Explosive synthesis: novel intrinsically safe method and application with micro-channel reactor

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Abstract. Novel Micro-channel method was introduced into explosive synthesis process. The method was discussed hereby with its intrinsic safety including marvelous inner-structure, high heat-transfer efficiency, and high mass-transfer efficiency compared to traditional kettle-based method. Micro-channel reactor for explosive synthesis was established with high precision control, the temperature difference of oil flow between import and export of micro-channel reactors was measured to be no more than 3 °C, and the flux fluctuation of reactant flow were measured to be no more than 0.1ml/min. Micro-channel reactor was experimented with TATB explosive synthesis process. Nitration reaction showed no residue of raw material PG and 91.62% HPLC area of target material TNPG, alkylation reaction showed no residue of raw material TNPG and 98.01% HPLC area of target material TETNB, amination reaction showed 5.28% HPLC area of raw material and output of target material TATB. It was concluded to be verifiable including micro-channel method, the apparatus, and application in TATB synthesis process.

1. Introduction

Explosive, which supplied high energy for munitions similarly as other energetic materials, should be always involved with high hazardous reagent and high hazardous synthesis process such as nitration reaction, azide reaction, amination reaction, denitrogenation reaction, and et al. Explosive synthesis process must be severely treated or would induce serious combustion or explosion [1-2]. Some of these hazardous processes were detailed with their reaction runaway and process risk [3-4].

Though classical process with kettle-based batch production manner owned so much risk as described above, it should be unparalleled within explosive synthesis till recent year.

2. Micro-Channel Reactor

2.1. Micro-Channel and Micro-Channel Reactor

Micro-channel was concerned with its magic which causes the intense disaggregation of fluid drop, turbulent mixing of ingredients, and molecular level homogeneity of fluid mixture [5]. Micro-channel was thereafter found attractive in chemical synthesis [6-7] and sequent researches enriched our comprehension on chemical reactors [8-10].

Some novel characteristics of micro-reactor were followed. Firstly, reactant flow inside micro-channel owned geometric characteristic entirely different from kettle reactor, such as slight diameter and disciplinary interior structure, tiny reaction room and huge specific surface area. Equivalent diameter of the channel was from micron to millimeter really. For example, channel fabricated in
Karlsruhe [11] owned cross-sections arc 75µm x 90µm, active volumes 1cm³, which was several grade less than kettle reactor. Secondly, heat transfer of reactant flow inside micro-channel should be severely strengthened due to huge specific surface area and turbulent mixing, which caused heat transfer coefficient up to 25KW·m⁻²·K⁻¹ [12-13], which was several grade higher than kettle reactor. Thirdly, narrow channel and slight flow diameter shortened the distance and period of mass transfer. The reactant inside sub-millimeter channel was discussed theoretically [14-16] to show sufficient mixing on millisecond scale radially. Simultaneously, the equivalent diameter round micron scale should be remarkably smaller than thickness of the fluid border lamina round millimeter scale, reactant flow owned smaller Renault value inside micro-channel and owned viscous force higher than inertial force, then reactant flow acted as laminar flow and sufficient mixing resulted from diffusion [17]. Practically, the synthesis could be completed round several to tens seconds in micro-channel which was adequately faster than in kettle. Fourthly, temperature and fluctuate was controlled precisely due to really sufficient heat transfer, even acute exothermic reaction would be also processed under nearly isothermal condition. Hotspot and temperature steep emerged hardly so that reaction was intrinsically safe [18]. Such the performance would obviously benefit for explosive synthesis which owned temperature-sensitive ingredient and acute exothermic reactions.

2.2. Micro-Channel Reactor: for Explosive Synthesis

Explosive synthesis owned always hazardous ingredient and reaction, which should be controlled carefully and show intrinsic safety within micro-channel reactor.

Reaction period was firstly concerned, which was decreased remarkably from several hours generally inside kettle to tens seconds inside micro-channel. It was considered that turbulent micro-mixing saved the majority of reaction period inside micro-channel and molecular level synthesis should be instantly.

Reaction temperature should be emphasized in hazardous explosive synthesis. For an example, a reaction temperature and fluctuate should be 150±10°C inside traditional kettle and 145±2°C inside micro-channel with the same conversion and yield. The accident probability of thermal runaway was estimated to decrease from “frequently” to “seldom”. In order to remove the violence sequence technically, the kettle reactor must be accompanied with emergency releasing system which counted for the loss of general production value. Comparatively, the reaction process inside micro-channel would be intrinsically safe and result in no product loss, no releasing waste, no sequent disposal fee but more benefit.

Reaction pressure should be also emphasized. Ordinary pressure reaction and high pressure reaction, which must employ different reaction kettle and different production line, could be processed meaningful and economically inside the same micro-channel.

2.3. Apparatus Establishment

Micro-channel reactor was then established for explosive synthesis ourselves [19]. As described in figure 1, the apparatus was divided to three frames. The three frames were mutually isolated to avoid the coupling of dangerous sources and decrease process risk of the apparatus.

The left frame was green region for operators, employed no reactant, and kept the operators out of chemical risk.

The middle frame was yellow region for micro-channel, employed baffle to keep accident inside without leakage. There placed dangerous sources such as high temperature and high pressure, which showed high frequency and low damage.

The right frame was red region for accessory modules including mixers, pumps, acceptor, and temperature controller, also employed baffle to keep accident inside. There placed dangerous sources such as voluminous reactant and solution, which showed low frequency and high violence.

Generally, the operators would be safe enough inside green region due to intrinsic safety of the apparatus principle and reasonable arrangement as given in figure 1.
The micro-channel in the context was made of borosilicate glass and regularized micro-structure with turbulent mixing effect. The micro-channel and accessory modules were designed with flux up to 10 ml/min.

Figure 1. Experimental arrangement of micro-channel reactor.

3. Application

3.1. Verification Trials
The verification trials were attempted to ensure security and reliability of the apparatus including blank trial, water trial, organic solvent trial, vitriol trial, and et al. The primary thing of the trials was resistance of the flow path materials within pipeline, valve, joint, connector, and et al. These materials should be chosen to endure the organic solvent such as methanol, acetone, and toluene, and the inorganic acid such as concentrated sulphuric acid, nitric acid, and their mixture. These trials were attempted under atmospheric circumstance, heating conditions, pressure conditions, and complex conditions in turn. Some adjustment and optimization were processed so that reactant leakage could be avoided well in explosive synthesis reaction.

The secondary thing of the trials was automation of the apparatus. The vast parameters ran automatically including value setting, real-time vision, and real-time feedback. The interlocking devices were also settled automatically so that the risks could be isolated from mutual-coupling or damage to operators.

3.2. High Precision of oil flow
High precision was the requirement of the verification trials and also the emphasis of the apparatus practicality. Anomalous deviation and precision degradation happened always with mutual-matching failure between modules.

The oil flow flux showed anomalous firstly from the trials. The temperature deviation (T2-T3) seemed to be round 10 ~ 15°C which was really higher than prospective. The flowmeter was added to show the flux about 20 ~ 30ml/min, which was evidently lower than prospective 300 ~ 500ml/min. The reason was considered that the oil pressure at temperature controller export was remarkably lower.
than rating pressure of channel import, which led to lower flux and insufficient heat exchange. A gear pump was then plugged between channel and temperature controller. The oil pressure was taken up to slightly higher than necessary with gear pump and overpressure was relieved with safety valve at the export of gear pump. Thereafter, the oil flow was adjusted carefully to remain its pressure, temperature, and flux within appropriate range. Together with coordinated adjustment of all oil path modules in figure 1, the fluctuation of T1 decreased to round 0.5 ℃, the fluctuation of T2 decreased to 2 ℃, the difference (T2-T3) decreased to no more than 3 ℃, and so that the high precision of oil flow was obtained.

3.3. High Precision of reactant flow
The reactant flow acted as the keystone of the apparatus and should be with precious control.

The upper limit of reactant flow pressure was firstly settled as 1.8MPa according to explosive synthesis application in our laboratory. Then all the reactant flow field material was chosen with sufficient pressure resistance. The pressure of pump A and pump B was also settled no more than 1.8MPa. The reactant flow should be pumped with constant flux and associated pressure fluctuation. The reactant flow should be reviewed with overall cooperation of its temperature, pressure, flux, fluid typicality, and et al so that they could be controlled precisely. The reactant flow flux were measured constant during running course with fluctuation no more than 0.1ml/min.

Caution: sludge would lead to overpressure of reactant flow and shutdown of the pumps.

3.4. Explosive Synthesis
TATB (1,3,5-triamino-2,4,6-trinitrobenzene), a well-known insensitive high explosives (IHEs) [20] and familiar in our lab [21-23], was chosen herby for micro-channel reaction.

The synthesis route was described in figure 2, phloroglucine was employed as raw materials, and TATB was obtained through nitrilation reaction, alkoxilation reaction, and amination reaction. The synthesis result showed excellent hereby compared to literature [24-26].

![Figure 2: The synthesis route of TATB](image)

3.4.1. nitration reaction. The nitration reaction was processed with the apparatus in figure 1. Mixture of PG / concentrated sulphuric acid (w/w=6:94) was prepared as reactant A. Mixture of concentrated nitric acid / concentrated sulphuric acid (w/w = 1:10, 1:8, 1:5) was prepared as reactant B. Reactant A and reactant B was mixed and reacted inside the micro-reactor to synthesize TNPG.

Reactant B (1:10), Reactant B (1:8), and Reactant B (1:5) were employed in turn in the nine trials as given in Table 1. Raw material PG were entirely translated in all the nine trials according to high performance liquid chromatography analysis and target material TNPG was obtained about 87.35% ~ 90.90%, 87.07% ~ 91.62%, and 78.38% ~ 86.57% according HPLC area respectively.

From the nitration trials it showed that, the temperature should be higher than 50 ℃ or the product should form stagnation at micro-channel export, Reactant B(1:10) and Reactant B(1:8) would lead to friendly reaction similarly, and Reactant B(1:5) would lead to incomplete nitration. Under optimization condition, target material TNPG could be up to 91.62% HPLC area.
Table 1. The trials of nitrations reaction.

| Entry   | Reactant A mL/min | Reactant B mL/min | T °C | Equiv. | P bar | HPLC Area% |
|---------|-------------------|-------------------|------|--------|-------|-------------|
|         |                   |                   |      |        |       | PG          |
| XH-10-01* | 0.3              | 0.62*             | 55   | 1::3.7 | 8     | 0 90.90     |
| XH-10-02* | 0.3              | 0.62*             | 60   | 1:3.7  | 8     | 0 90.19     |
| XH-10-03* | 0.3              | 0.70*             | 60   | 1:4.2  | 9     | 0 87.35     |
| XH-08-01◊ | 0.3              | 0.44              | 55   | 1:3.7  | 8     | 0 87.07     |
| XH-08-02◊ | 0.3              | 0.44              | 60   | 1:3.7  | 7.4   | 0 87.42     |
| XH-05-04Δ | 0.3              | 0.29              | 55   | 1:3.7  | 7.1   | 0 86.57     |
| XH-05-05Δ | 0.3              | 0.29              | 60   | 1:3.7  | 7.4   | 0 84.03     |
| XH-05-06Δ | 0.3              | 0.29              | 65   | 1:3.7  | 7.4   | 0 78.38     |

Re: * use Reactant B (1:10), ◊ use Reactant B (1:8), Δ use Reactant B (1:5).

3.4.2. Alkoxylation reaction. The alkoxylation reaction was processed with the apparatus in figure 1 and a mixture of TNPG / triethyl orthoformate (w/w = 5:95, 10:90) was prepared as reactant A. The import B of micro-channel was plugged. The trials were detailed in Table 2.

The triethyl orthoformate acted as both the solvent and the alkoxylation reagent here. The import of micro-channel should be heat isolated to avoid heat loss and stagnation.

With increase of temperature from 80 °C to 160 °C, the HPLC area of mono-ethyl substitute and di-ethyloxylate substitute decreased, and the HPLC area of target material TETNB increased.

Compared to Reactant A (5:95) under similar conditions, Reactant A (10:90) showed higher yield of target TETNB.

The optimization reaction condition showed 98.01% HPLC area of target material TETNB, which was excellent for sequent scale trials.

Table 2. The trials of alkoxylation reaction.

| Entry   | Reactant A mL/min | T °C   | Equiv. | P bar | HPLC Area% |
|---------|-------------------|--------|--------|-------|-------------|
|         |                   |        |        |       | TNPG       |
|         |                   |        |        |       | M-         |
|         |                   |        |        |       | D-         |
|         |                   |        |        |       | Tri-       |
| WJ-05-01* | 0.5              | 80–85  | 30     | 0     | 4.92 60.63 31.42 3.03 |
| WJ-05-02* | 0.5              | 100–105| 30     | 0     | 19.84 54.26 25.32 |
| WJ-05-03* | 0.5              | 120–125| 30     | 0     | 0.00            |
| WJ-05-04* | 0.5              | 140–145| 30     | 0     | 0.00            |
| WJ-05-05* | 0.5              | 160–165| 30     | 0     | 0.00            |
| WJ-10-01◊ | 0.5              | 79–80  | 16     | 0     | 17.45 69.05 13.50 0 |
| WJ-10-02◊ | 0.5              | 97–100 | 16     | 0     | 4.113 51.35 35.66 3.88 |
| WJ-10-03◊ | 0.5              | 120–125| 16     | 0     | 1.69 2.93 93.26 |
| WJ-10-04◊ | 0.5              | 140–145| 16     | 0     | 0.00            |
| WJ-10-05◊ | 0.5              | 160–163| 16     | 0     | 0.00            |

Re: * use Reactant A (5:95), ◊ use Reactant A (10:90).

3.4.3. Amination reaction. The amination reaction was processed with the apparatus in figure 1. The mixture of TETNB / toluene (w/w = 5:95) was prepared as reactant A and the ammonia (NH3 / H2O =
26 ~ 28 %) was prepared as reactant B. The trials were detailed in Table 3. TATB was obtained and residue of TETNB was measure with HPLC method as in the table 3.

**Table 3.** The trials of amination reaction.

| Entry | Reactant A mL/min | Reactant B mL/min | T ℃ | P bar | HPLC Area of TETNB % | Re |
|--------|-------------------|-------------------|------|-------|----------------------|----|
| AJ-08-01 | 1 | 1 | 80–83 | 0 | 96.18 | ultrasonic |
| AJ-08-02 | 1 | 1 | 80–83 | 3 | 97.38 | |
| AJ-08-03 | 1 | 1 | 100–105 | 3 | 101.41 | ultrasonic |
| AJ-08-04 | 1 | 1 | 100–105 | 3 | 100.63 | |
| AJ-11-01 | 1 | 1 | 80–83 | 12.4/8.8 | 87.97 | |
| AJ-11-02 | 1 | 1 | 100–108 | 12.4/8.8 | 37.63 | |
| AJ-11-03 | 1 | 1 | 120–123 | 13.3/8.8 | 27.77 | |
| AJ-11-04 | 1 | 1 | 120–124 | 15.5/11.8 | 5.28 | |
| AJ-11-05 | 1 | 1 | 130–132 | 15.8/12 | 22.46 | |

According to the former four trials in Table 3, residue rate of raw material TETNB was really high under 80–83 ℃ and nearly 100% under 100–105 ℃, ultrasonic showed no evidential difference within the trials. It was presumed that gasification of reactant induce the excessive velocity and insufficient reaction of the reactant flow.

The sequent trials in Table 3 were arranged with back pressure valve which added temperature, pressure, and more reaction time. Then the reaction looked ordinary according to the residue rate of raw material.

Some other solvent such as ethanol was observed to show less reaction activity than toluene.

The optimization reaction condition showed 5.28% HPLC area of residue raw material, which should benefit for scale-up.

### 4. Conclusion

Explosive synthesis was reviewed with high hazardous reagent and high hazardous synthesis process. Traditional kettle-based synthesis process was replaced by novel micro-channel method.

Micro-channel method was reviewed with its intrinsic safety including marvelous inner-structure, sufficient heat transfer, sufficient mass transfer, high precision control of temperature, and et al.

Micro-channel reactor for explosive synthesis was established. The apparatus was divided to three mutually isolatable frames with reactant flux up to 10 ml/min. The apparatus was attempted with verification trials, high precision control trials of oil flow, and high precision control trials of reactant flow. The temperature fluctuation of oil flow at export of temperature controller was decreased to be less than 0.5 ℃, The temperature fluctuation of oil flow at import of temperature controller was decreased to be less than 2 ℃, The temperature difference of oil flow between import and export of micro-channel reactors was decreased to no more than 3 ℃, the flux fluctuation of reactant flow were measured no more than 0.1 ml/min.

Micro-channel reactor was experimented with TATB explosive synthesis process. Under the nitration reaction of phloroglucine, target material TNPG could be up to 91.62% HPLC area. Under alkoxylation reaction of TNPG, target material TETNB showed 98.01% HPLC area. Under amination reaction of TETNB, target material TATB was obtained and residue TETNB showed 5.28% HPLC area.

It was concluded to be verifiable including micro-channel method, the apparatus, and application in TATB synthesis process.
References

[1] Yu Weifei and Huang Jinlun 2019 Journal of Ordnance Equipment Engineering 2016(9) 142 – 7

[2] Zhao Jingsong, Chen Wanghua and Lu Yi 2015 Chemical Process Safety Beijing: Chemical Industry Press

[3] Zhang Fan, Jiang Jie and Huang Fei etc. 2013 Occup Health & Emerg Rescue 31(4) 187-91

[4] Wang Xiaofeng, Chen Wanghua and Xue Yan 2007 Initiators & Pyrotechnics 03 18-22

[5] Baldyga J and Pohorecki R 1995 Chem. Eng. J. 58 183-95

[6] Ehfeld W, Hessel V and Mo K H 1996 Potential and Realization of Microreactors. In: Ehfeld W, Microsystem Technol. for Chem. and Biol. Microreact ors. Weinheim: Verlag-Chemie 1-28

[7] Lerous J J, Harold M P and Ryley J et al 1996 Microfabricated Minichemical Systems: Technical Feasibility. In: Ehfeld W Microsystem Technol. for Chem. and Biol. Microreact ors. Weinheim: Verlag-Chemie 51- 69

[8] Yang Kuan, Chu Guangwen and Shao Lei 2009 Chinese Journal of Chemical Engineering 17(4) 546-51

[9] Schubert K 1998 Chem. Ing. Tech. 27(10) 124-7

[10] Ehfeld W, Hessel V and Lowe H 2000 Microreactors: New Technology for Modern Chemistry, Weinheim: Willy-VCH

[11] Bier W, Keller W and Linder G etc 1993 Chemical Engineering and Processing 32 (1993) 33-43

[12] Schubert K, Bier W and Brandner J et al 1998 Realization and Testing of Microstructure Reactors Micro Heat Exchangers and Micromixers for Industrial Applications in Chemical Engineering In: Ehfeld W, Rinard I H, Wegeng R S. Process Miniaturization: 2nd International Conference on Microreaction Technology, IMERT2; Topical Conference Preprints, New Orleans, USA: AICHe, 88-95

[13] Brandner JJ, Emig G and Schubert K et al 2003 Chem. Eng. J. 101(1-3) pp 217-24

[14] Cussler E L 1997 Diffusion Mass Transfer in Fluid Systems Cambridge: Cambridge University Press

[15] Krog J P, Branebjerg J and Nielsen C R et al 1996 Experiment s and Simulations on a Micro- mixer Fabricated Using a Planar Silicon/Glass Technology Micro-electro-mechanical Systems (MEMS) 1996 International Mechanical Engineering Congress and Exposition, New York

[16] Ehfeld W, Golbig K and Hessel V,et al 1999 Industrial and Engineering Chemistry Research 38 1075-82

[17] Burns J R and Ramshaw C 1999 Chemical Engineering Research and Design 77 206-11

[18] Srinivasan R, Hsing I M and Berger P E et al 1997 AICHE J. 43 3059- 69

[19] Yu Weifei 2017 Energetic materials: development and feasibility of multi-channel synthesis reactors China Defence Report GF-A9018399M DEC 26

[20] B M Dobratz 1994Insensitive high explosive triaminotrinitrobenzene (TATB): development and characterization NTIS: LA-13014-H

[21] Yu Weifei 2002 TATB product quality manufactured with ammonium carbonate Beijing: Beijing Institute of Technology

[22] Rui Liu, Weifei Yu and Tonglai Zhang etc 2013 Phys. Chem. Chem. Phys. 15 7889-95 7889

[23] Yu Weifei, Zhang Tonglai and Huang Yigang etc 2009 Journal of Hazardous Materials 168 (2009) 952-4

[24] David Cantillo, Markus Damm and Doris Dallinger et al 2014 Org. Process Res. Dev. 18 1360–6
[25] N B Zuckerman, M Shusteff, P F Pagoria and A E Gash 2015 Microreactor flow synthesis of the secondary high explosive 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105). in New Trends in Research of Energetic Materials, Czech

[26] Ping Zhang, M Grace Russell and Timothy F Jamison 2014 Org. Process Res. Dev. 18 1567–70