

UTILIZATION OF FURFUROL. IV¹

Production of Pyrrole from Furfurol by means of a Contact Process in the Vapour Phase

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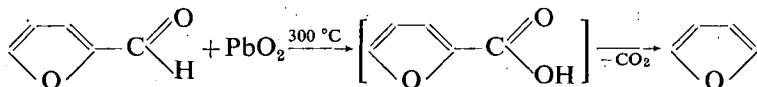
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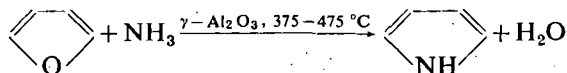
The one-step preparation of pyrrole from furfurol is dealt with. The procedure consists of the combination of two vapour-phase heterogeneous processes separated in space. In the first step the reaction of furfurol and lead oxides at about 300° gives rise to furan in about 40% yield, which is then subjected, without isolation, to ammonolysis on Al₂O₃ catalyst at 400–500°. Thus pyrrole could be produced in about 20% yield based on furan. The optimum parameters for the process have not been established. At the same time the procedure presented provides an example for the combination of vapour phase heterogeneous processes.

Y'UREV and coworkers [1] published the synthesis of pyrrole starting with furan in 1936. The authors [2] were successful in applying the procedure to a semi-plant scale in 1958. Since furan is accessible from furfurol under the effect of lead oxides in the vapour phase [3], through in a stepwise manner only, but reliably, the question arises whether the two processes could be combined, *i. e.* pyrrole could be synthesized from furfurol in one step. The advantage of such a procedure, in case of positive experimental results, are obvious. On the one hand, the combination of the single physical and chemical processes greatly facilitates the realization of promptness, simplicity and economicalness, as main points of view in the enlargement of the procedure. On the other, especially in the present case, the elimination of the isolation of furan is of great importance.

The principle of the procedure is that furfurol is oxidized to 2-furoic acid on passing through a mixture of lead oxides at about 300°. The latter undergoes decarboxylation to furan under the conditions applied. The pyrophoric lead formed as by-product may be re-oxidized by introduction of air and used again:



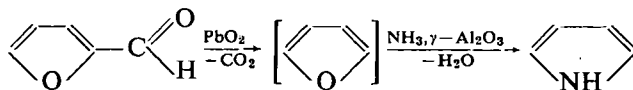
The end-gas containing mainly furan and carbon dioxide is passed through an alkaline medium to remove the latter, then mixed with a suitable amount of ammonia and finally passed through γ -aluminium oxide contact at 375–475°, when pyrrole is formed:



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The combination of the two processes may be illustrated as follows:



The one-step pyrrole production has been studied under those values of the parameters, which were found optimum in the syntheses of furan [3] and pyrrole [2], respectively. The preparation of furan was accomplished in 3000 ml. reactor space at 280°, adding furfural in 100 ml/hour rate of feed. Thus 40% yield could be achieved. The conversion of furan vapours to pyrrole was studied in 100 ml. catalyst-space at 375° and 475° with ammonia-furan mole ratio 2:1. The pyrrole yields were about 20%.

Temperature C°	Furan l/hr.	Ammonia l/hr	Yield %
375	5	10	17.5
475	10	20	19.5

The optimum parameters of the process have not been established. There is also possibility for the re-circulation of unchanged furan and ammonia.

Experimental

Starting materials:

- Furfural*: Commercially available technical grade product was used. It is worthy to note again that dilute aqueous solutions of furfural are also suitable.
- Lead oxides*: Commercially available technical grade lead oxides of different oxidation degree are utilizable.
- Ammonia*: The commercially available product, supplied in flasks was used.
- γ-Aluminium oxide*: Catalyst of type RB-13, prepared by the Research Institute of Organic Chemical Industry, Budapest, was applied. Other commercially available aluminium oxide catalysts were also used and no significant differences could be observed concerning the pyrrole yields. Each catalyst lost its activity relatively fast, but they could be regenerated by introduction of air [2].

Description of the apparatus and the procedure:

A simplified representation of the apparatus is given in Fig. 1; 1 injector, 2 reactor filled with lead oxides, 3 and 4 condensers, 5 transistronic manometer, 6 scrubbers, 7 gasometer, 8 differentiating manometer, 9 manometer, 10 pressure capillary tube, 11 ammonia valve, 12 needle valve rotameter, 13 manometer, 14 transistronic manometer, 15 reactor filled with aluminium oxide, 16 and 17 condenser systems, 18 rotameter, 19 gas meter, 20 electric heating. Detailed description of parts of the apparatus, their function and operation, except those of 6—10 are to be found in [4] and [5]. Gasometer 7 is necessary because of the stepwise nature of furan production.

The furfural injected with 100 ml/hr. rate of feed transforms in part to furan in reactor 2 (reactor space 3000 ml.). The unchanged furfural condenses in condensers 3 and 4 and it may be re-circulated. Reactor packing 2 is to be re-oxidized by two hours by introduction of air. The regeneration period is 0.5 hour. The end-product

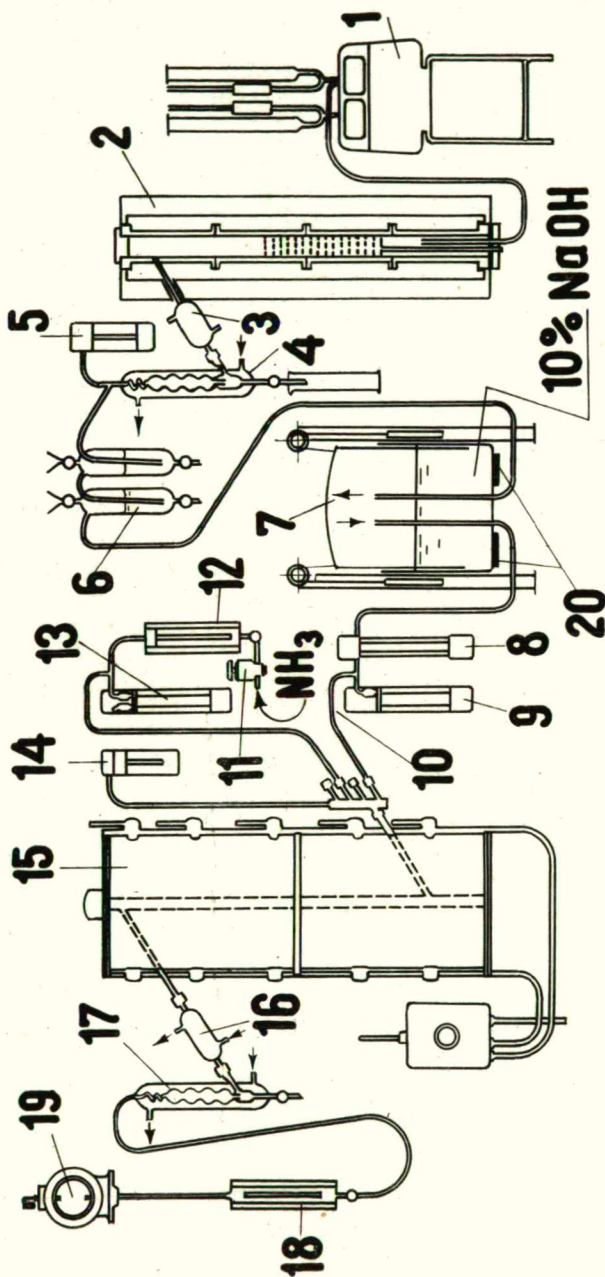


Fig. 1

(consisting mainly of furan and carbon dioxide) is subjected to alkaline treatment in scrubber 6 filled with 50% NaOH solution to remove carbon dioxide. The washing medium is continuously replaced with fresh alkaline solution on exhaustment. The removal of carbon dioxide can be accomplished by physical method, adsorption, as well. The purified furan is conducted to gasometer 7, filled with 10% NaOH solution and kept at about 45° with electric heater 20, from where it can be consumed continuously. Then it passes through differentiating manometer 8 adjustable with needle valve, pressure controlling manometer 9 and pressure capillary tube 10, and enters reactor 15 packed with aluminium oxide. Devices 8, 9 and 10 are heated at about 40—45° to avoid the condensing of furan. The diameter of the pipeline connecting the gasometer to the reactor should be min. 3—4 mm. to make possible the flow of sufficient amount of furan even under the low difference in pressure applied. The other reactant, ammonia is conducted into the reactor through reducing vent 11 and rotameter 12 equipped with needle valve. The pressure of ammonia is checked with manometer 13. Neither the entering pressure of ammonia, nor the pressure in reactor 15 may exceed the entering pressure of furan, to avoid the flowing back of ammonia to gasometer 7. The corresponding pressure are checked with manometers 9, 13 and 14. The automatic regulation of the pressure is also resolvable.

The rates of feed are 5 l/hr. furan and 10 l/hr. pyrrole at 375° reaction temperature and 10 l/hr. furan and 20 l/hr. pyrrole at 475° reaction temperature, respectively. The reaction proceeds in reactor 15 on the surface of Al_2O_3 catalyst and the crude product condenses in cooling systems 16 and 17. The flow velocity of the leaving end-gas is measured with rotameter 18 and, if necessary, with gasmeter 19. After two hours reaction period the activity of the catalyst considerably decreases, therefore the injection of the reactants is stopped.

The regeneration of the aluminium oxide catalyst is accomplished in the usual way [2]. The working up of the crude product is done as described in [2]. At 475° reaction temperature 10 g. (20%) A. R. pyrrole could be produced in two hours, b. p. 131° at 760 mm., n_D^{20} : 1.5035; and d_4^{20} : 0.9691.

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ПРИМЕНЕНИЕ ФУРФУРОЛА. IV

Получение пиррола из фурфурола в паровой фазе каталитическим методом

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Эта работа занимается получением пиррола из фурфурола. Сущность метода заключается в изолировании двух в пространстве парофазных гетерогенных процессов. В первом шагу при 300°C в реакции фурфурола с окисью свинца образуется фуран с выходом 40%. Пары фурана — без выхода — при 400—500°C подвергаются аммонолизу и получается пиррол с выходом около 20%. Оптимальные параметры процесса еще не установлены.