Abstract—A natural low silica bentonite was used as adsorbent for purifying biodiesel. The concentrations of sulfuric acid to activate bentonite were studied. Its composition and surface area was characterized by XRF and BET techniques. The high performance of activated bentonite was obtained by activating natural low silica bentonite with 0.1 M H₂SO₄ at 100 °C for 1 hour. By using 5% of activated bentonite with 120-200 mesh size, 47% of glycerin could be removed, and the adsorption isotherm was fit with Freundlich isotherm. Activated low silica bentonite was showed to be an efficiency adsorbent for purifying biodiesel and can be used to replace water washing.

Keywords—Biodiesel, Adsorption, Bentonite Clay

I. INTRODUCTION

The impurities left in the crude biodiesel after the reaction are dangerous to any combustion system and must be removed. The longest standing method for purification is water washing method. This method works very well, however, wastewater becomes difficult and costly to treat and dispose. Dry wash with adsorbent is an alternative method to biodiesel purification. The adsorbent has highly developed structure of pores on the surface of which is sites with easily trapped and released ions.

Bentonite is an absorbent which is mainly composed of montmorillonite. It is 2:1 type aluminium phyllosilicate, the unit layer structure of which consists of one octahedral sheet between two tetrahedral sheets. The octahedral sheet results in a net negative charge on the clay surfaces. The charge imbalance is offset by exchangeable cations of H⁺, Na⁺ or Ca²⁺ on the layer surfaces. In aqueous solutions, water molecules are intercalated into the interlamellar space of bentonite, leading to an expansion of the minerals. The chemical nature and pore structure of bentonite generally determine their adsorption ability.

Adsorption properties of bentonite are a function of the content of montmorillonite and the number of interlayer cations. In order to remove impurities and various exchangeable cations, bentonite was modified such as acid treatments can often replace exchangeable cations with H⁺ ions, followed by dissolution of the tetrahedral and octahedral sheets. Octahedral cations of Al³⁺, Fe²⁺, Fe³⁺, and Mg²⁺ can be depleted by acid treating the clay minerals [1]. The ion exchange capacity of clay minerals is attributed to structural defects, broken bonds. Also, acid treatment of bentonite has been shown to create enhanced mesoporosity depending on acid concentrations and treatment time which is important structural changes and partial decomposition of montmorillonite.

II. EXPERIMENTAL

A. Materials and preparation of acid activation bentonite

The natural low silica bentonite from the deposit of Lopburi Thailand was provided by Thai Nippon chemical industry Co.,Ltd. To activate this low silica bentonite, 50 g raw bentonite was slowly added to 200 ml 0.1-1.0 M H₂SO₄ in 500 millilitres of round bottom flask equipped with condenser. The reaction was heated to 100 °C for 1 h, 6 h, and 12 h, respectively. The activated bentonite slurry obtained was washed repeatedly with distilled water until the pH reached 6-7. The clay was dried in oven at 110 °C for 6 h and pulverized to pass through a sieve with a mesh size of 60 mesh, 80 mesh, 100 mesh, 120 mesh, and 200 mesh. Structure characteristics were studied by XRF, BET, and FTIR techniques.

B. Preparation of crude biodiesel by transesterification of refined palm oil

Five hundred grams of refined palm oil was added into 1000 ml of round bottom flask equipped with condenser. After the oil was heated to 65 °C, the solution of sodium hydroxide (5.0 g) in methanol (144.82 ml, 6:1 molar ratio of methanol to oil), was slowly added into the reaction and then the mixture was heated to 65°C for 1.50 h. The mixture was later brought to further purification.

C. Purification of crude biodiesel using activated bentonite adsorbent

Fifty grams of crude biodiesel were treated with 1, 5 and 10 %wt of activated bentonite adsorbents. The experiment was performed for 10 min with stirring rate of 200 rpm. The adsorbents were removed by filtration and the amount of soap content was determined by titration method.
D. Calculation of soap content

To the 250 ml of Erlenmeyer flask, biodiesel sample (5 g), isopropyl alcohol (100 ml) and 2 ml of 1% phenol red indicator solution were added. The mixture was subjected to titrate with 0.01 M HCl the colorless was occurred. Then 1 ml of 0.04% bromophenol blue indicator solution was added. The mixture was titrated with 0.01 M HCl until the yellow was occurred. The soap content in the biodiesel was calculated by using the equation:

\[
\text{Soap content (ppm)} = \frac{B \times 0.01 \times 303.4}{W \times 1000}
\]

Where:  
B = volume of HCl used in second step (ml)  
W = weight of crude biodiesel (g)

III. RESULT AND DISCUSSION

A. The adsorption efficiency of acid activated bentonite

The most important parameters affecting the efficiency of an absorbent are sulfuric acid treatment, particle size [2], activating time and amount of adsorbent. In order to study the combined effect of these factors, experiments were performed at different combinations of the physical parameters. The purified biodiesel was analyzed to determine residual soap content.

The effect of acid strength on soap removed and acid value were shown in Fig. 1 and Fig. 2. The results showed that 0.10–1.0 molar concentrations of acid gave similar results of soap removal, which acid value of biodiesel was proportional to acid strength. Due to the acid value accordingly to ASTM D6751-02 is 0.5 mgKOH/g Oil maximum [3]. As a result, sulphuric acid 0.1, 0.25, 0.5, 0.75, and 1.00 M of acid value were 0.34, 0.47, 0.57, 0.62, and 0.71 mgKOH/g Oil, respectively. The acid value was dramatically increased when the acid concentration was increased. In this experimental condition, 0.1 and 0.25 M H₂SO₄ could be used to activate bentonite. As the results of soap removed, 0.1 M of H₂SO₄ was found to be an appropriate concentration for activating bentonite.

The effect of particle size of activated bentonite was determined by varying in mesh size the range of 60-200 mesh. As shown in Fig. 3, % residue soap removal increased with particle size decreased. Significantly high adsorption was achieved at 120-200 mesh (54.93%). This can be explained by an increasing of surface area and better accessibility to pores.

The activating time was effected to soap removed. As can be observed in Fig. 4, the activating time at 1h, 6h, and 12h did not give significant different for soap removal. Therefore, 1 h of activating time is the optimal condition in this study. The effect of adsorbent dosage was studied by increasing the amounts of adsorbent from 1 to 10% activated bentonite. The percent residue soap removal for 5% activated bentonite (47.17%) is greater than 1% activated bentonite (39.61%) whereas 10% activated bentonite (50.14%) is nearly same 5% activated bentonite. Therefore, activating time at 1 hr and 5% activated bentonite was the most appropriate condition during the activated low silica bentonite purification.

Regarding adsorption isotherms, Fig. 5 and 6 showed a comparison of Langmuir and Freundlich isotherms [4], activated bentonite was better fit to Freundlich model because the r² value (0.9942) was closer to 1. This adsorption behavior indicated that the adsorption took place on a heterogeneous
surface. The overall adsorptive performance was dominated as a physical adsorption process.

![Fig. 5 Langmuir adsorption isotherms of activated bentonite](image)

![Fig. 6 Freundlich adsorption isotherms of activated bentonite](image)

B. Characterization of Raw and Acid-activated bentonite

The specific surface area ($S_{BET}$), pore volume ($V_p$) and pore diameter ($d_p$) of raw bentonite and activated bentonite was calculated using the BET method.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>SURFACE PROPERTIES OF RAW BENTONITE AND ACTIVATED BENTONITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>$S_{BET}$ [m$^2$ g$^{-1}$]</td>
</tr>
<tr>
<td>Raw</td>
<td>47.559</td>
</tr>
<tr>
<td>Activated</td>
<td>56.866</td>
</tr>
</tbody>
</table>

The obtained value was shown in Table I. A result show that the specific surface area and pore volume was increased by acid activation because of the decomposition of the crystal structure at some locations was occurred. Moreover, the acid/heat activation causes formation of smaller pores in solid particles resulting in a higher surface area (56.866 m$^2$ g$^{-1}$) and total pore volume (0.094247 cm$^3$ g$^{-1}$) relative to raw bentonite (47.599 m$^2$ g$^{-1}$ and 0.081585 cm$^3$ g$^{-1}$). This effect can be explained by FTIR.

![Fig. 7 IR spectrum of raw bentonite and activated bentonite](image)

The chemical analysis by XRF (X-ray fluorescence) was given in Table II, as the %wt of metal oxide. The amount of Ca$^{2+}$, Na$^+$, K$^+$ removal by acid treatment was decreased by exchangeable cations which are located out of the bentonite between layers. In Octahedral sheets, Fe$^{2+}$, Mg$^{2+}$, Al$^{3+}$ were also removed from bentonite.

<table>
<thead>
<tr>
<th>TABLE II</th>
<th>CHEMICAL COMPOSITION (%WT) OF THE RAW BENTONITE AND ACTIVATED BENTONITE BY XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Raw Bentonite</td>
<td>40.77</td>
</tr>
<tr>
<td>Activated Bentonite</td>
<td>41.04</td>
</tr>
</tbody>
</table>

The result from FTIR analysis (Fig.7) showed that bands involving octahedral Al$^{3+}$ were reduced in the montmorillonite structure. After the acid treatment, the only differences intensity of this band was decreased of the AlAlOH [5] band at 915 cm$^{-1}$ due to the loss of Al from it structure, as compared to intensity band of raw bentonite.

IV. SUMMARY

Chemical composition and adsorptive properties of the acid activated bentonites can be changed depending on the acid content and process time. The natural low silica was used to remove glycerin from crude biodiesel by activated with 0.1 M H$_2$SO$_4$ at 100 $^\circ$C for 1 hour. Using of 5% of activated bentonite with 120-200 mesh size. 47% of glycerin could be removed. The adsorption isotherm was fit with Freundlich isotherm. The dissolution of cations (Mg$^{2+}$, Fe$^{2+}$, Al$^{3+}$) and consequent decomposition of montmorillonite structure could be seen by FTIR at 915 cm$^{-1}$. The dry wash is becoming the method of choice for biodiesel purification.

ACKNOWLEDGMENT

The author gratefully acknowledges Department of Chemistry, Faculty of Science, Chulalongkorn University for this research

REFERENCES


