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KINETICS STUDY OF HYDRAZODICARBONAMIDE SYNTHESIS REACTION

In this study, the kinetics of hydrazodicarbonamide (HDCA) synthesis reaction were investigated. Hydrazodicarbonamide is prepared by reaction of urea and hydrazine in acidic medium. Synthesis of HDCA from urea and hydrazine is a two-step reaction. In the first step, semicarbazide is synthesized from the reaction of one mole of urea and one mole of hydrazine and in the second step, semicarbazide reacts with urea to produce hydrazodicarbonamide. By controlling the temperature and pH in the reaction, hydrazine concentration and the amount of produced hydrazodicarbonamide were measured and using this data, reaction rate constants were calculated. Based on this study, it was found that the semicarbazide formation reaction from hydrazine is the rate-limiting step. The rate of semicarbazide synthesis is $-r_1 = 0.1396[\text{NH}_2\text{NH}_2]^{0.5810}$ and the rate of hydrazodicarbonamide synthesis is $-r_2 = 0.7715[\text{NH}_2\text{NHCONH}_2]^{0.8430}$.

Keywords: hydrazodicarbonamide, azodicarbonamide, semicarbazide, synthesis, kinetics.

Polymer foams are widely used in the modern world in a variety of applications such as cushioning of the furniture, insulation materials, etc. [1]. The foams are made up of a solid and gas phase mixed together. The gas is generated by a blowing agent, which can be physical or chemical [2,3]. In physical blowing agents, the gas is generated through a physical phase change such as evaporation, but in chemical blowing agent, the gas is generated via a chemical reaction such as thermal decomposition. Azodicarbonamide (AZDC) with a molecular formula $\text{NH}_2\text{CONNCONH}_2$, is the most popular chemical blowing agent for making polymeric foams [4] and is made through oxidation of hydrazodicarbonamide (HDCA) with an appropriate oxidizing agent [5,6].

HDCA is a white solid with a molecular formula $\text{NH}_2\text{CONHNHCONH}_2$ and is prepared by reaction of urea and hydrazine or its salts. HDCA decomposes at 230–260 °C to produce gas, white solid and a viscous liquid. The gas comprises ammonia, carbon dioxide

and nitrogen, the solid is mainly urea and the viscous liquid is mainly urazole.

Various processes were proposed in the literature for HDCA synthesis. Some of these processes were summarized as follows:

1. Reaction of hydrazine or its salts with urea in the presence of a non-oxidizing acids such as sulfuric acid, phosphoric acid or hydrochloric acid [7–12].
2. Reaction of hydrazine or its salts with urea in the presence of an alkali and separating the produced ammonia from the reaction mixture [13,14].
3. Reaction of a ketazine with urea in the presence of a non-oxidizing acid [15–17].
4. Reaction of a ketazine with urea in the presence of an alkali and separating the produced ammonia and ketone and the un-hydrolyzed ketazine from reaction mixture [14,18].
5. Reaction of urea with semicarbazide [19].

HDCA production in commercial scale is mainly in batch reactor because the reaction time is long. Determination of the reactor volume and reaction time are important in reactor design, which requires the kinetic information of the synthesis reactions.

To the authors' best knowledge, no research has been done on the kinetics of the HDCA synthesis reaction. The reaction of urea and hydrazine under

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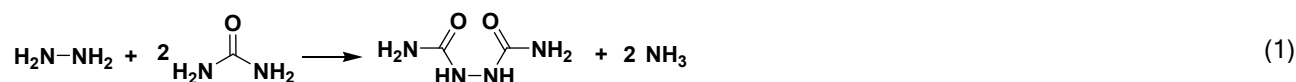
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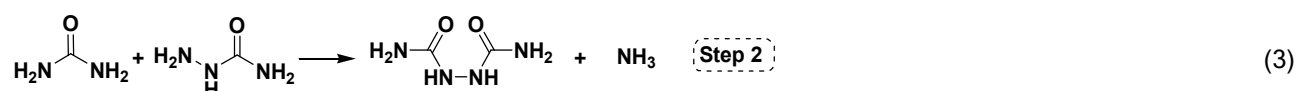
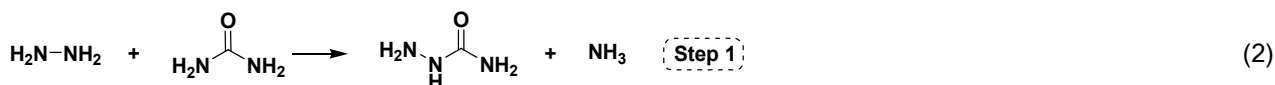
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acidic conditions is the commercial process for HDCA production, so the kinetics of this reaction were the subject of this research study. Hydrazine sulfate and urea were used for synthesis of HDCA and determination of reaction rate constants. The HDCA synthesis reaction can be written as:



which is a two steps reaction. In the first step, an intermediate compound named semicarbazide is produced and in the second step, HDCA is produced as presented in Eqs. (2) and (3):



It is necessary to consider that temperature and pH have an influence on the type of product, *e.g.*, if $T < 30 \text{ }^\circ\text{C}$ and $\text{pH} < 1$, hydrazine sulfate forms. If $50 \text{ }^\circ\text{C} < T < 90 \text{ }^\circ\text{C}$ and $7 < \text{pH} < 9$, semicarbazide forms and if $85 \text{ }^\circ\text{C} < T < 95 \text{ }^\circ\text{C}$ and $3 < \text{pH} < 6$, HDCA forms [20].

EXPERIMENTAL

Hydrazine sulfate, urea and sulfuric acid were purchased from Merck. The procedure for synthesis of HDCA is as follows: 0.1 mol hydrazine sulfate, 0.4 mol urea and 300 g water were mixed in the reactor. Then, the temperature was increased to 92–93 °C and kept constant during reaction period (1, 2, ..., 9 h) by gentle heating. By gradual addition of sulfuric acid solution, the pH of the reaction mixture was kept constant during reaction. After that, the temperature was lowered rapidly to room temperature and the precipitated HDCA was separated from the mother liquor by filtration and was weighed after drying. The concentration of unreacted hydrazine in the mother liquor was measured by the iodometric method, in which iodine was used to oxidize the hydrazine and the amount of unreacted iodine was measured by sodium thiosulfate solution, using starch as indicator [21,22].

The reactor setup used for HDCA synthesis consisted of a three-way flask and a condenser attached to it. Sulfuric acid solution was added during the reaction from one connection, and the other connection of the flask was used for thermometer attachment.

It was assumed that hydrazine decomposition was negligible during synthesis reaction. The concen-

tration of semicarbazide at the end of synthesis reaction period was calculated by mass balance through the hydrazine concentration and the weight of precipitated HDCA.

RESULTS AND DISCUSSION

Figures 1 and 2 represent hydrazine concentration and the weight of precipitated hydrazodicar-

bonamide versus time, while Figure 3 shows the calculated concentration of semicarbazide *versus* time.

Because the concentration of urea in the reaction mixture is high, it can be assumed that the concentration of urea in the reaction mixture is constant and the rate of reactions depend on the concentration of the other components (hydrazine and semicarbazide). That is, the method of excess is applicable. So the equations for rate of reactions can be written as follows:

$$\text{Step 1: } -r_1 = -\frac{dc_N}{dt} = K_1[\text{NH}_2\text{NH}_2]^n \quad (3)$$

$$\text{Step 2: } -r_2 = -\frac{dc_S}{dt} = K_2[\text{NH}_2\text{NHCONH}_2]^m \quad (4)$$

where K_1 and K_2 are the reaction rate constants and n and m are the orders of the reaction rate equations.

First step: reaction between urea and hydrazine

From Eq. (3), the following relations can be derived:

$$-\frac{dc_N}{dt} = K_1 c_N^n$$

$$\int_{c_{N0}}^{c_N} \frac{dc_N}{c_N^n} = \int_0^t -K_1 dt$$

$$\frac{c_N^{1-n} - c_{N0}^{1-n}}{1-n} = -K_1 t$$

where c_{N0} is the initial concentration of hydrazine in the reaction mixture. For the case of $n = 1$,

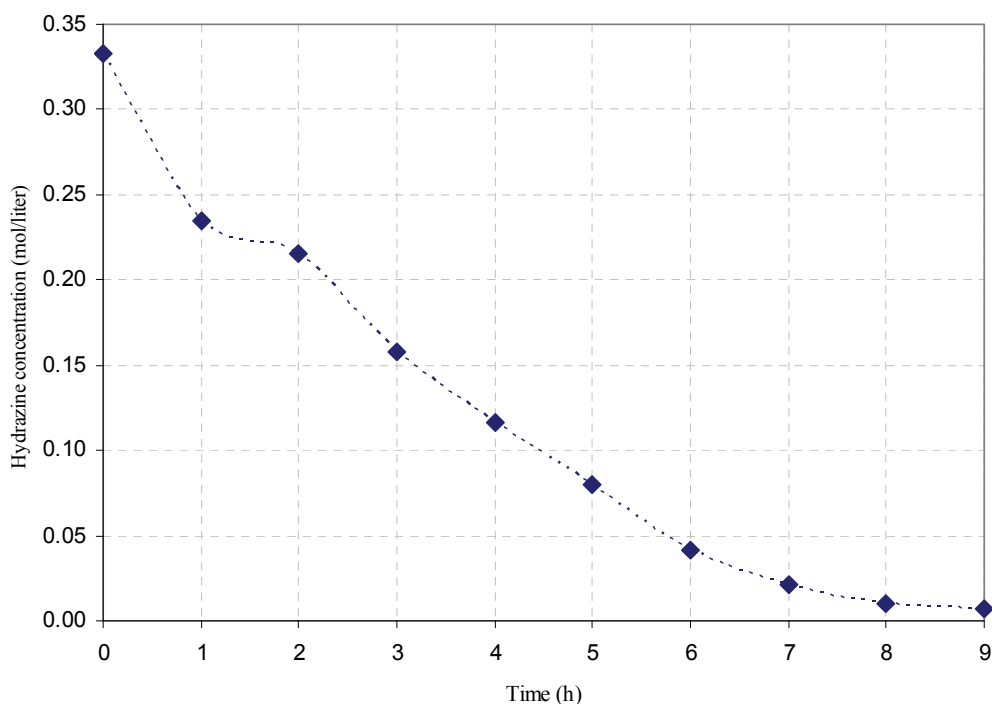


Figure 1. Hydrazine concentration versus time.

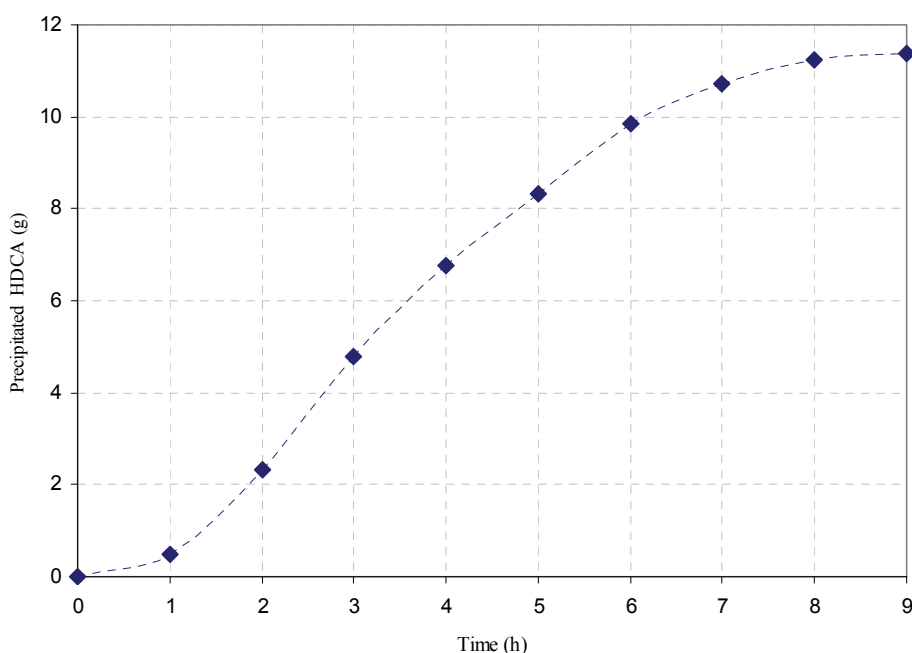


Figure 2. Mass of precipitated hydrazodicarbonamide versus time.

$\ln(c_N / c_{N_0}) = -K_1 t$. So, a plot of $\ln(c_N / c_{N_0})$ versus time (t) should result in a straight line if the order of reaction is unity.

From Figure 1 it can be found that the order of reaction (n) is a positive number and lower than unity. So, by using MATLAB software and optimization methods, optimum values for K_1 and n can be determined. For the optimum value of n , the graph of

$(c_N^{1-n} - c_{N_0}^{1-n}) / (1-n) = -K_1 t$ versus time is approximately linear with the slope of K_1 [23,24].

The calculation based on optimization methods of MATLAB software shows that the optimum values for K_1 and n are 0.1396 and 0.5810, respectively. The value of R^2 (coefficient of determination) for optimization is 0.9918. In Figure 4, the concentration of hydrazine versus time is shown for both the experimental

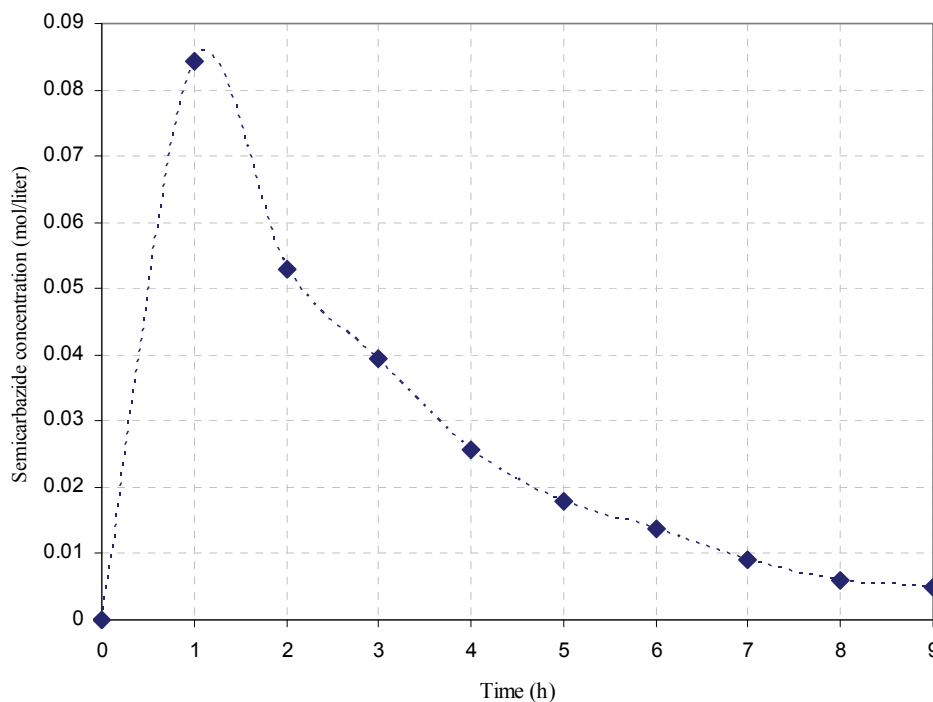


Figure 3. Semicarbazide concentration versus time.

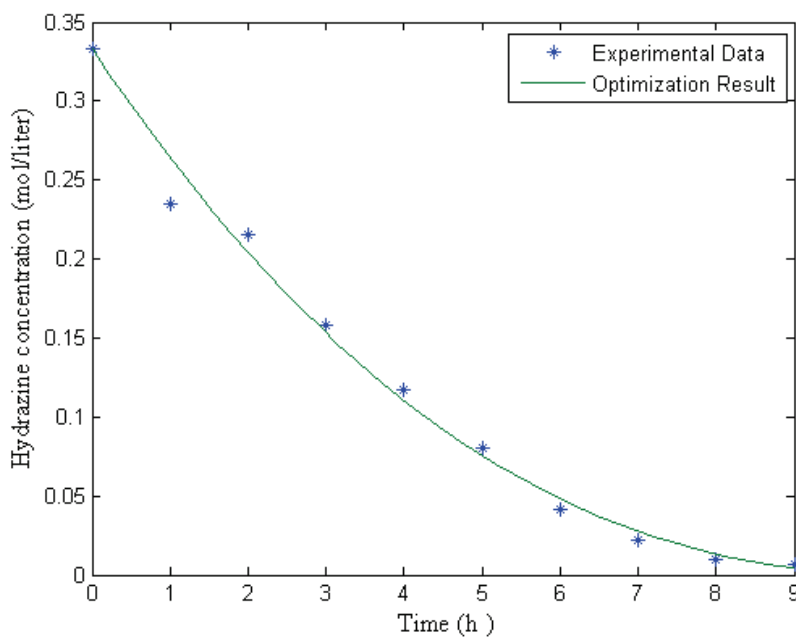


Figure 4. Comparison of experimental data and optimization result for hydrazine concentration.

data and the optimization results, which shows good fitting between these two sets of data.

The rate equation for the first reaction is:

$$-r_1 = K_1[\text{NH}_2\text{NH}_2]^n = 0.1396[\text{NH}_2\text{NH}_2]^{0.5810} \quad (5)$$

Second step: reaction between semicarbazide and urea

Because semicarbazide is an intermediate compound, its concentration depends on the rate of both

reactions (semicarbazide synthesis reaction and HDCA synthesis reaction). Based on the concentration-time diagrams for hydrazine and semicarbazide (Figures 1 and 3), it is obvious that the first reaction is the rate limiting step and rate of second reaction is higher than the first one. The change of semicarbazide concentration with time in the reaction mixture can be given as:

$$\frac{dc_s}{dt} = K_1 c_N^n - K_2 c_s^m \quad (6)$$

which is a parametric differential equation and by solving this equation, optimum values for K_2 and m can be obtained. Using optimization methods of MATLAB software, the optimum values of K_2 and m were determined which are 0.7715 and 0.8430, respectively. The value of R^2 (coefficient of determination) for optimization is 0.5912. In Figure 5, the concentration of semicarbazide *versus* time is shown for both the experimental data and the optimization results, which shows relatively good fitting between these two sets of data.

So, the rate equation for the second reaction (hydrazodicarbonamide formation reaction) is:

$$\begin{aligned} -r_2 &= K_2 [\text{NH}_2\text{NHCONH}_2]^m = \\ &= 0.7715 [\text{NH}_2\text{NHCONH}_2]^{0.8430} \end{aligned} \quad (7)$$

and the change of semicarbazide concentration with time can be calculated from:

$$\begin{aligned} \frac{d[\text{NH}_2\text{NHCONH}_2]}{dt} &= 0.1396 [\text{NH}_2\text{NH}_2]^{0.5810} - \\ &- 0.7715 [\text{NH}_2\text{NHCONH}_2]^{0.8430} \end{aligned} \quad (8)$$

CONCLUSIONS

Studying the kinetics of a chemical reaction allows for more accurate reactor design. The study of the hydrazodicarbonamide formation reaction from

urea and hydrazine shows that this reaction is a two-step reaction and each step has its own rate equation.

The plots of hydrazine concentration and semicarbazide concentration versus time show that the rate of semicarbazide synthesis reaction (reaction of urea with hydrazine) is lower than the rate of hydrazodicarbonamide synthesis reaction (reaction of semicarbazide with urea). In the plot of hydrazine concentration *versus* time and at $t = 1$ h, there is a sudden change in the decreasing trend of hydrazine concentration versus time which is due to an increase in semicarbazide concentration in the reaction mixture. This change shows that the first reaction is more sensitive to semicarbazide concentration. This confirms the conclusion that the rate of semicarbazide formation reaction is lower than the hydrazodicarbonamide formation reaction and the former reaction is the rate limiting step for hydrazodicarbonamide synthesis reaction.

The semicarbazide synthesis reaction has the following rate equation:

$$-r_1 = 0.1396 [\text{NH}_2\text{NH}_2]^{0.5810}$$

and the hydrazodicarbonamide synthesis reaction has the following rate equation:

$$-r_2 = 0.7715 [\text{NH}_2\text{NHCONH}_2]^{0.8430}$$

Nomenclature

c_N	hydrazine concentration in reaction media
c_S	semicarbazide concentration in reaction media
K_1	semicarbazide synthesis reaction rate constant

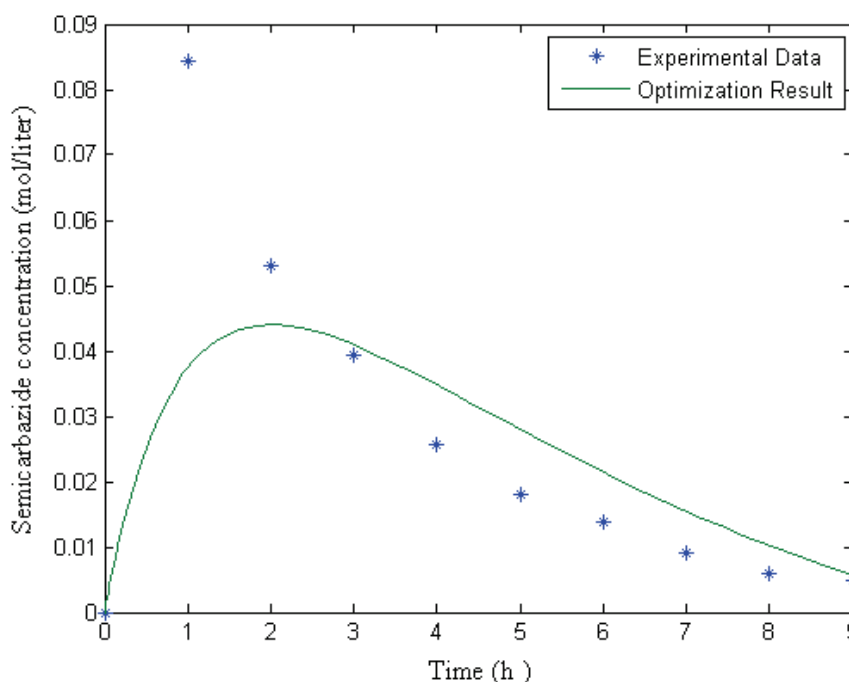


Figure 5. Comparison of the experimental data and optimization result for semicarbazide concentration.

K_2 hydrazodicarbonamide synthesis reaction rate constant
 m order of hydrazodicarbonamide synthesis reaction rate equation
 n order of semicarbazide synthesis reaction rate equation.

REFERENCES

- [1] S. Quinn, Chemical blowing agents: providing production, economic and physical improvements to a wide range of polymers, *Plastics, Additives and Compounding* **3**(5) (2001) 16-21
- [2] R.L. Heck, W.J. Peascoe, *Blowing Agents*. Encyclopedia of polymer science and technology, John Wiley & Sons Inc., 2011
- [3] H.W. Engels, H.J. Weidenhaupt, M. Pieroth, W. Hofmann, K.H. Menting, T. Mergenhagen, R. Schmoll, S. Uhrlandt, *Rubber, 9. Chemicals and Additives*. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KgaA, 2011
- [4] G.L.A. Sims, H.A.S. Jaafar, A chemical blowing agent system (CBAS) based on Azodicarbonamide, *Journal of Cellular Plastics* **30** (1994) 175-188
- [5] H. Hurnik, M. Finzenhagen, W. Jeblick, New blowing agent combination based on azodicarbonamide, production thereof and use thereof for foaming polymers, US Patent 4714568, Bayer Aktiengesellschaft, 1987
- [6] H. Motokawa, T. Hayashi, H. Kohara, Process for the preparation of azodicarbonamides modified with metallic compounds, US Patent 3876622, Eiwa Chemical Industrial Company, 1975
- [7] T.H. Newby, J.M. Allen, Preparation of hydrazodicarbonamide, US Patent 2692281, United States Rubber Company, 1954
- [8] Method for the preparation of hydrazodicarbonamide, GB Patent 740676, US Rubber (1955).
- [9] J. Miller, B.J. Needham, Process for the production of hydrazodicarbonamide and azodicarbonamide, GB Patent 1311480, Fisons Limited, 1973
- [10] Y. Hiroaki, M. Satoshi, K. Junichi, I. Makoto, A. Takayoshi, H. Yoshimitsu, Preparation of hydrazodicarbonamide, JP Patent 53056619, Asahi Denka Kogyo KK, 1978
- [11] C.H. Lee, S.J. Han, Method for synthesizing hydrazodicarbonamide, US Patent 6635785B1, J&J Chemical Co. Ltd., 2003
- [12] C.H. Lee, S.J. Han, Method for preparing hydrazodicarbonamide using biuret as starting material, US Patent 7465828, J&J Chemical Co. Ltd., 2008
- [13] Preparation of hydrazodicarbonamide and azodicarbonamide, GB Patent 1146233, Fairmount Chemical Co. Inc., 1969
- [14] S. Ohno, T. Kazuta, T. Iwata, Process for preparing hydrazodicarbonamide, US Patent 4176135, Otsuka Kagaku Yakuin Kabushiki Kaisha, 1979
- [15] J.P. Schirrmann, F. Weiss, Method for manufacturing hydrazodicarbonamide, US Patent 4049712, Produits Chimiques Ugine Kuhlmann, 1977
- [16] Process for making hydrazodicarbonamide, GB Patent 1371119, Pechiney Ugine Kuhlmann, 1974
- [17] K. Takashi, N. Toshihiro, Y. Kiyoshi, M. Isamu, Method for producing hydrazodicarbonamide, JP Patent 2002069049, Mitsubishi Gas Chem Co. Inc., 2002
- [18] R.W. Brown, B.A. Hunter, F.H. Barrows, Preparation of hydrazodicarbonamide, US Patent 3969466, Uniroyal Inc., 1976
- [19] C.H. Lee, S.J. Han, Method for preparing hydrazodicarbonamide using biuret as starting material, EP 1513798 B1, J&J Chemical Co. Ltd., 2011
- [20] C.P. Riley, Synthesis of hydrazine, semicarbazide, and hydrazinedicarbonamide, US Patent 3238226, National Polychemicals Inc., 1966
- [21] E.F. Rothgery, Hydrazine and its derivatives. Kirk-Othmer encyclopedia of chemical technology, John Wiley & Sons Inc., 2004
- [22] I.M. Kolthoff, R. Belcher, *Volumetric analysis*, Vol. 3, Wiley-Interscience, New York, 1957
- [23] *Chemical Reaction Engineering*, 3rd Edition, Octave Levenspiel, John Wiley & Sons Inc., 1999, USA
- [24] H.S. Fogler, *Elements of chemical reaction engineering*, 4th Ed., Prentice-Hall, 2006.

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NAUČNI RAD

PROUČAVANJE KINETIKE REAKCIJE SINTEZE HIDRAZODIKARBONAMIDA

U ovom radu je ispitivana kinetika sinteze reakcije hidrazodikarbonamida (HDCA). Hidrazodikarbonamid se priprema reakcijom uree i hidrazina u kiselj sredini. Sintaza HDCA iz uree i hidrazina se odigrava u dva stupnja. U prvom stupnju, reakcijom jednog mola uree i jednog mola hidrazina nastaje semikarbazid, koji u drugom stupnju reaguje sa ureom gradeći hidrazodikarbonamid. Kontrolom temperature i pH reakcije, merene su koncentracija hidrazina i količina nastalog hidrazodikarbonamida. Korišćenjem ovih podataka određene su konstante brzine reakcija. Na osnovu ovog istraživanja, utvrđeno je da je prvi stupanj formiranja semikarbazida limitirajući stupanj brzine reakcije. Brzina formiranja semikarbazida je $r_1 = 0,1396[\text{NH}_2\text{NH}_2]^{0,5810}$, a brzina formiranja hidrazodikarbonamida je $-r_2 = 0,7715[\text{NH}_2\text{NHCONH}_2]^{0,8430}$.

Ključne reči: hidrazodikarbonamid, azodikarbonamid, semikarbazid, sinteza, kinetika.