

Research about the Method of Synthesizing N,N-dimethyl-1,3-propanediamine Continuously

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N,N-dimethyl-1,3-propanediamine (DMAPA) is an important fine organic chemical intermediate, is widely used in the manufacturing of surfactants, cosmetics, detergents, textiles, and lubricating oil additives. Although market need is growing increasingly, but research report about the manufacturing process of DMAPA is not investigated explicitly. The current preparation of DMAPA is a two-step batch reaction. In the first step Dimethyl amine(DMA) and Acrylonitrile(ACN) as the starting materials lead to N, N-dimethyl-amino propionitrile(DMAPN). Then, DMAPN is hydrogenated to obtain DMAPA by Raney-Ni. Herein, we focus on realizing the two step in a continuous process using fixed bed. In the first step, the reaction conditions using fillers can achieve the effect of catalyst H-ZSM-5. Under an optimized the conditions 30 °C 1.0M Pa, LHSV 1.1~4h⁻¹ and molar ration of 1.00:1.00, the reaction conversion and selectivity were higher than 99.5 %. Later, we exploit hydrogenation of DMAPN in a continuous process catalyzed by ZL-311-R. Under an optimized the conditions 70 °C, 6 MPa, LHSV 0.3 h⁻¹, alkali liquor NaOH, the reaction conversion and selectivity were higher than 99.5 %. Realize synthesizing N,N-dimethyl-1,3-propanediamine continuously in the fixed bed and reaction conversion and selectivity were all higher than 99.5 % in the two step.

1. Introduction

N,N-dimethyl-1,3-propanediamine (DMAPA) is an important fine organic chemical. Betaines and amine oxide can be prepared from DMAPA which are surfactants widely used in personal care and household products (Taminco, 2011). DMAPA can be served as raw materials of textiles which are smooth, soft, water-resistant and stable to light. DMAPA and compounds based on it can also be used as addition of the gasoline to improve the properties of gasoline (HANTSMAN, 2012). Owing to DMAPA with mild character and excellent performance, DMAPA based surfactants show rapid growth (Taminco, 2011). Thus, DMAPA is widely used in our life and production. The research about DMAPA synthesis process has a very important practical significance. This paper focuses on research about the method of synthesizing DMAPA continuously. First, DMA and ACN as raw materials lead to raw reaction products 3-dimethyl aminopropionitrile (DMAPN)., then DMAPN hydrogenated to DMAPA. In the first step, because of DMA has only one active hydrogen, the reaction selectivity to DMAPN is very high. But in the second step, during the process of hydrogenated nitrile Intermediate imine will be formed which has high chemical active (Von Braun, 1923). This will lead to form a variety of byproducts. The N-alkylimine and enamine will be formed after NH₃ and proton releases. And then they will be hydrogenated to secondary or tertiary amine. The N-alkylimine and enamine also can react with water lead to alcohols (Barrault, 1997). Another tertiary amine will formed because there is a small amounts of DMA in the reaction system. Previous literature reported (Hui Chen, 2012) that supporter surface acidic and basic properties will affect the reaction selectivity. The basic properties will improve the selectivity of primary amine. The article (Hui Chen, 2012) also mentioned that the addition of base to the reaction can decreased the formation of secondary amine and tertiary amine. The nature of the supports showed great influence on the selectivity (Verhaak, 1994), but the selectivity is first determined by the nature of meta (Barrault, 1997). Raney cobalt

presents higher primary amine selectivity, but Raney nickel with lower price more widely used in the industrial production of primary amines (Chen, 2012). In this paper, our use Raney nickel as the catalyst and addition NaOH to the reaction medium can effective inhibition of secondary and tertiary amines formation.

2. Experiment

2.1 Reagent and equipment

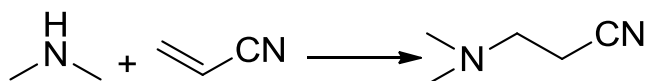
Reagent: dimethylamine ($\geq 99.0\%$, Jiangxi Chemical Plant in Dalian), acrylonitrile ($\geq 98.0\%$, AR, Tianjin. Fuchen Chemical Plant.)

Equipment: Gas Chromatograph (7890F, Shanghai Tian Mei Scientific Instruments Co., Ltd.)

2.2 General procedure : DMAPA preparation

The current preparation of DMAPA is a two-step batch reaction. In the first step DMA and ACN as the starting materials lead to DMAPN. Then, DMAPN is hydrogenated to obtain DMAPA by catalyst.

The first step: DMAPN was prepared by DMA and ACN Michael Reaction



The second step : DMAPA was prepared from DMAPN hydrogenated

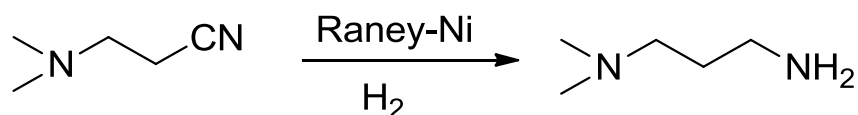


Figure.1 the reaction scheme for synthesizing DMAPA

2.3 Preparation of DMAPA

(1) In the first stage, we first put the catalyst or filler in the fixed bed reactor (50ml), and then sealed the entire reaction system after expelled the air in the reactor with nitrogen. Set up the experimental pressure and reaction temperature. Next, pump DMA and ACN according to a certain molar ratio with the two metering pumps to the reactor. The production DMAPN cooled by the gas-liquid separator. Sampled for gas chromatographic analysis. Process flow diagram shown in Figure 2.

(2) In the second stage, we put the catalyst in the fixed bed reactor (50ml) in the first, and then sealed the entire reaction system after expelled the air in the reactor with nitrogen. Set up the experimental pressure and reaction temperature. Next, pump alkaline liquor and DMAPN according to a certain molar ratio with the two metering pumps to the reactor. The production DMAPA cooled by the gas-liquid separator. Sampled for gas chromatographic analysis. The process flow diagram is similar to the Figure 2.

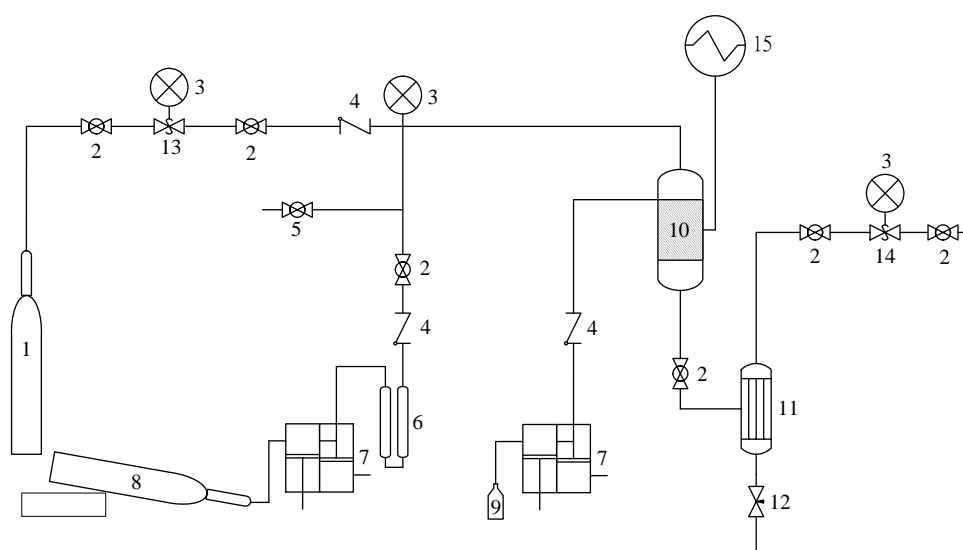


Figure 2: Flowchart of experiment setup

1. nitrogen 2. ball valve 3. piezometer orifice 4. check valve 5. Raw material emptying valve 6. drying pipe 7. Double plunger micro pump 8. Dimethylamine 9. Acrylonitrile 10. Reactor 11. gas-liquid separator, 12. sampling valve 13. constant pressure valve, 14. back-pressure valve 15. temperature controller

3. Results and discussion

In the first stage, DMA and ACN as the starting materials lead to DMAPN. Many factors may affect the results of the experiment, for example fillers, temperature, mole ratio, LHSV. First, the influence of fillers was investigated. Experiments were examined one catalyst and two fillers, namely HZSM5 catalyst, stainless steel and glass filler. The Table 1 results showed that H-ZSM-5 catalyst and stainless steel filler is better than glass filler because of the glass filler has a large aperture. The stainless steel filler can achieve the effect of H-ZSM-5 which lower and longer life than H-ZSM-5. In a word, stainless steel filler is more suitable for industrial production. Then, the effects of temperature were investigated. The experiment data was summarized in Table 2. The conversion rate was highest when initial temperature was 30 °C.

Table 1: The effect of different filler on the ACN conversion rate and DMAPN selectivity

Catalyst or filler	Conv. (ACN)	Sel.(DMAPN)
H-ZSM-5	99.6 %	≥99.5 %
Glass filler	93.7 %	≥99.5 %
Stainless steel filler	99.6 %	≥99.5 %

Reaction conditions: LHSV 0.8 h^{-1} , $P = 1.0 \text{ MPa}$, $T = 20 \text{ }^\circ\text{C}$, Time = 3.5 h, mole ratio = 1.0:1.0

When the temperature was lower, the reaction activity was low. When the temperature was higher, the reactants were easily detached from the surface of the filler with not long enough contact time. Next, the influence of the mole ratio of DMA and ACN was considered. The experimental results were listed in Table 3. The data indicated that when the mole ratio is greater than 1.1:1.0, ACN can be completely transformed. When the mole ratio fell to 1.0:1.0, there is a small amount of residual ACN. But slightly change the way of feeding can make ACN completely transformed. The last row of Table 3 adopted pumping DMA firstly. DMA excess 5 % existed in the reactor, and then pump DMA and ACN according to the mole ratio 1.00:1.00. Compared to the last row and the second to last row in the Table 3, it can be founded that pumping DMA firstly and excess 5 % in the reactor can make ACN completely transformed while general feeding way cannot.

Table 2: The effect of different temperature on the ACN conversion rate and DMAPN selectivity

Temperature	Conv. (ACN)	Sel.(DMAPN)
20 °C	94.5 %	≥99.5 %
30 °C	100.0 %	≥99.5 %
40 °C	99.4 %	≥99.5 %

Reaction conditions: LHSV 0.8 h⁻¹, P = 1.0 MPa, Stainless steel filler, Time = 4 h, mole ratio = 1.1:1.0

Table 3: The effect of different mole ratio on the ACN conversion rate and DMAPN selectivity

The mole ratio of DMA and ACN	Conv. (ACN)	Sel.(DMAPN)
1.5:1.0	100.0 %	≥99.5 %
1.3:1.0	100.0 %	≥99.5 %
1.1:1.0	100.0 %	≥99.5 %
1.0:1.0	99.6 %	≥99.5 %
1.0:1.0 ^a	100.0 %	≥99.5 %

Reaction conditions: LHSV 0.8 h⁻¹, P = 1.0 MPa, Stainless steel filler, Time= 4h, T = 30 °C

^aPumping DMA firstly and excess 5 % in the reactor

The results of different LHSV on the ACN conversion rate and DMAPN selectivity were listed in Table 4. The data showed that under this conditions ACN conversion rate and DMAPN selectivity were not sensitive to the change of LHSV. LHSV in the range of 1.1 to 4, ACN can be completely transformed. As a result, the industry can choose appropriate LHSV according to their own needs.

Table 4: The effect of different LHSV on the ACN conversion rate and DMAPN selectivity

LHSV/h ⁻¹	Conv. (ACN)	Sel.(DMAPN)
1.1	100.0 %	≥99.5 %
1.2	100.0 %	≥99.5 %
1.4	100.0 %	≥99.5 %
2.0	100.0 %	≥99.5 %
3.0	100.0 %	≥99.5 %
4.0	100.0 %	≥99.5 %

Reaction conditions: P = 1.0 MPa, Stainless steel filler, Time = 4 h, T = 30 °C, Pumping DMA firstly and excess 5 % in the reactor, mole ratio = 1.0:1.0

In the second step, DMAPN is hydrogenated to obtain DMAPA by catalyst. The autoclave experiments are screening the condition of the catalyst. The experimental data were showed in the Table 5. It can be founded that DCF-1 catalyst has highest conversion and selectivity under this conditions. The HFL series catalyst is not suitable for this hydrogenation system. After adding NaOH into the reaction system, The reaction almost didn't occur. So choose the DCF-1 as the fixed hydrogenated catalyst.

The autoclave experiments screening of DCF-1 catalyst used in fixed bed hydrogenation reaction. Fixed bed experiment takes into account the reaction way and reaction pressure affect DMAPN hydrogenation results. From Table 6, it can be drawn that the reflux reaction way is superior to the drip reaction way. Because the reflux reaction way it has longer residence time.

In the Figure.3 the conditions is that LHSV 0.3 h⁻¹, temperature 70 °C, alkali NaOH, reflux reaction way. The results in Figure.3 illustrated that pressure is less than 6 MPa, the reaction conversion rate and selectivity as the pressure rises, owing to hydrogen concentration is raised and the intermediate existence time is short lead to fewer by-products. When pressure is higher than 6 MPa, the reaction conversion and selectivity as pressure change is not obvious, and the higher reaction pressure will improve demand for equipments, so choose the reaction pressure is 6 MPa is more appropriate.

Table 5: The effect of catalyst on the DMAPN conversion rate and DMAPA selectivity

catalyst	NaOH/g	Hydrogen pressure/MPa	Time/h	Conv. (ACN)	Sel.(DMAPN)
DCF-1 ^a	0.1	2	3	100.0 %	99.4 %
DCF-2 ^b	0.1	2	3	87.0 %	97.0 %
DCF-3 ^c	0.1	2	6	66.7 %	99.7 %
HFL-3 ^d	0.1	4	6	0.6 %	30.0 %
HFL-3 ^e	0.0	4	6	64.3 %	16.7 %
HFL-1 ^f	0.0	4	6	100.0%	33.9 %

Reaction conditions: DMAPN = 10.00 g, a = 2.45 g; b = 2.50 g; c = 1.00 g; d = 2.00 g, e = 2.00 g, f = 2.00 g, T = 80 °C

Table 6: The influence of different reaction ways

Reaction ways	Conv. (DMAPN)	Sel.(DMAPa)
Drip reaction way	96.2 %	≥99.5 %
Reflux reaction way	100.0 %	≥99.5 %

Reaction conditions: LHSV 0.3 h⁻¹, P = 6.0 MPa, alkali liquor NaOH, T = 70 °C

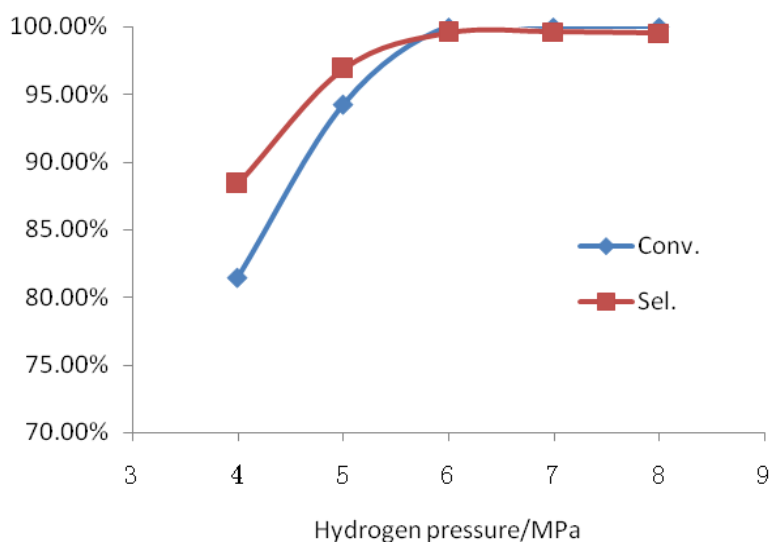


Figure.3: The effect of reaction pressure on the DMAPA conversion rate and selectivity

4. Conclusion

N,N-dimethyl-1,3-propanediamine is an important fine organic chemical intermediate, is widely used in our life and production. And market need is growing increasingly, so realizing the two steps in a continuous process using fixed bed has important significance.

This paper on the basis of summarizing the past literature focuses on exploiting hydrogenation of DMAPA in a continuous process. In the first step, under an optimized the conditions 30 °C 1.0 MPa, LHSV 1.1~4h⁻¹, Pumping DMA firstly and excess 5 % in the reactor DMA and ACN molar ratio of 1.0:1.0, with stainless steel filler as stuffing by fixed bed, the reaction conversion and selectivity were higher than 99.5 %. This method has a high selectivity and conversion rate, and low cost. N, N-dimethylaminopropionitrile is taken as one of raw materials, and then conduct hydrogenation experiment with fixed bed, Under an optimized the conditions 70 °C, 6 MPa, LHSV 0.3 h⁻¹, alkali liquor NaOH, the reaction conversion and selectivity were higher than 99.5 %.

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