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Process Optimization and Characterization of Methyl Ricinoleate by Orthogonal Design of Experiments

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Abstract: ***Methyl ricinoleate (MR) is an important bio-based chemical raw material. This study has changed the traditional pickling process and prepared MR by transesterification using castor oil and anhydrous methanol, with potassium hydroxide as catalyst. Orthogonal design of experiments were conducted to measure the multiple effects of reaction temperature, time, methanol/oil molar ratio, and catalyst dosage based on product yield and 40 ℃ kinematic viscosity, and the optimal reaction conditions were determined. After the structure of the products was characterized by FTIR, GC-MS, and NMR, it indicated that under the optimized conditions, the product yield was 96.7% and MR content was 84.1%.***

Keywords: Methyl ricinoleate, Orthogonal design, Transesterification, Structural characterization.

1. Introduction

Castor (*Ricinus communis* L.) is an industrial oil crop. Ricinoleic acid, a naturally occurring 12-hydroxy fatty acid, accounting for about 90% of the fatty acids in castor oil, fully named 12-hydroxy-9-octadecenoic acid, can conduct multiple reactions such as hydrogenation, oxidation, epoxidation, amidation, hydrolysis, esterification, and transesterification [1]. Castor oil derivatives are widely used in the fields of chemical industry, pharmaceutical industry, aviation, food, machinery manufacturing, etc. Castor oil provides abundant raw material for the production of methyl ricinoleate [2].

Methyl ricinoleate is an important bio-based chemical raw material that can be obtained by transesterification between castor oil and methanol. Methyl ricinoleate can be cracked to produce undecylenic acid methyl ester, which is then saponified, acidified and refined to obtain undecylenic acid, with byproducts such as heptanal and glycerol. Undecylenic acid has a wide range of applications. After bromination and ammonolysis reaction, amino undecylenic acid can be generated. After polymerization, PA11 can be produced, which has the advantages of low temperature resistance, good oil-resistance, low water absorption, and easy processing [3]. It is widely used in military industry, medical instruments, food manufacture, sporting goods industry, as well as surfactants and pharmaceuticals [4]-[5].

In the field of fuel, methyl ricinoleate can be used as bio-based diesel [6]. With the increasingly strict environment-protection requirements, there is a problem that the hydrodesulfurization degree of petroleum-based diesel has increased, resulting in a decrease in diesel lubricating performance. Methyl ricinoleate can be used as a bio-based diesel additive to enhance the lubricating performance of low sulfur diesel [7].

However, the methyl ricinoleate produced by traditional pickling process has high acid value, which directly affects the quality of subsequent deep processing products, not conducive to market application. Aiming to prepare high-quality methyl ricinoleate products, we have established a set of technological process flow. We used the orthogonal experiment method, set the product yield and 40 ℃ kinematic viscosity as the judgment basis, and comprehensively measured the effects of multiple factors including reaction temperature, reaction time, raw material ratio, and catalyst dosage. Based on the research above, we have determined the optimal preparation process conditions, and characterized the composition and structure of the product.

2. Experimental Part

2.1 Reagent Raw Materials

Castor oil (analytical pure), anhydrous methanol (analytical pure), potassium hydroxide (analytical pure), petroleum ether (90-120℃; analytical pure).

2.2 Analysis Instruments

The structural analysis was carried out by the Spectrum One-B Fourier transform infrared spectrometer (FTIR) from PE Company in US, the gas chromatography-mass spectrometry (GC-MS) from Shimadzu Company, and the AV300 300MHz nuclear magnetic resonance (NMR) spectrometer from Brooke Company in Switzerland.

The content analysis of methyl ricinoleate was carried out by the gas chromatograph (GC) from Shimadzu Company.

The 40 ℃ kinematic viscosity of the product is measured by a kinematic viscosity tester with GB/T 265 as the test method standard.

2.3 Experimental Principle

The schematic diagram of the overall synthesis route for the transesterification between castor oil and methanol is as follows:

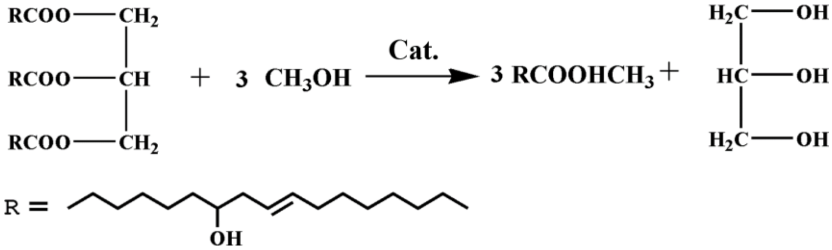

Figure 1: Schematic of the overall synthetic route

2.4 Preparation

Firstly, dissolve the measured KOH in anhydrous methanol to prepare KOH methanol solution. In a 250 ml three necked flask equipped with a reflux device, add 150 g of castor oil, heat to a specific reaction temperature, add the prepared KOH methanol solution, and stir for a while.

After the reaction is completed, transfer the reaction solution to a 500 ml separating funnel, add extraction solvent, shake evenly, and let it stand till the liquid separated. It can be observed that the lower layer is brownish red viscous liquid, and the upper layer is yellow liquid. Separate the two liquid layers, wash the upper layer liquid four times with water until the pH of the washing solution as same as the pH of distilled water.

Remove the residual water and extraction solvent by heating and vacuum distillation. The yellow transparent liquid obtained is methyl ricinoleate.

Calculate the prepared sample yield (=product mass/castor oil mass×100%), and measure the 40℃ kinematic viscosity.

2.5 Orthogonal Design

Liu Wenfeng and Liu Liangzheng have reported successively that the viscosity method can be used to test the conversion rate of transesterification, and the feasibility of this method has been verified [8]-[9]. The viscosity of castor oil is much higher than that of methyl ricinoleate. As a result, the lower the viscosity of the prepared sample, the higher the degree of reaction conversion. By comprehensively analyzing the sample yield and viscosity, it is practical to better measure the reaction process, which is conductive to exploring the optimal reaction conditions for ester exchange.

This study adopted a multi-factor orthogonal experimental design to investigate the conditions of transesterification (reaction temperature, reaction time, methanol/oil molar ratio, catalyst dosage) and select the optimal reaction conditions. The design of conditional factors and levels is shown in the Tab. 1 below, and the experimental factors are arranged by the L_9 (3^4) orthogonal table.

Table 1: Factors and level values of orthogonal design experiments

Factors *Levels*	*TEMP /℃ A*	*Time /h B*	*Molar Ratio C*	*Catalyst Dosage/% D*
1	30	2	3.9:1	0.6
2	45	4	6:1	0.9
3	65	6	9:1	1.2

3. Result and Discussion

3.1 Reaction Conditions

3.1.1 Effect of Reaction Conditions on Product Yield

Based on the analysis of product yield, it can be observed from Table 2 that $R_D>R_C>R_A>R_B$, indicating that the effect of catalyst dosage is almost consistent with the molar ratio of methanol/oil, which is greater than the reaction temperature and time. The product yields are higher at the levels of A1, B3, C2, and D1. The optimal reaction conditions for ester exchange are: reaction temperature 30℃, reaction time 6 hours, methanol/oil molar ratio 6:1, and catalyst dosage 0.6%.

Table 2: Effect of reaction conditions on the product samples' yield

No.	*A*	*B*	*C*	*D*	*Yield/%*
1	1	1	1	1	94.67
2	1	2	2	2	97.24
3	1	3	3	3	92.19
4	2	1	2	3	92.67
5	2	2	3	1	96.00
6	2	3	1	2	92.00
7	3	1	3	2	92.24
8	3	2	1	3	66.67
9	3	3	2	1	96.83
K1	94.700	93.193	84.447	95.833	
K2	93.557	86.637	95.580	93.827	
K3	85.247	93.673	93.477	83.843	
R (range)	9.543	7.036	11.133	11.990	

3.1.2 Effect of Reaction Conditions on Product Viscosity

Based on the analysis of product viscosity, it can be observed from Table 3 that $R_C>R_A>R_D>R_B$, indicating that the influence of the molar ratio of methanol/oil is greater than the reaction temperature, catalyst dosage, and reaction time. The yield is higher at the levels of A2, B3, C3, and D3. The optimal reaction conditions for ester exchange are: reaction temperature 45℃, reaction time 6 hours, methanol/oil molar ratio 9:1, and catalyst dosage 1.2%.

Table 3: Effect of reaction conditions on the product samples' kinematic viscosity

No.	A	B	C	D	*40 ℃ Viscosity* *(mm^2/s)*
1	1	1	1	1	22.26
2	1	2	2	2	17.88
3	1	3	3	3	16.28
4	2	1	2	3	15.45
5	2	2	3	1	16.94
6	2	3	1	2	18.38
7	3	1	3	2	16.71
8	3	2	1	3	19.71
9	3	3	2	1	17.31
K1	18.807	18.140	20.117	18.837	
K2	16.923	18.177	16.880	17.657	
K3	17.910	17.323	16.643	17.147	
R (range)	1.884	0.854	3.474	1.690	

In summary, taking product yield analysis as the main method and viscosity analysis as the auxiliary, while avoiding materials waste, the optimal reaction conditions are proposed as follows: reaction temperature 30°C, reaction time 6 hours, methanol/oil molar ratio 6:1, and catalyst dosage 0.6%. Under these conditions, the transesterification was carried out with a product yield of 96.7% and the 40 °C kinematic viscosity of 15.7 mm^2/s.

3.2 Product Composition and Structure Analysis

3.2.1 Analysis of Methyl Ricinoleate Content

The product composition has been analyzed by the gas chromatograph (GC). The substance with a retention time of 19.845 minutes is methyl ricinoleate, and its content was 84.1% calculated by the method of area normalization.

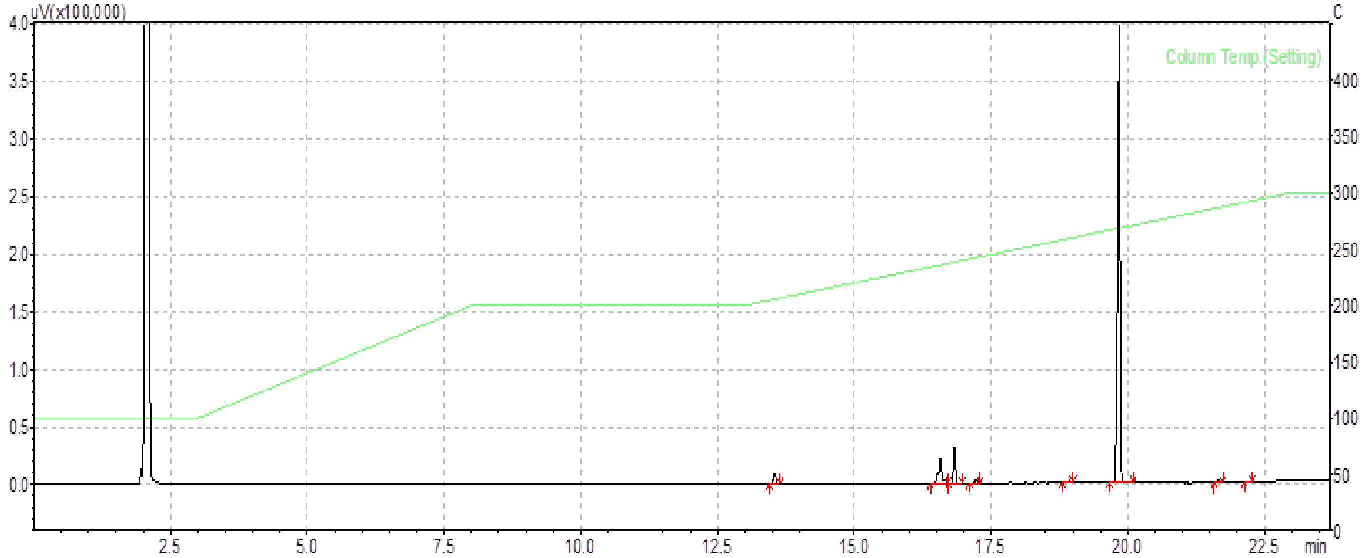

Figure 2: Gas chromatogram of product

3.2.2 FTIR Analysis

As shown in Figure 3, 3460 cm^{-1} is the characteristic strong absorption peak of hydroxyl groups, 3007 cm^{-1} is the stretching vibration absorption peak of the C-H bond on the olefin double bond, and 1742 cm^{-1} is the stretching vibration absorption peak of carboxyl groups in esters. The above characteristic peaks are consistent with the characteristic peaks of methyl ricinoleate.

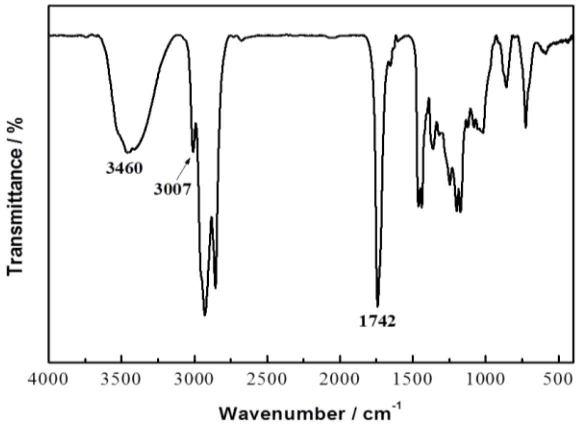

Figure 3: Infrared spectrogram of product

3.2.3 MS Analysis

The characteristic peaks of the product mass spectrometry are basically consistent with the methyl ricinoleate in the literature [10]. The molecular weight (M) of methyl ricinoleate is 312.49, and the hydroxyl groups in the molecule are easy to remove, which can be observed on the spectrum (Fig. 4) that an ion peak of M-18, with an M/Z value of 294.35.

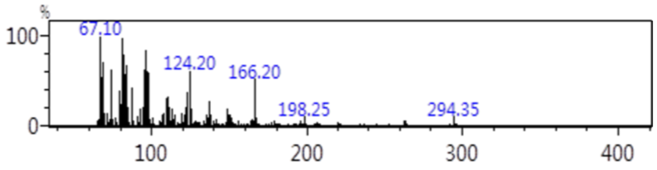

Figure 4: Mass spectra of product

3.2.4 Hydrogen and Carbon Spectrum Analysis

From the characteristic peak in Figure 5, it can be observed that, the chemical shift of the hydrogen proton in the methoxy group connected to the carboxyl group is 3.65 ppm, the chemical shift of the methylene hydrogen proton connected to the carboxyl group is a triple peak of 2.28 ppm, and the chemical shift of the proton in the double bond is a multiple peak of approximately 5.40 ppm. The hydrogen spectrum characteristic peaks of the product are consistent with the structure of methyl ricinoleate.

From the carbon spectrum (Figure 6), it can be observed that, the chemical shift of carboxyl carbon atoms is 174.34 ppm, the chemical shifts of double bonded carbon atoms are 125.26 ppm and 133.27 ppm, the chemical shift of carbon atoms connected to hydroxyl groups is 71.47 ppm, and the chemical shift of methoxy carbon atoms is 51.46 ppm. The carbon spectrum characteristic peaks of the product are consistent with the structure of methyl ricinoleate.

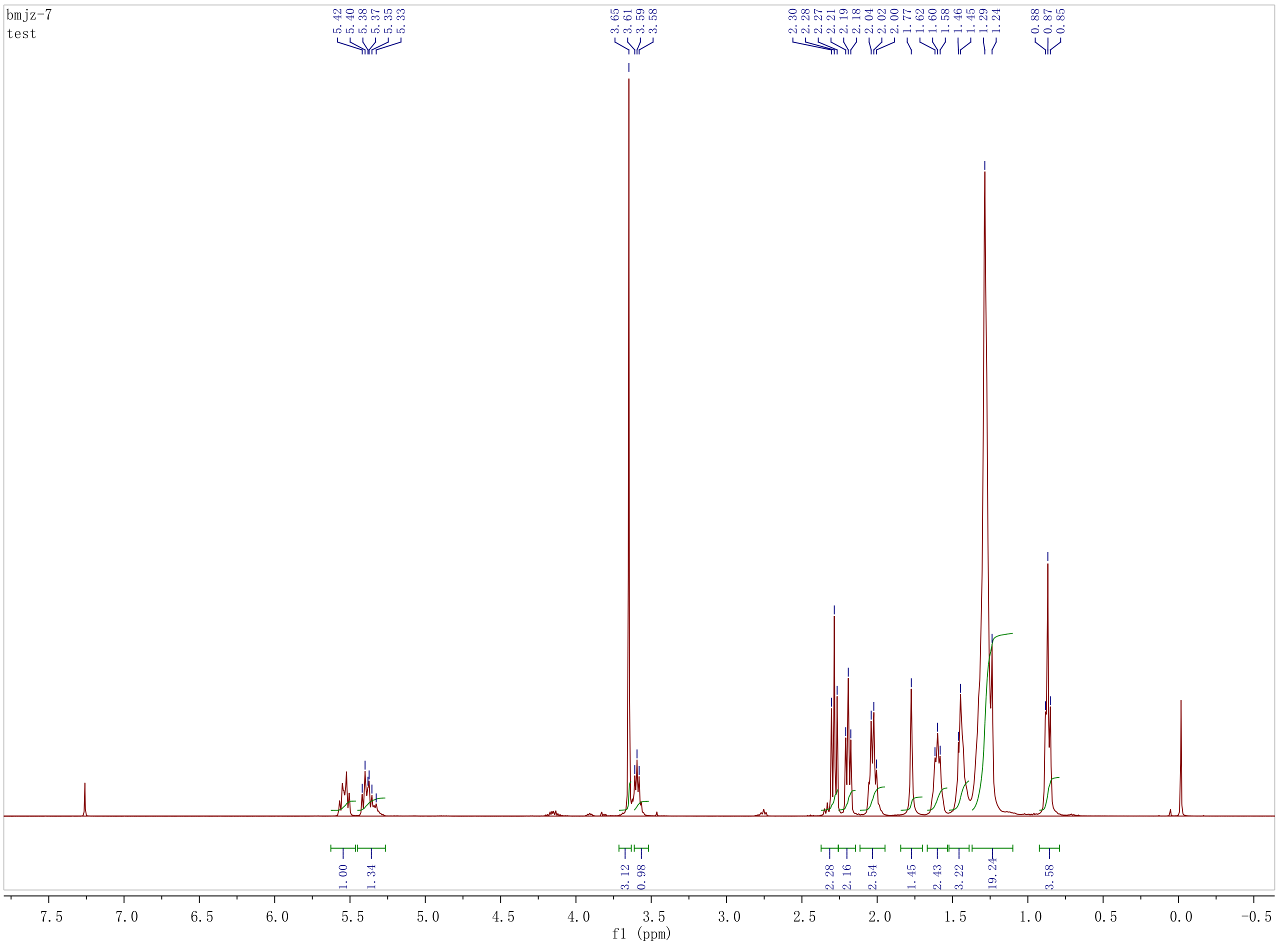

Figure 5: ^{1}H nuclear magnetic resonance spectrum of product

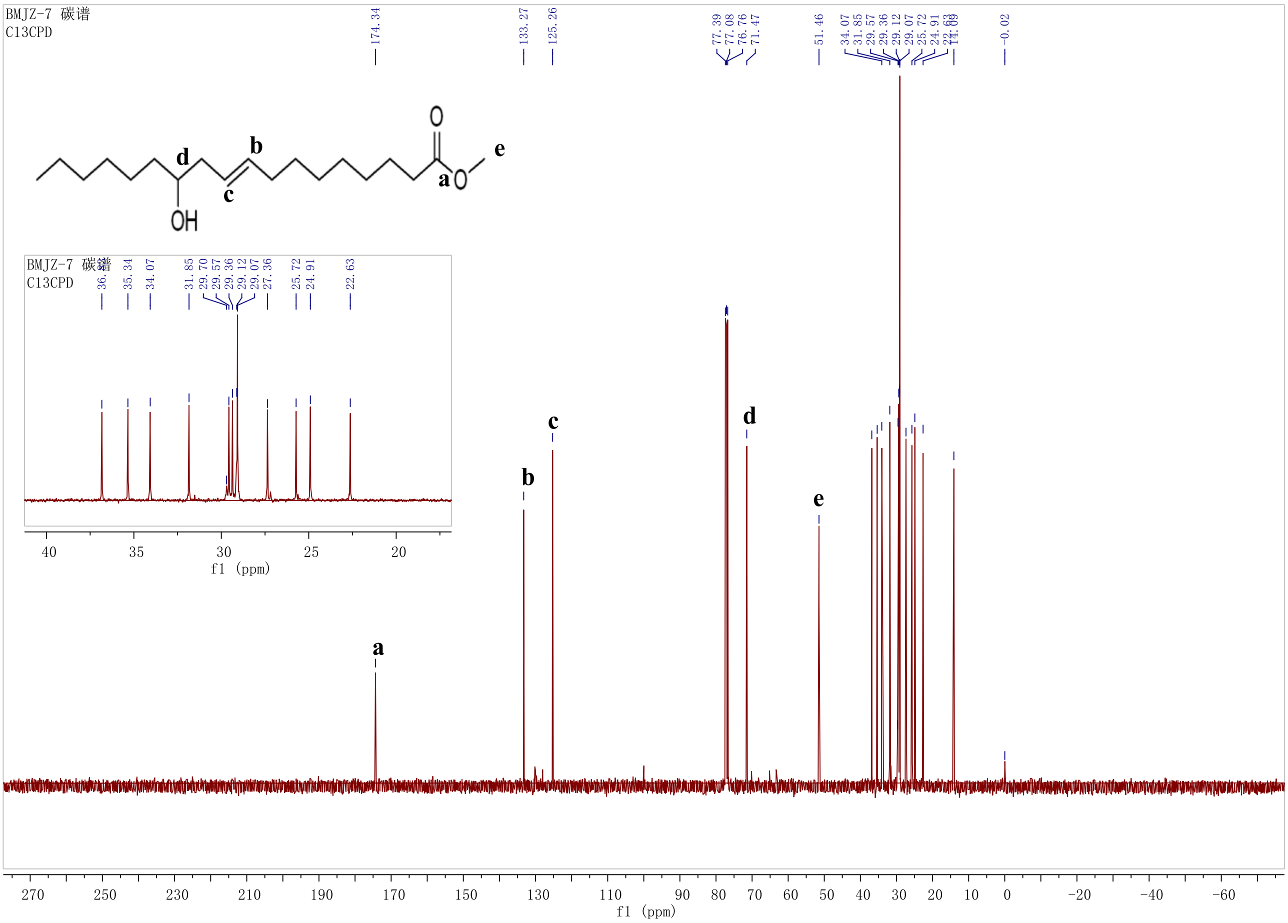

Figure 6: ^{13}C nuclear magnetic resonance spectrum of product

Gas chromatography analysis showed that the content of methyl ricinoleate in the product was 84.1%. The structure of the product was characterized by FTIR, GC-MS, hydrogen spectroscopy, and carbon spectroscopy, confirming that the product is methyl ricinoleate.

4. Conclusion

This study optimized the process of methyl ricinoleate by orthogonal experimental design. Based on product yield and 40℃ kinematic viscosity, simultaneously avoiding material waste, the optimal process conditions for methyl ricinoleate were determined to be: reaction temperature 30℃, reaction time 6 hours, methanol/oil molar ratio 6:1, and catalyst dosage 0.9%. The product structure was characterized by GC, FTIR, GC-MS, hydrogen spectroscopy, and carbon spectroscopy. It was determined that the product was methyl ricinoleate with the content of 84.1%.

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Author Profile

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