INTRODUCTION:

The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs has made biomass sources more attractive. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are on the verge of reaching their peak production. The scarcity of known petroleum reserves has made renewable energy sources more attractive. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines.

OBJECTIVES:

1. Synthesis of Heterogeneous Mg/Al Hydrotalcite catalyst.
2. Characterisation of Heterogeneous Mg/Al Hydrotalcite catalyst.
3. Biodiesel synthesis from different oils under optimum conditions like Reaction time and Catalyst concentration.
4. To draw a comparison for synthesis of Biodiesel from different oils using homogenous and heterogeneous catalysts.
5. Confirmation tests for Biodiesel

METHODOLOGY

For the production of Biodiesel and for the synthesis of Hydrotalcite catalyst, the various materials used are as follows:

Sunflower oil, Sesame oil, methanol, Magnesium nitrate, Aluminium nitrate, Sodium carbonate and Sodium hydroxide pellets were purchased from Merck India Ltd. All the chemicals were of analytical grade and used without any further purification.
The Experimental Setup included the following:

Round bottom flask, Condenser, Thermometer, Oil bath, Separating funnel, Magnetic stirrer with PID temperature control, Stir bar, Mechanical shaker, Centrifuge

PROCEDURE:

1. SYNTHESIS OF Mg/Al HYDROTALCITE CATALYST
   - 150 mmol (22.2g) of Mg(NO$_3$)$_2$ and 50 mmol (10.65g) of Al(NO$_3$)$_3$ were dissolved in 200 ml of distilled water.
   - This solution was added slowly into a 400 ml aqueous solution of 400 mmol (42.4g) of Na$_2$CO$_3$, which was then poured into a conical flask and pre-heated to 60 °C.
   - During co-precipitation, the slurry was vigorously stirred with a magnet bar with the drop-wise addition of a 1M solution of NaOH.
   - After complete addition of the metal nitrates solution, the suspension was stirred at 60 °C for 1 h, followed by ageing for 18 h, without stirring.
   - The synthesized solid was washed, filtered, dried at 80 °C. The dried solid was ground into a fine powder, which was further calcined in air at 500 °C to produce hydrotalcite as shown in Figure 1.

2. CHARACTERIZATION OF CATALYST

The characterization of the synthesized Mg/Al Hydrotalcite catalyst was done using X-Ray diffraction and Scanning Electron Microscope techniques.

The Figure 2 shows the X-Ray diffraction image of the synthesised Mg/Al Hydrotalcite catalyst. In the XRD analysis, which measures Intensity and 2θ has prominent 2θ peaks obtained at 11.8, 23.8, 35.2, 40, 48.5, 62.4, and 66.4. On comparison with JCPDS- Joint Committee on Powder Diffraction Standards data for Mg/Al Hydrotalcite, the formation of Mg/Al Hydrotalcite was confirmed and some other peaks were due to intermediate compounds. The XRD pattern of Mg/Al Hydrotalcite catalyst corresponds to a typical Hydrotalcite structure with strong, sharp and symmetric peaks for the (003), (006) and (012) planes as well as broad and symmetric peaks for the (015) and (018) planes. The three strong peaks are characteristic of a layered structure.

- The Mg/Al Hydrotalcite formation was analyzed by Scanning Electron Microscope-SEM technique.
The Figure 3 shows the SEM image of the synthesised Mg/Al Hydrotalcite catalyst having the ‘Rose Petals’ morphology characteristic of Hydrotalcite materials observed for the sample. Hydrotalcite had a relatively uniform hexagonal platelet like structure. Hydrotalcite has a well-developed platelet structure of a typical layered material with a uniform size of 1μm width.

**3. SYNTHESIS OF BIODIESEL BY TRANSESTERIFICATION**

**a) Estimation of acid value:**
Acid Value is the amount of NaOH required to neutralize free fatty acid per gram of oil.

Procedure for Acid value: 5 gm. of oil was taken in a conical flask and 2-3 drops of phenolphthalein indicator was added into it. The solution was then titrated against 0.1N NaOH until it turns from colourless to pale pink. The amount of rundown of NaOH to neutralize oil was noted down. The standard titrimetric method is as shown in Figure 4.

Acid value was calculated using the formula:

\[
\text{Acid value (mg NaOH/g of oil)} = \frac{\text{Titre value} \times \text{Normality of NaOH} \times \text{Molecular weight of NaOH}}{\text{Weight of oil (g)}}
\]

The acid value of oil should be <2 % to carry out the transesterification reaction. If the acid value is > 2%, an additional esterification step has to be carried out to reduce the free acid content of the oil.

**b) Esterification to decrease free acid content:**
To decrease free fatty acid content in non-edible unrefined oils, a three necked round bottom flask was charged with the oil and methanol in the mole ratio of 1: 6 and preheated at 60 °C for one hour. To this mixture, sulphuric acid was added in the mole ratio of 1: 0.07 and continuously stirred for 4 h at 60 °C. After stirring, the mixture was allowed to separate in a separating funnel overnight. The acid value of the oil was determined by a standard titrimetric method.

**c) Transesterification of oil with methanol:**
A three necked round bottom flask was charged with 50 ml of the oil and preheated at 60 °C for one hour with continuous stirring. After one hour, the calculated amount of catalyst, according to varying catalyst wt % (1wt%, 2wt%, 5wt%) and methanol were added slowly to the mixture, with continuous stirring at 60 °C for the required number of hours. The transesterification reaction is carried out as shown in Figure 5.

**Figure 3:** SEM image of Mg/Al Hydrotalcite catalyst

**Figure 4:** Estimation of acid value using the standard titrimetric method

**Figure 5:** Transesterification reaction
d) Isolation of biodiesel

Procedure followed using Homogenous NaOH catalyst:

After the completion of the transesterification reaction, the reaction mixture was transferred to a separating funnel, to obtain separate layers of biodiesel and glycerol, as shown in Figure 6.

**Figure 6:** Formation of biodiesel and glycerol layers after transesterification reaction

The reaction mixture contained glycerol at the bottom and methyl esters- Biodiesel at the top with impurities of unreacted oil and methanol, of which methanol was removed first by distillation as shown in Figure 7.

**Figure 7:** Distillation to remove Methanol

- After distillation, the residue was poured into a separating funnel and left there until the two layered mixture was formed.

- Petroleum ether (in order to completely separate glycerol) was added to the top layer, shaken well and allowed to settle for one hour as shown in Figure 8. Glycerol at the bottom was removed as a separate layer and weighed. Remaining petroleum ether was distilled out from the top layer to obtain Biodiesel as shown in Figure 9.

**Figure 8:** Separation after addition of petroleum ether

**Figure 9:** Distillation to remove Petroleum ether

- Methanol was added again in order to remove any unreacted oil in the mixture to the total esters in which biodiesel was completely miscible leaving unreacted oil as a separate layer. This mixture was allowed to settle in the separating funnel, as shown in Figure 10 for an hour and unreacted oil layer was removed and weighed.

**Figure 10:** Removal of unreacted oil using methanol

- Finally, methanol was distilled out as shown in Figure 11 from the biodiesel layer to get pure Biodiesel as shown in Figure 12.

**Figure 11:** Distillation to remove Methanol

**Figure 12:** Pure biodiesel obtained from Transesterification reaction
Procedure followed using Heterogeneous Mg/Al Hydrotalcite catalyst:

- After the completion of the transesterification reaction, the heterogeneous catalyst was separated from the reaction mixture by centrifugation as shown in Figure 13.

Figure 13: Centrifugation to separate heterogeneous catalyst

- The liquid mixture was then transferred to a separating funnel to obtain separate layers of biodiesel and glycerol as shown in Figure 14. The mixture contained glycerol at the bottom and methyl esters- Biodiesel at the top along with impurities of unreacted oil and methanol, of which methanol was removed first by distillation as shown in Figure 15.

Figure 14: Biodiesel and Glycerol  
Figure 15: Distillation to remove methanol layer formation after centrifugation

- After distillation, the residue was poured into a separating funnel and left there until the two layered mixture was formed.
- Petroleum ether was added to the top layer, shaken well and allowed to settle for one hour as shown in Figure 16. Glycerol at the bottom was removed as a separate layer and weighed. Remaining petroleum ether was distilled out from the top layer to obtain Biodiesel as shown in Figure 17.

Figure 16: Separation after addition of petroleum ether

Figure 17: Distillation to remove Petroleum ether
Methanol was added again in order to remove any unreacted oil in the mixture, to the total esters, in which biodiesel was completely miscible, leaving unreacted oil as a separate layer. This mixture was allowed to settle in the separating funnel as shown in Figure 18 for an hour and unreacted oil layer was removed and weighed.

**Figure 18:** Removal of unreacted oil using methanol

Finally, methanol was distilled out as shown in Figure 19 from the biodiesel layer to get pure Biodiesel as shown in Figure 20.

**Figure 19:** Distillation to remove Methanol  
**Figure 20:** Pure Biodiesel obtained from transesterification reaction

The yield of biodiesel was calculated using the formula:

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\text{Biodiesel Yield (\%)} = \left[ \frac{\text{wt. of biodiesel produced}}{\text{wt. of oil taken}} \right] \times 100
\]

**CONFIRMATION TESTS FOR BIODIESEL**

1. **Flash point** - The flash point is the lowest temperature at which vapors of a fluid will ignite. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the ignition source is removed.
   - For Biodiesel, Flash point is the lowest temperature at which it can form an ignitable mixture in air near the surface of the liquid. Biodiesel will ignite briefly as shown in Figure 21, but the vapor might not be produced at a rate to sustain the fire.

   **Figure 21:** Determination of Flash point

2. **Fire point** - The fire point of a fuel is the temperature at which the vapour produced by that given fuel will continue to burn for at least 5 seconds after ignition by an open flame as shown in Figure 22.
   - In general, the fire points can be assumed to be about 10 °C higher than the flash points.

   **Figure 22:** Determination of Fire point
3. **Cloud point** - Cloud Point is the temperature at which the crystals of solid biodiesel first become visible.

- Manual testing method involved: the test sample is first poured into a test jar to a level approximately half full. A cork carrying the test thermometer is used to close the jar. The thermometer bulb is positioned to rest at the bottom of the jar. The entire test subject is then placed in a constant temperature cooling bath. At every 1 °C, the sample is taken out and inspected for cloud then quickly replaced. Successively lower temperature cooling baths may be used depending on the cloud point.

4. **Pour point** - The pour point of a liquid is the temperature at which it becomes semi-solid and loses its flow characteristics.

- Manual testing method involved: The sample is cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9 °C above the expected pour point, and for every subsequent 3 °C, the test jar is removed and tilted to check for surface movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 sec. If it does not flow, 3 °C is added to the corresponding temperature and the result is the pour point temperature.

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