ABSTRACT

In light of the constantly increasing crude oil prices and growing environmental concerns, the replacement of fossil and petroleum fuels by renewable alternatives is becoming more and more important. While other renewable sources of energy, such as the sun and wind, can contribute to electricity capacity, in reality the vast majority of motor vehicles (transportation sector and distribution networks) require liquid fuel and will do so for the foreseeable future and therefore any attempts to sustainably power the world's millions of motor vehicles must include biofuels. Nonetheless, the main drawbacks preventing the large scale commercialization of these fuels are their higher production costs due to: (i) feedstock issues (expensive, food vs. fuel issues) and (ii) involvement of complex multi step synthesis and purification steps.

About 90% of all chemical manufacturing processes require the use of catalysts. Production of biofuels is no exception, as processing of biomass components into fuels and platform chemicals involve large number high energetic chemical and biochemical reactions. The present work focuses on the catalysis aspect of biofuel production. Next to feedstock, catalyst plays the most vital role in any industrial process as it directly affects production route and product cost, quality and yield. It is well accepted fact that uses of heterogeneous catalysts offer several process advantages over the homogeneous counterparts which include easy catalyst separation from product and reusability. However, most of the conventional heterogeneous catalysts (alumina, zeolites, amberlyst, sulfated zirconia etc) have shown poor performance in connection to applications in biofuel production. The main drawbacks are (i) poor activity (narrow pore structures restricting the interaction with large-size biomass building-blocks), (ii) high operational cost associated to the use of such materials and (iii) stability issues (leaching, thermal stability etc). Recently, attention has been given to biomass as renewable catalyst precursors in order to make the synthesis of heterogeneous catalyst “green” and “cost effective”. Within this concept, the carbon based catalysts and bio based CaO were reported, CaO prepared from Ca rich waste sources such as mollusk, snail, shrimp and egg shells have been successfully applied as catalysts for biodiesel production. Similarly, carbon based heterogeneous catalysts have been prepared from a variety of biomass sources such as starch, cellulose, glucose and
agro-industrial wastes. They are considered as ideal catalysts due to desirable features such as low material cost, chemical inertness, high surface area and thermal stability. Such catalysts were generally prepared in two steps: (i) carbonization followed by (ii) surface modification or functionalization with acids or bases.

In view of the above consideration, the present investigation was undertaken with the aim of developing heterogeneous catalysts from renewable sources using locally available bio-wastes. The prepared catalysts were examined for their catalytic activities in biofuel productions, which could eliminate the use of corrosive chemicals such as H₂SO₄, NaOH, KOH etc. thus, make the process environmentally benign, cost effective and greener one.

The work embedded in the thesis is arranged in seven chapters. The theme of the thesis is outlined in the introduction chapter (Chapter 1). The role of catalyst and the need for renewable source based ‘green’ heterogeneous catalysts in reference to biofuel production are discussed. While, in Chapter 2 the detailed discussion of various analytical methods used for characterization of the catalytic materials are presented.

In Chapter 3, the utilization of post harvest crop residues of Vigna radiata plant, Musa balbisiana pseudo stem for preparing a highly basic metal/mixed oxide catalyst is demonstrated. The materials were composed mainly of potassium and calcium in the form of oxides and carbonates, responsible for the high alkalinity and catalytic activity of such materials. The chapter also describes their application as a heterogeneous substitute to NaOH in biodiesel production. The Vigna radiata derived catalytic materials exhibited highest activity, FAME yield of 92% with 9:1 methanol to oil molar ratio in 8 h reaction time. Although such catalysts are cheap and could substantially reduce the biodiesel production costs, but they have disadvantages related to the reusability and requirement of a large catalyst amount for satisfactory FAME yield. Nonetheless, all the major fuel properties of biodiesel produced over such catalyst confer to the existing norms of biodiesel fuel.

In Chapter 4, the preparation, characterization and catalytic applications (in transesterification of vegetable oils) of a highly robust and reusable bio based CaO supported active carbon (ACaO) catalyst from Turbonilla striatula shells is demonstrated. Under optimized reaction conditions of 120 °C, 40:1 methanol to oil ratio, 11 wt% catalyst and 7 h of reaction time, FAME yield upto 96% could be reached. Although the catalyst
was less active than native CaO, ACaO was highly stable, reusable and maintained its initial activity up to five cycles under the investigated conditions. Consequently the reusability issues of the catalysts discussed in chapter 3 are successfully addressed by employing ACaO catalyst. The high stability of ACaO is attributed to the oxygen-containing groups (–COOH, –OH, lactones etc) present on the surface of active carbon which probably act as anchoring sites for the CaO molecules, thus preventing them from leaching out into the reaction mixture.

In Chapter 5, the preparation, characterization and catalytic applications (biodiesel production by simultaneous esterification and transesterification of acidic oils) of highly porous sulfonated carbon (Brønsted solid acid) catalysts from de-oiled waste cake (DOWC) residues generated in biodiesel production has been presented. The DOWC based catalytic materials exhibited high acid density, porosity, specific surface area, thermal stability and good reusability and outperformed homogeneous H₂SO₄ under similar conditions. The catalytic activity was found to be dependent on the reaction conditions and initial free fatty acid (FFA) content in oil. Higher FFA content leads to improved mutual solubility of the oil and methanol resulting in increased transesterification activity. Highest FAME yield of 71% was obtained from oil containing 43 wt% FFA in 8 h under mild conditions of 80 °C, 5 wt% catalyst and 43:1 methanol to oil molar ratio.

In Chapter 6, the effects of carbon source and preparation method on the structure, acidity and catalytic activity of DOWC based sulfonated carbons are described. The chapter also discusses the effect of catalyst structure on activity and selectivity through simultaneous and comparative evaluation of activities in oleic acid esterification and cellulose saccharification, two opposite but equally imperative reaction involved in biofuel synthesis. In the current work, preparation method strongly influenced the structure and surface properties of DOWC based sulfonated carbons, and hence their catalytic properties. In general, catalysts with a higher porosity, high surface area and acid site density always favor high activity. Use of chemical activation was necessary to facilitate porosity and functional group development, in order to enhance the catalytic performance. Structurally, these carbons are more complicated than previously reported sulfonated carbons and contain phosphates, nitrogen compounds in addition to –SO₃H, –COOH, –OH and lactones, typically present in carbohydrate, sugar or resin based sulfonated carbons.
Conventional H₂SO₄ sulfonation fails to produce catalysts with a high –SO₃H density and porosity simultaneously. Radical sulfonation on the other hand was found to be more effective and produced catalysts with tenfold higher –SO₃H densities than H₂SO₄ sulfonation even from graphitic and ordered AC. Carbon source and amount of sulfonating agent influenced efficiency of radical sulfonation, hence –SO₃H density and catalytic activity. A high density of –SO₃H groups resulted in higher esterification rates (FFA conversion up to 96% in 10 h under mild conditions of 65 °C, 3 wt% catalyst and 30:1 methanol to oil molar ratio) while a higher density of surface functional groups –COOH, –OH favored high saccharification activity as well as selectivity towards sugars (sugar yield 50.5 mol C% at 150 °C). Thus, the Mesua ferrea Linn. and Pongamia pinnata DOWC based catalysts with higher –SO₃H density and surface area were found to be more active in esterification of oleic acid whereas the Jatropha curcas cake based catalyst showed better activity and sugar selectivity in cellulose saccharification.

In Chapter 7, the main findings of work embedded in the thesis have been summarized and the prospective scopes for future work/development are discussed.