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Article

Kinetic Modelling of Nitration of Glycerol: Three Controlling Reactions Model

Erna Astuti^{1,2,a}, Supranto^{1,b}, Rochmadi^{1,c}, and Agus Prasetya^{1,d}

¹ Chemical Engineering Department, Gadjah Mada University, Indonesia

² Chemical Engineering Department, Ahmad Dahlan University, Indonesia

E-mail: ^aerna_uad@yahoo.com (Corresponding author), ^bsupranto@chemeng.ugm.ac.id,

^crochmadi@chemeng.ugm.ac.id, ^daguspras@chemeng.ugm.ac.id

Abstract. In the present study, a kinetic model of nitration between glycerol and nitric acid was developed. The presented model describes three controlling reactions model used elementary reactions consisting of three reversible reactions. The model utilizes first order reaction according to each reactant. The nitration of glycerol was modelled by fitting the kinetic model with 6 parameters, the rate constant at an average temperature and the activation energy. The reaction rate is assumed to be governed by three reactions, i.e. the formation of MNG (mononitroglycerin), the formation of DNG (dinitroglycerin) and the formation of TNG (nitroglycerin). The aim of this work is compare two models: seven controlling reactions model and three controlling reactions model. Two models have the similar trend. The three controlling reactions model gives better fit than seven controlling reactions model. The accuracy of three controlling reactions model is higher. The advantage of the seven controlling reactions model is this model can predict all products of nitration. So this model can be used at preliminary design plant. Three controlling reactions model can be used at next step, as design of reactor.

Keywords: Nitration, glycerol, three controlling reactions model, kinetic modelling.

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1. Introduction

Polyglycidyl nitrate (PGN) is an energetic polymer [1]. Energetic polymers are polymeric compounds that contain energetic functional groups, such as the azido group (-N₃), nitro group (C-NO₂), nitrate group (O-NO₂), nitramino group (N-NO₂), or the less common difluoroamino group (-NF₂) [2]. This polymer can be used as a binder in propellant and explosives to increase the explosive power in comparison with inert binders. Provatas [3] stated that PGN is the most energetic polymer. Willer and McGrath [4] made propellant with composition: PGN as binder of 60 – 85 % b/b, ammonium nitrate as oxidiser and a little amount of aluminium and or boron as additive. Willer and McGrath [5] used magnesium as additive. Talawar et al. [2] explained that this polymer has nitrate group. It made this compound as the promising polymer. Higsmitth et al. [6] proposed process for producing PGN from glycerol. This process comprise three reactions i.e. nitration, cyclization and polymerization. Reaction time of nitration is longest than the other reactions.

Basic knowledge of engineering is able to analyze and exploit fundamental reactions in production of polyglycidyl nitrate [7]. This paper focuses in nitration of glycerol. Glycerol is a by-product of the biodiesel production that need to handling immediately so as to not become the waste that polluted the environment [7-8]. Heat of reactions of nitration has known. Gibbs energies, enthalpies and entropies also have known [9]. Gas Chromatography is instrument that mostly used for identified nitroglycerin and its Derivatives [10-15]. Gas chromatography also can be used to quantify all product of nitration of glycerol [16]. It is necessary to study kinetic parameter of nitration.

At the previous study we proposed kinetic modelling of nitration of glycerol. The kinetic model was developed with seven reversible reactions (see Table 1) and namely as seven controlling reactions model. Nitration of glycerol produces five products: 1-MNG (1-mononitroglycerin), 2-MNG (2-mononitroglycerin), 1,3-DNG (1,3-dinitroglycerin), 1,2-DNG (1,2-dinitroglycerin) and TNG (trinitroglycerin) [6]. The concentration of eight compounds that consisted in nitration could be determined by analyzing the result of GC. The seven reversible reactions are [17]:

Table 1. Nitration reaction.

Reaction number	Reaction	Reaction
1	G + HNO ₃	↔ 1 MNG + H ₂ O
2	G + HNO ₃	↔ 2 MNG + H ₂ O
3	1 MNG + HNO ₃	↔ 1,3 DNG + H ₂ O
4	1 MNG + HNO ₃	↔ 1,2 DNG + H ₂ O
5	2 MNG + HNO ₃	↔ 1,2 DNG + H ₂ O
6	1,3 DNG + HNO ₃	↔ TNG + H ₂ O
7	1,2 DNG + HNO ₃	↔ TNG + H ₂ O

Nitration of some compounds has successfully been modelled as first order with respect to each reactant [18-21]. At seven controlling reactions model, the obtained experimental data were treated on the hypothesis that the rate of glycerol nitration was described by first order with respect to each reactant. For many reactions involving multiple steps and pathways, the powers in the rate laws agree with the stoichiometric coefficients indicating a simple kinetic mechanism. The equation rates of nitration are defined as:

$$-\frac{dC_G}{dt} = k_1 C_G C_{HNO_3} + k_2 C_G C_{HNO_3} - k_{-1} C_{1MNG} C_{H_2O} - k_{-2} C_{2MNG} C_{H_2O} \quad (2)$$

$$-\frac{dC_{1MNG}}{dt} = k_{-1} C_{1MNG} C_{H_2O} + k_3 C_{1MNG} C_{HNO_3} + k_4 C_{1MNG} C_{HNO_3} - k_1 C_G C_{HNO_3} - k_{-3} C_{1,3DNG} C_{H_2O} - k_{-4} C_{1,2DNG} C_{H_2O} \quad (3)$$

$$-\frac{dC_{2MNG}}{dt} = k_{-2} C_{2MNG} C_{H_2O} + k_5 C_{2MNG} C_{HNO_3} - k_2 C_G C_{HNO_3} - k_{-5} C_{1,2DNG} C_{H_2O} \quad (4)$$

$$-\frac{dC_{1,3DNG}}{dt} = k_{-3} C_{1,3DNG} C_{H_2O} + k_6 C_{1,3DNG} C_{HNO_3} - k_3 C_{1MNG} C_{HNO_3} - k_{-6} C_{1,2DNG} C_{H_2O} \quad (5)$$

$$-\frac{dC_{1,2DNG}}{dt} = k_{-4} C_{1,2DNG} C_{H_2O} + k_{-5} C_{1,2DNG} C_{H_2O} + k_7 C_{1,2DNG} C_{HNO_3} - k_4 C_{1MNG} C_{HNO_3} - k_5 C_{2MNG} C_{HNO_3} \quad (6)$$

$$-\frac{dC_{NG}}{dt} = k_{-6}C_{NG}C_{H_2O} - k_6C_{1,3DNG}C_{HNO_3} - k_7C_{1,2DNG}C_{HNO_3} \quad (7)$$

Parameter estimation has been done and gave 14 kinetic parameters. The parameter values describe that the 1st, 3rd, 5th and 7th reaction rates are very fast. On the contrary, the 2nd, 4th and 6th reaction rates are slow. The values of kinetic parameters and their 95% confidence intervals at various molar ratio of nitric acid/glycerol can be seen in Table 2.

Table 2. Kinetic parameters for nitration of glycerol calculated with seven controlling reaction model.

Reaction number	$K_{ref}, m^3/mol, s \cdot 10^{10}$			
	1/1	3/1	5/1	7/1
1	1034134.55±65373133.8	5.77±0.34	15.24± 0.64	235.38±19.03
2	0.02± 0.20	0.05 ± 0.10	1.59±0.30	4.17±1.32
3	86632.50± 313434.38	80.18±3.22	117.22±5.72	89.97± 1.21
4	3805.42± 8375.65	2.33± 3.65	4.90± 6.89	34.60± 8.38
5	3.72± 156.23	59.91±110.02	10803.65±150411.43	246130.55± 13263348.16
6	56.82±13.45	0.94±0.72	2.28±0.39	1.58± 0.06
7	857.40± 282.03	2.44±7.34	103.54± 33.07	716.19± 69.27
Activation energy, kJ/mol				
1	38.10±3692.52	38.10±4.21	38.15±2.56	38.12±5.52
2	117.23± 1441.48	117.23± 105.65	117.23± 11.62	117.23± 2.57
3	58.62± 332.69	58.62± 3.40	58.69± 3.97	58.64± 1.20
4	31.40± 129.65	31.40± 67.81	31.40± 79.80	31.38± 12.44
5	167.47± 3061.09	167.48± 147.73	167.48± 406.37	167.46± 880.47
6	104.67± 32.10	104.53± 50.04	104.51± 14.36	104.53± 2.97
7	71.18± 31.58	71.89± 192.41	71.90± 24.04	71.84± 6.61

Table 2 shows in most cases the confidence intervals are small compared to the magnitude of the parameter values, except confidence intervals for cases at molar ratio of 1/1 and reaction (5) at all molar ratio. At these conditions all reactions run very slowly therefore the compositions of nitration products are nearly equal. This caused the kinetic parameters at these conditions appear to be poorly defined.

The data in Table 2 showed that concentration of 2-MNG and 1,2-DNG at the mixture of reactions are very low. The primary hydroxyl group is more reactive than secondary hydroxyl group. Previous studies [22-23] showed that hydroxyl group at secondary position less reactive than primary position because of steric hindrance. Steric hindrance causes the transition state to be higher in energy and raise activation energy of reaction. The reaction that occurs at secondary hydroxyl group is slower than that at primary hydroxyl group. Reaction that nitrate group at first carbon atom is faster than that at secondary carbon atom. The 2nd reaction rate that includes secondary hydroxyl group is very slow, leading to the low concentration of 2-MNG. There are three reasons for low concentration of 1,2-DNG. Firstly in the 4th

reaction, the active functional group is a secondary nitrate group which is more difficult to form. Therefore the formation of 1,2-DNG from 1-MNG was very slow. Secondly even though the reaction rate of 5th reaction (the formation of 1,2-DNG from 2-MNG) is fast, however the concentration of 2-MNG is slow which causes low concentration of 1,2-DNG. Thirdly the reaction rate of 7th reaction (the formation of TNG from 1,2-DNG) is fast, however the 1,2-DNG disappear very quickly forming TNG.

HYSIS-Aspen data and NIST (National Institute of Standard and Technology) considered that two pair isomers, 1,3-DNG and 1,2-DNG and 1-MNG and 2-MNG, have the same physical properties i.e. boiling point, density, critical temperature, critical pressure etc. Basic characteristic of 1,3-DNG and 1,2-DNG explained that 1,3-DNG and 1,2-DNG have slightly different properties. The NMR spectra of 1,3-DNG and 1,2-DNG is also slightly different [24-25]. Two isomers have different physical properties but the formation of 2-MNG and 1,2-DNG are very low. The reactions that represent nitration of glycerol need to be reviewed. The model can be simplified based on the controlling mechanism. This paper assumed no distinction between two isomers (1-MNG and 2-MNG, 1,3-DNG and 1,2-DNG). The formation of 1-MNG and 2-MNG were regarded as one reaction. Therefore this paper describes kinetic modelling by reducing the reactions involving nitration. The 1st and 2nd reactions were merged into the equation of formation MNG. The 3rd, 4th and 5th reactions were merged into the equation of formation DNG. Furthermore the 6th and 7th reactions were merged into formation of TNG. The three controlling reactions model only considered three compounds as product of nitration, i.e. MNG, DNG and TNG. Nitration reaction proposed is a reaction in series as follows:

Table 3. Nitration reaction (three controlling reactions model).

Number	Reaction
1	$G + HNO_3 \leftrightarrow MNG + H_2O$
2	$MNG + HNO_3 \leftrightarrow DNG + H_2O$
3	$DNG + HNO_3 \leftrightarrow TNG + H_2O$

where $DNG=1,3-DNG+1,2-DNG$; $MNG=1-MNG+2-MNG$

The model then considers the following reaction rates:

$$-\frac{dC_G}{dt} = k_1 C_G C_{HNO_3} - k_{-1} C_{MNG} C_{H_2O} \quad (8)$$

$$-\frac{dC_{HNO_3}}{dt} = k_1 C_G C_{HNO_3} + k_2 C_{MNG} C_{HNO_3} + k_3 C_{DNG} C_{HNO_3} - k_{-1} C_{MNG} C_{H_2O} - k_{-2} C_{DNG} C_{H_2O} - k_{-3} C_{TNG} C_{H_2O} \quad (9)$$

$$-\frac{dC_{MNG}}{dt} = k_{-1} C_{MNG} C_{H_2O} + k_2 C_{MNG} C_{HNO_3} - k_1 C_G C_{HNO_3} - k_{-2} C_{DNG} C_{H_2O} \quad (10)$$

$$-\frac{dC_{DNG}}{dt} = k_{-2} C_{DNG} C_{H_2O} + k_3 C_{DNG} C_{HNO_3} - k_2 C_{MNG} C_{HNO_3} - k_{-3} C_{TNG} C_{H_2O} \quad (11)$$

$$-\frac{dC_{TNG}}{dt} = k_{-3} C_{TNG} C_{H_2O} - k_3 C_{DNG} C_{HNO_3} \quad (12)$$

$$-\frac{dC_{H_2O}}{dt} = -k_1 C_G C_{HNO_3} - k_2 C_{MNG} C_{HNO_3} - k_3 C_{DNG} C_{HNO_3} + k_{-1} C_{MNG} C_{H_2O} + k_{-2} C_{DNG} C_{H_2O} + k_{-3} C_{TNG} C_{H_2O} \quad (13)$$

The nitration of glycerol was modelled by fitting the kinetic model with 6 parameters, The rate constant ($k_{ref,1}$ - $k_{ref,3}$) and the activation energy ($E_{a,1}$ - $E_{a,3}$). All parameters were calculated at an average temperature, T_{ref} , of 20 °C.

The Arrhenius equation for the forward and backward reactions was:

$$k_i = k_{ref,i} e^{\frac{E_{a,i}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right)}$$

$$k_{-i} = k_i / K_i \quad (14)$$

where k_i is the rate constant and K_i the equilibrium constant at temperature T. Kazakov et al. [17] mentioned the equilibrium constants of all the reactions of nitration at different temperature and different nitric acid concentration. Experimental works also derived equilibrium constants for each experiment. The data indicates that Kazakov's constants do not fit properly. The backward reactions for each reaction were

calculated using the equilibrium constants that were obtained from experiments. The parameter estimation was performed with the objective function of minimizing was the residual sums of squares of errors (SSE) for the measured concentrations of glycerol, MNG, DNG and TNG. Since steady reaction conditions were not reached immediately the first measured data point was used as a starting value when solving the differential equations describing the reactions. However, this value is also prone to measurement errors and parameters P_i was introduced to estimate the true initial condition. A least squares minimization with respect to these parameters was also introduced.

$$SSE = \sum \frac{(Y_{calc,i} - Y_{dat,i})^2}{(MeanY_{dat,i})^2} + \sum \frac{(P_i - Y_{init,i})^2}{(MeanY_{dat,i})^2} \quad (15)$$

The weight factor $(MeanY_{dat,i})^2$ is to normalize the residual sum of squares assuming constant relative error in the concentration measurements. The lsqnonlin function with solver ode 15s in MATLAB 7.1 was used to obtain $k_{ref,i}$ and $E_{A,i}$. The relative errors of all concentrations of nitration product were calculated with this equation:

$$relative\ error = \sum \frac{Y_{calc,i} - Y_{dat,i}}{Y_{dat,i}} \quad (16)$$

2. Experimental Setup

The reactants used in the experiments are glycerol of $\geq 99\%$ purity from Sigma-Aldrich, nitric acid (for analysis EMSURE® ACS, Reag. Ph Eur) of 69% purity from Merck and 1,2-dichloroethane (ACS reagent) of purity $\geq 99.0\%$ from Sigma-Aldrich.

Experiments were carried out in a 5 cm³ flask that was immersed in cooling bath. Glycerol with a certain weight was placed in flask and was diluted with an equal volume of 1,2-dichloroethane and cooled to reaction temperature. Cooled nitric acid was added. The flask equipped with nitrogen purge for stirring. A thermocouple monitored the temperature in the flask. Samples were taken in time intervals between 45-60 minutes, 10 samples in each experiment.

2.1. Analytical Methods

Samples were analyzed with gas chromatography (430 GC, Bruker), equipped with flame ionization detector. The column was a VF-1 ms 30m x 0.25 mm, ID DF=1 capillary column from Factor Four. The injector and detector temperature were maintained at 175 °C and 225 °C, respectively. The oven temperature was kept at 60 °C during injection, after that increase to 140 °C and stable at that temperature. Chromatogram were recorded by computer that used Galaxies Chromatography System version 1.9.302.952 and gave the percent mass of 1-MNG, 2-MNG, 1,3-DNG, 1,2-DNG, TNG and glycerol of each samples, respectively.

A sampling procedure was developed to minimize the time between sampling and GC analysis and to be as reproducible as possible. Still the measured concentrations show large scattering.

3. Results and Discussion

The nitration between glycerol and nitric acid was modeled by three controlling reactions model. Figure 1 shows the comparison between the experimental data and calculated data points of the four compounds that are involved in seven controlling reactions model and three controlling reactions model.

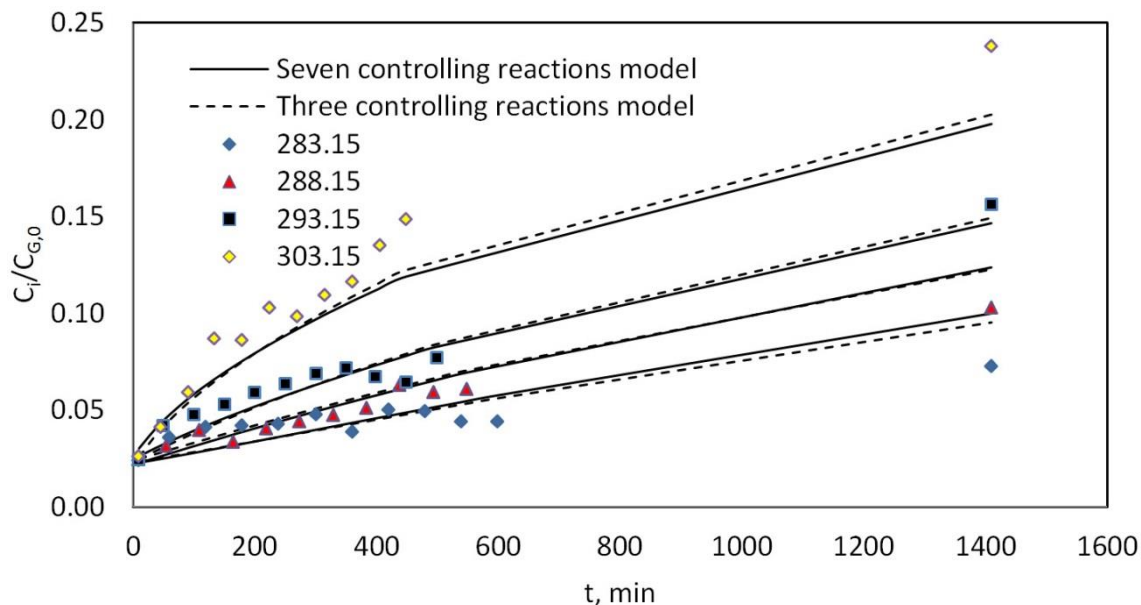


Fig. 1. Ratio $C_i/C_{G,0}$ of all products for nitration of glycerol at nitric acid of 69%, molar ratio (nitric acid/glycerol) 3/1 and temperature of reaction of 15 °C

The comparison between experimental data and calculated data of all compounds indicates that calculated data adequately fit the experimental data. Seven controlling reactions model and three controlling reactions model have the similar trend. The accuracy of two models is almost the same at the process condition reviewed. Calculation of three controlling reactions model can be done easier and faster than seven controlling reactions model. Three controlling reactions model can be used for practical purposes as design of reactor. On the other hand we can identify all products which can be synthesized from nitration by seven controlling reactions model. There are 2 pairs of isomer compounds (1-MNG and 2-MNG, 1,2-DNG and 1,3-DNG) and final product, TNG as the nitration products. The concentrations of all products can be known with seven controlling reactions model; therefore this model can be used at preliminary design plant.

Experimental works were done with reaction temperature of 10 to 30 °C. The influence of temperature to the conversion of DNG can be seen in Fig. 2.

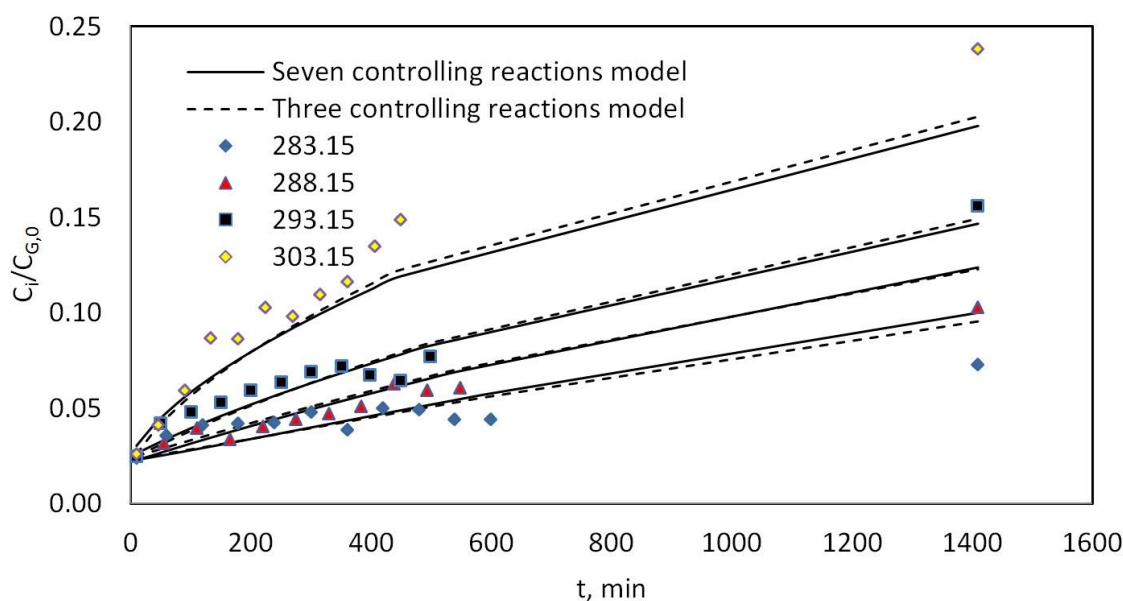


Fig. 2. The C_{DNG}/C_G at difference temperatures (nitric acid of 69%, molar ratio of 3/1).

An increase in temperature has tendency to increase the reaction rate. As a consequence the conversion of DNG also increases. This phenomenon can be seen in the result of estimation using both seven controlling reactions and three controlling reactions. Seven controlling reactions is suitable for high-temperature reaction while three controlling reactions is suitable for low-temperature reaction, as seen in Fig. 2.

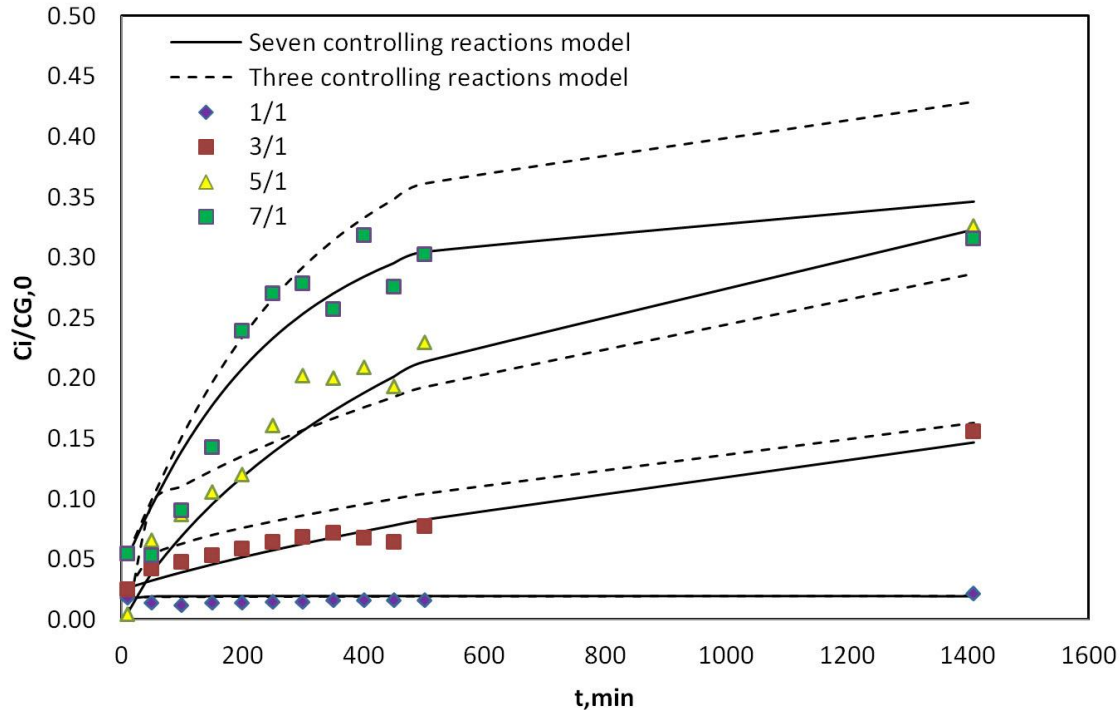


Fig. 3. The conversion of DNG at various mole ratio (nitric acid of 69%, temperature of 20 °C).

Experiments were carried out at molar ratio of nitric acid to glycerol 1/1 to 7/1. Figure 3 shows that increase in mole ratio will increase the concentration of nitric acid in the system. Increasing mole ratio clearly increased the $C_i/C_{G,0}$ of DNG. The seven controlling reactions model is appropriate at molar ratio of 1/1 to 5/1, while the three controlling reactions model is appropriate at molar ratio of 7/1.

The relative error of two models were calculated using equation (16), shown in Table 4. It can be seen that the relative error value of seven controlling reactions model is higher than three controlling reactions model at all molar ratio. The accuracy of seven controlling reactions model is lower than three controlling reactions model. It does not mean that three controlling reactions model is better than seven controlling reactions model. Each model has different uses.

Table 4. The relative error (%) of concentration of DNG at different molar ratio (Temperature of 20 °C, nitric acid of 69%).

Molar ratio	Seven controlling reactions model	Three controlling reactions model
1/1	18.55%	15.55%
3/1	24.44%	18.18%
5/1	32.82%	20.74%
7/1	41.62%	18.80%

The parameter estimation also has been done by three controlling reactions model. The resulting values of rate constants and activation energies are given in Table 5. Estimation was done at different mole ratio of nitric acid/glycerol.

Table 5. Kinetic parameters for nitration of glycerol (nitric acid concentration of 69%, 20 °C).

Reaction number	$k_{ref}, m^3/(mol.s) \cdot 10^{10}$			
	1/1	3/1	5/1	7/1
1	4.10E6±1.25E9	6.13±0.03	11.14 ± 0.02	42.22 ±0.06
2	1.55E4± 9.92E4	79.29 ± 0.3	131.31 ±0.65	206.87 ±1.10
3	4.67± 0.56	2.83±0.06	0.84±0.01	1541.03±708.69
Activation energy, kJ/mol				
1	37.68 ±1,035.3	35.66 ±0.35	33.49 ±0.16	54.01 ±0.13
2	50.24 ± 379.5	79.55 ± 0.35	79.55 ± 0.44	37.68 ± 0.44
3	29.31 ± 11.79	33.55 ± 0.21	33.49 ± 0.13	33.45 ± 1.65

Increase in mole ratio will increase the concentration of nitric acid in the system so the forward reaction rate will increase. Increase in mole ratio will increase the reaction rate constants as seen at Table 5. This fact supports the theory of the dependence of reaction rate on the concentration of the compounds present. Rate of reaction usually depends on concentration of reactants (and sometimes of products), and usually increases as concentration of reactants increases. The highest reaction constants were obtained at molar ratio 7/1.

The resulting kinetic parameter showed that the highest rate constant is formation of DNG. This phenomenon describe that DNG is main product of nitration of glycerol. The by-products of this reaction are MNG and TNG. This is similar with the result of seven controlling reactions model. Seven controlling reactions model and three controlling reactions model that developed represent the nitration process that occurs.

4. Conclusions

The seven controlling reactions model and the three controlling reactions model have the similar trend. Both two models can represent the nitration process. The three controlling reactions model gives better fit than the seven controlling reactions model. Calculation of the three controlling reactions model can be done easier and faster than the seven controlling reactions model. The accuracy of the three controlling reactions model is higher. The advantage of the seven controlling reactions model is this model can predict all products of nitration. So this model can be used at preliminary design plant. The three controlling reactions model can be used at next step, as design of reactor.

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