

Synthesis of Adipic Acid through Oxidation of K/A oil and Its Kinetic Study in a Microreactor System

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Abstract

Synthesis of adipic acid (AA) through the oxidation of cyclohexanol and cyclohexanone (K/A oil) with nitric acid was conducted in a capillary microreactor system. Effects of the temperature, the nitric acid concentration, the volumetric flow rate ratio of nitric acid to K/A oil, and the capillary length on the selectivity and the product yield were investigated systematically to achieve optimal reaction conditions. Notably, a high yield of adipic acid (i.e., 90%) was achieved just in 6 seconds at 85°C with the use of 55 wt% nitric acid. Gas components produced in this oxidation process and its total volumetric flow rate were determined under various operating conditions, which was beneficial for reaction mechanism characterization and process optimization.

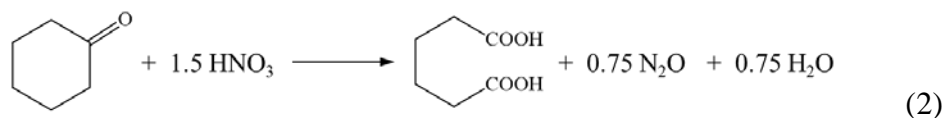
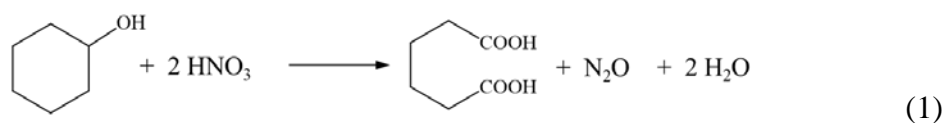
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Finally, a kinetic model was established, which was of crucial theoretical significance and practical value for optimizing the reactor design and better understanding such fast and highly exothermic multiphase processes with abundant gas production.

Keywords: Adipic Acid; Oxidation; Kinetics; Process Intensification; Microreactor

Introduction

As a crucial intermediate in the manufacture of Nylon 6,6 and many synthetic resins, adipic acid is produced almost exclusively via the oxidation of cyclohexanol or the mixture of cyclohexanol and cyclohexanone (K/A oil) with nitric acid as the oxidant in the presence of copper and vanadium catalysts in industry.¹⁻⁴ The reaction scheme for the oxidation of K/A oil with nitric acid can be represented theoretically as follows:



Reaction Equations (1) and (2) imply different pathways for the formation of adipic acid with different consumption of nitric acid when applying K/A oil as the substrate. Indeed, the reaction mechanism is much more complicated than that shown in this scheme. Cyclohexanol easily converts to cyclohexanone even at low temperatures, and then cyclohexanone takes part in further transformations at a much slower rate. Besides, nitric acid shows very complex activity associated with different steps such as acidifying, nitrating, nitrosating, and oxidizing, influencing the selectivity of this oxidation process. The activity of nitric acid is, in turn, greatly depends on

the operational conditions (e.g., temperature, pressure, and nitric acid concentration), catalysts and any impurities related to the transformation of nitric acid (i.e., HNO_2 , NO_2 , N_2O_3 , and N_2O_5).² In this oxidation process, a branch of intermediates are produced, while glutaric acid (GA) and succinic acid (SA) as two main by-products are generated in parallel and competing reaction steps. Moreover, a large amount of gas mixture is produced during the reaction process especially at high temperatures, and the analysis of the gas mixture composition indicates the presence of N_2O , NO , NO_2 , N_2 , and CO_2 .^{5,6} Nitrogen oxides (NO and NO_2) produced during the reaction process is considered to be due to the instability of nitrous acid (HNO_2) that is formed via the nitric acid reduction in the transformation of cyclohexanol to cyclohexanone.⁷

The reaction mechanism for the oxidation of cyclohexanol and cyclohexanone with nitric acid was first reported and discussed by van Asselt and van Krevelen^{2,7-9} in 1963. Castellan et al.^{1,3,10,11} described reaction networks and kinetics in a series of research papers at the beginning of the 1990s. This research generated a complete and detailed analysis of many possible reaction steps that could occur depending on operating conditions. Figure 1 is the overview of the proposed reaction pathways for the formation of AA from cyclohexanol with nitric acid as the oxidant, and it shows at least five paths leading to the formation of adipic acid. Cyclohexanol (A) is oxidized to cyclohexanone (B) in the presence of nitrous acid, followed by nitrosation of cyclohexanone via nitrous acid to produce 2-nitrosocyclohexanone (E). Moreover, Castellan et al.¹ considered cyclohexyl nitrite (C) as the first oxidation intermediate of cyclohexanol rather than cyclohexanone. Cyclohexyl nitrite (C) is then rearranged into

2-nitrosocyclohexanone (E), which is the critical intermediate in all the proposed mechanisms and can undergo various transformations as shown in Routes 1-5.^{12,13} All these five reaction routes are strongly dependent on the operating conditions (i.e., reaction temperature, pressure, concentrations of copper and vanadium catalysts, the concentration of nitric acid, and the molar ratio between reactants). High selectivity for the production of adipic acid (AA) can be achieved by optimizing these operational factors. Moreover, the high exothermicity of this oxidation process (the reaction enthalpy values of cyclohexanol to AA and cyclohexanone to AA are -215 kcal/mol and -172 kcal/mol respectively)^{12,13} and a large amount of gas generated have a decisive influence on the choice of technologies and the design of reactors.

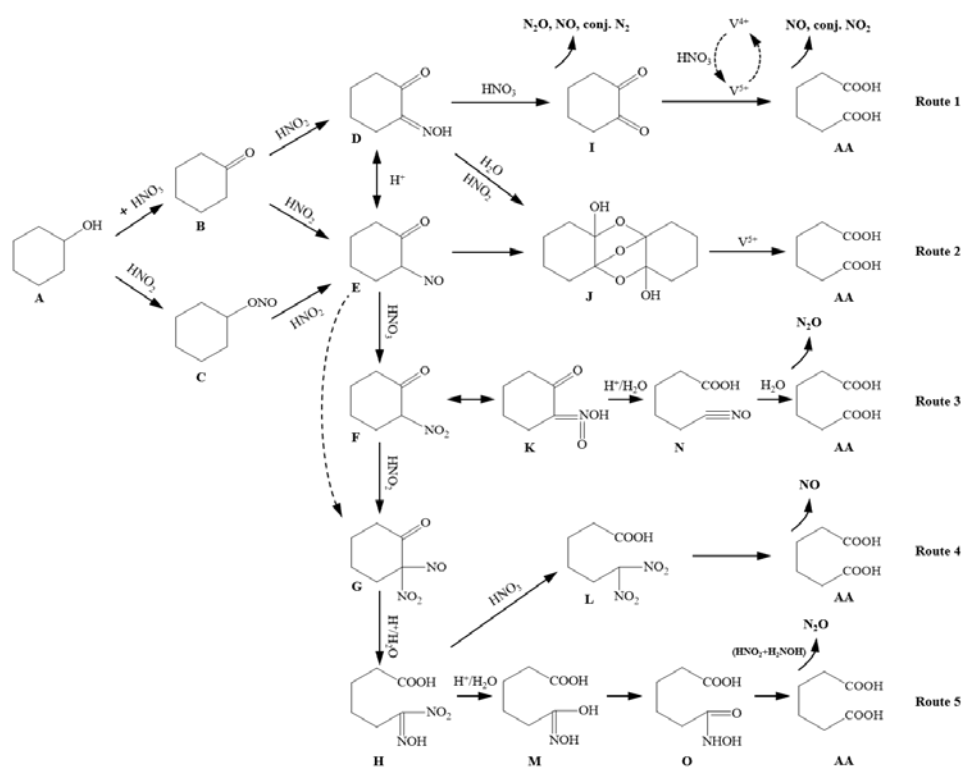


Figure 1 Main reaction steps and proposed routes for the formation of adipic acid (AA) through the oxidation of cyclohexanol with nitric acid (elaborated from refs^{1,2,5,12,13}).

In a typical industrial plant for the adipic acid production, the K/A oil reacts with 45–55% nitric acid containing copper (0.1–0.5 wt%) and vanadium (0.02–0.1 wt%) catalyst in four (or more) in-series stirred-tank reactors for each of which strict control over the temperature is required. Optimization of heat transfer performance in the oxidation reactors to achieve a high adipic acid yield has been the subject of considerable research and development over the years. In practice, it is necessary to control the K/A oil feed with a large excess of nitric acid in each bulky tank for better heat removal while the reaction time should be sufficiently long on purpose. In addition, negative pressure operation is required in each tank for venting the produced gas mixture out of the reaction system in case of an explosion. One can easily understand difficulties and safety risks of managing such a fast and highly exothermic oxidation process with the use of conventional reactors. To the best of our knowledge, all report studies^{1,5,7,14,15} concerning the adipic acid synthesis through the oxidation of cyclohexanol and cyclohexanone with nitric acid were carried out in batch reactors. In order to ensure the heat exchange rate adequate to compensate for the heat released in this oxidation process, it is essential to apply reactors with large specific surface areas.

Microreactor technology has experienced rapid development from fundamental research to industrial applications.¹⁶⁻²³ It benefits from much larger surface-to-volume ratio, higher heat and mass transfer rates and improved safety compared to traditional batch reactors, reforms the batch processing towards the continuous-flow processing to a remarkable extent, and currently has become a strong platform for process intensification of various reactions.²⁴⁻²⁹ Inspired by a series of landmark researches

about the direct synthesis of adipic acid from cyclohexene and hydrogen peroxide (H_2O_2) in packed-bed microreactors,³⁰⁻³² we surmised that the synthesis of adipic acid through the oxidation of K/A oil with nitric acid in continuous-flow microreactors would be advantageous as this fast and highly exothermic process has high requirements for heat and mass transfer efficiency. Moreover, the effects of operational conditions on the yields of AA, GA, and SA and the composition of the produced gas mixture have not been systematically investigated. Let alone, the reaction kinetics under operational conditions close to the industrial process for the oxidation of K/A oil to produce adipic acid has not been reported up to now. Such a reaction kinetics study would be of importance for process optimization and further understanding of reaction mechanisms. Besides, the gas mixture produced during the reaction process makes the intrinsic reaction rate determination more complicated due to multiphase hydrodynamics and the actual reaction time that could not be easily obtained.³³ A convenient method should be proposed to calculate the reaction rate in such a complex multiphase process with the production of substantial gas.

In this work, a continuous-flow microreactor system was developed to synthesis adipic acid through the oxidation of K/A oil using nitric acid as the oxidant. The main product, adipic acid, combining with the other two important by-products (GA and SA) in the liquid phase, was analyzed by HPLC. As a large amount of gas mixture was produced during the oxidation process, the composition of the gas mixture was confirmed by GC. Effects of the reaction temperature, the concentration of nitric acid, the volumetric flow rate ratio of nitric acid to K/A oil, and the length of the capillary

on the reaction performance were investigated systematically. Based on experimental data, a reaction kinetic model was developed to better understand this oxidation process.

Experimental Section

Materials

Cyclohexanol (98.5%, AR), cyclohexanone (99.0%, AR) were purchased from Yonghua Chemical Technology Co., Ltd (Shanghai, China). Nitric acid (AR) was obtained from Macklin Biochemical Co., Ltd (Shanghai, China). Copper (99.9%), vanadium pentoxide (99.0%), acetonitrile (99.9%, HPLC), succinic acid (RG), glutaric acid (RG), and adipic acid (RG) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemical reagents were used directly in the experiments without further purification.

Continuous synthesis of adipic acid in the capillary microreactor system

The schematic diagram of the microreactor system is shown in Figure 2. Nitric acid (HNO_3) solution and K/A oil (80 wt% cyclohexanol and 20 wt% cyclohexanone) were supplied from two glass vessels and separately delivered into the capillary microreactor system by two high precision piston pumps (Xingda 2PB-1040II, China) with the accuracy of 0.01 mL/min. The nitric acid solution with the concentration of 40~55 wt% was applied, and it contained the catalyst (i.e., 0.4 wt% Cu^{2+} and 0.04 wt% V^{5+}). Both these two solutions were preheated to the reaction temperature in coiled stainless capillaries before they were mixed in the micromixer (316L stainless steel). The stainless steel capillary loop was connected directly to the outlet of the micromixer. The

inner diameter of all applied capillaries and the micromixer was 1.0 mm. The whole microreactor system, which consisted of the preheating capillaries, the micromixer, and the capillary loop, was submerged in an electro-thermostatic water bath (BWS-0510, Shanghai Bluepard Instruments Co., Ltd. China) to achieve a set temperature (55-85°C). The reaction time could be easily controlled by verifying the length of the capillary loop ($L = 6\sim 22\text{m}$) and the total flow rate of two reactant solutions (Q_I). A pressure sensor (HUBA-691, Huba control, Switzerland) was placed in the inlet of the microreactor system for online monitoring the pressure drop (Δp) over the whole reactor system. For each experiment, it was repeated for three times with controlled experimental errors (5%) and average measurement values were provided as final results

Analysis

As shown in Figure 2, two analysis units were designed at the end of the stainless steel capillary loop controlled by a three-way change-over valve to analyze the gas mixture (N_2O , NO_2 , NO , N_2 and CO_2) and the products (adipic acid, glutaric acid and succinic acid) in the liquid mixture respectively.

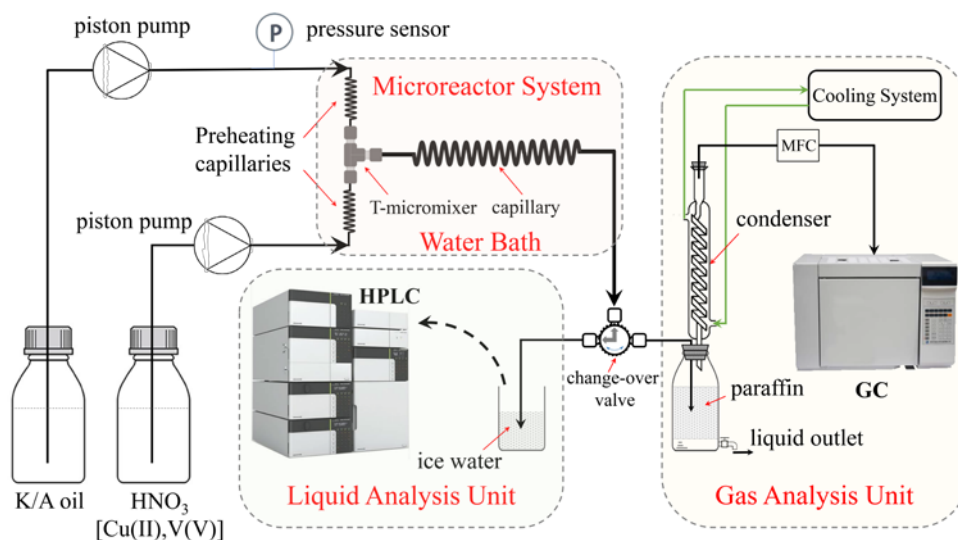


Figure 2 Schematic diagram of the experimental setup for the adipic acid synthesis.

In the liquid analysis unit, the reaction was quenched by diluting the liquid effluent in a collection vessel containing a known volume of ice water. The crystallization of succinic acid, glutaric acid and adipic acid was prevented in this sample collection process. A high-performance liquid chromatography (HPLC, Shimadzu LC-16, Japan) equipped with a C18 column (WondaSil C18-WR 5 μm , 4.6×150 mm) was used for determining the yield of SA, GA, and AA. The mobile phase was a mixture of ultrapure water (adjusting the pH to 2.5 by HPO_4) and acetonitrile with a flow rate of 0.8 mL/min. The detection wavelength of the UV-detector was set at 210 nm. The yield of SA, GA, and AA (Y_i) was calculated by the following equation:

$$Y_i = \frac{\frac{m_{\text{sample}}}{\rho_{\text{sample}}} \cdot C_i}{\frac{Q_{\text{K/A}} \cdot \rho_{\text{K/A}}}{M_{\text{K/A}}} \cdot t_{\text{sample}}} \quad (i = \text{SA, GA, or AA}) \quad (1)$$

where C_i is the concentration of dicarboxylic acid (SA, GA, or AA) in the liquid sample, m_{sample} is the weight of the liquid sample, ρ_{sample} is the density of the liquid sample, $Q_{\text{K/A}}$ is the volumetric flow rate of K/A oil, $\rho_{\text{K/A}}$ is the density of K/A oil, $M_{\text{K/A}}$ is the average molecular weight of K/A oil, and t_{sample} is the sampling time. The following equation is used to define the selectivity for the production of SA, GA and AA (S_i):

$$S_i = \frac{Y_i}{Y_{\text{SA}} + Y_{\text{GA}} + Y_{\text{AA}}} \quad (i = \text{SA, GA, or AA}) \quad (2)$$

As previously mentioned, the oxidation process of cyclohexanol converting to cyclohexane and intermediates is rapid. K/A oil disappeared almost immediately when it contacted with the nitric acid solution and was converted entirely to intermediates under all experimental conditions. The concentration of intermediates could not be

determined via HPLC. Thus, the possible intermediates in the reaction process were grouped as IM. The calculation of the IM concentration was based on the assumption that no other oxidation products were formed in the liquid mixture of the reaction system except for the intermediates, adipic acid, succinic acid, and glutaric acid, and the formation of SA and GA was only accompanied by the production of two-carbon compounds (C_2) and one-carbon compounds (C_1), respectively. According to the experimental results reported by W. J. Van Asselt et al.², further oxidation of these products (i.e., adipic acid, succinic acid, and glutaric acid) with nitric acid was unlikely occurred. The concentration of IM was calculated by the following equation:

$$\begin{aligned}
 [\text{IM}] &= [\text{IM}]_0(1 - X_{\text{IM}}) \\
 &= [\text{K/A}]_0 \left(1 - \frac{[\text{AA}] + [\text{GA}] + [\text{SA}]}{[\text{K/A}]_0}\right) \\
 &= [\text{K/A}]_0 - ([\text{AA}] + [\text{GA}] + [\text{SA}])
 \end{aligned} \tag{3}$$

where $[\text{IM}]_0$ is the initial concentration of IM, X_{IM} is the conversion of IM, $[\text{K/A}]_0$ is the initial concentration of K/A oil, $[\text{AA}]$, $[\text{GA}]$, and $[\text{SA}]$ are the concentrations of AA, GA, and SA in the liquid sample, respectively.

In the gas analysis unit, a gas-liquid separator containing enough volume of paraffin which prevented the reabsorption of gas was set to separate the gas and liquid products efficiently. In particular, the liquid phase was discharged from the separator by adjusting the bottom outlet valve while the gas phase was exhausted from the top outlet. A top-mounted condenser was used for cooling the vaporized nitric acid and water and drying the gas mixture. The coolant, namely a mixture of ethanol (80 %) and water (20 %), was kept at -5°C in the cooling system, ensuring the vaporized nitric acid and water to be sufficiently condensed and then fall back into the separator to the fullest

extent. Before the gas mixture was analyzed by a gas chromatography (GC, GC-6600, Shanghai Fanwei Instrument Equipment Co., Ltd, China), its total volumetric flow rate was measured by a gas mass flow controller (Beijing Sevenstar Electronics Co., Ltd., China, measurement range: 0–500 mL/min). The concentrations of N₂, NO, N₂O, and CO₂ were online determined directly by the GC with two TCD detectors using an autosampler. According to the previous discussion, the assumption that the rest of the gas could be calculated as NO₂ was made reasonably. The volumetric concentration of NO₂ in the gas mixture is calculated as follows:

$$[\text{NO}_2] = 1 - ([\text{N}_2] + [\text{NO}] + [\text{N}_2\text{O}] + [\text{CO}_2]) \quad (4)$$

Results and Discussion

The reaction performance in the microreactor system

To ensure cyclohexanol and cyclohexane being entirely converted under all experimental conditions (the reaction temperature = 55–85°C, the length of the capillary = 6–22 m and the residence time = 3.5–66 s), we analyzed liquid samples and found no residue of cyclohexanol and cyclohexane in the liquid samples. These results indicated that we could achieve 100% conversion for cyclohexanol and cyclohexane with very short residence times for this oxidation process under the involved experimental conditions using microreactor technology.

The flow rate needs to be determined to ensure efficient mass transfer performance in such a fast oxidation process. Figure 3 shows the variation of the adipic acid yield with different total flow rates at the same residence time and the same volumetric flow rate ratio of nitric acid and K/A oil (the details about the calculation of the residence

time can be seen in the part of the kinetic study). The mass transfer between two immiscible feed solutions increased in the T-micromixer and the following capillary when the volumetric flow rate increased.³⁴ As shown in Figure 3, the yield of adipic acid did not continued to increase when the total volumetric flow rate reached 10.5 mL/min, indicating that the mass transfer was no longer the limiting factor for this oxidation process even at high reaction temperature. In order to eliminate the mass transfer limitation, all the following experiments were operated with a total volumetric flow rate of 10.5 mL/min for this continuous-flow synthesis process.

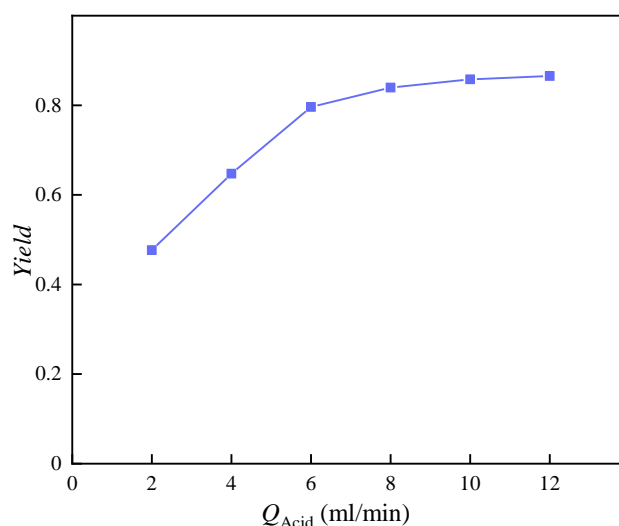


Figure 3 Yield of adipic acid with different total flow rates at the same residence time

($C_{\text{NA}} = 50$ wt%, $C_{\text{Cu}} = 0.4$ wt%, $C_{\text{V}} = 0.04$ wt%, $q = Q_{\text{NA}}/Q_{\text{KA}} = 20$, $T = 85$ °C and $t = 7$ s).

Effect of the volumetric flow rate ratio of nitric acid to K/A oil

In industry, nitric acid is considerably excess for the synthesis of adipic acid in tank-in-series processes. The volumetric flow rate ratio of nitric acid solution (50 wt% HNO_3) to K/A oil is 20-60, while the molar ratio of HNO_3 to K/A oil is around 22-30 in each batch reactor. As mentioned before, the selectivity for some side reactions such as the production of GA and SA will increase when the supply of nitric acid is not

enough. However, superabundant nitric acid would increase the load in subsequent separation sections after the oxidation process. Therefore, efficient and economical usage of nitric acid is of practical significance.

The effect of the volumetric flow rate ratio of HNO₃ to K/A oil ($q = Q_{NA}/Q_{KA}$) on the yield and selectivity for the production of adipic acid (AA) was studied for the oxidation process. As shown in Figure 4, the yield of adipic acid (AA) increased with the increase of the volumetric flow rate ratio. The selectivity for the adipic acid production firstly increased and then remained at a certain level (about 97%). The theoretical (or the least) consumption of nitric acid should be 1.5-2 mol per mole of K/A oil, as shown in Equations (1) and (2). Moreover, the concentration of nitric acid decreased sharply as the oxidation process proceeded especially at a high temperature. This oxidation process required a relatively high concentration of nitric acid for achieving high selectivity and high yield of adipic acid.^{3,11,12} Therefore, the volumetric flow rate ratio of HNO₃ to K/A oil should reach a reasonably high value. Experiments conducted in the microreactor system also proved that the yield and selectivity for adipic acid production decreased with decreasing the concentration of nitric acid. Besides, the adiabatic-temperature rise (ΔT_{ad}) of this oxidation process under the specific experimental condition ($q = Q_{NA}/Q_{KA}=20$, $Q_{NA}=10$ mL/min, $C_{NA} = 50$ wt%) is about 115°C according to the following equation:

$$\Delta T_{ad} = \frac{(-\Delta H_R)C_{A0}}{\rho \bar{C}_{pi}} \quad (5)$$

If the volumetric flow rate ratio of nitric acid to K/A oil decreases, the adiabatic-temperature rise would further increase, and more heat needs to be removed from the

reaction system demanding more capacity of the heat exchange for the reactor. Since this highly exothermic oxidation process is quite sensitive to the reaction temperature, the use of the large quantity of nitric acid would be beneficial for the control over the released heat and the temperature. In other words, the nitric acid solution could act as not only a reactant but also a coolant in this oxidation process. For saving the consumption of nitric acid, the volumetric flow rate ratio of nitric acid to K/A oil was optimized to be 20 for this oxidation process.

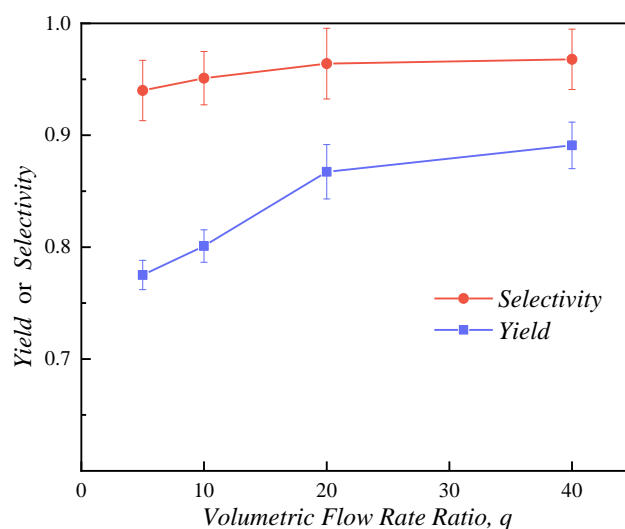


Figure 4 Effect of the volumetric flow rate ratio of nitric acid to K/A oil ($q = Q_{\text{NA}}/Q_{\text{KA}}$) on the selectivity and yield of adipic acid ($C_{\text{NA}} = 50$ wt%, $C_{\text{Cu}} = 0.4$ wt%, $C_{\text{V}} = 0.04$ wt%, $T = 85$ °C, $L = 22$ m and $Q_l = 10.5$ mL/min).

Effects of the reaction temperature and the capillary length

The oxidation of cyclohexanol and cyclohexanone is a highly exothermic reaction, and the intrinsic reaction rate constants usually increase with the temperature increase. Therefore, the reaction temperature has a critical influence on the reaction rate and the distribution of oxidation products. As shown in Figure 5, the effect of the reaction

temperature on the yield of AA, GA and SA and the selectivity for the AA formation was investigated in the capillary microreactors with four different lengths at a constant total volumetric flow rate of two reactant solutions. The residence time in the microreactor system was varied by changing the length of the capillary. The yield of oxidation products (i.e., AA, GA and SA), increased with the increase of the capillary length because of the continuous conversion of intermediates (IM) that was converted from K/A oil rapidly. The yield of AA increased from 13.5% to 40.9% with the capillary length varied from 6 m to 22 m at 55°C, and the yield of GA and SA increased from 0.5% to 2.2% and from 0 to 0.2% at the same condition respectively.

As can also be seen from Figure 5, the yield of AA, GA and SA increased with the increase of the reaction temperature from 55°C to 85°C. Notably, the yield of the target product, i.e., adipic acid, reached about 87.5% at 85°C in the microreactor system with the capillary length of 22 m. However, the promotion on the yield of AA was less significant with the further increase of the reaction temperature. For the selectivity for the AA formation (S_{AA}), it decreased slightly with the increase of the capillary length and the reaction temperature. The yield of SA was far lower than that of AA, and the formation of SA was less sensitive to the temperature compared with the formation of AA. The yield of AA was boosted more than five times from 13.1% to 66.7% when the temperature increased from 55°C to 85°C in the microreactor system with the capillary length of 6 m.

The results in Figure 5 also indicated that the side reactions could be suppressed by optimizing and precisely controlling the reaction temperature and the reaction time.

As previously mentioned, the oxidation of cyclohexanol to form AA is highly exothermic, and the adiabatic-temperature rise is relatively high even at a large volumetric flow rate ratio of nitric acid to K/A oil. Although the microreactor had a much larger surface-to-volume ratio, higher heat and mass transfer rates compared to the traditional reactors, the temperature at the microreactor outlet was still 2-3°C higher than the set temperature during the oxidation process at high temperatures. This again reflected the strict demand on a high heat exchange capacity of the reactor system for this oxidation process.

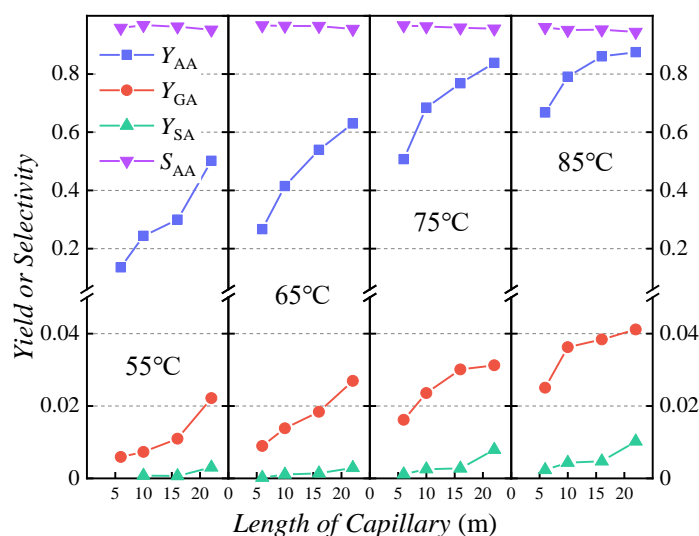


Figure 5 Effect of the reaction temperature and the capillary length on the yield of AA, GA and SA and the selectivity for AA (S_{AA}). ($C_{NA} = 50$ wt%, $C_{Cu} = 0.4$ wt%, $C_V = 0.04$ wt%, $Q_I = 10.5$ mL/min and $q = Q_{NA}/Q_{KA} = 20$).

Effect of the concentration of nitric acid

Figure 6 shows the effect of the concentration of nitric acid on the yield of AA, GA and SA and the selectivity for the AA production in the microreactor systems with various capillary lengths at 75°C. As the mass concentration of nitric acid increased from 40wt% to 55wt%, the yield of AA increased while the yield of GA and SA

decreased for all microreactor systems. Accordingly, the selectivity for the AA formation increased from 91.5% to 95.7% in the microreactor system with the capillary length of 22m. As stated before, nitrous acid plays a crucial role on the conversion of cyclohexanol, the nitrosation and hydrolyzation of a branch of intermediates. Nitrous acid would not be enough at a low concentration of nitric acid. In addition, the main routes especially Route 2 for the AA formation require a high concentration of nitric acid (e.g., 50wt%), as shown in Figure 2. The effect of the volumetric flow rate ratio of nitric acid to K/A oil on the selectivity and the yield of AA indicated that a high concentration of nitric acid could benefit to the formation of AA (see Figure 4).

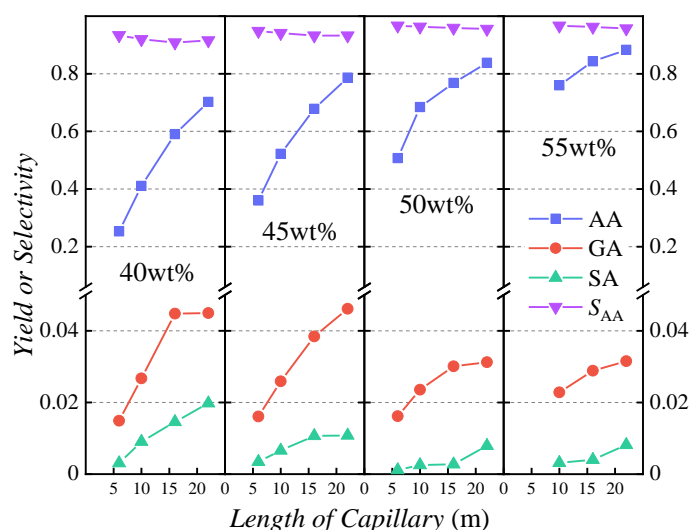


Figure 6 Effect of the concentration of nitric acid on the yield of AA, GA and SA and the selectivity for AA (S_{AA}) in microreactors with different capillary lengths ($T = 75^{\circ}\text{C}$, $C_{Cu} = 0.4 \text{ wt\%}$, $C_V = 0.04 \text{ wt\%}$, $Q_l = 10.5 \text{ mL/min}$ and $q = Q_{NA}/Q_{KA} = 20$).

A further increase in the concentration of nitric acid ($\geq 50\text{wt\%}$) had no significant contribution to the selectivity for the AA formation. However, the consumption of nitric acid would increase notably at high reaction temperatures due to the thermal decomposition of nitrous acid (HNO_2). Therefore, the optimal concentration of nitric

acid was considered to be in the range of 50wt%-55wt%.

According to the present investigation on the effects of operating conditions (the reaction temperature, the concentration of nitric acid, the volumetric flow rate ratio of nitric acid to K/A oil, and the capillary length) on the distribution of the oxidation products in the liquid mixture, it is crucial to precisely control and optimize the reaction temperature and the concentration of nitric acid for achieving high selectivity and desired yield of adipic acid.

Gas mixture and its composition

During the oxidation process, a great deal of gas mixture was produced, especially at high reaction temperatures. As mentioned before, in industrial continuous multi-reactor processes, negative pressure operation is required in each kettle venting the produced gas out of the reaction system. Few articles were concerning the total volumetric flow rate of the gas mixture (V_{gas}) under the condition close to industrial processes.⁸ Figure 7 shows the effect of the concentration of nitric acid and the reaction temperature on the total volumetric flow rate of the gas mixture in different microreactor systems with the capillary length variation. The total volumetric flow rate of the gas mixture increased with the increase of the concentration of nitric acid, the reaction temperature and the length capillary. At a low reaction temperature (55°C), the total volumetric flow rate of the gas mixture increased from 20.1mL/min to 63.2 mL/min when the concentration of nitric acid increased from 40wt% to 55wt%. As the reaction temperature raised to 85°C, a large amount of gas mixture was ejected from the outlet of the capillary microreactor together with the liquid effluent. The total

volumetric flow rate of the gas mixture reached 327 mL/min in the microreactor with the capillary length of 22 m when the concentration of nitric acid was 55 wt%, which was over 30 times higher than the inlet total volumetric flow rate of two reactant solutions (10.5 mL/min). In order to rule out the possibility of direct decomposition of nitric acid to produce gas, we only pumped nitric acid (with or without catalysts) into the capillary microreactor system without K/A oil under all the experimental conditions. No gas bubbles were observed at the end of the capillary microreactor. These results indicated that all the gases were produced due to the oxidation of K/A oil rather than the decomposition of nitric acid.

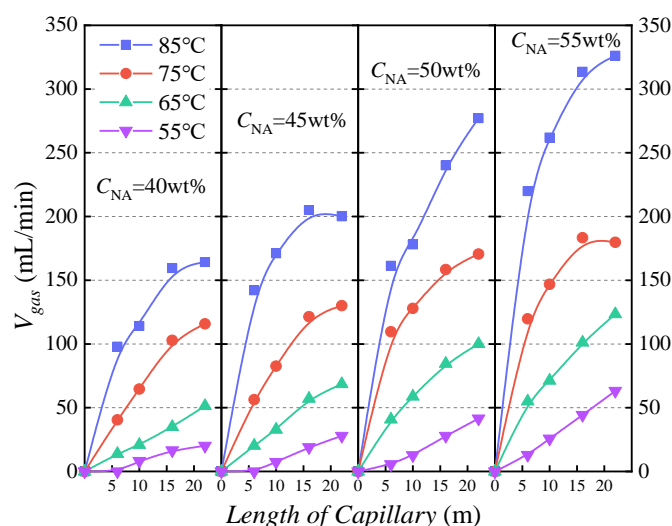
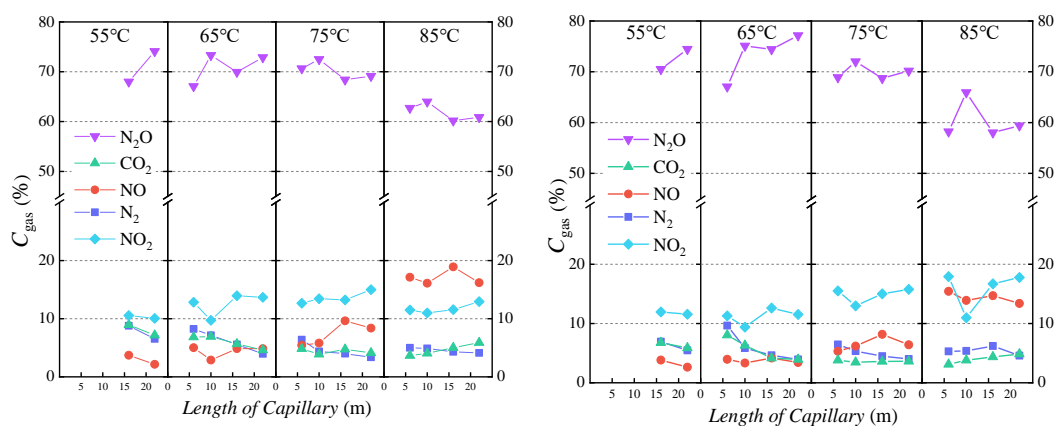


Figure 7 Effect of the concentration of nitric acid and the reaction temperature on the total volumetric flow rate of the gas mixture (V_{gas}) in microreactors with different capillary lengths ($C_{\text{Cu}} = 0.4\text{ wt\%}$, $C_{\text{V}} = 0.04\text{ wt\%}$, $Q_I = 10.5\text{ mL/min}$ and $q = Q_{\text{NA}}/Q_{\text{KA}} = 20$).

For the K/A oil oxidation process with 67 wt% nitric acid, the composition of the gas mixture was reported quantitatively in 1956 at relatively low reaction temperatures (55–60°C), indicating the presence of N_2O , NO , NO_2 , N_2 and CO_2 in an approximate

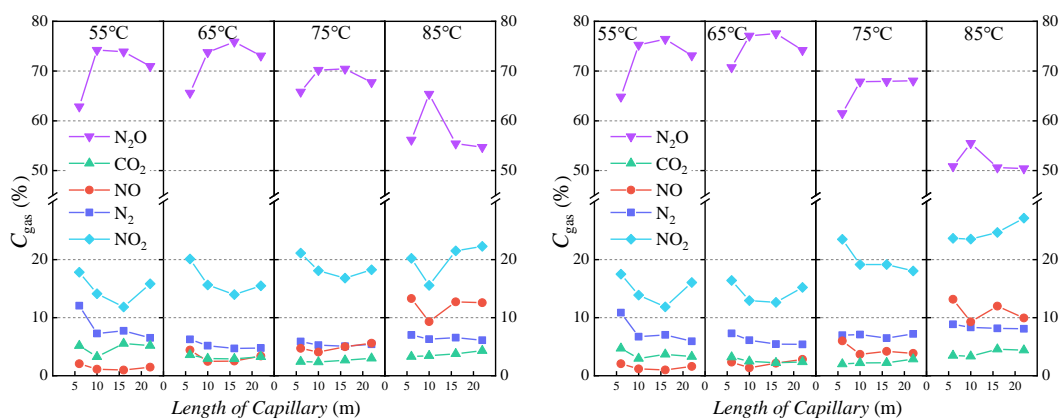
volumetric ratio of 11:5:2:1:1.⁵ Furthermore, more operating conditions (the concentration of acid, the reaction temperature and the reaction time) should be conducted for the study of the relationship between the gas mixture composition and the reaction performance. As previously mentioned, the reaction mechanism was much complex and no intermediate could be detected. The study of gas composition could be helpful for a better understanding of the reaction mechanism and the estimation of reaction routes. Figure 8 shows the effect of the concentration of nitric acid and the reaction temperature on the volumetric percentages of N₂O, NO, NO₂, N₂ and CO₂ in different microreactor systems with various capillary lengths. Since N₂O was the main gas product for the synthesis of adipic acid (AA) according to the reaction mechanism, it was found in the highest volumetric percentage (larger than 50%) under all involved experimental conditions. The volumetric percentage of N₂O firstly increased and then decreased with the increase in the capillary length, and it decreased with the increase in the reaction temperature and the concentration of nitric acid. NO₂ had the second-largest volumetric percentage in the gas mixture with an inverse trend of N₂O regarding the capillary length, the reaction temperature and the concentration of nitric acid. The volumetric percentage of NO₂ was in the range of 10-15% with a low concentration of nitric acid (40 wt%), but it increased 2-3 times when the concentration of nitric acid reached 55 wt% at 85°C in involved four microreactor systems with different capillary lengths. NO was more sensitive to the reaction temperature compared to NO₂. The volumetric percentage of NO increased 5-8 times when the reaction temperature increased from 55°C to 85°C for four different concentrations of nitric acid. It could be

estimated from the reaction mechanism that NO_2 and NO mainly came from the decomposition of nitrous acid. Thus, the quantity and decomposition rate of nitrous acid were boosted by increasing the concentration of nitric acid and the reaction temperature. The volumetric percentage of N_2 decreased with the increase of the capillary length for all involved concentrations of nitric acid, and it decreased with the increase of the reaction temperature at low concentrations of nitric acid (40 wt% and 45 wt%). However, at higher concentrations of nitric acid (50 wt% and 55 wt%), the volumetric percentage of N_2 slightly increased with the increase of the reaction temperature. The volumetric percentage of CO_2 kept the lowest in the gas mixture, with the range of 4–6% owing to the high selectivity for the AA formation.



(a) $C_{\text{NA}}=40\text{wt}\%$

(b) $C_{\text{NA}}=45\text{wt}\%$



(c) $C_{\text{NA}}=50\text{wt}\%$

(d) $C_{\text{NA}}=50\text{wt}\%$

Figure 8 Effect of the concentration of nitric acid and the reaction temperature on the volumetric ratio of N₂O, NO, NO₂, N₂ and CO₂ in the microreactors with different capillary lengths ($C_{Cu} = 0.4$ wt%, $C_V = 0.04$ wt%, $Q_l = 10.5$ mL/min and $q = Q_{NA}/Q_{KA} = 20$).

To better understand the relationship between the AA formation and the gas mixture composition, we tried to correlate the selectivity for AA (Figure 9(a)) with the volumetric percentages of N₂O, NO, NO₂, N₂ and CO₂ in the gas mixture (Figure 9(b)) at different reaction temperatures and concentrations of nitric acid. According to the comparison of Figure 9(a) and 9(b), only the volumetric percentage of N₂O had the same trend with the selectivity for AA, indicating that the formation of AA was mainly accompanied with the release of N₂O. Since CO₂ was mainly released from the formation of GA and SA with the loss of C₁ and C₂,¹⁴ the volumetric percentage of CO₂ had an inverse trend with the selectivity for the AA formation. However, the molar fraction of CO₂ in the gas mixture was much less than the total selectivity for GA and SA according to the carbon balance ($n_{CO_2} \ll n_{GA} + 2n_{SA}$), indicating that not all of C₁ and C₂ from GA and SA were converted to CO₂ and other carbonaceous products were formed in this oxidation process besides AA, GA and SA. As shown in Figure 8 and Figure 9, NO and NO₂ were sensitive to the reaction temperature and the concentration of nitric acid. Previous researches paid no attention to the generation of NO and NO₂ which can be recovered by a simple method in the industry. However, the generation of substantial NO and NO₂ would increase the pressure drop along with the microreactor system and the load of the subsequent separation and recovery units. Therefore, optimal

operating conditions (the reaction temperature and the concentration of nitric acid) should be precisely controlled to achieve the highest selectivity and yield of AA. Besides, it is necessary to take the energy consumption of the whole reactor system into consideration when performing such an oxidation reaction with a large amount of gas in continuous-flow reactors.

In general, the analysis of the gas composition, which was another crucial method combined with the analysis of the oxidation products in the liquid mixture, could be used as the guide for the estimation of reaction mechanism and the process optimization. The reaction selectivity and the yield of adipic acid could be optimized based on the results of the production of CO_2 and N_2O , and the adjustment of the operating conditions for less production of NO and NO_2 could contribute to the decrease of the nitric acid consumption. The route for the synthesis of N_2 cannot be determined by far, and it might be deduced from the investigation of intermediates in the future work.

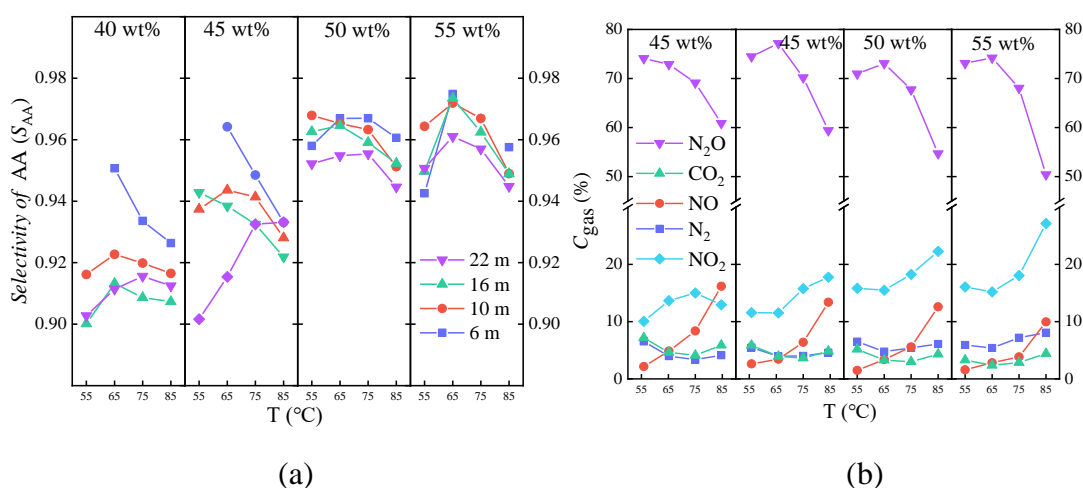


Figure 9 Effect of the reaction temperature and the concentration of nitric acid on (a) the selectivity of AA and (b) the volumetric ratio of N_2O , NO , NO_2 , N_2 and CO_2 in the microreactor system with the capillary length of 22 m ($C_{\text{Cu}} = 0.4 \text{ wt\%}$, $C_{\text{V}} = 0.04 \text{ wt\%}$,

$Q_l = 10.5 \text{ mL/min}$ and $q = Q_{\text{NA}}/Q_{\text{KA}} = 20$).

Moreover, such a large volume of complex gas mixture occupied the limited space and accelerated the superficial velocity of the reaction mixture in the microreactor system. Hence, the residence time of reactants was immensely shortened. For instance, the residence time should have been about 100 seconds treating the liquid as an incompressible fluid in the microreactor system with the capillary length of 22m. Nevertheless, the residence time decreased to about 5 seconds when considering the generation of the gas mixture in the microreactor system at 85°C with 55wt% nitric acid. Since the gas mixture was produced gradually with the oxidation process progress, it was difficult but necessary to measure the residence time in the microreactor system accurately for the study of reaction kinetics.

Apparent kinetic model of the oxidation reaction in the microreactor

According to previous researches,^{1,2,14} the mechanism for the oxidation of K/A oil with nitric acid is rather complicated with numerous uncertain elementary reactions and intermediates, which makes the description of the kinetics models based on reaction mechanisms difficult. We used the power-law kinetic model to correlate the experimental data involving both nitric acid and IM as follows:



$$r_i = \frac{dc_i}{dt} = k_0 \exp\left(\frac{-E_a}{RT}\right) [\text{NA}]^\alpha [\text{IM}]^\beta \quad (7)$$

where r_i is the reaction rate with the subscript i representing AA, GA, SA, N₂O, NO, NO₂, N₂ or CO₂, k_0 is the pre-exponential coefficient, E_a is the activation energy, [NA] is the concentration of nitric acid, [IM] is the total concentration of intermediates

calculating by Equation (3), α and β are the reaction orders with respect to nitric acid and intermediates, and R is the ideal gas constant.

Considering a large amount of gas mixture was produced during the reaction process, it was difficult to directly measure the actual residence time for the microreactor system in the absence of kinetic information. Herein, we replaced the residence time by the gas production rate along the capillary microreactor to describe the effect of the produced gas mixture on the residence time (reaction time) with two assumptions:

1. Gas was released from the beginning of the oxidation process conducted in the capillary microreactor system;
2. Under the identical operational conditions, the gas volumetric flow rate at the same fluid traveling distance was the same for the microreactor systems with different capillary lengths.

Hence,

$$\frac{AdL}{Q(L)} = \frac{AdL}{Q_l + Q_g} = dt \quad (8)$$

where $Q(L)$, Q_l and Q_g are the total volumetric flow rate, the volumetric flow rate of the liquid mixture and the volumetric flow rate of the gas mixture, respectively. $Q(L)$ is a function of the fluid traveling distance (L), which can be calculated by fitting the data in Figure 7. A is the cross-sectional area of the capillary microreactor.

The combination of Equation (7) with Equation (8) leads to the following equations:

$$\frac{Q(L)dc_i}{AdL} = k_0 \exp\left(\frac{-E_a}{RT}\right) [\text{NA}]^\alpha [\text{IM}]^\beta \quad (9)$$

$$\frac{dc_i}{A} = k_0 \exp\left(\frac{-E_a}{RT}\right) [\text{NA}]^\alpha [\text{IM}]^\beta \frac{1}{Q(L)} dL \quad (10)$$

Integration of both sides of Equation (10) leads to the following equation:

$$\frac{c_i}{\int_0^{L_0} \frac{1}{Q(L)} dL \cdot A} = k_0 \exp\left(\frac{-E_a}{RT}\right) [\text{NA}]^\alpha [\text{IM}]^\beta \quad (11)$$

where L_0 is the total length of the capillary microreactor.

Based on 144 experimental data points, the kinetic parameters in Equation (11) were regressed by the Levenberg–Marquardt method. The values of these kinetic parameters and the statistical test results are shown in Table 1. The correlation coefficient values (R^2) for all equations with regard to various products (i.e., products in the liquid mixture and the gas mixture) are higher than 0.95 except for the case of SA. As shown in Figure 10, the predicted values from Equation (11) well matched with the experimental results of concentrations for all products, confirming again the credibility of the reaction kinetic model established in this work.

Table 1 Parameters of the kinetic model and the statistical test results for the oxidation of K/A oil with nitric acid.

| r_i | Parameter | | | | Statistical test | | |
|-----------------------|--------------------------------|--------------------|------------------|------------------|------------------|----------------------|------|
| | k_0 | E_a (kJ/mol) | α | β | R^2 | $RMSE$ | F |
| AA | $2.93 \pm 0.45 \times 10^9$ | 93.96 ± 4.95 | 3.28 ± 0.21 | 0.24 ± 0.04 | 0.96 | 1.9×10^{-2} | 670 |
| GA | $2.94 \pm 0.62 \times 10^{11}$ | 103.32 ± 6.86 | 1.18 ± 0.20 | 0.08 ± 0.04 | 0.95 | 4.2×10^{-5} | 527 |
| SA | $2.84 \pm 0.86 \times 10^7$ | 64.18 ± 9.71 | -2.02 ± 0.37 | -0.63 ± 0.09 | 0.90 | 1.1×10^{-6} | 172 |
| N₂ | $6.49 \pm 0.23 \times 10^{12}$ | 148.36 ± 11.37 | 6.94 ± 0.34 | 0.26 ± 0.04 | 0.96 | 3.9×10^{-4} | 508 |
| NO | $4.43 \pm 0.32 \times 10^{27}$ | 225.78 ± 25.45 | 3.74 ± 0.20 | 0.26 ± 0.03 | 0.98 | 7.8×10^{-4} | 715 |
| CO₂ | $2.18 \pm 0.93 \times 10^{15}$ | 145.41 ± 14.29 | 3.46 ± 0.29 | -0.05 ± 0.05 | 0.95 | 1.0×10^{-4} | 399 |
| N₂O | $4.30 \pm 0.87 \times 10^{10}$ | 104.93 ± 6.57 | 3.65 ± 0.24 | 0.15 ± 0.04 | 0.96 | 2.2×10^{-2} | 548 |
| NO₂ | $1.77 \pm 0.66 \times 10^{13}$ | 144.91 ± 12.25 | 6.32 ± 0.35 | 0.11 ± 0.05 | 0.96 | 3.4×10^{-3} | 464. |

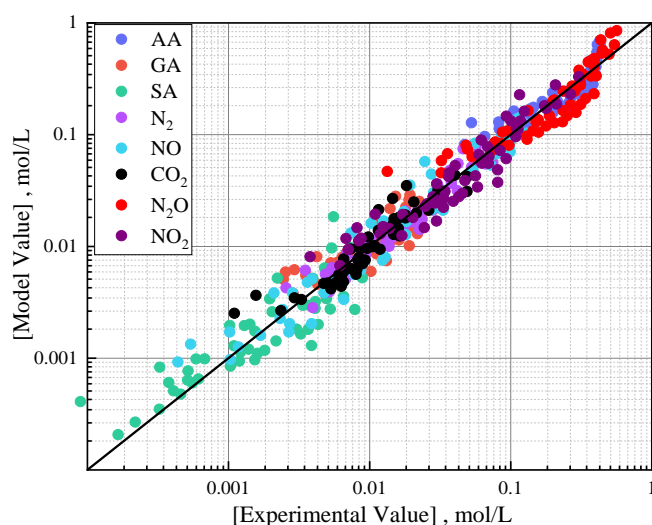


Figure 10 Comparison between experimental values and predicted values by the established kinetic model.

As shown in Table 1 Parameters of the kinetic model and the statistical test results for the oxidation of K/A oil with nitric acid, the values of the activation energy (E_a) for the formation of AA, GA and SA are 93.96 kJ/mol, 103.32 kJ/mol and 64.18 kJ/mol, respectively. The activation energy of the primary reaction, i.e., the formation of AA, was between those for the formation of GA and SA. Therefore, the precise control over the reaction temperature was crucial for achieving the high selectivity for adipic acid, which also well agreed with the conclusion from the experimental data.

To some extent, such findings in this work can guide the reactor design and process optimization in both batch reactors and continuous-flow microreactors or tubular reactors for the synthesis of adipic acid (AA) through the oxidation of K/A oil with nitric acid. For instance, to achieve the high yield and selectivity for adipic acid, novel reactors with excellent heat transfer should be designed for such a fast and highly exothermic oxidation process and multi-stage temperature control would be also needed

for better controllable process operation. Moreover, the capillary microreactor system showed excellent performance in the synthesis of adipic acid, the residence time estimated from Equation (11) for all involved experimental conditions was less than 1 minutes and only 6 seconds was needed to achieve a high yield of adipic acid (i.e., 90%) at 85°C with the use of 55 wt% nitric acid. In the future, we will work on further optimization of this oxidation process and design of the multi-type coupling reactors (e.g., microreactor coupled static mixer with high heat transfer performance) with for achieving higher yield of AA and larger throughput.

Conclusion

This work developed a continuous-flow capillary microreactor system to efficiently and safely synthesize adipic acid through the oxidation of K/A oil with nitric acid as an oxidant. The oxidation products including adipic acid and the two main by-products (glutaric acid and succinic acid) in the liquid mixture, were analyzed by HPLC while the gas mixture composition was confirmed by GC. The yield of adipic acid increased with the increase of the reaction temperature, the concentration of nitric acid, the volumetric flow rate ratio of nitric acid to K/A oil, and the capillary length. A high yield of adipic acid (90%) was achieved only in 6 seconds at 85°C with the use of 55wt% nitric acid in the microreactor system. The selectivity for adipic acid (AA) increased with the increase of the nitric acid concentration and decreased with the increase of the capillary length. In particular, the selectivity for adipic acid firstly increased and then decreased with the increase of the temperature, indicating the importance of precise

control over the reaction temperature and the capacity of the heat exchange of reactors. Moreover, a great deal of gas mixture was produced in this oxidation process. The largest total volumetric flow rate of the gas mixture could reach 327 mL/min in the microreactor system with the capillary length of 22 m for the nitric acid concentration of 55 wt%, which was over 30 times higher than the inlet total volumetric flow rate of the liquid mixture (10.5 mL/min). The volumetric ratio of each gas from high to low followed the order as N_2O , NO_2 , NO , N_2 and CO_2 under most of experimental conditions. The main gas component released from the reaction process was N_2O , and its volumetric ratio in the gas mixture had the same trend as the selectivity for the AA formation with the reaction temperature variation. Thus, the analysis on the relationship between the reaction selectivity and the gas mixture composition was beneficial for the estimation of reaction mechanism and process optimization. For example, when the operating conditions were adjusted for less production of NO and NO_2 , the nitric acid consumption would decrease.

The direct measurement of residence time was impossible due to the production of abundant gas mixture in the microreactor system. A power-law kinetic model was established based on the gas production rate along the capillary microreactor instead of the use of the residence time. Based on lots of experimental data for various operational conditions, kinetic parameters for various products in both the liquid mixture and the gas mixture were obtained through the regression by the Levenberg–Marquardt routine. The activation energy E_a for the formation of AA, GA and SA were respectively 93.96 kJ/mol, 103.32 kJ/mol and 64.18 kJ/mol, showing the high sensitivity of the reaction

temperature on the selectivity for the AA formation. Moreover, this kinetic model can well predict experimental results of concentrations for all products, indicating its potential application on process optimization and reaction mechanism understanding of such a fast and highly exothermic multiphase reaction process.

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