Chapter 5

Application of potassium - tin oxide (K-SnO_2) catalyst in biodiesel production from waste cooking oil and castor oil

5.1 Introduction

This chapter elaborates the catalytic behavior of potassium tin oxide (KSO) in transesterification of waste cooking oil and castor oil. Basically, four major studies namely optimization, reusability, kinetics and environmental studies were performed to discuss the efficacy of the KSO catalyst. In optimization studies, the reaction influencing parameters as calcination temperature, calcination time, oil to methanol molar ratio, catalyst weight %, reaction temperature, reaction time were optimized by following OVAT method. The stability and reusability of KSO catalyst was investigated for consecutive transesterification runs. Afterthat, kinetic and thermodynamic parameters were evaluated to describe the pathway and the nature of the reaction. Last, the green parameters 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 share of different methyl esters in biodiesel composition. The physicochemical and fuel properties were estimated by standard methods.

5.2 Optimization of influential reaction parameters

In optimization process, effect of various reaction variables on transesterification reaction was investigated in two sets of batch reactions for two feedstocks (WCO and CO). On account the best activity of the KSO catalyst in methyl esterification, the calcination temperature and calcination time of prepared catalyst were optimized to get the most active form of the catalyst. Then the activated catalyst was introduced in further optimization studies of oil : methanol molar ratio (1:4 to 1:24), catalyst weight % (0.5 to 4%), temperature (45 to 75^{o}C), and reaction duration (5 to 50 min). Each reaction was carried out for three times and the average of those three was considered as final value. Methyl ester of waste cooking oil and castor oil were designated as WCOME and COME.

5.2.1 Impact of catalyst (KSO) activation temperature and time on methyl ester conversion

Figure 5.1A demonstrates the effect of different catalyst activation (calcination) temperatures on FAME conversion (%) of WCOME and COME respectively. The catalytic efficacy of KSO catalyst activated at 500°C, 600°C, 700°C, 800°C and 900°C were investigated under the following reaction conditions: 1 : 16 oil to methanol molar ratio, 3 wt% of catalyst weight, 65°C reaction temperature, 35 min reaction duration for the batch reaction of WCO; similarly, 1 : 12 oil to methanol molar ratio, 2.5 wt% of catalyst weight, 65°C reaction temperature, 45 min reaction duration for the batch reaction of CO. This study reveals that raising the catalyst activation temperature improves the catalytic efficiency. The KSO catalyst showed the highest activity while it was activated at 800°C; however, above 800°C, the activity of this KSO catalyst was reduced. This observation can be explained by the XRD, BET and basicity analysis of KSO catalysts. In XRD, it was found that the carbonates were present in KSO catalysts activated at the temperature below 800°C, but the concentration of such carbonate species subsequently decreased with increasing the catalyst activation temperature and completely exhausted at 800°C. With the removal of carbonate species, BET surface area and basicity of the catalyst simultaneously increased, which in consequence improved the catalytic activity. KSO 800 possessed the best conversion because of its highest BET surface area and higher basicity. Beyond 800°C, the active component of the catalyst i.e. the potassium species started to decompose (Lehman et al., 1998), as a result, FAME conversion was affected and became lowered.

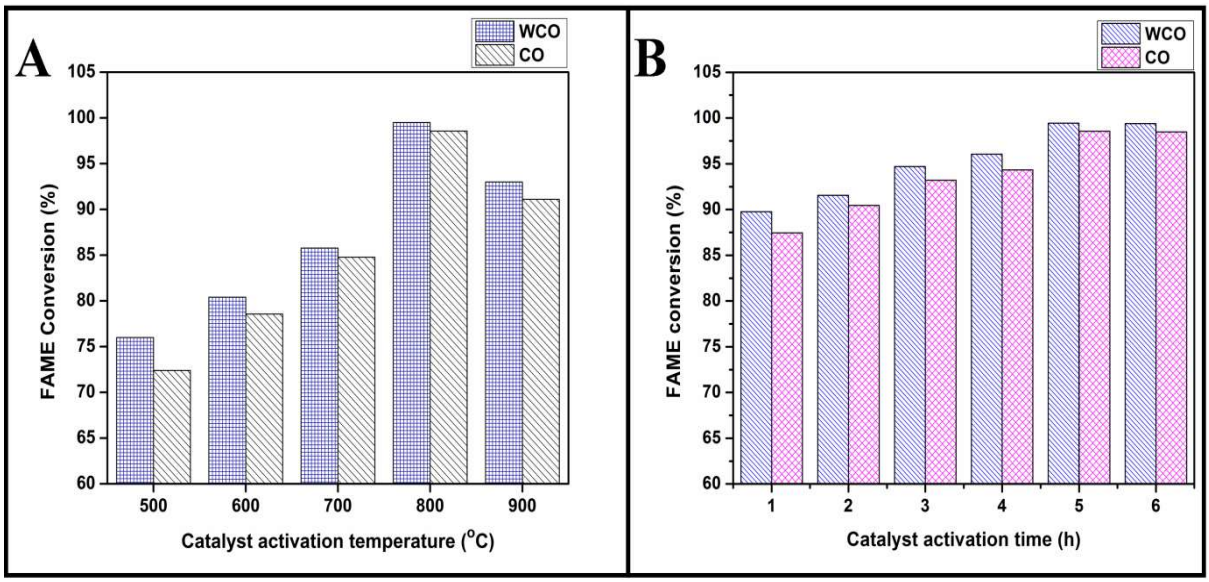

Figure 5.1 (A) Effect of catalyst activation temperature, and (B) effect of catalyst activation time on methyl esterification reaction of WCO and CO using KSO catalyst

The effect of activation time on FAME conversion (%) has been shown in Figure 5.1B. The catalyst KSO 800 was activated for different intervals, such as 1h, 2h, 3h, 4h, 5h & 6h. The activated catalysts were exposed in transesterification reaction under optimized conditions. It was observed that FAME conversion was improved with the increment in the calcination period up to 5h and then it became constant. This might have happened due to the phase transformation of native oxides of Sn and K to potassium stannate. In XRD analysis, it was noticed that the concentrations of tin oxide and potassium dioxide decreased with increasing calcination duration, whereas, the concentrations of potassium stannate phases increased with time. The particles of KSO 800 catalyst calcined for 5 h, showed good morphological view in SEM image; moreover, it also possessed high surface area and higher basicity. So, in the transesterification of WCO and CO, the best result of KSO 800 was found while it was activated for 5h.

5.2.2 Impact of oil : methanol molar ratio and catalyst weight percentage on methyl ester conversion

Figure 5.2A depicts the influence of oil to methanol molar ratio on FAME conversion (%) of WCO and CO in KSO catalysed transesterification reaction. The oil to methanol molar ratio was varied from 1 : 4 to 1 : 24; however, the reaction conditions were maintained as follows: 3 wt% of catalyst weight, 65^{o}C reaction temperature, 35 min reaction duration for the batch reaction of WCO; likewise, 2.5 wt% of catalyst weight, 65^{o}C reaction temperature, 45 min reaction duration for the batch reaction of CO. In this study, the optimum oil to methanol molar ratio has been obtained at 1 : 16 for WCOME, and 1 :12 for COME formation. Initially, the increment in methanol concentration promoted the methanolysis reaction which in consequence favored the biodiesel conversion. As soon as the requirement of methanol was fulfilled, the reaction proceeded in no time. At optimum oil to methanol molar ratio, the reaction achieved the most favored condition where the equilibrium was shifted to the product side at maximum extent. However, beyond the optimum molar ratio, by-product glycerol started to dissolve in excess methanol; thus the equilibrium was disturbed and reaction got disfavored again (Tan et al., 2015). As a result FAME conversion was hampered as shown in the optimization plot.

Next, the catalyst weight percentage was optimized under a range of 0.5 wt% to 4 wt% keeping other parameters constant as: 1 : 16 oil to methanol molar ratio, 65^{o}C reaction temperature, 35 min reaction duration for the batch transesterification of WCO; and 1 : 12 oil to methanol molar ratio, 65^{o}C reaction temperature, 45 min reaction duration for the batch transesterification of CO. In heterogeneous catalysis, catalyst plays the most important role to precede the reaction. The chemical reaction can only occur at the active sites present on the catalyst surface. This means the number of available active sites depend only on the concentration or the weight (%) of the catalyst present in the

reaction. So, it can be interpreted that increased catalyst weight (%) introduces larger number of active sites, which possibly reinforces the FAME conversion (Sahani et al., 2019). Figure 5.2B manifests that the transesterification reaction of WCO and CO using KSO 800 catalyst was accelerated to the maximum extent in presence of corresponding optimum catalyst concentration i.e. 3 wt% and 2.5 wt% respectively. But higher than optimum catalyst weight %, this reaction was obstructed because of enhancing fluid viscosity in the reaction medium (Kumar et al., 2018). Moreover, the mass transfer between three phases severely disrupted in viscose media, which can be evidentially found in the optimization plot as a reduction in FAME conversion at the high concentration of catalyst (i.e. 3.5 to 4 wt%).

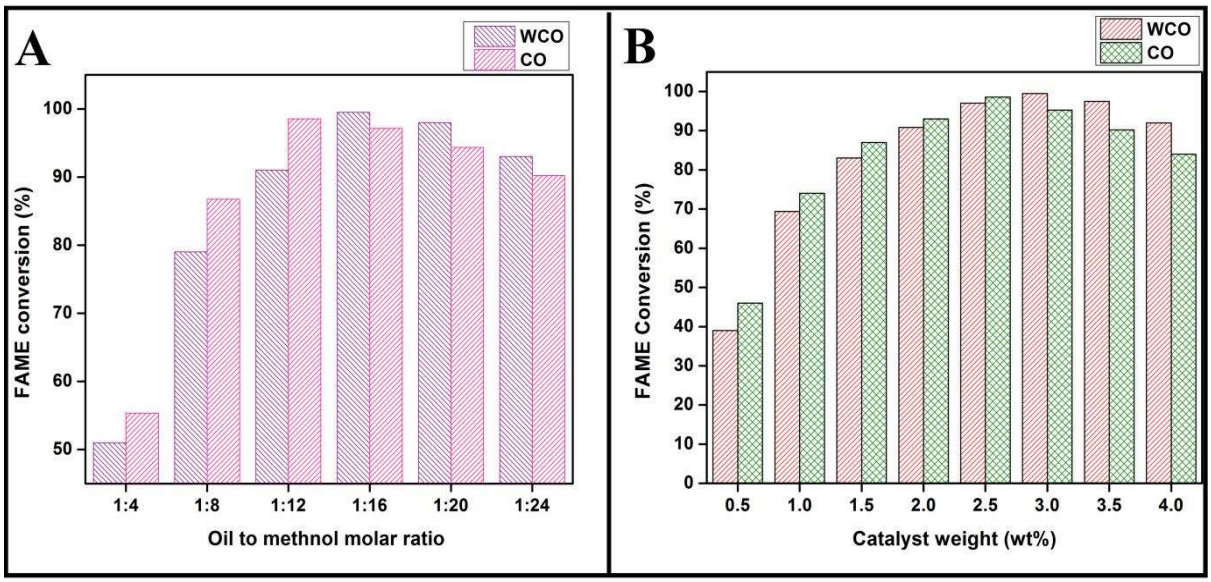

Figure 5.2 (A) Impact of oil : methanol molar ratio (1 : 4 – 1 : 24) (B) impact of catalyst weight (0.5 - 4.0) percentage on methyl esterification of WCO and CO

5.2.3 Impact of reaction temperature and time on methyl ester conversion

For any chemical reaction, two key parameters namely reaction temperature and time govern the kinetics of the process. The influence of temperature on FAME conversion (%) of WCOME and COME was investigated by executing numerous batch reactions over a temperature range starting from room temperature to 75°C. These batch reactions were carried out under the following reaction conditions: 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight and 35 min reaction duration for WCO transesterification, however, in case of CO transesterification, the reaction condition was 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight and 45 min reaction duration. The resultant data have been presented as Figure 5.3A, which depicts that in both the transesterification process, FAME conversion was improved with increasing reaction temperature 45°C to 65° but slightly decreased above 65°C. Therefore, the optimized reaction temperature of these transesterification processes was considered to be 65°C which was close to the boiling point of methanol (64.7°C). At this optimum temperature, the system acquired the external energy required to come across the threshold barrier for preceding the reaction towards the forward direction. Moreover, the acyl acceptor produced from methanol was fully activated at this temperature to interact with the triglyceride molecule with the highest efficacy (Gardy et al., 2018). However, at the temperature above 65°C, methanol started to vaporize and was lost in a significant amount from the triphasic reaction mixture. Thus, the FAME conversion was reduced subsequently with the increase in reaction temperature above the optimum value (Pullen and Saeed, 2015).

The second most important parameter for a kinetic reaction is reaction duration or time. The time of these transesterification processes was optimized by extending the reaction for 50 min under the following reaction conditions: 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65°C reaction temperature for methyl

esterification of WCO; 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature for methyl esterification of CO. The optimum time of the processes was ascertained in terms of the highest FAME conversion (%). Figure 5.3B displays that more than 90% methyl ester was formed within 15 min and the reaction completed in 35-45 min. The effect of time on FAME conversion can be elaborated by corroborating the above results with the previous studies (Sahani et al., 2019). Initially, the reaction was diffusion controlled; so, it was unable to produce a significant amount of methyl ester in 5 min. But whenever the reaction became kinetically controlled, a sharp amplification in FAME conversion was observed in the time optimization profile. Due time, the reactions approached equilibrium and became slowed down (Balat and Balat, 2010). In approximately 35 min and 45 min, WCO transesterification and CO transesterification respectively got the chemical equilibrium phase. Beyond the optimum time, FAME conversion was slightly reduced due to cracking followed by FAME oxidation to lower chain organic fractions (Enciner et al., 2018).

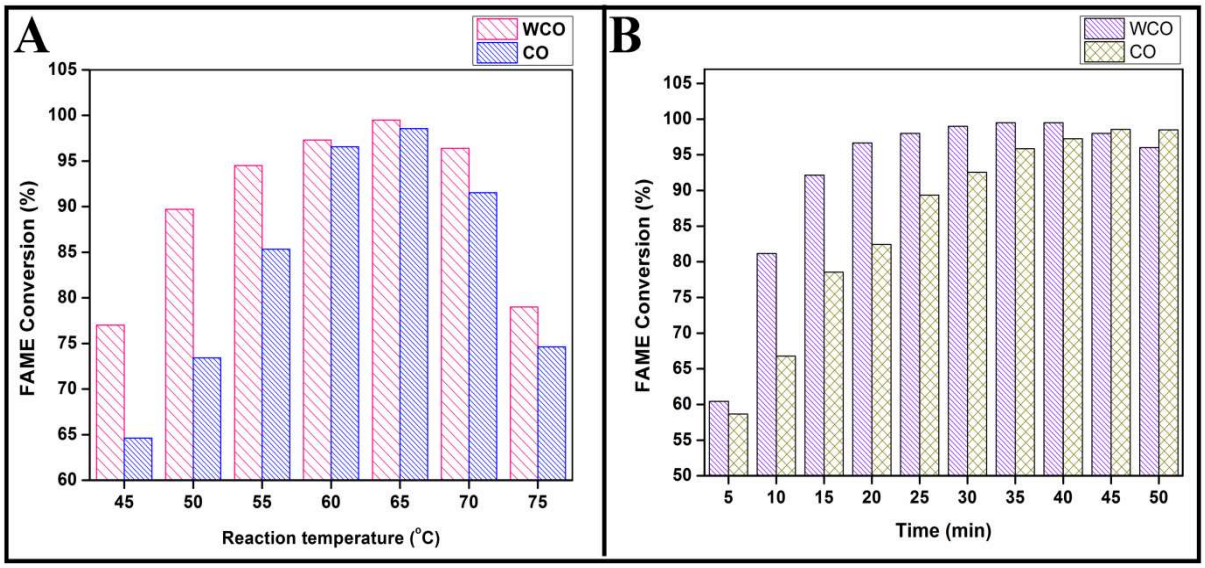

Figure 5.3 (A) Impact of reaction temperature (45 - 75°C), and (B) impact of reaction duration (5 – 50 min) on methyl esterification of WCO and CO

5.3 Reusability of KSO 800 catalyst

The key factor to choose heterogeneous catalyst over homogeneous catalyst is reusability or catalyst endurance ability. A reusable catalyst should cut the production cost to a larger extent. Thus, a catalyst that shows greater endurance with immense activity in terms of conversion or yield can be granted as a suitable catalyst for economic biodiesel production. The reusability of KSO 800 was investigated for five consecutive runs under the following reaction condition: 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65°C reaction temperature, 35 min reaction duration for methyl esterification of WCO; similarly, 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 35 min reaction duration for methyl esterification of CO. The endurance capability of KSO 800 for WCO and CO transesterification has been represented in terms of FAME conversion (%) in Figure 5.4.

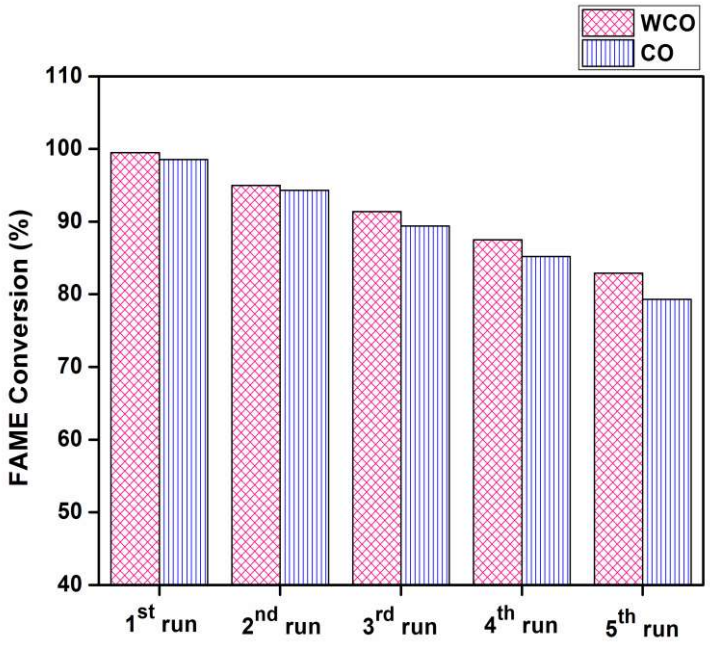

Figure 5.4 Reusability of KSO 800 catalyst in transesterification of WCO and CO at corresponding optimized reaction conditions

KSO 800 showed more than 80% conversion up to 5th run in both the cases. To check the leaching of active components, hot filtration test was performed after each cycle using the reused catalyst. Interestingly, no leaching of KSO 800 was noticed, but the slight decay (3% to 5%) in catalytic efficiency was recorded after each catalytic run, which possibly occurred due to weight loss of catalyst in filtration process or deformation of the catalytic site in recalcination process or unwanted glycerol deposition at the active site (Nayebzadeh et al., 2016). So, considering endurance potency, it can be confidently stated that KSO 800 is an efficient catalyst for economic biodiesel production.

5.4 Kinetic and thermodynamic study

The kinetic and thermodynamic parameters regarding transesterification of WCO and CO using KSO 800 catalyst were evaluated by the help of rate equation, Arrhenius and Eyring equations (Ahmad et al., 2014). Required optimum reaction conditions of the respective WCO and CO transesterification reactions (i.e. 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65^{o}C reaction temperature, 35min reaction duration for methyl esterification of WCO; similarly, 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65^{o}C reaction temperature, 35 min reaction duration for methyl esterification of CO) were maintained during kinetic study.

5.4.1 Determination of rate constants at different temperature and the order of the reaction

The rate of the reaction can be determined from the slope of the plot -ln(1- X_{ME}) vs t (in min) (Feyzi and Shahbazi, 2017). The two sets of batch reactions (WCO and CO transesterification) were performed at three different temperatures (45^{o}C, 55^{o}C, & 65^{o}C) under corresponding optimized reaction conditions. In the case of WCO, the FAME

conversion was estimated after 5 min interval; whereas, COME was evaluated after 10 min time interval. Then the resultant data was plotted following the rate equation [-ln(1-X_{ME}) = kt]. Figure 5.5A and Figure 5.5B represent the corresponding kinetic plots of the transesterification of WCO and CO using KSO 800 catalyst. The obtained rate constants at corresponding temperatures have been enclosed Table 5.1. The R^2 values of the resultant linear plots were found within a range of 0.966 to 0.998. These data approve that our pre-assumptions were correct; the rate of the reaction only depends on the triglyceride concentration; change in methanol concentration doesn't affect the overall reaction rate. Moreover, it proves that the aforementioned reactions were pseudo first order reaction. Furthermore, it was also observed that the reaction rate was enhanced around 2 fold with raising 10°C reaction temperature.

Table 5.1 Rate constants at different temperature for WCO and CO transesterification using KSO 800

Feedstock	**Waste cooking oil (WCO)**			**Castor oil (CO)**		
Temperature (°C)	45	55	65	45	55	65
rate constant k ($min^{-1)}$	0.0432	0.0818	0.1457	0.0231	0.0433	0.0823
R^2 value	0.966	0.982	0.994	0.992	0.998	0.978

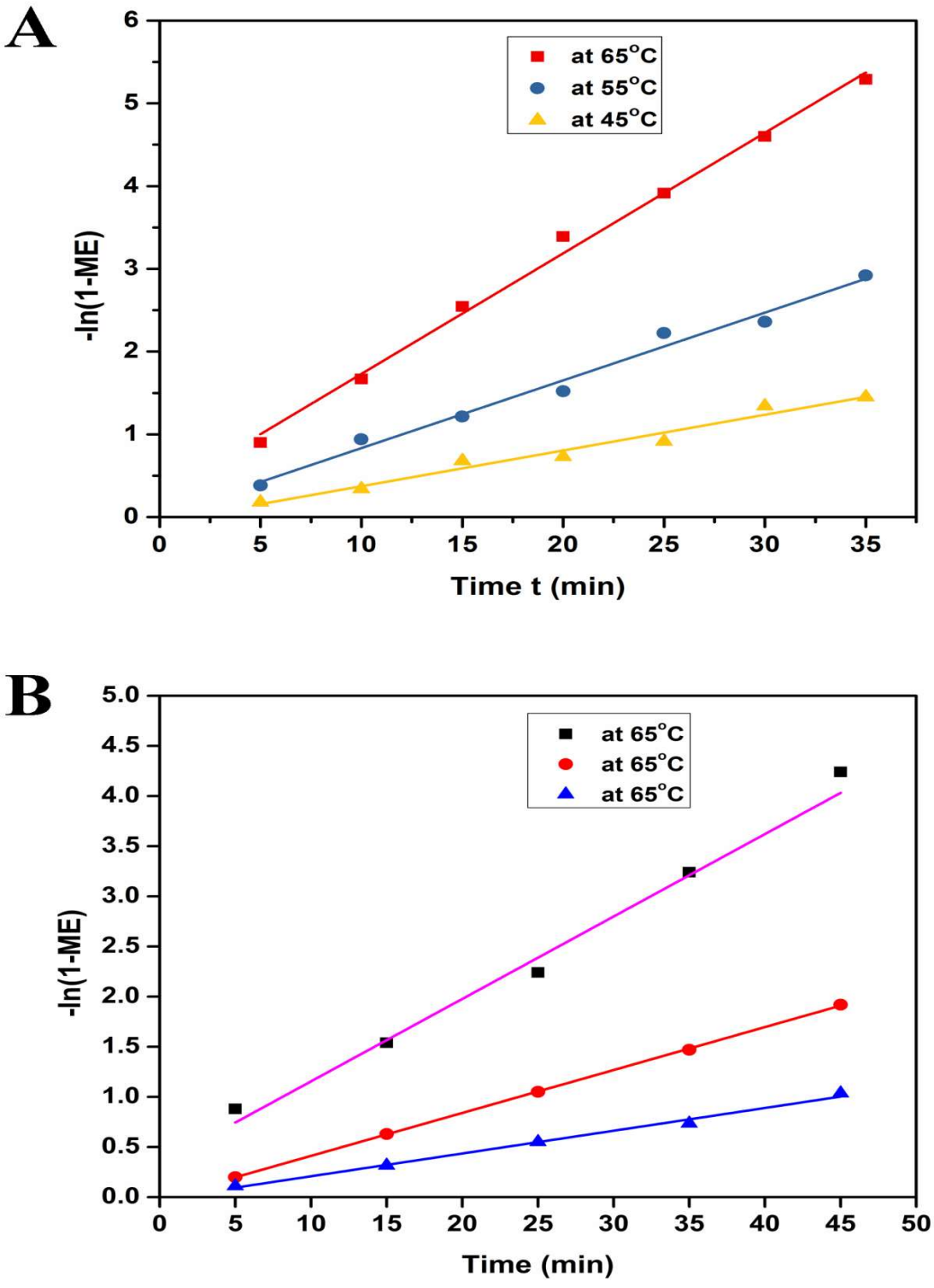

Figure 5.5 (A) Kinetic plot [-ln(1-ME) vs time] of WCO transesterification reaction, (B) kinetic plot [-ln(1-ME) vs time] of CO transesterification reaction using KSO 800 catalyst

5.4.2 Determination of reaction activation energy and pre-exponential factor

Following the Arrhenius equation, a linear plot of lnk vs $1/T$ was drawn to find out reaction the activation energy as shown in Figure 5.6A. From the slope (E_a/RT) of the linear plot, activation energies of the transesterification of WCO and CO, using KSO 800 catalyst were calculated to be 66.52 kJ/mol and 31.62 kJ/mol respectively. These exhibited in the range of basic heterogeneous catalysis i.e. 33.6-84 kJ/mol (Chen et al., 2020; Sahani et al, 2019). From the intercept ($ln\, k$) of the same plots, the frequency factor A was calculated to be 34.1×10^8 min^{-1} and 1.53×10^8 min^{-1} of WCOME and COME formation respectively. Basically, the frequency factor impacts on the reaction duration. In our case, we must say that the reaction has completed comparatively in shorter time (35 min) due to high frequency factor.

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

Following the Eyring-Polanyi's equation $[\ \ln(\frac{k}{T}) = [\ln\left(\frac{k_b}{h}\right) + (\frac{\Delta S^{\#}}{R})] - (\frac{\Delta H^{\#}}{RT}\ )]$, $\ln(\frac{k}{T})$ was plotted against $1/T$ as shown in Figure 5.6B. Enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were calculated respectively 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 the aforesaid linear plot [Bayat et al., 2018]. The $\Delta H^{\#}$ values of WCOME and COME formation were found to be 62.95 kJ/mol and 65.813 kJ/mol, whereas, $\Delta S^{\#}$ values were -74.07 J/mol/K and -70.44 J/mol/K obtained correspondingly. The positive sign of $\Delta H^{\#}$ and negative sign of $\Delta S^{\#}$ signify that the process followed an endothermic pathway and during the reaction, entropy of the system decreased. Next, $\Delta G^{\#}$ was found 88 kJ/mol and 89.62 kJ/mol for methyl esterification of

WCO and CO respectively at 65ºC. The positive value of $\Delta G^{\#}$ suggested that both transesterification processes were non-spontaneous and endergonic (Aziz et al., 2020).

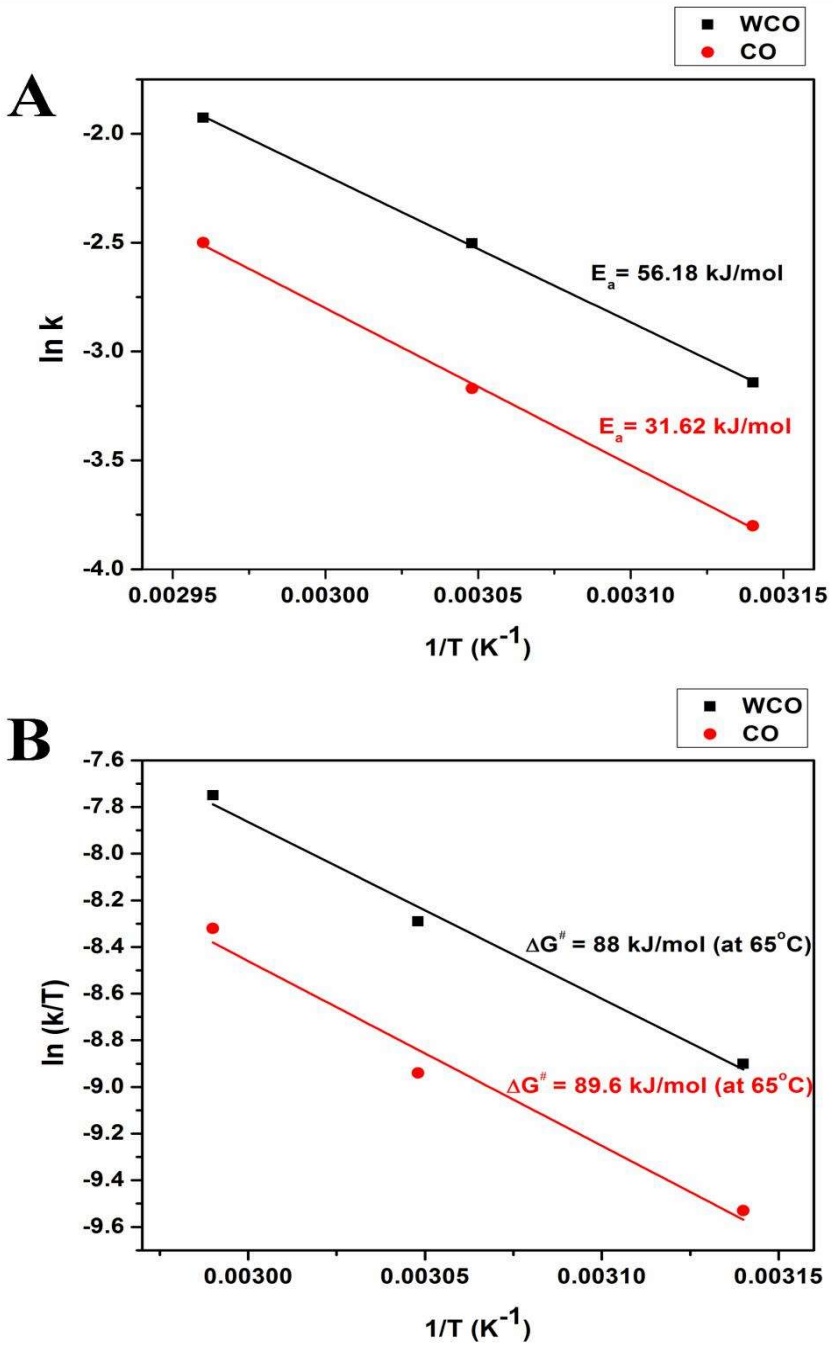

Figure 5.6 (A) Arrhenius plot ln k vs (1/T), and (B) Eyring-Polanyi's plot ln (k/T) vs (1/T) of transesterification of WCO and CO using KSO 800 catalyst

5.5 Green metrics study

Four important parameters such as yield (Y), turnover frequency (TOF), E-factor (E_f), and process mass index (PMI) were evaluated to ascertain the extent of greenness of the transesterification process. On account these parameters, the methyl esterification of WCO and CO were carried out using KSO 800 catalyst under optimized reaction conditions (i.e. 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65°C reaction temperature, 35 min reaction duration for methyl esterification of WCO; similarly, 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 45 min reaction duration for methyl esterification of CO). The experimental outcomes of green parameter study are enlisted in Table 5.2. The TOF of KSO 800 catalysts for both WCO and CO transesterification were found to be very high and comparable of homogeneous catalysts used in industry level biodiesel production (Sani et al., 2014). The E_f and PMI values were obtained in lower range that indicates the catalytic processes are non hazardous and eco-friendly.

Table 5.2 Green parameters for WCO and CO transesterification using KSO 800 catalyst

Parameter	WCO	CO
Maximum methyl ester conversion (%)	99.43	98.56
Maximum yield (%)	86	95.43
Turnover frequency TOF (s^{-1})	15.27×10^{-3}	12.1×10^{-3}
E-factor	0.453	0.409
Process mass intensity PMI	1.63	1.517

5.6 Characterization of derived biodiesel

5.6.1 ^{1}H NMR spectroscopy

Figure 5.7A and Figure 5.7B represent the ^{1}H NMR spectra of transesterification product WCO and CO. In these ^{1}H NMR spectra of the products, the following characteristic peaks were noticed at 5.5-5.3 ppm assigned for multiplet –C**H**=C**H** protons, 3.63 ppm assigned for singlet –OC**H**$_3$ proton, 3.59-3.57 ppm assigned for α hydroxy proton (in **COME**), 2.76-2.74 ppm assigned for triplet C=C-C**H**$_2$-C=C proton, 2.30-2.27 assigned for triplet –OCO-C**H**$_2$ (α-methylene) proton, 2.19-2.16 ppm assigned for –O**H** proton (in **COME**), 2.03-1.99 ppm assigned for multiplet –C**H**$_2$-C=C proton, 1.63 ppm assigned for multiplet –C**H**$_2$-C-C=O proton, 1.43-1.22 ppm assigned for rest –C**H**$_2$ protons, 0.88-0.85 ppm assigned for C**H**$_3$ (Ba et al., 2016).

The integral value of OCH_3 proton and α-CH_2 signals was analyzed to calculate the FAME conversion of respective oils (Madhu et al., 2017). The integral value of OCH_3 proton in WCOME and COME spectra were found to be 112 and 106.96 respectively; however, the integral value α-CH_2 proton was 75.08 in WCOME and 72.36 in COME.

At the optimized reaction conditions (i.e. 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65^{o}C reaction temperature, 35 min reaction duration for methyl esterification of WCO; similarly, 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65^{o}C reaction temperature, 45 min reaction duration for methyl esterification of CO) FAME conversion was calculated to be

$$\text{FAME conversion \% of WCO to WCOME} = \left(\frac{2\times112}{3\times75.08}\right) \times 100 = 99.45\ \% \quad (5.1)$$

$$\text{FAME conversion \% of CO to COME} = \left(\frac{2\times106.96}{3\times72.36}\right) \times 100 = 98.49\ \% \quad (5.2)$$

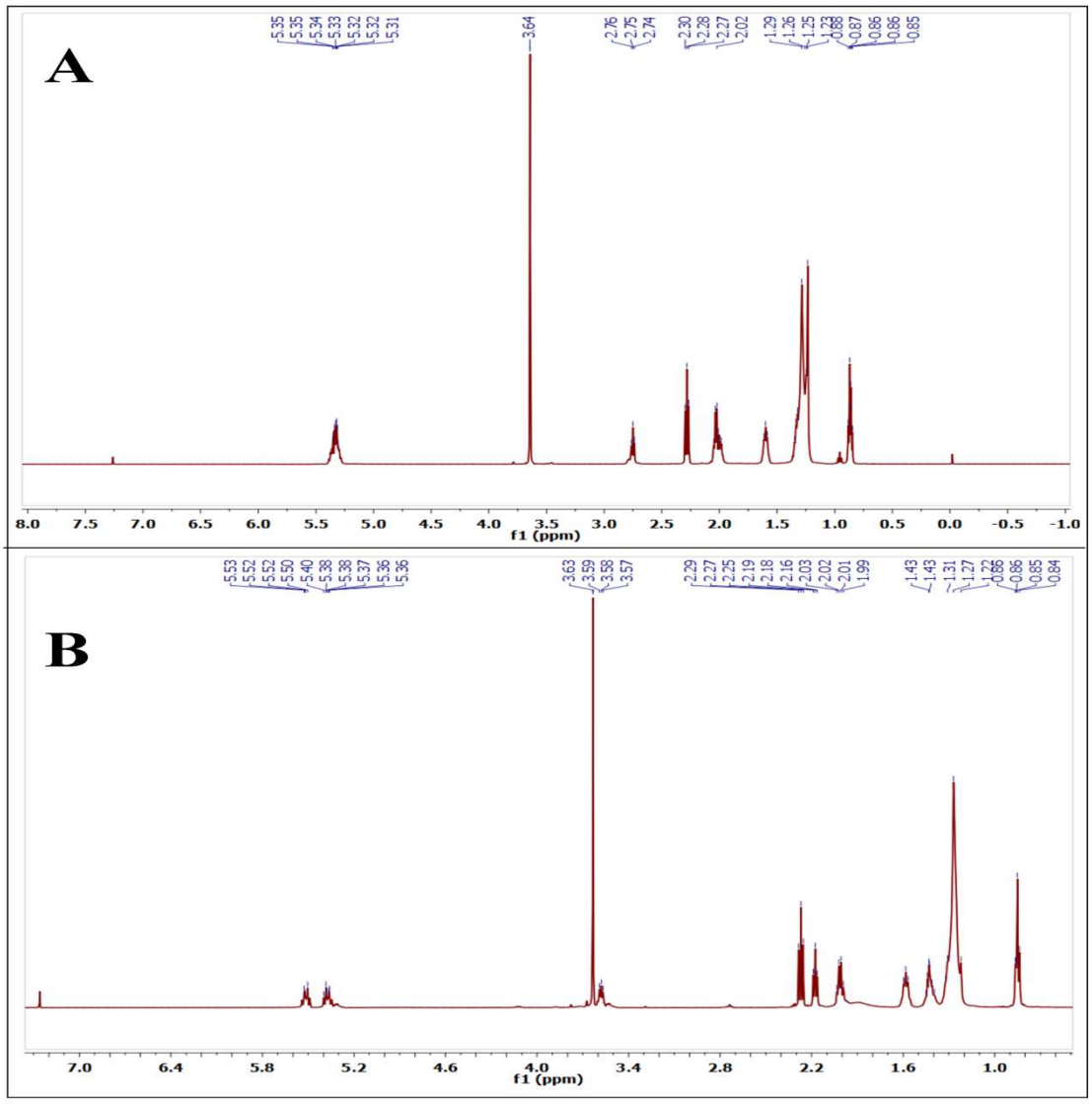

Figure 5.7 (A) ^{1}H NMR spectra of biodiesel derived from waste cooking oil and (B) ^{1}H NMR spectra of biodiesel derived from castor oil

5.6.2 ^{13}C NMR spectroscopy

Figure 5.8A and Figure 5.8B reveal the ^{13}C NMR spectra of transesterification product of WCO and CO respectively. The signals of ^{13}C NMR of WCOME and COME were recorded at chemical shift value of 174.3 ppm corresponds to single ester carbonyl carbon (O-**C**O-), 131 to 127 ppm corresponds to olefinic carbons (**C**H=**C**H), 77.2 to 76.8 ppm corresponds to solvent carbon (**C**DCl_3), 71.5 ppm corresponds to α-hydroxy proton (in

COME), 51.4 ppm corresponds to methyl ester carbon (**C**H_3O-), 31 to 22.6 corresponds to methylene carbon (**C**H_2), 14 corresponds to terminal methyl carbon (**C**H_3). The characteristic signal of methyl ester carbon (at 51.4 ppm) and single ester carbonyl carbon confirm the formation of fatty acid methyl ester (FAME) from WCO and CO (Roy et al, 2020c, Sahani et al., 2020; Ba et al., 2016).

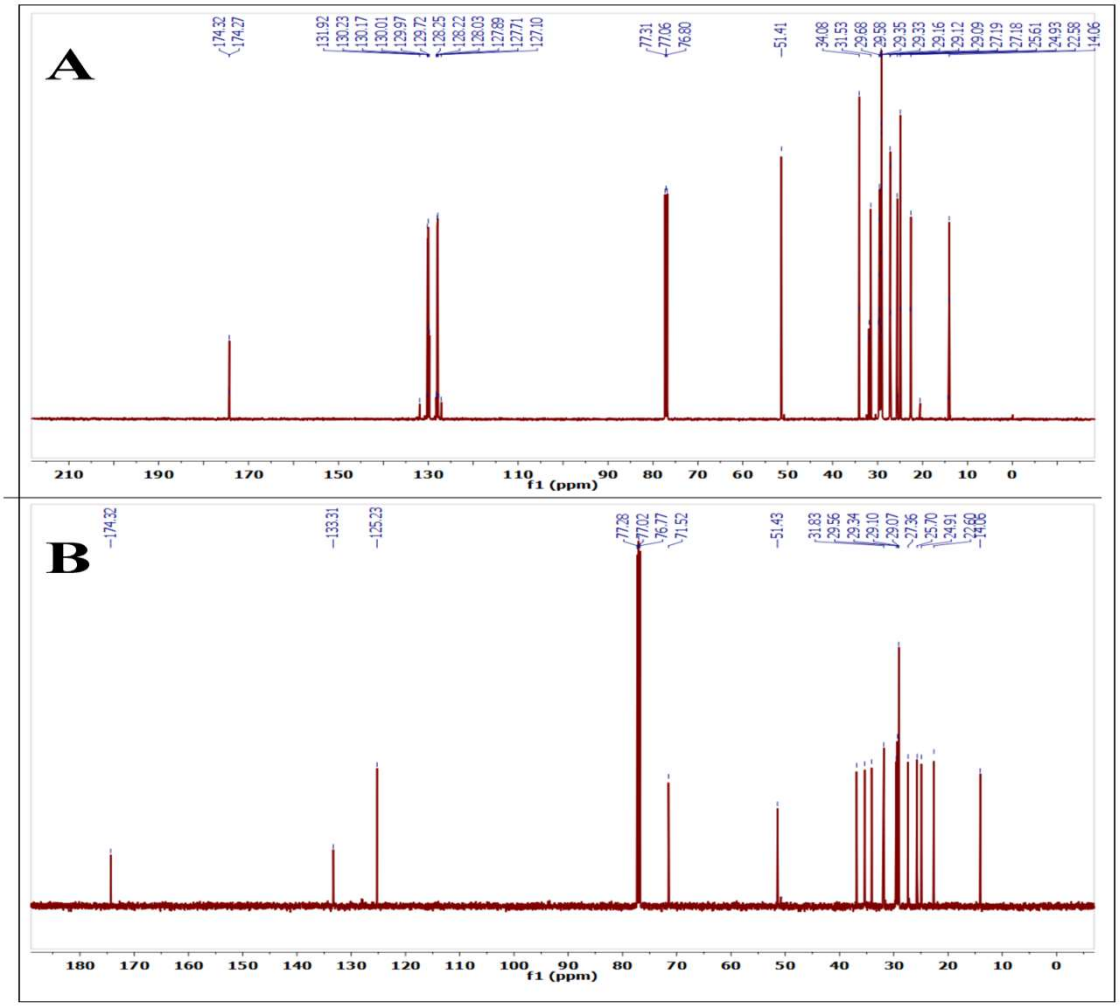

Figure 5.8 (A) ^{13}C NMR spectra of biodiesel derived from waste cooking oil and (B) ^{13}C NMR spectra of biodiesel derived from castor oil

5.6.3 GC-MS analysis

Table 5.3 comprises the constituent methyl esters present in COME. There are five components as methyl palmitate (1.012%), methyl linolate (4.191%), methyl oleate (3.568%), methyl stearate (1.105%) and methyl ricinolate (90.124%) found at the

corresponding retention time of 8.824, 10.446, 10.965, 11.512 and 12.433 min. Due to major contribution of methyl ricinolate (containing hydroxyl functional group) COME possesses comparatively higher kinematic viscosity than that of other biodiesel (Ramezani et al., 2010).

Table 5.3 FAME composion of the biodiesel derived from castor oil using KSO-800 catalyst

Retention time	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
8.824	Methyl palmitate	1.012	99	$CH_3(CH_2)_{14}COOMe$
10.446	Methyl linoleate	4.191	98	$CH_3(CH_2)_{12}(CH=CH)_2COOMe$
10.965	Methyl oleate	3.568	98	$CH_3(CH_2)_{14}CH=CHCOOMe$
11.512	Methyl stearate	1.105	99	$CH_3(CH_2)_{16}COOMe$
12.433	Methyl ricinoleate	90.124	99	$CH_3(CH_2)_{13}CH(OH)CH=CH$ COOMe
saturated FAME		2.117%		
monounsaturated FAME		93.692%		
polyunsaturated FAME		4.191%		

In Table 5.4**,** the constituent fatty acids methyl esters present in WCOME are enlisted with their compositional percentage. The major five components are methyl α-linolenate (13.12%), methyl palmitate (4.92%), methyl oleate (30.20%), methyl linolinate (44.70%), methyl stearate (4.72%). The saturated FAME content in WCOME is much higher than that of COME. This is soley responsible for better combusible property of WCOME compare to COME (Gurunathan and Ravi,2015).

Table 5.4 FAME composion of biodiesel derived from waste cooking oil using KSO-800 catalyst

Retention time	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
4.156	Methyl laurate	0.38	98	$CH_3(CH_2)_{10}COOMe$
6.132	Methyl myristate	0.06	99	$CH_3(CH_2)_{12}COOMe$
6.326	Methyl myristoleate	0.73	99	$CH_3(CH_2)_{10}(CH=CH)COOMe$
8.706	Methyl palmitate	13.12	98	$CH_3(CH_2)_{14}COOMe$
8.892	Methyl palmitoleate	0.28	98	$CH_3(CH_2)_{12}(CH=CH)COOMe$
11.458	Methyl stearate	4.92	98	$CH_3(CH_2)_{16}COOMe$
11.778	Methyl oleate	30.20	99	$CH_3(CH_2)_{14}(CH=CH)COOMe$
12.197	Methyl linoleate	44.70	98	$CH_3(CH_2)_{12}(CH=CH)_2COOMe$
12.901	Methyl α-linolenate	4.72	99	$CH_3(CH_2)_{10}(CH=CH)_3COOMe$
14.283	Methyl arachidate	0.32	99	$CH_3(CH_2)_{18}COOMe$
14.439	Methyl paullinate	0.24	99	$CH_3(CH_2)_{16}(CH=CH)COOMe$
17.211	Methyl behenate	0.33	99	$CH_3(CH_2)_{20}COOMe$
saturated FAME		19.13%		
monounsaturated FAME		31.45%		
polyunsaturated FAME		49.42%		

5.7 Fuel properties of synthesized biodiesel

Some of the most imperative properties of product biodiesel derived from WCO and CO have been evaluated by following ASTM standard methods and enlisted in Table 5.5 with mentioning their permissible limit as described in ASTM 6751. It is clearly shown in the above-mentioned table, the parameters of WCOME such as the density at 40°C (in g/l), kinematic viscosity (in mm^2/s), acid value (in mg KOH/g), calorific value (MJ/Kg), cetane number, cloud point (°C), flash point (°C), and pour point (°C) have found to be 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 engines.

Table 5.5 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	0.3	0.05
Density ($40^0C, g.l^{-1}$)	D 4052	0.86-0.90	0.87	0.935
Viscosity (mm^2/s)	D 7110	1.9 to 6.0	2.8	15.1
Cetane number	D 613	47	50	44.6
Calorific value (MJ/Kg)	D 240	35	42	39.01
Flash point (°C)	D 93	100 to 190	137	192
Pour point (°C)	D 97-05	-15 to 16	2	-28
Cloud point (°C)	D2500	-3 to 12	6	-15

5.8 Conclusions

In this present study, the activity of KSO catalysts in biodiesel production from WCO and CO was examined through various studies (optimization, reusability, kinetics and green parameter studies). In optimization study, we found the catalyst calcined at 800°C (KSO 800) showed the best activity in terms of FAME conversion as it had higher surface area as well as higher basic strength comparing with the catalysts calcined below 800°C. The OVAT study implied that using KSO 800 catalyst, the highest FAME conversion (99.45%) of WCO to WCOME can be achieved at the following optimized reaction conditions: 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65°C reaction temperature, and 35 min reaction duration. Likewise, the best result (98.49%) in CO transesterification was obtained at 1 : 12 oil to methanol molar ratio, 2.5 wt% catalyst weight, 65°C reaction temperature, 45 min reaction duration. In reusability study, it is found the catalyst KSO 800 has endurance ability for five catalytic runs with more than 80% efficiency in WCO as well as CO transesterification. Moreover, no leaching of K-species was registered during the complete endurance test that showed the stability of the catalyst. Kinetic and thermodynamic parameters of KSO 800 (potassium tin oxide activated at 800°C for 5h) catalyzed transesterification reactions were investigated at above mentioned optimized reaction conditions. Kinetic studies showed that both the reactions followed pseudo-first-order kinetics. Arrhenius plot (i.e. ln k Vs 1/T) and Eyring- Polanyi's plot (i.e. ln(k/T) Vs 1/T) helped to find out 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 66.52 kJ/mol, 62.95 kJ/mol, -74.07 J/mol/K and 88 kJ/mol respectively in WCO transesterification, and 31.62 kJ/mol, 65.81 kJ/mol, -70.44 J/mol/K and 89.62 kJ/mol respectively for CO transesterification. The green parameters such as yield, TOF, E-factor and PMI were of WCO and CO

transesterification using KSO 800 catalyst evaluated to analyze the 'Greenness' of these processes. High conversion, yield, TOF, and low value of environmental parameters (E factor and PMI) revealed that KSO 800 catalyzed transesterification process is a faster and cleaner route of biodiesel synthesis. Aftermath, the produced biodiesel was characterized. Methyl ester formation was confirmed by ^{1}H NMR and ^{13}C NMR. Furthermore, the product conversion was quantified by ^{1}H NMR and was found as 99.45% WCOME and 98.49% COME conversion at their corresponding most favored reaction conditions. The constituent methyl esters present in biodiesel were identified and quantified by GCMS. Methyl ricinoleate in COME and methyl α-linolenate, methyl palmitate, methyl oleate, methyl linolinate, methyl stearate in WCOME were obtained as the major components. Lastly, various physicochemical tests of the produced biodiesel were conducted following ASTM standard methods to check its compatibility and sustainability as substituted petrodiesel. WCOME showed better and compatible properties as compared to COME. So, considering the results of all the above studies, it is concluded that KSO 800 is efficient, stable, and leaching proof catalyst that can actively catalyze faster, cleaner and non hazardous transesterification process of WCO and CO to produce high quality biodiesel.