

6.1 Introduction

The present chapter deliberates the application of potassium aluminum oxide ($K_2Al_2O_4$) as heterogeneous base catalyst for biodiesel production via transesterification reaction of feedstocks used vegetable oil and kusum oil. To maximize the catalytic activity of $K_2Al_2O_4$, various reaction parameters influencing the conversion in transesterification such as methanol: oil molar ratio, catalyst dose, temperature, reaction time and stirring speed were optimized and deliberated with aids of graphs. The reusability of synthesized catalyst was also investigated as it is an important aspect in designing the economics of chemical reaction. In addition, the kinetics and thermodynamic analysis of transesterification reaction of both the feedstocks used vegetable oil and kusum oil were performed by using the Arrhenius and Eyring equations. The used vegetable oil biodiesel and kusum oil biodiesel were characterized by 1H and ^{13}C -NMR techniques as well as GCMS for its fatty acid methyl ester composition. Furthermore, the physicochemical properties of synthesized used vegetable oil biodiesel and kusum oil biodiesel such as acid value, density, kinematic viscosity (40 °C), calorific value, flash point, fire point and cetane number were investigated according to ASTM standards.

6.2 Biodiesel synthesis from used vegetable oil using $K_2Al_2O_4$ catalyst

6.2.1 Optimization of biodiesel production parameters

To attain the maximum performance, optimization studies were performed for transesterification of used vegetable oil using $K_2Al_2O_4$ catalyst and discussed here within. The parameters for optimization were methanol: oil molar ratio 9:1- 21:1, catalyst dose 1-3 wt%, reaction time 0-90 min, temperature 35-75±0.5 °C, and stirring speed 300-700 rpm. All

the experiments were conducted thrice and mean values were used for calculations and explained. **6.2.1 (a) Effect of methanol to oil molar ratio**

The effect of methanol: oil molar ratio was observed by executing a series of transesterification reactions by varying the molar ratio from 9:1- 21:1 for each reaction time 0-90 min, using catalyst dose 2.5 wt% at 65 ± 0.5 °C and stirring speed of 600 rpm. The higher product yield with accretion in molar ratio of methanol from 9:1 to 18:1 was owing to excess methanol in reaction mixture facilitates to shift the reaction to the product side. At a high molar ratio of reactant increases certain contact between the methanol and triglyceride molecules and methyl ester formation increases [Tan et al., 2015].

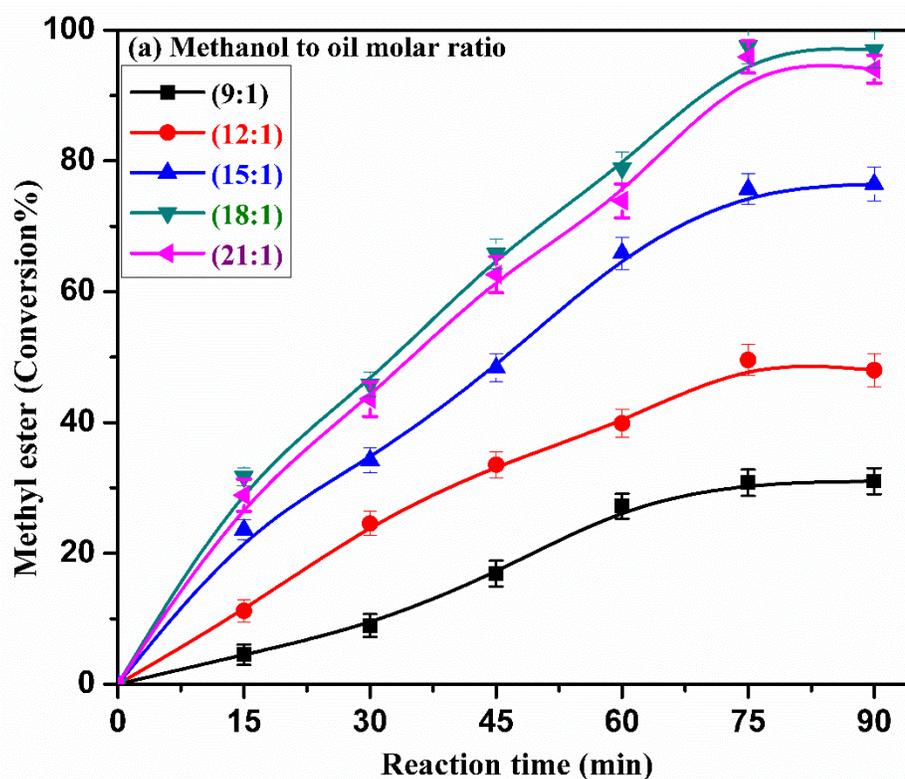


Figure 6.1 Effect of methanol: oil molar ratio (9:1 - 21:1) on methyl ester conversion (%) of used vegetable oil [catalyst dose (2.5 wt%); reaction time 0-90 min; temperature 65 ± 0.5 °C and stirring speed 600 rpm]

As observed in Figure 6.1, the maximum conversion 98.02% was achieved at methanol: oil molar ratio 18:1 and further increase in ratio beyond 18:1 resulted in lessening the biodiesel conversion to be 97.05% at 21:1 molar ratio of methanol: oil at the same reaction time. Beyond the optimum methanol: oil molar ratio, further addition of methanol in reaction media results in increased solubility of glycerol and unfavourable glycerolysis reaction of methyl ester that drives the equilibrium in the reverse direction resulting in a lower conversion of biodiesel [Xie and Huang, 2006]. Therefore, methanol to oil molar ratio of 18:1 was considered as optimal ratio in the present study.

6.2.1 (b) Effect of catalyst dose

In order to optimize the amount of catalyst $K_2Al_2O_4$, it was varied from 1 wt% to 3 wt% with respect to initial oil weight and keeping other parameters such as molar ratio of methanol: oil 18:1, temperature 65 ± 0.5 °C and stirring speed 600 rpm with varying reaction time 0-90 min. Increase in catalyst amount enhanced the contact of catalytically active sites and reactant. The maximum conversion (98.02%) was achieved at 2.5 wt% amount of catalyst as shown in Figure 6.2. Further increase in catalyst amount, there was a slight decrease in biodiesel conversion which could be attributed to mass transfer limitations caused by soap and emulsion formation. The soap and emulsions increase the viscosity, formation of foams and thus increase the liquid-solid mass transfer limitation in reaction media [Moggia et al., 2006].

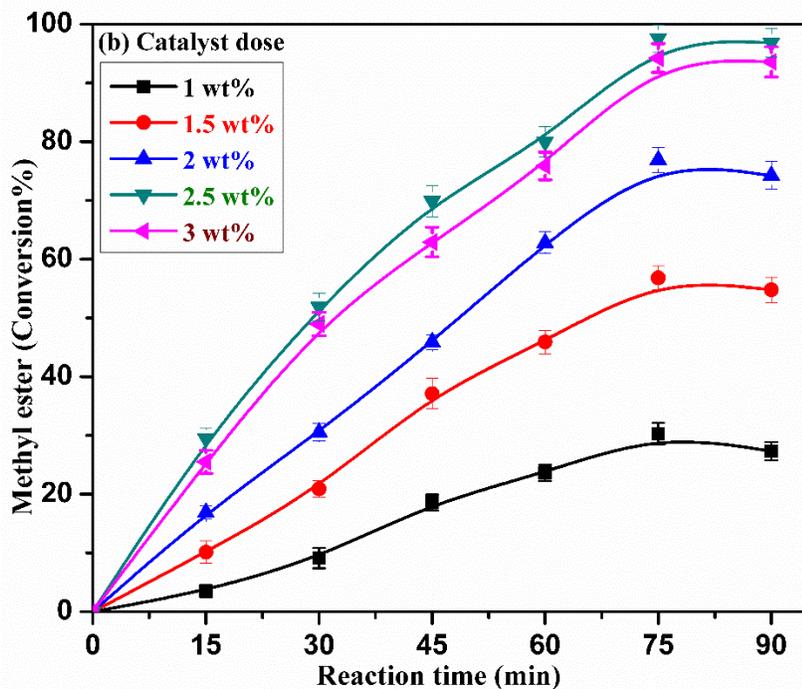


Figure 6.2 Effect of catalyst dose (1-3 wt%) on methyl ester conversion (%) of used vegetable oil [methanol: oil molar ratio 18:1; reaction time 0-90min; temperature 65 ± 0.5 °C and stirring speed 600 rpm]

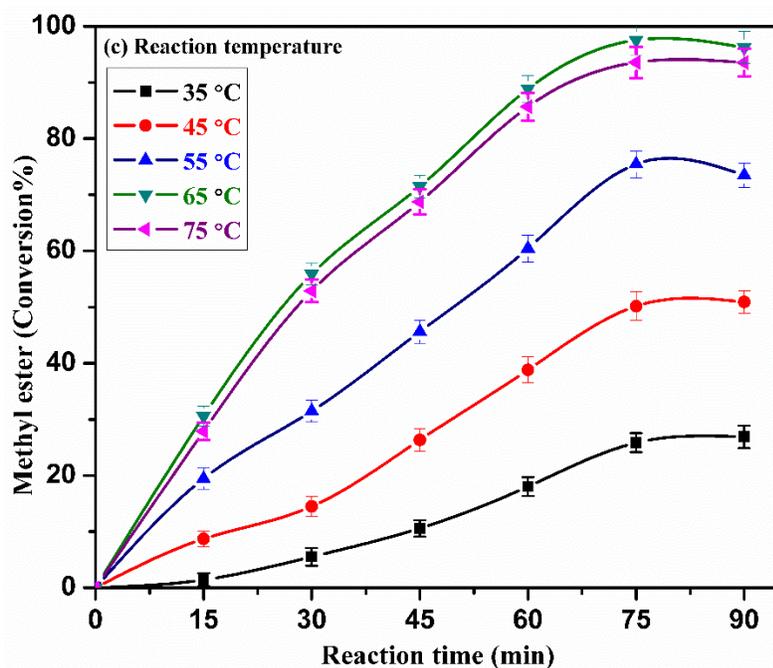


Figure 6.3 Effect of reaction temperature ($35-75 \pm 0.5$ °C) on methyl ester conversion (%) of used vegetable oil [methanol: oil molar ratio 18:1; catalyst dose 3 wt%; reaction time 0-90 min; and stirring speed 600 rpm]

6.2.1 (c) Effect of reaction temperature

Figure 6.3 illustrates the effect of temperature on methyl ester conversion of used vegetable oil. It was studied from 35 ± 0.5 °C to 75 ± 0.5 °C at interval of 10 °C with methanol: oil molar ratio 18:1, catalyst amount 2.5 wt%, at 600 rpm stirring speed with varying reaction time 0-90 min. The reaction temperature strongly affects the biodiesel production. The conversion gradually increases with the rise in the temperature from 35 ± 0.5 °C to 65 ± 0.5 °C as a result of high rate of reaction and further decreases beyond 65 ± 0.5 °C at the same reaction time. The optimum conversion 98.02% was attained at 65 ± 0.5 °C as it is methanol reflux temperature.

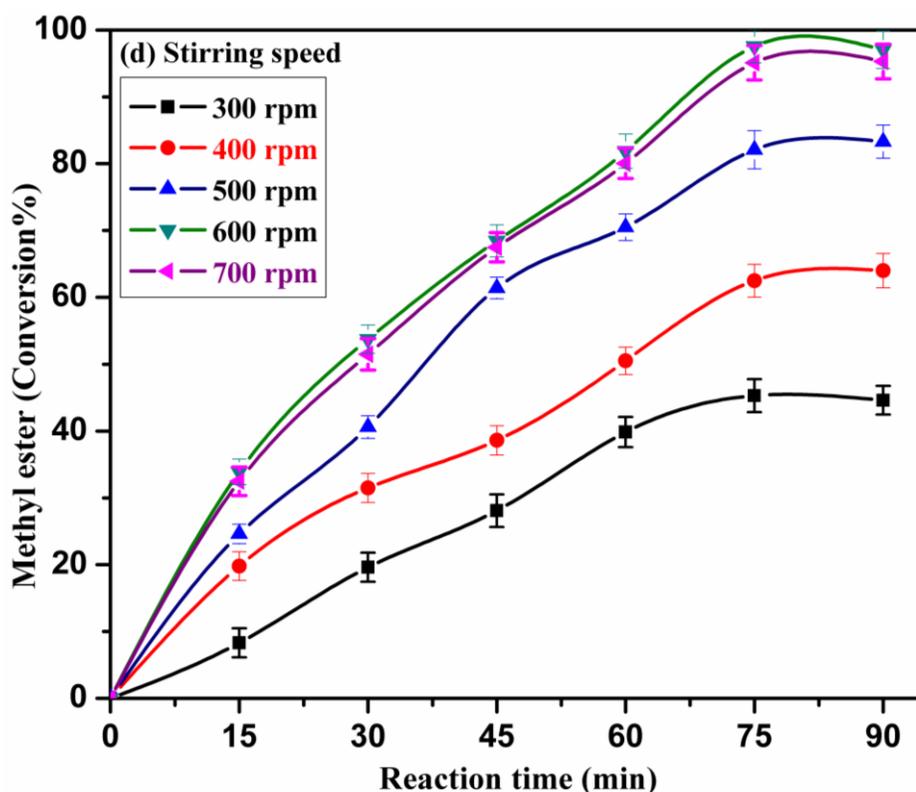


Figure 6.4 Effect of stirring speed (300-700 rpm) on methyl ester conversion (%) of used vegetable oil [methanol: oil molar ratio 18:1; catalyst dose 2.5 wt%; reaction time 0-90 min; temperature 65 ± 0.5 °C]

At high temperature ($> 65 \pm 0.5$ °C), methanol evaporation will form bubbles which inhibit the contact of reactants with catalyst at phase interface [Baskar and Soumiya, 2016].

6.2.1 (d) Effect of stirring speed

The stirring speed plays an important role as transesterification reaction is a biphasic reaction involving liquid phase; oil, methanol and solid phase $K_2Al_2O_4$ catalyst. Without stirring of reaction media, no biodiesel is produced. The stirring speed was studied by varying rpm 300 to 700 rpm at the reaction conditions methanol: oil molar ratio 18:1, catalyst dose 2.5 wt%, 65 ± 0.5 °C, reaction time 0-90 min. Below 600 rpm mixing speed, low methyl ester conversion was accomplished. Faster speed improves the mass transfer rate. Equilibrium conversion at 600 rpm was observed as shown in Figure 6.4. Further rise in mixing inhibits effective contact time to interact reactants so conversion decreases. Therefore, 600 rpm was appropriate for the transesterification [Costa et al., 2016].

6.2.2 Reusability

Figure 6.5 depicts the conversion results of reutilized and regenerated catalyst for transesterification reaction at optimized reaction conditions such as methanol: oil molar ratio 18: 1, catalyst dose 2.5 wt %, 65 ± 0.5 °C, reaction time 75 min and stirring speed of 600 rpm. For each transesterification reaction, fresh reactant substrates were used. The methyl ester conversion got dropped slowly from 98.02 % to 83.19 % at the end of fifth run indicating catalyst stability up to pertaining reaction cycle [Singh and Patel, 2014]. The stable and well crystalline structure may responsible for high reusability of catalyst sample ($> 80\%$

conversion in 5th reaction run). The catalyst exhibited to be very reusable under ambient conditions runs.

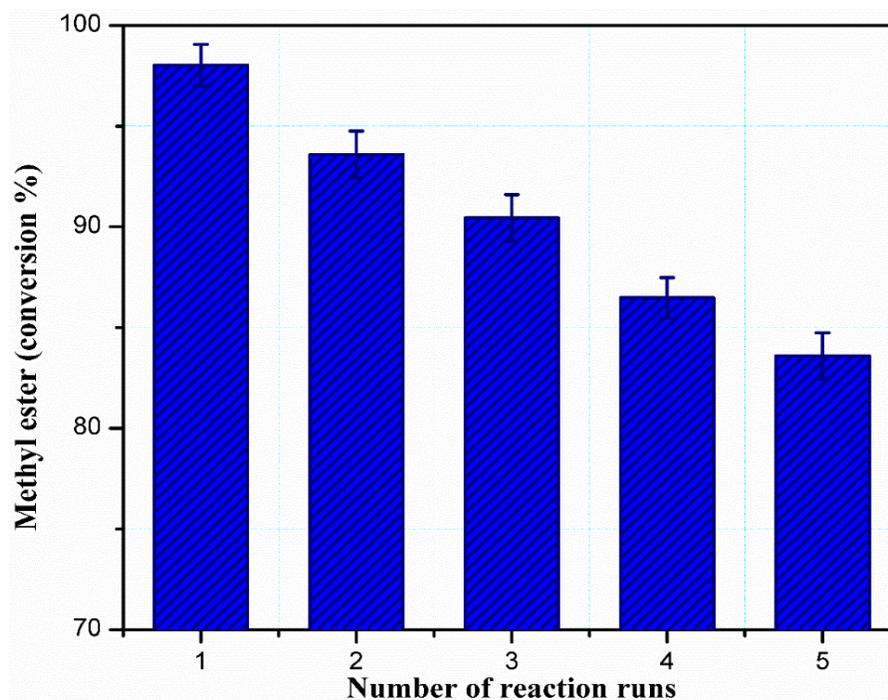


Figure 6.5 Reusability test for the $K_2Al_2O_4$ catalyst at optimized conditions [methanol: oil molar ratio 18:1; catalyst dose 2.5 wt%; reaction time 75 min; temperature 65 ± 0.5 °C and stirring speed 600 rpm]

The blockage of pore by irreversible adsorption of reaction molecules or loss of catalyst amount during reusability may responsible for slight loss of catalyst amount [Amani et al., 2016].

6.2.3 Kinetics and thermodynamic study

In order to elaborate the rate of reaction, required activation energy and free energy, the kinetics and thermodynamic studies were accomplished for transesterification reaction of used vegetable oil using Arrhenius and Eyring equation. Multiple batch reactions using isocondition (18:1 methanol: oil molar ratio, catalyst dose of 2.5 wt% of $K_2Al_2O_4$ and stirring

speed 600 rpm with varying reaction time 0-75 min and temperature 35-65±0.5 °C were carried out as depicted in Figure 6.3.

6.2.3 (a) First-order kinetics

The kinetic plot $-\ln(1-X)$ vs. time at varying reaction temperature exhibited a higher linear relationship as depicted in Figure 6.6 which favors the well-fitting of pseudo first-order kinetic model of transesterification of used vegetable oil in presence of $K_2Al_2O_4$ catalyst. The slope of these straight lines gives the value of the rate constant at different temperature and presented in Table 6.1 with their respective regression coefficients [Malani et al., 2017].

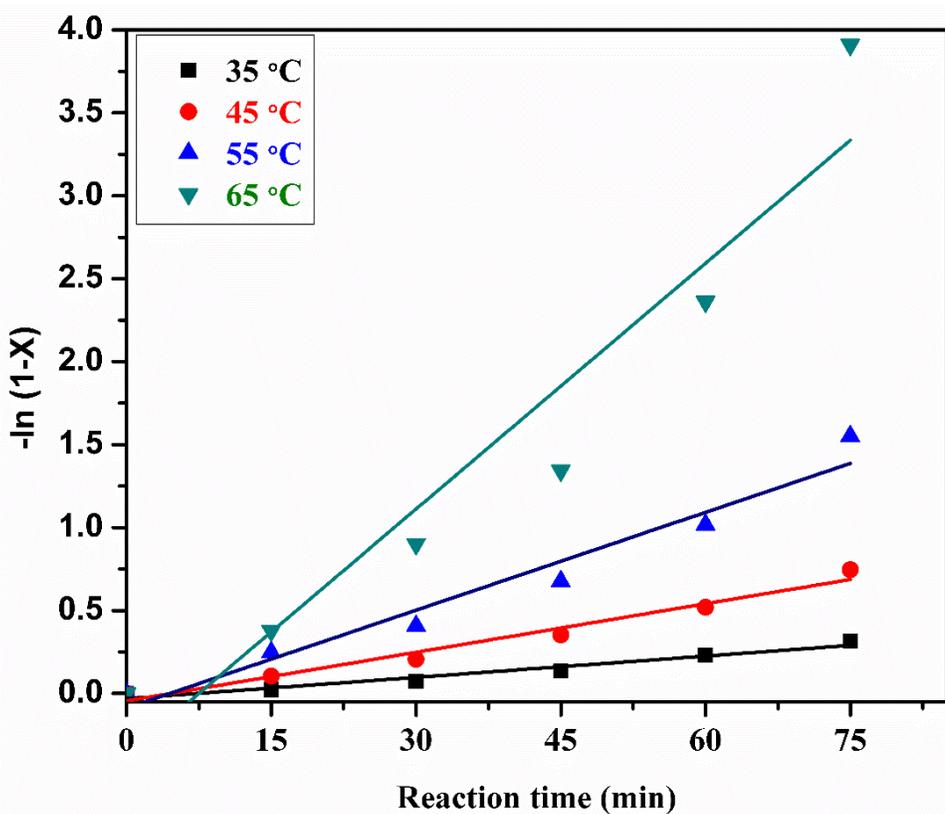


Figure 6.6 Kinetics plots of $-\ln(1-X)$ versus reaction time (min) at different reaction temperatures

Table 6.1 Reaction rate constants at different temperatures

Temperature (°C)	Reaction rate constant (10^{-2} , min^{-1})	Regression coefficient (R^2)
35	0.428	0.85
45	0.976	0.96
55	1.967	0.94
65	4.941	0.90

6.2.3 (b) Activation energy calculation

As we can see in Table 6.1, temperature exerts positive influence on rate of reaction. In addition, the activation energy of the reaction process was investigated using a relationship between the rate constant value (k), reaction temperature (T) in kelvin and activation energy (E_a). The plot of $\ln(k)$ vs. $1/T$ gives a straight line with negative slope by linear fitting and slope and intercept equal to $-E_a/R$ and $\ln(A)$ respectively as shown in Figure 6.7. The value of E_a and A were 71.169 kJ/mol and $4.57 \times 10^9 \text{ min}^{-1}$ respectively for transesterification of used vegetable oil and $\text{k}_2\text{Al}_2\text{O}_4$ catalyst [Choudhury et al., 2014].

6.2.3 (c) Thermodynamic study

In the present study, the thermodynamic parameters change in enthalpy (ΔH) and entropy (ΔS) were deliberated using the Eyring-Polanyi equation. The Eyring-Polanyi plot (Figure 6.7) in between $\ln(k/T)$ and $1/T$ exhibits intercept and slope equal to $\left[\ln \frac{kB}{h} + \frac{\Delta S}{R}\right]$ and $\frac{-\Delta H}{R}$ respectively. The value of ΔH and ΔS were found to be $66.57 \text{ kJ mol}^{-1}$ and $-0.0777 \text{ kJ mol}^{-1} \text{ K}^{-1}$ respectively [Malani et al., 2017]. The Gibbs free energy (ΔG) was inferred at different temperature and presented in Table 6.2.

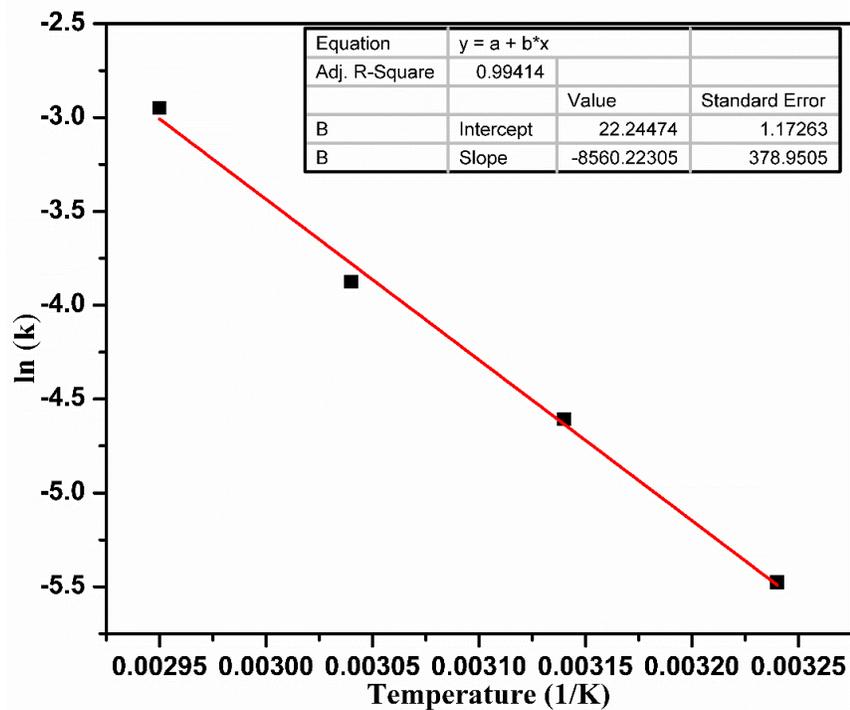


Figure 6.7 Arrhenius plot $\ln k$ vs. $(1/T)$ relation of transesterification of used vegetable oil using $K_2Al_2O_4$

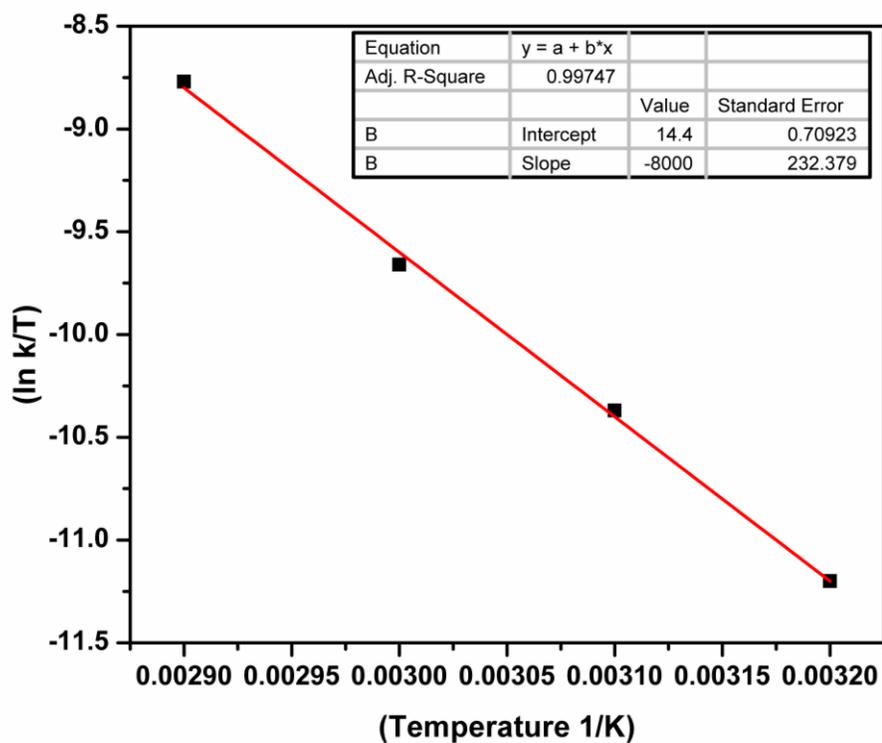


Figure 6.8. Eyring- Polanyi plot $(\ln k/T)$ versus $1/T$ of transesterification of used vegetable oil using $K_2Al_2O_4$

Table 6.2 Calculated values of various thermodynamic parameters

Thermodynamic Functions	Enthalpy (ΔH) (kJ mol ⁻¹)	Entropy (ΔS) (kJ mol ⁻¹ K ⁻¹)	Gibbs free energy (ΔG) (kJ mol ⁻¹)			
			308 K	318K	328K	338K
Values	66.57	-0.0777	90.28	91.05	91.82	92.59

In the present study, positive value of ΔG and ΔH , as well as negative value of ΔS , were obtained, which defines the unspontaneous and endothermic characteristics of transesterification of used vegetable oil in presence of $K_2Al_2O_4$ catalyst.

6.2.4 Green matrix formulation

To investigate the environmental impact of the present biodiesel synthesis reaction of used vegetable oil and $K_2Al_2O_4$ catalyst, *E*- factor and PMI values were determined. The minimum value of *E* factor and PMI value i.e. 2.91 and 3.91 respectively, indicates greener approaches of present biodiesel synthesis process.

6.2.5 Characterization of synthesized biodiesel

6.2.5 (a) NMR characterization (¹H and ¹³C)

Figure 6.9 depicts the ¹H NMR spectrum of used vegetable oil biodiesel synthesized from transesterification reaction using $K_2Al_2O_4$ catalyst. The synthesis of methyl ester in biodiesel was confirmed by characteristics peak of methoxy protons as a singlet at 3.68 ppm and α -methylene protons as a triplet at 2.32 ppm. The integration values of these peaks i.e. 3 and 2.04 respectively were used to calculate methyl ester conversion and it was found to be

$$98.02\% \text{ Methyl ester conversion } \% = \frac{2 \times 3}{3 \times 2.04} * 100 = 98.02\%$$

(6.1)

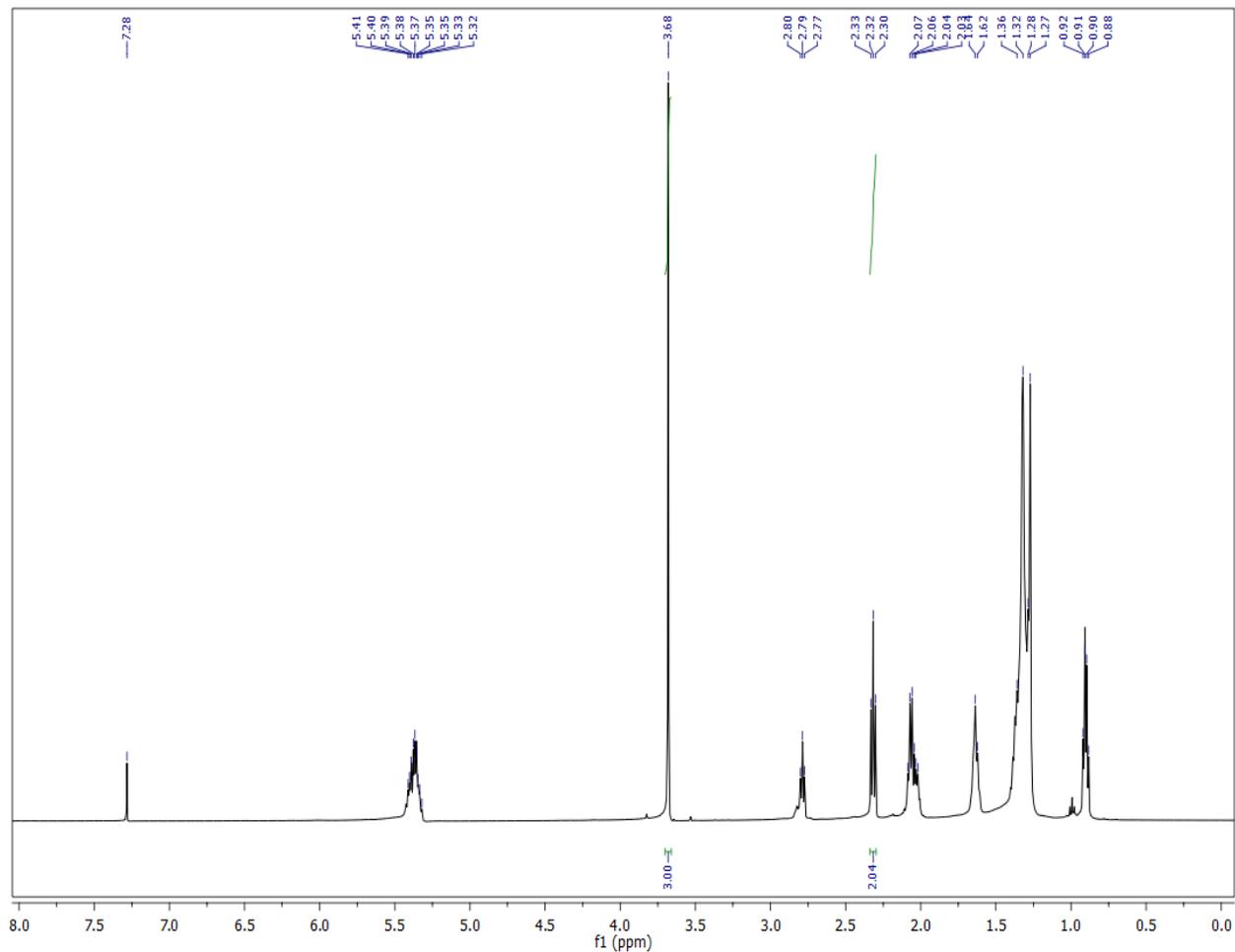


Figure 6.9 ¹H NMR spectrum of synthesized biodiesel from used vegetable oil

The other ¹H NMR peaks in spectrum at 0.88-0.90 ppm (multiplet); 1.27-1.36 ppm (multiplet); 1.62-1.64 ppm (doublet); 2.07-2.07 ppm (multiplet) and 2.77-2.80 ppm (triplet) were related to various kind of aliphatic protons as well as peaks at 5.32-5.41 ppm (multiplet) were due to olefinic protons in carbon chain of methyl ester.

A representative ^{13}C NMR spectrum of used vegetable oil biodiesel is presented in Figure 6.10. The peaks presented at 174.28 ppm and 51.40 ppm are characteristics peaks of ester carbonyl (-COO-) and (CO-) respectively. The peaks presented at 127.91-130.20 ppm were assigned to

unsaturation in carbon backbone. The other peaks in spectrum 22.56–34.10 ppm and 14.05-14.09 ppm presented due to methylene carbon of long carbon chain and terminal carbon of methyl group in biodiesel respectively [Mello et al., 2008].

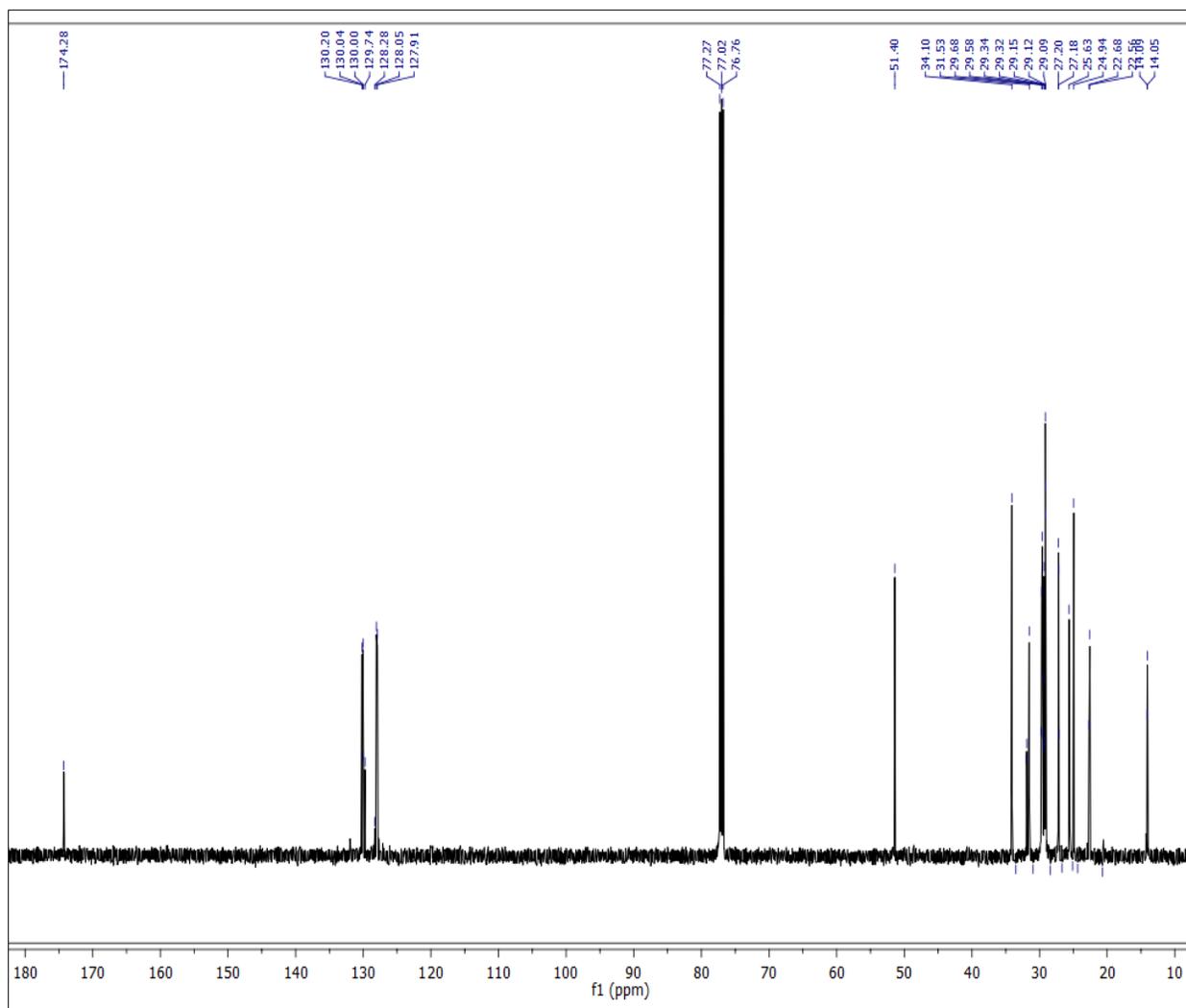


Figure 6.10 ^{13}C NMR spectrum of synthesized biodiesel from used vegetable oil

6.2.5 (b) Compositional analysis of FAME by GC-MS

The fatty acid composition of synthesized biodiesel was identified by GCMS analysis to investigate its suitability as fuel in the engine. The identified main compounds in biodiesel are presented in Table 6.3. The synthesized biodiesel contains three major constituents: Methyl hexadecanoate (39.21%); Methyl 9-octadecenoate (38.34%); Methyl(Z,Z,Z)-9,12,15-

octadecatrienoate (18.56%) followed by two minor constituents: Methyl cis-11-eicosenoate (1.94%) and Methyl docosanoate (1.92%). 39.21% of saturated, 42.20% of monosaturated and 18.56% of polysaturated fatty acid methyl esters were presented [Naureen et al., 2015]. The unsaturated compounds as major constituent reduce the viscosity of biodiesel and increase the cetane number [Tariq et al., 2011].

Table 6.3 Fatty acid methyl ester composition of Synthesized FAMES

Retention time (min)	% composition	Identified fatty acid methyl ester and their formula	Library Match	Corresponding acid
51.80	39.21	Methyl hexadecanoate (C ₁₇ H ₃₄ O ₂)	99	C16:0
57.72	38.34	Methyl 9-octadecenoate (C ₁₉ H ₃₆ O ₂)	99	C18:1
58.73	18.56	Methyl(Z,Z,Z)-9,12,15-octadecatrienoate (C ₁₉ H ₃₂ O ₂)	99	C18:3
63.42	1.94	Methyl cis-11-eicosenoate (C ₂₁ H ₄₀ O ₂)	99	C20:1
68.95	1.92	Methyl docosanoate (C ₂₃ H ₄₆ O ₂)	99	C22:1
Saturated fatty acid methyl ester				39.21%
Monounsaturated fatty acid methyl ester				42.20%
Polyunsaturated fatty acid methyl ester				18.56%

6.2.5 (c) Evaluation of fuel properties

The important fuel properties such as acid value, density, calorific value, flash point, kinematic viscosity (40 °C), fire point, cloud point, pour point and cetane number of used vegetable oil biodiesel were evaluated as per ASTM standards and results are shown in Table 6.4. The acid value of synthesized biodiesel was reduced to 0.3 mg KOH/g. Kinematic

viscosity and density are pivotal fuel quality parameter that directly influences the performance characteristics of fuel such as cetane number and calorific value. The kinematic viscosity and density of fuel were 0.878 g/cm^3 and $4.9 \text{ mm}^2/\text{s}$ which were within the range of standard. The calorific value of a fuel is the amount of energy (in form of heat) released during combustion of a unit quantity of fuel. The synthesized biodiesel had calorific value 44.80 MJ/kg which fails in ASTM standards limit [Ahmad et al., 2011].

Table 6.4 Comparison of fuel properties of synthesized biodiesel with diesel using ASTM specifications

Property	Units	Value	ASTM D 6751	Test method
Acid value	mg KOH/g	0.3	≥ 0.5	ASTM D 664
Density	g/cm^3	0.878	0.86 to 0.89	ASTM D 4052
Kinematic viscosity (40 °C)	mm^2/s	4.6	1.9 to 6.0	ASTM D 445
Calorific value	MJ/kg	44.80	>35	ASTM D 240
Flash point	°C	149	>120	ASTM D93
Fire point	°C	157	-	ASTM D93
Cloud point	°C	5	-3 to 12	ASTM D2500
Pour point	°C	7	-15 to 16	ASTM D97-05
Cetane number	-	48	>47	ASTM D976

The flash point and fire point of fuel i.e. 149 and 157 °C respectively are important characteristics related to the ignition temperature of fuel. The higher flash point and fire points than diesel fuel are responsible for fire safety. The cloud point and pour point are indicator of low-temperature applicability. The cloud point and pour point was found to be 5 and 7 °C which were within the standard limit. The ignitability of fuel is typically

characterized by its cetane index, and a high cetane index results in a shorter ignition delay. The synthesized biodiesel has 48 of cetane index which complies the recommended range for biodiesel as per ASTM standards. Based on above results of physicochemical characteristics, the synthesized biodiesel using UVO as feedstock and $K_2Al_2O_4$ catalyst can be a promising alternative for diesel engine assembly [Ahmad et al., 2011].

6.3 Biodiesel synthesis from kusum oil using $K_2Al_2O_4$ catalyst

6.3.1 Optimization of biodiesel production parameters

To achieve maximum performance of synthesized $K_2Al_2O_4$ catalyst on transesterification of kusum oil, reaction influencing variables such as methanol-to-oil molar ratio, catalyst dose, temperature, reaction time and stirring speed were optimized. Therefore, the reaction variables were varied as methanol: oil molar ratio 6:1-18:1, catalyst dose 0.5-2.5 wt%, temperature $35-75\pm 0.5$ °C, reaction time 0-90 min and stirring speed 300-700 rpm and all experiments were performed trice and their mean values were reported.

6.3.1 (a) Effect of methanol to oil molar ratio

Transesterification is reversible reaction, an excess of methanol is required to favour the forward reaction and improve the reaction rate. The effect of methanol: oil molar ratio on methyl ester conversion was investigated by performing a series of transesterification by varying the molar ratio from 1:6 to 1:18 for variable reaction time 0-90 min, 2.0 wt% of catalyst dose, 65 ± 0.5 °C temperature and stirring speed of 600 rpm. The conversion grew sharply and attained to maximum 97.56% when methanol: oil molar ratio was increased from 1:6 to 1:15 at 75 min of reaction time (Figure 6.11). High molar ratio of methanol promotes the formation of methoxy species on the base catalyst surface, leading to a shift in the equilibrium in the forward direction thereby, increased the methyl esters conversion [Singh et

al., 2016]. However, further increase in the methanol ratio beyond the optimum amount (>1:15), did not promote the reaction because of dissolution of glycerol in excess methanol, subsequently inhibited the reaction of methanol to the reactants and catalyst [Kafuku and Mbarawa, 2010].

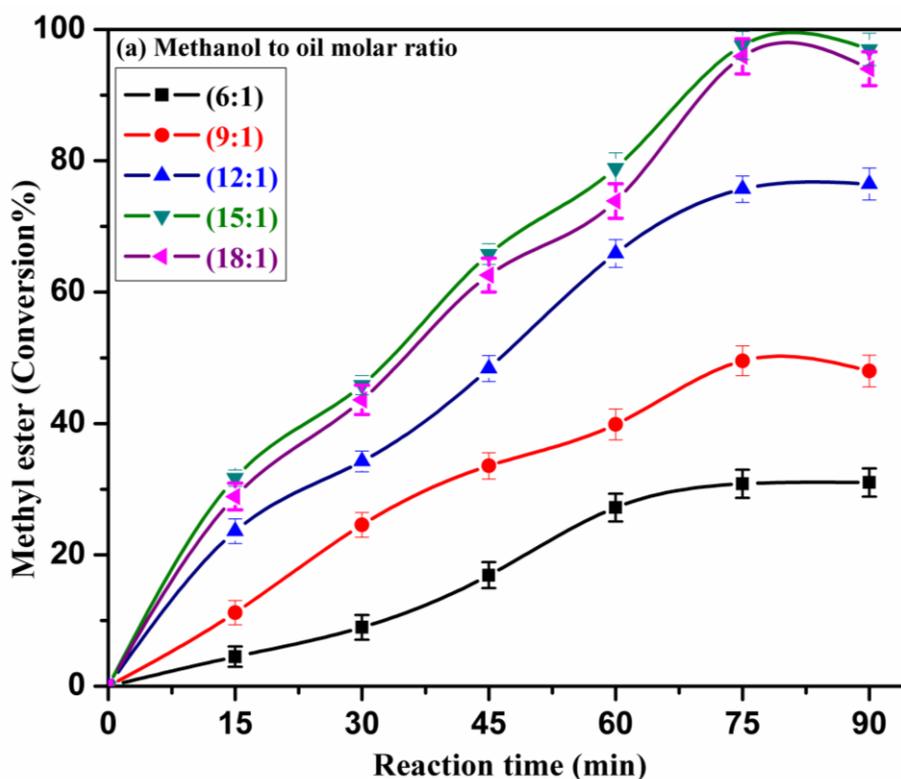


Figure 6.11 Effect of methanol: oil molar ratio (6:1-18:1) on methyl ester conversion (%) of kusum oil [catalyst dose (2.0 wt%); reaction time 0-90 min; temperature 65 ± 0.5 °C and stirring speed 600 rpm]

The unreacted methanol overturns the gravity decantation and decreased as the glycerol remains in the esters resulting in lower conversion. Therefore, methanol: oil 1:15 molar ratio was considered to be optimum [Zhang et al., 2015].

6.3.1 (b) Effect of catalyst dose

The methyl ester conversion is highly dependent on the amount of catalyst. The effect of catalyst dose (wt%) on conversion was investigated by varying the catalyst amount from 0.5 to 2.5 wt% with respect to initial oil weight at varying reaction time. The results clearly indicate (Figure 6.12) that the conversion of triglycerides increased as the catalyst was increased from 0.5 wt% to 2.0 wt% and attained to equilibrium conversion value 97.56% at 2.0 wt%. The increasing the catalyst amount, the availability of active sites increased for the transesterification reaction of oil [Wang et al., 2007]. However, further increase in the catalyst amount (>2.0 wt%) resulted in slight decrease in the conversion to 93.60%. At high catalyst concentration, the reaction mixture becomes viscous due to soap formation as well as mass transfer limitation between oil and methanol at increased solid interfaces in the reaction mixture, lowered the biodiesel production. Therefore, catalyst amount of 2.0 wt% was selected as the optimum value [Wan et al., 2010].

6.3.1 (c) Effect of reaction temperature

Rise in reaction temperature serves to overcome the energy barrier (i.e. activation energy) for a reaction to proceed. The effect of reaction temperature on methyl esters production was studied in the temperature range from 35 to 75 ± 0.5 °C as shown in Figure 6.13 whereas other reaction condition used were 15:1 methanol: oil molar ratio, 2.0 wt% catalyst dose, 0-90 min of reaction time and 600 rpm stirring speed.

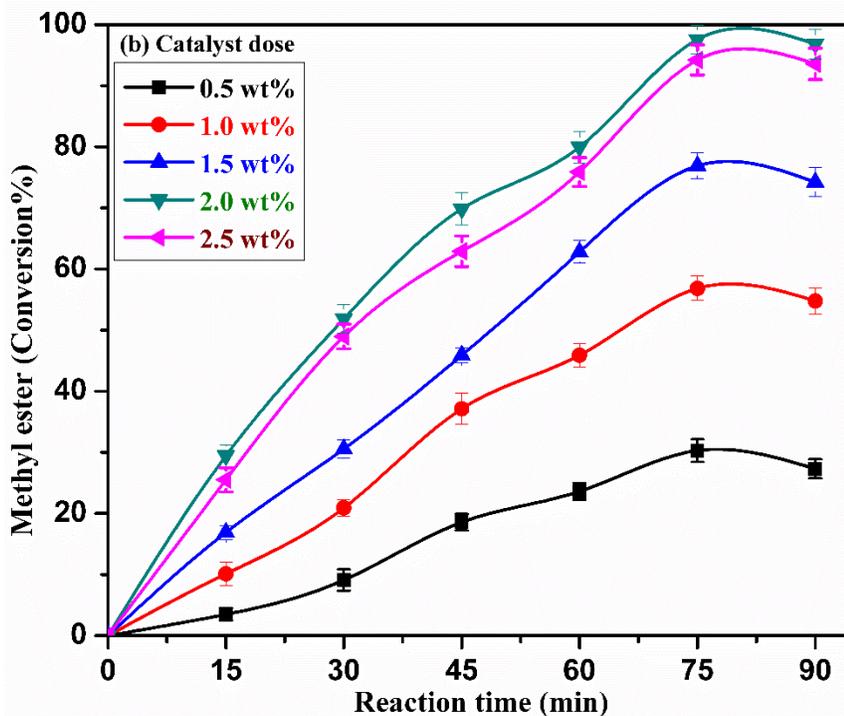


Figure 6.12 Effect of catalyst dose (0.5 – 2.5 wt%) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 15:1; reaction time 0-90 min; temperature 65 ± 0.5 °C and stirring speed 600 rpm]

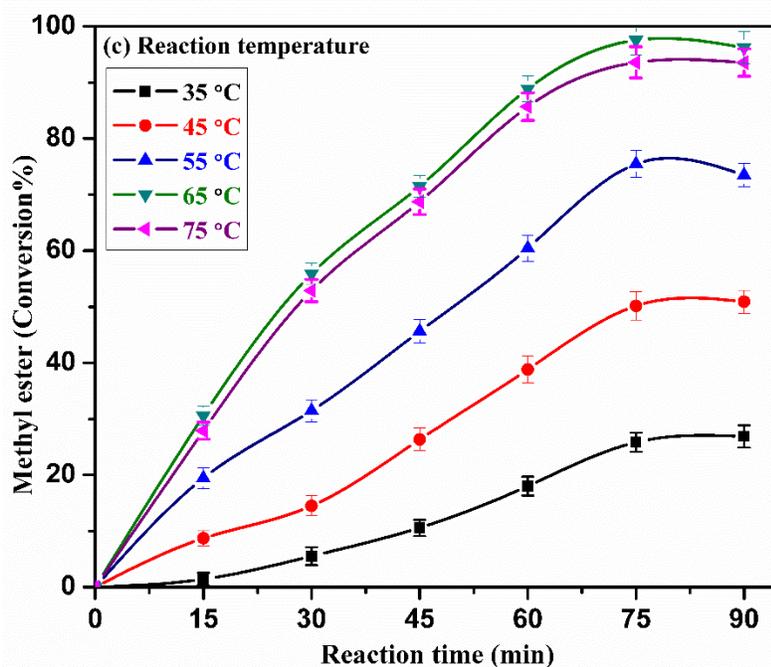


Figure 6.13 Effect of temperature ($35-65\pm 0.5$ °C) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 15:1; catalyst dose 2.0 wt%; reaction time 0-90 min; and stirring speed 600 rpm]

The results signify that the methyl ester conversion increased as the reaction temperature was augmented and the optimum conversion of 97.56% was obtained at 65 ± 0.5 °C. Because of endothermic nature of transesterification reaction, higher reaction temperature accelerates the chemical reaction by increasing the collision among the reactants molecules thereby enhances the miscibility and mass transfer. However, further rise in temperature beyond 65 ± 0.5 °C, low conversion of methyl esters was obtained because of vaporization of methanol the after the boiling point (64.5 °C), will form bubbles which inhibit the reaction on the three-phase interface [Chavan et a., 2017].

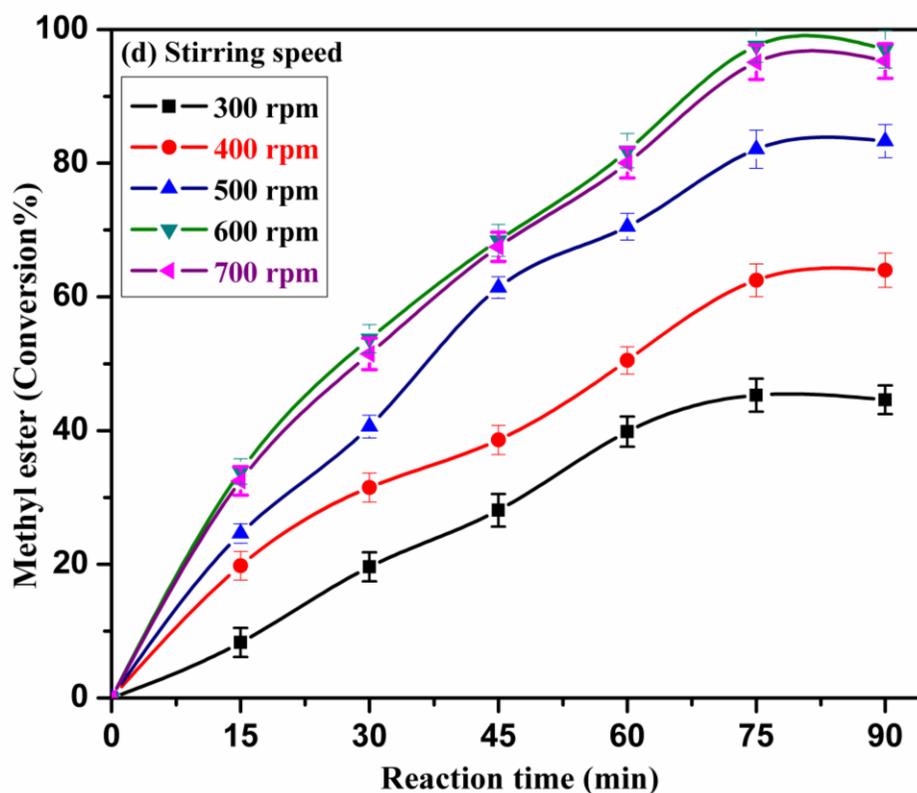


Figure 6.14 Effect of stirring speed (300-700 rpm) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 15:1; catalyst dose 2.0 wt%; reaction time 0-90 min; and temperature 65 ± 0.5 °C]

6.3.1 (d) Effect of stirring speed

The transesterification reaction of the oil in the presence of a heterogeneous catalyst involves multiphase properties and takes place at reactant interface. Therefore, the stirring speed is considered one of the most important parameter that affects the biodiesel conversion. Without stirring of reaction media, no product is formed. The effect of stirring speed was observed at different speed of mechanical stirrer ranging from 200 to 700 rpm using the reaction conditions of methanol: oil molar ratio 1:15, 2.0 wt% catalyst dose, reaction time 0-90 min at 65 ± 0.5 °C reaction temperature. As illustrated in Figure 6.14, the methyl ester conversion increased with increase in agitation speed and equilibrium conversion 97.56% was attained at 600 rpm. Faster agitation improves the diffusion resistance between these different phases in reaction media by increasing the intact area between the oil and catalyst-methanol solution. Nevertheless, continuously increasing the agitation speed from 600 to 700 rpm inhibits the effective contact time of the reactants and vaporization of methanol. These attribute the reduction of methyl ester conversion [Singh et al., 2016].

6.3.2 Reusability

The reusability of catalyst is an important parameter in designing the economics of the catalysis process in industrial purposes. The reusability of $K_2Al_2O_4$ catalyst in transesterification of kusum oil was investigated by using optimized reaction conditions such as methanol: oil molar ratio 15:1; catalyst dose 2.0 wt%; reaction time 75 min; temperature 65 ± 0.5 °C and stirring speed 600 rpm. Figure 6.15 presents the results of methyl ester conversion obtained from five successive transesterification experiments using the regenerated $K_2Al_2O_4$ catalyst. As shown in Figure 6.15 it is evident that the methyl ester

conversion was still 82.2% after five consecutive reaction cycles. The results revealed that the present catalytic system is reliably reusable with slight loss in its activity [Madhuvilakku et al., 2013]. The stability of the catalyst is accredited to the well-organized crystallite structure and morphology which resulted in stabilization of the catalyst phase after five reaction runs. However, after reusing some agglomeration in catalyst particles may responsible for slight loss of activity.

6.3.3 Kinetics and thermodynamic study

In order to investigate the rate constant, activation energy and free energy of activation of the transesterification reaction of kusum oil using $K_2Al_2O_4$ catalyst, kinetics and thermodynamic analysis were performed. For the purpose, multiple batch reactions were accomplished by

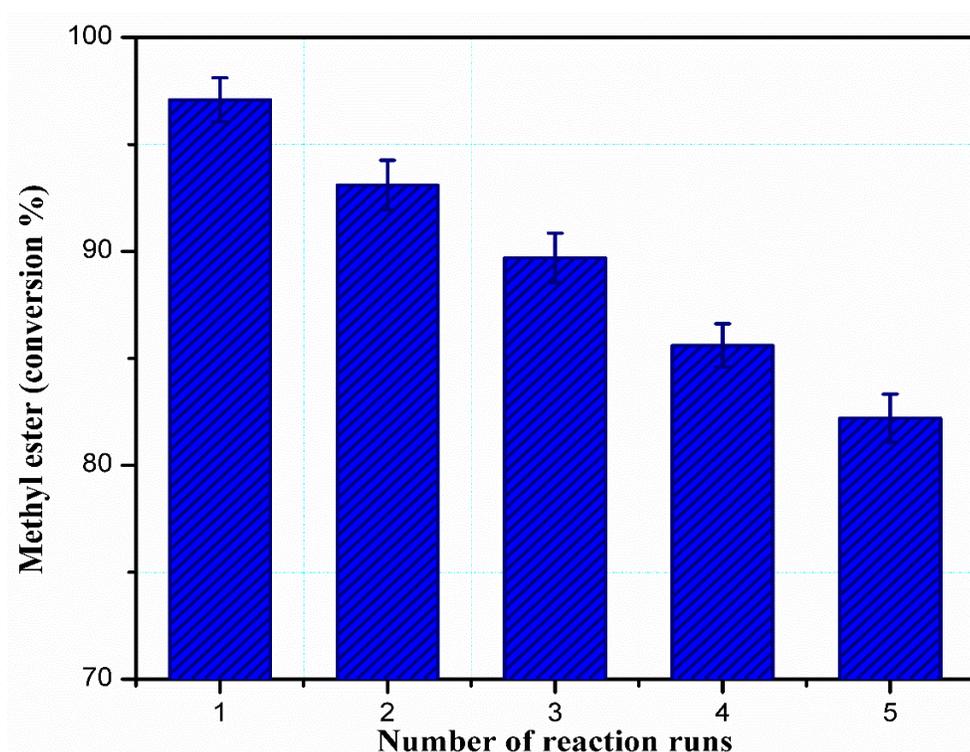


Figure 6.15 Reusability test for the $K_2Al_2O_4$ catalyst at optimized conditions [methanol: oil molar ratio 15:1; catalyst dose 2.0 wt%; reaction time 75 min; temperature 65 ± 0.5 °C; stirring speed 600 rpm]

varying reaction temperature from 35 to 65 °C and reaction time of 0-75 min at isocondition such as 15:1 methanol: oil molar ratio, catalyst amount 2.0 wt% and stirring speed 600 rpm as shown in Figure 6.13.

6.3.3 (a) First-order kinetics

The graph between $-\ln(1-X)$ against t at varying time and temperature gives a kinetic profile with linear relationship which confirms the pseudo-first-order kinetics of transesterification reaction of kusum oil using $K_2Al_2O_4$ catalyst. The rate constant values at varying temperature were calculated from the slop of the plot (Figure 6.16) and tabulated in Table 6.5 with their regression coefficient [Gurunathan and Ravi, 2015].

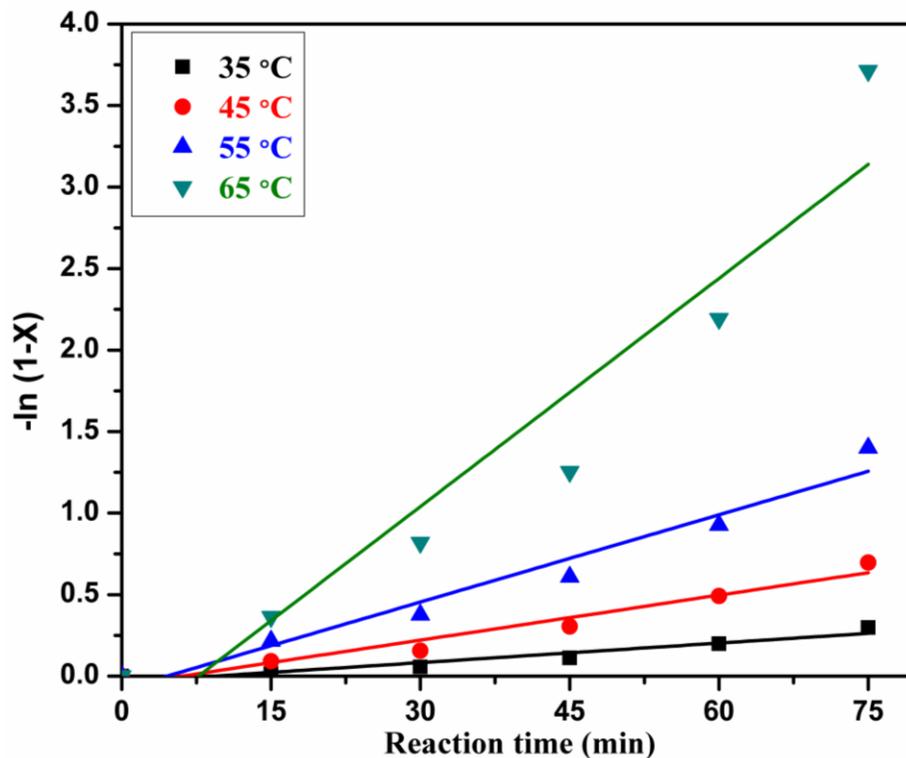


Figure 6.16 Kinetics plots of $-\ln(1-X)$ versus reaction time (min) at different reaction temperatures

Table 6.5 Reaction rate constants at different temperatures

Temperature (°C)	Reaction rate constant (10^{-2} , min^{-1})	Regression coefficient (R^2)
35	0.399	0.91
45	0.920	0.94
55	1.784	0.95
65	4.664	0.89

6.3.3 (b) Activation energy calculation

As tabulated in Table 6.5, reaction rate is positively dependent on reaction temperature. It implies that rate of methyl ester conversion increase with increasing temperature. Furthermore, Arrhenius relation between the activation energy and rate constant was used to

reveal the activation energy of reaction process. The graph in between $\ln(k)$ vs. $1/T$ (as shown in Figure 6.17) confer the activation energy from slope equal to $-E_a/R$ and pre-exponential factor A from intercept $\ln(A)$. The activation energy (E_a) required and pre-exponential factor (A) was calculated to be 68.73 kJ/mol and $1.67 \times 10^9 \text{ min}^{-1}$ respectively for the transesterification of kusum oil catalyzed by $\text{K}_2\text{Al}_2\text{O}_4$ catalyst [Hindryawati and Maniam, 2015].

6.3.3 (c) Thermodynamic study

The thermodynamic studies of present transesterification reaction of kusum oil using $\text{K}_2\text{Al}_2\text{O}_4$ catalyst was performed for calculating enthalpy, entropy and Gibbs free energy of activation by using Eyring-Polanyi equation. The Eyring plot between $\ln(k/T)$ vs. $1/T$ gives the straight line with negative slope as shown in Figure 6.18. The enthalpy can be calculated from the slope equal to $\frac{-\Delta H}{R}$ and entropy from intercept $[\ln \frac{kB}{h} + \frac{\Delta S}{R}]$ and these were found to be $64.45 \text{ kJ mol}^{-1}$ and $-0.084 \text{ kJ mol}^{-1}\text{K}^{-1}$ respectively.

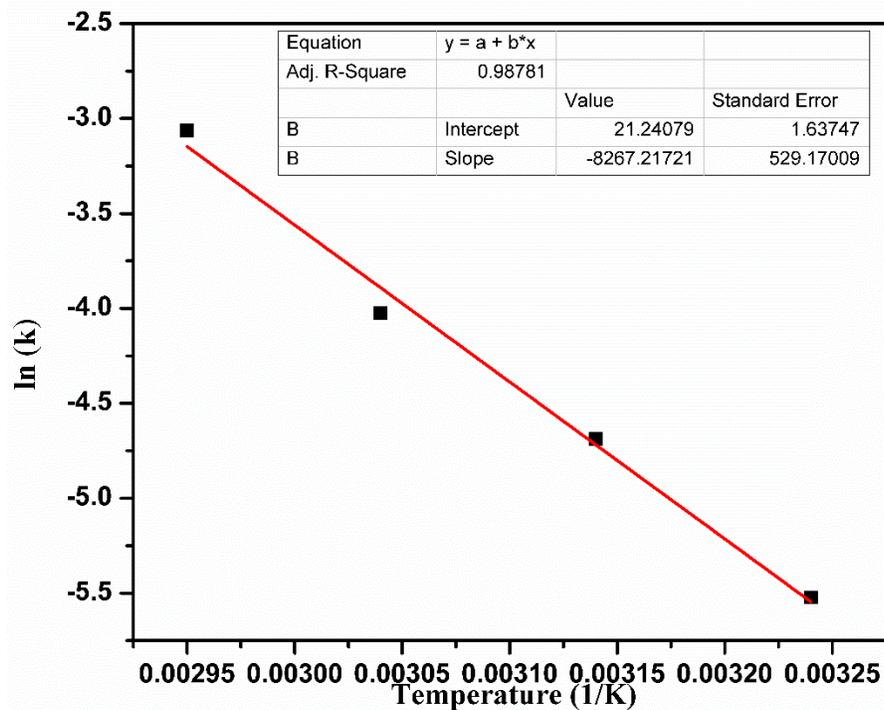


Figure 6.17 Arrhenius plot $\ln k$ vs. $1/T$ relation of transesterification of kusum oil using $K_2Al_2O_4$ catalyst

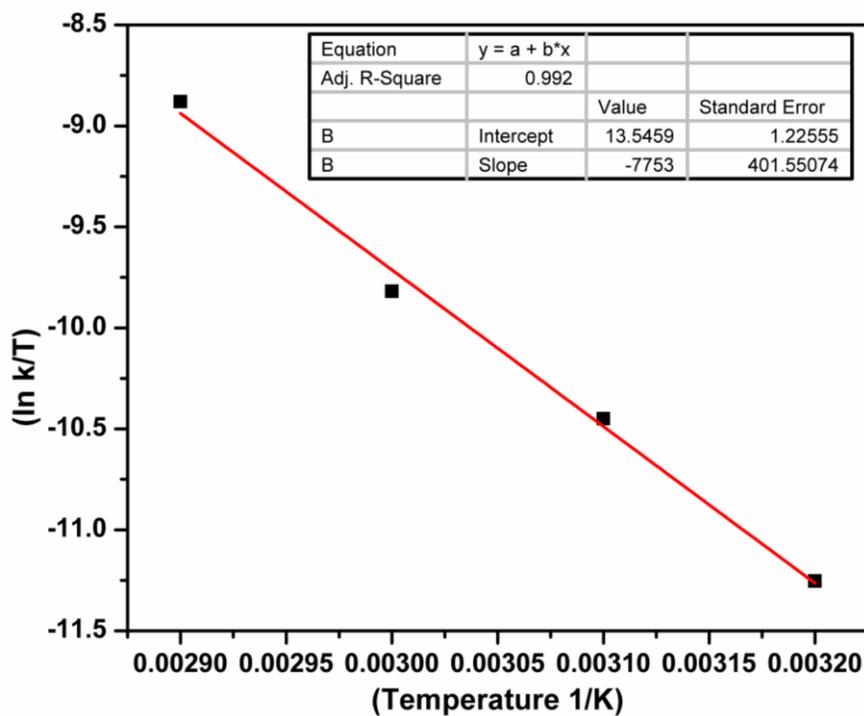


Figure 6.18. Eyring- Polanyi plot $(\ln k/T)$ versus $1/T$ of transesterification of kusum oil using $K_2Al_2O_4$

Furthermore, Gibb's free energy of activation was also calculated with the help of ΔH and ΔS [Suganya et al., 2013]. The Gibb's free energy measures the spontaneity of any chemical reaction. In the present work, Gibb's free energy and enthalpy has a positive value indicating endothermic and unspontaneous nature of the transesterification reaction of kusum oil with $K_2Al_2O_4$ catalyst.

Table 6.6 Calculated values of various thermodynamic parameters

Thermodynamic Functions	Enthalpy (ΔH) (kJ mol ⁻¹)	Entropy (ΔS) (kJ mol ⁻¹ K ⁻¹)	Gibbs free energy (ΔG) (kJ mol ⁻¹)			
			308 K	318K	328K	338K
Values	64.45	-0.084	90.32	91.16	92.00	92.84

6.3.4 Green matrix formulation

The 'green-ness' of present biodiesel synthesis process i.e. transesterification of kusum oil using $K_2Al_2O_4$ was measured by calculating 'E- factor' and PMI value at optimized conditions. The 'E- factor' and PMI value were calculated to be 3.99 and 4.99 respectively.

6.3.5 Characterization of synthesized biodiesel

6.3.5 (a) NMR characterization (¹H and ¹³C)

The representative ¹H NMR spectrum of synthesized kusum oil biodiesel using $K_2Al_2O_4$ catalyst is presented in Figure 6.19. The synthesized biodiesel has its characteristics peak at 3.66 ppm (singlet) and 2.30 ppm (triplet) of methoxy and α -methylene protons, respectively. The conversion of kusum oil into biodiesel was deliberated from the integration value of these peaks. The conversion value was 97.56%.

$$\text{Methyl ester conversion \%} = \frac{2 \times 3}{3 \times 2.05} * 100 = 97.56\% \quad (6.2)$$

The peak of methoxy proton presented at 3.66 (singlet) confirms the conversion of glycerides present in kusum oil into methyl esters. The other peaks in ^1H NMR spectrum are 0.87-0.90 ppm (multiplet); 1.25-1.30 ppm (doublet); 1.61-1.63 ppm (triplet); 2.02-2.06 ppm (triplet); 2.76-2.78 (triplet) were because of various type of aliphatic protons whereas peak at 5.34-5.38 ppm (multiplet) was because of olefinic protons [Kouame et al., 2012].

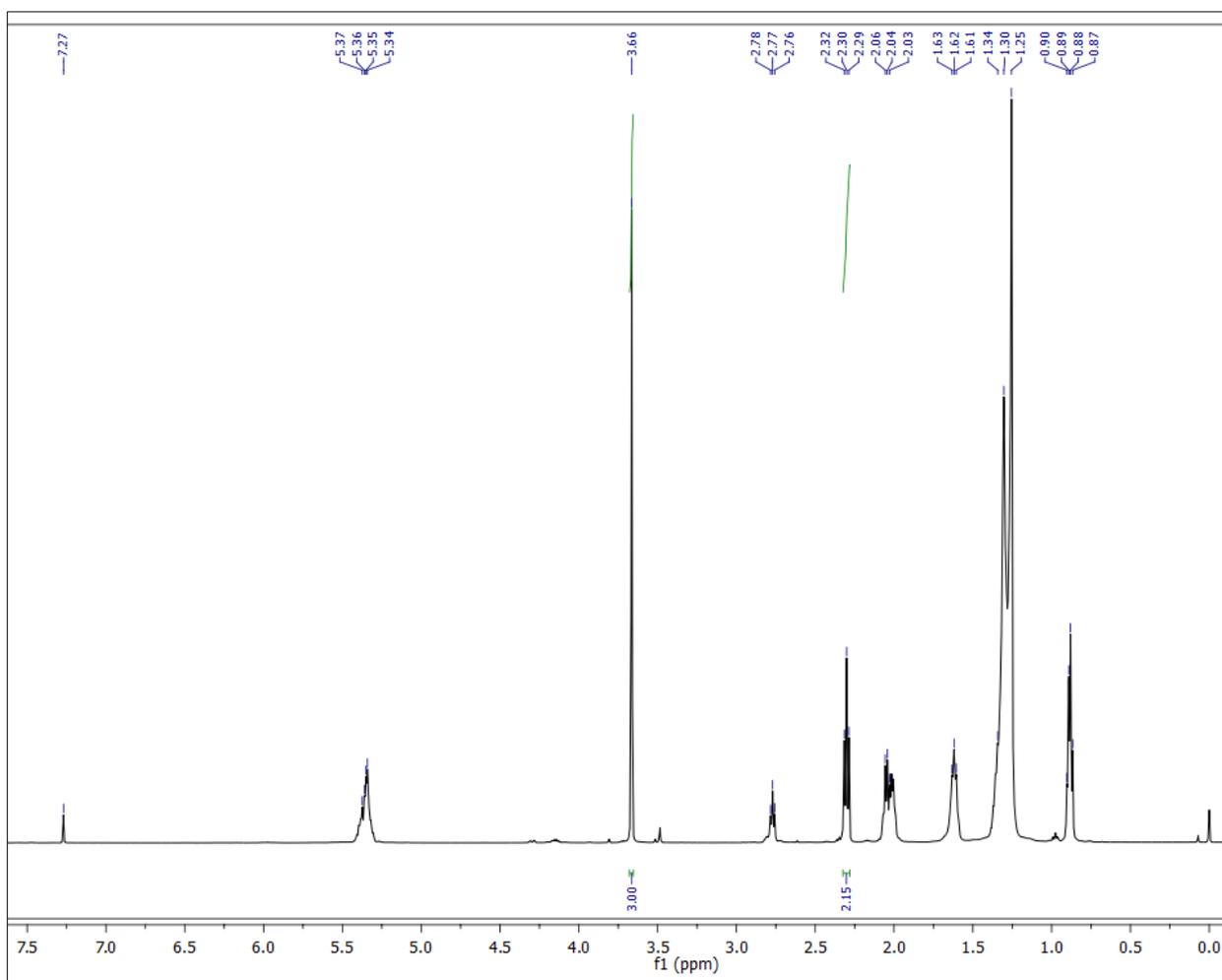


Figure 6.19 ^1H NMR spectrum of synthesized biodiesel from kusum oil

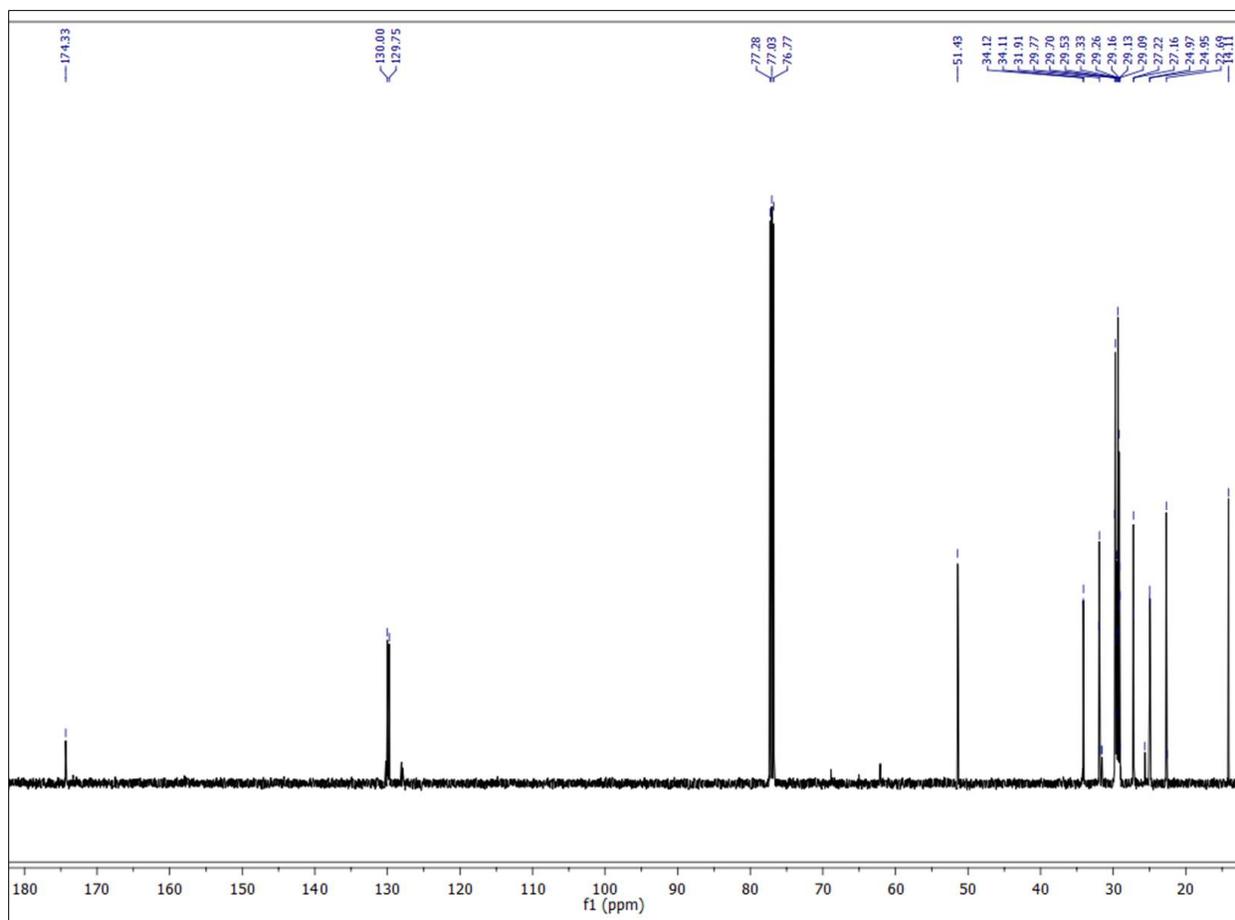


Figure 6.20 ^{13}C NMR spectrum of synthesized biodiesel from kusum oil

A typical ^{13}C NMR spectrum of as-synthesized kusum oil biodiesel is presented in Figure 6.20.

The peak at 174.33 ppm and 51.43 ppm in spectrum were characteristics peak of carbonyl ester carbon and ester carbon. The other peaks in spectrum at 130.00-129.75 ppm represents the olefinic carbons in long fatty acid chain; 34.12-22.69 ppm are due to the methylene carbons of long carbon chain in fatty esters and peak at 14.11 ppm signifies the terminal carbons of methyl group [Deka and Basumatary. 2011].

6.3.5 (b) Compositional analysis of FAME by GC-MS

The determination of kusum oil biodiesel composition helps to predict the suitability for its consumption as fuel. The biodiesel consists eight methyl esters; methyl 18-methylnonadecanoate in maximum amount, methyl 13-eicosenoate in second highest followed by methyl hexadecanoate, methyl (Z,Z)-9,12-octadecadienoate, methyl octadecanoate, methyl hexadec-9-enoate, methyl (Z)-docos-13-enoate and the least methyl docosanoate as shown in Table 6.7. The synthesized KOME sample comprises 44.2% unsaturated methyl esters and 55.8 % saturated methyl esters. Meanwhile, due to the presence of high saturated methyl esters, the combustible properties become better [Gurunathan and Ravi, 2015].

Table 6.7 Fatty acid methyl ester composition of Synthesized FAMES

Retention time (min)	%composition	Identified fatty acid methyl ester and their formula	Library Match	Corresponding acid
37.63	2.76	Methyl hexadec-9-enoate (C ₁₇ H ₃₂ O ₂)	99	C16:1
38.66	17.02	Methyl hexadecanoate (C ₁₇ H ₃₄ O ₂)	98	C16:0
43.24	9.30	Methyl(Z,Z)-9,12-octadecadienoate (C ₁₉ H ₃₄ O ₂)	99	C18:2
44.61	5.71	Methyl octadecanoate (C ₁₉ H ₃₈ O ₂)	99	C18:0
49.40	27.25	Methyl 13-eicosenoate (C ₂₁ H ₄₀ O ₂)	99	C20:1
50.35	28.72	Methyl 18-methylnonadecanoate (C ₂₁ H ₄₂ O ₂)	99	C20:0
54.26	4.89	Methyl (Z)-docos-13-enoate (C ₂₃ H ₄₄ O ₂)	99	C22:1
55.04	4.30	Methyl docosanoate	99	C22:0

(C ₂₃ H ₄₆ O ₂)	
Saturated fatty acid methyl ester	55.75%
Monosaturated fatty acid methyl ester	34.9%
Polysaturated fatty acid methyl ester	9.30%

6.3.5 (c) Evaluation of fuel properties:

Table 6.8 presents the physicochemical properties such as acid value, density, kinematic viscosity, calorific value, flash point, fire point, cetane number of synthesized biodiesel from kusum oil using K₂Al₂O₄ catalyst under optimized conditions. As shown in Table 6.12 acid value of biodiesel was 0.3 mg of KOH/g. Density and kinematic viscosity are a pivotally important parameter influencing fuel injection quality and combustion performance. The density and kinematic viscosity of the sample were 0.893 g/cm³ and 3.78 mm²/s respectively and satisfy the standard limit. The calorific value of the synthesized methyl ester was 41.24 MJ/kg.

Table 6.8 Comparison of fuel properties of synthesized biodiesel with diesel using ASTM specifications

Property	Units	Value	ASTM D 6751	Test method
Acid value	mg KOH/g	0.3	≥0.5	ASTM D 664
Density	g/cm ³	0.874	0.86-0.89	ASTM D 4052
Kinematic viscosity (40 °C)	mm ² /s	14.78	1.9-6.0	ASTM D 445
Calorific value	MJ/kg	41.24	>35	ASTM D 240
Flash point	°C	154	>120	ASTM D93
Fire point	°C	159	-	ASTM D93

Cloud point	°C	2	-3 to12	ASTM D2500
Pour point	°C	-4	-15 to16	ASTM D97-05
Cetane number		51.4	>47	ASTM D976

The flash point and fire point are ignition temperature of fuel and desired to be high due to handling safety. The synthesized kusum oil biodiesel has high value of flash point and fire point i.e. 154 and 159 °C. The cloud point and pour point of synthesized biodiesel was found to be 2 and -4 °C respectively [Sajjadi et al., 2016]. The cetane number of synthesized methyl esters was 51.4, which complies with ASTM standards that prescribe a minimum of 47. The methyl ester synthesized from kusum oil by transesterification reaction employing $K_2Al_2O_4$ catalyst satisfies the range of ASTM D6751 standard and has the potential to be used at industrial scale [Arbab et al., 2013].

6.4 Conclusions

As-synthesized potassium aluminum oxide $K_2Al_2O_4$ as heterogeneous base catalyst was deployed for biodiesel production from non-edible feedstocks used vegetable oil and kusum oil via transesterification reaction. The 98.02% conversion from used vegetable oil was achieved after optimization of reaction parameters such as methanol: oil molar ratio 18:1, catalyst dose of 2.5 wt%, reaction temperature of 65 ± 0.5 °C for 75 min of time and 600 rpm stirring rate whereas 97.56% conversion was obtained at the reaction conditions methanol: oil molar ratio 15:1, catalyst dose of 2.0 wt%, reaction temperature of 65 ± 0.5 °C for 75 min of time and 600 rpm stirring rate from kusum oil using $K_2Al_2O_4$ catalyst. The reusability studies revealed that catalyst can be recycled up to five reaction cycles with significant loss in catalytic activity (>80% conversion at the end of 5th cycle). For the transesterification of

used vegetable oil and kusum oil using $K_2Al_2O_4$ catalyst, the pseudo-first-order kinetic model was well-suited. The required activation energy (E_a) and frequency factor (A) were 71.16 kJ/mol and $4.57 \times 10^9 \text{ min}^{-1}$ for used vegetable oil feedstock as well as 68.73 kJ/mol and $1.7 \times 10^9 \text{ min}^{-1}$ for kusum oil

feedstock respectively. The thermodynamic studies of transesterification reaction exhibit enthalpy (ΔH) and entropy (ΔS) values 66.57 kJ mol⁻¹ and -0.077 kJ mol⁻¹K⁻¹ for used vegetable oil and 64.45 kJ mol⁻¹ and -0.084 kJ mol⁻¹K⁻¹ for kusum oil. The E- factor and PMI values were calculated to be 2.91 and 3.91 for transesterification of used vegetable oil whereas 3.99 and 4.99 for kusum oil respectively. The synthesized used vegetable oil biodiesel and kusum oil biodiesel were analyzed by NMR (¹H and ¹³C) spectroscopy and GCMS for compositional analysis. The important fuel characteristics such as acid value, density, kinematic viscosity (40 °C), calorific value, flash point, fire point, cloud point, pour point, and cetane number were investigated according to ASTM D6751 standard limits and found within the biodiesel standards. Hence, $K_2Al_2O_4$ catalyst for biodiesel production from used vegetable oil and kusum oil can be a fascinating substitute for large scale economical viable biodiesel.