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NANO HYDROTALCITE AS A NOVEL CATALYST FOR BIODIESEL CONVERSION

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Nano hydrotalcite (Mg–Al) was prepared and characterized by powder X–ray diffractrograme (XRD), infra red spectroscopy (FT–IR), thermal studies (TGA) and Scanning Electron Microcopy (SEM) techniques. The formation of hydrotalcite was confirmed by powder XRD technique. The prepared Mg-Al hydrotalcite was used as a catalyst for transesterification of Pongamia oil for the first time, and the conditions of the transesterification were optimized. 6:1 ratio of methanol and catalyst, and 65°C temperature gave a maximum biodiesel conversion of 90.8 %.

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1. Introduction

There is an increasing urgency to develop alternative energy resources. An immediately applicable option is the replacement of diesel fuel by biodiesel, which consists of simple alkyl esters of fatty acids. With a little modification, diesel engine vehicles can use biodiesel fuels. Its main advantage over fossil fuels is that it is renewable, biodegradable, and nontoxic. Its contribution to greenhouse gases is minimal, since the emitted CO_2 is equal to the CO_2 absorbed by the plants to create the triglycerides. Biodiesel has been defined as the Fatty acid methyl esters (FAME) which are derived from vegetable oils or animal fats (Triglycerides) by transesterification with methanol or ethanol. The use of biodiesel is encouraged by governments across the world to improve energy supply security, reduce greenhouse gas emissions, and boost rural incomes and employments [1,2].

The transesterification process can be catalyzed by both acids and bases. Base catalysts are preferred to acid catalysts because they have better activity and corrosion property. Base catalysis poses emulsification, separation difficulties, and side reactions like decompositionand polymerization may also occur during distillation after the reaction. To overcome these difficulties researchers have focused their attention on developing heterogeneous catalysts. The employment of heterogeneous catalysts helps to separate the products easily and have attracted much attention during the development of new environmentally friendly catalysts. [3,4]. [Fig 1]

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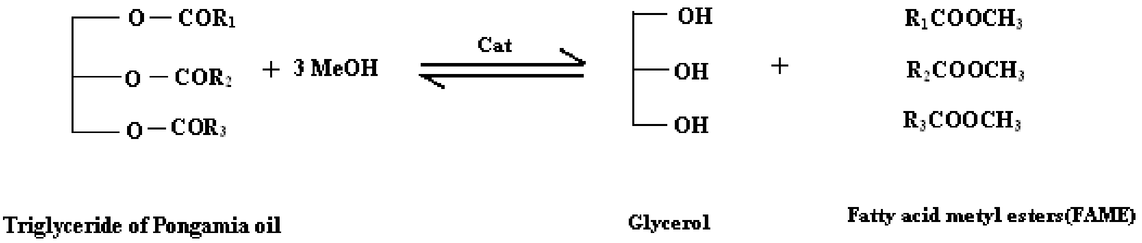

Fig 1. Transesterification reaction of Pongamia oil and methanol in the presence of Hydrotalciteas a catalyst

Heterogeneous catalysts such as zeolites, clays and ion exchange resins have been tried but their reaction rates are found to be very low. Therefore solid base catalysts i.e., metal oxides, mixed oxides and ion exchange resins have been used. At the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils. Hydrotalcite, ($Mg_6Al_2(OH)16SO_4.4H_2O$) have been used as catalysts for the biodiesel conversion. The structure of hydrotalcite resembles that of brucite, $Mg(OH)_2$, where the magnesium cations are octahedrally coordinated by hydroxyl ions, resulting in stacks of edge-shared layers of the octahedral. In the hydrotalcite structure, part of the Mg^{2+} ions are replaced by Al^{3+} ions forming positively charged layers. Charge-balancing anions (usually SO_4^{2-}) and water molecules are situated in the inter layers between the stacked brucite like cation layers. Calcinations at high temperature decomposes the hydrotalcite into interactive, high surface area and well-dispersed mixed Mg–Al oxides which present basic sites that are associated with structural hydroxyl groups as well as strong Lewis basic sites associated with O^{2-} Mn^{+} acid–base pairs [5-7].

Pongamia oil is non edible oil extracted from seeds of Pongamia pinnata. It is very easy to grow and needs little care, though till today ‘Pongamia’ is a much ignored tree. The transesterification of Pongamia oil to get biodiesel using a heterogeneous catalyst is attempted for the first time in our study. In the present work, calcined Mg–Al hydrotalcite were adopted for transesterification of Pongamia oil to Pongamia biodiesel. The catalytic efficiency was studied regarding the methyl ester conversion. The structure characterization of Mg–Al hydrotalcite was studied using analytical techniques like XRD, FTIR, TGA-DTA and SEM. In the optimized reaction conditions, the highest ester conversion was 90.8% using the Mg–Al hydrotalcite catalyst.

2. Experimental

2.1 Materials and Methods

The materials used in this study were commercially refined Pongamia oil obtained from Sakthi Sugars, Sathiyamangalam, Coimbatore, India, Magnesium nitrate (Merck, Germany), Aluminium nitrate (Merck, Germany) absolute alcohol (Jiangsu Huaxi, China), Na_2So_4 (Merck, Germany), $CDCl_3$ (Sigma Aldrich, USA) and Standard FAME was obtained from Sigma Aldrich, USA, Gas Chromatography (GC-2010, Shimadzu, Japan) and Powdered XRD (Shimadzu, Japan, LabX600Jeol) were the instruments used in our study.

2.2 Catalyst preparation

Mg-Al-SO_4 hydrotalcite was synthesized by the co-precipitation of Mg^{2+} and Al^{3+} ions in an alkaline solution containing NaOH. 1.0 M solution of $Mg_2(SO_4)6H_2O$ (0.3M) and $Al_2(SO_4).9H_2O$ (0.1M) were drop wise mixed in 3:1 ratio with 1M NaOH. The reaction time pH was maintained between 9 and 11 and the reaction was carried out under nitrogen atmosphere. The resultant mixture was aged at 90^0C for 72 hours. The hydrotalcite was separated by high speed centrifugation and washed with DI water. The hydrotalcite sample was dried at 100^0C and then calcined at 400^0C [8]. The prepared hydrotalcite was analyzed by XRD, FT-IR, SEM, Surface analysis, and TGA techniques.

2.3 Transesterification of Pongamia Oil

Pongamia oil and an appropriate volume of methanol with calcined Mg–Al hydrotalcite catalysts (0.5–1%) were placed into a 500 ml three necked flask equipped with reflux condenser and Teflon stirrer (100–500 rpm). The reaction mixture was blended for a period of time at 65^0C temperature under atmospheric pressure. The molar ratio of methanol to oil was taken as 6:1. After the reaction, the hydrotalcite catalyst was separated by filtration. Subsequently, the methanol was recovered by a rotary evaporator in vacuum at 45^0C and the ester layer was separated from the glycerol layer using a separating funnel. The fined ester layer was dried over sodium sulfate and analyzed by gas chromatography on a Shimadzu GC-2010 chromatograph with FID detector. The biodiesel conversion was compared with standard FAME [8-10].

3 Result and discussion

3.1 Characterization of catalyst

In the XRD analysis the prominent 2θ peaks obtained were at 11.8, 23.8, 35.2, 62.4, and 66.4. On comparison (JCPDS card no #:50-1684) the formation of Mg-Al hydrotalcite was understood and some other peaks were due to intermediate compounds. The basal spacing was calculated to be 0.739 nm. The sharp peak (003) indicates the formation of highly crystalline materials. Indexing of the diffraction peaks was done using a standard JCPDS file. The reflections were indexed in a hexagonal lattice with an R_3m rhombohedral symmetry. The parameter of hydrotalcite corresponding to the cation-cation distance within the brucite-like layer can be calculated as follows: a = 2 × d (110). On the other hand, the c parameter is related to the thickness of the brucite-like layer and the interlayer distance and can be obtained from the equation c = 3 × d (003) [11,12]. [Fig: 2]

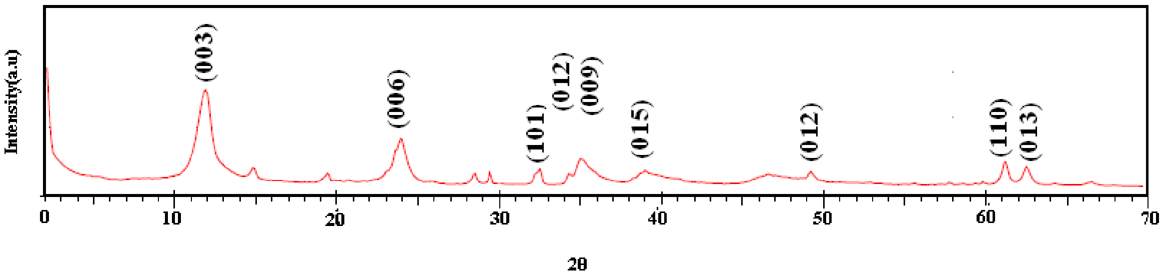

Fig 2. XRD pattern of Mg-Al Hydrotalcite

The values of the unit cell parameters, assuming rhombohedral symmetry, with the *c* parameter corresponding to three times the thickness of the expanded brucite like layer, are presented in Table 1. The *a* and *c* parameters decreased with increasing aluminum content, which can be explained by the substitution of larger Mg^{2+} ions by smaller Al^{3+} ions [13-15]. [Table 1]

Table 1: XRD calculation of interlayer distance

Mg-Al Hydrotalcite	(003) 2θ	d_{003} (Å)	d & c & Basal spacing
$d_{(003)}$	11.8	7.48	C=22.44
$d_{(110)}$	61.4	1.31	a = 3.03
$d_{(003)}$ crystal basal space	-	-	0.739 nm

Using Scherrers formula, one can find the size of the crystal or particle size.

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Where K is the shape factor, λ is the X-ray wavelength, typically 1.54 Å, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle; τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 µm, which precludes those observed in most metallographic and ceramographic microstructures. Using the Scherrer formula the crystal size was found to be within 4.66 nm to 21.2 nm [13, 15].

Fig. 3 shows the FT-IR spectrum of Mg-Al hydrotalcite. The spectrum was characterized with asymmetric and symmetric stretching vibrations of carboxyl group at 1425 cm^{-1}, along with the O-H stretching of the hydroxyl group and deformation vibration of H_2O at 3447.59 cm^{-1}. The spectrum is skewed on the right hand side and the net small peak at 2952 cm^{-1} is due to the hydrogen bonding of H_2O and interlayer of SO_4^{2-} anions. In the lower frequencies, the peak at 1637 cm^{-1} in all the samples can be attributed to the bending mode of the interlayer water. The main absorption band of the sulphate anions was observed at 1370 cm^{-1}. In the low energy ranges of the spectra 704 – 637cm^{-1}, peaks around 469cm^{-1} are attributed to the presence of Mg-O and Al-O bond. [Fig 3]

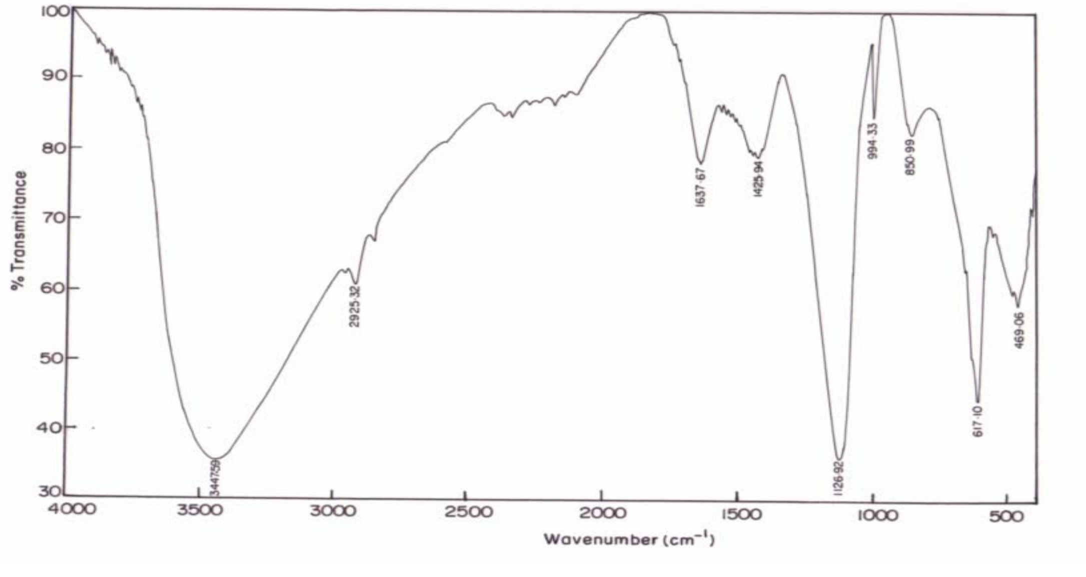

Fig 3: FT-IR spectrum of Mg-Al Hydrotalcite

The hydrotalcite formation by this preparative route was analyzed by SEM. Fig.4 shows the ‘Rose Petals’ morphology characteristic of hydrotalcite materials which was observed for all the samples [Fig 4]. The TGA-DTA curves of both the samples may be divided into two well differentiated main regions. In the first one, ranging from 120º C to 220º C there is an endothermic peak related to the dehydration of the sample, which is accompanied by a mass loss of 7.78%. The second region, ranging from 270 to 600º C corresponds to the weight loss due to the dehydroxylation and de-carbonation reactions, which resulted in a mass loss of 8.96%. The third endothermic region, ranging from 780^0C to 900^0C, has a weight loss of 5.06%. The weight loss corresponds to the decomposition of interlayer anion present in the brucite layer and the dehydroxylation of vicinal OH groups in the hydrotalcite [11, 18]. [Fig.5]

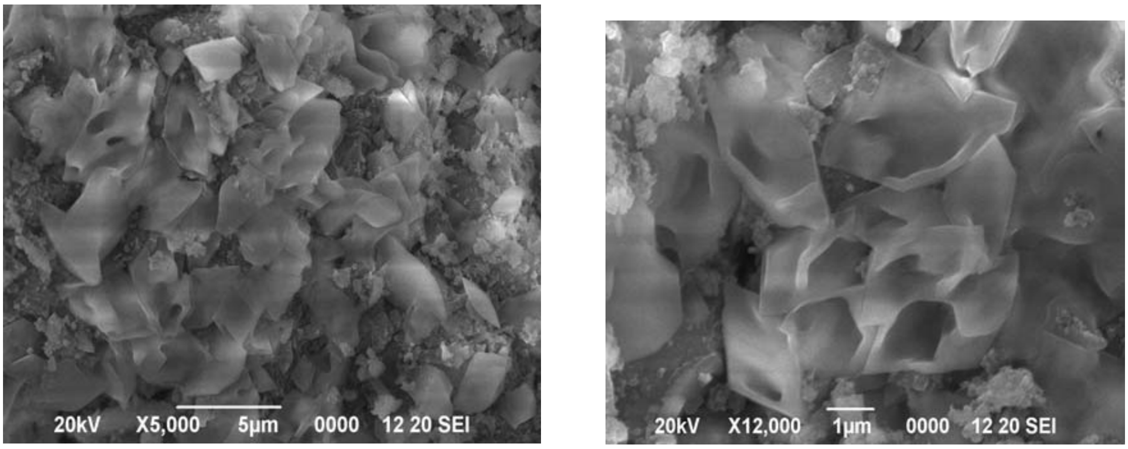

Fig 4: SEM picture of Mg-Al HT

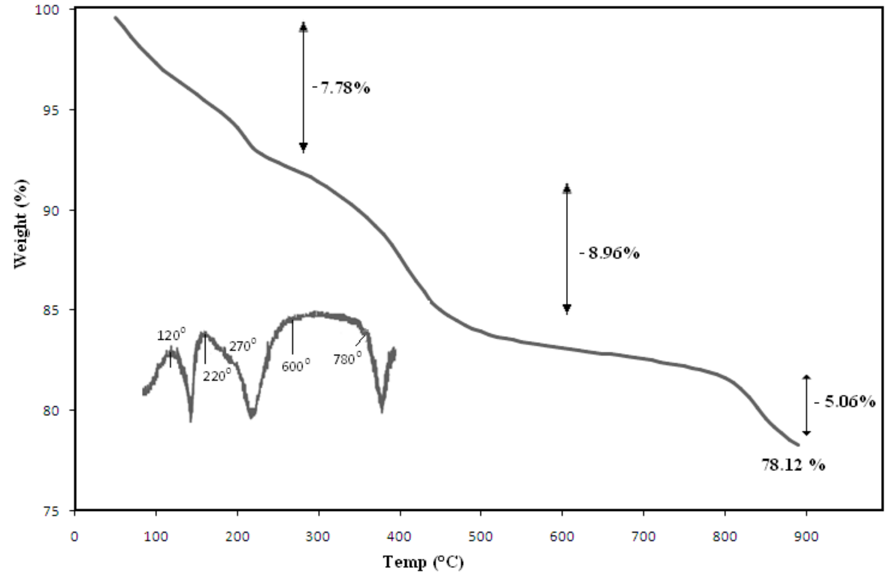

Fig 5: TGA-DTA curve of Mg-Al-HT

3.2 Application of Catalyst for transesterification of Pongamia Oil:

The molar ratio of methanol to vegetable oil was one of the most important variables that affect ester formation because the conversion and the viscosity of the produced ester depended on it. The stoichiometric molar ratio of methanol to oil is 3.0. But when mass transfer is limited due to problems of mixing, the mass transfer rate seems to be much slower than the reaction rate, so the conversion can be elevated by introducing an extra amount of the reactant methanol to shift the equilibrium to the right-hand side. Higher molar ratios result in greater ester conversions in a shorter time [16, 17]. From figure 6a it is evident that the optimum molar ratio of methanol to Pongamia oil is 6.0. Beyond the molar ratio of 6.0, the added methanol does not enhance significantly the ester conversion. In addition, the conversion increased sharply with reaction time, then reached a plateau value representative of a nearly equilibrium conversion after 4 h reaction. A nearly maximum conversion of 90.8% was obtained after 4 h reaction time. When increasing the amount of catalyst, the slurry (mixture of catalyst and reactants) becomes too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring. On the other hand, when the catalyst amount is not sufficient, maximum conversion cannot be reached. In most cases, sodium hydroxide or potassium hydroxide had been used in the process of alkaline methanolysis, both in concentrations ranging from 0.5% to 1.5% w/w of oil. In our work, the reaction profiles indicate that the ester conversion increased with the increase of catalyst amount from 0.5% to 1.5% (0.5% w/w of oil: 68.2%, 1.0: 79.5%, and 1.5: 90.5%).

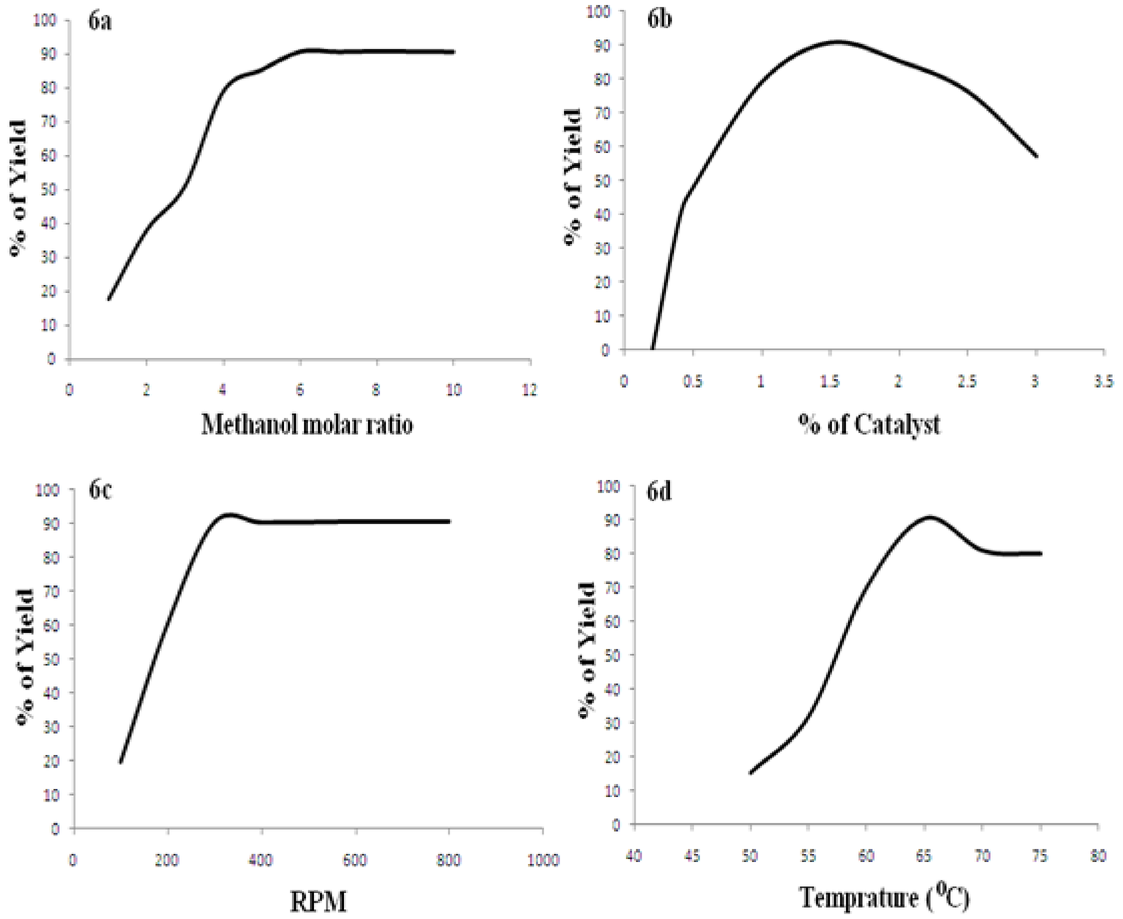

Fig 6: Transesterification reaction using Mg-Al-HT with pongamia Oil. 6a) Effect of Methanol molar ratio, 6b) Effect of Catalyst, 6c) Effect of RPM, 6d) Effect of Temprature.

However, figure 6b shows that the conversion to biodiesel decreased with increase of catalyst amount beyond 1.5 % (2.0: 85.0%, 2.5: 83.7%), which may possibly be due to the mixing problem of reactants, products and solid catalyst. The maximum ester conversion reached 90.5% when 1.5% catalyst was added. Mixing is very important for the transesterification of Pongamia oil, because pongamia oil and methanol solution are immiscible and the reactants and the solid catalyst are separated in the heterogeneous system. Generally, a more vigorous stirring speed causes better contact among the reactants and solid catalyst, resulting in the increase of the reaction rate. Figure 6c clearly shows that the reaction progressed only upon stirring and that the stirring of the reactants had a significant effect on the transesterification of the oil (100 rpm: 19.5%, 200: 60.2%, 300: 90.2%, 400: 90.2%, and 500: 90.3%). Adding solid catalyst to the reactants while stirring facilitated the chemical reaction, and the reaction started quickly. It quickly established a very stable emulsion of oil, MeOH and catalyst. The ester conversion increased rapidly with an increase of stirring speeds from 100 to 500 rpm. When the stirring speed was over 300 rpm, there was no significant enhancement in the conversions (above 90.2%). The effect of reaction temperature on the ester conversion was studied at six different temperatures, i.e. 50, 55, 60, 65, 70 and 75^{0}C. Figure 6d shows the variation of ester conversion with reaction temperature. Transesterification proceeded slowly at 50^{0}C, where the conversion was 19.6% in a 4 h reaction. Lower temperatures resulted in a drop of the ester conversion because only a small amount of molecules were able to get over the required energy barrier. The ester conversion increased up to 90.4% in 4 h reaction by increasing the reaction temperature to 65^{0}C (55^{0}C: 31.8%, 60^{0}C: 70.2%). Thus, the optimum temperature for the preparation of the ester was found to be 65^{0}C, which was near the boiling point of anhydrous methanol. The conversion fell to about 80.0% in the temperature range of 70–75^{0}C (70^{0}C: 80.9%, 75^{0}C: 80.0%), probably because the molar rate of methanol to oil decreased when the methanol reactant volatilized into gas phase above 65^{0}C, the boiling point of pure methanol. The catalytic transesterification of Pongamia Oil with methanol to form Biodiesel was investigated using the Mg/Al Hydrotalcite. The conversion of biodiesel was 90.8%. [Fig 6]

4. Conclusion

For the transesterification of Pongamia oil with methanol, calcined Mg–Al hydrotalcite was found to be effective as a solid base catalyst. The reaction conditions for the system were optimized to maximize the methanol ester conversion (about 90.8%). The optimum reaction conditions standardized are methanol to Pongamia oil molar ratio of 6.0, 1.5% catalyst (w/w of oil) and 300 rpm stirring speed for 4 h reaction time and an optimum temperature of 65^0 C. The catalyst used has a distinctive advantage in that it shows high catalytic activity, and it is easy to separate the catalyst at the end by simple filtration. It is a fact that the solid base catalyst can become a practical alternative to solution base catalyst.

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