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Studies on the Preparation of Biodiesel from *Zanthoxylum bungeanum* Maxim Seed Oil

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To reduce the cost of biodiesel production, the feasibility of *Zanthoxylum bungeanum* Maxim seed oil (ZBMSO) was studied to produce biodiesel. A methyl ester biodiesel was produced from ZBMSO using methanol, sulfuric acid, and potassium hydroxide in a two-stage process. The main variables that affect the process were investigated. The high level of free fatty acids in ZBMSO was reduced to < 1% by an acid-catalyzed (2% H_2SO_4) esterification with methanol to oil molar ratios of 20−25:1 for 1 h. A maximum yield of 96% of methyl esters in ZBMSO biodiesel was achieved using a 6.5:1 molar ratio of methanol to oil, 0.9% KOH (percent oil), and reaction time of 0.5 h at 55 °C. Further investigation has also been devoted to the assessment of some important fuel properties of ZBMSO biodiesel produced under the optimized conditions according to specifications for biodiesel as fuel in diesel engines. The fuel properties of the ZBMSO biodiesel obtained are similar to those of no. 0 petroleum diesel fuel, and most of the parameters comply with the limits established by specifications for biodiesel.

KEYWORDS: Biodiesel; *Zanthoxylum bungeanum*; methanolysis; seed oil; transesterification; free fatty acids

INTRODUCTION

Biodiesel, namely, fuel fatty acid methyl ester (FAME), has practically excellent characteristics; that is, it is renewable, biodegradable, and environmentally acceptable. It has been thought to be a good alternative to petroleum fuel and is receiving increasing attention throughout the world (*1, 2*). Vegetable oils and animal fats are the main feedstocks for biodiesel, among which vegetable oils such as soybean oil, peanut oil, and cottonseed oil are widely used, but most of these oils are edible, and the cost is greater using them as feedstocks to produce biodiesel fuel for many countries (*3*−*6*). As a future prospective fuel, the right choice of its raw materials must be always based on technical and economical aspects. At present, the essential techniques for producing biodiesel are approaching perfection; reducing the biodiesel production costs is the key problem, especially the cost of feedstock (*8, 9*). The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant in the delivery of a competitive biodiesel to commercial filling stations. Recently, researchers are paying more attention to wasted oils and nonedible tree seed oils (*10*−*14*). In this context, choosing a feedstock with high additive value and utilizing it synthetically also have great importance for producing biodiesel.

Zanthoxylum bungeanum Maxim, belonging to Ruta L., usually a small tree, is widely distributed in most parts of China. It grows quickly and matures after three years, yielding fruit that consists of *Z. bungeanum*, namely, the red shell, which is an important spice, and dark seed, a side product of *Z. bungeanum*. The yields of seeds and shells are nearly equal. A single tree is said to yield 2−3 kg of seed, and the total yield of the seed oil is about 160 million kilograms per year in China today. **Figure 1** shows close views of shells and seeds of the fruits of *Z. bungeanum*. Although the oil content in seed is 24−28% (percent dry basis), it is not fit for eating and easy metamorphosing etc. The oil mainly contains six fatty acids, namely, palmitic acid, stearic acid, palmitoleic acid, oleic acid, linoleic acid, and linolenic acid. Of these, the content of oleic and linoleic acids is >60%, and the total content of unsaturated fatty acids is >85%. Its fatty acid profile is shown in **Table 1**. According to previous works of many researchers (*13, 15, 16*), this oil is of great potential for providing an inexpensive source of triglycerides for conversion to biodiesel in terms of its fatty acid composition. Moreover, ZBMSO contains nearly 16% linolenic acid, which has high value in medical industry, but its methyl ester is not a favorable component for biodiesel

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Figure 1. Fruits, shells, and seeds of *Zanthoxylum bungeanum* Maxim.

production according to the specifications of biodiesel (*17*). At present, experiments are in progress to determine the optimum methods of extracting linolenic acid from crude ZBMSO before the production of biodiesel. Therefore, *Z. bungeanum* is a kind of multiple-use tree, and ZBMSO has great potential of use as a feedstock for biodiesel production in terms of reducing the producing cost, so the commercial production of biodiesel with ZBMSO is feasible.

Presently, an alkali-catalyzed transesterification process is adopted mostly on commercial scale for producing biodiesel. The acid value of ZBMSO produced by a mechanical expeller is higher (63.56 mg of KOH g^{-1}), but the alkali-catalyzed transesterification process with vegetable oil will have a low conversion if the free fatty acid content in the parent oil is >1% (w/w) (*18*−*20*). In addition, there are a few reports of the preparation of biodiesel from tree seed oil (*10, 13, 18, 20*−*22*); however, there is no report of the production of biodiesel from ZBMSO. This study was undertaken to determine the feasibility of producing biodiesel from ZBMSO. According to the quality of ZBMSO squeezing, a two-step esterification process (acid-catalyzed esterification and base-catalyzed methanolysis) was employed to produce ZBMSO biodiesel, and the optimal conditions were investigated. Furthermore, the biodiesel sample that presented the best results was analyzed,with the specifications for biodiesel as fuel in diesel engines taken into consideration.

MATERIALS AND METHODS

Materials and Reagents. The ZBMSO was obtained by mechanical expeller and donated by an oil company (Hanzhong, China). The acid value and the saponification value of the mechanically extracted oil were 63.56 and 199 mg of KOH g^{-1}, respectively. The oil was stored at 4−8 °C before use. Palmitic acid methyl ester, stearic acid methyl ester, oleic acid methyl ester, linoleic acid methyl ester, linolenic acid methyl ester, palmitoleic acid methyl ester, and tridecane acid methyl ester were purchased from Fluka and were chromatographically pure. All other chemicals were obtained commercially and were of analytical grade.

Two-Step Biodiesel Production Process. Because the ZBMSO has a high content of free fatty acids, a two-step process was adopted for the production of ZBMSO biodiesel (*11, 16, 18*−*21, 23, 24*). Both steps were carried out in a vacuum and thermostatic reaction flask (WZ-1809, Shanghai SENCO Technology Co., Ltd., China) with four necks, equipped with a reflux condenser, a digital rpm controlled mechanical stirrer, a thermometer, and an inlet for the reactants. The reaction flask was immersed in a thermostatic water bath. All experiments were performed at least in duplicate.

Acid-Catalyzed Esterification. About 80 g of crude ZBMSO was poured into the reaction flask and preheated to the desired reaction temperature before the reaction was begun. The H_2SO_4−methanol solution was prepared freshly and thermostated at reaction temperature. Then the methanolic solution was added to ZBMSO in the reaction flask, and the measurement of time was started at this point. Over the whole reaction process, the stirring speed was set at 600 rpm. After the required reaction time, the reaction mixture was poured into a separating funnel and was allowed to settle for 2 h. The excess alcohol, together with sulfuric acid and impurities, moved to the top layer and was removed. The lower layer (oily phase) was washed with hot distilled water after the remaining methanol had been boiled off by a Rota-Evaporator under 60 °C and 0.085 MPa in a water bath; then it was dried with anhydrous sodium sulfate at least for 4 h and used for further processing with the base-catalyzed transesterification. The efficiency of the esterification was routinely monitored by measuring the acid value.

Table 1. Fatty Acid Profiles of *Zanthoxylum bungeanum* Maxim Seed Oil (ZBMSO), Soybean Oil (*22*), and Rapeseed Oil (*25*)

fatty acid	ZBMSO (%)	soybean oil (%)	rapeseed oil (%)
		saturated	
C16	10.3	12.9	6.1
C18	1.1	3.7	2.3
C20		0.3	0.3
		unsaturated	
C16:1	10.8	0.1	
C18:1	35.9	22.2	56.0
C18:2	24.8	52.9	24.2
C18:3	15.9	7.9	6.5

Alkali-Catalyzed Transesterification. About 50 g of esterified ZBMSO was poured into the reaction flask and preheated to the desired reaction temperature. The solution of KOH and methanol was prepared freshly under cold reflux to maintain the catalytic activity and prevent moisture absorbance and then preheated to the reaction temperature. Finally, the methanolic solution was added to the esterified ZBMSO in the reaction flask, and the measurement of time was started at this point. Under constant stirring speed (600 rpm) for a required time, the reaction mixture was poured into a separating funnel and was allowed to settle overnight. The lower layer, containing glycerol and impurities, was drained off. The upper layer, which contained FAME, was vaporized with a Rota-Evaporator at 60 °C to eliminate most of the methanol. It was found that water washing was an inefficient method, because the water washing resulted in the soap emulsions which were difficult to remove. After all of the methanol had been boiled off, 3% (percent oil) silica gel was added to the FAME phase and stirred for about 0.5 h to remove the remaining trace amount methanol and KOH (*1*), and then it was filtered to remove the silica gel; finally, the ester phase was dried with 2% (percent oil) anhydrous sodium sulfate for at least 4 h. After removal of the sodium sulfate, the biodiesel produced was stored at 4−8 °C in a refrigerator for subsequent analyses. The biodiesel yield was determined by gas chromatography and expressed in terms of the percentage (weight percent) of fatty acid methyl esters formed.

Analytical Methods. Acid values of crude oil, esterified oil, and biodiesel were determined by the acid−base titration technique as the standards of the authorities of China. The amount of methyl esters in the product of ZBMSO biodiesel was analyzed on an Agilent 6890 gas chromatograph (Agilent Technologies) with a DB-Wax capillary column measuring 30 m × 0.32 mm i.d. × 0.25 μm (Agilent Technologies). The initial GC oven temperature was kept at 150 °C for 0.5 min, heated at 25 °C/min to 190 °C, and then heated at 3 °C/min to 240 °C, at which it was kept for 3 min. The detector was a flame ionization detector (FID) with a detecting temperature of 300 °C. A split ratio of 100:1 and the carrier gas of nitrogen (1 mL/min) were used. The biodiesel yield, described as the amount of FAMEs formed in the transesterification reaction, was quantified in the presence of tridecanoic acid methyl ester as internal standard. Approximately 0.16 g of the biodiesel products was weighed in a vial and dissolved with 5 mL of acetone. A sample of tridecane acid methyl ester solution (0.2 g/100 mL of acetone) was added. Then triplicate samples (1 μL) of the solution of tridecane acid methyl ester and biodiesel product were injected into the GC. All samples were analyzed at the same condition, and all peaks were quantified by internal standard method. The fatty acids were identified by comparison of retention times of the oil components with those of standards.

Fuel properties (flash point, cetane index, viscosity, etc.) of FAMEs were determined as per the standards prescribed by the authorities of China (GB standards, specifications for biodiesel and light diesel as fuel in diesel engines).

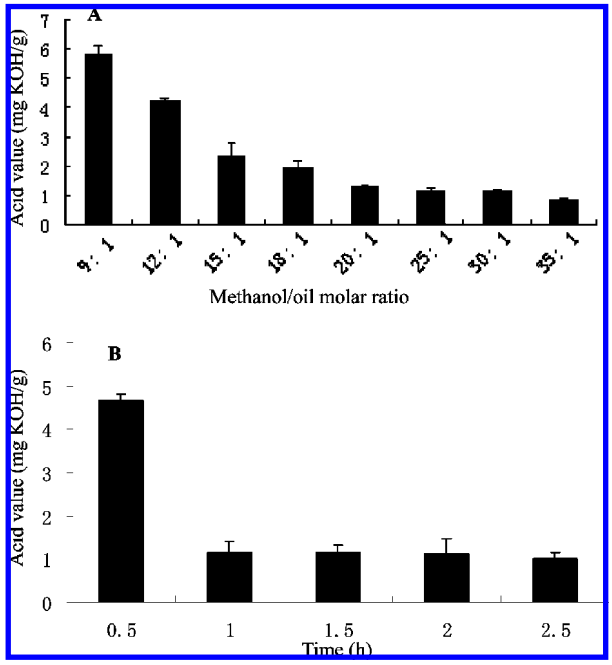

Figure 2. Influence of methanol quantity (**A**) and reaction time (**B**) on reduction of acid value of *Zanthoxylum bungeanum* Maxim seed oil during the esterifiction process.

RESULTS AND DISCUSSION

Characterization of ZBMSO. The quality of ZBMSO was expressed in terms of the physicochemical properties such as acid value and saponification value. These properties of crude ZBMSO were determined as per the Bureau of China Standard. The fatty acid composition of ZBMSO was determined by gas chromatographic method, and the fatty acid profiles of ZBMSO are given in **Table 1**. The base-catalyzed transesterification has been applied for biodiesel production successfully using oils such as rapeseed and soybean, and the ZBMSO has a very similar fatty acid composition, with oleic acid and linoleic acid being the major acids (>60%). Therefore, the ZBMSO could be potentially used as biodiesel-producing feedstock in terms of its chemical composition.

Acid-Catalyzed Esterification. The main factors affecting acid-catalyzed esterification are the amount of alcohol and catalyst, reaction temperature, and time. The optimum amount of catalyst (H_2SO_4) was studied previously (*26*), and the reaction temperature was maintained at 60 °C (*11, 19, 21*). Here, in order to reduce the FFA content below 1% for maximum biodiesel production, the effects of molar ratio of methanol to oil and reaction time on esterification of ZBMSO were studied in more detail as described below.

The molar ratio of alcohol to oil has a great effect on reducing FFA of vegetable oil using H_2SO_4 as catalyst. Molar ratios between 15:1 and 35:1 (*18*) and between 4.5:1 and 18:1 (*21*) were reported in the literature. According to the previous experimental results (*26*), using 2% H_2SO_4 and a reaction time for 1 h, the changes in the acid value of the esterified ZBMSO in relation to different molar ratios of methanol to ZBMSO are shown in **Figure 2A**. The rate of reaction was greatly influenced by the quantity of methanol. At a low methanol to oil ratio of 9:1, about 91% reduction was achieved and >97% was obtained for a high methanol to oil ratio of 20:1, when the acid value was reduced to 1.28 ± 0.3 mg of KOH g^{-1}. At a molar ratio of 25:1 the acid value of the esterified oil was reduced to 1.12 ± 0.3 mg of KOH g^{-1}. Beyond a molar ratio of 25:1 there was little reduction in the acid value with increasing methanol to oil ratio. Ghadge and Raheman (*19*) used a two-step esterifying process with H_2SO_4 to reduce the FFAs of mahua (*Madhuca indica*) oil from 38 mg of KOH g^{-1} to <2 mg of KOH g^{-1}. In this study the high content of FFA (63.56 mg of KOH g^{-1}) in the ZBMSO was decreased to <1% with the one-step esterification process used. Therefore, this esterifying method is fit for reducing FFA in the ZBMSO during the production of ZBMSO biodiesel, and a methanol to oil molar ratio of 20:1−25:1 is the recommended optimal quantity of methanol. Further studies proved that the optimum amount of methanol decreased with the decline of FFA content in the crude ZBMSO. In the whole reaction process a high amount of methanol was needed to decrease the acid value of ZBMSO to <2 mg of KOH g^{-1}. However, this high consumption of methanol can be reduced in commercial application by recovering part of it with fractional distillation.

Studies on the effect of reaction time on the oil esterification were performed at 0.5, 1, 1.5, 2, and 2.5 h with a methanol/oil molar ratio of 25:1 and 2% H_2SO_4 as catalyst. The effect of reaction time on the efficiency of ZBMSO esterification is indicated in **Figure 2B**. As can be seen, after 1 h, there was no significant reduction in the acid value, in accordance with the results obtained by Ghadge and Raheman (*19*), and this might be due to the effect of water produced during the esterification of FFAs, which prevented further reaction. Therefore, 1 h was the optimum reaction time.

Alkali-Catalyzed Transesterification. The variables affecting transesterification such as catalyst concentration (0.8−1.2 wt % of oil), methanol/oil molar ratio (4:1 to 7.5:1), temperature (45−65 °C), and reaction time were investigated to obtain an optimum reaction condition.

The alcohol to oil molar ratio is one of the important factors that affect the conversion efficiency of transesterification. Stoichiometrically, 3 mol of alcohol is required for each mole of triglyceride; in practice, a higher molar ratio is used for getting greater yields of fatty methyl esters. However, a too high molar ratio of alcohol to oil slows the separation of the glycerin phase and the methyl ester phase (*27, 28*) and lowers the yield of methyl esters (*3*). Commonly, the molar ratio has no effect on the acid value, peroxide, saponification, and iodine value of fatty acid methyl esters (*15*). The research results obtained from Muniyappa et al. (*29*) showed that the optimal methanol amount should be 2−10 times the stoichiometrical one. In the present work, the transesterification of esterified ZBMSO was carried out using KOH as an alkaline catalyst, and the amount was performed at a concentration of 1 wt % of oil, plus the amount needed to neutralize the free fatty acids in the esterified ZBMSO. The reaction was performed at 60 °C for 2 h, and the yields of methyl esters at different molar ratios of methanol/oil, such as 4:1, 4.5:1, 5.5:1, 6:1, 6.5:1, and 7.5:1, are demonstrated in **Figure 3A**. The yield of methyl esters at the methanol/oil molar ratio of 6.5:1 was the highest (94.2%), and the yield decreased greatly when the molar ratio was 7.5:1.

Methanolysis of esterified ZBMSO was carried out with KOH as a catalyst at a concentration of 0.8−1.2 wt % of oil at 60 °C with a methanol/oil molar ratio of 6.5:1 and a reaction time of 2 h. **Figure 3B** describes the yields of methyl esters at different catalyst concentrations. The lower catalyst concentration, that is, 0.8% of KOH, had lower catalytic activity and the yield of methyl esters was <90%, because the reaction was not finished completely. However, as 0.9% KOH was used, a yield of 95.2% methyl esters was obtained. With the increase in the concentration of catalyst, there was an obvious decrease in the yield of

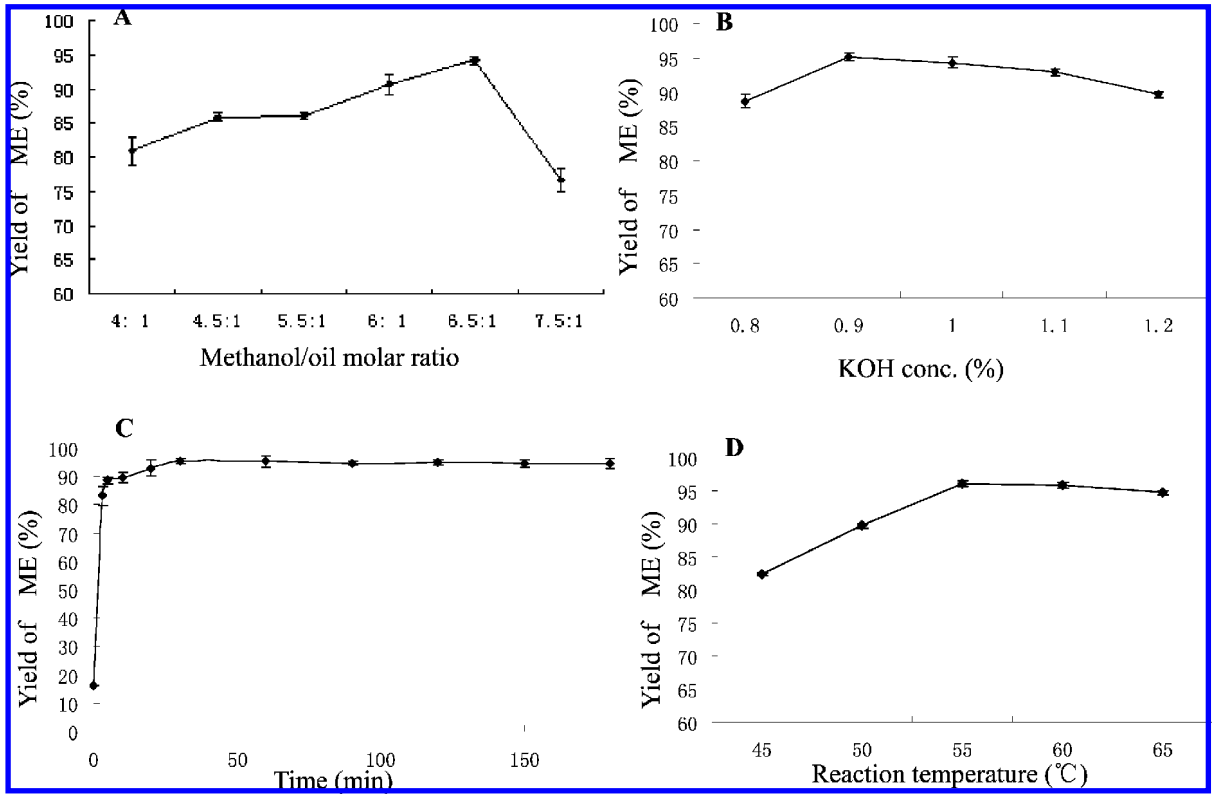

Figure 3. Influence of MeOH/oil molar ratio (**A**), KOH concentration (**B**), reaction time (**C**), and reaction temperature (**D**) on methanolysis of *Zanthoxylum bungeanum* Maxim seed oil ZBMSO.

methyl esters. This is in accordance with the results obtained by Mether et al. (*32*), Rashid et al. (*3*), and Sinha et al. (*30*). The reason for this was the formation of soap in the presence of high amount of catalysts, which increased the viscosity of the reactants and lowered the yield of ester. Vicente et al. (*2*) employed the factorial design of experiments and response surface methodology to optimize sunflower oil biodiesel production, and the results showed that the large catalyst concentrations should be avoided with NaOH as a catalyst. Therefore, 0.9% KOH was optimal in the reactions of this study.

The conversion rate of transesterification increases with reaction time. Mether et al. (*32*) transesterified *Pongamia pinnata* oil with methanol and KOH as a catalyst; the yield of methyl esters was >90% within 5 min, and from 0.5 to 3 h the yield of methyl esters increased slowly, about 96% at 0.5 h and 97% at 3 h. **Figure 3C** demonstrates the influence of reaction time on the methanolysis of ZBMSO; the yield of methyl esters increased with the reaction time. The content of methyl esters was about 90% at 10 min and reached the maximum yield (95.6%) at about 0.5 h; then from 0.5 to 3 h the yield of methyl esters fluctuated slightly. Freedman et al. (*7*) transesterified peanut, cottonseed, sunflower, and soybean oils under the condition of a methanol/oil molar ratio of 6:1, 0.5% NaOH catalyst, and 60 °C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93−98%). Therefore, the optimal time of ZBMSO transesterification was 0.5 h, which is consistent with the results of other researchers, such as Freedman (*7*) mentioned above.

Transesterification can occur at different temperatures, depending on the oil used. Studies were also carried out at different temperatures such as 45, 50, 55, 60, and 65 °C with 0.9% KOH as catalyst, a methanol/oil molar ratio of 6.5:1, and reaction time of 0.5 h. The yields of ZBMSO methyl esters at different reaction temperatures are shown in **Figure 3D**. It was observed that temperature had a positive influence on methanolysis of ZBMSO below 55 °C; above 55 °C, the influence was negative, and the yield of methyl esters decreased slowly. This might be

Table 2. Fuel Properties of ZBMSO Biodiesel

property	limit	test method	biodiesel A[a]	biodiesel B[b]	astm [c] d6751
density (15 °C) (kg/m^3)		GB/T1884	892.1	882.6	
kinematic viscosity (40 °C) (mm^2/s)	1.9−6.0	GB/T265	4.8	4.0	1.9−6.0
CFPP (°C)	≤4[d]	SH/T0248	−3	2	
cloud point (°C)	≤0[d]	GB/T510	−6	2	
cetane index	≥45[d]	GB/T11139	45	47	47 min
flash point (°C)	>130	GB/T261	>174	>174	130 min
acid value (mg of KOH/g)	≤0.8	GB/T258	0.3	0.3	0.8 max
carbon residue (10% dist residue)	≤0.3	GB/T268	0.3	0.1	
copper corrosion, 3 h at 50 °C	≤1	GB/T 5096	1	1	
90% distillation temperature (°C)	≤360	GB/T 6536	336.5	337.5	360 max

[a] Represents biodiesel produced under the optimum reaction condition without further processing. [b] Represents biodiesel produced under the optimum reaction condition with further distillation. [c] Represents biodiesel specification of the United States. [d] Represents the limit for no. 0 petroleum diesel fuel and the parameter determined as per the standards for light diesel fuel prescribed by the authority of China.

the reason that high temperatures tend to increase the saponification of glycerides by alkaline catalyst before completion of the methanolysis (*32*). This is in accordance with the results obtained by Sinha et al. (*30*). Thus, an optimal reaction temperature of 55 °C was used for ZBMSO transesterification in this study.

Fuel Properties of ZBMSO Biodiesel. Biodiesel fuel mainly consists of fatty acid alkyl esters, and its quality is specified according to the specifications of various countries. Further investigation verified that the effect of the amount of esterified oil used to produce ZBMSO biodiesel on the yield of methyl esters in biodiesel is small under optimum condition. Therefore, the biodiesel sample used to determine the fuel properties was prepared with 200 g of esterified ZBMSO, not the 50 g adopted when the reaction conditions were optimized. Some important fuel properties of ZBMSO biodiesel are presented in **Table 2**. Most of these parameters comply with the limits established by Chinese specifications for biodiesel as fuel in diesel engines.

The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. Research carried out by Knothe (*31*) indicated that important fuel properties of biodiesel, such as cetane number, cold flow, viscosity and so on, are strongly influenced by the fatty acid profiles, namely, chain length, degree of unsaturation, and branching of the chain of fatty acid. The results showed that cetane number, melting point, heat of combustion, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. In **Table 2**, biodiesel A represents the biodiesel that was produced under the optimum reaction condition without further processing, whereas biodiesel B was produced under the optimum reaction condition with further distillation to remove most of the linolenic acid methyl esters, because the EN standards of biodiesel (*17*) prescribed a maximum content of linolenic acid methyl ester 12% (mass percent), and the linolenic acid content of ZBMSO shown in **Table 1** is 15.9%. The results in **Table 2** demonstrate that the fuel qualities of the refined biodiesel, such as viscosity, cetane index, and carbon residue, were improved, but the cold flow property was decreased due to the decline of the content of unsaturated fatty acid methyl esters. This result is consistent with the report by Knothe (*31*). It is important to remove the excess amount of linolenic acid methyl ester in ZBMSO biodiesel, but the distillation means is not a favorable one because it may increase the production cost of biodiesel. At present, experiments are in progress in our laboratory to obtain the best extraction method of linolenic acid from crude ZBMSO before the production of biodiesel, and the elementary results would be exciting.

In summary, due to its high FFA content, in this study the ZBMSO was processed in two steps, that is, acid pretreatment was followed by alkali-catalyzed transesterification. The first acid-catalyzed esterification step reduced the FFA level from about 32 to <1% for 1 h at molar ratios of methanol to oil between 20:1 and 25:1. The second step converted the esterified ZBMSO into biodiesel. The maximum yield of methyl esters in the biodiesel product was about 96% under the optimum reaction conditions, namely, 600 rpm, 6.5:1 molar ratio of methanol to oil, 0.9% KOH, 55 °C, and a reaction time of 0.5 h. The ZBMSO biodiesel obtained has fuel properties that comply with the limits established by Chinese specifications for biodiesel and light diesel as fuel in diesel engines and is similar to no. 0 petroleum diesel fuel, except for a somewhat lower cetane index than that prescribed by the standards. Therefore, as a cheap byproduct in spice production, ZBMSO can be potentially used as a raw feedstock for producing biodiesel on a commercial scale in China.

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