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Orthogonal array design for biodiesel production optimization - using ultrasonic-assisted transesterification of *Camelina sativa* L. Crantz oil

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Abstract: Camelina seed oil has recently attracted great interest as a low-cost feedstock for biodiesel production because of its high oil content and environmental benefits. In the present study, an orthogonal array design was used to optimize the biodiesel production from camelina seed oil using ultrasonic-assisted transesterification. Four relevant factors are investigated: methanol to oil ratio, catalyst concentration, reaction time and temperature to obtain maximum fatty acid methyl ester (FAME) yield of biodiesel. An OA_{25} matrix was employed to study the effect of the four factors, by which the effect of each factor was estimated using statistical analysis. Based on the results of the statistical analysis after the orthogonal experiments, maximal biodiesel FAME yield (98.6 %) was obtained under the conditions of 8:1 methanol to oil molar ratio, 1.25 wt.% catalyst concentration (KOH), 50 min reaction time, and 55 ℃ reaction temperature. Other properties of the optimized biodiesel, including density, kinematic viscosity, and acid value, were conformed to the relevant ASTM and EN biodiesel standards and thus the optimized biodiesel from camelina oil basically qualified to be used as diesel fuel.

Keywords: Biodiesel, Orthogonal experiment, Optimization, Ultrasonic-assisted, Camelina oil.

1. Introduction

In recent years, biodiesel, as a low-emission renewable fuel, has attracted great public interest and there is a huge demand for biodiesel in the renewable fuel market. At present, most of biodiesel is produced from vegetable oils, such as soybean and rapeseed [1]. However, many vegetable oils for biodiesel production are edible and compete with the edible oil market. It will increase the cost of vegetable oils and cause deforestation since a lot of forests have to be felled for plantation purposes [2]. Moreover, the cost of raw materials accounts for 60-80 % of total biodiesel production [3]. Increasing cost of vegetable oils also causes the cost of biodiesel production higher. Therefore, many researchers focus on different feedstocks of biodiesel and explore non-edible vegetable oils for biodiesel production, such as jatropha curcas oil and algae oil [4].

Camelina (*Camelina sativa* L. Crantz), is a spring annual oilseed plant originated in Germany in about 600 B.C.. It grows well in temperate climates and matures earlier than other oilseed crops [5]. In comparison with common oilseed crops, camelina has lower agriculture inputs, such as lower water, pesticide and fertilizer requirements, and higher cold-weather tolerance. Therefore, camelina may avoid deforestation in certain extent since it can be cultivated in agriculturally undesirable lands which are not suitable for normal crops, hence improving the quality of lands [6]. Furthermore, camelina seeds have an oil content as high as 28 to 40 %, which makes camelina a high oil-bearing crop [7]. Therefore, the use of camelina oil as feedstock for biodiesel production can greatly reduce the production cost of biodiesel and offer some environmental benefits.

Frohlich and Rice [8] already evaluated the possibility of using camelina oil as a source for biodiesel production and Patil et al. [9] also tried to produce biodiesel from camelina oil using supercritical and subcritical methanol with cosolvents. Although there are some studies related to biodiesel produced from camelina oil, the optimal production conditions have never been investigated. Most optimal conditions were attained using a stepwise approach, which examined one process condition at a time [10]. This method was time-consuming and might

not get the right optimal conditions because some process conditions affect the yield of biodiesel simultaneously. This paper used an orthogonal array experimental design to optimize the biodiesel production conditions from camelina seed oil in order to avoid these problems. The use of the chemometric method: Orthogonal Array Experimental Design for process optimization has already found many applications elsewhere. It involves the selection of some representative combinations of factors and levels for the experiments to reflect the situation of the whole selected examined area. It is a cost-effective optimization strategy that can obtain the optimal level of each factor in a limited number of experimental trials [11]. This paper discussed the main process conditions in the transesterification reaction using orthogonal array experiments to optimize biodiesel production. To confirm whether or not the final product can be used as a qualified fuel, this study will also examined its compliance with international biodiesel standards.

Normally, a stirred reactor is used as the reaction vessel for continuous alkali-catalyzed biodiesel production. However, ultrasonic irradiation has proved to be a useful tool for strengthening the mass transfer of immiscible liquids. It can cause cavitation of bubbles near the phase boundary between immiscible liquid phases and then the asymmetric collapse of the cavitations bubbles disrupts the phase boundary and causes emulsification. Micro jets, which are formed by impinge one liquid to another, lead to intensive mixing of the system near the phase boundary and thus reactants can be produced more quickly [12, 13]. Therefore, assisted with ultrasound, the reaction time may be reduced dramatically and the high reaction temperature may be lower than in traditional mechanical stirring production process. That would reduce the production cost of biodiesel and save more energy.

2. Methodology

Reagents and catalysts

Cold-pressed camelina seed oil, obtained from Campressco Products Inc. (Saskatchewan, Canada), was used for the experiments. The main chemical compositon of the oil was, expressed in wt.%, 5 % palmitic acid, 16.7 % oleic acid, 16.9 % linoleic acid, 16.1 % cis-11-eicosenoic acid and 38.1 % linolenic acid. Analytical grade methanol (99.9 %) was used in the experiments and potassium hydroxide (>85 %) in pellet form was used as the catalyst for the alkaline transesterification reaction.

2.1. Experimental process

Around 100 g (±0.1) of camelina oil was weighted and placed in a 250 ml glass bottle. The amount of methanol used was calculated based on its molar ratio with oil. The catalyst was first dissolved completely in methanol with a prefixed amount using a standard mixer, and then the mixture was added into the oil. The whole reaction was carried out in an ultrasonic bath obtained from Jeio Tech Co., Ltd. (model: US-05; frequency: 40 KHz; volume: 5L) and operated at 40 KHz. To enhance mass transfer and the reaction rate, the bottle was shaken for about 20 seconds by hand for every 10 minutes. Until reaching the preset reaction time, the glass bottle was then removed from the bath and the products of the reaction were settled down overnight at the room temperature. Two major products was observed in the bottle: crude biodiesel phase at the top and glycerol phase at the bottom. These two phases were separated by centrifugation (rotating speed: 8000 r pm; time: 5 min). After that the crude biodiesel was washed several times by deionized water assisted with ultrasound to remove the impurities and unreacted catalyst. The use of ultrasound reduced the washing times.

2.2. Orthogonal experiment design

In the study, the experiments were based on an orthogonal array experimental design (OA_{25} matrix) where the following four variables were analyzed: methanol to oil molar ratio (factor A), catalyst concentration (factor B), reaction time (factor C) and reaction temperature (factor D). These variables were identified to have significant effects on the yield of biodiesel produced from other feedstocks [10]. An OA_{25} matrix was employed to assign the considered factors and levels as shown in Table 1. Twenty-five trials were carried out according to the OA_{25} matrix to complete the optimization process. Each row of orthogonal array represents a run, which is a specific set of factor levels to be tested. The run order of the trials was randomized to avoid any personal or subjective bias. Here the matrix denotes four factors each with five levels and the extra column remained could be used as experimental error to indicate the reliability of the whole experiments. Statistical analysis was carried out to reflect the optimal reaction conditions and their magnitudes.

Table 1 Levels and factors affecting the FAME yield of biodiesel.

| Level | Factors | | | |
	Alcohol quantity (Molar ratio) A	Catalyst concentration (wt.%) B	Reaction time /min C	Reaction temperature /°C D
1	2:1	0.75	10	25
2	4:1	1	30	35
3	6:1	1.25	50	45
4	8:1	1.5	70	55
5	10:1	1.75	90	65

2.3. Fuel properties of biodiesel

The whole experiments of biodiesel were aimed at increasing the fatty acid methyl ester (FAME) yield. This yield determines the quality of the biodiesel product and indicates the efficiency of oil conversion. The EN standard (EN14214) requires FAME content of biodiesel to be over 96 % [14]. In the present study, the FAME yield was analyzed by a Hewlett-Packard 6890 Series gas chromatograph (Palo Alto, USA) according to the AOCS official methods Ce 1-62 [15], equipped with a flame ionization detector (FID) operating at 300 ℃ and a capillary injection system operating at 250 ℃. The carrier gas was high-purity helium, with a constant flow of 1.0 ml/min, and samples of 1 μL were injected in split mode with a split ratio of 80:1. The column was a BD-EN14103 HP-INNOWax column (J&W Scientific, USA) with 30 m in length, 0.32 mm internal diameter and 0.25 μm film thickness. To minimize the experimental error, a known amount of a specific component methyl nonadecanoate (C19:0), used as the internal standard, was added into the sample prior to the GC injection. Other properties of the final biodiesel product, including density, kinematic viscosity and acid value, were determined in order to evaluate its suitability as diesel fuel substitute. The density was determined at the room temperature by using a density bottle while its kinematic viscosity was determined with an ubbelohde glass capillary kinematic viscometer according to the ASTM D445 method. The acid value (AV) was calculated according to the ASTM D644 method. All data reported were arithmetic means of triplicate assays.

2.4. Statistical analysis of orthogonal experiments

The statistical analysis included a range analysis and an analysis of variance (ANOVA). Range analysis was used to indicate the effect of each factor and determine the optimal level

of different factors. The mean value of the sum of the evaluation indexes of all levels in each factor ($\overline{K_{ji}}$) was used to determine the optimal level and the optimal combination of factors. The range (R_j) was defined as the range between the maximum and minimum value of the mean values and used to evaluate the importance of the factors. The optimal level for each factor could be obtained when $\overline{K_{ji}}$ is the largest and larger R_j means greater significance of the factor [16]. Although the optimal value of different factors can be easily determined by the range analysis, this method cannot distinguish whether the difference between the data fluctuation of each factor level was caused by experimental conditions or by experimental errors. Due to the limitation of the range analysis, analysis of variance was necessary to obtain the magnitudes of the factor affecting the result [17]. In the ANOVA, the data were analyzed by a F-test. The F value of each factor (F_j) implies the ratio of the variance for the each factor (V_j) to that of the experimental error (V_e) [16, 18]. During the F-test, F_α was a constant and defined as a critical value of the F-value for different inspection levels and can be found from the distribution table of the F-values [18]. When F_j is larger than F_α, the factor effect for the results is prominent; otherwise the factor effect for the results is not prominent. Moreover, the percentage contribution of each factor (P_j) was the percentage of the purified sum of square deviation for each factor (SS_j') in the total sum of square deviation (SS_T). It reflects the factor's influence and the percentage contribution due to experimental error providing an estimate of the adequacy of the whole experiments. Larger percentage contribution means more significant factor influence. When the percentage contribution due to error is low, say 15 % or less, it can be assumed that no important factor has been omitted and the whole experimental results are reliable [18, 19].

3. Results and discussion

3.1. Fatty acid methyl ester yield and statistical analysis

According to the OA_{25} matrix, twenty-five experiments were carried out and the results were shown in Table 2. As mentioned before, the extra column was used as the experimental error to indicate the reliability of the whole experiments. These data were taken as the original data and used in the statistical analysis.

The mean values ($\overline{K_{ji}}$) and the relative data of range analysis were shown in Table 3. The highest FAME yield of each level was clearly distinguished when methanol to camelina seed oil molar ratio was 8:1 (93.4 %), catalyst concentration was 1.25 wt.% (89.5 %), reaction time was 50 minutes (87.8 %) and reaction temperature was 55 ℃ (86.9 %) since $\overline{K_{ji}}$ at these combinations ($A_4B_3C_3D_4$) was the highest. Since larger R_j means bigger impact on the product yield, compared with the range values of different factors (R_j), the order of significant factors was: methanol to oil ratio (36.9) > catalyst concentration (14.8) > reaction time (10.3) > reaction temperature (7.3). The mean values of each factor ($\overline{K_{ji}}$) were shown in Fig.1. It should be noted that these lines were only used to show the trend of each factor, not for predicting other values that were not experimented [20]. Based on the changes of $\overline{K_{ji}}$, it can be observed that the FAME yield was dramatically increased from 56.5 % to 93.4 % with the ratio of methanol to oil increased from 2:1 to 8:1, and then slightly decreased. It indicated that increasing methanol amount immediately speeded up the transesterification reaction and shifted the reaction equilibrium toward the product side to form more FAME. However, further increasing the methanol amount beyond the optimal ratio reduced the yield since methanol also acts as an emulsifier that enhances emulsion. This caused a drop in FAME yield and complicated the washing process. The FAME yield increased with increasing catalyst concentration and reached maximum (89.5 %) at 1.25 wt.%. Beyond the optimal point, the yield slightly decreased to 86 %. It indicated that sufficient amount of catalyst was

required for complete conversion but excessive catalyst might activate the oil to react with the alkali catalyst, and thus formed more soaps and reduced the FAME yield. For reaction time, the FAME yield increased steadily first, and reached a maximum (87.8 %) at 50 min, and then the yield reduced slightly. Theoretically, FAME conversion would increase with reaction time. However, beyond the optimal time, the FAME yield slightly reduced because of the backward reaction and the saponification reaction [10]. Finally, reaction temperature seems to have little effect on the FAME yield with a change from 79.7 % to 86.9 %. Since the reaction was carried out in an ultrasonic bath, the cavitation led to a localized increase in temperature at the phase boundary and thus the influence of reaction temperature was small.

Table 2 FAME yield of biodiesel in OA_{25} matrix.

Trial no.	Factors					Results
	A	B	C	D	Experimental error level	FAME yield (wt.%)
1	2:1	0.75	10	25	1	28.5
2	2:1	1.00	30	35	2	53.6
3	2:1	1.25	50	45	3	68.4
4	2:1	1.50	70	55	4	67.6
5	2:1	1.75	90	65	5	64.2
6	4:1	0.75	30	45	4	84.1
7	4:1	1.00	50	55	5	93.4
8	4:1	1.25	70	65	1	95.2
9	4:1	1.50	90	25	2	90.5
10	4:1	1.75	10	35	3	85.9
11	6:1	0.75	50	65	2	88.5
12	6:1	1.00	70	25	3	91.6
13	6:1	1.25	90	35	4	95.8
14	6:1	1.50	10	45	5	92.5
15	6:1	1.75	30	55	1	96.2
16	8:1	0.75	70	35	5	88.5
17	8:1	1.00	90	45	1	94.6
18	8:1	1.25	10	55	2	93.6
19	8:1	1.50	30	65	3	96.9
20	8:1	1.75	50	25	4	93.3
21	10:1	0.75	90	55	3	83.8
22	10:1	1.00	10	65	4	87.1
23	10:1	1.25	30	25	5	94.4
24	10:1	1.50	50	35	1	95.6
25	10:1	1.75	70	45	2	90.3

Table 3 Range analysis data of biodiesel FAME yield.

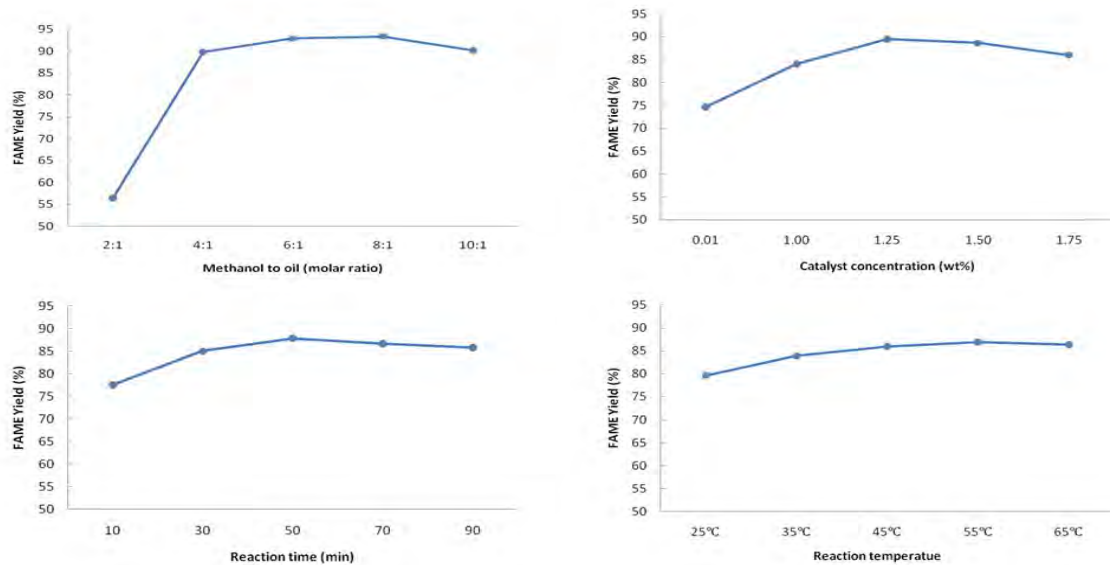|	Alcohol quantity (Molar ratio) A	Catalyst concentration (wt.%) B	Reaction time /min C	Reaction temperature /℃ D
$\overline{K_{i1}}$	56.5	74.7	77.5	79.7
$\overline{K_{i2}}$	89.8	84.1	85.0	83.9
$\overline{K_{i3}}$	92.9	89.5	87.8	86.0
$\overline{K_{i4}}$	93.4	88.6	86.6	86.9
$\overline{K_{i5}}$	90.2	86.0	85.8	86.4
R_j	36.9	14.8	10.3	7.3

Fig.1. Relationship between the mean values of various influence factor and FAME yield.

The data of ANOVA for the FAME yield was shown in Table 4. For the inspection level, $\alpha=0.05$, the critical value can be found from the distribution table of F-value: $F_a(4,4) = 6.39$. It was obvious that F_A (72.2) > F_a, F_B (10.2) > F_a. It indicated that methanol to oil ratio and catalyst concentration were the prominent factors affecting the FAME yield of biodiesel, when the regression curve and analysis were within a 95 % confidence level. Furthermore, from the percentage contribution, it was deduced that the most important factor contributing to the product yield was factor A (methanol to oil ratio, 78.5 %), followed by factor B (catalyst concentration, 10.1 %), whereas factors C (reaction time, 4.2 %) and factor D (reaction temperature, 1.7 %) were not the significant factors for the change of FAME yield. Since the percentage contribution due to error was low (5.5 %), it was assumed that no important factor had been omitted and the whole experimental results were reliable.

Table 4 ANOVA results of the FAME yield in OA$_{25}$ matrix.

Source	SS$_j$	df	V$_j$	F$_j$	F$_a$(4,4)=6.39	SS$_j$'	P$_j$ (%)
A	4986.1	4	1246.5	72.2	>	4917	78.5
B	702.9	4	175.7	10.2	>	633.8	10.1
C	331.8	4	83.0	4.8	<	262.7	4.2
D	176.9	4	44.2	2.6	<	107.8	1.7
e	69.1	4	17.3	—		345.5	5.5
T	6266.8	20				6266.8	100

3.2. Optimization of the experimental conditions

According to the statistical analysis, the four experimental conditions affected the FAME yield of biodiesel differently. The amount of methanol and catalyst influenced dramatically the FAME yield and reaction temperature had a few effect on the FAME yield. The results indicated that increasing the level of these factors speeded up the reaction and the FAME conversion. However, beyond the optimal level, the FAME yield slightly reduced because of the backward reaction, such as emulsion and saponification. On the other hand, reaction temperature had little effect on the FAME yield since assisted with ultrasound already led to a localized increase in temperature at the liquid phase boundary.

Finally, the experiment was repeated under the optimal process conditions to confirm the validity of the optimization. A FAME yield of 98.6 % was obtained, which was higher than any former orthogonal experimental result. Compared with the data of the Trial 18 experiment, it was obvious that there was slight difference in the FAME yield (93.6 %) because of the influence of reaction time (10 min in Trial 18 and 50 min under optimal conditions). This result was consistent with that of the statistical analysis. And compared with the results of the traditional mechanical stirring production process, the FAME yield under optimal conditions with ultrasonic-assisted was much higher. Both the reaction time and the amount of catalyst used were reduced [8]. Other properties of biodiesel produced under the optimal conditions were also measured. The density of biodiesel was 0.882 g/cm^3, while the kinematic viscosity was 3.66 cst at 40℃, and the acid value was 0.217 mg KOH/g. Compared with the ASTM D6751 and EN 14214 standards, all the tested fuel properties of biodiesel produced under the optimal production conditions met the requirements. Therefore, optimized biodiesel basically qualified to be used as the diesel fuel.

4. Conclusions

In this research, the alkali-catalyzed ultrasonic-assisted transesterification reaction of camelina seed oil was studied and optimized through the orthogonal experiments with an OA$_{25}$ matrix and a statistical analysis. According to the range analysis, the FAME yield of biodiesel increased sharply with increasing the amount of methanol used and catalyst concentration but was slightly reduced after the optimal point. The FAME yields also increased with increasing reaction time and temperature but the change was small. According to the ANOVA, the amount of methanol and catalyst used were significant factors for the FAME yield. After the whole statistical analysis, the optimal FAME yield of biodiesel (98.6 %) was obtained to be methanol to oil molar ratio of 8:1, catalyst concentration of 1.25 wt.%, reaction time of 50 min and reaction temperature of 55 ℃. Since the tested fuel properties of biodiesel conformed to the ASTM D6751 and EN 14214 standards, camelina seed oil biodiesel produced under the optimal conditions basically can be used as a qualified fuel.

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Reference

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