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A Thermodynamic Study of Parameters That Affect the Nitration of Glycerol with Nitric Acid

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Abstract**—**Biodiesel production from vegetable oil will produce glycerol as by-product about 10% of the biodiesel production. The amount of glycerol that was produced needed alternative way to handling immediately so as to not become the waste that polluted environment. One of the solutions was to process glycerol to polyglycidyl nitrate (PGN). PGN is synthesized from glycerol by three-step reactions i.e. nitration of glycerol, cyclization of 13-dinitroglycerine and polymerization of glycosyl nitrate. Optimum condition of nitration of glycerol with nitric acid has not been known. Thermodynamic feasibility should be done before run experiments in the laboratory. The aim of this study was to determine the parameters those affect nitration of glycerol and nitric acid and chose the operation condition. Many parameters were simulated to verify its possibility to experiment under conditions which would get the highest conversion of 1, 3-dinitroglycerine and which was the ideal condition to get it. The parameters that need to be studied to obtain the highest conversion of 1, 3-dinitroglycerine were mol ratio of nitric acid/glycerol, reaction temperature, mol ratio of glycerol/dichloromethane and pressure. The highest conversion was obtained in the range of mol ratio of nitric acid /glycerol between 2/1 – 5/1, reaction temperature of 5-25^{o} C and pressure of 1 atm. The parameters that need to be studied further to obtain the highest conversion of 1.3 DNG are mol ratio of nitric acid/glycerol and reaction temperature.

Keywords**—**Nitration, glycerol, thermodynamic, optimum condition.

I. INTRODUCTION

DUE to diminishing petroleum reserves, biodiesel has attracted attention during the past decade as a renewable energy that is capable of fulfilling an increasing energy demand. Biodiesel can be used in a diesel engine with little or no modification in the engine [1]. The advantages of biodiesel are good combustion efficiency, high-lubricity, biodegradability and low toxicity [2]. Generally, biodiesel is produced through the chemical reaction by the transesterification process of a vegetable oil or animal fat with alcohol in the presence of catalyst, to obtain methyl or ethyl esters (biodiesel) and concomitantly producing glycerol as a by-product [3], [4]. Approximately crude glycerol as many as 10% of total biodiesel by weight is produced from biodiesel industry [4]. In the EU, crude glycerol is generally classified as a hazardous waste, because of its contamination with methoxide, thereby increasing the cost of disposal [3]. Therefore, there was needed alternative way to handling immediately the crude glycerol so as to not become the waste that polluted environment and exactly generate value added products. Many routes for exploiting crude glycerol as a cheap feedstock have been explored. The traditional applications of glycerol are in cosmetics, food industries and pharmaceuticals [5]. Another applications are triacetin [6]-[8], propylene glycol [9], [10], and1, 3-propanediol [11], [12]. One of the glycerol promising applications is polyglycidyl nitrate (PGN) which is an energetic polymer that is used as a binder in propellant. Three steps in production of PGN from glycerol are nitration of glycerol, cyclization of 1, 3-dinitroglycerine and polymerization of glycosyl nitrate [13]-[15].

Nitration of glycerol with nitric acid produce five kinds of products: two isomers mononitroglycerin: 1 mononitroglycerin (1-MNG) and 2 mononitroglycerin (2-MNG), two isomers dinitroglycerin: 1, 3-DNG, 1,2 dinitroglycerin (1, 2-DNG) and nitroglycerin (TNG) with the main product is 1, 3-dinitroglycerine (see Fig. 1).

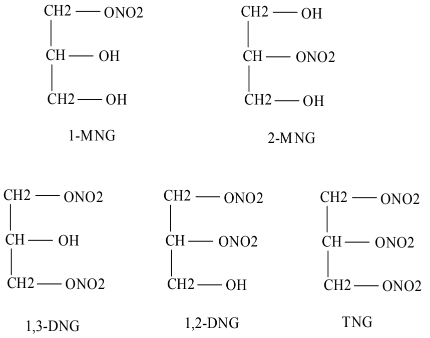

Fig. 1 The products of nitration of glycerol [15]

Nitration is defines as reaction between organic compound and nitrating agent, by entering one or more nitro groups (-NO_2). The reactions between glycerol and nitric acid are series parallel reactions [16]:

$$\mathrm{G} + HNO_3 \rightleftarrows \text{1-MNG} + H_2O \tag{1}$$

$$\mathrm{G} + HNO_3 \rightleftarrows \text{2-MNG} + H_2O \tag{2}$$

$$\text{1-MNG} + HNO_3 \rightleftarrows \text{1,3-DNG} + H_2O \tag{3}$$

$$\text{1-MNG} + HNO_3 \rightleftarrows \text{1,2-DNG} + H_2O \tag{4}$$

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

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

$$\text{1, 2 DNG} + HNO_3 \rightleftarrows \text{TNG} + H_2O \qquad (7)$$

Several studies about nitration of glycerol were reported. Nitration was run either with batch process [17], [18] or continues [14]. This reaction was done using nitrating agent such as nitric acid, mixed acids (such as nitric and sulphuric acids), acetyl nitrate, nitronium ion salts (such as NO_2BF_4, NO_2ClO_4, and or N_2O_5), tri fluoro acetic anhydride with ammonium nitrate, nitric acid and or Crivello reagents.

Another one of the advantages of nitration with nitric acid as nitrating agent is this reaction does not need to use pure nitric acid [13]. This reaction can be done using 53.8% to 87.6% purity of nitric acid. The reaction temperature is in the range of 0–48° C [16].

The scope of this study is many parameters that influence the equilibrium conversion of glycerol nitration. The proper operation condition of glycerol nitration was expected to obtain from the result of simulation. There are several well-known flow sheet soft-wares in process design, such as ASPEN, CADSIM Plus and CHEMCAD, Design II for windows and HYSYS.

This study uses HYSYS because it is powerful software to simulate chemical processes. Parameters which be observed were mol ratio of glycerol/nitric acid, reaction temperature, mol ratio of methyl chloride and pressure.

II. EXPERIMENTAL SETUP

Thermodynamic of nitration were reviewed by simulation with HYSYS. Physical properties and thermodynamic data for some components (glycerol, nitric acid, nitro-glycerine, water, dichloromethane) 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. Gibbs reactor with specify equilibrium reactions was chosen as type of reactor which was used for simulation. 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 given based on equilibrium constants were obtained from [16] as a function of temperature for specific HNO_3 concentrations. The experimental equilibrium constants were fitted to a polynomial.

The calculations were performed under various conditions: Mol ratio of nitric acid/glycerol, reaction temperature, mol ratio of dichloromethane/ glycerol and pressure. Fig. 2 shows the flow of material in the Gibbs reactor.

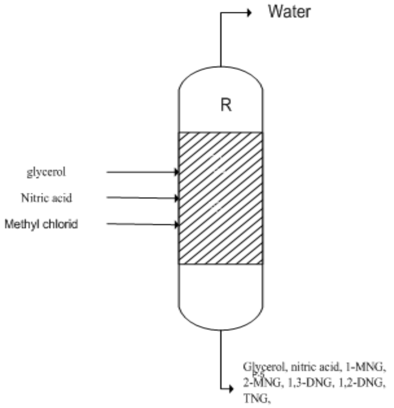

Fig. 2 Gibbs reactor (R) with specify equilibrium reactions type which was used for simulation

III. RESULTS AND DISCUSSION

A. Effect of mol Ratio of Nitric Acid/Glycerol

In this study nitric acid was used as nitrating agent and dichloromethane as an inert solvent. Fig. 3 shows the influence of mol ratio of nitric acid/glycerol to the conversion of all products of nitration. At low mol ratio, below 1.5/1, the largest conversion is 1-MNG. The highest conversion of 2-MNG is obtained in the range of 1/1and 1.5/1. The conversion of 1, 3-DNG is the greatest at the mol ratio. The conversion of 1, 3-DNG is higher than the other products for the greater mol ratio. The conversion of 1, 2-DNG have the same trend as 1, 3-DNG. While the TNG conversion increased with increasing mol ratio. The conversion of TNG is lowest than the other products at mol ratio of 0.5/1 to 2.5/1, then at mol ratio 2.5/1 to 7.5/1 the lowest conversion is 2-MNG.

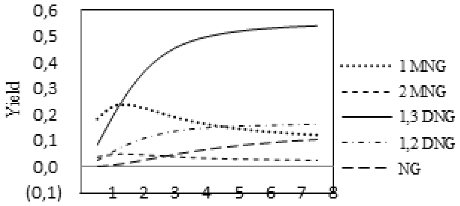

Fig. 3 Effect of mol ratio of nitric acid/glycerol to conversion of Products (HNO_3 71.35%, 20°C)

Le Chatelier principle can be used to predict the effect of a change in conditions on a chemical equilibrium. Changing the concentration of an ingredient will shift the equilibrium to the side that would reduce that change in concentration. Increase in mol ratio will increase the concentration of nitric acid in the system so that the equilibrium reaction will shift to the right [19]. Increase in mol ratio will increase the conversion of 1,3-DNG and 1,2 -DNG. However, different conditions occur at 1-MNG and 2- MNG. At the mol ratio of 1.5, both compounds were the highest conversion, and then decreased. The reason is the formation of 1, 3-DNG and1, 2-DNG from 1-MNG and 2-MNG is faster than the formation of 1-MNG and 2-MNG at the higher mol ratio. The highest conversion of product of nitration is 1, 3-DNG because equilibrium constant from reaction (3) that produced 1, 3-DNG is highest equilibrium constants of nitration.

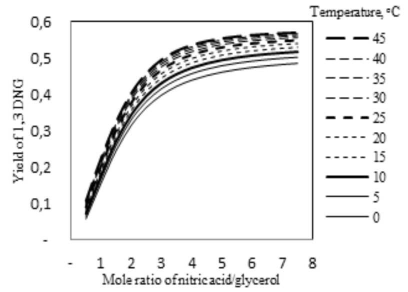

Fig. 4 Effect of mol ratio of nitric acid/glycerol to conversion of 1,3 DNG at concentration of HNO_3 71.35% at various temperature

Fig. 4 shows that increasing of mol ratio will increase conversion 1, 3-DNG. This trend applies to all temperatures (0-45 ^{0}C). Mol ratio has the same effect to the conversion of 1, 3-DNG at each temperature (0-45^{o}C).

The Calculations show that in the range of mol ratio of 0.5/1 to 7.5/1 increase in the mol ratio led to increase of conversion of 1, 3-DNG. At the mol ratio of 0.5/1 up to 2/1, conversion value increased significantly with increasing mol ratio. At mol ratio 2/1up to 5/1 it was slightly increasing. The conversion at mol ratio of 5/1 up to 7.5/1 is relatively equal. The conversion of 1, 3-DNG is optimum at mol ratio of 5/1.

B. Effect of Reaction Temperature

The influence of reaction temperature to the conversion of all products of nitration was described at previous paper [15]. Calculations were done at temperature of 0-45^{o}C to determine the effect of temperature on the nitration of glycerol. Increase in reaction temperature will increase the conversion of 1, 3-DNG and 1, 2-DNG (see Fig. 5). 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.

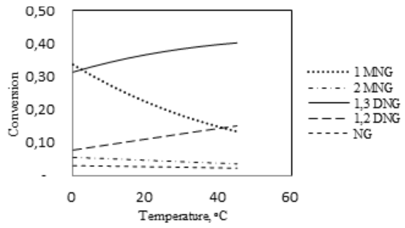

Fig. 5 The conversion of products of nitration at various temperature (concentration of HNO_3 71.35%, mol ratio of 2/1)

The dependence of the equilibrium constant of the reaction temperature is expressed by [20]. For endothermic reaction, the equilibrium constant increases with increasing temperature. If the reaction is exothermic, equilibrium constant will decrease if the temperature is raised. Fig. 5 shows that the reaction of formation of 1, 3-DNG and1, 2-DNG is an endothermic reaction, while the reaction of the formation of1-MNG, 2-MNG and TNG is an exothermic reaction.

Preferably, nitration is conducted at a relative low temperature. As shown at Fig. 5 the conversion of 1-MNG is more than 1, 3-DNG at temperature under 5^{o} C. So it is better to carry out nitration at the range of temperature 5-25^{o} C.

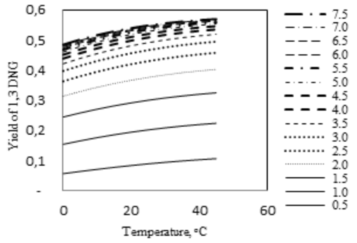

Fig. 6 The conversion of 1, 3- DNG at various temperatures (at various mol ratios) and nitric acid concentration of 71.35%

Calculations also were done at temperature of 0-45o C at many various mol ratios. Effect of temperature on the conversion of 1, 3-DNG at various HNO3 concentrations can be seen in Fig. 6. Increase in reaction temperature will increase the conversion of 1, 3-DNG for all mol ratios. At mol ratio above 5/1 increase in conversion is very slightly.

C. Effect of Ratio of Glycerol/Dichloromethane

An organic solvent may be added to the reactions in the inventive process to promote safety. The energetic nature of the mixed nitrate esters produced using the process of the present invention may lead to explosive reactions within the process. The addition of an organic solvent such as dichloromethane or dichloromethane, to the reaction process dilutes and moderates the reactions and provides a significant measure of safety to the process since the organic solvent absorbs the heat of the reaction and boils before dangerous temperatures are reached [14].

Calculations are performed with ratio of glycerol/ dichloromethane in the range of 1/0.5 and 1/2.5. The conversions of all products of nitration are the same for all mol ratios. It could be said that the amount of dichloromethane was used did not affect the conversion. However, the presence of dichloromethane is necessary in reaction to safety. Dichloromethane is commonly used at same volume with glycerol.

D. Effect of Pressure

Previous studies did not mention the pressure of the process. Calculations were performed to determine the effects of pressure on conversion of 1, 3-DNG. In accordance with the usual state of affairs for condensed phases, the dependence of ln K on the pressure is very small and is significant only when very large changes of pressure are considered [21]. The conversions of all products at pressure of 101,320 Pa up to

253,310 Pa are almost the same values. Reactions should be conducted at atmospheric temperature (101,320 Pa).

IV. CONCLUSION

The highest conversion will be obtained in the range of mol ratio of nitric acid /glycerol between 2/1 – 5/1, and reaction temperature of 5-25°C. Reactions should be run at atmospheric temperature (101,320 Pa). Thermodynamics calculations gave the optimum mol ratio of nitric acid/glycerol to produce 1, 3-DNG was 5/1. At a temperature of 5-25°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. The presence of dichloromethane is necessary in reaction to safety but has no influence in the conversion of 1, 3-DNG. The parameters that need to be studied further to obtain the highest conversion of 1.3 DNG are mol ratio of nitric acid/glycerol and reaction temperature.

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