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Comparison of Homogeneous Base Catalysts and Heterogeneous Base Catalysts for Biodiesel Transesterification of Waste Cooking Oil

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Abstract: This paper deals with the comparison of homogeneous base catalyst and heterogeneous base catalyst for the transesterification of waste cooking oil. The waste cooking oil was procured from university canteen. The homogeneous catalysts used were sodium hydroxide and potassium hydroxide and heterogeneous catalyst used were calcium hydroxide and magnesium hydroxide. It was found that homogeneous catalyst gave better yield than heterogeneous catalyst but would result in additional production cost for water washing. For every 100 ml of biodiesel produced 15 ml of water washing had to be done to discharge a neutral effluent from water washing. Heterogeneous catalyst gave a slightly less yield but there was no need for water washing steps. The catalyst could be recycled for eight times for the same operation .Hence it can be concluded that heterogeneous catalyst are better catalyst for transesterification reaction for waste cooking oil to yield an environmental friendly biodiesel.
Keywords: transesterification, biodiesel, base catalyst, homogeneous, heterogeneous.

Introduction

Sodium hydroxide and potassium hydroxide are the most commonly used base homogeneous catalysts for transesterification reactions for producing biodiesel. Traditional homogeneous catalysts (basic or acidic) possess advantages including high activity (complete conversion within 1 h) and mild reaction conditions (from 40 to 65°C and atmospheric pressure). However, the use of homogeneous catalysts leads to soap production[1]. Heterogeneous catalysts could improve the synthesis methods by eliminating the neutralization salts in the glycerol and therefore the number of separation steps can be reduced[2]. Also, heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed-bed reactor, leading to safer, cheaper and more environment-friendly operation[3]. Biodiesel production using heterogeneous catalysts has been carried out at industrial level and in such a process the employed catalyst has been reported to be a mixed oxide of zinc and aluminium[4]. Various studies have been carried out using acid catalysts[5-8]. The heterogeneous catalysts do not leave neutralization salts in the glycerol, and are plausible to be retained in the reactor by filtration[9-17]. The most commonly studied heterogeneous basic catalysts are alkaline metal carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and other oxides as ZnO [3,18-23] .Waste cooking oil was selected as the fatty acid resource for biodiesel. The use of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production [24],since the feedstock costs constitutes approximately 70-95% of the overall cost of biodiesel production [25]. As large amounts of waste cooking oils are illegally dumped into rivers and landfills, causing environmental pollution [26] the use of waste cooking oil to produce biodiesel as petrodiesel substitute offers significant advantages because of the reduction in environmental pollution[27].

Experimental Methodology

Materials

Waste cooking oil was procured from university canteen. Hydrochloric acid, methanol, sodium hydroxide, potassium hydroxide, magnesium carbonate and calcium carbonate used were of analytical grade.

Methodology

The waste cooking oil was appalam fried oil which was black in colour. The impurities in the oil were filtered off using muslin cloth. The used oil was having free fatty acid content more than 12%. In order to reduce the free fatty acid content, an acid pre-treatment was given by adding hydrochloric acid and methanol which resulted in the form of separate layers of esters, methanol, acid and water. The ester layer was transesterified using two homogeneous base and two heterogeneous base catalyst to find suitable catalyst for transesterification. The two homogeneous catalyst used were sodium hydroxide and potassium hydroxide. The two heterogeneous base catalysts used were magnesium carbonate and calcium carbonate. The waste cooking oil was transesterified according to procedure discussed in literature[28].All the experiments were done in triplicate for data reproducibility. The product was obtained as two layers comprising of biodiesel and glycerol. The two layers were separated, washed and dried according to procedure discussed in literature [29]. Water used for washing was tested for neutral pH for harmless disposal to the environment. The heterogeneous catalysts were reused for finding the reusability of catalyst.

Results and Discussion

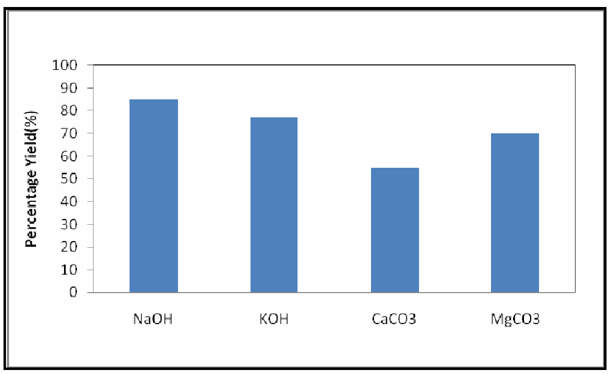

Figure 1. Biodiesel Yield percentage for Homogeneous and Heterogeneous base catalysts

From figure 1, it can be inferred that homogeneous catalyst gives the best yield. But, nevertheless, magnesium hydroxide which is a heterogeneous catalyst yield is also comparable to sodium hydroxide which is a homogeneous catalyst. Water washing is not needed for heterogeneous catalyst as the pH was 7.8. For homogeneous catalyst, three or four washing were done to get a neutral pH value which is indicated by table 1. Biodiesel obtained using sodium hydroxide was given four water washing and biodiesel obtained using potassium hydroxide required three water washing. The wash water for both catalysts for the first wash indicated it to be very acidic which will harm the environment. For every 100 ml of biodiesel produced 15 ml of water washing had to be done to discharge a neutral effluent from water washing.

Table 1. Wash water pH values for Homogeneous and Heterogeneous base catalysts

Catalyst wash water pH value	1^{st} wash	2^{nd} wash	3^{rd} wash	4^{th} wash
NaOH	9.22	8.43	7.61	7.52
KOH	9.14	8.25	7.40	-
$CaCO_3$	7.18	-	-	-
$MgCO_3$	7.75	7.34	-	-

From table 1, it can be inferred that homogeneous catalyst requires extensive washing because of soap formation whereas heterogeneous catalyst does not require water washing. This makes the process cost effective. Reusability is the recycling of catalyst without loss in efficiency. Homogeneous catalyst cannot be recovered since it becomes miscible with the reaction mixture. Heterogeneous catalyst can be recovered by filtering and drying the catalyst. The recovered heterogeneous catalysts were employed for tranesterification of waste cooking oil to yield biodiesel. From figure 2, it can be inferred that magnesium carbonate could be reused upto five times whereas calcium carbonate could be used upto nine times. This makes the process, economical as the catalyst could be reused. This is a major advantage of using heterogeneous catalyst.

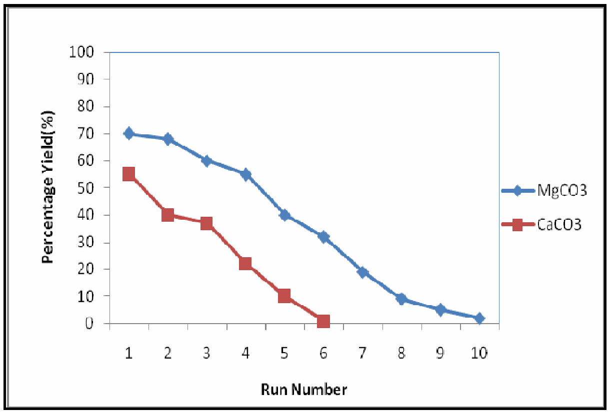

Figure 2. Reusability of heterogeneous base catalyst.

Conclusion

The research work indicates that the yield using homogeneous catalyst is higher than heterogeneous base catalysts. Homogeneous catalysts have the disadvantage of soap formation which increases the overall production cost. There is no recovery of catalyst and it requires large amount of catalyst for the production of biofuel in comparison to heterogeneous catalyst. However, heterogeneous base catalysts have the advantage of recycling and safe effluent disposal. Hence, it can be concluded that the heterogeneous base catalysts give a better eco friendly biofuel than homogeneous base catalysts.

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