Chapter 4

Application of potassium modified ceria oxide (K-CeO_2) catalyst in biodiesel production from waste cooking oil and castor oil

4.1 Introduction

The present chapter discusses the catalytic behavior of potassium modified ceria oxide (K- mod CeO_2) catalyst in lab scale biodiesel production from waste cooking oil and castor oil. The process optimization of various parameters namely, K/Ce atomic ratio, calcination temperature, oil : methanol molar ratio, catalyst weight %, temperature and duration were conducted to achieve the best catalytic efficiency of the catalyst. The catalytic reusability was investigated and thermo-kinetics parameters such as rate constant, activation energy, enthalpy of activation, entropy of activation and Gibb's free energy of activation were evaluated for the process of transesterification. The fatty acid methyl ester (FAME) formation in derived biodiesel was confirmed by ^{1}H and ^{13}C-NMR spectroscopy; in addition, the constitutional fatty acid methyl esters with their compositional % were analyzed by GCMS. Furthermore, the fuel characteristics of synthesized biodiesel were determined by ASTM standard methods, and lastly, yield %, turn over frequency, process mass index etc were investigated to check the 'Greenness" of the process.

4.2 Optimization of influential reaction parameters

In the process optimization, impact of different reaction variables of the transesterification reaction were investigated in two sets of batch reaction for WCO and castor oil following one variable at a time method (OVAT). First, the prepared catalyst was optimized to account the best performance in methyl esterification. So, K/Ce atomic ratio and catalyst activation temperature were optimized in the following range 0 to 3, and 600 to 1000^{O}C respectively. Then, the optimized catalyst was introduced in further optimization studies of oil : methanol molar ratio (1:8 to 1:18), catalyst loading % (0.5 to 3%), temperature (45 to 75^{o}C), and reaction duration (15 to 150 min). Methyl ester of waste cooking oil and castor oil were designated as WCOME and COME.

4.2.1 Impact of K/Ce atomic ratio and catalyst activation temperature on methyl ester conversion (%)

The K mod CeO_2 catalysts were prepared by sol-gel auto combustion method varying K/Ce atomic ratio from 0 to 3 with 0.5 increment of the atomic weight % of potassium. Then, the as-synthesized catalysts were introduced in two sets of batch reactions maintaining the following reaction conditions: 1:14 oil : methanol molar ratio, 1.5 wt% catalyst weight, $65^{\circ}C$ temperature, 75 min reaction duration for transesterification of waste cooking oil (1st set); and 1:16 oil to methanol molar ratio, 2.5 wt % catalyst weight, $65^{\circ}C$ reaction temperature, 120 min reaction duration for transesterification of castor oil (2nd set).

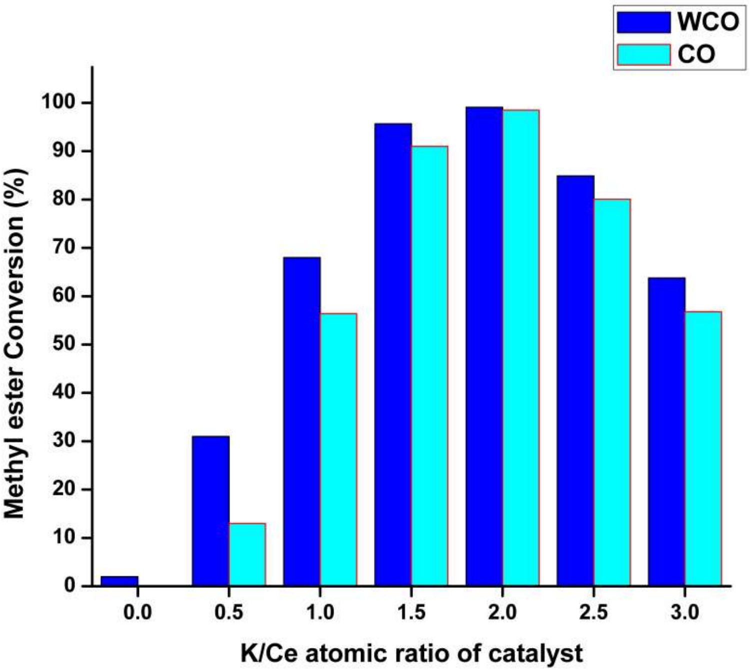

Figure 4.1A Impact of K/Ce atomic ratio (0.0-3.0) on methyl esterification reaction of waste cooking oil (WCO) and castor oil (CO)

Figure 4.1A has depicted the effect of K/Ce atomic ratio in FAME conversion of WCO and CO to WCOME and COME respectively. The increment in K/Ce atomic ratio has showed a positive impact on catalysis. This is because of increased availability of active sites with increasing K/Ce atomic ratio. At the optimum ratio, the maximum number of active components (i.e. K species) was uniformly distributed into the ceria oxide matrix; thus, the reactant molecules had singly and comfortably occupied the available active sites and best performance of the catalysts was obtained. The maximum FAME conversion of 99.09% WCOME and 98.49% COME were found at the K/Ce atomic ratio of 2. However, at a higher atomic ratio of K/Ce (>2), it was assumed that agglomeration of active species (K- species) on ceria oxide surface imposed molecular hindrance between the reactants and reduced the FAME conversion (Yadav and Sharma, 2018). The catalyst having K/Ce atomic ratio 2 was designated as 2K-CeO_2.

To obtain the desired phase, the pre-calcined catalyst sample (2K-CeO_2) was annealed at high temperature. The activation temperature was varied from 600 to 1000°C with an increment of 100°C. A set of batch reactions were carried out for WCOME formation at following optimum reaction conditions: 1: 14 oil to methanol molar ratio, 1.5 wt% of catalyst weight, 65°C reaction temperature, and 75 min reaction duration. Likewise, for COME formation, the following conditions i.e. 1: 16 oil to methanol molar ratio, 2.5 wt% of catalyst weight, 65°C reaction temperature, and 120 min reaction duration were maintained. Figure 4.1B shows the effect of catalyst activation temperature on methyl ester formation. FAME conversion increased with increase in activation temperature from 600 to 800°C. Maximum FAME conversions of 99.09% WCOME and 98.49% COME were observed at 800°C. A significant reduction in FAME conversion was noticed after increasing temperature to 900°C. The increment in catalyst activation temperature improvised the desired phase for methyl esterification reaction.

The ideal catalyst phase was formed at 800°C, confirmed by the XRD analysis. Beyond 900°C, the FAME conversion fell down because a significant amount of potassium species was volatilized during activation process at higher temperature (900 to 1218°C, confirmed by TGA-DTA analysis); in consequence, the number of active sites in the catalyst was reduced (Yadav et al. 2017). Thus, 800°C was taken as optimum activation temperature for the catalyst 2K-CeO_2. The catalyst activated at 800°C is termed as 2K-CeO_2-800.

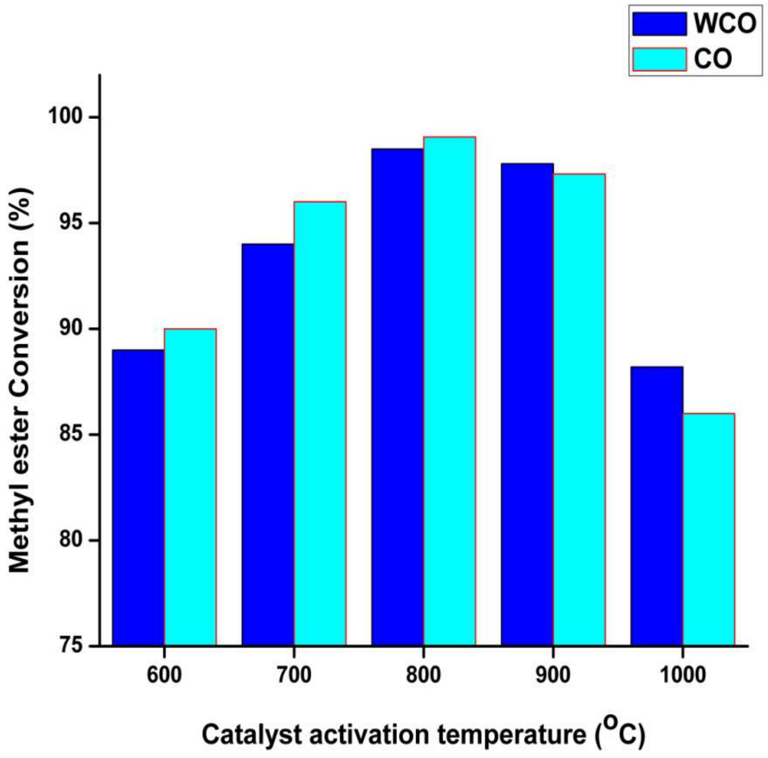

Figure 4.1B Effect of catalyst activation temperature (600 - 1000°C) on methyl esterification reaction of waste cooking oil (WCO) and castor oil (CO)

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

Optimization of oil to methanol is important for economic biodiesel production because this ratio has greater impact on driving the transesterification process as well as the production cost. The effect of oil to methanol molar ratio on FAME conversion of WCOME and COME formation has been shown in Figure 4.2A. The oil to methanol molar ratio was varied from 1: 8 to 1: 18, however, the other parameters like catalyst weight 1.5 wt%, temperature 65°C, reaction duration 75 min for WCOME formation and catalyst weight 2.5 wt%, temperature 65°C, reaction duration 120 min for COME formation were kept constant. The highest conversions of 99.09% WCOME and 98.49% COME were found at corresponding 1:14 and 1:16 oil to methanol molar ratio.

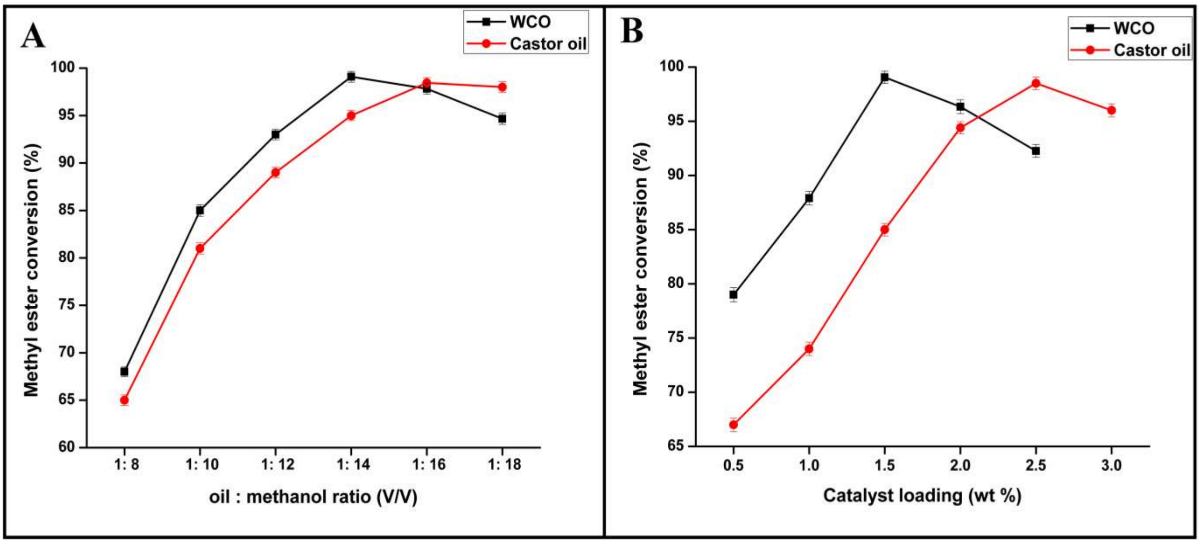

Figure 4.2 (A) Impact of oil : methanol molar ratio (1:8 - 1:18) (B) impact of catalyst weight percentage (0.5 - 3.0%) on methyl esterification of WCO and castor oil

FAME conversion was increased with increasing methanol concentration up to the optimum molar ratio. This might be occurred due to excess methanol accelerated the interaction between triglyceride and catalyst up to a optimum extent (Putra et al., 2018). After the optimum ratio, a further increase in oil to methanol molar ratio reduced the FAME conversion. It happened due to dissolution of glycerol (byproduct) in excess methanol, which ultimately troubled the proper glycerol-biodiesel phase separation (Singh et al., 2016).

Next, catalyst weight percentage predominantly influences the transesterification process as the optimum catalyst amount ensures the access of active sites for reactants. The impact of catalyst dose on FAME conversion (%) was examined by increasing the catalyst amount from 0.5 to 3 wt% (w/w), whereas the other reaction conditions namely oil to methanol molar ratio, temperature, reaction duration for WCOME formation and COME formation were set at the corresponding optimum value as mentioned earlier. Figure 4.2B has depicted that increasing catalyst loading enhanced the conversion till the optimum wt%, i.e. 1.5 wt% and 2.5 wt% in the corresponding WCOME and COME formation. Further increment in catalyst concentration dropped the methyl ester conversion due to increase the fluid viscosity in the reaction medium, induced poor mass transfer between three phases (Sahani et al., 2018).

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

For any kinetic reaction, both temperature and time play the most important role. To find out the optimized temperature for WCO and CO transesterification, two sets of batch reactions were executed between the temperature range of 45^{o}C to 75 ^{o}C for the two corresponding feedstock. The following reaction condition was maintained for optimization of temperature in WCO transesterification: oil to methanol molar ratio 1:14, catalyst weight 1.5 wt%, and reaction duration 75 min; however, in case of CO transesterification, it was oil : methanol 1:16, catalyst weight 2.5 wt%, and reaction duration 120 min. The influence of temperature in FAME conversion has been shown in Figure 4.3A. This implies that FAME conversion was accelerated with increasing temperature. Maximum conversions of both WCO and CO were obtained at 65°C, quite near to boiling temperature of methanol (64.8°C). At this optimum temperature, the reaction attained the required threshold energy, which in turn favored the mass transfer between reacting interfaces (Singh et al., 2016, Ayoub et al., 2017). Moreover, the rate of the reaction was enhanced with increasing temperature to the optimum extent. Beyond optimum temperature (65°C), methanol started to evaporate, causing effective loss of methanol from the reaction mixture, which in consequence displayed a significant fall in FAME conversion.

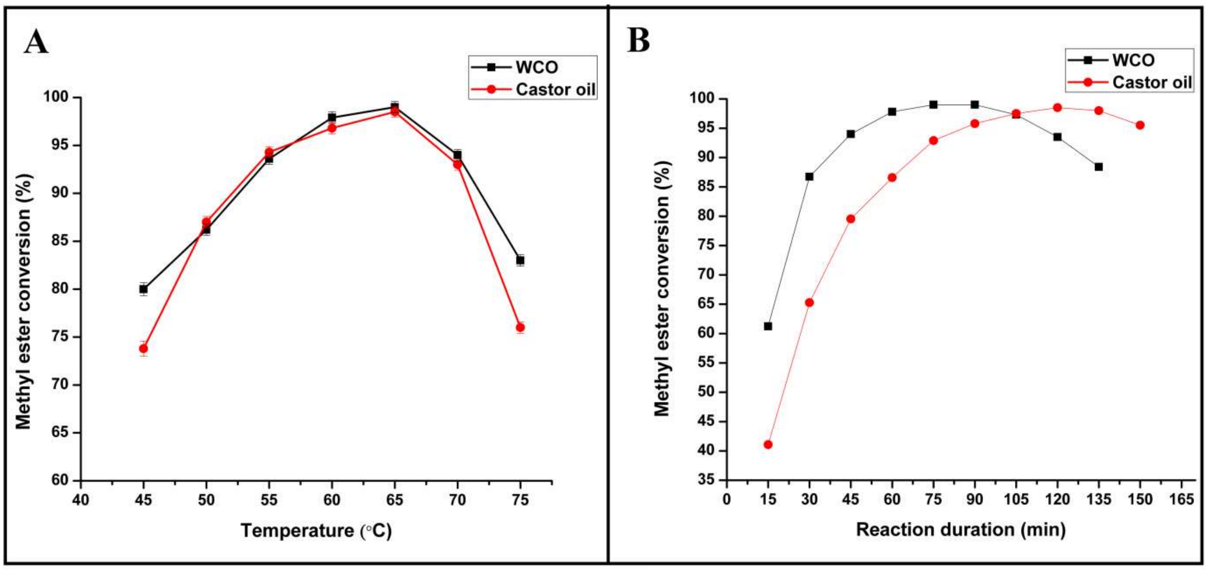

Figure 4.3 (A) Impact of reaction temperature (45 - 75°C), (B) impact of reaction duration (15 – 150 min) on methyl esterification of WCO and castor oil

Impact of time on methyl ester conversion of WCOME and COME was inspected by varying reaction duration from 15 to 150 min keeping other parameters constant. The batch reaction condition of WCO transesterification was 1:14 oil to methanol molar ratio, 1.5 wt% catalyst weight, and 65°C temperature; however, in case of

CO, it was 1:16 oil : methanol, 2.5 wt% catalyst weight, and 65°C temperature. Figure 4.3B manifests the effect of reaction time on biodiesel production from WCO and CO. For highest FAME conversion, reacting species in reaction mixture must be allowed to be in contact for an appropriate time period. The optimum reaction duration was observed as 75 min for waste cooking oil and 120 min for castor oil. At the initial stage of reaction, the reaction was diffusion controlled, so a poor FAME conversion was noticed within 15 min. But with time it was kinetically controlled, then the FAME conversion got sharply increased. When the reaction reached near to the equilibrium, the reaction was slowed down, and at the optimum time, it achieved the equilibrium and displayed constant rate upto a certain time limit. However, a significant drop in FAME conversion was also observed after the optimum time (i.e. 100 to 135 min for WCO and 135 to 150 min for CO). This might have happened due to reversal of the methanolysis reaction or acceleration of side reaction (dissolution of glycerol into methanol). Similar interpretations were also reported by Ma et al. (2017) and Tang et al. (2017).

4.3 Reusability of 2K-CeO_2-800 catalyst

Catalyst stability and reusability are the two significant properties of an efficient heterogeneous catalyst. The durability of the catalyst 2K-CeO_2-800 was examined to check its sustainability for the economic production of biodiesel. Two sets of transesterification reactions were carried out with two feedstock (WCO and CO) at their corresponding optimum reaction conditions: 1:14 oil to methanol molar ratio, 1.5 wt% catalyst weight, 65°C temperature, 75 min time for WCO transesterification, and 1:16 oil : methanol, 2.5 wt% catalyst weight, 65°C temperature, 120 min time for CO transesterification. Six consecutive runs were performed. The bar graph (Figure 4.4**)** represents the catalytic efficiency in terms of FAME conversion for consecutive six runs. The catalytic efficiency of the 2K-CeO_2-800 can be restored for five consecutive cycles.

After 5th run, the catalyst showed around 78% conversion of WCOME and 72% conversion of COME. After completion of each cycle, a small deterioration (2-3%) in conversion was observed that probably happened due to surface passivation and/or pore deformation during recalcination and/or weight loss during washing (Isahak et al. 2011). After the 5th cycle, a drastic fall in conversion was observed because of effective leaching of the active components from the catalyst surface. This aspect was confirmed by hot filtration test.

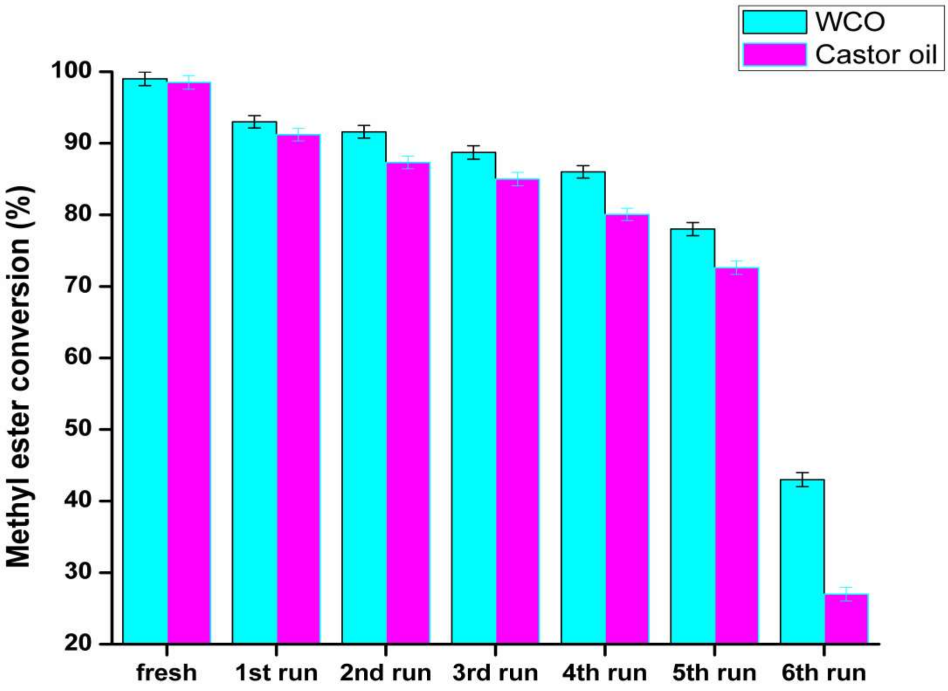

Figure 4.4 Reusability of 2K-CeO_2-800 catalyst in transesterification of WCO and CO at corresponding optimized reaction condition

4.4 Kinetic and thermodynamic study

The kinetic and thermodynamic parameters regarding transesterification of WCO and CO using K-mod CeO_2 catalyst were evaluated by the help of various equation and graphs. Required optimum reaction conditions of the respective WCO and CO transesterification reactions were maintained during kinetic study.

4.4.1 Determination of rate constants at different temperatures

To evaluate the value of rate constants (k) at different temperatures, $-\ln(1- X_{ME})$ was plotted against time (in min). Methyl esterification reactions of WCO and CO were conducted at five different temperatures as 45, 50, 55, 60 & 65°C. In case of WCO, the ME conversion was estimated after 15 min interval; whereas, COME conversion was evaluated after 20 min interval. Figure 4.5A and Figure 4.5B represent the corresponding kinetic plots of WCO and CO transesterification using 2K-CeO_2-800. The resultant values are shown in Table 4.1. The R^2 values of the linear plots were found in a range of 0.97 to 0.99. This ensures that the pre-assumptions for this kinetic model were very much correct (i.e. change of methanol concentration doesn't affect the rate of the reaction). Despite of two reactants (methanol and triglyceride), rate of reaction only depends on one reactant i.e. triglyceride. So, it is invariable stated that the methanolysis processes followed the pseudo-first-order kinetics.

Table 4.1 Rate constants at different temperature for WCO and CO transesterification

Feedstock	Waste cooking oil (WCO)					Castor oil (CO)				
Temperature (°C)	45	50	55	60	65	45	50	55	60	65
rate constant k (min^{-1})	0.02	0.027	0.036	0.051	0.062	0.011	0.017	0.023	0.029	0.035
R^2 value	0.99	0.997	0.996	0.988	0.976	0.999	0.997	0.989	0.992	0.987

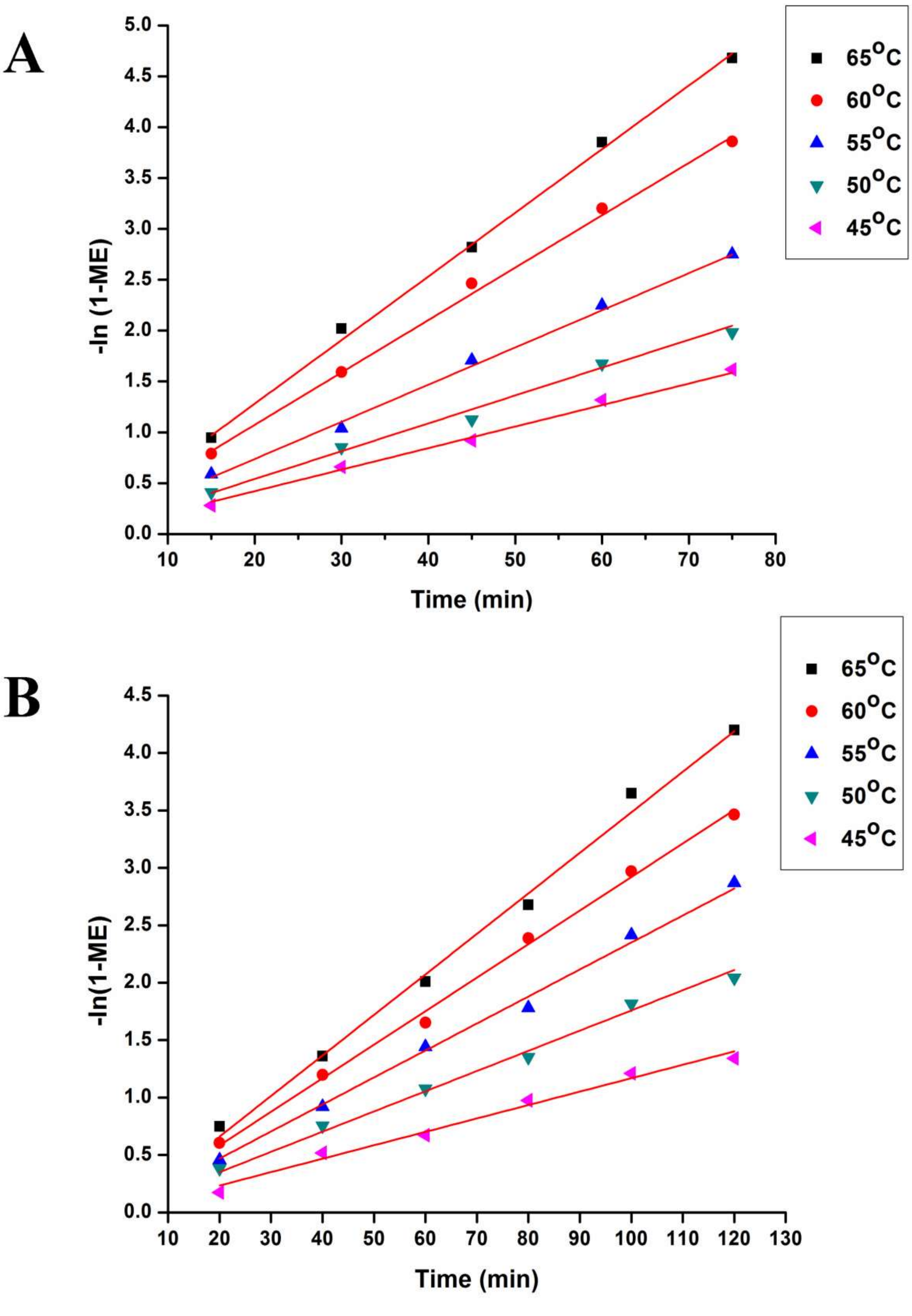

Figure 4.5 (A) Kinetic plot [-ln(1-ME) vs time] of WCO transesterification reaction, (B) kinetic plot of CO transesterification reaction using 2K-CeO_2-800 catalyst

4.4.2. Determination of reaction activation energy and pre-exponential value

Figure 4.6A represents the Arrhenius plot (lnk vs 1/T) of WCOME and COME formation. The activation energy of the transesterification of WCO and CO was found to be 50.1 kJ.mol^{-1} and 48.55 kJ.mol^{-1} respectively. Both the activation energies were found within the range of base-catalyzed transesterification reaction, i.e. 33.6 to 84 kJ.mol^{-1} (Sahani et al. 2019). The pre-exponential factors were determined as 35.4 $\times 10^5$ min^{-1} for WCO and 11.9 $\times 10^5$ min^{-1} for CO methyl esterification.

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

Figure 4.6B reveals the plot of ln(k/T) vs 1/T for both WCOME and COME formation. The enthalpy of the activation ($\Delta H^{\#}$) was determined from the slope of above mentioned plot. It was found to be 47.35 kJ.mol^{-1} and 45.98 kJ.mol^{-1} for the formation of WCOME and COME respectively using 2K-CeO_2-800 catalyst. The corresponding intercept implied the energy of entropy which was obtained as -128.69 J.K^{-1}.mol^{-1} for WCOME and -137.21 J.K^{-1}.mol^{-1} for COME formation. The Gibb's free energies of activation for methyl esterification (at 65°C) of WCO and CO were evaluated to be 90.85 kJ.mol^{-1} and 92.36 kJ.mol^{-1} respectively. The negative sign of $\Delta S^{\#}$ and positive sign of $\Delta H^{\#}$ & $\Delta G^{\#}$ imply that transesterification process using 2K-CeO_2-800 catalyst followed the endothermic non-spontaneous reaction pathway and entropy of the system was reduced during the transesterification process (Galvan et al., 2013).

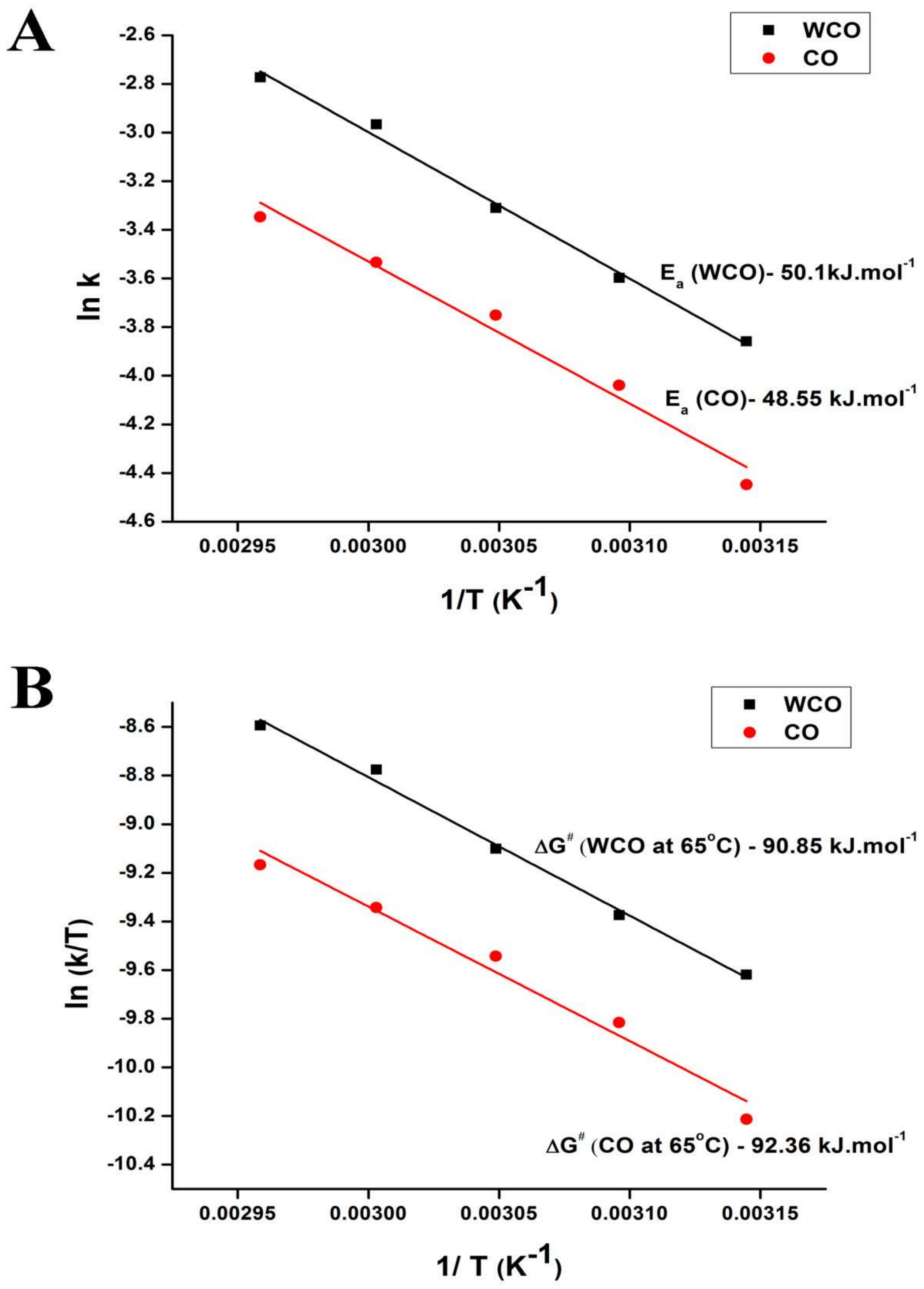

Figure 4.6 (A) Arrhenius plot ln k vs (1/T), and (B) Eyring-Polanyi plot ln (k/T) vs (1/T) of transesterification of WCO and CO using 2K-CeO_2-800 catalyst

4.5 Green parameters study

Some of the important 'Green' parameters like yield (Y), turnover frequency (TOF), E-factor (E_f) and process mass index (PMI) were investigated to know the extent of cleanness of the process. The transesterification reactions of WCO and CO were carried out at the corresponding optimum reaction conditions. The resultant values of such 'Green' parameters for biodiesel production from WCO and CO using 2K-CeO_2-800 catalyst are enlisted in Table 4.2. High yield percentage and high turnover frequency imply that the 2K-CeO_2-800 is an efficient heterogeneous catalyst for biodiesel production. In addition, the low value of E-factor and PMI suggest that both the transesterification processes produce negligible amount of waste during biodiesel production and follow a cleaner and greener pathway.

Table 4.2 Green parameters for WCO and CO transesterification using 2K-CeO_2-800 catalyst

Parameters	**WCO**	**CO**
Maximum methyl ester conversion (%)	99.09	98.49
Maximum yield (%)	83.34	95.15
Turnover frequency TOF (s^{-1})	4.80×10^{-4}	2.77×10^{-4}
E-factor	0.153	0.157
Process mass intensity PMI	1.813	1.698

4.6 Characterization of derived biodiesel

4.6.1 ^{1}H NMR spectroscopy

Figure 4.7A and Figure 4.7B display the ^{1}H NMR of biodiesel derived from waste cooking oil (WCOME) and castor oil (COME) respectively. The sharp intense signal at 3.68 ppm and triplet signal at 2.33-2.30 ppm are the characteristic peaks of methyl ester proton (OCH_3) and alpha-methylene (α-CH_2) proton respectively. The other obtained signals in ^{1}H NMR spectra of WCOME are assigned as follows: 5.39 to 5.35 ppm (multiplet **-C$\mathbf{H}$=C$\mathbf{H}$-)**, 2.80 to 2.77 ppm (triplet $C{=}C{-}C\mathbf{H}_2{-}C{=}C$), 2.06 ppm (multiplet $C\mathbf{H}_2{-}C{=}C$), 1.63 ppm (Singlet $C\mathbf{H}_2{-}C{-}C{=}O$), 1.32 to 1.27 ppm (rest $-C\mathbf{H}_2$), and `0.92 to 0.88 ppm (multiplet terminal $C\mathbf{H}_3$). The similar signals are also observed in ^{1}H NMR spectra of COME alongwith additional signals at 3.62 ppm and 2.22 assigned for α-hydroxy proton and hydroxyl proton respectively. The integral value of OCH_3 proton and α-CH_2 signals was analyzed to calculate the FAME conversion of respective oils. The integral value of OCH_3 proton in WCOME and COME spectra were found to be 19.62 and 17.02 respectively, similarly it was 13.20 and 11.54 for α-CH_2 proton of the same.

$$\text{FAME conversion (\%) of WCO} = \left(\frac{2\times19.62}{3\times13.20}\right)\times 100 = 99.09\ \% \tag{4.1}$$

$$\text{FAME conversion (\%) of CO} = \left(\frac{2\times17.05}{3\times11.54}\right)\times 100 = 98.49\ \% \tag{4.2}$$

At the optimum reaction conditions (1:14 oil to methanol molar ratio, 1.5 wt% catalyst weight, 65°C temperature, 75 min time for WCO transesterification, and 1:16 oil : methanol, 2.5 wt% catalyst weight, 65°C temperature, 120 min time for CO transesterification), the maximum conversion of WCO and CO to FAME were obtained as 99.09% and 98.49% respectively.

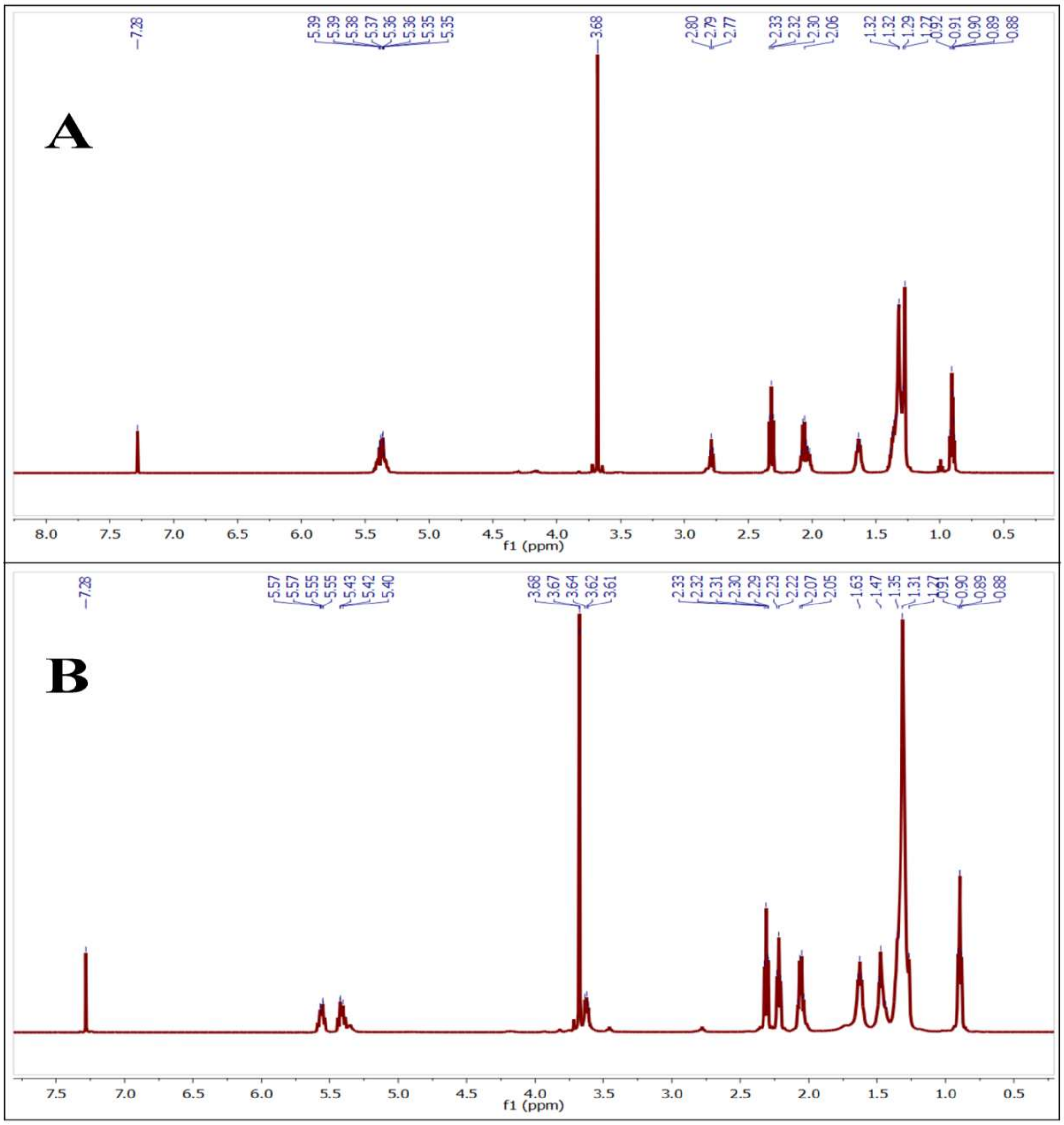

Figure 4.7 (A) ^{1}H NMR spectra of biodiesel derived from waste cooking oil and (B) ^{1}H NMR spectra of biodiesel derived from castor oil

4.6.2 ^{13}C NMR spectroscopy

Figure 4.8A and Figure 4.8B represent the ^{13}C NMR spectra of synthesized biodiesel from waste cooking oil (WCOME) and castor oil (COME) respectively. The ^{13}C NMR signals of WCOME are designated as: δ (ppm) = 174.3 corresponds to single ester carbonyl carbon (O-**C**O-), 130.2 to 127.9 corresponds to olefinic carbons (**C**H=**C**H), 77.2 to 76.7 corresponds to solvent carbon (**C**DCl_3), 51.4 ppm corresponds to methyl ester carbon ($\mathbf{C}H_3O$-), 34.1 to 24.9 corresponds to methylene carbon ($\mathbf{C}H_2$), 14 corresponds to terminal methyl carbon ($\mathbf{C}H_3$). In case of COME, above-mentioned signals are found with an additional signal at 71.5 corresponds to α-hydroxy carbon. The characteristic signal of methyl ester carbon (at 51.4 ppm) confirms the formation of fatty acid methyl ester (FAME) from WCO and CO (Yadav et al. 2017; Ba et al., 2016).

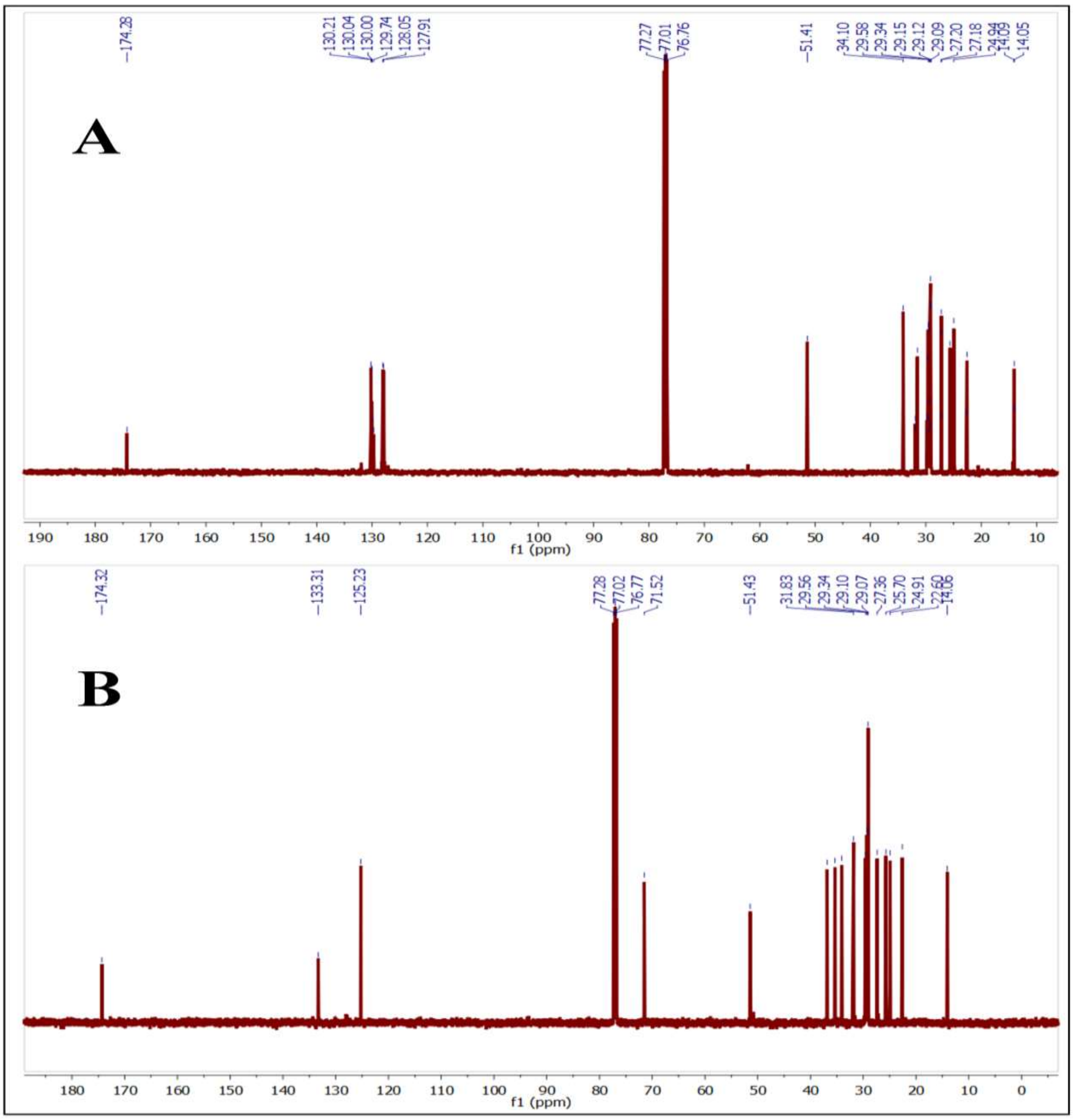

Figure 4.8 (A) ^{13}C NMR spectra of biodiesel derived from waste cooking oil and (B) ^{13}C NMR spectra of biodiesel derived from castor oil

4.6.3 GC-MS analysis

As summarized in Table 4.3, the composiotional FAME present in COME are methyl palmitate (1.005%), methyl linolate (4.198%), methyl oleate (3.898%), methyl stearate (1.204%) and methyl ricinolate (89.623%) found at retention time 9.224, 10.778, 10.855, 11.107 and 12.517 min. Methyl ricinolate has the largest share in COME composion. Table 4.4 compries the constituent fatty acids methyl esters present in WCOME; the major componanat are methyl palmitate (13.09%), methyl stearate (5.04%), methyl oleate (30.53%), methyl linolinate (45.86%), methyl α-linolenate (3.56%). These five constituents cummulatively contribute around 98% of total composition of WCOME. Both feedstock are composed by saturated and unsaturated fatty acid composition. The unsaturated FAME componants reduce the viscosity of the biodiesel and increase the cetane number (Sharma and Singh,2010).

Table 4.3 FAME composion of the biodiesel derived from castor oil using 2K-CeO_2-800 catalyst

Retention time (min)	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
9.224	Methyl palmitate	1.005	99	$CH_3(CH_2)_{14}COOMe$
10.778	Methyl linoleate	4.198	99	$CH_3(CH_2)_{12}(CH=CH)_2COOMe$
10.855	Methyl oleate	3.898	98	$CH_3(CH_2)_{14}CH=CHCOOMe$
11.107	Methyl stearate	1.204	98	$CH_3(CH_2)_{16}COOMe$
12.517	Methyl ricinoleate	89.623	98	$CH_3(CH_2)_{13}CH(OH)CH=CH$ $COOMe$
saturated FAME		2.209%		
monounsaturated FAME		93.521%		
polyunsaturated FAME		4.198%		

Table 4.4 FAME composion of biodiesel derived from waste cooking oil using 2K-CeO_2-800 catalyst

Retention time (min)	Fatty acid methyl ester (FAME)	Composition (%)	Library Match	Corresponding FAME structure
4.18	Methyl laurate	0.34	98	$CH_3(CH_2)_{10}COOMe$
6.02	Methyl myristate	0.08	99	$CH_3(CH_2)_{12}COOMe$
6.33	Methyl myristoleate	0.39	99	$CH_3(CH_2)_{10}(CH=CH)COOMe$
8.61	Methyl palmitate	13.09	99	$CH_3(CH_2)_{14}COOMe$
8.88	Methyl palmitoleate	0.16	99	$CH_3(CH_2)_{12}(CH=CH)COOMe$
11.47	Methyl stearate	5.04	98	$CH_3(CH_2)_{16}COOMe$
11.71	Methyl oleate	30.53	98	$CH_3(CH_2)_{14}(CH=CH)COOMe$
12.25	Methyl linoleate	45.86	98	$CH_3(CH_2)_{12}(CH=CH)_2COOMe$
12.85	Methyl α-linolenate	3.56	99	$CH_3(CH_2)_{10}(CH=CH)_3COOMe$
14.33	Methyl arachidate	0.38	99	$CH_3(CH_2)_{18}COOMe$
14.55	Methyl paullinate	0.28	99	$CH_3(CH_2)_{16}(CH=CH)COOMe$
17.18	Methyl behenate	0.27	98	$CH_3(CH_2)_{20}COOMe$
saturated FAME		19.20%		
monounsaturated FAME		31.36%		
polyunsaturated FAME		49.44%		

4.7 Fuel properties of synthesized biodiesel

The important physical and fuel properties such as acid value, density, viscosity, cetane number, calorific value, flash point, pour point and cloud point of derived biodiesels (WCOME & COME) were estimated by the standard methods laid by American Society for testing and material (ASTM). The experimental data regarding various parameters of fuel properties were accounted as per ASTM D 6751 standard as shown in Table 4.5. The acid values of WCOME and COME were found 0.5 mg KOH/g and 0.06 mg KOH/g within the ASTM standard range for biodiesel. Both density and viscosity of WCOME were obtained in the ASTM limits but in case of COME, both the values were greater than that of the standard range. Cetane number corresponds to the combustion quality and ignition delay time. The experimental cetane number 49 and 44.2 were observed for WCOME and COME respectively. Both the products showed standard calorific value and flashpoint. Low cloud point and pour point ascertained good cold flow properties of biodiesel COME.

Table 4.5 Comparison of fuel properties of WCOME and COME with ASTM standards for biodiesel

Parameters	ASTM test method used	ASTM-6751 biodiesel	WCOME	COME
Acid value (mgKOH/g)	D 664	<0.8	0.5	0.06
Density (40^0C,g.l^{-1})	D 4052	0.86-0.90	0.89	0.942
Viscosity (mm^2/s)	D 7110	1.9 to 6.0	4.3	15.8
Cetane number	D 613	47	49	44.2
Calorific value (MJ/Kg)	D 240	35	41.34	39.89
Flash point (°C)	D 93	100 to 190	140	192
Pour point (°C)	D 97-05	-15 to 16	3	-29
Cloud point (°C)	D2500	-3 to 12	6	-15

4.8 Conclusion

In this present study, the catalytic activity of K-mod CeO_2 catalyst in biodiesel production from waste cooking oil (WCO) and castor oil (CO) has investigated through various studies. In optimization study, it was found that catalyst having K/Ce atomic ratio 2, activated at 800ºC showed best activity in transesterification reaction. The highest fatty acid methyl ester (FAME) conversion from WCO was found to be 99.09% at the following optimum reaction conditions: 1:14 oil to methanol molar ratio, 1.5 catalyst wt%, 65ºC temperature and 75 min time. Similarly, the maximum FAME conversion from CO was obtained as 98.49% at the corresponding optimized reaction conditions such as 1:16 oil to methanol molar ratio, 2.5 catalyst wt%, 65ºC temperature and 120 min time. In reusability study, it was found that the catalyst (2K-CeO_2-800) is efficient for five consecutive runs with more than 75% efficacy. In kinetic study, it was found that both the processes followed pseudo first order kinetics. Activation energy E_a for WCO and CO transesterification were found to be 50.1 $kJ.mol^{-1}$ & 48.55 $kJ.mol^{-1}$ respectively with corresponding frequency factor 35.4×10^5 min^{-1} & 11.9×10^5 min^{-1}. Enthalpy of activation ($\Delta H^{\#}$) was obtained to be 47.35 $kJ.mol^{-1}$ and 46 $kJ.mol^{-1}$ with corresponding entropy of activation ($\Delta S^{\#}$) -128.69 $J.K^{-1}.mol^{-1}$ and -137.21 $J.K^{-1}.mol^{-1}$of methyl ester formation of WCO and CO respectively. The Gibb's free energy of activation ($\Delta G^{\#}$) of reactions (at 65ºC reaction temperature) was evaluated to be 90.85 $kJ.mol^{-1}$ (for WCOME formation) and 92.66 $kJ.mol^{-1}$ (for COME formation). The sign of the thermodynamic parameters suggested that the transesterification was non-spontaneous endothermic reaction. The catalyst showed high turnover frequency, and meager value of E-factor and PMI which imply the catalyst is well efficient for fast production of biodiesel with minute waste generation.