



THE STUDY ON VELOCITY TO GLYCEROL NITRATION REACTION RATE USING MICROCHANNEL HYDRODYNAMICS FOCUSED

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ABSTRACT

The article discusses the level of glycerol nitrate reaction based on flow rate. The purpose of this study was to determine the effect of flow velocity on the glycerol nitrate reaction rate with the correct experimental method. The Focal Channels ratio on microchannel uses a 1: 2 ratio (D Sheath = 300 μm). The flow rate variations used range from 50 μm/s, 100 μm/s, and 150 μm/s. The results of this study indicate that the rate of glycerol nitrate reaction is influenced by the flow rate of the reactants. The faster the flow rate of the reactants in the inlet the greater the rate of glycerol nitration reaction, because with the greater flow rate will increase the number of collisions between reactant molecules. The greater the number of collisions, the greater the molecular energy of the reactants to move, thus increasing the reaction rate. The results showed that the flow rate of 50 μm/s resulted in nitration reaction rate $r = - 0.00388 [C_3H_5(OH)_3]^{0.65142} [HNO_3]^{1.32858}$. While the flow rate is 100 μm/s, the reaction rate is $r = - 0.00388 [C_3H_5(OH)_3]^{0.6998} [HNO_3]^{1.3501}$. and for a flow rate of 150 μm/s, the reaction rate of glycerol nitrate is $r = - 0.00388 [C_3H_5(OH)_3]^{0.668276} [HNO_3]^{1.391724}$.

KEYWORDS : velocity, glycerol, nitrate acid, reaction rate

INTRODUCTION

The nitration reaction of the aromatic compounds occurs in the liquid phase, generally in the form of benzene compounds and their derivatives, naphthalene compounds, and their derivatives. One of these aromatic compounds is toluene or called methylbenzene or phenylmethane, the compound is insoluble in water and colorless.

With respect to nitration of glycerol and rate of reaction [7], [11] introduced a nitration balance system in glycerol-aqueous. [6] Whereas proposed several examples of glycerin synthesis of glycerin. [5] Then to produce of glycidyl nitrate from glycerol with 1.3 dinitroglycerin as the intermediate product. [8] found nitroglycerin kinetics parameters in the Continues stirred tank reactor process. The effect of temperature on glycerol nitration was studied [1]. Reaction order is required to set the rate equation of the reaction. The several compounds of nitration have been successfully modeled as the first order of each reactant.

[2] performed the nitration of benzene and several other reactive compounds used sulfuric acid, while [9] performed the nitration of benzene, chlorobenzene, toluene, and trimethyl benzene used trifluoroacetic acid. [10] performed the same nitration reactants used perchloric acid as the first-order reaction of each other [9]. The states that the rate of trinitroglycerin formation reaction of glycerol and nitric acid in the continues stirred tank reactor process of Biazzi is as follows:

$$-r_G = k C_G^m C_N^n = A e^{-E/RT} C_G^m C_N^n \quad (1)$$

Where the values of n and m are 0.9350 and 1.117.

[4] conducted a study on toluene nitration using microreactor and batch reactor, the study was conducted using nitric acid as a nitrating agent at constant reactor temperature. While the variables measured include reaction time, reaction temperature and acid concentration. It is used to know the performance of microreactor. The results of this study concluded that the use of microreactor to produce more reaction products than using reactor batch system. [12] conducted research and mathematical modeling of the nitration process of benzene compounds. The results of his research indicate that the reaction of nitration of aromatic compounds is influenced by reactant composition, reaction rate, reactant diffusivity, mass transfer coefficient, acidity

level, contact surface tension of the reactant and fluid properties change during nitration reaction. [3] conducted a study on toluene nitration using reactor batches. The results concluded that transition reactions occur at high concentrations from low to high speed, an increase in product per unit of acid volume, and the total mass transfer coefficient increases slowly at a fixed temperature.

METHODS

The study is used to know the effect of reactant velocity on the rate of glycerol nitration reaction in the microchannel. The microchannel geometry as in Fig. 1, While the specification of reactants seen in table 1.

Table-1 REACTAN SPECIFICATIONS

No.	Reactan	Molar mass (gr/mol)	Density (gr/cm3)	Reactan Volume (ml)
1	Glycerol	92,09	1,26	73
2	Nitric acid	63,01	1,51	186

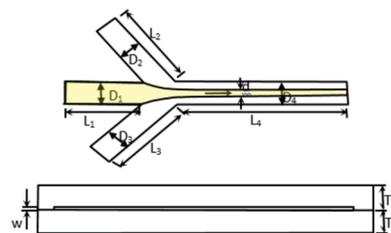


Fig. 1: Scheme two-dimensional of microchannel

- Where,
 Material = acrylic
 D1,D2,D3,D4 = 300 μm,
 w = 200 μm
 L1, L2, L3 = 2000 μm
 L4 = 4000 μm.
 T1, T2 = 5 mm.

Fig. 2 shows a scheme of research equipment, consisting of four parts: lighting, optics, camera, and control. Lighting using Fluorescent Bulb type lamp, Daylight MA305-05, serves to clarify the color of the image. Optics using BH2 BH-P Olympus type BH2 microscope. This microscope is equipped

with a 2 mm linear 2-way motion control. This microscope is integrated with AM7023B dino-capture camera. This serves to record reactant reactions in the output channel. The image data is stored as a jpg file on the computer. As for drain reactant using pump-type TS-1B / W0109-1B spryngje. This type consists of four channels. The four drive units can operate independently. This study used variations of a flow velocity of 50 μm/s, 100 μm/s, 150μm/s at a focal ratio of 1:2. Focus ratio is the discharge ratio focused on focusing discharge. The result is color data of reactants and reaction products. Then calculate the reaction rate by determining the empirical equation of the reaction rate n Order.

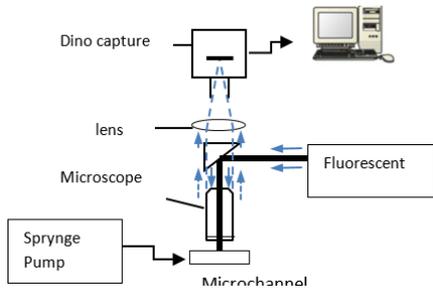
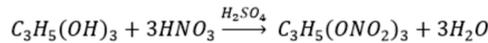


Fig. 2: Set up Research

Glycerol Nitration Reaction

The nitration process of glycerol uses glycerol and nitric acid as reactants with sulfuric acid as a catalyst. The equation of the glycerol nitration reaction process is as follows:

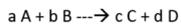


Reaction rate

In order for a collision, it must have enough energy to overcome the energy barrier of activation and the molecule must have the right geometry to form the bond back. The speed of the reaction is called the reaction rate. The more collisions, the faster the reaction rate. The reaction rate is measured by a number of reactants that become the product over time. The reaction rate is a change in the concentration of the reactant or product over time. The study of reaction rates is called reaction kinetics.

$$\text{Reaction rate} = \Delta [A] / \Delta t \text{ 3)}$$

The chemical reaction with the stoichiometric equation is as follows:



The reaction rate r is defined as

$$r = -\frac{1}{a} \frac{dA}{dt} = -\frac{dB}{b dt} = -\frac{1}{c} \frac{dC}{dt} \text{ 4)}$$

the unit of r is the concentration/time.

How to determine empirical equations rate of reaction n order. If the reaction mechanism is not known, the n-order rate equation adjusts the data with the form of the equation:

$$-r_A = -\frac{dC_A}{dt} = k C_A^n \text{ 5)}$$

Where the integration results are obtained:

$$C_A^{1-n} - C_{A0}^{1-n} = (n - 1)kt, \text{ where } n \neq 1$$

RESULT AND DISCUSSION

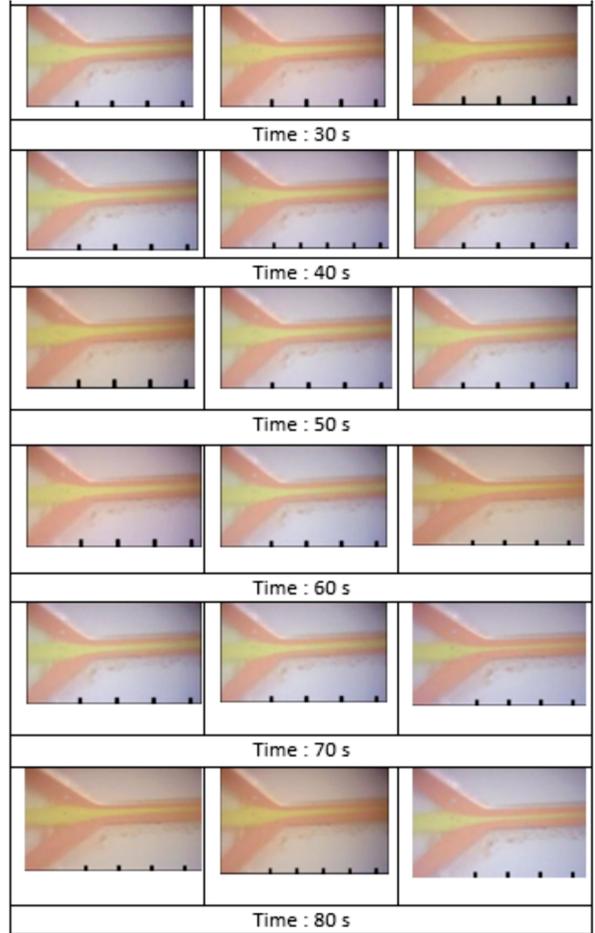
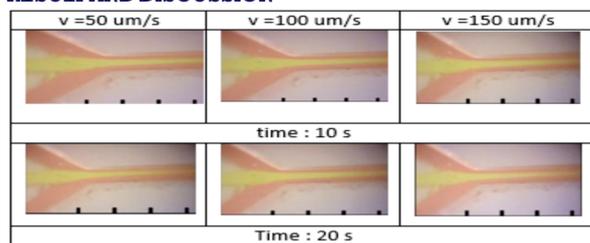


Fig. 3: The relationship of concentration change (mole) of nitric acid to time (s) at variation flow 50 m/s, 100 m/s and 150 μm/s.

Based on Fig. 3 can be calculated reaction rate using Guessing method to determining the order n. The data changes the concentration of reactants in the input into the equation 5. The results of nitrate acid reactant calculation at a velocity of 50 μm/s, 100 μm/s, 150 μm/s obtained data such as table 2, 3 and 4.

Table 4. The change of nitrate acid concentration to time using the n-th Order Guessing method at velocity 50 μm/s.

v = 50 μm/s				
n = 1,98				
t	CA	CA ⁽¹⁻ⁿ⁾ - CA0 ⁽¹⁻ⁿ⁾	A/(n-1)	B/t = k
0	3,0	0	0	0
10	2,12	0,1387	0,1321	0,01321
20	1,48	0,3470	0,3305	0,01652
30	1,13	0,5640	0,5371	0,01790
40	0,98	0,7059	0,6723	0,01680
50	0,82	0,9161	0,8725	0,01745
60	0,74	1,0563	1,0060	0,01676
70	0,67	1,2072	1,1497	0,01642
80	0,58	1,4562	1,3868	0,01733
			Variance	1,8E-06

Table 4. The change of nitrate acid concentration to time using the n-th Order Guessing method at velocity 100 μm/s

v = 100 μm/s				
n = 2,02				
T	CA	CA ⁽¹⁻ⁿ⁾ - CA0 ⁽¹⁻ⁿ⁾	A/(n-1)	B/t = k
0	3	0	0	0

10	2,2	0,1213	0,1178	0,0117
20	1,6	0,2937	0,2851	0,0142
30	1,18	0,5207	0,5055	0,0168
40	1,02	0,6572	0,6381	0,0159
50	0,88	0,8182	0,7943	0,0158
60	0,74	1,0410	1,0107	0,0168
70	0,64	1,2610	1,2243	0,0174
80	0,56	1,4945	1,4509	0,0181
			Variance	3,6E-06

Table 4. The change of nitrate acid concentration to time using the n-th Order Guessing method at velocity 150 μm/s.

v = 150 μm/s				
n=2,02				
t	CA	CA ⁽¹⁻ⁿ⁾ -CA0 ⁽¹⁻ⁿ⁾	A/(n-1)	B/t = k
0	3	0	0	0
10	2,3	0,1013	0,1034	0,0103
20	1,56	0,3060	0,3122	0,0156
30	1,2	0,4956	0,5057	0,0168
40	1,02	0,6400	0,6531	0,0163
50	0,88	0,7927	0,8089	0,0161
60	0,75	0,9849	1,0050	0,0167
70	0,67	1,1398	1,1631	0,0166
80	0,59	1,3363	1,3636	0,0170
			Variance	4,3E-06

Where, t = Reaction time, CA0 = Initial concentration of reactants Nitric acid (mol), CA = Concentration of reactants Nitric acid after t (mol), n = Order, and k = Rate of reaction constant.

From the calculation results can be made graph of concentration (CA⁽¹⁻ⁿ⁾-CA0⁽¹⁻ⁿ⁾)/((n-1)) to time as in Fig. 4, 5 and 6.

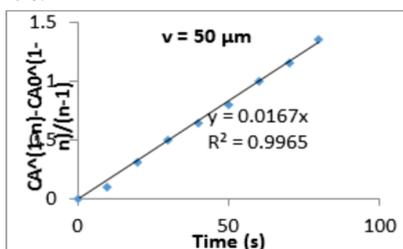


Fig. 4: The concentration relationship (CA⁽¹⁻ⁿ⁾ - CA0⁽¹⁻ⁿ⁾) / ((n-1)) over time at velocity of 50 μm/s.

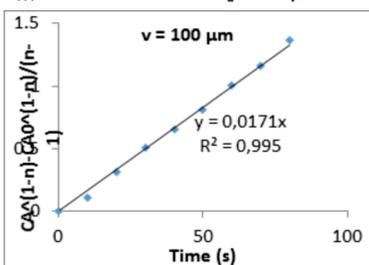


Fig. 5: The concentration relationship (CA⁽¹⁻ⁿ⁾ - CA0⁽¹⁻ⁿ⁾) / ((n-1)) over time at velocity 100 μm/s.

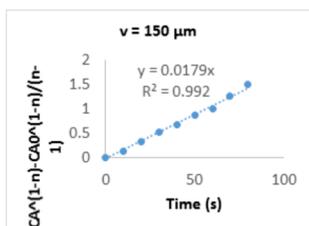


Fig. 6: The concentration relationship (CA⁽¹⁻ⁿ⁾ - CA0⁽¹⁻ⁿ⁾) / ((n-1)) over time at velocity 150 μm/s.

At Fig. 4, 5 and 6 obtained by value of the order, then calculate order value α and β. This is done by entering the value of the equation y at the value of k fitting. Then enter the value of mole coefficient of glycerol at α and coefficient of mole amount of nitric acid at β. After that do the trial and error method on the value of b that get the difference k = 0. Table 3 shows the results of the ordering of n, α and β.

Table 5. The results of ordering n, α and β at 50 μm/s

V = 50 μm/s			
n	1,98	k fitting	0,0167
α	1	k calculate	0,0167
β	3	k difference	-7,3E-13
b	1,32858		
α	0,65142		
k	0,00388		

Table 6. The results of ordering n, α and β at 100 μm/s

V = 100 μm/s		
2,02	k fitting	0,0171
1	k calculate	0,0171
3	k difference	9,82E-12
1,36071		
0,65929		
0,00388		

Table 7. The results of ordering n, α and β at 150 μm/s

V = 150 μm/s			
n	2,02	k fitting	0,0179
α	1	k calculate	0,0179
β	3	k difference	-9,1E-12
b	1,391724		
α	0,668276		
k	0,00388		

In table 5, 6 and 7 obtained, for flow rate 150 μm/s the calculation results obtained data α order = 0.668276 while β order = 1.391724 with the value k = 0.00388. Because the calculation of the rate of this reaction is based on the concentration of the reactant, and with increasing time there is a reduction of concentration so that the value of the constant is negative (-). So the equation of the reaction rate for glycerol nitration can be written as follows: r = - 0.00388 [C₃H₅(OH)₃]^{0.668276} [HNO₃]^{1.391724}. For flow rate 100 μm/s, the results α order = 0.65929, β order = 1.36071 and value k = 0.00388. So the equation of the reaction rate: r = - 0.00388 [C₃H₅(OH)₃]^{0.65929} [HNO₃]^{1.36071}. While flow rate 50 μm/s, the results α order = 0.65142, β order = 1.32858 with the value k = 0.00388. So the equation of the reaction rate for glycerol nitration can be written as follows: r = - 0.00388 [C₃H₅(OH)₃]^{0.65142} [HNO₃]^{1.32858}. It's because of the faster the flow rate of reactants, the greater the chance of collisions between molecules, the greater the reaction occurs with the collision between reactant molecules. Faster streams will provide a flow force that enlarges the activation of energy and the molecules easily form bonds again in the form of reaction products, thus increasing the reaction rate.

CONCLUSIONS

The results of the study concluded that the equation of the reaction rate for glycerol nitration was influenced by the flow rate of the reactants. The greater the flow rate will enlarge the reactant collision so as to enlarge the reaction order. It's seen that at a flow rate of 150 μm/s, the reaction rate is formulated r = - 0.00388 [C₃H₅(OH)₃]^{0.668276} [HNO₃]^{1.391724}, And respectively the reaction rate formed at a speed of 100 μm/s and 50 μm/s can be written as follows: r = - 0.00388 [C₃H₅(OH)₃]^{0.65929} [HNO₃]^{1.3501} and r = - 0.00388 [C₃H₅(OH)₃]^{0.65142} [HNO₃]^{1.32858}.

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REFERENCES

- [1] Astuti Erna, Supranto, Rochmadi, Prasetya Agus, Ström Krister & Andersson Bengt, 2014. Kinetic Modeling of Nitration Glycerol, *Modern Applied Science*, Vol. 8, No. 2; ISSN 1913-1844 E-ISSN 1913-1852, Published by Canadian Center for Science and Education.
- [2] Coombes, R. G., Moodie, R. B., & Schofield, K., 1968. Electrophilic Aromatic Substitution. Part I. The Nitration of Some Reactive Aromatic Compounds in Concentrated Sulphuric and Perchloric acids. *J. Chem. Soc. B*, 800-804.
- [3] Cox P.R., Strachan A.N. 1972, Two-Phase Nitration of Toluene-I, *Chemical Engineering Science*, Volume 27, Issue 3, 457-463.
- [4] Halder R., Lawal A., And Damavarapu, 2007. Nitration of Toluene in a Microreactor, *Catalysis Today* 125 (74-80) New Jersey Center for Microchemical Systems, Department of Chemical, Biomedical and Material Engineering, United States.
- [5] Highsmith, T. K., & Johnston, H. E., 2005. Continuous Process and System for Production of Glycidyl Nitrate from Glycerin, Nitric Acid and Caustic and Conversion of Glycidyl Nitrate to Poly (Glycidyl Nitrate). US Patent No. 6, 870061.
- [6] Highsmith, T. K., Sanderson, A. J., Cannizzo, L. F., & Hajik, R. M., 2002. Polymerization of Poly(glycidyl Nitrate) from High Purity Glycidyl Nitrate Synthesized from Glycerol. US Patent No. 6, 362, 311.
- [7] Kazakov, A. I., Kirpichev, E. P., Lagodzinskaya, G. V., Andrienko, L. P., Yunda, N. G., Korolev, A. M., Rubtsov, Y. I., Eremenko, L. T., 1990. Study of Nitration Equilibrium in the Glycerin—Aqueous Nitric Acid System. 2. Change in H and ΔS in The Nitration Reactions. *Russian Chemical Bulletin*, 39(8), 1565-1570.
- [8] Lu K. T., Luo, K. M., Yeh, T.F., & Lin, P.C., 2008. The Kinetic Parameters and Safe Operating Conditions of Nitroglycerine Manufacture in The CSTR of Biuzzi Process. *Process Saf. Environ. Prot.*, 86(1), 37-47.
- [9] Moodie R. B., Schofield, K., & Tobin, G. D., 1977. Electrophilic Aromatic Substitution. Part 17. Products, Kinetics, and Mechanism of Nitration in Trifluoroacetic Acid. *J. Chem. Soc. Perkin Trans.*, 2, 1688-1693.
- [10] Moodie R. B., Schofield, K., & Tobin, G. D., 1978. Electrophilic Aromatic Substitution. Part 19. The Nitration of Some Aromatic Compounds in Perchloric Acid. *J. Chem. Soc. Perkin Trans.*, 2, 318-323.
- [11] Yunda, N. G., Lagodzinskaya, G. V., Kazakov, A. I., Korolev, A. M., Rubtsov, Y. I., Anelis, G. B., & Eremenko, L. T., 1991. Nitration Equilibrium in The Glycerol-Aqueous-Nitric-Acid System 3. PMR Parameters, Conformational Structure, and Main Properties of Glycerol and Its Nitrates. *Russian Chemical Bulletin*, 40(2), 325-332.
- [12] Zaldivar J. M., Molga E., Alos M.A., 1995. Aromatic Nitrations by Mixed Acid. Slow liquid-liquid reaction regime, *Chem. Eng. & Proc. V. 34.*—P 543 – 559.