

# **Kinetics of Fructose Decomposition Catalyzed by Organic Acids in High Temperature Liquid Water**

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**ABSTRACT:** Biomass continues to be an important candidate as a renewable resource for energy, chemicals, and feedstock. Decomposition of biomass in high temperature liquid water is a promising technique for producing industrially important chemicals such as 5-hydroxymethylfurfural (5-HMF), furfural, levulinic acid (LA) with high efficiency. To further improve reaction rate and selectivity of the reactions, the kinetics of fructose decomposition catalyzed by organic acids in high temperature liquid water was studied at temperatures from 453.15K to 493.15K and pressure of 10MPa. The results show that the reaction rate is greatly enhanced with the addition of organic acids, especially formic acid. The effects of temperature, residence time, organic acids and their concentrations on the yields of 5-HMF and LA were shown. Interestingly, a yield of as high as 83% for 5-HMF can be achieved from fructose decomposition catalyzed by acetic acid. Fructose decomposition consists of two sequential reactions, first from fructose to 5-HMF, then from 5-HMF to LA. Based on the products profile, we speculate that acetic acid promotes the first step while has little influence on the second step. In contrast, both steps are accelerated by formic acid.

**Key words:** acid-catalysis kinetics, fructose decomposition, high temperature liquid water, organic acids

## **Introduction**

High Temperature Liquid Water (HTLW) is receiving increased attention as an environmentally benign reaction medium for biomass conversion and organic chemical reactions[1-4]. HTLW has two unique properties. First of all, the solubility of organics in water can be increased by several orders of magnitude because the dielectric constant of HTLW is significantly reduced compared to ambient water [5]. Secondly, HTLW itself is capable of acting

as an acid/base catalyst due to its higher ionization constant at elevated temperatures [6]. Many investigations [7-13] have been carried out on biomass conversion in sub-/super-critical water either without any catalyst or catalyzed with inorganic acids. Without any catalyst, we often encounter problems such as slow reaction rate, low conversion, and poor selectivity, which hinder industrial applications of the technique in practice. On the other hand, inorganic acid catalysts lead to serious environmental pollution problem. Here, we propose organic acids-enriched HTLW as a new environmental benign reaction medium, and report its applications in the decomposition of fructose.

## 1 Experimental

### 1.1 Reagents

D-fructose and glucose, A. R., Tianjin Guangfu Fine Chemical Research Institute; 5-HMF( $\geq 98\%$ ), Acros Organics; Formic acid ( $\geq 88\%$ ) and acetic acid ( $\geq 99.5\%$ ), A. R., Hangzhou Chemical Reagent Co. Ltd.; LA( $\geq 99.5\%$ ), Langfang Triple Well Chemicals Co., Ltd. All chemical were used as received.

### 1.2 Apparatus

The schematic diagram of the experimental apparatus is shown in Fig. 1, which mainly consists of a high pressure batch reactor (500mL), a plunger pump and a sampling line.

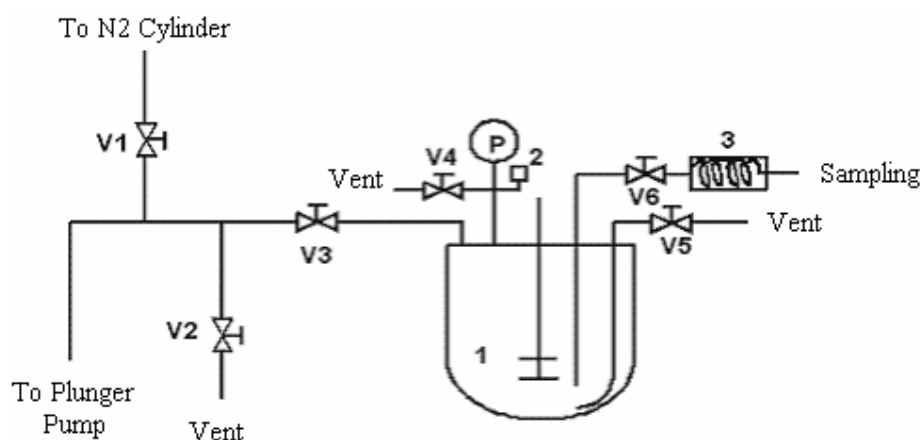


Fig. 1 Schematic diagram of the experimental apparatus

1 reactor; 2 safety valve; 3 cooler; V1~V6 high pressure valve; P pressure guage

The apparatus has the following features:

- Temperature up to 300°C, pressure 20MPa.
- Good temperature control  $\pm 1^\circ\text{C}$ .
- Small sampling line volume. The tubing used in the sampling line is 1/16" OD $\times$ 0.030" ID(SUS316), length 133cm, volume 0.60mL.
- Resistance to corrosion. The reactor is made of 00Cr17Ni14Mo2 austenitic stainless steel.

Experimental procedure: first, the system was degassed with vacuum pump, and then filled with high purity nitrogen. 300 mL of deionized water was added into the reactor by plunger pump, and the system pressure was increased to 5MPa by high pressure nitrogen cylinder. After the temperature inside the reactor reached the reaction temperature, 50 mL of fructose-organic acid mixed solution was quickly injected and the line was rinsed with 20ml deionized water. The reactor reached the reaction temperature within several minutes. The system pressure was maintained at 10MPa by the high pressure nitrogen cylinder. Finally, the samples (2-3 mL) were collected at certain reaction time and directly analyzed with HPLC after filtration. Prior to the sampling, 2-3 mL solution was vented to wash the sampling line. The pressure drop (0.1~0.2 MPa) during sampling was compensated by high pressure nitrogen cylinder. The cooler in the sampling line was used to prevent evaporation of the sample. The reaction content was constantly agitated at 400 rpm using a mechanical impeller throughout the reaction.

### 1.3 Analysis

The liquid sample was quantitatively analyzed by HPLC (Agilent 1100) with RI detector. HPLC column was Sugar SH1011 (Shodex, 8mmID $\times$ 300mm).  $0.5 \times 10^{-3}$  mol/L sulfuric acid solution was used as the mobile phase (flow rate at 0.5ml/min). Column temperature was set up at 60°C, and RI detector temperature at 40°C. Injection volume was 20 $\mu$ L.

## 2 Results and discussion

### 2.1 Products of fructose decomposition

A typical HPLC chromatograph of fructose decomposition products is shown in Fig. 2. The main products include organic acids (formic acid, acetic acid, LA), glucose, fructose, 5-HMF, and furfural. Peak identification was made by comparison of sample peak retention times with the standard solutions of pure compounds, and conformed with GC/MS (Agilent 6890GC/5973MSD).

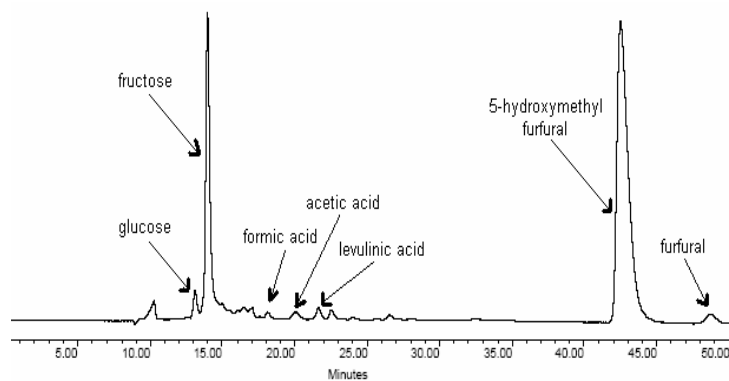


Fig. 2 Typical HPLC chromatograph of fructose decomposition products (without catalyst)

(P = 10 MPa, T = 473.15K, t = 20 min)

## 2.2 Effects of different organic acids on the kinetics of fructose decomposition

The effects of different organic acids on the decomposition kinetics of fructose in HTLW were determined at temperatures from 453.15K to 493.15K and pressure of 10 MPa. As shown in Fig. 3, the three conditions studied are without any catalyst, with formic acid, and with acetic acid. The initial concentration of fructose and the organic acid are both 10.8 mg/mL.

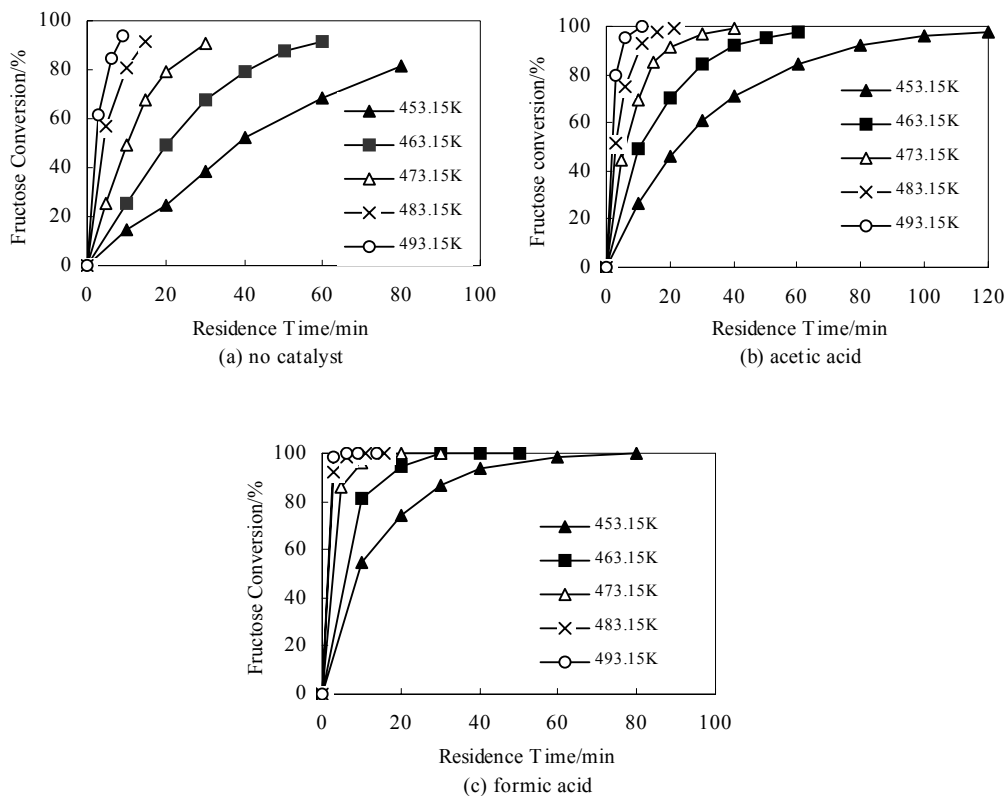


Fig. 3 The effects of temperature, organic acids and residence time on fructose conversion

Based on the first-order reaction assumption, the equation  $-\ln(1-x) = kt$  was used to correlate the data. Comparison of the rate constants for fructose decomposition under different conditions is illustrated in Fig. 4. Figs. 3 and 4 show that the reaction rates are greatly enhanced with the addition of organic acids. At the same concentration, formic acid demonstrates stronger ability to accelerate the fructose decomposition than acetic acid.

Arrhenius plot for fructose decomposition was used to evaluate the apparent activation energy of the fructose decomposition: 126.16 kJ/mol without any catalyst, 111.99 kJ/mol catalyzed with formic acid, and 125.64 kJ/mol catalyzed with acetic acid, respectively.

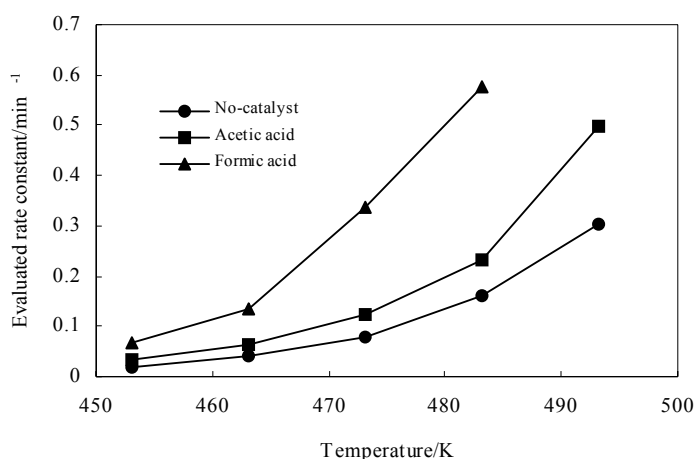


Fig. 4 Comparison of the rate constants for fructose decomposition at different temperatures (10 MPa)

### 2.3 Product distribution

The effects of temperature, organic acids and residence time on the yield of 5-HMF are depicted in Fig. 5. At the experimental range of temperature and residence time, the maximum yields of 5-HMF reach 51% without any catalyst, 58% catalyzed with formic acid, and 83% with acetic acid, respectively. Interestingly, higher 5-HMF yield is obtained from fructose decomposition when acetic acid is used as the catalyst.

The effects of temperature, organic acids and residence time on the yield of levulinic acid are shown in Fig. 6. The highest yields of LA are 3.6% without any catalyst, 22% catalyzed with formic acid, and 7.5% with acetic acid, respectively. No maximum in yield was observed at the experimental range of residence time.

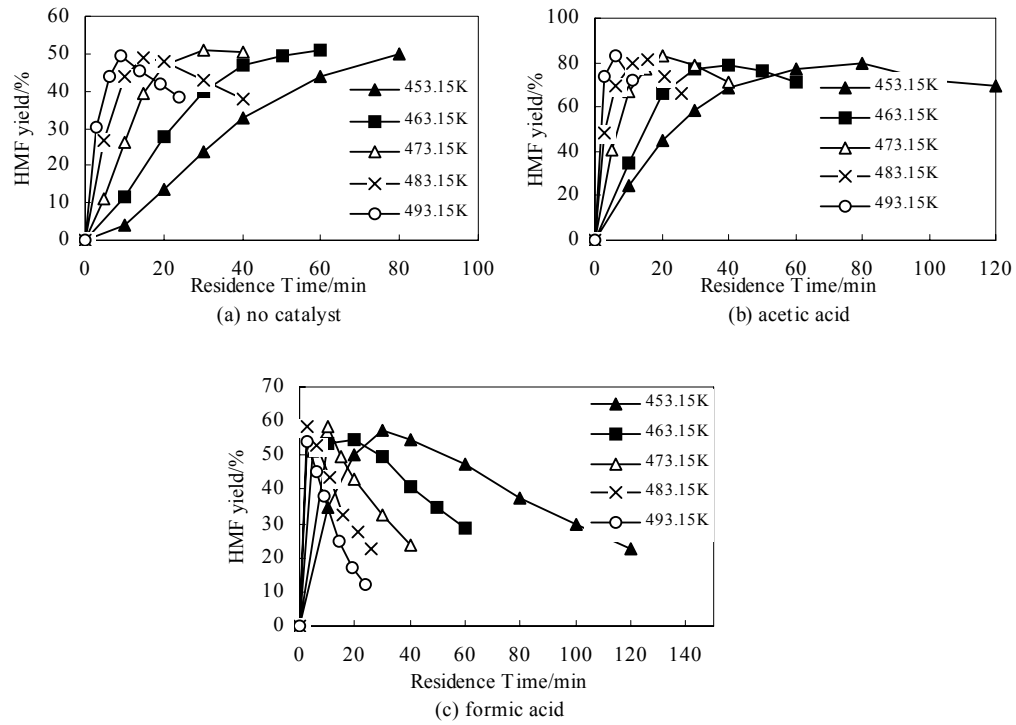


Fig. 5 The effects of temperature, organic acids and residence time on the yield of 5-HMF

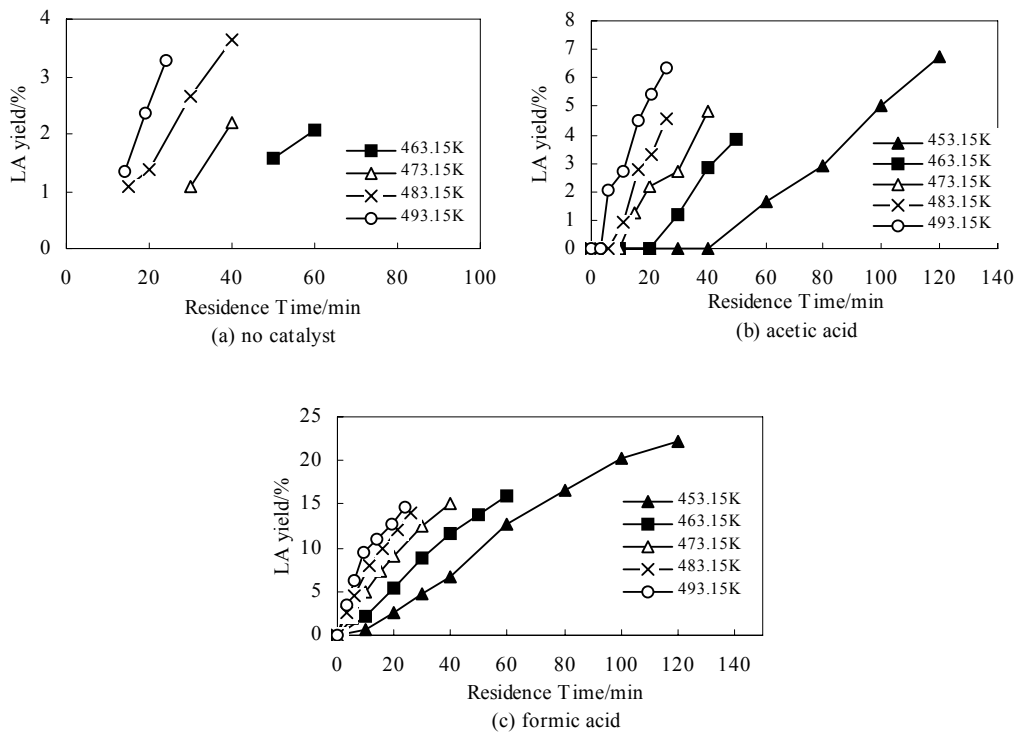


Fig. 6 The effects of temperature, organic acids and residence time on the yield of levulinic acid

Fructose decomposition consists of two sequential reactions: first from fructose to 5-HMF, then from 5-HMF to levulinic acid. Based on the products profile, we speculate that acetic acid promotes the first step, while has little influence on the second step. In contrast, both steps are accelerated by formic acid.

#### 2.4 Effects of formic acid concentration on the fructose decomposition

The effects of formic acid concentration and residence time on the fructose conversion, and the yields of 5-HMF and LA are shown in Figs. 7-9. The reaction temperature was at 473.15K, pressure 10 MPa, and the initial concentration of fructose 10.8 mg/mL. As the formic acid concentration increases, it is noted that the fructose conversion and the yield of LA increase, and shorter residence time is needed to reach the maximum yield of 5-HMF.

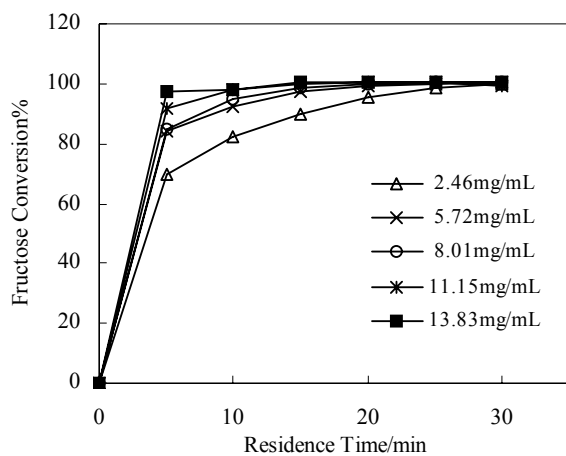


Fig. 7 The effects of formic acid concentration and residence time on fructose conversion (T=473.15K)

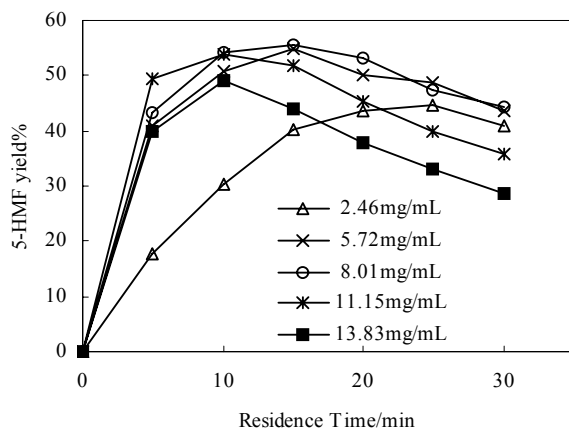


Fig. 8 The effects of formic acid concentration and residence time on the yield of 5-HMF (T=473.15K)

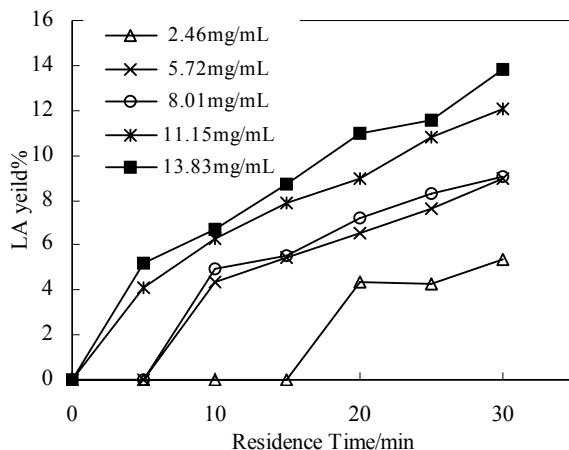


Fig. 9 The effects of formic acid concentration and residence time on yield of the levulinic acid (T=473.15K)

### 3 Conclusion

Although HTLW itself exhibits weak acidity/basicity, it is often not sufficient to act as an effective catalyst for acid/base-catalyzed chemical reactions. Environmentally-benign organic acids, such as formic acid and acetic acid, were proposed to be used as acid catalysts in HTLW. In addition, these organic acids itself are products in some reactions, for example, biomass decomposition. In this work, the effects of different organic acids on the kinetics of fructose decomposition have been investigated. The following conclusions may be made:

- The rate of fructose decomposition can be greatly enhanced with the addition of organic acids. At the same concentration, formic acid demonstrates stronger ability to accelerate fructose decomposition than acetic acid.
- The evaluated apparent activation energy of fructose decomposition is 126.16 kJ/mol without any catalyst, 111.99 kJ/mol catalyzed with formic acid, and 125.64 kJ/mol catalyzed with acetic acid, respectively.
- A high yield of 83% for 5-HMF can be achieved from the fructose decomposition catalyzed by acetic acid.

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