B. Space-Time Yields and Questions of Equipment Construction.

In most of the laboratory tests described, pressure tubes with an internal diameter of 12 - 13 mm were used for reactor tubes. The catalysts was uniformely distributed in an iron or copper boat, and the boat was pushed into the middle of the tube (arranged at some slant for the partial draining of the paraffin formed). The normal catalyst charge was 10 g of Fe, which corresponds to 15 - 16 mls of a freshly prepared so-called "normal catalysts". The empty space in the reaction zone of the tube (30 centimeters in length) amounted to about 35 mls. When considering the space occupied by the boat, 35 mls of this reaction space or about 1/2 of the space was filled with the catalysts, while the upper half remained free. The scheme I, figure 19 was drawn to illustrate these conditions.

When different amounts of synthesis gas per unit time were conducted over the catalysts arranged as above, the reaction temperature had to be kept the higher, the more gas was to be converted in a unit time. Thus according to figure 20, a 50 percent contraction was obtained with a thruput of only 1.7 li (measured at 1 atm) at a temperature of 220°C; at 233°C 4.1 li/hr had to be led, at 250°C - 8 li/hr, and at 275°C 16 li/hr.

In another test 4 li/hr were passed over the catalyst at 235°C, and 20 li/hr at 280°C, to produce a contraction of 50 percent.

It is preferable to conduct a synthesis at the lower temperatures as long as possible, which will result in a greater life of the catalyst, higher hydrocarbons, and for industrial considerations; on the other hand it would be preferable for space-time yields to operate at higher temperatures and use higher temperatures. With hourly gas thruputs of 10 - 20 li/10 g Fe, the heat removal on a large scale industrial operations becomes a problem, when trying to avoid overheating of the catalysts and deposition of carbon, which would cause a more rapid dying-off of the activity of the catalyst. This was the reason for selecting an average rate of flow of 4 li of synthesis gas per hr and per 10 g Fe. In thearrangement shown in figure 19, the catalysts were active for one to two years without any reactivation of the catalysts, and producing a satisfactory conversion.

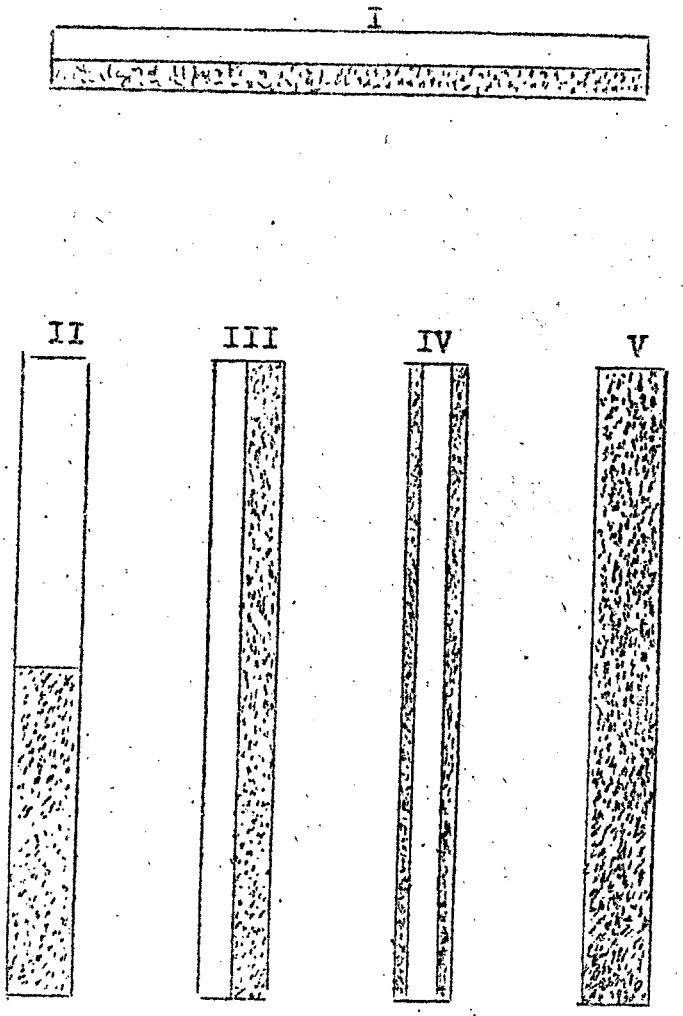
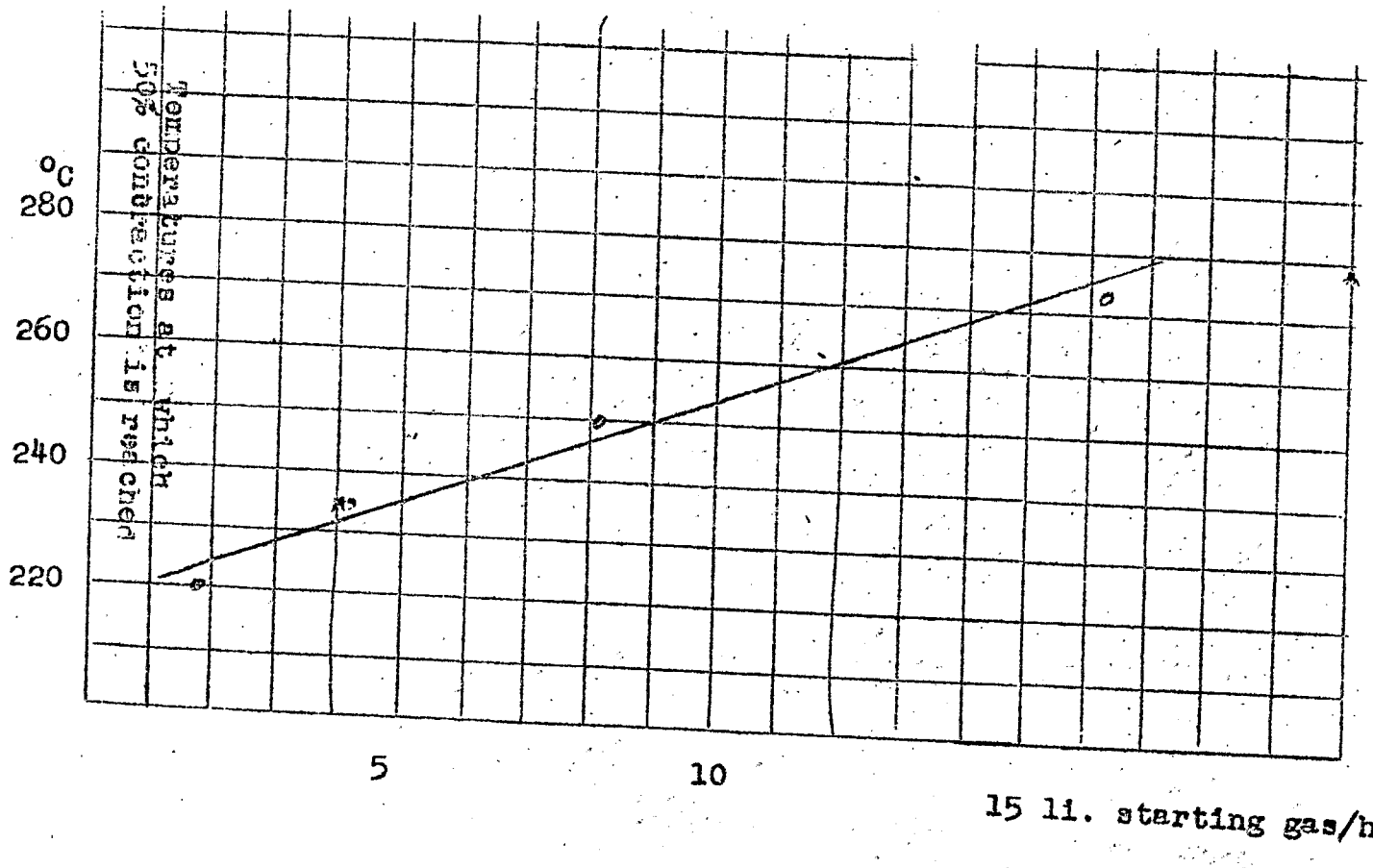


Fig. 19. Schematic presentation of various filled catalyst tubes

Fig. 20, Relation between reaction temperature and gas thruput(for the same contraction of 50%)



It has also been shown in the iron middle pressure synthesis, that without increasing the pressure, the gas thruput, i.e. the weight of gas converted per unit weight of the catalysts, could not be increased. Many processes occur on the surface of the catalysts (the transportation of the participant and products of the reaction to and form the catalysts, etc.) and the processes which determine the rate of the reaction are not accelerated by increasing the pressure.

When the reaction tube is set vertically (figure 19, scheme 2), then the catalysts distributed in a layer 30 centimeters long becomes compressed to 10 - 15 centimeters, and the gas which tarried relatively long over the catalysts passes now more rapidly through the narrower channels between the grains of the catalysts. The empty space available to gas in the region of the catalysts in the two schemes, I and II, is therefore in proportion of about 4 : 1. The relationship between the gas thruput and the temperature shown in figure 20 may be understood to mean that equally good results can not be obtained according to scheme II as to scheme I. There is a further difficulty in that the volume of the catalysts increases as a result of the absorption of reaction products and of carbon. This results in a further shortening of the residence time of the gases because of the narrowing of the hollow spaces inside the catalysts.

It may be impossible industrially to avoid using vertical reactors, and a solution of the problem was at first sought according to schemes III and IV. The broken lines represent perforated sheets. In case 3 a perforated sheet separates the reaction tube into two equal parts, in case 4 a second tube made of perforated sheets is set inside the reaction tube. The catalyst here is placed between the two tubes. In both cases the length of the layer, the space filled by the catalyst and the empty space correspond to the proportion in case 1. The results were also at first similar. The perforated sheets caused no noticeable slowing down of the conversion. (The catalyst was formed in a separate apparatus and the catalyst was transferred in an atmosphere of carbon dioxide). After a few weeks of operation a retardation of conversion was observed in methods III and IV in comparison with the method according to scheme I. The reason for it may be in the chance for the catalysts in case I to expand

during synthesis, which could happen in cases III and IV only at the expense of the empty spaces between the catalyst grains.

The scheme shown in drawing V figure 19 was based on the addition of a substance tending to increase the porosity of the catalyst, e.g. of kieselguhr. 4 g of kieselguhr was normally used with 10 g of iron, in which case the iron-kieselguhr catalyst fills 12 to 13 mls of space in the reaction tube to a length of approximately 30 centimeters. The free gas space is smaller than in the case I by the space occupied by kieselguhr, but the increased porosity of the catalysts resulted in a considerable increase of its activity. A relatively smaller percent increase in the iron volume through absorption of carbon can no longer affect the process as adversily in case 5 as in cases 2 and 4. A test run in this way (figure 11) proceeded satisfactorily for several weeks.

We may in general point out that the volume increases distinctly observable in tests II and IV were not observed in all cases. Thus aniron catalyst precipitated with ammonia and formed with mischgas at atmospheric pressure, and used in vertical reaction tubes could be used in the temperature range from 240 - 260°C for three months with out reactivation and with a good conversion. Tests to explain these results are still in process.

It must be mentioned with reference to the iron-keiselguhr-catalysts that the space-time yields obtained with them were approximately the same as with the cobalt catalysts. With this catalyst the same industrial equipment could be used as in the cobalt synthesis. In the laboratory, water cooled tubes could be used. The steam pressure was naturally higher because of the higher reaction temperatures. It was equal to 30 - 50 atm, depending on the length of operation.

C. Forming the Catalysts

The iron catalysts described in the first part of this paper and precipitated by sodium carbonate from ferric nitrate solution as well as the catalysts precipitated with ammonia from ferric nitrate solution were hard after drying and broke with a lustrous fracture, and their strength satisfied industrial requirements.

Tests were nevertheless made of grinding the iron catalysts and compressing them into tablets.

The brownish - black color of the grains of the catalysts are changed during grinding into a reddish brown color which is retained by the compressed tablets. It has been found that the activity of the original catalysts was not always retained in the tablets. This may have been connected with the heating during compression, and from phenomena produced by a pressure during the tableting.

Iron catalyst tablets of very good activity and life have been prepared when paraffin was added to the catalysts powder to be pressed. Synthetic paraffin, shaved to fine scales was used in these tests.

Test 1 table 35 shows a test with tablets which contained 25 percent paraffin referred to iron. Test 2 has been performed for the sake of comparison without any addition of paraffin. Paraffin does not interfere with the forming and can also be mostly recovered during that step. The tablets retained their shape even after many months of synthesis.

Table 35

Experiments with Catalysts Compressed into Tablets

Days of operation	Experiment 1 Temp. °C	Experiment 1 Contr. %	Experiment 2 Temp. °C	Experiment 2 Contr. %
1	235	53	234	55
2	235	54	235	56
10	235	51	236	54
16	234	53	236	50
20	235	52	235	49
25	235	47	240	48
31	235	46	246	47
47	240	49		
60	240	45		

	CO_2	Heavy hydrocarbons	O_2	CO	H_2	Hydrocarbons	Carbon number	N_2
Experiment 1								
Starting gas:	2.1	0.0	0.2	53.8	35.7	0.2	1.0	8.0
End gas:	59.7	3.9	0.1	1.1	10.2	7.6	1.9	17.4
Experiment 2								
Starting gas:	2.1	0.0	0.1	53.7	38.0	0.4	1.0	5.7
End gas:	61.5	3.5	0.0	1.8	13.2	7.2	1.8	13.0

The conversion at the start of the operation was practically the same in the two series of tests (as may be seen from the two parallel gas analyses printed at the bottom of the table). However, the catalyst tablets prepared without paraffin addition required a more rapid rise in temperature after a few weeks, than the tablets made with paraffin. The activity of the catalyst in series 1 is the same after fifty days of operation as after twenty-five days of operation of the catalyst 2.

An improvement in the catalytic behavior of the catalysts tablets was also found upon the addition of 5 and 10 percent of paraffin.

D. On the Subsequent Working up of the Primary Products.

Great variety of reaction products are obtained in the middle pressure synthesis with iron catalysts, as has already been discussed in a special section. In most cases they could be used for the same purposes as the products of synthesis with cobalt catalysts. It remains to discuss a little more closely the possibilities of the utilization of the products. The products of the iron-synthesis differ naturally in certain respects from those of the cobalt synthesis. One such instance is the formation of the synthol-like by-products, such as the different alcohols, and an other one is the increased formation of unsaturated hydrocarbons. The oxygen-containing and the unsaturated compounds produce a higher knock resistance in the iron gasolines. These compounds show no tendency to form gum. The gasoline formed with iron-catalysts remains completely colorless and clear after months of storage.

The amount of unsaturated gasol hydrocarbons is greater in the middle pressure synthesis with iron-catalysts; they may permit a polymerization to the knock-resisting liquid hydrocarbons, which appears to indicate that the iron catalysts synthesis is suited for the production of high grade gasoline.

We have performed a few tests on the catalytic polymerization of the olefin hydrocarbon which has been primarily developed by Ipatiev of the Universal Oil Products Company and his collaborators 23/ who worked on the problem of a combination of synthesis and polymerization. A solid phosphoric acid catalyst, namely $Cd_3(PO_4)_2 \cdot 4H_3PO_4$, was used for that purpose.

The cadimum phosphate $Cd_3(PO_4)_2$ was used as a carrier and was obtained by precipitation of cadimum nitrate solution at the boiling point with a calculated amount of Na_2HPO_4 and NaOH. It was washed with hot water and mixed while still moist with the calculated amount of the 89 percent phosphoric acid, evaporated, dried, and granulated.

When a gasol containing 35 to 40 percent of unsaturated hydrocarbons (obtained in cobalt synthesis) led over this catalyst (1 l gaseous gasol/hr/10g catalyst), under a pressure of 7 atm, 40 percent of the unsaturated hydrocarbons were converted at 140°C, 60 percent at 160°C and 70 - 80 percent at 180°C. A polymere gasoline was formed which was distilled, and 10 - 20 percent of compounds boiling 180 - 200°C were separated and found to have an octane number of 97 to 99 without the addition of any volatile hydrocarbons, with a Reid vapor pressure of 0.1 to 0.2 atm., and without any additional hydrogenation.

Tests were carried out in which the total reaction gas of the iron middle pressure synthesis was led into a second stage synthesis under pressure with phosphoric acid catalysts, after separating the products condensible at room temperature. About equal volumes of catalysts were used in the synthesis and the polymerization. The synthesis was in operation for about two months before the different tests were started. An ammonia precipitated iron catalyst with 1/4 K_2CO_3 was used after being formed with mischgas at atmospheric pressures. The yield of solid, liquid and gasol hydrocarbons amounted to about 140 g per ncbm of the ideal gas. Table 36a shows a few analyses of the reaction gases after the synthesis and after the polymerization. This series of experiments was run at pressures of 15 atm. The temperatures of the synthesis were at 250°C, of polymerization at 200 - 220°C.

Table 36

Composition of the Reaction Gases after Synthesis and after Polymerization.

	CO_2	Heavy hydrocarbons	O_2	CO	H_2	Hydrocarbons	Carbon number	N_2
a	58.3	3.7	0.2	8.7	12.8	6.7	1.6	9.6
b	59.8	1.1	0.2	9.1	13.0	6.2	1.7	10.6
a	62.9	3.7	0.2	7.0	10.1	7.7	1.8	8.4
b	64.8	1.2	0.3	7.1	10.0	7.6	1.8	9.0
a	58.4	4.2	0.0	10.9	5.1	6.4	1.7	15.0
b	60.6	1.2	0.4	10.8	5.0	6.0	1.8	16.0

Analyses show that 2/3 to 3/4 of the heavy hydrocarbons disappeared during polymerization.

Table 37 shows the number of g of solid, liquid and gasol hydrocarbons per ncbm ideal gas produced during synthesis with and without polymerization. The top values represent an average of three weeks of operation, the bottom series is an average of the next week of operation during which the polymerization step was omitted. The AK gasoline was obtained only once at the end of the conversions (that is not between the synthesis and the polymerization stages).

Table 37

Combination of Synthesis and Polymerization

Polymerization	Yield g/ncbm Wt. percent of the liquid hydrocarbons (including paraffin)	Gasol	% of liquid hydrocarbons by wt. After Synthesis	After Polymerization	As AK gasoline
With	125	14	70	20	10
Without	105	30	85	0	15

139 g of liquid and gasol hydrocarbons (including paraffin) were formed in the synthesis during the first period, 135 g/ncbm during the second period (without polymerization). The synthesis therefore produced about 3 percent more products during the first period, while the amount of liquid hydrocarbons was 19 percent greater, largely produced from gasol by polymerization. In the containers cooled to room temperature, 70 percent of the liquid products separated in the polymerization experiment after the synthesis and 20 percent after the polymerization, with 10 percent as AK gasoline. The so-called AK gasoline obtained during synthesis and not condensed in the first container, was led with the reaction gases over the phosphoric acid catalyst and polymerized part of the unsaturated gasoline hydrocarbons. While the amount of gasol hydrocarbons was reduced from 30 to 14 g/ncbm by polymerization, the proportions of the AK gasoline was reduced only from 16 to 13 g/ncbm. We may explain this by assuming that the olefinic hydrocarbons of the C_4 hydrocarbons are more readily polymerized than the hydrocarbons with lower or higher molecular weights which

react at a slower rate. For this reason the dimers of olefins are largely formed in this polymerization over phosphoric acid esters.

Unlike the "iron gasoline", the polymer gasoline can be advantageously hydrogenated, and it would therefore be preferable to remove as perfectly as possible the synthetic gasoline from the reaction gas before the polymerization stage.

It becomes therefore possible to complete the working up of the reaction gases of the middle pressure synthesis with the iron catalysts for the manufacture of polymer gasoline in one continuous operation. It will have to be left to practical experience whether such a process is more economical then a second polymerization stage of the gasol hydrocarbons freed from the other gases.

A closer connection between synthesis and polymerization might be obtained by mixing the synthesis catalysts with the one used in polymerization, but it results in a gradual weakening of both processes especially if the contact of the two types of the catalysts is very intimate (by the interaction of the acid phosphoric acid catalysts and iron).

Tests in which acid iron phosphate was used for polymerization instead of cadimum phosphate produced similar results.

The gasolines obtained by stabilization and washing of the two liquid reaction products in table 37 with sodium hydroxide have been tested for knock resistance in the I. G. test motor. About 2/3 of the total liquid products in this test boiled within the range of 30 - 180°C. Table 1 shows :

1. Gasoline not followed by polymerization:

2. Gasoline -180°C obtained in a combination of synthesis and polymerization:

3. Gasoline b.p. -150°C obtained by polymerization following synthesis:

The density, olefin content, boiling point curve and vapor pressures at 37.8°C as well as the octane numbers are given for all three samples

Summary

A review is given of the work on middle pressure synthesis with iron catalysts. It includes investigation of the precipitation, alkalization and forming of the catalysts, the finding of the optimum synthesis conditions (composition of gas, pressure, temperature, additions, catalysts reactivation etc.); the third topic was a discussion of the reaction products and the fourth was treatment of general problems such as the production of synthesis gases, equipment construction problems, tableting the catalysts and the subsequent treatment of the original products.

The principal results of these investigations are the following:

1. Precipitation of the iron catalysts:

The catalysts were generally produced by precipitation of iron with sodium carbonate or ammonia from ferric nitrate solution, obtained by solutions of technical grade of iron in dilute nitric acid. The catalysts precipitated from ferric solutions were

superior to those obtained from ferrous solutions.

2. Alkalization of the Catalysts:

The presence of alkalies is not necessary for synthesis, nor does it regulate the amount of conversion. However, the presence of increasing amounts of alkalies favors the formation of higher molecular weight hydrocarbons. The addition of alkali is therefore important for the production of solid paraffin. Potassium carbonate was generally used but different alkali salts produced the same results.

3. Forming the Catalysts:

Forming (pretreating the catalysts with gases containing carbon monoxide, best with pure carbon monoxide)is necessary for the production of active catalysts. Forming is conducted at pressures below the synthesis pressure, e.g. at atmospheric pressure, but best at a reduced pressure.

The gas used for forming is best conducted at a high rate and at temperatures over 250°C, best at 300 to 350°C, until the carbon dioxide formed in the reaction passes through a maximum and then reaches an approximate constant minimum value .

4. Synthesis:

The optimum proportion of carbon monoxide to hydrogen in the synthesis gas is 3 : 2. The optimum synthesis pressure is between 10 and 20 atm. The optimum synthesis temperatures are between 230 and 240°C. At the start catalysts synthetized the gas at considerably lower temperatures. This is not however, of advantage to the life of the catalysts, nor are temperatures in excess of 280°C (the latter because of a deposition of carbon).

The addition of kieselguhr (after alkalizing) results in a considerable increase in the activity of the catalysts.

No advantages were found in treating catalysts with hydrogen before synthesis, but an occasional treatment with hydrogen during the synthesis results in a reactivation of the iron catalysts.

5. Optimum Yields:

The best yields in solid, liquid and gasol hydrocarbons amounted to about 150 g/ncbm ideal gas. The longest life was obtained with a catalyst which still brought about a conversion of 140 g/ncbm gas at a temperature of 260°C after 1 1/2 years of operation.

6. Reaction Products:

The nature of the reaction products can be modified within wide limits by changing the operating conditions.

5 to 50 percent of the total solid and liquid hydrocarbons were solid paraffin. Low melting point paraffins are formed as well as particularily high melting paraffins with melting points up to 125°C.

The liquid reaction products differ from those obtained with the cobalt catalysts by their increased content of unsaturated hydrocarbons and by their content of synthol-like products among which alcohols and esters of different molecular weights have been proven.

The octane number of the 180°C cuts of primary gasoline is 60 to 63. It can be increased further 10 octane numbers by combining synthesis with the polymerization of the gasol hydrocarbons, and the addition of 0.7 mls of tetraethyl lead per li of gasoline will increase it by an additional 10 O.N.

10 to 30 percent of the solids, liquids and gasol hydrocarbons consist of gasol. Its olefin content reaches 80 percent. When the temperature or the activity of the catalyst are increased, the total gasol yield is increased, but its olefin content is lowered.

Iron catalysts have been found suitable also for the production of a gas meeting specifications of the gas manufactures.

7. Production of Synthesis Gas:

A synthesis gas with the carbon monoxide and hydrogen in proportion of 3 : 2 is obtained by a simultaneous conversion of carbon dioxide and steam in a water gas producer, with the carbon dioxide required obtained from the synthesis products. Another

suitable synthesis gas is obtained by gasification of coke or coal with oxygen.

8. Equipment Construction:

Connections between the shape of the equipment and the life and activity of the catalysts has been discussed. The best results are obtained in horizontal or slightly inclined reactor. The removal of the positive heat of the reaction with water requires steam pressures of 30 to 50 atm on the water side of the reactor.

/s/ Pichler
July 1, 1940