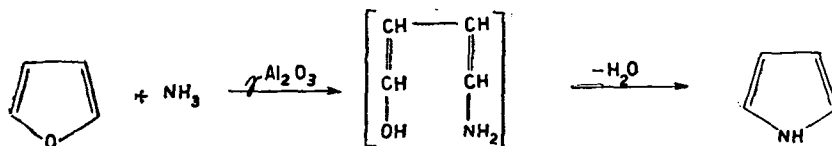# UTILIZATION OF FURFURAL. III.

PREPARATION OF PYRROLE FROM FURANE IN THE VAPOUR PHASE

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The values of yield of the conversion furane-pyrrole were investigated under various physical and physico-chemical conditions. The optimum conditions of obtaining pyrrole and the changes in the activity of catalyst as a function of temperature were established.

YUREV and co-workers [1], [2] prepared pyrrole by reacting furane and ammonia on alumina catalyst at 400—450°.

$$\text{furane} + NH_3 \xrightarrow{Al_2O_3} \begin{bmatrix} CH{=}CH \\ | \quad\quad | \\ CH \quad CH \\ | \quad\quad | \\ OH \quad NH_2 \end{bmatrix} \xrightarrow{-H_2O} \text{pyrrole}$$

The reaction was carried out by BISHOP and DEUTON [5] in the presence of molybdenum oxide and vanadium pentoxide catalysts on alumina carrier. Results obtained by these authors are disclosed by Table I.

Table I

No.	Furane moles/hour	Ammonia moles/hour	Temperature °F	Pressure mm Hg	Space velocity	Contact time sec.	Catalyst	Rate of conversion %
1	2,4	4,8	700	760	1/2	3	Activated alumina	0,5
2	2,4	4,8	700	760	1/2	3	20% MoO_3 on activated alumina	7,0
3	1,2	2,4	800	760	1/4	6	alumina	10,0
4	2,4	4,8	800	760	1/2	3	10% V_2O_5 on activated alumina	8,0

In addition to the mentioned authors, also other research workers studied the conversion of furane into pyrrole [3], [4], [6].

In the present experiments the dependence of pyrrole formation on the temperature, on the space velocity of furane fed into the reactor and on the
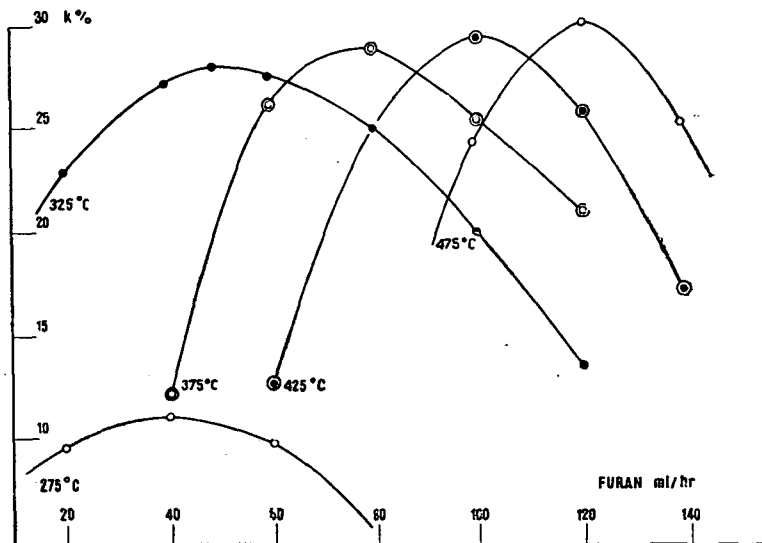

Fig. 1

ratio furane to ammonia were subjected to systematic investigation. The obtained results are shown by Figs. 1 and 2.

In Figs. 1 and 2, the following notations were used:

K: percentage of conversion into pyrrole, %,

v: feed rate of furane, ml/hour,

c: mole ratio ammonia: furane,

t: temperature, °C.

It can be seen that values of pyrrole yields plotted against the relative concentrations of ammonia and the space velocities of furane show a maximum curve in the temperature interval studied. On raising the temperature, the maximum of the yields of pyrrol shifts to higher space velocities and tends to increasing values. When, under otherwise identical conditions, the ratio furane: ammonia was varied,
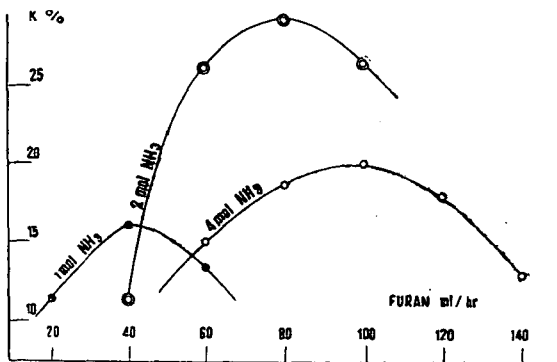

Fig. 2. t = 375° C

maximum yield was attained with the ratio mole 2:1 of ammonia:furane. Thus, it appears from the figure that maximum yields obtained at various relative concentrations of ammonia follow a maximum curve as well.

The optimum yield (30%) of the conversion furane-pyrrole was attained at 475°, with a feed rate of 120 ml furane/hour, applying a mole ratio 2:1 of ammonia to furane.

Experiments were carried out in an iron tube reactor of 200 ml catalyst area to establish the period of activity and duration of life of alumina catalyst. It was found that this catalyst relatively quickly loses its activity which, however, can readily be recovered by activation with air. The duration of life of the catalyst is long. From the point of view of the production of pyrrole, it proved to be practical to apply alternately operation periods of two hours and activation periods of two hours.

Experimental

Substances applied :

Furane: b. p. 760:32 °C; d: 0,937; n_D^{20}:1,4225.

Gaseous ammonia, technical grade.

Catalyst: the same γ-alumina catalyst was used as in the experiments to prepare pyrrolidine [7]. The catalyst was activated at 400° by a current of air. Processing is completed when no carbon dioxide can be detected in the leaving gases by the barite-water test.

Description of the apparatus

The apparatus described at the preparation of pyrrolidine [7] was applied in the present experiments, with the difference, however, that at the conversion of furane into pyrrole the connecting tube 17 was inserted, due to the high tension of furane. Details of operation of the apparatus are given in our earlier paper.

In connection with the reaction furane-pyrrole, our tentative experiments were carried out in a reactor of 200 ml catalyst area, whilst the systematic investigations were conducted in an iron tube reactor of 2460 ml catalyst area. Results of the latter series are shown by Figs. 1 and 2 [7]. Each experiment was conducted with freshly activated catalyst.

Isolation of reaction products

Crude products formed in these reactions always consisted of two phases. On separating the aqueous phase, the oil phase was dried over potassium carbonate and fractionated by a 40 cm Widmer column and the obtained pyrrole re-distilled from potassium hydroxide. The distilled pyrrole showed the physical constants: b. p. 760:131 °C; n_D^{20}:1,5035; d_4^{20}:0,9691.

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