5.1 Introduction

The present chapter discusses the utilization of barium aluminum oxide (BaAl$_2$O$_4$) as heterogeneous base catalyst in transesterification reaction of used vegetable oil and kusum oil feedstocks. The optimization of various reaction parameters influencing the conversion efficiency of catalyst in transesterification; namely methanol: oil molar ratio, catalyst dose, temperature, reaction time and stirring speed was carried out. Furthermore, the kinetics and thermodynamics of biodiesel synthesis process were aptly investigated. The synthesis biodiesel was characterized by ^{1}H and ^{13}C-NMR techniques and fatty acid methyl ester composition was evaluated by GCMS. Moreover, the important physicochemical properties such as acid value, density, kinematic viscosity, calorific value, flash point, fire point and cetane number of synthesized biodiesel were appraised according to ASTM standards.

5.2 Biodiesel synthesis from used vegetable oil using BaAl$_2$O$_4$

5.2.1 Optimization of biodiesel production parameters

On account of the highest performance of as-synthesized catalyst BaAl$_2$O$_4$ in methyl-transesterification of UVO, the effect of reaction parameters used, on biodiesel conversion (%) was investigated. For the purpose, multiple experiments at varying methanol to oil molar ratio (12:1 to 24:1), catalyst dose with respect to oil weight 1.0 to 5.0 wt%, reaction temperature 35 to 75±0.5 °C and stirring rate 300 to 700 rpm were executed with respect to time 0-180 min to attain the optimum condition for maximum incorporation of triglyceride into biodiesel. All experiments were performed thrice and their mean values were reported.

5.2.1 (a) Effect of methanol to oil molar ratio

Methanol is the basic reactant and its molar ratio to oil controls the process of transesterification affecting the biodiesel conversion as well as cost of production. Stoichiometrically methanol to oil molar ratio required for transesterification reaction is 3:1 but higher molar ratios improve the biodiesel conversion because of shifting the equilibrium towards product formation as well as regenerates, the catalytic active site by removing the product molecules from catalyst surface.

Figure 5.1 depicts the effect of methanol: oil molar ratio varying (12:1 to 24:1) at variable reaction time on the biodiesel conversion. Other reaction conditions such as temperature 65 ± 0.5 °C, catalyst dose 4 wt% of $BaAl_2O_4$ and stirring rate at 600 rpm were kept constant [Shrirame et al., 2011]. The results indicate that biodiesel conversion efficiency augments at any reaction time significantly with increasing methanol: oil molar ratio from 12:1 to 21:1 and attains a maximum conversion (93.45%) at 21:1 molar ratio in 150 min of time. Below 21: 1 ratio, methanol amount was insufficient to move the equilibrium towards the forward direction resulting low biodiesel conversion. Further rise in methanol to oil molar ratio beyond 21:1, conversion would decrease because high methanol amounts interfere with separation of glycerol because of an increase in solubility drives the equilibrium in backward reaction direction. Besides, excess methanol involves extra energy to heat and separate the methanol and glycerol resulting in increased production cost [Tan et al., 2015].

5.3.1 (b) Effect of catalyst dose

Transesterification reaction using heterogeneous catalyst is a three- phasic system and reaction occurs after transport of reactant to the active sites of catalyst. Thus, catalyst dosage is one of the most significant parameter affecting biodiesel conversion. To investigate the optimum amount of catalyst, a series of transesterification of UVO with methanol (21:1 molar ratio) was performed by varying catalyst amount 1-5 wt% and reaction time 0-180 min at 65±0.5 °C. Figure 5.2 depicts the effect of catalyst dose on biodiesel conversion. It is clear that increasing the catalyst dose, biodiesel conversion increases sharply. For a catalyst concentration of 1 wt%,
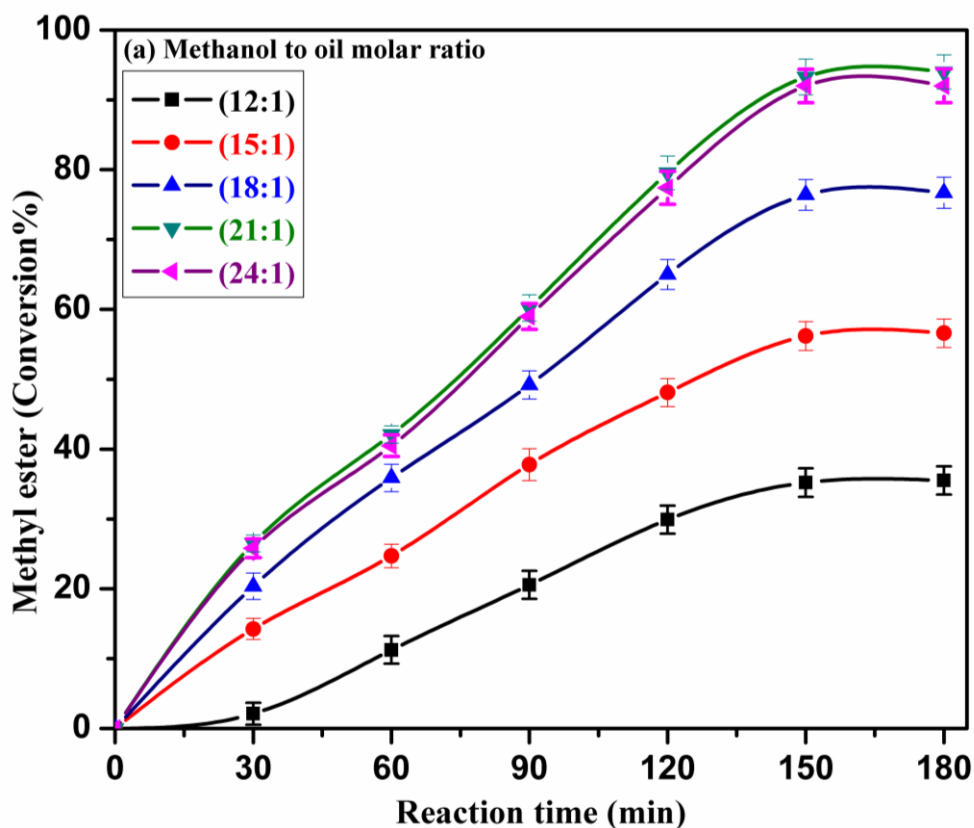
Figure 5.1 Effect of methanol: oil molar ratio (12:1 - 24:1) on methyl ester conversion (%) of used vegetable oil [catalyst dose (4 wt%); reaction time 0-180 min; temperature 65±0.5 °C and stirring speed 600 rpm]

9.23% conversion was achieved and it increases to 93.45% with 4 wt% catalyst at the same reaction time. Increasing the catalyst amount in reaction, the available catalyst active site increase which was responsible for high conversion efficiency. Our findings are supported by the previous literature. However, further rise in catalyst amount beyond its optimum value i.e. 4 wt%, biodiesel conversion was decreased at the same time. This was attributed to the saponification reaction, a side reaction in between the FFA present in feedstock and base catalyst. The formation of soap and emulsion leads to mass transfer limitation as well as difficulties in separation process eventually reduction in conversion efficiency [Kumar et al., 2018].
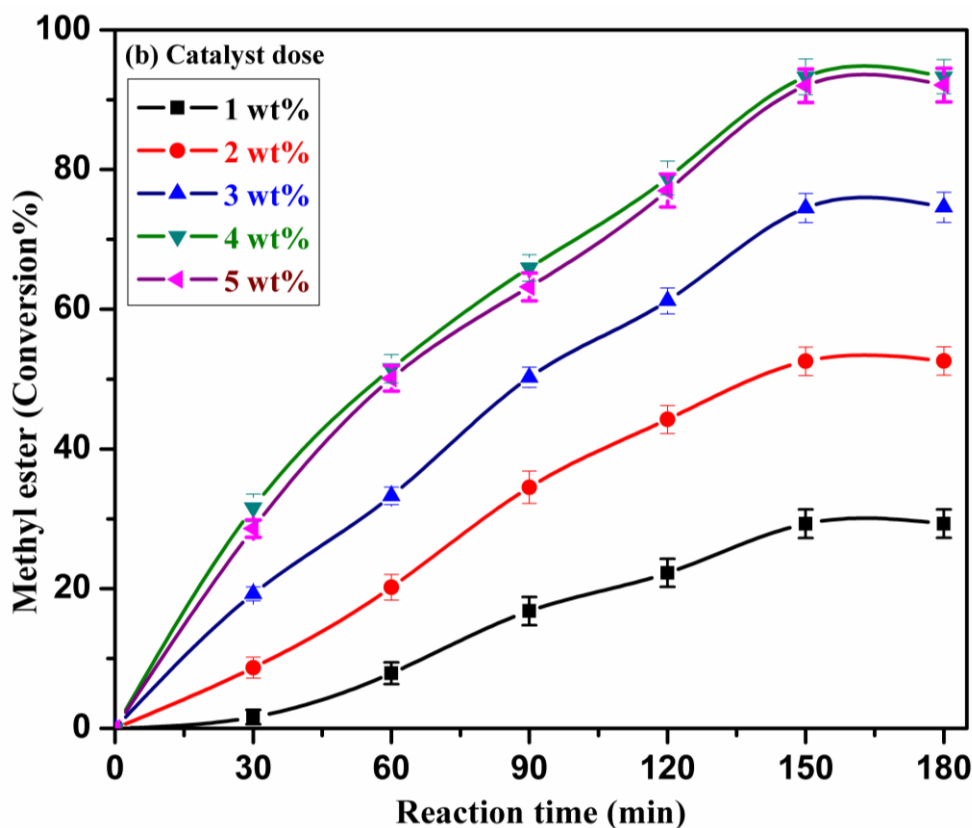

Figure 5.2 Effect of catalyst dose (1-5 wt%) on methyl ester conversion (%) of used vegetable oil [methanol: oil molar ratio 21:1; reaction time 0-180 min; temperature 65±0.5 °C and stirring speed 600 rpm]

5.2.1 (c) Effect of reaction temperature

Reaction temperature plays an important role on conversion of biodiesel. Endothermic reactions are thermodynamically favoured by increase in reaction temperature. To study the effect of reaction temperature, a series of experiments were performed by varying temperature from 35-75±0.5 °C at the interval of 10 °C using methanol: oil 21:1 molar ratio, 600 rpm stirring rate and 0-180 min time. The results shown in Figure 5.3 imply that at lower temperature, such as 35-45±0.5 °C, only 26.90–48.0% of methyl ester conversion was observed at the same time because of the diffusion resistance among different phases oil-methanol-catalyst. Increasing reaction temperature 55 to 65±0.5 °C, collision among the reactant molecules also augmented and enhanced miscibility as well as reduced mass transfer limitations are responsible for the higher conversion of methyl ester (74.89- 93.45%). When the temperature was further increased beyond 65±0.5 °C, the conversion was decreased [Birla et al., 2012]. This might have occurred as after boiling point of methanol, 64.5 °C, large number of bubbles were formed which inhibited the reaction at interface; therefore, reduced the biodiesel conversion [Pullen and Saeed, 2015].

5.2.1 (d) Effect of stirring speed

The transesterification reaction of used vegetable oil (UVO) using methanol and heterogeneous base catalyst, $BaAl_2O_4$ is bi-phase system and takes place at reactants interface. Therefore, the stirring rate plays an important role to facilitate the initiation of the reaction. Without mixing of reactants, no methyl ester is produced since oil and methanol are

immiscible. To examine the effect of stirring rate of mechanical stirrer on biodiesel conversion, it was varied within
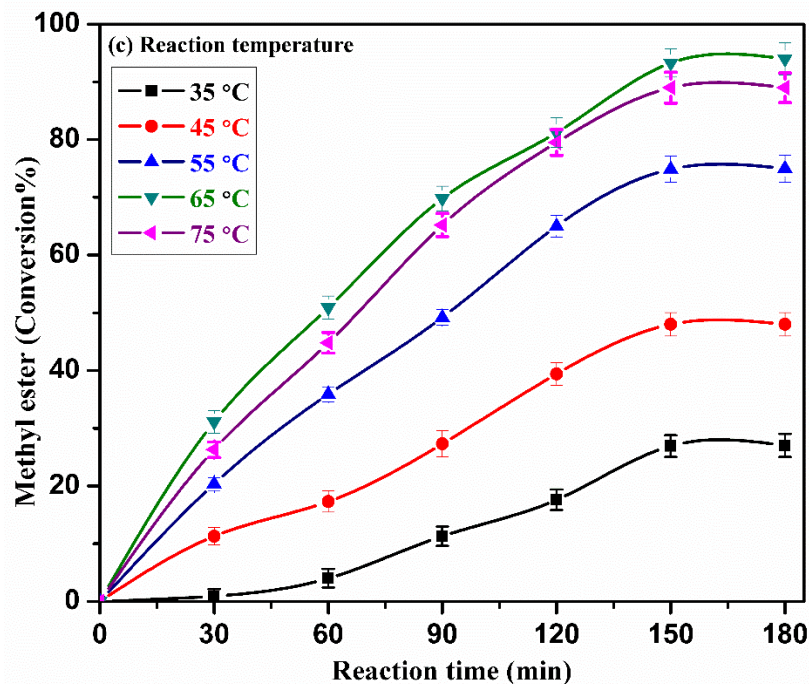

Figure 5.3 Effect of reaction temperature (35-65±0.5 °C) on methyl ester conversion (%) of used vegetable oil [methanol: oil M ratio 21:1; catalyst dose 4 wt%; reaction time 0-180 min; and stirring speed 600 rpm]
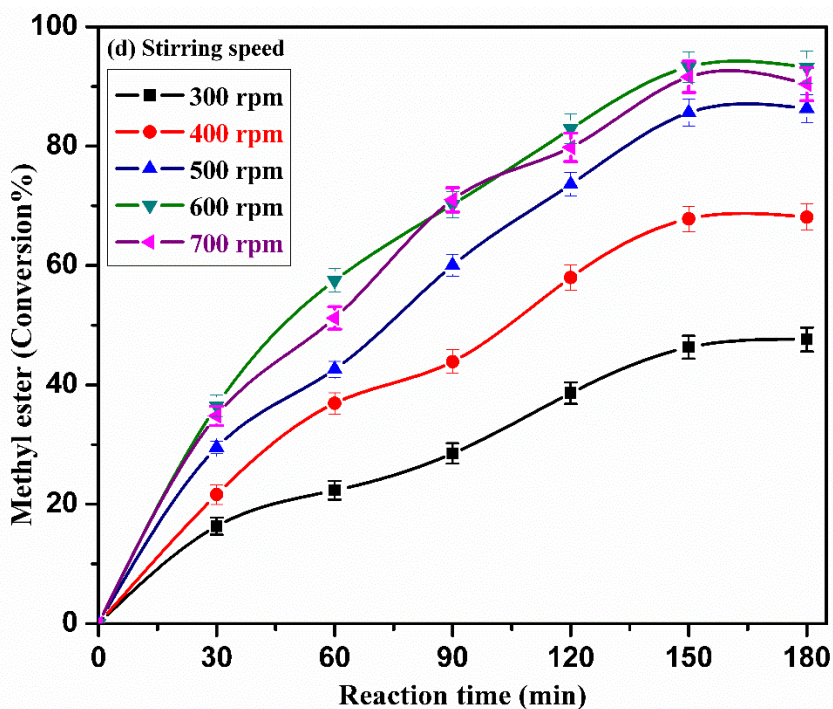
Figure 5.4 Effect of stirring speed (300-700 rpm) on methyl ester conversion (%) of used vegetable oil [methanol: oil molar ratio 21:1; catalyst dose 4 wt%; reaction time 0-180 min; temperature 65±0.5 °C]

300-700 rpm range with methanol: oil 21:1 molar ratio, 4 wt% of catalyst dosage and 0-180 min of reaction time at 65±0.5 °C temperature [Madhu et al., 2016]. As depicted in Figure 5.4, at lower stirring rate, the difficulties of achieving a uniform distribution of catalyst particle are responsible for low methyl ester conversion. The optimum conversion 93.45% was achieved at 600 rpm. Proper mixing improves the mass transfer between the different phases; oil and catalyst-methanol solution by increasing the reaction area. However further increase in stirring rate, effective contact time to interact reactant molecules reduced as well as vibration of the mechanical rotor leads to loss of methanol by evaporation and so conversion decreased [Agrawal et al., 2012].

Above study divulgated that methanol to oil molar ratio of 21:1, a catalyst dose of 4 wt%, at reaction temperature of 65±0.5 °C for 150 min of reaction time and 600 rpm stirring rate

were found to be optimum reaction conditions for maximum methyl ester conversion over the $BaAl_2O_4$ catalyzed trans-esterification reaction.

5.2.2 Reusability

In designing the economics of a catalytic system, the repeated use of the catalyst is desirable to reduce the process cost. The reusability results of regenerated $BaAl_2O_4$ catalyst at optimized reaction conditions for five successive runs are presented in Figure 5.5. After five runs, catalyst resulted up to 75% conversion of methyl ester. The well-organized crystallite structure was responsible for stability of catalyst. A small decay in conversion (2-3%) after each cycle was noticed which could be due to loss in catalyst amount or blockage of active sites or pore filling. However, quite better reusability with reasonable conversion (%) established the present catalytic system as cost-effective for biodiesel synthesis [Nayebzadeh et al., 2016].
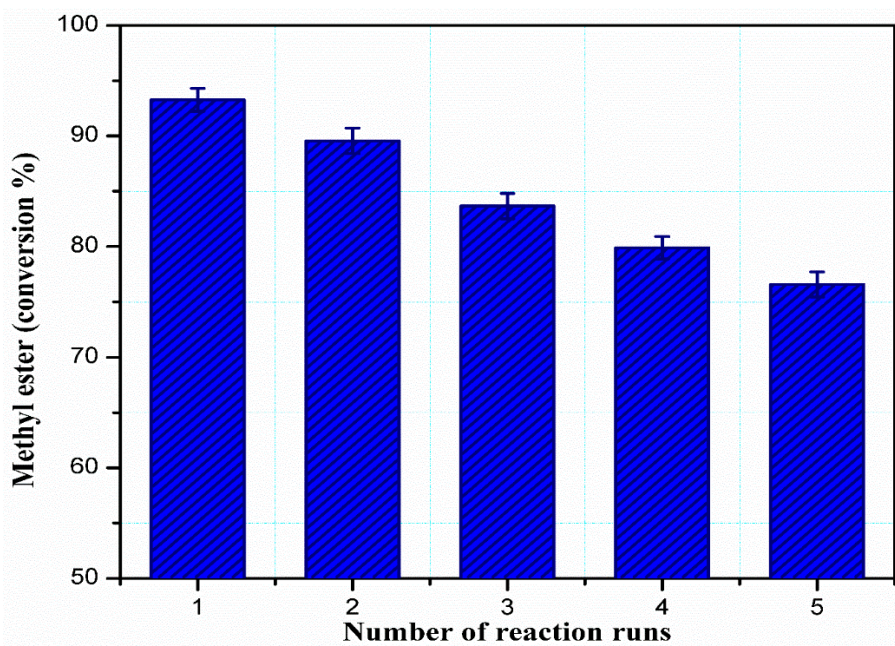

Figure 5.5 Reusability test for the $BaAl_2O_4$ catalyst at optimized conditions [methanol: oil molar ratio 21:1; catalyst dose 4 wt%; reaction time 0-180 min; temperature 65±0.5 °C]

5.2.3 Kinetics and thermodynamic study

To investigate rate, required activation energy and free energy, the kinetics and thermodynamic studies were performed for transesterification reaction of used vegetable oil using Arrhenius and Erring equations. For the purpose, reactions were performed at variable temperature (35-65 °C) and time (0-150 min) using parameter methanol: oil molar ratio 21:1, 4 wt% $BaAl_2O_4$ catalyst and 600 rpm stirring rate as shown in Figure 5.3.

5.2.3 (a) First-order kinetics

As shown in Figure 5.6, a high linear correlation of reaction time in function of –ln (1-X), at the different reaction temperatures was observed that supports the hypothesis of pseudo-first order kinetics of transesterification of used vegetable oil using $BaAl_2O_4$ catalyst [Feyzi and Shahbazi, 2017]. The rate constant values calculated from the slope of these straight lines and their respective regression coefficients at various temperatures are presented in Table 1.
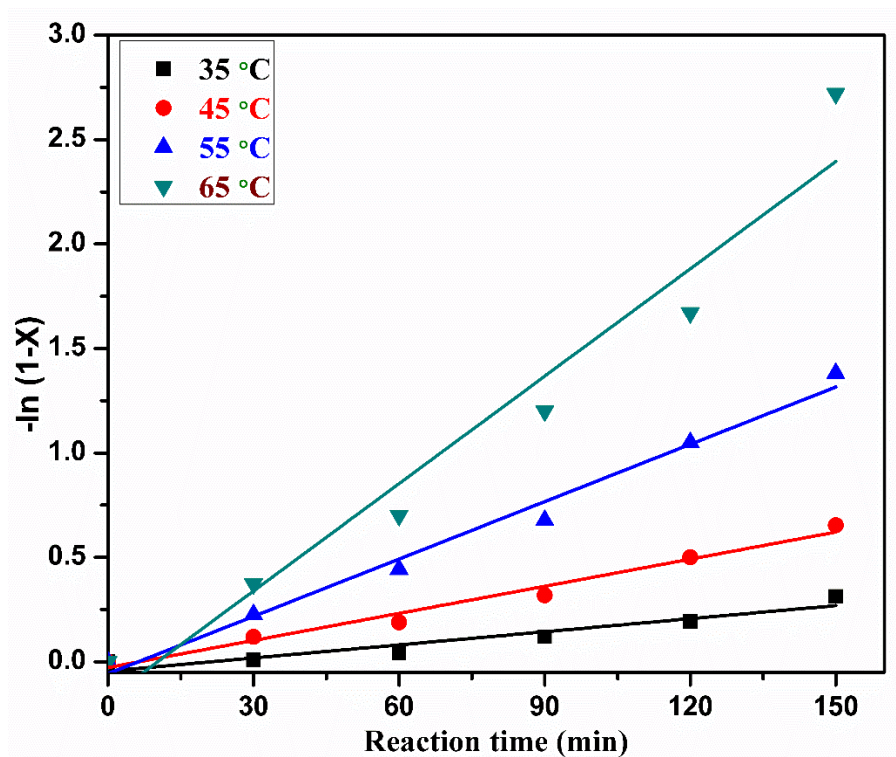
Figure 5.6 Kinetic plots of –ln (1-X) versus reaction time (min) at different reaction temperatures

Table 5.1 Reaction rate constants at different temperatures

Temperature (°C)	Reaction rate constant (10^{-2}, min^{-1})	Regression coefficient (R^2)
35	0.209	0.89
45	0.433	0.97
55	0.915	0.98
65	1.714	0.94

5.2.3 (b) Activation energy calculation

The values of rate constants of the transesterification process using $BaAl_2O_4$ catalyst have significant favourable dependence to temperature as shown in Table 5.1. Furthermore, required activation energy was inferred by using Arrhenius theory to establish quantitative relationship between the activation energy, temperature and rate constants. The Arrhenius plot of ln k versus 1/T (1/K) gives a straight line with negative slope by linear fitting as shown in Figure 5.7. The activation energy and frequency factor (A) were quantified from the slope (-Ea/R) and intercept (ln A) respectively. The obtained values of the activation energy (Ea) and frequency factor (A) for the methyl transesterification of used vegetable oil in presence of $BaAl_2O_4$ catalyst were 60.55 kJ/mol and 3.73×10^7 min^{-1} which is in good agreement with reported literature [Nautiyal et al., 2014].
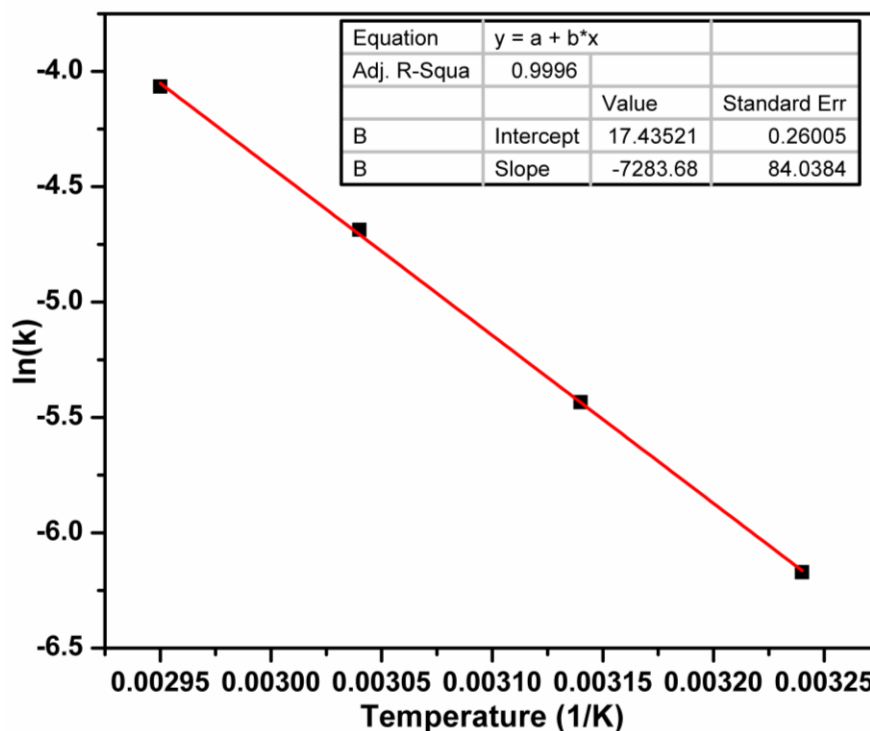

Figure 5.7 Arrhenius plot ln k vs. (1/T) of transesterification of used vegetable oil using $BaAl_2O_4$ catalyst

5.2.3 (c) Thermodynamic study

Eyring-Polanyi equation was used to deliberate the relationship between enthalpy and entropy with the rate constants. The value of enthalpy and entropy were inferred from intercept [$\ln \frac{kB}{h} + \frac{\Delta S}{R}$] and slope $\frac{-\Delta H}{R}$ of the Eyring-Polanyi plot as shown in Figure 5.8 and found to be 55.873 kJ mol^{-1} and -0.136 kJ mol^{-1} K^{-1} respectively. The value of Gibbs free energy quantified at different temperature is presented in Table 5.2. The ΔG of a chemical reaction is related to the spontaneity and its negative sign indicates spontaneity and vice-versa [Deshmane and Adewuyi, 2013]. In present study, the obtained ΔG of transesterification reaction of used vegetable oil showed the positive values indicating non-spontaneity of the reaction.
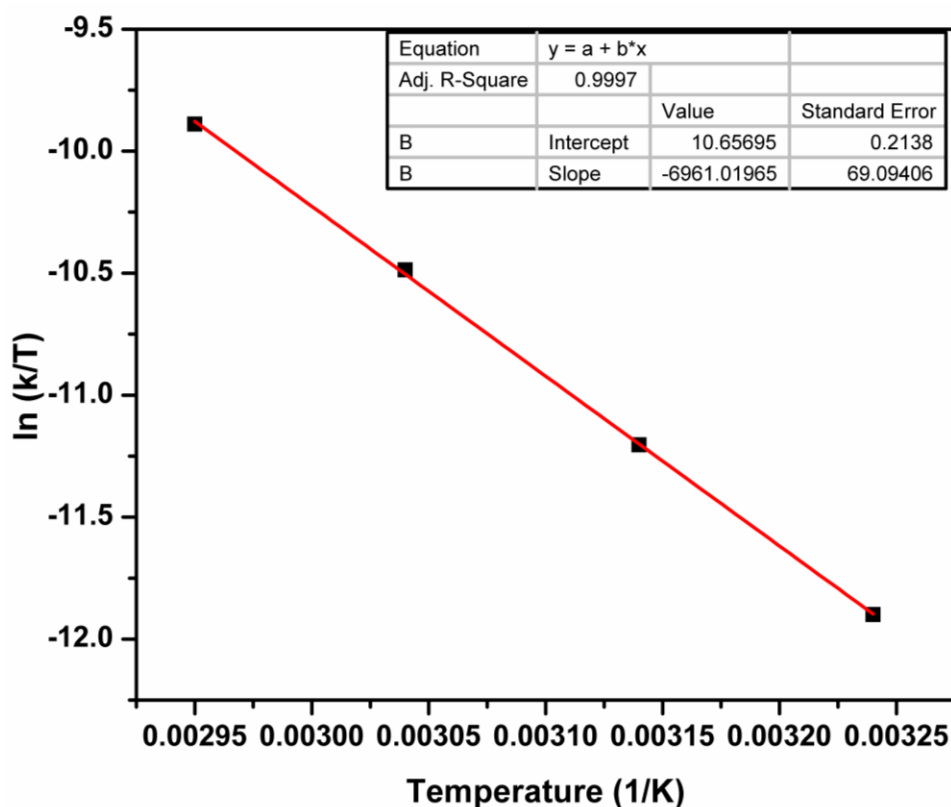

Figure 5.8 Eyring- Polanyi plot (lnk/T) versus 1/T of transesterification of used vegetable oil using BaAl$_2$O$_4$ catalyst

Table 5.2 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})			
Values	57.873	-0.103	**308 K**	**318K**	**328K**	**338K**
			91.40	92.49	93.57	94.66

5.2.4 Green matrix formulation

The "green-ness" of the present biodiesel synthesis process i.e. transesterification of used vegetable oil using $BaAl_2O_4$ catalyst was investigated by calculating green chemistry metrics *E*- factor and Process mass intensity. A lower E-factor and PMI values of present biodiesel synthesis process i.e. 3.85 and 4.85 imply less waste generation and more green approach [Das et al., 2013].

5.2.5 Characterization of synthesized biodiesel

5.2.5 (a) NMR characterization (^{1}H and ^{13}C)

A typical ^{1}H NMR spectrum of used vegetable oil biodiesel produced from transesterification using $BaAl_2O_4$ is presented in Figure 5.9. The spectrum of biodiesel has characteristics peak of methoxy protons as a singlet at 3.68 ppm and α-methylene protons as a triplet at 2.32 ppm, respectively which confirm the presence of methyl ester. The conversion (%) of methyl ester was calculated using integration values i.e. 3.0 and 2.14 respectively of these peaks and 93.45% conversion was found at optimized conditions.
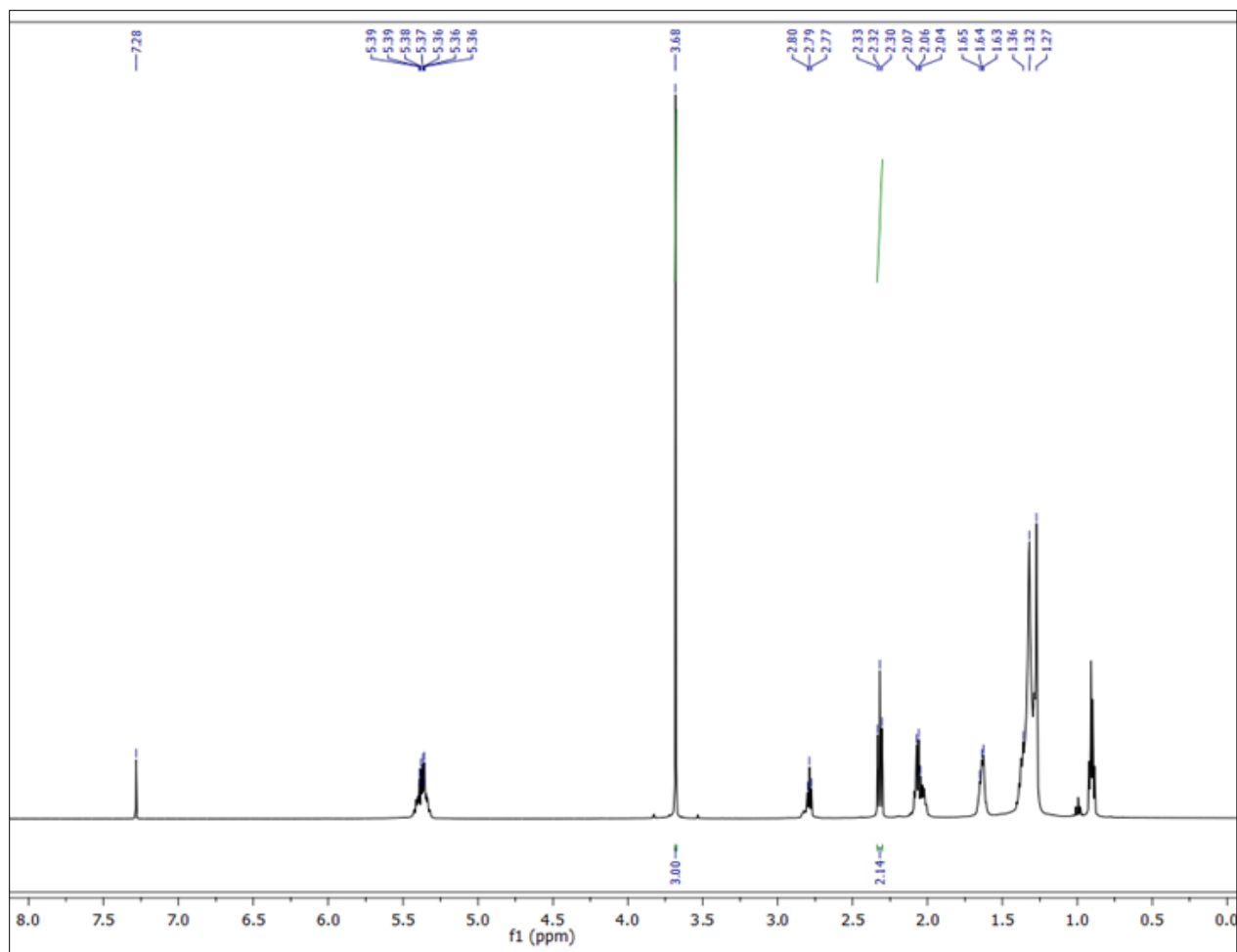
Figure 5.9 ^{1}H NMR spectrum of synthesized biodiesel from used vegetable oil

Methyl ester conversion % $= \frac{2*3}{3*2.14} * 100 = 93.45\%$ (5.1)

Other observed peaks in ^{1}H NMR spectrum of biodiesel; multiplet at 0.88–0.90 ppm; multiplet at 126–1.31 ppm; triplet at 1.62–1.64 ppm; multiplet at 2.01–2.06 ppm; multiplet at 2.75–2.78 ppm were to due aliphatic hydrogens while multiplet peaks at 5.33–5.38 were related to olefinic hydrogens in long carbon chain of methyl esters [Satyarthi et al., 2009].

The ^{13}C NMR spectrum of methyl esters produced from used vegetable oil is shown in Figure 5.10 which shows the peak of ester carbonyl carbon at 174.33 and 173.28 ppm. The

peaks at 130.21–127.73 ppm indicated the unsaturation in carbon backbone. The other peaks available at 22.57–31.53 ppm are related to methylene carbons of long carbon chain and peaks of terminal carbon of methyl groups are at 14.09 and 14.05 ppm. Moreover, the additional characteristic peaks of ester carbonyl groups were exhibited at 174.31 and 51.36 ppm, respectively [Tahira et al., 2012].
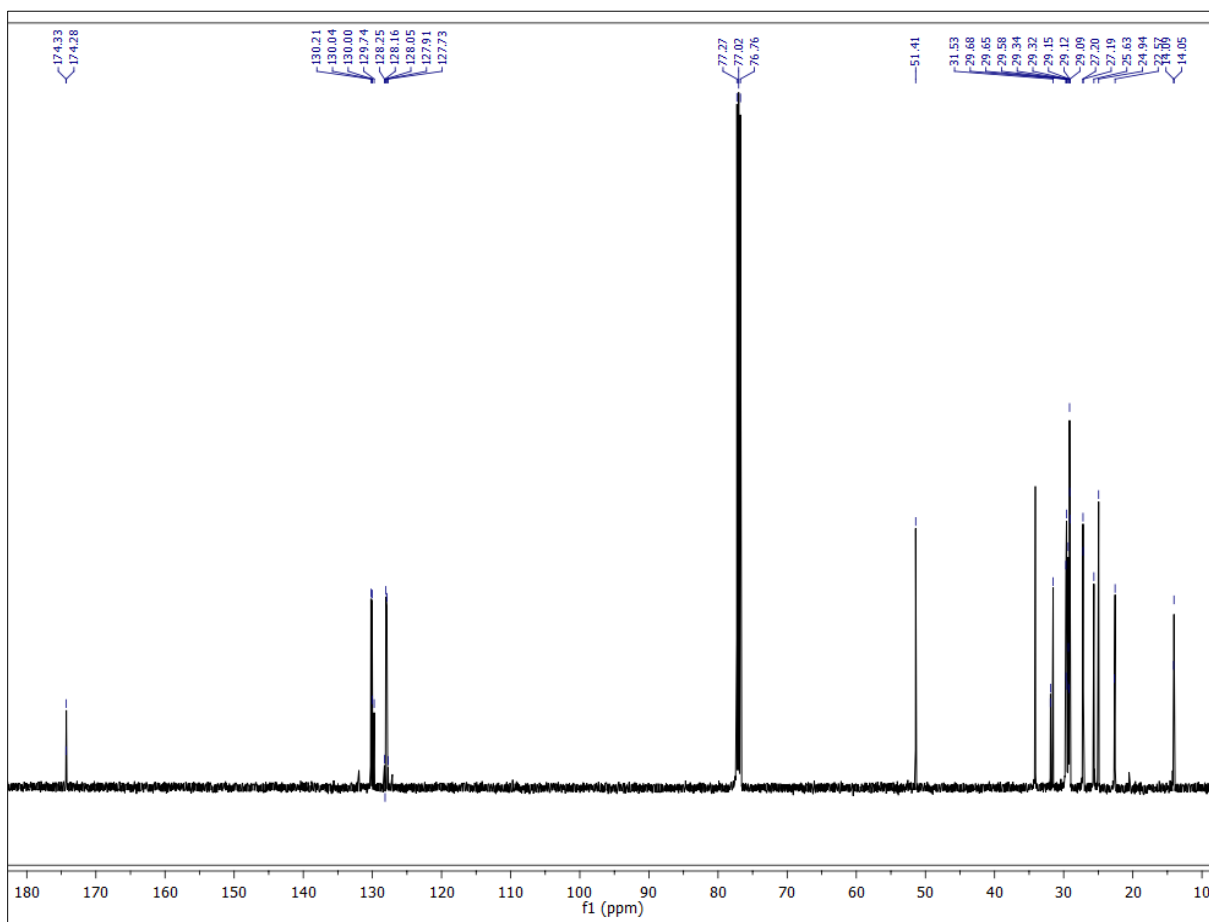

Figure 5.10 ^{13}C NMR spectrum of synthesized biodiesel from used vegetable oil

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

The chemical composition of fatty acid methyl esters (FAME) was analyzed by GCMS which reveals its suitability as fuel in diesel engine. As summarized in Table 5.3 FAMEs comprises three major constituents: methyl hexadecanoate (15.96%), methyl 9-octadecenoate (32.15%), methyl (Z,Z)-9,12-octadecadienoate (41.73%) followed by four minor constituents: Methyl(Z,Z,Z)-9,12,15-octadecatrienoate (8.03%), methyl cis-11-eicosenoate (0.42%), methyl eicosenate (0.82%), and methyl docosanoate (0.78%). FAMEs comprises saturated (16.78%), monounsaturated (33.35%) and polyunsaturated (49.76%) fatty acid methyl esters. The presence of these unsaturated compounds as major constituent decreases the viscosity of biodiesel and increases cetane number [Sharma and Singh, 2010].

Table 5.3 Fatty acid methyl ester composition of synthesized biodiesel

Retention time (min)	% composition	Identified fatty acid methyl ester and their formula	Library Match	Corresponding acid
52.065	15.96	Methyl hexadecanoate ($C_{17}H_{34}O_2$)	98	C16:0
58.08	32.15	Methyl 9-octadecenoate ($C_{19}H_{36}O_2$)	99	C18:1
58.31	41.73	Methyl(Z,Z)-9,12-octadecadienoate ($C_{19}H_{34}O_2$)	99	C18:2
59.02	8.09	Methyl(Z,Z,Z)-9,12,15-octadecatrienoate ($C_{19}H_{32}O_2$)	99	C18:3
68.48	0.42	Methyl cis-11-eicosenoate ($C_{21}H_{40}O_2$)	99	C20:1
63.72	0.82	Methyl eicosenate ($C_{21}H_{42}O_2$)	99	C20:0
68.96	0.78	Methyl docosanoate ($C_{23}H_{46}O_2$)	99	C22:1
Saturated fatty acid methyl ester				16.78
Monounsaturated fatty acid methyl ester				33.35
Polyunsaturated fatty acid methyl ester				49.76

5.2.5 (c) Evaluation of fuel properties

Table 5.4 represents the significant fuel properties such as acid value, density, calorific value, flash point, kinematic viscosity, fire point, cloud point, pour point and cetane number of as-synthesized biodiesel of used vegetable oil as feedstock. The acid value of synthesized biodiesel was 0.5 mg KOH/g and falls in the ASTM limit. Kinematic viscosity and density of biodiesel significantly affect the engine performance and combustion properties. The values of density and viscosity were found to be 0.881 g/cm^3 and 4.9 mm^2/s which were within the range of fuel standard. The calorific value i.e. energy content of the synthesized biodiesel was found to be 43.40 MJ/kg. The values of flash point and fire point, 151 and 159 °C respectively were found to be higher than diesel fuel which are responsible for fire safety. The cloud point and pour points give indication of minimum operating temperature of the fuel which were found to be 6 and 8 °C, respectively. The ignition quality of synthesized biodiesel depends on cetane number [Azam et al., 2005]. The cetane number of synthesized UVO biodiesel was 49 which complies with recommended range for biodiesel (>47). The synthesized biodiesel from UVO feedstock using BaAl$_2$O$_4$ catalyst via methyl transesterification satisfy ASTM D 6751 norms.

Table 5.4 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	0.5	≥0.5	ASTM D 664
Density	g/cm^3	0.881	0.86 to 0.89	ASTM D 4052
Kinematic viscosity (40 ºC)	mm^2/s	4.9	1.9 to 6.0	ASTM D 445
Calorific value	MJ/kg	43.40	>35	ASTM D 240
Flash point	°C	151	>120	ASTM D93
Fire point	°C	159	-	ASTM D93
Cloud point	°C	6	-3 to 12	ASTM D2500
Pour point	°C	8	-15 to 16	ASTM D97-05

Cetane number	-	49	>47	ASTM D976

5.3 Biodiesel synthesis from kusum oil using $BaAl_2O_4$ catalyst

5.3.1 Optimization of biodiesel production parameters

The catalytic activity of synthesized $BaAl_2O_4$ catalyst in transesterification of kusum oil is influenced by reaction parameters such as methanol: oil molar ratio, catalyst dose, reaction time, temperature and stirring speed. Therefore, a series of transesterification reactions at varying methanol: oil molar ratio 9:1–21:1, catalyst dose 0.5-4.5 wt%, 35-75±0.5 °C temperature, reaction time 0-180 min and stirring speed 300-700 rpm was performed and effect on methyl ester conversion was investigated with aids of graphs. All experiments were performed thrice and their mean values were reported.

5.3.1 (a) Effect of methanol to oil molar ratio

Stoichiometrically, transesterification requires methanol to oil molar ratio of 3:1. Since transesterification reaction is reversible in nature, thus excess of methanol is required to drive the equilibrium in methyl ester formation direction. Optimum methanol: oil molar ratio will form high amount of methoxide ion in presence of catalyst which facilitates high rate of forward reaction. In this work, methanol: oil molar ratio was varied from 9:1 to 21:1 at variable reaction time as depicted in Figure 5.11. The other reaction parameters such as catalyst dose of $BaAl_2O_4$ 3.5 wt%, temperature 65±0.5 °C and stirring speed 600 rpm. It was observed that conversion was increased continuously for all reaction time with increasing methanol: oil molar ratios of 9:1 to 18:1. The maximum conversion 93.02% was achieved at 150 min of time using 18:1 methanol to oil molar ratio. Beyond 18:1 molar ratio, further

increment in methanol quantity imparted adverse effect on conversion reaction [Kaur et al., 2018].

This may be due to the shift of equilibrium in backward direction because of dissolution of produced glycerol in excess methanol. As excess of methanol enhances viscosity of the reaction mixture, this impedes gravity based decantation as well as separation [Guldhe et al., 2017].

5.2.1 (b) Effect of catalyst dose

To investigate the effect of catalyst dose on methyl ester conversion (%), a sequence of transesterification reaction raising mass of catalyst from 0.5 wt% to 4.5 wt% with respect to oil at various studied time (0-180 min) were performed, whereas other reaction conditions remained constant such as methanol: oil molar ratio 18:1, temperature 65±0.5 °C and stirring
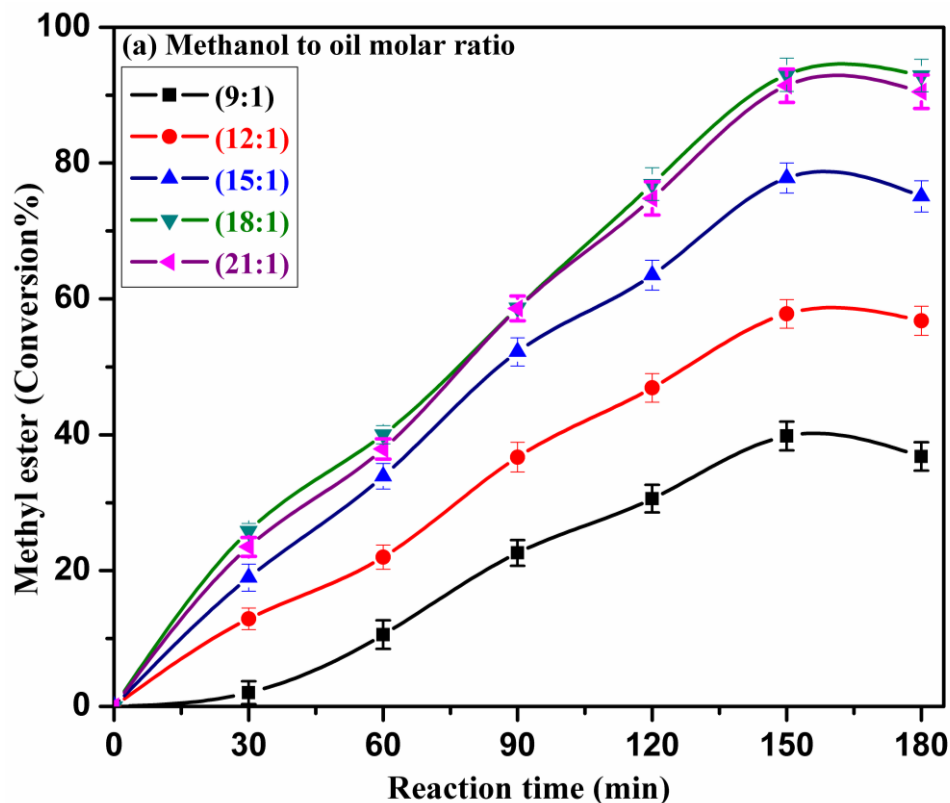
Figure 5.11 Effect of methanol: oil molar ratio (9:1 - 21:1) on methyl ester conversion (%) of kusum oil [catalyst dose (4 wt%); reaction time 0-180 min; temperature 65±0.5 °C and stirring speed 600 rpm]

speed 600 rpm. From Figure 5.12, conversion profile demonstrated increasing trend with increasing amount of catalyst from 0.5 to 3.5 wt% at each reaction time and maximum conversion (93.02%) was obtained at 3.5 wt%. At higher catalyst loading, high biodiesel conversion was obtained due to enhanced interaction between active sites of catalyst and reactants. Whereas, at low catalyst loading, numbers of active sites are relatively lower to effectively catalyze the reaction. Further, as the catalyst dose increases beyond 3.5 wt%, conversion efficiency reduced remarkably as large amount of catalyst increases viscosity of reaction mixture because of soap formation [Singh et al., 2016]. High viscosity of reaction

mixture renders ineffective mass transfer in the triphasic reaction system. Moreover, saponification also diminishes the ease of phase separation of biodiesel and glycerol.
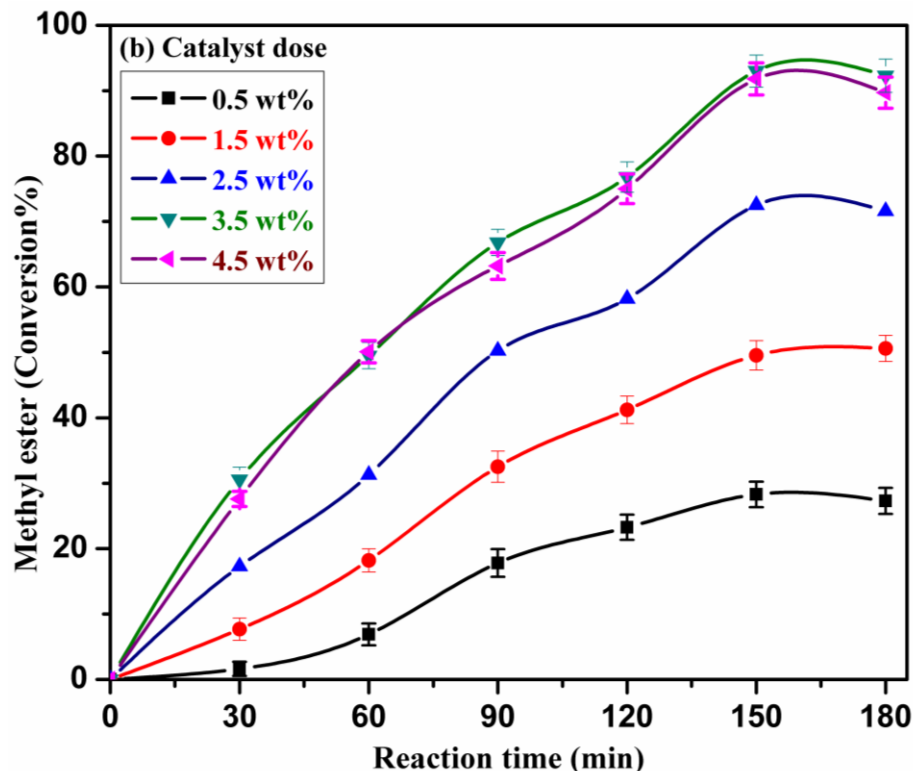

Figure 5.12 Effect of catalyst dose (0.5 – 4.5 wt%) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 18:1; reaction time 0-180 min; temperature 65±0.5 °C and stirring speed 600 rpm]

5.3.1 (c) Effect of reaction temperature

Figure 5.13 clearly demonstrates that reaction temperature positively influences biodiesel conversion. Elevated temperature augmented the solubility of methanol with enhanced diffusion rate in triphasic reaction system. In order to study the effect of reaction temperature on biodiesel production, temperature was varied from 35±0.5 °C to 75±0.5 °C using optimum reaction conditions as methanol: oil molar ratio 18:1, 3.5 wt% catalyst dose and 600 rpm stirring speed for 0-180 min reaction time. Maximum 93.02% of FAME conversion was obtained at 65±0.5 °C as optimum temperature [Gardy et al., 2018].
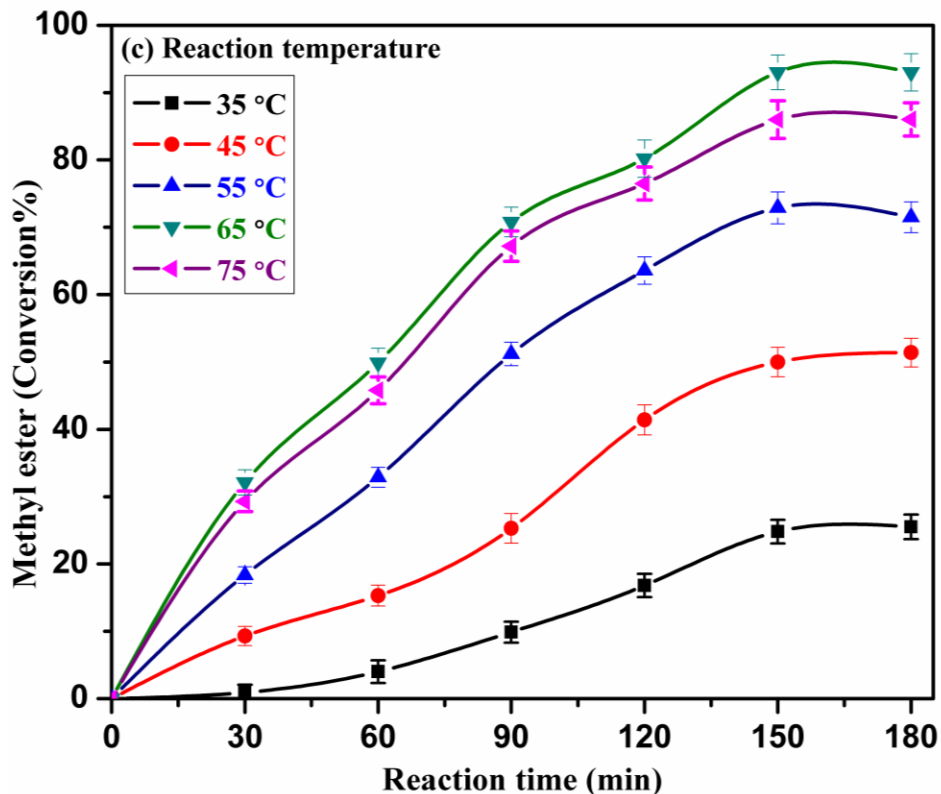
Figure 5.13 Effect of temperature (35 - 65±0.5 °C) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 18:1; catalyst dose 3.5 wt %; reaction time 0-180 min; and stirring speed 600 rpm]

At 64.5°C methanol starts to boil and enhances the collision possibilities between the reactant molecules that resulted in higher biodiesel conversion. When the temperature was further increased to 75±0.5 °C, conversion (%) significantly declines as at temperature greater than 65±0.5 °C, methanol started to evaporate and above its boiling point bubble formation takes place which further inhibits the reaction on three-phase interface (solid catalyst-oil-alcohol) and consequently conversion decreases [Singh et al., 2016].

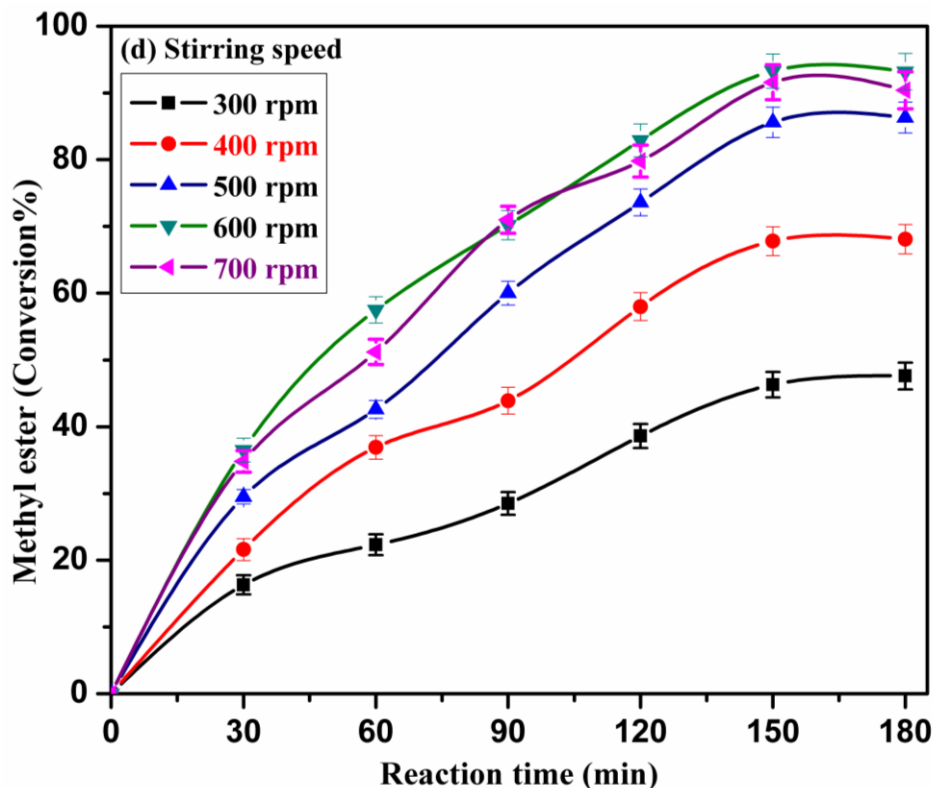**5.3.1 (d) Effect of stirring speed**

Figure 5.14 Effect of stirring speed (300-700 rpm) on methyl ester conversion (%) of kusum oil [methanol: oil molar ratio 18:1; catalyst dose 3.5 wt%; reaction time 0-180 min; and temperature 65±0.5 °C]

As transesterification reaction is two immiscible phase system: liquid phase contains oil and methanol; solid phase is catalyst, the reaction is purely diffusion controlled and takes place only at reactant interface, therefore, mixing plays important role in reducing the mass transfer limitation at the surface of the solid catalyst. The effect of stirring speed was studied at different stirring rates ranging from 300 to 700 rpm at studied reaction time (0-180 min) using the reaction conditions (methanol: oil molar ratio 18:1, 3.5 wt% catalyst dose at 65±0.5 °C reaction temperature). It was found that without stirring of reaction mixture, no biodiesel

conversion was achieved. At 300 rpm, 44.30% conversion was achieved which gradually increased to 93.02% at 600 rpm at the same reaction time (Figure 5.14). Further rise in stirring speed inhibits effective contact of the reactants to transform into product hence no further increment in the conversion was observed at 700 rpm as shown in Figure 5.14 [Mansir et al., 2018].

5.3.2 Reusability

The reuse of catalyst conveys prime information regarding designing of the catalysis for industrial purpose in an economical way. The $BaAl_2O_4$ catalyst reusability was investigated by performing five reaction cycles using optimum transesterification conditions (18:1 methanol: oil molar ratio; 3.5 wt% catalyst dose, 150 min of reaction time at 65±0.5 °C temperature) as depicted in Figure 5.15. The results revealed that catalyst can be reused up to five successive reaction cycles by producing more than 75% of FAME conversion in 5th cycle. The high reusability of catalyst was due to its stable crystalline structure [Feyzi and Norouzi, 2016].
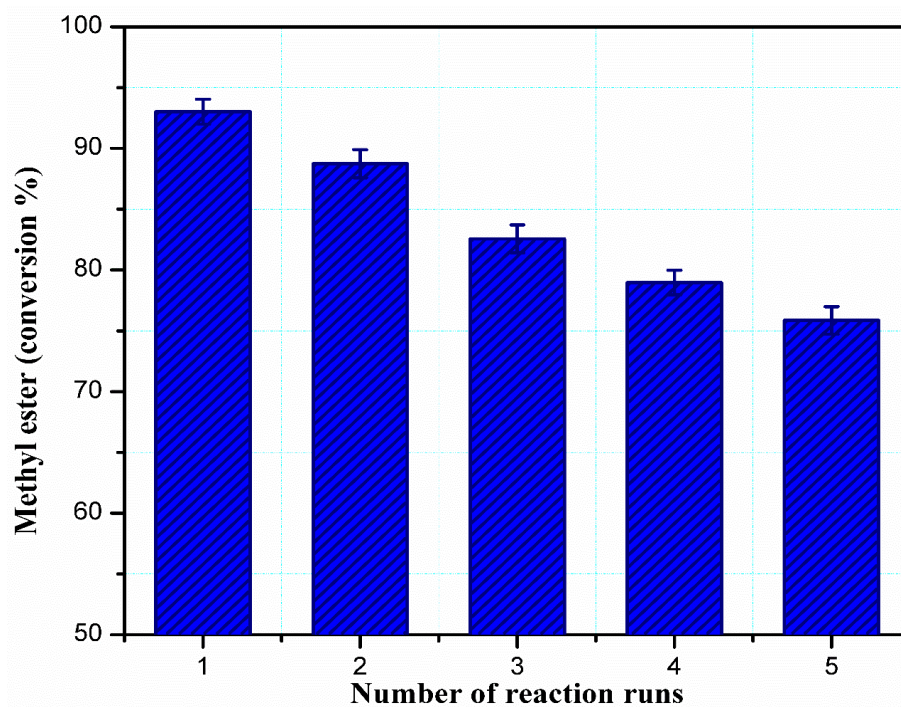
Figure 5.15 Reusability test for the $BaAl_2O_4$ catalyst at optimized conditions [methanol: oil molar ratio 21: 1; catalyst dose 4 wt%; reaction time 0-180min; temperature 65±0.5 °C]

Thus, present catalytic system can be used as cost-effective biodiesel synthesis. The reactant molecules got adsorbed on the catalyst surface and loss of catalyst during washing steps may responsible for small decay in conversion.

5.3.3 Kinetics and thermodynamic study

The kinetic and thermodynamic data help in determining the overall rate constant, activation energy and free energy of the transesterification of kusum oil using $BaAl_2O_4$ catalyst. Therefore reactions were carried out under experimental conditions such as temperature (35-65 °C) and time (0-150 min) using parameter methanol: oil molar ratio 18:1, catalyst dose of 4 wt% of $BaAl_2O_4$ and 600 rpm stirring rate as shown in Figure 5.13.

5.3.3 (a) First-order kinetics

The kinetic profile as shown in Figure 5.16 comprises of a plot of $-\ln(1-X)$ against t at different interval of time and temperature and resultant linear relation validates the hypothesis of pseudo-first order kinetics of transesterification of kusum oil using $BaAl_2O_4$ catalyst. From the slope of these plots, rate constant values at different temperature were also determined and presented in Table 5.5 with their regression coefficients [Feyzi and Shahbazi, 2017].
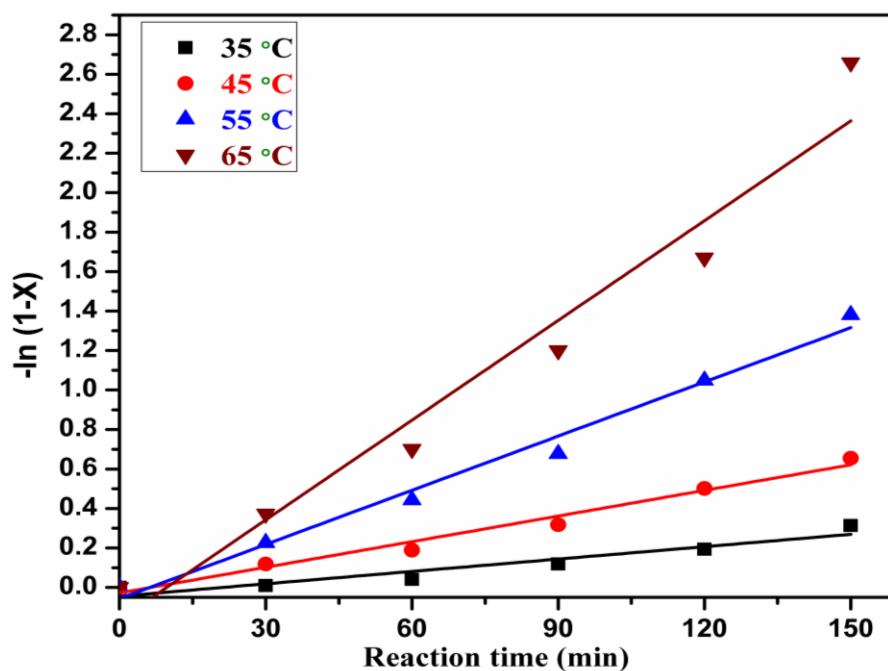

Figure 5.16 Kinetics plots of $-\ln(1-X)$ versus reaction time (min) at different reaction temperatures

Table 5.5 Reaction rate constants at different temperatures

Temperature (°C)	Reaction rate constant (10^{-2}, min^{-1})	Regression coefficient (R^2)
35	0.198	0.90
45	0.401	0.98
55	0.882	0.99
65	1.462	0.90

5.3.3 (b) Activation energy calculation

From the rate constant values in Table 5.7, it is evident that reaction rate increases steadily with the rise in reaction temperature which indicates that reaction temperature greatly controlled the rate of the conversion process in transesterification reaction. In addition, the activation energy of the reaction process was also investigated using Arrhenius relation between the activation energy, temperature and rate constants. The values of activation energy Ea, and pre-exponential factor A can be calculated from the slope and intercept of the plot ln(k) versus 1/T as shown in Figure 5.17 [Kostić et al., 2018]. The activation energy Ea required and pre-exponential factor A for the transesterification of kusum oil catalyzed by $BaAl_2O_4$ catalyst was found to be 61.78 kJ/mol and 5.97×10^7 min^{-1} respectively.

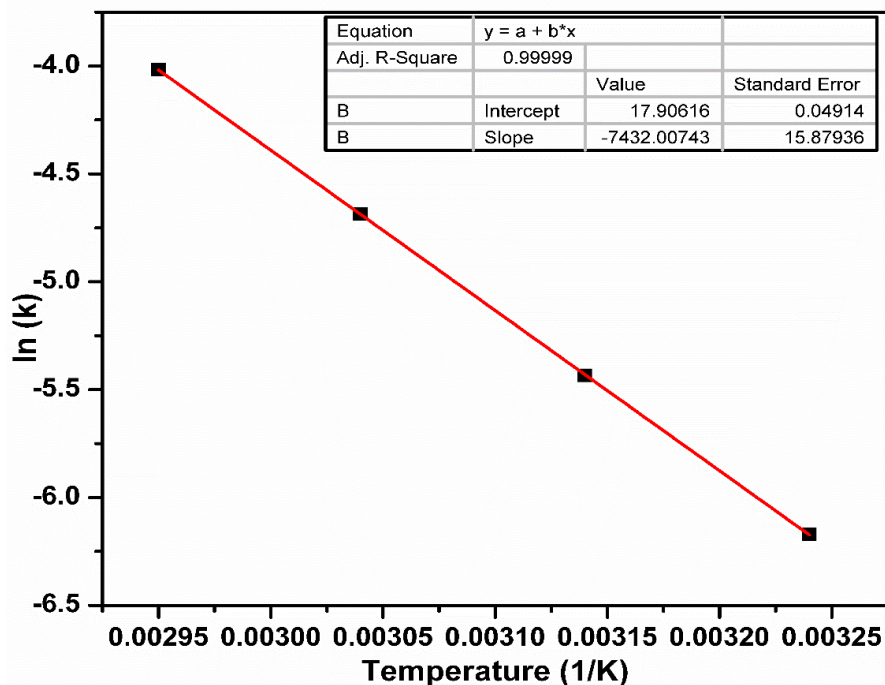| Equation	y = a + b*x		
Adj. R-Square	0.99999		
		Value	Standard Error
B	Intercept	17.90616	0.04914
B	Slope	-7432.00743	15.87936

Figure 5.17 Arrhenius plot ln k vs. 1/T relation of transesterification of kusum oil using $BaAl_2O_4$ catalyst

5.3.3 (c) Thermodynamic study

To evaluate the change in enthalpy, entropy and Gibbs free energy of activation, the thermodynamic analysis was performed by applying Eyring-Polanyi equation. The enthalpy and entropy were obtained from the slope $\frac{-\Delta H}{R}$ and intercept [$\ln \frac{kB}{h} + \frac{\Delta S}{R}$] of linear Eyring plot of 1/T vs. ln (k/T) as shown in Figure 5.18. The values of enthalpy (ΔH) and entropy (ΔS) were found to be 57.44 kJ mol^{-1} and -0.110 kJ mol^{-1}K^{-1} respectively [Lamba et al., 2018]. The Gibbs free energy of activation (ΔG) was also inferred at different temperature and presented in Table 5.6. The Gibbs free energy is a parameter to measure the spontaneity of any chemical reaction. In present study the positive values of Gibbs free energy were observed indicating endergonic and unspontaneous character of the transesterification reaction of kusum oil with $BaAl_2O_4$ catalyst [Gupta et al., 2018].
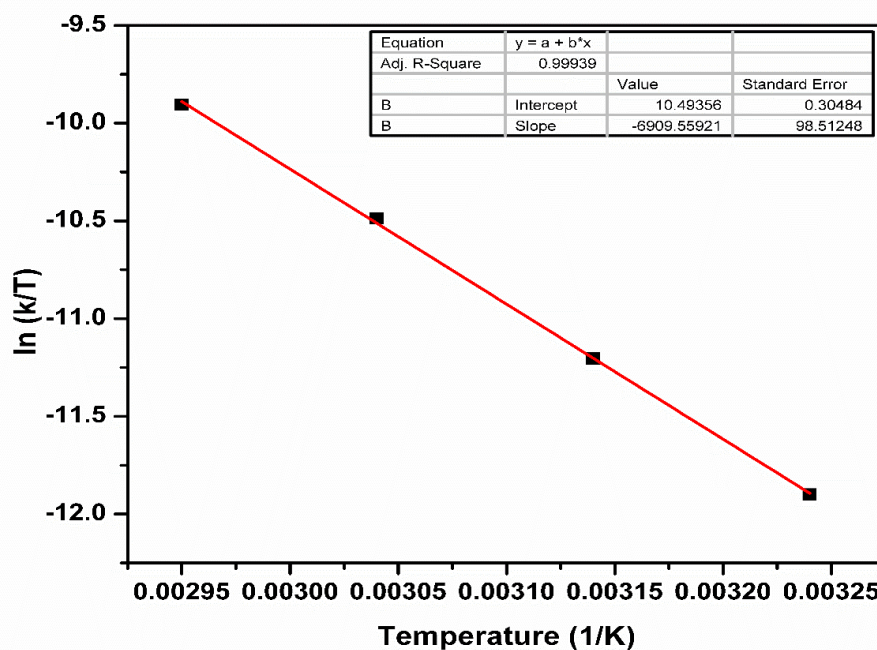

Equation	y = a + b*x		
Adj. R-Square	0.99939		
		Value	Standard Error
B	Intercept	10.49356	0.30484
B	Slope	-6909.55921	98.51248

Figure 5.18 Eyring- Polanyi plot (ln k/T) versus 1/T of transesterification of kusum oil usong BaAl$_2$O$_4$ catalyst

Table 5.6 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})			
Values	57.44	-0.110	**308 K**	**318K**	**328K**	**338K**
			91.42	92.50	93.60	94.70

5.3.4 Green matrix formulation

To measure the "green-ness" of biodiesel synthesis from kusum oil using BaAl$_2$O$_4$ catalyst, *E-* factor and PMI were calculated using experimentally optimized conditions. The values of *E-* factor and PMI were found to be 4.52 and 5.52 respectively. Near to unity values of *E-*factor and PMI indicated least waste generation in the process [Cote et al., 2009].

5.3.5 Characterization of synthesized biodiesel

5.3.5 (a) NMR characterization (^{1}H and ^{13}C)

^{1}H NMR spectrum of kusum oil biodiesel is shown in Figure 5.19. The spectrum of biodiesel has characteristics peaks of methoxy protons and α-methylene group of ester at approximately 3.66 ppm singlet and 2.302 ppm triplet, respectively. The conversion of biodiesel was calculated from integration values of these peaks and it was found to be 93.02% at optimized reaction conditions.

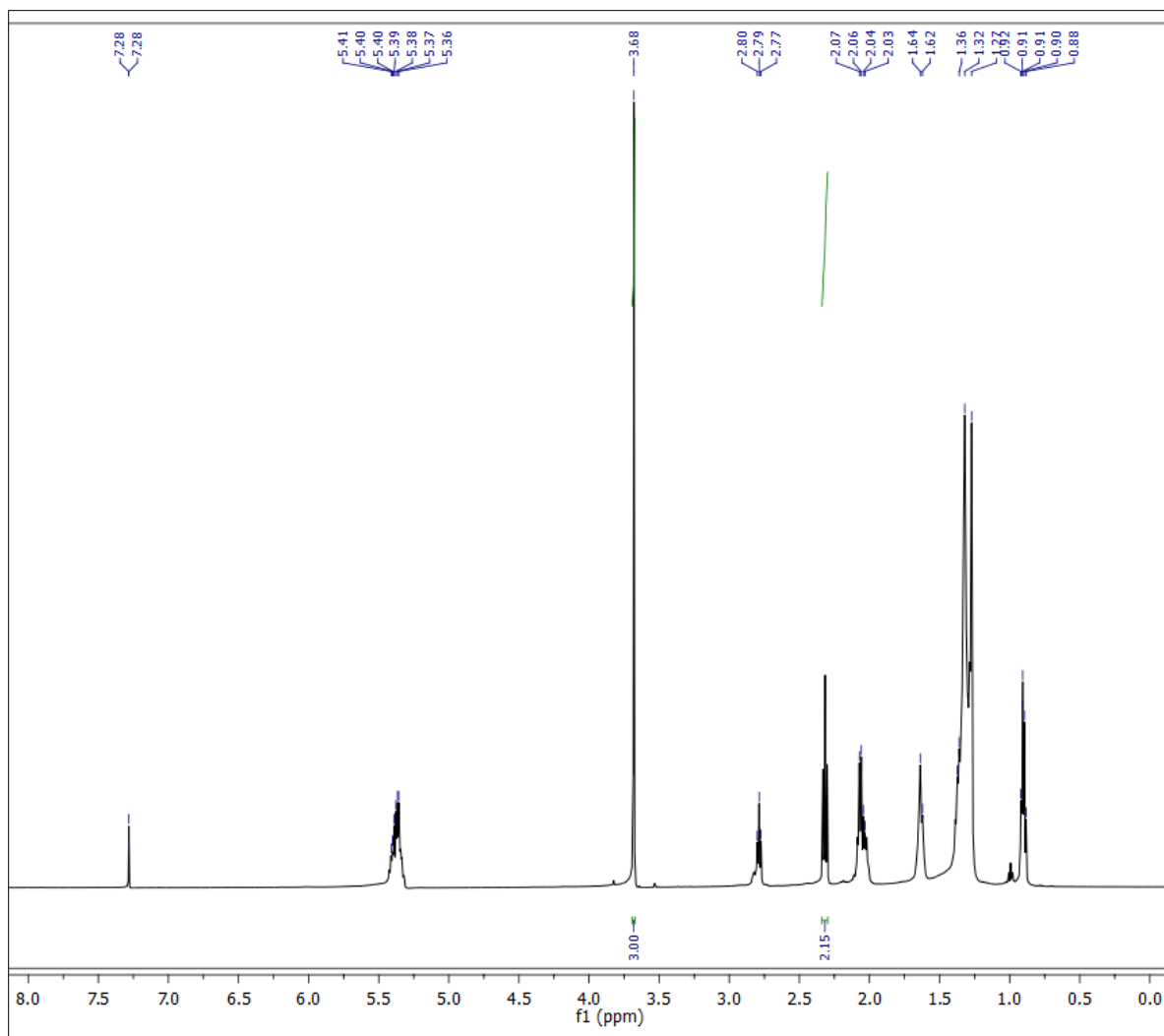Methyl ester conversion % $= \frac{2*3}{3*2.15} * 100 = 93.02\%$ (5.2)

Figure 5.19 ^{1}H NMR spectrum of synthesized biodiesel from kusum oil

These methyl ester related signals confirm the conversion of triglycerides in kusum oil into methyl esters. The other signals observed in spectrum are multiplet form at 5.36–5.41 ppm, are due to olefinic hydrogens and remaining peaks (2.77–2.80 ppm, triplet; 2.03–2.07 ppm, multiplet; 1.62–1.64 ppm, doublet; 1.27–1.36 ppm, multiplet; 0.88–0.92 ppm, multiplet) are related to aliphatic hydrogens of alkyl chain in long chain fatty ester [Ghesti et al., 2007].
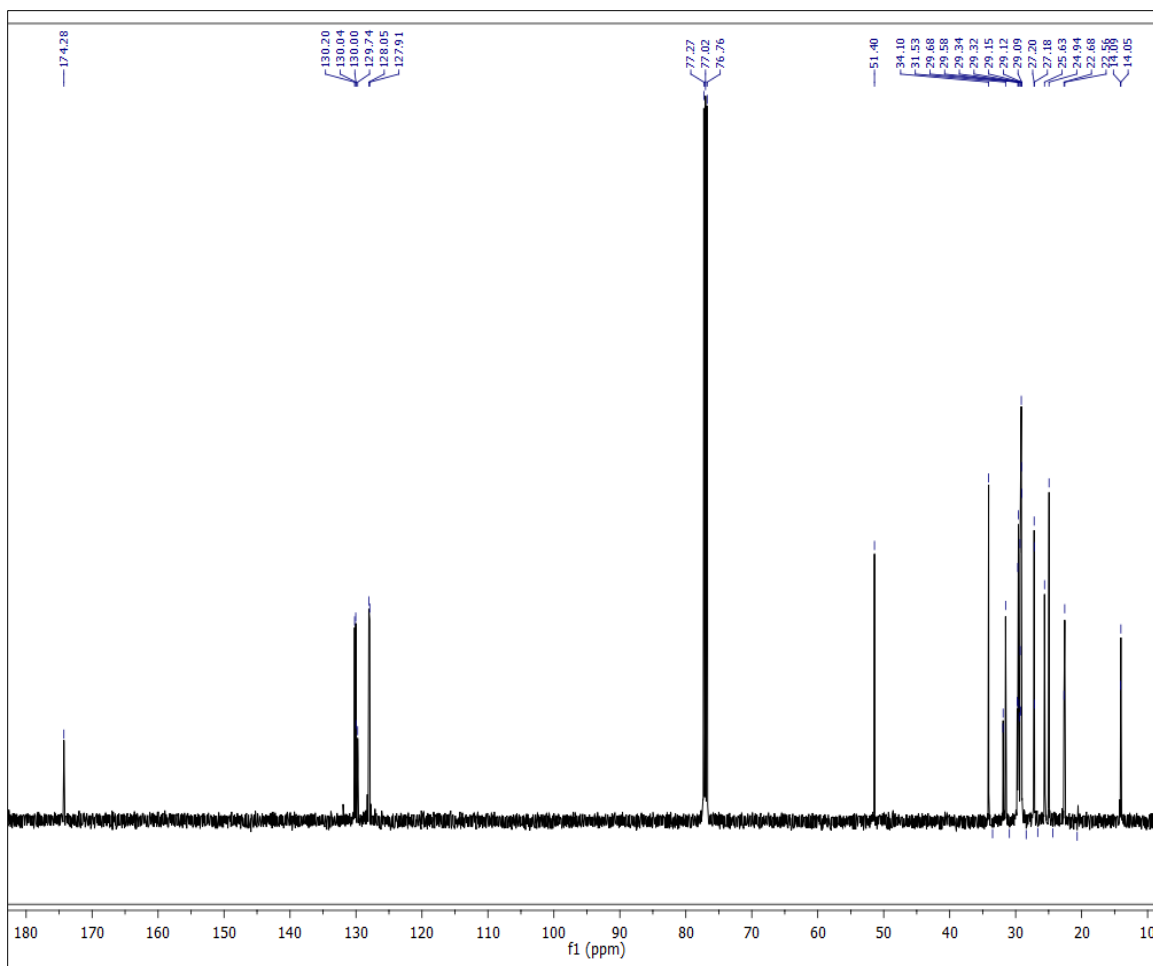
Figure 5.20 ¹³C NMR spectrum of synthesized biodiesel from kusum oil

A representative ¹³C NMR spectrum of kusum oil biodiesel is given in Figure 5.20. The spectrum shows the characteristics singlet peaks of carbon of carbonyl esters at 174.28 ppm. The peaks at 130.20–127.91 ppm are related to the olefinic carbons in long fatty acid chain. The peak at 51.39 ppm was due to the ester carbon (O-C). Peaks available at 34.10–22.56 are related to methylene carbons of long carbon chain in fatty esters. Other peaks at 14.09 and 14.05 signify the terminal carbons of methyl group [Ghesti et al., 2007].

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

The fatty acid profile of synthesized methyl esters from kusum oil is illustrated in Table 5.7 which gives the information of its suitability as fuel in engines. As summarized in Table 5.7, FAMEs comprise four major constituents: Methyl hexadecanoate (16.78%), Methyl 13-eicosenoate (26.59%), Methyl 18-methylnonadecanoate (39.88%) and Methyl(Z,Z)-9,12-octadecadienoate (10.10%) followed by four minor constituents: Methyl hexadec-9-enoate (3.26 %), Methyl octadecanoate (4.48%), Methyl (Z)-docos-13-enoate (5.03%), and Methyl docosanoate (3.59%). FAMEs comprises saturated (61.14%), monounsaturated (34.88%) and polyunsaturated (10.10%) fatty acid methyl esters [Lu et al., 2009].

Table 5.7 Fatty acid methyl ester composition of synthesized biodiesel

Retention time (min)	%composition	Identified fatty acid methyl ester and their formula	Library Match	Correspon-ding acid
36.43	3.26	Methyl hexadec-9-enoate ($C_{17}H_{32}O_2$)	99	C16:1
39.23	16.78	Methyl hexadecanoate ($C_{17}H_{34}O_2$)	98	C16:0
42.44	10.10	Methyl(Z,Z)-9,12-octadecadienoate ($C_{19}H_{34}O_2$)	99	C18:2
46.39	4.48	Methyl octadecanoate ($C_{19}H_{38}O_2$)	99	C18:0
50.70	26.59	Methyl 13-eicosenoate ($C_{21}H_{40}O_2$)	99	C20:1
52.49	39.88	Methyl 18-methylnonadecanoate ($C_{21}H_{42}O_2$)	99	C20:0

55.30	5.03	Methyl (Z)-docos-13-enoate ($C_{23}H_{44}O_2$)	99	C22:1
56.78	3.59	Methyl docosanoate ($C_{23}H_{46}O_2$)	99	C22:0
Saturated fatty acid methyl ester				61.14
Monounsaturated fatty acid methyl ester				34.88
Polyunsaturated fatty acid methyl ester				10.10

5.3.5 (c) Evaluation of fuel properties

The results of important fuel quality parameters such as acid value, density, calorific value, flash point, kinematic viscosity, fire point, cloud point, pour point and cetane number of synthesized biodiesel from kusum oil using $BaAl_2O_4$ catalyst are illustrated in Table 5.8 and compared with ASTM specifications. The acid value of synthesized biodiesel was 0.4 of mg KOH/g and is within the ASTM limit. Kinematic viscosity and density are important measurement and affect the incomplete atomization of fuel in combustion chamber resulting in deposition of particles in engine parts and ultimately reducing engine performance. The value of density and viscosity were found to be 0.885 g/cm^3 and 4.95 mm^2/s which satisfy the range of ASTM standard. The calorific value of the synthesized biodiesel was 40.35 MJ/kg which is lower than diesel fuel due to higher oxygen content. The higher flash point and fire points of fuel ensure greater safety in handling storage, and transportation. The flash point and fire point values of i.e. 155 and 161 °C respectively are found to be higher than diesel fuel. Cloud point of a fuel is the temperature at which the liquid fuel becomes cloudy because of solidification of saturates. The pour point is the temperature at which liquid loses its flow characters and becomes semi-solid. The values of cloud point and pour point of synthesized

biodiesels were observed to be higher than the diesel fuel i.e. 3 and -2 respectively which limits the application of biodiesel in cold environment. The ignition delay of fuel depends on cetane number. The cetane number of synthesized kusum oil biodiesel was 51.9 which complies with recommended range for biodiesel (>47). As mentioned earlier, the synthesized biodiesel using kusum as feedstock and $BaAl_2O_4$ catalyst via methyl transesterification satisfied the range of ASTM D 6751 and can be an alternative of diesel fuel [Essamlali et al., 2017].

Table 5.8 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	0.4	$\geq$0.5	ASTM D 664
Density	g/cm^3	0.885	0.86 to 0.89	ASTM D 4052
Kinematic viscosity (40 °C)	mm^2/s	4.95	1.9 to 6.0	ASTM D 445
Calorific value	MJ/kg	40.35	>35	ASTM D 240
Flash point	°C	155	>120	ASTM D93
Fire point	°C	161	-	ASTM D93
Cloud point	°C	3	-3 to12	ASTM D2500
Pour point	°C	-2	-15 to16	ASTM D97-05
Cetane number	-	51.9	>47	ASTM D976

5.4 Conclusions

The heterogeneous base catalyst $BaAl_2O_4$ was successfully utilized for biodiesel production from transesterification of non-edible feedstocks using vegetable oil and kusum oil. The optimization studies revealed that maximum conversion of used vegetable oil biodiesel was

93.45% at reaction conditions; methanol: oil molar ratio 21:1, catalyst dose of 4 wt%, reaction temperature of 65±0.5 °C for 150 min of time and 600 rpm stirring rate whereas, 93.02% biodiesel conversion was obtained for kusum oil feedstock at optimized reaction conditions; methanol: oil molar ratio 18:1, catalyst dose of 3.5 wt%, reaction temperature of 65±0.5 °C for 150 min and 600 rpm. The catalyst can be reused up to five reaction cycles in transesterification of UVO and kusum oil by producing >75% conversion. A pseudo-first order kinetic model was fitted well for transesterification of used vegetable oil and kusum oil using $BaAl_2O_4$ catalyst. The required activation energy and frequency factor (A) were 60.55 kJ/mol and 3.73×10^7 min^{-1} as well as 61.78 kJ/mol and 5.97×10^7 min^{-1} respectively for used vegetable oil and kusum oil feedstocks. The enthalpy (ΔH) and entropy (ΔS) values transesterification reaction were 57.873 kJ mol^{-1} and -0.103 kJ mol^{-1}K^{-1} for used vegetable oil and 57.44 kJ mol^{-1} and -0.110 kJ mol^{-1}K^{-1} for kusum oil respectively. The E- factor and PMI values were found to be 3.85 and 4.85 for transesterification of used vegetable oil, whereas 4.52 and 5.52 for kusum oil respectively. The synthesized used vegetable oil biodiesel and kusum oil biodiesel were characterized by NMR (^{1}H and ^{13}C) and GCMS for compositional analysis. The important fuel characteristics such as acid value, density, kinematic viscosity (40 ℃), calorific value, flash point, fire point, cloud point, pour point, and cetane number were within ASTM D6751 standards. Synthesis of biodiesel from used vegetable oil and kusum oil using $BaAl_2O_4$ catalyst was economically feasible and retained the superior quality and can be utilized for large scale biodiesel production.