

Optimum Conditions for the Formation of Glycidyl Nitrate from 1,3-Dinitroglycerin

By Erna Astuti

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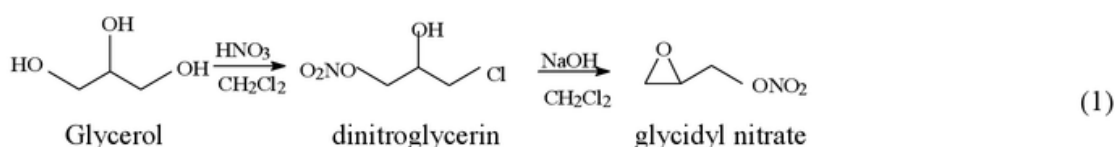
Keywords: Glycidyl nitrate; Cyclization; 1,3-Dinitroglycerine; Optimum Condition

Abstract. One of the utilization of glycerol as byproduct of the biodiesel industry is to produce polyglycidyl nitrate, the most energetic polymer. The synthesis of polyglycidyl nitrate from glycerol includes three steps: nitration, cyclization and polymerization. The aim of this study is to obtain the optimum conditions of cyclization. The cyclization was carried out in a 5 ml reactor and equipped with Hickman distillation head and nitrogen purge with variations the variables are mole ratio of sodium hydroxide/glycerol of 1/1 to 1.5/1, reaction temperature of 283.15 to 293.15 K and sodium hydroxide concentration of 15%. Each sample was analyzed by gas chromatography to determine the composition of products. The optimum conditions are temperature of 288.15 K and the mole ratio of sodium hydroxide /glycerol of 1.5.

Introduction

Glycerol is a renewable resources which is formed as a byproduct in the biodiesel industry; approximately 1 ton of a crude glycerol is formed for every 10 tons of biodiesel produced [1]. Because of its large volume production, there is an opportunity to convert this compound into higher value products. One alternative is to produce polyglycidyl nitrate (PGN), the most energetic polymer that can be used as a propellant binder. Three steps to make PGN from glycerol are nitration of glycerol, cyclization of 1,3-dinitroglycerin (1,3-DNG) and polymerization of glycidyl nitrate. A thermodynamic study, kinetic modeling and optimum condition of nitration have been described in the previous studies [2-5]. This paper proposes the optimum condition of cyclization of 1,3-DNG to synthesize glycidyl nitrate.

Glycidyl nitrate can be produced from several processes. There are some materials to synthesize glycidyl nitrate: glycidyl tosylate [6-9], epichlorohydrin [10] and glycerol [11]. The Cyclization of 1,3-DNG into glycidyl nitrate is performed using inorganic hydroxide such as sodium hydroxide, potassium hydroxide, and lithium hydroxide [10,12]. Highsmith et al [11] react glycerol with nitric acid and sodium hydroxide to get glycidyl nitrate. The reaction occurs:



Research on the cyclization reaction of 1,3- DNG was very rarely done. Highsmith et al [11] proposed seven receipts of the cyclization. The difference between the variations is the concentration of sodium hydroxide, the mole ratio of sodium hydroxide/glycerol, the reaction temperature and the separation process. The reactions that occur during the cyclization and kinetics

are unknown. The study to predict that mechanism of reactions will be proposed in the next paper. Furthermore optimum conditions of cyclization reaction were obtained from interpretation of literature data and experimental results.

Materials and methods

The reactants used in the experiments are nitrated glycerol solution, the products of glycerol nitration, which are get from experimental before. The nitrated glycerol solution contain glycerol, 1-mononitroglycerin (1-MNG), 2-mononitroglycerin (2-MNG), (1,3-DNG), 1,2-dinitroglycerin (1,2-DNG), nitroglycerin (TNG) and water. The other reactant is sodium hydroxide of $\geq 99.98\%$ from Merck.

All experiments were run in a batch reactor that has diameter of 2.12 cm and volume of 5 ml. The reactor was equipped with a nitrogen purge gas and NO_x absorber. The nitrated glycerol solution was placed in the reactor and sodium hydroxide solution with a certain concentration was added slowly while maintaining temperature below 298.15 K until the reaction had a pH of 14. Then sodium hydroxide was added in a certain mol ratio of sodium hydroxide and glycerol. Samples were taken in time intervals 2.5 minutes, 7 samples in each experiment. Experimental works were done with 2 variables i.e. reaction temperature (283.15 to 293.15 K), mol ratio of sodium hydroxide and glycerol (1.0, 1.25 and 1.5).

The samples were analyzed using GC with internal standard method. The 1-butanol was used as internal standard. 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 448.15 K and 498.15 K, respectively. The oven temperature was kept at 333.15 K during injection, after that increase to 413.15 K and stable at that temperature.

Result and Discussion

The purpose of this study is to find the optimum conditions for the cyclization. The parameters studied are the reaction temperature and mole ratio of glycerol/sodium hydroxide. The experimental results cyclization in the form of the mass concentration of the compounds which present in the cyclization solution is glycerol, 1-MNG, 2-MNG, 1,3-DNG, 1,2-DNG, TNG, glycidyl nitrate (GN) and glycidol at different reaction temperature and mole ratio of sodium hydroxide / glycerol. A chromatogram showing all the component in product of cyclization of 1,3-DNG is presented in figure 1.

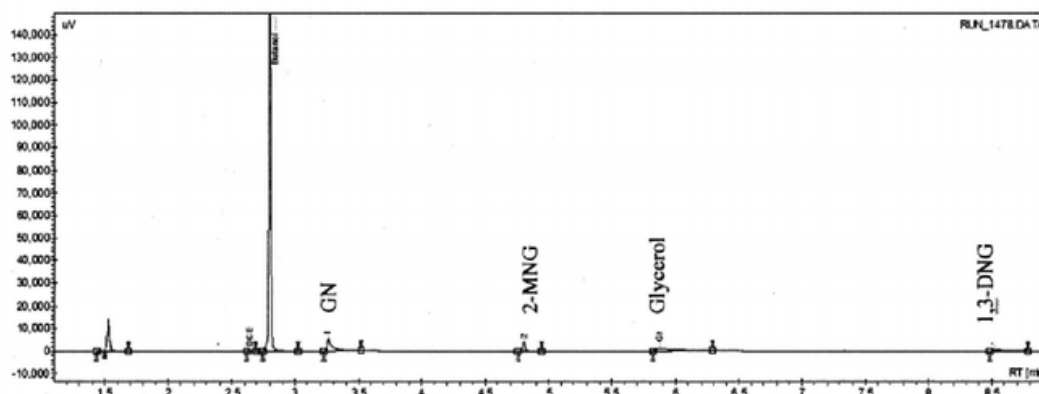
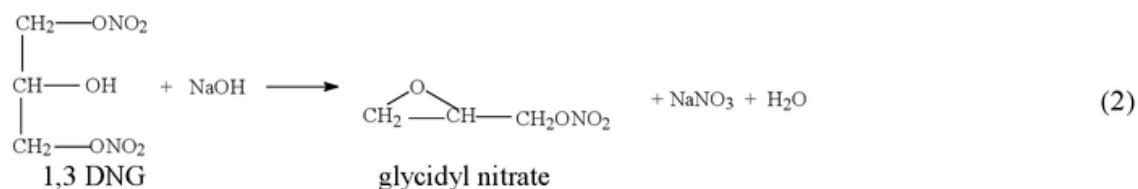


Figure 1. A chromatogram from cyclization

Research on the cyclization of 1,3-DNG is still very rare. Until now there have been found few journals that discuss the cyclization of 1,3-DNG. Some literatures only reported molecular structure of glycidyl nitrate and how to conduct cyclization of 1,3-DNG. This paper proposes the reaction between the 1,3-DNG and sodium hydroxide as reaction:



The formation of glycidyl nitrate occurs fast. Previous researchers [11, 13] were conducted cyclization with a reaction time of 0.5 to 3 hours. Figure 2 and Figure 3 shows glycidyl nitrate formation run quickly. The increase in the conversion of glycidyl nitrate (GN) significantly occurs in the order of minutes.

Cyclization can be carried out at a temperature of 273.15 to 298.15 K and preferred to be done at a temperature of 297.15 K [11, 13]. This research was carried out at a temperature of 283.15 to 293.15 K with a temperature interval of 2.5 K and NaOH concentration of 15%. The temperature range was selected for the cyclization because this reaction is exothermic, whereas the epoxide ring is unstable and susceptible to heat so the glycidyl nitrate which is produced will be decomposed. This effect is minimized by choosing the reaction temperature of 283.15 to 293.15 K. The influence of temperature on the conversion of 1,3-DNG is represented in Figure 2.

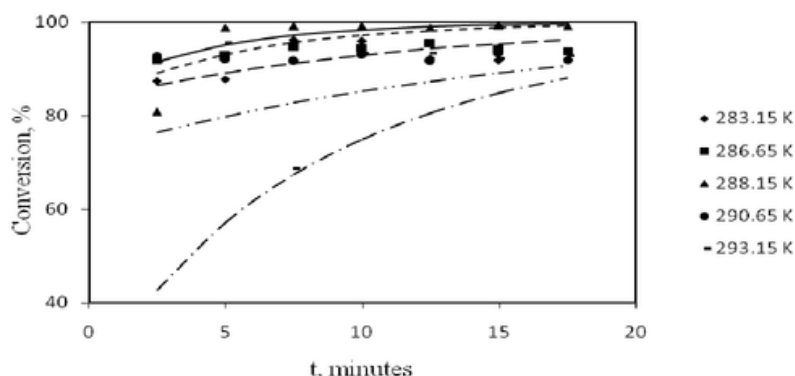


Figure 2. The 1,3-DNG conversion into glycidyl nitrate at various reaction temperature

The higher the temperature of the reaction, the conversion of 1,3-DNG is increased. The increases in the reaction temperature of 2.5 K lead to increased conversions by 2.98%. At a temperature of 288.15 K, the maximum conversion is reached, after that the rises of reaction temperature precisely decrease conversion of 1,3-DNG. This phenomenon occurs because the equilibrium has not been achieved in a reaction time of 17.5 minutes so this experiment results did not report the equilibrium conversion of cyclization. The highest conversion is obtained at the reaction temperature 288.15 K.

The ratio of reactant is one of the factors that determine the rate of reaction. The reaction can be accelerated by using one of the reactants in excess. The previous research [11] conducted the cyclization of 1,3-DNG at mole ratio of NaOH / glycerol of 1 to 9. In this study, the experiments were carried out with a mole ratio of sodium hydroxide / glycerol 1, 1.25 and 1.5. The experiments cannot be run on a mole ratio greater than 1.5 because of the high viscosity of the solution and the reaction proceeds very quickly at the beginning of the reaction so conversion for a reaction time of 2.5 minutes is unidentified. The higher mole ratio cause the cyclization solution is more viscous so

the sample of cyclization is more difficult to take. The syringe clogs very easily. The influence of increase in the mole ratio of sodium hydroxide / glycerol can be seen in Figure 3.

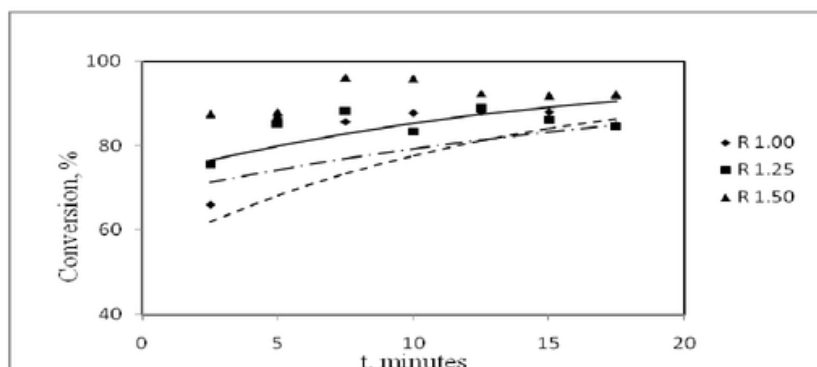


Figure 3. 1,3-DNG conversion into glycidyl nitrate at NaOH 15% and a temperature of 283.15 K with a variation of the mole ratio of NaOH / glycerol (R).

The addition amount of sodium hydroxide in the cyclization cause in increased product of glycidyl nitrate, that is marked by the increase in the conversion of 1,3-DNG. Increase in mole ratio of sodium hydroxide/glycerol raise amount of glycidyl nitrate, main product of cyclization. The optimum conversion was obtained from experiments with a mole ratio of NaOH / glycerol of 1.50. The use of sodium hydroxide is effective to increase the conversion of 1,3-DNG into glycidyl nitrate. The increase in the ratio of 0.25 led to rise 1,3-DNG conversion of 4.21%.

Summary

Cyclization of 1,3-DNG is an exothermic reaction. The formation of glycidyl nitrate runs very quickly, the increasing conversion of 1,3-DNG significantly occurs in the order of minutes. The epoxide ring which is in the structure of glycidyl nitrate is unstable and susceptible to heat. This study indicates that the optimum temperature for the cyclization of 1,3-DNG is 288.15 K. The addition amount of sodium hydroxide in the cyclization cause in increased product of glycidyl nitrate, but there is restrictiveness to add sodium hydroxide during cyclization. The optimum mole ratio of NaOH/glycerol is 1.5 with NaOH concentration of 15%.

Acknowledgement

The authors thank to Prof. Bengt Andersson and Assoc. Prof. Krister Ström for all the help and guidance, to the Erasmus Mundus Programme EuroAsia and Chemical Engineering Division, Chemical and Biological Department, Chalmers University of Technology, Sweden which supported this work.

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