

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 0.1 ml/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, alkoxylation 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, should be always involved with high hazardous reagent and high hazardous synthesis process such as nitration, oxidization, amination, denitrogenation, and et al. Explosive synthesis process must be severely or would induce reaction runaway and process risk. As described above, classical process with kettle-based batch production manner owned so much risk and seemed irreplaceable till recent year.

2. Micro-Channel Reactor

2.1. Micro-Channel and Micro-Channel Reactor

Micro-channel, causes intense disaggregation of fluid drop, turbulent mixing of ingredients, and molecular level homogeneity of fluid mixture. Should be attractive in chemical synthesis and improve our comprehension on chemical reactors. **Micro-channel reactor**, Firstly reactant flow hereby owned geometric characteristic entirely different from kettle-reactor such as slight diameter and disciplinary interior structure, tiny reaction room and huge specific surface area. Micro-channel reactor owned active volumes several grade less than kettle reactor. Secondly, heat transfer of reactant flow should be severely strengthened due to huge surface area and turbulent mixing. Thirdly, narrow channel and slight flow diameter shortened the distance and period of mass transfer. The reactant showed sufficient mixing on millisecond scale theoretically. Simultaneously, reactant flow owned smaller Renault value hereby and viscous force higher than inertial force, then acted as laminar flow and sufficient mixing. The synthesis hereby could be completed practically within several to tens seconds remarkably faster than in kettle. Fourthly, parameters fluctuate was controlled precisely due to really sufficient heat transfer, even acute exothermic reaction would be also processed under nearly isothermal condition. Such these would obviously benefit for explosive synthesis.

2.2. Micro-Channel Reactor: for Explosive Synthesis

Explosive synthesis always owned hazardous ingredient and reaction and showed safety improvement within micro-channel reactor. Reaction period decreased remarkably from several hours inside kettle to tens seconds inside micro-channel. Reaction temperature should be emphasized in hazardous explosive synthesis and temperature fluctuate would reduce remarkably here to diminish thermal runaway risk and accident probability. Comprehensively reaction process here 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.

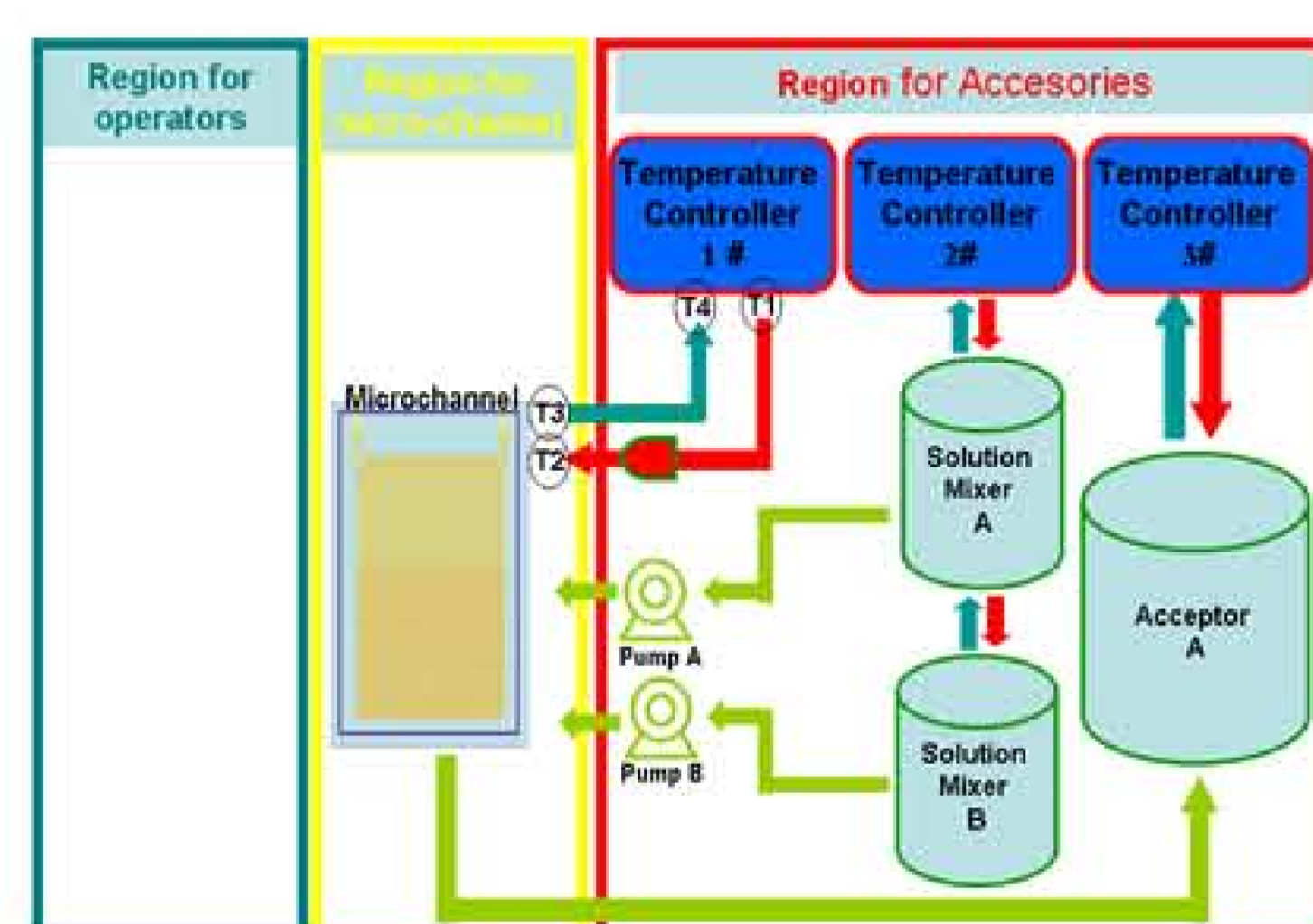


Figure 1. Experimental arrangement of micro-channel reactor.

2.3. Apparatus Establishment

Micro-channel reactor was then established for explosive synthesis as described in figure 1, the apparatus was divided to three frames mutually-isolated to avoid the coupling of dangerous sources and decrease process risk of the apparatus. The left frame was green for operators, employed no reactant, and kept the operators out of chemical risk. The middle frame was yellow for micro-channel, employed baffle to keep accident inside without leakage. There placed dangerous sources including high temperature and high pressure, which showed high frequency and low damage. The right frame was red 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.

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.

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.

Primarily, resistance of the flow path materials to endure the organic solvent, inorganic acid, and their mixture under atmospheric circumstance, heating conditions, pressure conditions, and complex conditions in turn. Some adjustment should be processed.

Secondarily, automation of the apparatus including value setting, real-time vision, real-time feedback, and interlocking devices so that the risks could be isolated from mutual-coupling or damage to operators.

3.2. High Precision of oil bath

High precision, the requirement of verification trials and the emphasis of practical apparatus. The oil flow flux showed anomalous firstly from the trials. The temperature deviation (T2-T3) seemed really higher than prospective. The flowmeter was added to show the flux evidentially lower than prospective.

The **reason** was considered that temperature controller export oil with lower pressure, led to lower flux and insufficient heat exchange. Novel pressure adaptor was introduced and the oil flow was adjusted to remain flux, pressure, and temperature within appropriate range. Together with coordinated adjustment of all oil path modules in figure 1, fluctuation of T1 decreased to ~0.5 °C, fluctuation of T2 decreased to ~2 °C, difference (T2-T3) decreased to no more than 3 °C, and so that the high precision of oil bath was obtained.

3.3. High Precision of reactant flow

The **reactant flow** acted as the keystone hereby and should be controlled preciously. The **upper limit** of reactant flow pressure was firstly settled as 1.8MPa. Then all the reactant flow field material would be chosen with sufficient pressure resistance. The pressure of pump A and pump B was settled less than 1.8MPa. The reactant flow should be with constant flux and less fluctuation. The reactant flow was then reviewed with overall cooperation of its temperature, pressure, flux, fluid typicality, and et al so that they could be controlled preciously.

3.4. Explosive Synthesis

TATB synthesis route was attempted within micro-channel reaction.

3.4.1 nitration reaction. Mixture of PG / H₂SO₄ (w/w=6:94) was prepared as reactant A. Mixture of HNO₃ / H₂SO₄ (w/w = 1:10, 1:8, 1:5) was prepared as reactant B. A and B was mixed and reacted to synthesize TNPG. The nine trials was given in Table 1 with HPLC result. Raw material PG were entirely translated and target material TNPG was obtained with high yield. Conclusively, reaction temperature should be higher enough to avoid flow stagnation at export, optimization condition would lead to target TNPG with yield up to 91.62%.

3.4.2. alkoxylation reaction. Mixture of TNPG / triethyl orthoformate (w/w = 5:95, 10:90) was prepared as reactant A. The import B was plugged. The triethyl orthoformate acted as both the solvent and the alkoxylation reagent. The import of micro-channel should be heat-isolated to avoid heat loss and stagnation. Conclusively, with increase of temperature from 80 °C to 160 °C, mono-ethyl substitute and diethoxyethyl substitute decreased, and target material TETNB increased. A(10:90) showed higher yield compared to A (5:95). Optimization condition showed TETNB with yield up to 98.01%.

3.4.3. amination reaction. 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 former four trials in Table 3 showed residue TETNB really high, ultrasonic showed no beneficial result. Gasification of reactant was presumed to lead to insufficient reaction. The sequent trials in Table 3 were arranged with back pressure valve which optimized the conditions and made the reaction ordinarily. Other solvent such as ethanol was trialed with less reaction activity. Optimization condition showed 5.28% HPLC area of residue raw material.

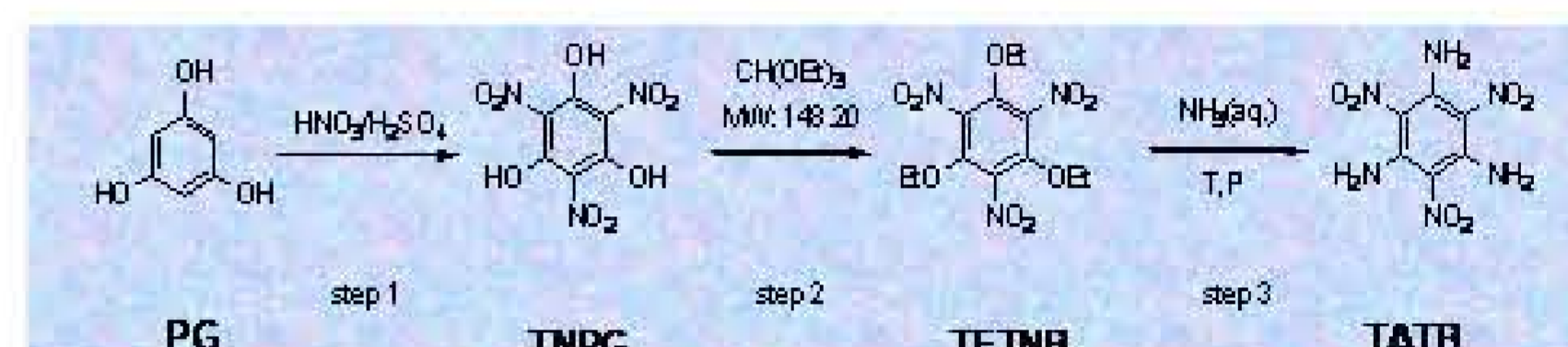


Figure 2. The synthesis route of TATB

Table 1. The trials of nitration reaction

Entry	Reactant A mL/min	Reactant B mL/min	T °C	Equiv.	P bar	HPLC Area%	
						PG	TNPG
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-08-03‡	0.3	0.44	65	1:3.7	7.4	0	91.62
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).

Table 2. The trials of alkoxylation reaction

Entry	Reactant A mL/min	T °C	Equiv.	P bar	HPLC Area%		
					TNPG	M-	D-
WJ-05-01*	0.5	80~85	30	0	4.92	60.63	31.42
WJ-05-02*	0.5	100~105	30	0	0	19.84	54.26
WJ-05-03*	0.5	120~125	30	0	0	0.00	8.36
WJ-05-04*	0.5	140~145	30	0	0	0.00	0.00
WJ-05-05*	0.5	160~165	30	0	0	0.00	0.00
WJ-10-01‡	0.5	79~80	16	0	17.45	69.05	13.50
WJ-10-02‡	0.5	97~100	16	0	4.113	51.35	35.66
WJ-10-03‡	0.5	120~125	16	0	0	1.69	2.93
WJ-10-04‡	0.5	140~145	16	0	0	0.00	0.00
WJ-10-05‡	0.5	160~163	16	0	0	0.00	0.00

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

Table 3. The trials of amination reaction

Entry	Reactant A mL/min	Reactant B mL/min	T °C	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	

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 owned 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 reactant flow. The temperature fluctuation of oil flow at export decreased to be less than 0.5 °C, the temperature difference of oil flow between import and export of micro-channel reactors decreased to no more than 3 °C, the flux fluctuation of reactant flow were measured no more than 0.1 ml/min.

TATB explosive synthesis was processed within Micro-channel reactor. Nitration reaction could lead to TNPG yield up to 91.62%. Alkoxylation reaction showed yield up to 98.01%. Amination reaction showed residue 5.28%.

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