

# Comparison of Membrane Extraction with Traditional Extraction Methods for Biodiesel Production

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**ABSTRACT:** Three traditional methods for the refining step in biodiesel production were compared: (i) washing with distilled water; (ii) washing with acid (HCl); and (3) dissolving and extracting in a solvent (hexane or petroleum ether) and then washing with distilled water. Biodiesel with a high purity (97.5%) could be obtained by all three methods, but serious emulsification occurred during the refining processes, which led to high refining losses. A novel refining method was developed by using hollow fiber membrane extraction, and polysulfone was selected as the most suitable membrane. This process effectively avoided emulsification during refining and decreased the refining loss. The purity of the biodiesel obtained was about 99%; and other properties, such as density, kinematic viscosity, water content, and acid value, conformed to the standards.

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**KEY WORDS:** Biodiesel, hollow fiber extraction, production refining, transesterification.

Biodiesel, a clean, renewable fuel, has recently arisen as a potential candidate for diesel fuel substitution. It is made from nontoxic, biodegradable resources, such as vegetable oils, animal fats, or used cooking oils. The most commonly used method for preparing biodiesel is the transesterification reaction (1–8). Fat and oil react with alcohol (methanol or ethanol) to produce FAME or FA ethyl esters, namely, biodiesel, whose molecular sizes and properties are similar to those of diesel fuel.

Although the esters are the desired products of the reactions, the recovery of glycerin is also important due to its numerous applications in different industrial products. Besides the main products (esters and glycerin), there are some impurities in the final products because of the existence of impurities in the oil and incompleteness of the reaction. As noted in the literature (9), the presence of these minor contaminants can be detrimental to both engines and the environment.

Current limits on the concentrations of these compounds in biodiesel are set out in guidelines, such as those published by ASTM. In European countries, the component concentrations of biodiesel are restricted according to European Union standards. The purity of biodiesel must be at least 96.5% (10). Methanol, FFA, glycerol, and water contents in the biodiesel must be under specified limits.

To conform to these strict restrictions, a refining step after transesterification is necessary. The objective of the present study was to investigate the effectiveness of various refining methods in biodiesel production. Three traditional refining methods were carried out and compared: (i) washing with distilled water; (ii) washing with acid (HCl); and (iii) extracting with solvent (*n*-hexane or petroleum ether). Furthermore, a novel refining method using membrane extraction was developed.

## EXPERIMENTAL PROCEDURES

**Materials.** Edible-grade soybean oil used in the experiment was produced in Shanxi Province, China. Anhydrous methanol, petroleum ether, *n*-hexane, sodium hydroxide, and sodium sulfate were purchased from Beijing Chemicals Company (Beijing, China). Methyl esters of palmitic, heptadecanoic, oleic, linoleic, linolenic, and eicosenoic acids as well as heptadecanoic acid methyl esters used as internal standards in the gas chromatograph were supplied by Sigma (Beijing, China).

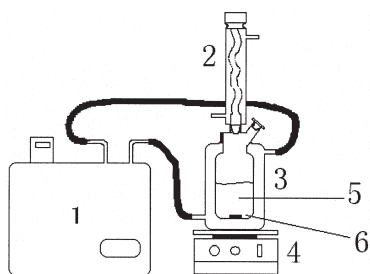
**Analysis.** The products of transesterification were analyzed by GC in a Hewlett-Packard 6890 chromatograph equipped with an FID, using an HP-INNOWAX capillary column (30 m × 0.15 mm). Nitrogen was used as carrier gas. Methyl esters of palmitic, stearic, oleic, linoleic, linolenic, and erucic acids were analyzed by using this procedure. The following parameters were determined in the crude and refined biodiesel products using ASTM procedures: density (D 1480-02), kinematic viscosity (D 445-03), water content (D 2709-96), and acid value (indicated by the pH value of distilled water in contact with biodiesel, D 1293-99).

**Refining method.** Experiments were carried out in two steps.

(i) *Preparation of crude biodiesel.* The device is depicted in Figure 1. The calculated amount of soybean oil (18.9 g) was placed in the dry reaction flask and heated to the predetermined temperature. An appropriate amount of methanol (5.8 g) with sodium hydroxide (0.1 g) was then added to the reaction flask to start the reaction. At a constant stirring rate (300 rpm), the reaction mixture was blended at (65°C) for 1 h. Some properties of the crude biodiesel were as follows: density at 20°C, 0.871 g/cm<sup>3</sup>; kinematic viscosity at 40°C, 3.915 mm<sup>2</sup>/s; water, 0.085 wt%; alkaline pH; FAME yield (wt%): 16:0, 10.6; 18:0, 3.8; 18:1, 19.0; 18:2, 53.0; 18.3, 9.9; total, 96.3. Impurities, unreacted oil, and middle products were 3.7%

(ii) *Investigation of biodiesel refining by different methods.* Three traditional refining methods (9)—washing with distilled water, washing with acid (HCl), and extracting with a solvent

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**FIG. 1.** Experimental device for transesterification: (1) constant temperature bath; (2) condenser; (3) glass tank reactor; (4) magnetic stirrer; (5) reaction mixture; and (6) rotor.

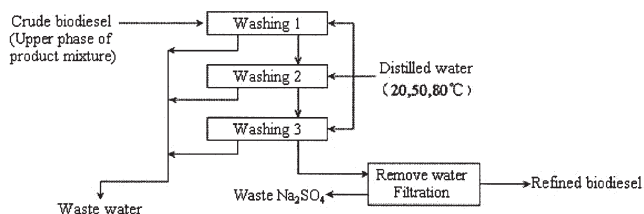
(hexane or petroleum ether)—were compared with extraction with hollow fiber membranes, in which hollow fiber membranes were applied in the refining step of biodiesel production.

**Washing with distilled water.** Crude biodiesel was washed with distilled water at different temperatures in a 1:1 volume ratio. Figure 2 shows the processing scheme for this method. The washing process was carried out in a water bath oscillator at 125 rpm for 20 min, and then the ester and water phases were separated in a separatory funnel. After washing three times, the ester phase was placed over heated  $\text{Na}_2\text{SO}_4$  (10% of the amount of the ester product) in a beaker, left for 12 h, and then filtered.

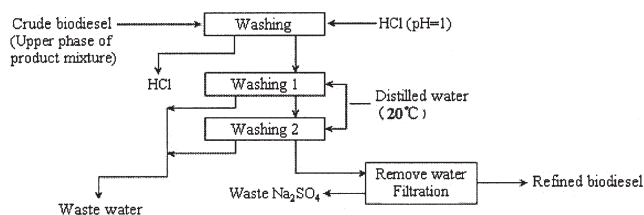
**Washing with acid.** This method was applied first by washing with HCl (pH = 1) at room temperature in a 1:1 ratio at different stirring rates and then washing twice with distilled water at a 1:1 volume ratio. The procedure is illustrated in Figure 3.

**Extracting with solvent.** Crude biodiesel was first extracted with solvent (petroleum ether or *n*-hexane) at a 1:1 ratio at room temperature, and then the mixture was washed three times using distilled water at a 1:1 volume ratio, as in the method described before. The organic solvent was then removed. The procedure is illustrated in Figure 4.

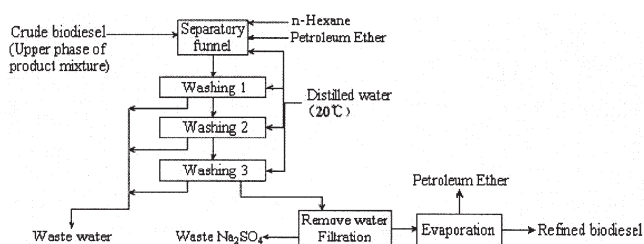
**Hollow fiber membrane extraction.** In this method, a hollow fiber membrane (1 m long, 1 mm diameter) was immersed in a 200-mL beaker filled with distilled water (20°C). The crude biodiesel was pumped into the hollow fiber membrane (flow rate: 0.5 mL/min, operating pressure: 0.1 MPa). The refined biodiesel was placed over heated  $\text{Na}_2\text{SO}_4$  (10% of the amount of the ester product), left for 12 h, and then filtered. The refining procedure is shown in Figure 5.



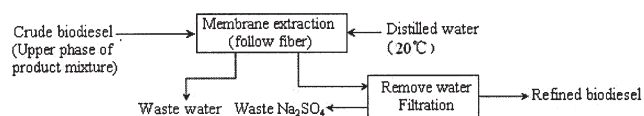
**FIG. 2.** Process scheme for washing with distilled water.



**FIG. 3.** Process scheme for washing with acid.



**FIG. 4.** Process scheme for extracting with solvent.



**FIG. 5.** Process scheme for membrane extraction.

The densities, kinematic viscosities, water contents, acid values, methyl ester composition of refined biodiesel, and ester losses were determined to evaluate the effectiveness of the refining methods. Ester loss was calculated by dividing the amount of ester loss during the refining process by the total amount of esters before refining according to Equation 1:

$$\text{Ester loss (wt\%)} = \frac{m_{\text{crude biodiesel}} \times C(\text{wt\%})_{\text{FAME before refining}} - m_{\text{refined biodiesel}} \times C(\text{wt\%})_{\text{FAME after refining}}}{m_{\text{crude biodiesel}} \times C(\text{wt\%})_{\text{FAME before refining}}} \times 100\% \quad [1]$$

## RESULTS AND DISCUSSION

**Washing with distilled water.** Table 1 shows the results of the refining method using distilled water. The properties of the refined biodiesel were similar when distilled water of different temperatures was used. Biodiesel with a purity of 97.5% could be obtained by using this method, but the highest yield was achieved at 50°C. At 20°C, serious emulsification was encountered, and at 80°C more esters dissolved in the water. Both temperatures led to more serious ester loss. So, 50°C was judged to be the optimal temperature for washing in this method.

**Washing with acid.** Methyl ester losses, densities, kinematic viscosities, water content, pH, and methyl ester compositions of biodiesel at two different mixing rates are shown in Table 1. After being mixed with HCl, the crude ester became somewhat acidic, which alleviated the emulsification. The ester loss re-

**TABLE 1**  
**Results of Refining by Different Methods**

Refining method	Ester loss (wt%)	Density at 20°C (g/cm)	Kinematic viscosity at 40°C (mm/s)	Water content (wt%)	pH	Fame yield (wt%)					Total
						16:0	18:0	18:1	18:2	18:3	
Washing with distilled water	15.2 ± 0.2	0.890 ± 0.003	3.931 ± 0.006	0.112 ± 0.004	9.44 ± 0.05	10.9 ± 0.2	3.9 ± 0.2	18.4 ± 0.5	54.3 ± 0.3	10.1 ± 0.2	97.6 ± 1.1
	10.1 ± 0.3	0.873 ± 0.005	3.952 ± 0.005	0.056 ± 0.002	8.53 ± 0.04	11.0 ± 0.1	3.9 ± 0.1	18.5 ± 0.3	54.5 ± 0.4	10.1 ± 0.1	98.0 ± 0.9
	10.8 ± 0.2	0.887 ± 0.005	3.944 ± 0.008	0.071 ± 0.005	8.76 ± 0.05	11.0 ± 0.2	4.0 ± 0.1	18.5 ± 0.3	54.5 ± 0.2	10.1 ± 0.2	98.1 ± 1.3
Washing with acid	12.4 ± 0.3	0.887 ± 0.008	3.902 ± 0.003	0.054 ± 0.003	7.41 ± 0.05	11.0 ± 0.2	3.9 ± 0.1	18.5 ± 0.2	54.4 ± 0.5	10.1 ± 0.1	97.9 ± 1.0
	13.2 ± 0.1	0.888 ± 0.006	3.918 ± 0.006	0.066 ± 0.002	3.02 ± 0.06	11.0 ± 0.3	3.9 ± 0.1	18.5 ± 0.3	54.4 ± 0.4	10.1 ± 0.1	97.9 ± 1.2
Solvent extraction	13.0 ± 0.2	0.883 ± 0.004	3.929 ± 0.005	0.073 ± 0.004	7.43 ± 0.03	11.0 ± 0.1	4.0 ± 0.2	18.3 ± 0.3	54.2 ± 0.4	10.1 ± 0.2	97.6 ± 1.1
	13.6 ± 0.3	0.884 ± 0.005	3.946 ± 0.004	0.071 ± 0.002	7.35 ± 0.04	11.0 ± 0.2	4.0 ± 0.1	18.4 ± 0.3	54.3 ± 0.3	10.1 ± 0.1	97.8 ± 0.8
Membrane extraction	8.1 ± 0.2	0.876 ± 0.007	3.906 ± 0.006	0.042 ± 0.004	6.87 ± 0.03	11.0 ± 0.3	4.0 ± 0.1	18.5 ± 0.1	54.8 ± 0.5	10.2 ± 0.1	98.5 ± 0.9
	10.3 ± 0.1	0.887 ± 0.003	3.937 ± 0.007	0.107 ± 0.004	6.91 ± 0.02	11.0 ± 0.2	3.9 ± 0.1	18.5 ± 0.3	54.5 ± 0.3	10.1 ± 0.2	98.0 ± 1.2

sulting from this method was less than that when washing directly with distilled water at 20°C, but the acid value of refined biodiesel by this method was slightly higher owing to the addition of acid. The rotational rate of the water bath oscillator greatly affected the refining process. If the rotational rate was low, the ester and water phases could not contact effectively; thus, many impurities remained in the biodiesel. If the rotational rate was too high, serious emulsification occurred, leading to higher ester loss and higher acid value in the biodiesel. The experimental results showed that 125 rpm was the most suitable rotational rate.

*Solvent extraction.* The ester loss and the results of biodiesel properties are shown in Table 1. In the experiment, serious emulsification occurred at the interface of the ester and water phases, and the solvent in the biodiesel had to be evaporated out after refining. Both steps increased the loss of methyl esters.

*Hollow fiber membrane extraction.* Biodiesel with purity of 97.5% could be obtained by all three methods, and properties of the refined biodiesel were similar. Serious emulsification, however, occurred during refining, which led to high ester loss. To avoid emulsification and decrease ester loss, we used a membrane extraction method.

Applications for a membrane separation process have been developed in a wide range of industries and in pharmaceuticals. Membrane separation is a process that achieves gas/liquid or liquid/liquid mass transfer without dispersion of one phase with another. This approach offers a number of important advantages over conventional dispersed phase separation, including the following: there is no emulsification, no density difference is required between fluids for hollow fiber membranes, and the interfacial area is surprisingly high (11). In this investigation, we made use of the advantages of the hollow fiber membrane to avoid the emulsification of water and methyl esters and obtain high-purity methyl esters.

Two types of hollow fiber membranes, polysulfone and polyacrylonitrile, which are hydrophilic and hydrophobic respectively, as well as readily available and inexpensive, were used. The biodiesel properties and the ester loss resulting from this method are shown in Table 1. Membrane extraction effectively avoided emulsification during refining and decreased the refining loss compared with the three traditional refining methods. In the refining process using polysulfone, the refining loss decreased to 8.1% (by wt), which was the lowest refining loss for all methods, while the highest refining loss was 15.2% by washing with distilled water at 20°C. We found that after refining with polyacrylonitrile membranes, refined biodiesel had a higher water content, 0.107%, than for the other methods. Thus, we concluded that polyacrylonitrile was not suitable for refining biodiesel, however, polysulfone showed effective behavior in refining biodiesel. When the refining experiment was carried out with polysulfone, the refined ester flowing out of the polysulfone hollow fiber was transparent and clear. The purity of the biodiesel, about 99%, obtained by polysulfone membrane extraction was the highest among the refining methods, and other properties, such as density, kinematic viscosity, water

content, and acid value, conformed to standards (ASTM PS121-99). The water content of the refined biodiesel of polyacrylonitrile hollow fiber membrane extraction was less than the maximum value of 500 mg/kg (ASTM PS121-99), and the water content of the refined biodiesel for other refining methods was higher than the maximum value (ASTM PS121-99). All these results show that membrane extraction is a very promising method for refining of biodiesel.

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