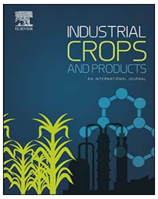
Industrial Crops & Products 108 (2017) 336–347

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Research Paper

Methyl ester synthesis of *Pistacia khinjuk* seed oil by ultrasonic-assisted cavitation system

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ARTICLE INFO

Keywords:
Pistacia khinjuk oil
Optimisation
Ultrasonic cavitation
Mass transfer
Fuel properties

ABSTRACT

Synthesis of biodiesel from a non-edible source as *Pistacia khinjuk* seed oil via ultrasonic cavitation (UC) system is reported in this study. A heterogeneous catalyst sulphated tin oxide impregnated with silicon dioxide (SO_4^{2-}/SnO_2–SiO_2) was employed during the transesterification reaction in an UC reactor. Parametric optimisation results revealed the maximum *Pistacia khinjuk* methyl ester (PiKME) yield was 88 wt.% at reaction time of 50 min, amplitude of 50%, catalyst amount of 3.5 wt.% and molar ratio of 13:1 (alcohol:oil). Performance of UC at optimised values was compared with mechanical stirring (MS). UC proved advantageous over MS with 3 times more time efficient. Hence, the superiority of UC over MS was established. About 3.2 fold higher reaction rate constant using UC (0.029 min^{-1}) compared to MS (0.009 min^{-1}). PiKME production via UC can potentially subsidise the overall cost of production by having 3.2 fold higher reaction rate constant than MS. PiKME met most of the fuel properties enlisted in EN14214 and ASTM D6751 standards.

1. Introduction

Anthropogenic emissions of greenhouse gas are reckoned as chief contributors towards drastic climatic changes. These changes coupled with growing levels of carbon dioxide are likely to affect the developed and developing countries in a different manner. However, regions located at low latitude are more vulnerable to such change (Chuah et al., 2015a). Researchers are fretful about the potential peril to treasured ecosystems and expect that climate change would increase the probability of large-scale ecological instabilities (Chuah et al., 2016a). Mitigation and stabilisation of the carbon footprint in response to fossil-fuel utilisation, technology developments, and industrial revolution (Bokhari et al., 2017) demand for cleaner and sustainable fuel options. Serious environmental penalties pinned with fossil fuels usage have spurred the quest for renewable and environmentally benign bio-fuels (Chuah et al., 2016b). Meanwhile, biodiesel is acknowledged worldwide as a cleaner and a better replacement fuel in a diesel engine (Chuah et al., 2016c). Biodiesels from indigenous renewable bio waste oils (Rozina et al., 2017) via intensified technologies are a recent and innovative addition in feasible alternatives fuels.

Abbreviation: PiKSO, *Pistacia khinjuk* seed oil; PiKME, *Pistacia khinjuk* methyl ester; TG, triglyceride; UC, ultrasonic cavitation; MS, mechanical stirring; FFA, free fatty acid; FAME, fatty acid methyl ester; AOCS, American oil chemist's society; FTIR, Fourier transform infrared spectroscopy; X, methyl ester conversion; RSM, response surface methodology; CCD, central composite design; KOH, potassium hydroxide; CaO, calcium oxide; H_2SO_4, sulphuric acid; SO_4^{2-}/SnO_2–SiO_2, sulfated tin oxide impregnated with silicon dioxide; SnO_2–SiO_2, sulfated tin oxide; 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.indcrop.2017.06.046
Received 14 February 2017; Received in revised form 22 May 2017; Accepted 17 June 2017
0926-6690/

Current work explores the viability of relatively under utilised oil seed feedstock, *Pistacia khinjuk* seed oil (PiKSO), a nonconventional indigenous feedstock towards biodiesel production. *Pistacia khinjuk* belongs to genus *Pistacia* (Anacardia ceae/cashew family). It is an important genus because of the economic value of its member namely; *Pistachia vera* (Kafkas et al., 2002). PiKSO is native to Irano-Turanian regions and its plantation is widely spread across Pakistan, Afghanistan, Syria, Iran and Turkey. The *Pistacia khinjuk* trees are 2–5 m long. These trees are highly adapted to irradiated and low nutrient soils, hot and arid conditions even with an annual rainfall of 100–600 mm. Trees of PiKSO potentially can withstand the severest climatic conditions also (Behboodi, 2003). Locations having the temperature range within T = 10–25 °C are suitable for seeds growth. Researchers are of the view that PiKSO plant is not much sensitive towards extensive heat, the amount of rain, dryness, height and other climatic conditions of the region. *Pistacia khinjuk* is the best species which can be cultivated in many regions with diverse climates (Behboodi, 2003). It is a rich gene pool species due to its scatteredness across harsh climatic zones and among local populations. Anemophily is another significant characteristic which adds to its diversity. (Taran et al., 2009). It has been reported that *Pistacia khinjuk* trees occupy approximately $2.5–3 \times 10^6$ ha areas in several parts of Iran and its seeds are the waste (Alaei et al., 2012). It contains about 60 wt.% oil. Under these conditions, the use of PiKSO hold a better potential for a renewable energy source for future.

Processing of cleaner biodiesel is hinged on the development of process intensification technology (Chuah et al., 2016d). Process intensification technique offers many primacies like; less reaction time, a low molar ratio (MR) of oil and alcohol, high conversion rate, low catalyst concentration and lower energy consumption hence less operating cost. Among intensification technologies, ultrasonic cavitation (UC) is usually considered as one of the most suitable ones for transesterification reaction (Chuah et al., 2016e). UC surges the emulsification rate of immiscible reactants (oil and alcohol) and solves the poor mass transfer problem between reactant species (Chuah et al., 2017b). Reaction kinetics of intensification process was obeyed the pseudo first order reaction kinetics as a conversion of triglycerides (TG) to respective methyl ester for transesterification process. The detailed reaction kinetics mechanisms for intensification transesterification process has been discussed in our previous publish research (Chuah et al., 2017a). Homogenous (Samani et al., 2016) and heterogeneous (Salamatinia et al., 2010) catalysts for transesterification via UC have been studied by several researchers. Samani et al. (2016) synthesised the Pistacia atlantica Desf. methyl ester (96.6 wt.% yield) via UC system under homogenous catalysed transesterification reaction. UC increased the methyl ester conversion by 7.5 wt.% as compared to mechanical stirring (MS). The UC work on biodiesel synthesis by calcium oxide (CaO) heterogeneous catalyst on *Salvadora alii* and *Thespesia populneoides* oil has been conducted. More than 90 wt.% biodiesel yield was reported for both non-edible feedstocks. The UC was found to be 3 fold more efficient in reaction rate and reduced 3 fold reaction time compared to MS (Asif et al., 2017). Free fatty acid (FFA) content of kapok seed oil was reduced by acid esterification process using UC reactor and it is found to be 4.5 times efficient as compared to MS approach (Chuah et al., 2017c).

Transesterification of PiKSO was steered to optimise several process variables. The response surface methodology (RSM) was statistically confirmed the significance of mathematical model for heterogeneously catalysed transesterification process variables. The central composite design (CCD) was designed the experimental runs for transesterification process. It is capable to give a parametric effect of a solo independent variable or with the combination of other variables with respect to output response. It gives affirmative responsive results for parametric interactions and considered for being cost, time and material effective (Ahmad et al., 2014). Later, the effect of these parameters on fatty acid methyl ester (FAME) yield was monitored also. Experimentally obtained results were processed by RSM to estimate optimum reaction conditions. Reaction kinetics at optimum results was conducted along comparison with MS approach. Hence prepared biodiesel from indigenous non-edible oil was tested to meet the standard fuel properties. Obtained results were compared with EN 14214 and ASTM D6751 biodiesel standards.

Fig. 1. *Pistacia khinjuk* mature seeds.

2. Experimental section

2.1. Materials

Mature seeds for PiKSO extraction (Fig. 1) were collected from different parts of Baluchistan, located in the southwestern region of Pakistan. Seeds were dried under shade for several days. Dried seeds were later kept in a controlled ambience of a laboratory to avoid any humid effects. Prior to oil content estimation seeds were dried at 60 °C in an oven for overnight. Oil estimation was carried out with the help of soxhlet apparatus by using organic solvent (*n*-hexane) extraction method (Ahmad et al., 2011).

2.1.1. Chemicals

Sigma Aldrich, Malaysia provided the standard mixture containing 37 FAME. Utilised analytical grade chemicals were; sulphuric acid (H_2SO_4), wijs solution, cyclohexane, acetic acid (glacial), potassium iodide, starch, acetone, ethanol, hydrochloric acid, anhydrous methanol, anhydrous sodium sulphate, toluene, potassium hydroxide (KOH) pellets, chloroform, sodium thiosulphatepentahydrate, phenolphthalein and 2-propanol. All the aforementioned chemicals were procured from Merck Malaysia.

2.2. Oil estimation

Dried seeds (50 g) were ground by mortar and pestle till fine powder was obtained. Obtained powder was fed to a soxhlet type apparatus comprised of three neck round flasks (250 mL) and a reflux condenser. Oil was extracted with *n*-hexane at T = 45–55 °C for 6–8 h. The difference in sample weight before and after extraction was accounted as the weight of the oil possessed (oil content) by seed. All the experiments were performed in triplicate and the average values are reported for further consideration. Once extraction was accomplished, the remaining solvent was removed at 55 °C under moderate vacuum conditions by using a rotary evaporator. American Oil Chemists Society (AOCS-Cd 3d-63) official method was conformed to estimate the acid values and water contents of both oils.

2.3. Catalyst selection and preparation

In this study super acid solid heterogeneous catalyst–sulphated tin oxide impregnated with silicon dioxide ($SO_4^{2-}/SnO_2–SiO_2$) was used for transesterification reaction. Literature review supported the selection of this catalyst for one step transesterification of feedstock with high FFA value. Lam et al. (2009) synthesised, characterised and applied the said

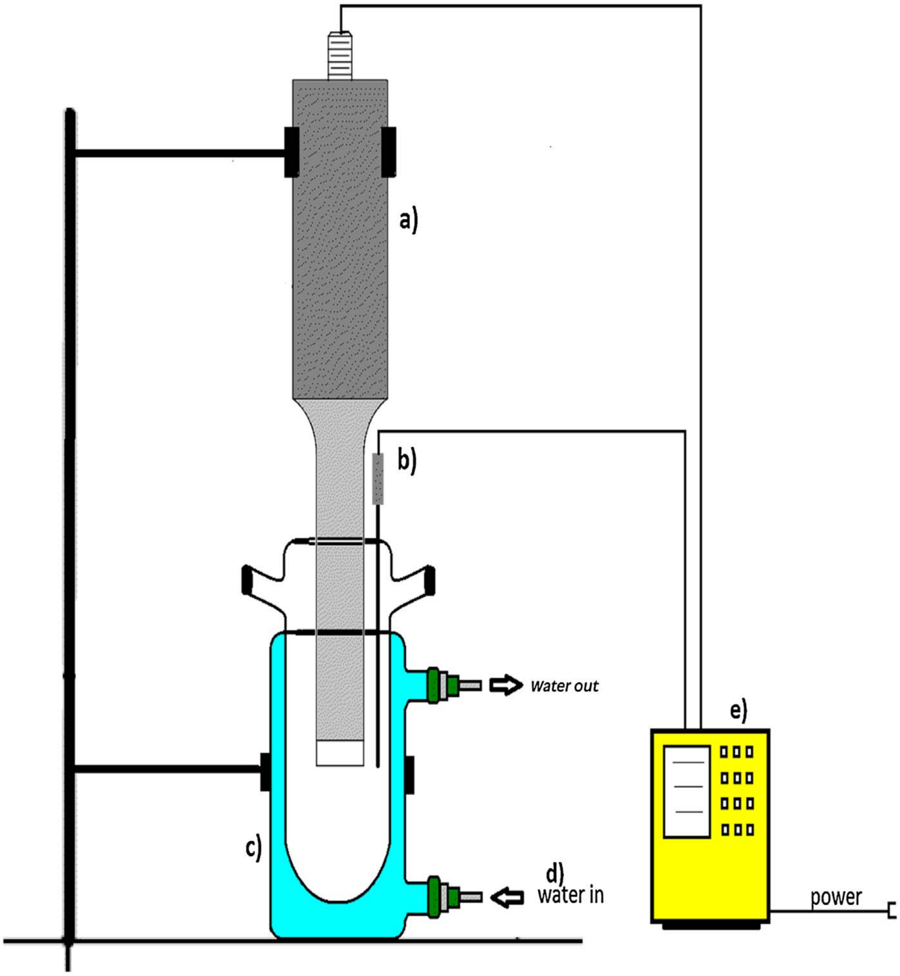


Fig. 2. A schematic diagram of ultrasonic cavitation system.

catalyst for the transesterification of waste cooking oil and reported 92.3 wt.% yield of biodiesel under optimum reaction conditions. This bi-metallic superacid catalyst has also been utilised for biodiesel synthesis from Moringa oleifera with an optimum yield up to 84 wt.% under suitable reaction parameters (Kafuku et al., 2010b). The same catalyst was employed successfully to obtain a yield ≈ 95 wt.% from Croton megalocarpus oil also without any pre-treatment step (Kafuku et al., 2010a).The catalyst was prepared by gradually adding 30 g tin oxide to 2.0 M H_2SO_4 solution while it was stirred at 600 rpm for 6 h. Alongside, 10 g of SiO_2 was also added to the solution (SnO_2 to SiO_2 ratio utilised was 3:1). The mixture was later filtered by using filter paper and precipitated solid was calcined in a muffle furnace. Operating conditions for calcination were as: heating at 10 °C/min, maximum temperature of 300 °C and holding time of 2 h. The super solid heterogeneous catalyst was stored in desiccator cabinet prior to further usage (Lam et al., 2009).

2.4. *Ultrasonic experiment setup*

Three neck glass reactor was utilised for transesterification process. It was partially submerged in a water bath as shown in Fig. 2 to regulate the temperature. The condenser was attached to the reaction vessel to control the evaporative loss of methanol. UC to the reaction mixture was provided by Branson (USA) ultrasonic processor having frequency of 20 kHz. In a typical run, the reactor was fed with a known amount of oil while it was placed inside the water bath. Later, known amount catalyst and finally suitable ratio of methanol to oil was fed inside the reactor. Evaporated methanol was recovered by using a condenser. The reactor was then exposed to the ultrasonic energy at a pattern of 10 s pulse on and 3 s pulse off. The temperature of the water bath was maintained at 56 °C. Ultrasonic probe generated heat and hence the temperature of reaction mixture was maintained at 65 ± 1 °C. By using rotary evaporator excess methanol was distilled out from the reaction mixture upon completion of reaction. Reaction mixture was placed in a centrifuge for 20 min (3,000 rpm) to split it into two phases. An upper layer of the split phases was collected and subjected to gas chromatography (GC) analysis.

2.5. *Fatty acid profile*

Properties of PiKSO are listed in Table 1. GC (7890-A, FID-Agilent Technologies) system and methylpolysiloxane capillary column (DB-23) (60 m × 0.25 mm × 0.25 μm) were used to estimate the quantitative conversion of methyl ester. The procedure listed in EN 14103 standards were strictly followed for accurate estimation. Operating conditions were as: $T_{initial}$ = 100 °C, initial holding = 2 min, heating = 10 °C/min, T_{final} = 240 °C, final holding = 7 min. Carrier gas was helium (flow rate = 4 mL/min). For flame production air and hydrogen were used at flow rate = 50 and 400 mL/min (Bokhari et al., 2016a). All the experiments were performed in triplicate and the average values were taken for further considerations. EN 14214 and ASTM D 6751 standards were subscribed while estimating the properties of obtained methyl ester.

2.6. *Experimental design and statistical analysis*

Experimental plot was planned to appraise the effect of independent variables: MR (methanol:oil) of 6:1–18:1, reaction time (20–60 min),

Table 1
Properties of *Pistacia khinjuk* seed oil.

Analysis		Mean ± standard deviation (n = 3) PiKSO
Acid value (mg KOH/g)		**4.22. ± 0.03**
Oil content (wt.%)		**60 ± 0.01**
Saponification value (mg KOH/g)		**151 ± 1.11**
Molecular weight (g/mol)		**875.21 ± 3.48**
FFA (%)		**2.10 ± 0.03**
Higher Heating Value (MJ/kg)		**39.43 ± 0.04**
Density (g/cm^3)	at 20 °C	**0.873 ± 0.000**
	at 40 °C	**0.866 ± 0.000**
	at 60 °C	**0.857 ± 0.000**
Kinematic Viscosity (mm^2/s)	at 20 °C	**45.20 ± 0.08**
	at 40 °C	**37.82 ± 0.06**
	at 60 °C	**24.30 ± 0.04**
Oxidative Stability (h)		**13.50 ± 0.21**
Iodine value (g I_2/100 g)		**117 ± 0.88**
Moisture content (wt.%)		**0.16 ± 0.00**
Flash point (°C)		**266 ± 1**
Cetane number		**48 ± 0.05**
Glycerides (wt.%)	Monoglycerides	**0.96 ± 0.03**
	Diglycerides	**5.37 ± 0.01**
	Triglycerides	**93.67 ± 0.05**
Fatty acid composition (wt.%)	Palmitic acid, C16:0	**0.91 ± 0.35**
	Palmitoleic acid, C16:1	**0.84 ± 0.01**
	Stearic acid, C18:0	**1.30 ± 0.24**
	Oleic acid, C18:1	**50.65 ± 0.01**
	Linolenic acid, C18:3	**1.14 ± 0.01**
	Linoleic acid, C18:2	**12.92 ± 0.01**
	Tricosanoic acid, C23:0	**32.24 ± 0.31**
Fatty acid composition of PiKME (wt.%)	**Methyl esters**	**PiKME**
	Palmitic acid, C16:0	**0.27 ± 0.01**
	Palmitoleic acid, C16:1	**0.61 ± 0.01**
	Stearic acid, C18:0	**0.41 ± 0.08**
	Oleic acid, C18:1	**48.22 ± 0.06**
	Linolenic acid, C18:3	**0.86 ± 0.01**
	Linoleic acid, C18:2	**9.99 ± 0.01**
	Tricosanoic acid, C23:0	**27.64 ± 0.20**

Table 2
Experiment design by central composite design for transesterification process.

Process Parameters	−2	−1	0	+1	+2
Alcohol to oil molar ratio	3	8	13	18	23
Reaction time (min)	20	30	40	50	60
Catalyst loading (wt.%)	0.5	2	3.5	5	6.5
Amplitude (%)	30	40	50	60	70

catalyst concentration (2–5 wt.%) and ultrasonic amplitude (30–70%) on yield of methyl ester (wt.%) by utilising RSM, which relies upon a CCD Table 2. Methyl ester yield was calculated using the following Eq. (1).

$$\text{Methyl ester yeild (wt.\%)} = \frac{\text{Amount of methyl ester produced(g)}}{\text{Amount of oil required(g)}} \times 100 \tag{1}$$

Two-level factorial design based on CCD (for 4 independent variables) was used and in total experiments was 30 ($=2^k + 2k + 6$), where k represents a number of independent experimental variables. Regression coefficients obtained by CCD for optimisation of the reaction settings. These coefficients were estimated by using fitting experimental data to second-order multiple regression models. Analysis of variance (ANOVA) was applied to the engendered data for insight into the interaction among the variables. Response surfaces were generated using Design Expert 8 software.

3. Results and discussion

3.1. Oil properties

The seeds were found to contain 60 wt.% PiKSO after soxhlet extraction with *n*-hexane (Table 1). Earlier reports have shown the influence of various parameters affecting oil yield. The maximum yield of 77.5 wt.% oil was obtained by using the pulsed mood of UC assisted solvent extraction (PULSE) technique at 50% amplitude and at 50 °C (Hashemi et al., 2015). However, this potential feedstock has not been explored earlier for biodiesel production. This is supposed to be the first work reporting the viability of this potential candidate for biodiesel synthesis. Among fatty acids, oleic acid (18:1) was found to be most suitable with a value of (50.65 ± 0.01) wt.%. This was in line with the values reported in open literature. Tricasonoic acid (23:0) was found be another important fatty acid, which contributes a sizeable share of (32.24 ± 0.31) wt.%. It was found to be a leading saturated fatty acid in the oil which has not yet been reported in earlier studies. The fatty acid composition of PiKSO also depicted in Table 1 and GC analysis shown in Fig. 4.

PiKSO and *Pistacia khinjuk* methyl ester (PiKME) were further characterised for via Fourier transform infrared spectroscopy (FTIR). The spectrum of PiKSO is shown in Fig. 3(a). The range of absorption band from 2,922 to 2,853 cm^{-1} confirmed the symmetric and anti-symmetric stretching vibration of the CH_2 and CH_3 bonds. At 1,744 cm^{-1}, stretching vibration of carbonyl (C=O) group was confirmed the presence of TG. The stretching from 1,461 to 1,237 cm^{-1} indicated the presence of $-CH_2$ and $-CH_3$. The ester (C−O) peaks from 1,195 to 1,031 cm^{-1} were revealed the presence of ester. PiKME spectrum was depicted in Fig. 3(b). The bands were fallen in the range of 3,009–2,853 cm^{-1} while portrait symmetric and asymmetric stretching confirms the vibration of the methyl bonds ($-CH_3$). The stretching of the carbonyl group (−C=O) was depicted by peak 1,742 cm^{-1}. While the region from 1,243 to 1,118 cm^{-1} was depicted the (C−O−C) group. The hydrocarbon was observed in the range of 1,031–721 cm^{-1}. The FTIR results of Ahmad et al. (2014) confirms the PiKSO conversion to PiKME.

3.2. Optimisation of process parameters by response surface methodology

Detailed experimental results of methyl ester yield with actual values are shown in Table 3. For process optimisation, four independent factors with minimum and maximum ranges: i.e., MR (A) of 6:1–18:1, reaction time (B) of 20–60 min, catalyst loading (C) of 2–5 wt.% and amplitude (D) of 30–70% were planned and 30 experiments were executed by Design of Expert 8 software. The obtained results were further tested by ANOVA. This was expedient to validate the fitness and significance of the model. It also gave valuable information about the precision of the model. Table 3 bears the effects of individual variables and interactions on yield (response). Coded values obtained from the estimation of data were utilised to establish a quadratic regression model. Eq. (2) represents the established model. It can be seen that the model is based upon the coded values for biodiesel yield. Methods (*p*-values, student *t*-test) suggested by Montgomery (2008) were utilised to evaluate the significance of each coefficient. ANOVA result (Table 4) revealed that the model was significant for a probability of error (*p*-value) value of < 0.0001 to successfully predict yields of methyl ester. According to Table 4, catalyst loading and amplitude were found to be

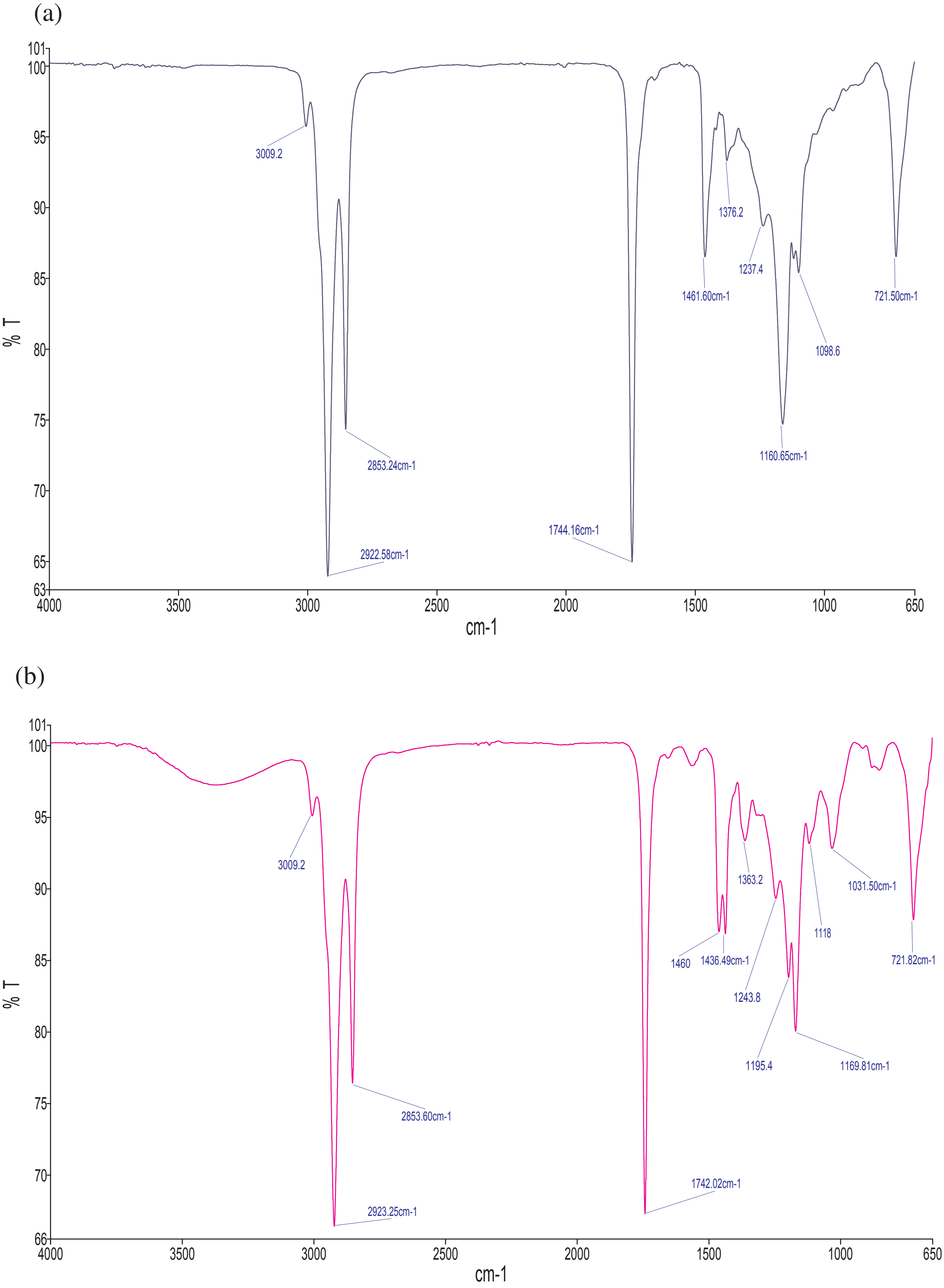


Fig. 3. FTIR analysis of (a) PiKSO and (b) PiKME.

the most significant factors and showed momentous impact on biodiesel yield. Among the parametric interaction, alcohol to oil ratio (A) x amplitude (D) and reaction time (B) x amplitude has been found most significant (p-value < 0.05) while the quadratic term of reaction time D^2 was observed to be least significant (p-value > 0.05). The coefficient of determination, R^2, measures that how accurately the model predicts values for the response. A value, $R^2 = 0.93$ was reasonably good for methyl ester validating the experimental data and the model

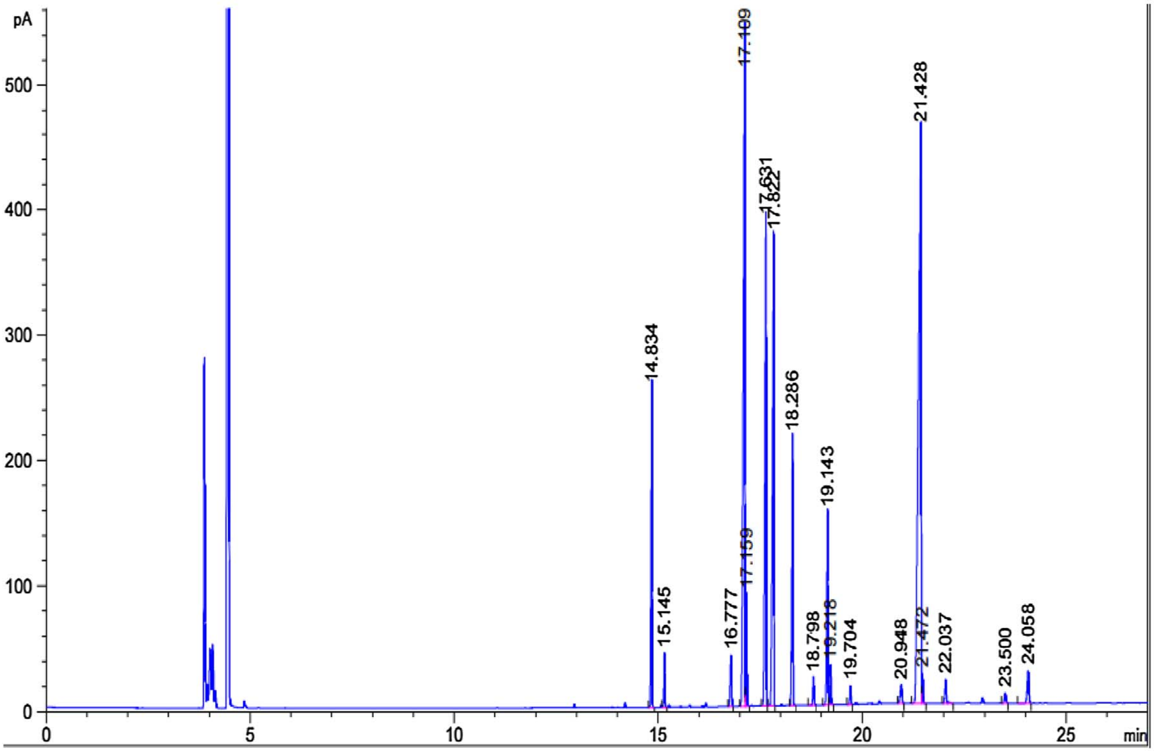


Fig. 4. GC analysis of PiKME.

Table 3
Detailed experimental results for transesterification process.

Run	Type	A:Alcohal to oil ratio	B:Reaction Time (min)	C:Catalyst loading (wt.%)	D:Amplitude	PiKME yield (wt.%)
1	Center	13	40	3.5	50	86
2	Factorial	8	50	2	40	67
3	Center	13	40	3.5	50	80
4	Center	13	40	3.5	50	83
5	Factorial	8	30	5	40	72
6	Axial	13	40	3.5	30	79
7	Axial	13	40	6.5	50	70
8	Factorial	18	30	5	60	66
9	Center	13	40	3.5	50	85
10	Factorial	8	30	2	40	62
11	Factorial	8	30	2	60	71
12	Center	13	40	3.5	50	88
13	Factorial	8	30	5	60	70
14	Axial	3	40	3.5	50	44
15	Center	13	40	3.5	50	83
16	Factorial	18	50	2	40	70
17	Factorial	18	30	5	40	75
18	Axial	23	40	3.5	50	50
19	Axial	13	60	3.5	50	90
20	Factorial	8	50	5	40	69
21	Factorial	18	50	5	40	68
22	Factorial	18	30	2	40	65
23	Factorial	18	50	5	60	76
24	Factorial	8	50	2	60	83
25	Axial	13	40	3.5	70	88
26	Factorial	8	50	5	60	80
27	Axial	13	40	0.5	50	42
28	Factorial	18	50	2	60	70
29	Factorial	18	30	2	60	61
30	Axial	13	20	3.5	50	88

Table 4
Analysis of variance for transesterification process.

Sample	Source	Sum of squares	df	Mean square	*F*-value	Prob. > *F*
PiKME	Model	4229.883	14	302.1345	14.23298	< 0.0001
	A-Alcohol to oil ratio	5.041667	1	5.041667	0.237503	0.6331
	B-Reaction time	84.375	1	84.375	3.974745	0.0647
	C-Catalyst loading	287.0417	1	287.0417	13.52198	0.0022
	D-Amplitude	92.04167	1	92.04167	4.335907	0.0549
	AB	3.0625	1	3.0625	0.144269	0.7094
	AC	7.5625	1	7.5625	0.356255	0.5595
	AD	95.0625	1	95.0625	4.478213	0.0515
	BC	27.5625	1	27.5625	1.298417	0.2724
	BD	105.0625	1	105.0625	4.949293	0.0419
	CD	10.5625	1	10.5625	0.497579	0.4914
	A^2	2247.503	1	2247.503	105.8756	< 0.0001
	B^2	57.50298	1	57.50298	2.708855	0.1206
	C^2	1269.074	1	1269.074	59.78367	< 0.0001
	D^2	0.145833	1	0.145833	0.00687	0.9350
	Residual	318.4167	15	21.22778		
	Lack of fit	279.5833	10	27.95833	3.599785	0.0850
	Pure error	38.83333	5	7.766667		
	Cor Total	4548.3	29			

R^2 = 0.93, C.V. = 6.34%, Std. dev. = 4.61, Adeq precision = 14.32.

exactitude. Adequate precision measures the ratio of signal to noise; it relates the range of the predicted values at the design points to the average prediction error of the model, a ratio of greater than 4 is required. In this model, obtained ratio ≈ 14.324 specifies the sufficient model PiKME discrimination. Lack of Fit *F*-value of 3.599 infers that Lack of Fit is not prominent compared to the pure error and the model was significant. The equation in terms of coded factors can be expressed as Eq. (2).

$$\begin{aligned}&\text{PiKME yield}\\&(\text{wt.\%}) = +84.17 - 0.46 * A + 1.87 * B + 3.46 * C + 1.96 * D\\&- 0.44 * A * B + 0.69 * A * C - 2.44 * A * D - 1.31 * B * C + 2.56 *\\&B * D - 0.81 * C * D - 9.05 * A^2 + 1.45 * B^2 - 6.80 * C^2\\&+ 0.073 * D^2\end{aligned} \quad (2)$$

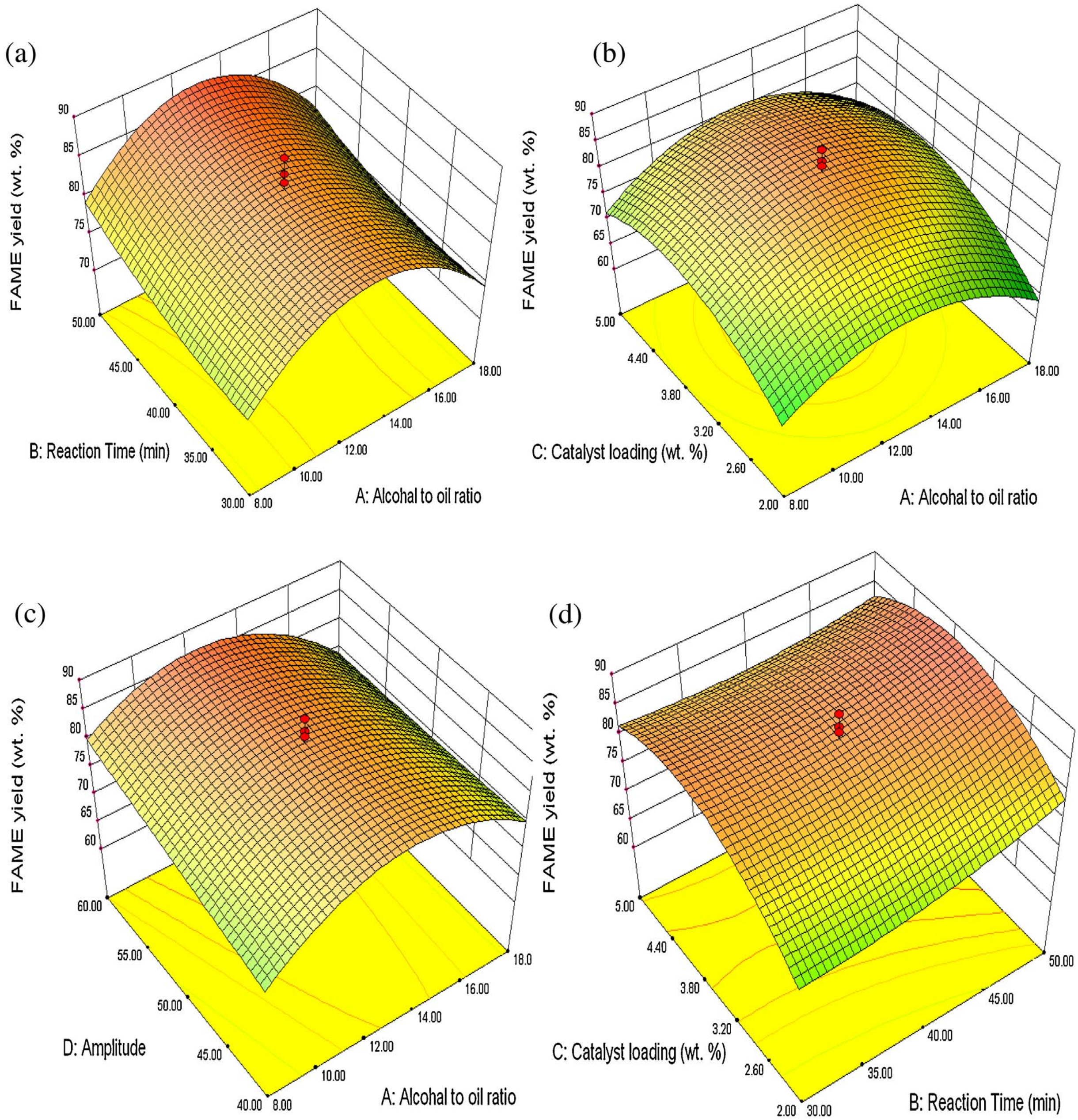


Fig. 5. Reaction parametric effects for PiKME.

3.3. Parametric interactions of transesterification

3.3.1. Influence of methanol to oil ratio

3D (a-f) plots were generated from the experimental data. Response surface 3D plots represent the effect of parametric interaction on methyl ester yield while keeping the other parameters at their respective centre points. Fig. 5(a) shows the interaction between reaction time and reactants' MR while keeping the other parameters at their centre values (ultrasonic amplitude of 50%, catalyst amount of 3.5 wt.% and explains the effect on PiKME yield). Alcohol to oil ratio is considered to be one of the most important parameters impelling the biodiesel yield. Stoichiometric calculations suggest that transesterification requires 3 mol of methanol to 1 mol of oil to yield 1 mol of glycerol and 3 mol of biodiesel. The surplus volume of methanol is inevitable in this equilibrium reaction to move methanolysis in a forward direction. By this equilibrium becomes favourable for biodiesel formation. In order to attain maximum FAME yield, many researchers suggest that MR of 6:1 is sufficient (Chuah et al., 2015b). In this study, MR's were studied from 6:1 to 18:1. Maximum methyl ester yield (88 wt.%) for PiKSO was recorded at MR of 13:1, in an about 45 min, while other variables were kept constant. A considerable decrease in yield was noticed with increase in MR. Beyond MR of 13:1 the separation of glycerol from ester was problematic. Higher MRs > 13:1, resulted in the diluted product of biodiesel and glycerol. Diluted products can initiate the reverse reaction and implicate no significant change in the conversion. UC intensifies the mass transfer between two phases by a formation of a fine emulsion. By this, the interfacial area between two phases is enhanced. Mass transfer coefficient is also escalated due to the presence of acoustic streaming and jet formation at the end of cavitation bubble collapse near the phase boundary of the methanol and oil. Interfacial area and mass transfer coefficient depending upon the amount of methanol and oil. Stavarache et al. (2007) also noticed the similar effects on yield due to the increase of methanol quantity in transesterification of vegetable oil in continuous mode.

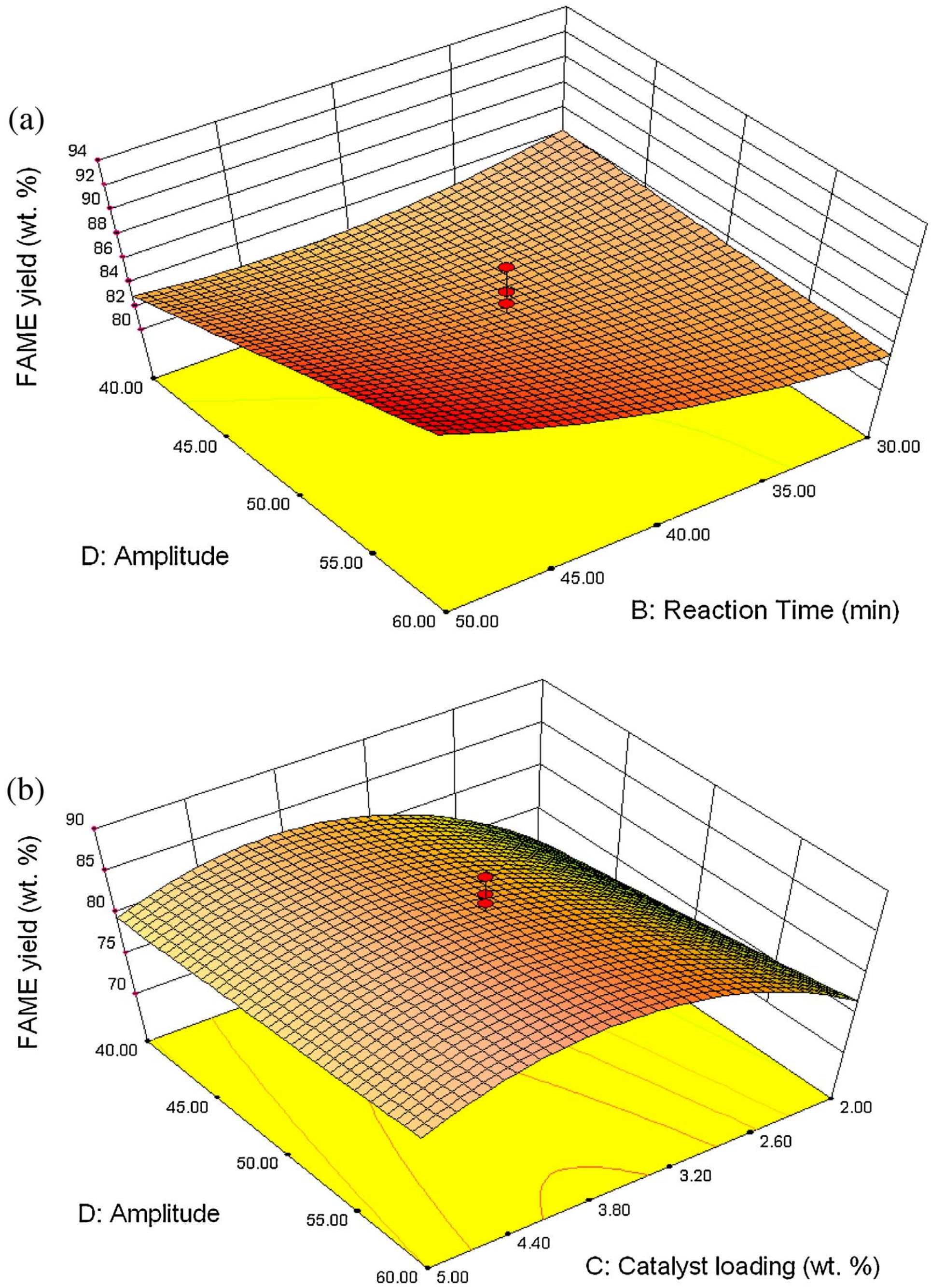
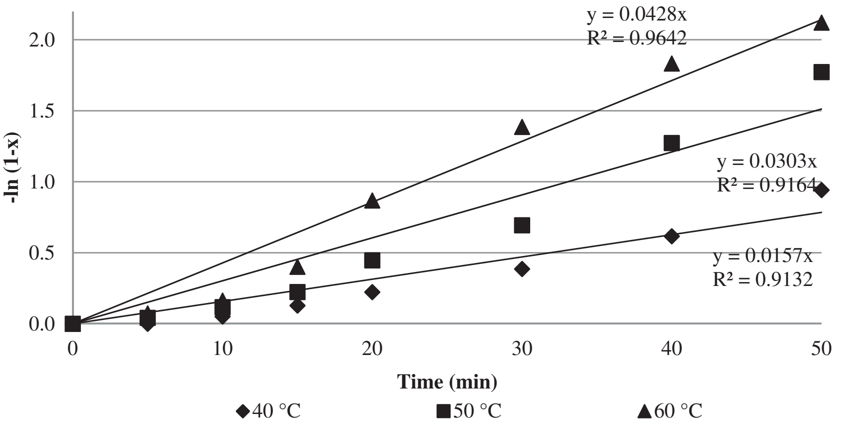


Fig. 6. Reaction parametric effects for PiKME.

3.3.2. Influence of catalyst loading

In transesterification process, the concentration of catalyst plays a vital role. From among available catalysts for biodiesel synthesis from low-grade oils with high FFA content, a heterogeneous acid catalyst was opted. Sulphated tin oxide (SO_4^{2-}/SnO_2) is among the few well- versed contender for esterification reactions owing to its very high acidity, which is called super acidity (Matsuhashi et al., 2001). $SO_4^{2-}/SnO_2–SiO_2$ was selected for this study due to its easy availability and good performance under mild reaction conditions. Due to its promising acidic properties, it has garnered considerable attention towards its applicability in one-step transesterification reaction (Lam et al., 2009). The strong acid sites of catalyst were provided a higher rate of reaction for transesterification process in the intensification environment via UC. This activity is significantly enhanced by sulphate concentration and calcination temperature. In order to study the effect of catalyst ($SO_4^{2-}/SnO_2–SiO_2$) loading on the conversion and rate of reaction, the transesterification reaction was conceded with calcined catalyst concentration of 2–5 wt.% at constant reaction temperature (T = 65 °C) using ultrasound irradiation. Literature references report that the utilisation of SO_4^{2-}/SnO_2 impregnated with an appropriate ratio of SiO_2 gives promising results in transesterification process via conventional methodology. However, up till now this very potential super acidic catalyst has not yet been explored/tested for UC intensification process. Figs. 5b and Fig. 66b show that reaction rate gradually increased with the increase in catalyst concentration from 2 to 3.5 wt.%. After attaining the optimum plateau, yield started to drop with the surge of catalyst loading. Similar results were observed while using $SO_4^{2-}/SnO_2–SiO_2$ (3 wt.%) for the transesterification of waste cooking oil (Lam et al., 2009), *Croton megalocarpus* oil (Kafuku et al., 2010a), *Moringa oliefera* oil (Kafuku et al., 2010b), *Jatropha curcas* oil (Kafuku et al., 2010c) and waste cooking oil with 6 wt.% of the $SO_4^{2-}/SnO_2–SiO_2$ catalyst (Lam and Lee, 2010). A significant parametric

a. Ultrasonic cavitation



b. Mechanical stirring

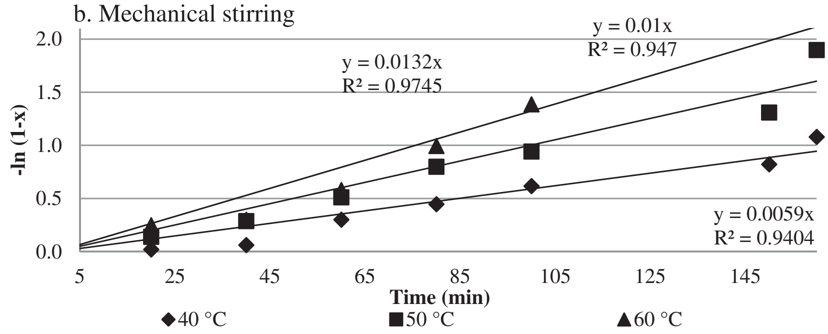


Fig. 7. Reaction kinetic for establishing the rate constant.

interaction between catalyst loading and amplitude can be seen from Fig. 6(b). PiKME yield has reached an optimum value with the catalyst amount up to 3.5 wt.% around 50% amplitude. The leading decisive factor for heterogeneous catalytic systems is the contact between the catalyst and the reactants. UC energy generated much smaller reactant droplets resulting in improving the utilisation between the reactants and the catalyst (Kumar et al., 2010).

3.3.3. *Influence of amplitude*

Fig. 5(c) illustrates the interactive effect between MR and ultrasonic amplitude while other parameters were kept at their centre values (reaction time of 40 min, the catalyst of 3.5 wt.%). Reasonable increments in PiKME yield can be seen with increasing ultrasonic amplitude from 40 to 60%. Further Fig. 6(a) explains the interactive effect between ultrasonic amplitude and reaction time; it can be established that at low reaction time, increasing ultrasonic amplitude led to an increase in the yield. This was so as increment in the ultrasonic amplitude at the initial stage of the reaction could lead to a noticeable increase in the reaction rate. Meanwhile, increasing amplitude beyond 60% under maximum reaction time (range) led to a decrease in the yield. This could be attributed to the generation of a large sized acoustic bubble at high ultrasonic amplitude (above 60%) (Kumar et al., 2010). These large sized cavitation bubbles are more stable and act as a barrier to the transfer of ultrasonic energy to reacting species and lead to poor emulsification. Similar behaviour of UC assisted biodiesel production systems could be observed at high UC energy (Stavarache et al., 2007). The role of moderate ultrasonic amplitude was also reported for different catalytic processes (Badday et al., 2013).

3.3.4. *Influence of reaction time*

UC was aided to overcome the mass transfer between alcohol and oil phase by supplements the energy by cavitation phenomena occurred. It results in a reduction of reaction time. Many researchers have reported that ultrasound reduces the processing time up to three times as compared to MS. For the comparison purpose, PiKME was synthesised under conventional mixing (600 rpm) for 3 h using the optimum UC reaction conditions. It was observed that PiKME yield was still below the optimum yield obtained by UC. Since this study focused on biodiesel production under UC, which has proven to be a function of time, therefore additional experiments were not performed at other reaction time for conventional mixing.

Lam et al. (2009) studied the conversion of waste cooking oil to biodiesel via MS reactor system using the same type of catalyst ($SO_4^{2-}/SnO_2–SiO_2$). They obtained an optimum yield of 92.35 wt.% at 150 °C and 10 bar of pressure for 3 h reaction time. Fig. 5(a,c,d) represent the interaction of reaction time with other parameters, it can be seen that with the escalation of reaction time the reaction rate has gradually increased at an optimum MR. This observation suggested that specified residence time is required for achieving optimum kinetic energy necessary to overcome the mass transfer limitation between oil and alcohol (Bokhari et al., 2016b). It was observed that a yield up to 84 wt.% of *Moringa oleifera* methyl ester could be obtained with the same catalyst at 150 °C after 150 min of conventional stirring reaction in pressurised container (Kafuku et al., 2010b).

4. Kinetics

Proposed mechanism for the PiKME production is a heterogeneous catalytic reaction. Pseudo first order kinetic acts as a function of TG concentration and governs this process. Limiting reactant designate is methanol due to its excess concentration (two times more). Excess methanol drives this equilibrium reaction to forward direction i.e. towards the formation of FAME.

Asif et al. (2017) transesterified non-edible feedstock in presence of CaO heterogeneous catalyst. They proposed a pseudo-first order kinetic model to correlate their experimental results.

Fig. 7 shows the plots of $-\ln(1\text{-}x)$ vs. time at different reaction temperature by using UC and MS, and the obtained rate constant from

Table 5
Comparison of reaction rate constants between ultrasonic cavitation and mechanical stirring.

Sample	Method	Temperature (°C)		
		40	50	60
PiKME	Rate constant for transesterification processing, min^{-1}			
	UC	0.015	0.030	0.042
	MS	0.005	0.010	0.013

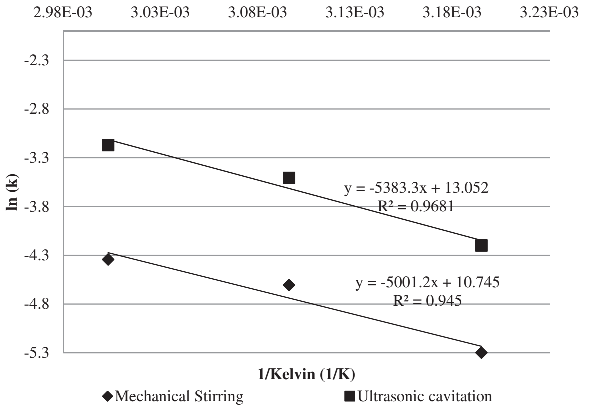


Fig. 8. Activation energy for mechanical stirring and ultrasonic cavitation.

these plots have been given in Table 5. Rate constant values for UC system were approximately 4.8 times higher than MS system when temperature raised from 40 to 60 °C. Deshmane and Adewuyi (2013) pseudo first order kinetic fitting's results resemble with the reported results of this work. The research focused on the synthesis of biodiesel from soybean oil in presence of sodium methoxide as a catalyst via UC system at various operating amplitudes and temperatures.

Conventional MS system usually requires extensive temperature and pressure conditions for heterogeneously catalysed transesterification reaction. Tri-phasic (oil, methanol and catalyst) behaviour of heterogeneous catalytic reaction slows down the reactivity of methanol on the surface of catalyst. UC remarkably enhances the adsorption of methanol over the catalyst to generate methoxide ion and increased the mass transfer between the reaction mixture. Oscillating cavities generated high-intensity micro level turbulences and thereby enhanced the synthesis of methyl ester. In UC process the high interfacial area efficiently eliminated the mass transfer resistance between methanol and TG during transesterification reaction. High local pressure and temperature are generated as cavities expand and compress intensely in few µs. By this, the forward reaction is favoured. High turbulence intensity of fluid flow is generated by the sudden collapse of cavities due to intensive compression and expansion. The rate of transport process is enhanced by the high turbulence intensity which leads to better yield. Temperatures ranged from 40 to 60 °C were selected and estimated rate constant for this range were further utilised to evaluate energy for PiKME. The plot of 1/K *vs* ln k is depicted in Fig. 8. For present study, Arrhenius expression for methyl ester synthesis using UC and MS can be expressed using Eqs. (3) and (4).

$$k = 4.65 \times 10^{5} e^{\frac{-44.7\ \text{kJ/mol}}{RT}} \quad (\text{for UC}) \tag{3}$$

$$k = 4.60 \times 10^{4} e^{\frac{-41.5\ \text{kJ/mol}}{RT}} \quad (\text{for MS}) \tag{4}$$

5. Comparison

Table 6 bears the optimised operating conditions for heterogeneous catalytic transesterification of PiKME. These values were estimated by numerical optimisation tool in RSM. Under same conditions, these optimised parameters were compared to MS. Prior their comparison these

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

	Current Study		Asif et al. (2017)	Mostafaei et al. (2015)
Parameters Optimum conditions	UC PiKME	MS	UC Salvadora alii oil	UC Waste cooking oil
1. Alcohol to oil molar ratio	13:1	13:1	10:1	1:6
2. Catalyst	$SO_4^{2-}/SnO_2–SiO_2$		CaO	KOH
3. Catalyst loading (wt.%)	3.5	3.5	3	1
4. Amplitude (%)	50	–	50	56
5. RPM	–	600	–	–
6. Time (min)	50	150	30	14
7. Pressure (bar)	–	10	–	–
8. Ester yield (wt.%)	88	88	92	97.21
9. Order of reaction	1st	1st	1st	–
10. Reaction rate constant for first order (min^{-1})	0.029	0.009	0.067	–
11. Reaction rate constant for second order ($L\,mol^{-1}\,min^{-1}$)	–	–	0.221	–

Biodiesel properties	EN 14214	ASTM D 6751	UC		
1. Density (15 °C, g/cm^3)	0.86–0.90	–	0.89	0.83	0.87
2. Kinematic viscosity, (40 °C, mm^2/s)	3.5–5.0	1.9–6.0	3.52	3.70	3.89
3. Flash point (°C)	≥120	≥130	147	136	172
4. Acid value (mg KOH/g oil)	≤0.5	≤0.8	0.10	0.20	0.42
5. Cloud point (°C)	–	–	8.0	11	–
6. Pour point (°C)	–	–	3.0	4	–
7. Oxidation stability (h)	–	≥6	17	21	6.09
8. Cold filter plugging point (°C)	–	–	4.9	–	–
9. Cetane number	≤51	≤47	53	–	–
10. Free glycerin (wt.%)	≥0.02	≥0.02	0.004	–	–
11. Total glycerin (wt.%)	≥0.24	≥0.24	0.01	–	–
12. Iodine value ($gI_2/100$ g)	< 120	–	88	–	98.26
13. Sulphur content (wt.%)	< 0.020	< 0.020	0.006	–	0.014

parameters were verified. For both MS and UC processes, the optimum conditions for methyl ester synthesis from PiKSO are listed in Table 6. For UC process within 50 min, PiKME showed 88 wt.% yield. At MS, drastically higher reaction time was required to attain better yield (150 min). MS relies upon propeller, which cannot homogenise reaction media as much as UC can do. The rate of mass transfer between immiscible alcohol and oil phase is increased by incremented homogenisation of reactants, which results in enhanced PiKME conversion. Biodiesel synthesised in a laboratory can only be used commercially if it is able to successfully fulfill the set standards for such fuels. These EN 14214 and ASTM D 6751standards contain the set of requirements for viable usage of biodiesels on the commercial scale. Any synthesised biodiesel, which meets the requirements of these standards possess the full potential for its large scale commercial usage. UC technology is capable of producing a biodiesel with a maximum yield at a minimum amount of catalyst and alcohol for transesterification reaction. Moreover, UC revealed excellent energy efficiency as compared to hydrodynamic cavitation and MS. The UC technology needed to be 1.4 kWh/m^3 for biodiesel synthesis. While, the hydrodynamic cavitation technology required was 32.0 kWh/m^3 and MS required 4.4 kWh/m^3 on identical reaction conditions (Asif et al., 2017). However, it is not necessary that any biodiesel which meets the set standards be immediately utilised in commercial diesel engines. A comprehensive database of other physiochemical properties and knowledge of present impurities is imperative in addition to the listed requirements.

6. Conclusion

Novel non-edible bio-waste (*Pistacia khinjuk* seed) was utilised for biodiesel synthesis. In this study, methyl ester has been successfully produced by using UC reactor. Transesterification reaction occurred well in the presence of heterogeneous acid catalyst viz. $SO_4^{2-}/SnO_2–SiO_2$. RSM identified the optimised conditions and parametric behaviour. Optimum conditions for PiKME has been revealed as MR of 13:1, catalyst amount of 3.5 wt.%, the amplitude of 50% and reaction time of 50 min. Under these conditions maximum ester yield ≈ 88 wt.% was attained. UC is more efficient in the triphasic behaviour of a heterogeneous catalyst in comparison to MS. It has been proved to provide an enough interfacial area to overcome mass transfer region and ultimately results in higher methyl ester yield. UC is concluded to be three-fold time saving and 3 fold higher reaction rate constant than MS. Majority of the PiKME fuel properties agreed well with EN 14214 and ASTM D6571 standards. It is further recommended to broaden the research area of methyl ester production by numerous non-identified waste seeds from non-edible plants. The waste seeds will be further investigated in depth and convert to methyl ester under consideration of various technologies and multiple catalysts.

Acknowledgments

The authors would like to thank Higher Education Commission (HEC) of Pakistan, Prof Dr Keat Teong Lee, Mr Niaz Mohammad Tareen, Universiti Sains Malaysia, Biomass Processing Lab of Universiti Teknologi PETRONAS, Universiti Malaysia Terengganu and to the EU project Sustainable Process Integration Laboratory – SPIL, funded as project No. CZ.02.1.01/0.0/0.0/15_ 003/0000456, by Czech Republic Operational Programme Research and Development, Education, Priority 1: Strengthening capacity for quality research.

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