

## $T_{cf}$ and MTSR of Toluene Nitration in Mixed Acid

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Toluene nitration with mixed acid is a very complex process, because there are many reactions involved in the nitrotoluene production process, such as mononitration as a main reaction, dinitration, trinitration, oxidation, and decomposition of products as side reactions. Therefore, it is difficult to calculate an accurate MTSR for thermal hazard evaluation of the desired reaction. Here, isothermal reactions at 30 °C -70 °C were carried out by reaction calorimeter RC1e, and products in the organic phase were analyzed by GC-MS. Results show that the heat generation and dinitrotoluenene ratio both increased with the increasing reaction temperature. Afterwards,  $T_{cf}$  curves and MTSRs of the reactions at 30 °C, 40 °C and 50 °C were obtained with different methods, which were: method 1:  $T_{cf}$  and MTSR were obtained based on the equations described as  $T_{cf} = T_r + X_{ac} \Delta T_{ad} \frac{M_{r,t}}{M_{r(0)}}$ , MTSR = max( $T_{cf}$ ); method 2:  $\Delta T_{ad}$  in method 1 is replaced with  $\Delta T_{ad}/\text{yield}$ ; method 3: the

reaction heat measured at 70 °C was used to calculate  $\Delta T_{ad}$ , so as to calculate  $T_{cf}$  and MTSR; method 4:  $T_{cf}$  was calculated by  $T_{cf} = T_r + \left[ \frac{X_{HT} \Delta H_{HT} - X_{LT} \Delta H_{LT}}{C_p M_r} \right]_{\text{with the same mass of toluene}}$ . The results indicate that, method 1, 2 and 3 are

established based on the assumption that potential energy is in direct proportion to the amount of toluene added, however in fact, nitration and dinitration are both easier to occur in excess nitric acid at the early stage of toluene feeding, namely, latent energy of per unit mass of toluene at this time is higher. Therefore,  $T_{cf}$  and MTSRs calculated by the first, second and third methods are not applicable for the complex toluene nitration. And the method 4 takes the exothermic reaction without heat accumulation at high temperature as a reference, which the desired reaction would achieve when cooling failure occurred, and thus obtains more reasonable  $T_{cf}$  and MTSR. It also can be found, MTSRs obtained based on the first method was the lowest, and that obtained by method 4 were the highest, which also indicates the result obtained by method 4 is more conservative.

### 1. Introduction

Toluene nitration in mixed acid of nitric acid and sulfuric acid is a very complex process. The overall reaction rate is limited by the combined effect of both mass transfer and chemical reaction (Lu, 1993). Mononitrotoluene (MNT), as a main product of the reaction, has three isomers, i.e., o-nitrotoluene, m-nitrotoluene, and p-nitrotoluene. At the same time, the reaction process also includes side reactions, such as dinitration and trinitration reactions, as well as oxidation reactions, which generate dinitrotoluene DNT, trinitrotoluene TNT, and some oxidation products (Chen et al., 2003), and these side reactions are often aggravated with the increasing temperature. Moreover, toluene nitration is also a dangerous reaction, with violent heat release, and many scholars have studied the thermal runaway hazard. For example, Chen, Wu (1996), Luo and Chang(1998) all derived kinetic parameters from reaction calorimetry experiments, and evaluated thermal stability of this reaction. D'Angelo et al. (2003) developed a methodology for toluene mononitration which was carried out in a batch reactor, and gave an optimum procedure to maximize conversion. We have also previously tested the reaction for its exothermic characters within a range of 30-50 °C, and calculated MTSR (Maximal Temperature attainable by runaway of the desired Synthetic Reaction) of the reaction, based on the method proposed by Gyax and Stoessel (Chen, 2008). However, the above

evaluations are all performed based on the thermodynamics and kinetics parameters obtained under normal process. Taking the MTSR calculation under a semi-batch reaction for example, this evaluation is carried out based on the cooling failure scenario (Gygax, 1990, and Stoessel, 2008), and the calculation formulae for a simple reaction are listed in formulae (1)-(3) (Stoessel, 2008):

$$T_{cf} = T_r + X_{ac} \Delta T_{ad} \frac{M_{r,f}}{M_{r(0)}} \quad (1)$$

$$\text{MTSR} = \max(T_{cf}) \quad (2)$$

$$X_{ac} = X_{fd} - \frac{\int_0^t q_r d\tau}{\int_0^\infty q_r d\tau} \quad (3)$$

$$\Delta T_{ad} = \frac{\int_0^\infty q_r d\tau}{C_p M_{r,f}} = \frac{\Delta H}{C_p M_{r,f}} \quad (4)$$

where,  $T_{cf}$  is the temperature after cooling failure,  $T_r$  is the temperature of reaction mass,  $X_{ac}$  is an accumulation degree,  $\Delta T_{ad}$  is adiabatic temperature rise,  $M_{r,f}$  is the total mass after feeding,  $M_{r(0)}$  is the total

mass during feeding, and  $q_r$  is the rate of heat release.

Apparently, this calculation is based on the test results under a certain reaction process, however, when side reactions are triggered by the increase of temperature, the impact of heat generated from the side reactions on the reaction system is not taken into account (Lerena et al., 1996). Particularly, for the toluene nitration process, both main and side reactions are very complex, thus it is actually difficult to predict the thermal accumulation and hazard just based on the measurement results under normal operation condition. Therefore, here we attempt to analyze the heat accumulation during toluene nitration based on the results of reaction calorimetry. As known, toluene nitration is performed during 30 °C-50 °C. Thus, the reactions at 30 °C, 40 °C, and 50 °C are tested, as well as that at higher temperatures (60 °C and 70 °C), so as to explore the calculation method of MTSR for the toluene nitration system.

## 2. Experimental

Reagents: nitric acid, 65-68 %; sulfuric acid, 95-98 %; and toluene, ≥99.5 %. All of the above reagents were analytically pure, and were manufactured by Shanghai Lingfeng Chemical Reagent Co., LTD. 630 g of mixed acid were employed in the tests with a mass ratio of: nitric acid/sulfuric acid/water = 13/66/21.

Equipment: Reaction Calorimeter RC1e, manufactured by Mettler-Toledo Co., Switzerland, equipped with an MP10 glass reactor.

Experimental conditions:

Rotation rate: 250 rpm

Feeding rate: 2 g·min<sup>-1</sup> or 1 g·min<sup>-1</sup>

Feeding mass of toluene: 100g

The isothermal experiments were carried out at the temperatures of 30 °C, 40 °C, 50 °C, 60 °C, or 70 °C.

After RC experiments, the two phases product, i.e., an acid phase and an organic phase, were separated. The organic phase was washed with a 2 % (wt %) NaHCO<sub>3</sub> solution and deionized water, then the water in the organic phase was removed with anhydrous magnesium sulfate, and finally, the products were analyzed by gas chromatography-mass spectrometry.

## 3. Results and discussion

### 3.1 RC test results

The experiment results are shown in Figure 1 and Table 1. The feeding rate used in the experiments of 30 °C, 40 °C, and 50 °C was 2 g·min<sup>-1</sup>. As the test result of 50 °C showed that the temperature difference between the reactant and the jacket was very great, in order to prevent damage of the glass reactor caused by the great temperature difference, a feeding rate of 1 g·min<sup>-1</sup> was employed to the 60 °C and 70 °C reactions.

The straight line marked 1 in Figure 1 corresponds to the termination time of the feeding with 2 g·min<sup>-1</sup>, and the line marked 2 is the termination time of the feeding rate 1 g·min<sup>-1</sup>. As found from Figure 1, the maximum heat release rate  $q_r$  appears at the beginning of feeding, then  $q_r$  decreased gradually with the dosing of

toluene; And for the tests at 30 °C, 40 °C, and 50 °C, there are still a lot of heat accumulation at the point of charging termination; whereas heat generation has been terminated even before the end of the feeding in the 60 °C and 70 °C reactions.

Analysis results of the products are summarized in Table 2. Obviously, the yield of DNT increases with the reaction temperature, it indicates that the toluene dinitration increases with the reaction temperature. Also, the amount of nitric acid consumed is calculated according to the amount of the products, wherein it is assumed that, when 1 mol MNT is generated, 1 mol HNO<sub>3</sub> is consumed, and when 1 mol DNT is generated, 2 mol HNO<sub>3</sub> is consumed. The amount of pure HNO<sub>3</sub> in mixed acid before the experiment was about 81.9 g, so that it can be considered that nitric acid had been consumed up before charging termination in the 60 °C and 70 °C reactions, in conjunction with Figure 1 and Table 2.

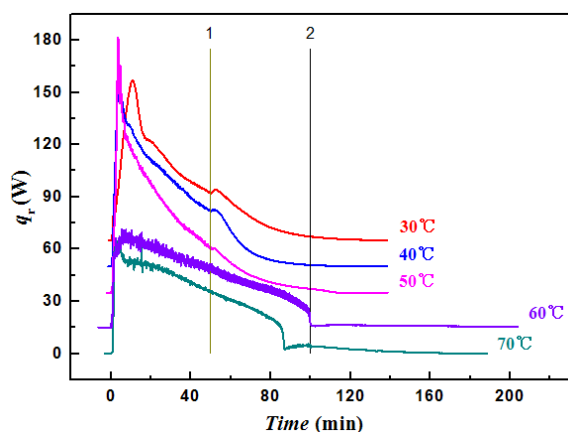


Figure 1: heat generation rate of toluene mononitration

Table 1: RC test results of toluene mononitration under different experimental conditions

Isothermal temperature (°C)	Feeding rate (g·min <sup>-1</sup> )	average value of specific heat capacity C <sub>p</sub> (J·g <sup>-1</sup> ·K <sup>-1</sup> )	maximum heat release rate q <sub>r,max</sub> (W)	ΔH (kJ)
30	2	1.84	92.0	180.7
40	2	1.89	107.7	196.1
50	2	1.92	146.6	198.7
60	1	1.93	60.7	199.5
70	1	1.98	64.2	207.6

Table 2: Yield of MNT and the by-product DNT under different reaction conditions

Isothermal temperature (°C)	Yield of MNT (%)	Yield of DNT (%)	Yield of (MNT + DNT) (%)	HNO <sub>3</sub> consumption (g)
30	92.2	4.3	96.5	69.0
40	86.1	10.1	96.2	72.8
50	82.7	13.2	95.9	74.7
60	63.8	26.0	89.8	79.3
70	53.2	35.6	88.8	85.2

At the same time, as can be found from Table 2 that, no TNT was detected in the product system, and moreover the total yield of the main product MNT and the by-product DNT is not equal to 100%, which is due to the presence of chemical equilibrium and thus unreacted toluene all along. In addition, main products of the oxidation side reaction in toluene mononitration process are cresol and derivatives thereof. Phenolic byproducts were removed when the organic phase was treated by alkaline wash, and thus a small amount of byproducts of oxidation and resinification were not detected by the instrument.

### 3.2 MTSR calculation of semi-batch reaction

Calculations of T<sub>cf</sub> and MTSR are performed here for the reactions at 30 °C, 40 °C, and 50 °C by employing 4 methods. Each method is described as follows.

1) Method 1: T<sub>cf</sub> and MTSR are calculated based on formulae (1), (2), (3) and (4).

2) Method 2: adiabatic temperature rise  $\Delta T_{ad}$  is corrected by the yield, so as to calculate  $T_{cf}$  and MTSR. That is,  $\Delta T_{ad}$  in formula (1) is replaced with  $\Delta T_{ad}/\text{yield}$ . Because there is DNT, in addition to MNT, in the toluene reaction products, the yield here is the sum of MNT and DNT yields.

3) Method 3: the maximum reaction heat obtained in 5 tests, i.e., the heat measured at 70 °C is used to calculate  $\Delta T_{ad}$ , so as to calculate  $T_{cf}$  and MTSR.

The results obtained by method 1, 2, and 3 are shown in Figures 2, 3 and 4, and the  $T_{cf}$  curves marked with (1), (2), (3) corresponds to  $T_{cf}$  obtained by method 1, 2 and 3.

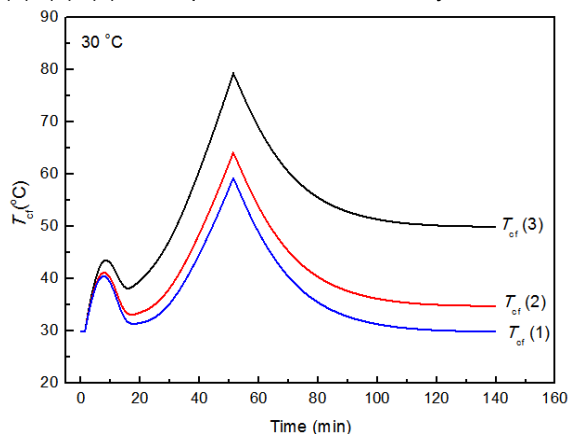


Figure 2  $T_{cf}$  of 30 °C reaction by method 1, 2 and 3

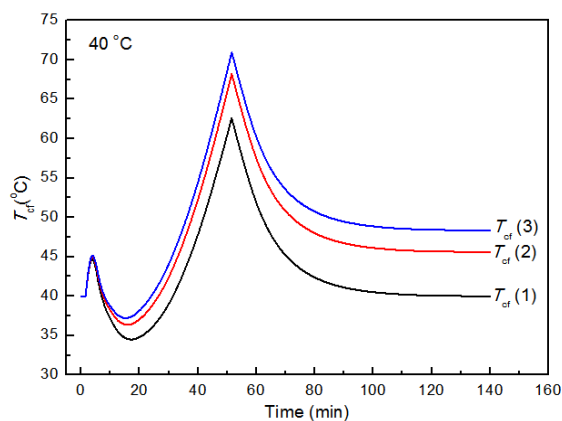


Figure 3  $T_{cf}$  of 40 °C reaction by method 1, 2 and 3

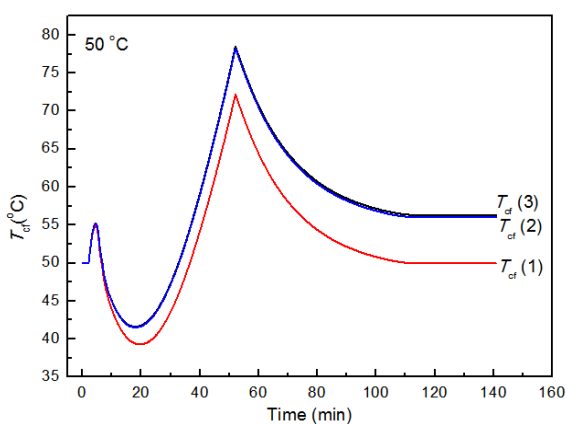


Figure 4  $T_{cf}$  of 50°C reaction by method 1, 2 and 3

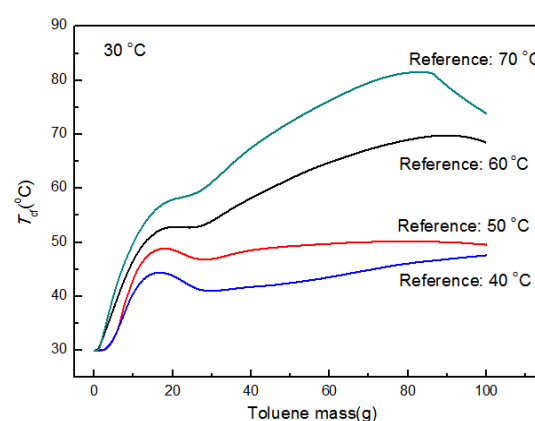


Figure 5  $T_{cf}$  of 30°C reaction obtained by method 4

Table 3: MTSR obtained by four methods

Isothermal temperature (°C)	MTSR1(°C)	MTSR2(°C)	MTSR3(°C)	MTSR4(°C)
30	59	64	79	80
40	63	68	71	75
50	72	78	79	80

Note: subscripts 1, 2, 3, and 4 correspond to the results by methods 1, 2, 3, and 4, respectively.

4) Method 4:

As discussed above, the side reaction, dinitration, will increase with the reaction temperature. Thus here, the reactions tested at high temperatures are thought as the final status or the reference reactions, which the toluene nitration system could achieve as the thermal runaway of the desired reaction occurred.  $T_{cf}$  calculated by method 4 is proposed from this viewpoint:

$$T_{cf} = T_r + \left[ \frac{X_{HT}\Delta H_{HT} - X_{LT}\Delta H_{LT}}{C_p M_r} \right]_{\text{with the same mass of toluene}} \quad (5)$$

where,  $T_r$  refers to the temperature of the reactant;  $X_{HT}$  and  $X_{LT}$  refer to the thermal conversion of the reaction at high temperature and low temperature respectively;  $\Delta H_{HT}$  and  $\Delta H_{LT}$  refer to the total heat of the reaction at high temperature and low temperature respectively;  $C_p$  is specific heat capacity of the reactant; and  $M_r$  refers to corresponding total mass of the reaction system.  $X_{HT}$ ,  $X_{LT}$  and  $M_r$  in the square bracket corresponds to the values at the same point when the same mass of toluene is dosing into the reactor. And it should be noted that, this equation is only appropriate for the process of feeding.

$T_{cf}$  calculated with equation (5) for the reactions of 30 °C, 40 °C and 50 °C are shown in Figures 5 to 7, wherein the maximum values of  $T_{cf}$ , shown as  $MTSR_4$  in Table 3, are obtained just taking the reaction at 70 °C as the final status of nitration system for calculation.

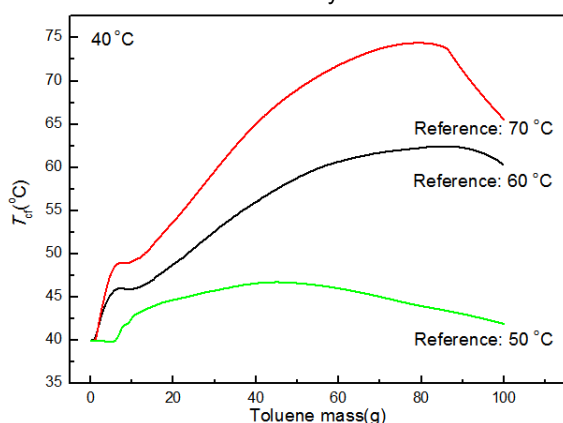


Figure 6  $T_{cf}$  of 40 °C reaction obtained by method 4

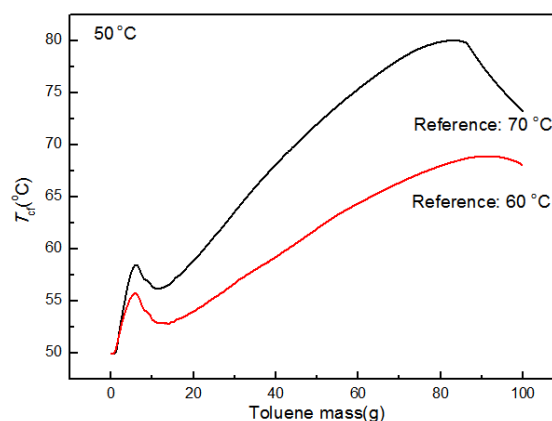


Figure 7  $T_{cf}$  of 50 °C reaction obtained by method 4

### 3.3 Discussion for the calculation results

Apparently,  $T_{cf}$  curves of the method 1 are obtained based on the measured results, the values of  $MTSR_1$  is the lowest in Table 3, and it is located at the termination of feeding. Once cooling failure is occurred, the accumulated materials will necessarily cause the system temperature increase to  $MTSR_1$ ; and the increased temperature will accelerate the reaction rate, so that the time to  $MTSR_1$  when cooling failure is far shorter than the time during which the accumulated heat is released under the isothermal mode. However, just because temperature will rise under the adiabatic condition, the toluene that is not consumed under the normal process temperature is likely to react with the excess nitric acid, and even entirely for the worst-case assumption. Therefore, the reaction heat and adiabatic temperature rise is corrected with the total yield of MNT and DNT in the method 2, to obtain a more conservative  $MTSR$  value. For the same purpose, the maximal value of adiabatic temperature rise among 5 tests is employed to calculate  $T_{cf}$ , to obtain a conservative  $MTSR$  value by method 3. However, this kind of correction still can not give a right  $T_{cf}$  curve.

In the above three methods, it is hypothesized that the potential heat is proportional with the addition of toluene. In fact, when the nitric acid is of a high concentration and is excess, toluene will be subjected to mononitration to generate MNT, and it will additionally be further nitrated to DNT, which have been detected in the product. Namely, at the initial stage of feeding, dinitration is easier to occur with the excess nitric acid. As the concentration of nitric acid decreases, dinitration will be attenuated gradually. Thus the heat release rate  $q_r$  at the beginning stage is far higher than that at the later stage though the dosing rate is constant. Therefore, the inappropriate assumption of the potential heat proportional to toluene mass, results in the negative  $X_{ac}$  at the beginning stage of reaction, causes part values of  $T_{cf}$  is even below  $T_r$ , and then shows the corresponding concave shape in all the  $T_{cf}$  curves (in Figure 2, 3 and 4).

When calculating by method 4, the negative  $X_{ac}$  are eliminated, and all the values of  $T_{cf}$  become greater than  $T_r$ . (shown in Figures 5, 6 and 7). It is because the heat generation of the reaction at high temperature is really greater than that of the reaction at normal operation temperature as the same mass of toluene is charging. For this complex nitration reaction, the reaction tested at high temperature is closer to the real scenario that the runaway nitration system could achieve. And it is also found that the value of  $MTSR_4$  in Table 3 is greater than the other. Namely, the results calculated by method 4 are more conservative for the thermal hazard evaluation.

It can also be found from Figures 5, 6 and 7 that, the maximum value of  $T_{cf}$  does not appear at the end of feeding, it is different from the results calculated by the above 3 methods. For the reactions at 60 °C and 70 °C, all the heat has been released before the end of the dosing, and the maximum value of  $T_{cf}$ , taken these two reactions as the runaway scenario, appears at the time when the nitric acid is consumed up. And for the reaction at 40 °C or 50 °C, there is a lot of heat accumulated during dosing, thus this released heat considered as the potential energy is too low for the worst case prediction, as the calculation based on equation (5) is only appropriate for the process of charging. Then it could be concluded that when method 4 is used for the calculation of  $T_{cf}$ , the reactions used as the runaway scenario should be a reaction without heat accumulation during charging, otherwise the predicted results won't be conservative enough for the thermal hazard evaluation.

Of course, there are still defects for the fourth method. All values of  $MTSR_4$  in Table 3 are greater than 70 °C, the highest tested temperature. And if the reaction temperature is further increased, more DNT and even TNT may be generated, the heat release is possibly further increased, and the  $MTSR$  is likely to be greater and be achieved earlier. But it is not practical that performing test at a very high temperature, for the long exploring time and the possibility of triggering decomposition and accident. Therefore, further work should be performed for answering the problem: when the RC test could be stopped?

#### 4. Conclusions

Semi-batch nitration of toluene is a very complex reaction, because there are many products and by-products, and side reactions are aggravated and heat release is increased with increasing temperature. Therefore, 4 methods are employed here to obtain  $T_{cf}$  and  $MTSR$  of the desired reaction. Results show that, in methods 1 to 3, it is assumed that latent energy in the reaction system is in direct proportion to the amount of toluene added, however in fact, nitric acid has a high concentration at the early stage of toluene feeding, so that nitration and dinitration are both easier to occur, namely, latent energy of per unit mass of toluene at this time is higher; and the method 4 is established taking the exothermic reaction without heat accumulation at high temperature as a reference, and thus obtains more reasonable  $T_{cf}$  and  $MTSR$ . It can also be found  $MTSR$ s obtained by the fourth methods are the highest and the most conservative.

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#### Reference

- Chen C. Y., Wu C. W., 1996, Thermal Hazard assessment and macrokinetics analysis of toluene mononitration in a batch reactor. *Journal of Loss Prevention Industries*, 9, 309-316.
- Chen L. P., Chen W. H., Liu Y., Peng . H., Liu R. H., 2008, Toluene mono-nitration in a semi-batch reactor. *Central European Journal of Energetic Materials*, 5, 37-47.
- Chen L. T., Xiao H. M., Xiao J. J., Gong X. D., 2003, DFT Study on Nitration Mechanism of Benzene with Nitronium Ion. *Journal of Physical Chemistry A*, 107, 11440-11444.
- D'Angelo F. A., Brunet L., Cognet P., Cabassud M., 2003, Modeling and Constraint Optimisation of an Aromatic Nitration in Liquid-Liquid medium. *Chemical Engineering Journal*, 91, 75-8.
- Gygax R., 1990, Scale up principles for assessing thermal runaway risks. *Chemical Engineering Progress*, February, 53-60.
- Lerena P., Wehner W., Weber H., 1996, Assessment of hazards linked to accumulation in semi-batch reactors. *Thermochimica Acta*, 289, 127-142.
- Lu, C. X., 1993, Nitration theory. Jiangsu Science and Technology Publishing House. Nanjing, China, 125-131.
- Luo K. M., Chang J. G., 1998 The stability of toluene mononitration in reaction calorimeter reactor. *Journal of Loss Prevention Industries*, 1998, 11, 81-87.
- Stoessel F., 2008, Thermal safety of chemical processes - risk assessment and process design. 1st ed, Wiley-VCH, Mörlenbach, The FEDERAL Republic of Germany.