



# Reaction Kinetics Study of Catalytical Hydrogenation of Furfural in Liquid Phase

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## Abstract

Hydrogenation of furfural in the presence of Raney nickel catalyst is employed for the preparation of tetrahydrofurfuryl alcohol. The effects of stirring rate, reaction time and reaction temperature on the yield of tetrahydrofurfuryl alcohol are studied. The reaction kinetic is also studied and the data are modeled by zero-, first- and second-order reaction equations. The results show that the hydrogenation reaction is of first order with respect to furfural concentration and is of zero order with respect to tetrahydrofurfuryl alcohol concentration. The activation energy of the two reaction steps is found to be 24.7 kJ/mol and 27.7 kJ/mol.

## Subject Areas

Chemical Engineering & Technology

## Keywords

Hydrogenation, Furfural, Raney Nickel, Kinetic, Liquid Phase

## 1. Introduction

The liquid phase hydrogenation of furfural is commonly used to produce furfuryl alcohol, tetrahydrofurfuryl alcohol and 2-methylfuran [1] [2] [3]. Furfuryl alcohol is widely used in producing various synthetic fibers, rubbers, resins, and farm chemicals. It can also be used as a good solvent for furan resin, pigment and varnish and as rocket fuel [4]. In the case of hydrogenation of furfural to tetrahydrofurfuryl alcohol in the absence of solvent or in an aqueous solution highly active are the supported nickel catalysts. The hydrogenation of furfural has been carried out in either liquid or vapor phase. Most companies adopt gas phase hydrogenation. However, in some countries, e.g. in China, liquid phase hydrogenation is frequently employed [5]. The catalyst mainly used for furfural

hydrogenation in the industry is a Cu-Co catalyst modified with various promoters [6]. As Cu-Co catalysts have high toxicity and thus cause severe environmental pollution, many attempts have been made to develop new catalysts that are environmentally friendly. Applications of PtCu [7], Ru [8], Ni<sub>2</sub>P [9] have been reported.

This paper describes a study on the catalytic hydrogenation of furfural using Raney Ni, besides an investigation of the effect of reaction time, reaction temperature on the yield of tetrahydrofurfuryl alcohol and the kinetics of this reaction. Provide reference for the industrial application of liquid phase hydrogenation of furfural.

## 2. Experimental Section

### 2.1. Experimental Reagents

Furfural (supplied by Shanghai Jinshan Tingxin Chemical Reagent Factory) of purity 99% was used for the preparation of furfuryl alcohol. Hydrogen (supplied by Hangzhou today's industrial goods and Materials Co., Ltd.) of purity 99% was used for furfural hydrogenation. Raney nickel catalyst (supplied by Shanghai Sun Chemical Technology Co., Ltd.) of an average pore size 3 μm, and surface area 1000 m<sup>2</sup>/g was used for the hydrogenation of furfural.

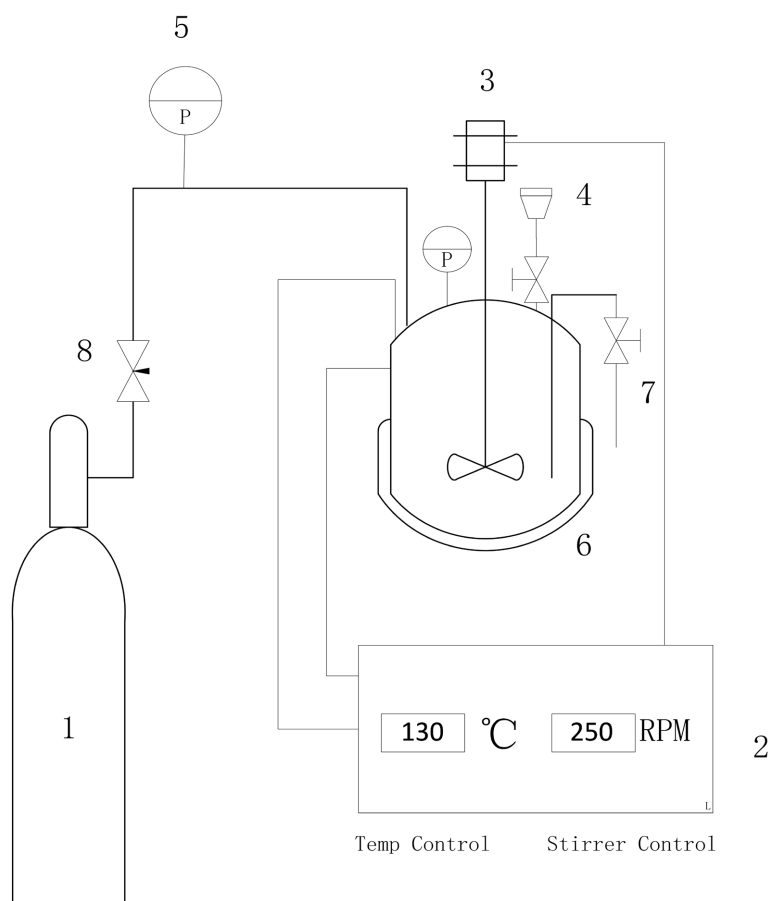
### 2.2. Experimental Apparatus

A schematic diagram of laboratory experimental unit used for the hydrogenation of furfural is shown in **Figure 1**. This unit consists of a 100 ml stainless steel autoclave equipped with a mechanical stirrer and an electric heating system.

The composition of product is measured by an automatic on-line valve and analyzed with a gas chromatograph (GC) and PEG-30m column and FIT detector. Furfural, furfuryl alcohol and tetrahydrofurfuryl alcohol are identified and quantified with the response factor method using model compounds.

### 2.3. Experimental Procedure

Catalytic hydrogenation of furfural was performed in a 100 ml stainless steel autoclave equipped with a mechanical stirrer and an electric heating system. 70 ml of ethanol, which were first transferred into the autoclave, were used as the solvent. Then 5 ml of furfural and a mount of Raney nickel catalyst were added to the autoclave. After the necessary connection between the autoclave and hydrogen gas cylinder was duly made, H<sub>2</sub> gas passed into the autoclave until H<sub>2</sub> pressure reached 1.0 MPa. Then pressurization and successive depressurization were repeated 5 times so as to completely replace the air in the autoclave. Then the reactor was filled with H<sub>2</sub> up to the prescribed pressure, followed by heating slowly until the prescribed temperature. The first product sample for analysis was taken after 10 min of reaction (period needed to reach reaction steady-state). After reaction for 3 h, the reaction products were analyzed to determine the conversion of furfural and the selectivity to furfuryl alcohol. The identification



**Figure 1.** Schematic diagram of furfural hydrogenation unit. 1: Hydrogen cylinder; 2: Controller; 3: Pulsator; 4: Exhaust head; 5: Pressure gauge; 6: Reactor; 7: Bleeder valve; 8: Needle valve.

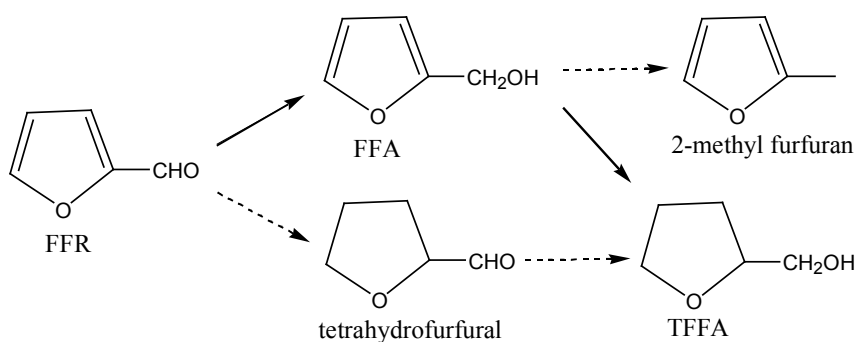
and analysis of the reaction product mixtures were performed by means of GC. Conversion of furfural was measured directly by the comparison of its concentration in the inlet stream with the outlet stream. Selectivity was calculated as the ratio of the number of moles of tetrahydrofurfuryl alcohol to number of moles of all products formed in the reaction.

### 3. Results and Discussion

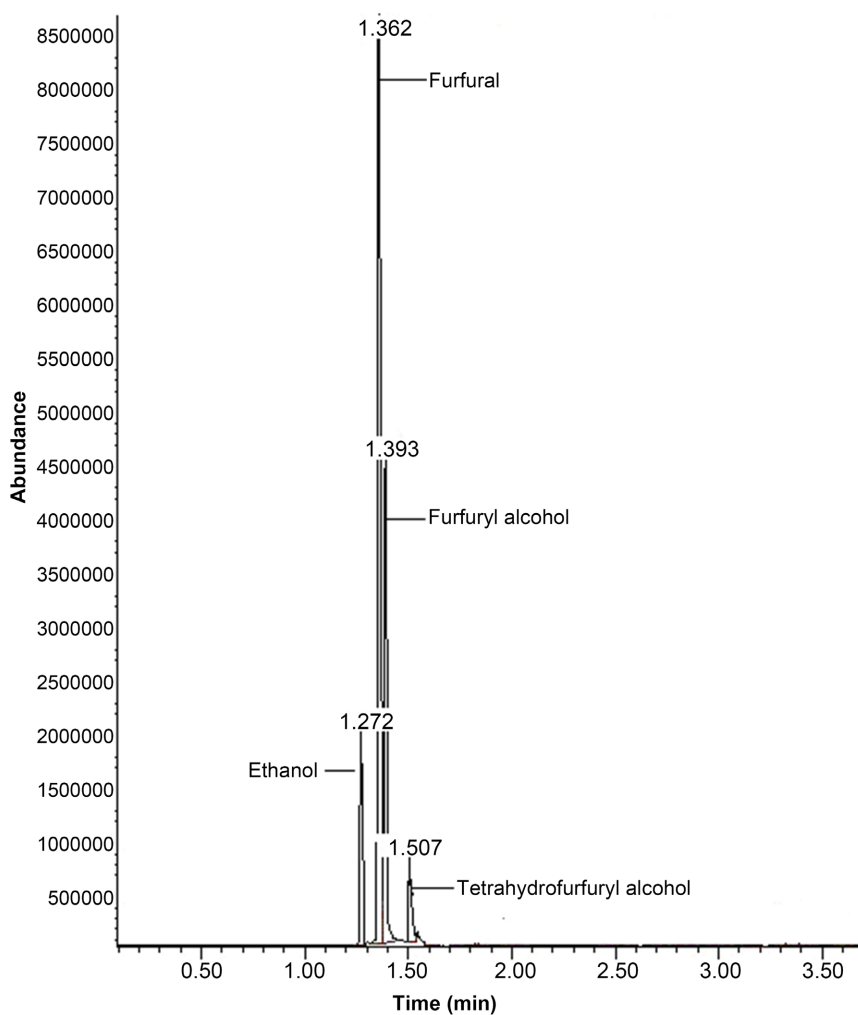
#### 3.1. Reaction Pathways of Furfural Hydrogenation in Liquid Phase

As shown in **Scheme 1**, the formation of furfuryl alcohol and tetrahydrofurfural are parallel reactions, which are competitive, while tetrahydrofurfuryl alcohol is the final product of further hydrogenation of both furfuryl alcohol and tetrahydrofurfural.

In the process of catalytic hydrogenation of furfural to tetrahydrofurfuryl alcohol, the sample was taken out and analysis by GC-MS, **Figure 2** shows that products of sample comprise furfural, furfuryl alcohol and tetrahydrofurfuryl alcohol. It has been claimed that reaction pathway for furfural catalytic hydrogenation was form furfuryl alcohol first then to tetrahydrofurfuryl alcohol.



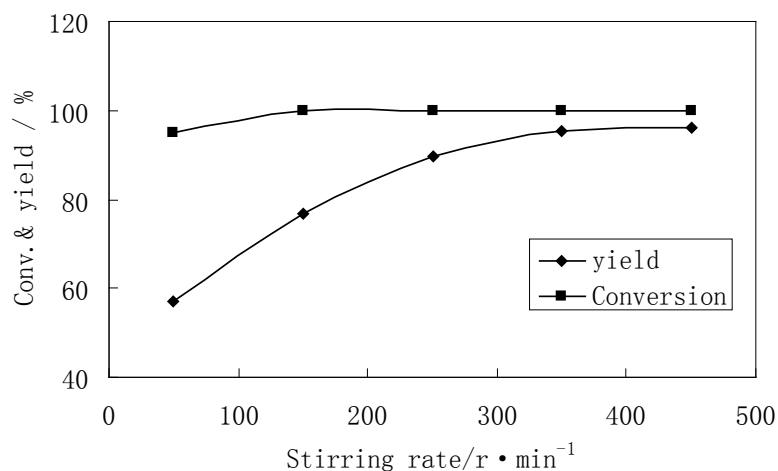
**Scheme 1.** Reaction pathway for furfural catalytic hydrogenation, (...) possible pathway; (-) actual reaction pathway.



**Figure 2.** GC-MS analysis of the products.

### 3.2. Effect of Stirring Rate

Figure 3 shows that the effect of stirring rate on furfural hydrogenation reaction under the reaction conditions. It shows that the yield of tetrahydrofurfuryl alcohol increases with increasing stirring rate. However, the influence of stirring rate becomes weak when the stirring rate reaches  $450 \text{ r}\cdot\text{min}^{-1}$ .



**Figure 3.** Effect of stirring rate on furfural hydrogenation reaction. Reaction conditions:  $T = 383 \text{ K}$ ;  $P = 1.5 \text{ MPa}$ ;  $t = 180 \text{ min}$ ;  $m(\text{cat.}) = 2.0 \text{ g}$ .

### 3.3. Effect of Reaction Time

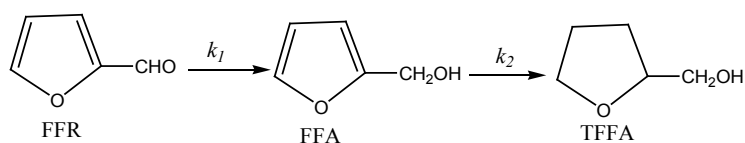
**Figure 4** shows the effect of reaction time on the conversion of furfural and the selectivity for tetrahydrofurfuryl alcohol. It shows that, within 40 min of reaction time, the conversion increases to 100%, while the selectivity raises slowly. As reaction time is prolonged, the selectivity increases to more than 80% and then falls appreciably. This could be attributed to the fact that some compounds derives from hydrogenation of tetrahydrofurfuryl alcohol.

### 3.4. Effect of Reaction Temperature

Increase in temperature of a reaction usually causes an increase in reaction rate. From **Figure 5**, it is seen that as the reaction temperature is increased, the selectivity for tetrahydrofurfuryl alcohol increases obviously at temperature below 403 K. However, the selectivity for tetrahydrofurfuryl alcohol falls when the reaction temperature rises to 418 K. This could be attributed to the fact that many other compounds derived from secondary reactions, such as hydrogenolysis of the C-O bond, decarbonylation, hydrogenation and furan ring opening, may appear.

### 3.5. Hydrogenation Kinetics

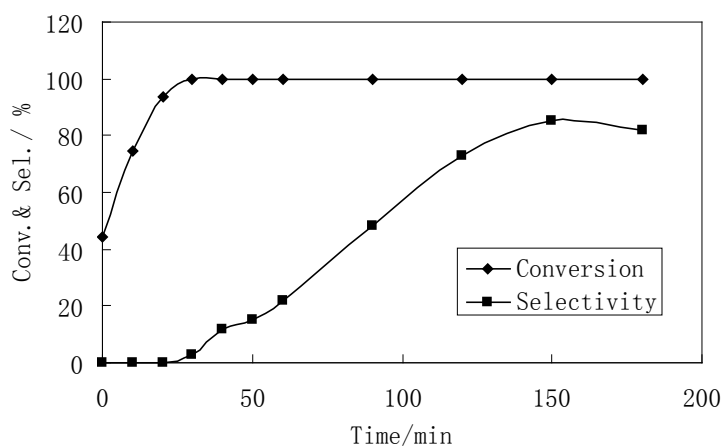
Determination of reaction order



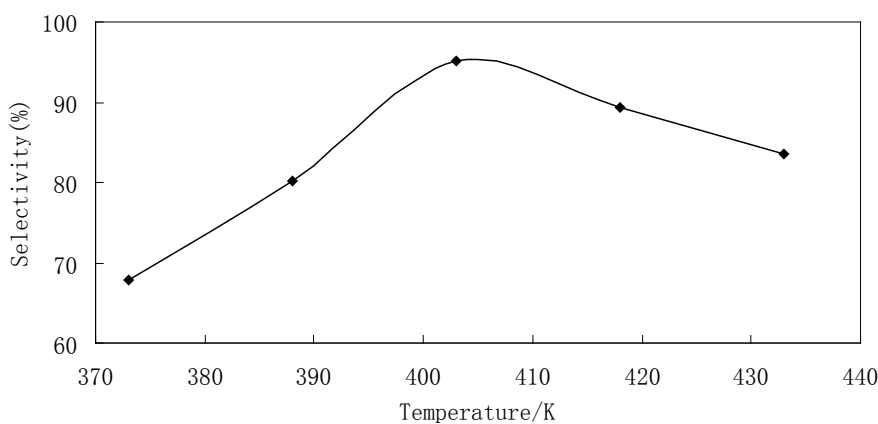
For the determination of the order of reaction, equations of zero-, first- and second-order reactions was used. These equations can be written as follows:

Zero-order reaction equation:

$$C_A = C_{A,0} - kt \quad (1)$$



**Figure 4.** Conversion of furfural and selectivity for tetrahydrofurfuryl alcohol as a function of reaction time. Reaction conditions:  $T = 433 \text{ K}$ ;  $P = 1.5 \text{ MPa}$ ;  $m(\text{cat.}) = 2.0 \text{ g}$ .



**Figure 5.** Influence of reaction temperature on selectivity for tetrahydrofurfuryl alcohol. Reaction conditions:  $P = 1.5 \text{ MPa}$ ;  $t = 180 \text{ min}$ ;  $m(\text{cat.}) = 2.0 \text{ g}$ .

First-order reaction equation:

$$\ln(C_{A,0}/C_A) = kt \quad (2)$$

Second-order reaction equation:

$$1/C_A = 1/C_{A,0} + kt \quad (3)$$

**Table 1** shows time against furfural concentration data using 2.0 g catalyst at a temperatures of 373, 378, 383, 388 and 393 K.

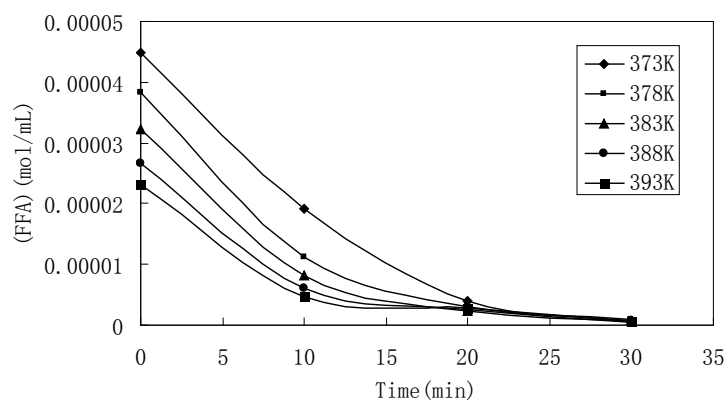
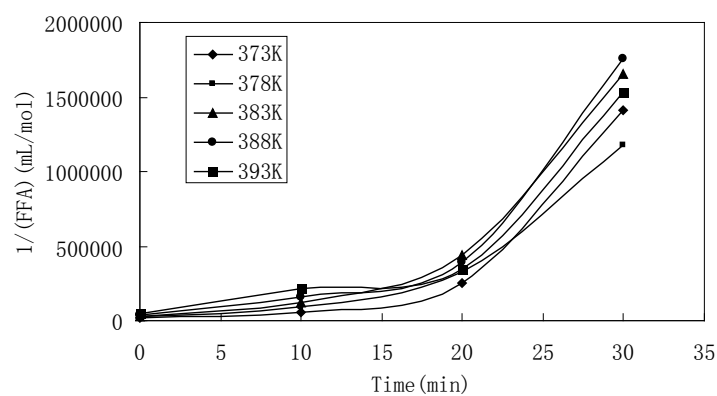
Plot of  $(FFA)$  and  $[1/(FFA)]$  vs. time for Equations (1) and (3), respectively are nonlinear as shown in **Figure 6** and **Figure 7**, while plot of  $\ln((FFA)_0/(FFA))$  vs. time for Equation (2) is linear as shown in **Figure 8**. This proves that the furfural hydrogenation follows the first-order nature.

**Table 2** shows time against tetrahydrofurfuryl alcohol concentration data using 2.0 g catalyst at a temperatures of 373, 378, 383, 388 and 393 K.

Plot of  $(TFFA)$  vs. time for Equation (1) respectively is linear as shown in **Figure 9**. This proves that the furfuryl alcohol hydrogenation follows the zero-order nature.

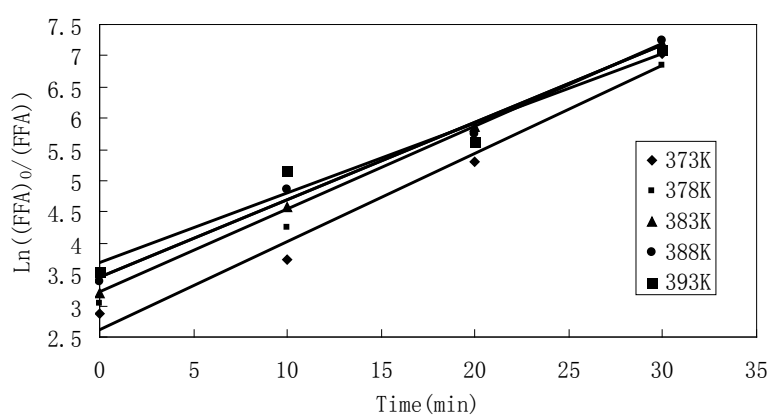
**Table 1.** Time vs. furfural concentration data.

Temperature (K)	Time (min)	(FFA) * 10 <sup>-6</sup> (g·mol/l)	Ln((FFA) <sub>0</sub> /(FFA))	1/(FFA)(1/g·mol)
373	0	44.90	2.876	22,270.7
373	10	19.18	3.727	52,133.9
373	20	3.978	5.310	251,355.9
373	30	0.7068	7.028	1,414,904.0
378	0	38.21	3.037	26,170.8
378	10	11.25	4.260	88,851.0
378	20	1.199	6.499	833,900.4
378	30	0.8486	6.845	1,178,423.0
383	0	32.13	3.211	31,120.3
383	10	8.237	4.572	121,398.7
383	20	2.272	5.860	440,049.1
383	30	0.6040	7.185	1,655,699.0
388	0	26.65	3.398	37,526.0
388	10	6.162	4.862	162,273.1
388	20	2.531	5.752	395,157.5
388	30	0.5689	7.245	1,757,731.0
393	0	23.03	3.544	43,426.3
393	10	4.574	5.160	218,644.6
393	20	2.884	5.621	346,690.6
393	30	0.6534	7.106	1,530,512.0

**Figure 6.** Test for zero-order reaction.**Figure 7.** Test for second-order reaction.

**Table 2.** Time vs. tetrahydrofurfuryl alcohol percentage concentrations.

Temperature (K)	Time (min)	( <i>FFA</i> )/%
373	40	0.4789
373	50	0.8930
373	60	0.9792
373	90	2.076
373	120	3.552
373	150	4.697
378	30	0.2361
378	40	0.9290
378	50	1.183
378	60	1.728
378	90	3.237
378	120	4.808
383	30	0.3588
383	40	1.044
383	50	1.581
383	60	2.305
383	90	3.889
383	120	5.564
388	20	0.5532
388	30	1.406
388	40	2.428
388	50	2.913
388	60	3.347
388	90	5.189
393	0	0.0600
393	10	0.9266
393	20	1.543
393	30	2.351
393	40	3.247
393	50	4.088

**Figure 8.** Test for first-order reaction.

### 3.6. Determination of Activation Energy

The activation energy is calculated by the use of Arrhenius equation which can be written as follows:



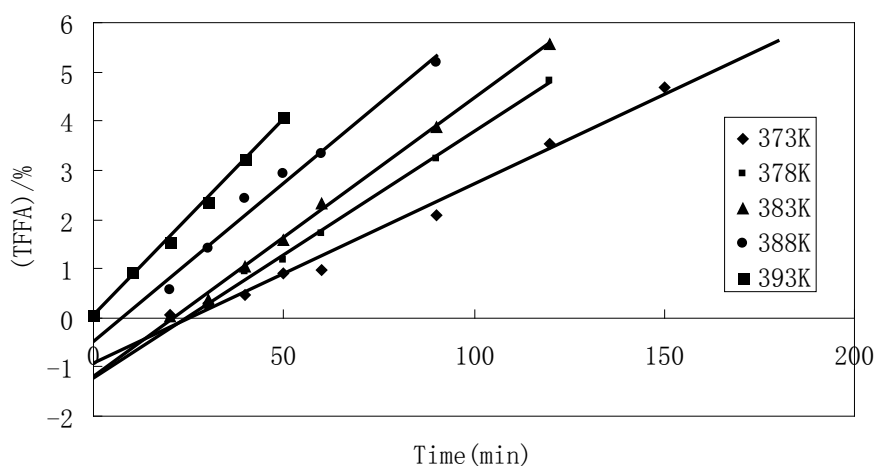
$$k = k_0 \exp(-E/RT) \quad (4)$$

The first-order reaction rate constant calculated from Equation (2) and **Figure 8** at different temperatures is shown in **Table 3**. **Figure 10** shows a plot of  $\ln k_1$  vs.  $[1/\text{Temp.}](1/\text{K})$ . Linear equation is obtained with slope of  $(E/R)$ , and activation energy is calculated as 24.7 kJ/mol.

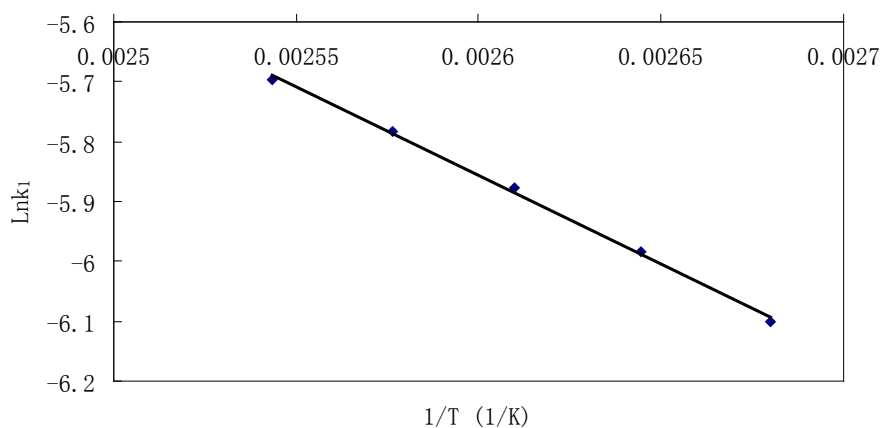
The zero-order reaction rate constant calculated from Equation (1) and **Figure 9** at different temperatures is shown in **Table 4**. **Figure 11** shows a plot of  $\ln k_2$  vs.  $[1/\text{Temp.}](1/\text{K})$ . Linear equation is obtained with slope of  $(E/R)$ , and activation energy is calculated as 27.7 kJ/mole.

**Table 3.** Effect of temperature on furfural hydrogenation.

Temperature (K)	$k_1$ ( $\text{min}^{-1}$ )	$1/(\text{Temp.})$ (1/K)	$\ln k_1$
373	0.00224	0.00268	-6.101
378	0.00252	0.00264	-5.984
383	0.00280	0.00261	-5.878
388	0.00308	0.00258	-5.783
393	0.00336	0.00254	-5.696



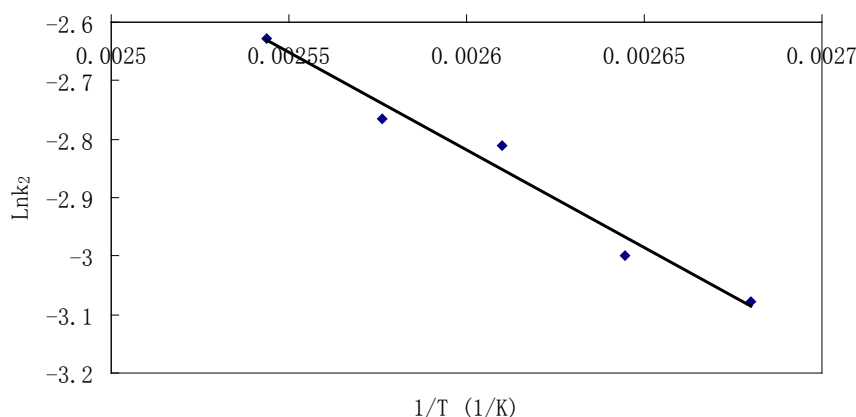
**Figure 9.** Test for zero-order reaction.



**Figure 10.** Effect of temperature on reaction rate.

**Table 4.** Effect of temperature on furfuryl alcohol hydrogenation.

Temperature (K)	$k_2$ (gmole/liter/min)	1/(Temp.) (1/K)	$\text{Ln}k_2$
373	0.0461	0.00268	-3.078
378	0.0498	0.00264	-2.999
383	0.0602	0.00261	-2.811
388	0.0630	0.00258	-2.765
393	0.0723	0.00254	-2.627

**Figure 11.** Effect of temperature on reaction rate.

## 4. Conclusions

- 1) Below the stirring speed of  $450 \text{ r}\cdot\text{min}^{-1}$ , the yield of tetrahydrofurfuryl alcohol increases with increasing stirring rate.
- 2) A maximum tetrahydrofurfuryl alcohol yield of 96% is obtained at a 180 min reaction time, 383 K reaction temperature, 1.5 MPa  $\text{H}_2$  and 2.0 g catalyst.
- 3) The corresponding order is first-order with respect to furfural concentration and zero-order with respect to tetrahydrofurfuryl alcohol concentration for the hydrogenation of furfural and the hydrogeoxygenation of furfuryl alcohol, respectively.
- 4) The corresponding values are 24.7 kJ/mole and 27.7 kJ/mole for the hydrogenation of furfural ( $E_1$ ) and the hydrogeoxygenation of furfuryl alcohol ( $E_2$ ), respectively.

## Acknowledgements

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## Conflicts of Interest

The authors declare no conflicts of interest.

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## Notation

$E$ : activation energy (kJ/mol)

$k$ : reaction rate constant

$k_1$ : first-order reaction rate constant ( $\text{min}^{-1}$ )

$k_2$ : zero-order reaction rate constant (gmole/liter/min)

$T$ : temperature (K)

$t$ : time (min)

$R$ : gas constant (8.314 J/gmole/K)

$FFR$ : furfural

$FFA$ : furfuryl alcohol

$TFFA$ : tetrahydrofurfuryl alcohol

$C_{A,0}$ : initial concentration of component A in reaction solution (mol/mL)

$C_A$ : final concentration of component A in reaction solution (mol/mL)