Optimum Operating Conditions Of Glycerol Nitration to Produce 1, 3-Dinitroglycerin

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OPTIMUM OPERATING CONDITIONS OF GLYCEROL NITRATION TO PRODUCE 1, 3-DINITROGLYCERIN

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ABSTRACT

The 1, 3-dinitroglycerin is an important compound to synthesize glycidyl nitrate, monomer of polyglicidyl nitrate (PGN). PGN is the most energetic polymer which can be used as binder of propellant. This compound was produced from the nitration of glycerol with nitric acid. This paper aims to obtain optimum conditions nitration of glycerol with nitric acid. The reaction was run in a flask equipped with a nitrogen purge for stirring. Nitration of glycerol to 1,3-dinitroglycerin was studied in the temperature range of 10-30 ^{0}C, the molar ratio of nitric acid to glycerol 1/1 to 7/1 and nitric acid concentration of 69%. %. From experiments it is known that the optimum conditions of nitration of glycerol with nitric acid is a reaction temperature of 20 ^{0}C, the mole ratio of nitric acid / glycerol 5/1 and the concentration of nitric acid 69%.

Keywords: nitration, glycerol, optimum, operation condition.

1. INTRODUCTION

1, 3-dinitroglycerin (1, 3–DNG) is an important compound to produce polyglicidyl nitrate (PGN). PGN is the most energetic polymers [1] and useful as a propellant binder. The advantages of PGN are this polymer is not easily broken [2], has nitrato group which oxygen rich contained [3] and has relative value of specific impulse higher than the other composites [4]. On the other hand, glycerol is a major byproduct of the biodiesel industry; approximately crude biodiesel as much as 10% weight of biodiesel is formed [5]. The amount of glycerol that was produced needed alternative way to handling immediately so as to not become the waste that polluted the environment. One of the solutions was to process glycerol to polyglicidyl nitrate (PGN). This may contribute to the improvement of the economical viability of the biodiesel production itself [6].

The PGN formation from glycerol includes three reaction steps; nitration of glycerol and nitric acid to produce 1,3-DNG, 1,3- DNG cyclization to form glycidyl nitrate, and polymerization of glycidyl nitrate to produce PGN. Nitration of glycerol with nitric acid consist of 7 parallel- serial reactions and produce 5 kinds of products: 1 mononitroglycerin (1-MNG), 2 mononitroglycerin (2-MNG), 1,3 dinitroglycerin (1,3-DNG), and 1,2 dinitroglycerin (1,2-DNG) and nitroglycerin (TNG) [7]. The 1,3 dinitroglycerin is the main product of the reaction. The design of PGN plant needs the technical information about the reaction of glycerol to PGN. The kinetics of nitration has already presented in the previous paper [7, 8]. This paper aims to obtain optimum conditions nitration of glycerol with nitric acid.

Research on the nitration of glycerol has been done by Kazakov *et al.* [9] at the reaction temperature 0 ^{0}C to 48 ^{0}C and the concentration of nitric acid 53.80% to 87.06%. Highsmith *et al.* [10] stated nitration reaction of glycerol with nitric acid should be carried out at a temperature of 0 ^{0}C to 25 ^{0}C, the mole ratio of nitric acid / glycerol 4 to 5 and the concentration of nitric acid 90%.

Sanderson and Martins [11] states glycerol nitration reaction takes place between 0 to 25 ^{0}C, usually preferred at a temperature of 10 to 20 ^{0}C. The study of thermodynamics of glycerol of nitration has been reported [12]. The highest equilibrium conversion of the nitration reaction will be obtained at the reaction temperature range of 5 to 25 ^{0}C and the ratio of nitric acid / glycerol 2/1 to 7/1. The mole ratio of dichloromethane (solvent) / glycerol and the pressure does not affect the equilibrium conversion. Thermodynamic study of the effect of the concentration of nitric acid to the equilibrium conversions will be presented in this paper. The parameters which reviewed in this paper are the reaction temperature, mole ratio of nitric acid / glycerol and the concentration of nitric acid.

2. METHOD

a) Reagent

Experiments were carried out in two 5 cm^3 flask that was immersed in cooling bath. The flask equipped with nitrogen purge for stirring. A thermocouple monitored the temperature in the cooling bath. Glycerol with a certain weight was placed in flask and was diluted with an equal volume of dichloroethane and cooled to reaction temperature. Nitric acid was added. Samples were taken in time intervals between 45-60 minutes, 10 samples in each experiment. Experimental works were done with two variables i.e. reaction temperature (10 to 30 ^{0}C) and molar ratio (1/1 to 7/1).
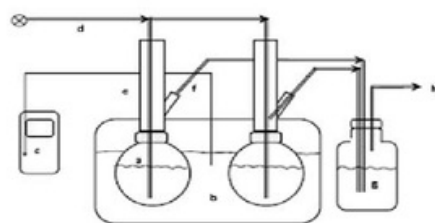
Caption:
a. Microscale reactor with a   d. Nitrogen hose
   volume of 5 mL   e. Hickman distillation head
b. Water bath   f. Gas hose
c. Termometer with   g. the Griess-Saltzman solution
   accuracy of 0.1O° C   h. exhaust gas

Figure-1. The equipment of glycerol nitration.

b) Analysis method

The samples were analyzed using GC with internal standard method. Samples were analyzed with gas chromatography (430 GC, Bruker), equipped with flame ionization detector. The column was a VF-1 ms 30 m x 0.25 mm, ID DF=1 capillary column from Factor Four. The injector and detector temperatures were maintained at 175 and 225 ^{0}C, respectively. The oven temperature was kept at 60 ^{0}C during injection, after that increase to 140 ^{0}C and stable 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 sample, respectively.

3. RESULTS AND DISCUSSION

a) Quantitative analysis of products of glycerol nitration

Gas chromatography (GC) method usually used for qualitative analysis, identifying the presence of a compound in the sample. When used for quantitative analysis, there are two kinds of interpretation of the results of the analysis are considered as mass percent or mole percent. Preliminary research was conducted to prove that the results of the analysis with a GC is mass percent. This method is then used for quantitative analysis of the results of the nitration reaction of glycerol with nitric acid.

Calculation of concentration by GC can be done in three different ways, namely normalization, ESTD (i.e. quantitative way using a standard solution) and the ISTD (i.e. quantitative way using internal standard solution). Internal standard is very useful for quantitative analysis of samples that are difficult to control. The type of material used as an internal standard to identify compounds nitroglycerin and their derivates are various kinds: o-iodobenzyl alcohol [13], o-chloronitrobenzene [14] and 2,4-dinitrotoluene [15]. This research used 1-butanol as internal standard because retention time of 1- butanol is fastest compared to other compounds present in the sample. Chromatogram of glycerol nitration obtained can be seen in Figure-2.
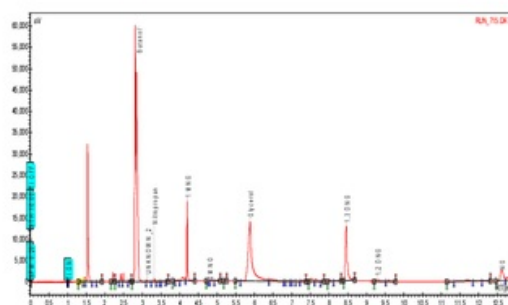

Figure-2. Chromatogram form GC analysis of glycerol nitration.

Figure-2 shows the peaks of 1-MNG, 2-MNG, 1,3-DNG, 1,2-DNG and NG. All the compounds are expected to appear in the analysis can be identified by GC. Analysis successfully identifies isomers present in the sample as two separate peaks. Peak of 2-MNG appears after peak of 1-MNG. Similarly, 1,2-DNG peak appears after the peak of 1,3 DNG.

This study also used the GC method for quantitative analysis of compounds in the sample. This method was chosen because the GC and HPLC method is a method that can be used to analyze the nitroglycerin in the slightly sample. Moreover, both methods are highly sensitive, selective and have a tiny error rate [16]. Results chromatogram (Figure-2) states that GC methods can also be used to identify derivative compounds of nitroglycerin,so this method can also be used to determine the quantity of compounds.

On the use of GC for quantitative analysis method, there are two kinds of interpretation of the results, which are considered as mass percent or mole percent. To know the exact interpretation of the research analyzed three samples of a mixture of propanol, and butanol dichloroethane and 3 samples of mixture nitropropana, dichloroethane and butanol. Propanol and nitropropana was chosen because its structure is not much different from the structure of the products of nitration. Results of the analysis are listed in Table-1:

The results of analysis prove that the peak area is proportional to the mass and not the mole. Comparison between the mass of a compound and internal standard compound mass and peak area is expressed as a ratio of RRF (*relative response factor*). Table-2 states that the RRF of propanol is 1.13 while the RRF of nitropropana is 1.04. It could be said that the RRF for a compound that has a molecular structure similar to the internal standard is one, according to the ideal value of RRF. The average error of the mixture of propanol-dichloroethane-butanol is 11.64% and the average error of the mixture of nitropropane-dichloroethane-butanol is 4.24%. The average error of all samples is 7.94%. If the molecular structure of the compounds analyzed and internal standard is different, RRF value is not equal to one. RRF for dichloroethane is 2.42. In a subsequent study, RRF value

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of 1-MNG, 2-MNG, 1,3-DNG, 1,2-DNG and TNG are considered to the RRF ideal value.

Table-1. Results of Analysis the mixture of propanol, and butanol DCE and the mixtures of nitropropane, DCE and butanol.

Sample	Compound	vol, μl	mass, gram	mass (GC)	RRF	error, %
I	Propanol	200	0,1590	0,1404	1,1322	11,68
	DCE	200	0,2423		2,4225	
	Butanol	100	0,0768			
II	Propanol	300	0,2349	0,2064	1,1379	12,12
	DCE	100	0,1198		2,3507	
	Butanol	100	0,0778			
III	Propanol	100	0,0791	0,0703	1,1254	11,14
	DCE	300	0,3657		2,4803	
	Butanol	100	0,0782			
IV	Nitropropana	100	0,1034	0,1016	1,0177	1,74
	DCE	100	0,1145		*	
	Butanol	100	0,0430			
V	Nitropropana	100	0,1003	0,0922	1,0879	8,08
	DCE	100	0,1206		*	
	Butanol	100	0,0780			
VI	Nitropropana	100	0,1001	0,0972	1,0298	2,90
	DCE	100	0,1238		*	
	Butanol	100	0,0798			

*No data

b) Operating conditions of glycerol nitration

i. The influence of temperature

Experiments were done at reaction temperature of 10 °C, 15 °C, 20 °C dan 30 °C. The reaction rate usually increases exponentially if the reaction temperature increases. The formation of 1,3-DNG is an endothermic reaction [17].
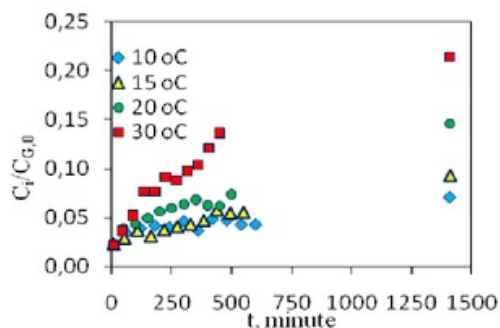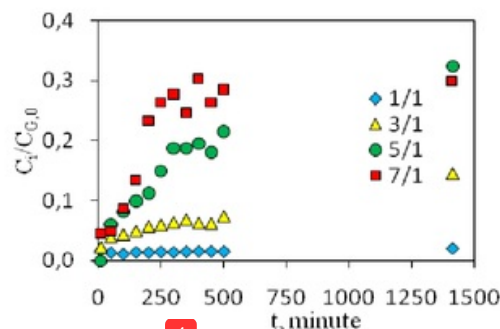
Figure-3. $C_i/C_{G,0}$ of 1,3-DNG at various temperatures (HNO$_3$ concentration of 69%, mole ratio of nitric acid/glycerol of 3/1).

The experimental results stated that the reaction temperature increases cause 1,3-DNG conversion increase (see Figure-3). The rising temperatures are likely to increase the reaction rate by reducing the resistance factor [18]. Nitration of glycerol can only run up to a certain temperature. On the heating of 18 to 20 °C, TNG started to decompose by releasing NO$_2$ gas which has brown color. Decomposition can run very fast and can lead to an explosion. When placed in an enclosed space and heated quickly or initiated with a detonator, TNG will explode accompanied by a huge release of energy [19]. At this experiment, the decomposition reaction has not happened at reaction temperature of 20 °C. Decomposition occurs in some experiments which carried out at a temperature of 30 °C, characterized by the presence of brown gas above the solution nitration. Therefore nitration reaction of glycerol should be run until the temperature of 20 °C.

ii. The influence of the mole ratio

This study did nitration with a mole ratio of nitric acid/glycerol of 1/1, 3/1, 5/1 and 7/1. The greater mole ratio cause concentration of nitric acid in the nitration solution will be increased so that the equilibrium will shift to the right. The increase in the mole ratio increases the conversion of 1,3-DNG. The greater the mole ratio, the 1,3-DNG conversion is greater. The highest conversion is in mole ratio of 7/1. However, in that mole ratio, the process is difficult to control so that the optimum mole ratio is 5/1. This is in line with Highsmith *et al.* [10] which states that the mole ratio between the nitrating agent and the glycerol is in the range of 4/1 and 5/1.

Figure-4. $C_i/C_{G,0}$ of 1,3-DNG at various mole ratio of nitric acid/glycerol (HNO$_3$ concentration of 69%, temperature of 20 °C).

This research also studied the influence of temperature and mole ratio to 1,3-DNG conversion as seen in Table-2.

Based on the data in Table-2, can be calculated the average increase in the conversion of 1,3-DNG at the reaction temperature rise of 10° C and an increase in the mole ratio of nitric acid/ glycerol amounted of 2/1. The reaction temperature is 10° C rise would increase 1,3-DNG conversion of 13.6%, whereas the increase in the

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mole ratio of nitric acid/glycerol 2/1 will raise 1,3-DNG conversion of 5.1%. The highest conversion obtained at a temperature of 30° C reaction and the mole ratio of nitric acid / glycerol amounted to 7/1. However, for security reasons process, nitration reaction should be run at a temperature of 20° C reaction and the mole ratio of 5/1

Table-2. Maximum Conversion of 1,3-DNG.

Mole ratio	T, °C	Maximum conversion, %	Mole ratio	T, °C	Maximum conversion, %
1/1	10	1,64	5/1	10	1,57
	15	5,13		15	8,28
	20	11,05		20	22,26
	30	22,93		30	28,57
3/1	10	1,53	7/1	10	1,68
	15	6,15		15	13,42
	20	15,14		20	32,94
	30	25,09		30	38,7

iii. The influence of the concentration of nitric acid

Nitric acid as nitrating agent determines the acidity of the reaction mixture. Effect of acidity on the equilibrium constant was reported by Danov *et al.* [20] which states that the use of nitric acid concentration the higher the benzene nitration reaction rate constant increases. The influence of the concentration of nitric acid to 1,3-DNG conversion equilibrium, 1,2-DNG, 1-MNG, 2-MNG and TNG studied thermodynamics and simulations using HYSIS at different reaction temperature (0 to 45° C). The simulation was done using AspenHYSYS v7.2 under license for Chalmers University of Technology, Sweden. A method for simulation has been described in previous papers [12]. The influence of the concentration of the equilibrium conversion nitration reaction products can be seen in Figure-5.
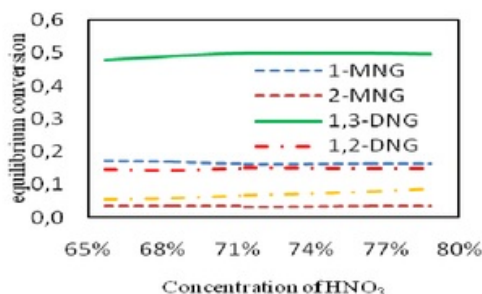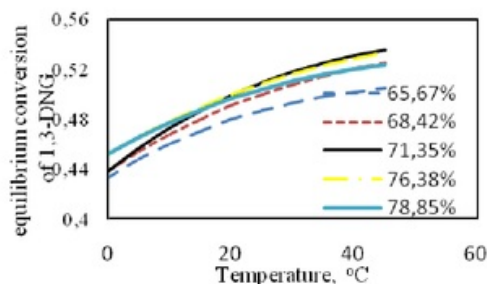

Figure-5. Equilibrium conversion of all nitration products at various concentrations (temperature of 20 °C and a mole ratio of 4/1).

Figure-5 shows that increasing concentrations of HNO3 will slightly improve the equilibrium conversion of 1,3-DNG. Conversion equilibrium 1-and 2-MNG MNG

declined with increasing concentrations of HNO3. The equilibrium conversion of 1,2-DNG relatively fixed on all variations of HNO3 concentration while TNG result increased with increasing concentrations of HNO3. These results suggest that the equilibrium conversion value nitration reaction product is influenced by the concentration of HNO3 which are used.

In general, the equilibrium constant will not remain at the temperatures and pressures remain, its value varies depending on the composition of the mixture at equilibrium [21]. If the reactants and products make the ideal solution in all the range of composition, the equilibrium constant will be a constant in the range of the composition. The equilibrium constant will be constant in very dilute solutions [22].

Figure-6. Equilibrium conversion of 1.3 DNG at various reaction temperature and HNO3 concentration (at mol ratio nitric acid/glycerol of 4/1)

If the HNO3 concentration rises, the equilibrium conversion of 1,3-DNG has also increased. The highest increase in equilibrium conversion occurs at a concentration range of 71.35%. After concentration, the equilibrium conversion of 1,3-DNG decreased. This indicates a different equilibrium conversion value for the different concentrations of HNO3. The mixture involved in the nitration process can be categorized as non-ideal solution.

Nitration was run at a concentration of nitric acid used by 65% to 69%. The results of a review of thermodynamics states optimal concentration of nitric acid is 71.35% to 78.85%. Previous [10, 11] using 90% nitric acid. The concentration of nitric acid used in the experiment chosen with consideration of the availability of materials and safety. Reaction using nitric acid 69% gave higher conversion of 1,3-DNG than the reaction using 65% nitric acid. Therefore, the optimum concentration of nitric acid is 69%.

4. CONCLUSIONS

Based on the highest conversion of 1,3-DNG which is reached, the maximum conversion is achieved at a temperature of 30 °C, the mole ratio of nitric acid / glycerol 7/1 and the concentration of nitric acid 90%. However, the process in these conditions requires a much higher safety standards and possible decomposition TNG

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and NOx are formed. Therefore, based on consideration of process safety, the recommended conditions for the nitration of glycerol with nitric acid is a reaction temperature of 20 ^{0}C, the mole ratio of nitric acid / glycerol 5/1 and the concentration of nitric acid 69%.

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