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MODELING OF THE SYNTHESIS OF PYRROLES IN CHEMICAL PRODUCTION

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Abstract. This work has studied the reaction of catalytic conversion of butyn-2-diol-1,4 and ammonia in the presence of complex mixed polyfunctional catalysts. It was found that in order to take into account uncertainties of various nature, it was proposed to solve the problem of ensuring the safety of chemical production at a qualitatively new level using new information technologies based on the creation of intelligent decision support systems for managing the safety of chemical technological processes and systems at all stages of occurrence. These systems make it possible to formulate recommendations for various decision-makers on the management of the safety of chemical production, both on the basis of operational observation data and using methods and models based on artificial intelligence embedded in expert systems, including the knowledge of specialists and experience in operating chemically dangerous objects.

Keywords: pyrrole, acetylene, ammonia, amines, catalyst, dehydration, heterocyclization.

Introduction.

The operating chemical industrial plants are high-risk facilities that pose a serious danger to humans and the environment, operating under conditions of uncertainty associated with the lack or incompleteness of information about the processes of occurrence. To solve the problems of analyzing industrial hazards, identifying pre-emergency situations and managing the safety of chemical industries, it is promising to use artificial intelligence methods which allow, due to the learning and adaptation algorithms embedded in them, to reduce the errors of existing models associated with the absence or incompleteness of information, and are applicable for safety management in real time mode [1,2]. In this regard, further intensification of chemical processes in various industries and an increase in their efficiency are inextricably linked with the development of mathematical modeling of chemical production processes. The great interest in the chemical industry to the synthesis of nitrogen-containing organic compounds is due to the wide practical application of the latter in such areas of science and technology as medicine and pharmacology, biotechnology, polymer composite materials technology, in the fuel and energy complex, etc. Therefore, the development of effective methods for calculating and choosing the designs of an industrial reactor in the synthesis of pyrroles in chemical production are of great practical importance.

Nitrogen-containing heterocyclic compounds of the pyrrole and pyridine series are very valuable raw materials for the production of a number of practically important medicines [3,4].

The pyrrole ring is part of the molecules of many natural and biologically active compounds. Derivatives of pyrrole include a number of important plant alkaloids, such as nicotine, atropine, cocaine, etc. The pyrrole ring is present in the molecules of the blood dye - hemoglobin and the green substance of higher plants - chlorophyll, vitamin B12, bile pigment, and a number of antibiotics [5-6].
The widespread use of pyrrole, pyridine and their derivatives is delayed due to the lack of convenient methods for their synthesis. The various methods for the synthesis of the pyrrole and pyridine rings available in the literature are multistage. In addition, the starting compounds for their synthesis are difficult to obtain in many cases.

There are many different ways of forming a pyrrole cyclic system from aliphatic intermediates [7-14]. The main impetus for these studies was the need for pyrrole intermediates for the synthesis of paraffins and related structures of biological significance. Using the most important synthetic methods, substituted pyrroles are obtained from which, as appropriate, the side chains are modified or completely removed.

We have studied the reaction of pyrrole synthesis by catalytic heterocyclization of butyn-2-diol-1.4 and ammonia in the presence of a Cadmium-Zinc-Chromium-Aluminum (CZCA-1) catalyst [15-17].

**Experimental part.**

*Method for Preparing Catalysts.* 60 ml of 5% hydrochloric acid and 50 ml of 3.0-5.9% hydrofluoric acid were added to 120 g of aluminum hydroxide TU-03714-78 (PPP-33%). 7 g of cadmium fluoride, 7 g of zinc oxide and 6 g of chromium oxide were added to the resulting suspension with stirring. The catalyst mass was molded in the form of a "cylinder" by passing through a filter with a diameter of 4 mm. The molded catalyst mass was dried at room temperature (20-30 °C) for 12-16 hours and dried at 100±5 °C for 3 hours. Then the temperature was gradually raised by 30-50° hour to 500-550°C for 5 hours. Then it was cut into cylinders 4-5 mm long and sifted out of dust. The finished catalyst had a composition; wght%: ZnO-10.0; CdF₂-10.0; Al₂O₃-80.0.

*Method for Synthesis of Pyrroles Based on Butyn-2-Diol-1.4.* A 50% solution of butyn-2-diol-1.4 in DMSO was passed through a layer of Cadmium-Zinc-Chromium-Aluminum (CZCA-1) catalyst with ammonia at a ratio of butyn-2-diol-1.4: NH₃ = 1:2 mol at a speed of 0.3-0.5 hour⁻¹. The resulting vapor-gas mixture was cooled in a refrigerator and collected in a receiver. After passing through 200 cm³ of a solution of 2-diol-1.4 and ammonia, 105 cm³ of a solution containing 62% pyrrole was obtained. A fraction boiling at 125-135°C in the amount of 72 g was isolated from the mixture by fractional distillation. Pyrrole was isolated in an amount of 60.0 g by rectification on a rectification column with 20 theor. trays. The yield was 63.9% of theoretical amount. The isolated pyrrole has a boiling point °С (130.5 h = 0.960) (0.963), 1.4420 (1440). Literature data for purity 93.0-95% are in parentheses.

![Fig. 1. Chromato-Mass Spectrum of Heterocyclization Catalyze of Butyn-2-Diol-1.4 and Ammonia.](image-url)
The liquid products of the object were analyzed on Agilent Technology GC/MS AT 5973N gas chromatography-mass spectrometer according to the DRUGSP-SHORT.M method using a capillary column 30 m × 0.25 mm in size with 5% phenylmethylsiloxane at an injector temperature of 280°C; sample size is 1 mcL (Fig. 1).

The conditions of the chromatography-mass spectrum are: temperature 280°C when programming the temperature of the thermostat column from 70 to 280°C; sample size is 1 mcL.

The chromatogram-mass spectrum of the product gives a variety of proposed products, among which pyrrolidone, morpholine, pyrrole and DMSO series products prevail, as well as the presence of traces of unidentified heterocyclization products is available.

The IR spectrometer of the obtained heterocyclization product of butyn-2-diol-1.4 was taken on an Agilent Technology FTIR-640 instrument under the following analysis conditions: registration range 4000-400 cm⁻¹, number of scans is 12 (Fig. 2).

![IR spectrometer of Butyn-2-Diol-1.4 Heterocyclization Product.](image)

The IR spectrum of the preparation contains a band at 2500-2700 cm⁻¹ which refers to the stretching vibrations of the group of the fully deprotonated CH₃ group; there are also bands at 1070-1150 cm⁻¹ with stretching vibration of CO groups, 3200-3400 cm⁻¹ with bending vibration of OH-groups, 650-900 and 1560-1640 cm⁻¹ with stretching vibration of NH₂-groups, 1490-1580 cm⁻¹ with stretching vibration of the NH-group.

**Results and discussion thereof.**

The synthesis of pyrroles from butyn-2-diol-1.4 was carried out using two methods: from an aqueous solution of butanediol-1.4 and a solution of butynediol-1.4 in DMSO. Synthesis of pyrroles from an aqueous solution of butyn-2-diol-1.4.

The synthesis of pyrroles from a 50-60% aqueous solution of butyn-2-diol-1.4 and amines has been studied. When studying the process of heterocyclization of an aqueous solution of butyn-2-diol-1.4 with ammonia, it was found that, along with pyrrole, butanediol-1.4-on-2, 3-pyrrolidone and other. were identified in the reaction products.

Under reaction conditions of 320-380°C in the presence of catalysts containing cadmium and zinc compounds, butyne-2-diol-1.4 adds water and forms butanediol-1,4-on-2 according to the following scheme:

\[
HOCH₂ – C ≡ C – CH₂OH + H₂O \xrightarrow{t, Cd^{2+}} \xrightarrow{O} HOCH₂ – C – CH₂ – CH₂OH
\]
Pyrrrole is formed from butynediol-1.4 and ammonia; 2-pyrrolidone is formed from ammonia and butanediol-1.4-on-2 according to the following scheme:

\[
\text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow{-2\text{H}_2\text{O}} \text{H}_\text{N} \text{H}
\]

\[
\text{HOCH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow{-2\text{H}_2\text{O}} \text{H}_\text{N} \text{=O}
\]

The synthesis of pyrrole from an aqueous solution of butyn-2-diol-1.4 and ammonia was studied. The effect of temperature, volumetric velocity, butyn-2-diol-1.4 ratio: ammonia, catalyst bed height on the pyrrole yield was studied (Fig. 1).

![Fig. 3. Influence of Temperature on Pyrrole Yield. CZCA-1 Catalyst. \( V_{\text{tot.}} = 0.4 \text{ hour}^{-1} \).](image)

As it can be seen from the data in the table, the pyrrole yield changes insignificantly with increasing temperature. At the same time, a gradual increase in the yield of butanediol-1.4-on-2 and 3-pyrrolidone is observed. The conversion of butyn-2-diol-1.4 increases reaching from 51 to 81%.

<table>
<thead>
<tr>
<th>№</th>
<th>Temperature, °C</th>
<th>Pyrrole Yield, % of Theoretical Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>320</td>
<td>28.0</td>
</tr>
<tr>
<td>2</td>
<td>340</td>
<td>35.0</td>
</tr>
<tr>
<td>3</td>
<td>360</td>
<td>42.0</td>
</tr>
<tr>
<td>4</td>
<td>380</td>
<td>48.0</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>53.0</td>
</tr>
<tr>
<td>6</td>
<td>420</td>
<td>56.0</td>
</tr>
<tr>
<td>7</td>
<td>440</td>
<td>52.0</td>
</tr>
<tr>
<td>8</td>
<td>460</td>
<td>44.0</td>
</tr>
</tbody>
</table>

Table 1. Effect of temperature on the yield of pyrrole from butyn-2-diol-1.4: DMSO=60% vol, \( V = 0.4 \text{ hr}^{-1} \). DB ratio: DMSO: \( \text{NH}_3 = 1: 2 \) vol.
Table 2.

<table>
<thead>
<tr>
<th>Syntheses</th>
<th>Finished Product Name</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{DMSO}} )</td>
<td>Pyrrole</td>
<td>56</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{CH}_3\text{NH}_2 )</td>
<td>N-methyl-pyrrole</td>
<td>42</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{NH}_2 )</td>
<td>N-vinyl-pyrrole</td>
<td>35</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NH}_2 )</td>
<td>N-finyl-pyrrole</td>
<td>35</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_2\text{OH} )</td>
<td>N-ortho-hydroxy-phenyl-pyrrole</td>
<td>32</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_2\text{NH}_2 )</td>
<td>N-ortho-aminophenyl-pyrrole</td>
<td>28</td>
</tr>
<tr>
<td>( \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_3 )</td>
<td>2-pyrro-lidone</td>
<td>62</td>
</tr>
</tbody>
</table>

Conclusion.
Thus, the reaction of catalytic conversion of butyn-2-diol-1.4 and ammonia in the presence of complex mixed polyfunctional catalysts has been studied. It was found that when passing butyn-2-diol-1.4 and ammonia through the catalyst bed at a high temperature, a complex mixture of nitrogen-containing compounds is formed such as: acetonitrile, pyrrolidone, morpholine, pyrrole, pyridine bases with a moderate content in the catalyzate. It was found that carrying out heterocyclization reactions in superbasic media in the presence of DMSO greatly simplifies the process and increases the yield of the target products. A one-step method for the preparation of pyrrole and its N-substituted derivatives with good yield has been developed.

Based on the results obtained, it can be said that in order to take into account uncertainties of various nature, it is proposed to solve the problem of ensuring the safety of chemical production at a qualitatively new level using new information technologies based on the creation of intelligent decision support systems for managing the safety of chemical technological processes and systems at all stages of occurrence. These systems make it possible to formulate the recommendations for various decision-makers on the management of the safety of chemical production, both on the basis of operational observation data and using methods.

\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{DMSO}} \text{Pyrrrole} \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{CH}_3\text{NH}_2 \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{NH}_2 \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NH}_2 \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_2\text{OH} \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_2\text{NH}_2 \]
\[ \text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH} + \text{NH}_3 \]
and models based on artificial intelligence embedded in expert systems including the knowledge of specialists and experience in operating chemically dangerous facilities.

References