

Study on Preparation of P-Phenylenediamine from Wasted Polyester

Sun Chengjun^{1,2}, Yan Shenghu^{1,2,*}, He Weigang^{1,2}, Gu Shunlin^{1,2}, Shen Jiefa^{1,2}, Liu Jianwu^{1,2}, Zhang Yue^{2,3}

¹*School of Pharmacy, Changzhou University, Changzhou, 213164, China*

²*Continuous Flow Technology Engineering Laboratory for Petroleum and Chemical Industry, Changzhou, 213164, China*

³*School of Environmental Science and Engineering, Changzhou University, Changzhou, 213164, China*

**Corresponding author*

Keywords: Polyester, p-phenylenediamine, microchannel, ammonolysis, hofmann rearrangement

Abstract: The important fine chemical intermediate p-phenylenediamine (PPA) was prepared by a two-step process of catalytic ammonolysis and Hoffmann rearrangement from polyester fiber waste (WP) as raw material. The catalysts, solvents, water, solvent dosage, reaction temperature and other factors in the ammonolysis process were investigated respectively. As well as the solvents, reaction temperature, sodium hydroxide dosage, sodium hypochlorite dosage, residence time and other factors in the rearrangement process. The optimum process condition was obtained as follows: the ratio of m(WP):m(nano-copper oxide, N-Cu):m(NH₃)=1:0.1:11 for catalytic ammonolysis, reaction temperature of 150 °C, reaction time of 24 h, and anhydrous environment; the reaction temperature of microchannel rearrangement was 60 °C, residence time of 300 s, and the ratio of n(terephthalamide, DMA):n(NaOH):n(NaClO)=1:3.2:2.1. The conversion of polyester fiber waste yarn was 71.2% and the yield of p-phenylenediamine was 58.2%.

1. Introduction

P-phenylenediamine is a widely used fine chemical intermediate with an irreplaceable role in dyestuff, pharmaceutical and pesticide industries. The main industrial methods for producing p-phenylenediamine are chlorobenzene nitration reduction, benzene nitration reduction, and nitrobenzene urea condensation^[1-2]. At present, the mainstream process for the production of p-phenylenediamine in China is still the chlorobenzene nitration reduction method, but this process has many reaction steps, a long process and low atomic economy; the process involves a high risk of the nitration reaction step and low para-selectivity of the nitration reaction; the production process of the raw material used, chlorobenzene, also has the disadvantages of heavy environmental pollution and low process safety. The reaction speed and production efficiency of benzene nitration reduction method are high, but the hazardous factors in the nitration reaction step are still unavoidable, and the para-products in dinitrobenzene obtained from the secondary nitration of benzene are not the main

products. The nitrobenzene urea condensation method is a relatively new synthetic method with milder process conditions, but the production of raw nitrobenzene is unstable in supply due to the hazardous process involved in the nitration reaction^[3-5]. With the further strengthening of chemical process safety risk control in China, the traditional nitration reaction has been included as a key regulated hazardous process^[6], making the industrial production of p-phenylenediamine limited to meet the growing market demand, and it is particularly important to find new alternative synthetic process routes. In recent years, it has been reported that p-phenylenediamine was obtained from polyester fiber waste by ammonolysis followed by Hoffmann degradation, but these synthesis methods are intermittent processes with long reaction times, the process requires tedious operations of cooling down and then heating up, more by-products and difficult separation, which do not have industrial application prospects.

Continuous flow microchannel synthesis process is a hot topic of research and application in recent years, which is mainly realized by microchannel reactor equipment. Unlike traditional intermittent reactors or simple continuous reactors, microchannel reactors have a more complex fine structure inside, which makes the heat and mass transfer efficiency of such reactors much higher than that of traditional reactors^[7]. According to the relevant literature, the use of microchannel reactors to enhance the existing reaction process can effectively shorten the reaction time, control the occurrence of side reactions, and reduce the unnecessary reaction heating and cooling process^[8-9]. In recent years, studies using microchannel reactors to enhance Hoffman degradation reactions have also been reported, all of which have achieved good results^[10-12].

In this paper, using polyester fiber waste yarn as raw material, we firstly carried out ammonolysis reaction using nano-copper oxide and then Hoffmann rearrangement using microchannel reactor to finally obtain the fine chemical intermediate p-phenylenediamine. Compared with the existing synthesis process, this new process can synthesize p-phenylenediamine in a simple, mild, continuous and efficient manner.

2. Materials and methods

2.1 Experimental materials

Table 1: Experimental materials.

Name	Purity	Manufacturers
Polyester fibre waste	-	A chemical plant in Changzhou
Cuprous oxide nanoparticles	-	Laboratory homemade
Deionised water	-	Laboratory homemade
Copper oxide	Analysis pure	Sinopharm Chemical Reagent
Copper sulfate	Analysis pure	Sinopharm Chemical Reagent
Cuprous oxide	Analysis pure	Sinopharm Chemical Reagent
Sodium hydroxide	Analysis pure	Sinopharm Chemical Reagent
Copper powder	Analysis pure	Sinopharm Chemical Reagent
Copper chloride	Analysis pure	Sinopharm Chemical Reagent
10% sodium hypochlorite solution	Analysis pure	Shanghai Aladdin Biochemical
Chlorobenzene	Analysis pure	Shanghai Shenbo Chemical
Ethylene glycol	Analysis pure	Shanghai Shenbo Chemical
Glycerine trioxide	Analysis pure	Shanghai Shenbo Chemical
Dioxane	Analysis pure	Shanghai Shenbo Chemical
DMSO	Analysis pure	Shanghai Shenbo Chemical
DMF	Analysis pure	Shanghai Shenbo Chemical
Ammonia	-	Changzhou Huayang Gases

The information about each raw material used in the experiment is shown in Table 1, and the reagents used were not further purified. Among them, the polyester fiber waste yarn was the polyester fiber that was determined to have a polymerization degree lower than the minimum standard after the polymerization reaction in the chemical plant, and otherwise contained no other impurities, and the purity was considered to reach the analytical purity level of the experimental drug.

2.2 Experimental equipment

The information about each equipment used in the experiment is shown in Table 2.

Table 2: Experimental equipments.

Name	Model	Manufacturers
HPLC	20A	Shimadzu Corporation
Thermostatic circulation heat exchangers	HR-50	Wuxi Shengze P&C Instruments
Analytical scales	FA2004	Changzhou Keyuan Instruments
Liquid phase metering pumps	NP7030P	Jiangsu Hanbang Technology
Low temperature baths	DC-3030	Shanghai Hengping Instruments
Pipes and valves	PFA	Swagelok Corporation
Pressure reactors	RC-HP-VS	Shenzhen Kejing Technology
General laboratory equipment	-	The laboratory offers

The microchannel reactor, supplied by Jiangsu Diyuan Precision Instruments Co., Ltd, can be functionally divided into a material transfer zone, a preheating zone, a mixing zone, a reaction zone, a heat exchange zone, a safety control zone and a combination of related connection components. The microchannel module consists of a number of capillary units with full mixed flow characteristics and a microchannel pipe size of 1 mm. different materials first enter the different preheating zone modules and then the mixing zone modules before entering the reaction zone for reaction. A simple schematic diagram is shown in Figure 1.

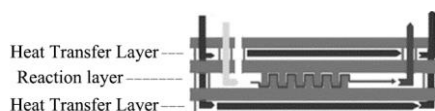


Figure 1: Schematic diagram of the microchannel reactor

2.3 Reaction Mechanisms

The reaction mechanism and route for the preparation of p-phenylenediamine from polyester fibre waste is shown in Figure 2.

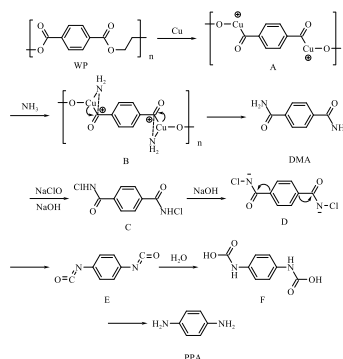


Figure 2: Reaction mechanism and route

The production of terephthalamide from polyester fibre waste, i.e. polyethylene terephthalate, is a catalytic ammonolysis reaction. The α -carbon atom in polyethylene terephthalate is conjugated to the benzene ring electron cloud because it also has a p-electron cloud. Intermediate A has a nucleophilic centre, which is attacked by ammonia as a nucleophilic reagent to give Intermediate B. Finally, Intermediate B is partially stripped of its groups to give back the copper catalyst and eventually terephthalamide. The formation of p-phenylenediamine from terephthalamide (DMA) is a Hoffmann degradation reaction. The amide is first replaced by chlorine in the presence of sodium hypochlorite to form intermediate C. Intermediate C is then stripped of its hydrogen in a basic environment to form intermediate D. Intermediate E is then rearranged to give intermediate E. Intermediate E is finally hydrolysed to give intermediate F and further decarboxylated to give the product p-phenylenediamine^[13-15].

2.4 Experimental procedure

The experimental process flow diagram is shown in Figure 3.

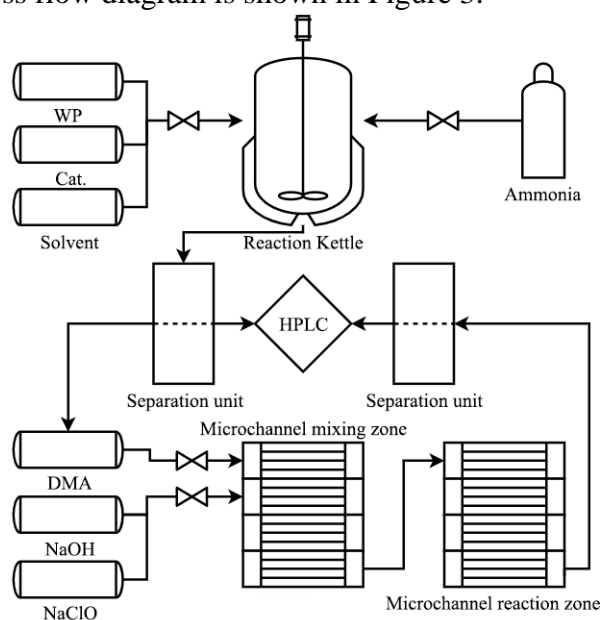


Figure 3: Reaction process flow chart

The reaction is carried out in a pressure reaction kettle by weighing and mixing a suitable amount of polyester fibre waste powder with a suitable amount of catalyst, then pouring a suitable amount of solvent into the kettle and sealing it, and finally passing a suitable amount of ammonia into the kettle and heating it up. The filtrate was subjected to HPLC and the pH was adjusted to precipitate the terephthalamide, which was then separated for use.

The terephthalamide obtained in the previous step is dissolved in chlorobenzene in a certain molar ratio as material A. Sodium hydroxide and sodium hypochlorite are added to deionised water in a certain molar ratio to prepare material B. The two streams of material are transferred to the storage tank separately. The two materials are mixed in the reaction zone after preheating and reacting with each other. The temperature of the reaction system is precisely controlled by heating or cooling of the heat transfer oil by a thermostat. The reaction residence time and the molar ratio of the material can be effectively controlled by changing the flow rate of the metering pump or the length of the microchannel reactor. Immediately after completion of the reaction, the material exits the reactor and is quenched using low temperature sodium thiosulphate, and the organic phase is taken for use after the two phases have been stratified. The results were determined by high performance liquid

chromatography analysis.

2.5 Analysis methods

The information about analysis methods used in the experiment is shown in Table 3.

Table 3: Analysis methods

Item	Condition
HPLC	Shimadzu Model 20A
Chromatographic columns	Welch Ultimate XB-C18
Column length and diameter	4.6×250 mm
Filling specifications	5 μm
Detection wavelength	254 nm
Flow rate	1.0 mL/min
Column temperature	25°C
Column pressure	15±2 MPa
Sampling volume	20 μL
Mobile phase A	100% methanol
Mobile phase B	70% acetonitrile aqueous solution

The analysis was carried out using mobile phase A for 5 min, followed by a gradient elution so that mobile phase A was 50% and mobile phase B was 50%. The results for the standard samples of polyester waste, terephthalamide and p-phenylenediamine under these analytical conditions are shown in Figure 4.

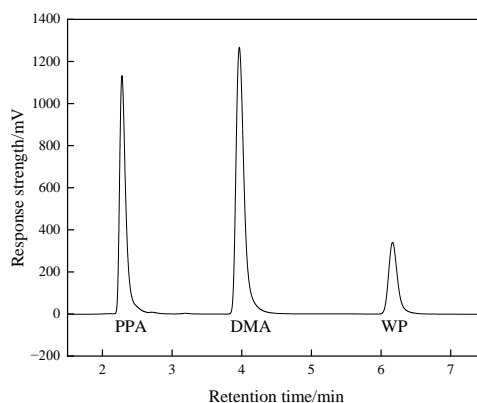


Figure 4: Reference spectrum

The feedstock conversion (C) and product selectivity (S) of the reaction are used as the main indicators to be investigated, which are calculated according to the following equations.

$$C = \frac{P_{r1} - P_{r2}}{P_{r1}} \times 100\% \quad (1)$$

$$S = \frac{P_p}{P_p + P_o} \times 100\% \quad (2)$$

In the formula: P_{r1} is the peak area of the raw material before the reaction, P_{r2} is the peak area of the raw material after the reaction, P_p is the peak area of the target product after the reaction and P_o is the sum of the peak areas of all the peaks after the reaction except the target product peak.

3. Results and Discussion

3.1 Catalytic ammonolysis of polyester fibre waste

3.1.1 Influence of catalyst type

The effect of different catalyst types on the results was investigated at $m(\text{WP}):m(\text{catalyst}):m(\text{NH}_3) = 1:0.1:11$, with polyester fibre waste yarn as the raw material and terephthalamide as the product, at a solvent dosage of 50 mL, a reaction temperature of 150 °C and a reaction time of 24 h. The results are shown in Figure 5.

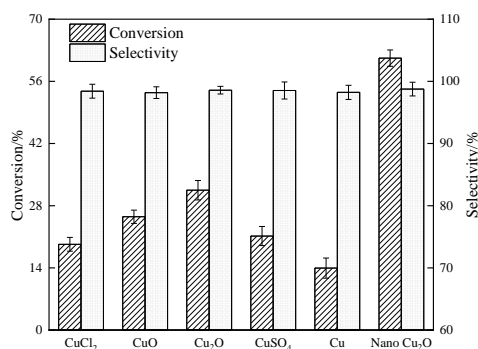


Figure 5: Effect of catalyst type on catalyzed ammonolysis reaction

Figure 5 shows that the selectivity of the products catalyzed by each catalyst is relatively consistent, while the conversion of the feedstock varies considerably. This indicates that the different valence states of copper have a certain catalytic effect on all, but different catalyst morphology, structure, copper valence state and other factors directly affect the conversion of the feedstock under the action of the catalyst. Among copper oxide, copper chloride, cuprous oxide, copper sulphate and copper monomers, it can be found that copper monomers have the weakest catalytic effect, copper oxides have a better catalytic effect than copper salts, and monovalent copper has a better catalytic effect than divalent copper. The nano-copper oxide is significantly smaller than the other catalyst types and is more likely to bind to the reaction feedstock to form Intermediate A, so its feedstock conversion rate is significantly better than the other catalyst types. On balance, nano-copper oxide (N-Cu) should be selected as the catalyst in the process^[16-17].

3.1.2 Influence of solvent type

The effect of different solvent types on the results was investigated at $m(\text{WP}):m(\text{N-Cu}):m(\text{NH}_3) = 1:0.1:11$, with polyester fibre waste yarn as raw material and terephthalamide, an ammonolysis product, as product, at a solvent dosage of 50 mL, a reaction temperature of 150 °C and a reaction time of 24 h. The results are shown in Figure 6.

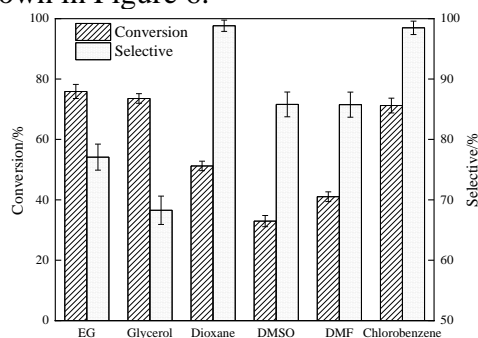


Figure 6: Effect of solvent type on catalytic ammonolysis reaction

Figure 6 shows that ethylene glycol and propanetriol have high conversion but low selectivity; dioxane, DMSO and DMF have good selectivity but low conversion; and chlorobenzene has a good combination of conversion and selectivity. This is due to the fact that ethylene glycol and propanetriol, in addition to their role as solvents, also tend to compete with ammonia for the binding of intermediate A, resulting in the production of a large number of non-target compounds and thus a significant decrease in selectivity. Dioxane, DMSO and DMF are less soluble in the feedstock, resulting in significantly lower feedstock conversions than other solvents with better solubility in the same time frame. On balance, chlorobenzene has a better performance in terms of feedstock conversion and product selectivity, so it should be chosen as the solvent in the process.

3.1.3 Influence of water in the reaction system

The effect of water present in the system on the results was investigated at $m(\text{WP}):m(\text{N-Cu}):m(\text{NH}_3) = 1:0.1:11$, with polyester fibre waste yarn as raw material and terephthalamide, a product of ammonolysis, at a solvent dosage of 50 mL, a reaction temperature of 150 °C and a reaction time of 24 h. The results are shown in Figure 7.

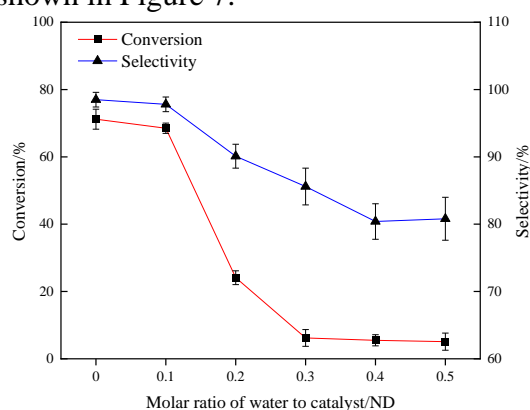


Figure 7: Effect of Water on Catalyzed Ammonolysis Reaction

As can be seen in Figure 7, the presence of water significantly reduces the feedstock conversion and product selectivity of the reaction, with a greater decrease in feedstock conversion. This is due to the fact that the ammonia produced by the combination of water and ammonia further combines with the active part of the copper-based catalyst to produce the complex complex dihydrate tetraamminated cuprous ion. The spatial resistance of this complex is significantly greater than that of the original catalyst, making it significantly more difficult to bind to the active site of the feedstock; the complex is also positively charged, further preventing ammonia from binding to the intermediate as a nucleophilic reagent. In summary, the presence of water can significantly hinder the reaction and therefore a water-free environment should be chosen as an important reaction condition or a control of $n(\text{water}):n(\text{catalyst}) < 0.1:1$.

3.1.4 Influence of solvent dosage

The effect of solvent dosage on the results was investigated at $m(\text{WP}):m(\text{N-Cu}):m(\text{NH}_3) = 1:0.1:11$, with polyester fibre waste yarn as the raw material and terephthalamide, a product of ammonolysis, at a reaction temperature of 150 °C and a reaction time of 24 h. The results are shown in Figure 8.

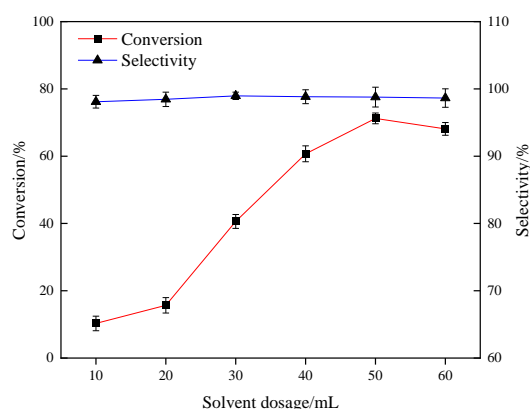


Figure 8: Effect of solvent dosage on catalytic ammonolysis reaction

Figure 8 shows that the product selectivity of the reaction has basically no effect on the change of solvent dosage, but the product conversion rate is significantly higher when the solvent dosage is less than 50 mL and slightly decreases when it is more than 50 mL. On the whole, the product selectivity remains the same, the product conversion rate is lower before and after the solvent dosage of 50 mL, so the solvent dosage of 50 mL should be chosen in the process.

3.1.5 Influence of reaction temperature

The effect of reaction temperature on the results was investigated at $m(\text{WP}):m(\text{N-Cu}):m(\text{NH}_3) = 1:0.1:11$, with polyester fibre waste yarn as raw material and terephthalamide, a product of ammonolysis, at a solvent dosage of 50 mL and a reaction time of 24 h. The results are shown in Figure 9.

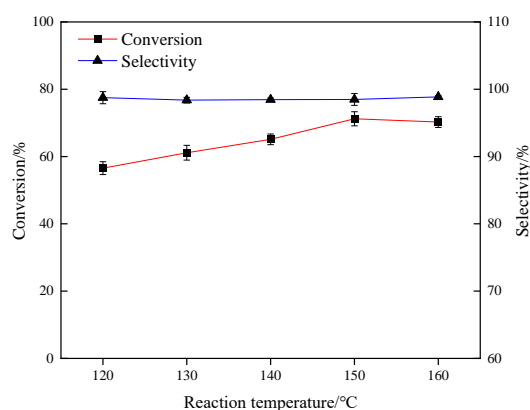


Figure 9: Effect of reaction temperature on catalyzed ammonolysis reaction

Figure 9 shows that the change in reaction temperature does not have a significant effect on product selectivity, while the feedstock conversion increases steadily until the reaction temperature reaches 150 °C and decreases slightly beyond 150 °C. This is due to the fact that the increase in reaction temperature directly increases the average kinetic energy of molecules in the reaction system, and the increase in average kinetic energy of molecules directly leads to an increase in the probability of intermolecular collision, while the reaction itself is a heat-absorbing reaction, and the combined effect of the two ultimately directly increases the reaction conversion of the product. However, with the further increase of the reaction temperature, Intermediate A and Intermediate B gradually become unstable in the system, leading to the interruption of the reaction chain, thus making the conversion of raw materials begin to decline. On balance, the reaction product selectivity remains basically unchanged, while the reaction temperature shows a peak of 150 °C. Therefore, the reaction

temperature of 150 °C should be chosen in the process.

3.2 Microchannel Hoffmann rearrangement of terephthalamide

3.2.1 Influence of solvent type

The effect of solvent type on the results was investigated at $n(\text{DMA}):n(\text{NaOH}):n(\text{NaClO}) = 1:3.5:2.5$, with polyester fibre waste yarn as the raw material and terephthalamide as the product, at a reaction temperature of 50 °C and a residence time of 300 s. The results are shown in Figure 10.

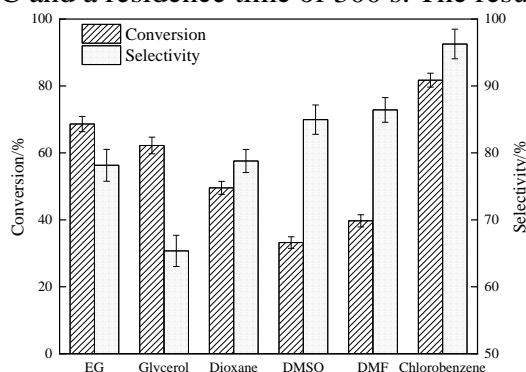


Figure 10: Effect of solvent type on microchannel rearrangement reaction

Figure 10 shows that ethylene glycol reacts with propyleneglycol with better feedstock conversion but poorer product selectivity; dioxane, DMSO and DMF react with slightly better product selectivity than feedstock conversion; and chlorobenzene reacts with better feedstock conversion and product selectivity than other solvent types. This is due to the fact that ethylene glycol and propyleneglycol not only play the role of solvent, but also facilitate the reaction of intermediate C and intermediate D to produce non-target products, making the product selectivity decreased. Dioxane, DMSO and DMF are less soluble as solvents for the feedstock terephthalamide, which directly leads to low product conversion, but they do not react with other reaction intermediates, so the feedstock selectivity is better. On balance, chlorobenzene has a better performance in both feedstock conversion and product selectivity, so it should be chosen as a solvent in the process.

3.2.2 Influence of reaction temperature

The effect of reaction temperature on the results was investigated at $n(\text{DMA}):n(\text{NaOH}):n(\text{NaClO}) = 1:3.5:2.5$, with polyester fibre waste yarn as raw material and terephthalamide, an ammonolysis product, as product, at a residence time of 300 s. The results are shown in Figure 11.

As can be seen in Figure 11, the reaction feedstock conversion increases rapidly with temperature before remaining essentially constant after 60 °C; product selectivity, on the other hand, remains essentially constant up to 60 °C and decreases significantly beyond that. In the traditional batch process, the Hoffmann rearrangement reaction generally takes the form of a low-temperature mixture of feedstocks, which is then warmed up to carry out the reaction. This is due to the instability of sodium hypochlorite and intermediate C in the reaction chain at higher temperatures and the fact that this step itself is exothermic, while subsequent reaction processes need to occur at higher temperatures. The microchannel reactor has a very strong heat transfer performance, which can be increased by about 100 times compared to the traditional reactor. This excellent feature makes it possible to complete the reaction in the microchannel without the need for tedious cooling and warming operations according to the traditional process steps, and at only one temperature. In the microchannel reactor, sodium hypochlorite and the raw material terephthalamide rapidly form intermediate C,

which immediately reacts with sodium hydroxide to form intermediate D. During this time, the reactor precisely controls the temperature of the reaction system through high heat transfer efficiency, effectively avoiding the dilemma of decomposition of intermediate C at higher temperatures or the inability to continue the reaction at lower temperatures^[18-19]. However, as the reaction temperature is further increased, the reactor has reached the limit of heat transfer efficiency, at which time overheating decomposition of the reaction intermediate still occurs, which leads to interruption of the reaction chain making the product selectivity decrease. On balance, both reaction feedstock conversion and product selectivity peak at 60 °C, so a reaction temperature of 60 °C should be selected in the process.

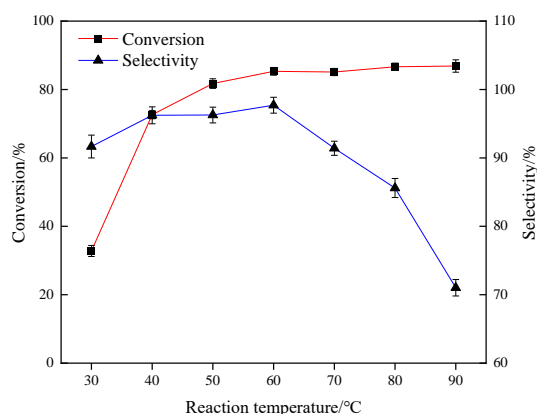


Figure 11: Effect of reaction temperature on microchannel rearrangement reaction

3.2.3 Influence of sodium hydroxide dosage

The effect of sodium hydroxide dosage on the results was investigated at $n(\text{DMA}):n(\text{NaClO}) = 1:2.5$, with polyester fibre waste yarn as the raw material and terephthalamide as the product, at a reaction temperature of 60 °C and a residence time of 300 s. The results are shown in Figure 12.

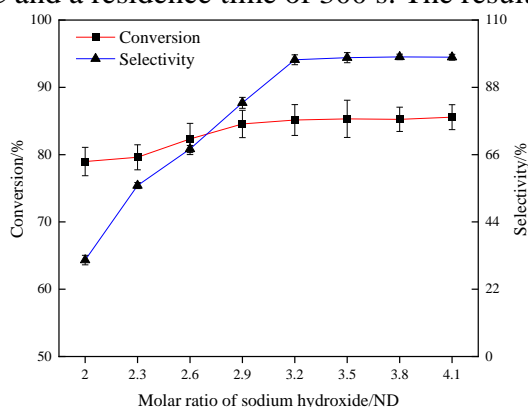


Figure 12: Effect of sodium hydroxide dosage on microchannel rearrangement reaction

In the subsequent conversion of intermediate C to intermediate D and intermediate F to product, sodium hydroxide needs to be directly involved in the reaction and consumed, so a lower amount of sodium hydroxide will cause the suspension of the reaction chain and eventually lead to low product selectivity. On balance, the product selectivity peaks at $n(\text{DMA}):n(\text{NaOH}) = 1:3.2$, so $n(\text{DMA}):n(\text{NaOH}) = 1:3.2$ should be chosen in the process, as shown in Figure 12.

3.2.4 Influence of sodium hypochlorite dosage

The effect of sodium hypochlorite dosage on the results was investigated at $n(\text{DMA}):n(\text{NaOH}) =$

1:3.2, with polyester fibre waste yarn as the raw material and terephthalamide as the product, at a reaction temperature of 60 °C and a residence time of 300 s. The results are shown in Figure 13.

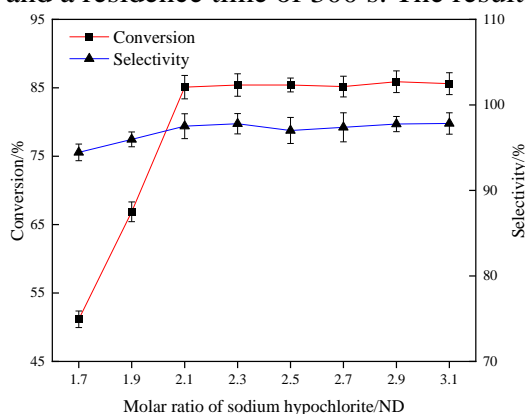


Figure 13: Effect of sodium hypochlorite dosage on microchannel rearrangement reaction

As can be seen in Figure 13, the feedstock conversion and product selectivity of the reaction increased to some extent until $n(\text{DMA}):n(\text{NaClO}) = 1:2.1$, and the increase in feedstock selectivity was limited and remained essentially constant beyond this amount. This is due to the fact that sodium hypochlorite is directly involved in the reaction process when the feedstock is converted to Intermediate C, and plays little role in the subsequent reaction process. Therefore, the lower dosage of sodium hypochlorite does not allow the complete conversion of the product to intermediate C, which directly leads to a low conversion rate. For product selectivity, the effect of sodium hypochlorite is not significant. On balance, the product conversion reaches a peak level at $n(\text{DMA}):n(\text{NaClO}) = 1:2.1$, so $n(\text{DMA}):n(\text{NaClO}) = 1:2.1$ should be chosen for the process.

3.2.5 Influence of residence time

The effect of residence time on the results was investigated at $n(\text{DMA}):n(\text{NaOH}):n(\text{NaClO}) = 1:3.2:2.1$, with polyester fibre waste yarn as raw material and terephthalamide, an ammonolysis product, as product, at a reaction temperature of 60 °C. The results are shown in Figure 14.

As can be seen in Figure 14, the reaction feedstock conversion increases significantly with increasing residence time, but remains essentially constant after reaching 300 s; while the product selectivity fluctuates within a certain range and is not sensitive to changes in residence time. In a conventional batch process, the Hoffmann rearrangement reaction typically requires a total reaction time of several hours. In addition to the operating time associated with the need to raise and lower the temperature, this is due to the fact that the reaction itself is a two-phase reaction system and the poor mass transfer efficiency of the conventional batch process results in less than optimum mixing of the two phases, significantly slowing the reaction process. Similar to the heat transfer efficiency, the mass transfer efficiency of the microchannel reactor is much higher than that of the traditional batch process, and the two streams of material can reach a homogeneous mixing state close to one phase in the reactor, so the reaction time can be significantly reduced^[20]. After a residence time of more than 300 s, the majority of the products have been reacted to give the target product and further extension of the residence time does not continue to significantly increase the feedstock conversion. Since the products of this reaction do not react with the individual reaction materials, extending the residence time does not result in a decrease in reaction selectivity. On balance, the feedstock conversion reaches its peak level after a residence time of more than 300 s. Therefore, a residence time of 300 s should be chosen for the process.

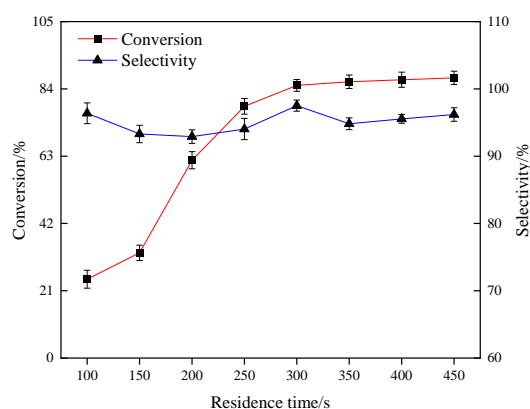


Figure 14: Effect of residence time on microchannel rearrangement reaction

4. Conclusion

Polyester fiber waste as raw material, through the catalytic ammonolysis, Hoffmann rearrangement two-step reaction, you can get important fine chemical intermediates p-phenylenediamine, catalytic ammonolysis process for the best process parameters: reaction temperature of 150°C, reaction time of 24 h, the ratio of each material is m (WP):m (N-Cu):m (NH₃) = 1:0.1:11, when the raw material conversion rate of The optimum process parameters for the microchannel Hoffmann rearrangement process were: reaction temperature of 60 °C, residence time of 300 s, and the ratio of each material was $n(\text{DMA}):n(\text{NaOH}):n(\text{NaClO})=1:3.2:2.1$, which resulted in a feedstock conversion of 85.1% and a product selectivity of 97.5%. Under the optimum process conditions, the conversion of the raw material polyester fiber waste was 71.2% and the product p-phenylenediamine yield was 58.2%.

Compared with the traditional intermittent kettle reactor, the use of microchannel reactor for the Hoffmann rearrangement reaction of p-phenylenediamine, a product of the ammonolysis of polyester fiber waste yarn, to obtain p-phenylenediamine has the advantages of simple operation, high product production efficiency and safe and controllable reaction process, which has accumulated important experience for the effective utilization of polyester fiber waste yarn in the future.

Acknowledgements

The authors gratefully acknowledge the financial support from National Key Research and Development Program of China (2021YFC3001104-01).

References

- [1] Aldrich Chemical Company, *Aldrich [M]*. Milwaukee: Sigma-Aldrich Co, 2008: 156-158.
- [2] Zheng Renhua, Jiang Huajiang, *Progress of chemical research on p-phenylenediamine[J]*. Zhejiang Chemical Industry, 2005(04): 24-26.
- [3] Hong Zhongling, *Deep processing of organic chemical raw materials [M]*. Beijing, Chemical Industry Press, 1997: 593-596
- [4] Faiz Ahmed Khan, Jyotirmayee Dash, Ch Sudheer, Rakesh Kumar Gupta. *Chemoselective reduction of aromatic nitro and azo compounds in ionic liquids using zinc and ammonium salts[J]*. Tetrahedron Letters, 2003, 44(42): 7783-7787.
- [5] Chamberlin Kim S. *Process for coproduction of arylene diamine dihalides and alkyl halides: US5025107[P]*. 1991-6-18.
- [6] State Administration of Work Safety, *State administration of work safety on the publication of the first batch of key regulatory hazardous chemical process directory [Z]*. 2009.
- [7] Zhang Jingwei, Zhou Yiwei, Chen Zhuo, Xu Jianhong. *Frontiers of organic synthesis in microreactors[J]*. Journal of Chemical Engineering, 2022, 73(08): 3472-3482.

- [8] Yan S.H., Han L.L., Shen W., Shen J.F., Liu J.W., Zhang Y. A continuous flow process for the oxidative synthesis of ϵ -caprolactone from cyclohexanone in microchannels[J]. *Chemical Progress*, 2014, 33(11): 3061-3066.
- [9] Liu Jianwu, Yan Shenghu, Zhang Yue, Shen Jiefa. A continuous flow process for the liquid phase oxidation of benzaldehyde from benzyl alcohol[J]. *Chemical Progress*, 2021, 40(01): 394-400.
- [10] Jinpei Huang, Funing Sang, Guangsheng Luo, Jianhong Xu. Continuous synthesis of Gabapentin with a microreaction system [J]. *Chemical Engineering Science*, 2017, 173: 507-513.
- [11] Fajun Wang, Yuncheng Ding, Jianhong Xu. Continuous-Flow Synthesis of Pigment Red 146 in a Microreactor System[J]. *Industrial & Engineering Chemistry Research*, 2019, 58(36): 16338-16347.
- [12] Hernando Marcos Veguillas, Moore Jonathan C, Howie Rowena A, Castledine Richard A, Bourne Samuel L, Jenkins Gareth N, Licence Peter, Poliakoff Martyn, George Michael W. High Yielding Continuous-Flow Synthesis of Norketamine [J]. *Organic process research & development*, 2022, 26(4): 1145-1151.
- [13] Matsumura Y, Satoh Y, Shirai K, et al. New reaction conditions using trifluoroethanol for the EI Hofmann rearrangement[J]. *Journal of the Chemical Society, Perkin Transactions 1*, 1999 (15): 2057-2060.
- [14] Hansu Georuku Tsuengeru, Manfureeto Berukufueruto. Manufacture Of M-And P-Phenylenediamine: JPS6029695B[P]. 1985-07-12.
- [15] Liu Yi et al. Preparation of metal organic framework hybridizing with poly(p-phenylene terephthalamide) fiber and adsorption properties for anionic dye[J]. *Pigment & Resin Technology*, 2023, 52(1): 60-72.
- [16] Pascal Gesse and Thomas J. J. Müller. Consecutive Five-Component Ugi-4CR-CAL B-Catalyzed Aminolysis Sequence and Concatenation with Transition Metal Catalysis in a One-Pot Fashion to Substituted Triamides[J]. *European Journal of Organic Chemistry*, 2019, 2019(11) : 2150-2157.
- [17] Linda P. Seiwel. Copper-catalyzed nonaqueous ammonolysis of p-chlorobenzotrifluoride. Effect of potassium fluoride[J]. *J. Org. Chem.*, 2002, 44(25) : 4731-4733.
- [18] Qiu Yunlong et al. Flow and heat transfer characteristics in a microchannel with a circular synthetic jet[J]. *International Journal of Thermal Sciences*, 2021, 164.
- [19] Ying Xiang et al. Experimental investigation of Fischer-Tropsch synthesis in a microchannel reactor[J]. *Abstracts of Papers of The American Chemical Society*, 2015, 249.
- [20] Yi Jiao et al. Hydrogen-Rich Syngas Production by Toluene Reforming in a Microchannel Reactor Coated with Ni/MgO-Al₂O₃ Multifunctional Catalysts[J]. *Industrial & Engineering Chemistry Research*, 2019, 58(43) : 19794-19802.