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 1, 3-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°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 not to 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], and 1, 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-DNG and nitroglycerin (TNG) with the main product is 1, 3-dinitroglycerine (see Fig. 1).

![Fig. 1 The products of nitration of glycerol](image)

Nitration is defines as reaction between organic compound and nitrating agent, by entering one or more nitro groups (-NO2). The reactions between glycerol and nitric acid are series parallel reactions [16]:

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

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

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

\[
1\text{-MNG} + HNO_3 \rightleftharpoons 1,2\text{-DNG} + H_2O \quad (4)
\]
Several studies about nitration of glycerol were reported. Nitration was run either with batch process \cite{17}, \cite{18} or polynomial.

The calculations were performed with an equilibrium reactor model under isothermal conditions for the seven reactions discussed. Gibbs reactor with specify equilibrium reactions type of chloromethane/ glycerol and pressure. Fig. 2 shows the flow of material in the Gibbs reactor.

![Gibbs reactor](Image)

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 1/1 and 1.5/1. The conversion of 1, 3-DNG is the greatest at the 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 for the greater mol ratio.

![Graph](Image)

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 \cite{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 and 1,2-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.

**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°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.

**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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REFERENCES


