Chapter 6

Application of barium - tin oxide ($Ba-SnO_2$) catalyst in biodiesel production from waste cooking oil and castor oil

6.1 Introduction

This chapter includes the activity of barium stannate (BSO) catalyst for the methyl esterification of waste cooking oil (WCO) and castor oil (CO). Firstly, Ba : Sn atomic ratio and activation temperature of the catalyst were optimized, then reaction parameters like oil to methanol molar ratio, catalyst weight %, reaction temperature, time were optimized to get the best catalytic outcome. Aftermath, reusability of the catalyst BSO was investigated. Kinetic and thermodynamic parameters such as rate constants at different temperatures, reaction activation energy, enthalpy of activation, entropy of activation and Gibb's free energy of activation were evaluated. The green parameters like yield, turnover frequency, E-factor and process mass index were determined to know the impact of this catalytic reaction on environment and economics. The formation of product biodiesel was confirmed by NMR characterization technique. However, GC-MS helped to find out the methyl esters contribution in biodiesel composition. The physicochemical and fuel properties were estimated by ASTM standard methods.

6.2 Optimization of influential reaction parameters

The entire optimization process was designed by the means of various parameters under the consideration of their significant contribution in FAME conversion. To investigate the individual impact of the following factors on FAME conversion, a series of transesterification reactions were conducted over a precise range following one variable at a time (OVAT) method: Ba/Sn atomic ratio (1 : 1, 2 : 1, 1 : 2), catalyst activation temperature (550 to 950ºC), oil to methanol molar ratio (1 : 4 to 1 : 24), catalyst weight % (0.5 to 3 wt%), reaction temperature (35 to 75ºC), and time (5 to 35 min). Derived biodiesel from waste cooking oil and castor oil were termed as WCOME and COME respectively. Each reaction was performed for three times and the mean of three outcomes was considered as final result. The experimental events of such optimization studies are discussed elaborately in the following subheads with the respective plots.

6.2.1 Impact of Ba : Sn atomic ratio and catalyst activation temperature on methyl ester conversion (%)

For immense catalytic activity in transesterification, it is necessary to optimize the Ba/Sn atomic ratio and calcination temperature of the as-synthesized catalysts. Thus, to verify the optimum stoichiometric ratio in catalyst, both metal (Ba & Sn) concentrations were varied. Figure 6.1A displays that among all catalyst samples, Ba/Sn atomic ratio 1 : 1 (i.e. BSO) was obtained as the best stoichiometric ratio for transesterification of WCO and CO. This might have occurred due to synergistic effect of large surface area and higher basicity on transesterification. In case of 2BSO, catalyst having 2 : 1 Ba/Sn atomic ratio, showed lower catalytic activity due to lower surface area and lower basic strength as compared to BSO. However, B2SO (Ba/Sn 1 : 2) catalyst showed meager FAME conversion as the excess and catalytically inactive SnO_2 was randomly accumulated over the surface of $BaSnO_3$ and blocked the active sites. Thus, it caused poor accessibility of the triglyceride molecules at the active sites (Sahani et al., 2019).

The optimum calcination temperature of the catalyst BSO was explored by conducting a set of batch reactions using BSO catalyst calcined at different temperature varying from 550°C to 950°C at following reaction conditions: oil to methanol molar ratio 1 : 16, catalyst dose 2.5 wt%, reaction temperature 65°C for 25 min time duration for WCO transesterification, and oil to methanol molar ratio 1 : 16, catalyst dose 2 wt%, reaction temperature 65°C for 30 min time duration for castor oil transesterification. Figure 6.1B has depicted that fatty acid methyl ester conversion was accelerated with elevating calcination temperature from 550°C to 850°C but slightly decreased at 950°C.

The maximum FAME conversions (98% of WCOME and 97.51% COME) were obtained at 850ºC which has been considered as optimum calcination temperature for BSO catalyst. This observation can be corroborated by the information getting from TGA and XRD analysis of the catalyst BSO. Increment in catalyst activation temperature up to 850ºC endorsed pure $BaSnO_3$ perovskite phase which was supposed to be the active phase in methyl esterification reaction. On the other hand, reduction in FAME conversion at a calcination temperature beyond 850ºC might have occurred due to significant deformation in active sites at high temperature. Finally, it is concluded that the catalyst having Ba : Sn atomic ratio 1 : 1 and calcined at 850ºC has the most active form for the transesterification reaction.

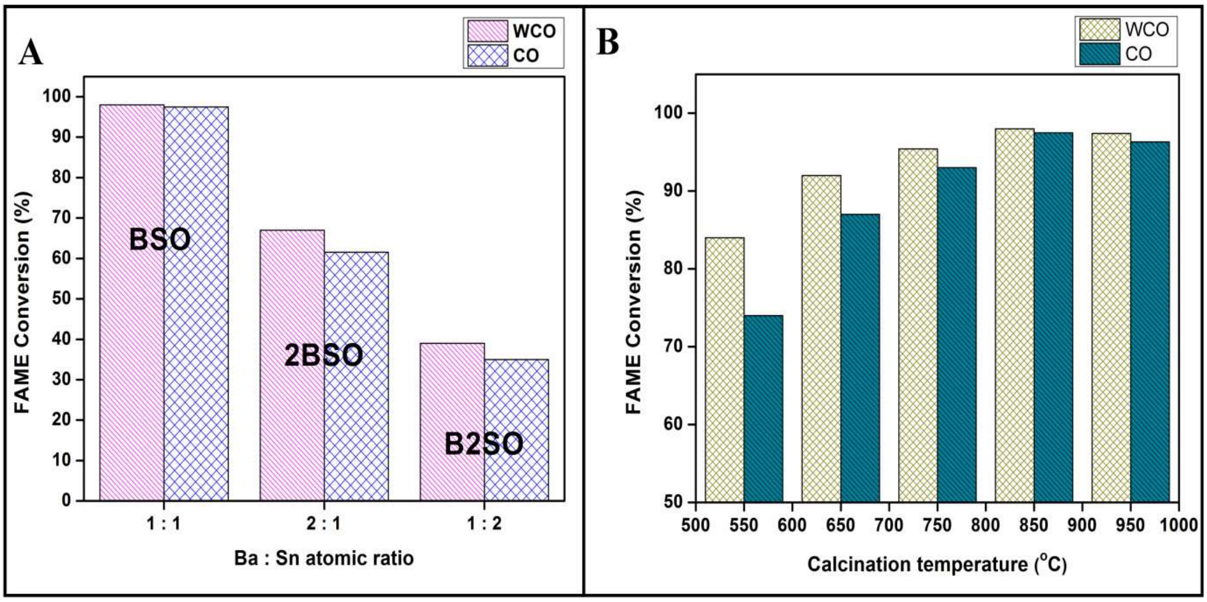

Figure 6.1 A) Effect of Ba : Sn atomic ratio and B) catalyst calcination temperature on methyl esterification of waste cooking oil (WCO) and castor oil (CO)

6.2.2 Impact of oil : methanol molar ratio and catalyst weight percentage on methyl ester conversion (%)

According to the literature, heterogeneous transesterification demands relatively more time and higher molar concentration of alcohol for prominent mass transfer between different phases like solid catalyst, polar methanol and non polar triglyceride (Xie and Huang, 2006). The influence of oil to methanol molar ratio on FAME conversion (%) was investigated by varying the molar ratio from 1:4 to 1:24 under the following reaction conditions: catalyst weight 2.5 wt%, temperature 65±0.5°C, time 25 min for WCO transesterification, and catalyst dose 2 wt%, reaction temperature 65±0.5°C, time 30 min for CO transesterification. Figure 6.2A reveals that the highest FAME conversion of both WCO and CO was obtained at oil to methanol molar ratio 1: 16. Initially, FAME conversion was enhanced with increasing oil to methanol molar ratio, but after getting the optimum molar ratio it started to decrease with further increment in molar ratio. This whole phenomenon can be elaborated on the basis of previous studies and hypothesis. Initially, rising methanol concentration probably stimulated the mass transfer between three phases oil-methanol-catalyst up to the optimum molar ratio (Vyas et al., 2011). Beyond the optimum molar ratio, there were two possibilities for reducing FAME conversion; one was the shifting of reaction equilibrium towards the reactant side which might have stimulated the backward reaction and second was the partial dissolution of glycerol in over-ecxess methanol which complicated the product phase separation and reduced the FAME conversion (Dai et al., 2015).

The effect of catalyst weight (%) in transesterification was investigated by varying catalyst amount from 0.5 to 3 wt% (w/w) with 0.5 wt% increment; however, other reaction parameters were kept constant. The impact of catalyst weight (%) on methyl esterification has been shown in Figure 6.2B, which has depicted that methanolysis is highly influenced by the amount of catalyst as it accounts the number of available active sites exposed on the catalyst surface. Larger amount of catalyst provides more accessibility of the reactants to accommodate and carry out the desired reaction (Likozar and Levec, 2014). Thus, transesterification was accelerated with increasing catalyst amount to the extent of the optimum value, i.e. 2.5 wt % for WCO and 2 wt% for CO tranasesterification. However, larger amount than that of optimum catalyst weight percentage increased the viscosity in reaction medium which consequently decreased the mass transfer between the heterogeneous phases (catalyst-oil-methanol). Thus it showed slight decrement in FAME conversion after the optimum catalyst weight %. Similar phenomenon has also been reported by Sahani et al. (2018) and Roy et al. (2020a).

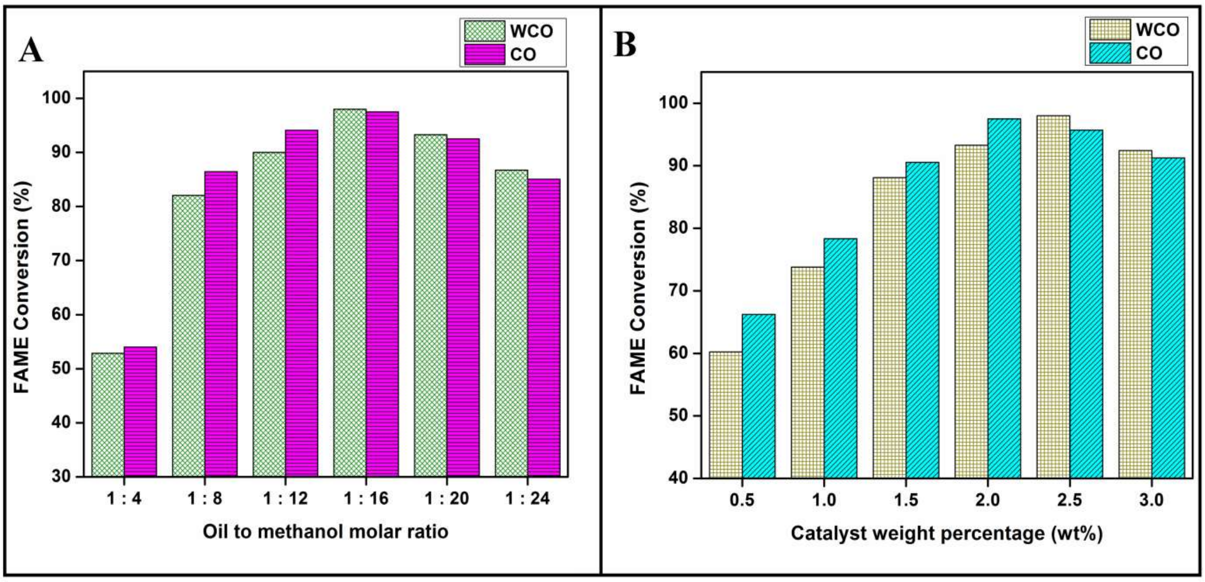

Figure 6.2 A) Effect of oil to methanol molar ratio and B) effect of catalyst weight percentage on methyl esterification reaction of waste cooking oil (WCO) and castor oil (CO)

6.2.3 Impact of reaction temperature and time on methyl ester conversion (%)

In transesterification reaction, temperature is one of the key parameters which require to be optimized to acquire the most favorable condition for the reaction. An optimum temperature provides the require energy to overcome the threshold energy barrier. The optimized temperature was acquired by conducting two sets of transesterification reactions (WCO and CO) over a temperature range of 35ºC to 75ºC. The influence of temperature on FAME conversion using BSO catalyst has represented in Figure 6.3A which implied that FAME conversion was accelerated when temperature was enhanced from ambient to optimum extent but at higher temperature above the optimum temperature it fell down instantly. Here, the optimum temperature of the WCO transesterification using BSO catalyst was found at 65ºC near the boiling temperature of methanol (64.7ºC). Many reports regarding on kinetics of transesterification have stated that this type of reactions are passing through endothermic pathway (Roy et al., 2019). It is known that the reaction equilibrium of an endothermic reaction will be shifted more towards the product side by enhancing reaction temperature. At optimum temperature, the reaction gets the threshold energy for completion of the transesterification reaction. But when the reaction was performed at high temperature above the boiling temperature of methanol (64.7ºC), a significant amount of methanol evaporated which could not take part in the reaction and consequently FAME conversion fell down (Ayoub et al., 2017; Singh et al., 2016).

Optimization of reaction time is also important for economic biodiesel production. For this purpose, two sets of transesterification reactions (WCO transesterification and CO transesterification) were carried out for 35 min keeping other reaction parameters (oil to methanol molar ratio, catalyst weight % and reaction temperature) constant and the FAME conversion was evaluated after 5 min interval.

Figure 6.3B displays the change of FAME conversion due times in methyl esterification reaction of WCO and CO. For heterogeneous catalysis, the rate of the mass transfer invariably depends on effective contact period between interactive phases. Due to poor miscibility of three phases (solid catalyst, polar methanol and non polar triglyceride), heterogeneous transesterification takes comparatively more time than homogeneous and enzymatic transesterification (Singh et al., 2019). Thus, it is obvious that FAME conversion will definitely be promoted with extending the reaction period due to better mass transfer. The maximum WCOME and COME were formed at 25 min and 30 min respectively. Beyond the optimum extent the reaction got the equilibrium and no further change in FAME conversion was observed.

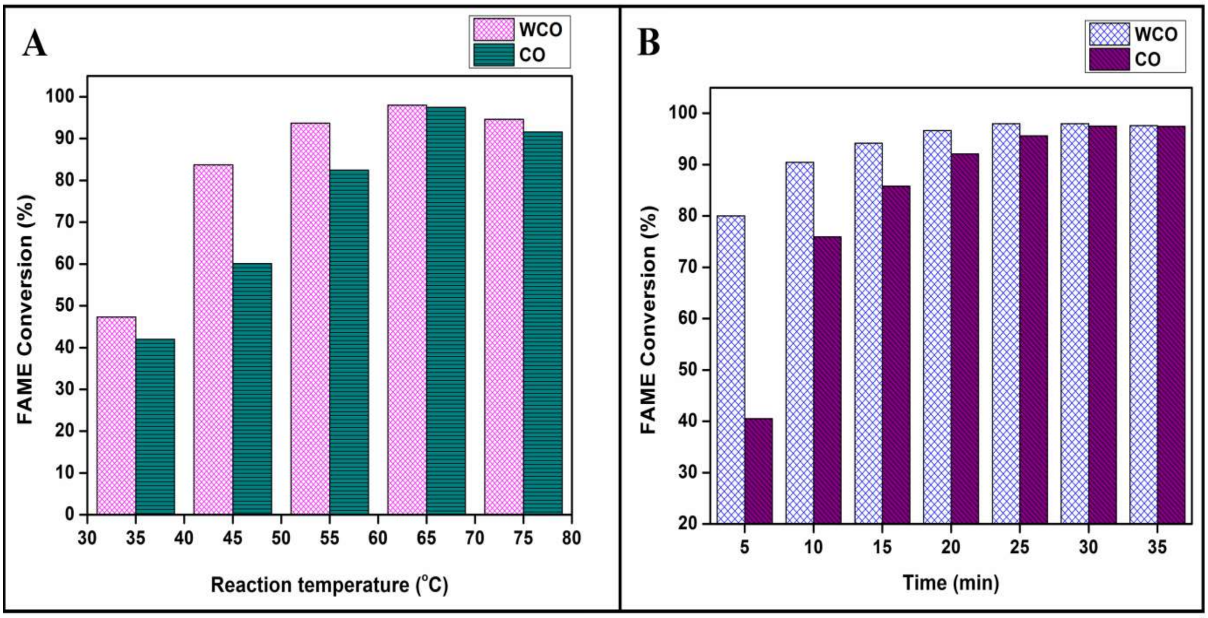

Figure 6.3 A) Effect of reaction temperature and B) reaction time on methyl esterification reaction of waste cooking oil (WCO) and castor oil (CO)

6.3 Reusability of BSO catalyst

One of the important reasons to choose heterogeneous catalyst over homogeneous catalyst for transesterification is its reusability or endurance capacity. Figure 6.4 represents the catalytic endurance of BSO catalyst for six consecutive transesterification of WCO and CO. the transesterifications were performed at optimum reaction conditions as: 1 : 16 oil to methanol molar ratio, 2.5 catalyst weight %, 65°C temperature, 25 min time for WCO transesterification, and 1 : 16 oil to methanol molar ratio, 2 catalyst weight %, 65°C temperature, 30 min time for CO transesterification. After completion of each run, the catalyst was recovered and reactivated through recalcination process. It was found that the activity of the catalyst was almost unchanged (>95%) upto three consecutive run. This means the catalyst is stable for three catalytic cycles. After 3rd run, its efficacy became started to go down. This might have happened due to increasing concentration of acidic carbonate species into the catalyst through surface passivation. Barium has high affinity towards acidic CO_2. During the recalcination process, the organic impurities were decomposed into CO_2 which was further re-adsorbed as carbonate by the Ba-O site. The presence of such carbonate species consequently decreased the basic strength of the catalyst. Despite this, the catalyst showed more than 85% FAME conversion at the 6th catalytic run for both WCO and CO transesterification reactions. This is an impressive result, which implies the catalyst is highly efficient, reusable and stable. Herewith, considering the endurance potency and the conversion capability, it is confidently stated that the catalyst BSO is an efficient catalyst for economic production of biodiesel from waste cooking oil and castor oil.

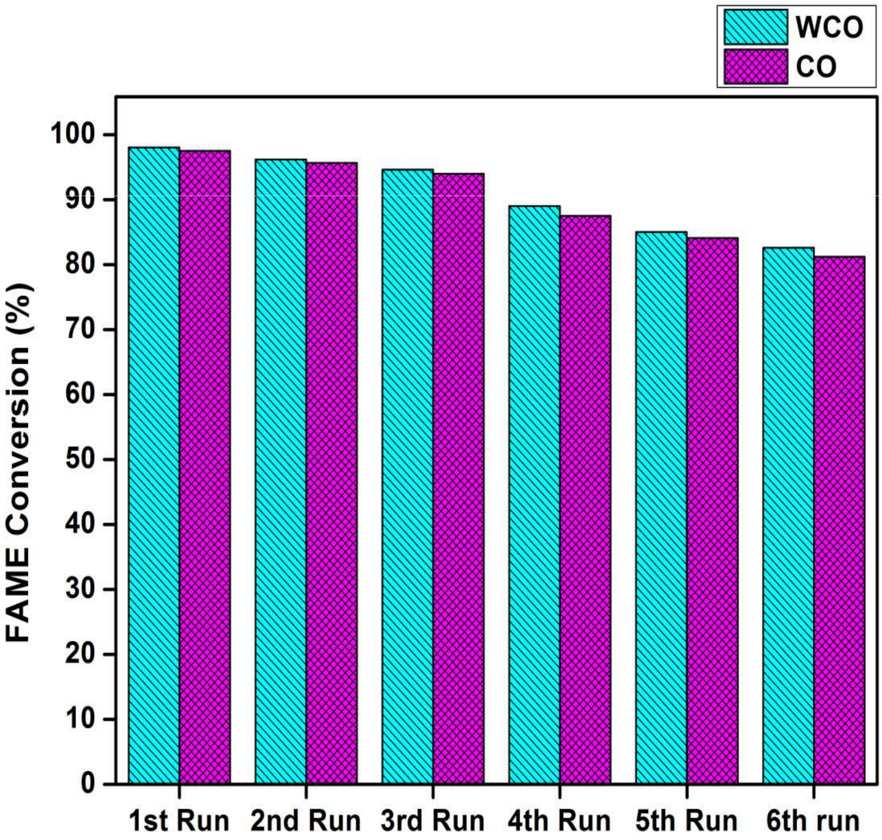

Figure 6.4 Reusability of the BSO catalyst for WCO and CO transesterification at corresponding optimized reaction condition

6.4 Kinetic and thermodynamic studies

The kinetic and thermodynamic parameters corresponding to the transesterification of WCO and CO using BSO catalyst were evaluated by the help of Arrhenius equation and Eyring equation respectively (Ahmad et al., 2014). Required optimum reaction conditions of the respective WCO and CO transesterification reaction (i.e. 1 : 16 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 25 min reaction duration for methyl esterification of WCO; similarly, 1 : 16 oil to methanol molar ratio, 2 wt% catalyst weight, 65°C reaction temperature, 30 min reaction duration for methyl esterification of CO) were maintained during kinetic study.

6.4.1 Determination of rate constants at different temperatures

To evaluate the rate constants at different temperatures, three sets of transesterification reactions for each feedstock were employed at 45°C, 55°C & 65°C under the above mentioned (in section 6.4) reaction conditions. Figure 6.5A and Figure 6.5B are the respective kinetic plots of WCO and CO transesterification using BSO catalyst. The obtained values of the rate constants corresponding to the temperatures have been given in Table 6.1. For both WCO and CO transesterification using BSO catalyst, the regression values of the linear plots lie between 0.985 - 0.998. This clearly demonstrates that our pre-assumptions for the kinetic modeling are very much true. The rate of the reaction only depends upon triglyceride concentration and it is not influenced by the change of methanol concentration as it was really taken in excess amount. So, it can be stated the transesterification reaction of WCO and CO using BSO catalyst followed pseudo first order kinetics. It was also found that rate constant of these reactions (WCO and CO transesterification) will be increased 2 to 3 fold by increasing reaction temperature 10 to 20°C.

Table 6.1 Rate constants for transesterification of WCO and CO at different temperature using BSO catalyst

Feedstock	Waste cooking oil (WCO)			Castor oil (CO)		
Temperature (°C)	45	55	65	45	55	65
rate constant k (min^{-1})	0.0278	0.0531	0.1129	0.0305	0.0579	0.1229
R^2 value	0.993	0.985	0.992	0.993	0.998	0.989

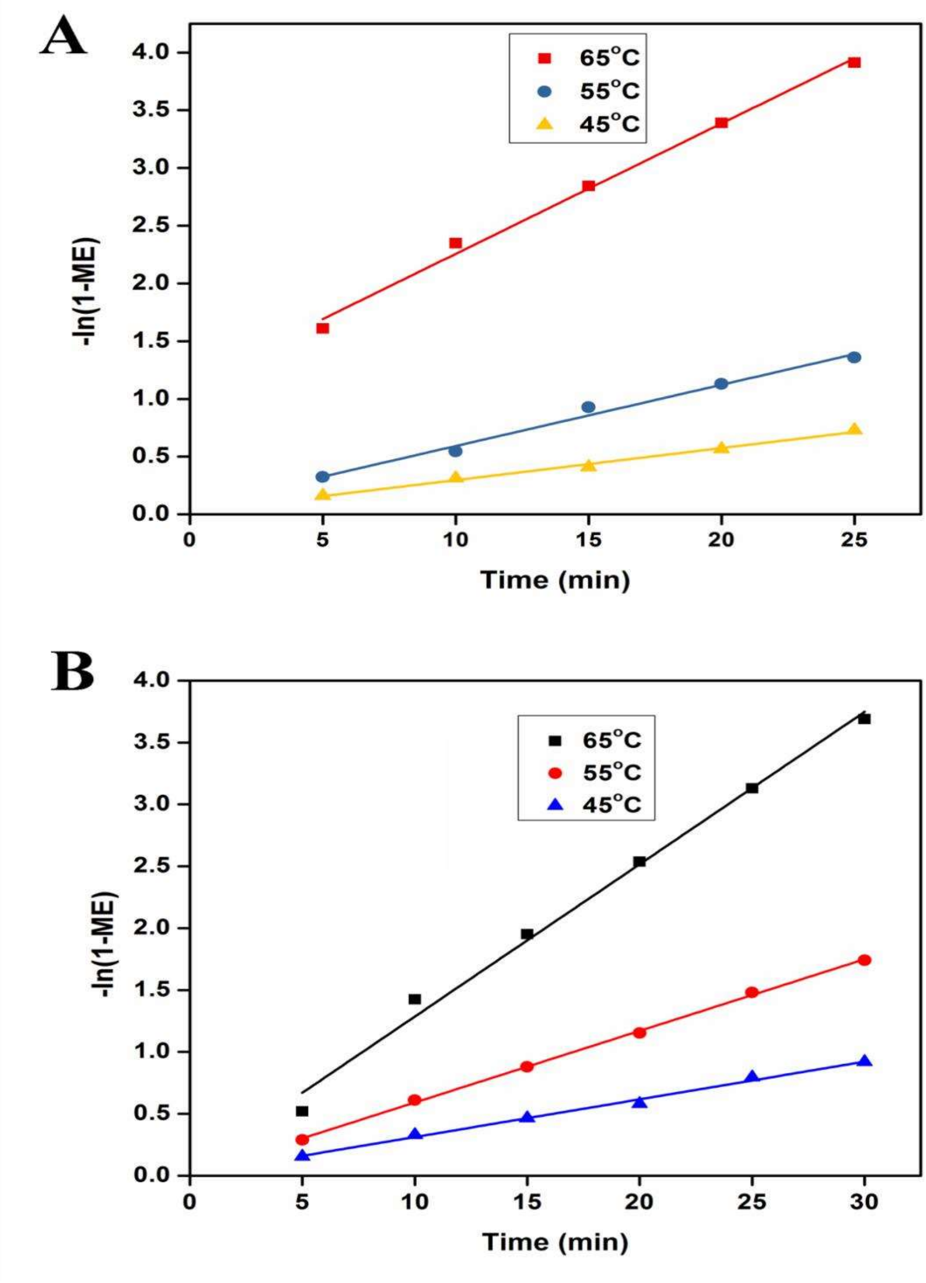

Figure 6.5 (A) Kinetic plot [-ln(1-ME) vs time] of WCO transesterification reaction, (B) kinetic plot [-ln(1-ME) vs time] of CO transesterification reaction using BSO catalyst

6.4.2. Determination of reaction activation energy and pre-exponential factor

Activation energy and pre-exponential factor were respectively derived from the slope and the intercept of the liner plot lnk vs $1/T$ constructed by following Arrhenius equation. Figure 6.6A displays the linear plots or Arrhenius plots of WCO and CO transesterification. The activation energies regarding WCOME and COME formation using BSO catalyst were calculated to be 61.57 kJ/mol and 61.97 kJ/mol respectively. The activation energy endures in range of the base catalyzed heterogeneous reaction which is 33.6-84 kJ/mol (Lee et al., 2014; Moura et al., 2016). From the intercept (lnk) of the same plots, the frequency factor was calculated to be 36.55×10^{7} min^{-1} and 45.05×10^{7} min^{-1} of WCOME and COME formation respectively. The high frequency factors have significant impact on the reaction duration. Thus, within 25 to 30 min, the transesterification reactions acquire equilibrium.

6.4.3. Determination of enthalpy of activation, the entropy of activation and Gibb's free energy of activation

The thermodynamic parameters for the transesterification reactions were evaluated from the Eyring-Polanyi plot ln(k/T) Vs ln(1/T) as shown in Figure 6.6B. From the slope (i.e. $\Delta H^{\#}/R$) and the intercept (i.e. $\ln\left(\frac{k_b}{h}\right)+\frac{\Delta S^{\#}}{R}$) of this plot, enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for the transesterification reaction were calculated respectively. The $\Delta H^{\#}$ values of WCOME and COME formation were found to be 59.76 kJ/mol and 60.61 kJ/mol respectively, whereas, $\Delta S^{\#}$ were obtained as - 87.19 J/mol/K and -84.13 J/mol/K correspondingly. Moreover, $\Delta G^{\#}$ for methyl esterification of WCO and CO were found to be 89.23 kJ/mol and 89.03 kJ/mol at 65°C reaction temperature respectively. The sign of these thermodynamic parameters imply that both reactions were non-spontaneous and endergonic; during reaction entropy of the system reduced (Aziz et al., 2020, Banerjee etal, 2019).

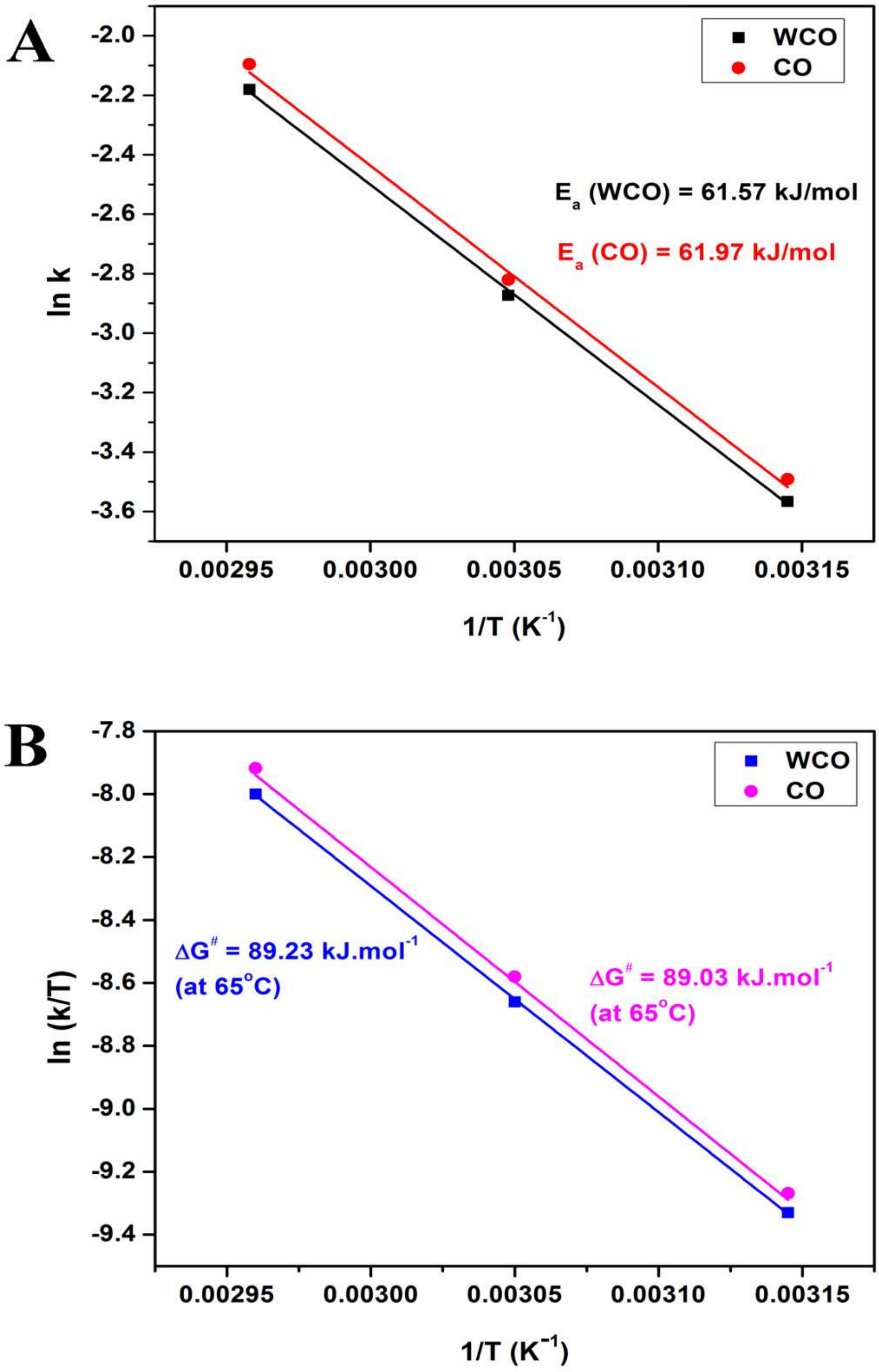

Figure 6.6 (A) Arrhenius plot ln k vs (1/T), and (B) Eyring-Polanyi's plot ln (k/T) vs (1/T) of transesterification of WCO and CO using BSO catalyst

6.5 Green metrics study

The contribution of the catalyst in green chemistry has been evaluated in terms of four basic parameters such as yield (Y), turnover frequency (TOF), E-factor (E_f), and process mass index (PMI). On account these parameters, the methyl esterification of WCO and CO were conducted using BSO catalyst under optimized reaction condition (i.e. 1 : 16 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 25 min reaction duration for methyl esterification of WCO; similarly, 1 : 16 oil to methanol molar ratio, 2 wt% catalyst weight, 65°C reaction temperature, 30 min reaction duration for methyl esterification of CO). The experimental outcomes are presented in Table 6.2. The TOF of BSO catalysts for both methyl esterification of WCO and CO were obtained within the comparable range of homogeneous catalysts (like H_2SO_4, H_3PO_4 etc) used in industry level biodiesel production (Sani et al., 2014). However, E_f and PMI values were procured as minute values that indicates, during the reactions very low amount of waste was generated and the catalytic processes has no harmful effect on environment.

Table 6.2 Green parameters for WCO and CO transesterification using BSO catalyst

Parameter	WCO	CO
Maximum methyl ester conversion (%)	98	97.51
Maximum yield (%)	96.6	92.33
Turnover frequency TOF (s^{-1})	29.63×10^{-3}	22×10^{-3}
E-factor	0.252	0.388
Process mass intensity PMI	1.431	1.725

6.6 Characterization of derived biodiesel

6.6.1 ^{1}H NMR spectroscopy

Figure 6.7A represents the ^{1}H NMR spectra of biodiesel (WCOME) derived from waste cooking oil (WCO). The NMR signals of WCOME were assigned as: chemical shift δ (ppm) = 5.39 to 5.35 (m, **-CH**=**CH-)**, 3.67 (s, -OC**H**$_3$), 2.79 to 2.77 (t, C=C-C**H**$_2$-C=C), 2.33 to 2.30 (t, -OCO-C**H**$_2$), 2.05 (m, C**H**$_2$-C=C), 1.63 (s, C**H**$_2$-C-C=O), 1.32 to 1.26 (m, rest -C**H**$_2$), 0.91 to 0.88 (m, terminal C**H**$_3$) (Yadav et al., 2017). In case of ^{1}H NMR spectra of COME (biodiesel derived from castor oil) presented as Figure 6.7B, the above mentioned all signals associated with different type of protons were found with additional two more signals. These two signals are assigned for α-hydroxy proton and hydroxyl proton of methyl ricinoleate obtained at 3.62 ppm and 2.20 ppm (Sembiring et al., 2018). The presence of –OCH$_3$ proton (at 3.67 ppm) and absence of glyceride proton (expected to be found at 4.2 ppm) confirmed the formation of fatty acid methyl ester.

At the optimized reaction conditions (i.e. 1 : 16 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 25 min reaction duration for methyl esterification of WCO; similarly, 1 : 16 oil to methanol molar ratio, 2 wt% catalyst weight, 65°C reaction temperature, 30 min reaction duration for methyl esterification of CO) FAME conversion was calculated to be

$$\text{FAME conversion \% of WCO to WCOME} = \left(\frac{2\times 27.07}{3\times 18.42}\right)\times 100 \cong 98\ \% \qquad (6.1)$$

$$\text{FAME conversion \% of CO to COME} = \left(\frac{2\times 23.95}{3\times 16.37}\right)\times 100 \cong 97.5\ \% \qquad (6.2)$$

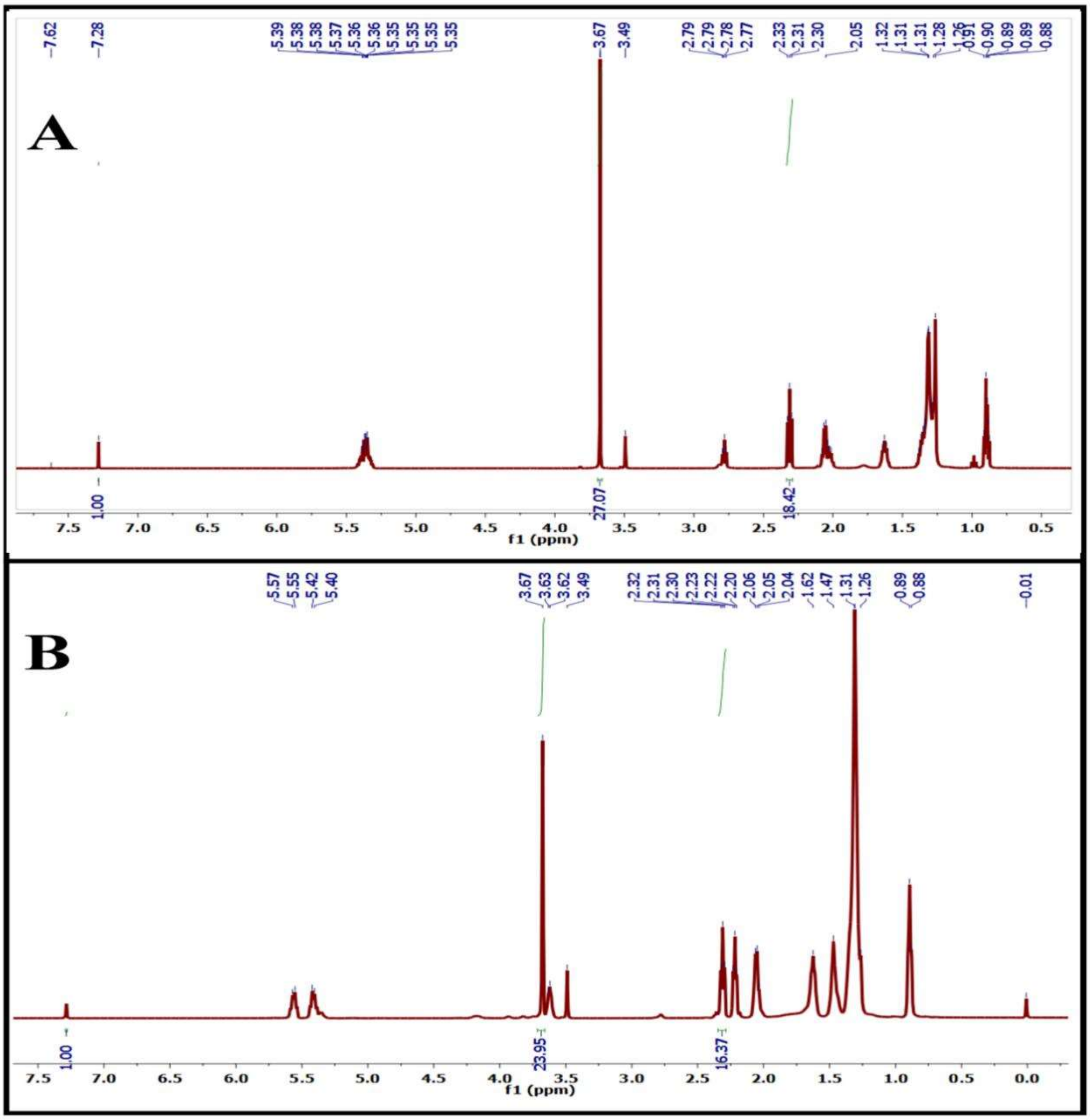

Figure 6.7 (A) ^{1}H NMR spectra of biodiesel derived from waste cooking oil and (B) ^{1}H NMR spectra of biodiesel derived from castor oil using BSO catalyst

6.6.2 ^{13}C NMR spectroscopy

Figure 6.8A displays the ^{13}C NMR spectra of derived biodiesel from WCO. The following sharp signals in ^{13}C NMR spectra of WCOME were observed at chemical shift value of 174.28 ppm corresponds to single ester carbonyl carbon (O-**C**O-), 130.21 to 127.91 ppm corresponds to olefinic carbons (**C**H=**C**H), 77.27 to 76.76 ppm corresponds to solvent carbon (**C**DCl3), 51.41 ppm corresponds to methyl ester carbon (**C**H3O-), 34.10 to 22.56 ppm corresponds to different methylene carbon (**C**H2), 14.05 ppm corresponds to terminal methyl carbon (**C**H3) (Ba et al.,2016). In case of COME, the similar types of carbon signals were found in ^{13}C NMR. In addition, a signal at 71.5 ppm corresponds to α-hydroxy proton (in COME) was observed due to presence of hydroxyl group in methyl ricinoleate. The characteristic signal of methyl ester carbon (at 51.46 ppm) and single ester carbonyl carbon confirm the formation of fatty acid methyl ester (FAME) from WCO and CO (Sembiring et al., 2018;).

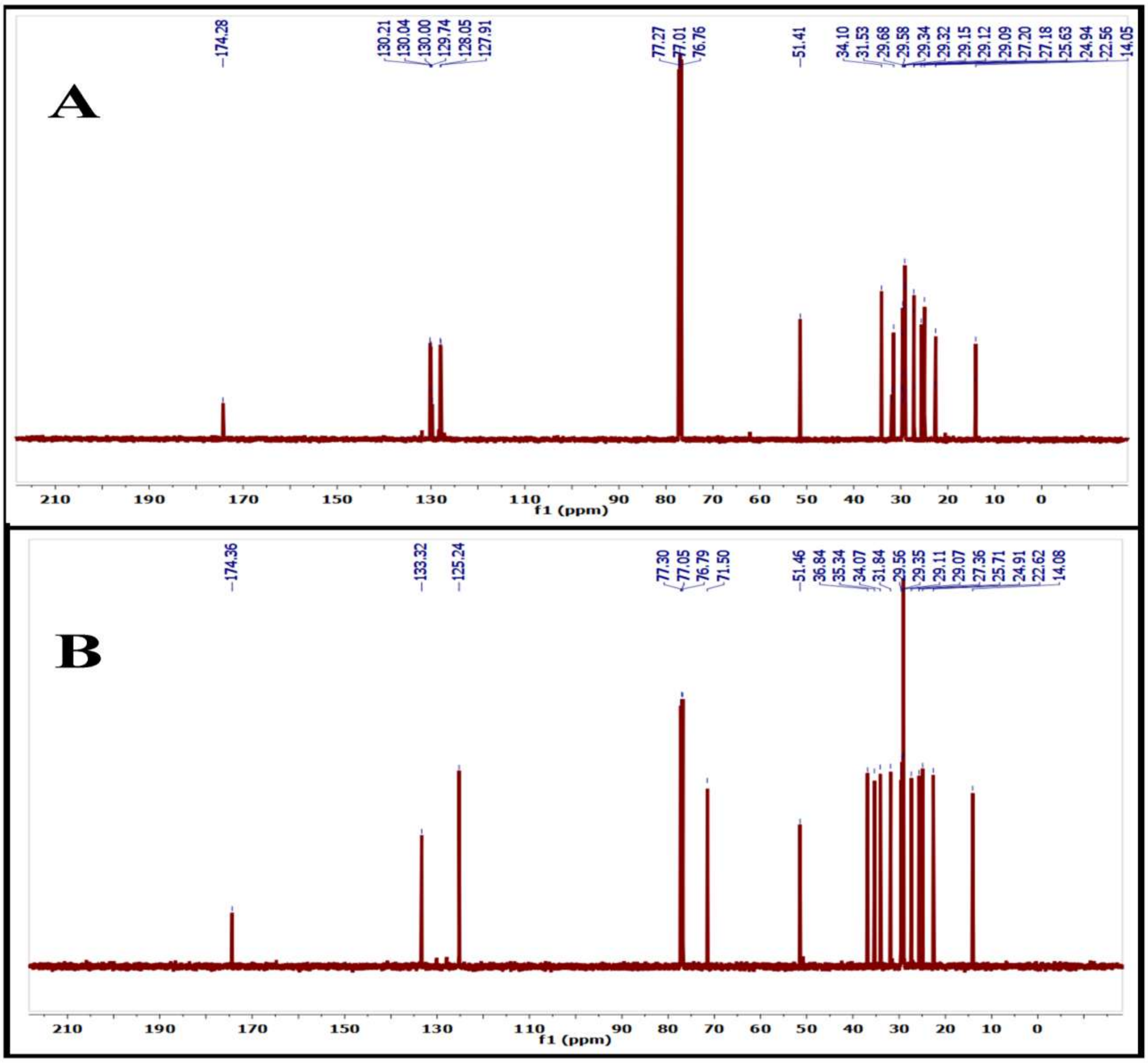

Figure 6.8 (A) ^{13}C NMR spectra of biodiesel derived from waste cooking oil and (B) ^{13}C NMR spectra of biodiesel derived from castor oil using BSO catalyst

6.6.3 GC-MS analysis

Table 6.3 includes the constituent fatty acid methyl esters present in COME. Among the five constituent FAME, found in GC of COME, methyl ricinoleate was obtained as the major constituent. The –OH functional group present in methyl ricinoleate responsible for hydrogen bonding between the fatty acid molecules, which shows adverse effect on physicochemical properties (like higher kinematic viscosity, high density etc) of the biodiesel (Keera et al.,2018).

Table 6.3 FAME composion of biodiesel derived from castor oil using BSO catalyst

Retention time	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
9.117	Methyl palmitate	1.022	99	$CH_3(CH_2)_{14}COOMe$
10.429	Methyl linoleate	4.491	98	$CH_3(CH_2)_{12}(CH=CH)_2COOMe$
11.089	Methyl oleate	3.117	98	$CH_3(CH_2)_{14}CH=CHCOOMe$
11.523	Methyl stearate	1.421	98	$CH_3(CH_2)_{16}COOMe$
12.418	Methyl ricinoleate	89.958	99	$CH_3(CH_2)_{13}CH(OH)CH=CH COOMe$
saturated FAME		2.443%		
monounsaturated FAME		93.075%		
polyunsaturated FAME		4.491%		

In Table 6.4, the constituent fatty acids methyl esters present in WCOME are enlisted with their compositional percentage. The major five components are methyl α-linolenate, methyl palmitate, methyl oleate, methyl linolinate, methyl stearate shared cumulatively 97.13% of total contribution in WCOME. The saturated FAME content in WCOME is much higher than that of COME. Thus, it is expected that WCOME will show better combusible property compare to COME (Gurunathan and Ravi,2015).

Table 6.4 FAME composion of biodiesel derived from waste cooking oil using BSO catalyst

Retention time	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
4.178	Methyl laurate	0.29	98	$CH_3(CH_2)_{10}COOMe$
6.031	Methyl myristate	0.16	99	$CH_3(CH_2)_{12}COOMe$
6.318	Methyl myristoleate	0.77	98	$CH_3(CH_2)_{10}(CH{=}CH)COOMe$
8.712	Methyl palmitate	14.21	98	$CH_3(CH_2)_{14}COOMe$
8.935	Methyl palmitoleate	0.39	98	$CH_3(CH_2)_{12}(CH{=}CH)COOMe$
11.491	Methyl stearate	5.36	99	$CH_3(CH_2)_{16}COOMe$
11.683	Methyl oleate	29.03	99	$CH_3(CH_2)_{14}(CH{=}CH)COOMe$
12.225	Methyl linoleate	43.35	98	$CH_3(CH_2)_{12}(CH{=}CH)_2COOMe$
12.839	Methyl α-linolenate	5.18	99	$CH_3(CH_2)_{10}(CH{=}CH)_3COOMe$
14.277	Methyl arachidate	0.22	98	$CH_3(CH_2)_{18}COOMe$
14.625	Methyl paullinate	0.43	99	$CH_3(CH_2)_{16}(CH{=}CH)COOMe$
17.191	Methyl behenate	0.61	99	$CH_3(CH_2)_{20}COOMe$
saturated FAME		20.85%		
monounsaturated FAME		30.62%		
polyunsaturated FAME		48.53%		

6.7 Fuel properties of synthesized biodiesel

To ascertain the compatibility of the synthesized biodiesel for using as substituted fuel, there are standard ranges of some important physicochemical and fuel properties or parameters prescribed by ASTM standard. Such properties of WCOME and COME are intimated in Table 6.5 with mentioning their permissible limits as described in ASTM 6751. It is clearly observed that the parameters of WCOME such as the density at 40ºC (in g/l), kinematic viscosity (in mm^2/s), acid value (in mg KOH/g), calorific value (MJ/Kg), cetane number, cloud point (ºC), flash point (ºC), and pour point (ºC) have obtained in the acceptable range for biodiesel defined by ASTM standard, however, in case of COME (B100), obtained physicochemical values are not up to the mark. But in literature, it is reported that when castor biodiesel is blended with petrodiesel (maximum up to 20%), it shows compatible physicochemical properties (Bueno et al., 2017). So, we can say that WCOME can be used in pure form and COME can be used in blended form in C.I engine.

Table 6.5 Comparison of fuel properties of WCOME and COME with ASTM standard for biodiesel

Parameters	ASTM test method used	ASTM-6751 biodiesel	WCOME (B100)	COME (B100)
Acid value (mgKOH/g)	D 664	<0.8	0.4	0.07
Density ($40^0C, g.l^{-1}$)	D 4052	0.86-0.90	0.896	0.932
Viscosity (mm^2/s)	D 7110	1.9 to 6.0	4.3	14.08
Cetane number	D 613	47	49.2	44.3
Calorific value (MJ/Kg)	D 240	35	41.57	39.48
Flash point (ºC)	D 93	100 to 190	139	190
Pour point (ºC)	D 97-05	-15 to 16	3	-26
Cloud point (ºC)	D2500	-3 to 12	6	-15

6.8 Conclusions

In this chapter, the catalytic property of synthesized Ba-SnO_2 catalyst for biodiesel synthesis from WCO and CO has been demonstrated. Among the analogs, BSO catalyst calcined at 850°C and having Ba : Sn atomic ratio 1 : 1, showed the highest activity in transesterification reaction. This BSO catalyst was then introduced in the optimization studies of reaction parameters. The maximum FAME conversion, 98% of WCO to biodiesel was found at optimized conditions of oil to methanol molar ratio 1 : 16, catalyst concentration 2.5 wt%, temperature 65°C, and time 25 min; whereas, the maximum 97.51% biodiesel conversion from CO was obtained at following reaction conditions as 1 : 16 oil to methanol molar ratio, 2 wt% catalyst concentration, 65°C temperature, and 30 min duration. Catalyst endurance test suggested that the $BaSnO_3$ has the appreciable catalyzing potency and stability for several reuses (sustain for 5th catalytic cycle with more than 85% FAME conversion). Kinetic study of the transesterification process by using BSO revealed that this process followed pseudo first order kinetics as well as a non spontaneous endothermic pathway. The reaction activation energy, enthalpy of activation, entropy of activation, and Gibb's free energy of activation of the reaction and these were obtained to be 61.57 kJ/mol, 59.76 kJ/mol, -87.19 J/mol/K and 89.23 kJ/mol respectively for WCO transesterification, and 61.97 kJ/mol, 60.61 kJ/mol, -84.13 J/mol/K and 89.03 kJ/mol respectively for CO transesterification. The TOF of BSO was found to be comparable that of homogeneous catalyst which means that BSO is as efficient as homogeneous catalyst. Furthermore, the low E factor and PMI values indicate that BSO can efficiently produce biodiesel from WCO and CO following the environmentally benign pathway.