Study of Reaction and Kinetics in Pyrolysis of Methyl Ricinoleate

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ABSTRACT: The effects of pyrolysis temperature, space-velocity, and dilution ratio of starting materials on the reaction have been studied in the pyrolysis of methyl ricinoleate. The reaction parameters were optimized to obtain yield ranges of 25.8–26.7% for heptaldehyde and 45.7–46.5% for methyl undecenoate. The kinetic study showed that pyrolysis of methyl ricinoleate is a first-order reaction at 828–878 K, and the activation energy is 1.729×10^5 J/mol.
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KEY WORDS: Heptaldehyde, kinetics, methyl ricinoleate, methyl undecenoate, pyrolysis.

Heptaldehyde and undecenoic acid have many broad applications. They are important raw materials for the manufacture of perfumery chemicals, as well as pharmaceutical and polymeric compounds. Further, heptaldehyde serves as a solvent for rubber, resins, and plastics and as a source of emulsifiers, plasticizers, and insecticides. Undecenoic acid is used in bactericides and fungicides (1–3).

Castor is an important, inedible oilseed crop in China. The pyrolysis of castor oil yields heptaldehyde and undecenoic acid. Castor oil can be directly pyrolyzed, or methyl ricinoleate can be synthesized by methanolysis from castor oil and then thermally split (4–6). Because castor oil is viscous, direct pyrolysis is restricted in technical applications, because it is difficult to use, easily causing tarry materials and poisonous gases with acrolein (7). However, thermal splitting of methyl ricinoleate overcomes these disadvantages and yields the side product glycerin.

Several reports have considered pyrolysis of castor oil at 400–700°C under reduced pressure to obtain yields of heptaldehyde and undecenoic acid at 16.0–24.0% and 17.0–35.0%, respectively (8,9). A French patent of ORGANCO Company reported that methyl ricinoleate was pyrolyzed at 575°C in the presence of superheated vapor to yield 25.4% heptaldehyde and 44.2% methyl undecenoate (10).

To increase the yield of desired products of methyl ricinoleate pyrolysis, we have improved the pyrolytic reactor and investigated the effects of temperature, space-velocity, and dilution ratio of starting materials on the pyrolysis. Optimization and kinetics have also been examined in this work.

EXPERIMENTAL PROCEDURES

Materials. Methyl ricinoleate was obtained from our laboratory. Its characteristics were: appearance, light-yellow oily liquid; specific gravity d_4^{20}, 0.9253; viscosity (20°C) μ, 32 Cp; refractive index N_D^{20}, 1.4632. In the kinetic study, refined methyl ricinoleate [d_4^{20}, 0.9240; μ (20°C), 26 Cp; N_D^{20}, 1.4624] was used.

Procedure. Methyl ricinoleate (0.9–4.25 g/min) and dilution water (water/methyl ricinoleate, 0.8:1.4, vol/vol) were pumped into an electrically heated stainless-steel tubular reactor (100 cm long, 3.0 cm i.d.), which was packed with porcelain rings (ϕ 5 × 10 mm) in the preheating section (~50 cm long) and without porcelain rings (~50 cm long) in the pyrolytic section, preheated to 400 ± 1°C and pyrolyzed at 558–638°C under atmospheric pressure. The pyrolysis products were condensed and collected, and qualitatively analyzed by means of a chromatograph–mass spectrometer (HP 5988 A, Hewlett-Packard, Palo Alto, CA). The quantitative analysis of products was performed by gas chromatography (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

Effect of temperature on pyrolysis. For a volume ratio of H_2O to methyl ricinoleate of 1:1, the effect of temperature on the yields of heptaldehyde and methyl undecenoate at fixed space-velocity is shown in Figure 1. It shows that pyrolysis of methyl ricinoleate has an optimum temperature. When the temperature is lower than this optimum temperature, the yield of pyrolysis products could reach 95–98%, and in the pyrolysis products, the molar ratio of methyl undecenoate to heptaldehyde approaches the theoretical value of 1.0; there are almost no side products except unreacted methyl ricinoleate. These facts show that almost no parallel and consecutive side reactions occur during pyrolysis. On the contrary, when the temperature is higher, the yield decreases from 95 to 79.07%, and the productive rate of noncondensable gas increases from 0.05 to 0.13 L/g methyl ricinoleate. The molar ratio of methyl undecenoate to heptaldehyde rises from 1.0 to 1.12. This indicates that parallel and consecutive side reactions will occur at a higher temperature, and that the thermostability of heptaldehyde is worse than that of methyl undecenoate, which results in a lower yield of heptaldehyde.
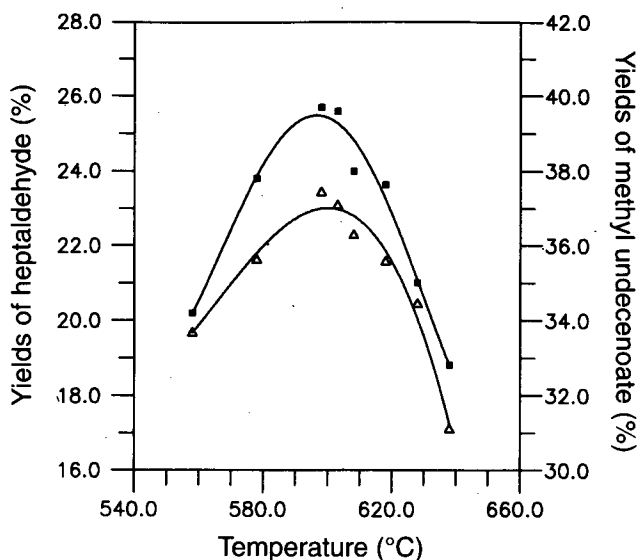
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FIG. 1. The effect of temperature on yields: yield of methyl undecenoate (■); yield of heptaldehyde (△).

FIG. 3. Effect of space-velocity on yields: yield of methyl undecenoate (■); yield of heptaldehyde (△).

Effect of dilution ratio of H_2O to methyl ricinoleate on pyrolysis. Dilution ratios (H_2O/methyl ricinoleate,vol/vol) vs. yields of heptaldehyde and methyl undecenoate were obtained by changing feed rate of H_2O at a fixed feed rate of methyl ricinoleate. The results are shown in Figure 2, which shows that below the ratio of 1.10, the yields of heptaldehyde and methyl undecenoate will be improved with increasing H_2O. It shows that decreasing partial pressure of methyl ricinoleate benefits the main reaction of pyrolysis. But, when the ratio is higher than 1.10, the yield of desired products drops. It may be that the heat needed for vaporation and superheating increases due to the increase of H_2O, so that the heat needed for pyrolysis of methyl ricinoleate is insufficient.

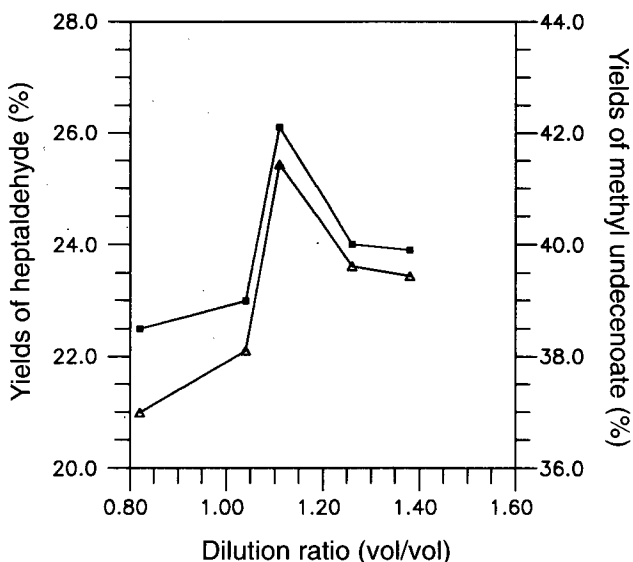*Effect of space-velocity on pyrolysis.* Space-velocity vs.

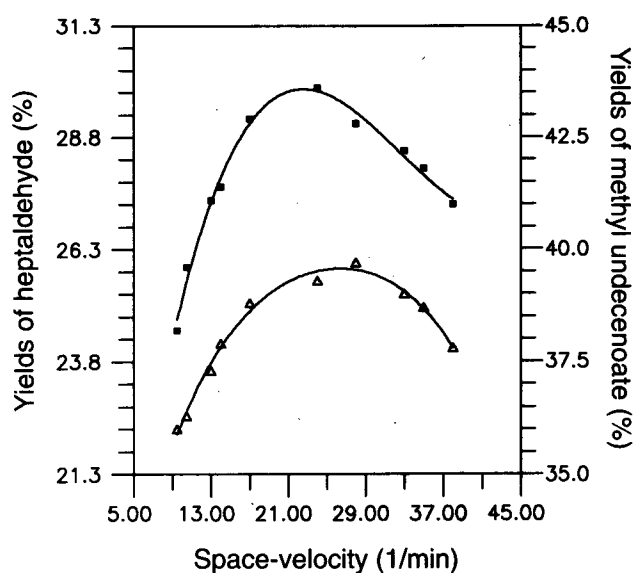**FIG. 2.** Effect of dilution ratio on yields: yield of methyl undecenoate (■); yield of heptaldehyde (△).

yields of heptaldehyde and methyl undecenoate is shown in Figure 3. The results indicate that methyl ricinoleate has an optimum space-velocity under given conditions. When the space-velocity is lower, residence time is longer, and consecutive side reactions will increase. On the contrary, when the space-velocity is higher than the optimum, residence time is shorter, and the conversion of methyl ricinoleate and yields of desired products will decrease.

Optimization. Taking the yields of heptaldehyde and methyl undecenoate as the object function, and conditions such as temperature, space-velocity, and dilution ratio of H_2O to methyl ricinoleate as variable factors, we evaluated the effects of these three factors on the function. Experiments were carried out by using the orthogonal table of L_{27} (3^{13}) [i.e., an orthogonal table of 27 rows (27 times of test),13 columns, and 3 levels] (11). With the variance analysis of effects of each factor on the function, we found that temperature and space-velocity were the dominant factors for influencing the yield of desired products, and temperature was the most notable. By analyzing the interaction of these factors, we found that temperature and space-velocity depended on each other, and that a given temperature corresponded to an optimum space-velocity. Generally, the higher the temperature, the higher the optimum space-velocity will be.

According to the conclusion of the orthogonal test, the optimum conditions are determined by this test. Repeated tests gave yields of heptaldehyde and methyl undecenoate as 25.8–26.7 and 45.7–46.5%, respectively.

Kinetics. Formulation of model. Experiments indicated that methyl ricinoleate was pyrolyzed into heptaldehyde and methyl undecenoate at an appropriate temperature and space-velocity. The overall rate was written as

$$(-r_A) = k \cdot P_A \qquad \qquad [1]$$

Because pyrolysis is a gas-phase reaction of variable volume at constant temperature, with balancing of materials of ingredient A in the infinitesimal reactor (12,13), we had

$$\frac{V_R}{F_{A0}} = \int_0^{x_A} \frac{dx_A}{(-r_A)} \qquad [2]$$

Equation 1 was substituted into Equation 2 to give

$$\frac{V_R}{F_{A0}} = \int_0^{x_A} \frac{dx_A}{k \cdot p_A} \qquad [3]$$

Because

$$p_A = \frac{F_{A0}(1-x_A)p}{F_0(1+\delta_A y_{A0} x_A)} \qquad [4]$$

it was substituted into Equation 3 to give

$$k = \frac{F_0}{pV_R} [(1+\delta_A y_{A0})\ln \frac{1}{1-x_A} - \delta_A y_{A0} x_A] \qquad [5]$$

Let $a = [(1+\delta_A y_{A0})\ln \frac{1}{1-x_A} - \delta_A y_{A0} x_A]$ and

Equation 5 would be

$$F_0 = pV_R k/a \qquad [6]$$

where k is rate constant, F_{A0} is molar volume of methyl ricinoleate, F_0 is total initial molar volume, p is total pressure of system (atm), V_R is reaction volume (L), x_A is conversion rate of methyl ricinoleate, δ_A is expansion coefficient, p_A is partial pressure of methyl ricinoleate, and y_{A0} is initial molar ratio of methyl ricinoleate.

Solution of kinetic parameters. When methyl ricinoleate is used as the initial material and the volume ratio of H_2O to methyl ricinoleate is 1.10, the feed rate at fixed temperature vs. the composition of pyrolysis products is obtained. The results are indicated in Table 1. F_0 is plotted against $1/a$ at different

TABLE 1
Kinetic Experiment Data

| Test number	Pyrolysis temperature (K)	F_0 (mol/h)	Y_{A0}	x_A	a
1	828	12.987	0.0452	0.392	0.502
2	828	13.487	0.0466	0.378	0.479
3	828	15.103	0.0444	0.340	0.419
4	828	16.378	0.0460	0.327	0.399
5	858	13.594	0.0482	0.574	0.867
6	858	14.587	0.0459	0.548	0.805
7	858	15.739	0.0465	0.516	0.735
8	858	16.843	0.0451	0.490	0.681
9	878	13.085	0.0447	0.703	1.235
10	878	14.361	0.0453	0.668	1.122
11	878	14.989	0.0460	0.654	1.080
12	878	16.560	0.0443	0.618	0.978
13	905	12.418	0.0471	0.689	1.195
14	905	12.910	0.0472	0.682	1.177
15	905	13.835	0.0483	0.680	1.161
16	905	16.867	0.0470	0.676	1.148
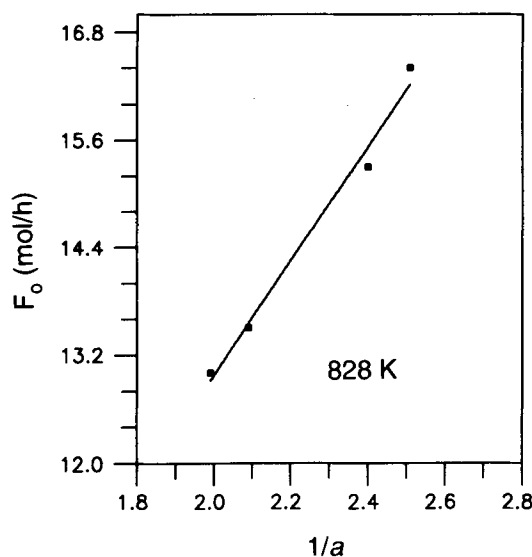
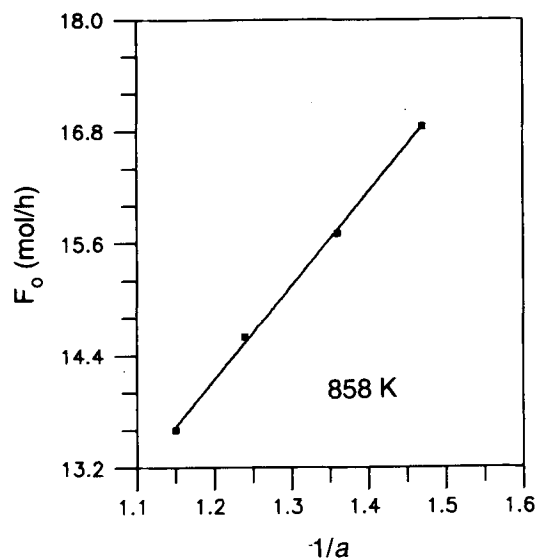
FIG. 4. Plot of F_0 vs. $1/a$ at 828 k.

FIG. 5. Plot of F_0 vs. $1/a$ at 858 k.

temperatures (see Figs. 4–7). Figures 4–7 show that F_0 vs. $1/a$ is a straight line at 828–878 K, and that pyrolysis fits a first-order reaction. From calculation, the values of k are 0.381, 0.687, and 0.953 at 828, 858, and 878 K, respectively. But, when the temperature is higher than 905 K, the relationship between F_0 and $1/a$ will be a curved line, and pyrolysis does not follow a first-order reaction. According to analysis of the pyrolysis products, some other major pyrolysis products, such as CO_2, CO, CH_4, C_2H_4, C_2H_6, and C_3H_6, were present besides heptaldehyde and methyl undecenoate.

When the values of k at different temperatures are put into Equation 6, the calculated values of F_0 can be obtained. From a comparison of F_0 (calc.) with F_0 (exp.), error analysis is given in Table 2, which shows that the maximum relative error is 2.06%, which fits kinetic regulations.

TABLE 2
Error Analysis

| Test number	Temperature (K)	k	F_0 (exp.)	F_0 (calc.)	$\dfrac{F_0 \text{(exp.)} - F_0 \text{(calc.)}}{F_0 \text{(exp.)}} \times 100$
1	828	0.381	12.987	12.869	0.91
2	828	0.381	13.478	13.487	-0.07
3	828	0.381	15.107	15.418	-2.06
4	828	0.381	16.378	16.191	1.14
5	858	0.687	13.594	13.440	1.13
6	858	0.687	14.587	14.471	-0.80
7	858	0.687	15.739	15.849	-0.70
8	858	0.687	16.843	17.105	-1.56
9	878	0.953	13.085	13.084	0.01
10	878	0.953	14.361	14.402	-0.28
11	878	0.953	14.989	14.962	0.18
12	878	0.953	16.560	16.520	0.24
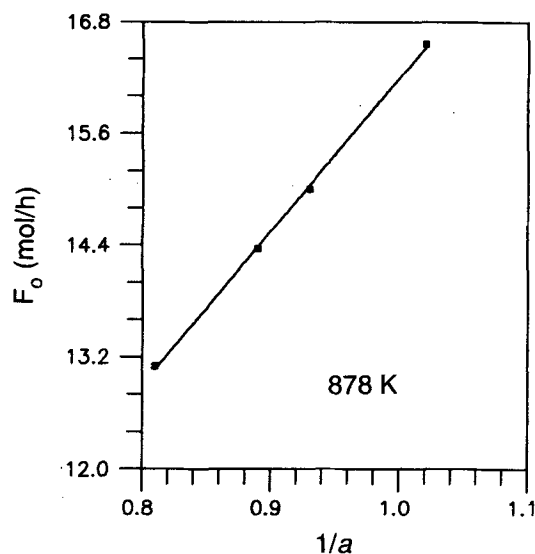
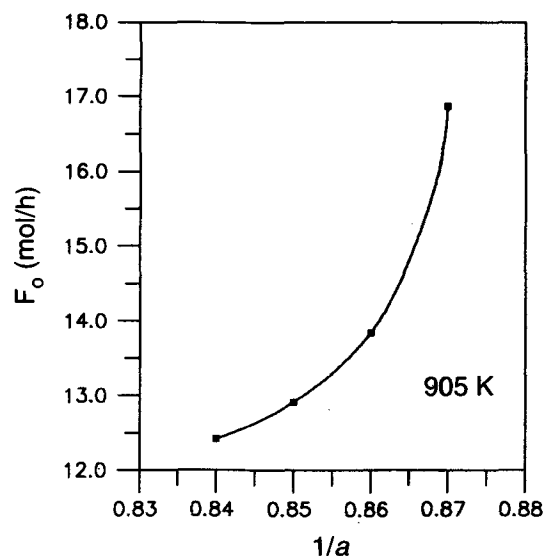**FIG. 6.** Plot of F_0 vs. $1/a$ at 878 k.

FIG. 7. Plot of F_0 vs. $1/a$ at 905 k.

Pyrolysis of methyl ricinoleate is described by a first-order rate equation at 828–878 K. The kinetic parameters are calculated as: apparent activation energy, $E = 1.729 \times 10^5$ J/mol; pre-exponential,

$$k_0 = 3.943 \times 10^8 \text{ [mol/(atm} \cdot \text{L} \cdot \text{min)]} \qquad [7]$$

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