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Synthesis of Biodiesel Using Solid heterogeneous Catalyst Mg-Al Hydrotalcite by Transesterification from Waste Cooking Oil

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ABSTRACT

The rise of interest in biodiesels has enumerated certain environmental effects like biodegradability and decrement in greenhouse gas emission, pollution deforestation etc. The conventionally used liquid metal oxide catalysts are now replaced with the heterogeneous catalysts like Mg-Al hydrotalcite which gives the same conversion as that of the homogeneous one. The other advantages of the solid catalysts include high selectivity, environment friendly and different preparation methods. In this project the catalyst is synthesized by Urea Hydrolysis and Co-precipitation methods and characterized using XRD. Transesterification reaction is carried out first using KOH as catalyst then by the synthesized solid catalysts, followed by addition of co-solvent Hexane and Glycerol. The conditions are optimized for different parameters such as temperature, reaction time, amount of catalyst and reactants. Characterization of synthesized biodiesel is done using FTIR and the properties like density, kinematic and dynamic viscosities are compared with ASTM standard.

Keywords: Mg-Al, heterogeneous catalyst, hydrotalcite, transesterification, ASTM, FTIR, XRD, urea hydrolysis, co-precipitation.

1. INTRODUCTION

The scarcity of conventionally used fossil fuels, increasing emissions of combustion-generated harmful gases and their multiplying costs has made biomass sources more preferred when compared to other resources. Petroleum-based fuels are exhaustible reserves concentrated in certain regions of the world. These sources are on the verge of depletion. The scarcity of existing petroleum reserves has created more interest on renewable energy sources. Biodiesel fuels are gaining more attention worldwide not only as a blending component but also as direct replacement for diesel in vehicle engines.

Biodiesel is an environment friendly renewable fuel, devoid of any noxious emissions which is synthesized from animal fats, vegetable oils, and waste cooking oil and greases. It has a clear amber-yellow colour and properties like viscosity almost close to that of petrol and diesel. Biodiesel can be synthesized from a large range of natural crops like sunflower, rapeseed, palm, castor, soybean, canola, sesame, mustard, jatropa, flax and waste vegetable oils.

Biodiesel is an effective replacement to the conventionally used petroleum derived diesel and is useful in a number of ways. It is used either by blending it with petroleum diesel or in its natural form. The chemical and physical characteristics of biodiesel are very close to that of conventionally used petroleum-based diesel. It is an inexhaustible source of energy which can help in reducing emission of greenhouse gases and does not contribute to global warming. The oxygen content in biodiesel is higher than that present in petroleum based diesel and its usage in diesel engines resulted in considerable reduction in release of particulate matter, sulphur, carbon monoxide, hydrocarbons, polyaromatics, smoke and noise. Biodiesel does not contain toxic substances and hence it is safe to use. Studies have found that the biodegradability of biodiesel is much more than that of conventional fossil fuels.

The lubricating properties of the biodiesel blends are much better than the conventional diesel resulting in reduced wear and also longer component life.

Biodiesel is synthesized by the transesterification reaction of a triglyceride with a primary alcohol in the presence of a catalyst. Among primary alcohols, methanol is most commonly used for the transesterification process because of its low cost and high reactivity. Heterogeneous solid catalysts like zeolites, metal oxides, γ-alumina and hydrotalcites are being used recently because these catalysts can be separated easily from the reaction mixture, reducing the purification costs, and can be reused. The usage of solid base and acid catalysts for biodiesel production also offers improved process efficiency, allowance of continuous operation and enhancement of the purity of the glycerol by-product. Base catalysts are more active than acids in transesterification, and hence are more suitable for high purity oils with low free fatty acid content.

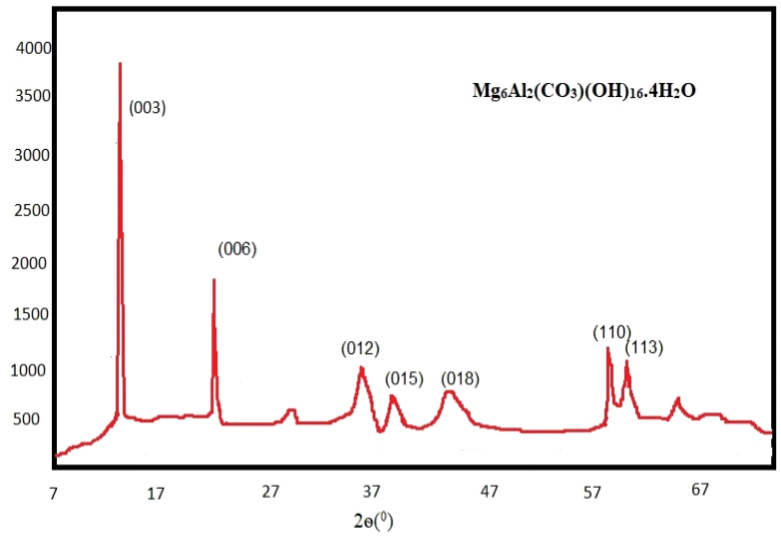
2. MATERIALS AND EXPERIMENTAL SETUP

Waste cooking oil was obtained from a restaurant .Chemicals used were of analytical grade. Magnesium Nitrate(Mg(NO3)2 .6H2O , Aluminium nitrate (AL(NO3)3.4H2O ,Urea, Sodium Hydroxide (NaOH),Sodium Carbonate(Na2CO3).

2.1. Synthesis of Catalyst: Co-precipitation method

The Mg-Al Hydrotalcite was synthesized in 3:1 ratio.150mmol of magnesium nitrate and 50mmol of aluminium nitrate were dissolved in 200ml of distilled water. The resultant solution was added into 400ml of sodium carbonate and heated at 600C for 60 minutes with constant stirring at 200rpm, followed by ageing for 18hrs at room temperature. The solution was washed and filtered .The filtered solid was dried at 900C.

2.1.1. Characterization of the Catalyst



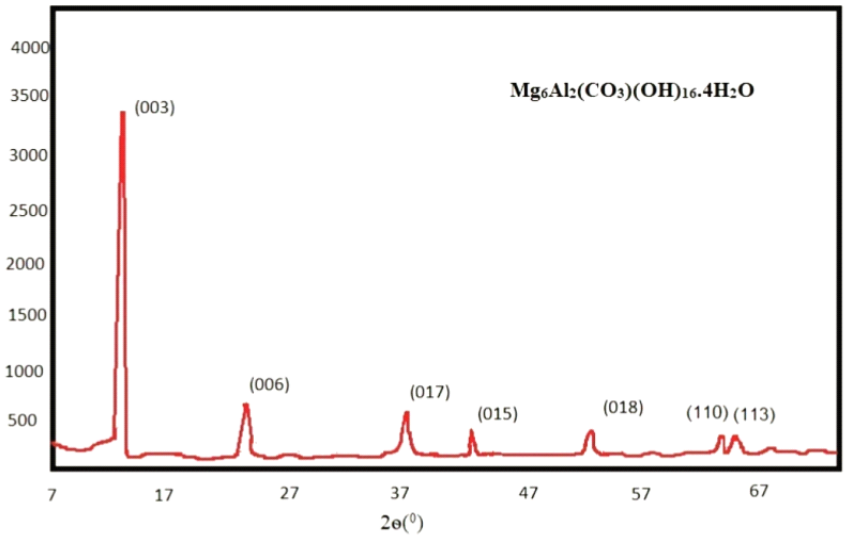
The synthesized catalyst was characterized using XRD. In the analysis the peaks obtained at 11.9, 23.9, 35.3, 40, 48.5, 62.4 and 66.4 were prominent. On comparing with the standards it was confirmed that the compound

synthesised was Mg-Al Hydrotalcite .The other peaks were due to impurities and intermediate compounds. The predominant peaks correspond to a layered structure.

2.2. Synthesis of catalyst: Urea Hydrolysis method

All reagents used were of analytical grade. The Mg/Al ratio was chosen to be 4:1; these were dissolved in 200ml of distilled water. The above solution was added to urea solution with urea to nitrate ratio being 0.6.The resultant solution was heated with constant stirring at 900C and aged for 18hrs.The solution was washed, filtered and dried at 1000C.

2.2.1. Characterization of the catalyst



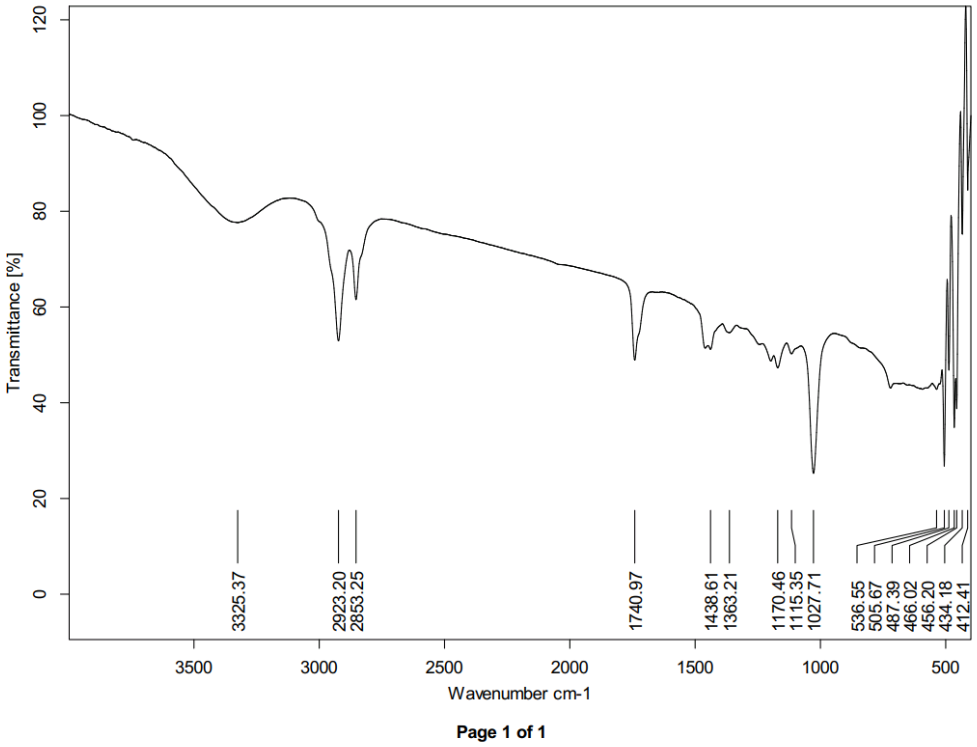
The crystallinity was checked using XRD and found that the peaks obtained were comparable to that of standards and showed double layered structure.

3. Transesterification for production of biodiesel

The waste cooking oil was obtained from nearby restaurant, and oil was pre-treated by filtering it and further heating at 700C.Transesterification was carried with methanol to oil ratio of 6:1 at 600 C ,with constant stirring at 300rpm,1.5wt% catalyst for 60minutes.The reaction mixture was poured into a separating funnel, after 24hrs clear distinction between the ester layer, glycerol, unreacted oil and catalyst particles were obtained. The ester layer was further purified to remove impurities and unreacted components.

Transesterification was carried out at varying temperatures, catalyst concentration, reaction time, and methanol to oil molar ratio to study the effect on yield obtained. Further studies were done effect of addition of co-solvent Hexane.

3.1. Characterisation of Biodiesel



The biodiesel obtained was characterized using FTIR. The spectra illustrated characteristic peaks of biodiesel. With broad and strong absorption band in the range of 3400-3200cm-1 which shows OH stretching, followed by methyl groups in the range of 2810-2930 cm-1 and ester groups in the range of 1725-1750 cm-1.Other intermediate peaks for impurities and unreacted components present

4. RESULTS AND DISCUSSION

4.1. Effect of temperature

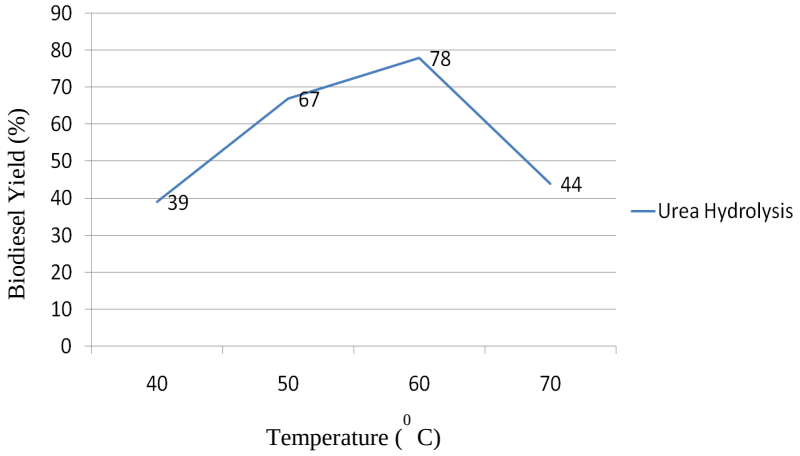


Figure: 4 Effect of Temperature on Biodiesel Production. Reaction Conditions: Methanol to oil molar ratio(6:1),Catalyst concentration:1.5%,reaction time:60minute.

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The reaction was carried out varying temperatures of 400C, 500C, 600C and 700C.The yield obtained vs. temperature was plotted and it was seen that the yield increased with increase in temperature until 600C and beyond this temperature there was a dip because the boiling point of methanol was 650C and higher temperature results in evaporation of methanol consequently affecting equilibrium and reducing the yield.

4.2. Effect of Catalyst concentration

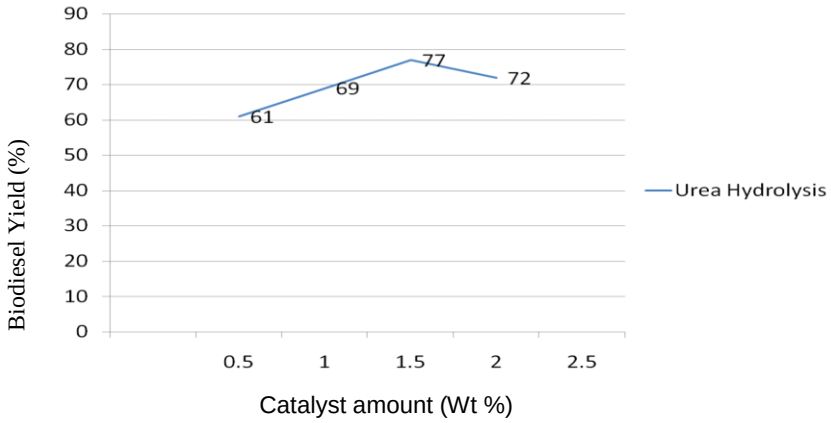

Figure : 5 Effect of catalyst concentration on the biodiesel production. Reaction Conditions: Temperature 60^0 C. Methanol to oil molar ratio:6:1, reaction time:60minutes

Transesterification was carried out at different catalyst concentration from 0.5wt%, 1wt%, 1.5wt% and 2wt%.The yield obtained was plotted against the different catalyst concentrations and it was seen that yield increased with amount of catalyst only until a specific value here 1.5wt% further increase in catalyst concentration causes a decrease in yield this might be because the solution became too viscous thus introducing mixing and consequently mass transfer problems leading to lower yields.

4.3. Effect of Methanol to oil molar ratio

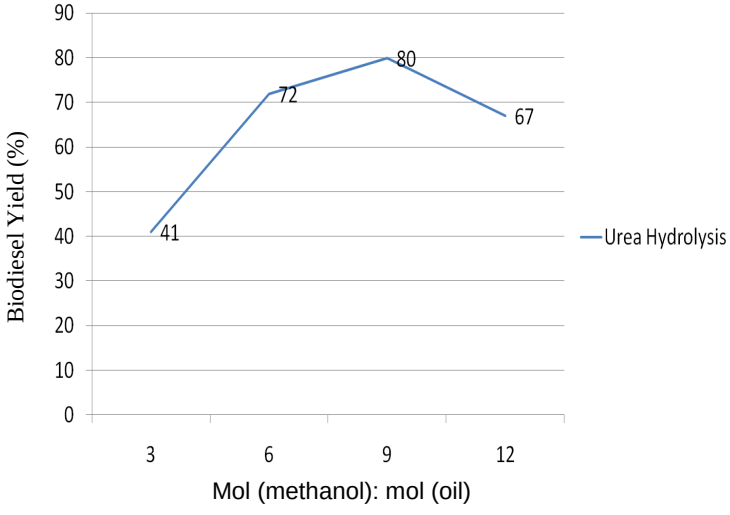

Figure :6 Effect of Methanol to Oil molar ratio on biodiesel production.
Reaction Conditions: Temperature of 60^{0}C, Catalyst concentration 1.0%, Reaction time: 80minutes.

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The reaction was carried out at different methanol to oil molar ratios, 3:1, 6:1, 9:1 and 12:1. Since the reaction is reversible increase in methanol content would lead to increase in forward reaction, thus when yield vs. molar ratio is plotted curve gradually increases until a value here 9:1,after which there is a drop this might be because increase in methanol content enhances dissolution of glycerol in methanol and formation of emulsion thus reducing the yield.

4.4. Effect of reaction time

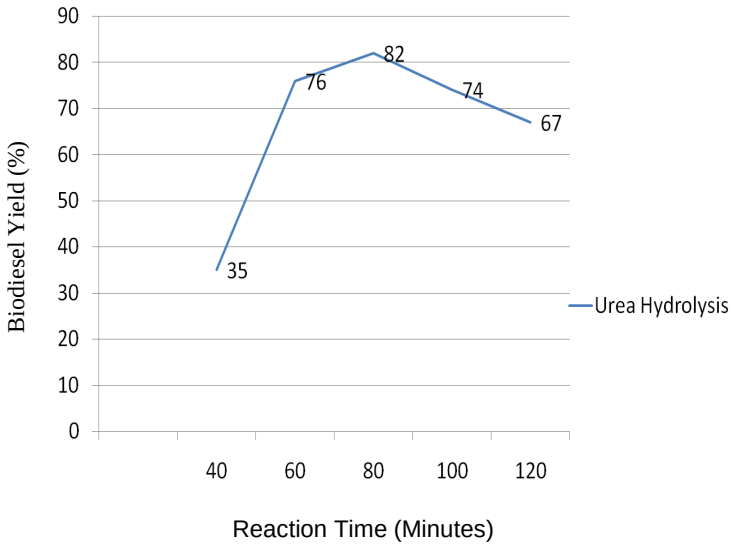

Figure :7 Effect of reaction time on production of Biodiesel. Reaction Conditions: Temperature 60^{0}C, Methanol to oil molar ratio:6:1, Catalyst concentration:1.5wt%

4.5 Effect of addition of co-solvent

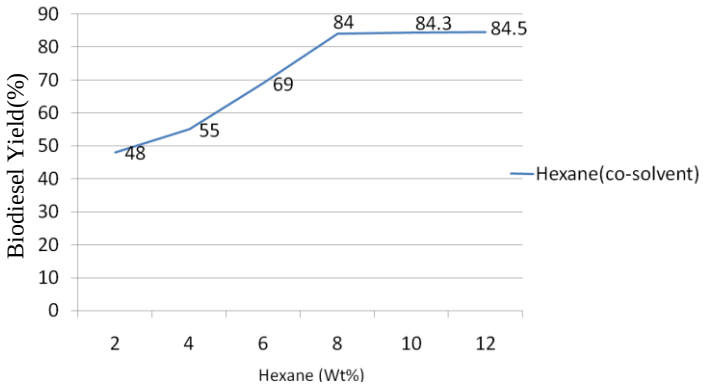

Figure: 8 Effect of addition of Co-Solvent on synthesis of Biodiesel.
Reaction Conditions: Temperature: 60^{0}C, Catalyst concentration: 1.5(wt %),
Methanol to oil molar ratio:6:1,reaction time:60minute

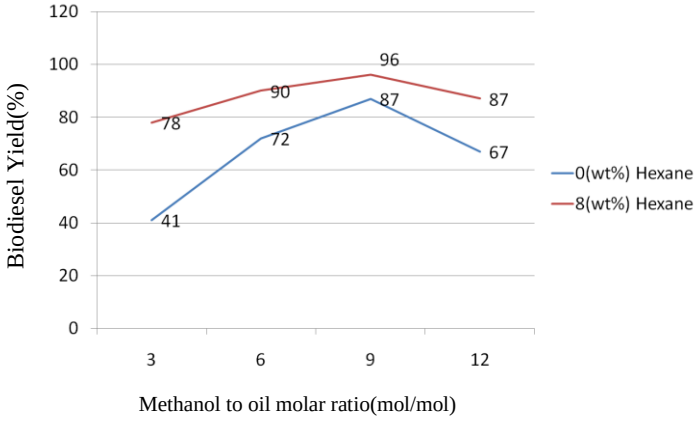

Figure: 9 Comparison of Biodiesel Yield with and without addition of Co-Solvent, with varying amounts of methanol to oil molar ratio.

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Transesterification was carried out at varying reaction times 40, 60 , 80, 100 and 120 minutes. The yield obtained versus reaction time was plotted and similar to other cases there was an increase in yield until a value here 80 minutes above this yield decreases this may be because of hydrolysis of the esters resulting in generation of more fatty acids and thus formation of soap.

Hexane to oil ratio at different weight percents of 2wt%, 4wt%, 6wt%, 8wt% and 10wt% is taken and transesterification is carried out. The yield vs. Hexane wt% is plotted and it seen that the conversion increases until 8wt% and becomes constant even after further addition. Another trial of transesterification is carried out with 8wt% Hexane and varying amounts of methanol to oil molar ratio. It is seen that higher conversions are obtained at lower methanol to oil ratio when Hexane is added, this may be due to solubility of oil in these solvents and their miscibility in methanol thus enhancing the mixing of both the reactants.

Table 4.6 Characteristics of biodiesel

Specific Gravity	0.866
Kinematic Viscosity(m^2/s)	$1.399*10^{-5}$
Saponification Value(mgKOH/gOil)	193
Iodine Value($gI_2/100$)	9.39
Acid Value(mgKOH/gOil)	0.32

5. CONCLUSIONS

From the studies it was concluded that the optimum conditions for more maximum yield were Temperature: 60 0C, Catalyst concentration: 1.5 wt%, Methanol to oil molar ratio: 9:1, Reaction time: 80 minutes. The effect of addition of co-solvent Hexane at different wt% was also studied and found to yield a maximum at 8 wt%. Studies were conducted for effect of Hexane at different molar ratios of methanol to oil, and found to yield a maximum at 9:1 ratio.

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