Supporting Information

Efficient Dehydration of C_{6-10}-\alpha, \omega-alkanediols to Alkadienes as Catalyzed by Aliphatic Acids

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1. parameters of reactor

![Diagram of the device of ester pyrolysis]

Figure S1. The device of ester pyrolysis

1. The raw material container ; 2. Injection pump ; 3. Preheater tube ; 4. Silica wool ; 5. Electric heating wire ; 6. Tubular reactor ; 7. Temperature tube ; 8. Thermoelectric thermometer ; 9.
Transformer tank; 10. Condenser; 11. Receiving flask; 12. Bubbler.

The Tubular reactor has a diameter of 3 cm and a height of 70 cm. The quartz Raschig ring with a filler type of 3 mm × 7 mm was filled into the tubular reactor to afford a desired residence time and a uniform radical distribution of temperature; the filler void fraction was about 0.7. The temperature measuring covered the whole reactor. We can detect the temperature of different sections by placing there the thermoelectric thermometer probes. The reactor is evenly wrapped with an electric heating wire and the reaction temperature is adjusted by a transformer tank. Silica wool was used to improve the thermal insulation of reactor.

2. The specific data figures of diester pyrolysis

![Graph showing the yield of products at different temperatures and flow rates](image)

Figure S2a. Pyrolysis of 1,10-Dimethyloxydecane
Figure S2b. Pyrolysis of 1,10-Diacetoxydecane

Figure S2c. Pyrolysis of 1,10-Bis(propionyloxy)decane
Figure S2d. Pyrolysis of 1,10-Bis(isobutyryloxy)decane

Figure S3a. Pyrolysis of 1,8-Diacetoxyoctane
3. Establishment of kinetic equation for dehydration of 1,10-decanediol as catalyzed by acetic acid

3.1 Selection of Reactor

Gasous species in tubular reactor usually flows in turbulent form. Assuming that temperature, velocity or concentration do not diffuse in the axial direction and there is no radial gradient, the flow in tubular reactor can be regarded as plug flow. Thus, different feed rates only result in different residence times. When there is no pressure drop in the reactor and no heat exchange with the outside, the integral form of the design equation of the plug flow reactor is as follows,

\[ V = F_{A0} \int_{0}^{X} \frac{dX}{x - \tau_a} \]  \hspace{1cm} (1)

V is reactor volume and X is conversion rate.
3.2 Calculation of residence times

The Tubular reactor has a diameter of 3 cm and a height of 70 cm. The filler void fraction is about 0.7. We can get the reactor volume \( V \).

\[ V = 0.7 \times \pi \times r^2 \times h = 346.5 \text{cm}^3 \]

Through formula transformation of the design equation of plug flow reactor (1), we can get the residence time calculation formula (2).

\[
\int_{V_{F_0}}^{V} \frac{1}{F_{A_0}} dV = \int_{X_{A_0}}^{1} \frac{dX_A}{1 - r_A} \\
\frac{V}{F_{A_0}} = \frac{\tau}{C_{A_0}} = \int_{X_{A_0}}^{1} \frac{dX_A}{1 - r_A} \\
\tau = \frac{VC_{A_0}}{F_{A_0}} = C_{A_0} \int_{X_{A_0}}^{1} \frac{dX_A}{1 - r_A} \quad (2)
\]

\( F_{A_0} \) is the feed rate, \( X_A \) is the conversion rate of A, \( r_A \) is the reaction rate of A, and \( \tau \) is the residence time.

An example of the residence time calculation (feed rate \( v_{A_0} = 15 \text{ g/h} \), \( T = 450^\circ\text{C} \)):

\[
F_{A_0} = \frac{v_{A_0}}{M_{AO}} = \frac{15\text{ g/h}}{258\text{ g/mol}} = 0.06\text{mol/h}
\]

Assuming that the gas is an ideal gas, then:

\[
C_{A_0} = \frac{P}{RT} = 16.8\text{mol/m}^3 = 1.68 \times 10^{-2}\text{mol/L}
\]

\[
\tau = \frac{VC_{A_0}}{F_{A_0}} = 0.097\text{h}
\]

\( M_{AO} \) is the molar mass of 1,10-diacetoxydecane.

3.3 Order of reaction

A represents for 1,10-diacetoxydecane, B represents for 9-decen-1-ol, 1-acetate, C represents
for 1,9-decadiene. Most acetic acid is rapidly decomposed and discharged at high temperature, so the effect of acetic acid on the reaction process is not considered. Thus, this reaction is considered as a consecutive reaction, and the reaction from A to B and B to C is a decarboxylation reaction with the same mechanism. It is assumed that the two reactions have the same order of reaction \( n \).

Then:

\[
\begin{align*}
    r_A &= \frac{dC_A}{dt} = -k_1C_A^n, \quad (3) \\
    r_B &= \frac{dC_B}{dt} = k_1C_A^n - k_2C_B^n, \quad (4) \\
    r_C &= \frac{dC_C}{dt} = k_2C_B^n \quad (5)
\end{align*}
\]

In order to obtain the order of reaction \( n \) and the reaction rate constants \( k_1 \) and \( k_2 \), according to the formula (3), we can get the formula (6).

\[
- k_1 \tau = \int^{C_A} C_A^0 \frac{dC_A}{C_A^0} \quad (6)
\]

When \( n \neq 1 \), formula (6) is integrated into formula (7).

\[
- k_1 \tau = \frac{1}{n + 1} \left( C_A^{-n + 1} - C_A^{-n + 1} \right) \quad (7)
\]

When \( n=1 \), formula (6) is integrated into formula (8).

\[
k_1 \tau = \ln \left( \frac{C_A}{C_A^0} \right) = - \ln (1 - X_A) \quad (8)
\]

| \( F_{A0} \) (g/h) | \( \tau \) (h) | \( X_C \) (%) | \( X_B \) (%) | \( X_A \) (%) | \(- \ln (1-X_A)\) |
|-----------------|----------------|--------------|--------------|--------------|----------------|
| 45              | 0.032          | 36.0         | 33.2         | 69.2         | 1.177655       |
| 37.5            | 0.039          | 41.5         | 30.7         | 72.2         | 1.280134       |
| 30              | 0.049          | 48.9         | 28.5         | 77.4         | 1.48722        |
| 22.5            | 0.065          | 63.1         | 22.5         | 85.6         | 1.937942       |
| 15              | 0.097          | 90.3         | 1.9          | 92.2         | 2.551046       |

Assuming \( n=1 \), a linear graph of \( \tau \) with \(- \ln (1-X_A)\) is constructed, and \( k_1 \) can be obtained by slope as shown in Figure S4:
When $n=1$, the fitted formula is $y=21.764x+0.4593$. And the coefficient of determination $R^2$ is about 0.994, which has a high reliability. So, the order of reaction is about 1, $k_1$ is about 21.764h$^{-1}$ (T=450°C).

3.4 Reaction rate constant

Due to $n=1$, we can get formula (9), (10) and (11) from formula (3), (4) and (5) respectively:

$$C_A = C_{A0} \cdot e^{-k_1 \tau} \quad (9)$$

$$C_B = C_{A0}k_1\left(\frac{e^{-k_2 \tau}}{k_2-k_1} + \frac{e^{-k_2 \tau}}{k_1-k_2}\right) \quad (10)$$

$$C_C = C_{A0}\left(1 + \frac{k_2e^{-k_1 \tau}}{k_1-k_2} + \frac{k_3e^{-k_2 \tau}}{k_2-k_3}\right) \quad (11)$$

The expression of fitting function is formula (11), in which $k_1$ is about 21.764h$^{-1}$ (T=450°C) and the corresponding data of $X_C$ varying with $\tau$ can be obtained from Table 1. Using Origin to fit the data, the fitted data can be obtained as shown in Figure 2.
It can be seen from the Figure S5 that the fitted value of $k_2$ is about 74.199 h$^{-1}$ ($T=450^\circ$C), the coefficient of determination $R^2$ is about 0.9567, and the reliability is high.

**Table S2** Variations in Yields with Feed Rates ($T=430^\circ$C)

| $F_{A_0}$ (g/h) | $\tau$ (h) | $X_C$ (%) | $X_B$ (%) | $X_A$ (%) | $-\ln (1-X_A)$ |
|-----------------|------------|-----------|-----------|-----------|----------------|
| 45              | 0.033      | 25.3      | 41.2      | 66.5      | 1.093625       |
| 37.5            | 0.040      | 32.1      | 37.2      | 69.3      | 1.180908       |
| 30              | 0.050      | 39.8      | 35.6      | 75.4      | 1.402424       |
| 22.5            | 0.067      | 55.1      | 27.5      | 82.6      | 1.7487         |
| 15              | 0.100      | 83.5      | 7.5       | 91.6      | 2.476938       |

**Table S3** Variations in Yields with Feed Rates ($T=400^\circ$C)

| $F_{A_0}$ (g/h) | $\tau$ (h) | $X_C$ (%) | $X_B$ (%) | $X_A$ (%) | $-\ln (1-X_A)$ |
|-----------------|------------|-----------|-----------|-----------|----------------|
| 45              | 0.042      | 8.2       | 34.0      | 42.2      | 0.548181       |
| 37.5            | 0.052      | 12.8      | 38.9      | 51.7      | 0.727739       |
| 30              | 0.069      | 18.0      | 40.7      | 58.7      | 0.884308       |
| 22.5            | 0.104      | 33.3      | 38.1      | 71.3      | 1.248273       |
| 15              | 0.156      | 44.5      | 32.9      | 77.3      | 1.482805       |

**Table S4** Variations in Yields with Feed Rates ($T=380^\circ$C)

| $F_{A_0}$ (g/h) | $\tau$ (h) | $X_C$ (%) | $X_B$ (%) | $X_A$ (%) | $-\ln (1-X_A)$ |
|-----------------|------------|-----------|-----------|-----------|----------------|
| 30              | 0.054      | 2.7       | 23.4      | 26.1      | 0.302457       |
| 22.5            | 0.071      | 5.3       | 29.3      | 34.6      | 0.424648       |
| 15              | 0.107      | 10.9      | 32.0      | 42.9      | 0.560366       |
| 7.5             | 0.214      | 23.2      | 33.9      | 57.1      | 0.846298       |

**Table S5** Variations in Yields with Feed Rates ($T=360^\circ$C)

| $F_{A_0}$ (g/h) | $\tau$ (h) | $X_C$ (%) | $X_B$ (%) | $X_A$ (%) | $-\ln (1-X_A)$ |
|-----------------|------------|-----------|-----------|-----------|----------------|
| 22.5            | 0.075      | 1.3       | 17.3      | 1.3       | 17.3           |
At different temperatures, the yields corresponding to different feed rates are shown in Tables S2, S3, S4 and S5. According to the above algorithm, the values of \( k_1 \) and \( k_2 \) at different temperatures are calculated as shown in Figure S6 and S7.

According to Arrhenius equation: 
\[
k = k_0 \cdot e^{-E_a/RT}
\]
where \( k \) is the reaction rate constant, \( k_0 \) is the pre-exponential factor, and \( E_a \) is the apparent activation energy. \( E_a \) is regarded as a constant when
the temperature range is not large, then we get $E_a = RT^2 \frac{d\ln k}{dT}$ and the indefinite integral form of this formula is $\ln k = \frac{E_a}{RT} + \ln k_0$. A linear graph of $\frac{1}{T}$ with $\ln k$ is constructed as shown in Figure S8. Then, $-\frac{E_a}{R}$ can be obtained by slope and $\ln k_0$ can be obtained by intercept.

| T (°C) | $\frac{1}{T}$ (K$^{-1}$) | $k_1$ (h$^{-1}$) | $\ln k_1$ | $k_2$ (h$^{-1}$) | $\ln k_2$ |
|--------|-----------------|-----------------|------------|-----------------|------------|
| 360    | 0.001579        | 1.187           | 0.171      | 4.2307          | 1.442      |
| 380    | 0.001531        | 3.2078          | 1.166      | 6.3838          | 1.854      |
| 400    | 0.001486        | 8.0530          | 2.140      | 14.370          | 2.665      |
| 430    | 0.001422        | 20.977          | 3.043      | 42.385          | 3.747      |
| 450    | 0.001383        | 21.764          | 3.080      | 74.199          | 4.307      |

From the Figure S8, $E_{a1}$ is about 127.9 kJ/mol, $k_{0,1}$ is about $\exp(24.697)$, $E_{a2}$ is about 126.8 kJ/mol, $k_{0,2}$ is about $\exp(25.384)$. we can get the reaction rate constant equation of $k_1 = \exp\left(\frac{-15388}{T} + 24.697\right)$ and $k_2 = \exp\left(\frac{-15256}{T} + 25.384\right)$.

3.5 Kinetic equation

According to the formula (3), (4) and (5), the kinetic equation (12), (13) and (14) can be established by substituting $k_1$ and $k_2$. 

S11
\[ r_A = - \exp\left(\frac{-15388}{T} + 24.697\right)C_A \]  
(12)

\[ r_B = \frac{dC_B}{dt} = \exp\left(-\frac{15388}{T} + 24.697\right)C_A - \exp\left(-\frac{15256}{T} + 25.384\right)C_B \]  
(13)

\[ r_C = \frac{dC_B}{dt} = k_2 = \exp\left(\frac{-15256}{T} + 25.384\right)C_B \]

(14)4. MS spectral data

Figure S9. Mass spectrometry results of 1,5-hexadiene
Figure S10. Mass spectrometry results of 1,7-octadiene

Figure S11. Mass spectrometry results of 1,9-decadiene
5. NMR spectral data

**Figure S12.** $^1$H NMR spectrum of 1,5-hexadiene

**Figure S13.** $^1$H NMR spectrum of 1,7-octadiene
**Figure S14.** $^1$H NMR spectrum of 1,9-decadiene

**Figure S15.** $^{13}$C NMR spectrum of 1,5-hexadiene
Figure S16. $^{13}$C NMR spectrum of 1,7-octadiene

Figure S17. $^{13}$C NMR spectrum of 1,9-decadiene