Production of Biodiesel from Waste Cooking Oil using Indigenous Copper Impregnated Graphene Oxide Supported Catalyst

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Abstract:
With increasing the energy demand and rapid depletion of non-renewable energy resources the search of new and renewable energy is gaining more and more interest in recent years. In this study we have focused on production of biodiesel using heterogeneous catalyst. Waste cooking oil was taken as the feed stock and Cu impregnated graphene oxide (GO) was taken as the heterogeneous catalyst. Synthesized GO was characterized by field emission scanning electron microscope (FESEM). Different process parameters, such as catalyst dose, Cu-impregnation, time, temperature, and methanol to oil (MO) ratio has been studied. The maximum yield of biodiesel was obtained at 3% catalyst dose along with 5% Cu impregnation. The optimum value of reaction time was 45 min and temperature was found to be 55°C.

Keywords: Biodiesel, Graphene Oxide (GO), Transesterification, Waste cooking oil, Yield.

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1.   Introduction

To reduce the dependency of fossil fuel for energy consumption, environmental pollution and global warming associated with their burning leads to the search for viable alternative fuels to meet the current world energy demand. Therefore, the replacement of petroleum fuel as source of energy by biofuels is urgent. In this regard, biodiesel has gained considerable attention as a good alternative fuel to petroleum-based diesel because it is non-toxic, renewable, clean burning fuel compared to petroleum diesel. In addition, the favorable properties of biodiesel such as low sulphur content, high flash point, and high cetane number have made it suitable as potential source of renewable energy [1, 2]. Among the various renewable alternatives, biodiesel can be used directly in diesel engine without any modification [3, 4]. Generally there are four major types of feedstock available for biodiesel production including oil seed (vegetable oil), animal fats, algae and different low quality material such as waste cooking oil [5, 6].

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature. They have practically no sulfur content, no storage difficulty and excellent lubrication properties. Currently, more than 95% of world's biodiesel is produced from vegetable oils (edible oils) like sunflower oil, soybean oil, palm oil, rapeseed oil, canola oil, cotton seed oil etc. which are easily available on large scale from agricultural industry. However, continuous and excess use of vegetable oils leads to food versus fuel crisis. The use of edible oil to produce biodiesel in India is not feasible because of big gap in its demand and supply [7- 9].

But considering the cost effectiveness, waste utilization and environmental aspects, waste cooking oil can be used as appropriate raw material for biodiesel production. As the viscosity of waste cooking oil is much higher than diesel fuel, there is the need for reduction in viscosity for use as fuel in IC engines. The commonly employed methods to reduce viscosity of oil are blending with diesel, emulsification, pyrolysis, cracking and transesterification. Among these, transesterification of vegetable oils appears to be more suitable because the by-product glycerol has commercial value. Transesterification process is the use of oil and alcohol (e.g. methanol, ethanol) in presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break long and branched chain triglyceride molecules of raw oil chemically into methyl or ethyl esters of oil (biodiesel), with glycerol as a byproduct. Transesterification of vegetable oils can be performed using both homogeneous (acid or base) [10] and heterogeneous (acid, base, and enzymatic) catalysts [11-14].

For industrial biodiesel production, homogeneous basic catalysts such as NaOH, KOH, or CH$_3$ONa are usually employed in transesterification process. However, these catalysts, although effective, are shown to be sensitive to water and FFA present in feedstock due to formation of unwanted soap by-products, which makes product separation difficult and also reduces catalyst performance. As a result, a tedious and environmental unfriendly water washing process is required to remove the catalyst from final product biodiesel [15]. To avoid this problem, heterogeneous catalysis approach is expected to replace homogeneous one owing to the ease of catalyst separation, less downstream process and environmental benign, thereby making the transesterification process practical from both commercial and environmental point of view. Up to now, variety heterogeneous basic catalysts have been investigated, including alkali earth metal oxides, supported alkali earth metals, rare metal oxides, zeolites, hydrotalcites and anion exchanged resins which exhibit high catalytic activity [16 - 21]. Among heterogeneous bases, calcium-based catalysts appear to be a promising catalyst for transesterification reaction due to their high activity, reusability and low cost [22, 23]. Heterogeneous acid catalysts are capable of esterifying fatty acids in vegetable oils. Many acid heterogeneous catalysts have been reported such as sulphated metal oxide, heteropolyacid, sulphonated amorphous carbon, and acid ion exchange resin [24 - 27]. However, heterogeneous acid catalysts generally exhibit weak catalytic activity, require high reaction temperatures and long reaction times [28].

Few researchers have worked on activated carbon as catalyst support such as palm shell derived carbon, bio-char based solid acid catalyst [29, 30], sulphonated carbon nanotubes were also reported to be efficient catalyst for biodiesel production at very high temperatures [31, 32]. But the literature regarding biodiesel production over graphene based catalyst is scare. Recently few authors reported the research works on production of biodiesel from vegetable oils and waste cooking oil using various graphene oxide supported metal oxide composite heterogeneous catalysts [33 - 37]. Till now, no report has been found on Cu impregnated GO catalyst used for transesterification of waste cooking oil to produce biodiesel.

The aim of this study is to synthesize Cu impregnated graphene oxide catalyst and to investigate the effect of catalyst loading, and process parameters on yield of biodiesel.

2.   Experimental
2.1   Materials
Sulphuric acid (H$_2$SO$_4$) was taken from Fischer Scientific, Mumbai, India. Potassium permanganate (KMnO$_4$) was obtained from High Media Laboratories Pvt. Ltd, Mumbai, India. Sodium nitrate (NaNO$_3$) was supplied by Merck Life Science Pvt. Ltd. H$_2$O$_2$ was collected from Qualigens Fine Chemicals, Mumbai, India. Cupric sulphate extra pure (CuSO$_4$, 5 H$_2$O) was bought from S D Fine-Chem Limited, Mumbai, India. All the chemicals were used as it was received without any further purification.

2.2   Methods
Graphene oxide (GO) was synthesized from graphite powder using modified Hammer's method. To prepare GO, 1.5 gm of pure graphite powder and 0.75 gm of NaNO$_3$ was mixed with 34.5 ml of sulphuric acid with continuous stirring. The mixture was kept in an ice bath, then 4.5 g KMnO$_4$ was added gradually and stirred slowly for 30 mins to avoid the sudden rise in temperature to 20-35° C. Then the reaction mixture was diluted by adding 69 ml double distilled water under heating condition to maintain the reaction temperature at 98 ^{o} C. After that, the mixture was cooled in diluted condition using approximately 200 ml water with 1.5 ml H$_2$O$_2$ and stirred continuously at room temperature. Then the solution was kept for settling and after decantation of water, finally the sample was filtered. Then the filtered solid was dried for overnight in oven. The morphological and structural characterizations of the synthesized graphene oxide were done by field emission scanning electron microscope (FESEM) (ZEISS).

3.   Results and discussion
3.1   Characterization of graphene by FESEM
Field emission scanning electron microscopic (FESEM) characterization was done for the morphological and structural studies of the synthesized graphene oxide. Fig. 1a present the FESEM image of the graphene oxide (GO).

The images show that the GO sheets are smooth and are closely associated with each other. Fig. 1b is the more magnified image of the GO.
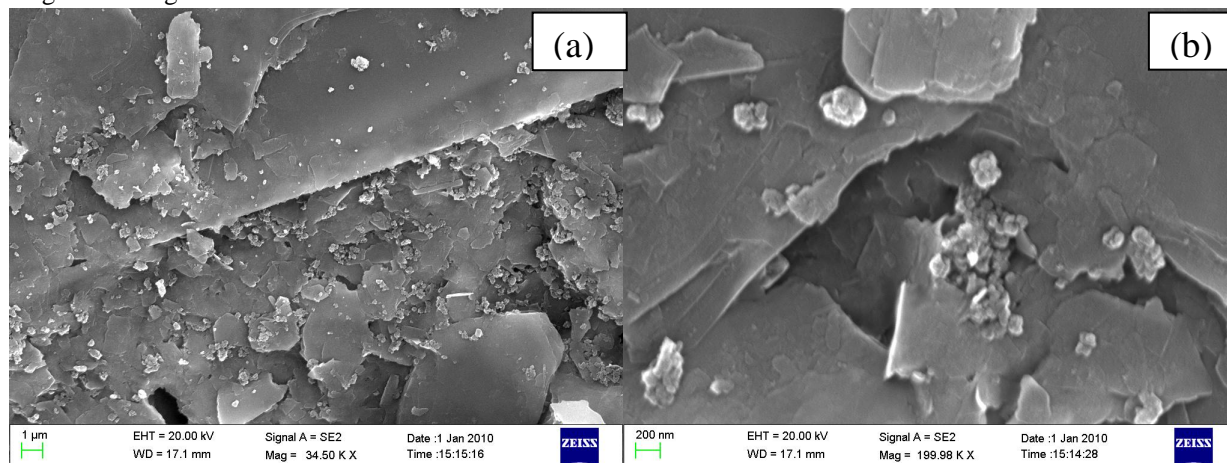

Fig. 1. (a, b) FESEM images of the synthesized Graphene oxide

3.2   Transesterification of waste cooking oil with methanol

Transesterification reaction was carried out under different parametric conditions, such as catalyst dose, copper impregnation, time, temperature, and methanol to oil ratio. In the catalyst dose study reaction was carried out under different concentration (1 to 5%) of graphene (Fig. 2). At 1% graphene concentration the yield of biodiesel was obtained 28%. Then with increasing the graphene concentration there was increase in biodiesel yield up to 3% graphene. After 3% there is decrease in biodiesel yield with increasing concentration of graphene. Maximum product yield was obtained 50% at 3% graphene. Increasing yield with increasing graphene concentration is because of the higher active sites of the heterogeneous catalyst, which favours the transesterification reaction. Decreasing biodiesel yield at higher graphene concentration might be because of increased viscosity in the reaction mixture, which resists the mass transfer in the reaction mixture [38]. However, 3% graphene concentration was chosen as the optimum catalyst dose for further parameter studies.
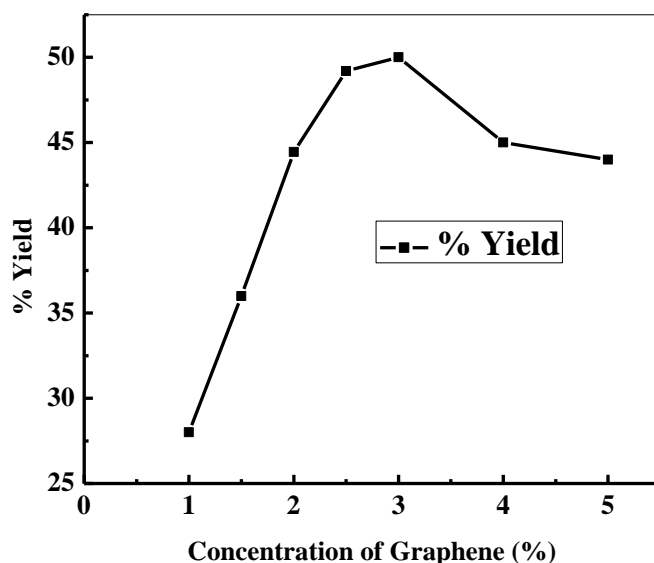

Fig. 2. Effect of Catalyst (graphene) dose on yield of biodiesel produced

Effect of copper impregnation on the transesterification reaction was studied to evaluate the optimum value of Cu required for getting maximum conversion of waste cooking oil to biodiesel. For this study catalyst dose was maintained at 3%. Copper concentration was varied from 0.5 to 10% as shown in Fig. 3. At 0.5% Cu concentration the yield was obtained 51.6%, which clearly indicates the effect of Cu on the catalytic properties of graphene. It was observed that the yield increased further with increasing concentration Cu till 5%, after that there is sharp declined in the yield value with further increased in Cu concentration. Declining in yield value at higher Cu concentration might be because of destroying the lattice structure of the graphene, which is a common problem at higher impregnation concentration due to the serious lattice mismatching and the loss of stoichiometry in the base material. This lattice mismatching further enhances quantum tunnelling and structural instability in the material [39]. Maximum product yield was obtained 56% at 5% Cu impregnation.
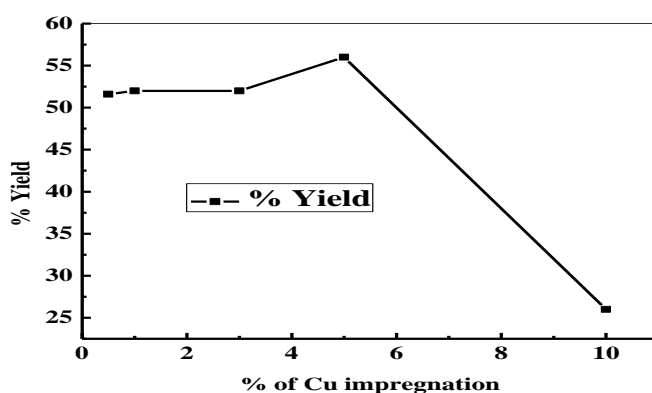

Fig. 3. Effect of Cu impregnation on yield of biodiesel produced

To study the dependence of the conversion of waste cooking oil to biodiesel was tested in different time duration. The reaction was conducted for 15, 30, 45, and 60 min. The obtained product yield was plotted against different time interval in Fig. 4. It has been seen that the yield value increases with increasing the time up and the maximum yield was achieved after 45 min. So, 45 min reaction time can be taken as the optimum value for this transesterification reaction.
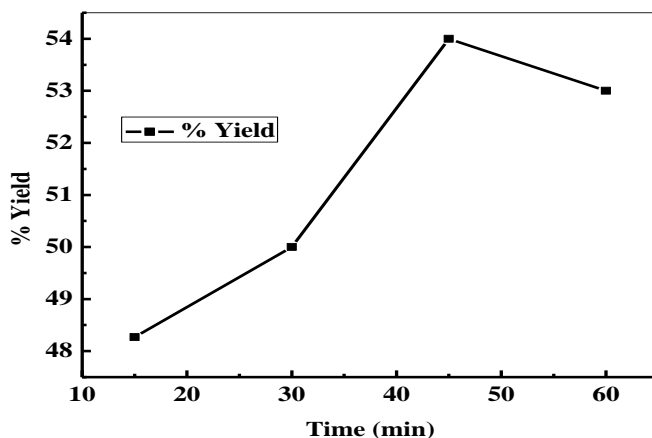

Fig. 4. Effect of time on yield of biodiesel produced

Optimization of reaction temperature of the transesterification was done by carrying out the reaction at different temperature such as 35, 40, 50, 55, and 70°C. The results are shown in Fig. 5. The yield was obtained 38.75% at 35°C then there is increase in yield with increasing the temperature up to 55°C. The maximum yield was obtained 54% at 55°C. Beyond 55°C there is sharp decrease in the product yield of the biodiesel. The sharp decrease in product yield at higher temperature is because of the lower conversion of waste cooking oil to biodiesel due to deficiency of the methanol in the reaction mixture. The deficiency of the methanol in reaction mixture is because of the vaporization of methanol at higher temperature. So, 55°C can be taken as the optimum value of temperature in the transesterification reaction.
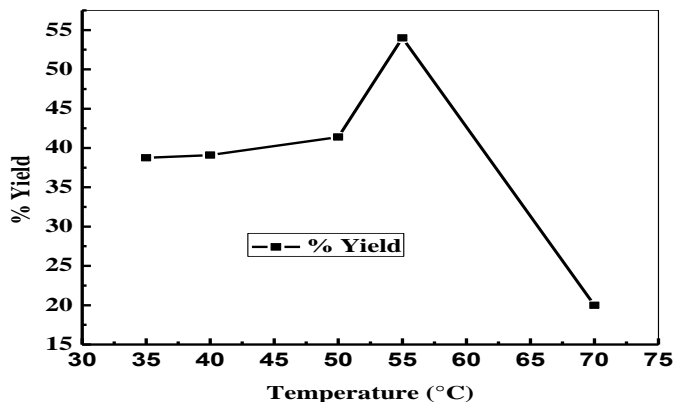

Fig. 5. Effect of temperature on the yield of biodiesel produced

Effect of methanol to oil (MO) ratio on the biodiesel production was tested at different ratio such as 5:1, 10:1, 20:1, 30:1, and 40:1. The production yield with different methanol to oil ratio is presented in Fig. 6. From the results it has been found that at low MO ratio the yield was very less which is because of the methanol deficiencies in the reaction mixture. With increasing the MO ratio there is increase in the biodiesel yield. The maximum yield reached to 54% at 20:1 MO ratio. Above this ratio there is no further improvement in the yield value of the product. No change in yield value at higher MO ratio might be because of the dissolution of glycerol by product in excess methanol which inhibits the transesterification [40]. So, it can be pointed out that 20:1 MO ratio is sufficient for completion of the reaction.
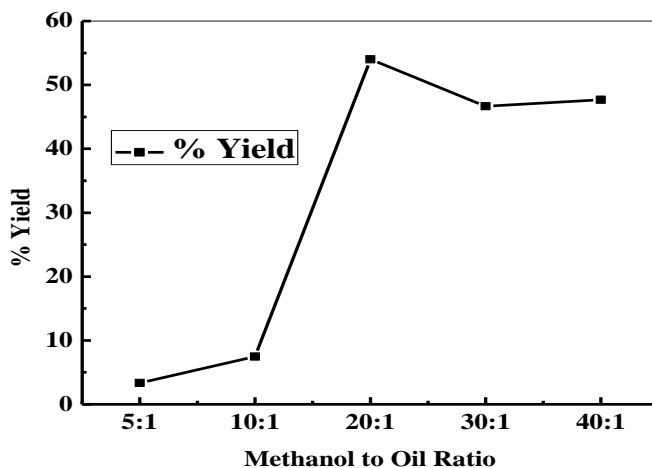

Fig. 6. Effect of methanol to oil ratio on the yield of biodiesel produced

4.   Conclusions

Biodiesel was produced from waste cooking oil through transesterification reaction. Graphene oxide (GO) was taken as the heterogeneous catalyst for the reaction. The synthesized GO sheets were found to be smooth and closely associated with each other. The transesterification reaction was carried under different parametric conditions. 3% graphene concentration was found to be optimum catalyst dose for the reaction. Maximum yield of biodiesel was seen in the presence of 5% Cu impregnation with graphene. Time taken for the completion of the transesterification reaction was 45 min. The optimum value of temperature for the reaction was 55°C and methanol to oil (MO) ratio was 20:1.

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