

Rapid In Situ Transesterification of Sunflower Oil

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A rapid in situ transesterification process of sunflower oil with methanol assisted by diethoxymethane (DEM) is described in this article. DEM served as both extraction solvent and reaction promoter in the process. The effects of moisture content of sunflower seeds, catalyst category, molar ratio of catalyst/oil, molar ratio of methanol/oil, molar ratio of DEM/oil, reaction time, reaction temperature, and agitation speed on the in situ transesterification were investigated. The most important factors which influenced the crude biodiesel yield, free fatty acid (FFA) content, and fatty acid methyl ester (FAME) purity were the molar ratio of DEM/oil, molar ratio of catalyst/oil, and molar ratio of catalyst/oil, respectively. An empirical model of the rapid in situ transesterification process was established and used to determine the optimal reaction conditions. When the in situ transesterification was carried out at the molar ratio of catalyst/oil of 0.5:1, the molar ratio of methanol/oil of 101.39:1, the molar ratio of DEM/oil of 57.85:1, the agitation speed of 150 rpm, and reaction temperature of 20 °C, a product containing 97.7% FAME and 0.74% FFA was obtained within 13 min.

1. Introduction

The simple alkyl esters of fatty acids, derived from oils by transesterification with simple aliphatic alcohols, are widely used in food, textile, cosmetic, rubber, and synthetic lubricant industries, etc. Among these esters, FAME is the predominant one, especially when it is used as biodiesel. However, FAME is not economically feasible as biodiesel nowadays despite lots of environmental benefits.^{1–3} The conventional process of producing FAME involves oil extraction, purification (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.), and transesterification. The cost of oil contributed over 70% of the total cost of FAME product when refined oil was used.^{4–6} So the simplification of the oil extraction and purification will be a useful way to reduce the cost of FAME production. Hence, more researchers pay attention to the study on the in situ transesterification now.

In situ transesterification, involving the direct reaction of oil-bearing materials instead of purified oils with alcohol, was at first adopted to detect the fatty acid composition of materials from different organisms.^{7–11} Harrington and D'Arcy-Evans^{12,13} first evaluated the possibility of producing FAME via acid-catalyzed in situ transesterification. More FAME was obtained by the in situ transesterification than that by the conventional oil extraction and transesterification process. The same results were also obtained by other researchers.¹⁴ The factors which influenced the acid-catalyzed in situ transesterification, such as molar ratio of alcohol/oil, catalyst amount, reaction time, and temperature, were investigated by different researchers.^{15–18} Özgül-Yücel and Türkay^{16–18} found that the overall reaction rate of the in situ transesterification was mainly determined by the parameters affecting the extraction rate.

Considering that the acid-catalyzed in situ transesterification was a time-consuming process, Haas et al.^{19,20} developed an alkali-catalyzed in situ transesterification process. About 95% of the total oils were extracted from the raw material, and 84% of those oils were converted into FAME under the optimal conditions.¹⁹ When

the moisture content of flaked soybean dropped from 7.4% to 2.6% and 0, the volume of required methanol to convert 5 g of soybean flakes decreased from 30 mL to 18 mL and 12 mL,²⁰ respectively. The alkali-catalyzed in situ transesterification was also extended to other oil-bearing materials, for example, distillers dried grains, meat, and bone meal.²¹

In the process of either acid-catalyzed or alkali-catalyzed in situ transesterification, the methanol/oil molar ratio was much higher than the value calculated according to stoichiometry of the transesterification reaction, for example, 532:1,¹² 300:1,¹⁵ and 543:1.¹⁹ The redundant methanol would probably play the role of extraction solvent,^{16–18,22} providing access of alcohol and alkaline catalyst to the substrate, altering the permeability of the solid substrate, etc.²⁰ As simple aliphatic alcohols were not good solvents for dissolving oil, the reaction times of in situ transesterification were usually several hours. If a proper solvent was added to accelerate the oil extraction, the reaction efficiency might be improved greatly.

Tetrahydrofuran (THF)^{23–27} and DEM²⁸ had been proved to be good cosolvents for methanol and oil and, furthermore, could improve the mass transfer of oil and methanol and intensify the transesterification of oil and aliphatic alcohols. In this paper, a rapid in situ transesterification process assisted by a cosolvent was investigated. The cosolvent might play the roles of both extraction solvent and reaction promoter in the process and accelerate the in situ transesterification.

The in situ transesterification process could be influenced by many factors, for example, the moisture content of sunflower seeds, the catalyst category, the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of cosolvent/oil, etc. It would be very difficult to investigate the effect of each factor by factorial design or orthogonal design. In order to reduce the enormous number of test points and to obtain results reflecting the major characteristics of the experimental system, the uniform design^{29,30} was used in our research.

2. Experimental Section

2.1. Materials. Newly harvested sunflower seeds were obtained from Inner Mongolia. Oil content of the sunflower seeds, determined by Soxhlet extraction with n-hexane, was 45.63%. Moisture

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Table 1. Principal Fatty Acid Composition and Its Contribution to the Molecular Weight of Sunflower Oil

fatty acid	M_r	content (%)	M_r contribution
palmitic (16:0)	256	4.84	12.39
stearic (18:0)	284	68.60	192.08
oleic (18:1)	282	22.49	63.39
linoleic (18:2)	280	4.08	11.59

Table 2. Oil Extraction with Different Solvents

extraction method	weight of oil extracted (g)	extraction rate (%)	FFA content (%)
soxhlet extraction	9.1270	100	0.43
extracted by n-hexane	8.4932	93.06	0.33
extracted by DEM	8.7477	95.85	0.44
extracted by THF	8.4757	92.87	0.55
extracted by methanol	≤0.8621	≤9.44	ND ^b

^a The datum was calculated by subtracting the weight of oil left in the methanol-pre-extracted sunflower seed residue (determined by re-extracting the methanol-pre-extracted material with n-hexane by Soxhlet method) from that of total oil. ^b Not detected.

content of the seeds was 4.63%. The principal fatty acid composition of the sunflower oil extracted from the sunflower seeds was assayed and is presented in Table 1. The mean molecular weights of fatty acid and triglyceride calculated according to the fatty acid composition were 279.45 and 876.35. The following experiments were all designed based on these molecular weights.

DEM purchased from Yangzhou Hengsheng Chemical Co., Ltd., was dehydrated with calcium oxide and distilled. THF, anhydrous methanol, and n-hexane purchased from Beijing Beihua Fine Chemical Co., Ltd., were all of analytical grade. The reference standards for gas chromatography analysis were purchased from Sigma (methyl palmitate, methyl oleate, methyl linoleate, 1-oleoyl-*rac*-glycerol, glyceryl trioleate, glyceryl trioctanoate), Merck (methyl tridecanoate), and Accustandard (diolein), respectively. The silylation reagent (BSTFA + 1%TMCS) was purchased from Supelco. Other reagents were of analytical grade.

2.2. Experimental Procedures. 2.2.1. Oil Extraction. Four extraction solvents, including n-hexane, DEM, THF, and methanol, were tested to extract oil from sunflower seeds (Table 2). Oil extraction was carried out using 200 mL of solvent and 20 g of milled sunflower seeds at 25 °C with 400 rpm magnetic stirring for 1 h. The extraction rates of different solvents were calculated by the following formula:

$$\text{extraction rate} = \frac{\text{the weight of oil extracted by solvent in 1 h}}{\text{the weight of oil determined by Soxhlet method}} \times 100\%$$

2.2.2. In Situ Transesterification. The in situ transesterification was carried out with the whole seeds according to the following process. About 20 g of sunflower seeds were weighed and milled by 3×20 s in a coffee grinder. The ground sunflower seeds were then transferred into a 250-mL three-necked spherical reactor equipped with a mechanical stirrer, a reflux condenser, and a sampling outlet and preheated in a constant-temperature water bath. An accurate amount of NaOH or KOH catalyst was weighed and dissolved in methanol (if the methanol used was not enough to dissolve the catalyst, for example, R6 in Table 4, the catalyst was added into the reactor directly). A certain volume of DEM was added to the alkaline methanol solution, and the mixture was then added into the reactor and the reaction was timed (The experiment designs are presented in Tables 3, 4, 5, 6). At the end of the reaction, a proper amount of 1 mol/L HCl was added to neutralize the alkaline catalyst, adjust the pH value to about 4, and convert all soap formed in the transesterification into FFA.

Table 3. Factor-Level List for Preliminary In Situ Transesterification

	1	2	3	4	5	6
moisture content, %	2.51	4.63				
catalyst category	KOH	NaOH				
molar ratio of catalyst/oil	0.2:1	0.6:1	1.0:1	1.4:1	2.0:1	2.4:1
molar ratio of methanol/oil	23.8:1	71.4:1	119.0:1	166.6:1	214.2:1	261.8:1
molar ratio of dem/oil	5.64:1	16.92:1	28.20:1	39.48:1	50.76:1	62.04:1
reaction time, min	10	20	30	40	50	60
temperature, °C	20	35	50	65		
agitation speed, rpm	150	300	450	600		

The neutralized reaction mixture was centrifuged (5000 rpm, 5 min) in a TDL-5-A low speed centrifuger (Shanghai Anting Experimental Instrument Factory, Shanghai, China) to separate liquid from solid residue. The liquid was collected in a flask. The residue was washed (with 20 mL of methanol) and centrifuged (5000 rpm, 5 min) twice to extract the FAME absorbed on the solid residue. All supernatants were mixed with the former liquid. The combined liquid was then vacuum-dried to recover methanol and DEM, and the remaining liquid was extracted by n-hexane to transfer FAME, glycerides, and FFA to another flask. The flask was first vacuum-dried to recover n-hexane and then dried at 105 °C to constant weight. The weight of the sample was recorded as the yield of crude biodiesel.

The influences of eight factors, including the moisture content of sunflower seeds, the catalyst category, the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of cosolvent/oil, the reaction time, the reaction temperature, and the agitation speed, on the in situ transesterification were investigated. The value range of each factor was designed according to the references.^{19–21} The biodiesel yield, FFA content, and FAME purity were set as responses.

2.3. Analysis Methods. A high temperature gas chromatograph^{31,32} was adopted to determine the FAME and glyceride contents of the crude biodiesel. After silylation with BSTFA + 1%TMCS, the internal standards and samples were diluted to proper concentrations and analyzed by a Shimadzu GC-14C gas chromatograph. A VF-5ht (Supelco) column (15 m × 0.25 mm i.d.) coated with 0.25 μm film of 5% phenyl and 95% dimethylpolysiloxane was used in the high temperature gas chromatograph analysis. The operating parameters were as follows: the injector temperature, 350 °C; the FID detector temperature, 385 °C; the temperature program, 1 min at 150 °C, heating at a rate of 5 °C/min to 190 °C first, and then at a rate of 20 °C/min to 370 °C and holding for 10 min.

The acid value of the crude product was determined by titration with KOH solution, and phenolphthalein was used as an indicator. FFA content could be calculated based on the acid value.

2.4. Experimental Design and Statistical Analysis. Uniform design, based on the quasi-Monte Carlo method and number-theoretic method, is a new experimental design method proposed by Fang and Wang.²⁹ The characteristics of uniform design take no account of regular comparability, ensuring the uniformity completely and distributing the test point in the experimental scope adequately and uniformly. Uniform design has at least the following merits:³⁰ (1) space filling: it is capable of producing samples with high representativeness in the studied experimental domain; (2) robustness: it imposes no strong assumption on the model and is against changes of the model in a certain sense; (3) multiple levels: it accommodates the largest number of levels for each factor among all experimental designs. Therefore, uniform design was increasingly used in chemistry and chemical engineering research to reduce experi-

Table 4. U12 ($2^2 \times 6^4 \times 4^2$) Uniform Design of Preliminary In Situ Transesterification and the Experiment Results

test times	factors									responses		
	moisture content (%)	catalyst category	molar ratio of catalyst/oil	molar ratio of methanol/oil	molar ratio of DEM /oil	reaction time (min)	temperature (°C)	agitation speed (rpm)		Y_{yield} (g)	Y_{FFA} (%)	Y_{purity} (%)
R1	1	2	1	3	4	1	4	2		8.5229	0.67	30.51
R2	2	2	3	6	2	2	3	4		8.2347	1.35	98.58
R3	1	1	2	6	5	5	2	3		8.5422	0.83	98.59
R4	1	2	4	2	6	3	1	4		8.6954	1.45	98.36
R5	2	2	2	4	3	6	1	1		8.6817	0.85	98.59
R6	2	2	5	1	5	5	3	2		8.7036	3.68	92.25
R7	2	1	6	4	4	1	1	3		8.2249	1.21	98.50
R8	2	1	4	5	6	3	4	1		8.5975	4.20	98.66
R9	1	2	6	5	1	4	2	2		5.4732	3.84	98.79
R10	1	1	5	3	3	6	4	4		8.6542	9.61	98.48
R11	2	1	1	2	1	4	3	3		6.5036	0.76	5.26
R12	1	1	3	1	2	2	2	1		8.2286	1.52	94.03

Table 5. Factor-Level List for the Second Run In Situ Transesterification

	1	2	3	4	5	6	7	8
molar ratio of catalyst/oil	0.3:1	0.4:1	0.5:1	0.6:1				
molar ratio of methanol/oil	47.6:1	71.4:1	95.2:1	119.0:1				
molar ratio of DEM/oil	22.56:1	28.20:1	33.84:1	39.48:1	45.12:1	50.76:1	56.4:1	62.04:1
reaction time, min	2	4	6	8	10	12	14	16

Table 6. U8 ($4^2 \times 8^2$) Uniform Design of the Second Run In Situ Transesterification and Experiment Results

test times	factors				responses		
	molar ratio of catalyst/oil	molar ratio of methanol/oil	molar ratio of DEM/oil	reaction time (min)	Y_{yield} (g)	Y_{FFA} (%)	Y_{purity} (%)
R1	4	1	2	5	8.6205	0.90	95.86
R2	3	2	4	1	8.1806	0.74	69.60
R3	1	4	3	6	8.5909	0.63	66.57
R4	2	3	1	2	7.623	0.60	66.51
R5	2	2	8	7	8.8621	0.78	91.20
R6	3	3	5	8	8.5221	0.66	96.21
R7	1	1	6	3	8.5272	0.67	66.39
R8	4	4	7	4	8.6628	0.79	93.54

ment times.^{30,33,34} It was employed to investigate this multifactor and multilevel in situ reaction system in our research.

Combined with partial least-squares (PLS) regression method, uniform design can easily determine the effects of factors on responses and optimize the conditions of those factors, especially when many factors and interactions affect the desired responses.³⁵ The regression relations of the responses and the factors are usually expressed in the following formula:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j$$

where Y is the predicted response, β_0 is constant coefficient, β_i are linear coefficients, β_{ii} are quadratic coefficients, β_{ij} are interaction coefficients, x_i and x_j are the independent factors.

The software named Data Processing System (DPS, version 6.5.5.8) was used to generate the experiment designs and analyze the results.³⁶ The standard regression coefficient (SRC) of each factor and factor combination was calculated when the experimental data were analyzed by DPS. The factors or factor combinations with positive SRC values ($\text{SRC} > 0$) had positive effects on the response; the factors or factor combinations with negative SRC values ($\text{SRC} < 0$) had negative effects on the response. The absolute value of SRC (ISRC) of different factors or factor combinations reflected the influence degree on the response by that factor or factor combination.

3. Results and Discussions

3.1. Oil Extraction Using Different Solvents. The extraction results with different solvents are shown in Table 2. Though n-hexane was usually recommended to extract oil from oilseeds, DEM showed the highest extraction rate (98.85%) among the four solvents, and methanol was the lowest one. About 90.56%

of the total oil was detected in the methanol-pre-extracted sunflower seeds. The FFA contents of the oils extracted by n-hexane, DEM, or THF were very low; hence, it could be deduced that an alkaline catalyst would not cause very serious saponification and that the alkali-catalyzed in situ transesterification process was feasible. The acid value of the oil extracted by methanol was not given because the oil was extracted together with sugar and protein, and the amount of the oil was too small.

It had been proved in our previous research that DEM could intensify the transesterification of oil and methanol.²⁸ Therefore, DEM was chosen to establish the rapid in situ transesterification process in the following experiments. The oil amount (9.1270 g) determined by Soxhlet method was regarded as the theoretical oil content of the 20 g of sunflower seeds, and the corresponding theoretical weight of FAME was 9.1687 g.

3.2. Preliminary In Situ Transesterification. The major aims of this section are to describe the main factors that greatly influenced the responses and determine the proper values or value ranges of these factors. Eight factors, including the moisture content of sunflower seeds, the catalyst category, the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of cosolvent/oil, the reaction time, the reaction temperature, and the agitation speed, were investigated based on a U12 ($2^2 \times 6^4 \times 4^2$) uniform table (Table 4). Levels of these factors are presented in Table 3; results of these experiments are shown in Table 4.

The SRC values of each factor for the three responses are shown in Figure 1 (A: the yield of the crude biodiesel; B: the FFA content of the crude biodiesel; C: the FAME purity of the crude biodiesel). According to the SRC values, the influences of these eight factors on the three responses are discussed below.

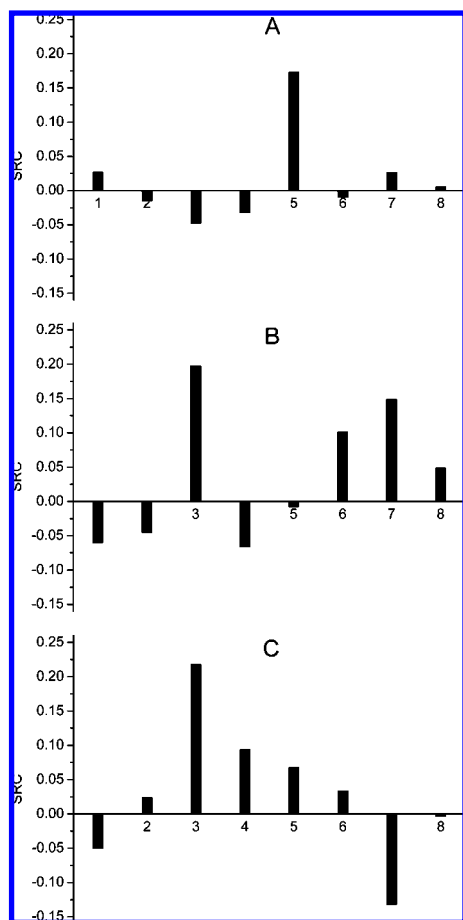


Figure 1. SRC of each factor when the responses were the biodiesel yield (A), the FFA content (B) and the FAME purity (C) of the crude biodiesel. 1, 2, 3, 4, 5, 6, 7, 8 are the linear coefficients of the moisture content of sunflower seeds, the catalyst category, the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, the reaction time, the reaction temperature, and the agitation speed, respectively.

As described in other papers,^{20,22} the moisture content (1 in Figure 1) had great effects on the in situ transesterification when there was no cosolvent used. For example, the required methanol was greatly reduced if the moisture was removed.²⁰ Both the oil yield and the ester purity were markedly influenced by the water content of alcohol.²² Similarly, moisture had negative effects in the conventional oil-based transesterification.³⁷ The main reason might lie in the fact that the strong polar KOH or NaOH catalyst was more likely to be dissolved in the strong polar water and hence there was less catalyst to catalyze the transesterification reaction of triglyceride and methanol. But the moisture content showed few effects on the three responses ($|SRC| \leq 0.060$) when DEM was used in the in situ transesterification. In our previous research, DEM could convert the oil/methanol/water multiphase system into a single phase system when it was added over the critical volume. When DEM was used in the in situ transesterification process, its volume was much higher than the critical volume. The extracted oil, methanol, and water could also form a homogeneous solution. The catalyst was then distributed uniformly in the whole reaction system rather than dissolved mainly in water. So the sunflower seeds with a moisture content of 4.63% were used in the later experiments to avoid the drying process.

Because KOH and NaOH were both strong alkali, the catalyst category (2 in Figure 1) had few effects on the three responses ($|SRC| \leq 0.045$). The products catalyzed by NaOH had lower

FFA content than that by KOH, and NaOH was less expensive than KOH. So NaOH was used in the later research.

The molar ratio of catalyst/oil (3 in Figure 1) hardly affected the biodiesel yield ($|SRC| = 0.048$) but influenced FFA content ($|SRC| = 0.198$) and FAME purity ($|SRC| = 0.217$) greatly. If the molar ratio of catalyst/oil was 0.2:1, the FAME purities were very low (R1, R11 in Table 4). If the molar ratio of catalyst/oil was over 0.6:1, the FAME purities were all over 98%. A high catalyst dosage was beneficial to yield a product with high FAME purity but, meanwhile, resulted in high FFA content ($SRC_{FFA} > 0$). To limit FFA content, further experiments were carried out at the molar ratio of catalyst/oil ranging from 0.3:1 to 0.6:1.

When DEM was used, methanol was no longer the main extraction solvent, so the molar ratio of methanol/oil (4 in Figure 1) had few effects on biodiesel yield ($|SRC| = 0.032$). The effects of the molar ratio of methanol/oil on FFA content ($|SRC| = 0.066$) and FAME purity ($|SRC| = 0.094$) were also insignificant, so the amount of methanol could be decreased. FAME purities of the products with a methanol/oil molar ratio of 23.8:1 (R6, R12 in Table 4) were all less than 94.1%. When the molar ratio of methanol/oil reached 119.0:1, the FAME purities exceeded 98%. So the molar ratio of methanol/oil in further experiments was set from 47.6:1 to 119.0:1.

The amount of DEM (5 in Figure 1) showed significant effects on the biodiesel yield ($|SRC| = 0.173$) but few effects on FFA content ($|SRC| = 0.008$) and FAME purity ($|SRC| = 0.068$). The molar ratio of DEM/oil was also the only single factor that greatly influenced the biodiesel yield among the eight factors. The result proved that the extraction was really the key step to obtain high biodiesel yield. If the molar ratio of DEM/oil was below 28.20:1, the yields of crude biodiesel were all less than 8.3 g. When the molar ratio of DEM/oil reached 28.20:1, some experiments got a biodiesel yield of 8.65 g (R5, R10 in Table 4). So the molar ratios of DEM/oil in further experiments were set from 22.56:1 to 62.04:1.

When the reaction times were all longer than 10 min, reaction time (6 in Figure 1) had a few effects on FFA content ($|SRC| = 0.101$) but tiny effects on biodiesel yield ($|SRC| = 0.010$) and FAME purity ($|SRC| = 0.034$). Long reaction time tended to generate more FFA; hence, a long reaction time should be avoided in the later experiments.

The reaction temperature (7 in Figure 1) had few effects on the biodiesel yield ($|SRC| = 0.026$) but great effects on the FFA content ($|SRC| = 0.149$) and the FAME purity ($|SRC| = 0.132$). An abnormal conclusion that the temperature showed a negative effect on the FAME purity ($SRC < 0$) was drawn from the experiment results. The main reason for this was that several high temperature levels were just combined with low catalyst concentration levels. However, at least one of three FAME purities at each temperature reached 98% (R4, R5, R7 at 20 °C; R3, R9 at 35 °C; R2 at 50 °C; R8, R10 at 65 °C). Anyway, a low reaction temperature was better to get low FFA content. The reaction temperature was fixed at 20 °C in the following experiments.

Agitation speed (8 in Figure 1) barely influenced both the biodiesel yield ($|SRC| = 0.005$) and FAME purity ($|SRC| = 0.003$), and only a few effects on FFA content ($|SRC| = 0.059$) were seen. The reason was probably that DEM decreased the mass transfer resistance of methanol and oil in the in situ transesterification reaction so that high agitation speed was not necessary. Thus, the lowest agitation speed of 150 rpm was sufficient.

3.3. Modeling of the In Situ Transesterification. On the basis of the results of the preliminary experiments, some factors were set as follows: the moisture content, 4.63%; the catalyst,

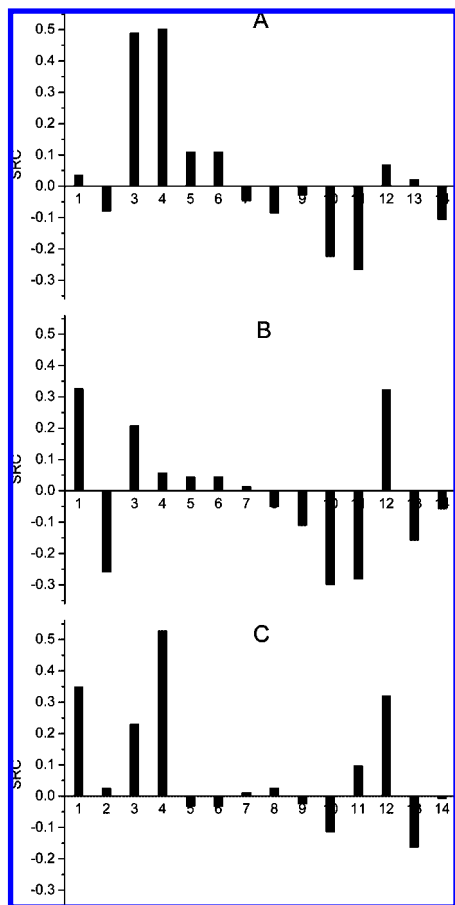


Figure 2. SRC of different factors or factor combinations when the responses were the biodiesel yield (A), the FFA content (B), and the FAME purity (C) of the crude biodiesel. 1–4 are the linear coefficients for the molar ratio of catalyst/oil (X_1), the molar ratio of methanol/oil (X_2), the molar ratio of DEM/oil (X_3), and the reaction time (X_4), respectively; 5–8 are the quadratic coefficients for X_1X_1 ... X_4X_4 ; 9–14 are the interaction coefficients for X_1X_2 ... X_3X_4 .

NaOH; the reaction temperature, 20 °C; the agitation speed, 150 rpm. Four important factors, namely, the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, and the reaction time, were reevaluated in the new value ranges according to Table 5 and Table 6. To establish the empirical model of this rapid in situ transesterification, the values of the four factors are represented by X_1 , X_2 , X_3 , and X_4 respectively.

The SRC of various factors (1–4 are linear coefficients for X_1 , X_2 , X_3 , X_4 , respectively) or factor combinations (5–8 are quadratic coefficients for X_1^2 , X_2^2 , X_3^2 , X_4^2 , respectively; 9–14 are interaction coefficients for X_1X_2 , X_1X_3 , X_1X_4 , X_2X_3 , X_2X_4 , X_3X_4 , respectively) for the three responses are shown in Figure 2 (A: the yield of the crude biodiesel; B: the FFA content of the crude biodiesel; C: the FAME purity of the crude biodiesel).

The molar ratio of DEM/oil (3 in Figure 2A) and reaction time (4 in Figure 2A) were the two single factors which greatly influenced the biodiesel yield. The molar ratio of catalyst/oil affected the biodiesel yield in the form of the combination of X_1X_3 (10 in Figure 2A) and X_1X_4 (11 in Figure 2A) rather than in the form of a single factor.

As described in the former section, the catalyst dosage was the most effective factor that influenced the FFA content. When the molar ratio of catalyst/oil was restricted in the range of 0.3:1 to 0.6:1, the effects of catalyst dosage (1 in Figure 2B) on the FFA content were similar to those of methanol (2 in Figure

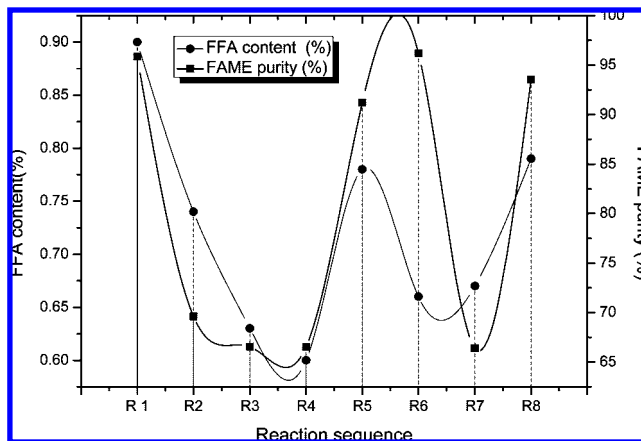


Figure 3. FFA contents and the corresponding FAME purities of some products.

2B) and DEM dosage (3 in Figure 2B). However, the factor combinations which contained catalyst factor, such as X_1X_2 (9 in Figure 2B), X_1X_3 (10 in Figure 2B), and X_1X_4 (11 in Figure 2B), showed significant effects on the FFA content. The fact indicated that catalyst dosage was still the most important factor which influenced the FFA content.

The FAME purity was mainly influenced by the molar ratio of catalyst/oil (1 in Figure 2C), the molar ratio of DEM/oil (3 in Figure 2C), the reaction time (4 in Figure 2C), and the combination of the molar ratio of methanol/oil and the molar ratio of DEM/oil (12 in Figure 2C). The effect of reaction time on FAME purity (4 in Figure 2C) was remarkable, and in contrast, the effect of reaction time on the FFA content (4 in Figure 2B) was very limited. It indicated that saponification was a much faster process in comparison with transesterification.

Regression equations of the three responses, including biodiesel yield, FFA content, and FAME purity, were obtained by PLS regression method and presented as follows:

$$Y_{\text{yield}} = 6.9402 + 0.2525X_1 - 0.2765X_2 + 0.2074X_3 + 0.3146X_4 + 0.0393X_1^2 + 0.0393X_2^2 - 0.0036X_3^2 - 0.0066X_4^2 - 0.0063X_1X_2 - 0.0340X_1X_3 - 0.0597X_1X_4 + 0.0105X_2X_3 + 0.0051X_2X_4 - 0.0088X_3X_4 \quad (R^2 = 0.999) \quad (1)$$

$$Y_{\text{FFA}} = 0.3497 + 0.1469X_1 - 0.0423X_2 + 0.0094X_3 + 0.0834X_4 + 0.0044X_1^2 + 0.0044X_2^2 + 0.0003X_3^2 - 0.0011X_4^2 - 0.0057X_1X_2 - 0.0119X_1X_3 - 0.0165X_1X_4 + 0.0127X_2X_3 - 0.0098X_2X_4 - 0.0012X_3X_4 \quad (R^2 = 0.995) \quad (2)$$

$$Y_{\text{purity}} = 51.8278 + 6.1428X_1 + 1.2353X_2 - 1.7999X_3 + 4.1184X_4 - 0.4349X_1^2 - 0.4349X_2^2 + 0.0334X_3^2 + 0.0765X_4^2 - 0.2013X_1X_2 - 0.6520X_1X_3 + 0.8204X_1X_4 + 1.8393X_2X_3 - 1.4513X_2X_4 - 0.0239X_3X_4 \quad (R^2 = 0.999) \quad (3)$$

where X_1 , X_2 , X_3 , and X_4 were the level values (row 1 in Table 5) of the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, and the reaction time, respectively. The conversion relations of these level values (row 1 in Table 5) and the real values (row 2–5 in Table 5) were as follows:

$$X_1' = 0.1X_1 + 0.2 \quad (4)$$

$$X_2' = 23.8X_2 + 23.8 \quad (5)$$

$$X_3' = 5.64X_3 + 16.92 \quad (6)$$

$$X_4' = 2X_4 \quad (7)$$

where X_1' , X_2' , X_3' , and X_4' were the real value of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, and the reaction time.

3.4. Validation of the In Situ Transesterification Models.

The FFA contents and the FAME purities of the products generated from experiments in Table 6 are shown in Figure 3. It could be seen that the products with high FAME purity also had high FFA content and vice versa. It was impossible to obtain a product with high FAME content but low FFA content. So, it was important to get balance among the three responses. Anyway, it was desirable that less reagent was used. Especially, the unreacted methanol and DEM should be less, because they would determine the energy consumption for recovery.

Here we proposed a method to solve those problems: by minimizing the volume sum of methanol and DEM when the biodiesel yield was more than 8.62 g (about 94% of the theoretical yield), the FFA content was less than 0.75% and the FAME purity was more than 96%. These statements are illustrated in the following formulas:

$$\min[(10X_2 + 10) + (10X_3 + 40)] \quad (8)$$

$$\text{subject to: } 1 \leq X_1 \leq 4 \quad (9)$$

$$1 \leq X_2 \leq 4 \quad (10)$$

$$1 \leq X_3 \leq 4 \quad (11)$$

$$1 \leq X_4 \leq 4 \quad (12)$$

$$8.62 \leq Y_{\text{yield}} \leq 9.17 \quad (13)$$

$$0 \leq Y_{\text{FFA}} \leq 0.75 \quad (14)$$

$$96 \leq Y_{\text{purity}} \leq 100 \quad (15)$$

where X_1 , X_2 , X_3 , and X_4 were the level values of the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, and the reaction time respectively. The computation expression of $(10X_2 + 10)$ and $(10X_3 + 40)$ in eq 8 were the volume of methanol and DEM, respectively.

Because the factors of the molar ratio of catalyst/oil (X_1) and reaction time (X_4) were not included in eq 8, the solution would not be unique. Some of the calculated solutions and the experimental results are presented in Table 7. Though there were some differences between the experimental values and the calculated values, especially when low dosage of catalyst or short reaction time were adopted, good results were obtained in solution 3, solution 4, and solution 5 in Table 7. So the rapid

in situ transesterification process of sunflower seeds was well-simulated by the empirical models established above.

Taking solution 4 as an example, 8.79 g of crude biodiesel containing 97.7% FAME and 0.74% FFA was obtained by the in situ transesterification of 20 g of sunflower seeds containing 4.63% moisture and 45.63% oil at the molar ratio of catalyst (NaOH)/oil of 0.5:1, the molar ratio of methanol/oil of 101.39:1, the molar ratio of DEM/oil of 57.85:1, the agitation speed of 150 rpm, the reaction temperature of 20 °C, and the reaction time of 13 min. With the help of DEM, the reaction time was shortened from 8 h¹⁹ to 13 min, the efficiency was greatly improved. The molar ratio of catalyst (NaOH)/oil was reduced from 2.0:1¹⁹ to 0.5:1. The molar ratio of methanol/oil was reduced from 543:1 to 101.39:1. The volume sum of methanol and DEM in the rapid in situ transesterification process was 145.25 mL, whereas the volume of methanol used in the process without any assistant cosolvent was 120 mL.¹⁹ It seemed that more liquid was used in the DEM-assisted in situ process than that without any colvents, but taking account of the oil content differences between the sunflower seed (45.63%) and the soybean (23.9%), less liquid was needed to produce per unit mass of biodiesel. To produce 1 g of biodiesel, the methanol volume of about 25.0 mL was needed when no DEM was used, and the sum of methanol and DEM volume was about 16.9 mL.

Given the oil content of 45.63% for the sunflower seeds, an overall FAME recovery of 93.7% was obtained in the rapid in situ transesterification in about 10 min. The overall FAME recovery of the current standard process was about only 92%, and the total operation time was several hours.¹⁹

There was an oil extraction process in the conventional oil-based transesterification process, while the oil extraction and transesterification were simultaneously accomplished in the in situ transesterification process. That was the reason why the molar ratio of methanol/oil (from about 65:1 to 120:1, see Table 7) in the in situ process was greatly higher than that of oil-based transesterification (usually about 6:1). In the oil extraction process, the ratio of liquid (usually n-hexane) to solid was usually 4:1–10:1 (volume of n-hexane:weight of oilseed). Taking a soybean oil extraction as an example, if the oil content was 18% and the ratio of liquid to solid was 6:1, the molar ratio of extractant (n-hexane)/oil reached 224:1. So there was no significant difference between the amount of the total solvent used in the DEM-assisted in situ transesterification (including DEM and methanol) and conventional oil-based process (including n-hexane used in oil extraction and methanol used in transesterification). On the other hand, after exposure to

Table 7. Some Calculated Solutions of the In Situ Transesterification Model and Experimental Results

	solution 1	solution 2	solution 3	solution 4	solution 5	solution 6	solution 7
volume sum of methanol and DEM (mL)	100.91	111.17	139.36	145.25	148.40	149.97	151.33
molar ratio of catalyst/oil, calculated level value/real value	2.46/0.45:1	2.70/0.47:1	2.87/0.49:1	3.02/0.50:1	3.50/0.55:1	3.67/0.57:1	4.00/0.60:1
molar ratio of methanol/oil, calculated level value/real value	1.95/70.21:1	1.76/65.69:1	2.68/87.58:1	3.26/101.39:1	4.00/119.00:1	4.00/119.00:1	3.92/117.10:1
molar ratio of DEM/oil, calculated level value/real value	4.14/40.27:1	5.36/47.15:1	7.25/57.81:1	7.26/57.85:1	6.84/55.50:1	7.00/56.4:1	7.22/57.64:1
reaction time (min), calculated level value/real value	8.0/16.0	7.5/15	7.0/14	6.5/13	6.0/12	5.5/11	5.0/10
Y_{yield} (%), predicted value/experimental value	8.62/8.44	8.62/8.59	8.62/8.76	8.62/8.79	8.62/8.68	8.62/8.69	8.62/8.74
Y_{FFA} (%), calculated value/ experimental value	0.75/0.71	0.75/0.70	0.72/0.73	0.72/0.74	0.71/0.75	0.73/0.79	0.75/0.81
Y_{purity} (%), calculated value/ experimental value	96.0/94.4	96.0/95.6	96.0/96.2	96.0/97.7	96.0/98.5	96.0/97.4	96.0/96.7

methanol and DEM, whether the residue of the sunflower seeds would cause any health problem is a new question worth further study.

4. Conclusions

Compared with the in situ transesterification without any cosolvent, the DEM-assisted rapid in situ transesterification showed great advantages in shortening reaction time and reducing the addition amounts of catalyst and methanol. The moisture content of sunflower seeds, the catalyst category, and the agitation speed showed very limited influence on the rapid in situ transesterification, while the molar ratio of catalyst/oil, the molar ratio of methanol/oil, the molar ratio of DEM/oil, and the reaction time were the important factors affecting the biodiesel yield, the FFA content, and the FAME purity. The results calculated from the empirical models for the rapid in situ transesterification were basically consistent with the experiments results. A crude biodiesel product with 97.7% FAME and 0.74% FFA was obtained in 13 min by the rapid in situ transesterification.

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Nomenclature

DEM = diethoxymethane

DPS = data processing system

FAME = fatty acid methyl ester

FFA = free fatty acid

PLS = partial least-squares

SRC = standard regression coefficient

THF = tetrahydrofuran

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