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A new procedure for sulfuric acid manufacture by the contact process[☆]

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In this article a description is given of investigations during which contact sulfuric acid was manufactured by an altogether new process. As contact mass a liquid melt was used, consisting of alkaline pyrosulfates and sulfur trioxide, wherein the active compounds were dissolved. Relative to the theoretical considerations which brought about the development of this method, we refer to the first article.

The best conversions were obtained by letting the liquid contact mass circulate over Raschig rings in counter-current with the gas mixture.

By this new sulfuric acid process conversions of 95–98% have been reached at temperatures and space velocities equivalent to those ordinarily applied in connection with the contact process.

The trial set-up was, except for the converter, similar to the one used when measuring the activity of catalyst bodies, which is described in the first article. Also the analytical methods were the same.

The liquid catalyst used consisted of a potassium pyrosulfate-sulfurtrioxide melt in which the active vanadium compounds were dissolved. The sulfurtrioxide content of the melt was finally established during the reaction and, therefore, the percentual content of vanadium also changed during the activating period. The content of vanadium compounds calculated as V_2Q_5, however, amounted to approximately 14%.

The first tests were made by bubbling the gas mixture through, the liquid catalyst in a laboratory converter of Pyrex glass which is shown in Fig. 1. The melt was only a few centimetres high and nothing had been done to reduce the size of gas bubbles passing the catalyst.

With this technically very imperfect apparatus only small conversions were obtained; for instance, at a temperature of 520 °C, a melt 5 cm high, and a rate of flow of 0.13 1 7% SO_2/h per cubic centimetre a conversion of 27% was obtained. At the same temperature and rate of flow, but with twice the melt height, the conversion was 34%, which fits in quite well with the fact, that the contact period in the latter case is about 1.4 times as long as the contact period of the first one.

In spite of the small conversions obtained, we have reasons for believing that, for instance by arranging the converter according to the principle applied in ordinary plate columns and bubble cap columns, a technically satisfactory degree of conversion may be obtained.

The next reaction apparatus which was tried out, was also a laboratory apparatus of glass—this in order to allow observation of the catalyst. It was arranged in such a way that the melt by means of a glass air lift was circulated over a layer of Raschig rings, past which the sulfur dioxide gas passed against the downward flow of catalyst fluid. The arrangement of this reaction apparatus is shown in Figs. 2 and 3. All parts, also the outside circulation tube and the inlet for the gas mixture, were electrically heated by resistance coils so that they could maintain the desired temperature. The total capacity of the converter was about 400 cm^3, the maximum height of the layer of Raschig rings was in our investigations 20 cm.

In spite of the fact that this apparatus, for instance as regards the current conditions, was not as appropriate as might be desired, we obtained excellent conversions.

1. The investigation results and their interpretation

With the apparatus described above, and with a catalyst containing approximately 14% Y_2O_5 conversions were measured at varying space velocities and composition of the gas mixture, varying circulation of the liquid catalyst, and

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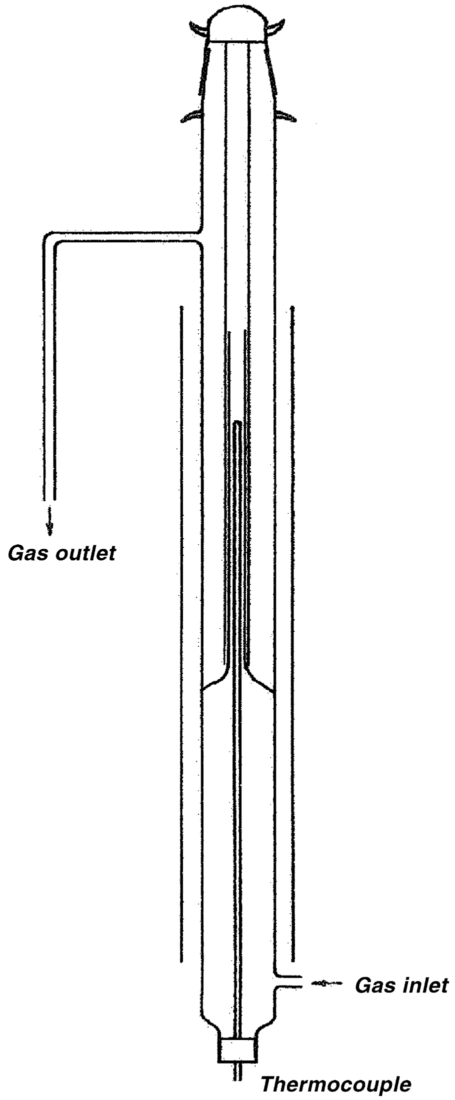

Fig. 1.

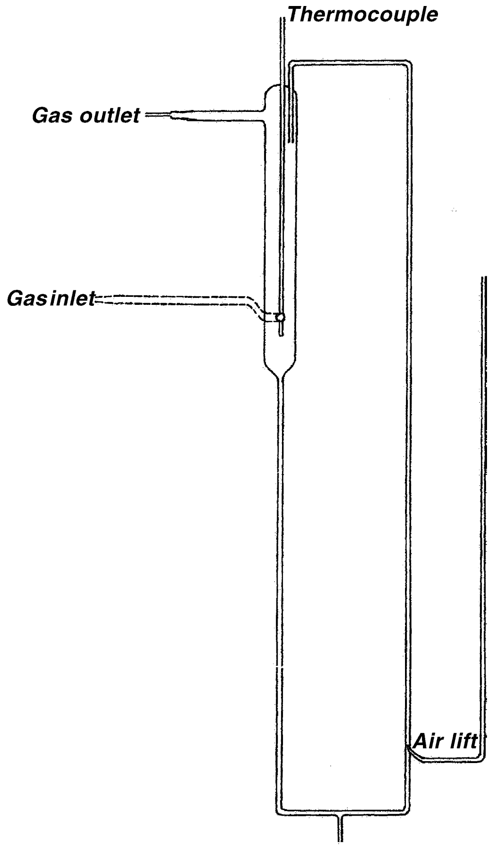

Fig. 2.

different temperatures. The temperature pertaining to an investigation is indicated by a single number. This represents the temperature in the middle of the converter.[1]

The temperatures at which the measurements were made, vary from 480 to 495 °C. These variations are, as we have proved by experiments, only of slight importance as regards the conversion. Also the circulation of the liquid catalyst has taken place at about the same rates during the different investigations mentioned herein. Consequently the different measurements give direct information as to the variation of conversion with speed and composition of the gas mixture.

It seems conclusive that according to the new method the same high degree of conversion may be obtained as by using catalyst bodies. However, with the laboratory converter described herein, we reached this conversion only at an essentially lower space time yield than may be obtained with the apparatus in general use today.

Two things must be brought to mind, however. Firstly, the active catalyst volume in a typical sulfuric acid converter for catalyst bodies is only about 20–30% of its total volume, and thus the outer dimensions of converters for the same production, arranged according to the new and the old method, respectively, may not differ as greatly as might be expected from the space time yield measured.

Secondly, the conditions in the described laboratory apparatus for the current of gas mixture as well as for the liquid catalyst were far from ideal.

In this respect we may mention that a series of investigations which are presently being made indicate that an essentially higher space time yield than the above mentioned may be reached.

Finally we wish to point out some of the advantages that may be gained by using a liquid catalyst.

One characteristic fact that speaks for the new method is, that the contact mass, constantly or at intervals, may be replaced without disrupting the operation. Furthermore, when the mass is poisoned, it may easier be regenerated than the catalyst which is presently used, in which even the regeneration

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[1] As the temperature varied somewhat along the converter and, for instance, was somewhat lower in the outlet than in the middle of the oven, there are at some investigations measured conversions higher than the equilibrium at the observed temperature, which however may be explained by the above circumstances.

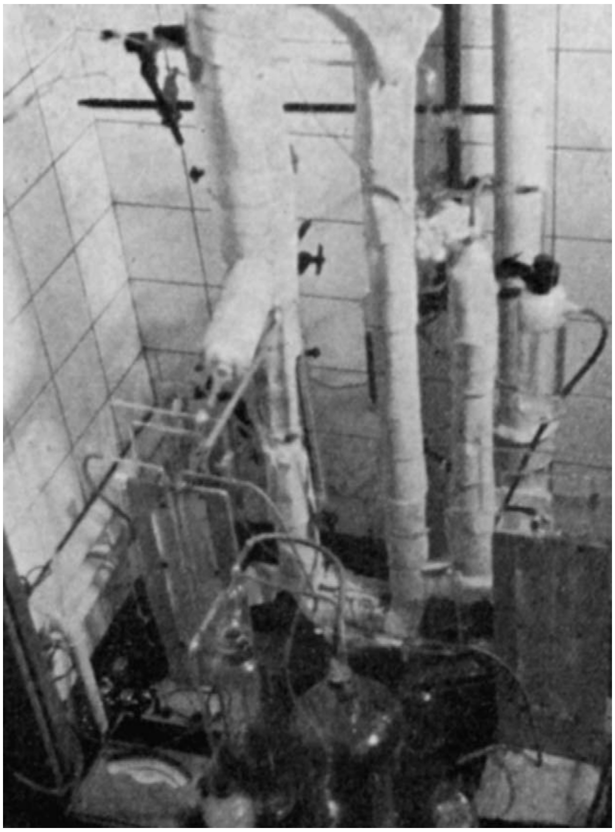

Fig. 3.

Table 1
Measurements with normal roaster gas (11% O_2, 82% N_2, 7% SO_2)

Temperature (°C)	Rate of flow (N), $N = 13.5$ l 7% SO_2/h	Conversion (%)
490	0.9	92
495	1.0	85
490	2.0	ca. 50

Table 2
Measurements with mixtures of air and SO_2

Temperature (°C)	Rate of flow (N)		Conversion (%)
	Air, $N = 12.5$ l air/h	SO_2, $N = 950$ cm^3 SO_2/h	
480	0.91	0.82	98.7
480	0.92	1.0	97.1
490	0.92	1.3	91
485	0.94	1.55	89

Table 3
Measurements with mixtures of oxygen and SO_2

Temperature (°C)	Rate of flow (N)		Conversion (%)
	Oxygen, $N = 12.5$ 1/h	SO_2, $N = 950$ cm^3/h	
485	0.61	3.0	97.5
495	0.52	4.0	93.5
490	0.61	5.4	82.7
485	0.51	0.86	98.9
485	0.9	4.0	96.0
485	0.23	4.0	81.5

of the vanadium is a difficult and expensive process, so expensive, indeed, that under normal conditions it is not carried out (Tables 1–3).

Hereby the poisoning of the catalyst is easily met, causing the demands for dust cleansing to be reduced considerably. In this respect attention is drawn to the fact that the catalyst cannot be clogged by dust from the outside, passed in with the gas. Nor can dust originating from abrasion of the contact mass cause difficulties as may be the case when using catalyst bodies.

The method also brings up new possibilities in a different field.

During recent years considerable efforts have been exerted, especially in Russia [1], to use oxygen in the sulfuric acid contact process. The above-mentioned article by Boreskov states that by using oxygen, the capacity is increased by a factor of 5–6. As the results of the measurements indicate, this has also been found to apply to the new sulfuric acid process. This process, however, offers a good chance of controlling the thermic conditions in the converter or the converters as the circulating catalyst fluid may be instrumental in the cooling and equalisation of the temperature.

Acknowledgment

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Reference

[1] G.K. Boreskov, Kislorod 4 (1944) 16; C. A. 40 (1946) 3859.