DETERMINATION OF THE TEMPERATURE EFFECT ON GLYCEROL NITRATION PROCESSES USING THE HYSYS PREDICTIONS AND THE LABORATORY EXPERIMENT

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Received December 2, 2013; Accepted January 16, 2014

ABSTRACT

Determinations of the temperature effect on glycerol nitration processes have been done with two methods: the HYSYS predictions and the laboratory experiment. The aim of this study was to compare prediction method and laboratory experiment method. The highest equilibrium conversion from HYSYS predictions was obtained in the range of equilibrium temperature of 10 to 20 °C. The laboratory experiments also described that nitration of glycerol with nitric acid should be carried out at reaction temperature of 10 to 20 °C. HYSYS that was used to predict the results of experiments in the laboratory can reduce the laboratory work with minimize the range of operating conditions studied. HYSYS exactly predict temperature of nitration of glycerol. The difference in conversion between two methods due to the equipment that was used in the experiments, procedure of experiments and the accuracy of analysis.

Keywords: *nitration; glycerol; thermodynamic process; numerical prediction*

ABSTRAK

Penentuan pengaruh suhu pada proses nitrasi gliserol telah dapat dilakukan dengan dua metode: prediksi HYSYS dan percobaan laboratorium. Tujuan dari penelitian ini adalah untuk membandingkan kedua metode tersebut. Konversi kesetimbangan tertinggi dari prediksi HYSYS diperoleh di dalam kisaran suhu kesetimbangan 10 sampai 20 °C. Hasil percobaan laboratorium juga menyatakan bahwa nitrasi gliserol dengan asam nitrat sebaiknya dilakukan pada suhu reaksi 10 sampai 20 °C. HYSYS yang digunakan untuk memprediksi hasil eksperimen di laboratorium dapat mengurangi pekerjaan laboratorium dengan meminimalkan kisaran kondisi operasi yang dipelajari. HYSYS memprediksi dengan tepat suhu nitrasi gliserol. Perbedaan konversi antara dua metode disebabkan oleh peralatan yang digunakan pada percobaan, prosedur percobaan dan keakuratan analisis.

Kata Kunci: *nitrasi; gliserol; proses termodinamika; prediksi numeris*

INTRODUCTION

Due to the depletion of the world's petroleum reserves and the increasing environmental concerns, the need to search for an alternative energy is necessary. Biodiesel has shown great promise as an alternative energy [1-2]. Biodiesel is currently produced via transesterification of vegetable oils, animal fat or waste cooking oil. This reaction consists of transforming triglyceride into biodiesel, in the presence of alcohol and catalyst with glycerol as by product [3-7]. Several processes to synthesize glycerol into a wide variety of value-added special and fine chemicals were proposed by Pagliaro and Rossi [8], Bonet et al. [9], Galan et al. [10], Kurosaka et al. [11], Malero et al. [12], Maris et al. [13] and Dasari et al. [14]. Nitration of glycerol is a good alternative to utilize the glycerol produced by biodiesel process. Highsmith et al. [15], Sanderson and Martins [16] and Highsmith and Johnston [17] used glycerol to produce polyglycydyl nitrate (PGN). PGN is an energetic polymer that is used as a binder in propellant [18], plasticizer [19] and explosives [20]. Provatas [21] stated that PGN is the most energetic polymer. This polymer can be used as a binder in propellant and explosives to increase the explosive power in comparison with inert binders.

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PGN is synthesized from glycerol by three-step reaction i.e. nitration, cyclization and polymerization. Nitration of glycerol with nitric acid produce five kinds of products i.e. two isomers mononitroglycerin: 1-mononitroglycerin (1-MNG) and 2-mononitroglycerin (2-MNG), two isomers dinitroglycerin: 1,3-dinitroglycerin (1,3-DNG), 1,2-dinitroglycerin (1,2-DNG) and nitroglycerin (TNG), as shown in Fig. 1. The cyclization of 1,3-DNG into glycidyl nitrate is performed in excess of sodium hydroxide. The last reaction is polymerization of glycidyl nitrate with the Lewis acid as catalyst to produce PGN [15-17].

The reactions between glycerol and nitric acid are series parallel reactions [22] as follows:

$$G + HNO_3 \rightleftharpoons 1\text{-MNG} + H_2O \quad (1)$$

$$G + HNO_3 \rightleftharpoons 2\text{-MNG} + H_2O \quad (2)$$

$$1\text{-MNG} + HNO_3 \rightleftharpoons 1,3\text{-DNG} + H_2O \quad (3)$$

$$1\text{-MNG} + HNO_3 \rightleftharpoons 1,2\text{-DNG} + H_2O \quad (4)$$

$$2\text{-MNG} + HNO_3 \rightleftharpoons 1,2\text{-DNG} + H_2O \quad (5)$$

$$1,3\text{-DNG} + HNO_3 \rightleftharpoons TNG + H_2O \quad (6)$$

$$1,2\ DNG + HNO_3 \rightleftharpoons TNG + H_2O \quad (7)$$

There have been several studies related to the nitration equilibrium in glycerol-aqueous nitric acid [22-25]. Experimental results that Kazakov et al. [23] were done stated that several reactions of nitration reactions above are exothermic reactions. Otherwise the other reactions are endothermic reactions. On the other hand all real enthalpies are exothermic. So evaluation of temperature parameter that suitable for nitration is needed to determine the proper temperature.

Moore [25] determined the temperature dependence of equilibrium constant as the equation (8):

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^o}{RT^2} \quad (8)$$

If the reaction is endothermic (ΔH^o positive) the equilibrium constant increases with temperature. If reaction is exothermic (ΔH^o negative) the equilibrium constant will decrease when temperature is raised. Kazakov et al. [22] described the temperature dependences of equilibrium constants of all the reactions above. The experimental equilibrium constants were fitted to a linear equation. Relationship between equilibrium constants and temperature are presented at figure 2. The equilibrium constants show that 4 reactions are exothermic reaction (eq. 1, 2, 6 and 7), while 3 reactions are endothermic reactions reaction (eq. 3, 4 and 5).

The proper temperature for the nitration reaction can be determined from the evaluation of thermodynamic nitration and from experimental work. The aim of this study was to compare prediction method and laboratory experiment method on determination of temperature effect of glycerol nitration. The prediction was done by HYSYS. There are several well-known flow sheet softwares in process design, such as ASPEN, HYSYS and CHEMCAD. HYSYS is powerful software that simulates chemical processes. The built-in property packages in HYSYS provide accurate thermodynamic, physical and transport property predictions for hydrocarbon, non-hydrocarbon, petrochemical and chemical fluids. Modeling reactor can be done in HYSYS to study how chemical reactions and reaction kinetics affect a process. Modeling reactor also can be used to study the influence of many parameters (temperature, pressure, mole ratio, concentration) to the composition of products.

EXPERIMENTAL SECTION

Estimation

Thermodynamic of nitration were reviewed with HYSYS. Physical properties and thermodynamic data for some components (glycerol, nitric acid, nitroglycerin, water, methylene chloride) provided by HYSYS databank. HYSYS databank does not provide physical properties and thermodynamic data for 1-MNG, 2-MNG, 1,3-DNG and 1,2-DNG. Therefore the data were obtained from the component hypotheses (hypothetical components). Fluid package used was NRTL (Non-Random Two Liquid).

The calculations were performed with an equilibrium reactor model under isothermal conditions for the seven reactions discussed. The outlet streams of the reactor are in a state of chemical and physical equilibrium. Equilibrium reactions maybe calculated either sequentially or simultaneously. The equilibrium reactor model calculated the composition of the products for the reactions and stoichiometry given based on equilibrium constants were obtained from Kazakov et al. [22] as a function of temperature for specific HNO_3 concentrations. The calculations were performed under equilibrium temperature.

Materials

The reactants used in the experiments are glycerol of ≥ 99% purity from Sigma-Aldrich, nitric acid of 69% purity from Merck and 1,2-dichloroethane of purity ≥ 99.0% from Sigma-Aldrich.

Instrumentation

Experiments were carried out in a 5 cm^3 flask that was immersed in cooling bath. Samples were analyzed with gas chromatography (430 GC, Bruker), equipped

Table 1. Heat of reaction of nitration

	Reaction						
	1	2	3	4	5	6	7
ΔH_{expt}[1]	-17.2±1.3	-8.8±0.8	15.9±1.3	20.1±1.3	11.7±0.8	-6.3±0.8	-10.5±1.3
ΔH_{real}[1]	-18.8±2.1	-10.5±2.5	-12.1±1.7	-7.1±2.5	-15.5±2.9	-5.4±1.3	10.5±1.3
ΔH[2]	-59.4	-50.6	-51.5	-46.4	-55.6	-44.4	-49.4
ΔH[3]	-15.0	-5.8	-12.1	-7.1	-16.3	-4.1	-9.1
ΔH[4]	-20.0	-10.8	-12.1	-7.1	-16.3	-4.2	-9.2

[1]Kazakov ([9]

[2]Calculated by HYSYS and hand calculation, data of heat of formation of all components are from NIST

[3]Calculated by hand calculation using heat of formation of glycerol, nitric acid and water from HSC Chemistry, heat of formation of 1 MNG, 2 MNG, 1.3 DNG, 1.2 DNG are from Kazakov et al. [23] and NG from NIST

[4]Calculated by hand calculation using heat of formation of nitric acid and water from HSC Chemistry, heat of formation of all products and glycerol are from Kazakov et al. [23]

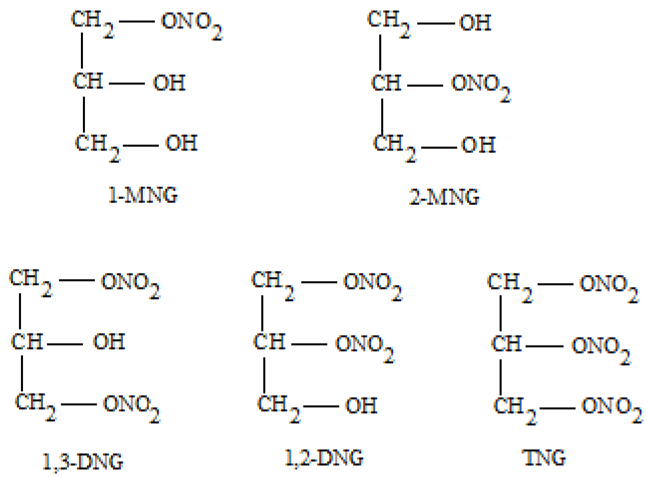

Fig 1. The products of nitration of glycerol

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 and 225 °C, respectively. The oven temperature was kept at 60 °C during injection, after that increase to 140 °C and stabile at that temperature. Chromatogram were recorded by computer that used Galaxie Chromatography System version 1.9.302.952 and gave the mass percent of 1-MNG, 2-MNG, 1,3-DNG, 1,2-DNG, TNG and glycerol of each samples, respectively.

Procedure

Glycerol with a certain weight was placed in flask and was diluted with an equal volume of 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 min, 10 samples in each experiment, and were analyzed with GC.

RESULT AND DISCUSSION

Thermodynamic Aspects

Thermodynamics can be used to predict the equilibrium concentration under any conditions of reaction. Conversely, equilibrium concentration can be used to know the condition of reaction to get maximum equilibrium conversion of the desired product. Table 1 presents the heat of reaction from the experimental results and the real heat of reaction indeed [23]. The heat of reaction is also calculated by HYSYS and by hand calculation.

Le Chatelier principle describe that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised, then energy is absorbed as heat and the rise in temperature is opposed. Conversely, equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, then energy is released and the reduction in temperature is opposed [26]. For exothermic reactions, increased temperature favors the reactants. For endothermic reactions, increased temperature favors the products and increased the equilibrium constants. Table 1 exhibit that heat of reactions from experimental result for reaction (1), (2), (6) and (7) have negative values. It means those reactions are exothermic reactions. Otherwise reactions (3), (4) and (5) have positive values of enthalpies of reactions. These reactions are endothermic reactions. It relates K_{3expt}, K_{4expt}, and K_{5expt} [22] increase with an increase in the temperature. But the real heat of reaction [23] and heat of reaction from calculation (ΔH^3, ΔH^4) for all reactions have negative values with different values. All reactions are exothermic reactions.

The HYSYS Predictions

Calculations were done at temperature of 0 to 45 °C to determine the effect of temperature on the

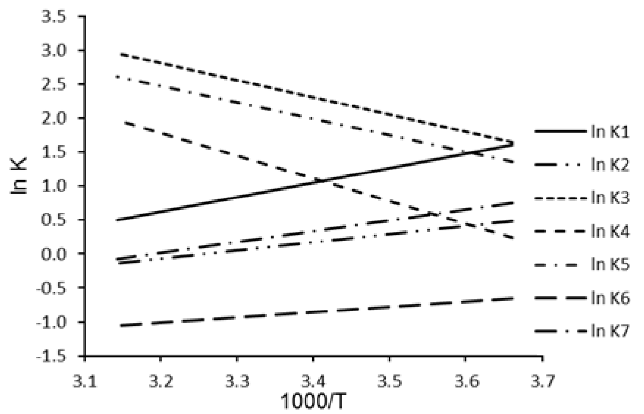

Fig 2. Relationship between equilibrium constants and temperature at nitric acid concentration of 71.35%

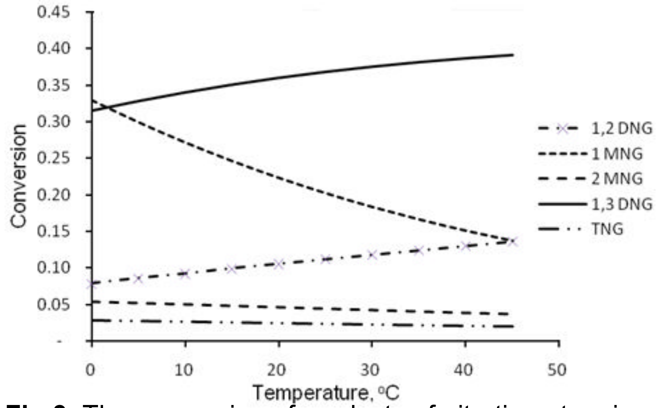

Fig 3. The conversion of products of nitration at various temperatures (nitric acid of 68.42%, mole ratio of 4/1)

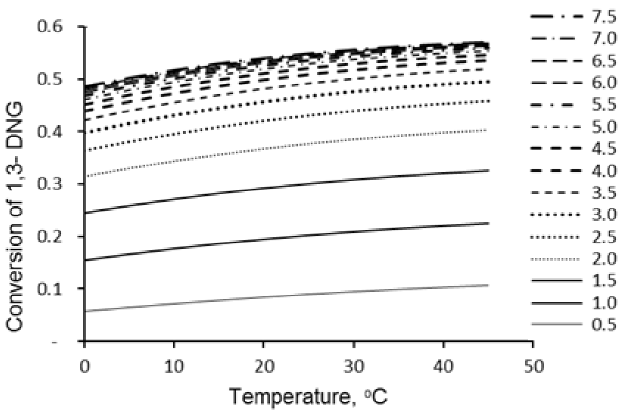

Fig 4. The conversion of 1,3-DNG at various temperatures and nitric acid of 71.35%

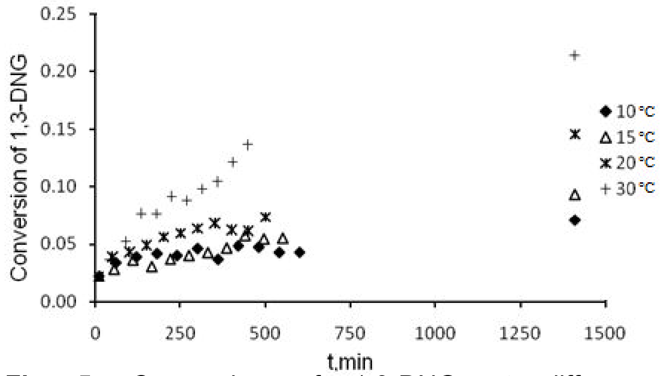

Fig 5. Conversion of 1,3-DNG at difference temperatures from experimental work at nitric acid of 69% and molar ratio of 3/1

nitration of glycerol. Increase in reaction temperature will increase the conversion of 1,3-DNG and 1,2-DNG (see Fig. 3). Conversely, the conversion of 1-MNG will decrease. The conversion of 2-MNG also slightly decrease. The conversion of TNG slightly decreases and tends to fix for all temperature. It means that equilibrium constants for reactions 3, 4 and 5 (that produce 1,3-DNG and 1,2-DNG) increase with temperature and equilibrium constants for reaction 1-2 (that produce 1-MNG and 2-MNG) and reaction 6-7 (that produce TNG) decrease with temperature.

Preferably, nitration is conducted at a relative low temperature, not higher than room temperature, more preferably 0 to 25 °C and still more preferably 10 to 20 °C [15-16]. Fig. 3 shows the conversion of 1-MNG is higher than 1,3-DNG at temperature under 5 °C. So it is better to carry out nitration at temperature above 5 °C.

Calculations were also done at temperature of 0 to 45 °C at many various mole ratios. Effect of temperature on the conversion of 1,3-DNG at various HNO_3 concentrations can be seen in Fig. 4. Increase in reaction temperature will increase the conversion of 1,3-DNG for all mole ratio. At temperatures above 25 °C increased temperature give a small effect on conversion of 1,3-DNG and at mole ratio above 5/1 increase in conversion is very slightly. TNG can be decomposed at 30 °C. Therefore nitration should be carried at temperature range 10 to 20 °C.

The Laboratory Experiments

Laboratory experiments were carried out at reaction temperature of 10 to 30 °C, nitric acid of 69% and molar ratio of 3/1. The range of temperature were widen from estimation to get the optimum temperature. The experimental results were presented as conversion of 1,3-DNG at various temperature. It can be seen in Fig. 5.

According Fig. 2 the formation of 1,3-DNG (eq. 3) is an endothermic reaction. Moore [25] declared the equilibrium constant increases with temperature for an endothermic reaction. Rate of reaction usually increases nearly exponentially as temperature increases. The experimental work described that theory. It can be seen in Fig. 5 that higher reaction temperature cause significant increase in the conversion

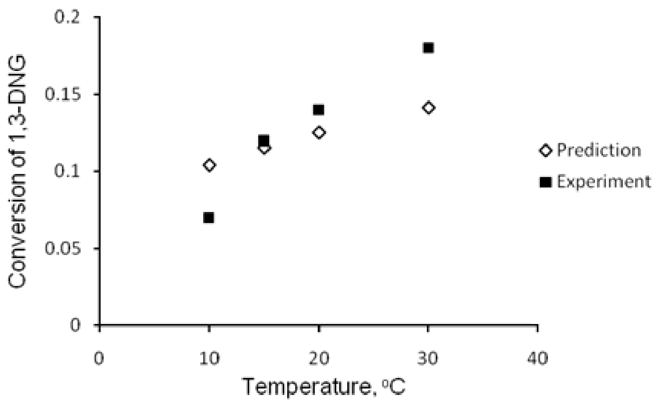

Fig 6. Equilibrium conversion of 1,3-DNG at difference temperatures from the HYSYS predictions and experimental work at nitric acid of 69% and molar ratio of 3/1

of 1,3-DNG. An increase in temperature has tendency to increase the reaction rate. The restriction of reaction temperature in nitration is the decomposition of TNG that occurred at temperature above 20 °C which is dangerous for safety. The nitration of glycerol should be carried out in the low temperature (10 to 20 °C).

Comparison of Two Methods

The comparison between the HYSYS prediction and experimental results were presented as equilibrium conversion of 1,3-DNG at various temperature, shown in Fig. 6.

Rate of reaction usually increases nearly exponentially as temperature increases. The HYSYS predictions and laboratory experiments described that theory. It can be seen in Fig. 6 that higher reaction temperature cause significant increase in the conversion of 1,3-DNG. An increase in temperature has tendency to increase the reaction rate. The relationship between the predictive conversion and the experimental conversion follows this equation:

$$X_{experimental} = X_{prediction} - 0.3 \quad (9)$$

The laboratory experiments have the different trend with the HYSYS predictions because the HYSYS prediction used equilibrium constants from Kazakov et al. [22] that was different from equilibrium constants which calculated from laboratory experiments. Therefore the conversion of 1,3-DNG from the laboratory experiments are lower than the conversion from the HYSYS predictions as seen in Fig. 6 because of many factors i.e. the equipment that was used at experiments, procedure of experiments and the accuracy of analysis. The reactor which was used in the experiments is a 5 cm^3 flask. This flask is a part of micro scale. The experiments were done using this flask due to the process safety. The defectiveness experiments could be occurred because of the size of reactor. The samples were taken from the flask by manual sampling. The reaction still continues during sample preparation until 1,3-DNG partly convert to TNG. The relative error of quantitative analysis of nitration products with Gas Chromatography is 7.94% [27]. However, the predictions qualitatively give the proper range temperature of nitration. The prediction results can drive laboratory experiments. It has significant contribution to minimize trial and error in laboratory experiments.

CONCLUSION

Thermodynamics calculations gave the proper temperature to produce 1,3-DNG. At a temperature of 0 to 20 °C increase in temperature would increase conversion of 1,3-DNG and reduce conversion of TNG. At temperatures above 25 °C increased temperature give a small effect on conversion of 1,3-DNG. Nitration is preferable conducted in the temperature range of 10 to 20 °C. The laboratory experiments also described that nitration of glycerol with nitric acid should be carried out at reaction temperature of 10 to 20 °C. The equipment that was used at experiments, procedure of experiments and the accuracy of analysis are the causal factors that caused the difference in conversion between the HYSYS predictions and the laboratory experiment. The predictions have significant contribution to minimize trial and error in laboratory experiments.

ACKNOWLEDGEMENT

The authors thankfully acknowledge Directorate General of Higher Education, Ministry of National Education Indonesia which has awarded scholarships of doctorate program (BPPS) at Universitas Gadjah Mada. The authors also convey our sincere gratitude to Chemical and Biological Department, Chalmers University of Technology, Sweden for providing equipment and chemicals for this research.

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