

Technology for the production of disubstituted pyrroles

Megli Djumayevich Safarov^{1*}

¹Karshi Engineering economic institute, 180100, Karshi, Uzbekistan

Abstract. In this work, we studied the catalytic synthesis of pyrrole and their derivatives from ketoximes and acetylene in the liquid phase under normal conditions in the presence of homogeneous catalysts. Mathematical modeling of the experiment was carried out using the Box-Wilson method and the optimal conditions for the synthesis of a number of pyrroles were found. The catalytic synthesis of pyrrole under vapor phase conditions in the presence of heterogeneous catalysts has been studied. Low-temperature polyfunctional catalysts have been developed that provide the highest yield of pyrroles.

Keywords. technology, synthesis, pyrrole, monoethanolamine and diethanolamine, catalyst, heterocyclization of amino alcohols and amines, dehydration.

1 Introduction

The rational use of local raw materials, natural resources, the development of a waste-free, resource-saving and environmentally friendly technology for the production of practically important products based on local raw materials and industrial waste is one of the urgent tasks of modern chemical technology.

Nitrogen-containing heterocycles, mainly pyrrole and its derivatives, are of great value as raw materials for the production of a number of practically important drugs, and the pyrrole core, as the dominant subunit, provides the whole play of colors in both the animal and plant worlds.

The pyrrole ring is part of the molecules of many natural and biologically active compounds. Pyrrole derivatives include a number of important plant alkaloids, such as nicotine, atropine, cocaine, etc. The pyrrole ring is contained in the molecules of the blood coloring substance - hemoglobin and the green substance of plants - chlorophyll, vitamin B12, bile pigment, a number of antibiotics, etc.

The widespread use of pyrrole and their derivatives is delayed due to the lack of cheap and convenient methods for their production. Known diverse methods for the synthesis of

* Corresponding author: shavkat0006@mail.ru

the pyrrole cycle under normal conditions with a moderate yield of the target product are multistage, the starting materials are in many cases difficult to obtain. The service life of the catalysts used is limited, and there are certain difficulties in separating the resulting complex mixture.

In this regard, it is of practical interest to develop effective synthetic methods for the production of pyrrole and its homologues based on industrially available compounds, in particular from industrial wastes of monoethanolamine and diethanolamine, using homogeneous and polyfunctional low-temperature heterogeneous catalysts based on local raw materials.

Pyrrole derivatives attract the attention of many researchers due to the diversity and uniqueness of their properties [1].

The pyrrole structure is the basis of such vital compounds as chlorophyll and hemoglobin, which play an important role in the processes of basic metabolism. Of considerable interest are polymeric compounds of the pyrrole series, which have found application in various industries.

Many works are devoted to various aspects of the preparative, theoretical and applied chemistry of pyrrole and its derivatives [14-23].

2 Methods

The revival and growth of interest in the chemistry of pyrrole is currently directly related to the preparation of new compounds of the pyrrole series from natural sources, and, moreover, of a relatively simple structure. At present, questions of the structure, reactivity, and synthesis of pyrroles, as well as the possibility of polymerization of the pyrrole core, have been studied.

The discovery of the reaction of ketoximes with acetylene, leading to various types of NH- and N-vinylpyrroles, presented unlimited possibilities in terms of the synthesis and detailed study of polymers of this class.

The synthesis of pyrrole and its derivatives is carried out under liquid-phase conditions using homogeneous catalysts. The feedstock for the synthesis is acetylene.

Acetylene is obtained from calcium carbide, after which it was purified with an aqueous solution of monoethanolamine (MEA). The content of the main substance is not less than 99.0%.

The synthesis of pyrrole and its derivatives from MEA and ketones, and acetylene with ketoximes was carried out on a laboratory setup, schematically shown in Fig. 1.

The reaction of the interaction of MEA and ketones in the liquid phase at atmospheric pressure in the presence of KOH was carried out in a flask (9) with a stirrer (8) on a setup equipped with automated control systems.

Heterocyclization of acetylene with ketoximes was carried out in a flask (9) with an electric stirrer (8) with a continuous supply of acetylene from the gas supply system and the reaction mixture was fed in various ratios of acetoxime: DMSO. Sodium hydroxide (NaOH, KOH) was used as the alkali metal hydroxide.

To establish the process parameters, the study was carried out in their various concentrations in the reaction mixture at a temperature range of 80-140°C. The flask was heated through a vessel (13) by a resistance furnace (2). The temperature was measured with a chromel-alumel thermocouple on a potentiometer (11).

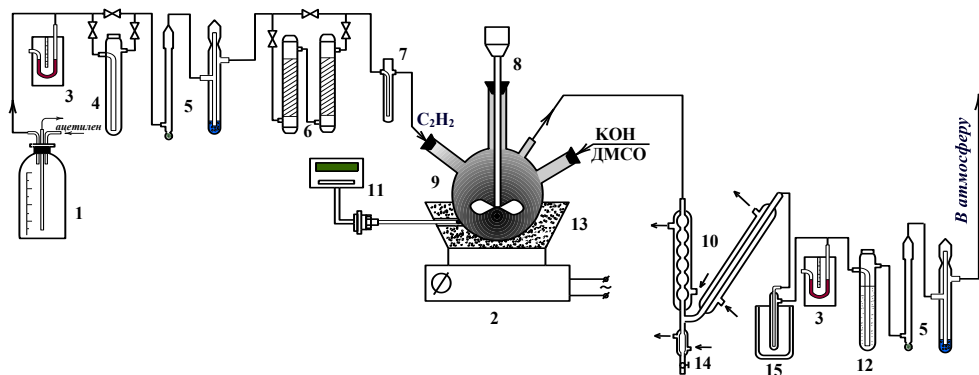


Fig. 1. Scheme of a laboratory setup for the synthesis of pyrrole and its derivatives in the presence of homogeneous catalysts. 1 – control gas meter of acetylene; 2 – resistance furnace; 3 - manometer; 4 – scrubber with MEA; 5 – gas flow measurement and control system; 6 – gas drying system; 7 - barometer; 8 - mixer; 9 - glass flask; 10 - cooling system; 11 - potentiometer; 12 - packed scrubber; 13 - vessel with sand; 14 - refrigerator - collection; 15 is a trap.

Currently, there is no unified theory for the selection of catalysts. Although the authors [2] put forward a hypothesis about the selection of catalysts, changing the nature of their active centers, and also proposed a developed method for studying catalysts with predetermined properties, etc., a large number of catalytic reactions require a rational selection of catalysts to achieve the desired result.

The developed catalysts must have high catalytic activity, selectivity, mechanical strength, thermal stability, resistance to the action of catalytic poisons, long service life, easy regeneration, certain hydrodynamic characteristics, and low cost [3].

Known catalysts used in industry are selected, mainly, empirically, based on ideas about the mechanism of catalysis for certain types of reactions [4-8].

The heterocyclization reactions of amino alcohols and amines is a complex series-parallel process, including addition, dehydration, dehydrogenation, and dehydrocyclization reactions. Obviously, for such a process, the catalyst must be polyfunctional or, with a small choice of components, successfully combine various catalytic properties.

Synthesis of compounds of the pyrrole series by heterocyclization of ethanolamines was carried out on a laboratory setup, which is schematically shown in Fig. 2.2.

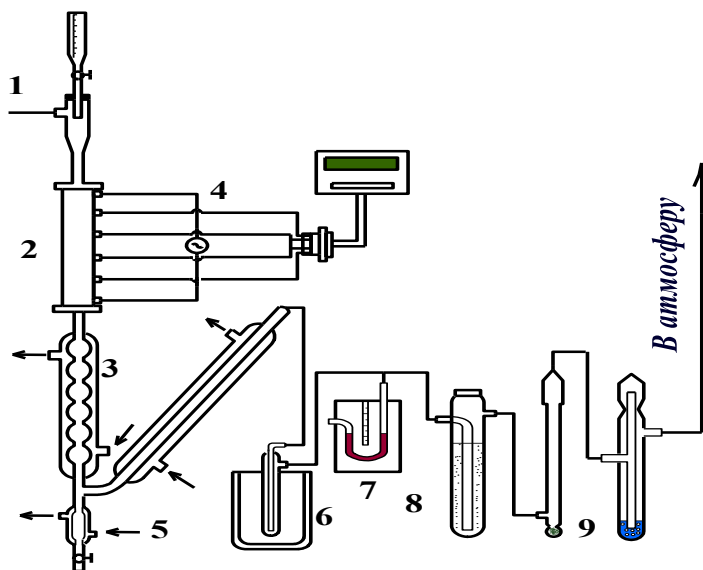


Fig. 2. Scheme of a laboratory setup for the synthesis of compounds of the pyrrole series in the presence of heterogeneous catalysts. 1 - burette; 2 - reactor; 3 - cooling system; 4 - reactor temperature control unit; 5 - refrigerator-collector; 6 - trap; 7 - pressure gauge; 8 - packed scrubber; 9 - gas measurement and control system.

The plant mainly consists of the following functional systems:

- systems for supplying initial components and synthesis;
- temperature control and maintenance systems in the working volume of the reactor, equipped with KSP-5;
- cooling systems and condensation of reaction products.

Liquid components are fed from the brutka (1), the resulting mixture enters the evaporator - in the upper part of the reactor) (2). The reactor is a hollow stainless steel tube $\text{dBH} = 32$ mm in size, 1000 mm long with a grid for the catalyst. To maintain the set temperature, it is equipped with an external electric heater controlled by an autotransformer. The temperature is measured by a thermocouple (4) with a millivoltmeter at 4 points of the reactor. In the reactor (2) there are 7 samplers, which are located along the length through 100-150 mm. The vapor-gas mixture formed as a result of contacting enters the ball cooler (3) and the condensed reaction products are collected in the receiver (5), while the non-condensed ones enter the trap for further cooling. (Cooling with a mixture of ice and sodium chloride). It was found that the reaction products are completely condensed in this case.

The gas mixture, which consists mainly of acetylene, hydrogen and ammonia, is sent after the traps to wash off ammonia in a packed scrubber (8), periodically filled with distilled water. Next, the gas passes through the foam and liquid rheometers and is directed to the gasometer or to the atmosphere.

The condensed reaction products are collected through a receiver into a separate vessel, which undergoes further analysis.

3 Results and Discussion

In the synthesis of compounds of the pyrrole series by heterocyclization of ketoximes with acetylene and ketones with monoethanolamine, the reaction conditions play an important role: the solvent, the nature of the catalyst and its concentration, the temperature and

duration of the process. The synthesis of various 2-, 2,3-, 2,5-substituted pyrroles and their N-vinyl derivatives proceeds in the temperature range of 70-140°C, more often 90-100°C [9-10].

During the condensation of ketoximes with acetylene in alcohols, hydrocarbons, dimethylformamide, dioxane, pyrroles are not formed. Using hexamethanolsulfolane or dioxane-dimethyl sulfoxide (DMSO) as a solvent, the reaction can be carried out selectively.

Compared to DMSO, its aprotic dipolar analogs, hexamethanol and sulfolane, form less active catalytic media. In solvents such as dioxane, alcohols, hydrocarbons, the reaction does not take place at all. In an aqueous medium, acetylene and ketoxime interact in a completely different way, forming pyridines instead of pyrroles. In the H₂O-DMSO medium (1:2 by volume), ketoximes and acetylene form tertiary acetylenic alcohols (up to 50% yield) [11].

In the heterocyclization of ketoximes with acetylene, the catalytic function of DMSO is especially evident when using its mixtures with dioxane. For the reaction according to the above scheme (dioxane, 20% KOH, 120°C, 2 hours) of cyclohexanone oxime with acetylene, by varying the concentration of DMSO, it is possible to actively influence the selectivity of the process and obtain either NH-pyrrole (with a low content of DMSO), or only N-vinylpyrrole (in pure DMSO). The reaction proceeds most efficiently to dimethyl sulfoxide (DMSO).

The reactions of ketoximes with acetylene are specifically catalyzed by the superbasic pair strong base-DMSO. Oxymates, alcoholates, quaternary ammonium bases and alkali metal hydroxides are used as strong bases.

There is a clear dependence of the activity of the catalytic system on the nature of the cation - it increases with an increase in its atomic number, but the maximum activity for potassium:

$$K^+ \geq Cs^+ \geq Rb^+ \geq [-N^+ -] \geq Na > Li \quad (1)$$

The sequence given (1), which is valid for many oximes of aliphatic and alicyclic ketones, is not, however, an absolute and, apparently, may vary depending on the reaction conditions and the type of ketoxime.

Superbasic systems, consisting of a strong base and a solvent or reagent, are able to specifically bind the cation, "exposing" the conjugated anion.

Lithium hydroxide (LiOH) selectively catalyzes the heterocyclization of alkylalkylketoximes with acetylene, but is inactive at the stage of vinylation of the formed pyrroles.

For alicyclic ketoximes, LiOH is inefficient at both stages – the construction of the pyrrole ring in this case is selectively accelerated by rubidium and tetrabutylammonium hydroxides [81]. The reaction rate increases with increasing base concentration in the reaction mixture [12].

For the synthesis of pyrroles by heterocyclization of monoethanolamine with ketones from a number of compounds tested as catalysts (alkali metal hydroxides, potassium, zinc and cadmium acetates, zinc, copper and cobalt chlorides), only alkali metal hydroxides turned out to be effective. Their activity increases in the series: LiOH < NaOH < KOH < CsOH.

By varying the amount of catalyst, temperature and duration of the process, it is possible to establish the optimal conditions for the synthesis of pyrrole compounds by heterocyclization of carbonyl compounds with acetylene and amines.

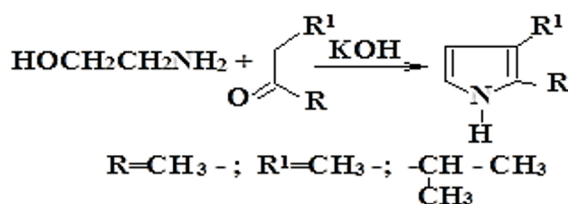
The presence of an excess density (lone pair of electrons) on a heteroatom, concentrated positive charges of the hydrogen atoms of functional groups, as well as the strongly

electron-withdrawing ability of the oxygen atom of the hydroxyl group in the molecule of monoethanolamine makes it possible to judge its specific interaction with ketones.

On the other hand, dialkyl ketones have C=O bonds of high reactivity due to the presence of an active carbonyl group. Due to polarization, the carbon atom of the carbonyl group, having electrophilic properties, is able to react with nucleophilic reagents.

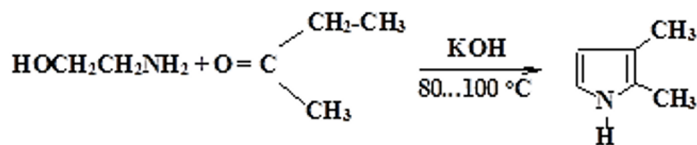
We have developed a method for the synthesis of disubstituted pyrroles by cyclocondensation of monoethanolamine (MEA) and ketones, the distillation residue of MEA formed during the production of ammonia and ketones [13].

In the course of studying the process of condensation of monoethanolamine with dialkyl ketones, a previously unknown reaction for the formation of disubstituted pyrroles was established.



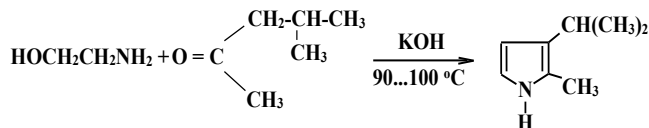
The reaction proceeds smoothly at a temperature of 80-100°C. The use of caustic potash as a catalyst makes it possible to speed up the process and obtain end products - pyrroles unsubstituted at the nitrogen atom in 30-42% yield.

When monoethanolamine is condensed with methyl ethyl ketone, 2,3-dimethylpyrrole is formed:



Condensation of monoethanolamine with methyl isobutyl ketone in the presence of potassium hydroxide at a temperature of 90-100°C and the ratio of the initial components MEA:MIBK=1:0.5 mol/mol isolated 2-methyl 3-isopropylpyrrole with a 30% yield (Fig. 2.3).

The reaction is carried out according to the scheme:



It was determined by GLC that liquid condensation products consist of monoethanolamine, 2-methyl-3-isopropylpyrrole and water.

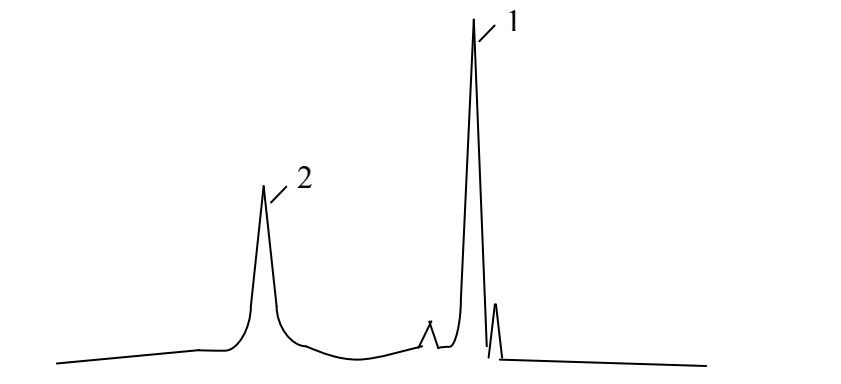
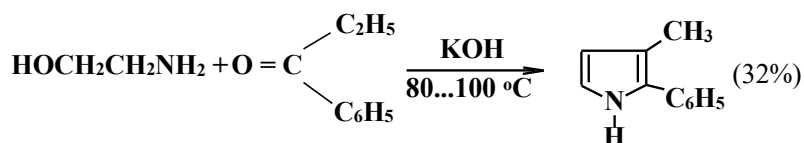
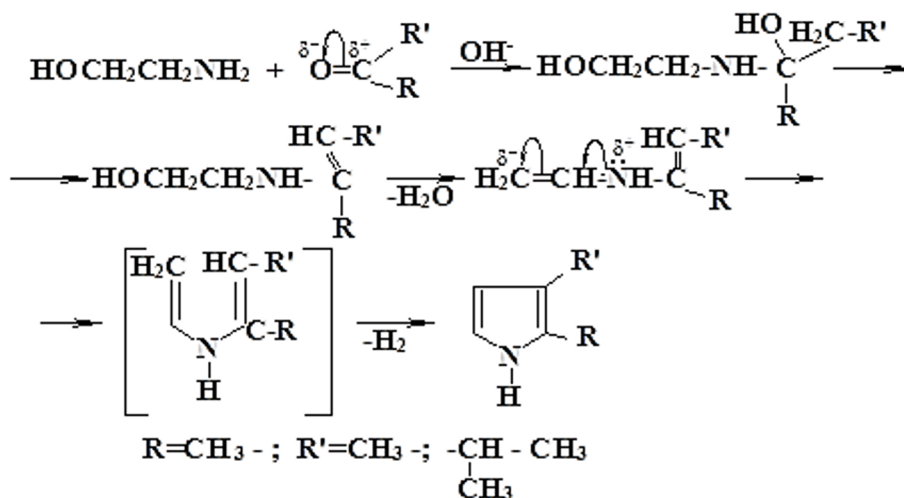


Fig. 3. Chromatogram of liquid condensation products MEA:MIBK ; 1-monoethanolamine, 2-methyl-3-isopropylpyrrole, 3 – water.

During the interaction of monoethanolamine with phenylethyl ketone in a ratio of 1:1 at a temperature of 80-100°C for 8-10 hours, in a medium of 40% KOH, 2-phenyl-3-methylpyrrole was obtained as the main product with a yield of 32%:



The studies carried out make it possible to judge the probable mechanism for the formation of di-mixed pyrroles:

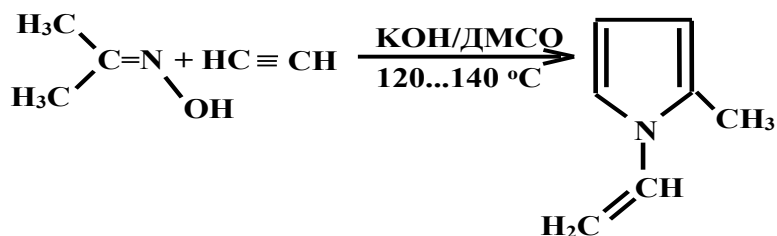


One of the features of the proposed reactions is that, depending on the structure of the introduced ketones, it is possible to synthesize various hard-to-reach disubstituted pyrroles and their homologues.

The widespread use of pyrrole and its derivatives is delayed due to the lack of cheap and convenient methods for their synthesis. The known production methods are mainly multi-stage, and the starting compounds are expensive and difficult to obtain.

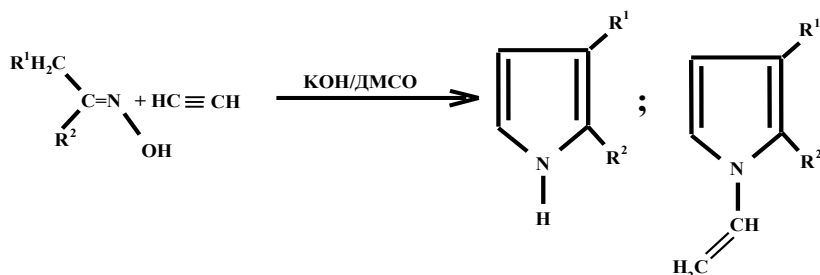
In this regard, the development of convenient one-step methods for the synthesis of compounds of the pyrrole series and their derivatives is a very urgent task.

We have studied the interaction of acetylene with oximes of symmetrical and unsymmetrical ketones. A method has been developed for the preparation of pyrroles and their N-vinyl derivatives from acetoxime and acetylene in the liquid phase.



The reactions were carried out in a flask with a stirrer with a continuous supply of acetylene at atmospheric pressure under the following conditions (temperature 120-1400C, process duration in the range of 2-14 hours, KOH concentration 10-100% relative to the reaction mixture, and various ratios of ketone oximes with DMSO were taken).

A probable scheme for the formation of pyrroles has been proposed:



Where: R1=H, -CH3, -CH2-CH3, -CH2-CH2-CH3;

R2= -CH3; -CH2, -CH3 ; -H2C – CH2 – CH3 ; -CH2 -CH2 -CH2 -CH3 .

The reaction makes it possible to obtain a variety of 2-, 2,3-substituted pyrroles and their N-vinyl derivatives.

The effect of the process temperature, time, and ratio of KOH and DMSO concentrations on the yield of N-vinyl-2-methylpyrroles was studied (Table 1):

Table 1. Dependence of the yield of N-vinyl-2-methylpyrrole on the reaction conditions and the volume ratio of acetoxime and the superbasic medium.

№	Number of KOH, %	Volume ratio of acetoxime and DMSO	Reaction temperature, °C	Reaction time, h	Yield, %
1	10	1:8	140	3	20
2	20	1:10	120	2-3	20
3	30	1:10	130	3	38
4	30	1:15	130	4	42
5	30	1:20	120	4	40
6	40	1:10	120-140	6	50
7	40	1:10	120-140	8	54
8	50	1:15	130	4	37
9	50	1:10	120-140	3	24
10	50	1:10	100	6	17
11	100	1:10	97	14	7

From Table. 1 shows that the highest yield of 54% occurs with continuous supply of acetylene to the reaction mixture (acetoxime:DMSO ratio = 1:10, temperature 120-1400C, time 8 hours) and addition of 40% KOH in portions after 4-5 hours. If you increase the

concentration of KOH to 50% and add alkali not in portions, but immediately, then, all other things being equal, all acetoxime reacts in 4 hours. With an increase in the duration of the process, the yield of N - vinyl - 2 - methylpyrrole drops to 17%. With a further increase in the concentration of KOH to 100%, the yield of products decreases to 7%.

Analysis of the reaction products using the GLC method showed that acetoxime under these conditions completely reacts.

Thus, under normal conditions, the catalytic synthesis of N-vinyl-2-alkylpyrroles by the reaction of acetylene with ketone oximes was studied for the first time, and a probable scheme for the formation of individual reaction products was proposed.

In order to clarify the effect of the amount of KOH in the reaction mixture on the mechanism of the reaction, we studied the changes in the yield of N-vinyl-2-methylpyrrole depending on the duration of the process at a ratio of acetoxime: DMSO=1:10 in the temperature range of 120-140°C (Fig. 2.4).

In the amount of 30% KOH, the yield of N-vinyl-2-methylpyrrole, depending on time, increases from 20% to 32% (Fig. 2.4., a). The highest yield of pyrrole is achieved at the amount of 40% KOH, reaching up to 54% (Fig. 2.4., b).

With an increase in the amount of KOH (50% KOH) during the first 2-6 hours, the yield of pyrroles drops to 17%.

With a further increase in the concentration of KOH to 100%, the yield of products decreases to 7%.

Analysis of the reaction products using GLC methods showed that acetoxime under these conditions completely reacts.

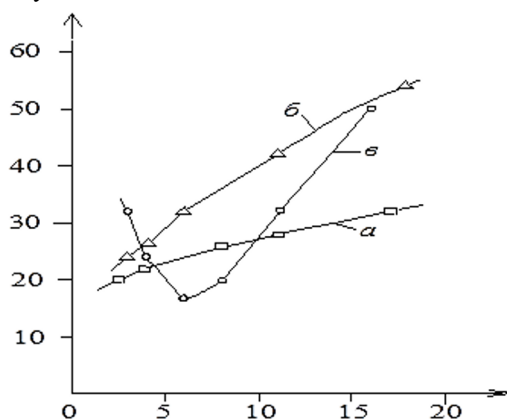


Fig. 4. Change in the yield of N-vinyl-2-methylpyrrole depending on the duration of the process under the conditions: acetoxime:DMSO=1:10 mol/mol, at a temperature range of 120-140°C. a –30% KOH; b –40% KOH; in -50% CON.

In order to use these wastes, we studied the condensation reactions of monoethanolamine, which is present in the VAT residue with ketones, to obtain compounds of the pyrrole series.

The analysis established the composition of the distillation residue of monoethanolamine.

Formic acid concentration - 0.75 g/dm³

Mass fraction of monoethanolamine - 17-20%

Mass fraction of water - 24-25%

Oil concentration - 245 mg/dm³

In the course of studying the process of MEA condensation with dialkyl ketones, the reaction of the formation of disubstituted ketones was carried out.

4 Conclusions

Cyclocondensation proceeds at a temperature of 80-100°C. The use of caustic potassium as a catalyst makes it possible to speed up the process and obtain unsubstituted end products - unsubstituted pyrroles with a 30-42% yield. During the process of condensation of MEA with MEK, 2,3-dimethylpyrrole is formed. It has been established that after boiling the reaction mixture for an hour, a product yield of 40-42% is achieved at a ratio of initial components MEK:MEA of 0.1-0.2 mol, a temperature of 90°C and a contact time of 5-6 hours.

The model laboratory setup consists of a steel closed reactor with a volume of 100 l, equipped with a stirrer. The reactor was heated with nitrogen heated to 100–140°C by an electric heater. Synthesis of pyrrole was carried out as follows: the corresponding containers were loaded with the calculated amount of a solution of caustic potassium, dimethyl sulfoxide, MEA and ketones, which passed through the mixer and entered the reactor. Subsequently, during the synthesis, the distillation residue formed during the production of ammonia was fed. VAT residue contains 17.5-20.0% pure monoethanolamine.

As a result of the reactions carried out, the heterocyclization of MEA contained in the VAT residue with dialkyl ketones was carried out to obtain disubstituted pyrroles. The reaction conditions and product yield are given in table. 2.

Table 2.

№	Ratio of similar components, mol/mol	Reaction temperature, °C	Reaction time, hour	target product	Exit, %
1	Distillation residue MEA:IEC	100	10	2,3-dimethylpyrrole	18

Based on the conducted laboratory studies, the developed technology for the production of disubstituted pyrroles using the distillation residue of MEA with dialkyl ketones is recommended for implementation.

We thank all our colleagues who worked closely with us on this paper.

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