CHAPTER 7

7.1 Summary of the work

The thesis entitled "*Synthesis of biodiesel from indigenous non-edible feedstocks (used vegetable oil and kusum oil) using heterogeneous base catalysts*" demarcated the biodiesel synthesis from used vegetable oil and kusum oil feedstocks using heterogeneous aluminum-based catalyst barium aluminum oxide ($BaAl_2O_4$) and potassium aluminum oxide ($K_2Al_2O_4$).

Rising world population, increasing industrialization, continuously deteriorating environment, and reducing energy security have announced global interest in the exploration of various renewable energy sources based on green technologies. Currently, the energy need of the world is fulfilled primarily by the fossil-based fuels such as coal, petroleum, and natural gas. But these are non-renewable sources and also cause environmental pollution. Their uneven distribution over the world, 63% of the oil reserves are located in the Middle East is also leading to inequality and dominance. To mitigate these problems renewable energy sources such as solar, wind, tidal, hydroelectric, bio-renewable energy such as biodiesel and bioethanol are receiving considerable attention because of their more or less even distribution and potential to maintain zero or almost zero emission of greenhouse gases and other pollutants. Among various renewable energy sources, the biodiesel has attracted academic and commercial researcher's interests substantially due to its biodegradability, availability, and high energy returns (~90%). Biodiesel, an alternative to petroleum diesel fuel is a clean burning, oxygenated sulphur-free fuel and has lesser emissions of harmful gases, viz. sulfur dioxide, carbon monoxide and unburnt hydrocarbons in comparison to petroleum diesel fuel. It can be used in the existing internal combustion diesel engines for transport and power generation with or without little engine modifications. For biodiesel production.

transesterification is the well accepted and best-suited method in which conversion of triglycerides present in oil into its respective alkyl esters occurs by the base-catalyzed consecutive chemical reaction. Stoichiometrically, it involves 3 moles of alcohol and 1 mole of triglyceride to produce 3 mole of fatty acid alkyl ester and 1 mole of glycerol via stepwise conversion of triglyceride into diglyceride and monoglycerides take place. Transesterification reaction of triglycerides in presence of base catalyst follows SN_2 mechanism.

Transesterification process has been carried out in presence of a homogeneous or heterogeneous catalyst. The commercial-scale biodiesel production technologies are based on the use of a homogeneous catalyst such as hydroxide and alkoxides of sodium and potassium. These homogeneous catalyst leads to cause undesirable soap formation, toxic waste generation, high cost, additional washing steps to remove contamination and residual catalyst. These problems can be avoided by the utilization of heterogeneous catalyst for the synthesis of biodiesel. Heterogeneous catalysts can be easily separated and the final product does not contain impurities of the catalyst. Usage of heterogeneous catalyst is an environmental friendly process since it does not require washing steps and economical by mean of regeneration and then regenerated catalyst is reused as well. The main feature of these catalysts are that these share basic sites on their surface to catalyze the basic transesterification.

Barium aluminum oxide ($BaAl_2O_4$) and potassium aluminum oxide ($K_2Al_2O_4$) were synthesized via co-precipitation and physicochemical method respectively, and these are used as heterogeneous base catalyst for biodiesel production. The catalysts were characterized by

various techniques. Used vegetable oil and kusum oil were collected and physicochemical properties of both oils were studied according to ASTM standards. Direct transesterification was carried for used vegetable oil and esterification followed by transesterification was performed for the synthesis of biodiesel from kusum oil using the above-mentioned catalyst. Furthermore, the reaction parameters such as methanol: oil molar ratio, catalyst dose, reaction temperature, time and stirring speed were optimized to obtain the maximum conversion of FAMEs. Reusability of the synthesized catalysts was also investigated using optimized reaction conditions. The kinetics and thermodynamic studies of transesterification process were also performed to investigate the reaction order, rate constants, activation energy and free energy. Moreover, the fuel properties of synthesized used vegetable oil biodiesel and kusum oil biodiesel such as acid value, density, kinematic viscosity (40 ºC) calorific value, flash point, fire point, cloud point, pour point, and cetane number were analyzed in order to compare diesel fuel and ASTM standards. The green chemistry matrices Environmental-factor (*E*-factor) and Process mass intensity (PMI) were also deliberated for the transesterification process.

This is a well-organized thesis based on heterogeneous catalyst synthesis and characterization, physicochemical properties of feedstocks, transesterification reactions for biodiesel production and influence of reaction variables on FAME conversion, kinetics and thermodynamics studies, physicochemical properties of biodiesel have been properly addressed. The summary of the thesis has been listed below:

Chapter 1 includes general introduction to world energy production and consumption statistics. World energy production from various fossil fuels and renewable sources were also described. Global energy crises due to non-renewable nature and hazardous environmental

problems by fossil fuels uses were also discussed. Thus utilization of potential, renewable and sustainable energy resource biodiesel was mentioned in this chapter. Biodiesel is non-toxic,

renewable, environmentally friendly fuel and has similar operational properties with diesel fuel but more inquisition, as well as technological evolvement, is required in this direction. The policies based on production and usage of biofuels in various nations including India encourage to establish them rival of conventional energy sources were deliberated in detail. The objectives of present work have been demarcated as synthesis and application of heterogeneous catalysts for production of biodiesel production using non-edible oil feedstocks as well as effect of various reaction parameters, kinetics and thermodynamic studies, and characterization of biodiesel.

Chapter 2 discuss the literature review. This chapter describes the biodiesel production technologies such as blending, microemulsion, thermal cracking or pyrolysis, and transesterification reaction in detail. The latest literature related to various biodiesel feedstocks categorized as first, second and third generation as well as homogeneous and heterogeneous acid/base catalyst including enzymes been reviewed and presented in the chapter.

In **Chapter 3**, materials and methodology adopted for synthesis and characterization of catalyst namely barium aluminum oxide ($BaAl_2O_4$) and potassium aluminum oxide ($K_2Al_2O_4$), transesterification for biodiesel production and biodiesel characterization have been discussed. The catalysts for the present study were synthesized via co-precipitation and physicochemical methods. Then physicochemical characterization of catalysts was

investigated using various spectroscopic techniques. Furthermore, the catalytic activity of synthesized catalysts in transesterification of the feedstock namely used vegetable oil and kusum oil was assessed through optimization and reusability study. The kinetics and thermodynamic studies along with green chemistry matrix were studied for biodiesel synthesis. The synthesized biodiesel samples were characterized by NMR (^{1}H and ^{13}C), GC-MS and physicochemical properties by using ASTM standards.

Chapter 4 includes the synthesis of heterogeneous base catalysts $BaAl_2O_4$ and $K_2Al_2O_4$ by co-precipitation and physicochemical route and characterization by various spectroscopic techniques. The thermal characterization TGA-DTA reveal the thermal stability of synthesized catalyst samples, $BaAl_2O_4$ and $K_2Al_2O_4$ at 600 °C and 950 °C as calcination temperatures and XRD data well supported the formation of single crystalline phases of catalyst samples. The crystallite size of synthesized catalysts $BaAl_2O_4$ and $K_2Al_2O_4$ were found to be 75.02 nm and 34.19 nm respectively. The particle morphology was confirmed by HRSEM analysis and $BaAl_2O_4$ catalyst had flower shape morphology whereas $K_2Al_2O_4$ has a spherical morphology. The EDX spectra of catalysts confirm the respective composition of synthesized catalyst samples. The surface area and pore diameter were determined by BET-BJH analysis and were found to be 22.3 m^2/g and 2.029 nm for $BaAl_2O_4$ and 5.86 m^2/g and 5.0 nm for $K_2Al_2O_4$ catalyst respectively. Both the catalyst samples were mesoporous in nature. The catalysts $BaAl_2O_4$ and $K_2Al_2O_4$ have high basicity i.e. 4.12 $mmolg^{-1}$ and 4.37 $mmolg^{-1}$ and can be applied as heterogeneous base catalyst in transesterification reaction.

In **chapter 5**, the synthesized heterogeneous base catalyst $BaAl_2O_4$ was successfully utilized for biodiesel production from transesterification of non-edible feedstocks used vegetable oil

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

Chapter 6 describes the application of as-synthesized potassium aluminum oxide K_2Al2O4 as heterogeneous base catalyst for biodiesel production from non-edible feedstocks used

vegetable oil and kusum oil via transesterification reaction. The 98.02% conversion from used vegetable oil was achieved after optimization of reaction parameters such as methanol: oil molar ratio 18:1, catalyst dose of 2.5 wt%, reaction temperature of 65±0.5 °C for 75 min of time and 600 rpm stirring rate whereas 97.56% conversion was obtained at the reaction conditions methanol: oil molar ratio 15:1, catalyst dose of 2.0 wt%, reaction temperature of 65±0.5 °C for 75 min of time and 600 rpm stirring rate from kusum oil using K_2Al2O4 catalyst. The reusability studies revealed that catalyst can be recycled up to five reaction cycles with a significant loss in catalytic activity (>80% conversion at the end of 5^{th} cycle). For the transesterification of used vegetable oil and kusum oil using $K2Al_2O_4$ catalyst, the pseudo-first-order kinetic model was well-suited. The required activation energy and frequency factor (A) were 71.16 kJ/mol and 4.57×10^9 min^{-1} for used vegetable oil feedstock as well as 68.73 kJ/mol and 1.7×10^9 min^{-1} for kusum oil feedstock respectively. The thermodynamic studies of transesterification reaction exhibit enthalpy (ΔH) and entropy (ΔS) values 66.57 kJ mol^{-1} and -0.077 kJ $mol^{-1}K^{-1}$ for used vegetable oil and 64.45 kJ mol^{-1} and -0.084 kJ $mol^{-1}K^{-1}$ for kusum oil. The E- factor and PMI values were calculated to be 2.91 and 3.91 for transesterification of used vegetable oil whereas 3.99 and 4.99 for kusum oil respectively. The synthesized used vegetable oil biodiesel and kusum oil biodiesel were analyzed by NMR (^1H and ^{13}C) spectroscopy and GCMS for compositional analysis. The important fuel characteristics such as acid value, density, kinematic viscosity (40 ºC), calorific value, flash point, fire point, cloud point, pour point, and cetane number was investigated according to ASTM D6751 standard limits and found within the biodiesel standards. Hence, $K_2Al_2O_4$ catalyst for biodiesel production from used vegetable oil and kusum oil can be a fascinating substitute for large scale economical viable biodiesel.

All the results obtained from experimental work has been summarized in Table 7.1. Table shows the use of synthesized heterogeneous catalyst barium aluminum oxide ($BaAl_2O_4$) and potassium aluminum oxide ($K_2Al_2O_4$) in biodiesel production, optimized conditions for transesterification reaction of used vegetable oil and kusum oil, reusability, various kinetics and thermodynamic parameters, and green chemistry metrics. It is concluded that heterogeneous catalyst barium aluminum oxide ($BaAl_2O_4$) and potassium aluminum oxide ($K_2Al_2O_4$) have been found to be very effective in transesterification reaction for biodiesel synthesis from selected feedstocks and give high FAME conversion results. The important fuel properties of synthesized biodiesel from the feedstocks used vegetable oil and kusum oil was found within the ASTM standard limit. Hence the presented results are beneficial for academic and commercial researcher substantially for pilot scale and at large scale biodiesel production.

7.2 Economic analysis

Recently, biodiesel grabbed significant attention as promising alternative fuel for diesel engine because of its environmentally friendly nature and made of renewable biological sources such as vegetable oil and animal feedstocks. A major hurdle in the commercialization of biodiesel is its high manufacturing cost mainly the raw materials cost in comparison to petroleum diesel. The economic assessment of inexpensive feedstocks is key driving force in development of production technology of biodiesel. The cost of biodiesel is mainly decide by the feedstocks cost, plant size, and value of the glycerol by-production. The production of biodiesel from non-edible feedstocks such as kusum, Jatropha, karanja, waste oils and fats in comparison to edible oils is one of the better way to use it efficiently and economically. The

glycerol byproduct significantly affect the net value of the total manufacturing cost. The glycerol value has potential in reduction of production cost of biodiesel by 6-6.5%.

In the present work, direct transesterification was employed for used vegetable oil feedstock and esterification followed by transesterification reaction was performed for kusum oil feedstock. The esterification leads to 96% reduction in free fatty acid content of kusum oil feedstock. The synthesized catalyst

$K_2Al_2O_4$ and $BaAl_2O_4$ were used for transesterification reaction of the both the feedstocks and catalyst reusability up to 5 reaction cycle was consideration in calculation the cost of production of biodiesel. A highly efficient methanol recovery system was assumed with 99% recovery of excess of methanol used in the production process. The fixed capital investments (FCI) of the production process was calculated by using the methodology given by Apostolakou et al. (2009) and cost of used raw materials, chemical reagents as well as utility cost (electricity and heat) were calculated according to current market value. The final purity of synthesized biodiesel was assumed to be 99% after water washing and drying steps. The glycerol credit was also incorporated in the cost of produced biodiesel by assuming >95% of purity after filtration process. Based on the economic analysis of produced process, the unit cost of of biodiesel from kusum oil feedstocks was calculated 1.03-1.12 USD kg^{-1} while the cost of biodiesel produced from used vegetable oil feedstock was estimated to be 0.68-0.75 USD kg^{-1}. The cost of biodiesel produced from used vegetable oil is significantly lower than kusum oil feedstock whereas the cost both the feedstocks accounts 70-80% cost of total production process. The present economic assessment concludes the biodiesel production process via $BaAl_2O_4$ and $K_2Al_2O_4$ catalyzed transesterification reaction of used vegetable oil

and kusum oil feedstocks can be scale-up at industrial setup implementing the extensive simulation based studies.

7.3 Future scope

The opportunities for expanded biodiesel production are bright considering the high demand for petroleum products in both industrialized and developing regions of the world. As a result, the increased awareness of the negative environmental factors associated with petroleum fuels and a desire to move to renewable fuels, biodiesel production is growing significantly worldwide. However, small fraction of the current diesel fuel demands meet the biodiesel production. Therefore, the following are the recommendations for extending this work further.

1. Efforts could be taken to determine the competitiveness of biodiesel as a direct substitute for petroleum diesel on the basis of feedstock availability, the price, and the resulting by-products, combined with government incentives based on economic or environmental issues.

2. Investigation on the industrial applications of vegetable oils, animal fats and microalgal oils as feedstock will not disturb food supply and its price.

3. Implementation of improved conversion technologies for competitive and economically feasible biodiesel production as government incentives are phased out.

Table 7.1 Summary of experimental work

	$BaAl_2O_4$		$K_2Al_2O_4$	
Feedstocks	**Used vegetable oil**	**Kusum oil**	**Used vegetable oil**	**Kusum oil**
Optimized conditions	Methanol: oil mole ratio 21:1; Catalyst dose 4 wt%; Temperature 65±0.5 °C; Reaction time 150 min; Stirring rate 600 rpm.	Methanol: oil molar ratio 21:1; Catalyst dose 3.5 wt%; Temperature 65±0.5 °C; Reaction time 150 min; Stirring rate 600 rpm.	Methanol: oil molar ratio 18:1; Catalyst dose 2.5 wt%; Temperature 65±0.5 °C; Reaction time 75 min; Stirring rate 600 rpm.	Methanol: oil molar ratio 15:1; Catalyst dose 2.0 wt%; Temperature 65±0.5 °C; Reaction time 75 min; Stirring rate 600 rpm.
Conversion	93.45%	93.02%	98.02%	97.56%
Reusability	Five cycles (>75%)	Five cycles (>75%)	Five cycles (>80%)	Five cycles (>80%)
Kinetic parameters	Ea = 60.55 kJ/mol $A = 3.73\times10^{7}$ min^{-1}	Ea = 61.78 kJ/mol $A = 5.97\times10^{7}$ min^{-1}	Ea = 71.16 kJ/mol $A = 4.57\times10^{9}$ min^{-1}	Ea = 68.73 kJ/mol $A = 1.67\times10^{9}$ min^{-1}
Thermo-dynamic parameters	ΔH = 57.873 kJ mol^{-1} ΔS = -0.103 kJ $mol^{-1}K^{-1}$ $\Delta G_{(338K)}$ = 94.66 kJ mol^{-1}	ΔH = 57.44 kJ mol^{-1} ΔS = -0.110 kJ $mol^{-1}K^{-1}$ $\Delta G_{(338K)}$ = 94.70 kJ mol^{-1}	ΔH = 66.57 kJ mol^{-1} ΔS = -0.077 kJ $mol^{-1}K^{-1}$ $\Delta G_{(338K)}$ = 92.59 kJ mol^{-1}	ΔH = 64.45 kJ mol^{-1} ΔS = -0.084 kJ $mol^{-1}K^{-1}$ $\Delta G_{(338K)}$ = 92.84 kJ mol^{-1}
Green chemistry metrics	E- factor = 3.85 PMI = 4.85	E- factor = 4.52 PMI = 5.52	E- factor = 2.91 PMI = 3.91	E- factor = 3.99 PMI = 4.99