Optimizing Biodiesel Synthesis: From Process Parameters to the Distinct and Sub-Additive Effects of Water and Iron in Supercritical Methanol

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1. Calibration of Methyl Oleate Standard Curve

Different amounts of methyl oleate standard samples were accurately weighed and dissolved in 2 mL of ethyl acetate to prepare mixed solutions with varying concentration gradients. For each standard solution, 1.5 μL was injected into the gas chromatograph (GC) for detection and analysis. The resulting chromatograms were recorded, and the peak areas corresponding to methyl oleate were obtained. The methyl oleate standard curve (peak area vs. concentration) was then constructed, as shown in **Figure S1**. The calibration curve exhibited excellent linearity with a correlation coefficient $R^2 > 0.99$.

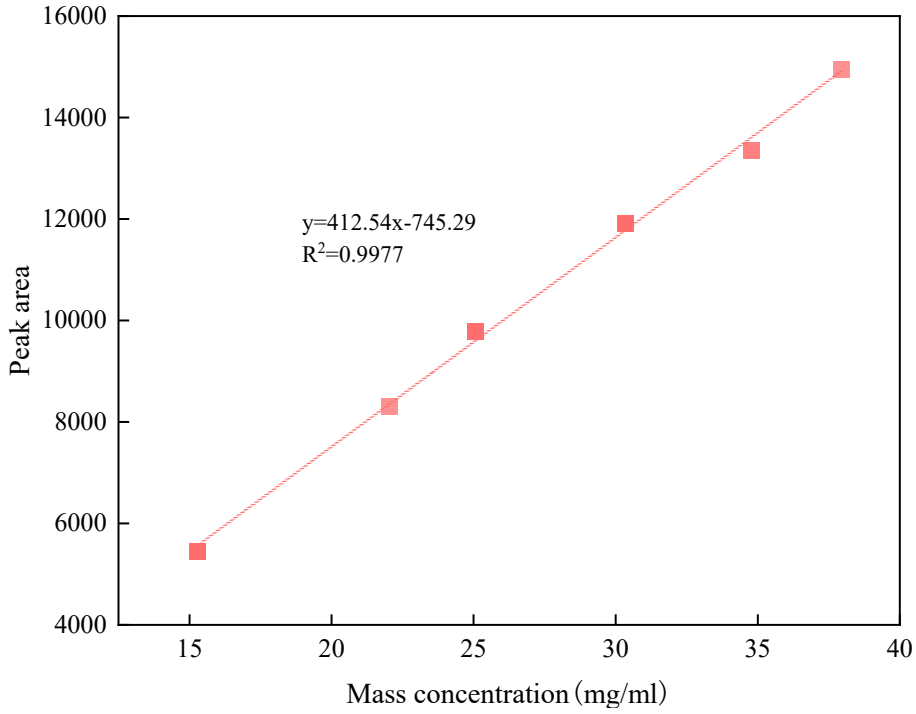

Figure S1 Standard curve of methyl oleate

2. Determination of Methyl Oleate Concentration in Reaction Products

A specified mass of oleic acid was placed into the autoclave to react with methanol under the designated conditions. After the reaction was completed, the final product was weighed. A known mass of the product was dissolved in 2 mL of ethyl acetate to prepare a homogeneous solution. An aliquot of 1.5 μL of this solution was injected into the GC for analysis, and the peak area of methyl oleate was recorded. Using the pre-established standard curve, the mass concentration of methyl oleate in the solution was determined. From this concentration and the known volume of the solution, the mass of methyl oleate in the dissolved product aliquot was calculated. Based on the ratio of this mass to the mass of the product aliquot taken, the mass fraction of methyl oleate in the total product was obtained. Multiplying this mass fraction by the total mass of the product gave the total mass of methyl oleate produced, which was then converted to the corresponding amount of substance (moles).

3. Quality Control and Replicates

For each product sample was performed by GC analysis, and the average peak area was used for concentration determination. The reported conversion values represent the mean of the independent experiments with standard deviations. Taking the test data obtained under conditions of 275°C, 30 min, and a methanol-to-oleic acid molar ratio of 15 as an example, the detailed data are provided in **Table S1**.

Table S1 Test data and conversion rate calculations for methyl oleate

No	Temperature/℃	Residence time/min	Molar ratio/mol·mol-1	Peak area	Mass concentration/mg·ml-1	Proportion/%	Product quality/g	Amount of methyl oleate/mol	Amount of oleic acid/mol	Conversion rate/%
1	275	30	15	9156	24.00	74.1%	7.452	0.019	0.025	75.2%
2	275	30	15	9025	23.68	74.6%	7.452	0.019	0.025	75.7%
3	275	30	15	8861	23.29	73.5%	7.452	0.018	0.025	74.8%