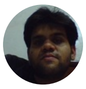
Pilot Scale Intensification of Rubber Seed (Hevea brasiliensis) Oil via Chemical Interesterification using...

Article *in* Bioresource Technology · March 2017

DOI: 10.1016/j.biortech.2017.03.046



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Bioresource Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

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Pilot scale intensification of rubber seed (*Hevea brasiliensis*) oil via chemical interesterification using hydrodynamic cavitation technology

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HIGHLIGHTS

- HC system for interesterification of RSO at pilot scale (50 L/batch).
- Interesterification was carried out on four new designed orifice plates.
- Optimisation of orifice plate geometry and interesterification variables.
- HC found to be 3-fold shorter time compared to MS.

ARTICLE INFO

Article history:
Received 12 January 2017
Received in revised form 5 March 2017
Accepted 7 March 2017
Available online xxxx

Keywords:
Interesterification
Process intensification
Hydrodynamic cavitation
Rubber seed oil
Optimisation

ABSTRACT

Chemical interesterification of rubber seed oil has been investigated for four different designed orifice devices in a pilot scale hydrodynamic cavitation (HC) system. Upstream pressure within 1–3.5 bar induced cavities to intensify the process. An optimal orifice plate geometry was considered as plate with 1 mm dia hole having 21 holes at 3 bar inlet pressure. The optimisation results of interesterification were revealed by response surface methodology; methyl acetate to oil molar ratio of 14:1, catalyst amount of 0.75 wt.% and reaction time of 20 min at 50 °C. HC is compared to mechanical stirring (MS) at optimised values. The reaction rate constant and the frequency factor of HC were 3.4-fold shorter and 3.2-fold higher than MS. The interesterified product was characterised by following EN 14214 and ASTM D 6751 international standards.

1. Introduction

Energy is a major factor to boost societies and maintain a high standard of living (Tangy et al., 2017). The unsteady and fluctuating cost of fossil fuel drew the attention of researchers towards the prospective development of renewable energy technologies (Park et al., 2016). Fossil fuel is adequately criticised for its failure to give a clear refutation of being cleaner and greener fuel (Chuah et al., 2016a). Urge to curtail greenhouse gas emissions for a cleaner environment has brought biodiesel to a higher level of acceptance in the world (Chuah et al., 2016b). Biodiesel is benign towards atmospheric ecology (Leite et al., 2013). It can be utilised

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Abbreviations: RSO, rubber seed oil; RSOME, rubber seed oil methyl ester; TG, triglyceride; HC, hydrodynamic cavitation; MS, mechanical stirring; FFA, free fatty acid; FAME, fatty acid methyl ester; X, methyl ester conversion; RSM, response surface methodology; CCD, central composite design; KOH, potassium hydroxide; MR, methanol to oil molar ratio; GC, gas chromatography; ANOVA, analysis of variance; p-Value, probability of obtaining result; F-value, variance of group means; C.V, coefficient of variation; Adeq. Precision, adequate precision; Std. dev, standard deviation.

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http://dx.doi.org/10.1016/j.biortech.2017.03.046
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Please cite this article in press as: Bokhari, A., et al. Pilot scale intensification of rubber seed (*Hevea brasiliensis*) oil via chemical interesterification using hydrodynamic cavitation technology. Bioresour. Technol. (2017), http://dx.doi.org/10.1016/j.biortech.2017.03.046

solely in an engine or with any blending ratio to fossil diesel (Chuah et al., 2015a). Biodiesel production can be initiated with numerous available edible and non-edible organic feedstock (Chuah et al., 2016c). Biodiesel is widely produced from edible oils. To avoid food vs. fuel imbalance, utilisation of non-edible oils is the best option for effective biodiesel production (Ahmad et al., 2014a).

Usage of rubber seed oil (RSO) as the potential non-edible alternative raw material for biodiesel production (Ahmad et al., 2014b). RSO gained great attention in Southeast Asian and Sub-Saharan African regions (Onoji et al., 2016). Oil derived from rubber seed was extracted via mechanical press, hydraulic press and chemical solvent extraction. Studies depict that rubber seeds contain 40–50 wt.% oil content via soxhlet extraction, which make it superior and tough contender among other non-edible sources (Bokhari et al., 2012). Association of Natural Rubber's figures reveals that around 1.2 M ha of oil bearing rubber seed is available for biodiesel production. Malaysia has the advantage being in a tropical region. The Tropical weather has proven beneficial for rubber trees growth (Ahmad et al., 2014c). Rubbers seeds are ellipsoidal in shape having length between 2.5 and 3 cm. Approximately 5,000 t of RSO can be obtained from annual production of 30,000 t of seeds (Ramadhas et al., 2005).

Transesterification reaction has an abrupt issue of profitability and by-product utilisation. Glycerol as a by-product normally is considered as a waste due to its market saturation and selling consideration (Subhedar and Gogate, 2016). Biodiesel production via chemical interesterification is a reaction between triglycerides and methyl acetate with the formation of triacetin as a valued by-product (Sustere et al., 2016). Lab scale chemical interesterification for sunflower oil was studied by Casas et al. (2011a). Its kinetics has been studied in detail for biodiesel and triacetin production by Casas et al. (2011b).

Biodiesel production has resorted to numerous intensification technologies for conversion of value added respective methyl esters (Gogate, 2008). Intensification can be generated in a process via various techniques namely; microwave (Bokhari et al., 2015), sonochemical (Asif et al., 2017), oscillatory baffle and hydrodynamic cavitation (HC) reactors (Chuah et al., 2017a). Meanwhile microwave and ultrasonic cavitation techniques are not mature enough for biodiesel production at industrial scale (Chuah et al., 2016d). HC offers a number of advantages over other intensification technologies (Chuah et al., 2017b). It shows good performance with respect to product yield, reaction time, energy consumption and product quality (Chuah et al., 2016e). HC is the most potential intensification technology for eliminating mass transfer resistance between immiscible reactants viz. oil and methyl acetate (Gole et al., 2013). HC offers easy scale-up, low energy consumption, high yield efficiency and low reaction time (Bokhari et al., 2016a). High pressure fluid passing through a small constriction (orifice plate) drives a destructive force which produces highly turbulent cavities (Chuah et al., 2015b). Cavities formation gives a high interfacial area when implosion of bubbles happen. As local pressure fall below the vapour pressure generated cavities will collapse for recovery of pressure (Kelkar et al., 2008).

Maddikeri et al. (2013) conducted pioneering study featuring chemical interesterification of waste cooking oil via ultrasound intensified technology in presence of potassium methoxide. They obtained maximum fatty acid methyl ester (FAME) yield (90 wt.%) for 1:12 methyl acetate to oil molar ratio (MR) with 1 wt.% catalyst amount and at 40 °C. Kinetics study revealed that interesterification followed second order rate equation. Subhedar and Gogate (2016) used ultrasound assisted intensification of waste cooking oil for enzymatic interesterification. Their maximum (96.1 wt.%) reported biodiesel yield was at MR of 9:1, enzyme amount of 3%w/v at 3 h.

Only a single study by Maddikeri et al. (2014) reported the chemical interesterification of waste cooking oil using HC reactor having 15 L capacity. Three different cavitation devices namely; orifice plate (2 mm one hole), circular and slit venture were investigated. Maximum biodiesel yield (90 wt.%) was obtained with slit venturi for MR of 1:12, catalyst amount of 1 wt.% and inlet pressure of 3 bar. Details of orifice plate hole spacing, distribution patterns and design were not taken into account. These are the crucial factor while designing interesterification HC reactor for large scale. The current study is a continuation of our previous research (Bokhari et al., 2016a), in which we have investigated the esterification of RSO (72.36 mg KOH/g) in a pilot HC reactor. In this work viability of HC for chemical interesterification of high free fatty acid (FFA) non-edible RSO at the pilot scale of 50 L capacity has been studied. Besides this, effects of newly designed four different orifice plates assisted by double diaphragm pump have been estimated. From the foregoing literature review, it is evident that it will be the first study featuring HC application on such scale to the best of our knowledge. Effects of inlet pressure (1–3.5 bar) and geometrical parameters has been investigated also. Response surface methodology (RSM) was used for the optimisation of chemical interesterification conversion from RSO via HC. Both international standards ASTM D 6751 and EN 14214 were referred to the fuel properties of produced rubber seed oil methyl ester (RSOME) in pilot scale HC reactor.

2. Methods

2.1. Materials

Pretreatment of RSO was conducted on the optimum conditions from our previous studies (Bokhari et al., 2016a). Treated RSO chemical properties are summarised in Table 1. Most of the analytical grade chemicals were supplied by Merk, Malaysia. Following were the reagents that utilised in experiments; methyl acetate, methanolic potassium methoxide (32 wt.% of methanolic solution), potassium hydroxide pellets, anhydrous sodium sulphate, Wijs solution, phenolphthalein, sulphuric acid, acetic acid (glacial), cyclohexane, toluene, potassium iodide, 2-propanol, sodium thiosulphate pentahydrate, starch, acetone, hydrochloric acid, chloroform, and ethanol. The progress of interesterification was examined by GC-FID, which measures the concentration of methyl esters produced. The methyl ester conversion was analysed by following the EN 14103 method and detailed methodology has been described by (Bokhari et al., 2016b). All the experiments were conducted thrice and the average values were reported.

2.2. Reactor setup and methodology

The chemical interesterification experiments were conducted in a pilot scale of 50 L double jacketed HC reactor made up of borosilicate glass. The upstream pressure of the system was controlled by the aid of double diaphragm pump, which circulated the reaction

Table 1
Properties of treated rubber seed oil.

Analysis		This study mean ± standard deviation (n = 3) Rubber seed oil
Acid value (mg KOH/g)		2.64 ± 0.04
Density (g/cm^3)		0.87 ± 0.03
Saponification value (mg KOH/g)		200 ± 1.10
FFA (%)		1.3 ± 0.03
Higher heating value (MJ/kg)		37.1 ± 0.06
Kinematic viscosity (mm^2/s)	at 20 °C	95 ± 0.07
	at 40 °C	36 ± 0.06
Moisture content (wt.%)		0.04 ± 0.00
Flash point (°C)		201 ± 1
Methyl ester content (wt.%)		40.75

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mixture through orifice plate in a close loop. The double diaphragm pump is the key device to regulate the energy through an entire HC pilot plant. The downstream part of a pump was assorted into two lines. The upstream pressure and fluid flow through the orifice plate were controlled by valves at main line and bypass. Fig. 1 illustrates the schematic configuration of HC pilot reactor. When inlet pressure was regulated to 3 bar, mass flow rates were 25.8 and 5.1 L/min at main and bypass lines. The whole pilot plant is equipped with pressure gauges and flow meters. The heat was dissipated in HC reactor via heating oil, which surrounded the space between the double jacketed glass. Digital temperature controller maintained the desired temperature for a period of reaction. Detail description of newly designed four orifice plates have been presented in our previous papers, i.e. waste cooking oil (Chuah et al., 2016d) and RSO (Bokhari et al., 2016a). Experiments for the orifice plate and inlet pressure optimisation were carried out at MR of 10:1 and catalyst amount of 0.75 wt.% at 50 °C. The HC reactor was charged with a certain quantity of RSO and methyl acetate. Uniform mixing of reactants was achieved by circulating it in a close loop using pumping energy. The initiate reaction point was considered, where the catalyst was charged to the system. The methanolic potassium methoxide catalyst was supplied in a liquid form, which has an affirmative impact as it dissolved completely in RSO and methyl acetate. Solid potassium methoxide was posed catalyst mixing problems and resulted in lower biodiesel yield (Casas et al., 2013). To develop the constructive conditions for various newly designed orifice geometries, elevated pressure up to 3.5 bar was created by passing reaction mixture. The known quantity of sample was withdrawn from the system in order to examine the progress of a reaction. Collected samples were separated under gravity and impurities were washed by warm ionised water. Remaining methyl acetate and water in the biodiesel were evaporated by using a vacuum rotary evaporator.

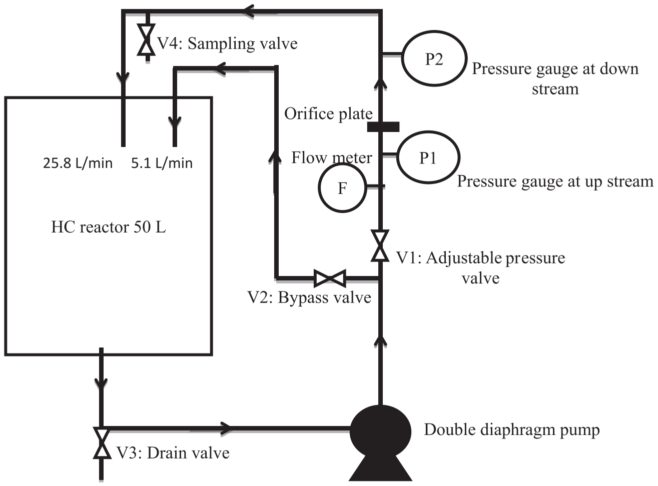

Fig. 1. Schematic diagram of cavitation reactor system.

2.3. Yield efficiency calculation

It is also known as energy efficiency. It is an estimation of the required pumping energy for dissociation of a specific amount of oil. Yield efficiency was calculated by using the following Eq. (1) (Chuah et al., 2016d).

$$\text{Yield efficiency} = \frac{\text{Amount of product produced(g)}}{\text{Pumping energy(J)}} \tag{1}$$

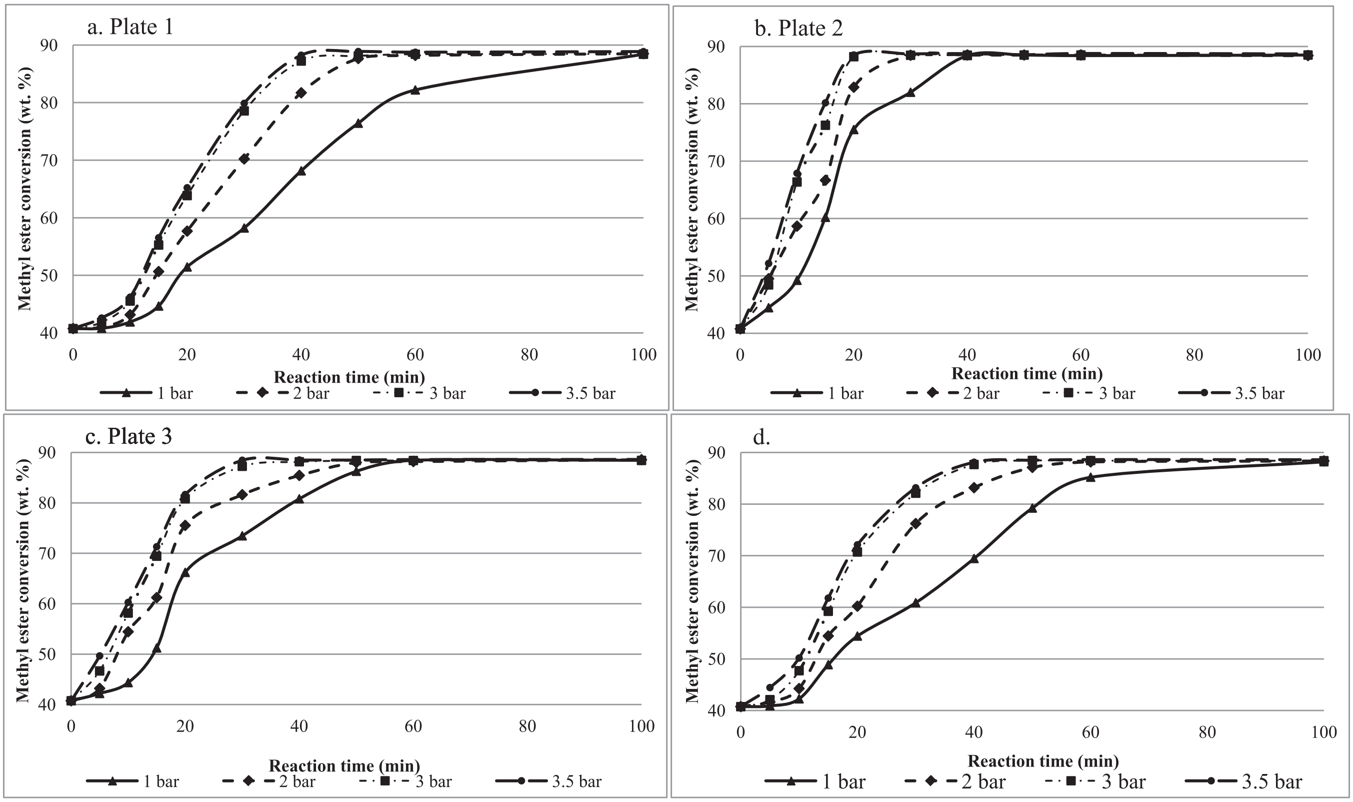

Fig. 2. Effect of inlet pressure on RSOME conversion.

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3. Results and discussion

3.1. Effect of inlet pressure on methyl ester conversion

Effects of inlet/upstream pressure on methyl ester conversion for four orifice plates of different geometries are shown in Fig. 2 at an upstream pressure ranging between 1 and 3.5 bar at 55 °C. The increase in inlet pressure from 1 to 3 bar resulted in enhanced interesterification reactions for all orifice plates. However, raised in pressure from 3 to 3.5 did not significantly altered the reaction rate. Formation of large cavities at downstream area of orifice plate was the reason. Coalescence of a huge number of cavities result in cavitation chocking (Ghayal et al., 2013).

Inlet pressure when attained certain high value of >3.5 bar, slowered the reaction rate as observed by many researchers (Chuah et al., 2016d). The decrement in degradation rate was noticed by Bagal and Gogate (2014) when inlet pressure reached as high as 4 bar. Likewise, at pressure of 3.8 bar, Vichare et al. (2000) observed a significant decreased in the reaction rate.

Hence, an optimised inlet pressure of 3 bar was chosen for rest of the experiments. For optimised methyl ester conversion of ≥88 wt.%, the time required were 100, 20, 40, 60 min for plates 1, 2, 3, 4. Conversion rate increased with a decreased in cavitation number. Cavitation number's value as lower as 0.301 appeared to show maximum benefits for methyl ester production. Mixture is exposed to cavitational zone for a longer period of time when the cavitation number is lower. It resulted in maximum conversion. Ghayal et al. (2013) noted that with increased collapse intensity of cavities the inlet pressure also increased. Decrement in mass transfer resistance among immiscible reactant was noted as speed-

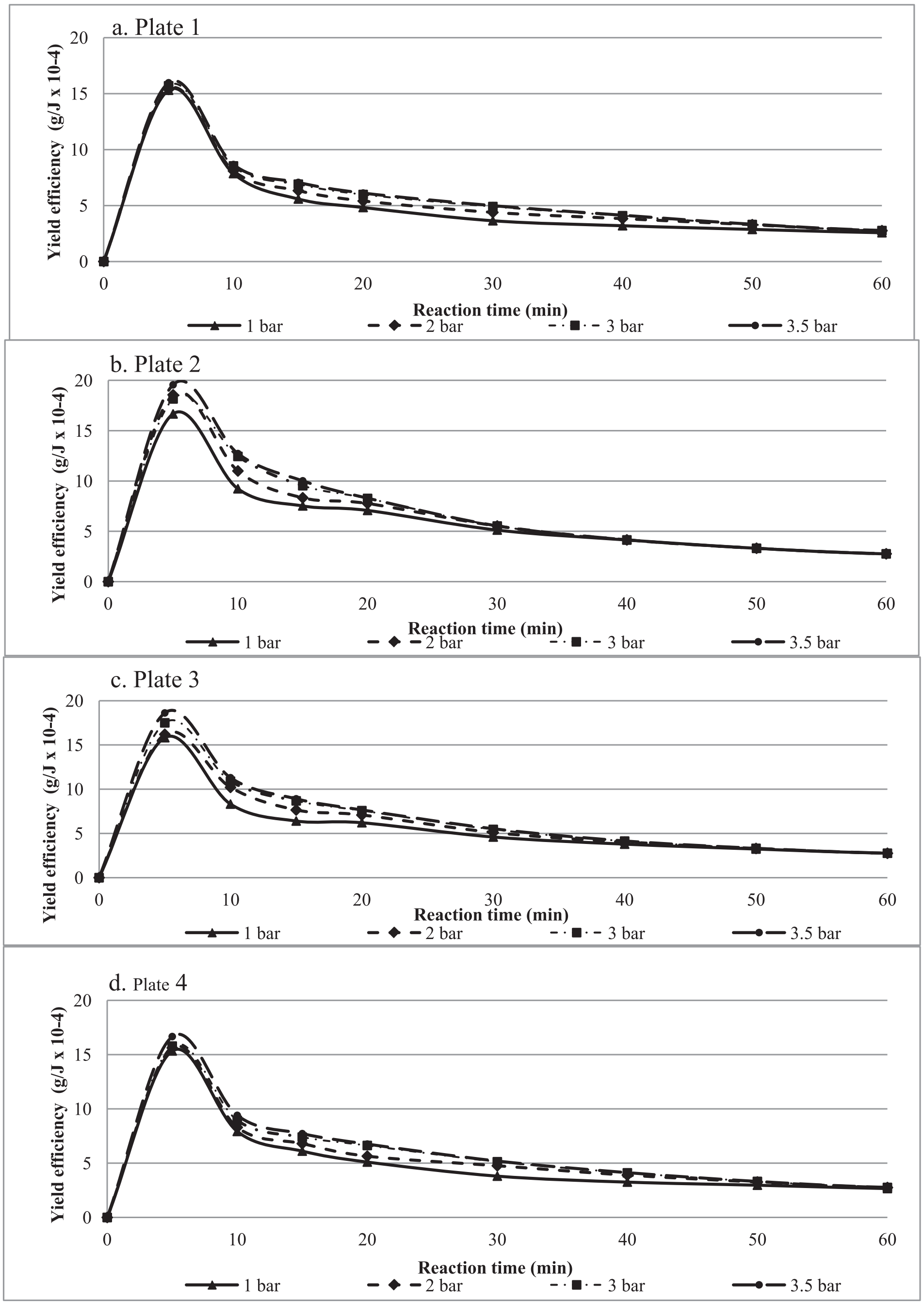

Fig. 3. Effect of inlet pressure on yield efficiency.

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ily collapsed cavities occurred in the system. Enhanced transport rate is achieved due to sudden collapsed of cavities. This sudden collapsed produce high turbulence intensity in the fluid. The increment in fluid rates resulted in lower cavitation number (Vichare et al., 2000). Rest of the experiments were carried out with plate 2, as it resulted in maximum methyl ester of $\geq$88 wt.% conversion within a short span of time of 20 min at pressure of 3 bar, compared to other plates.

3.2. Yield efficiency dependence on inlet pressure

Yield efficiency is defined as the product obtained per unit energy. Energy is required for completion of the reaction. The price of raw material plus energy summed up the total production cost of biodiesel.

Plates were selected on the basis of their yield efficiencies. Yield efficiency performances on each orifice plates are illustrated in Fig. 3. Gradual increased in yield efficiency was observed with an increase in pressure until 3 bar. However, after this point, marginal increased was observed till 3.5 bar. Yield efficiency of plates at pressure of 3 bar can be ranked as; plate 1 (6.0×10^{-4} g/J) < plate 4 (6.6×10^{-4} g/J) < plate 3 (7.5×10^{-4} g/J) < plate 2 (8.2×10^{-4} g/J).

3.3. Effect of the orifice plate geometries on methyl ester conversion

Effect of each parameters on chemical interesterification reaction has been discussed in this section. Reaction time of 20 min, was a bench mark in this study to monitor the effect of total hole perimeter on methyl ester conversion. All orifice geometries were studied at this time span. Plate 2 achieved more than 88 wt.% conversion within 20 min of reaction time.

Effects of total hole perimeter on methyl ester conversion at different inlet pressure are illustrated in Fig. 4(a). Total hole perimeter ranges of four orifice plates was between 14.39 and 65.98 mm. Cavitational events are greatly affected by the number of holes (Senthil Kumar et al., 2000). Methyl ester conversion increased with increase in total hole perimeter between pressure of 1–3 bar as depicted in Fig. 4a. The ratio of total hole perimeter to flow area of the reaction mixture passing through orifice plate is represented by α (Ghayal et al., 2013). The relationship between methyl ester conversion and α has been shown in Fig. 4(b) at $t = 20$ min and at pressure of 3 bar. Higher α value occurs when holes are larger in number, with smaller hole size. For higher α values greater methyl conversion is achieved. Estimated α values were within a range of 0.87 to 4 mm^{-1} for this work. The affect of α on methyl ester conversion in relation to plates at pressure of 3 bar followed the order: plate 1–63.85 wt.% < plate 4–70.71 wt.% < plate 3–80.80 wt.%

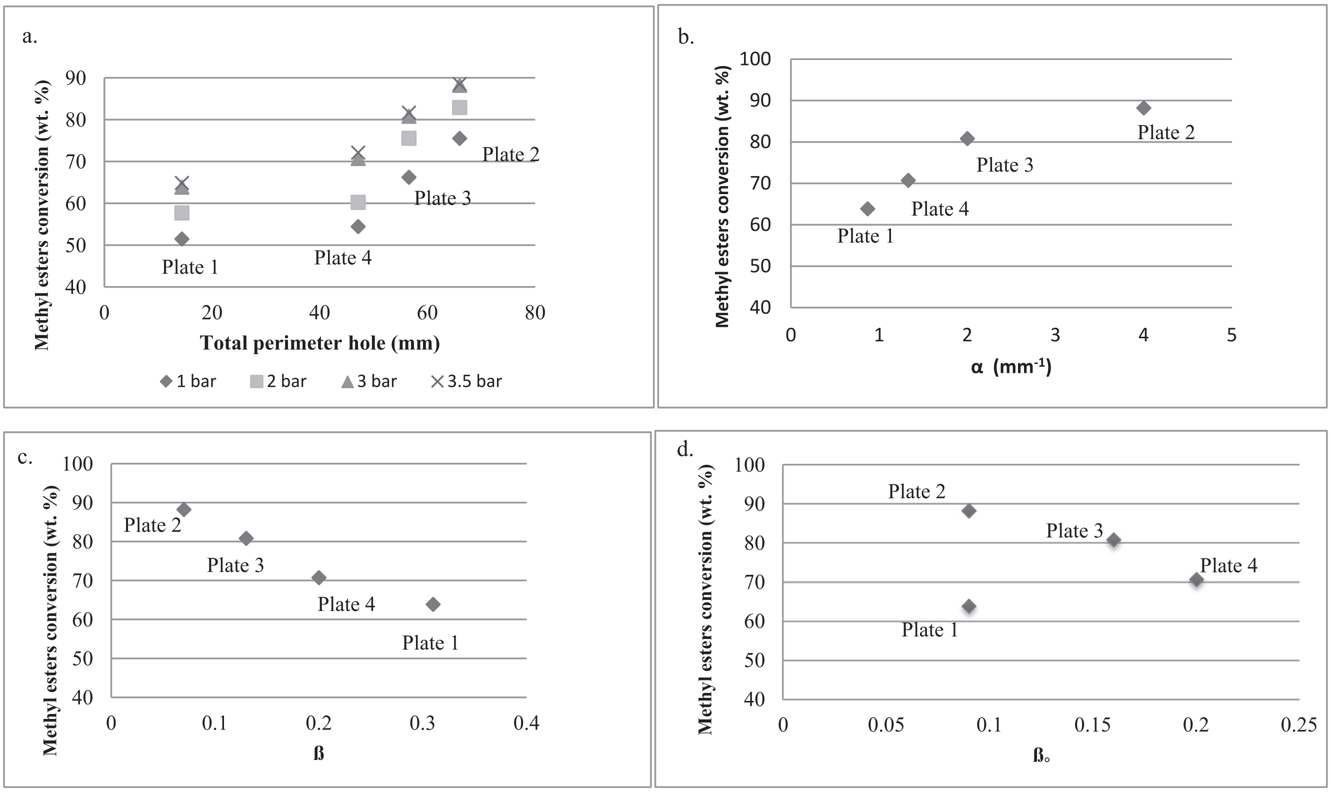

Fig. 4. Effect of the plate geometries on RSOME conversion.

Table 2
Central composite experimental design for chemical interesterification process.

Process Parameters	−2	−1	0	+1	+2
Methyl acetate to oil ratio (molar ratio)	8	10	12	14	16
Catalyst amount (wt.%)	0.63	0.75	0.88	1	1.13
Reaction time (min)	5	10	15	20	25
Reaction temperature (°C)	35	40	45	50	55

Note: Inlet pressure = 3 bar and plate 2 = 21 holes with 1mm diameter.

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< plate 2–88.20 wt.%. Plate 2 showed around 7.4 and 17.49% more methyl ester conversion compared to plates 3 and 4. Total flow areas of orifices were 16.5, 16.5, 28.3 and 35.3 mm^2 for plates 1,2,3 and 4. Though plates 1 and 2 have same total flow area yet plate 2 with 21 small holes diameter of 1 mm gave better conversion compared to plate 1 having a single hole with diameter of 4.58 mm. This could be attributed to increase in number of holes. It has been observed that with increased in hole number the cavity generating sports viz. shear layer area, frequency of turbulence and collapse pressure also increased. These factors result in higher number of cavities. Increased cavitation supports the mass transfer due to better emulsification and hence results in enhanced conversion. Ratio of hole dia to pipe dia is represented by β which is a dimensionless geometrical parameter (Ghayal et al., 2013). The relationship between β and methyl ester conversion is illustrated in Fig. 4(c) at reaction time of 20 min and pressure of 3 bar. Estimated β values were 0.31, 0.07, 0.13 and 0.20 for plates 1, 2, 3 and 4. An inverse relation was found between β value and conversion i.e. smaller the β value, the greater the conversion. Plate 2 shows the least β value with highest conversion rate of 88.20 wt.%.

This is due to the fact that smaller hole orifice plate diameter triggers higher numbers of smaller bubbles. These cavitational events give better emulsification. This leads to larger mass transfer and hence better conversion. Increased in turbulence‘s intensity with the decreased in β value has been observed by Vichare et al. (2000). Greater turbulence resulted in intensified cavities collapsed and hence generated higher magnitude pressure pulses. The ratio of total flow area to the pipe’s cross sectional area is represented by a dimensionless parameter $\beta_{\circ}$. The relationship between $\beta_{\circ}$ and conversion is represented in Fig. 4(d). $\beta_{\circ}$ values estimated for the present work varied between 0.09 and 0.20. The lower is the value of $\beta_{\circ}$ the higher is the conversion. In other words higher reaction rate will occur at lower $\beta_{\circ}$ value. At same value of $\beta_{\circ}$ Comparison between plate 1 and 2 at same $\beta_{\circ}$ value revealed that plate 2 gave better conversion than plate 1. It is note worthy to mention that plate 2 has smaller and more number of holes than plate 1 which has a single large hole. This could be attributed to higher cavitation intensity and turbulence frequency. Ghayal et al. (2013) claimed that a plate which has smaller holes but greater in number results in even distribution of mixture across the pipe’s cross sectional area. This even distribution resulted in larger probability for the cavity to experience the shear zone and collapsed intensity. Smaller holes of plate 2 yielded larger shear layer area and maximum turbulence, which resulted in greater collapse pressure and better conversion in a shorter reaction time.

3.4. Statistical analysis

Estimated parameters for chemical interesterification for RSO were analysed by using RSM viz. Design Expert 8.0. The central composite design (CCD) was applied base on RSM to design and optimise the interesterification reaction variables. These statistical designed tools help in minimising the experimental runs for generating the effect of all independent factors and their corresponding interactions. RSM identified four independent parameters such as; A = (methyl acetate:oil) MR, B = catalyst amount (wt.%), C = reaction time (min) and D = reaction temperature (°C). The output of each experimental run resulted in terms of methyl ester conversion, HC reactor at inlet pressure of 3 bar using orifice plate of 1 mm diameter and 21 holes. Table 2 shows the levels of four parameters which were studied in current work and its experimental ranges. Table 3 presented the design matrix of CCD with total of 30 experimental runs. Regression in Eq. (2) was generated by RSM based on a second-order polynomial of which predicted the response values independently and including all interactive terms.

Table 3
Detailed experimental results for transesterification process with orifice plate 2 at inlet pressure of 3 bar.

Run No.	Type	Methyl acetate to oil molar ratio (MR)	Catalyst amount (wt.%)	Reaction time (min)	Reaction temperature (°C)	Methyl ester conversion (wt.%)
1	Axial	12.0	0.88	15.0	55.0	77.8
2	Center	12.0	0.88	15.0	45.0	55.7
3	Center	12.0	0.88	15.0	45.0	62.2
4	Factorial	14.0	0.75	10.0	40.0	51.3
5	Factorial	10.0	0.75	10.0	50.0	48.7
6	Axial	8.00	0.88	15.0	45.0	55.4
7	Factorial	14.0	0.75	20.0	50.0	88.2
8	Center	12.0	0.88	15.0	45.0	64.7
9	Center	12.0	0.88	15.0	45.0	64.3
10	Axial	12.0	0.88	15.0	35.0	54.9
11	Axial	12.0	0.88	25.0	45.0	86.2
12	Axial	12.0	0.63	15.0	45.0	57.7
13	Factorial	14.0	1.00	20.0	50.0	88.9
14	Center	12.0	0.88	15.0	45.0	64.4
15	Factorial	14.0	1.00	10.0	40.0	73.8
16	Factorial	10.0	1.00	10.0	40.0	60.6
17	Factorial	10.0	0.75	10.0	40.0	45.1
18	Axial	12.0	1.13	15.0	45.0	72.8
19	Factorial	10.0	1.00	10.0	50.0	68.4
20	Factorial	14.0	0.75	20.0	40.0	80.2
21	Factorial	10.0	1.00	20.0	40.0	84.3
22	Center	12.0	0.88	15.0	45.0	63.3
23	Factorial	10.0	0.88	20.0	50.0	86.7
24	Factorial	10.0	1.00	20.0	50.0	87.9
25	Factorial	10.0	0.75	20.0	40.0	76.1
26	Factorial	14.0	1.00	20.0	40.0	75.1
27	Factorial	14.0	1.00	10.0	50.0	77.7
28	Factorial	14.0	0.75	10.0	50.0	75.3
29	Axial	12.0	0.88	5.00	45.0	55.4
30	Axial	16.0	0.88	15.0	45.0	68.3

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Table 4
Analysis of variance for chemical interesterification process.

	Sum of Squares	df	Mean square	F-value	p-Value Prob > F
Source					
Model	4320.34	14.00	308.59	9.74	<0.0001
A-Methyl acetate to oil (molar ratio)	256.30	1.00	256.30	8.09	0.0123
B-Catalyst amount (wt.%)	378.97	1.00	378.97	11.96	0.0035
C-Reaction time (min)	2175.70	1.00	2,175.70	68.67	<0.0001
D-Reaction temperature	610.54	1.00	610.54	19.27	0.0005
AB	36.45	1.00	36.45	1.15	0.3004
AC	208.73	1.00	208.73	6.58	0.0215
AD	36.51	1.00	36.51	1.15	0.3000
BC	189.40	1.00	189.40	5.97	0.0273
BD	17.99	1.00	17.99	0.56	0.4627
CD	0.70	1.00	0.70	0.02	0.8830
A^2	28.12	1.00	28.12	0.88	0.3610
B^2	95.15	1.00	95.15	3.00	0.1036
C^2	289.06	1.00	289.06	9.12	0.0086
D^2	125.33	1.00	125.33	3.95	0.0653
Residual	475.20	15.00	31.68		
Lack of Fit	415.83	10.00	41.58	3.50	0.0895
Pure Error	59.36	5.00	11.87		
Cor Total	4,795.54	29.00			

R-squared = 0.90, Adj *R*-squared = 0.81, Adeq precision = 13.54.
Std. dev. = 5.62, Mean = 69.03, C.V% = 8.15.

$$\begin{aligned}\text{Methyl esters conversion}(\text{wt.}\%) \\ &= 62.43 + 3.27\text{A} + 3.97\text{B} + 9.52\text{C} + 5.04\text{D} - 1.51\text{AB} \\ &\quad - 3.61\text{AC} + 1.51\text{AD} - 3.44\text{BC} - 1.06\text{BD} - 0.21\text{CD} \\ &\quad + 1.01\text{A}^2 + 1.86\text{B}^2 + 3.25\text{C}^2 + 2.14\text{D}^2 \qquad (2)\end{aligned}$$

Experimental results of analysis of variance (ANOVA) was fitted by mean square method and the response model coefficients analysed using F-test are presented in Table 4. The model F-value of 9.74 corresponding to lowest p-value of <0.0001 shows the reliability of the model fitting with FAME conversion. Higher F-value of reaction time followed by catalyst amount has the most influential effects on FAME conversion. Least significant p-values behaviour confirmed that results are statistically significant. R^2 value of 0.90 indicated that 90% experimental data gives compatibility with the predicted results of the model. The lower value of a coefficient of variation (C.V) is 8.15, which further confirmed the reliability of the model applied based on experimental design.

3.5. Parametric effects of chemical interesterification process

The combined effect of two interactive variables on FAME conversion was illustrated in Fig. 5(a-f). At constant catalyst amount of 0.75 wt.%, RSOME concentration increased from (10:1–14:1) MR as depicted in Fig. 5(a). MR is one of the key variable which enhanced the concentration of FAME conversion. On the basis of stoichiometric reaction, for the production of three moles of FAME and one mole of triacetin, three moles of methyl acetate react with one mole of triglyceride (TG) via chemical interesterification reaction. Due to natural reversibility of interesterification reaction, higher MR is preferred in order to keep reaction equilibrium towards desired FAME conversion. (Maddikeri et al., 2014). In pilot HC system, an effect of MR on FAME conversion at constant reaction temperature of 45 °C, 0.75 wt.% of methanolic potassium methoxide catalyst and reaction time of 15 min were studied. Results revealed that the FAME conversion experienced the increment at MR of 10:1–14:1. This could be due to excess of MR, which limiting the backward nature of the reaction and promoted towards the conversion of RSO to methyl esters. There is no significant increased in FAME conversion was observed above MR of 12:1. The lower amount of MR is worthwhile to refrain from the product separation issues (Maddikeri et al., 2013). Casas et al. (2011a) reported that mechanical stirring (MS) for interesterification revealed that excessive MR of 50:1 resulted in the 76.7% of biodiesel yield. Similarly, Fig. 5(a) revealed that constant MR of 10:1 promoted the RSOME concentration with catalyst amount between 0.75 and 1.0 wt.% while keeping constant reaction time of 15 min at 45 °C. Methanolic potassium methoxide catalyst is one the most influential variable that affects the chemical interesterification reaction. The catalyst amount is an essential variable to study to avoid its excessive usage in rate determine step, which uplifts the separation process associated problems. For catalyst amount from 0.75 to 1 wt.% at 15 min of reaction time, the RSOME conversion increased from 60 to 85 wt.%. However, no significant product conversion was obtained beyond 1 wt.% of methanolic potassium methoxide. Casas et al., (2011a) obtained maximum biodiesel yield of 76.7 wt.% at catalyst amount of 1.04 wt.% for sunflower oil interesterification. Similar results was supported by the work of Maddikeri et al. (2014) for biodiesel synthesis in a HC reactor at laboratory scale to study interesterification using three different cavitating devices.

The combined effect of reaction time and temperature on FAME conversion is depicted in Fig. 5(f). Reaction temperature is the essential form of energy to carry out the interesterification successfully. The driving force which drive the reaction rate is directly associated with this variable. The effect of reaction temperatures between 45 and 55 °C was investigated under preset operation conditions; MR of 12 and catalyst amount of 0.88 wt.%. Results revealed that when the reaction temperature increased from 45 to 55 °C, FAME conversion was increased from 55.8 to 86.3 wt.% at 15 min of reaction time. Viscosity was reduced due to quick dispersion of methyl acetate in treated RSO at elevated reaction temperature. Interesterification reaction rate and mass transfer between methyl acetate and treated RSO phase was improved at the higher reaction temperature. Meanwhile, adequate reaction time was required to give enough residential period to intensify the interesterification process. FAME conversion increased with an increment of reaction time to a specified period. Reaction time of 20 min in HC was sufficient to overcome the mass transfer between treated RSO and methyl acetate. FAME conversion was slightly increased after 20 min of a residential period.

3.6. Interesterification reaction kinetics

Pseudo-first order kinetics which is a function of TG concentration governs the homogenous catalytic reaction of interesterifica-

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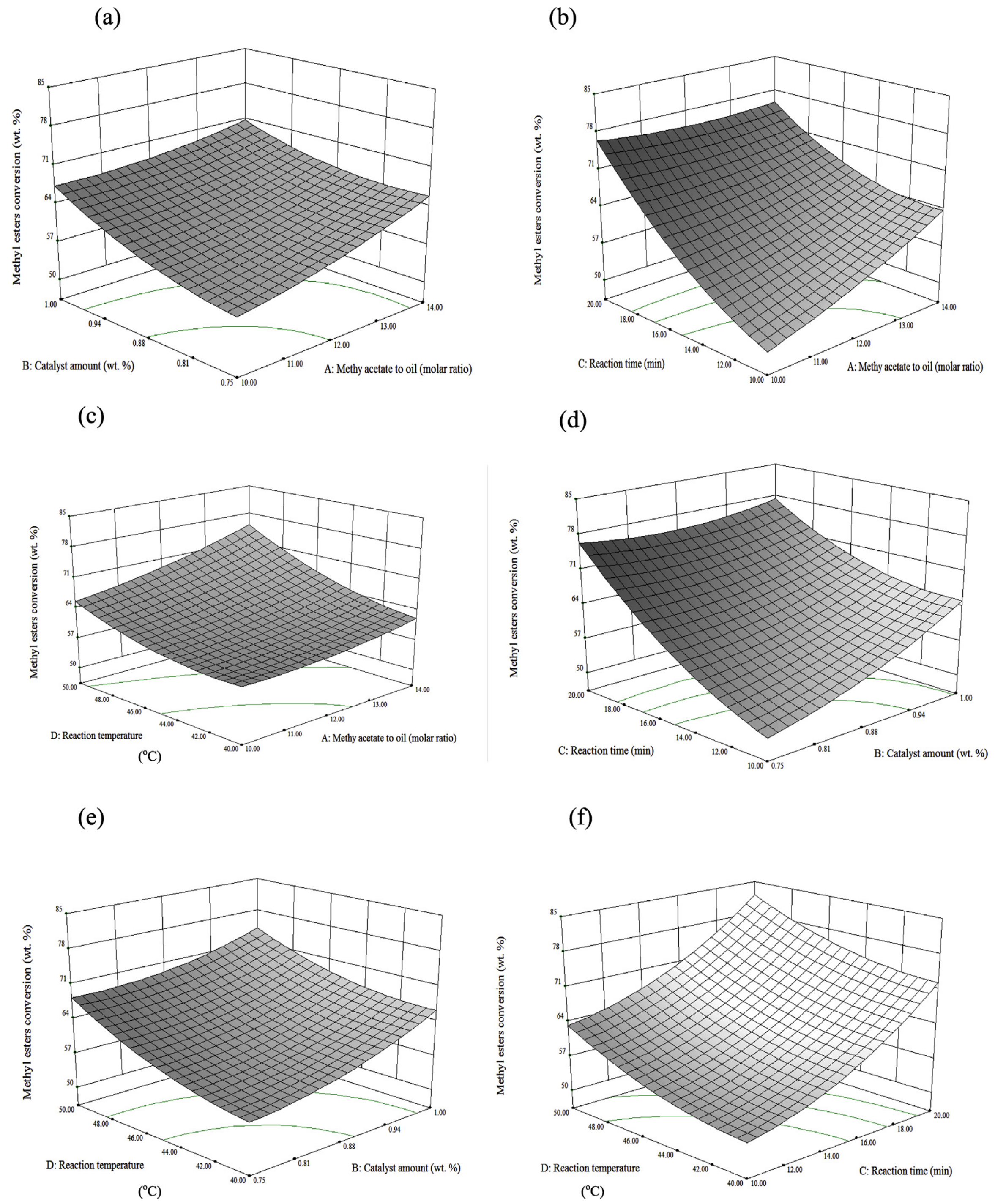

Fig. 5. Reaction parametric effects on RSOME conversion.

tion. The limiting reactant is methyl acetate. Excess methyl acetate is favourable in this reversible reaction, as it shifts the reaction towards favourable products i.e. FAME. Plot of −ln (1-X) vs reaction time at various operating temperatures while using HC and MS pilot system is shown in Fig. 6. The rate constant values obtained from these plots have been summarised in Table 5. HC showed 3.4 (average value) fold higher rate constant than MS with increased in process temperature from 45 to 55 °C. Pseudo second order kinetics fitting was reported by Casas et al. (2011b) while studying the chemical interesterification of sunflower oil using conventional method at various temperatures. Maddikeri et al. (2014) reported second order kinetics of interesterification of waste cooking oil via HC reactor. In their work the kinetics was studied at laboratory scale using venturi as the cavitating media. While in current study the rate of reaction has been increased using various orifice plates and 21 holes of 1 mm diameter plate to generate the cavitational effect. Oscillating cavities generated high intensity micro level turbulence which raised the rate of methyl ester synthesis. Mass transfer resistance between RSO and methyl acetate during interesterification reaction is successfully eliminated by the high interfacial area in HC. In micro seconds the cavities expanded and compress at elevated pressure and temperature which favoured forward reaction. Due to intensive expansion and compression sudden collapsed of cavities process

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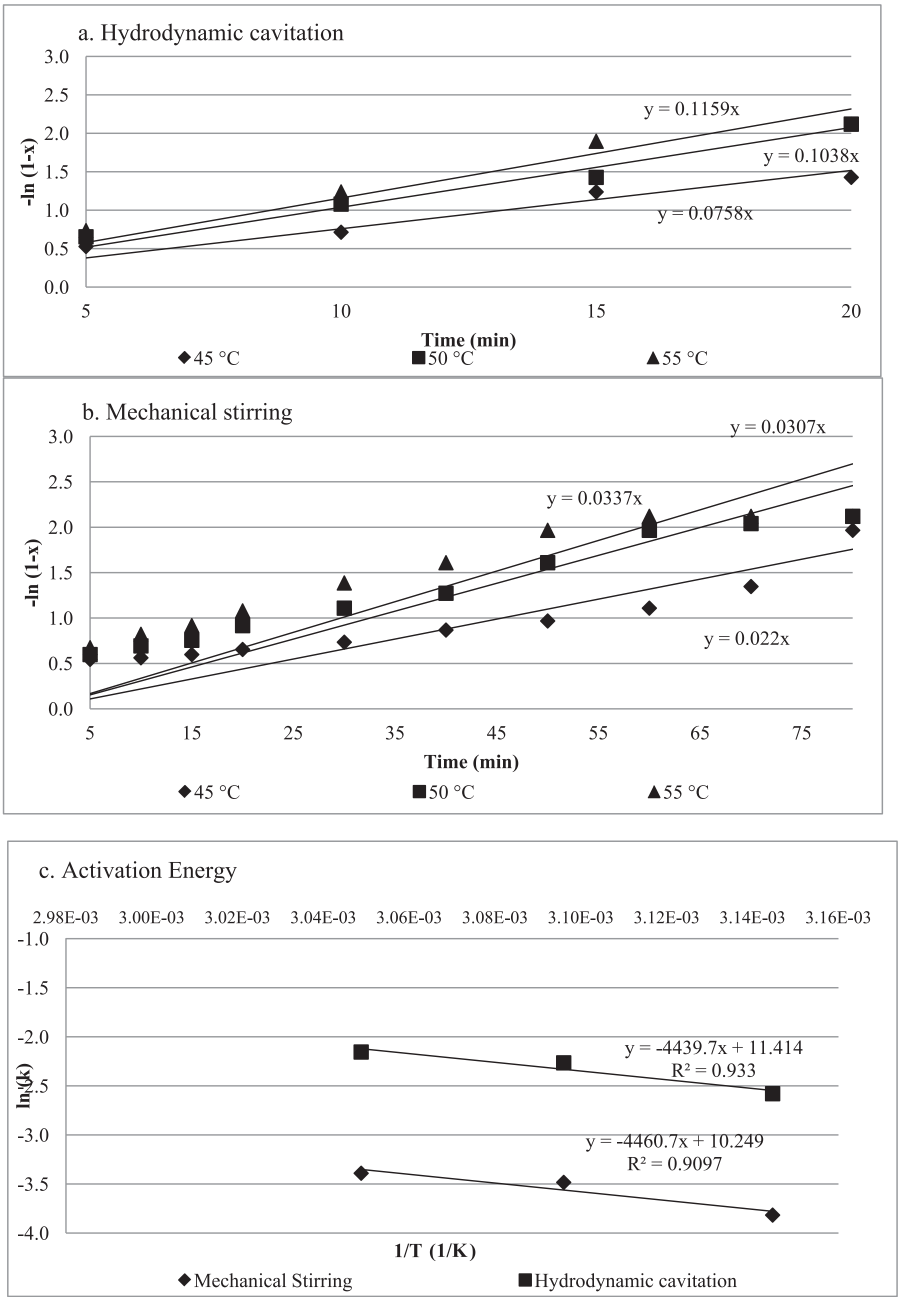

Fig. 6. Kinetic studies for establishing the rate constants and activation energy.

Table 5
Comparison of reaction rate constants and yield efficiency between hydrodynamic cavitation and mechanical stirring.

Method	Temperature (°C)		
	45	50	55
Rate constant for interesterification processing, k, min^{-1} × 10^{-2}			
HC	7.58	10.38	11.59
MS	2.20	3.07	3.37
Yield efficiency, × g/J 10^{-4}			
HC	7.13	8.25	12.5
MS	1.30	1.50	1.70

experienced. This enhanced rate ultimately lead to better conversion. Activation energy for both MS and HS was estimated from the calculated rate constant at each reaction temperature between 45 to 55 °C.

Fig. 6 (c) shows a plot of ln k vs 1/T. Based on this research, the Arrhenius expression for FAME synthesis using HC and MS are given by $k = 9.02x10^4 e^{\frac{-36.9\ kJ/mol}{RT}}$ and $k = 2.8x10^4 e^{\frac{-37.1\ kJ/mol}{RT}}$.

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Table 6
Comparison of optimum conditions and fuel properties between hydrodynamic cavitation and mechanical stirring.

Parameters	HC	MS		
Optimum conditions				
Oil to methyl acetate ratio	1:14	1:14		
Catalyst amount (wt.%)	0.75	0.75		
Temperature (°C)	50	50		
RPM	–	600		
Inlet pressure (bar)	3 bar	–		
Time (min)	20	80		
Yield efficiency (mg/J)	0.0825	0.015		
Reaction rate constant (min^{-1})	0.104	0.031		
Biodiesel properties			EN 14214	ASTM D 6751
Density (15 °C, g/cm^3)	0.87	0.87	0.86–0.90	
Kinematic viscosity, (40 °C, $\text{mm}^2\text{/s}$)	3.80	3.82	3.5–5.0	1.9–6.0
Flash point (°C)	151	152	≥120	≥130
Acid value (mg KOH/g oil)	0.30	0.42	≤0.5	≤0.8
Ester conversion (wt.%)	88	88	≥96.5	

3.7. Comparative performance of hydrodynamic cavitation and mechanical strirring

The regression Eq. (2) was solved by numerical optimisation tool and the predicted operating conditions were obtained for chemical interesterification of RSO as; methyl acetate to oil molar ratio of 14:1, catalyst amount of 0.75 wt.%, reaction temperature of 50 °C and reaction time of 20 min. These optimised predicted variables were validated for HC and compared to MS in triplicate runs for data reliability. Table 6 summarised the optimum reaction variables for chemical interesterification of RSO through HC and MS. Results revealed that both HC and MS system interesterified up to ≥88.20 wt.% of methyl ester conversion in 20 and 90 min reaction time. This is due to high intensity of micro level turbulence generated by oscillating cavities with high interfacial area in HC system. HC technology has affirmative effect in eliminating the mass transfer resistance during the reaction and results in higher conversion within less time. In MS system methyl acetate- oil interface was only dependent on the stirrer bar (MS),which produced poor mass transfer between the immiscible reactants and resulted in slow conversion rate. Reaction rate constant using HC is 3.4-fold higher than MS. Majority properties of RSOME complied with ASTM D 6751 and EN 14214 standards.

4. Conclusions

Chemical interesterification has been successfully implemented using RSOME via HC in a 50 L reactor. Orifice plate with 1 mm diameter of 21 holes and 3 bar upstream pressure was identified as the optimum cavitating device. The optimum conditions from RSM were 14:1 of MR in the presence of 0.75 wt.% catalyst for 20 min reaction time at 50 °C. Comparison of HC and MS results has been reported. HC reaction rate and yield efficiency is 3.4 and three fold higher than MS. Majority of the fuel properties met the EN 14214 and ASTM D 6751 standards.

Acknowledgements

The authors would like to thank Universiti Teknologi Petronas, Public Service Department of Malaysia, Marine Department Malaysia, PRGS Grant (No. 0153AB-K19), MyRA Grant (No. 0153AB-J19) and Pázmány Péter Catholic University in Budapest, for supporting the research.

References

Ahmad, J., Yusup, S., Bokhari, A., Kamil, R.N.M., 2014a. Study of fuel properties of rubber seed oil based biodiesel. Energy Convers. Manage. 78, 266–275.

Ahmad, J., Bokhari, A., Yusup, S., 2014b. Optimization and parametric study of free fatty acid (FFA) reduction from rubber seed oil (RSO) by using response surface methodology (RSM). Aust. J. Basic Appl. Sci. 8 (5), 299–303.

Ahmad, J., Yusup, S., Bokhari, A., Kamil, R.N.M., 2014c. Biodiesel production from the high Free fatty acid "Hevea brasiliensis" and fuel properties characterization. Appl. Mech. Mater. 625, 897–900.

Asif, S., Chuah, L.F., Klemeš, J.J., Ahmad, M., Akbar, M.M., Lee, K.T., Fatima, A., 2017. Cleaner production of methyl ester from non-edible feedstock by ultrasonic-assisted cavitation system. J. Clean. Prod. http://dx.doi.org/10.1016/j.jclepro.2017.02.081.

Bagal, M.V., Gogate, P.R., 2014. Degradation of diclofenac sodium using combined process based on hydrodynamic cavitation and heterogeneous photocatalysis. Ultrason. Sonochem. 21, 1035–1043.

Bokhari, A., Yusup, S., Ahmad, M.M., 2012. Optimization of the parameters that affects the solvent extraction of crude rubber seed oil using response surface methodology (RSM). In: Dmitriev, A., Camarinhas, C.L. (Eds.), Recent Advance in Engineering. WSEAS, Paris, pp. 28–30.

Bokhari, A., Chuah, L.F., Yusup, S., Ahmad, J., Shamsuddin, M.R., Meng Kiat Teng, M. K., 2015. Microwave-assisted methyl esters synthesis of kapok (Ceiba pentandra) seed oil: parametric and optimization study. Biofuel Res. J. 7, 281–287.

Bokhari, A., Chuah, L.F., Yusup, S., Klemeš, J.J., Kamil, R.N.M., 2016a. Optimisation on pretreatment of rubber seed (Hevea brasiliensis) oil via esterification reaction in a hydrodynamic cavitation reactor. Bioresour. Technol. 199, 414–422.

Bokhari, A., Chuah, L.F., Yusup, S., Klemeš, J.J., Akbar, M.M., Kamil, R.N.M., 2016b. Cleaner production of rubber seed oil methyl ester using a hydrodynamic cavitation: optimisation and parametric study. J. Clean. Prod. 136, 31–41.

Casas, A., Ramos, M.J., Pérez, Á., 2011a. New trends in biodiesel production: Chemical interesterification of sunflower oil with methyl acetate. Biomas Bioenergy 35, 1702–1709.

Casas, A., Ramos, M.J., Pérez, Á., 2011b. Kinetics of chemical interesterification of sunflower oil with methyl acetate for biodiesel and triacetin production. Chem. Eng. J. 171, 1324–1332.

Casas, A., Ramos, M.J., Pérez, Á., 2013. Methanol-enhanced chemical interesterification of sunflower oil with methyl acetate. Fuel 106, 869–872.

Chuah, L.F., Abd Aziz, A.R., Yusup, S., Bokhari, A., Klemeš, J.J., Abdullah, M.Z., 2015a. Performance and emission of diesel engine fuelled by waste cooking oil methyl ester derived from palm olein using hydrodynamic cavitation. Clean Techn. Environ. Policy 17, 2229–2241.

Chuah, L.F., Yusup, S., Abd Aziz, A.R., Bokhari, A., Klemeš, J.J., Abdullah, M.Z., 2015b. Intensification of biodiesel synthesis from waste cooking oil (palm olein) in a hydrodynamic cavitation reactor: effect of operating parameters on methyl ester conversion. J. Chem. Eng. Process. Process Intens. 95, 235–240.

Chuah, L.F., Bokhari, A., Yusup, S., Klemeš, J.J., Abdullah, B., Akbar, M.M., 2016a. Optimisation and kinetic studies of acid esterification of high free fatty acid rubber seed oil. Arab. J. Sci. Eng. 41 (7), 2515–2526.

Chuah, L.F., Abd Aziz, A.R., Yusup, S., Klemeš, J.J., Bokhari, A., 2016b. Waste cooking oil biodiesel via hydrodynamic cavitation on a diesel engine performance and greenhouse gas footprint reduction. Chem. Eng. Trans. 50, 301–306.

Chuah, L.F., Yusup, S., Abd Aziz, A.R., Klemeš, J.J., Bokhari, A., Abdullah, M.Z., 2016c. Influence of fatty acids content in non-edible oil for biodiesel properties. Clean Technol. Environ. Policy 18 (2), 473–482.

Chuah, L.F., Yusup, S., Abd Aziz, A.R., Bokhari, A., Abdullah, M.Z., 2016d. Cleaner production of methyl ester using waste cooking oil derived from palm olein using a hydrodynamic cavitation reactor. J. Clean. Prod. 112, 4505–4514.

Chuah, L.F., Amin, M.M., Yusup, S., Raman, N.A., Bokhari, A., Klemeš, J.J., Alnarabiji, M.S., 2016e. Influence of green catalyst on transesterification process using ultrasonic-assisted. J. Clean. Prod. 136, 14–22.

Chuah, L.F., Klemeš, J.J., Yusup, S., Bokhari, A., Akbar, M.M., Zhong, Z.K., 2017a. Kinetic studies on waste cooking oil into cleaner biodiesel via hydrodynamic cavitation. J. Clean. Prod. 146, 47–56.

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Chuah, L.F., Klemeš, J.J., Yusup, S., Bokhari, A., Akbar, M.M., 2017b. A review of cleaner intensification technologies in biodiesel production. J. Clean. Prod. 146, 181–193.

Ghayal, D., Pandit, A.B., Rathod, V.K., 2013. Optimization of biodiesel production in a hydrodynamic cavitation reactor using used frying oil. Ultrason. Sonochem. 20, 322–328.

Gogate, P.R., 2008. Cavitational reactors for process intensification of chemical processing applications: a critical review. Chem. Eng. Process. 47, 515–527.

Gole, V.L., Naveen, K.R., Gogate, P.R., 2013. Hydrodynamic cavitation as an efficient approach for intensification of synthesis of methyl esters from sustainable feedstock. Chem. Eng. Process. 71, 70–76.

Kelkar, M.A., Gogate, P.R., Pandit, A.B., 2008. Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. Ultrason. Sonochem. 15, 188–194.

Leite, G.B., Abdelaziz, A.E.M., Hallenbeck, P.C., 2013. Algal biofuels: Challenges and opportunities. Bioresour. Technol. 145, 134–141.

Maddikeri, G.L., Pandit, A.B., Gogate, P.R., 2013. Ultrasound assisted interesterification of waste cooking oil and methyl acetate for biodiesel and triacetin production. Fuel Process. Technol. 116, 241–249.

Maddikeri, G.L., Gogate, P.R., Pandit, A.B., 2014. Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil. Fuel 137, 285–292.

Onoji, S.E., Iyuke, S.E., Igbafe, A.I., Nkazi, D.B., 2016. Rubber seed oil: A potential renewable source of biodiesel for sustainable development in sub-Saharan Africa. Energy Convers. Manage. 110, 125–134.

Park, J., Kim, B., Lee, J.W., 2016. In-situ transesterification of wet spent coffee grounds for sustainable biodiesel production. Bioresour. Technol. 221, 55–60.

Ramadhas, A.S., Jayaraj, S., Muraleedharan, C., 2005. Biodiesel production from high FFA rubber seed oil. Fuel 84 (4), 335–340.

Senthil Kumar, P., Siva Kumar, M., Pandit, A.B., 2000. Experimental quantification of chemical effects of hydrodynamic cavitation. Chem. Eng. Sci. 55, 1633–1639.

Subhedar, P.B., Gogate, P.R., 2016. Ultrasound assisted intensification of biodiesel production using enzymatic interesterification. Ultrason. Sonochem. 29, 67–75.

Sustere, Z., Murnieks, R., Kampars, V., 2016. Chemical interesterification of rapeseed oil with methyl, ethyl, propyl and isopropyl acetates and fuel properties of obtained mixtures. Fuel Process. Technol. 149, 320–325.

Tangy, A., Pulidindi, I.N., Perkas, N., Gedanken, A., 2017. Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil. Bioresour. Technol. 224, 333–341.

Vichare, N.P., Gogate, P.R., Pandit, A.B., 2000. Optimization of hydrodynamic cavitation using a model reaction. Chem. Eng. Technol. 23 (8), 683–690.