CHAPTER 8

Summary of the work and future scope

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8.1 Summary of the work

Extreme accession in industrialization and urbanization is responsible for huge demand of fossil fuels which are depleting day by day. Hence, search for renewable energy resource has come up as a considerable challenge in recent years. Biodiesel has been recognized as an alternative fuel, non-toxic and biodegradable which is capable to replace the diesel fuel. In developing countries such as India, there is crisis of edible oils and the edible oil is imported to accomplish the demand. The search for biodiesel sources should consider the feedstocks that do not require fertile land, do not compete with food crops, help in reduction of greenhouse gases (GHG) emission as well as decrease the dependency on other nations. Present thesis entitled **"Synthesis of biodiesel from non-edible oil feedstocks using mixed metal oxides"** deals with the systematic analyses and includes synthesis, characterization of various mixed metal oxides as heterogeneous catalysts and their application in biodiesel production from waste vegetable oil (WVO) and *Pongamia pinnata* (Karanja) oil. Though, biodiesel is economically viable, more inquisition as well as technological evolvement is required in this direction. To overcome on these problems, policies based on usage of bio fuels derived by various nations encourage biodiesel production, making them rival of conventional energy sources are desired.

Perpetual demand of fuels worldwide has been increasing tremendously and relies partly on fossil fuels. However, concern about global warming due to carbon emissions from burning of fossil fuel has also been increasing. Concentrating on this aspect, researchers have derived biofuels, such as biodiesel based on renewable resources as a possible substitute for fossil fuels. Biodiesel plays a vital role since transportation, agriculture and industrial sectors require huge quantity of diesel, which could be replaced by biodiesel. Biodiesel is non-flammable, non-toxic, and biodegradable as well as has lesser emissions of harmful gases, viz. sulphur dioxide, carbon monoxide and unburnt hydrocarbons in comparison to petroleum diesel fuel. Among all the methods for biodiesel production; transesterification is the best suited method and is mostly used for biodiesel production on commercial scale. It involves 3 mol of alcohol and 1 mol of triglyceride to attain 3 mol of fatty acid alkyl ester and 1 mol of glycerol. Usually, acid or base catalyst has been used in transesterification reaction in which stepwise conversion of triglyceride into diglyceride and mono-glyceride take place. Transesterification reaction of triglycerides in presence of base catalyst follows SN_2 mechanism.

Transesterification process has been carried out in presence of homogeneous or heterogeneous catalysts. The major drawbacks of homogeneous catalyst are that they cannot be regenerated since catalyst is used up in the reaction due to which separation is difficult and it needs expensive equipment. To overwhelm on these demerits of homogeneous catalyst and to diminish environmental along with financial cost of biodiesel production, alternative heterogeneous catalysts are better materials. Heterogeneous catalysts can be easily separated from the product and as a result, final product does not contain impurities of the catalyst. Usage of heterogeneous catalyst is environment friendly process, since it does not require water for separation and ultimately reduces the cost by regeneration and then regenerated catalyst is reused as well. This decrement in cost is adequate for biodiesel to compete with fossil diesel. The main characteristics of these catalysts are that they share basic sites on their surface in case of basic transesterification reaction.

Beta-potassium dizirconate, barium zirconate, calcium aluminate and beta-tricalcium phosphate were synthesized and were used as heterogeneous solid base catalyst. The catalysts were characterized by various techniques. Waste vegetable oil (WVO) and *Pongamia pinnata* (Karanja) oil were collected and physical and chemical properties of both oils were studied according to ASTM standards. Direct transesterification was carried for waste vegetable oil and esterification followed by transesterification was performed for the synthesis of biodiesel from Karanja oil using the catalysts mentioned above. Influence of reaction variables such as catalyst concentration, oil:methanol molar ratio, reaction temperature, reaction time, stirrer speed and catalyst reusability on biodiesel conversion were studied to obtain optimum reaction conditions at each stage. Physical and chemical properties of biodiesel were studied as per ASTM standards.

This is a well-organized thesis based on heterogeneous catalyst synthesis and characterization, physical and chemical properties of feedstocks, transesterification reactions for biodiesel production and influence of reaction variables on FAME conversion, physical and chemical properties of biodiesel have been properly addressed. The summary of the thesis has been presented as follows:

Chapter 1 includes general introduction and deals with the systematic analyses of energy demand, production and consumption statistics of various nations. In addition to this global energy crises as well as GHG emission statistics were also described. Overview of biofuels and the policies in different countries were presented. Especially India's biodiesel policy and production were described in this chapter. Problems based on energy scarcity, biodiesel production were mentioned in this chapter. Though, biodiesel is economically viable, more inquisition as well as technological evolvement is required in this direction. To overcome on these problems, policies based on usage of bio fuels derived by various nations which encourage biodiesel production, making them rival of conventional energy sources are needed. The objectives of the thesis have been demarcated in this chapter. Application of heterogeneous catalysts for production of biodiesel by using non-edible oil feedstocks as well as effect of various reaction parameters and fuel properties of biodiesel were included in the objectives.

Chapter 2 provides a distinctively clear literature review. Various feedstocks for biodiesel production starting from first generation to third generation have been deliberated in this chapter. This chapter also described different homogenous and heterogeneous catalysts previously used for biodiesel production. The literature related to the methods used for production of biodiesel such as blending, micro-emulsion, thermal cracking, supercritical methanol and transesterification were described in detail. Latest literature in the topic has been reviewed and presented in the chapter.

Chapter 3 is methodology which describes materials and methods employed for present work. Methods adopted for the catalyst synthesis, characterization by various techniques such as TGA, XRD, ATR-FTIR, SEM, EDS, BET, BJH, particle size, basicity were briefly discussed. This chapter also mentioned different feedstocks for biodiesel production via transesterification and effect of reaction parameters on FAME conversion. Analytical instruments used for characterization of feedstock and synthesized biodiesel were GC-MS, FT-NMR and ASTM standards.

Chapter 4 includes the synthesis of beta-potassium dizirconate (β-$K_2Zr_2O_5$) by solid state method and its characterization by various techniques. Production of biodiesel from waste vegetable oil and Karanja oil using beta-potassium dizirconate has also been discussed in this chapter. Influence of reaction parameters such as catalyst concentration, molar ratio (oil:methanol), reaction temperature, reaction time, and stirrer speed on FAME conversion were studied. High FAME conversion of 96.61±0.2% was observed for WVO at optimum catalyst concentration (4.0 wt%), oil to methanol molar ratio (1:10), reaction temperature (65 °C), reaction time (120 min) and stirrer speed (600 rpm). FAME conversion of Karanja oil was achieved as 97.24±0.31% at catalyst concentration (3.0 wt%), oil to methanol molar ratio (1:8), reaction temperature (65 °C), reaction time (120 min) and stirrer speed (600 rpm). Synthesized biodiesel was characterized with ^{1}H-NMR and FAME conversion was calculated. Catalyst reusability was performed up to seven runs and a high catalytic activity has been obtained. Physico-chemical properties of synthesized biodiesel were characterized as per ASTM standards.

Chapter 5 explores the synthesis of barium zirconate ($BaZrO_3$) by co-precipitation method and its characterization by several techniques. Production of biodiesel from waste vegetable oil and Karanja oil using barium zirconate has also been deliberated in this chapter. Effect of reaction parameters such as catalyst concentration, molar ratio (oil: methanol), reaction temperature, reaction time, and stirrer speed on FAME conversion was studied. FAME conversion of 96.91±0.42% was obtained for WVO at catalyst concentration of 1.2 wt%, oil to methanol molar ratio 1:27, reaction temperature 65 °C, reaction time 180 min and stirrer speed of 600 rpm. While, FAME conversion of Karanja oil was attained as 97.82±0.5% at catalyst concentration 1.0 wt%, oil to methanol molar ratio 1:27, reaction temperature 65 °C, reaction time 180 min and stirrer speed 600 rpm. Synthesized biodiesel was characterized through ^{1}H-NMR and FAME conversion was calculated. Catalyst reusability was performed up to nine runs. Physico-chemical properties of synthesized biodiesel were studied and observed within ASTM standards range.

Chapter 6 comprises the synthesis of calcium aluminate ($Ca_2Al_2O_5$) by solid state method and characterized by different techniques. Biodiesel production from waste vegetable oil and Karanja oil using calcium aluminate has also been presented in this chapter. Consequence of reaction parameters such as catalyst concentration, molar ratio (oil:methanol), reaction temperature, reaction time, and stirrer speed on FAME conversion were discussed. FAME conversion of 95.24±0.1% was attained by using WVO at catalyst concentration of 3.0 wt%, oil to methanol molar ratio 1:21, reaction temperature 65 °C, reaction time 150 min and stirrer speed of 700 rpm. Whereas, FAME conversion of Karanja oil was achieved 97.05±0.21% at 2.5 wt% catalyst, 1:18 oil: methanol molar ratio, 65 ºC reaction temperature, 150 min time of reaction and 700 rpm of stirring speed. Synthesized biodiesel was characterized by ^{1}H-NMR for FAME conversion calculation. Catalyst reusability was studied up to seven runs. Physico-chemical properties of synthesized biodiesel were determined and were found to be within ASTM standards.

Chapter 7 presents biodiesel production from waste vegetable oil and Karanja oil by using beta-tricalcium phosphate as a heterogeneous base catalyst. Beta-tricalcium phosphate was obtained via calcination of waste guinea fowl bone and characterized by various techniques. Effect of reaction parameters such as catalyst concentration, molar ratio (oil:methanol), reaction temperature, reaction time, and stirrer speed on FAME conversion were studied. Maximum conversion of 93.02±0.6% was obtained for waste vegetable oil by using 4.0 wt% catalytic concentration, 1:21 oil: methanol molar ratio, 65 ºC reaction temperature, 180 min time of reaction and 700 rpm of stirring speed. On the other hand Karanja oil shows FAME conversion of 94.84±0.51% at 4.0 wt% catalyst, 1:18 oil:methanol molar ratio, 65 ºC reaction temperature, 180 min of reaction time and 700 rpm of stirring speed. Synthesized biodiesel was characterized by ^{1}H-NMR to obtain FAME conversion. Catalyst reusability was found satisfactory up to seven runs. Physico-chemical properties of synthesized biodiesel were studied and obtained as per ASTM standards.

All the data obtained from experimental work has been summarized in Table 8.1. Table shows the heterogeneous catalyst (beta-potassium dizirconate, barium zirconate, calcium aluminate and beta-tricalcium phosphate) synthesis techniques and optimized conditions for transesterification reaction of WVO and Karanja oil.

On the basis of outcomes of this thesis, it can be concluded that the different heterogeneous catalysts (beta-potassium dizirconate, barium zirconate, calcium aluminate and beta-tricalcium phosphate) have been found to be effective for transesterification reactions. In addition to this, it has been observed that selected feedstocks Waste vegetable oil (WVO) and *Pongamia pinnata* (Karanja) oil show high FAME conversion. Most of the fuel properties of the biodiesel from selected feedstock confirms to the ASTM D6751standards. Hence, the data obtained has academic as well as industrial importance for pilot scale and at large scale biodiesel production.

8.2 Future scope

The economic and environmental inducements for developing and executing biofuels are desirable. In the coming years, biofuels are likely to be expected to come up as big industry. But, any single biofuel will not resolve complete energy problems. The production of some biofuels is still energy intensive and in addition to this, biofuel industries are associated with too many problems. As a recommendation, policies by different nations are essential to encourage the production of biodiesel and associated Governmental efforts are also requisite to meet these challenges.

Though, biodiesel could be an alternative fuel and good fuel additive, but this may not eliminate the world's energy problem yet. The present research work displays the feasibility of biodiesel derived from waste vegetable oil and Karanja oil by using heterogeneous base catalyst. In addition to this, the enhancement in quality of biodiesel should be performed in the future to promote usage of biodiesel in diesel engine. Consequently, further investigations on additional fuel properties and wear analysis of biodiesel fuelled engine are also obligatory. The outlook of extensive use of biodiesel appears optimistic at this stage: but then if the complete potential of this selection is to be employed sufficiently, vibrant strategies as well as policies need to be developed and placed for ensuring quick results. The partial substitution of diesel fuel with biodiesel will lessen the stress on remaining diesel oil resources and reduction in import of crude diesel. Furthermore, it is anticipated that the cost of biodiesel will be lesser than the conventional diesel fuel in nearby future caused by linear growth in cost of conventional diesel fuel with the increment in its demand and restricted supply.

8.3 Future of Biodiesel in India

As the fossil fuels are getting exhausted, prominence should be given to the renewable energy sources such as sustainable biofuel crops. As such, biodiesel seems to be one of the resources that have the adequate potential to contribute in India's energy security. In that case, research and development based on sustainable agricultural management, biodiesel production as well as environmental and social effect assessment for biodiesel utilization is essential. India has great potential for biodiesel production. In India, wild crops cultivated in wastelands can act as source of biodiesel production and according to Economic Survey of Government of India, around 175 million hectare land area has been categorized as degraded and waste land out of the cultivated land area. Consequently, based on demand, India can certainly knock its potential and produce biodiesel at industrial scale. All non-conventional energy sources and agriculture shows prominent role in this program. In addition to this, research institutes and industries can also play significant role for the clear supply chain mechanism and success with consumption plan is essential at national level resembling elsewhere across the world. Research organizations should be promoted to carry out life cycle analysis application in biodiesel production.