

Technological parameters of the ammonolysis of waste 1,2-dichloropropane

Marcin Bartkowiak, Grzegorz Lewandowski, Eugeniusz Milchert*

Institute of Organic Chemical Technology, Technical University of Szczecin, Pulaskiego 10, PL 70-322 Szczecin, Poland

Received 21 July 2003; received in revised form 13 October 2003; accepted 13 October 2003

Abstract

The ammonolysis of waste 1,2-dichloropropane (DCP) using liquid ammonia has been investigated. The influence of temperature, molar ratio of NH_3 /1,2-dichloropropane and reaction time was examined. The highest yield of the synthesis was achieved at a temperature of 140°C , for the reaction time of 3 h and the molar ratio of NH_3 /1,2-dichloropropane as 20:1. Under these conditions the degree of 1,2-dichloropropane conversion amounted to 97.1 mol% and the selectivity of transformation to 1,2-diaminopropane (DAP) in relation to consumed 1,2-dichloropropane was 25.3 mol%, whereas in relation to consumed ammonia 17.9 mol%. The remaining 1,2-dichloropropane reacts to form polypropyleneamines.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Ammonolysis; 1,2-Dichloropropane; 1,2-Diaminopropane; Polypropyleneamines; Amines

1. Introduction

The production process of propylene oxide is still based on the chlorohydrin method. The global production of propylene oxide by this method amounts about 65%. Two by-products: 1,2-dichloropropane (DCP) and bis(1-chloroisopropane) ether are formed in the amount of 0.1–0.4 t per tonne of produced propylene oxide [1]. Due to their limited applications these compounds are usually incinerated with recovery of hydrogen chloride. Apart from incineration there are some chemical methods for utilization of waste chloroorganic compounds. For instance DCP can be utilized by catalytic dechlorination to propane and HCl [2] or by reductive dechlorination to propene and HCl [3]. Catalytic partial or complete dechlorination of 1,2,3-trichloropropane to propane, propene and allyl chloride (AC) on Pt-Sn catalyst has been described [4]. The ammonolysis is the method of utilization the wide spectrum of waste from chemical industry. This method is effective and gives many useful intermediates for organic synthesis [5].

A concept of integration of the propylene oxide plant with the production of 1,2-diaminopropane (DAP) and

polypropyleneamines through the ammonolysis of waste DCP has appeared in the recent years as a result of the transformation from the currently used technologies to the waste-free processes [6].

The main reason for such actions is very harmful influence of DCP on the environment. This compound is used nowadays only as intermediate in chemical industry, but in the past DCP was used as a soil fumigant for nematodes, insecticide for stored grain, solvent in some paint strippers, varnishes, and furniture finish removers, metal degreasing agent in electroplating etc. During the last two decades applications of DCP have been gradually decreased, especially in farming, but due to its slow chemical breakdown in both the air and the soil, most of the DCP released into the environment finally ends up in the air and in the groundwater. The half-life of DCP in air is longer than 23 days, in groundwater it is estimated to be between 6 and 24 months. The Environment Protection Agency has set a MCL (Maximum Contaminant Level) of 0.005 mg/kg for DCP in drinking water and recommends that the level of DCP in surface water should be limited to 0.00052 mg/kg to prevent possible human health effects. Drinking DCP or breathing high levels of DCP by humans has produced poisoning. At these high levels of exposure, effects include dizziness, headache, nausea, injury to the liver and kidneys, anemia, coma and ultimately, death. In animal experiments, low amounts of DCP

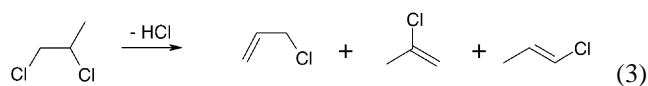
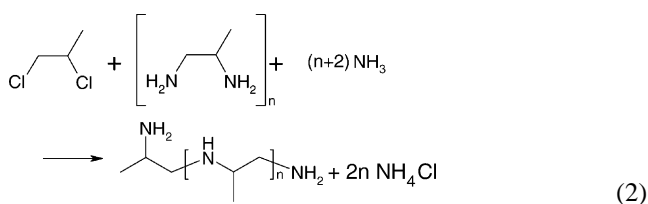
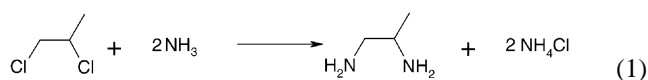
* Corresponding author. Tel.: +4891-449-4855; fax: +4891-449-4365.
E-mail address: eugeniusz.milchert@ps.pl (E. Milchert).

breathed in long-term periods result in damage to the liver, kidney, and respiratory system, while high amounts resulted in death [7].

Both DAP and polypropyleneamines are the valuable intermediates in the organic synthesis. These compounds are used in the production of surfactants [8], improvers for liquid fuels, mineral oils and lubricants [9], improving agents in the textile industry (for impregnation and softening of fabrics) and plastics [10], and in the building industry, among others, for the production of agents improving the adhesion of asphalts to the mineral aggregates [11].

The solutions of ammonia in water or organic solvents are most frequently used in the ammonolysis process. In the case of the processes carried out at the critical temperature of ammonia (131 °C) or above, the appropriate amination agent is the gaseous NH₃ or its solution in the organic solvent or in the substrate [12,13]. The ammonolysis of 1,2-dichloropropane by aqueous ammonia solution was also described [14,15].

In this work, the investigations of the ammonolysis process of DCP with liquid ammonia under the autogenic pressure were performed. The influence of temperature, molar ratio of ammonia to DCP and the reaction time on the degree of DCP conversion and the selectivity of this transformation to DAP in relation to consumed DCP and ammonia has been determined. The equations below describe the ammonolysis of DCP.



2. Experimental

2.1. Procedure of ammonolysis

The ammonolysis of DCP with liquid ammonia was carried out in a laboratory autoclave made by Berghof (Germany). After the introduction of the appropriate amount of DCP the autoclave was cooled in a cryostat to -50°C and air was evacuated by using the vacuum pump (1 mmHg). The autoclave was then weighted, filled with liquid ammonia and weighted again. The excess of ammonia was removed to achieve an assumed mass of the substrates. The charged autoclave was then placed in a heating jacket with regulated temperature. After the synthesis was completed,

the autoclave was weighted again in order to determine the loss of ammonia, subsequently it was then placed in a cryostat and cooled to -50°C and then the outlet valve was open. The cryostat was switched off and the autoclave was kept in the cryostat for the purpose to warm up and a slow distilling off unreacted ammonia. The reaction products were weighted and dissolved in chloroform. The two phases were obtained: the liquid containing DAP, allyl chloride, polypropyleneamines, unreacted DCP, and the solid phase ammonium chloride. After centrifugations and filtering off a liquid layer was analyzed by the gas chromatography method. Thus, the concentration of organic compounds (DCP, DAP, AC) in the reaction mixture were determined. Moreover, a concentration of the chloride ions in the reaction mixture was determined by argentometric titration. This allows to determine the amount of consumed ammonia, since the amount of the chloride ion moles in the reaction mixture is equal to the amount of consumed ammonia moles. The quantity of polypropyleneamines was calculated from the difference between the amount of used DCP and obtained organic products (DAP, AC) and unreacted DCP.

2.2. Analytical methods

The chromatographic analyses were performed on a Chrom 5 apparatus with a flame-ionization detector (FID). A steel column (2.5 mm × 4 mm) filled with 10% Pennwalt + 4% KOH on GCR 80/100 mesh was used. Analyses were carried out in the temperature gradient: isothermally at 50°C for 6 min, then increase to 180°C at the rate of 6°C min^{-1} and isothermally for 10 min. The carrier gas (N₂) flow rate was $27\text{ cm}^3\text{ min}^{-1}$, the air flow rate was $300\text{ cm}^3\text{ min}^{-1}$ and the hydrogen flow rate was $40\text{ cm}^3\text{ min}^{-1}$. A quantitative analysis was performed by the absolute calibration method. The argentometric determination of the chloride ions concentration was performed using a potentiometer TELEKO N5170E. The determinations were performed using the two electrode system: silver AgP-201W and calomel RL-200.

3. Results and discussion

The literature [6] reveals, that the most significant parameters influencing the ammonolysis process by an aqueous solution of ammonia are the molar ratio of ammonia to DCP and the temperature. The reaction time and the amount of catalyst (as well as the type and amount of emulsifier in heterogenic systems) have significantly less pronounced effect. The ammonolysis process was evaluated after the performance of the mass balance for each synthesis and the calculation of the following magnitudes describing the process: the degree of conversions of each substrate, the selectivities of transformation to DAP in relation to consumed DCP and NH₃.

3.1. Influence of NH_3/DCP molar ratio

A series of syntheses was carried out in order to investigate the influence of variable molar ratio of the substrates on the course of the process. Each synthesis was performed twice or more times at a temperature of 150°C , for 3 h, varying a molar excess of ammonia to DCP in the range from 5:1 to 50:1. The conversion of DCP and NH_3 and the selectivity of transformation to DAP as the function of the molar ratio NH_3/DCP are shown in Figs. 1–3.

As can be seen in Fig. 1 the degree of DCP conversion exceeds 99.9 mole% when the molar ratio of

NH_3/DCP is higher than 10:1. The degree of conversion exceeds 99.8 mole% over the entire range of studied molar ratios. During increase an excess of ammonia in relation to DCP, the degree of conversion also increases, reaching 100 mol% above the molar ratio $\text{NH}_3/\text{DCP} = 20:1$. For such a high degree of DCP conversion over the entire examined range of molar ratios, conversion is not a decisive indicator in the selection of the optimum technological parameters of the process operation.

The degree of NH_3 conversion decreases significantly together with an increase of the molar ratio of NH_3/DCP

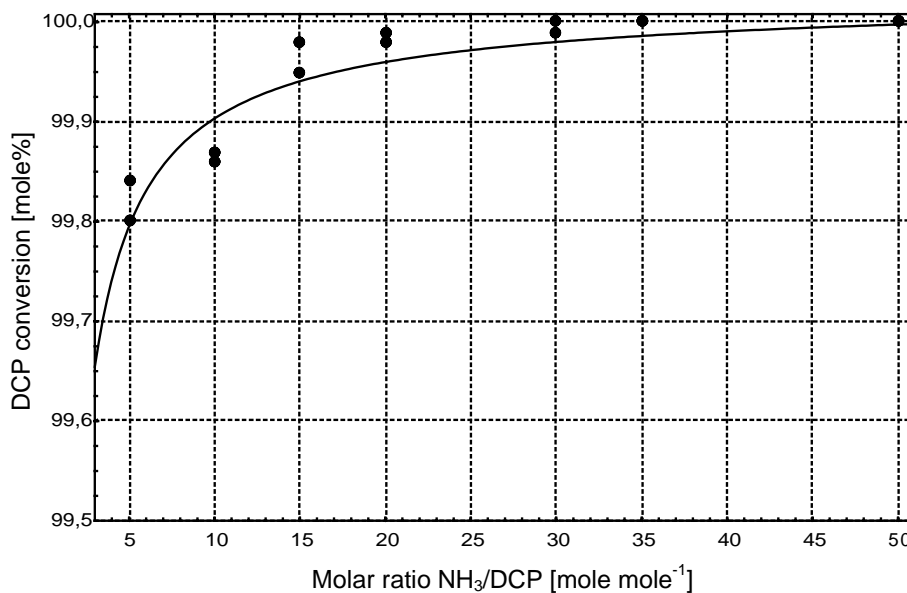


Fig. 1. Influence of molar ratio NH_3/DCP on degree of DCP conversion.

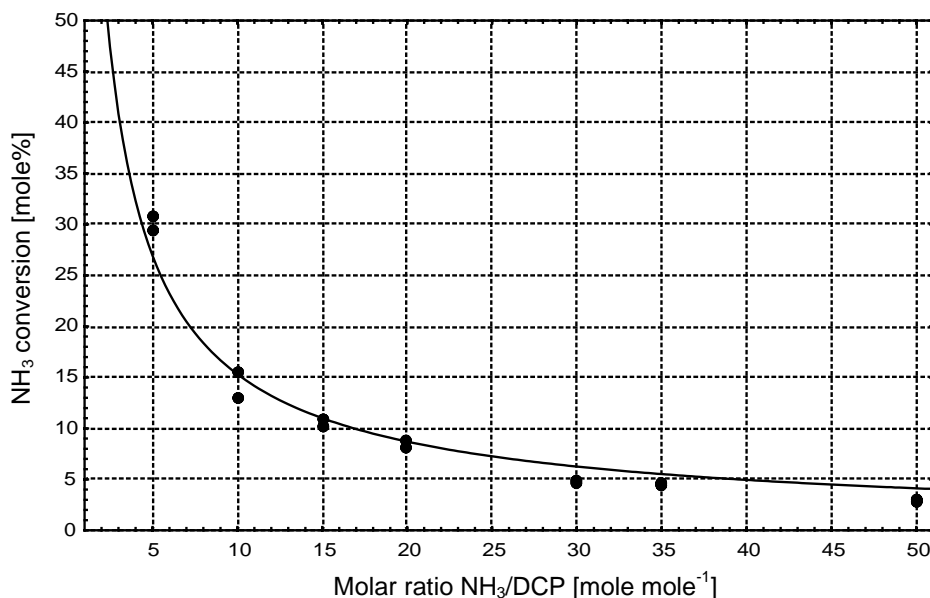


Fig. 2. Influence of molar ratio NH_3/DCP on degree of NH_3 conversion.

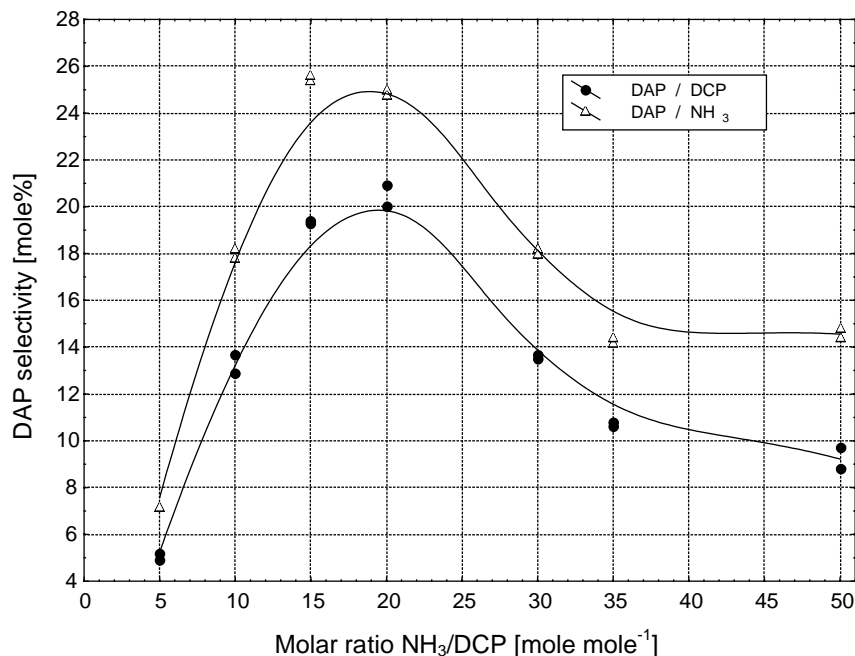


Fig. 3. Influence of molar ratio NH_3/DCP on selectivity of transformation to DAP in relation to consumed substrates.

(Fig. 2). However, this technological parameter has a less significant meaning when the parameters optimal with regard to NH_3 excess are established. Changes of the degree of ammonia conversion above the molar ratio $\text{NH}_3/\text{DCP} = 30:1$ are insignificant. The maximum degree of NH_3 conversion amounted to 30.7 mol% ($\text{NH}_3/\text{DCP} = 5:1$), whereas a minimum degree was 2.7 mole% ($\text{NH}_3/\text{DCP} = 50:1$). The degree of NH_3 conversion amounts 9 mole% at the highest degree of DCP conversion (100 mol%).

The most important indicators to establish the optimal technological parameters are the selectivities of transformation to DAP in relation to consumed DCP and NH_3 . Fig. 3 shows this influence which is similar both in relation to consumed DCP and NH_3 . The maximum selectivity of transformation to DAP in relation to consumed DCP amounts 20.9 mol% and occurs at the molar ratio of $\text{NH}_3/\text{DCP} = 20:1$. The selectivity of transformation to DAP in relation to consumed ammonia at the molar ratio $\text{NH}_3/\text{DCP} = 20:1$ amounts 25.0 mol%. This magnitude is slightly different

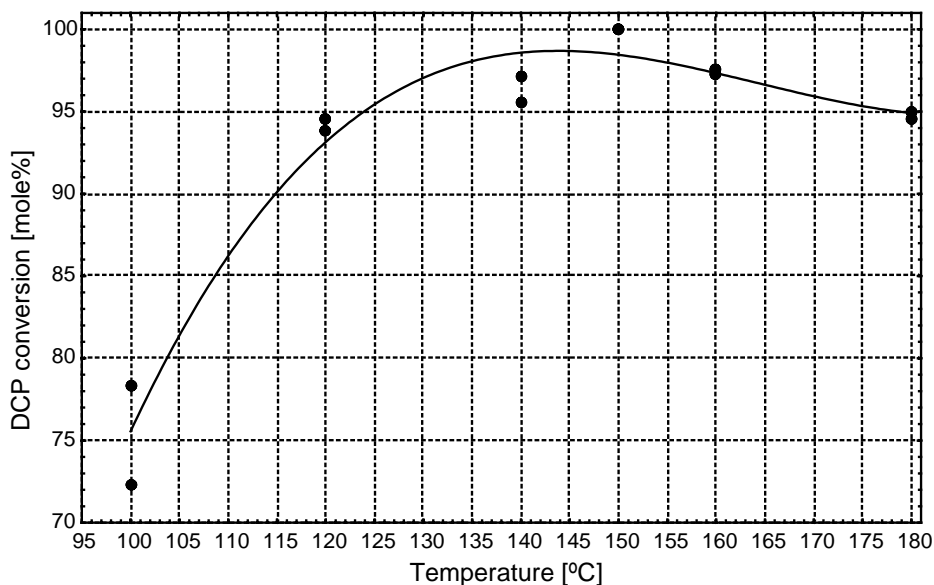


Fig. 4. Influence of temperature on degree of DCP conversion.

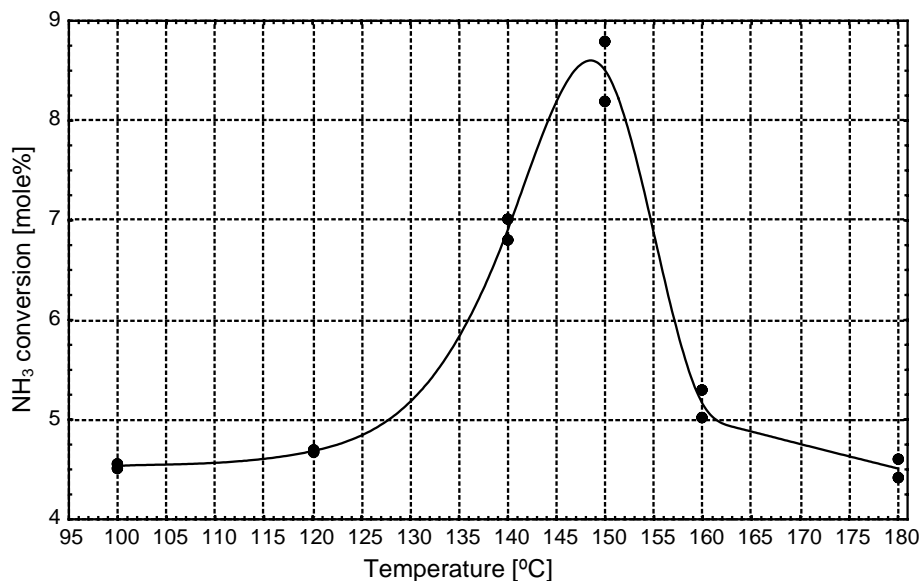


Fig. 5. Influence of temperature on degree of NH₃ conversion.

from a maximum (25.6 mol%) achieved at the molar ratio NH₃/DCP = 15:1.

3.2. Influence of temperature

A series of syntheses was performed in order to determine the influence of temperature on the ammonolysis of waste DCP with liquid ammonia, with each experiment repeated at least twice. The process time was 3 h and the molar ratio of NH₃ to DCP was established as equal to 20:1 in accordance with the results of the previous series of experiments. A

temperature was varied in the range from 100 to 180 °C. The influence of temperature is presented in Figs. 4–6.

As can be seen from Fig. 4 the degree of DCP conversion is highest at 145 °C for the molar ratio of substrates equal to 20:1. This temperature is close to that used in the previous series of experiments. The degree of DCP conversion initially increases rapidly together with elevation of temperature to 120 °C, and then slowly decreases above 150 °C.

The degree of NH₃ conversion (Fig. 5) is also increasing rapidly in the temperature range 125–150 °C and reaches a maximum (8.8 mol%) at 150 °C. A further increase of

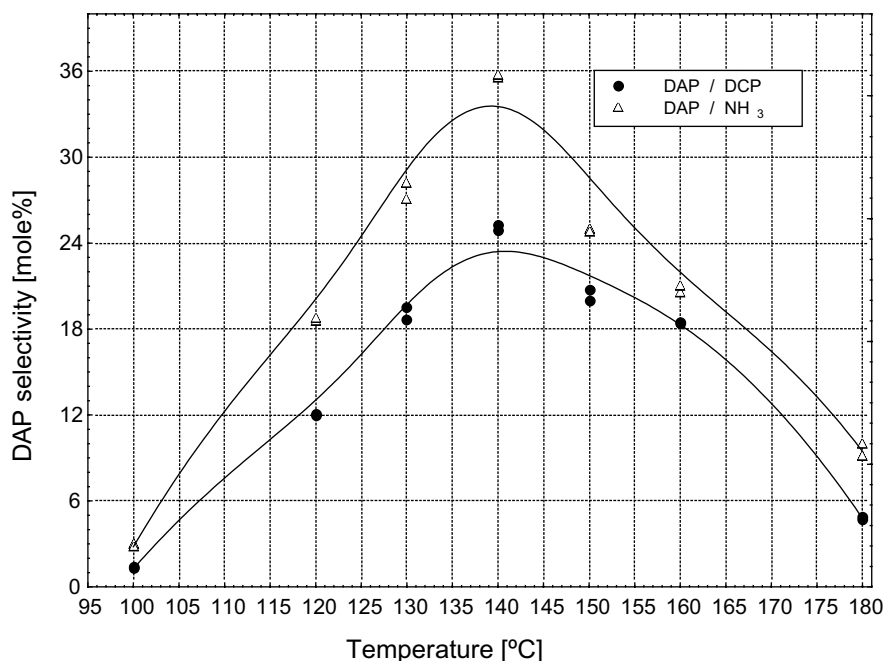


Fig. 6. Influence of temperature on selectivity of transformation to DAP in relation to consumed substrates.

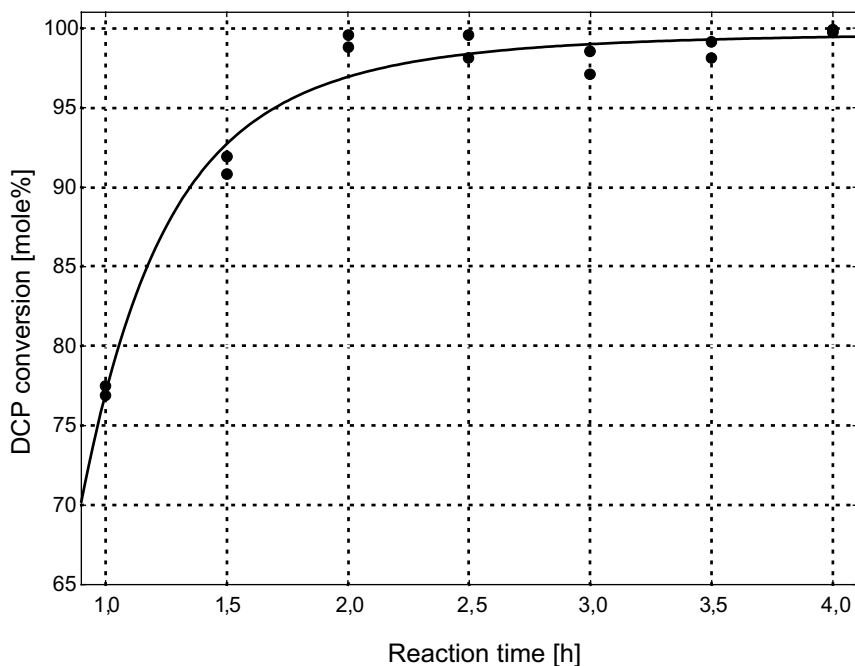


Fig. 7. Influence of reaction time on degree of DCP conversion.

temperature has a significant impact on the degree of conversion of both substrates. A decrease of the degrees of conversion above 150 °C results most probably from the transformation of ammonia from the liquid phase to gaseous one. For temperatures above 150 °C the ammonolysis of DCP to DAP and polypropyleneamines proceed in the gaseous phase. The reactions in liquid ammonia were prevailing at lower temperatures.

The selectivity of transformation to DAP in relation to consumed substrates (Fig. 6) varies during the increase of

process temperature. The highest selectivity of transformation to DAP in relation to consumed DCP as well as NH_3 occurs at temperature of 140 °C and amounts 25.3 and 35.8 mol% respectively.

3.3. Influence of the reaction time

The influence of the reaction time on the course of DCP ammonolysis was investigated in a consecutive series of syntheses. The experiments were performed over the time

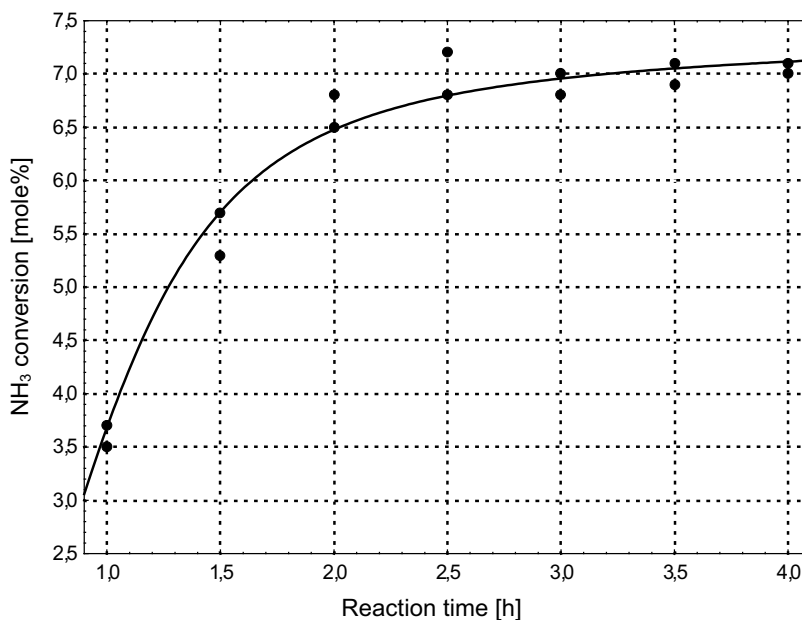


Fig. 8. Influence of reaction time on degree of NH_3 conversion.

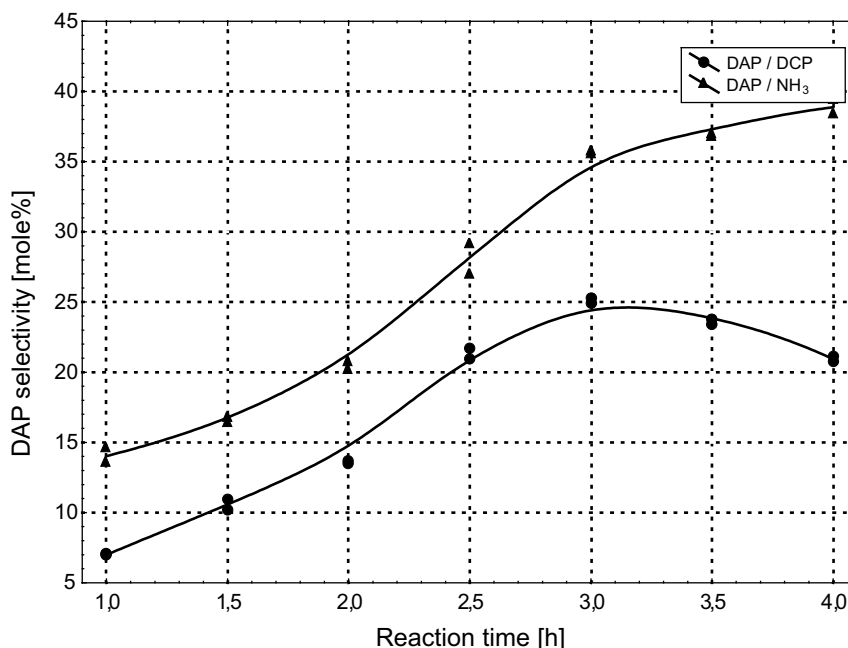


Fig. 9. Influence of reaction time on selectivity of transformation to DAP in relation to consumed substrates.

of: 1, 1.5, 2, 2.5, 3, 3.5, and 4 h, while the remaining parameters have the most favorable values established in the previous series: molar ratio $\text{NH}_3/\text{DCP} = 20:1$, temperature equal to 140°C . The obtained results are shown in Figs. 7–9.

As shown in Fig. 7 the degree of DCP conversion changes along with an increase of the reaction time, rapidly growing from 76.9 mol% (for the reaction time equal to 1 h) to 99.6 mol% after 2 h. The largest increase of the degree of conversion takes place over the period of time from 1 to 1.4 h. Almost a complete transformation of DCP to DAP and polyamines was achieved after 2 h. A similar dependence occurs in Fig. 8, which presents the influence of the reaction time on the degree of NH_3 conversion. The degree of NH_3 conversion initially increases very rapidly from the minimum value of 3.5 mol% after 1 h, to the maximum value of 7.2 mol% after 2.5 h. For experiments carried out over a period of 3–4 h these values are within the range of 7.0–7.1 mol%. From Figs. 7 and 8 results that the degree of conversion of both substrates is practically invariable at reaction time higher than 2.5 h.

The selectivity of transformation to DAP in relation to consumed DCP varies together with a change of the reaction time, increasing from 7.0 mol% after 1 h to the maximum value of 25.3 mol% after 3 h of the reaction (Fig. 9). The prolongation of the reaction time causes a slow increase of the selectivity of transformation in relation to consumed NH_3 . A minimum value (14.6 mol%) was achieved after 1 h. A gradient of increase of the selectivity of transformation to DAP in relation to consumed NH_3 is the smallest over a period of time 3–4 h.

4. Conclusions

The investigations performed to determine the influence of technological parameters of waste DCP ammonolysis by liquid ammonia on the degree of substrates conversion and the selectivity of transformation to DAP in relation to consumed DCP and NH_3 allowed to establish that the process proceeds favorably at a temperature of 140°C , molar ratio NH_3/DCP equal to 20:1, for the reaction time of 180 min. Under these conditions the degree of DCP conversion reaches 97.1 mol%, whereas for NH_3 7.0 mol%. The selectivity of transformation to DAP in relation to consumed DCP and NH_3 amounts to 25.3 and 35.8 mol% respectively. A low degree of NH_3 conversion is justified by its large excess. Unreacted ammonia is easy to recover and recycle back to the process. A described method was found to be a more effective in comparison with known methods [4,6] utilizing ammonia water. This method allows to transform DCP to DAP significantly more selectively, without a loss of organic material. The remaining amount of DCP transforms to polypropyleneamines, an intermediate with similar applications as DAP. Thus, the mass of organic raw material is not wasted. The developed method creates the convenient conditions for the separation of pure DAP and polypropyleneamines, due to an anhydrous reaction environment. For this reason this method comprises a considerable advance in relation to the ammonolysis by ammonia water.

References

- [1] E. Milchert, Technology of chloroorganic compounds production. The wastes utilization, WUPS, Szczecin, 1997, p. 50.

- [2] Patent USA 5625110 (1997).
- [3] Patent USA 4943671 (1990).
- [4] K.O. Early, W.D. Rhodes, V.I. Kovalchuk, J.L. d'Itri, *Appl. Catal. B: Environ.* 26 (2000) 257–263.
- [5] M. Bartkowiak, E. Milchert, *Przem. Chem.* 81 (2002) 708–712.
- [6] J. Zieńko, J. Myszkowski, *Przem. Chem.* 69 (1990) 252–253.
- [7] Agency for Toxic Substances and Disease Registry, *Toxicological Profile for 1,2-Dichloropropane*, Public Health Service, U.S. Dept. of Health and Human Services, 1989.
- [8] Patent USA 3251882 (1966).
- [9] Patent USA 5405543 (1995).
- [10] Patent USA 5362432 (1994).
- [11] J. Pombszky, O. Dobozy, *Zur. Prik. Chim.* 46 (1973) 1214.
- [12] J. Zieńko, E. Milchert, J. Myszkowski, *Przem. Chem.* 68 (1989) 219–223.
- [13] *Unit processes in organic synthesis*, P.H. Groggins (Ed.), McGraw Hill, New York, 1958.
- [14] M. Mungo, M. Bornengo, *La Chimica & L'Industria* 46 (1964) 1037–1040.
- [15] J. Zieńko, E. Milchert, J. Myszkowski, *Chemia Stosowana* 33 (1989) 721–724.