Abstract

The world has relied heavily on non renewable crude oil for more than a century. In recent years the rapid growth in industrialization and world population has increased the demand for energy. To date the fossil fuels accounts for 80 % of the world energy needs; out of which nearly 57% is utilized in transportation sector. At present, there is a big gap between world energy requirement and energy demand. Therefore, the world is facing twin problem of depleting fossil fuel reserves and increasing environmental degradation because of fossil fuel utilization. This depletion in oil reserves has resulted into decrease in world oil supply and increase in petroleum prices. The unstable increasing petroleum prices, limited fossil fuel reserves and increasing concerns about environment have escalated the search for alternative energy sources especially in the transportation sector. Because of these problems, in recent years, liquid biofuels such as biodiesel have become very attractive because of their environmental benefits.

Chemically biodiesel is defined as the mixture of methyl esters with long chain fatty acids and is typically made from nontoxic, biological resources such as vegetable oils, animal fats and waste cooking oils. Compared to conventional diesel fuel, biodiesel is technically and economically more competitive because of its renewability, liquid nature-portability, biodegradability, low emission profiles, high flashpoint and lower sulfur and aromatic content. Biodiesel has properties very similar to diesel fuels. The biodiesel blends up to B20 could be used in all the diesel equipments without any engine modifications. Biodiesel is produced by transesterification of triglycerides with alcohol in the presence of a catalyst. At present the most popular catalysts used on industrial basis for commercial biodiesel production are homogeneous base catalysts such as KOH or NaOH. The advantage of with alkali catalyst is that very high conversion is obtained under mild conditions and reaction in just 1 h. Moreover the reaction is 4000 times faster than the same amount of homogeneous acidic catalysts. However, transesterification in the presence of base catalysts has many disadvantages. The primary problem is the separation of catalyst from final reaction product, which is very difficult. In order to remove the catalyst from the product, large amount of waste water is generated. Moreover even a little amount of moisture can initiate oil hydrolysis to form free fatty acids and glycerol. The FFA then reacts with base catalyst to form soap, which is again an unwanted side-reaction. These limiting factors of homogeneous catalysts can be overcome by using solid catalysts instead of homogeneous catalysts.
Utilization of heterogeneous catalysts offers several process advantages which includes easy catalyst separation from final product, reusability and regenerability of the catalyst. In addition unlike homogeneous catalysts, these catalysts are less sensitive to water which makes them even more attractive for biodiesel production from a variety of feedstocks. Large number of heterogeneous catalysts such as metal oxides, alkaline earth metal oxides, transition metal oxides, mixed metal oxides, ion exchange resins, sulfated oxides, carbon based heterogeneous catalysts, enzyme supported heterogeneous catalyst have been reported in literatures for biodiesel production.

Among the reported heterogeneous catalysts vast study has been done in the field of different metal oxides for biodiesel production. Among the different metal oxides reported, the most popular metal oxide was found to be calcium oxide which was due to its easy availability, cheapness, low toxicity and high catalytic activity. Recently researchers have introduced a novel method of preparing CaO from waste mollusk and egg shells and used it for biodiesel production. However, the properties of CaO prepared from these shells were not reported to be altered for better catalytic activity in transesterification of vegetable oil.

Based on these findings we have undertaken the study for the preparation of solid catalyst from the waste shells of Turbonilla striatula. In our investigation we observed that the waste shells of Turbonilla striatula acted as an excellent raw material for the preparation of CaO because it was mainly composed of calcium carbonate. The CaO was prepared by calcining the raw material at temperature above 800 °C for 4 h. Therefore the catalyst preparation route was only one step method and less time consuming. In this study the shells calcined at 900 °C was considered to be the best catalyst as it exhibited maximum activity.

The catalyst calcined at 900 °C was employed for transesterification of mustard oil. It was observed that maximum yield of 93.3% was obtained with 9:1 methanol to oil ratio, 3.0wt% catalyst amount at 65±5 °C. The same catalyst was then used in the transesterification of waste cooking oil (WCO). It was observed that maximum conversion of 98% was achieved in 8 h with 12:1 methanol to oil ratio and 5 wt% catalyst amounts.

In order to increase the catalytic activity of the parent catalyst, it was doped with Li from (0.5-1.5) wt%. The results indicated that the basicity of the catalyst increased with increasing amount of Li loading and which in turn influenced the catalytic activity. It was observed that very high conversion of 98% was obtained with 1 wt% Li doped waste shell derived CaO in 4 h with 9:1
methanol to oil ratio and 2.0 wt% catalyst amounts. Similar to this investigation, the parent catalyst was also doped with Ba, which has a very high basicity. Doping with Ba resulted in significant enhancement of the catalyst basicity. It was observed that the Ba doped waste shell derived CaO were highly basic in nature. Complete conversions were obtained with 1% Ba doped CaO catalyst in only 3 h with 6:1 methanol to oil ratio and 1.0 wt% catalyst amount. This excellent conversion is also comparable with the conversions obtained with conventional catalysts such as NaOH and KOH.