

The Intensification of Rapid Reactions for Multiphase Systems in a Microchannel Reactor by Packing Microparticles

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In this study, the nitration of o-nitrotoluene (NT) with mixed acid as a model fast liquid–liquid multiphase reaction was conducted in the packed and nonpacked microchannel reactors. Better reaction performance could be obtained in the packed microchannel reactor compared with the nonpacked microchannel reactor because of its excellent mass transfer performance. The conversion of NT reached 94% in the packed microchannel reactor even when the reaction time was less than 3 s. A parameter, which represented the coupling of mass transfer and residence time in microdevices, was proposed for explaining and anticipating nitration process in microchannel reactors. In addition, the effects of some operating parameters on reaction performance, such as the composition of mixed acid and reaction temperature, were also investigated experimentally. © 2010 American Institute of Chemical Engineers AICHE J, 57: 1409–1418, 2011

Keywords: microchannel, mass transfer, nitration, packed bed, multiphase flow, dispersion

Introduction

Aromatics nitration with mixed acid is one of the most important processes for the production of pharmaceuticals, dyes, explosives, pesticides, etc.¹ These liquid–liquid reactions involve an aqueous phase and an organic phase. The nitration reaction has been validated to take place in the aqueous phase, where the mixed acid generates nitronium ions (NO_2^+) by the catalyzing of the sulfuric acid. The generation of NO_2^+ is strongly dependent on the sulfuric acid strength, so it determines the type of reaction developed,

slow or fast reaction regime.^{2,3} These nitronium ions attack organic molecules diffusing from the interface of immiscible two phases, produce nitrated product and finally diffuse back into the organic phase. It is obvious that mass transfer processes and chemical reactions compete between themselves in a way for fast reaction regime, that is, the sulfuric acid strength and the hydrodynamics of immiscible liquid–liquid two phases strongly impact on nitration reaction process.

In addition, these nitration reactions are highly exothermic, and the temperature runaway can easily occur in conventional stirred tank reactors.^{4,5} For these reasons, the less efficient mass transfer and heat transfer in these conventional reactors can lead to the formation of undesirable by-products due to excess nitration and oxidation, the phenomena of reaction runaway and even explosion. Therefore, the reaction temperature and the

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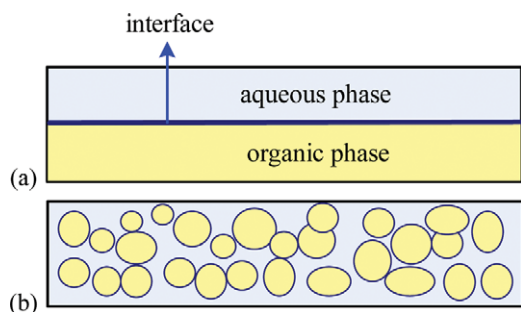


Figure 1. The schematic diagrams of parallel flow and dispersed droplets flow.

(a) Parallel flow in the nonpacked microchannel and (b) dispersed droplets flow in the packed microchannel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reactant concentration are usually limited to obtain mild reaction states for safety and higher product yield in the industry. However, these can decrease the reaction rate and lead to the increasing of the reaction time, even up to several hours.

During the last decade, microreaction technology has experienced spectacular development as one of the most important process intensification technologies.^{6–10} Its extremely large surface-to-volume ratio and the short transport path in microchannels enhance heat and mass transfer dramatically and, hence, provide many potential opportunities in chemical process development and intensification.^{11–14}

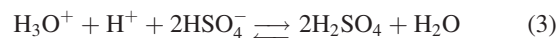
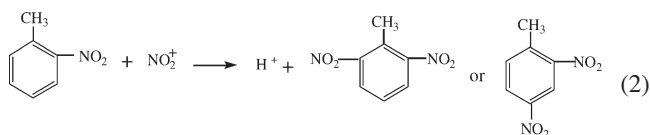
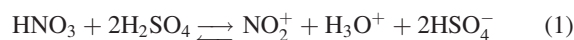
Burns and Ramshaw¹⁵ investigated the nitration of benzene and toluene with mixed acid in microreactors. Their results showed that the mixed acid composition had a strong influence on reaction behavior, and slug flow within the microchannel reactor can provide enough effective interfacial area for fast liquid–liquid multiphase reaction. Halder et al.¹⁶ demonstrated that the nitration of toluene could proceed rapidly by self-protonation of nitric acid in a microreactor without sulfuric acid, and its reaction rate was much higher than the batch reactor rates. Ahmed et al.¹⁷ thought that the reaction rates could be improved by slug flow for the hydrolysis reaction of *p*-nitrophenyl acetate in microchannel reactors. The nitration of *iso*-octanol with mixed acid in the microchannel reactor was also investigated in our group.¹⁸ The results showed that the reaction could be almost completed in the microreactor system because of the enhanced heat and mass transfer rates.

Liquid–liquid two-phase flow patterns are formed when two immiscible fluids are brought in contact in the microchannels. There are two kinds of flow regimes, that is, the continuous phase flow pattern (parallel flow) and the dispersed phase flow pattern (slug flow).¹⁹ Due to internal circulation in slug droplet, the mass transfer between immiscible liquid–liquid two phases is enhanced compared to parallel flow.^{20,21} Although slug flow in the microchannel has provided a feasible method for fast liquid–liquid multiphase reactions, the slug flow can be obtained only under very low total flow rate or extremely large volumetric flux ratio of immiscible liquid–liquid two phases in microchannels. Therefore, this flow pattern is not suitable for fast liquid–liquid multiphase reactions in microchannel reactors considering high throughput in production in practical application.

In our previous work,²² we investigated the mass transfer intensification of immiscible liquid–liquid two phases in the

microchannel by packing microparticles. In the packed microchannel, the parallel flow of high throughput can easily transform to the dispersed droplets flow, and thus larger effective interfacial area is achieved. The schematic diagrams of parallel flow in the nonpacked microchannel and dispersed droplets flow in the packed microchannel are shown in Figure 1. From the schematic diagrams, it can be seen that one phase is highly dispersed in another phase in the packed microchannel, and the hydrodynamics and contact of the immiscible liquid–liquid two phases are improved for achieving excellent mass transfer performance.

In this study, the nitration of *o*-nitrotoluene (NT, C₇H₇NO₂) with mixed acid was conducted in packed and nonpacked microchannel reactors to understand the effects of mass transfer on the fast liquid–liquid multiphase reaction system, and its reaction equations are shown as follows:



The main products are 2,4-dinitrotoluene (DNT) and 2,6-DNT in the nitration of NT with mixed acid.²³ Trace amounts of trinitrotoluene (TNT) maybe occur in the products because of further nitration. The effect of the sulfuric acid concentration on the solubility of NT in the aqueous phase was studied, which was relevant to complicated interfacial phenomena and mass transfer between immiscible reaction phases. And different reaction behaviors in packed and nonpacked microchannel reactors were compared based on the liquid hourly space velocity (LHSV). Some other key operating conditions for this nitration reaction, such as the composition of mixed acid, the reaction temperature, the ratio of reactants, the length of eduction tube connected to microchannel, were also investigated.

Experimental Section

Material and apparatus

The typical T-shaped microchannel was fabricated in the stainless steel plate by micromachining technology (FANUC KPC-30a) in our CNC Machining Center. The depth, width, and length of the microchannel were 600 μm, 600 μm, and 60 mm, respectively. Another stainless steel plate was used as cover plate. The thickness of two stainless steel plates was only 3 mm, which was beneficial to heat transfer. The irregular quartz sand microparticles were used as packing particles, their average diameter was about 300 μm. The weight of microparticles was 3.0 mg, and the packing length was 10 mm. The distance between T-junction and threshold of packing section is 6 mm. To prevent the loss of microparticles, a microparticle whose diameter approximately equals to the hydraulic radius of the microchannel was packed in the rear of packing section as shown in Figure 2(a). The width of the irregular big particle fitted the width of the channel so that both sides of the particle could contact

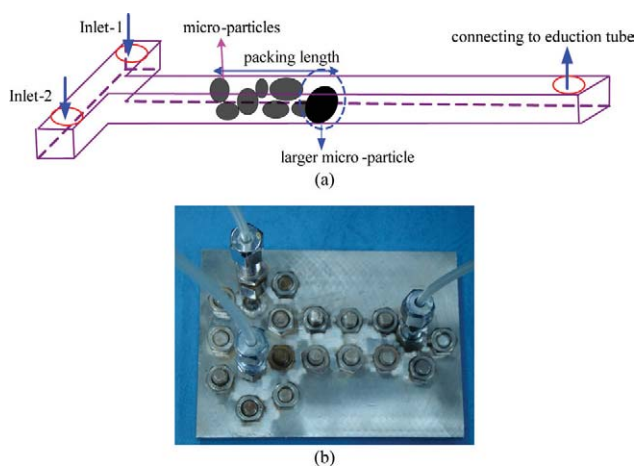


Figure 2. (a) Schematic diagram of packed microchannel and (b) picture of packed microchannel reactor.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

closely with the microchannel wall and then the particle fixed itself in the channel. Because the big particle was irregular, so there was void for fluid flowing through. After packing microparticles in the microchannel, the plates were compressed each other by bolts. A PTFE eduction tube with an inner diameter of 3 mm connected to the outlet of microchannel. The microchannel reactor is shown in Figure 2(b).

Experimental Setup

The schematic diagram of the experimental apparatus is shown in Figure 3. To maintain continuous flow without pulsation, two high precision piston pumps were used to feed mixed acid and NT (nitric acid and NT, AR, Sinopharm Chemical Reagent Company; sulfuric acid, AR, Tianjin No.3 Chemical Reagent Factory). The microchannel reactor and the eduction tube were immersed in water bath with constant temperature to obtain uniform reaction temperature.

Analytical procedure

After attaining steady state during a run, the small beaker was directly used to collect the products from the outlet of eduction tube, which contained the mixture of ice and water to stop the reaction. When reaction conversion was large, DNT was deposited in collector due to temperature decreasing. Enough hot water (about 330 K) was added to the collector, and then precipitates dissolved. Separatory funnel was used to separate aqueous phase and organic phase as the two phases formed clear interface. Hot water was used to wash the organic phase to extract the dissolved trace acid, and the washing time was at least three times. A fraction of the organic phase was diluted using excess acetone, and then the composition of diluted organic phase was analyzed by a gas chromatograph (Fuli Analytical Instrument Co., LTD, column: SE-54, 50 m × 0.2 mm × 0.33 μm) with nitrogen as the carrier gas and the flame ionization detector. The temperature of the column was maintained at 483.2 K, whereas that of the injector and the detector was kept at 453.2 K and 483.2 K, respectively. The area normalization method was used to determine the concentrations of the components quantitatively. The maximum error of the measurements did not exceed ±3%.

For determining the solubility of NT in the aqueous phase, an excess amount of NT was added to the sulfuric acid solution, and the mixture in a sealed conical flask (placed inside a water bath) was agitated for about 1 h under magnetic stirring. The standing time was over 2 h, and then the aqueous and organic phases were separated by separatory funnel. A fraction of sample from the aqueous phase (1 ml) was collected and dissolved in ethanol. The amount of NT present in the sample was determined by UV spectroscopy ($\lambda_{\max} = 297 \text{ nm}$). The amount of sulfuric acid dissolved in the organic phase was determined by acid–base titration using standardized NaOH solution.

The composition of products is determined by gas chromatograph. The conversion of NT is calculated as the following equation:

$$X = 1 - \frac{w_{\text{NT}}}{w_{\text{NT}} + w_{\text{DNT}} \times \frac{M_{\text{NT}}}{M_{\text{DNT}}}} \times 100\% \quad (4)$$

where X is the conversion of NT, w_{NT} and w_{DNT} are the mass fractions of NT and DNT in the product organic phase, respectively. M_{NT} and M_{DNT} are the molecular weight of NT and DNT, respectively. LHSV and superficial residence time in microchannel reactor are defined as following equations, respectively.

$$\text{LHSV} = \frac{Q_{\text{aq},i} + Q_{\text{or},i}}{V} \quad (5)$$

$$t = \frac{1}{\text{LHSV}} \quad (6)$$

where $Q_{\text{aq},i}$, $Q_{\text{or},i}$, V are aqueous volumetric flow rate, organic volumetric flow rate, and microchannel reactor volume, respectively. Here, the effect of packed microparticles on superficial residence time was neglected due to small volume percent of microparticles in the whole microchannel.

The sulfuric acid strength is an important parameter and is defined as following equation:

$$\varphi = \frac{w_s}{w_s + w_w} \times 100\% \quad (7)$$

where w_s and w_w are the mass fractions of sulfuric acid and water in the mixed acid, respectively.

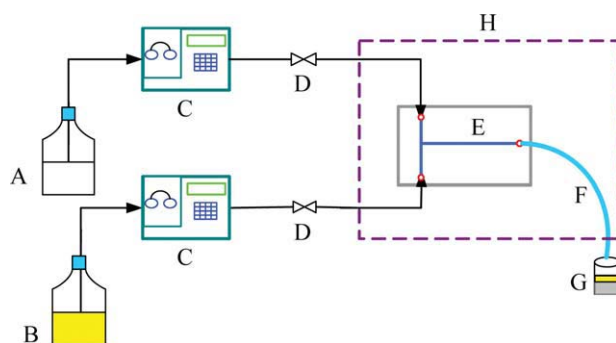


Figure 3. Schematic diagram of experimental setup.

(A) mixed acid tank; (B) NT tank; (C) piston pump; (D) check valve; (E) packed microchannel reactor; (F) eduction tube; (G) products collector; (H) water bath. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

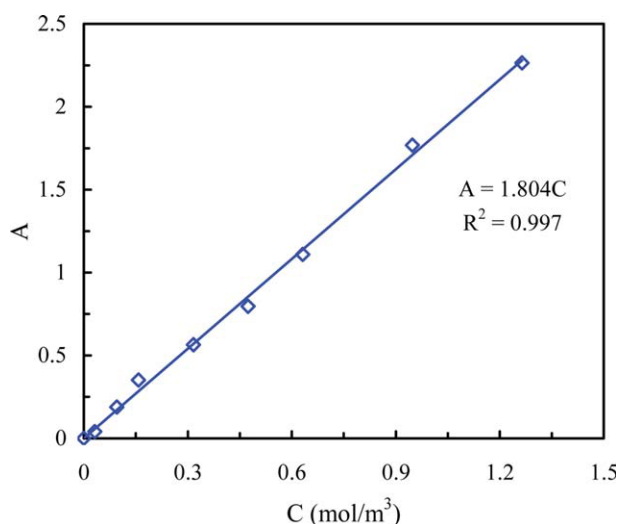


Figure 4. Relationship of absorbance and concentration of NT in ethanol solution.

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For discussing the effects of mass transfer on reaction, the mass transfer flux of NT (M) and the overall volumetric mean mass transfer coefficients (ka) are defined as Eqs. 8–10. Here, we assume that the velocity field of two flows is plug flow, the volume of the organic phase remains constant after reaction and the concentration of NT in the mixed acid is much lower than that in organic phase.

$$M = Q_{or} (C_{or,0} - C_{or,1}) = kaV\Delta C_m \quad (8)$$

$$ka = \frac{Q_{or} (C_{or,0} - C_{or,1})}{V\Delta C_m} \quad (9)$$

$$\Delta C_m = \frac{\Delta C_{or,0} - \Delta C_{or,1}}{\ln \frac{\Delta C_{or,0}}{\Delta C_{or,1}}} = \frac{C_{or,0} - C_{or,1}}{\ln \frac{C_{or,0}}{C_{or,1}}} \quad (10)$$

where $C_{or,0}$, $C_{or,1}$, and ΔC_m are the original concentration of NT in organic phase, the concentration of NT in organic phase after reaction, and logarithmic mean concentration driving force.

Results and Discussion

Solubility of NT in the sulfuric acid solution

Because the reaction mainly takes place in the aqueous phase, the concentration of NT in the aqueous phase is one of the important factors influencing nitration reaction rate. Also, the solubility characteristic of liquid–liquid multiphase reaction system is relevant to complicated interfacial phenomena and mass transfer between immiscible reaction phases.²⁴ Therefore, it is necessary to study the solubility of NT in the acid phase. As shown in Figure 4, there is linear relationship between the absorbance and the concentration of NT in ethanol solution, which means that the solubility of NT in the sulfuric acid solution can be properly measured by UV spectroscopy.

From Figure 5, we can see the solubility of NT in acid phase depended strongly on the content of sulfuric acid. The solubility increased dramatically with the increase of the con-

tent of sulfuric acid. The solubility of sulfuric acid in the NT also increased in a similar manner, which was also depicted in Figure 5. A sharp increase in solubility was observed around 83.5 wt % H_2SO_4 for both two lines. This trend was similar to the results of Rahaman et al.,²⁵ who used sulfuric acid and nitrobenzene as a testing system. Rahaman had demonstrated a fine dispersion of the nitrobenzene droplets in the sulfuric acid phase after enough agitation. And the size of the droplets decreased as the content of sulfuric acid increased, which was due to the decrease in the interfacial tension between nitrobenzene and sulfuric acid. The system of NT and sulfuric acid was similar to sulfuric acid and nitrobenzene system. Therefore, we speculate that it is easy to obtain better dispersion performance of NT and acid phase at the same agitation intensity with the increase of sulfuric acid content.

Effect of mass transfer on reaction performance

To demonstrate the effects of mass transfer on the nitration reaction performance, the nitration of NT was carried out in the packed and nonpacked microchannel reactors, respectively. Two kinds of mixed acid compositions were used and the reaction temperature was kept at 328.2 K. The length of eduction tube was 160 mm, and the mole ratio of HNO_3 to $C_7H_7NO_2$ was 1. The compositions of mixed acid were 62.8 wt % (H_2SO_4)-27 wt % (HNO_3) and 68.5 wt % (H_2SO_4)-29.5 wt % (HNO_3), respectively. Their corresponding sulfuric acid strengths were 86 wt % and 97.2%, and mole ratios of HNO_3/H_2SO_4 were both 0.67.

It is well known LHSV has great effects on the hydrodynamics and mass transfer of the immiscible liquid–liquid two phases, that is, the reaction behaviors of liquid–liquid multiphase systems partially depends on LHSV. Figure 6 shows the effect of LHSV on the conversion of NT in the packed and nonpacked microchannel reactors, it can be seen the conversion of NT decreased slightly as LHSV increased. According to our previous investigation,²² an increase of flow rate or LHSV can lead to better dispersion of immiscible liquid–

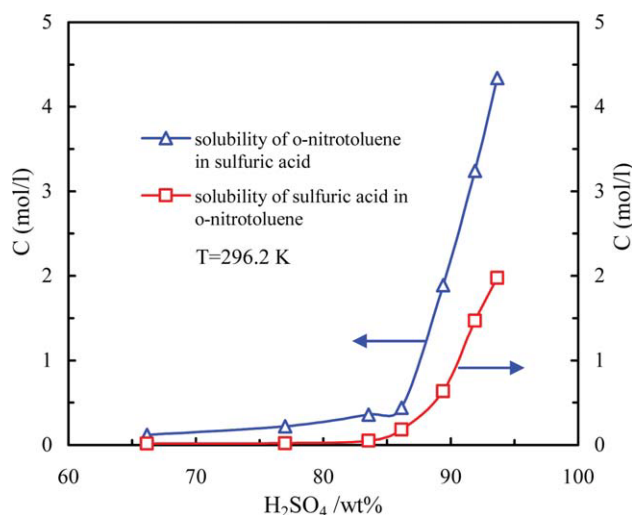


Figure 5. Effect of the content of sulfuric acid on solubility of NT in acid phase and solubility of sulfuric acid in NT phase.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

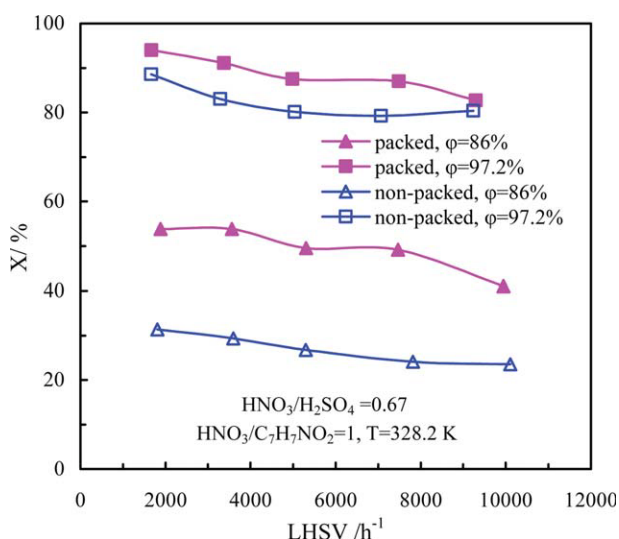


Figure 6. Comparison on conversion of NT between the packed and nonpacked microchannel.

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liquid two phases and the increase of mass transfer performance in the packed and nonpacked microchannel. Therefore, the nitration reaction rate increased with increasing of LHSV because of the intensification of mass transfer. However, the conversion of NT in microchannel reactor is not only dependent on the mass transfer performance but also the residence time of reaction fluids within microreactor, that is, the values of ka and t are all dependent on LHSV. The negative effect of the decrease in residence time could not be completely counteracted by the increase of nitration reaction rate, so the conversion of NT decreased slowly.

From Figure 6, it can also be seen that the conversion in the packed microchannel were higher than in the nonpacked microchannel. This attributed to better mass transfer performance in the packed microchannel reactor.

From Figure 7, it can also be seen that the overall volumetric mean mass transfer coefficients in the packed microchannel were much larger than those in the nonpacked microchannel. Moreover, the flow pattern for nitration reaction in the nonpacked microchannel reactor was considered as parallel flow.¹⁹ The two phases flowed side-by-side, and the transfer of NT from organic phase to aqueous phase was principally through diffusion and weak disturbance in the nonpacked microchannel reactor. In comparison to the parallel flow in nonpacked microchannel, the two phases flowed into the confined and crooked interstices between microparticles in the packed microchannel. In the extremely narrow microspace, the two immiscible phases interwove and sheared, mixed dramatically and happened reaction. The irregular microparticles also sheared the fluids drastically, which was beneficial to the mixing and reaction of two immiscible fluids. High dispersion could be formed easily in the packed microchannel, thus the effective interfacial area and surface renewal velocity increased and the mass transfer performance was improved.

As Figure 7 shown, the composition of mixed acid has great effects on the overall volumetric mass transfer coefficient. When conducting in the same reactor, the values of ka with

97.2 wt % sulfuric acid strength were much larger than that with 86 wt % sulfuric acid strength. The mass transport increases if the substance transfers into the other phase where reaction occurs in liquid–liquid multiphase systems.²⁴ In addition, the nitration reaction rate increases with the increasing of the sulfuric acid strength. Therefore, the mass transfer rate is higher as sulfuric acid strength increases, which results in higher values of ka .

The increased degree of ka under two kinds of mixed acid composition is shown in Figure 8, where the factor $(ka)_p/(ka)_n$ represents the ratio of ka between the packed and nonpacked microchannel reactors. From Figure 8, the values of $(ka)_p/(ka)_n$ were almost independent on LHSV therefore of Reynolds number. It is attributed to that an increase of Reynolds number can lead to better mixing of immiscible or miscible reaction system both in the packed and nonpacked microchannels. So, the values of $(ka)_p/(ka)_n$ changed little as LHSV rises. It can also be seen the amplitude of ka was more obvious for lower sulfuric acid strength. Based on the solubility characteristic of sulfuric acid and NT system, the two phases were immiscible for lower sulfuric acid strength. So, the mixing between them became difficult, and the effect of mass transfer on nitration was more obvious. Moreover, the reactant fluids were partially mutually soluble with higher sulfuric acid strength. It was considered there was not clear interface between two phases in the nitration process even in nonpacked microchannel, and the reaction characteristics maybe fall into the transition zone from heterogeneous to homogeneous reaction. Therefore, the mixing of two phases was somewhat easier, and the amplitude of ka was smaller with high sulfuric acid strength.

It is well known the reaction behavior of fast liquid–liquid multiphase reaction (or extraction efficiency) is not only dependent on the mass transfer rate but also the residence time of fluids within the reactor (t). In microdevices, the values of ka and t are all dependent on LHSV. The overall volumetric mass transfer coefficients (ka) usually increase with the increase of

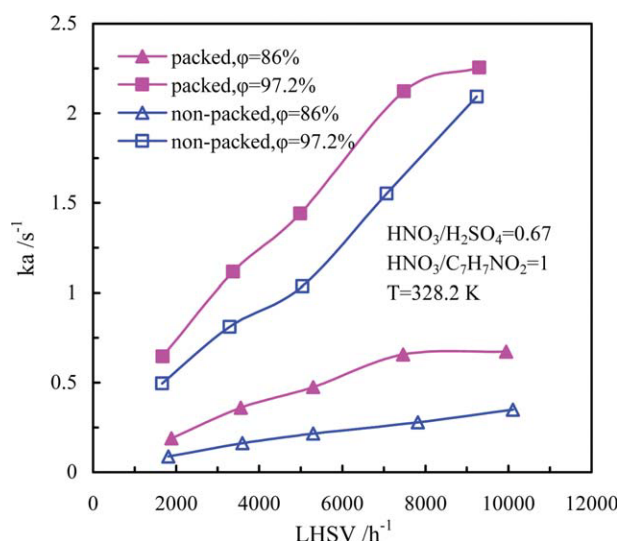


Figure 7. Comparison on overall volumetric mean mass transfer coefficient between the packed and nonpacked microchannel.

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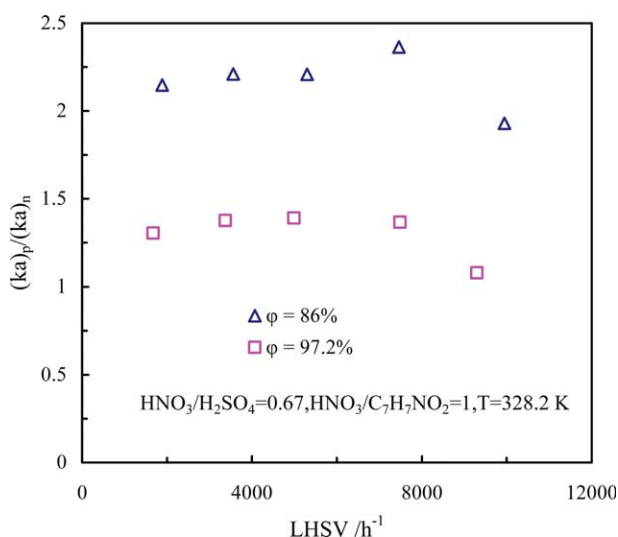


Figure 8. Comparison of the increased amplitude of ka for different mixed acid strength.

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LHSV, whereas t is just the opposite. The ratio of the residence time to the characteristic reaction time is expressed by the first Damköhler number (Da').²⁶ Here, we define a parameter (Da') which is analogous to the first Damköhler number as given in the following:

$$Da' = \frac{ka}{LHSV} = ka \cdot t \quad (11)$$

Da' is the function of the overall volumetric mean mass transfer coefficient and the residence time, that is, the coupling of the mass transfer performance and the residence time. Figure 9 shows the effect of Da' on the conversion and the extraction efficiency, where the data of extraction efficiency was obtained from the previous work.²² The conversion and the extraction efficiency all increased with the increasing of Da' , and the relationship between Da' and X (or E) generally accorded with Eqs. 12 and 13, respectively ($0.1 < Da' < 1.4$).

$$X = 30.8 \ln(Da') + 85.9 \quad (12)$$

$$E = 38.8 \ln(Da') + 103 \quad (13)$$

The results demonstrated that Da' is an important parameter in microreactors for liquid–liquid multiphase systems, and it must increase Da' to obtain higher conversion or extraction efficiency. In Figure 9, the whole zone was divided to two zones for reaction system, which was relative to different sulfuric acid strength. Zone-1 was more sensitive to Da' compared to Zone-2, which could be explained from two aspects. First, the reaction characteristics maybe fall into the transition zone from heterogeneous to homogeneous reaction in Zone-2, and the intensification amplitude of mass transfer was relatively low, as shown in Figure 8. Second, the effect of residence time becomes weaker as it reaches to a certain value for fast reaction. From Figure 9, it also can be seen that the extraction efficiency was higher than the reaction conversion at the same value of Da' . This is because that the physical extraction process is considered as ultra fast reaction, which is more sensitive to mass transfer compared to actual chemical reaction processes.

The increased mass transfer rate and reaction conversion in packed microchannel reactor were at the expense of increased pressure drop which was relevant to energy consumption. In packed microchannels reactor, the fluids only could flow through the confined interstices between microparticles, which led to higher pressure drop. Therefore, more appropriate packing method and more optimized microparticles fixing method are required for the optimization design of packed microchannel reactor.

Effect of composition of mixed acid on the conversion

Figure 10 shows the effect of the initial sulfuric acid strength on the conversion of NT when the reaction temperature was kept at 296.2 K, and the length of eduction tube was 160 mm. It is clear that the conversion of NT increased as the sulfuric acid strength increased at the same reaction time. It is well known the generation of NO_2^+ is catalyzed by the sulfuric acid in the mixed acid, and the nitration rate is strongly dependent on the sulfuric acid strength according to the intrinsic kinetics of nitration.²⁷ As the sulfuric acid strength increased, more NO_2^+ ions were provided for nitration, so the conversion increased. Table 1 shows the change of sulfuric acid strength in aqueous phase before and after reaction. For the mixed acid with 68.5 wt % H_2SO_4 , the sulfuric acid strength was still high after reaction (88.5 wt %), even higher than the initial sulfuric acid strength for the mixed acid with 58.3 wt % H_2SO_4 , thus the higher conversion could be obtained. Here, the NT could form dispersed droplets in the nitration reaction process based on the surface characteristics of the packed microchannel reactor. Actually, the microchannel wall and packed quartz sand microparticles were all hydrophilic, so the NT phase was prone to form dispersed droplets. In addition, the sulfuric acid content had influence on the dispersion of NT in the mixed acid phase based on above discussion. As the sulfuric acid strength increased, the smaller dispersed droplets of NT could be obtained. Therefore, the mass transfer rate, reaction rate and

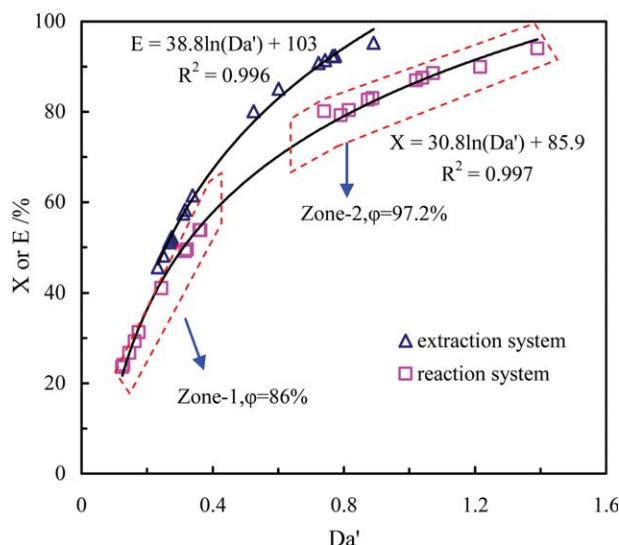


Figure 9. The effects of Da' on conversion and extraction efficiency.

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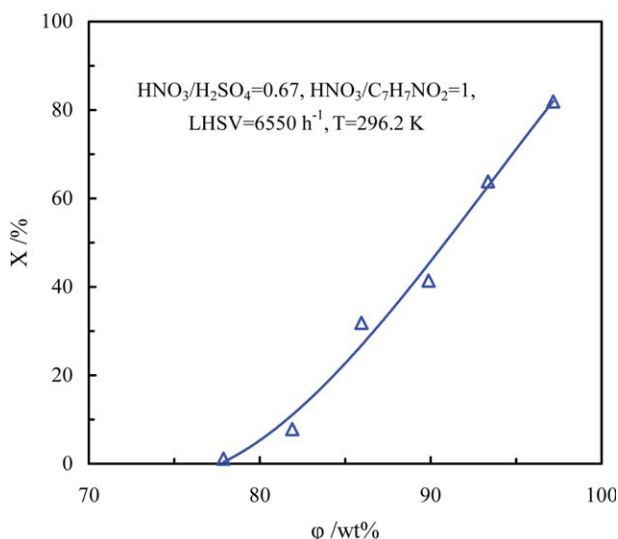


Figure 10. Effect of the sulfuric acid strength in mixed acid on the conversion of NT.

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the conversion for the nitration of NT increased with the increase of the sulfuric acid strength.

Figure 11 shows the effect of mole ratio of HNO_3 to H_2SO_4 in mixed acid on the conversion of NT. The reaction temperature was kept at 296.2 K, and the length of eduction tube was 160 mm. It can be seen the conversion of NT decreased sharply with the increasing of mole ratio of HNO_3 to H_2SO_4 , and then decreased slightly. As the mole ratio of HNO_3 to H_2SO_4 increased, the content of HNO_3 in mixed acid increased, and the content of H_2SO_4 decreased. The sulfuric acid molecules provided for per mole of nitric acid was reduced. The chance of collision between sulfuric acid molecule and nitric acid molecule decreased, and less NO_2^+ was produced and provided for the nitration of $\text{C}_7\text{H}_7\text{NO}_2$. Therefore, the nitration reaction rate of NT was decreased, and the conversion of NT was reduced.

Effect of the mole ratio of nitric acid to NT on the conversion

The conversion of NT increased with the increasing of mole ratio of $\text{HNO}_3/\text{C}_7\text{H}_7\text{NO}_2$ at the same reaction time shown in Figure 12. This is attributed to more NO_2^+ ions provided for nitration. There was not any TNT in products even though the nitric acid was much excess. The reason is that the mixing of the two phases in the packed microchannel reactor was excellent, and the mass transfer rate was large. The DNT produced could diffuse back into the organic phase quickly. Second, the

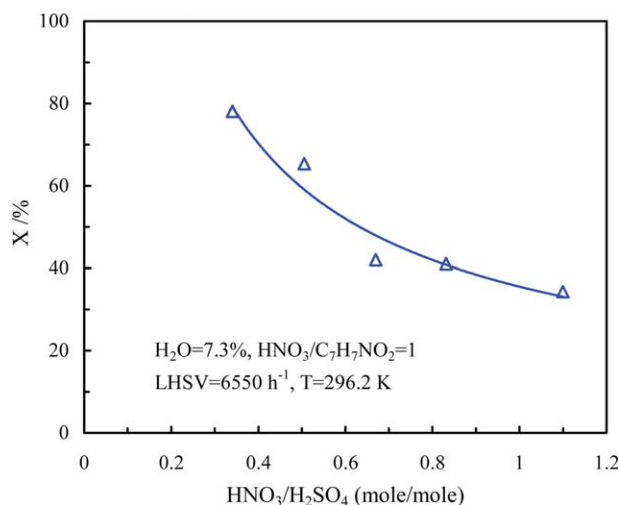


Figure 11. Effect of $\text{HNO}_3/\text{H}_2\text{SO}_4$ on the conversion of NT.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DNT had much lower activity compared to NT according to reaction characteristics. Therefore, it was hard to further nitrify the DNT, and TNT did not occur in products.

Effect of reaction temperature on the conversion

It is well known that the reaction temperature has a great important effect on the reaction, and the intrinsic rate constant usually increases with the increasing of reaction temperature according Arrhenius Equation. Figure 13 demonstrates the effect of temperature on the conversion of NT. The conversion of NT first increased with the increasing of reaction temperature and then decreased, and the highest conversion was obtained at 340.2 K. The interaction between NT molecules and NO_2^+ ions increased with an increase in reaction temperature. The mass transfer rate of NT also increased and the reaction rate with the increase of temperature, as reported by Rahaman et al.²⁸ However, NO_2^+ ions concentration decreased with an increase in temperature according to the reports by Edwards et al.²⁹ The generation of NO_2^+ ions is through the catalysis of sulfuric acid, and the reaction is exothermic reaction. Therefore, the conversion would decrease as the reaction temperature reached a certain values in the nitration process of NT. Precise temperature control could be obtained in microchannel reactors even though the nitration with mixed acid was highly exothermic, which was due to fast heat transfer rate and small internal reaction volume. Therefore, the safety for the nitration process was ensured, and temperature-sensitive side reactions such as oxidation were inhibited.

Effect of eduction tube length on the conversion

Figure 14 shows the effect of the eduction tube length on the conversion of NT at different mixed acid composition. The conversion of NT increased slightly as the length of eduction tube increased when the sulfuric acid strength was low (86 wt %). As the sulfuric acid strength was relatively higher (97.2 wt %), the conversion of NT was hardly changed with an increase in the length of eduction tube. Actually, the residence time in eduction tube was much larger than that in packed microchannel reactor as shown in Table 2. Zaldivar et al.²⁷ had indicated

Table 1. The Change of Sulfuric Acid Strength after Reaction

Sulfuric Acid Content (wt %)		Sulfuric Acid Strength (wt %)
Before Reaction	Before Reaction	After Reaction
58.3	77.9	77.8
60.6	81.9	81.3
62.8	85.9	83.2
64.8	89.9	85.9
66.5	93.4	87
68.5	97.2	88.5

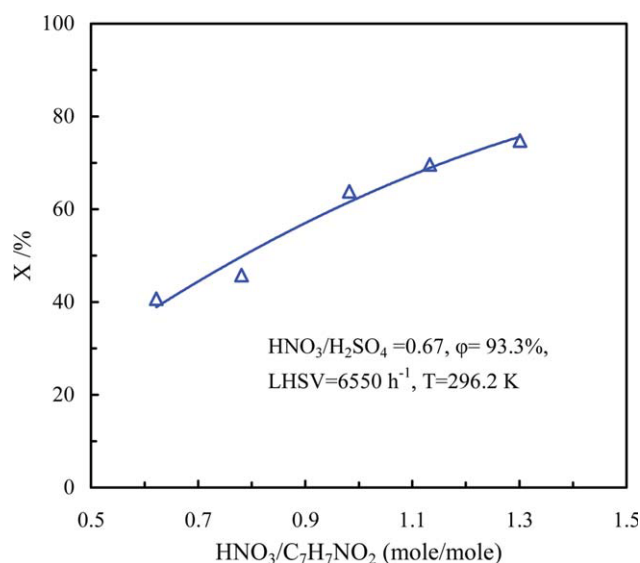


Figure 12. Effect of $\text{HNO}_3/\text{C}_7\text{H}_7\text{NO}_2$ on the conversion of NT.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the nitration of aromatics falls into the fast reaction regime as sulfuric acid strength exceeds 70%. The sulfuric acid strengths both exceeded 80% for the two kinds of mixed acid composition in this work; therefore, the reactions were limited by mass transfer. In the packed microchannel reactor, high liquid–liquid dispersions can be obtained, and so the effective interfacial area and mass transfer rate are large. The mass transfer in the packed microchannel reactor between two phases was much better than that in the eduction tube. The concentration of reactants also became lower after the nitration in the packed microchannel reactor. So, the nitration reaction rate in the

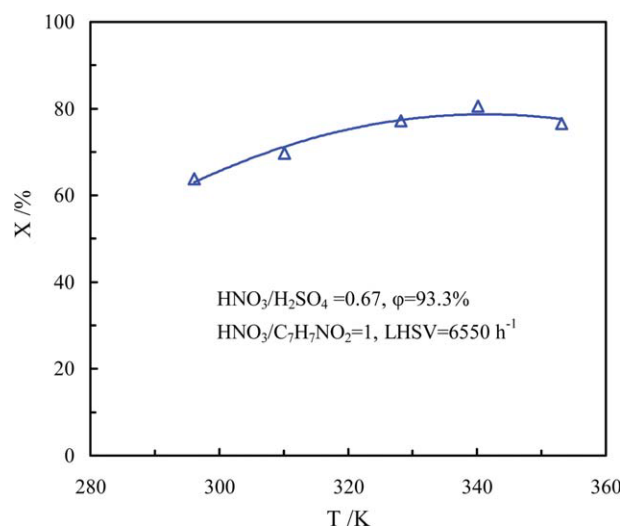


Figure 13. Effect of reaction temperature on the conversion of NT.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

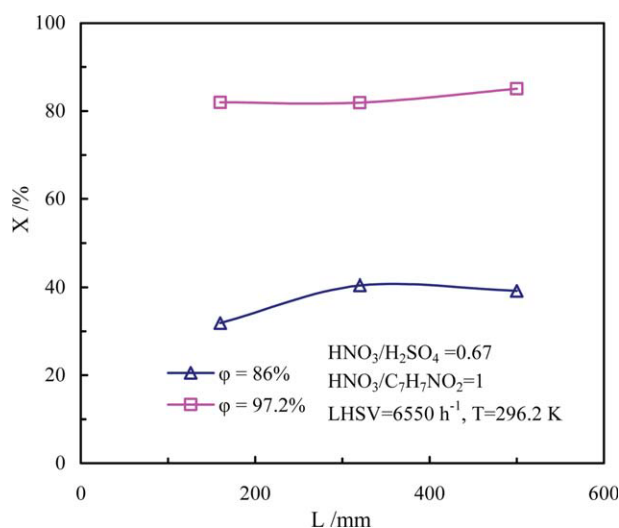


Figure 14. Effect of length of eduction tube on the conversion of NT.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

packed microchannel reactor was much higher compared with that in eduction tube, and the nitration reaction mostly took place in the packed microchannel reactor. As the sulfuric acid strength was higher, the difference of mass transfer rates in the packed microchannel reactor and the eduction tube was more obvious, and thus, the reaction taking place in the eduction tube could be neglected.

In addition, the eduction tube had an influence on determining the values of ka . From Figure 14, we also can see that the effect of eduction tube on conversion was relatively obvious for lower sulfuric acid strength (86 wt %). In this situation, the conversion of NT in the eduction tube could not be neglected. That is, the conversion of NT in the packed microchannel reactor was overestimated. However, the calculation of ka was only based on the volume of the microchannel and did not consider the volume of the eduction tube. Therefore, it must result in overestimating ka in Figure 7. For higher sulfuric acid strength (97.2 wt %), the conversion of NT was over 80%, and hardly changed with an increase in the length of eduction tube. It could be speculated that the concentration of NT and nitronium ions (NO_2^+) was low in the outlet of packed microchannel reactor, and the conversion of NT in the eduction tube was extremely low. In other words, the eduction tube did not affect the calculation of ka . Actually, the overestimating of ka can be eliminated by using packed microchannel reactor without eduction tube. However, the eduction tube is necessary when the packed microchannel reactor is immersed in water bath for constant temperature operation.

Table 2. Residence Time in Packed Microchannel Reactor and Eduction Tube

	Packed Microchannel	Eduction Tube with Different Lengths (cm)		
		16	32	50
Residence time (s)	0.55	28.78	57.57	87.95

Conclusions

The nitration of NT with mixed acid as a fast liquid–liquid multiphase reaction model was conducted in the packed and nonpacked microchannel reactors. It was speculated that better dispersion of NT phase and acid phase could be obtained as the content of sulfuric acid in aqueous phase increased according to the solubility characteristics. Better reaction performance could be found in the packed microchannel reactor compared with the nonpacked microchannel reactor because of its higher dispersion and excellent mass transfer performance. The conversion of NT even reached 94% in the packed microchannel reactor when the reaction time was less than 3 s. A new parameter, which represented the coupling of mass transfer and residence time in microdevices, was proposed for explaining and anticipating nitration process in microchannel reactors. It must increase the values of Da' to obtain higher conversion or extraction efficiency in microdevices for liquid–liquid multiphase systems. Some operational parameters such as mixed acid composition and reaction temperature affected intrinsic kinetic, mass transfer, and finally the reaction performance. By-product and temperature runaway did not appear in the reaction process because of superior heat and mass transfer rate in the microchannel reactor. The effect of education tube on the reaction performance was dependent on the sulfuric acid strength and the reactor characteristics.

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Notation

- a = interfacial area, m^2/m^3
 $C_{or,0}$ = original concentration of NT in organic phase, mol/l
 $C_{or,1}$ = concentration of NT in organic phase after reaction, mol/l
 Da = the first Damköhler number, 1
 Da' = a parameter similar to first Damköhler number for micro-devices, 1
 k = overall mean mass transfer coefficient, m/s
 ka = overall volumetric mean mass transfer coefficient, 1/s
 L = length of education, mm
LHSV = Liquid hourly space velocity, h^{-1}
 M_{DNT} = molecular weight of DNT, g/mol
 M_{NT} = molecular weight of NT, g/mol
 $Q_{aq,i}$ = aqueous phase volume flow rate, m^3/s
 $Q_{or,i}$ = organic phase volume flow rate, m^3/s
 t = residence time in microchannel reactor, s
 V = volume of microchannel, m^3
 M_{DNT} = mass fractions of DNT in the product organic phase, 1
 M_{NT} = mass fractions of NT in the product organic phase, 1
 w_s = mass fraction of sulfuric acid in mixed acid, 1
 w_w = mass fraction of water in mixed acid, 1
 X = conversion of NT, %

Greek letters

- φ = sulfuric acid strength, %

Subscripts

- aq = aqueous phase
 i = inlet
or = organic phase
0 = original
1 = after reaction

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