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Research paper

# Esterification of oleic acid and high acid content palm oil over an acid-activated bentonite catalyst

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ABSTRACT

The esterification of oleic acid with methanol and that of a high acid content palm or Jatropha oil with methanol or ethanol were evaluated with different acid-activated bentonite catalysts. Na-bentonite was acid-activated by either $H_2SO_4$ at varying concentrations from 0.25 to 2.0 M or with 0.5 M $HNO_3$. The characterization of the raw and acid-activated bentonite was then conducted by nitrogen adsorption, XRD, XRF, SEM and acid–base titration analysis. The 0.5 M $H_2SO_4$ acid-activated bentonite exhibited the best catalytic activity with 100% methyl oleate yield and 99% free fatty acid conversion in the esterification of pure oleic acid and oleic acid in palm oil with methanol, respectively. Both conversions were higher than that obtained from esterification via commercial Amberlyst-15 catalyst.

## 1. Introduction

Because of the limited supply of non-renewable fossil fuel and the corresponding increase in diesel oil price, an increasing trend in current research has centered upon developing alternative fuels to petroleum. Among the different possible resources, biodiesel is one popular alternative as a renewable replacement of the non-renewable petroleum diesel. Biodiesel is comprised of the alkyl esters of fatty acids and is produced from either the transesterification of triglycerides or the esterification of free fatty acids (FFA) with short chain alcohols in the presence of a catalyst to produce fatty acid alkyl esters (biodiesel) and glycerol (Ma and Hanna, 1999; Pintoa et al., 2005). The advantages of biodiesel are that it is biodegradable, non-toxic to nature and has a low emission profile aided by being essentially free from sulfur (Dorado et al., 2003; Labeckas and Slavinskas, 2006; Ulusoy et al., 2004).

Esterification has been performed using conventional homogeneous acidic catalysts, such as $H_2SO_4$, HCl and $HNO_3$ (Koono et al., 1993) since it gives a high conversion level of alkyl esters in a short time. However, the catalyst is difficult to remove from the product and is inconvenient to regenerate. Therefore, it would be desirable to perform the esterification reaction with a heterogeneous acidic catalyst. These catalysts can be separated easily from the system at the end of the reaction and can also be reused. A large number of heterogeneous acidic catalysts have been reported in the literatures, including ion-exchange resins (Russbueldt and Hoelderich, 2009), heteropolyacids (Xu et al., 2008), sulfated zirconia (Nuttapol et al., 2011), polymers with sulfonic acid groups (Caetano et al., 2009; Melero et al., 2010), heteropolyacids immobilized on silica (Caetano et al., 2008), zeolites (Carmo et al., 2009) and clays (Moraes et al., 2011; Nascimento et al., 2011; Wypych et al., 2011).

The use of various clays as a catalyst has expanded rapidly in recent years due to their advantageous properties, such as their mechanical and thermal stabilities, their high specific surface area and ion-exchange capacity (Lagaly and Bergaya, 2001). Major clay minerals in bentonite (Bent) are smectites such as montmorillonite (Mt), beidellite, saponite, nontronite, and hectorite. Bent might also contain other clay minerals and nonclay minerals (Grim and Guven, 1978; Murray, 2000). Each smectite is comprised of a 2:1 layer, containing two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet (Grim and Guven, 1978). The net negative electric charge of the 2:1 (TOT) layers, which arise from the isomorphic substitution of $Al^{3+}$ with $Fe^{2+}$ or $Mg^{2+}$ in the octahedral sites and of $Si^{4+}$ with $Al^{3+}$ in the tetrahedral sites, is balanced by the presence of cations, such as $Na^+$ and $Ca^{2+}$, located between the layers and surrounding the edges. Bent may be used either in its natural form or after some physicochemical treatments, such as acid-activation, ion-exchange and calcination, according to the desired application (Breen and Watson, 1998; Lagaly and Bergaya, 2001). Acid-activated Bent powders have been used in many applications, such as adsorbents, catalysts and bleaching clay, also in the preparation of pillared clay, organoclay and nanocomposites (Hart and Brown, 2004). Some physicochemical properties of Bent, such as the crystallinity of its smectite, chemical composition, ion-exchange capacity, adsorption capacity, selectivity, surface acidity and catalytic power change, depend on the activation conditions (Komadel et al., 1990).

The first aim of this study was to investigate the variation in some of these properties, namely the chemical composition, morphology, specific surface area, pore volume and pore diameter of Bent with

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different acid activations. The second aim was to study the resultant catalytic activity of the acid-activated Bent in the esterification of oleic acid or the FFA in *Jatropha curcas* oil or palm oil with methanol and to compare their catalytic activities with that of the commercial Amberlyst-15 catalytic resin.

## 2. Experimental

### 2.1. Chemicals

Oleic acid (Aldrich), refined palm oil (Olein Co., Ltd., Thailand), *Jatropha curcas* oil (Lam Soon (Thailand) Public Company Limited, Thailand), and methanol or ethanol (Merck), were used as the reactants for the esterification reaction. $H_2SO_4$ (Merck) and $HNO_3$ (Merck) were used for the acid activation. The commercial Amberlyst-15 in dry form (Rohm & Hass, France) was dried in an oven at 100 °C for 24 h before use.

### 2.2. Catalyst preparation

#### 2.2.1. Clay source

The Bent source of this study was obtained from Siam Valclay Co., Ltd. (Thailand) in the Na form, and had a chemical composition of (mass/mass) $SiO_2$ 68.5%, $Al_2O_3$ 17.0%, $TiO_2$ 1.1%, $Fe_2O_3$ 4.9%, $Na_2O$ 3.0%, $K_2O$ 1.3%, CaO 0.9% and MgO 2.8%. In addition, kaolin was obtained from the Industrial Mineral Development Ltd. (Thailand), and had a chemical composition of (mass/mass) $SiO_2$ 48.5%, $Al_2O_3$ 38.5%, $TiO_2$ 0.9%, $Fe_2O_3$ 0.7%, $Na_2O$ 0.1%, $K_2O$ 1.1%, CaO 0.1% and MgO 0.1%, as determined by X-ray fluorescence spectrometry (XRF) analysis.

#### 2.2.2. Clay acid activation

The $Na^+$-Bent sample was prepared by acid-activation with either $H_2SO_4$ at varying concentrations from 0.25 to 2.0 M or with 0.5 M $HNO_3$. Acid-activated Bent was prepared by refluxing dried Bent powder with $H_2SO_4$ or $HNO_3$, as appropriate, at 120 °C for 1 h at a Bent:acid solution ratio of 1.0 g:30 ml. At the end of each run, the mixture was separated by centrifugation and then the harvested Bent was refluxed twice more as above with a fresh sample the same acid type/concentration. Finally, the acid-activated Bent was dried in an oven at 100 °C overnight. The activated-Bent samples with 0.25, 0.5, 1.0 and 2.0 M $H_2SO_4$ were denoted as TBS-0.25, TBS-0.5, TBS-1.0 and TBS-2.0, respectively, whilst that activated with 0.5 M $HNO_3$ was denoted as TBN-0.5. Acid-activated kaolin samples were prepared in the same way except only with 0.5 M $H_2SO_4$ or 0.5 M $HNO_3$, and were denoted as TKS-0.5 and TKN-0.5, respectively.

#### 2.2.3. Catalyst characterization

The X-ray diffraction (XRD) pattern of each catalyst preparation was determined by a Rigaku, Dmax 2200/Ultima$^+$ diffractometer equipped with a monochromator and Cu Kα radiation. The specific surface area was calculated using the BET method, and the pore volume and pore size distribution using the BJH method, based on the desorption data obtained by a BEL Japan BELSORP-mini 28SP adsorptometer. Philips, PW 2400 model X-ray fluorescence by dispersive wavelength spectrophotometer (XRF) was used to investigate the chemical composition of clay. The morphology of the catalyst particles was identified by scanning electron microscopy (SEM) using a JSM-5410 LV. The acidity of activated Bent samples was identified the chemical band variations by using Nicolet 6700 FT-IR model, Thermo Scientific and was quantified using standard acid-base titration, where a known mass (~0.05 g) of the sample was added to 15 ml of 2.0 M NaCl solution and allowed to equilibrate for 30 min. Thereafter, it was titrated by the dropwise addition of 0.01 M NaOH (aq) (Mbaraka et al., 2003).

### 2.3. Esterification

#### 2.3.1. Esterification of oleic acid

The reaction was carried out in a 100 mL stainless steel autoclave reactor with a stirrer using oleic acid and methanol as starting materials with 10% (mass/mass) of catalyst (based on the reactant mass) and stirred at 200 rpm. After completion of the reaction, the used catalyst was separated from the liquid phase by centrifugation. The reaction mixture was analyzed using a Varian CP-3800 gas chromatography with a CP-8 column, following the EN 14105:2003 procedure. The content of the methyl ester yield was calculated based on the eicosane internal standard. The methyl oleate yield is reported as the mean ± 1 standard deviation (SD), derived from four independent repeats.

#### 2.3.2. Esterification of vegetable oil

The esterification of 85% (mass/mass) refined palm oil mixed with 15% (mass/mass) oleic acid, Jatropha oil or waste cooking palm oil, was performed in a 100 mL round-bottom flask equipped with a magnetic stirrer and water cooling condenser at various molar ratios of oil to methanol (1:9, 1:23, 1:30, 1:50 and 1:70), reaction times (15, 30, 45 and 60 min) and catalyst amounts (0.125, 0.25, 0.5, 1, 5 and 10% (mass/mass)). After reaction, the FFA content in the sample was determined by the titration technique following the ASTM D5555-95. The FFA conversion is shown as the mean ± 1 SD, derived from four independent repeats.

## 3. Results and discussion

### 3.1. Characterization of catalysts

#### 3.1.1. XRD analysis

From the obtained XRD patterns (Fig. 1), the raw Bent consisted of Mt (d001-value = 1.29 nm) and a substantial amount of the crystalline quartz (Q), similar to that previously reported by Noyan et al. (2007). The crystallinity of Mt decreased as the Bent was activated with increasing concentration of $H_2SO_4$, being essentially lost after activation with 1 and 2 M $H_2SO_4$. In addition, the intensity of the quartz reflection decreased with increasing $H_2SO_4$ concentration. In contrast, the XRD pattern of TBN-0.5 still revealed the Mt and quartz phases that were almost the same as in the raw Bent, except that the lazulite (L) phase

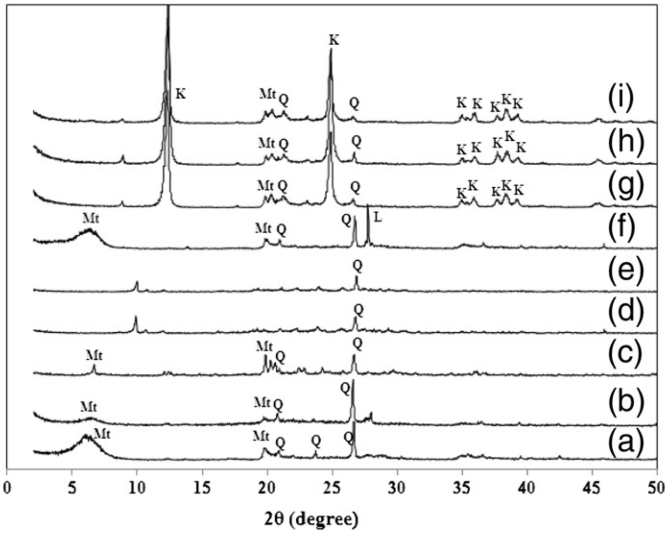

**Fig. 1.** Representative (of four independent repeats) XRD patterns of (a) raw Bent, (b) TBS-0.25, (c) TBS-0.5, (d) TBS-1.0, (e) TBS-2.0, (f) TBN-0.5, (g) raw kaolin, (h) TKN-0.5 and (i) TKS-0.5. Mt, Q, L and K represent montmorillonite, quartz, lazulite and kaolinite, respectively.