E-Smoking Liquids as Precursors for Liquid Nitroesters

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Abstract: Currently, E-smoking cigarettes are widely used and occur within all classes of society. This work investigated the use of E-smoking liquids for the synthesis of Nitroglycerin (NG) and 1,2-Propylene Glycol Dinitrate (PGDN), both considered as nitroester liquid high explosives. Two kinds of E-smoking liquids (10 mL) were investigated: nicotine free and with nicotine (10 mg/mL). Quantitative analysis of the glycerin and propylene glycol (PG) present in the E-smoking liquids was carried out by gas chromatography-mass spectrometry (GCMS), with calculation of the accuracy and precision parameters. The percentage of glycerin was (10-13 wt.%) and percentage of propylene glycol was (40-70 wt.%) The synthesis of pure NG and pure PGDN were performed with laboratory grade glycerin and propylene glycol and compared to the samples obtained from the E-smoking liquid. Differential Scanning Calorimetry (DSC) was used for the determination of the activation energy and the heat of decomposition for each synthesized explosive, using the Ozawa and Kissinger models. The brisance index was assessed by the witness plate test and compared with some conventional explosives (TNT and C4). Finally, the influence of nicotine (less than 2 wt.%) on the synthetic process and the detonic properties of the explosive mixture was studied.

Keywords: E-smoking liquid, nitroesters, nitroglycerin, 1,2-propylene glycol dinitrate, brisance test, activation energy

1 Introduction

In recent years, the consumption of the electronic cigarettes, also named E-smoking cigarettes, has increased [1] and some surveys show a continued

increase. In the United Kingdom, for example, 2.1 million adults use electronic cigarettes [2]. The E-smoking cigarette is composed of two components, an electronic part and a chemical part called the E-smoking liquid. This latter contains a rechargeable product composed of propylene glycol, glycerol, nicotine, water and some additives [3]. However, the presence of nicotine is not required. The use of propylene glycol is for the vaping effect when it is heated by the electronic part, the propylene glycol spreads a white vapour similar to the one produced by real cigarettes [4]. The greatest advantage of E-smoking is the diminution of toxic gases and the control of the concentration of nicotine [5]. Nevertheless, the propylene glycol and glycerin can be used as precursors in the synthesis of nitroglycerin (NG) and propylene glycol dinitrate (PGDN), respectively, for subversive purposes.

PGDN and NG (see Figure 1) are nitroester liquid explosives used in military and commercial explosive/propellant formulations. The liquid state of these substances facilitates their use in mixtures as gelatinating agents [6-8].

NG   PGDN
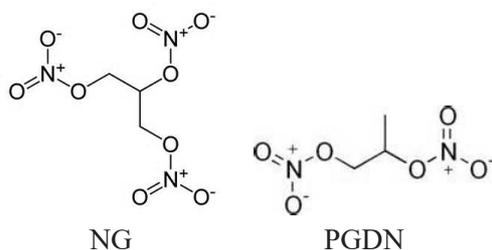
Figure 1.   NG and PGDN molecules.

The aim of the present work was to assess the use of the E-smoking liquid as a precursor in NG and PGDN synthesis. Two types of E-smoking liquid were investigated, with (10 mg/mL) and without nicotine. The objective of this twofold investigation was to look for the influence of the presence of nicotine in both the synthetic behaviour and the explosive performance.

In order to study the mixture (NG + PGDN) synthesized from E-smoking liquid with and without nicotine, the physicochemical characterizations were determined using GCMS and DSC. The detonation characterization of the explosive mixtures were realized by the determination of the brisance index and compared to the brisance index of pure PGDN, pure NG and some other conventional explosives (TNT and C4).

2　Experimental Part

2.1　Reagents and materials

The nitroglycerin standard (1% in methanol) and sodium carbonate (purity > 99.9%) were purchased from Merck. 1,2-Propylene glycol dinitrate (100 µg/mL) was obtained from Accu-Standard, and N,O-bis(trimethylsilyl)trifluoroacetamide containing trimethylchlorosilane (BSTFA-TMCS (1%)) from TCI.

Dichloromethane (purity > 99.8%) was purchased from Fluka Analytical and pure glycerin from UCB. 1,2-Propylene glycol (purity > 98%) and ethylene glycol were obtained from Fluka Chemika. The sulfuric acid used (99-100%) was purchased from VEL and the nitric acid (purity > 70%) from Riedel De Haen.

The commercial E-smoking liquids (10 mL), with nicotine (10 mg/mL) and nicotine free, were purchased from Shisha Time.

The GCMS analyses were performed with an Agilent 6890 series Gas Chromatograph (GC) and Agilent 5973 Mass Spectrometer (MS). The GC separations were performed with a DB5 column (30 m × 0.32 mm × 0.5 µm) and helium gas (1.5 mL/min).

Before the GCMS analysis, a quantity (2 µL) of each sample was dissolved in dichloromethane (2 mL) and an aliquot (2 µL) of this solution was introduced using the splitless mode. The inlet heater was fixed at 250 °C, the pressure at 3.77 psi and the total flow was 24.2 mL/min. The oven temperature was initially kept at 90 °C for 3 min, then heated at a linear rate of 15 °C/min until 280 °C, and finally kept at this temperature for 5 min.

The MS quadrupole temperature was set at 150 °C and the MS source temperature was 250 °C. The solvent delay time was 1.3 min. The MS was operated in the scan mode (30-600 amu).

DSC822 Mettler Toledo equipment was used. It was calibrated with indium and zinc, and cylindrical high pressure crucibles were used under nitrogen flow. The operating conditions consisted of heating the samples from 50 to 280 °C at four heating rates (β = 1, 3, 5 and 8 °C/min). The activation energies (E_a) of the synthesized NG and PGDN were obtained by applying the Ozawa and Kissinger models.

The brisance index of all of the synthesized explosives was assessed according to the witness plate test [9]. The brisance index of the mixture (NG + PGDN) synthesized from the two E-smoking liquids investigated was compared to the brisance index of NG and PGDN synthesized from pure laboratory grade ingredients. Two conventional explosives (TNT and C4) were also tested with the same testing procedure in order to calibrate the brisance of the mixed explosives from the E-smoking liquids.

2.2 Derivatization and calibration

The derivatization process was achieved by adding BSTFA-TMCS (500 µL) to a vial (2 mL) of each polyol sample (ethylene glycol, propylene glycol and glycerin). The vials were then heated at 65 °C during 30 min.

In order to assay the propylene glycol and glycerin present in the E-smoking liquid, a GCMS calibration curve was constructed using five concentrations (40, 80, 200, 400, 800 mg/L). Silylated ethylene glycol was used as an internal standard (IS-silylated; 200 mg/mL) for both propylene glycol and glycerin quantification. The percentage of the relative standard deviation (%RSD) and the relative response factor (RRF) relating to the area and to the retention time, were calculated by injecting each concentration five times. The calculation of these parameters was performed using the following equations [11, 12].

The RRF factors related to the area (RRF_{area}) and to the retention time (RRF_{tr}) are given in Equations 1 and 2, respectively:

$$RRF_{area} = \frac{(A_A)(C_{IS})}{(A_{IS})(C_A)} \tag{1}$$

$$RRF_{tr} = \frac{tr_A}{tr_{IS}} \tag{2}$$

where: A_A: area of the analyte, A_{IS}: area of the internal standard, tr_A: retention time of the analyte, tr_{IS}: retention time of the internal standard, C_A: known concentration of the analyte, C_{IS}: known concentration of the internal standard.

The relative standard deviation (RSD) and its percentage were calculated using Equations 3 and 4, respectively.

$$RSD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{(n-1)}} \tag{3}$$

where: x_i: each *RRF* value used in the calculation, $\overline{x}$: average of *n* values (in the case of this work, $n = 5$)

$$\%RSD = \frac{RSD}{average\ of\ the\ RRF} \ X\ 100 \tag{4}$$

When the RRF_{tr} is used instead of the RRF_{area} in Equation 3, the relative standard deviation related to the retention time (RSD_{tr}) is obtained. Its percentage (%RSD_{tr}) was obtained using Equation 4 with RRF_{tr} and RSD_{tr}.

2.3 Explosive synthesis

Four explosive samples were synthesized:
- nitroglycerin (NG) from pure glycerin, laboratory grade;
- propylene glycol dinitrate (PGDN) from pure propylene glycol, laboratory grade;
- a mixture NG + PGDN (Mixt 1) from E-smoking liquid, nicotine free;
- a mixture NG + PGDN (Mixt 2) from E-smoking liquid, with nicotine (10 mg/mL).

All of the explosives were synthesized by following a strict process, using a sulfonitric mixture, appropriate control of the physical parameters and adhering to all safety precautions. After the synthesis, purification was carried out by washing with distilled water. The products were then further washed with a sodium carbonate solution to neutralize residual acids. This operation was followed by washing the samples with distilled water until the pH became neutral. The yields from the four syntheses were between 58% and 65%.

3 Results and Discussion

3.1 GCMS analysis

All of the precursors and the synthesised products were analyzed by GCMS, the silylation process being used for all of the samples. The importance of silylation for GCMS analysis, using the BSTFA reagent, was to transform the hydrogen of a polar compound, polyol in our case, into a trimethylsilyl derivative (see Figure 2). The purpose of this chemical transformation was to make the target molecule more volatile and less thermolabile [10]. After silylation, the peak became symmetrical, as shown in Figures 3 and 4, which represent the glycerin and the silylated glycerin chromatograms respectively. Consequently, the quantification of the peak area after silylation becomes tractable.

a   b   c
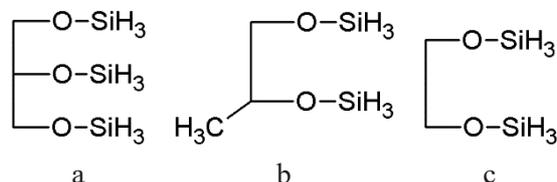
Figure 2.   Silylated glycerin, propylene glycol and ethylene glycol:
a: Trimethylsilyl ether of glycerin;
b: 1,2-Bis(trimethylsiloxy)propane;
c: 1,2-Bis(trimethylsiloxy)ethane.
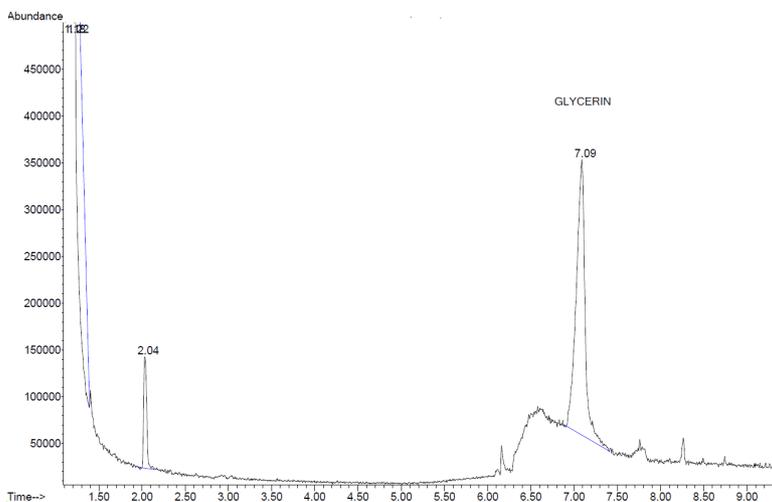
Figure 3.   Chromatogram of NG without silylation.

Analyses of glycerin and propylene glycol were calibrated in the silylated form using ethylene glycol as an internal standard. Figures 4 and 5 show the corresponding chromatograms. The retention times (*tr*) of IS-silylated, PG silylated and glycerin silylated are 4.02, 4.23 and 7.93 min, respectively.
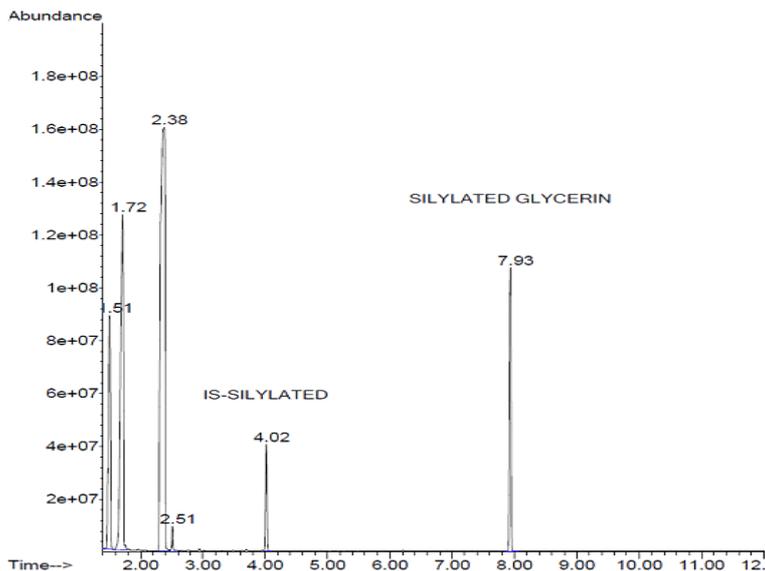

**Figure 4.**   Chromatogram of silylated NG with internal standard.
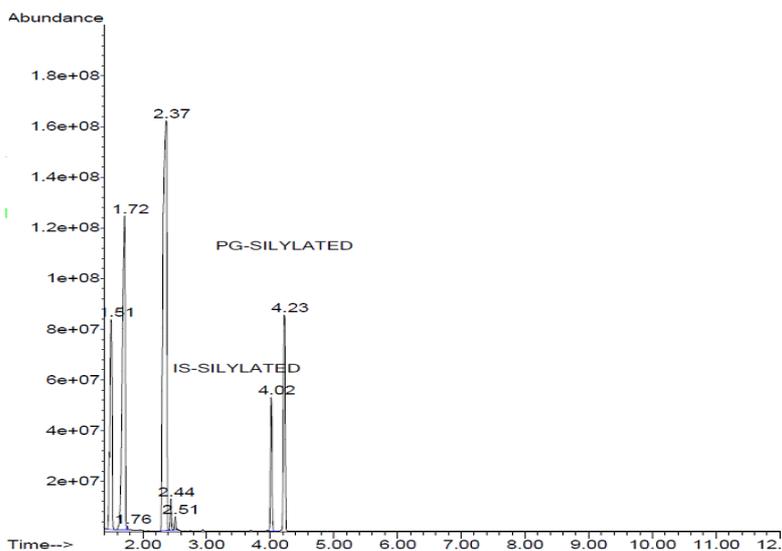
Figure 5. Chromatogram of silylated PG with internal standard.

The area ratios against concentration for glycerin and propylene glycol are represented in Figures 6 and 7, respectively. It is clear that both the glycerin and propylene glycol calibration curves had good linearity with a high correlation coefficient. Nevertheless, in order to validate the GCMS analysis, the calculation of %*RSD* was still necessary.
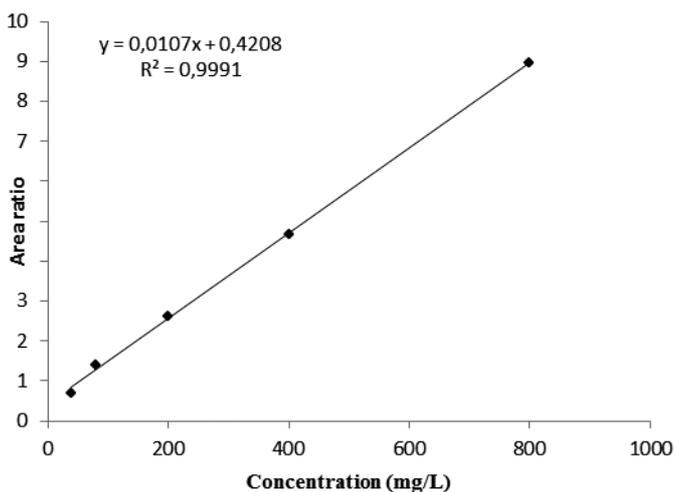
**Figure 6.** Calibration curve for glycerin.

y = 0,008x - 0,0015
R² = 0,9992
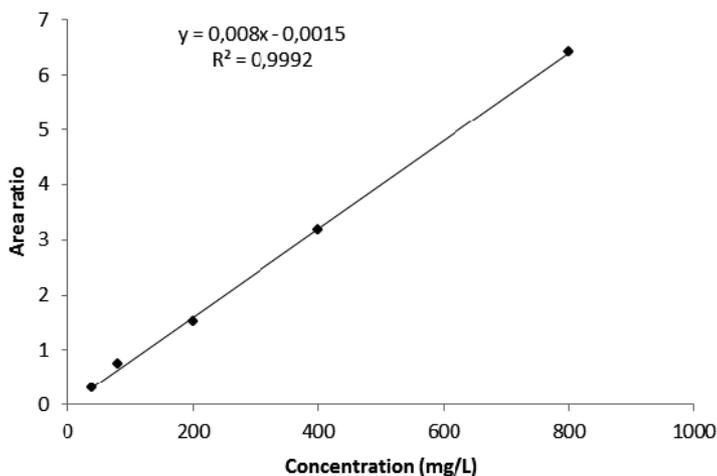
Figure 7. Calibration curve for propylene glycol.

**Table 1.** Validation of the calibration parameters of glycerin and propylene glycol

Compound	RRF_{area}	RRF_{tr}	$\%RSD_{area}$	$\%RSD_{tr}$
Glycerin	3.29	1.97	6.90	0.070
PG	1.65	1.05	1.84	0.073

Table 1 shows the calibration validation of the peak area and retention time. We concluded that the result was acceptable for both parameters, the $\%RSD$ for neither glycerin nor the one for propylene glycol exceeding 15%.

Figures 8 and 9 represent the chromatograms of the E-smoking liquid, both nicotine free and with nicotine (10 mg/mL), respectively. The first observation was the presence of glycerin ($tr=7.94$ min) and propylene glycol ($tr=4.23$ min) in both chromatograms.
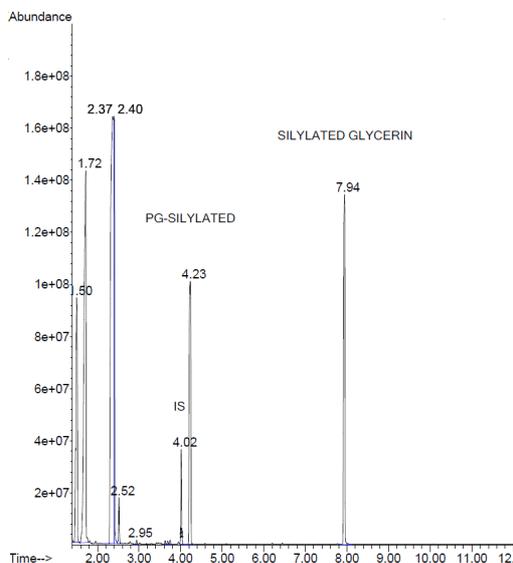
Figure 8. Chromatogram of E-smoking liquid, nicotine free, silylated.
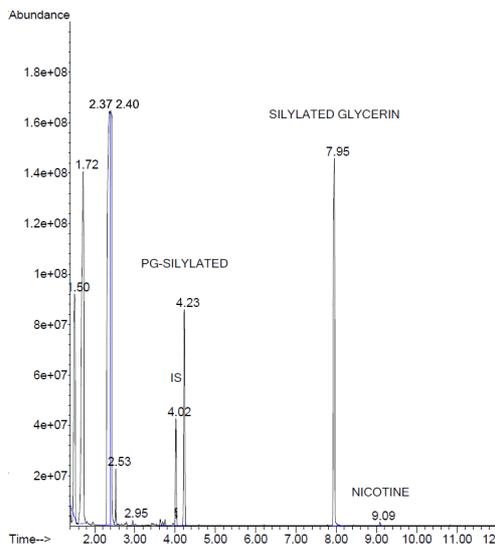
Figure 9. Chromatogram of E-smoking liquid, with nicotine (10 mg/mL), silylated.

The peak at $tr = 9.09$ min in Figure 9 is related to nicotine [13]. Despite the silylation process, the nicotine was identified in the E-smoking liquid and is unaffected by silylation.

The quantification of the volumes of glycerin ($V_{glycerin}$) and propylene glycol (V_{PG}) in both types of E-smoking liquid (10 mL) was performed using the calibration curves in Figures 6 and 7, respectively. The results obtained are represented in Table 2.

Table 2.   Quantification result of glycerin and propylene glycol

| Type of E-smoking liquid	$V_{glycerin}$	V_{PG}
Nicotine free	1.07	6.96
With nicotine (10 mg/mL)	1.35	4.78

In the case of the E-smoking liquid without nicotine, the volume of propylene glycol was 46% higher than the one in the second kind of the E-smoking liquid. This difference can be explained by the fact that the presence of nicotine needs aqueous solvation, therefore, the volume of propylene glycol is diminished in favour of water [14]. In addition, the presence of a high V_{PG} produces a better "vaping" effect, so that the consumer reproduces the same gestures as with real cigarettes [3].

Figure 10 shows the chromatograms of NG and PGDN, respectively, synthesized from pure laboratory grade ingredients. A comparison of these results with those of NG and PGDN standards indicated identical retention times (8.92 min for NG and 5 min for PGDN) and mass fragments. The chromatograms and mass spectra of both the standard and synthesized NG and PGDN are given as supplementary material.


a   b
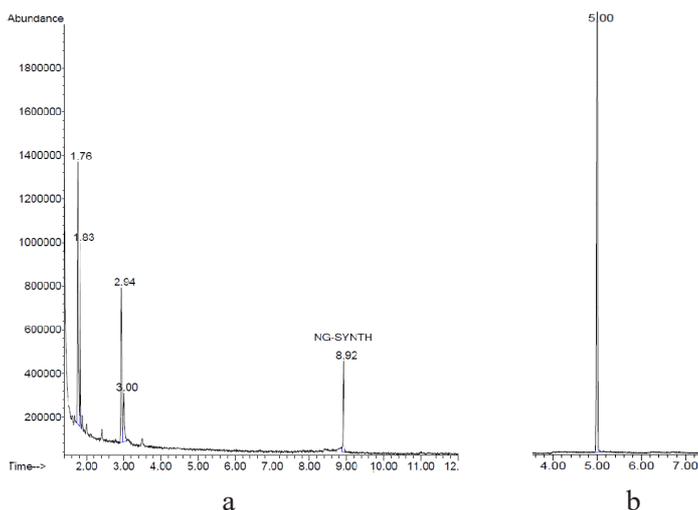
Figure 10.   Chromatograms of NG and PGDN synthesized from glycerol and propylene glycol, laboratory grade, (a) NG, (b) PGDN.

Figures 11 and 12 represent the chromatograms of Mixt 1 and Mixt 2, respectively. It is clear that NG and PGDN have been successfully synthesized and similar retention times were observed when compared with those of the NG and PGDN standards. However, in the case of the E-smoking liquid with nicotine (Mixt 2), the intensity of NG was higher. This is probably due to the presence of more glycerin in the precursor (Table 2). In addition, the lower propylene glycol content allows additional nitration of NG.
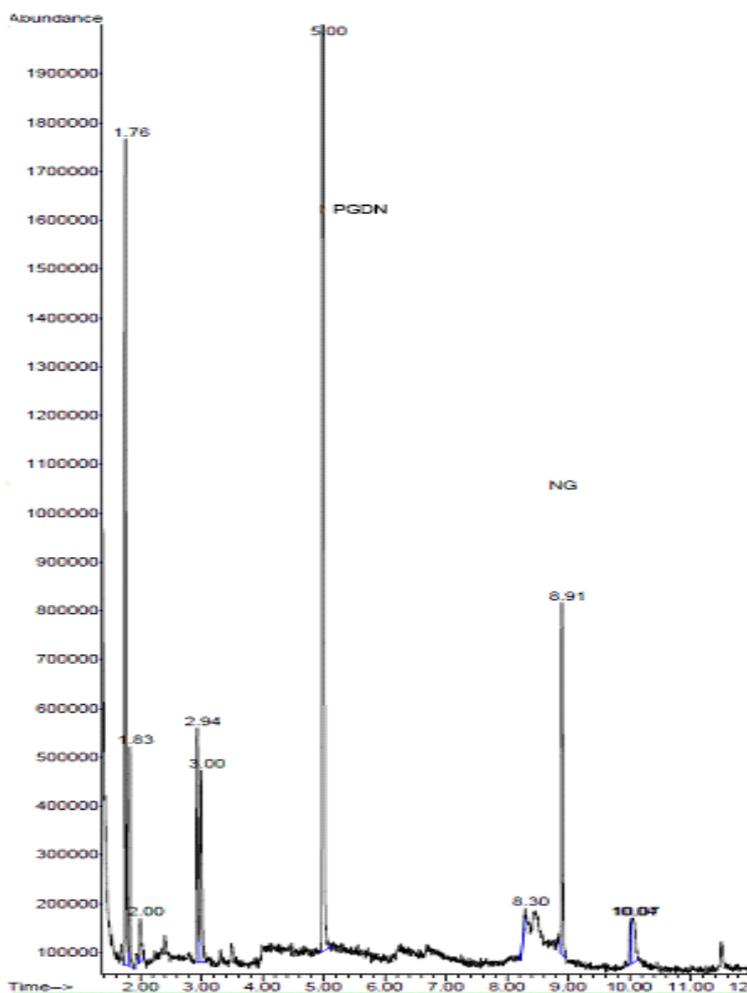
Figure 11. Chromatogram of the mixture (NG + PGDN) synthesized from E-smoking liquid, nicotine free.
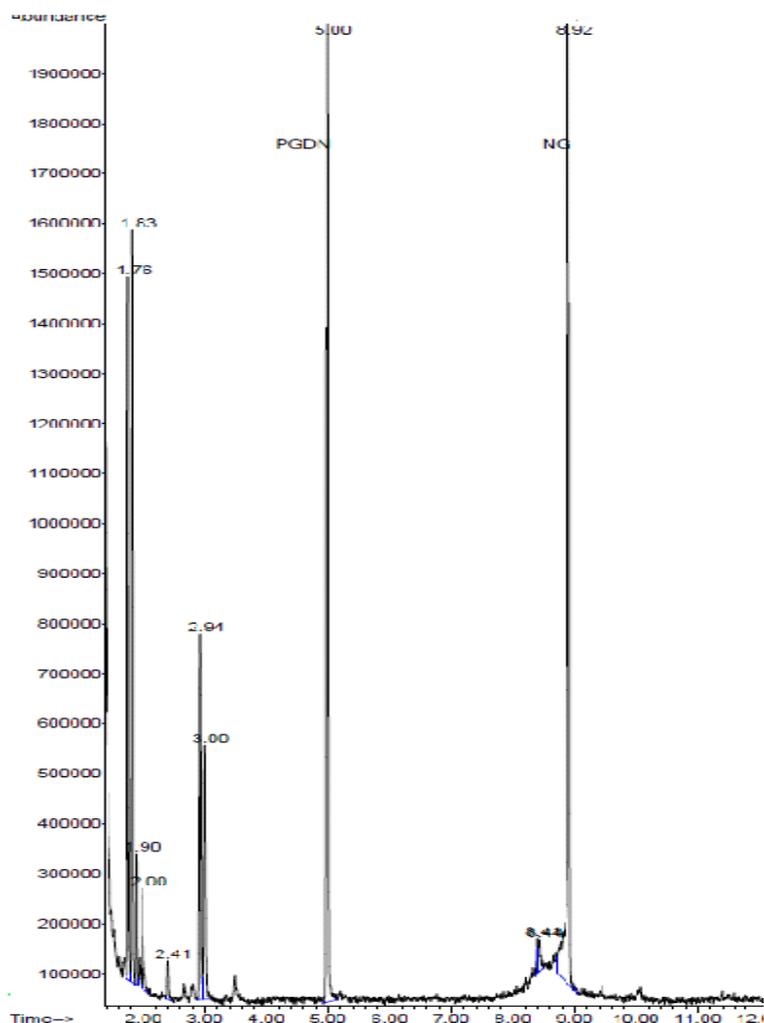
Figure 12. Chromatogram of the mixture (NG + PGDN) synthesized from E-smoking, liquid, with nicotine.

The peak for nicotine was not observed in the chromatogram related to the mixture synthesized from the E-smoking liquid with nicotine (Figure 12). This indicates that the purification process after synthesis was correctly carried out.

3.2 DSC analysis

Figure 13 shows the DSC thermograms of the synthesized explosives; we noted the evolution of the onset temperature when the heating rate was raised,

for both NG and PGDN. However, the decomposition of NG starts at a lower temperature than the one for PGDN. In fact, at a slow heating rate of 1 °C/min, NG decomposition starts at 116 °C, and for PGDN at 173 °C (Table 3). This behavior was observed at all heating rates (3, 5 and 8 °C/min). This accounts for the high temperature sensitivity of NG.

Table 3. Heat of decomposition and temperatures of the onset of NG and PGDN

| β, [°C/min]	T_{onset}, [°C]	T_{max}, [°C]	ΔH, [J/g]
NG			
1	115.93	122.08	3144.88
3	122.75	135.82	2937.02
5	134.78	142.61	3255.51
8	146.03	149.72	2990.58
Average			3082
PGDN			
1	172.83	182.19	4121.91
3	180.50	196.67	4134.39
5	182.00	203.00	4003.21
8	192.68	208.48	3788.00
Average			4011.87

β : Heating rate

Table 4. E_a determination of NG and PGDN by the Ozawa and Kissinger methods

Explosives	Ozawa		Kissinger		Literature values [17] [kJ/mol]
	Correlation factor (R^2)	E_a [kJ/mol]	Correlation factor (R^2)	E_a [kJ/mol]	
NG	0.9995	97.68	0.9994	97.86	167.2
PGDN	0.9982	133.07	0.9980	134.78	168.45

According to Table 4, both the Ozawa and Kissinger models [15] give similar values for the activation energies (E_a) of each explosive (NG and PGDN). However, the NG activation energy is lower than that of PGDN; it seems that NG is more sensitive to heat [16]. The literature [17] gives quasi-equal activation energy values for NG and PGDN (Table 4). However, the activation energies of the synthesized explosives (NG and PGDN) are lower, especially for the NG. This can be explained by the fact that the values presented in the literature relate to industrially synthesized materials.

Thermograms of Mixt 1 and Mixt 2 (Figure 13) show a lag of the peaks towards the PGDN decomposition for the mixture synthesized using the E-smoking liquid without nicotine, and towards the NG decomposition for the mixture synthesized using the E-smoking liquid with nicotine (10 mg/mL). It is clear that Mixt 2 is more sensitive to heat, this can be explained by the higher NG content, as confirmed by the GCMS results. In the other words, the DSC analyses allowed us to speculate about the composition of the mixture, and this could be useful in forensic analysis of explosive mixtures [18].
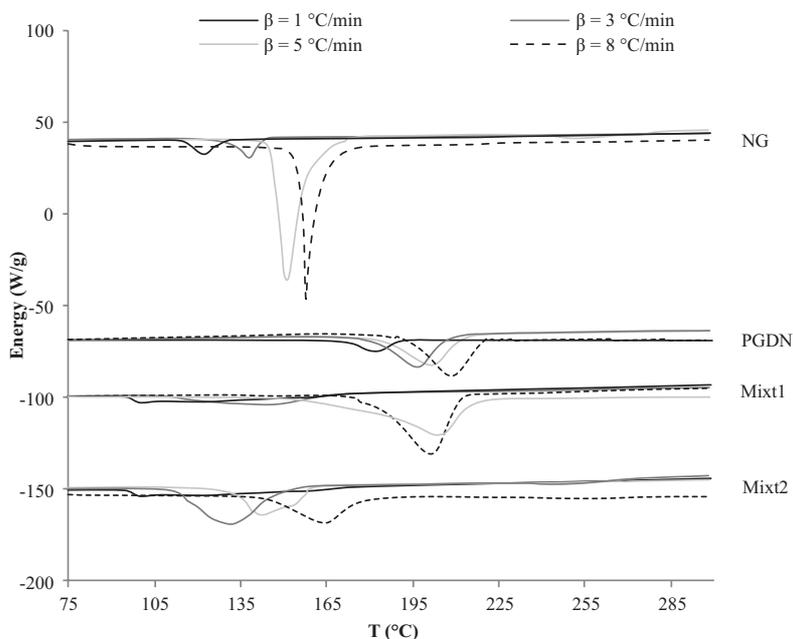
Mixt 1: NG + PGDN synthesized from E-smoking liquid, nicotine free.
Mixt 2:   NG + PGDN synthesized from E-smoking liquid, with
nicotine (10 mg/mL).

Figure 13. DSC Thermograms of the synthesized explosives, at different heating rates.

3.3 Brisance test

The brisance test was performed for all of the synthesized explosives. In addition and for comparison purposes, the test was also done with two conventional explosives (TNT and C4).

According to Figure 14, the detonation steady state is reached after about 25 to 30 mm for all of the explosives, with the highest brisance for C4 and the

lowest for TNT. The result obtained with PGDN was very close to that obtained with TNT. However, for the same length of charge, the NG indents are higher than the corresponding PGDN indents. In addition, the Mixt 1 and Mixt 2 indents are also higher than that of PGDN.
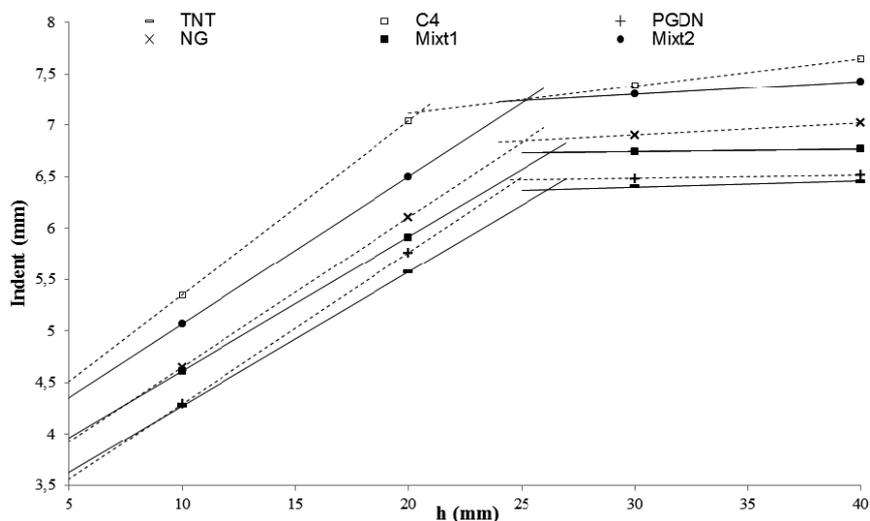
Figure 14. Brisance curves of the synthesized explosives, expressed as depth of the indent on the witness plate as a function of the length of the explosive charge. The asymptotic value was assumed to be representative of the brisance of the explosive.

Table 5. Brisance index of NG, PGDN and mixtures

Tube dimensions (Length × Φ_{inter} × Φ_{extr}) mm	B_{TNT}	B_{NG}	B_{PGDN}	B_{Mixt1}	B_{Mixt2}	B_{C4}
10 × 9.8 × 13.9	1	1.089	1.005	1.080	1.187	1.250
20 × 9.8 × 13.9	1	1.095	1.034	1.061	1.167	1.340
30 × 9.8 × 13.9	1	1.078	1.012	1.053	1.141	1.150
40 × 9.8 × 13.9	1	1.088	1.009	1.049	1.150	1.190
Average B	1	1.087	1.015	1.061	1.161	1.23

B: Brisance index = $h_{explosive}$ / h_{TNT}.
Mixt 1: NG + PGDN synthesized from E-smoking liquid, nicotine free.
Mixt 2: NG + PGDN synthesized from E-smoking liquid, with nicotine (10 mg/mL).

For better understanding, the brisance index (B), largely studied in previous work [19], was calculated for each explosive (Table 5). The results showed that

Mixt 2 is more brisant than all of the other synthesized explosives. This can be explained by the fact that this mixture, synthesized from the E-smoking liquid with nicotine, contained more NG (as confirmed by the DSC and GCMS analyses). The fact that Mixt 2 is more brisant than NG seems logical; the synthesized NG probably contains impurities, and the NG mixed with PGDN is certainly more brisant than the NG containing impurities which are not explosives. Mixt 1 is more brisant than PGDN and less brisant than NG. This is due to the fact that this mixture is composed mainly of PGDN, so the presence of the NG allows a higher brisance without reaching the brisance of NG.

4   Conclusions

The quantitative analysis of glycerin and propylene glycol used in two kinds of E-smoking liquids enabled us to quantify the compositions present in 10 mL rechargeable bottles. The main compounds present in the rechargeable E-smoking liquid are propylene glycol (50-70%) and glycerin (10-14%). The percentage of propylene glycol depends on the presence or absence of nicotine. Nevertheless, the PG content is sufficient for PGDN synthesis.

The values of the relative response factors and the relative standard deviations of the areas and retention times are acceptable and have helped us to speculate about the volume of glycerin and propylene glycol existing in the E-smoking liquids.

A study of the use of an E-smoking liquid for the synthesis of NG and PGDN explosives has been carried out. Analyses with different techniques has demonstrated that the presence of nicotine in the E-smoking liquid affects neither the synthesis nor the explosive performance of the NG and PGDN.

The synthetic procedure was similar for both explosives. The yield was about 58-65%, without any pretreatment of the E-smoking liquid. Nevertheless, the final composition of the explosive mixture depends on the type of E-smoking liquid.

The brisance test has shown proportionality between the brisance index and the NG concentration.

These results demonstrate the need to control these precursors to prevent their misuse in creating explosive charges. A technical solution could consist in the introduction of an inhibitor for nitration. Such a study is part of our ongoing work and investigation.

References

[1] de Andrade M., Hastings G., Angus K., Dixon D., Purves R., *The Marketing of Electronic Cigarettes in the UK*, Cancer Research, UK, Report No. 115991, November **2013**.

[2] Use of Electronic Cigarettes in Great Britain, *Action on Smoking and Health*, in press.

[3] Britton J., Bogdanovica L., *Electronic Cigarettes,* Division of Epidemiology and Public Health, University of Nottingham, Report No. 2014079, **2014**.

[4] Erbach G., *Electronic Cigarettes*, Library of the European Parliament, Report No.130494, **2013**.

[5] Vansickel A.R., Cobb C., Weaver M., Eissenberg T., A Clinical Laboratory Model for Evaluating the Acute Effects of Electronic "Cigarettes": Nicotine Delivery Profile and Cardiovascular and Subjective Effects, *Cancer Epidemiol., Biomarkers Prev.*, **2010**, *19*(8), 45-53.

[6] Matyáš R., Šelesovsky J., Jalový Z., Roháčová J., Synthesis and Characterization of Polyethylene Glycol Dinitrates, *Cent. Eur. J. Energ. Mater.*, **2011**, *8*(3), 145-155.

[7] Meyer R., Köhler J., Homburg A., *Explosives*, Sixth Completely Revised Edition, Wiley-VCH, Weinheim, **2007**, pp. 226-228; ISBN 3-527-60051-5.

[8] Akhavan J., *The Chemistry of Explosives*, RSC Ed, UK, **2004**, pp. 32-33; ISBN 0-85404-640-2.

[9] Fettaka H., Lefebvre M., Investigation of Commercial Precursors for the Synthesis of Liquid Nitroesters, *New Trends Res. Energ. Mater., Proc. Semin., 17th*, Pardubice, Czech Republic, **2014**, *18*-26 .

[10] Molever K., Simplified Assay of Diethylene Glycol and Ethylene Glycol in Various Raw Materials by Capillary Gas Chromatography, *J. Cosmet. Sci.*, **2010**, *61*, 225-234.

[11] Scanlon T.J., Willis D.E., Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept, *J. Chromatogr. Sci.*, **1985**, *23*, 333-340.

[12] Edgerley A., Techniques for Improving the Accuracy of Calibration in the Environmental Laboratory, *WTQA − 14th Annu. Waste Testing & Quality Assurance Symp.*, **1998**.

[13] Iwai M., Ogawa T., Hattori H., Zaitsu K., Ishii A., Suzuki O., Seno H., Simple and Rapid Assay Method for Simultaneous Quantification of Urinary Nicotine and Cotinine Using Micro-extraction by Packed Sorbent and Gas Chromatography-Mass Spectrometry, *Nagoya J. Med. Sci*., **2013**, *75*, 255-261.

[14] Purwono S., Murachman B., Wintoko J., Simanjuntak B.A., Sejati P.P., Permatasari N.E., Lidyawati D., The Effect of Solvent for Extraction for Removing Nicotine on the Development of Charcoal Briquette from Waste of Tobacco Stem, *Journal of Sustainable Energy & Environment*, **2011**, *2*, 11-13.

[15] Wu S., Chi J., Wu Y., Huang Y, Chu F., Horng J., Shu C., Charpentier J., Thermal Hazard Analysis of Triacetonetriperoxide (TATP) by DSC and GC/MS, *J. Loss*

Prev. Process Ind., **2012**, *25*, 1069-1074.

[16] Jones M.L., Lee E., Impact Sensitivity of Nitroglycerin, *J. Energ. Mater.*, **1997**, *15*, 193-204.

[17] Manelis G.B., Nazin G.M., Rubtsov I.Y.U., Strunin V.A., *Thermal Decomposition and Combustion of Explosives and Propellants*, Taylor and Francis, **2003**, pp. 128; ISBN 9780415299848.

[18] Kunzel M., Yan Q.L., Selesovsky J., Zeman S., Matyáš R., Thermal Behavior and Decomposition Kinetics of ETN and its Mixtures with PETN and RDX, *J. Therm. Anal. Calorim.*, **2014**, *115*, 289-299.

[19] Fettaka H., Lefebvre H.M, Ethylene Glycol Dinitrate (EGDN): from Commercial Precursors, Physicochemical and Detonation Characterizations, *Cent. Eur. J. Energ. Mater.*, **2015**, *12*(2), 287-305.