Investigation of Solid Catalyst Poisoning Characteristics for Biodiesel Fuel (BDF) Synthesis by Using Ultrasonic Irradiation

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Abstract. So far, a method of employing ultrasound irradiation and zeolites as solid catalyst for BDF synthesis has been suggested and experimentally verified. However, since catalyst poisoning will occur due to the repeated use of the same zeolite for BDF synthesis, hence at current paper, the catalyst poisoning characteristics of zeolite was investigated as the study target. During the study, firstly several zeolites of were selected and prepared to increase their basic characteristics. Secondly, the basic characteristics of the prepared zeolites were characterized by using SEM and X-ray diffractometer. Thirdly, BDF synthesis experiment was carried out by using the selected zeolite based on ultrasonic irradiation for several times. It was found that BDF yield ratio decreased as the number of the BDF synthesis experiments repeated while the same catalyst was used.

1. Background and purpose
It is extremely important to promote using alternative fuel such as alcohol or BDF for automobile in the era when mankind is facing the crisis of global warming while at the same time crude oil price is soaring so high. Recently many literatures[1-6] have being published focusing on the methods of synthesizing biomass fuels and their applications.
So far, a method of employing ultrasound irradiation and zeolites as solid catalyst for BDF synthesis has been suggested[7]. However, since catalyst poisoning will occur due to the repeated use of the same zeolite for BDF synthesis, hence at current paper, to investigate catalyst poisoning characteristics of zeolite is the study objective. During the study, several zeolites of were selected and were prepared to increase their basic characteristics. Then the basic characteristics was characterized by using SEM and X-ray diffractometer. Beside, BDF synthesis experiment was carried out by using the selected zeolite based on ultrasonic irradiation. It was found that BDF yield ratio decreased as the number of the BDF synthesis experiments repeated while the same catalyst was used.

2. BDF synthesis principle
The zeolite-catalyzed transesterification equation for producing BDF is shown in Figure 1. When vegetable oil (triglyceride) is mixed with alcohol (methanol) under the condition of ultrasonic irradiation and zeolite for some time, BDF and the by-product of glycerin are yielded.

![Figure 1 BDF synthesis principle](Image)

3. BDF synthesis experiment

3.1. Catalyst preparation and evaluation

Since base strength could properly influence the BDF yield ratio, before BDF synthesis, zeolite was prepared as follows:

Step 1: Soak samples A3, A4, A5 and F9 with different NaOH concentration (3, 6 and 9 mol) respectively for 24 hours

Step 2: Wash the samples by using methanol and then dry the samples

Step 3: Sinter the samples by an electric furnace at the temperature of 400 °C for 2 hours

Before and after zeolites were prepared, SEM and X-ray diffractometer are used to character their base strength characteristics.

3.2. BDF synthesis

During batch type BDF synthesis (Figure 2), firstly, the mixture of the reactants of vegetable oil and methanol are prepared inside a glass tube. Secondly, the glass tube is put inside an ultrasonic reactor (Hondex frequency = 28kHz) in which hot water is prepared. In order to decrease BDF synthesis time, the temperature of the hot water is set to be around 70 degree.

Condition of BDF synthesis is listed in Table 1. The zeolites of A3, A4, A5 and F9 as catalysts were used respectively. Volume ratio of vegetable oil to methanol is 5:1.

The sample of the BDF product is taken out after reaction time of 60 mins and BDF yield ratio is detected by using a GC (Shimazu GCMS-QP2020) system. The total BDF yield ratio is calculated based on the GC detection results.

| Physical quantities                  | Condition           |
|--------------------------------------|---------------------|
| Volume ratio of vegetable oil to methanol | 5:1                 |
| Methanol purity                      | 99.5%               |
| Types of Zeolite                     | A3, A4, A5 and F9   |
| Quantity of Zeolite                  | 0.33wt%             |
3.3. Catalyst poisoning characteristics
Based on the BDF synthesis result, we selected A5 as the catalyst for catalyst poisoning investigation. The same amount of A5 was repeatedly used four times to produce BDF by the method described above. The BDF yield ratio was calculated based on the GC results.

4. Results and discussions
4.1. Catalyst evaluation
The solid catalysts used for BDF synthesis in this paper are 5 kinds of zeolites (A3, A4, A5 and F9) produced by Wako of Japan. Figure 3 shows the size and shape of zeolite A5 and its SEM analysis result. A5 has the round shape whose average external diameter is around 5-7 mm. According to the SEM analysis result, the surface area of A5 is very large which could absorb large amount of liquid. Na\(^+\) content change after zeolite preparation is shown in Figure 4 based on SEM analysis. As for surface investigation, the Na\(^+\) content increased if the high NaOH concentration is used. In case of A4, A5 and F9, the Na\(^+\) content are over 20%. In regard of inner investigation, the Na\(^+\) content is lower than that of the surface because less NaOH is infiltrated in the inner of the zeolite.

![Figure 2 BDF synthesis by using batch method](image)

![Figure 3 Shape of zeolite A5 and its SEM analysis.](image)
Figure 4 Na+ content for prepared zeolites

![Na+ content graph](image)

Figure 5 X-ray diffractomete results for A5

(a)Before preparation  
(b) After preparation for 3mol

Analysis result based on X-ray diffractomete are shown in Figure 5 for zeolite A5. It can been seen that the X-ray diffractomete results are different before preparation and after preparation. It seems that the X-ray diffractomete result changed because the soaked Na+ content changed its structure to some extent, which could likely effect the BDF synthesis efficiency.

4.2. BDF synthesis

In Figure 6, BDF yield ratio produced by different zeolites with different preparing method. It was found that by using A5 with 6mol NaOH in preparation, the BDF yield ratio reached the maximum value of 62%. Besides it could conclude that with the higher concentration of the NaOH for zeolite preparation, the more BDF yield ratio will be, which indicated that preparation was an effective way to increase BDF yield ratio. However, even 9 mol NaOH was used, the BDF yield ratio was not bigger than that of 6 mol. It appeared that there existed an optimum NaOH concentration for zeolite preparation.

4.3. Catalyst poisoning investigation

In Figure 7, the BDF yield ratio(right y axis) as well as change in Na+ (left y axis)content changed with the number of times of BDF synthesis reaction by using the same A5 are shown. At the beginning, the BDF ratio was 9%, however when it was used for the fourth time, the BDF ratio almost dropped to 0%,
which means the effect of the catalyst poisoning. While at same time it is found that the Na+ content decreased from 12.7% to 10.8%. It appeared that the Na+ content would likely influence the BDF yield ration to some extent and how to keep the Na+ remain on the surface of the zeolite and how to reuse zeolites is a task to be challenged in the near future.

Figure 6 BDF yield ratio

Different zeolites

Figure 7 Change in BDF yield ratio and Na+ content after A5 was repeatedly used

5. Conclusion

In order to investigate the catalyst poisoning characteristics of the solid zeolite, a series of experiments including zeolite preparing, basic characteristics evaluation, BDF synthesis by repeatedly using the same prepared zeolite and some conclusions are obtained as follows:

(1) By using zeolite A5 with 6 mol NaOH preparation, the BDF yield ratio reached 62%;
(2) When zeolite A5 was used as catalyst for BDF synthesis at fourth time, the BDF could not be synthesized due to the influence of the catalyst poisoning.

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