



Kinetic Parameters Evaluation of Furfural Degradation Reaction Using Numerical and Integral Methods

Jabosar Ronggur Hamonangan Panjaitan^{1,*}, Guna Bangun Persada¹, Didik Supriyadi²

¹Energy System Engineering, Institut Teknologi Sumatera, Lampung 35365, Indonesia

²Chemical Engineering, Institut Teknologi Sumatera, Lampung 35365, Indonesia

*E-mail: jabosar.panjaitan@tse.itera.ac.id

ABSTRAK

Furfural adalah salah satu bahan kimia penting yang dapat diubah menjadi berbagai bahan kimia seperti furfuryl alkohol dan asam levulinat. Furfural dapat diproduksi dari biomassa lignoselulosa dalam kondisi asam dengan mengkonversikan fraksi hemiselulosa dalam biomassa menjadi gula pentosa dan selanjutnya menjadi furfural. Reaksi degradasi furfural tidak diinginkan karena dapat mengurangi hasil furfural yang telah dihasilkan. Tujuan dari penelitian ini adalah untuk menghitung parameter kinetika dari reaksi degradasi furfural menggunakan metode numerik dan integral. Hasil penelitian menunjukkan bahwa nilai konstanta laju reaksi dan energi aktivasi dari perhitungan metode numerik dan integral berbeda karena perbedaan dalam metode perhitungan. Pada metode integral, reaksi degradasi furfural pada suhu yang lebih tinggi (170°C) sesuai dengan model orde nol karena sebagian besar furfural telah terdegradasi dalam reaksi, akan tetapi reaksi degradasi furfural pada suhu yang lebih rendah (150°C dan 160°C) sesuai dengan model *non-second order*.

Kata kunci: Degradasi furfural, reaksi kinetik, konstanta laju reaksi, orde reaksi.

ABSTRACT

Furfural is one of the important building block chemicals that can be converted into various chemicals such as furfuryl alcohol and levulinic acid. Furfural can be produced from lignocellulosic biomass in acidic condition which hemicellulose fraction in biomass can be converted into pentose sugar and subsequently became furfural. Furfural degradation reaction is not desirable because it can reduce the yield of furfural that had been produced. The purpose of this study was to calculate kinetic parameters of furfural degradation reaction using numerical and integral methods. The results showed that the value of reaction rate constants and activation energies from numerical and integral methods calculation were different due to the differences in calculation methods. Using integral method, reaction order of furfural degradation at higher temperature (170°C) follows zero order because most of the furfural had been degraded in the reaction, but reaction order of furfural degradation at lower temperature (150°C and 160°C) follows non-second order.

Keywords: Furfural degradation, kinetic reaction, reaction rate constant, reaction order.

1. PENDAHULUAN

Furfural is one of 12 building block chemicals that can be converted into various chemicals [1]. The most widely used furfural application was furfuryl alcohol which used for adhesive applications in sand casting [2]. Furfuryl alcohol can be hydrolyzed with acid to produce levulinic acid [3]. Levulinic acid can be converted into biofuels such as ethyl levulinate, γ -valerolactone, and 2-methyltetrahydrofuran [4]. Therefore,

furfural had a lot of potential as fuel and chemicals.

Lignocellulosic biomass can be used as reactant for furfural production. Under acidic condition, hemicellulose fraction in biomass can be converted into pentose sugar and subsequently became furfural [5]. Sulfuric acid catalyst and biomass can be reacted at 170 - 185°C in batch resulting furfural yield around 40-50% [4].

Furfural can be degraded at high temperature. Formic acid and tar were

produced from furfural degradation reaction [6]. In furfural production, furfural degradation reaction is not desirable because it can reduce the yield of furfural that had been produced.

Degradation reaction of furfural can be evaluated to determine furfural kinetic degradation reaction. Kinetics of furfural degradation in formic acid media has been carried out by Lamminpaa [5]. They showed that reaction order change when formic acid catalyst concentration change. The method to determine reaction rate constants and reaction orders can be calculated using many methods. Six methods can be used to analyze reaction rate constants and reaction order such as differential method, integral method, half-live method, initial reaction rate method, linear regression method and non-linear regression method [7]. The differential method can be divided into graphical, numerical and polynomial fit methods. Numerical and integral methods are the simple and fast methods that can be used to determine reaction rate constants and reaction orders. On the other side, non-linear regression method is more complex, and it has a lot of assumptions. Therefore, it is very interesting to evaluate kinetic parameters using numerical and integral method.

The purpose of this study was to investigate kinetic parameters in furfural degradation reaction such as reaction rate constant, activation energy and reaction order using numerical and integral methods. Data from furfural degradation were obtained from the study of Gozan et al [8], which furfural was obtained from empty fruit bunches acid hydrolysis that had been treated with ammonia.

2. METHODS

2.1 Kinetic Experiments And Analytical Method

In this study, furfural concentration data were obtained from Gozan et al [8]. They analyzed furfural concentration using

HPLC which obtained from kinetics experiment of empty fruit bunches hydrolysis using a 0.5M sulfuric acid catalyst. Furfural degradation reaction can be showed in Figure 1, which furfural degraded in resinification products [8,9].

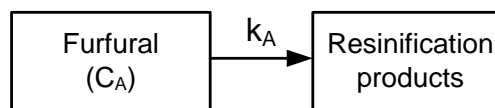


Figure 1. Furfural Degradation Reaction Scheme

From Figure 1, we can make kinetic equation for furfural degradation reaction:

$$\frac{dC_A}{dt} = -k_A \cdot C_A \quad (1)$$

Where k_A was reaction rate constant for furfural degradation reaction and C_A was furfural concentration.

2.2 Numerical Method Calculation

Furfural concentration data were taken in the 30 to 120 minutes reaction with 30 minutes data interval. $(-dC_A/dt)$ calculation can be done using three-point differentiation formulas [7]:

- Initial point:

$$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \quad (2)$$

- Interior point:

$$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t} [(C_{A(i+1)} - C_{A(i-1)})] \quad (3)$$

- Last point:

$$\left(\frac{dC_A}{dt}\right)_{t_5} = \frac{C_{A3} - 4C_{A4} + 3C_{A5}}{2\Delta t} \quad (4)$$

where $\ln(-dC_A/dt)$ is furfural concentration change per time, C_{A1-5} is the furfural concentration in the 30 to 120 minutes reaction, and Δt is 30 minutes reaction interval.

Reaction rate constants can be calculated using the formula:

$$\ln\left(\frac{dC_A}{dt}\right) = \ln k_A + \alpha \cdot \ln C_A \quad (5)$$

The plot between $\ln(-dC_A/dt)$ and $\ln C_A$ can produce reaction rate constant (k) and the reaction order (α).

Activation energy can be calculated using the Arrhenius:

$$k = A \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (6)$$

where k is reaction rate constant, A is the pre-exponential factor, E_A is activation energy (kJ/mol), R is gas constant (kJ/mol.K), and T is reaction temperature ($^{\circ}\text{K}$).

2.3 Integral Method Calculation

Kinetic parameters calculation using integral method is a trial method of reaction order to determine reaction rate constant value based on the suitability of graph.

- Zero order reaction rate constant calculation:

$$C_A = C_{A0} - kt \quad (7)$$

The plot between C_A and t can produce reaction rate constant (k).

- First order reaction rate constant calculation:

$$\ln \frac{C_{A0}}{C_A} = kt \quad (8)$$

The plot between $\ln C_{A0}/C_A$ and t can produce reaction rate constant (k).

- Second order reaction rate constant calculation:

$$\frac{1}{C_A} = kt + \frac{1}{C_{A0}} \quad (9)$$

The plot between $1/C_A$ and t can produce reaction rate constant (k).

Activation energy calculation can be calculated using reaction rate constants between two reaction temperatures:

$$E_A = -\frac{2.3(R) \log(k_2/k_1)}{(1/T_2) - (1/T_1)} \quad (10)$$

where k is reaction rate constant, A is the pre-exponential factor, E_A is activation energy (kJ/mol), R is gas constant (kJ/mol.K), and T is reaction temperature ($^{\circ}\text{K}$).

3. RESULTS AND DISCUSSION

Reaction rate constants from simultaneous model in Gozan et al [8] were compared with numerical and integral methods in this study. Table 1 showed reaction rate constants and activation energies which calculated using numerical and integral methods.

Table 1. Reaction rate constant and activation energy evaluation with numerical and integral methods.

Parameters	Gozan et al [8]		This study		
	Non-linear regression	Numerical	Integral zero order	Integral second order	
Reaction rate constant	150 $^{\circ}\text{C}$	0.04	2.83	0.0003	0.1082
	160 $^{\circ}\text{C}$	0.22	1.55	-	-
	170 $^{\circ}\text{C}$	0.16	5.73	0.0008	0.1480
Activation energy (kJ/mol)	98.21	53.685	76.318	24.372	

Reaction rate constant, reaction order and activation energy calculation using zero, first and second order integral method was carried out at reaction temperature of 150 $^{\circ}\text{C}$, 160 $^{\circ}\text{C}$ and 170 $^{\circ}\text{C}$. Based on the

calculation, there are error value in reaction rate constant and reaction order at 160 $^{\circ}\text{C}$. In addition, error value was also obtained in determining reaction rate constant using first order integral method.

Therefore, in this study reaction temperature of 160°C and first order integral method were not evaluated.

Based on Table 1, reaction rate constants were higher using numerical methods at temperatures of 150, 160, and 170°C which are 2.83, 1.55 and 5.73. In addition, reaction rate constants calculation using zero order and second order integral methods produced values at 150°C reaction temperature were 0.0003 and 0.0008 and at 170°C reaction temperature were 0.1082 and 0.1480. Reaction rate constants value using numerical and integral methods at 170°C is higher than the temperature of 150°C and 160°C. This can be happened because reaction rate constants were affected by reaction temperature according to Arrhenius equation. On the other side, Gozan et al [8] showed lower reaction rate constants at temperatures of 150, 160, and 170°C, which are 0.04, 0.22 and 0.16.

Activation energy of furfural degradation reaction was also calculated based on numerical and integral methods and compared with Gozan et al [8]. Activation energies produced in this study were lower than Gozan et al [8]. Numerical methods, zero order integral and second order integral methods produced activation energies values which are 53.685, 76.318, and 24.3372 kJ/mol. However, Gozan et al

[8] obtained 98.211 kJ/mol in activation energy.

The difference in reaction rate constant and activation energy values that produced in this study can be due to differences in the calculation method. Numerical method is a differential method that evaluated uncertainty data, but integral method is a method that smoothed data. On the other side, non-linear regression method is a method that minimizes errors between measured value and data [7].

Based on numerical calculation method, reaction order at temperatures of 150, 160 and 170°C were 2.84, 2.48 and 3.84. Higher reaction order value ($\alpha > 2$) indicated that the effect of reactants which are water and furfural had high impact on the rate of furfural degradation reaction. Higher reaction temperature produced higher reaction order and accelerated the rate of furfural degradation reaction.

Integral method analysis of reaction order can be seen in Figure 2. Based on Figure 2, zero order integral method model suitable to furfural concentration data at 170°C with R-square value about 0.99. This happened because at temperature of 170°C most of furfural had been degraded, so that there is almost no effect of reactant in the reaction which produced a zero-order reaction equation. Furfural degradation can produce formic acid and tar [6].

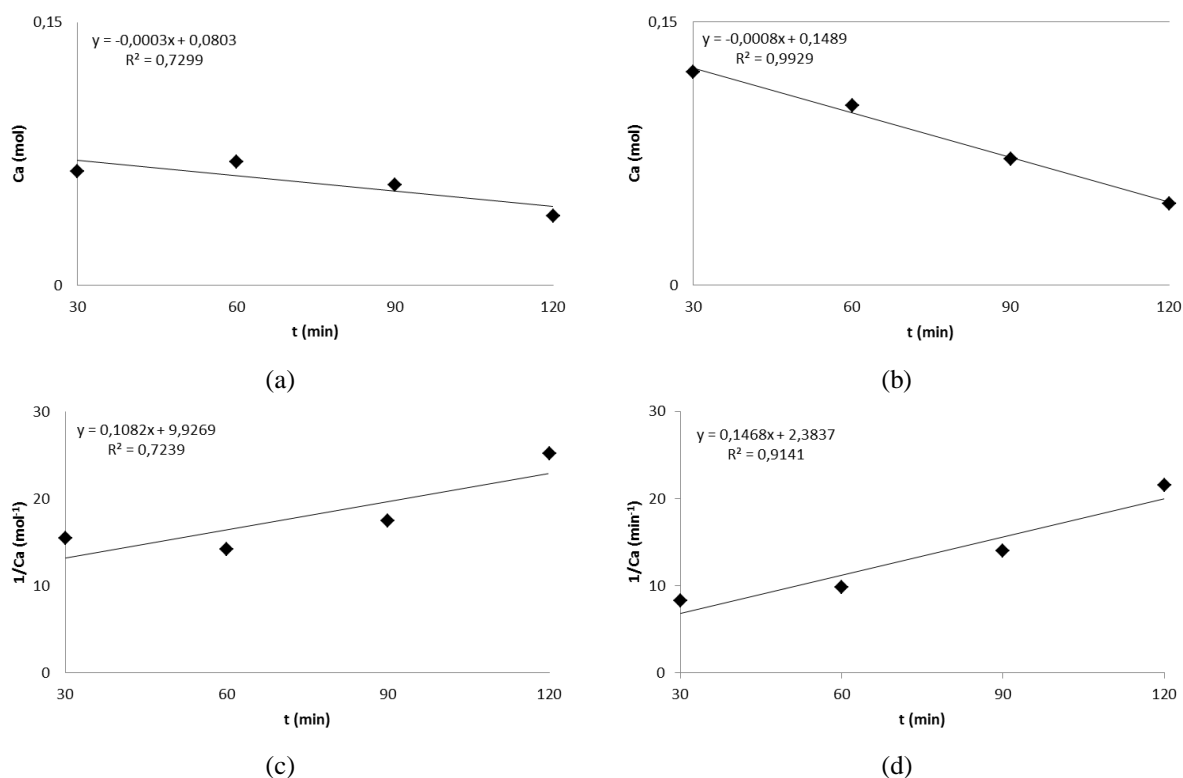


Figure 2. Reaction order analysis using integral method (a) Zero order at temperature 150°C, (b) Zero order at temperature 170°C, (c) Second order at temperature 150°C, (d) Second order at temperature 170°C.

4. CONCLUSION

The purpose of study was to calculate kinetic parameters of furfural degradation reaction using numerical and integral methods. The results showed that the value of reaction rate constants and activation energies from numerical and integral methods calculation were different due to the differences in calculation methods. Based on integral method, reaction order of furfural degradation at higher temperature (170°C) follows zero order because most of the furfural had been degraded in the reaction. On the other side, the order of furfural degradation reaction at lower temperatures (150°C and 160°C) follows non-second order integral method.

REFERENCES

- [1] S. Choi, C. W. Song, J. H. Shin, S. Y. Lee, Biorefineries for The Production of Top Building Block
- [2] B. M. Barbosa, J. L. Colodette, C. P. T. Cabral, J. C. Silva, F. B. Gomes, F. N. Oliveira, Furfural Production From Lignocellulosics, (In Proceedings of 7th International Colloquium on Eucalyptus Pulp), Vitória, Espírito Santo, Brazil, May 2015.
- [3] A. Morone, M. Apte, R. A. Pandey, Levulinic Acid Production From Renewable Waste Resource: Bottlenecks, Potential Remedies, Advancements And Applications, *Renewable and Sustainable Energy Review*, vol. 51, pp. 548–565, 2015.
- [4] K. Yan, G. Wu, T. Lafleur, C. Jarvis, Production, Properties and Catalytic

Chemicals and Their Derivatives, *Metabolic Engineering*, vol. 28, pp. 223–239, 2015.

- Hydrogenation of Furfural to Fuel Additives and Value-Added Chemicals, *Renewable and Sustainable Energy Review*, vol. 38, pp. 663–676, 2014.
- [5] K. Lamminpaa, J. Aloha, J. Tanskanen, Acid-Catalysed Xylose Dehydration Into Furfural in The Presence of Kraft Lignin, *Bioresource Technology*, vol. 177, pp. 94–101, 2015.
- [6] B. Danon, L. van der Aa, W. de Jong, Furfural Degradation in a Diluted Acidic and Saline Solution in The Presence of Glucose, *Carbohydrate Research*, vol. 375, pp. 145–152, 2013.
- [7] H. S. Fogler, *Elements of Chemical Reaction Engineering*, 4th Edition, New Jersey: Prentice Hall, 2006.
- [8] M. Gozan, J. R. H. Panjaitan, D. Tristantini, R Alamsyah, Y. J. Yoo, Evaluation of Separate and Simultaneous Kinetic Parameters for Levulinic Acid and Furfural Production from Pretreated Palm Oil Empty Fruit Bunches, *International Journal of Chemical Engineering*, vol. 2018, no. 1920180, pp. 1–12, 2018.
- [9] K. Dussan, B. Girisuta, D. Haverty, J. J. Leahy, M. H. B. Hayes, Kinetics of Levulinic Acid and Furfural Production from *Miscanthus x giganteus*, *Bioresource Technology*, vol. 149, pp. 216–224, 2013.