CATALYTIC SYNTHESIS OF PYRIDINE DERIVATIVES AND THEIR CORROSION INHIBITION PROPERTIES

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Abstract. The study established that acetaldehyde reacts with ammonia in an autoclave in the presence of a catalyst with a mass fraction of 1-20% for 3 hours at 130-160°C, at a mol ratio of $CH_3CHO:NH_3$ = 1:3, 2-methyl-5-ethylpyridine is formed as the main product.

Keywords: ammonia, acetaldehyde, catalyst, alkylpyridines, catalytic synthesis, heterocycles, heterocycles, carbonyl compounds

Foreign synthetic industrial processes for obtaining pyridine bases are based on the catalytic gas-phase cyclocondensation of aldehydes and/or ketones with ammonia in the presence of amorphous aluminosilicates promoted by Ni, Cr, Cd, Zn or Th compounds. The yield of pyridine bases in these processes is 40-60% [1]. In these processes, zeolite ZSM-5 was used as a catalyst in the synthesis of N-heterocycles, including pyridines.

The author [2] investigated catalytic compositions for the synthesis of pyridine and pyridine bases on hierarchically porous zeolites (micro/meso; micro/macro; micro/meso/macro) and showed that the condensation of carbonyl compounds with ammonia proceeds with a high yield in the presence of 4 zeolite catalysts. It was also established that the reaction of acetaldehyde with ammonia in an autoclave in the presence of 1-20% by mass of the catalyst for 3 hours at a temperature of 130-160 °C, in a molar ratio of $CH_3CHO:NH_3$ = 1:3, leads to the formation of 2-methyl-5-ethylpyridine as the main product.

These studies also showed that the MEP yield in the micro-meso-macro-porous structure sample was 1.5 times higher than in the initial micro-porous sample H-ZSM-5, which indicates the influence of mesoporousness formation on catalytic properties and increased selectivity towards heterocycles.

In the case of N-Yh zeolite samples with different (0.70; 0.87; 0.95) showed that the selectivity for MEP increases somewhat with the increase in αNa and reaches 93% in the sample 0.95H-Yh, and it was concluded that the MEP yield also changes equally from 58% (0.70H-Yh) to 63% (0.95H-Yh). Optimal conditions for changing the decationization stage of H-Yh zeolite were established, along with an increase in the number of high-molecular-weight compounds (up to 10 wt.%), which ensured an increase in the MEP yield by 63%:150 C, with a 3-mol ratio of $CH3CHO:NH_3$ = 1:3.

To date, methods for the technical synthesis of alkylpyridines from various organic compounds have been developed. All alkylpyridine production plants in the world use only carbonyl compounds and ammonia as raw materials..

The process of obtaining a mixture of pyridine and 3-methylpyridine from carbonyl compounds and ammonia is well-studied. "Navoiazot" JSC launched

production of 20 thousand tons of formaldehyde per year and 7 thousand tons of formaldehyde per year. In this regard, the process of jointly obtaining pyridine and 3-methylpyridine from acetaldehyde, formaldehyde, and ammonia was of interest.

The heterocyclization reaction of carbonyl compounds with ammonia (and amines) includes complex parallel-sequential reactions, including nucleophilic addition reactions of ammonia, isomerization, dehydrocyclization, and others. All these processes can be combined in the vapor phase using catalysts with multifunctional properties. Based on this, the role of each component in the pyridine and methylpyridine formation reaction was considered when selecting the catalyst composition.

The heterocyclization reaction of the croton fraction with aniline and o-aminofenol in the presence of mixed polyfunctional catalysts was investigated, composition, wt.%: Cd - 3.0-5.0; ZnO - 5.0-10.0; Cr_2O_3 - 3.0-5.0; Fe_2O_3 - 3.0-5.0; - Al_2O_3 - 75.0-86.0.

Composition of the croton fraction, wt.%: croton aldehyde - 57.4 - 66.95; paraldehyde - 13.45 - 29.47; acetone - 0.63 - 10.56; the rest - water.

Catalysts were prepared by methods of suspension, molding, washing, drying, and purification. Aluminum oxide (PPP-33%) was used as a hydrate carrier. 3-5% solutions of fluic and acetic acids were used as peptizers. The textural properties of the developed catalysts were determined (Table 1).

Table 1

Physicochemical and operational properties of the developed catalysts

№	Composition, % by mass..	Relative surface area, mg/h	Mechanical strength, MPa	Service life until regeneration, hour	Output, g/kg*time*h
1.	CdF_2 – 3,0 ZnO – 5,0 Cr_2O_3 – 5,0 Al_2O_3 – 87,0	225	6,8	68,0	81,0
2.	CdF_2 – 5,0 ZnO – 5,0 Cr_2O_3 – 3,0 Fe_2O_3 – 3,0 Al_2O_3 – 84,0	240	7,8	96,0	101,0
3.	CdF_2 – 5,0 ZnO – 5,0 Cr_2O_3 – 5,0 Fe_2O_3 – 3,0 Al_2O_3 – 82,0	225	7,3	72,0	98,0
4.	CdF_2 – 5,0 ZnO – 10,0 Cr_2O_3 – 3,0 Fe_2O_3 – 5,0	196	8,0	120	122
5.	CdF_2 – 5,0 ZnO – 5,0	184	8,2	184	130

	Cr_2O_3 – 5,0 Fe_2O_3 – 5,0 Al_2O_3 – 80,0				

The condensation reaction of the croton fraction with ammonia and amines was carried out in a stainless steel reactor with dimensions δl = 25×1000 mm under flow conditions with external electric heating and a catalyst volume of 100 cm3. The analysis of liquid products was carried out by the GJX method (LXM-8MD chromatograph, I-modification, heat conductivity modification, detection, mobile phase - zelit 545, column temperature - 120, absolute calibration).

Table 2

Influence of temperature on the yield of target products
croton fraction: ammonia = 1: 2; Gav. = 200 h-1, catalyst No. 6

№	Tempera-ture, °C	Amount in the catalyst, %			by-products	Croton fraction conver-sion
		2-methylpyri-dine	4-methyl-pyridin	2-methyl-5-ethylpyridine		
1.	370	18,0	12,0	11,0	14,0	56,0
2.	380	22,0	16,0	14,0	18,0	64,0
3.	390	32,0	22,0	20,0	26,0	85,0
4.	400	38,0	25,0	25,0	12,0	95,0
5.	410	36,0	24,0	26,0	14,0	98,0
6.	420	37,0	23,0	25,0	15,0	98,0
7.	430	33,0	22,0	20,0	25,0	99,0

The reaction of the croton fraction with ammonia was carried out at a temperature of 360 - 420 C in the presence of catalyst No. 6. The main products of the reaction were a mixture of 2 and 4 - methylpyridine (up to 50%), 2-methyl-5-ethylpyridine 360 - 420 C (up to 26%). As byproducts, acetonitrile, a mixture of di- and trimethylpyridine, resins, and water are formed.

The influence of temperature, volumetric velocity, the ratio of initial reagents, the height of the catalyst layer, etc., on the yield of target products and the conversion of the croton fraction was studied. The influence of temperature was studied in the range of 360-420C (Table 2).

As can be seen from the table, the reaction does not proceed at temperatures below 360°C. With an increase in temperature to 400°C, the yield of the target products gradually increases and reaches its maximum at 400°C. This leads to a decrease in the output of the target product.

The study of the volumetric rate of target products, crotone fraction conversion, and process selectivity showed that with an increase in the volumetric rate of ammonia from 150 to 300 h-1 and an increase in the crotone fraction from 0.1 to 0.7 h-1, the pyridine yield gradually decreases. This indicates that the process occurs in the region of internal diffusion.

To improve solubility, extraction phosphoric acid was added to the obtained mixtures in a ratio of 1:0.25. The obtained products were tested as

corrosion inhibitors in a hydrochloric acid environment. To study the inhibitory properties, compounds No. 2 and No. 3 were selected, which ensure maximum yield of heterocyclization products. The influence of the inhibitor concentration on the corrosion rate of St.20 steel in 15% hydrochloric acid (t = 50°C; τ = 42 hours) was studied.

Table 3

Influence of inhibitor concentration on the corrosion rate of St.20 steel grade

Inhibitor concentration, %	Corrosion rate, g/m2.h	Protection level, %
Mix № 6		
No additions	13	-
0,8	2,0	41,0
1,0	1,4	43,3
1,2	2,4	47,8
1,6	3,2	63,7
2,1	4,2	83,6
2,2	4,4	87,5
Mix № 7		
0,8	2,0	51,0
1,0	1,4	52,2
1,2	2,4	53,6
1,6	3,2	71
2,1	4,4	98
2,2	4,46	99,5

Table 4

Influence of temperature on corrosion rate and degree of inhibitory protection during corrosion of St.3 steel in 15% HCl in 3% hydrochloric acid. The inhibitor concentration is 2.2%.

№	HCl acid solution	Corrosion rate, g/m²h	Protection efficiency, %
Room temperature, τ=24 hours			
1	No additions	4,7	-
	Inhibitory	1,4	71,0
Temperature 40°C, τ=4 hours			
2	No additions	46,2	-
	Inhibitory	0,5	99,0
Temperature 80°C, τ=4 hours			
3	No additions	131,0	-
	Inhibitory	2,0	98,0
Temperature 100 °C, τ=1 hours			
4	No additions	1020	-
	Inhibitory	4,9	99,5

As can be seen from the table data, "mixture No. 7" is a more effective corrosion inhibitor at a concentration of 0.8-2.2% for 42 hours, protecting the

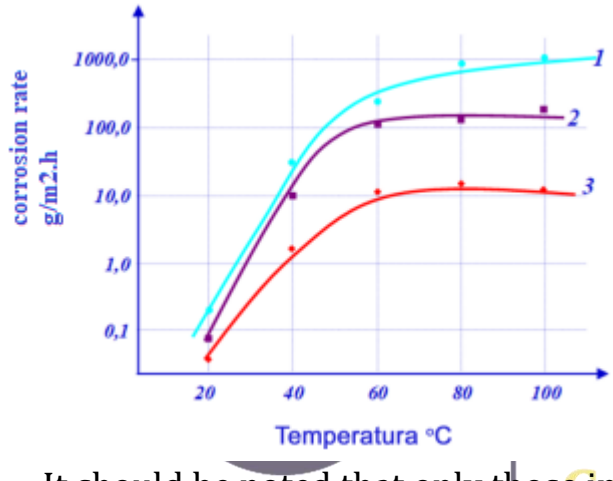
metal from corrosion up to 99.5%, and the protective effect of "mixture No. 6" is less than 90%.

To obtain stable and highly effective corrosion inhibitors, compositions based on a more effective heterocyclization product - "mixture No. 7" were prepared:

1)"mixture No7" (0.6%) + urotropin (0.3%) + acrylic emulsion (0.1%) - "composition 1."

2)"mixture No7" (0.5%) + thiourea (0.3%) + copper salt (0.2%) - "ingredient2."

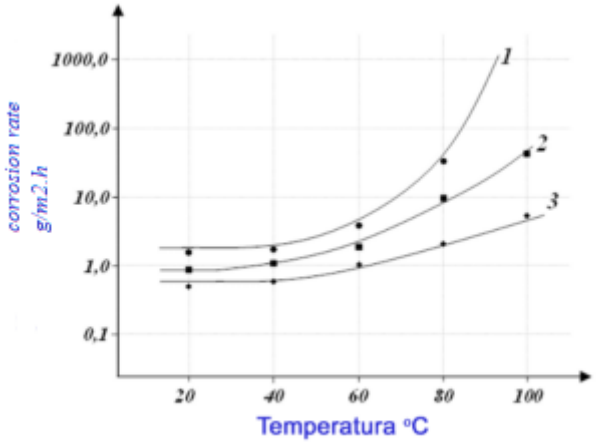
** In brackets, the mass percentage of the inhibitor added to 12% hydrochloric acid is indicated.*



HCl (1); HCl "mixture No7" (2); HCl "Mixture 1" (3).
Figure 1. Dependence of corrosion rate on temperature

It should be noted that only those inhibitors of hydrochloric acid corrosion that have a raw material base and are not scarce have been studied. In addition, the possibility of reducing the corrosive activity of hydrochloric acid by emulsifying it in a hydrocarbon medium was studied.

As can be seen from Figure 1, the most effective of the investigated corrosion inhibitors in the temperature range from 20 to 100 C is "Composition 1." The corrosion coefficient with "Composition No. 7" in a 12% hydrochloric acid medium at 90°C is 130 g/m².h (or 76.9%), and with "Composition 1" is 17 g/m2.h (or 91.0%). Compared to "No7 Mixture," the composition consisting of "No7 Mixture," urotropin, and acrylic emulsion has several advantages, the main one being that the latter does not clog the lower plaster zone during treatment.



HCl (1); HCl mixture No7 (2); Mixtures of HCl 2 (3). Figure 2. Temperature dependence of corrosion rate 20

As can be seen from Figure 2, the corrosion rate of 20% HCl acid in a hydrophobic emulsion medium with a phase ratio of 75/25 decreased 4 times compared to the corrosion rate in a 12% HCl acid medium at the same temperature for "mixture No7."

Thus, the corrosive activity of "mixture No. 7," inhibited by hydrochloric acid, decreases 20 times compared to the addition of urotropin and acrylic emulsion at 100C.

We are conducting targeted research on the development of new highly effective methods for obtaining pyridine and quinoline bases based on local raw materials.

At Navoiazot JSC, the production of acetylene, acetaldehyde, methanol, ammonia, and other potential raw materials for the production of synthetic pyridine bases has been mastered. Previously, the processes of obtaining pyridine and its homologs based on acetylene and ammonia (methanol) were studied.

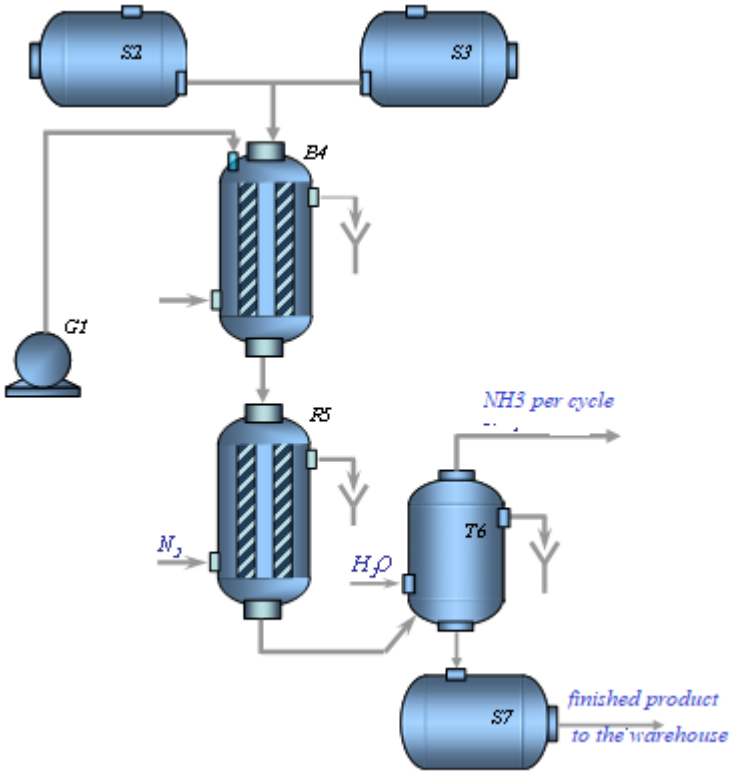


Figure 3. Technological scheme for the production of pyridine and pyridine bases: G - gas holder for ammonia; E2, E3 - croton fraction capacities; T4 - evaporator; R5 - reactor; T6 - cooler; E7 - Catalyst Capacity

The working amount of ammonia from the gas holder (pos. G) and the croton fraction from the container (pos. E2) enter the mixer-evaporator (position. T4), where the mixture is heated to a temperature of 100-120 °C. Further, the mixture enters the upper part of the reactor (pos. P5). The steam-gas mixture exiting the reactor is cooled in a cooler (pos. T6) and is collected in a container (pos. E7).

The work is devoted to obtaining pyridine bases based on a large amount of acetaldehyde production waste - croton fraction.

Individual products are separated by rectification in a rectification column. The cubic volume of the rectification column is 1.9 m3, the column height is 6000 mm, the diameter is 200 mm, and the nozzles are made of Rashig rings measuring 20 x 20 mm.

Thus, we studied the heterocyclization reactions of the croton fraction with ammonia and acetylene. The optimal parameters of the studied processes have been established, and a flexible technology for obtaining pyridine bases has been developed.

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