Investigation of Kinetic Parameters for Methanolysis of Para Rubber Seed Oil by CH$_3$/SO$_3$H-MCM41 Catalyst

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The methanolysis of para rubber seed oil in the presence of the catalyst CH$_3$/SO$_3$H-MCM-41 was investigated with the aim of improving catalytic stability. Using 5.06 wt% of CH$_3$/SO$_3$H-MCM-41, we obtained a 95 % yield of the fatty acid methyl ester. A kinetic study was conducted in which the reaction time and temperature were varied in the range of 30-150 min and 120-160 °C, respectively. The activation energy, pre-exponential factor, and reaction order were determined. It was shown that the reaction approached first order kinetics (n = 1.08, R$^2 > 0.99$). The activation energy (E$_a$) and frequency factor (A) were found to be 29.2 kJ/mol and 129.3 min$^{-1}$ (mol/g)$^{-0.0807}$, respectively.

Key Words

Kinetic, Biodiesel, Para rubber seed oil

1. Introduction

The finite nature of fossil fuel resources has the potential to lead to an energy crisis unless alternatives are found. Moreover, the combustion of such fuels has a grave environmental impact, releasing many pollutants into the atmosphere. Sustainable and renewable energy sources are thus of huge importance for the replacement of fossil fuels. Biodiesel is an example of a promising renewable energy source as it is non-toxic, readily available, eco-friendly and biodegradable. Currently, biodiesel is produced from edible oils such as palm oil, soybean oil, and sunflower oil. However, the use of edible oils has a direct effect on the supply chain of the food industry. For this reason, non-edible oils such as Jatropha curcas oil, sea mango oil, castor oil, and tobacco oil have drawn attention. Para rubber seed oil (RSO) is non-edible oil that is of particular interest for biodiesel production as the rubber seed contains up to 40-60 wt% oil. In Thailand, more than a million kilograms of para rubber seed is discarded at the cultivation area. Therefore, utilization of para rubber seed oil (RSO) as a raw material for biodiesel production has huge potential. Rubber seed oil consists of 10.2 % palmitic acid (C16:0), 8.7 % stearic acid (C18:0), 24.6 % oleic acid (C18:1), 39.6 % linoleic acid (C18:2) and 16.3 % linolenic acid (C18:3). The amount of free fatty acid (FFA) in RSO is relatively high, which causes saponification problems in the presence of alkaline catalysts. Acid catalysts are thus used to prevent such reactions. Many types of acid catalyst have been employed for biodiesel production including ferric alginate beads, aminophosphonic acid resin D418, acid-activated carbon and sulfonic acid-functionalized SBA-15 catalysts. In this work, CH$_3$/SO$_3$H-MCM-41 (Fig. 1) is used as a catalyst for biodiesel production from RSO as it offers advantageous characteristics such as high surface area, high activity in transesterification and the potential for reuse. The presence of a methyl group (-CH$_3$) at the active site (SO$_3$H-group) encourages efficient mass transfer and maintains the durability of the catalyst due to the anti-adsorption of polar molecules such as glycerol and water on the surface of the catalyst during transesterification reactions. In previous work, methanolysis of RSO using CH$_3$/SO$_3$H-MCM-41 as a catalyst was optimized by a Box-Behnken design. A 95 % yield of the fatty acid methyl ester (FAME) was obtained using the optimum conditions (5.06 wt% catalyst, 153 °C, 120 min, 0.266 moles 3-mercaptopropyl (methyl) dimethoxysilane)}
Kansedo et al. and Kiakalaieh et al. have previously investigated the kinetics of biodiesel production from sea mango oil and waste cooking oil using sulfated zirconia and heteropoly acid catalysts. The results revealed first order kinetics with activation energies ($E_a$) of 36.03 and 53.99 kJ/mol at 90-180 °C and 50-70 °C respectively. However, the kinetics of RSO methanolysis in the presence of CH$_3$/SO$_3$H-MCM-41 has been not reported. In this research, the kinetic parameters of RSO methanolysis are investigated.

2. Experimental

2.1 Materials

Rubber seed oil was obtained by cold press extraction of para rubber seed (Hevea brasiliensis) from the Ranong province (Southern Thailand). RSO contains 14.5 wt% free fatty acid, 0.041 wt% water, and 2.3 wt% unsaponified matter. Tetraethyl orthosilicate (TEOS, 99 %), MPMDS (95 %) and tetramethylammonium hydroxide (TMAOH, 25 wt% in water) were supplied from Sigma Aldrich. Cetyltrimethylammonium bromide (CTAB, 98 %) was obtained from APS Methanol (AR grade), hydrogen peroxide (H$_2$O$_2$, 30 wt% in H$_2$O) from QR and Amberlyst-15 from Sigma-Aldrich. Activated carbon was purchased from Fluka which was treated with acid using the sulfonation method. All chemicals were used as received.

2.2 Synthesis of CH$_3$/SO$_3$H-MCM-41 catalyst

CH$_3$/SO$_3$H-MCM-41 was synthesized via the one-step co-condensation of TEOS and MPMDS in the presence of CTAB following the procedure of Diaz et al. The molar composition of reaction mixture was 0.734 TEOS: 0.266 MPMDS: 0.12 CTAB: 0.27 TMAOH: 18.8 CH$_3$OH: 77.7 H$_2$O. CTAB (2.2 g) was first dissolved in a mixture of deionized water (70.0 g) and methanol (32.0 g) and stirred for 30 min at 30 °C. A mixture of TEOS and MPMDS was added dropwise followed by TMAOH (1.0 g) as co-structuring agent. The reaction was stirred for a further 16 h. The mixture was then subjected to hydrothermal treatment at 95 °C for 48 h, filtered, and dried to obtain solid product. The solid (1.5 g) was refluxed with a mixture of ethanol (205 mL) and aqueous HCl (20 mL of 37 wt% HCl) at 70 °C for 24 h to remove the CTAB template and then dried at 70 °C to obtain CH$_3$/SH-MCM-41. The sulfhydryl group (SH) was converted to the sulfonic acid group ($-$SO$_3$H) by the oxidation of CH$_3$/SH-MCM-41 (1.0 g) with 30 wt% aqueous H$_2$O$_2$ (20 mL) to obtain the CH$_3$/SO$_3$H-MCM-41 catalyst. The catalyst was obtained from the mixture by filtration.

2.3 Characterization of catalyst

The physical properties of the CH$_3$/SO$_3$H-MCM-41 catalyst were characterized using a N$_2$ sorption technique on an Autosorb-iQc instrument (Quantachrome, USA). The surface area was calculated from N$_2$ isotherm data using the BET model. Pore volume and pore diameter were obtained using the BJH model. The small-angle X-ray scattering (SAXS) was carried out using a Rigaku TTRAX III X-ray diffraction spectrophotometer operating at a low angle using Cu K$_\alpha$ radiation in the 2$\theta$ angle range of 1-10°. The thermal stability of the catalyst was determined using a Perkin-Elmer TGA7 instrument in the temperature range 100- 800 °C (heating rate of 10 °C/min) under air flow. The number of SO$_3$H-groups on the MCM-41 surface was determined by a back titration technique. The sulfur content of the catalyst was quantified using a Thermo Scientific™ FLASH 2000 series CHNS/O elemental analyzer.

2.4 Comparison of catalytic activity in the RSO methanolysis reaction

The activity of the CH$_3$/SO$_3$H-MCM-41 catalyst was compared to that of other acid catalysts commonly used in the RSO methanolysis reaction: Amberlyst-15 and acid-activated carbon. The acid-activated carbon was prepared by sulfonation reaction of activated carbon. A mixture of activated carbon (5 g) and 15 % aqueous H$_2$SO$_4$ (100 mL) was heated to 100 °C for 24 h under N$_2$. The solid was then filtered, washed with deionized water, and dried in an oven at 110 °C.

The methanolysis reaction was carried out in an autoclave reactor (Amar Equipments, India) to which a mixture of RSO (200 g), methanol (120 g, 1:16 molar ratio of oil to methanol) and catalyst (1.012 g, 5.06 wt.% with respect to oil) was charged. A schematic diagram of the autoclave reactor employed is shown in Fig. 2. The reaction was carried out at a stirring speed of 600 rpm for various reaction times and temperatures. After the reaction was complete, running water was used to cool the system. The residual methanol and catalyst were separated by evaporation and filtration, respectively. The yield of FAME was determined by gas chromatography according to the standard testing method EN 14103.
2.5 Kinetic study of methanolysis

The kinetic parameters of the RSO methanolysis reaction were investigated by varying the reaction temperature and time in the range of 120-160 °C and 30-150 min respectively. The oil to methanol molar ratio was maintained at 1:16, at which levels it was assumed that methanol would be present in excess. The reaction order with respect to oil concentration was thus determined.

3. Results and Discussion

3.1 Characterization of catalyst

The pore structure of the catalysts can be represented by N2 isotherms. IUPAC type IV isotherms of MCM-41 and CH3/ SO3H-MCM-41 were obtained (Fig. 3). The hysteresis loop (H1) of MCM-41 corresponds to cylindrical pore channels where as hysteresis loop (H2), disordered porous structure, were presented by CH3/ SO3H-MCM-41. The physical properties of the catalyst are reported in Table 1. The presence of sulfonic and organic molecules on the MCM-41 structure resulted in decreased surface area, pore volume, and pore diameter as the pores of MCM-41 were occupied by sulfonic acid groups (-SO3H).

The SAXS pattern of MCM-41 is presented in Fig. 4. Three diffraction peaks at 2θ of 2.2°, 3.8° and 4.4° were designated as (1 0 0), (1 1 0), and (2 0 0) planes. However, the SAXS pattern of CH3/ SO3H-MCM-41 did not share the two diffraction peaks at 2θ of 3.8° and 4.4°, which indicates that the long-range hexagonal regularity of MCM-41 was greatly reduced by MPMDS. This phenomenon could be attributed to the steric effect of the alkyl sulfonic chains (CH3/ SO3H). Such chains possibly hinder the pore arrangement during the preparation of MCM-41.

The results of a thermogravimetric study of CH3/ SO3H-MCM-41 are shown in Fig. 5. The TG-DTG profile of CH3/ SO3H-MCM-41 shows a two-step weight loss at temperatures of 300 and 500 °C, which are believed to represent the decomposition of the thiol group (-SH) and the sulfonic acid group (SO3H) respectively. The high decomposition temperature (up to 300 °C) suggests that CH3/ SO3H-MCM-41 will have thermal stability under methanolysis conditions.

The acid capacity and sulfur content of CH3/ SO3H-MCM-41 were determined by titration and elemental analysis, respectively. The results are summarized in Table 2. The thiol conversion was calculated using Eq. 1.

\[
\text{Thiol conversion (\%)} = \frac{\text{mol of SO3H titrated}}{\text{mol of sulfur analyzed}} \times 100
\]
The thiol conversion of the obtained catalyst was found to be 95.30%, suggesting that the majority of the sulfhydryl (SH-) groups were converted to sulfonic acid (SO₃H).

### 3.2 Comparison of catalytic activity

The activity of each catalyst in RSO methanolysis was compared in reactions conducted for 120 min at 153°C. Fig. 6 shows the yield of FAME after the first use, and subsequent uses, when methanolysis was carried out using CH₃/SO₃H-MCM-41, Amberlyst-15 and acid-activated carbon catalysts. The results show that CH₃/SO₃H-MCM-41 outperforms the other catalysts in terms of both catalytic activity and reusability. The yield of FAME decreased only 1.5% after being reused twice.

### 3.3 Kinetic modeling

The kinetic parameters of RSO methanolysis were investigated. Fig. 7 shows the conversion of RSO to biodiesel over time at various reaction temperatures.

The initial reaction rate increased with an increase in reaction temperature. To determine the reaction rate, the equation was summarized and expressed as Eq. 2, which was obtained from integral method. Thereafter, the various reaction times were placed in linear equation (Eq. 2) to obtain the reaction rate constant (k).

\[
\frac{1 - (1-X)^{1-n}}{1-n} = Kt
\]

where \( X \) is the conversion of RSO to biodiesel, \( t \) is the reaction time (min), \( n \) is reaction order, \( K = k/\left(C_0\right)^{1-n} \) (where \( k \) is the reaction rate constant (min⁻¹(mol/g)⁻ⁿ), and \( C_0 \) is the initial concentration of the reactant (mol/g)).

A trial and error method was applied for the calculation with the initial value of \( n = 0 \). Fig. 8 presents the relationship between \( [1-(1-X)^{1-n}]/(1-n) \) and \( t \) at different reaction temperatures.

From the calculation, the value of \( n = 1.0807 \) was determined to fit well with experimental data. The correlation coefficient \( R^2 \) was shown to be greater than 0.99 in all cases for the plot between \( [1-(1-X)^{1-n}]/(1-n) \) and \( t \) at different reaction temperatures.

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The Arrhenius relationship (Eq. 3) was used to determine the activation energy (Eₐ) and frequency factor (A) for the reaction, making use of the reaction temperature and rate constant.

\[
lnk = -\frac{E_a}{RT} + lnA
\]
where $k$ is the reaction rate constant, $A$ is the frequency factor, $E_a$ is the activation energy, $T$ is the reaction temperature, and $R$ is the gas constant ($8.314 \text{ J/Kmol}$).

Based on data in Table 3 and the linear equation of the Arrhenius relationship in Eq. 3, $\ln k$ versus $1/T$ was plotted as shown in Fig. 9.

A linear fit ($R^2 = 0.9800$) was obtained for the Arrhenius plot. From this, the activation energy ($E_a$) was calculated to be $29.2 \text{ kJ/mol}$ and frequency factor ($A$) found to be $129.3 \text{ min}^{-1}(\text{mol/g})^{-0.0807}$.

### Table 3 Reaction rate constant at different temperatures

| Temperature (°C) | Rate constant ($\text{min}^{-1}(\text{mol/g})^{-0.0807}$) | $R^2$ |
|------------------|---------------------------------------------------------|-------|
| 120              | 0.0175                                                  | 0.9986|
| 140              | 0.0244                                                  | 0.9991|
| 160              | 0.0401                                                  | 0.9984|

### 4. Conclusion

The activity and stability of the catalyst CH$_3$/SO$_3$H-MCM-41 in RSO methanolysis was studied. The catalyst was shown to have good catalytic activity giving FAME in a yield of over 95 %. Moreover, the catalyst performance was only slightly diminished after being reused twice. Following a kinetic study, the reaction was shown to approach first order kinetics ($n=1.08$). The activation energy ($E_a$) and frequency factor ($A$) were found to be 29.2 kJ/mol and 129.3 min$^{-1}(\text{mol/g})^{-0.0807}$, respectively ($R^2 = 0.98$).

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