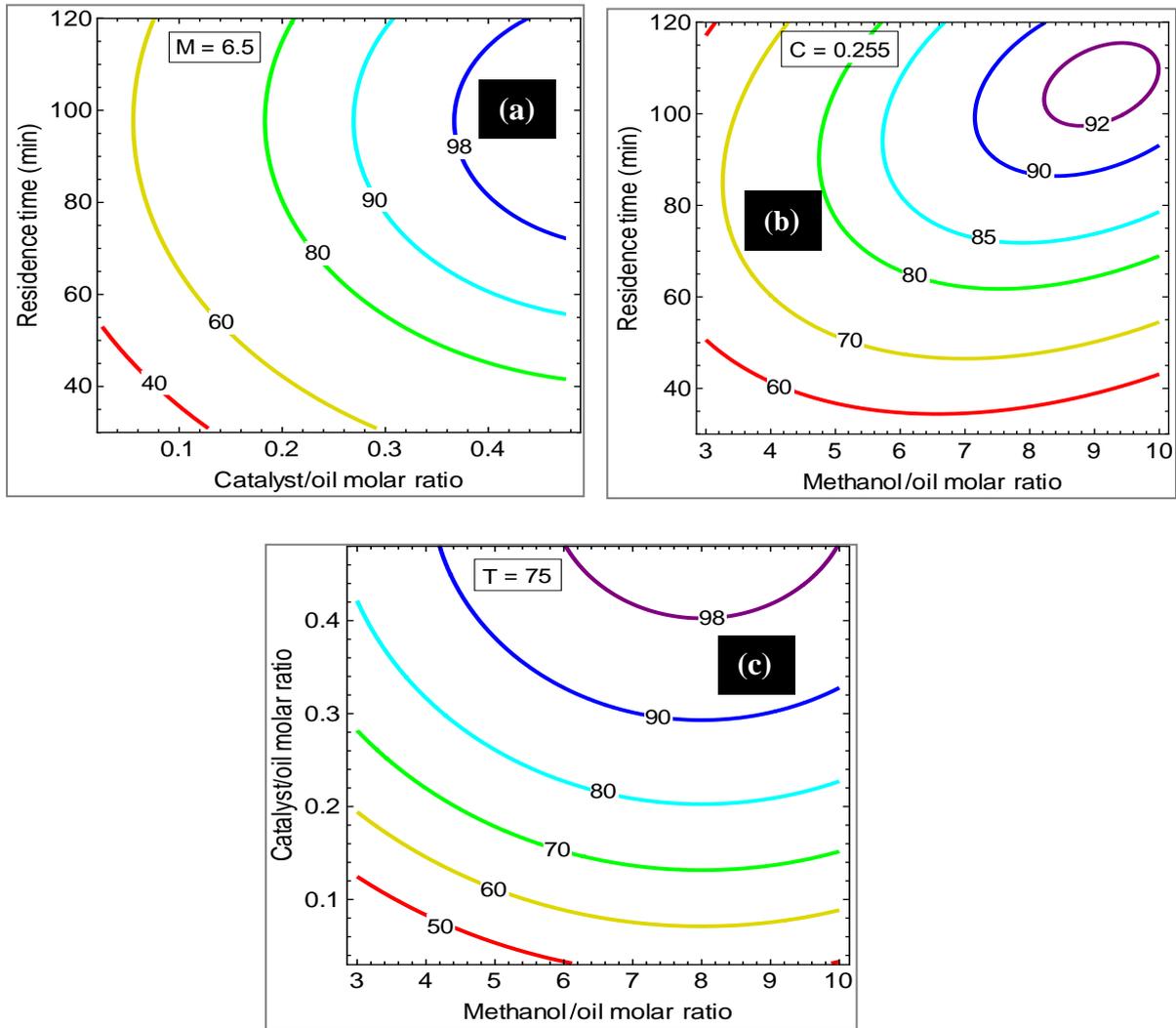


Figure 8: Contour plots showing the values of FAME Yield calculated from equation 5 as a function of the values of two of the factors: at M (6.5:1) of methanol-to-oil molar ratio, C catalyst concentration at 0.255 and T residence time of 75 min

It can be seen from *Figure 8 (a)* that at a given catalyst concentration, longer residence times lead to higher FAME yields. At a fixed residence time yield increases with methanol-to-RSO molar ratio: at the catalyst concentration used here, to ~90% at ~7.5:1. *Figure 8(c)* shows that high FAME yields can be achieved at low methanol-to-oil molar ratios and high catalyst

concentrations, while increasing the methanol-to-oil molar ratio leads to reductions in the amounts of DBSA catalyst required to attain same level of FAME yield.

The findings in this study are compared to existing work on various acid catalysts in *Table 3* below. Generally far less DBSA is required than trifluoroacetic acid [54]. The practical disadvantages of using H₂SO₄ are described in the introduction. The rapid acid-catalysed biodiesel process developed in this study compares favourably with the conventional base-catalysed process, which typically in practice requires operating conditions of 60°C, 6:1 methanol-to-oil molar ratio and 1h reaction time. Furthermore, the DBSA can catalyse both FFA esterification and triglyceride transesterification. Therefore, biodiesel production using DBSA catalysis has potential applications in processing of low grade triglyceride feedstock containing high levels of FFA and water, whereas such feedstock cannot be processed using the conventional base-catalysed method, and is extremely slow when using sulphuric acid.

Table 3: comparison between current catalysts with that reported in literature

Catalyst type	Catalyst amount	Residence conditions					FAME Yield (%)	References
		Residence time (h)	Temperature (°C)	Alcohol:oil molar ratio	Reactor Type	Oil		
DBSA	0.095M	3	80	6:1	Batch	Refined sunflower seed oil	>99.5	[31]
Trifluoroacetic acid (CF ₃ CO ₂ H)	2M	5	120	20:1	Electric nominal drier	Soybean oil	98.4	[54]
H ₂ SO ₄	0.045 M	8	100	9:1	Batch	Soybean oil	99	[35]
DBSA	1.25M	1	60	10:1	Meso-OBR	RSO	100	Current work
DBSA	0.99M	1	60	10:1	Meso-OBR	RSO	100	Current work
DBSA	0.499M	2	60	6.5:1	Meso-OBR	RSO	99.8	Current work

3.3 One-variable-at-a-time Studies

For more detail on certain points, extra experiments were performed to investigate specific variables. The DBSA catalyst concentration exhibited the most significant effect on the FAME yield, according to Equation 8. *Figure 9(a)* shows that when the catalyst concentration was

increased, the FAME yield increased until it reached a plateau at ~98.3%, at DBSA catalyst concentration of 0.718mol/L.

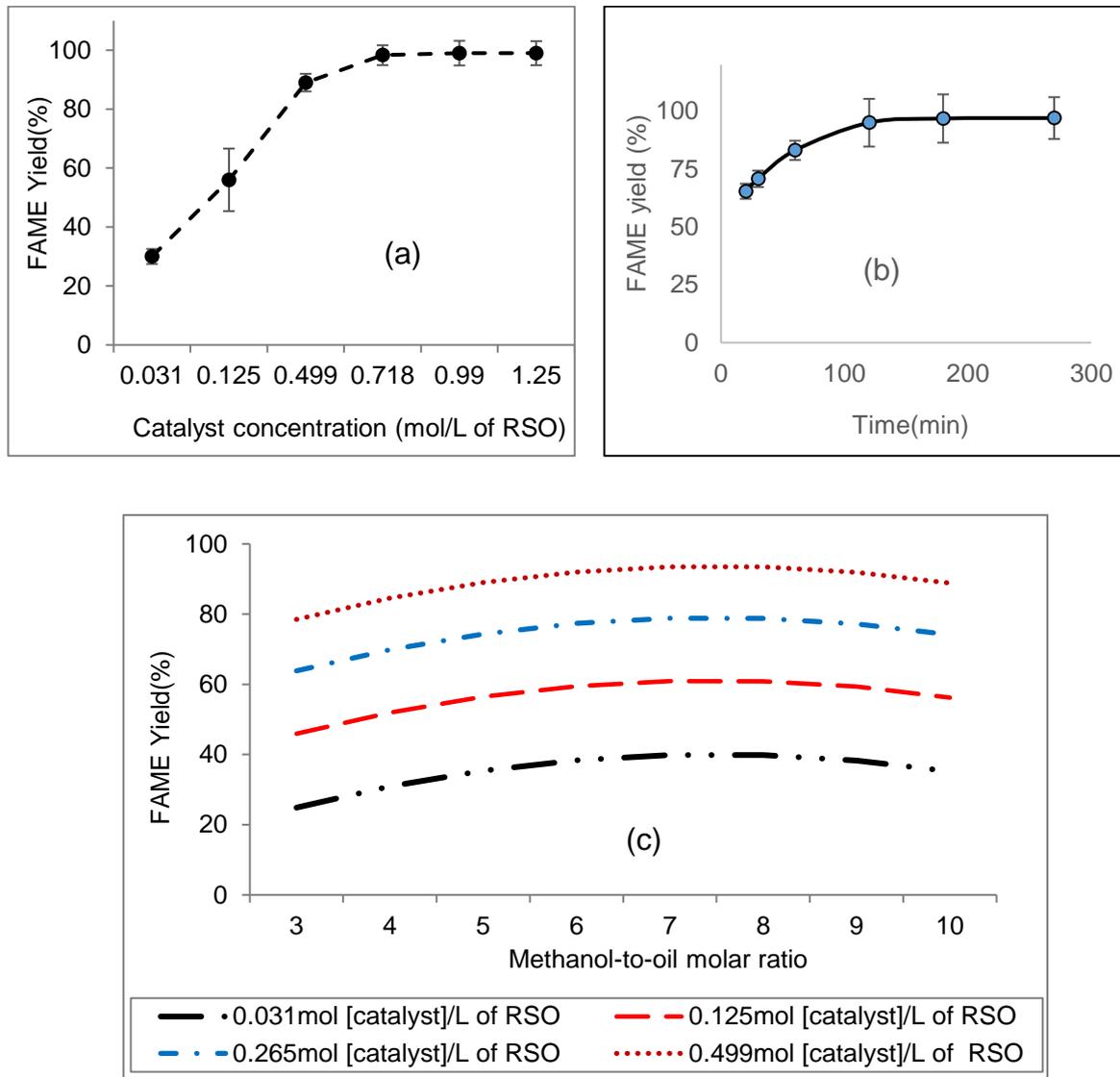


Figure 9: Effects of the process parameters on FAME Yields for RSO transesterification at 60 °C and oscillatory mixing condition, Reo = 124, (a) catalyst concentration at methanol-to-oil molar ratio of 10:1 and 60min, (b) residence time at methanol-to-oil molar ratio of 10:1 and 0.499 mole of catalyst per litre of RSO using a batch reactor, and (c) methanol to RSO molar ratio at different catalyst concentrations and 120min.

In acid-catalysed transesterification, there is no secondary reaction to reduce yield with time, as there is (saponification) when the reaction is base-catalysed [48, 51, 55]. Therefore, reductions in the FAME yield at moderate increase in the DBSA catalyst concentration would

not be expected, however, they have been previously observed in Alegria *et al.* (2014). Here, the FAME yield was observed to increase monotonically with residence time, as would be expected. *Figure 9(b)*, for example, shows the time profile for a batch reactor at 0.499mol catalyst/L of RSO at 10:1 of methanol to oil molar ratio and 60min. The FAME yield increased from 65.4% after 20min to > 95% after 120 min reaction time, for RSO transesterification at 60°C temperature, 10:1 methanol-to-oil molar ratio and 0.499mole of catalyst per litre of RSO. The maximum FAME yield observed was 97%. This was achieved after 180 min reaction time, a substantially lower reaction time than when using sulphuric acid. Thus, one of the merits of the DBSA catalyst is that it operates at shorter residence times (up to 84% shorter) at a lower temperature of 60°C, than when using sulphuric acid catalyst (typically at 120°C), where a typical residence time is 19h [35]. A key advantage of operation at 60 °C is that there are significant capital and operating cost savings in operating below methanol's ambient pressure boiling point. Note that previous studies on DBSA have operated at higher temperatures.

The effects of residence time on the conversion to FAME can be quantified using Equation 9, a partial derivative of Equation 8, with respect to residence time.

$$\left[\frac{dx}{dT}\right]_{M, C} = 1.049 - 0.0144 * T + 0.053 * M \quad \text{Equation 9}$$

The global quantitative effect of the methanol-to-RSO molar ratio was calculated from a partial derivative of Equation 8, as shown in Equation 10, below. This indicates that a high methanol-to-oil molar ratio is desirable for high conversion. It can be observed from *Figure 9 (c)* that the effect of methanol-to-oil molar ratio on the FAME conversion tends to be small (6% or less – within the chosen parameter space), similar to what has been reported elsewhere [38]. The methanol-to-RSO molar ratio passes through a maximum value at ~6.5:1.

$$\left[\frac{dx}{dM}\right]_{C, T} = 8.12 - 1.514 * M + 0.05324 * T$$

Equation 10

It has been reported that the optimum value of methanol-to-oil molar ratio for sulphuric acid catalysis is 9:1 [35] and 245:1 of methanol:canola oil [26]. The optimum methanol to RSO molar ratio in this study was 6.5:1.

3.4 Catalyst Recovery

It was demonstrated, using the procedure given in 2.4, that DBSA could largely be recovered and reused. The recovered DBSA catalyst was shown to be active in catalysis of RSO transesterification, however, there was some loss of catalyst: 17% less FAME yield was achieved at 0.03 mole of DBSA to oil, 3:1 of methanol to oil molar ratio and 60 °C, compared to the fresh DBSA catalyst. This is due to the reduced sulphonic acid content of the recovered catalyst, measured via sulphur content analysis (8.9 wt% of sulphur compared with 9.8 wt% for fresh DBSA), indicating that further development of the catalyst regeneration process would be necessary.

4 Conclusion

DBSA-catalysed biodiesel production from RSO was evaluated in a continuous mesoscale oscillatory baffled reactor. A design of experiments study was conducted based on three variables: methanol-to-RSO molar ratio, catalyst-to-oil molar ratio and residence time.

The main outcomes of this research were as follows:

- i.** For the first time, a method of *continuous* biodiesel production using a DBSA catalyst has been demonstrated. Continuous production is generally desirable for production at large scale, and OBR scale-up is broadly understood.
- ii.** Good agreement (96%) was achieved between the experimental results and the DoE model, and the model was validated. Hence (within this parameter space) the model is a useful predictive tool for process design.

- iii.** The DoE and experimental results show areas of the parameter space FAME that meets biodiesel purity standards ($\text{FAME} \geq 97\%$). Hence, acceptable biodiesel can be reliably produced by operation in this region.
- iv.** The meso-OBR attained steady states within reaction times in the range of $1.1 - 1.5\tau$ indicating short start-up time, therefore minimal waste of resources during the induction time.
- v.** The oscillatory mixing requirement of $\text{Re}_o \geq 83$ for the DBSA-catalysed rapeseed oil transesterification, was below the 107 required for similar processes using homogeneous base catalysis, probably due to the surfactant properties of the catalyst. This represents a small but significant reduction in the cost of energy required for the reactants mixing.
- vi.** Methanol-to-oil molar ratios were similar to that of conventional base-catalysed transesterification at 6.5:1. This is substantially lower than that of sulphuric acid (typically at least 9:1, and often much higher, at higher temperatures and longer residence times). 98.7% FAME yield was the maximum observed, at 120min residence time. This is substantially lower than the typical 19h for H_2SO_4 in stirred tank batch reactors.
- vii.** DBSA catalyst can be recovered using an ion exchange resin, and reused, in contrast to other homogenous catalysts used in conventional biodiesel processes. However, the process has not been optimised, and would require further development prior to commercial use. Nonetheless, this represents basic “proof-of-concept”, and is potentially a significant advantage over conventional acid and base catalysts.
- viii.** The continuous screening has identified regions of the parameter space where the conditions for acceptable conversion are preferable to those identified in batch reactions. Notably, the temperature is $60\text{ }^\circ\text{C}$ rather than 80 or 90°C . This represents a significant advantage as it allows operation close to ambient pressure (the ambient pressure boiling point of methanol is $65\text{ }^\circ\text{C}$), leading to significant capital cost savings.

Overall, this work demonstrates the use of a mesoOBR for screening the biodiesel reaction with a surfactant catalyst, and provides proof-of-concept for a continuous acid-catalysed process with substantially more desirable operating conditions than H_2SO_4 , and some improvements over existing conditions for batch DBSA catalysis.

Note that the rapid, lower temperature, acid-catalysed biodiesel process developed in this study could be used for biodiesel production from both refined triglyceride sources, and low-grade triglyceride feedstock that contains high levels of FFA and water.

Acknowledgment

The authors would like to thank the higher committee for education development in Iraq (HCED) for their financial support. Alexandra Alegría thanks the University of Salamanca for a Research Staff Training Fellowship.

Abbreviations

<i>ANOVA</i>	<i>analysis of variance;</i>
<i>DBSA</i>	<i>4-Dodecylbenzenesulfonic acid;</i>
<i>FAME</i>	<i>fatty acid methyl ester;</i>
<i>FFA</i>	<i>Free fatty acid;</i>
<i>GC</i>	<i>Gas chromatography;</i>
<i>H₂SO₄</i>	<i>Sulphuric acid;</i>
<i>MeOH</i>	<i>Methanol;</i>
<i>OBR</i>	<i>Oscillatory baffled reactor;</i>
<i>Re_n</i>	<i>Net flow Reynold number;</i>
<i>RSO</i>	<i>Rapeseed oil;</i>
<i>St</i>	<i>Strouhal number;</i>
<i>TG</i>	<i>Triglyceride.</i>

References

- [1] D. Darnoko, M. Cheryan, Kinetics of palm oil transesterification in a batch reactor, *JAOCS, Journal of the American Oil Chemists' Society* 77 (2000) 1263-1267.
- [2] M. Mittelbach, B. Trathnigg, Kinetics of Alkaline Catalyzed Methanolysis of Sunflower Oil, *Lipid / Fett* 92 (1990) 145-148.
- [3] G. Vicente, M. Martínez, J. Aracil, A. Esteban, Kinetics of Sunflower Oil Methanolysis, *Industrial & Engineering Chemistry Research* 44 (2005) 5447-5454.
- [4] A. Demirbas, *A Realistic Fuel Alternative for Diesel Engines*, 1 ed., Springer London 2008.
- [5] Z. Helwani, M.R. Othman, N. Aziz, W.J.N. Fernando, J. Kim, Technologies for production of biodiesel focusing on green catalytic techniques: A review, *Fuel Processing Technology* 90 (2009) 1502–1514.
- [6] M.E. Bambase, N. Nakamura, J. Tanaka, M. Matsumura, Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters, *Journal of Chemical Technology & Biotechnology* 82 (2007) 273-280.
- [7] M. Balat, H. Balat, Progress in biodiesel processing, *Applied Energy* 87 (2010) 1815-1835.
- [8] S.R. Mishra, M.K. Mohanty, S.P. Das, A.K. Pattanaik, Optimisation of base-catalysed transesterification of *Simarouba glauca* oil for biodiesel production, *International Journal of Sustainable Energy* (2013) 1-8.
- [9] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering, *Chemical Reviews* 106 (2006) 4044-4098.

- [10] H. Hoydonckx, D. De Vos, S. Chavan, P. Jacobs, Esterification and Transesterification of Renewable Chemicals, *Topics in Catalysis* 27 (2004) 83-96.
- [11] K. Wilson, A.F. Lee, Rational design of heterogeneous catalysts for biodiesel synthesis, *Catalysis Science & Technology* 2 (2012) 884-897.
- [12] B. Moser, Biodiesel production, properties, and feedstocks, *In Vitro Cellular & Developmental Biology - Plant* 45 (2009) 229-266.
- [13] G.T. Jeong, D.H. Park, Lipase-catalyzed transesterification of rapeseed oil for biodiesel production with tert-butanol, *Applied Biochemistry and Biotechnology* 148 (2008) 131-139.
- [14] C.-C. Lai, S. Zullaikah, S.R. Vali, Y.-H. Ju, Lipase-catalyzed production of biodiesel from rice bran oil, *Journal of Chemical Technology & Biotechnology* 80 (2005) 331-337.
- [15] M.K. Lam, K.T. Lee, A.R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review, *Biotechnology Advances* 28 (2010) 500-518.
- [16] D. Kusdiana, S. Saka, Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel* 80 (2001) 693-698.
- [17] K.T. Lee, C. Ofori-Boateng, *Sustainability of Biofuel Production from Oil Palm Biomass*, Springer, Singapore, 2013.
- [18] S. Glisic, D. Skala, The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions, *The Journal of Supercritical Fluids* 49 (2009) 293-301.
- [19] J.M. Cervero, J. Coca, S. Luque, Production of biodiesel from vegetable oils, *Grasas y Aceites* 59 (2008) 76-83.
- [20] M. Canakci, J. Van Gerpen, A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks, *Transactions of the American Society of Agricultural Engineers* 46 (2003) 945-954.
- [21] V.C. Eze, A.N. Phan, A.P. Harvey, A more robust model of the biodiesel reaction, allowing identification of process conditions for significantly enhanced rate and water tolerance, *Bioresource Technology* 156 (2014) 222-231.
- [22] A. Demirbas, Progress and recent trends in biodiesel fuels, *Energy Conversion and Management* 50 (2009) 14-34.
- [23] V.C. Eze, A.N. Phan, A.P. Harvey, Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils, *Fuel* 220 (2018) 567-574.
- [24] P. Lu, Z. Yuan, L. Li, Z. Wang, W. Luo, Biodiesel from different oil using fixed-bed and plug-flow reactors, *Renewable Energy* 35 (2010) 283-287.
- [25] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin, Synthesis of Biodiesel via Acid Catalysis, *Industrial & Engineering Chemistry Research* 44 (2005) 5353-5363.
- [26] S. Zheng, M. Kates, M.A. Dubé, D.D. McLean, Acid-catalyzed production of biodiesel from waste frying oil, *Biomass and Bioenergy* 30 (2006) 267-272.
- [27] Y. Wang, S.O. Pengzhan Liu, Z. Zhang, Preparation of biodiesel from waste cooking oil via two-step catalyzed process, *Energy Conversion and Management* 48 (2007) 184-188.

- [28] A.L. Cardoso, S.C.G. Neves, M.J. da Silva, Kinetic Study of Alcoholysis of the Fatty Acids Catalyzed by Tin Chloride(II): An Alternative Catalyst for Biodiesel Production, *Energy & Fuels* 23 (2009) 1718-1722.
- [29] M. Balat, H. Balat, Progress in biodiesel processing, *Applied Energy* 87 (2010) 1815-1835.
- [30] T. Issariyakul, M.G. Kulkarni, A.K. Dalai, N.N. Bakhshi, Production of biodiesel from waste fryer grease using mixed methanol/ethanol system, *Fuel Processing Technology* 88 (2007) 429-436.
- [31] A. Alegría, Á.L.F.d. Arriba, J.R. Morán, J. Cuellar, Biodiesel production using 4-dodecylbenzenesulfonic acid as catalyst, *Applied Catalysis B: Environmental* 160–161 (2014) 743-756.
- [32] L. Li, C. Zou, L. Zhou, L. Lin, Cucurbituril-protected Cs_{2.5}H_{0.5}PW₁₂O₄₀ for optimized biodiesel production from waste cooking oil, *Renewable Energy* 107 (2017) 14-22.
- [33] P. Bondioli, The Preparation of Fatty Acid Esters by Means of Catalytic Reactions, *Topics in Catalysis* 27 (2004) 77-82.
- [34] M. Naik, L.C. Meher, S.N. Naik, L.M. Das, Production of biodiesel from high free fatty acid Karanja (*Pongamia pinnata*) oil, *Biomass and Bioenergy* 32 (2008) 354-357.
- [35] M. Goff, N. Bauer, S. Lopes, W. Sutterlin, G. Suppes, Acid-catalyzed alcoholysis of soybean oil, *J Amer Oil Chem Soc* 81 (2004) 415-420.
- [36] L. Li, C. Zou, L. Zhou, L. Lin, Cucurbituril-protected Cs_{2.5}H_{0.5}PW₁₂O₄₀ for optimized biodiesel production from waste cooking oil, *Renewable Energy* 107 (2017) 14-22.
- [37] S. Vasanthakumar, I. Janajreh, Sulphuric acid modified biomass: A novel acid catalyst for effective esterification of free fatty acids for biodiesel production, *Renewable and Sustainable Energy Conference (IRSEC), 2013 International, 2013*, pp. 453-455.
- [38] Y.S. Pradana, A. Hidayat, A. Prasetya, A. Budiman, Biodiesel production in a reactive distillation column catalyzed by heterogeneous potassium catalyst, *Energy Procedia* 143 (2017) 742-747.
- [39] N. Reis, A.P. Harvey, M.R. Mackley, A.A. Vicente, J.A. Teixeira, Fluid Mechanics and Design Aspects of a Novel Oscillatory Flow Screening Mesoreactor, *Chemical Engineering Research and Design* 83 (2005) 357-371.
- [40] X. Ni, N.E. Pereira, Parameters affecting fluid dispersion in a continuous oscillatory baffled tube, *AIChE Journal* 46 (2000) 37-45.
- [41] M.R. Mackley, K.B. Smith, N.P. Wise, Mixing and separation of particle suspensions using oscillatory flow in baffled tubes, *Chemical Engineering Research and Design* 71 (1993) 649-656.
- [42] N. Reis, A.A. Vicente, J.A. Teixeira, M.R. Mackley, Residence times and mixing of a novel continuous oscillatory flow screening reactor, *Chemical Engineering Science* 59 (2004) 4967-4974.
- [43] P. Stonestreet, A.P. Harvey, A mixing-based design methodology for continuous oscillatory flow reactors, *Chemical Engineering Research and Design* 80 (2002) 31-44.
- [44] A.P. Harvey, M.R. Mackley, T. Seliger, Process intensification of biodiesel production using a continuous oscillatory flow reactor, *Journal of Chemical Technology & Biotechnology* 78 (2003) 338-341.

- [45] V.C. Eze, A.N. Phan, C. Pirez, A.P. Harvey, A.F. Lee, K. Wilson, Heterogeneous catalysis in an oscillatory baffled flow reactor, *Catalysis Science & Technology* 3 (2013) 2373-2379.
- [46] K. Boodhoo, A. Harvey, *Process Intensification for Green Chemistry: Engineering Solutions for Sustainable Chemical Processing*, 2013.
- [47] D. Reay, C. Ramshaw, A. Harvey, *Process Intensification Engineering for Efficiency, Sustainability and Flexibility*, Butterworth-Heinemann, 2013.
- [48] A.N. Phan, A.P. Harvey, V. Eze, Rapid Production of Biodiesel in Mesoscale Oscillatory Baffled Reactors, *Chemical Engineering & Technology* 35 (2012) 1214-1220.
- [49] V.C. Eze, J.C. Fisher, A.N. Phan, A.P. Harvey, Intensification of carboxylic acid esterification using a solid catalyst in a mesoscale oscillatory baffled reactor platform, *Chem. Eng. J.* 322 (2017) 205-214.
- [50] BS EN 14103, Fat and oil derivatives - Fatty acid methyl esters (FAME) for diesel engines - Determination of esters and linolenic acid methyl ester contents, Designation BS EN 14103 Chiswick High Road, London, 2003.
- [51] V.C. Eze, A.P. Harvey, A.N. Pha, The Use of Mesoscale Oscillatory Baffled Reactors for Rapid Screening of Heterogeneously Catalysed Biodiesel Production Reactions, School of Chemical Engineering and Advanced Materials, Newcastle University, University of Newcastle upon Tyne, 2014.
- [52] A.P. Harvey, M.R. Mackley, P. Stonestreet, Operation and Optimization of an Oscillatory Flow Continuous Reactor, *Industrial & Engineering Chemistry Research* 40 (2001) 5371-5377.
- [53] D.U. Jung, H.Y. Yoo, S.B. Kim, J.H. Lee, C. Park, S.W. Kim, Optimization of medium composition for enhanced cellulase production by mutant *Penicillium brasilianum* KUEB15 using statistical method, *Journal of Industrial and Engineering Chemistry* 25 (2015) 145-150.
- [54] X. Miao, R. Li, H. Yao, Effective acid-catalyzed transesterification for biodiesel production, *Energy Conversion and Management* 50 (2009) 2680-2684.
- [55] A.B. Fadhil, M.M. Dheyab, L.A. Saleh, Conversion of Fish Oil into Biodiesel Fuels via Acid-base Catalyzed Transesterification, *Energy Sources, Part A*, 36 (2014) 1571-1577.