Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater., 2016, *13*(3), 579-591; DOI: 10.22211/cejem/65024

Improved Synthesis of Glycidyl Nitrate in the Presence of 5-Aminotetrazolium Nitrate: a New Method Optimised Using the Taguchi Method

Yadollah BAYAT,* Mahvash Mossahebi MOHAMMADI

Department of Chemistry and Chemical Engineering,
Malek-Ashtar University of Technology,
P.O. Box 16765-3454, Tehran, Iran
**E-mail: Y_bayat@Mut.ac.ir*

Abstract: This paper describes a method for increasing the yield of glycidyl nitrate from chloro-epoxypropane and dilute nitric acid, in the presence of 5-aminotetrazolium nitrate. The presence of 5-aminotetrazolium nitrate as catalyst and co-nitrating agent, enabled glycidyl nitrate to be produced smoothly and in excellent yield under mild condition. The optimal reaction conditions were obtained by the Taguchi method, increasing the yield from 66 to 81%. The product was characterized by FTIR and ^{1}H NMR spectroscopy.

Keywords: glycidyl nitrate, 5-aminotetrazolium nitrate, chloro-epoxypropane, Taguchi method

1 Introduction

Polyglycidyl nitrate (PGN) is widely used in propellants, explosives and pyrotechnics due to its energetic content, derived from the ONO_2 function in the glycidyl nitrate monomer, and its polyisocyanate curability *via* the terminal hydroxyl groups [1, 2]. This polymer was the first energetic prepolymer to be investigated for binder applications. Initial studies on PGN were carried out by Thelen *et al.* in the 1950s at the Naval Surface Warfare Center (NSWC) [3]. This prepolymer was later evaluated as a propellant at the Jet Propulsion Laboratory (JPL) [4, 5]. The development of PGN into an energetic binder was delayed due to the hazardous processes of monomer preparation, purification and polymerization. Thus, an investigation of the synthesis and modification of

glycidyl nitrate is welcomed by many researchers.

Moreover, medicinal use of glycidyl nitrate in treating some diseases, such as cancer, has been reported by Bednarski [6].

Glycidyl nitrate is a transparent liquid with vapour pressure 1.26 mmHg at 25 °C, refractive index 1.46 at 20 °C and boiling point 180 °C at 760 mmHg [7].

Glycidyl nitrate was synthesized for the first time in 1907 by Naoum [8] *via* hydrolysis of dinitroglycerin in the presence of potassium hydroxide. Many efforts have been made in the development of the synthesis of glycidyl nitrate. All of the studies in this area can be summarized under three general methods of nitration.

1. The first method is nitration of glycerine. In this method, 1,2-dinitroglycerin is simply prepared by nitration of glycerine with nitric acid. The dinitroglycerin is then reacted with a strong base to form the epoxide *via* ring closure [9-11].
2. The second method is based on the selective nitration of glycidol with a nitrating agent [12-15]. Hong Chang *et al*. have synthesized glycidyl nitrate using HNO_3/AcO_2 as the nitrating agent [15]. $NaNO_3$ and N_2O_5 have also been used as the nitrating agent [12-14].
3. The last method for glycidyl nitrate synthesis is the nitration of chloro-epoxypropane (epichlorohydrin) in two steps. In the first step, the chloro-epoxypropane ring is opened by the nitrating agent. This reaction is then followed by ring closure using a strong base [16, 17].

These methods have some disadvantages, such as low yield [9-11, 17], production of significant amounts of nitroglycerine and dinitroglycerin as by-products [9-11], extreme sensitivity to temperature during the reaction [12, 13] and laborious purification processes [12, 13].

In order to overcome these shortcomings, we have modified the glycidyl nitrate synthesis *via* a one-pot reaction of chloro-epoxypropane with dilute nitric acid and 5-aminotetrazolium nitrate as the nitrating agent. In order to optimize the reaction conditions, the Taguchi method was applied as a simple, efficient and powerful tool in experimental design for obtaining higher yields, which makes this the preferred method in many applications [18-20]. Among the advantages of the Taguchi method, the possibility of performing parallel experiments is the most significant [21, 22]. The product structure was analysed by FT-IR and ^{1}H NMR spectroscopy and the product purity was demonstrated by gas chromatography.

2 Material and Methods

Chloro-epoxypropane (epichlorohydrin > 99%), boric acid, HCl (37%) solution, sodium azide, dicyandiamide and HNO_3 (65 wt.%) were used in the experiments, were all analytical grade and purchased from Merck, Fluka and Sigma-Aldrich. The products were characterized by FTIR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were obtained using a DRX-Avance Bruker instrument (100 MHz) using $CDCl_3$ as the solvent at room temperature. The IR spectra were recorded with a Nicolet 950 spectrometer in the range 500-4000 cm^{-1} using 32 scans. Gas chromatography (GC) was performed with an Agilent Technologies 6890N instrument.

2.1 Preparation of 5-aminotetrazole [23]

Dicyandiamide (10.00 g, 0.12 mol), sodium azide (7.74 g, 0.12 mol) and boric acid (11.00 g, 0.18 mol) in water (100 mL) were placed in a 1-litre single-neck, round-bottom flask equipped with a magnetic stirrer bar and reflux condenser. The solution was refluxed until its colour turned slightly orange. The reaction was allowed to reflux for 24 h and then concentrated HCl (15 mL) was added while the solution was still hot. A white crystalline solid formed upon cooling. The product was isolated by filtration and washed twice with portions of ice-cold distilled water (50 mL). The 5-aminotetrazole (CH_3N_5) obtained was dried in a vacuum oven at about 60 °C for 12 h to achieve pure white, fine crystals in 96.3% yield.

2.2 Preparation of 5-aminotetrazolium nitrate [24]

5-Aminotetrazole (1.03 g, 0.01 mol) was placed in a 100 mL single-neck flask and dissolved in boiling water (2 mL). After complete dissolution, 65% nitric acid (2.0 mL) was added to the solvent over 1 min and stirred for 10 min. The external heating was then immediately removed. Within a few minutes feathery white crystals were observed. After 5 min cooling, the reaction vessel was transferred to an ice-water bath and resulted in the crystallization of an increased amount of the feathery white crystals of 5-aminotetrazolium nitrate. This material was filtered off, washed three times with diethyl ether, recrystallized once from boiling water, washed three additional times with diethyl ether and then dried in a vacuum oven below 60 °C, to give dried 5-aminotetrazolium nitrate ($CH_4N_6O_3$) (1.24 g, 84%).

2.3 Preparation of glycidyl nitrate

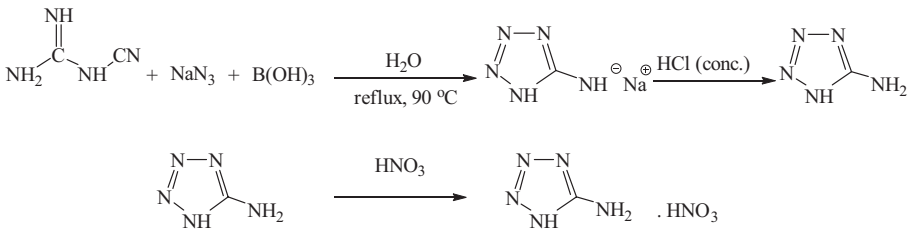
A solution of 45 wt.% nitric acid (12 mL, 0.15 mol) was added to 5-aminotetrazolium nitrate (0.74 g, 5.00×10^{-3} mol) in a 100 mL flask equipped

with thermometer and magnetic stirrer. Chloro-epoxypropane (9.20 g, 0.10 mol) was then added dropwise to the stirred solution over a period of 60 min, while the solution temperature was kept at 20 ± 2 °C. After the chloro-epoxypropane addition, the solution was stirred at room temperature for 2.5 h. The solution was then cooled to 0 °C and aqueous sodium hydroxide (8.00 g, 0.20 mol in 10 mL H_2O) was added dropwise; the temperature was kept below 15 °C during the addition of the sodium hydroxide solution. The reaction solution was stirred for an additional 60 min. After completion of the reaction, the organic layer was extracted three times with dichloromethane. The solvent was evaporated from the combined extracts and the product was distilled under vacuum at 60 °C to obtain glycidyl nitrate ($C_3H_5NO_4$) (9.7 g, ~81%) of purity > 96% (as determined by GC).

3 Results and Discussion

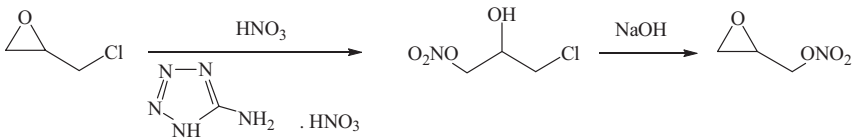
In this study of a one-pot synthesis of glycidyl nitrate, the first step is reaction of chloro-epoxypropane with nitric acid in the presence of 5-aminotetrazolium nitrate as a catalyst and co-nitrating agent, at room temperature, to form 1-nitrato-3-chloropropan-2-ol. This compound was reacted with NaOH solution in the next step to produce glycidyl nitrate.

5-Aminotetrazole was prepared first and then converted to the nitrate salt, 5-aminotetrazolium nitrate, with nitric acid (Scheme 1).



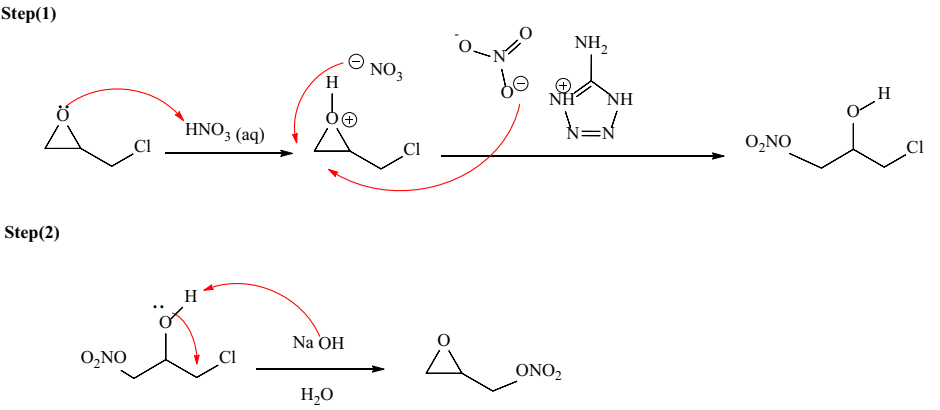
Scheme 1. Preparation of 5-aminotetrazolium nitrate.

Nitric acid and the 5-aminotetrazolium nitrate were then reacted with chloro-epoxypropane to form glycidyl nitrate. For this purpose, chloro-epoxypropane was added dropwise to dilute nitric acid, resulting in ring-opening. Ring-closure occurred *via* reaction of this intermediate with aqueous saturated NaOH solution (Scheme 2).



Scheme 2. One pot synthesis of glycidyl nitrate in the presence of 5-aminotetrazolium nitrate.

The mechanism of the reaction consists of two steps. In the first, the epoxide ring is opened in order to effect nitration of the chloro-epoxypropane, which is then followed by ring closure. Epoxide ring nitration was considered as the main step of the reaction that was carried out in low yield in presence of dilute nitric acid [17]. Therefore, 5-aminotetrazolium nitrate was added in order to increase the yield of the reaction. It seems that 5-aminotetrazolium nitrate facilitates this step by increasing the NO_3^- concentration (Scheme 3). This mechanism was proved by quenching the reaction after the first step and separating the intermediate product, which was characterized by ^1H NMR spectroscopy and by comparison with an authentic sample [25].



Scheme 3. Proposed mechanism for glycidyl nitrate synthesis in the presence of 5-aminotetrazolium nitrate.

Finally, the Taguchi method was applied in order to optimize the various parameters affecting the reaction, and to evaluate the effects of these parameters on the reaction yield. Six factors were selected and three levels for each factor were employed to illustrate the effect of each variable in order to increase the yield of glycidyl nitrate, using Qualitek 4 software (Nutek, Inc., Michigan, USA). The design factors included nitric acid concentration, moles of HNO_3, moles of NaOH,

the time required for the nitration reaction and the amount of 5-aminotetrazolium nitrate. The factors and their tested levels are listed in Table 1.

Table 1. The design factors and the levels of the variables in the Taguchi method

	Factors [a]	Level 1	Level 2	Level 3
a	Nitric acid concentration [wt.%]	25	35	45
b	Reaction time of stirring with nitric acid [min]	120	165	210
c	Amount of nitric nitric acid [mol]	1	1.2	1.5
d	Amount of NaOH [mol]	1.5	2	2.5
e	Reaction time of stirring with NaOH [min]	45	60	75
f	5-Aminotetrazolium nitrate [mol]	0.05	0.1	0.2

[a] for 1 mole chloro-epoxypropane

18 experiments were designed for optimizing the six individual parameters by the Taguchi method. All of the designed experiments and the design matrix can be seen in Table 2. The reaction yields achieved are also reported in this table.

Table 2. Design matrix together with the corresponding reaction yields

Trial conditions	a	b	c	d	e	f	Yield [%]
1	1	1	1	1	1	1	41
2	1	2	2	2	2	2	32
3	1	3	3	3	3	3	29
4	2	1	1	2	2	3	45
5	2	2	2	3	3	1	57
6	2	3	3	1	1	2	30
7	3	1	2	1	3	2	37
8	3	2	3	2	1	3	48
9	3	3	1	3	2	1	63
10	1	1	3	3	2	2	43
11	1	2	1	1	3	3	28
12	1	3	2	2	1	1	48
13	2	1	2	3	1	3	37
14	2	2	3	1	2	1	68
15	2	3	1	2	3	2	36
16	3	1	3	2	3	1	70
17	3	2	1	3	1	2	45.5
18	3	3	2	1	2	3	29

Figures 1(a-f) show the average yields and the levels of the factors required for the glycidyl nitrate synthesis reaction. As shown in the curves, the average yield for each factor changes as the level of that factor is varied.

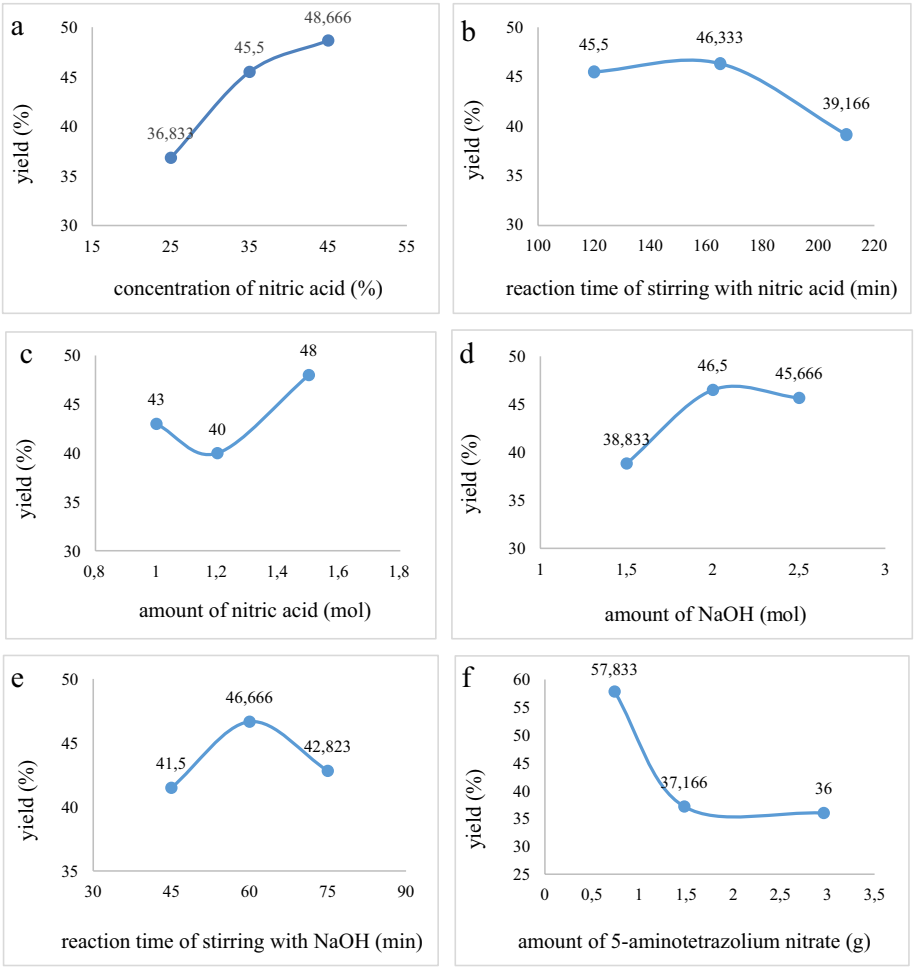


Figure 1. (a) Yields for the concentration of nitric acid; (b) Yields for the time of stirring with nitric acid; (c) Yields for the moles of nitric acid; (d) Yields for the moles of NaOH; (e) Yields for the time of stirring with NaOH; (f) Yields for the amount of 5-aminotetrazolium nitrate.

The data obtained by an analysis of the variance (ANOVA) of the effects of the factors on the reaction yield are shown in Table 3. According to the table of an analysis of the variance (ANOVA), it can be concluded that by increasing the F-ratio, the impact parameter can be partially recognized.

Table 3. ANOVA table

	Factors	DOF*	Sums of squares	Variance	F-Ratio	Percent
a	Nitric acid concentration	2	450.333	225.166	12.193	13.634
b	Reaction time of stirring with nitric acid	2	184.333	92.166	4.990	4.861
c	Moles of nitric acid	2	196.000	98.000	5.306	5.246
d	Moles of base	2	212.333	106.166	5.749	5.784
e	Reaction time of stirring with NaOH	2	86.333	43.166	2.337	1.629
f	Amount of 5-aminotetrazolium nitrate	2	1,810.333	905.166	49.400	58.489
	Other errors	5	92.333			10.357
	Total	17	3,032.000			100.000%

* DOF − Degree of Freedom

The results of ANOVA showed that the optimum conditions for the production of glycidyl nitrate were: concentration of nitric acid 45 wt.%, molar ratio of nitric acid/chloro-epoxypropane 1.5/1, molar ratio of NaOH/ chloro-epoxypropane 2/1, and 8 wt.% of 5-aminotetrazolium nitrate relative to chloro-epoxypropane, for 2.5 h, and the optimum amount of NaOH was 2 mole. Considering the ANOVA table, the highest effect of all of the factors was exhibited by the amount of 5-aminotetrazolium nitrate. The yield of the reaction decreased on increasing the amount of this factor. The interactions between the variables were not considered. In addition, the results showed that the reaction time of stirring with base is not an important parameter in glycidyl nitrate synthesis.

Finally, the study of the main factors showed that the optimum conditions proposed according to the results of ANOVA were as shown in Table 4.

The best level for each factor is listed in Table 4. The yield obtained under these conditions was 72.64%, according to the software. A reaction performed under these conditions gave a yield of about 81%.

Table 4. Optimum conditions and performance

Factors	Proposed	Level
Concentration of nitric acid	45	3
Time of stirring with nitric acid	165	2
Moles of nitric acid	1.5	3
Moles of NaOH	2	2
Amount of 5-aminotetrazolium nitrate	0.05	1
Total contribution from all factors		28.998
Current grand average of performance		43.666
Expected result under optimum conditions		72.664

Glycidyl nitrate was not formed in good yield in preliminary reactions carried out with dilute HNO_3 and chloro-epoxypropane. Therefore, 5-aminotetrazolium nitrate was used as both catalyst and co-nitrating agent. The results showed that 5-aminotetrazolium nitrate played an efficient role in the reaction and increased the yield up to 81%. A comparison between glycidyl nitrate synthesis from chloro-epoxypropane without 5-aminotetrazolium nitrate and the optimized method showed an improvement of about 21% in the yield. Hence, in this study, we have used chloro-epoxypropane as the starting material and HNO_3 as the nitrating agent in the presence of 5-aminotetrazolium nitrate as an effective reagent for the synthesis of glycidyl nitrate. Higher yields and purity can be achieved by using dilute nitric acid and 5-aminotetrazolium nitrate as both catalyst and co-nitrating agent. We have presented an optimized method using the Taguchi method, which increases the reaction yield by using 5-aminotetrazolium nitrate as the nitrating agent, for the first time in the synthesis of an explosive material. The results showed that the yield of the glycidyl nitrate synthesis reaction can be enhanced significantly, by adjusting the amount of 5-aminotetrazolium nitrate, to 81% with > 96% purity as determined by gas chromatography. The products were identified by FTIR and ^{1}H NMR spectroscopy and were found to be identical to those described in the literature [14, 17].

The FTIR spectra of glycidyl nitrate and chloro-epoxypropane are shown in Figure 2. Bands at 3069~2905 cm^{-1} were assigned to the CH_2 and CH groups. The epoxide ether absorption was observed at 859 cm^{-1}. The disappearance of the C−Cl stretching band in the FTIR spectrum of chloro-epoxypropane at 760 cm^{-1} and the appearance of a band attributed to the asymmetric NO_2 stretching mode at 1636 cm^{-1} in the FTIR spectrum of glycidyl nitrate indicates that the reaction was successful.

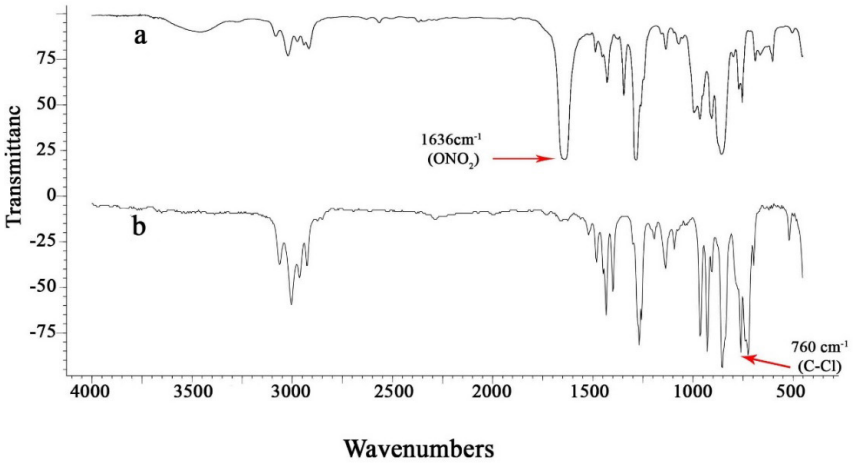


Figure 2. FTIR spectra of: (a) glycidyl nitrate, (b) chloro-epoxy propane.

Figure 3 shows the ^{1}H NMR spectrum of glycidyl nitrate. The double peak of the CH_2 group bearing the ONO_2 group was observed at $\delta = 4.2$ and 4.7. The signal at $\delta = 3.1 \sim 3.3$ was assigned to the ring C–H group, and the multiple peaks of the ring CH_2 group were at 2.9 and 2.6.

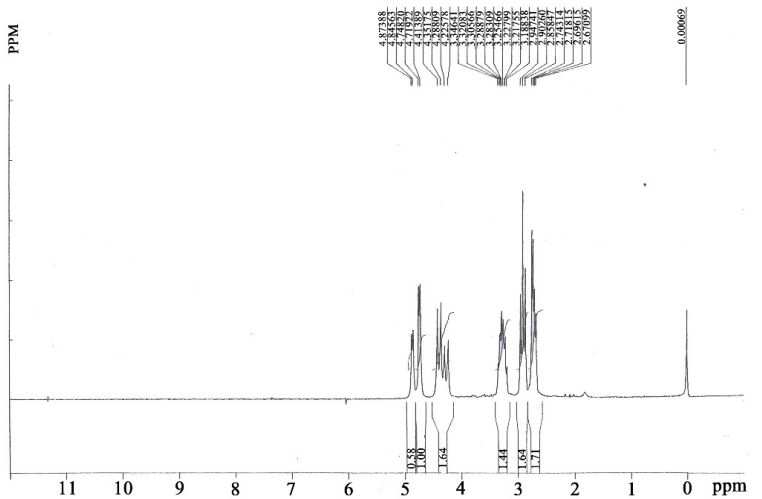


Figure 3. ^{1}H NMR spectrum of glycidyl nitrate.

4 Conclusions

In this paper we have reported a novel method for the synthesis of glycidyl nitrate in higher yield and purity, by nitrating chloro-epoxypropane in the presence of dilute nitric acid and 5-aminotetrazolium nitrate as an effective material as both catalyst and co-nitrating agent. In this research, 5-aminotetrazolium nitrate was introduced for the first time as an efficient weak nitrating agent. Six effective factors in the synthesis of glycidyl nitrate have been investigated by the Taguchi method. The effects of these six factors on the yield of glycidyl nitrate were quantitatively evaluated by the analysis of variance (ANOVA). Applying the Taguchi method significantly enhanced the yield of the reaction. Experiments were undertaken to confirm the effectiveness of the Taguchi method. Through this study, the main factors that affect the yield of glycidyl nitrate were identified, together with their optimal factor levels. It was shown that the amount of 5-aminotetrazolium nitrate was the most significant factor affecting the yield of glycidyl nitrate, followed by the concentration of nitric acid. The optimum factor levels were: a mixing time of 2.5 h, a concentration of nitric acid of 45 wt.%, 8 wt.% of 5-aminotetrazolium nitrate relative to chloro-epoxypropane, a molar ratio of HNO_3 to chloro-epoxypropane of 1.5, and a molar ratio of NaOH to chloro-epoxypropane of 2. Finally, the optimal conditions for the synthesis of glycidyl nitrate *via* a one pot method was proposed, and a yield of 81% was obtained under these optimal factor levels. This result agrees well with the predicted yield. In the presence of 5-aminotetrazolium nitrate and using the Taguchi method for optimizing the yield, it was increased from 60% to 81%.

Acknowledgment
This work was supported by the Malek-Ashtar University of Technology and we are grateful for this support.

References

[1] Hinshaw C.J., Wardle R.B., Highsmith T.K., *Propellant Formulations Based on Dinitramide Salts and Energetic Binders*, Patent US 5 741 998, **1998**.
[2] Willer R., Stern A.G., Day R.S., *Polyglycidyl Nitrate Plasticizers*, Patent US 5 380 777, **1995**.
[3] Ang H.G., Pisharath S., *Energetic Polymers*, Wiley, New York, **2012**, p. 8; ISBN 9783527331550.
[4] Provatas A., *Energetic Polymers and Plasticizers for Explosive Formulations – a Review of Recent Advances*, Defence Science and Technology Organization,

DTIC Document, Report No. DSTO-TR-0966, Melbourne, Australia, **2000**, 13.
[5] Ingham J.D., Nichols P.L., *High Performance PGN-polyurethane Propellants*, Jet Propulsion Laboratory, Publication No. 93, **1959**.
[6] Bednarski M.D., Oehler L.M., Knox S., Cannizzo L., Warner K., Wardle R., Velarde S., Ning S., *O-Nitro Compounds, Pharmaceutical Compositions Thereof and Uses Thereof*, Patent US 0,135,380, **2007**.
[7] Liu J., *Liquid Explosives*, Springer, Berlin, **2015**, p. 211; ISBN 978-3-662-45847-1.
[8] Cannizzo L.F., Hajik R.M., Highsmith T.K., Sander A.J., Martins L., Wardle R.B., A New Low-cost Synthesis of PGN, *31st Int. Conf. ICT*, Karlsruhe, Germany, **2000**, 1-36.
[9] Highsmith T.K., Sanderson A.J., Cannizzo L.F., Hajik R.M., *Polymerization of Poly(Glycidyl Nitrate) from High Purity Glycidyl Nitrate Synthesized from Glycerol*, Patent US 6 362 311, **2002**.
[10] Sanderson A.J., Martins L.J., Dewey M.A., *Process for Making Stable Cured Poly(Glycidyl Nitrate) and Energetic Compositions Comprising Same*, Patent US 6 861 501, **2005**.
[11] Sanderson A.J., Martins L.L., *Method for Making Stable Cured Poly(Glycidyl Nitrate)*, Patent US 0,133,128, **2005**.
[12] Wang Q., Shi F., Zhang X., Wang L., Mi Z., Green Synthesis of Glycidyl Nitrate (in Chinese), *Chinese J. Explos. Propellants*, **2009**, *32*(2), 14-16.
[13] Desai H.J., Cunliffe A.V., Lewis T., Millar R.W., Paul N.C., Stewart M.J., Amass A.J., Synthesis of Narrow Molecular Weight α, ω-Hydroxy Telechelic Poly(Glycidyl Nitrate) and Estimation of Theoretical Heat of Explosion, *Polymer*, **1996**, *37*(15), 3471-3476.
[14] Ochoa-Gómez J.R., Blanco-Gómez J.J., A Safe Two-step Process for Manufacturing Glycidyl Nitrate from Glycidol Involving Solid-Liquid Phase-transfer Catalysis, *Org. Process Res. Dev.*, **2011**, *15*(6), 1454-1457.
[15] Hong-Chang M., Xiao-Xian G., Xian-Ming L., Shao-jun Q., Qing L., Synthesis and Characterization of Glycidyl Nitrate (in Chinese), *Chinese J. Energ. Mater.*, **2009**, *17*(4), 396-398.
[16] Young-Gu Ch., Jae-Kyung K., Derk-Soon H., Young-Hwan K., Jin-Seuk K., A Study on the Polymerization of Energetic Poly(Glycidyl Nitrate) (in Korean), *Polymer (Korea)*, **1993**, *17*(3), 233-241.
[17] Qiu S., Gan X., Fan. H., One-pot Synthesis of Glycidyl Nitrate, *Energ. Mater.*, **2005**, *13*(4), 211-213.
[18] Tehrani Matin K., Bastani D., Kazemian H., Applying the Taguchi Method to Develop an Optimized Synthesis Procedure for Nanocrystals of T-type Zeolite, *Chem. Eng. Technol.*, **2009**, *32*(7), 1042-1048.
[19] Yu X., Li Y., Wu D., Microencapsulation of Tannase by Chitosan-alginate Complex Coacervate Membrane: Synthesis of Antioxidant Propyl Gallate in Biphasic Media, *J. Chem. Technol. Biotechnol.*, *79*(5), 475-479.
[20] Ata O.N., Yeşilyurt M., Çolak S., Beşe A.V., Determination of the Optimum Conditions for Zinc Extraction from Ore Containing Sphalerite by HCl Solutions,

Can. J. Chem. Eng., **2002**, *80*(4), 1-11.
[21] Montgomery D.C., *Design and Analysis of Experiments*, Wiley, New York, **2008**, pp. 1-22; ISBN 9780470128664.
[22] Zhou J., Wu D., Guo D., Optimization of the Production of Thiocarbohydrazide Using the Taguchi Method, *J. Chem. Technol. Biotechnol.*, **2010**, *85*(10), 1402-1406.
[23] Highsmith T.K., Lund G.K., *Method for Synthesizing 5-Aminotetrazole*, Patent US 5,451,682, **1994**.
[24] Von Denffer M., Klapötke T.M., Kramer G., Spieß G., Welch J.M., Heeb G., Improved Synthesis and X-ray Structure of 5-Aminotetrazolium Nitrate, *Propellants Explos. Pyrotech.*, **2005**, *30*(3), 191-195.
[25] Iranpoor N., Salehi P., Ceric Ammonium Nitrate: a Mild and Efficient Reagent for Conversion of Epoxides to β-Nitrato Alcohols, *Tetrahedron*, **1995**, *51*(3), 909-912.