

Mg-Al hydrotalcite as solid base catalyst for biodiesel production from pongamia oil

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This study presents preparation, characterization and use of Mg-Al hydrotalcite as a catalyst for transesterification of pongamia oil and optimization of transesterification conditions. Mg-Al hydrotalcite was characterized by powder X-ray diffraction (XRD), infra red spectroscopy (FT-IR), thermal studies (TGA) and Scanning Electron Microcopy (SEM) techniques. Methanol and catalyst (6:1) and 65°C temperature gave a maximum biodiesel conversion (90.8%). Transesterification of pongamia oil using Mg-Al hydrotalcite was compared with conventional base catalyst.

Keywords: Biodiesel, Hydrotalcite, Pongamia oil, Solid base catalyst, Transesterification

Introduction

Pongamia oil, extracted from seeds of *Pongamia pinnata*, can be transesterified with methanol and catalyst to give pongamia oil methyl ester (POME) to be used as biodiesel. Use of biodiesel is encouraged to improve energy supply security, reduce greenhouse gas (GHG) emissions, and boost rural incomes and employments^{1,2}. Under transesterification process, base catalysts are preferred to acid catalysts because they have better activity and corrosion property, but poses emulsification, separation difficulties, and side reactions like decomposition and polymerization during distillation after the reaction. To overcome these difficulties, employment of heterogeneous catalysts helps to separate products easily^{3,4}. Many heterogeneous catalysts have been developed to catalyze transesterification of vegetable oils with methanol. Calcinations at high temperature decomposes 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 O²⁻ Mn⁺ acid-base pairs⁵⁻⁷.

This study presents calcined Mg-Al hydrotalcite (MAH) as catalyst for transesterification of pongamia oil to POME and the optimized reaction conditions. The

catalytic efficiency of MAH was compared with conventional base catalyst and the MAH was characterized using X-ray diffraction (XRD), infra red spectroscopy (FT-IR), thermal studies (TGA) and scanning electron microcopy (SEM), and reaction conditions were optimized.

Experimental Section

Refined pongamia oil was obtained from Sakthi Sugars, Sathiyamangalam, Coimbatore, India. Chemicals used were Magnesium nitrate (Merck, Germany), Aluminium nitrate (Merck, Germany), absolute alcohol (Jiangsu Huaxi, China), NaOH (Merck), Na₂SO₄ (Merck, Germany), CDCl₃ (Sigma Aldrich, USA) and C₄ to C₂₄ FAME (fatty acid methyl esters) mix (Sigma Aldrich, USA). Instruments used in the study were Gas Chromatography (GC-2010, Shimadzu, Japan) and Powdered XRD (Shimadzu, Japan, LabX600Jeol).

Catalyst Preparation

Mg-Al-SO₄ hydrotalcite was synthesized by co-precipitation of Mg²⁺ and Al³⁺ ions in an alkaline solution containing NaOH. 1.0 M solution of Mg₂(SO₄)6H₂O (0.3M) and Al₂(SO₄)₃·9H₂O (0.1M) were drop wise mixed in 3:1 ratio with 1M NaOH. Reaction time pH was maintained at 9-11 and the reaction was carried out under nitrogen atmosphere. The resultant mixture was aged at 90°C for 72 h. Hydrotalcite was separated by high speed centrifugation and washed with DI water.

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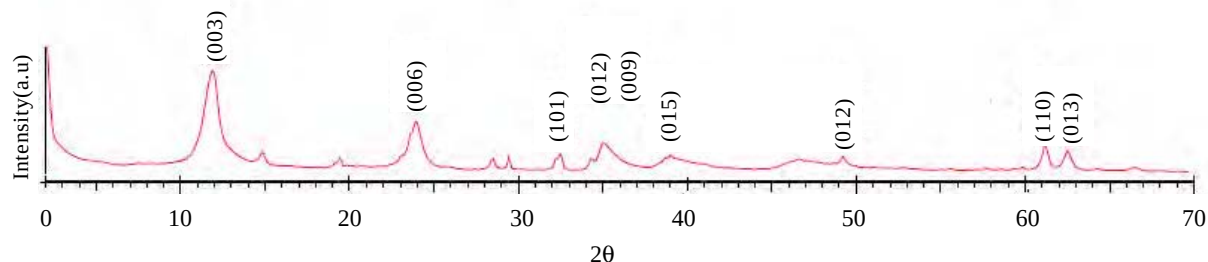


Fig 1—XRD pattern of Mg-Al hydrotalcite (MAH)

Hydrotalcite sample was dried at 100°C, calcined at 400°C⁸ and then analyzed by XRD, FT-IR, SEM, Surface analysis, and TGA.

Transesterification of Pongamia Oil

Pongamia oil and an appropriate volume of methanol with calcined MAH catalysts (0.5-1%) were placed into a 500 ml three necked flask equipped with reflux condenser and Teflon stirrer (100-500 rpm). Reaction mixture was blended for a period of time at 65°C under atmospheric pressure. Molar ratio of methanol to oil was taken as 6:1. After reaction, MAH was separated by filtration. Subsequently, methanol was recovered by a rotary evaporator in vacuum at 45°C and ester layer was separated from glycerol layer using a separating funnel. Fined ester layer was dried over sodium sulfate and analyzed by GC on a Shimadzu GC-2010 chromatograph with FID detector. Oven temperature program consisted of start at 40°C to final at 360°C. The same procedure was followed in alkaline method of transesterification using NaOH instead of MAH. Internal standard used was C₄ to C₂₄ FAME (fatty acid methyl ester) mix (Sigma Aldrich, USA) (Sigma Aldrich, USA)⁸⁻¹⁰.

Result and Discussion

Characterization of Catalyst

In XRD analysis, prominent 2θ peaks obtained were at 11.8, 23.8, 35.2, 62.4, and 66.4 (Fig. 1). On comparison (JCPDS card no #:50-1684), formation of MAH was understood and some other peaks were due to intermediate compounds. Basal spacing was calculated to be 0.739 nm. Sharp peak (003) indicates formation of highly crystalline materials. Reflections were indexed in a hexagonal lattice with an R_3m rhombohedral symmetry. Parameters of MAH corresponding to cation-cation distance within brucite-like layer can be calculated as follows: $a = 2 \times d(110)$. On the other hand, c parameter

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

is related to thickness of brucite-like layer and interlayer distance, and can be obtained as $c = 3 \times d(003)$ ^{11,12}. Basal reflections from (003), (006), and from (110) planes in XRD patterns (Fig. 1) are indicative of Mg-Al-SO₄, proving hydrotalcite formation with an interlayer spacing of 0.739 nm¹². Sharp XRD lines were detected in the precursor with $r = 0.75$, which has composition of stoichiometric hydrotalcite, Mg₆Al₂(OH)₁₆SO₄·4H₂O. All other hydrotalcite containing precursors showed broader XRD lines, corresponding to smaller crystallites or less ordered structures^{13,14}. The a and c parameters decreased with increasing aluminum content, which can be explained by substitution of larger Mg²⁺ ions by smaller Al³⁺ ions¹⁵ (Table 1). Using Scherrers formula, one can find crystal size or particle size as $\tau = K\lambda / \beta \cos\theta$, where K is shape factor, λ is X-ray wavelength, typically 1.54 Å, β is line broadening at half the maximum intensity (FWHM) in radians, and θ is Bragg angle; T is mean size of ordered (crystalline) domains, which may be $\leq$ to grain size. Dimensionless shape factor has a typical value of 0.9, but varies with actual shape of the crystallite. Scherrer equation is limited to nano-scale particles. It is not applicable to grains $> 0.1 \mu\text{m}$, which precludes those observed in most metallographic and ceramographic microstructures. Using Scherrer formula, crystal size was found to be within 4.66 nm to 21.2 nm^{13,15}.

FT-IR spectrum (Fig. 2) of MAH was characterized with asymmetric and symmetric stretching vibrations of

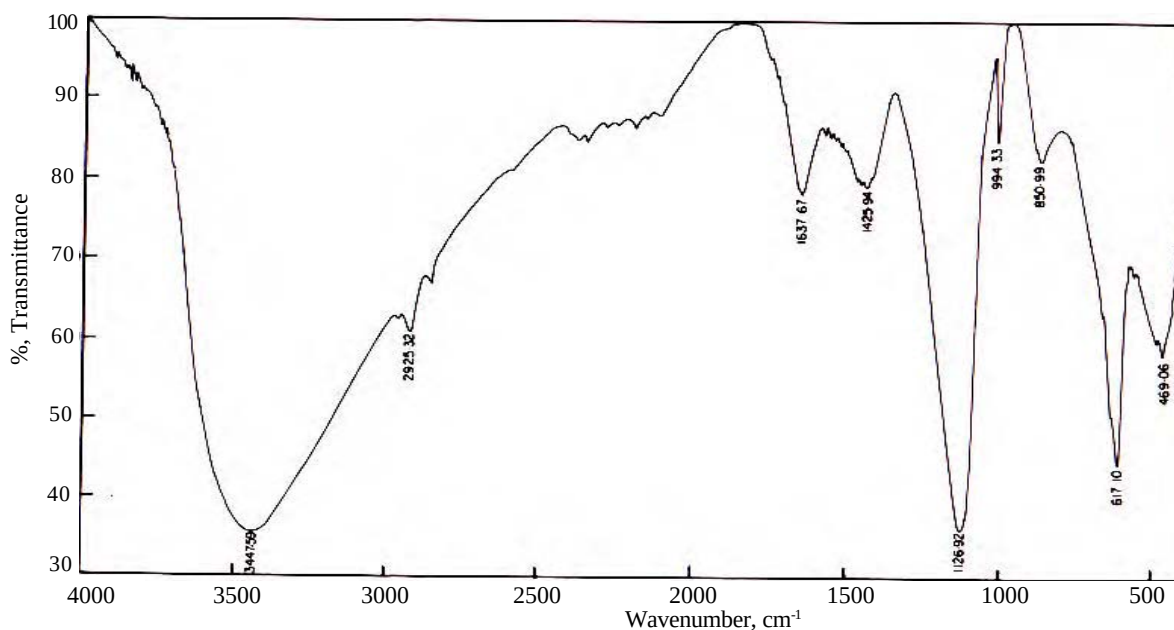


Fig 2—FT-IR spectrum of Mg-Al hydrotalcite (MAH)

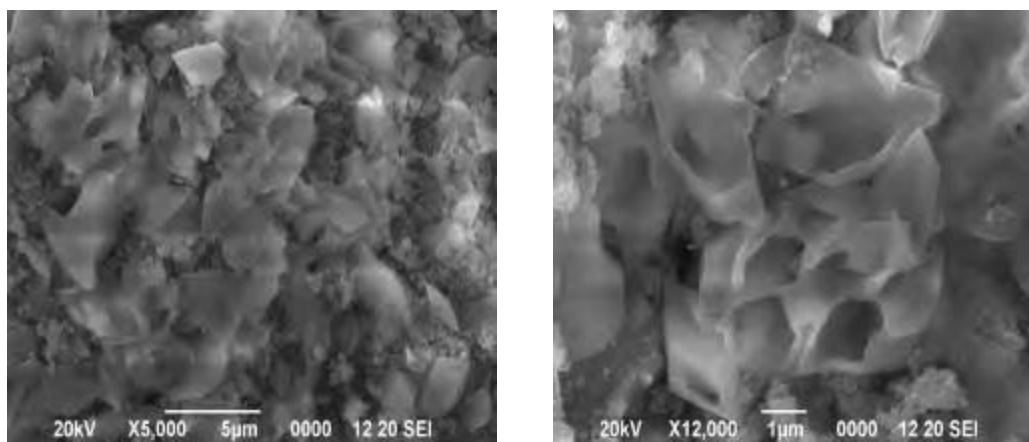


Fig 3—SEM picture of Mg-Al hydrotalcite (MAH)

carboxyl group at 1425 cm^{-1} , along with O-H stretching of hydroxyl group and deformation vibration of H_2O at 3447.59 cm^{-1} . Spectrum is skewed on the right hand side and net small peak at 2952 cm^{-1} is due to hydrogen bonding of H_2O and interlayer of SO_4^{2-} anions. In lower frequencies, peak (1637 cm^{-1}) in all samples can be attributed to bending mode of interlayer water. Main absorption band of sulphate anions was at 1370 cm^{-1} . In low energy ranges of $704\text{--}637\text{ cm}^{-1}$, peaks at 469 cm^{-1} are attributed to the presence of Mg-O and Al-O bond (Fig. 2). MAH formation by this route was analyzed by SEM (Fig. 3). TGA-DTA curves (Fig. 4) of both samples may be divided into two well differentiated main regions. In the first one ($120\text{--}220^\circ\text{C}$), there is an endothermic

peak related to dehydration of the sample, which is accompanied by a mass loss of 7.78%. Second region ($270\text{--}600^\circ\text{C}$) corresponds to the weight loss due to dehydroxylation and de-carbonation reactions, which resulted in a mass loss of 8.96%. Third endothermic region ($780\text{--}900^\circ\text{C}$) has a weight loss of 5.06%. Weight loss corresponds to decomposition of interlayer anion present in brucite layer and dehydroxylation of vicinal OH groups in MAH^{11,16}.

Application of Catalyst for Transesterification of Pongamia Oil

Conventional Method

For transesterification of pongamia oil, optimum quantity was determined by varying concentrations of

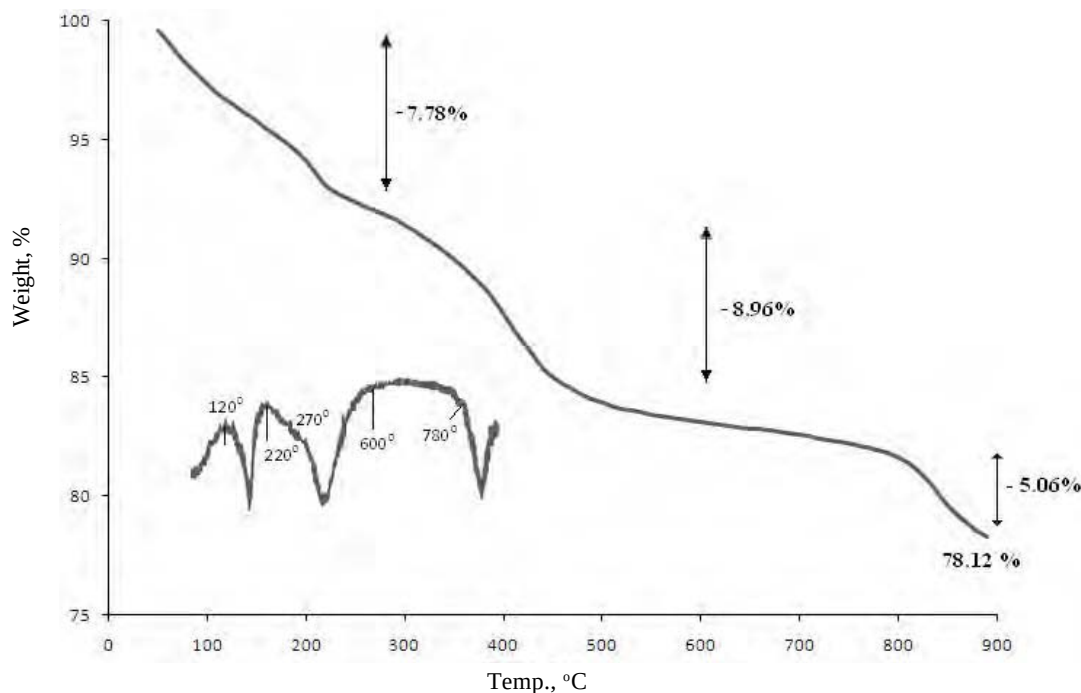


Fig 4—TGA-DTA curve of Mg-Al hydrotalcite (MAH)

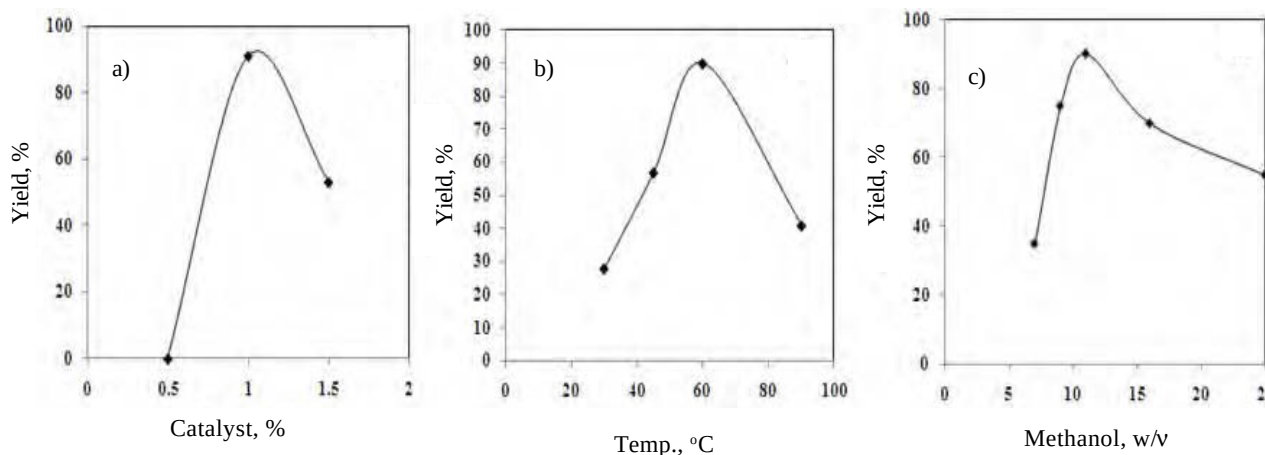


Fig 5—Transesterification reaction using NaOH with pongamia Oil: a) Effect of catalyst; b) Effect of temperature; and c) Effect of methanol molar ratio

methanol (8-25 w/v) and NaOH (0.5-1.5%) and reaction temperature (30-60°C (Fig. 5). Maximum ester yield (89.1%) was obtained at the following optimum conditions: NaOH conc., 1.0% (Fig. 5a); reaction temp., 60°C (Fig. 5b); methanol conc., 11 w/v (Fig. 5c); and reaction time, 90 min. It was observed that if NaOH and methanol concentrations were reduced below or increased above the optimum, there was no significant

increase in biodiesel production, but there was increased formation of glycerol and emulsion. Reaction temperature should always be below the boiling point (65°C) of methanol and so reaction temperature was fixed at 60°C. When stirring speed was over 300 rpm, there was no significant enhancement in the conversion. In conventional method, there is no scope of reusing the catalyst, as excess alkali get saponified with oil, leading to soap formation.

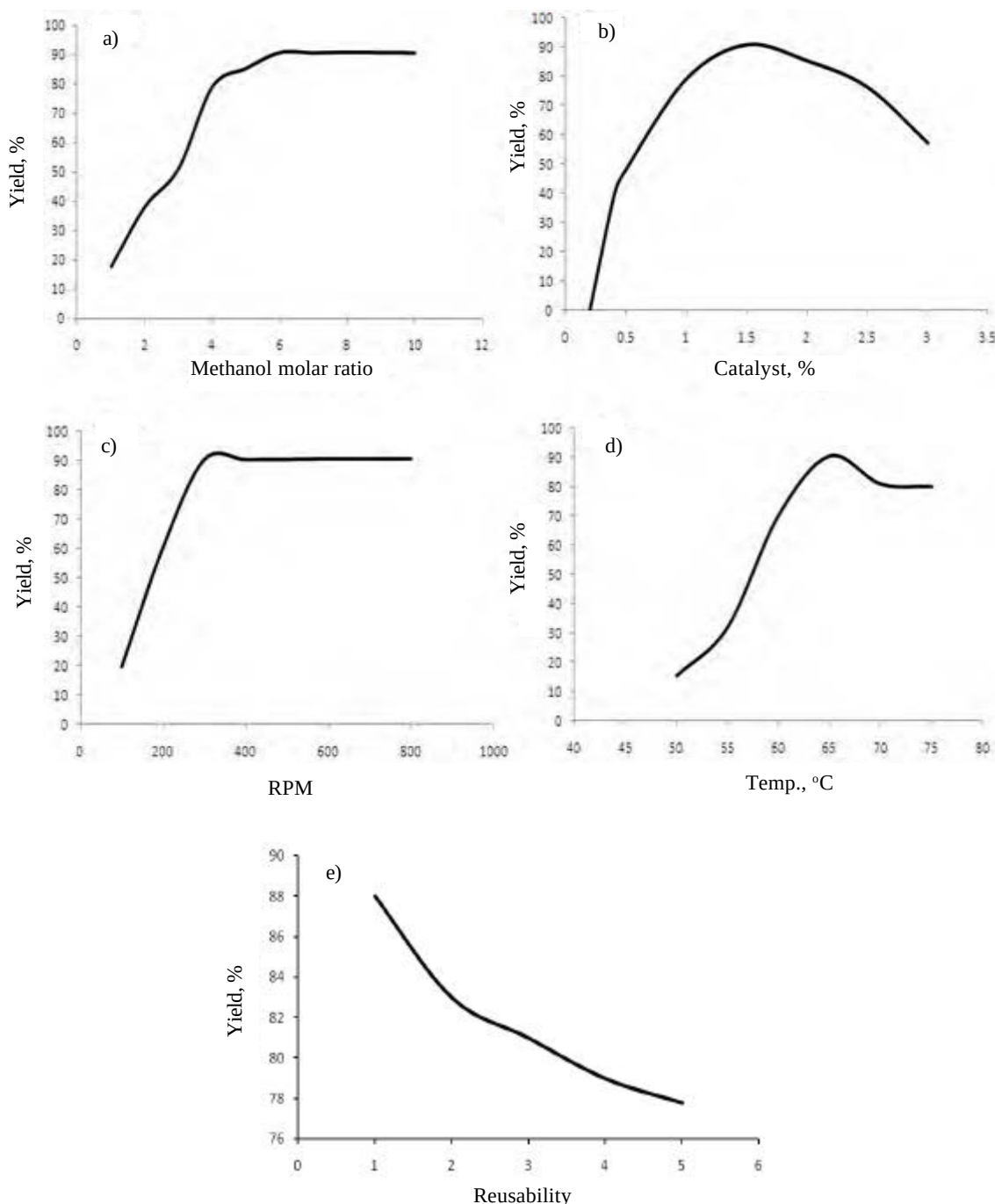


Fig 6—Transesterification reaction using MAH catalyst with pongamia oil: a) Effect of methanol molar ratio; b) Effect of catalyst; c) Effect of RPM; d) Effect of temperature; and e) Reusability

Proposed Method

Molar ratio of methanol to vegetable oil affect ester formation because conversion and viscosity of produced ester depend on it. Stoichiometric molar ratio of methanol to oil is 3.0. But when mass transfer is limited due to problems of mixing, mass transfer rate seems to be slower than reaction rate, so the conversion can be elevated by

introducing an extra amount of reactant methanol to shift equilibrium to the right-hand side. Higher molar ratios result in greater ester conversions in a shorter time^{17,18}. Optimum molar ratio of methanol to pongamia oil is 6.0 (Fig. 6a), beyond which added methanol does not enhance significantly the ester conversion. In addition, conversion increased sharply with reaction time, a nearly maximum

conversion (90.8%) was obtained after 4 h reaction time. When increasing the amount of catalyst, 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 catalyst amount is not sufficient, maximum conversion cannot be reached. In most cases, NaOH or KOH (0.5-1.5% w/w) had been used in alkaline methanolysis.

In the present work, reaction profiles indicate that ester conversion increased with 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%). However, conversion to biodiesel decreased with increase of catalyst amount beyond 1.5% (2.0: 85.0%, 2.5: 83.7%), possibly due to mixing problem of reactants, products and solid catalyst. Maximum ester conversion (90.5%) reached when 1.5% catalyst was added. Mixing is very important for transesterification of pongamia oil, because pongamia oil and methanol solution are immiscible and reactants and solid catalyst are separated in heterogeneous system. Generally, a more vigorous stirring speed causes better contact among reactants and solid catalyst, resulting in the increase of reaction rate. Stirring of reactants (Fig. 6c) had a significant effect on transesterification of pongamia oil (100 rpm: 19.5%, 200: 60.2%, 300: 90.2%, 400: 90.2%, and 500: 90.3%). Adding solid catalyst to reactants while stirring facilitated chemical reaction, and reaction started quickly. It quickly established a very stable emulsion of oil, MeOH and catalyst. When stirring speed was over 300 rpm, there was no significant enhancement in conversions (above 90.2%). Effect of reaction temperature on ester conversion was studied at six different temperature (50, 55, 60, 65, 70 and 75°C). Transesterification proceeded slowly at 50°C, where conversion was 19.6% in a 4 h reaction. Lower temperatures resulted in a drop of ester conversion because only a small amount of molecules were able to get over the required energy barrier. Ester conversion increased up to 90.4% in 4 h reaction by increasing reaction temperature to 65°C (55°C: 31.8%, 60°C: 70.2%). Thus, optimum temperature for ester preparation was found to be 65°C (Fig. 6d), which was near the boiling point of anhydrous methanol. Conversion fell to 80.0% between 70-75°C (70°C: 80.9%, 75°C: 80.0%), probably because molar rate of methanol to oil decreased when methanol reactant volatilized into gas phase above 65°C, the boiling point of pure methanol. Catalytic (MAH) transesterification of pongamia oil with

Table 2—Gas chromatography result of pongamia biodiesel

S. No	FAME Profile	Pongamia biodiesel	
		Using MAH ^a	Using NaOH
1	16:0	0.525	0.489
2	16:1	-	-
3	18:0	10.37	9.94
4	18:1	58.69	61.72
5	18:2	8.81	8.009
6	18:3	1.29	1.172
7	20:0	2.23	1.13
8	20:1	5.7	4.39
9	22:0	1.18	1.19
10	24:1	1.47	1.67

^aMAH-Mg-Al hydrotalcite

methanol resulted in conversion of biodiesel to 90.8%. Catalysts was separated after 4 h from reaction mixture and washed with double distilled water and finally washed with acetone and dried in an oven at 50°C. Reusability of catalyst for transesterification in subsequent reaction cycles (Fig. 6e) indicated that after 5th cycle of transesterification, biodiesel conversion dropped to 77.8%.

The obtained biodiesel was analyzed by a Shimadzu GC 2010 using C₄ – C₂₄ FAME MIX., as standard. All relative percentages determined by GC for each FAME sample are means of triplicate runs. Using proposed method (Table 2), composition (%) of five important FAMES found in biodiesel samples [palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3)] acid methyl esters were determined and reported. Table 2 also shows that linoleic and oleic acid methyl esters are the major components in synthesized biodiesel samples. GC study shows clearly that catalyst MAH is efficient in transesterification of pongamia oil to biodiesel.

Conclusions

For transesterification of pongamia oil with methanol, calcined MAH was found to be effective as a solid base catalyst. Maximum POME (90.8%) was obtained under following optimized reaction conditions: methanol to pongamia oil molar ratio, 6.0; catalyst (w/w of oil), 1.5%; stirring speed, 300 rpm; reaction time, 4 h; and temp., 65°C. MAH catalyst has a distinctive advantage in that it shows high catalytic activity, and is easy to separate at the end by simple filtration.

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