UTILIZATION OF FURFURAL. I.

PRODUCTION OF MALEIC ANHYDRIDE BY VAPOUR-PHASE OXIDATION

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Instead of the small volume reactors described in literature and in patent specifications, the authors carried out experiments to convert furfural into maleic anhydride by the vapour-phase heterogeneous catalytic method in an increased volume. The optimum parameters of the reaction were established by thermochemical calculations and by experiments. By this way, they succeeded in securing a mean yield of 37 % with V_2O_5 as catalyst and of 85 % with a promoted type of V_2O_5 catalyst.

The vapour-phase oxidation of benzene, of various derivatives of furane, of butadiene and of other compounds to maleic acid and maleic anhydride, respectively, is described in literature and in patent specifications. Under conditions prevailing in Hungary, utilization of furfural as a cheap initial substance appears to be practical. The majority of conversion methods are patents with rather scarce and schematic descriptions which cannot be reproduced. The most important methods of oxidizing furfural can be summarized as follows.

BOEHRINGER [1] prepared maleic acid from furane and furane derivatives in the presence of vanadic acid as catalyst at a temperature of 180° in 90 % yield. ZUMSTEIN [2] reported a yield of 41 % on using vanadium pentoxide to catalyze the conversion. MILAS and WALS [3] prepared maleic acid by the oxidation of furfurylalcohol, furfural, furane carboxylic acid and furane, in yields varying between 22 and 65 %. These authors were of the opinion that higher yields cannot be obtained, due to polymerization. On studying the thermochemistry of the conversion, they found that the control of the course of the exothermic reaction cannot be carried out in an industrial scale without special apparature. JAEGER [4] observed in connection with the oxidation of compounds of the diene type that oxidation to carboxyl groups on the carbon atoms 1,4 takes place uneasily, at temperatures between 300 and 500°. NIELSEN [5] later patented a method and published a paper on the oxidation of furfural. Oxidation was carried out by air, using various contact tubes, the maximum oxidation being attained in a nickel tube. TARVIDA [6] produced maleic acid from furfural in similarly fair yields. According to the descriptions, throughout vanadium pentoxide is applied as catalyst, complemented by various promoters and stabilizers, at temperatures varying from 250 to

550°, using quantities of air varying from the 20-fold to the 200-fold amount of that calculated by stoichiometry. Although the composition of catalyst is published, no details of the method of preparation are given. End gases are absorbed by water, maleic acid being obtained therefrom by distillation. A great number of authors deal with the analysis of end gases and with the isolation of products [7]—[12]. The methods differ from each other mainly in the ways of converting maleic acid into maleic anhydride.

In the knowledge of these antecedents and data, we started our experiments to the vapour-phase heterogeneous catalytic production of maleic anhydride with the aim to attain a size of reactor volume, using furfural of Hungarian origin as initial substance, the data of which can be utilized in designing an apparature of semi-industrial scale. Thus, investigations were needed with respect to the thechnique of oxidation: under adiabatic conditions, in the presence of a great excess of air as diluting agent. Further, conditions of preparing catalysts, changes in the quantities of end products, variations of temperature as a function of amounts applied, and changes in yields in the presence of methanol were to be examined as well. In the following, a report will be given of the experimental results obtained so far and of the conclusions drawn of these results and of the data of literature.

Our experiments were started by determining the optimum temperature of the entering gas mixture, i. e. the temperature at which the reaction starts in a broad interval of contact period, in a utilizable manner. This temperature was found to be 250°. The entering gas mixture was preheated by an evaporator of small cross section but of a large heat exchange surface, the flow being turbulent.

In the knowledge of this temperature, the heat of reaction (Q) of the
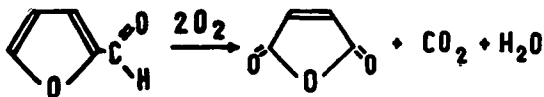
process was approximately calculated (123,6 Kcal/mole.) In our thermochemical calculations the sum of the heats of reactions taking place at the stoichiometric conversions of furfural was considered. Owing to the low concentrations of furfural applied, its specific heat was taken as equal to that of air, neglecting the factors of the radiation of heat as well. The value obtained by this way for Q was obviously considered as an approximate date within a given order of magnitude since the reaction is not quantitative in that a part of the substance remains unchanged, whereas another part converts into the desired product and the residual part is overoxidized. On applying this approximate value, optimum parameters which could be used in practice were obtained by theoretical and experimental operations.

In the knowledge of the heat of reaction, the value of t_2 can be calculated with the use of the equation $Q = n \bar{C}_p (t_2 - t_1)$ where t_1 is the temperature (250°) of the mixture air-furfural entering the reactor, t_2 the temperature of the gas mixture heated by the heat quantity Q, $\bar{C}_p$ the mean molar heat of air and n the number of moles of air.

Values of t_2 (indicating the degree of heating) calculated by the described way plotted against values of n are shown by points marked by circles in Fig. 1. (The quantities of air mixed to 1 mole of furfural are plotted in moles (n) on axis x and values calculated for t_2 on axis y).

It appears from the curve that in the case of an adequately chosen catalyst the optimum temperature (from the point of view of volume increase of reactor) ranges about 270°, and the optimum mole ratio for air: furfural about 800. At this temperature the reaction takes place without appreciable overoxidation, whilst the mole ratio is favourable with respect to isolation since it is not too dilute. The given parameters chosen by theoretical way are in fair accordance with the experimental results of NIELSEN [5]. These
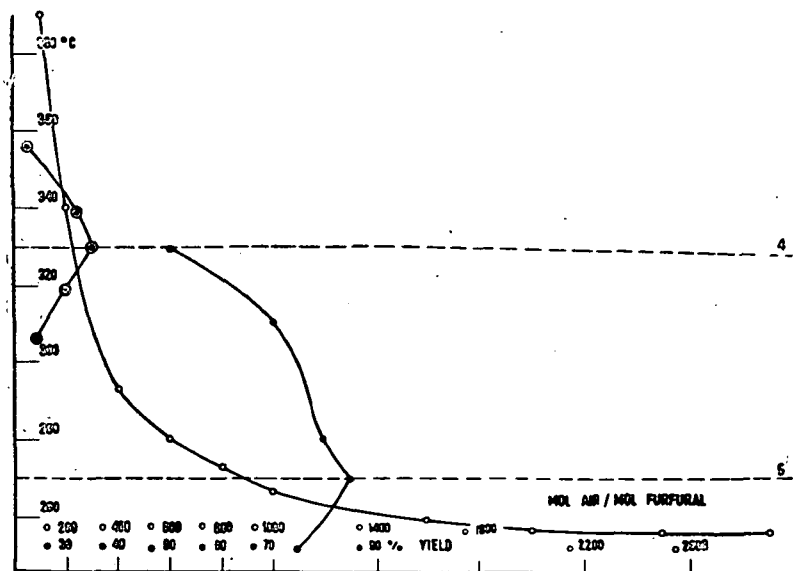

Fig. 1

latter indicated that only small yield increases appear by dilutions over the mole ratio 800 and thus it is not favourable to apply higher dilutions. Therefore, in our experiments throughout a mole ratio air: furfural 800 was used.

The experiments were conducted under constant conditions (4000 l of air hour and 20 ml of furfural hour, *i. e.* 740 moles of air to 1 mole of furfural). The effect of vanadium pentoxide catalyst (points marked by double rings in Fig. 1) and of a promoted type of vanadium pentoxide catalyst (points marked by black circles in Fig. 1) on the reaction as a function of temperature and yield were investigated at the given parameters. (Yields obtained are plotted in axis x and temperatures of catalyst area applied in axis y. Thus, units and scales of axis y are identical for all three curves.)

It appears from our experimental results that the conventional type of vanadium pentoxide catalyst is unsuitable for our purposes. Namely, its
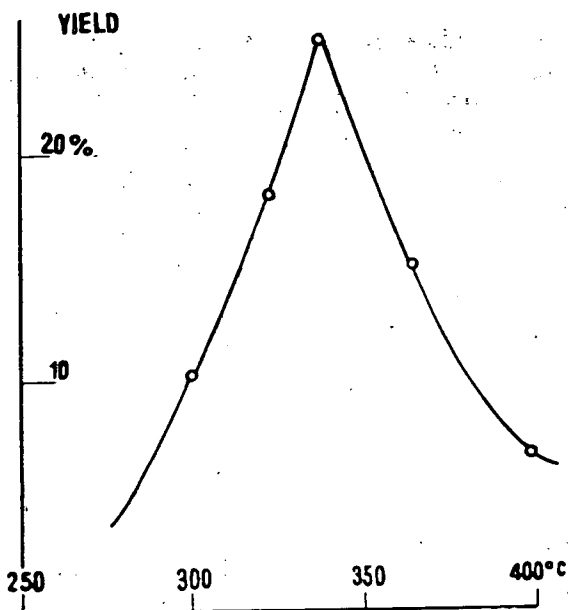
Fig. 2. Yield of maleic anhydride *versus* temperature. Katalyst: V_2O_5.
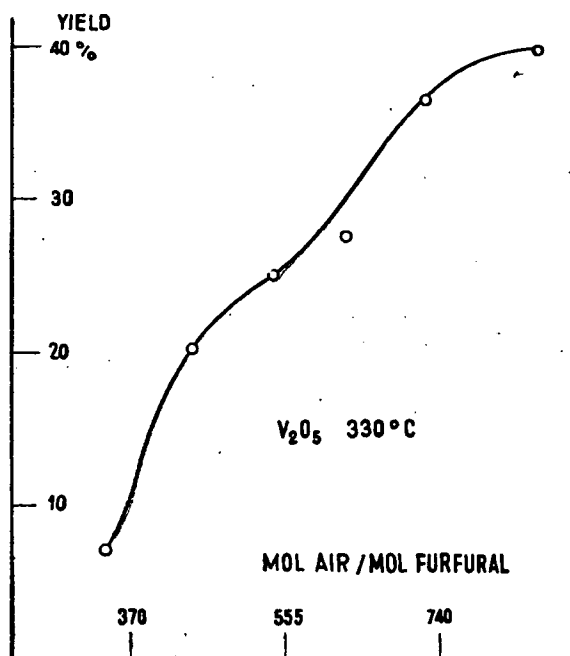Ratio air : furfural $= 500 : 1$

Fig. 3. Yield of maleic anhydride *versus* amount of air

operation requires high temperature (330°) obviously leading to overoxidation and reducing thus the level of the optimum yield attainable to 37 % (line 4 in Fig. 1). We succeeded, however, in securing an excellent yield (85 %) (line 5 in Fig. 1) in the presence of the promoted type of vanadium pentoxide catalyst at the prescribed parameters (mole ratio 740 of air: furfural and 270°). This is mainly due to the lower temperature of processing, at which the overoxidation is of a smaller extent and the course of reaction is steadier.

The systematic variation of parameters proved to be practical in securing these results. Using *e.g.* vanadium pentoxide catalyst at lower mole ratios (500) of air:furfural, the optimum yield (of only 23 %) appeared at 330°.
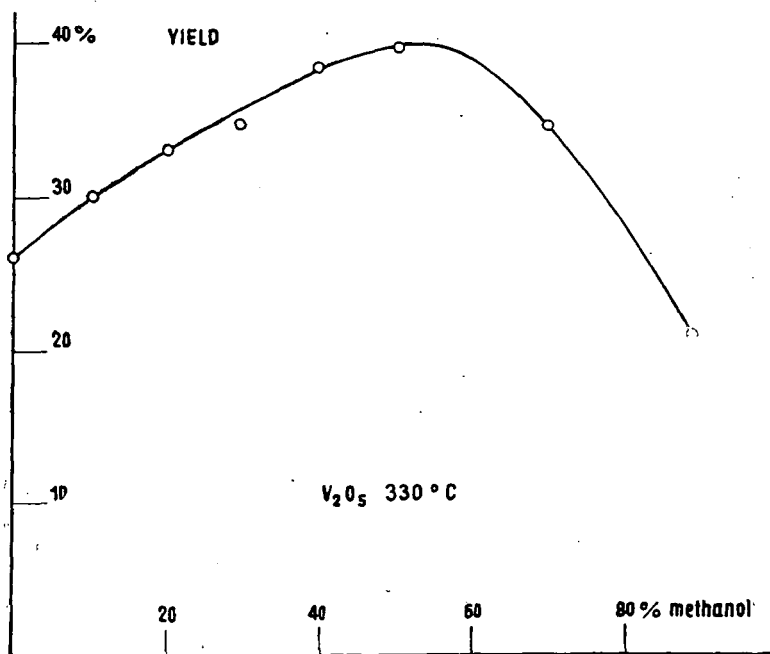

Fig. 4. Yield of maleic anhydride *versus* amount of methanol.
Ratio air:furfural = 500:1

On varying the mole ratio of air to furfural at a constant temperature (330°), optimum yield (38 %) was obtained at a mole ratio of 740:1 of air: furfural.

JAEGER [4] and other authors add methanol to the system in order to inhibit overoxidation of furfural. However, using vanadium pentoxide as catalyst, only yields not exceeding 40 % could be attained at 330° in the presence of methanol (optimum concentration 50 %), either.

The effect of lower rates of air (mole ratio 500:1 of air to furfural) in the presence of a promoted type of vanadium pentoxide catalyst is shown

by Fig. 5 (similarly to Fig. 2), indicating reduction of yield (63 %) and increase of temperature (290°).

Experimental results and calculated values (points marked by single rings in Fig. 1) clearly demonstrate that the unusually great excess of air applied in the reaction is required, in place of oxidizing the compound, rather for removing the heat developed during the reaction, further that the reaction is sensitive against temperature and thus it must take place in a narrow region of temperature. It follows of this that the reaction is independent of the cross section of the reactor since the removal of the heat of reaction is secured by the great excess of air. Accordingly, it is theoretically possible to carry out the reaction at a given length of reactor with any cross section desired, which fact is of a great advantage when designing industrial plants.
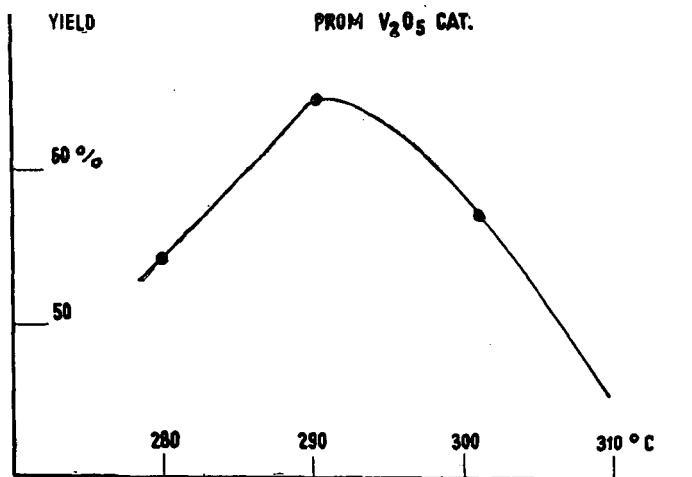

Fig. 5. Yield of maleic anhydride *versus* temperature.
Ratio air : furfural = 740 : 1

In the case of oxidation reactors, overoxidation in a qualitative sense is denoted by isotherms of paraboloid shape, the cones of which face the axis and the direction of gas flow. In a reactor of V volume, the value of v (the volume between the isotherms at both sides of optimum temperature interval of the reaction) is only 10—15 % of V. In the discussed case V is practically equal to v (similarly to reactors of fluid and moving bed), due to the steady distribution of heat.

It is planned to conduct experiments with reactions taking place in the vapour phase at high temperatures in metals and other melts, in the presence and in the absence of catalysts. Similarly, it is expected to reduce the long periods required for the preparation of promoted catalysts by using metal baths [13].

Experimental

Substances applied: Furfural (99,5 %), technical grade, freshly distilled.
B. p. of main fraction 161—162°, n_D^{20}:1,5261. Ammonium metavanadate
(NH_4VO_3) puriss. Chinoin.

Catalysts

a) Vanadium pentoxide. The suspension of 70 g of ammonium meta-
vanadate in 500 ml of water was mixed with 1000 ml of pumice stone, the
mixture stirred and dried to an airdry state. Catalyst transferred into the
reaction area was first gradually heated in 8 hours to 350°, then activated
at 400° for 30 minutes. During activation, 50 liters of air were led through
the reactor.

b) Vanadium pentoxide promoted by ferric molybdenate on pumice stone
carrier, prepared according to NIELSEN [5], U. S. P. 2,464.825.

Description of the apparatus (Fig. 6)

Air is fed to the bottom of the evaporator (3) through a needle valve,
rotameter and mercury manometer, with the use of an air compressor (1)
of 4 cu. m./hour and 7 atm. output, equipped with a 30 l buffer container
with adjustable pressure control. (The manometer indicates the resistance of
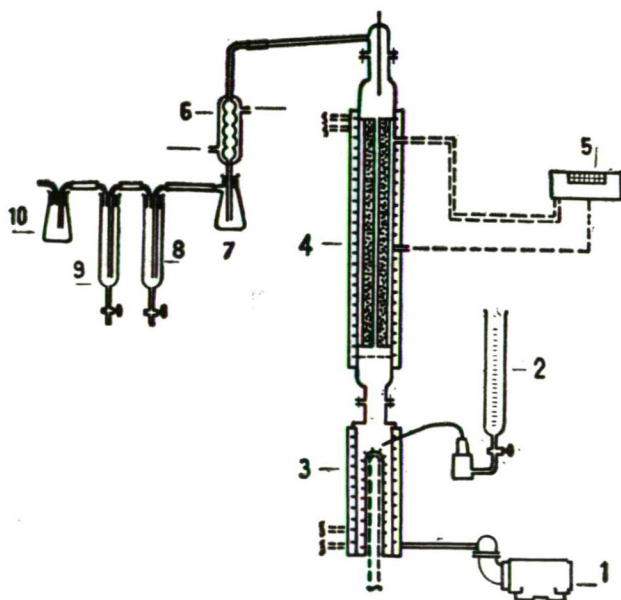the system, pressure rise signing eventual cloggings.)

Fig. 6

Evaporators of two types of structural design were applied:

a) (Fig. 6. 3) Evaporation takes place in the area between an externally heated iron cylinder of 90 cm length, 10 cm inner diameter and 3 mm wall thickness and an internally ribbed tube of 70 cm length and 4 cm external diameter, soldered at the centre of the external tube. The evaporation area is filled up by ceramic Raschig rings of 8 mm.

b) An iron tube of 70 cm length, 4 cm inner diameter and 3 mm wall thickness.

Both types of evaporator are equipped with temperature control and electric heating (high resistance coils).

Furfural is sucked up from a dosing burette by an independent Diesel pump, and pressed into the evaporation area (in the case of type a) at the head and in the case of type b) at the bottom of the evaporator), subsequent to admixture, in a Y-tube, of the required amount of air.

A portion of the introduced furfural can be returned to the burette through a needle valve located at the branching of the tube which connects the dosing burette with the evaporator. By this way it is possible to dose extremely small amounts (several milliliters per hour) as well.

The gas mixture is introduced into the reactor (4). Reactors of two structural types were applied:

a) (Fig. 6. 4) For gas mixtures of high furfural concentration: four square-shaped tubes of 20×20 mm, 90 cm length located in an iron cylinder of 10 cm diameter. The area between tubes and cylinder is filled up with cast aluminium. (Experiments conducted with this apparatus will be reported in our next communication).

b) For gas mixtures of low furfural concentration: an iron tube of 80 cm length and 55 mm diameter.

Both types of reactor were heated electrically by resistance coils, temperature being controlled by electric devices (5).

The gas mixture leaving the upper portion of the reactor passes a conderser (6) to reach a sublimation area (7), then passes consecutively two alkaline traps (8, 9) and leaves the system through a buffer flask (10).

Description of the process

The present experiments were carried out in the apparatus under b).

Throughout the experiments 100 g of furfural were introduced into the evaporator at a rate of 20 ml of furfural per hour. The volume rate of air applied can be read from Fig. 2—5. On investigating the effect of methanol, furfural was previously mixed up with the corresponding quantities of methanol (Fig. 4). End gases leaving the reactor passed traps containing 20 ml of 0,1 N sodium hydroxide and 200 ml of water.

Calculation of data of yield (Fig. 2—5):

In the case of a low mole ratio (about 1:25) of air, also solid substance precipitates in the sublimation flask. This is combined with the content of traps and titrated back with 0,1 N hydrocloric acid in the presence of

phenolphthalein. According to analytical investigations, other acidic by-products formed cause a total error of $2-3\%$. In the case of a high mole ratio of air, no solid substances appear in the sublimation flask, and approximate yields can be calculated from the decolouration of the first alkaline trap containing an indicator and from the furfural value read on the dosing burette, considering that 95% of the formed products are absorbed by the first trap, according to our experiences.

Data of yield found by analysis were controlled by the preparative isolation of maleic anhydride. For this purpose, aqueous traps were applied, the obtained solutions evaporated and the residue distilled over phosphorus pentoxide under atmospheric pressure or without phosphorus pentoxide under a pressure of 10 mm Hg. Maleic anhydride of $94-95.\%$ purity was obtained.

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