



## Study on characteristics of toluene/chlorobenzene nitrification in different microreactors

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### ARTICLE INFO

**Keywords:**  
Microreactor  
Aromatic nitrification  
Structural feature  
Selectivity

### ABSTRACT

Aromatic nitrification with mixed acid is an important industrial reaction with fast, strong-exothermic, and high-risk reaction characteristics. To investigate the promotion for the preparation of nitrotoluene (MNT) and nitrochlorobenzene (NCB), three microreactors with different structural features, namely, heart-shaped, diamond-shaped, and zigzag-shaped microreactors, are designed and fabricated. Firstly, the effects of temperature, residence time, and molar ratio on toluene (TOL) and chlorobenzene (CB) nitrification are investigated, and orthogonal experiments are further conducted to determine the optimum reaction conditions. Results showed that channel structures and the residence time  $\tau$  have negligible effects on the isomers selectivity of the three microreactors, and higher reaction temperatures and mole ratios would lead to the substantial occurrence of side reactions and byproducts in the zigzag microreactor. The heart-shaped microreactor has the highest value of 91.49 % for the MNT's optimal yield, followed by the diamond-shaped and zigzag-shaped microreactors (89.91 % and 89.81 %, respectively). The heart-shaped microreactor provides the maximum amount of NCB preparation (93.95 %), while the yields of the diamond-shaped and zigzag-shaped microreactors are 91.51 % and 88.25 %, respectively. This work provides the experimental basis for the efficient preparation and industrial scale-up of aromatic nitrification in microreactors.

### 1. Introduction

Nitroaromatics often act as flexible intermediates and reactive raw materials in the production of dyes, plastics, medicine, pesticides, and explosives (Jin et al., 2023). Despite the usefulness of nitroaromatics and the significance of nitrification of aromatics, challenges remain in the efficient, safe preparation and industrial scale-up of aromatics nitrification (Cui et al., 2022). Aromatics are nitrated with mixed acid to produce nitroaromatics in the modern chemical industry. The nitrification reactions are complex liquid-liquid heterogeneous reactions, which mainly occur in the bulk aqueous phase or the phase interfaces, and have the characteristics of rapid and strong heat release (Song et al., 2022). Therefore, the coupling effect of interphase mass transfer, flow, and heat transfer are fundamental reasons affecting the efficiency of the aromatic nitrification.

Nitrification reaction is one of the 18 hazardous chemical processes under key supervision in China. At present, the industrial toluene (TOL) preparation of mononitrotoluene (MNT) and chlorobenzene (CB)

preparation of nitrochlorobenzene (NCB) processes are multi-stage series batch reactor nitrification processes carried out at specified low temperatures. There are challenges in the following aspects (Russo et al., 2023): (1) Due to the limited mass transfer capacity and relatively long residence time mostly at the hour level, many undesirable side-reactions and byproducts are produced, resulting in lower quality of the target product, greater separation difficulty and cost, and insufficient market competitiveness; (2) The small-scale screening and optimization process in the laboratory makes it difficult to scale-up directly at the industrial production scale; (3) The large holdup capacity, volume of the stirred-tank reactor and the regulatory difficulty in temperature fluctuations, if not properly controlled, can easily cause thermal runaway, reaction splash, and even explosion (Yang et al., 2022a). Therefore, the development of safer, greener, and more efficient MNT and NCB preparation processes has become an urgent goal for process capability improvement of aromatics nitrification.

Microreactor technology has recently expanded the boundaries of academics and industry, offering a more consistent and sustainable alternative scheme for aromatics nitrification. Microreactor is named

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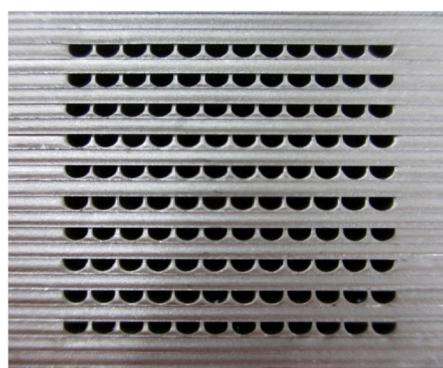
<b>Nomenclature</b>	
<i>Variables</i>	
<i>c</i>	the molar concentration, mol/L
<i>Q</i>	the volume flow rate, mL/s
<i>S</i>	the selectivity of the reaction product
<i>V</i>	the liquid holdup of the reaction sheet, mL
<i>X</i>	the conversion rate
<i>Y</i>	the yield of the reaction product
<i>Greek letters</i>	
$\tau$	the residence time, s
<i>Subscripts and abbreviations</i>	
<i>aq</i>	the aqueous phase
<i>i</i>	the reaction substrates
<i>j</i>	the reaction products
m-MNT	1-methyl-3-nitrobenzene
m-NCB	1-chloro-3-nitrochlorobenzene
or	the organic phase
o-MNT	1-methyl-2-nitrobenzene
o-NCB	1-chloro-2-nitrochlorobenzene
p-MNT	1-methyl-4-nitrobenzene
p-NCB	1-chloro-4-nitrochlorobenzene
CB	chlorobenzene
DNT	dinitrotoluene
HNO <sub>3</sub>	nitric acid
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid
MNT	mononitrotoluene
MR	microreactor
NCB	nitrochlorobenzene
PCHE	printed circuit heat exchanger
TNT	trinitrotoluene
TOL	toluene

after the microchannel cavity of reactants which can realize the continuous flow reaction and chemical production. The characteristic size of the internal channel is generally between 10 and 1000  $\mu\text{m}$ , therefore, the low flow velocity can maintain a laminar flow, and the large specific surface area facilitates the high heat and mass transfer efficiency, avoiding local overheating (Masoni et al., 2023). The dead-zone-free microchannel design minimizes the axial back-mixing, precisely regulating the reactant residence time, and inhibiting the occurrence of side reactions to the greatest extent (Karaghiosoff et al., 2023). Moreover, due to the milliliter-level holdup volume in a single reaction channel, it has significant advantages in dealing with high-risk reactions and improving intrinsic safety (Zhan et al., 2023). Moreover, the potential in heat and mass transfer enhancement of microreactors made them suitable for fluidization of catalyst solid particles (Latifi et al., 2014), adsorption bed (Grabowska et al., 2018; Grabowska et al., 2021a; Grabowska et al., 2021b; Krzywanski et al., 2021; Krzywanski et al., 2023; Kulakowska et al., 2020; Sosnowski et al., 2018), and the porous media (Grabowska et al., 2021a; Krzywanski, 2019) in reactors.

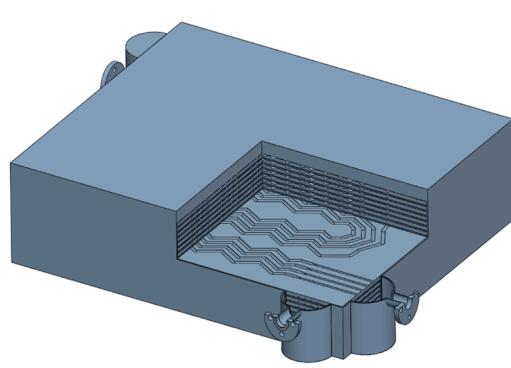
In recent years, many microfluidic systems have been built to achieve the process intensification and to obtain the reaction kinetic models of various nitrification reactions, such as p-Nitrotoluene (Song et al., 2022), nitrobenzene (Jin et al., 2023), o-xylene (Guo et al., 2023b), trifluoromethylbenzen (Guo et al., 2023a), and chlorobenzene(Cui et al., 2022), etc. Scholars have proposed a variety of structures to enhance reactant mixing and mass transfer. Many novel structures have been reported, T-shaped (Masoni et al., 2023), capillary-shaped (Zhan et al.,

2023), grooved-shaped (Rahmannezhad and Mirbozorgi, 2019), rhombic-shaped (Zhang and Chen, 2022), honeycomb-shaped (Zou et al., 2020), diamond-shaped (Rehman et al., 2021), for instance. Among them, the heart-shaped structure is the most well-known, which firstly proposed by Corning Co., Ltd., stands out for its excellent mass transfer performance and mixing (Guo et al., 2023a; He et al., 2023).

When scaling up the laboratory-level chemical production process in microreactors, in theory, there is no amplification effect in microreactor or microchemical systems (Fu et al., 2022; Stee et al., 2023). There are currently two technical routes for numbering-up (Shen et al., 2018): 1) External numbering-up route by increasing the number of parallel microchemical systems or the channel structure size, the product output can be scaled up linearly (Karaghiosoff et al., 2023). However, the complex parallel microchemical systems need to be equipped with the relevant auxiliary equipment, electronic control, and monitoring instruments simultaneously; 2) Internal numbering-up route by increasing the number of the internal parallel channels (the size of metal sheets), the number of metal reaction sheets stacked to form a block, the number of functional blocks to form a core, and further coupled with conventional industrial size heads, nozzles and distributors (Seris et al., 2005). By the multiplication of linear numbering-up in each stage, the overall assembled microreactor can implement a “cubic-level” scaleup. The whole microchemical system shares a set of hot or cold utilities, control and monitoring auxiliary systems, and has low system investment and compact footprint, the sectional view of the core and the internal amplification concept of PCHE are depicted in Fig. 1.

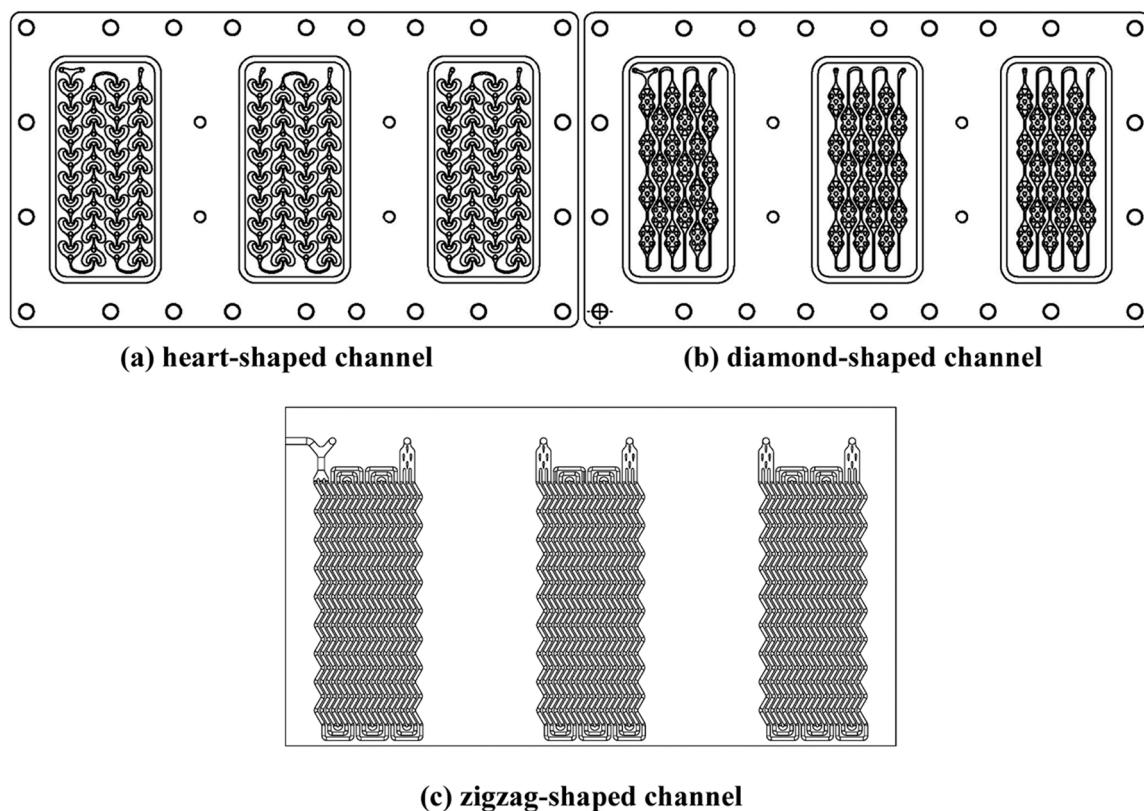


(a) sectional view



(b) internal amplification concept

Fig. 1. Sectional view and the internal amplification concept of PCHE.



**Fig. 2.** Diagram of channel structures for the three microreactors.

The representative equipment for the internal numbering-up route is a printed circuit heat exchanger (PCHE), which is a highly compact and efficient heat exchanger of an industrial size layout and integrated core composed of a large number of parallel semicircular microchannels dimensions of 100–2000  $\mu\text{m}$ . Manufactured utilizing two advanced techniques, chemical etching, and diffusion bonding, PCHE has characteristics of excellent temperature and pressure resistance (20–1000 K,  $\leq 100 \text{ MPa}$ ), high heat transfer efficiency, and modular block layout. For PCHE, typical channel structures includes straight, zigzag, sinusoidal, S-shaped, airfoil, etc., and have achieve industry applications such as CO<sub>2</sub> Brayton power generation systems, hydrogen energy, nuclear energy, offshore oil and gas platforms, etc (Chung et al., 2023; Yang et al., 2022b).

At present, on the one hand, the PCHE has been widely used in scientific research and engineering under high Reynolds number flow conditions. However, the integrated effects of enhanced momentum transport, energy transport, quality transport, and reaction engineering in typical PCHE channels remain unclear; On the other hand, although it is generally recognized that microreactors have certain advantages over conventional stirred tank reactors for aromatics nitrification, there are few studies for the influences of different microchannel structures and reactions on the efficiency and performance comparison of aromatic nitrification.

Based on the above analysis, a continuous flow comprehensive performance testing system for aromatics nitrification has been constructed, and three kinds of Hastelloy microreactors with different structural features are designed and fabricated to investigate the promotion for the preparation of MNT and NCB in microreactors, this paper explores the influences of channel structures, reaction conditions, and operation process parameters on MNT and NCB preparation. This work aims to provide experimental data support for channel layout optimization, reaction parameters selection, scale-up process, and equipment development of aromatics nitrification.

## 2. Experimental section

### 2.1. Chemicals and materials

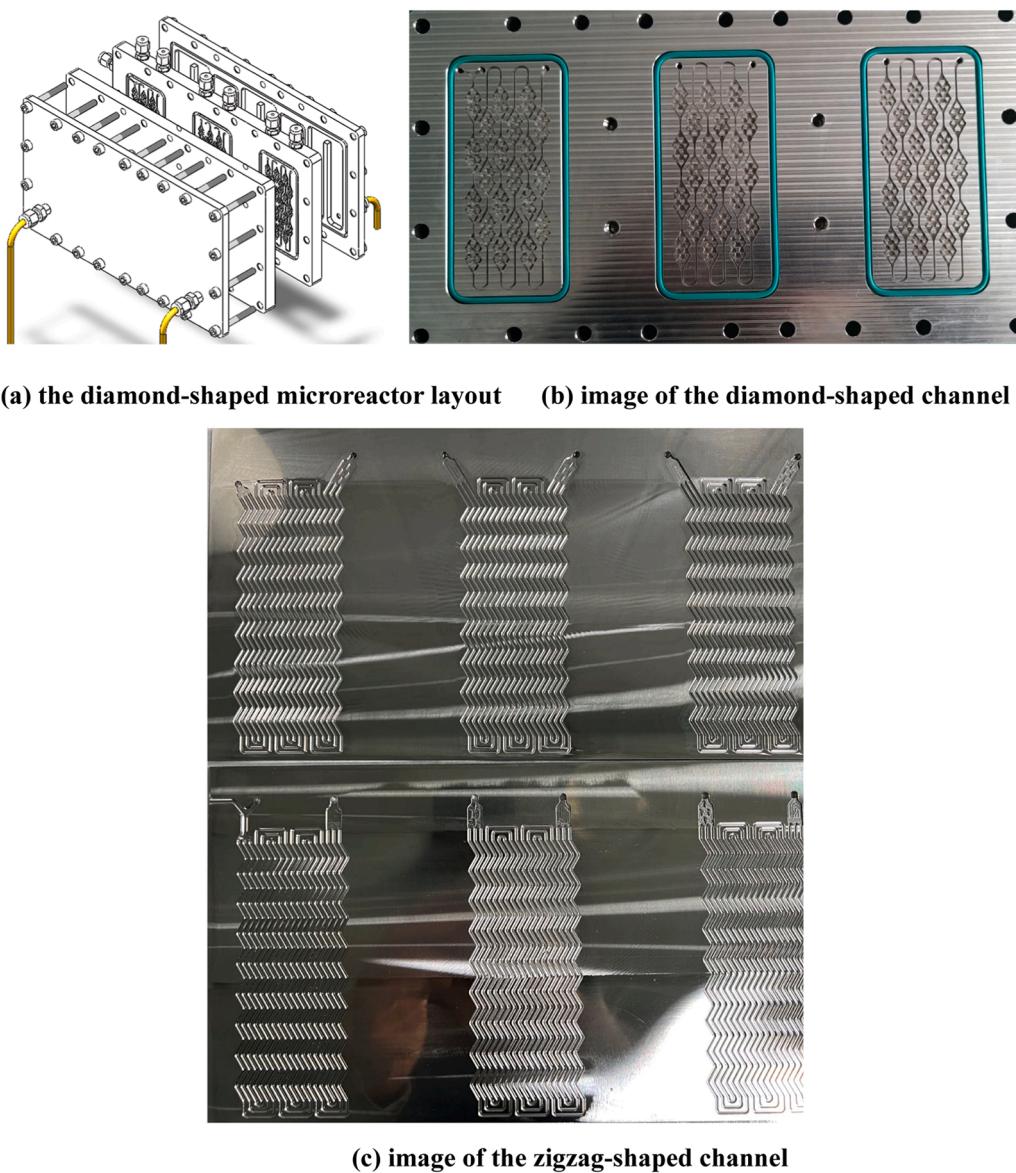
TOL (99 %), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 %), and nitric acid solution (HNO<sub>3</sub>, 65–68 %) were purchased from Sinopharm Chemical Reagent Co., Ltd, and CB (99 %) was purchased from Macklin Biochemical Technology Co., Ltd.

The mixed acid of different molar ratios was prepared by weighting the 98 % H<sub>2</sub>SO<sub>4</sub> and 65–68 % HNO<sub>3</sub> solution respectively, and the 98 % H<sub>2</sub>SO<sub>4</sub> was slowly added to the 65–68 % HNO<sub>3</sub> solution drop by drop in a dry conical bottle which was placed in an ice water mixture bath and cooled to room temperature after adequate stirring.

### 2.2. Microreactors and experimental test system

In this study, three Hastelloy microreactors with different geometrical characteristics, namely the heart-shaped, the diamond-shaped, and the zigzag-shaped reaction channels are designed and fabricated. The channel structures for the three microreactors are illustrated in Fig. 2.

The dimension of each reaction sheet is 270 mm × 150 mm (length × width), and each sheet consists of three series reaction units, for the heart-shaped and the diamond-shaped, the minimum flow regions are rectangle cross-sections of 1.5 mm × 0.75 mm. For the heart-shaped microreactor, each microcavity is partly occupied by cylindrical and arc-cylindrical solid metal obstacles and uniformly distributed in a single pass through the reactant-side inlets and outlets, likewise, the diamond-shaped microreactor is partly occupied by staggered diamond-shaped obstacles of inconsistent sizes. For the heat transfer side channels, heart-shaped and diamond-shaped microreactors are rectangular channels with a width × height of 10 mm × 1.5 mm, which is much larger than the reaction side in liquid holdup volume and cross-section areas, and the overall serpentine co-flow arrangement is the most



**Fig. 3.** Diagram of sheet layout and physical drawings of the microreactors.

frequently used configuration although the energy consumption is extremely high, and cause adverse consequence for production amplification.

Meanwhile, the reaction channels and heat supply side channels of the zigzag-shaped microreactor of internal numbering-up type are identical semicircular cross-sections of radius 0.75 mm, and the zigzag angle is 30. The liquid holdup volume and cross-section areas on two sides are the same and the countercurrent flow arrangement can obtain larger heat exchange capacity and thus better energy saving effect.

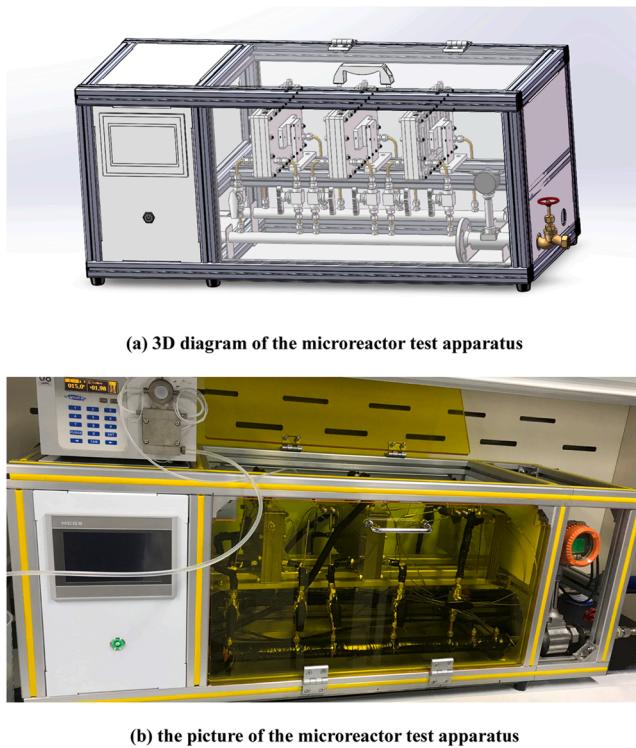
Therefore, to explores the influences of channel structures, reaction conditions, and operation process parameters on MNT and NCB preparation, the heart-shaped and the diamond-shaped microreactors have the co-flow arrangement with unequal liquid holdup volume and cross-section areas, and the zigzag-shaped microreactor has a countercurrent flow arrangement with an identical liquid holdup volume and cross-section areas for two sides. The sheet layout and physical drawings of the microreactors are depicted in Fig. 3.

The total holdups of three microreactors are 6.74, 6.65, and 6.82 mL respectively. The chemical reaction sheet (side A) and the heat transfer sheet (side B) are stacked into a “BAB” double banking layout to ensure better temperature control for each microreactor. For the test apparatus,

the three microreactors are in a parallel layout.

The experimental test system for TOL and CB nitrification is equipped with two PTFE metering pumps, PTFE connection pipes, a high and low-temperature circulation device, a thermal oil gear pump, and a quenching and sampling module. The diagram and the picture of the microreactor test apparatus part are shown in Fig. 4.

The general experimental procedure is as follows: Wait until the thermal oil of the heat transfer side is heated to the preset temperature, open the inlet stop valve of the microreactor to be tested, and pump aromatic and mixed acid solution into the microreactor for mixing and reaction, after at least 5 times the residence time and the system is stable, sampling and drop it into the sample bottle pre-filled with a mixture of water and ethyl acetate which was placed in an ice-water mixture bath, and after 5 minutes of magnetic stirring, stationary for 10 minutes until the aqueous phase and the organic phase is completely stratified. During the test procedure, the flow rates of thermal oil on the heat transfer side of the microreactors are adjusted to the maximum by the gear pump and valves, for the heart-shaped and diamond-shaped microreactors, the flow rates of thermal oil are 550 L/h, for the zigzag-shaped microreactor, the flow rate is 155 L/h.



**Fig. 4.** The diagram and the picture of the microreactor test apparatus.

### 2.3. Sample analyses

The organic phase mixtures are diluted by ethyl acetate and delivered to the gas chromatograph (SHIMADZU GC-2030) equipped with a SE-54 capillary column (0.22 mm i.d.×50 m) and an FID hydrogen flame detector, the injection volume is 0.2  $\mu\text{L}$ . The separation ratio was 20:1, and the column temperature and the SPL1 temperature are 80 °C and 280 °C respectively. The flow rates of carrier gas (nitrogen), hydrogen, and air are set as 32 mL/min, 40 mL/min, and 300 mL/min, respectively. The molar fraction of the toluene and chlorobenzene nitrification reaction products and the concentration of the remaining reactants are determined by the area normalization method.

### 2.4. Performance definitions and evaluation criterion

During the toluene and chlorobenzene nitrification reaction test, firstly, the effects of residence time  $\tau$ , reaction temperature  $T$ , TOL/CB-nitrate-sulfur molar ratio on the conversion and selectivity of MNT and NCB are investigated. Then, the orthogonal experimental design is conducted to determine the optimal process conditions.

The residence time  $\tau$  is defined as:

$$\tau = \frac{V_{\text{MR}}}{Q_{\text{aq}} + Q_{\text{or}}} \quad (1)$$

where  $\tau$  is the residence time, s;  $V_{\text{MR}}$  is the liquid holdup of the reaction sheet for microreactors, mL;  $Q_{\text{aq}}$  and  $Q_{\text{or}}$  are the volume flow rates of the aqueous phase(mixed acid) and the organic phase (TOL/CB), mL/s, respectively.

The TOL/CB conversion  $X$  is defined as:

$$X_i(\%) = \left( 1 - \frac{c_i}{c_i + \sum_1^n c_{jn}} \right) \times 100\% \quad (2)$$

where  $c_i$  is the molar concentration of reaction substrate(toluene/chlorobenzene), mol/L;  $c_{jn}$  is the molar concentration of reaction products, mol/L.

The selectivity of each reaction product is expressed as:

$$S_j(\%) = \frac{c_j}{\sum_1^n c_{jn}} \times 100\% \quad (3)$$

where  $c_j$  is the molar concentration of the analyzed target product (MNT/NCB, or each isomer), mol/L.

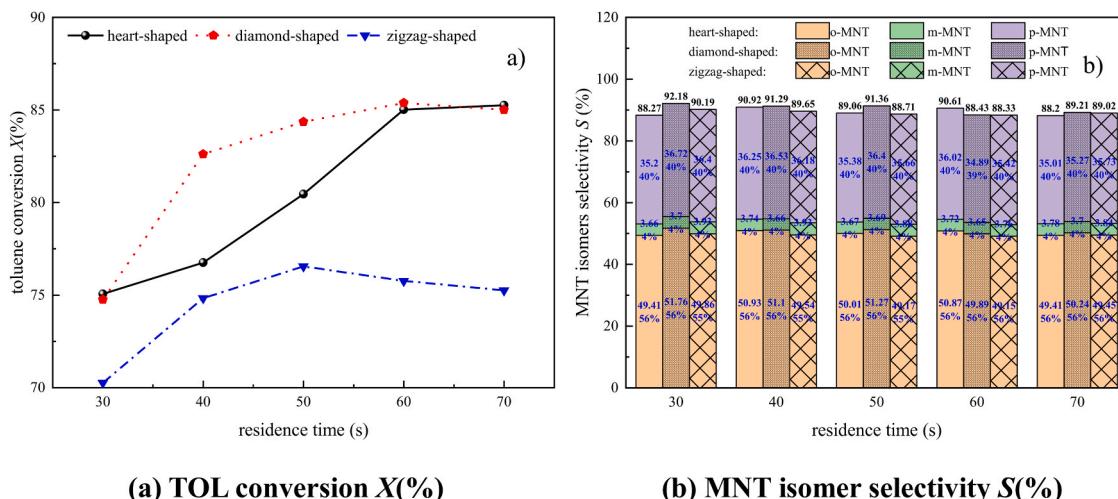
The yield of the MNT/NCB is calculated as:

$$Y_j(\%) = X_i \times S_j \quad (4)$$

## 3. Results and discussions

### 3.1. TOL/CB nitrification mechanism

Aromatic nitrification with mixed acid is a well-known reaction which extensively utilized both on a laboratory research scale and an industrial production scale, therefore, the reaction mechanisms of toluene and chlorobenzene nitrification are very similar(Cox, 1971; Jin et al., 2023). Previous works of literature suggest that the nitronium ion  $\text{NO}_2^+$  is the activation nitrating and the  $\text{NO}_2^-$  is formed by the hydroxyl group protonation of nitric acid solution in the presence of sulfuric acid, sulfuric acid acts as an activating nitrification agent and a dehydrating



**Fig. 5.** Effects of residence time  $\tau$  on the conversion of toluene and MNT isomer selectivity.

agent, combining with the water molecules generated by the nitrification reaction to form sulfuric acid hydrate, maintaining the concentration of nitric acid and improving the  $\text{NO}_2^+$  utilization rate. and the reaction equations are expressed as follows (Cui et al., 2022; Jin et al., 2023):



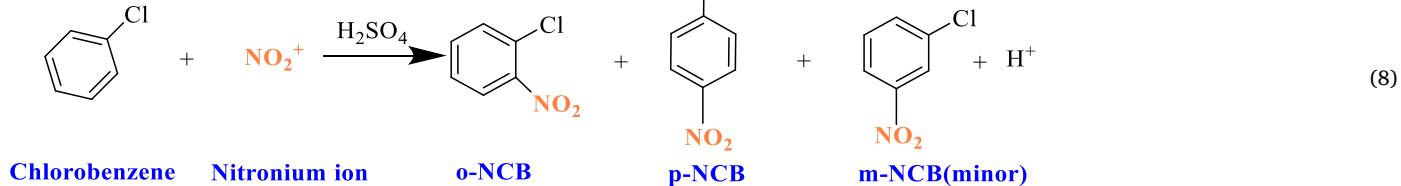
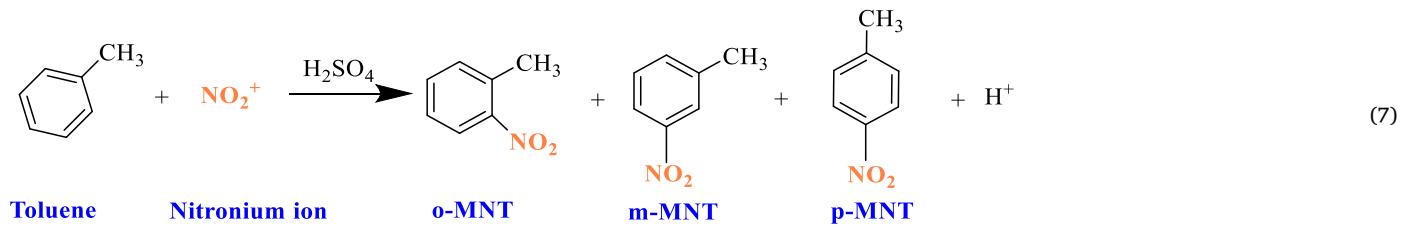
Afterward, an electrophilic reaction occurs between the nitronium ion  $\text{NO}_2^+$  and the toluene/chlorobenzene molecules which diffuse into the aqueous phase, and different isomers are produced at the different positions on the benzene ring where the reaction takes place, and the relevant reaction equations are listed in Eqs.(6–7). For the TOL nitrification, 1-methyl-2-nitrobenzene (*o*-MNT), 1-methyl-3-nitrobenzene (*m*-MNT), and 1-methyl-4-nitrobenzene (*p*-MNT) are the three mono-nitrobenzene products of benzene nitrification. For the CB nitrification, 1-chloro-2-nitrochlorobenzene (*o*-NCB), 1-chloro-3-nitrochlorobenzene (*m*-NCB, minor), and 1-chloro-4-nitrochlorobenzene (*p*-NCB), and MNT/NCB can be further nitrated to be DNT/DNCB in the presence of excess  $\text{NO}_2^+$  respectively.

irregularly designed obstacles during the flow process. On the one hand, the reaction mainstream breaks and disperses into smaller tributary streams, shortening the mass transfer distance of the two phases and increasing the effective contact time. On the other hand, the interphase boundary layer is destroyed by the collision between the streams and generates shear force instantaneously, causes local pressure fluctuation, and promotes interphase mass transfer (Zheng et al., 2021). When the zigzag flow channel is used, small vortices are formed at each bend of the zigzag paths, which produces local turbulence and the destruction of the boundary layer, and the formation of low Reynolds number turbulence, thus enhancing the interphase mass transfer (Wang et al., 2022). However, when the flow rate increases, the more complex flow structure of the heart-shaped and diamond-shaped channels would cause greater flow resistance, and the energy consumption will be higher than that of the zigzag flow path.

### 3.3. Reaction characteristics of TOL/CB nitrification in microreactors

#### 3.3.1. Effects of residence time $\tau$ on TOL/CB nitrification

As mentioned in (Cui et al., 2022), a shorter residence time can promote the mixing performance and the reaction rate, but results in a

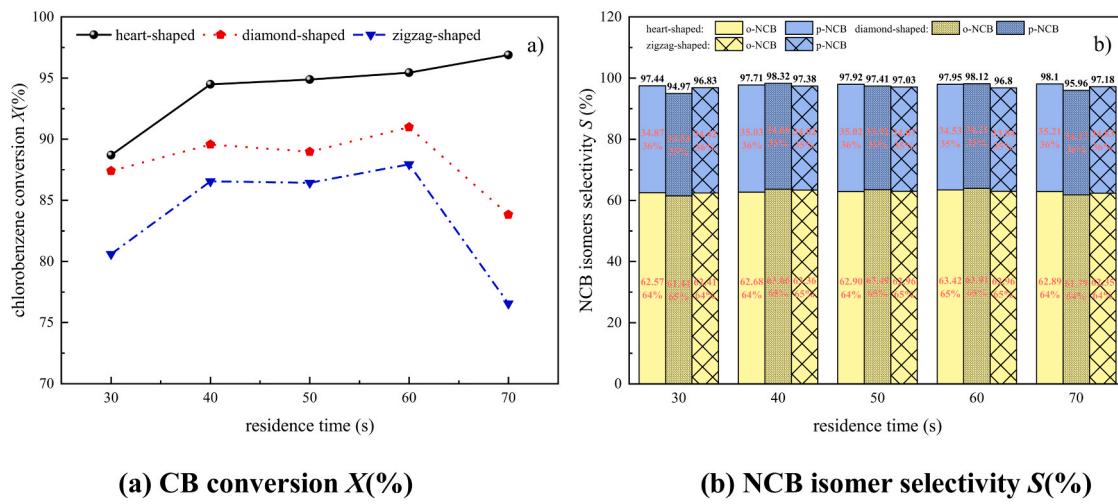


### 3.2. The mixing and mass transfer mechanisms in three microreactors

The mixing and mass transfer mechanisms of Aromatic nitrification which has been extensively investigated and reported in previous literature(Cox, 1971; Song et al., 2022). The liquid-liquid two-phase nitrification reaction of TOL and CB occurs in the mixed acid phase, therefore, the interphase mass transfer effect determines the reaction rate of the nitrification process. The channel dimensions of the micro-reactors are in submillimeter magnitude, and the viscosity of the acid phase is high. For the flat micro-channel, the flow pattern is laminar flow with a low Reynolds number, and the mass transfer mainly depends on molecular diffusion, and the residence time required for complete mixing is long, consequently, the chemical reaction effect is unsatisfying. When a heart-shaped or diamond-shaped reaction channel is used, the organic phase and the mixed acid phase constantly collide with

inadequate conversion rate, and a longer residence time can cause undesirable side reactions and byproducts. The preparation of MNT/NCB by aromatics nitrification with mixed acid are rapid, strong-exothermic reaction, and the flow rate of the reactant is a crucial factor for interphase mass transfer and flow pattern, in which the effects of residence time on the conversion and selectivity of MNT and NCB preparation are investigated by changing the total volume flow rate of the aqueous phase and the organic phase.

For the MNT preparation, the reaction temperature  $T$  is set as 60 °C, the TOL-nitric-sulfur molar ratio is fixed at 1:1.2:1.7, and the residence time  $\tau$  is 30 s, 40 s, 50 s, 60 s, 70 s, respectively. Fig. 5 shows the toluene conversion rate and MNT isomers selectivity under different residence time  $\tau$ s. Generally, the shorter residence time  $\tau$  means a tighter reactant contact time, a higher total volume flow rate, and more adequate mixing, the combined influence on the TOL conversion rate is different for



**Fig. 6.** Effects of residence time  $\tau$  on the conversion of CB and NCB isomers selectivity.

the three microreactors. As can be inferred from Fig. 5a, the  $\tau$  has a positive effect on the  $X$  for three microreactors, which is consistent with that observed by (Jin et al., 2023; Yang et al., 2022a), and the heart-shaped and diamond-shaped microreactors are superior to the zigzag-shaped microreactor for the comparison of  $X$ s. Moreover, in the range of 60–70 s, the rate of variation decreases for the heart-shaped and diamond-shaped microreactors, and the maximum  $X$  under the process parameters is around 85 %. For the zigzag-shaped microreactor, there exists an optimal  $X$  of 76.6 % at the residence time of 50 s.

For the MNT isomers selectivity  $S$ , due to the excellent heat transfer performance and temperature control property of microreactors, the channel structures have little effect on the molar ratio of the *o*-MNT, the *m*-MNT, and the *p*-MNT, and from the MNT selectivity results in Fig. 5b, the microreactors demonstrate satisfying suppression of the side reactions and the generation of dinitrotoluene (DNT), the average MNT isomers selectivity  $S$  is around 90 %, and the percentages of the *o*-MNT, the *m*-MNT, and the *p*-MNT are 56 %, 4 %, and 40 %, respectively. The optimal residence time range is 40–60 s.

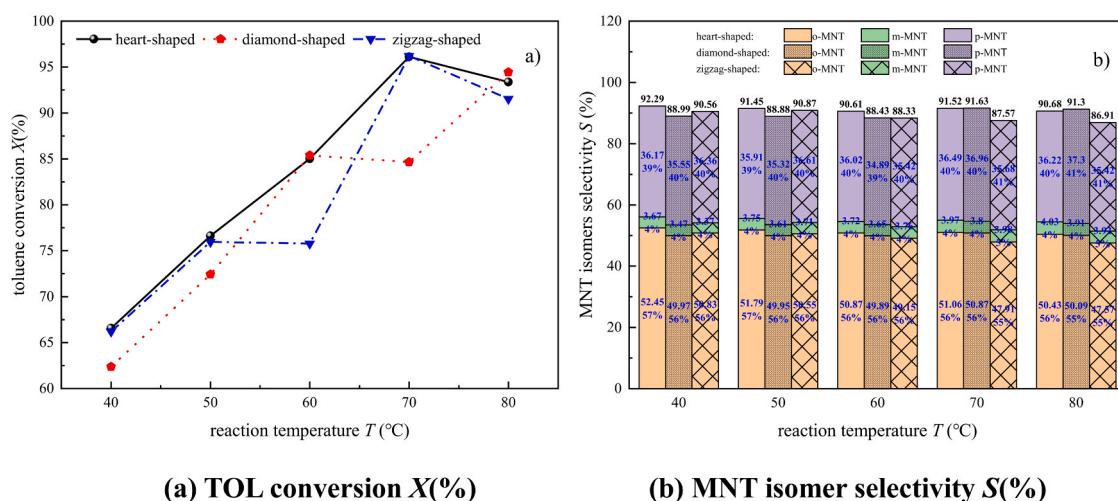
For the NCB preparation, the reaction temperature  $T$  is set as 60 °C, the chlorobenzene-nitric-sulfur molar ratio is fixed at 1:1.2:2.0, and the residence time  $\tau$  is kept at the 30 s, 40 s, 50 s, 60 s, 70 s, 80 s, respectively. Fig. 6 shows the chlorobenzene conversion rate and NCB isomer selectivity under different residence time  $\tau$ s. and the sort from best to worst is the heart-shaped microreactor, the diamond-shaped microreactor, and

the zigzag-shaped microreactor. Although the  $\tau$  has a positive effect on the  $X$  for the heart-shaped microreactor, the maximum  $X$  reaches 96.9 %, but the promotion is less obvious than that of the toluene nitrification. For the diamond-shaped and the zigzag-shaped microreactors, with the increase of  $\tau$ , the conversion rate of chlorobenzene first increases and then decreases, and reaches 83.8 % and 77.6 % respectively at the residence time of 70 s, which the conversion rate is also the lowest. The optimal residence time range for chlorobenzene conversion is 50–60 s.

As depicted in Fig. 6b, the channel structures have little effect on the selectivity  $S$  of the *o*-NCB, and the *p*-NCB. The selectivity  $S$  of NCB for the three microreactors reaches over 95 %, which is superior to that of MNT selectivity. The percentages of the *o*-NCB and the *p*-NCB are 64 %, and 36 %, respectively.

Through horizontal comparison of MNT and NCB preparation, it can also be found that the mixing effect and interphase mass transfer of the zigzag flow channel at a low Reynolds number is worse than that of the other two microreactors. and the nitrification reaction of toluene is more intense than that of chlorobenzene. Side reactions and byproducts (DNT, TNT, etc) are more likely to occur, therefore, the MNT selectivity is worse.

Considering the conversion rate, the selectivity, and the economy of production, the residence time  $\tau$  of 60 s is selected for subsequent performance comparison experiments.



**Fig. 7.** Effects of reaction temperature  $T$  on the conversion of toluene and MNT isomers selectivity.

### 3.3.2. Effects of reaction temperature $T$ on TOL/CB nitrification

The reaction temperature has a significant impact on the aromatic nitrification efficiency of the microreactors because of their superior heat transfer performance and temperature control feature. To investigate the effects of reaction temperature  $T$  on the MNT preparation, the residence time  $\tau$  is set as 60 s, the toluene-nitric-sulfur molar ratio is fixed at 1:1.2:1.7, and the reaction temperature  $T$  is set at 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C, respectively. Fig. 7 shows the toluene conversion rate and MNT isomer selectivity under different reaction temperatures  $T$ s.

As shown in Fig. 7, the variation of toluene conversion  $X$  shows similar trends for the three microreactors, according to the kinetics model of aromatics nitrification, a higher reaction temperature  $T$  can accelerate the rate of each reaction, thus, the overall conversion rate  $X$  of toluene increases significantly in the beginning, however, for the heart-shaped and zigzag-shaped microreactors, the promotion of higher temperature decreases gradually within the range of reaction temperature 70–80 °C, the reason behind maybe in two aspects, as the nitrification reaction proceeds, the concentration of toluene and nitric acid decreases gradually, and the reaction rate decreases accordingly, moreover, some nitronium ion  $\text{NO}_2^+$  continued to react with MNT to generate 2,6 and 2,4 dinitrotoluene (DNT), resulting in a decrease in MNT selectivity, which can be concluded from the slight decrease in overall MNT isomer selectivity at 80 °C and 90 °C in Fig. 7b.

For the MNT isomer selectivity  $S$ , with the increase of reaction temperature  $T$ , the relative proportion of *m*-MNT and *p*-MNT increase, and the *o*-MNT decreases. Moreover, for the zigzag-shaped microreactor, the overall MNT selectivity decreases gradually, this is due to the countercurrent flow arrangement between the reaction side and the thermal oil side, and the thermal oil side are identical zigzag microchannels with a much smaller flow rate of 155 L/h, which is much lower than that of 550 L/h for the rectangular large channel of the heart-shaped and diamond-shaped microreactors. Even though the energy consumption has dropped a lot when the reaction temperature exceeds 60 °C, the MNT selectivity slowly decreases, and the amount of DNT gradually begins to accumulate. In addition to studying trends with temperature changes, conversion and selectivity, whether the raw material can be consumed completely is a matter of great concern to chemical engineers, as it is often highly correlated with the economics of production. Since toluene has not been completely converted in all reactors, in order to explore the limitation of the performance of the microreactors and comprehensively consider MNT selectivity and energy consumption, the reaction temperature of 80 °C is selected.

According to the related literatures (Cui et al., 2022; Wen et al.,

2018), the reaction rate increases with the higher reaction temperatures, and due to the difference in activation energy for parallel competing reactions of *o*-NCB and *p*-NCB, the selectivity for *o*-NCB dominates. For the NCB preparation, the residence time  $\tau$  is set as 60 s, the chlorobenzene-nitrate-sulfur molar ratio is fixed at 1.0:1.2:2.0, and the reaction temperature  $T$  is kept at 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C, respectively. Fig. 8 shows the chlorobenzene conversion rate and NCB isomers selectivity under different reaction temperatures  $T$ s. The selectivity of *m*-NCB was lower than 5%, which is in accordance with that analyzed by (Cui et al., 2022).

The results showed that the reaction temperature  $T$  has a positive effect on the chlorobenzene conversion rate  $X$  for both microreactors. At the same reaction temperate  $T$ , the mass transfer and mixing effect of the heart-shaped microreactor are superior to that of the diamond-shaped microreactor and the zigzag-shaped microreactor, the chlorobenzene conversion rate  $X$  is the optimal, followed by the diamond-shaped microreactor and the zigzag-shaped microreactor. As depicted in Fig. 8, the impacts of the reaction temperature  $T$  on the NCB selectivity  $S$  are not obvious, but the counter flow arrangement of the zigzag-shaped microreactor does make the NCB selectivity only slightly lower than that of the other two, therefore, the energy conversation effect is prominent. As can be seen from Fig. 8a-b, because CB nitrification reaction is milder than toluene, the inhibition effect of the side reaction of microreactors is more obvious, and the overall selectivity is much higher. The reaction temperature of 80 °C is selected for aromatics-nitric-sulfur molar ratio experimental investigation.

### 3.3.3. Effects of aromatics-nitric-sulfuric molar ratio on TOL/CB nitrification

Based on the relevant literatures (Edwards and Fawcett, 1994; Song et al., 2022), the concentration of  $\text{NO}_2^+$  increases with the molar fraction of  $\text{HNO}_3$  under the dominant occupation of  $\text{H}_2\text{SO}_4$ , and decreases with increasing molar concentration of  $\text{HNO}_3$ . While increasing the molar ratio of nitric-toluene molar ratio can promote the nitrification of toluene, it would also enhance the DNT or even trinitrotoluene (TNT) selectivity, meanwhile, increasing the molar ratio of sulfuric-nitric would enhance the hydroxyl group protonation of nitric acid and the production of the  $\text{NO}_2^+$ , accelerate the reaction rate. However, the subsequent waste acid treatment chemical process will be challenging because of the existence of excessive sulfuric.

To investigate the effects of aromatics-nitric-sulfur molar ratio on the MNT preparation, the residence time  $\tau$  is set as 60 s, the reaction temperature  $T$  is kept at 80 °C, and the toluene-nitric-sulfur molar ratio is set at 1.0:1.0:1.8, 1.0:1.1:1.8, 1.0:1.2:1.8, 1.0:1.3:1.8, and 1.0:1.4:1.8,

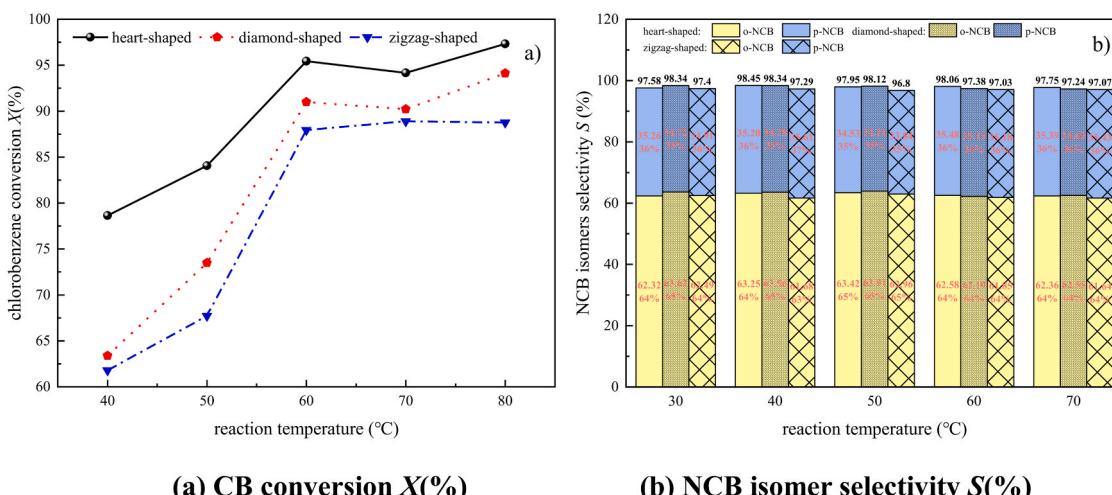


Fig. 8. Effects of reaction temperature  $T$  on the conversion of chlorobenzene and NCB isomers selectivity.

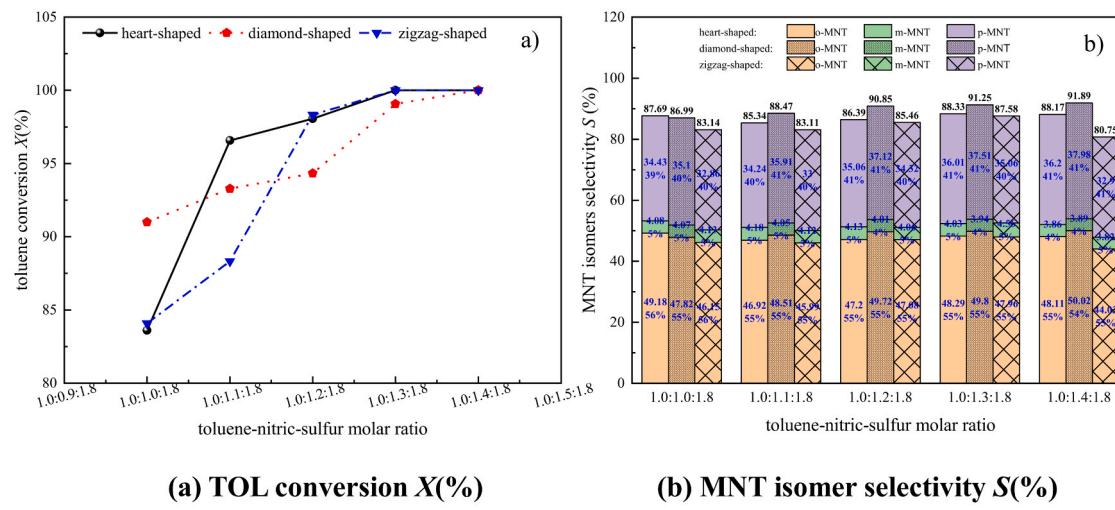


Fig. 9. Effects of TOL-nitric-sulfur molar ratio on the conversion of toluene and MNT isomer selectivity.

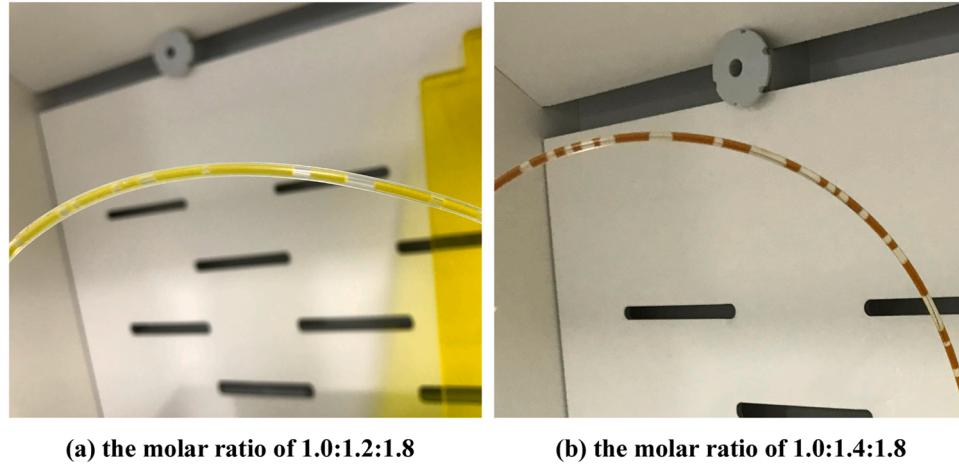


Fig. 10. The reaction effluent of the zigzag-shaped microreactor.

respectively. The toluene conversion rate and MNT isomer selectivity under different molar ratios are illustrated in Fig. 9.

With the increase of the aromatics-nitric-sulfur molar ratio, the conversion rate  $X$  of toluene increases, and reaches 100 % for each microreactor at the molar ratio of 1.0:1.4:1.8. In general, the increase of molar ratio has a more significant improvement effect on the heart-shaped and the zigzag-shaped microreactors.

It can be seen from Fig. 9 that, the overall MNT isomer selectivity  $S$  of the heart-shaped microreactor is unimpacted by the increase of molar ratio, while the concentration of the *o*-MNT decreases from 49.18 to 48.11, and the *p*-MNT increases from 34.43 to 36.2. Therefore, a higher molar ratio can promote the production of the *p*-MNT, moreover, the MNT selectivity  $S$  for the diamond-shaped microreactor increases from 86.99 % to 91.89 %. For the zigzag-shaped microreactor, the MNT selectivity increases from 83.14 % to 87.58 %, and decreases sharply to 80.75 % at the molar ratio of 1.0:1.4:1.8. And the reason is that the counter flow configuration of the zigzag-shaped microreactor has the maximum heat exchange capacity and the highest end temperature difference, while the temperature variation of the co-current flow is the smallest, and the variable temperature means the substantial occurrence of side reactions and byproducts of DNT. The reaction effluent from the outlet PTFE pipe of the zigzag-shaped microreactor are shown in Fig. 10, at the molar ratio of 1.0:1.2:1.8 and 1.0:1.4:1.8, respectively.

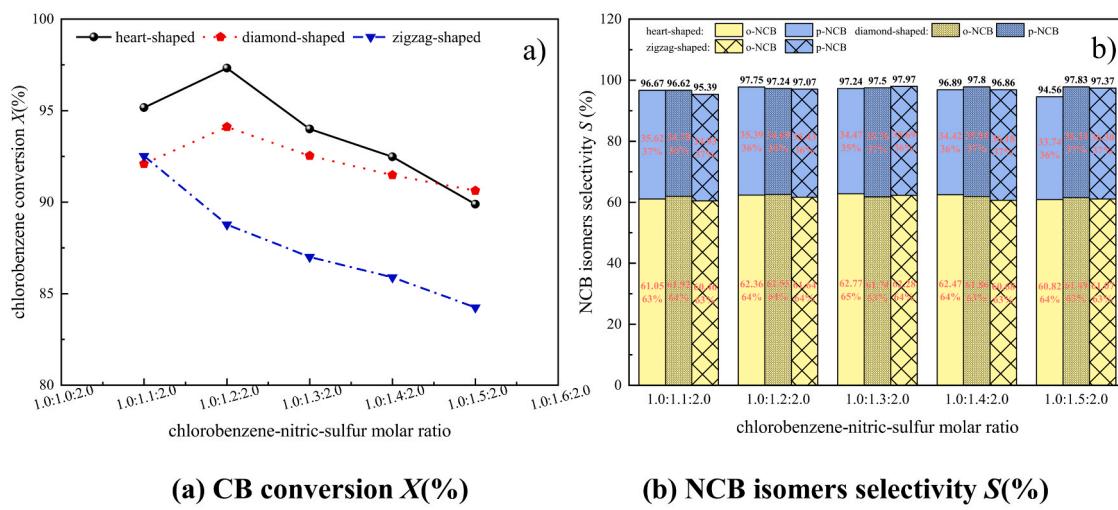
For the NCB preparation, the residence time  $\tau$  is set as 60 s, the reaction temperature  $T$  is kept at 80 °C, and the CB-nitric-sulfur molar

ratio is set at 1.0:1.1:2.0, 1.0:1.2:2.0, 1.0:1.3:2.0, 1.0:1.4:2.0, and 1.0:1.5:2.0, respectively. Fig. 11 shows the chlorobenzene conversion rate and NCB isomer selectivity under different CB-nitric-sulfur molar ratios.

With the increase of the CB-nitric-sulfur molar ratio, the conversion rate  $X$  of the CB increases firstly and reaches the maximum at the molar ratio of 1.0:1.2:2.0, then the  $X$  decreases gradually, for the zigzag-shaped microreactor, however, the molar ratio harms the  $X$  for that the hydroxyl group protonation of nitric acid is suppressed as the relative quantity of sulfuric acid is on the decrease, and the concentration of the chlorobenzene is inadequate for the continuous conversion, and the overall NCB selectivity decreases to 94.56 % as a consequence of side reactions and byproducts such as 1-chloro-2,4-dinitrobenzene (DNBC).

### 3.3.4. Orthogonal optimization of TOL/CB nitrification process

According to the results of the above univariate performance test analysis, to find the multi-parameter optimum nitrification process conditions, the three-factor three-level orthogonal tables are designed, namely, for the TOL nitrification, the orthogonal input parameters are listed as follows: reaction temperatures of 60 °C, 70 °C, and 80 °C, residence times of 50 s, 60 s, and 70 s, molar ratios of 1.0:1.2:1.8, 1.0:1.3:1.8, and 1.0:1.4:1.8. For the CB nitrification, the orthogonal input parameters are listed as follows: reaction temperatures of 70 °C, 80 °C, and 90 °C, residence times of 50 s, 60 s, and 70 s, molar ratios of 1.0:1.0:2.0, 1.0:1.1:2.0, and 1.0:1.2:2.0. The orthogonal design



**Fig. 11.** Effects of CB-nitric-sulfur molar ratio on the conversion of chlorobenzene and NCB isomers selectivity.

**Table 1**

The orthogonal design conditions and test numbers for MNT/NCB preparation.

(a) The MNT preparation			
No.	T (°C)	$\tau$ (s)	Molar ratio
1	60	50	1.0:1.2:1.8
2	60	60	1.0:1.3:1.8
3	60	70	1.0:1.4:1.8
4	70	50	1.0:1.3:1.8
5	70	60	1.0:1.4:1.8
6	70	70	1.0:1.2:1.8
7	80	50	1.0:1.4:1.8
8	80	60	1.0:1.2:1.8
9	80	70	1.0:1.3:1.8

(b) The NCB preparation			
No.	T (°C)	$\tau$ (s)	Molar ratio
1	70	50	1.0:1.0:2.0
2	70	60	1.0:1.1:2.0
3	70	70	1.0:1.2:2.0
4	80	50	1.0:1.1:2.0
5	80	60	1.0:1.2:2.0
6	80	70	1.0:1.0:2.0
7	90	50	1.0:1.2:2.0
8	90	60	1.0:1.0:2.0
9	90	70	1.0:1.1:2.0

conditions and test numbers are shown in **Table 1**. The orthogonal optimization experiments are carried out for the three microreactors.

Through the orthogonal experimental results and mean value analysis of the MNT and NCB selectivity, the optimum process conditions of the three microreactors are listed in **Table 2**.

According to the above results, the MNT/NCB preparation performance and repeatability verification tests are conducted under the optimum process conditions of microreactors, and the consistency is satisfying after multiple samplings. The average results are shown in **Table 3**.

As can be seen from **Table 3a**, for the yield of the MNT, the heart-shaped microreactor has the highest value of 91.49, followed by the diamond-shaped and the zigzag-shaped microreactors, which is 89.91 and 89.81 respectively, and the differences in performance are not obvious, the TOL conversion rates are 100 % for the former two reactors. For the NCB preparation, the highest yield of 93.95 is obtained by the heart-shaped microreactor, and the yields of the diamond-shaped and the zigzag-shaped microreactors are 91.51 and 88.25, respectively.

#### 4. Conclusions

In this paper, to study the promotion for MNT and NCB preparation,

**Table 2**

The optimum process conditions for MNT/NCB preparation.

Reaction	Microreactors	T (°C)	$\tau$ (s)	Molar ratio
MNT	heart-shaped	70	70	1.0:1.2:1.8
	diamond-shaped	80	60	1.0:1.3:1.8
	zigzag-shaped	70	70	1.0:1.4:1.8
NCB	heart-shaped	90	60	1.0:1.2:2.0
	diamond-shaped	80	50	1.0:1.1:2.0
	zigzag-shaped	80	70	1.0:1.0:2.0

heart-shaped, diamond-shaped, and zigzag-shaped microreactors, are designed and fabricated, effects of temperature, residence time, and molar ratio, on TOL and CB nitrification are investigated, and the orthogonal experiments are further conducted to determine the optimum reaction conditions.

Due to the excellent heat transfer performance and temperature control property of microreactors, the channel structures, residence time  $\tau$ , have little effect on the isomer molar ratio of MNT and NCB, which demonstrate satisfying suppression of the side reactions.

At relatively higher temperatures and molar ratios, the counter flow and identical microchannel configuration of both sides for the zigzag-shaped microreactor has the maximum temperature difference, which means the substantial occurrence of side reactions and byproducts.

For the TOL nitration of heart-shaped, diamond-shaped, and zigzag-shaped microreactors, the optimum process conditions are obtained at reaction temperatures of 70 °C, 80 °C, and 70 °C, residence times of 70 s, 60 s, and 70 s, molar ratios of 1.0:1.2:1.8, 1.0:1.3:1.8, and 1.0:1.4:1.8, respectively. For the CB nitrification, the optimum process conditions are obtained at reaction temperatures of 90 °C, 80 °C, and 80 °C, residence times of 60 s, 50 s, and 70 s, molar ratios of 1.0:1.2:2.0, 1.0:1.1:2.0, and 1.0:1.0:2.0, respectively.

For the optimum yield of the MNT, the heart-shaped microreactor has the highest value of 91.49, followed by the diamond-shaped and the zigzag-shaped microreactors, which is 89.91 and 89.81 respectively; For the NCB preparation, the highest yield of 93.95 is obtained by the heart-shaped microreactor, and the yields of the diamond-shaped and the zigzag-shaped microreactors are 91.51 and 88.25, respectively.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Table 3**

The optimum MNT/NCB preparation performance for three microreactors.

(a) The MNT preparation		TOL	o-MNT	m-MNT	p-MNT	DNT	X(%)	MNT S(%)	DNT S(%)	Y(%)
Microreactors										
heart-shaped	0	50.07	3.79	37.62	8.33	100	91.49	8.33	91.49	
diamond-shaped	0	48.75	3.97	37.19	9.86	100	89.91	9.85	89.91	
zigzag-shaped	0.89	49.08	3.92	36.81	9.10	99.12	90.62	9.18	89.81	
(b) The NCB preparation										
Microreactors	CB	o-NCB	p-NCB	DNCB	X(%)	NCB S(%)	DNCB S(%)	Y(%)		
heart-shaped	3.61	59.61	34.34	1.68	96.39	97.47	1.74	93.95		
diamond-shaped	5.89	58.86	32.65	1.71	94.11	97.24	1.82	91.51		
zigzag-shaped	7.48	55.94	32.31	1.90	92.52	95.38	2.05	88.25		

**Acknowledgments**

We gratefully acknowledge the financial support for the Key Research and Development Project of Anhui Province (No. 2023z04020020); the grants of the Doctoral Science and Technology Foundation of Hefei General Machinery Research Institute (No. 2020011748), and the Youth Science and Technology Fund of Hefei General Machinery Research Institute Co., Ltd (2023010773).

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