Development of basic technology of non-catalytic and non-phosgene reduction method for the synthesis of isocyanates by thermal decomposition of carbamates

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Abstract

This work is dedicated to phosgene-free route to isocyanates by carbamates thermal decomposition. In accordance with policy of the government of the Russian for the development of low-tonnage chemical production in the Russian Federation for the period up to 2030, active development of the country's own technologies for producing chemical products, including low-tonnage ones, is required. The list of priority product lines includes crop protection products, adhesives, sealants, reagents and solvents, plastics and special purpose rubbers. Most of these products include in their composition derivatives of carbamic acids, especially isocyanates, whose production is highly toxic This is the main reason for organization of environmentally friendly, efficient and safe technologies that allow producing products at competitive prices. This task requires a thorough study of physical and chemical processes' patterns, which ensure the creation of safer processes with the avoiding highly toxic and explosive substances that require increased safety measures. As a result, it will allow getting a lower cost and high quality of the target products.

The growing practical demand of the Russian market for isocyanates, which is currently almost completely met by imports, against the background of the general trend towards import substitution is associated with a wide range of applications of isocyanates in the chemical industry. Another difficulty is the lack of competitive domestic isocyanate production technologies, which means that foreign licensors must be involved in projects. The implementation of this thesis in the framework of the Federal program on priority directions of development of scientific-technological complex of Russia (project № 2019-05-579-0001 "Development of import-substituting technology for methylene diphenyl diisocyanate (MDI)") was one of solutions of this problem. This is certainly officially confirms the relevance of the topic of this qualification work.

The main goal of the present work was to develop methods and technology of aliphatic isocyanate synthesis for low-tonnage manufacturing by investigation into quantitative patterns of carbamates thermal decomposition as an economically viable technology on phosgene-free basis.

The main tasks were:

1. Creation of a laboratory research facility for aliphatic isocyanates production by carbamates thermal decomposition;

2. Studying the processes of thermal decomposition of carbamates by the example of *n*-butyl isocyanate, cyclohexyl isocyanate and benzyl isocyanate;

3. Development of analytical methods for composition identification of the resulting products;

4. Creation of analytical and mathematical models of the process of carbamates thermal decomposition in a tube reactor with a non-isothermal mode;

5. Generalizing the kinetic trends of the process and getting the kinetic parameters (activation energy and pre-exponential multiplier), which allow calculating the process equipment when scaling the technology;

7. Technical and economic calculations of the technology for obtaining *n*-butyl isocyanate in the fungicide “benomyl” (Methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate) synthesis.

Scientific novelty:

1. The analytical model for dependence of the conversion degree from the temperature profile, flow rate and length of the reactor was developed based on investigation into the physical and chemical features of the process in a non-isothermal displacement reactor with varying exposure time, temperature profile along the length of the reactor at the created laboratory research facility for thermal decomposition of O-methyl-N-alkylcarbamates. The mathematical model of process in tubular reactor was also developed in the software suite COMSOL Multiphysics. Using both of these models allows one to determine process parameters at each point of the reactor.
2. Kinetic parameters — activation energy and pre-exponential multiplier — were obtained for the first time using aforementioned analytical model for the thermal decomposition reactions of O-methyl-N-butylcarbamate, O-methyl-N-cyclohexylcarbamate and O-methyl-N-benzylcarbamate.

Theoretical significance of the work

Adequacy of foregoing analytical and mathematical models which was proven by experimental data, allows them to be used in theoretical modeling and kinetic parameters

(activation energy and pre-exponential multiplier) calculation not only for isocyanate synthesis but also in other non-isothermal processes.

Practical significance of the work

The developed laboratory facility for thermal decomposition of carbamates allows running the two-step process: carbamate decomposition and consequent derivatization of obtained isocyanate with alkylamine to obtain corresponding N-alkyl-N'-methyl-N'-benzyl urea as the analytical form suitable for HPLC with UV-detector. The laboratory setup allows to obtain practically significant carbamates and urea without isolating isocyanate. The interface of the SCADA system of the laboratory plant was developed, that automatize process control and data-gathering, which in turn reduces investigation time consumption. Analytical methods have been developed to determine not only the main product of the reaction, but also by-products and the initial reagents. Newly developed phosgene-free isocyanate production method by non-catalytical carbamates thermal decomposition in tubular reactor with non-isothermal mode in gas phase is much safer unlike known ways utilizing phosgene and its analogues. Technical and economic calculations of the process may be used in realization of developed 3-step fungicide "benomyl" production with productive capacity 1500 tons per year.

Investigations methods

The structures of substances were proven by means of NMR spectroscopy and mass-spectrometry; compositions of reaction masses were determined by HPLC with UV and refraction index detector. Analytical standards of intermediates and final products were obtained synthetically and purified by preparative HPLC. Computational and project design works were carried using modern CAE programs: MathCAD, COMSOL Multiphysics, ChemCAD.

Confidence limit

Reliability of obtained results is ensured by using precise and modern methods of analysis (^{1}H NMR spectroscopy, HPLC with UV and refraction index detector) and correct applying of math tools in kinetic model development.

Defense provisions:

1. Development of research facility for the thermal decomposition of carbamates;

2. Kinetic patterns of the thermal decomposition process of O-methyl-N-butylcarbamate, O-methyl-N-cyclohexylcarbamate, O-methyl-N-benzylcarbamate;

3. Mathematical model of a displacement reactor under non-isothermal conditions;
4. The basic technological scheme of an industrial plant for obtaining benomil.