Study on Synthesis Method of Biodiesel from Epoxy Gutter Oil

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Abstract. Using waste oil biodiesel as raw material, using formic acid as oxygen carrier, using trace concentrated sulfuric acid as catalyst, epoxy waste oil biodiesel was prepared without solvent. The effects of the dosage of formic acid, hydrogen peroxide, reaction time and reaction temperature on the epoxidation of biodiesel were investigated. The results showed that the epoxy value of biodiesel was 5.56% and the conversion rate was 80.03% after 3.5h reaction at 500 r/min speed and 50 ℃ reaction temperature according to the mass ratio of biodiesel, 30% hydrogen peroxide, 88% formic acid and concentrated sulfuric acid of 15:13.5:2. 9:0.075.

1. Introduction
With the shortage of fossil energy, waste cooking oil has increasingly become the focus of research[1]. If waste cooking oil was poured directly into the sewer, it would not only cause environmental pollution, but also led to energy waste[2]. If waste cooking oil (gutter oil) was pretreated, it can be used to prepare epoxy resin[3], mold release agent[4], surfactant[5], plasticizer, etc., and then methylated to obtain gutter oil biodiesel, which can be used for engine drive. Vegetable oil can be epoxidation by referring to the methods of epoxidation, mainly including liquid acid catalysis, solid acid catalysis, ionic liquid catalysis and enzyme catalysis.

In this paper, using waste oil biodiesel as raw material and trace concentrated sulfuric acid as catalyst, the preparation of epoxy waste oil biodiesel can shorten the reaction time, improve the conversion rate and avoid the corrosion of equipment after the use of a large amount of sulfuric acid. The product can be used to prepare flame retardant polyurethane hard foam, used in construction, automotive and other fields.

2. Materials and methods
2.1. Materials and instruments
Gutter oil biodiesel; Hydrogen peroxide (30%), formic acid, concentrated sulfuric acid, potassium iodide, starch, sodium thiosulfate, iodine monochloride, glacial acetic acid, cyclohexane, KOH, phthalic anhydride, imidazole, pyridine, hydrochloric acid, acetone, NaHCO₃, NaOH and dichloromethane were all pure.

HH-ZK constant temperature water bath; S212-90c constant speed agitator; S212-90c constant speed agitator; 7890A /5975C Mass spectrometer; Fourier transform microscopy infrared VERTEX 70, Raman spectrometer; A V400 NMR spectrometer.
2.2. Experimental methods
The formic acid was mixed with trace concentrated sulfuric acid, and then added into a 250 mL tri-flask containing gutter oil biodiesel, heated in a water bath at 45℃. The reaction was conducted at a speed of 500 r/min, and hydrogen peroxide was added slowly as the reaction proceeded for 3 hours. Remove it, wash it with NaHCO₃ aqueous solution, then wash it with deionized water to neutral, and then layer it statically. The biodiesel was obtained by spinning on the rotary evaporator.

2.3. Determination of biodiesel acid value and epoxy value of epoxy gutter oil
According to GB /T 5530-2005 "determination of acid value and acidity of animal and vegetable oils", the acid value of epoxy gutter oil biodiesel was determined. According to GB/t1677-2008 "determination of epoxy value of plasticizer", the epoxy value of biodiesel of epoxy gutter oil was determined.

3. Results and discussions

3.1. Influence of stirring rate
At 65℃, at different stirring rates, the reaction was conducted for 3 hours according to the mass ratio of biodiesel, 88% formic acid, 30% hydrogen peroxide and concentrated sulfuric acid of 15:1.95:10.5:0.06. The results were shown in Figure 1.

![Figure 1. Effect of stirring rate on epoxidation of gutter oil biodiesel](image)

As can be seen from Figure 1, when the stirring rate was 500 r/min, the epoxy value reached the maximum value of 4.57%. Therefore, the optimal stirring rate was 500 r/min.

3.2. Influence of reaction temperature
At 500 r/min and at different temperatures, the reaction was conducted for 3 hours according to the mass ratio of biodiesel, 88% formic acid, 30% hydrogen peroxide and concentrated sulfuric acid of 15:1.95:10.5:0.06, as shown in Figure 2.
As can be seen from Figure 2, the epoxy value first increased and then decreased with the increase of reaction temperature. When the temperature was low, it was not conducive to the formation of peroxyformic acid, leading to a slow epoxidation rate and a low epoxidation value. When the temperature was too high, the decomposition of hydrogen peroxide and peroxyformic acid would be accelerated, and the resulting epoxy oil was prone to ring-opening side reactions. When the temperature was 45℃, the maximum epoxy value was 4.63%. When the temperature was lower than 45℃ or higher than 45℃, the epoxy value would decrease.

3.3. Influence of reaction time
At 500 r/min, the reaction temperature was 45℃, and at different reaction times, the mass ratio of biodiesel, 88% formic acid, 30% hydrogen peroxide and concentrated sulfuric acid was 15:1.95:10.5:0.06, as shown in Figure 3.

As can be seen from Figure 3, the epoxidation value of biodiesel from gutter oil first increased and then decreased with the increase of reaction time. Short time and incomplete reaction result in low epoxidation value. When the reaction time was too long, the side reaction of the reaction increased, resulting in the decrease of the reaction epoxy value. When the reaction time was 3 h, the maximum epoxy value was 4.63%, so the best reaction time was 3 h.
3.4. Influence of concentrated sulfuric acid dosage
At 500 r/min, the reaction temperature was 45℃. Different concentrated sulfuric acid mass (measured by biodiesel) was added. the mass ratio of biodiesel, 88% formic acid and 30% hydrogen peroxide was 15:1.95:10.5. The reaction took 3 hours.

![Graph showing the effect of sulfuric acid dosage on epoxy value of gutter oil biodiesel.](image)

Figure 4. Effect of sulfuric acid dosage on epoxidation of gutter oil biodiesel

As can be seen from Figure 4, with the increase of concentrated sulfuric acid consumption, the epoxy value of the product first increased and then decreased. When the amount of concentrated sulfuric acid consumption was 0.5% of the raw oil mass, the product had the maximum epoxy value of 4.79%. Therefore, the best concentrated sulfuric acid consumption was selected as 0.5% of the raw oil quality.

3.5. Influence of hydrogen peroxide dosage
At 500 r/min, the reaction temperature was 45℃, 30% hydrogen peroxide of different mass was used, and the mass ratio of biodiesel, 88% formic acid and concentrated sulfuric acid was 15:1.95:0.075. The results were shown in Figure 5.

![Graph showing the effect of 30% hydrogen peroxide on epoxy value of gutter oil biodiesel.](image)

Figure 5. Effect of 30% hydrogen peroxide on the epoxidation of gutter oil biodiesel

As can be seen from figure 5, with the increase of hydrogen peroxide consumption, the epoxy value of biodiesel in epoxy gutter oil first increased and then decreased. Because less hydrogen peroxide was used, although hydrogen peroxide would increase the utilization rate, the concentration was too low, was not conducive to the epoxy process of raw materials. More hydrogen peroxide increased the contact between the epoxy group and water, which aggravated the side reaction and led to the decrease of the epoxy value.; When the molar ratio of hydrogen peroxide to biodiesel was 1.5:1, the maximum epoxy value of the product was 4.86%.
3.6. Influence of formic acid dosage
At 500 r/min, the reaction temperature was 45℃, and the reaction was conducted for 3 hours with different mass formic acid, according to the mass ratio of biodiesel, 30% hydrogen peroxide and concentrated sulfuric acid of 15:12.45 and 0.075, as shown in figure 6.

![Figure 6. Effect of formic acid on epoxidation of gutter oil biodiesel](image)

As can be seen from figure 6, with the increase of the dosage of formic acid, the epoxy value of the product first increased and then decreased. When the molar ratio between formic acid and biodiesel was 0.8:1, the product had a maximum epoxy value of 5.19%. When the dosage of formic acid was too small, its concentration was low, which affected the process of epoxidation of raw oil. When the amount of formic acid was too much, the decomposition of hydrogen peroxide was more serious and the side reaction was accelerated. Therefore, the molar ratio of the double bond of waste oil biodiesel was 0.8 times that of the optimal formic acid.

4. Conclusion
In the solvent-free condition, the reaction temperature was 45℃ at 500 r/min, and the mass ratio of biodiesel, 30% hydrogen peroxide, 88% formic acid and concentrated sulfuric acid was 15:13.5:2. After the reaction for 3.5 h, the epoxy value of biodiesel was 5.56% and the conversion rate was 80.03%.

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