New Heterogeneous Catalysts for Green and Faster Biodiesel Production

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By

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Chapter 7

Summary of the work

7.1 Synopsis of the work

The thesis entitled "New heterogeneous catalysts for faster and cleaner biodiesel production" illustrates the study of biodiesel synthesis from waste cooking oil and an indigenous feedstock castor oil using three new heterogeneous catalysts, namely potassium modified ceria oxide, potassium tin oxide, and barium tin oxide catalysts.

Current issues like population explosion, high energy demand, fast depletion of non-renewable energy resources, and the concern for future energy crisis have insisted to explore sustainable resources for continuous energy supply. As a supplementary, biodiesel has been appreciated throughout the world because of its physicochemical compatibility that of conventional petrodiesel. Biodiesel is a nontoxic, less polluting, and biodegradable fuel. Combustion of biodiesel possesses lower carbon dioxide gas emissions along with other exhausting gas emissions. Besides, introduction of biodiesel blends into the existing Compression-Ignition (C.I) engine is quite feasible without any major modification in engine design.

Chemically biodiesel is a mixture of alkyl esters of saturated or unsaturated fatty acids having carbon number 10 to 22. It is derived from different feedstock like vegetable oils (like soybean oil, sunflower oil, etc), lignocellulosic biomass (like Ricinus communis oil, Jatropha curcas oil, etc), waste oil, and animal fats. Cost analysis of biodiesel production estimates that 70% to 80% of total production cost is shared by its feedstock. So, it is important to choose a sustainable feedstock for the economic production of biodiesel. Waste frying oil (WFO) is one of the best feedstocks as it is abundantly available and much cheaper than other feedstocks. The discarded oil creates severe ecological damage in the aquatic environment and its carcinogenic and mutagenic nature is equally harmful for human beings. Therefore, the use of waste oil to biodiesel is admirable for waste to wealth transformation. According to India's biodiesel policy, it is declared that India will recover approx 220 core liters of waste oil to produce biodiesel (Roy et al., 2020). Besides, sulfur less, pale yellow coloured, highly viscous oil extracted from the castor (*Ricinus communis)* seed which possesses a high content of oxygen and higher cetane number can also be used as potential feedstock for biodiesel production. Currently, castor is cultivated mostly in Gujarat and Andhra Pradesh on above 7,00,000 hectares. India is world's largest producer and exporter of castor oil. The Indian breed of castor seed has 42% to 48% oil content, which can be extracted by simple mechanical pressing. The average yield of castor seed oil is 550 lit/hectare. Moreover, the cultivation cost of castor is around 50% and 25% that of rapeseed and Jatropha. So, considering this facts, it must be stated that in India, waste frying oil and castor oil would be evolved as potential and sustainable resource for mass scale biodiesel production.

Biodiesel can be produced by various techniques as dilution, pyrolysis, microemulsion, and transesterification, etc. But among all these processes, transesterification is simpler, economic, and more reliable. In the transesterification process, two basic components are required for converting triglyceride (feedstock) to alkyl ester of fatty acid (biodiesel); these are alcohol and catalyst. Generally, methanol and ethanol are used as alcohols in the transesterification reaction. But methanol is extensively used because of its easy abundance and cost-effectiveness. Thus, the product biodiesel derived by using methanol as alcohol is the mixture of fatty acid methyl ester or FAME. Next, the catalyst is one of the most important components in transesterification as it pushes the reaction to achieve the ultimate goal by acquiring the lower energy path. Basically, three types of catalysts like homogeneous, heterogeneous, and enzymatic catalysts are used in the transesterification process. Till now in industry level biodiesel production, homogeneous catalysts like NaOH, KOH, H_2SO_4, $NaOCH_3$, etc are deployed as they all are cheap and efficient, though it is associated with number of demerits as wastewater production, toxic contamination, additional purification step etc. Moreover, such corrosive homogeneous catalysts can also disturb the environmental diversity. On the other hand, the enzymatic catalysts possess low reaction rate, poor reproducibility, high synthesis cost, alcohol sensitivity etc. However, heterogeneous catalysis is far advantageous than homogeneous and enzymatic catalysts as it neither demands any additional purification for catalyst separation nor intensive care for preventing any type of contamination. Moreover, it can be used several times with good efficiency. So, from the commercial point of view, the synthesis of an efficient heterogeneous catalyst is much profitable for biodiesel production. In literature, it is reported that both K and Ba based heterogeneous catalysts are highly efficient for transesterification but there also some issues like long reaction time, leaching of the active component, surface passivation, poor recyclability, etc. which have to be improved. In this thesis, all such aforementioned problems are addressed. The thesis contains new heterogeneous catalyst synthesis, characterization and application in biodiesel production. The application segment includes optimization study, kinetic study, reusability study, physicochemical characterization of product biodiesel and green parameter study. The summary of the research work has been presented here.

Chapter 1 is general introduction and literature review. It introduces global energy scenario, renewable energy resources and biodiesel. The statistics and projections of world’s energy consumption with time from different non renewable resources are described in this chapter. In addition, the future energy crisis, uneven distribution of fossil fuels, the environmental issues regarding exhaust gas emissions and importance of renewable energies are also discussed with statistical report. Additionally, the energy scenario of India and the status of biodiesel as a substituted biofuel in India are discussed in details. This chapter presented a critical literature survey on feedstocks of biodiesel, technologies for biodiesel production, and the recent reported heterogeneous catalysts for lab scale biodiesel production. On the basis of literature review, the viability gap and research motivation are proposed. Furthermore, the prime objectives of this research work have been demarcated as the selection of suitable feedstocks for economically viable biodiesel production, synthesis and characterization of some new heterogeneous base catalysts and its application including optimization, reusability, kinetics, and green parameter studies in biodiesel production.

Chapter 2 discusses the required materials and adopted methodologies for the present research work. The important chemicals used in catalyst synthesis and biodiesel production have been mentioned with specification and purity. The sources of feedstocks (waste cooking oil and castor oil) along with the purification process have been discussed. After purification the important physicochemical properties of the feedstocks were investigated by ASTM methods. Thus, the resultant data has been enlisted with mentioning the standard methods for characterization of feedstocks. Next, the different catalyst synthesis procedures (as sol-gel auto combustion method, polymer precursor auto combustion method, and wet impregnation method) and the different catalyst characterization techniques (as TGA-DTA, XRD, XPS, BET adsorption – desorption, SEM-EDAX, Hammett indication titration) are discussed. After that, the biodiesel production process viz. transesterification adopted for the studies in application part of the catalyst have been described with schematic diagram. Additionally, the methodologies of optimization studies (one variable at a time, OVAT), reusability study, kinetic study and green parameters study are deliberated in details. Then, various characterizations techniques, such as ^{1}H NMR, ^{13}C NMR and GC-MS of synthesized biodiesel are disclosed with the instrumental specification and analytical condition. At the last in this chapter, the standard methods adopted to evaluate the physicochemical as well as fuel properties of the derived biodiesel are described.

Chapter 3 includes synthesis methods and characterizations of three new heterogeneous base catalysts for biodiesel production. Potassium modified ceria oxide (K-mod CeO_2), potassium tin oxide (KSO) and barium tin oxide (BSO) catalysts were synthesized via sol-gel auto combustion process, polymer precursor auto combustion process and wet impregnation process respectively. The thermal stability of the catalysts were investigated by TGA-DTA, revealed that K-mod CeO_2, KSO, and BSO catalysts were thermally stabilized at 739°C, 765°C, and 758°C respectively. The powder XRD confirmed the chemical phases present in catalysts calcined at different calcination temperatures. In case of K mod CeO_2, it was found that when the catalyst was calcined below 800°C, cerium was present in form of Ce_2O_3 along with $Ce(OH)_3$; however, when it was calcined at 800°C, cerium existed as CeO_2. The potassium species were accommodated at the interstitial points of the cerium oxide lattice, and it was confirmed by the XRD data. In KSO, it was observed that in catalysts calcined at 500, 600 and 700°C, the metals (K and Sn) existed in their individual native oxide forms, but in the catalyst calcined at 800°C, metals formed three distinct compound phases as K_2SnO_3, $K_2Sn_2O_3$, and $K_2Sn_3O_7$. The XRD of barium tin oxide catalysts were quite interesting. The XRD of BSO (having Ba:Sn atomic ratio 1:1) revealed the single phase formation of $BaSnO_3$, however, in XRD of 2BSO (Ba:Sn = 2:1) and B2SO (Ba:Sn = 1:2) depicted that chemically excess Ba and Sn were present in $BaCO_3$ and SnO_2 along with $BaSnO_3$ in 2BSO and B2SO respectively. The oxidation state of each individual species present in catalysts was identified by XPS analysis, and the resultant XPS data was cross verified by XRD of the same. Morphological interpretation was delivered by SEM-EDAX analysis. It was found that the small sized rod shaped pure ceria oxide particles were transformed into large sized spherical particles after modification. However, in case of KSO 800 catalyst (calcined at 800°C), three different types of particles were found. Further EDAX confirmed that K_2SnO_3 possessed solid block like structure, $K_2Sn_2O_3$ particles were small sized spherical shaped agglomerated topology, and $K_2Sn_3O_7$ particles were needle shaped morphology. Comparing the SEM images of different barium tin oxide catalysts, it was confirmed that chemically excess $BaCO_3$ and SnO_2 were heterogeneous agglomerated over the surface of $BaSnO_3$ particles in 2BSO and B2SO respectively. BET surface area and basicity of the catalysts were investigated to predict the activity of such catalysts. After modification the surface area of the ceria oxide reduced due to increase the particle size, but the basicity increased due to incorporation of alkaline potassium species into the ceria matrix. In case of KSO catalyst, both the surface area and the basicity of the KSO 800 were obtained to be greater than that of other potassium tin oxides as the particles of KSO 800 were in less agglomeration and had particular shape and size, moreover KSO didn't contain the acidic carbonate species; thus, the basic property wasn't hampered. Similarly, the surface properties of BSO were found to be far better than 2BSO and B2SO for the same reason as mentioned in KSO catalysts. In addition, the basic strength of 2BSO and B2SO were observed to be quite low than that of BSO. This happened due to both carbonate and tin oxide possessed acidic character that lowered the basic strength of the respective catalysts.

In **Chapter 4,** the catalytic activity of K-mod CeO_2 catalyst in biodiesel production from waste cooking oil (WCO) and castor oil (CO) has been discussed. In optimization study, it was found that catalyst having K/Ce atomic ratio 2, activated at 800°C 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%, 65°C 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%, 65°C 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 65°C 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.

In **Chapter 5**, 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, 65ºC 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 800ºC 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.

In **Chapter 6**, the catalytic properties of synthesized Ba-SnO_2 catalyst for biodiesel synthesis from WCO and CO has been demonstrated. Among the analogs, BSO catalyst calcined at 850ºC 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.

The major findings of the present work have been summarized in Table 7.1. On reviewing the outcomes of this present work, it can be concluded that new heterogeneous base catalysts, namely, K-mod CeO_2, KSO, and BSO catalysts are highly efficient, stable and reusable for biodiesel production from waste cooking oil and castor oil. Moreover, the catalysts need moderated reaction conditions to acquire the most favorable conditions to display the highest FAME conversion. These catalysts produced high quality biodiesel within a very short time range of 25 min to 120 min. The biodiesel produced from WCO showed greater compatibility as a substituted biofuel according to the ASTM 6751 standards than that of the biodiesel derived from CO. High TOF and low E-factor suggested that transesterification reactions of WCO and CO using above catalysts were economic, clean and non-hazardous. Among the three catalysts, BSO and KSO 800 are found as efficient as of homogeneous catalysts. So, it is invariably stated that the newly synthesized catalysts can be used for faster and high quality biodiesel production from WCO and CO, adopting environmentally benign pathway.

7.2 Economic feasibility and cost analysis

Economic feasibility of biodiesel production is an important factor which actually governs the sustainability of biodiesel. Though, using biodiesel has many advantages but still biodiesel could not substitute the petrodiesel completely because of its shorter supply and relatively high cost. In commercial scale biodiesel production, the basic production cost is contributed by the feedstock, chemicals, and equipment cost (Gebremariam and

Marchetti, 2018). As 70 -85% of total production cost is shared by the feedstock cost; so, economic viability of biodiesel production is mainly depends on the feedstock that is used to produce biodiesel (Singh et al., 2018). In present work, the high quality biodiesel is produced from cheap feedstocks as waste cooking oil and castor oil using highly efficient heterogeneous catalysts (K mod CeO_2, K-Sn mixed metal oxide, Ba-Sn mixed metal oxide). Thus, the overall production cost has been mitigated to a large extent by reducing feedstock cost, utility cost and equipment cost. Moreover, the additional cost regarding purification step of biodiesel has been cut by using heterogeneous catalyst. Anuar and Abdullah (2016) reported that the application of heterogeneous catalyst has given the concession of the cost involved in the purification of biodiesel by reducing the production cost up to 5-10% and equipment costs about 25%. Furthermore, the heterogeneous catalysts were reused for five times, which ultimately upgrade the process to more sustainable level. Hence, in present study, the solid base catalysts were applied in ceramics after their deactivation in the transesterification reaction. Apart from biodiesel production, transesterification of oil also produces glycerol as the only side product which has been extensively used in pharmaceutical, personal care product, and chemical industries. The fixed capital investments (FCI) required in biodiesel production was investigated by using the standard methodology given in the literature (Apostolakou et al., 2009). This prescribed cost analysis included the cost of raw materials, chemicals, equipment and utility cost (water and electricity). The recyclability factor was also considered during cost analysis. Owing to the solid-liquid separation method, excess methanol and ethanol were recovered thoroughly. After thorough investigation of physicochemical characterization, the purity of produced biodiesel and glycerol were anticipated to be 99% and more than 95% respectively after purification. Finally, considering above factors, the tentative cost of biodiesel production from waste cooking oil was estimated to be 0.51-0.59 USD/L whereas the cost of biodiesel from castor oil was found to be 0.89- 0.92 USD/L. Easy abundance of WCO with zero investment shows the discrepancy in the cost of biodiesel produced. The current economic analysis suggested that the lab-scale production of biodiesel can be upgraded at the industry level using extensive and precise simulation techniques.

7.3 Future scope of the work

The high demand of petroleum in transportation sector is brightening the opportunities for expanding the biodiesel industries. In southern Asia, biodiesel industry has greater scope of marketing and profiting because of huge demand and low competition. The present work is mainly focused on faster and high quality biodiesel synthesis from abundant resources. To make this study more impactful in this field, some additional studies are further required in the extended version. The extended work of the present study must include the parametric study of scale up reaction, simulation study of cost analysis for industry level production, emission study of prepared FAME (pure and blended form), and value addition of glycerol.

Table 7.1 Summary of the work reported

Catalyst	Feedstock	Reaction condition (oil to methanol molar ratio, catalyst wt%, temperature, time)	Activation energy (E_a kJ/mol) & Gibb's free energy of activation at 65°C ($\Delta G^{\#}$- kJ/mol)	FAME Conversion (C %) & Yield (Y %)	E- factor (E_f), PMI & TOF (10^{-3}/S)	Reusability
K mod-CeO_2 (2K-CeO_2 800)	WCO	O:M -1:14, cat - 1.5 wt%, temp - 65°C, time -75 min	E_a - 50.1 kJ/mol, $\Delta G^{\#}$ - 90.85 kJ/mol	C- 99.09% Y- 83.34%	E_f - 0.153 PMI - 1.813 TOF - 0.48	5th (C - >75%)
	CO	O:M -1:16, cat - 2.5 wt%, temp - 65°C, time -120 min	E_a - 48.55 kJ/mol $\Delta G^{\#}$ - 92.36 kJ/mol	C- 98.49% Y- 95.15%	E_f - 0.157 PMI - 1.698 TOF - 0.277	5th (C - >75%)
K-Sn oxide (KSO 800)	WCO	O:M -1:16, cat - 3 wt%, temp - 65°C, time -35 min	E_a - 56.18 kJ/mol $\Delta G^{\#}$ - 88 kJ/mol	C- 99.43% Y- 96%	E_f - 0.453 PMI - 1.63 TOF - 15.27	5th (C - >80%)
	CO	O:M -1:12, cat - 2.5 wt%, temp - 65°C, time -45 min	E_a - 31.62 kJ/mol $\Delta G^{\#}$ - 89.62 kJ/mol	C- 98.56% Y- 95.43%	E_f - 0.409 PMI - 1.517 TOF - 12.09	5th (C - 80%)
Ba-Sn oxide (BSO)	WCO	O:M -1:16, cat - 2.5 wt%, temp - 65°C, time-25 min	E_a - 61.57 kJ/mol $\Delta G^{\#}$ - 89.23 kJ/mol	C- 98% Y- 96.6%	E_f -0.252 PMI - 1.43 TOF - 29.63	5th (C - >85%)
	CO	O:M -1:14, cat - 2 wt%, temp - 65°C, time -30 min	E_a - 61.97 kJ/mol $\Delta G^{\#}$ - 89.03 kJ/mol	C- 97.51% Y- 92.33%	E_f - 0.388 PMI - 1.725 TOF - 22	5th (C - >85%)