When a Dellwig-Fleischer-Generator is used, one requires 550 g. of coke per cubic meter of water-gas, that is, twice as much as is theoretically necessary. The temperature and heat requirements for the production of the CO-rich gases are approximately the same as that for the water-gas production.

We were able to produce 100 m^3 of CO-rich gas per hour in our water-gas generator for several years without interruptions. The composition of the synthesis gas, for example, was as follows: 2% CO_2, 55% CO, 37% H_2, and 6% N_2. In several instances, in order to determine the expressed contraction more accurately, a little more nitrogen than given above was added to the synthesis gas.

The purification of the gases was carried out in the same manner as with H_2-rich gas.

Another way for producing the desired synthesis gas, consists in the gasification of coke or coal with the addition of oxygen. It is not necessary to discuss this here.

B. Space-time Yields and Apparatus Details.

For most of the experiments in the laboratory, we used reaction tubes of 12 to 13 mm, I.D. The catalyst was distributed evenly over a length of 30 cm, within the tube. A normal catalyst charge contained 10 g. of iron. This corresponds to 15 to 16 cm^3 of freshly-prepared normal catalyst. The free space in the tube amounted to 35 cm^3 (in the reaction zone). Consequently, the catalyst filled approximately half of the reaction space. The upper half of the tube remained empty. Drawing 1 in Figure 19 shows the relationships schematically.

If various synthesis gas quantities are thus passed over the catalyst under the conditions of the synthesis, the reaction temperature has to be kept higher if it is desired to convert more gas per unit of time. According to Figure 20, contractions of around 50 percent were obtained at an hourly gas rate of 1.7 liters (referred to one atmosphere pressure) at a temperature of 220°C. When 4.1 liters per hour of gas were used, the temperature was 233°C. At 8 liters per hour, it was 250°C,, and it was 275°C. for 16 liters per hour of gas. In another experiment, 4 liters per hour of gas were passed over at 235°C., and a contraction of 15 percent was obtained, at 280°C. and 20 liters per hour, the same contraction was reached.

With respect to the lifetime of the catalyst, the magnitude of the yields of higher hydrocarbons and for other technical reasons, it is advantageous to carry the synthesis through at as low a temperature as possible for as long a time as possible. With respect to the space-time yields, however, it appears more favorable to work at higher temperatures and higher gas rates. We found that at gas rates between 10 and 20 liters per hour per 10 g. of iron, serious difficulties arise when the reaction is carried out on the large scale. The difficulties encountered are chiefly due to the fact that the heat of reaction cannot be carried away fast enough. This causes the catalyst to overheat and free carbon is formed which rapidly causes a decrease in the catalyst activity. For this reason we chose to work at a flow velocity of 4 liters of synthesis gas per hour per 10 g. of iron. Drawing #1 in Figure 19 shows the arrangement of the catalyst in the tubes, and it is to be observed that it was possible to operate for one to 2 years with the same catalyst without regeneration, and a satisfactory degree of conversion was always obtained.
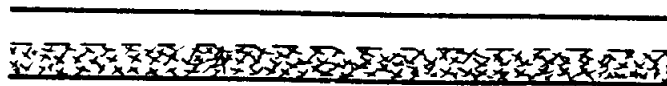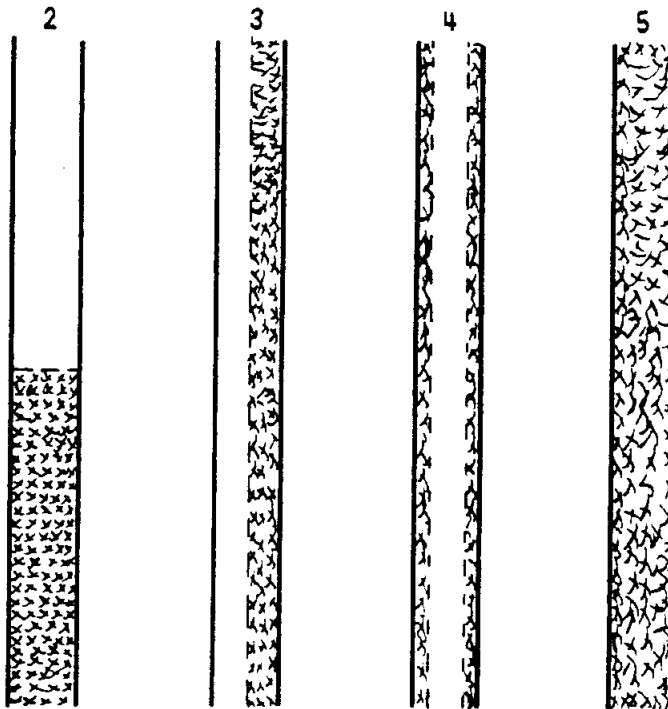
Figure 19. - Schematic representation of positions of reaction tubes.

For the iron middle-pressure synthesis, we have discovered also that with increased pressure, the gas rate per unit weight of catalyst may not be increased. We have found that processes occurring on the surface of the catalyst are controlling the reaction velocity (transportation of the reaction products away from the catalyst, respectively carrying the reactants to the catalyst surface). These processes are not accelerated by increasing the pressure.

If the reaction tube is arranged at a vertical position (Figure 19, Schematic Drawing #2), the catalyst layer length only amounts to 10 to 15 cm., instead of 30 cm as compared to a horizontal arrangement. The contact time of the gases going through the catalyst is much shorter therefore when the tube is arranged in a vertical position. The empty space through which the gas flows is approximately 4 times as large in the case of a horizontal tube than it is in a vertical tube. By taking into consideration the relationship between rate of gas flow and temperature (shown in Figure 20), it may be understood that the same favorable results are not obtained when the work is carried out with an apparatus arranged according to Drawing #2. In addition to that, we found that the catalyst takes up considerable quantities of the reaction products and large quantities of carbon are deposited on the catalyst. This causes the percentage voids in the catalyst to decrease with a consequent shortening of the contact time between the gas and the catalyst.

Since on the large scale, one would be chiefly interested in working with vertical reaction tubes, we have attempted to find a solution to the problem according to the Schematic Drawings #3 and #4. The dotted lines represent perforated plates. In case 3, a perforated plate divides the reaction tube into two equal sections. In case 4, a perforated reaction tube is concentrically arranged within the larger reaction tube. The catalyst is distributed in the annulus between the two tubes. In both cases, the catalyst layer length and the percentage free-space correspond to the conditions of case 1. The results were similar for case, 1, also. The perforated plates did not cause a noticeable decrease in conversions (the induction of the catalyst had been carried out in a separate apparatus, and the catalyst was transferred in an atmosphere of CO_2). After several weeks of operation, the experiments carried out according to cases 3 and 4 showed a decline in the conversion as compared to the procedure of Drawing #1. The reason for this, we believe, might be that the catalyst in case 1 had the possibility to expand during the synthesis, whereas in cases 3 and 4, this expansion occurred mainly at the expense of the internal voids between the catalyst particles.

The Schematic Drawing 5 of Figure 9, shows the arrangement when a catalyst was used the structure of which was loosened up by the addition of kieselguhr. When the normal quantity of iron, namely 10 g., is diluted with 4 g. of kieselguhr, then this iron-kieselguhr catalyst fills a 12 to 13 mm. I.D. reaction tube up to a length of 30 cm. The percentage free-space is smaller than in case 1, in amount approximately equal to the quantities of kieselguhr used, on the other hand, the loosening of the catalyst by the kieselguhr causes a considerable improvement in its activity. A small percentage expansion of the iron on account of the deposition of carbon does not produce as unfavorable a result in case 5, as it has caused in cases 2 to 4. An experiment which has been under investigation for several weeks gives a satisfactory conversion (Figure 11).
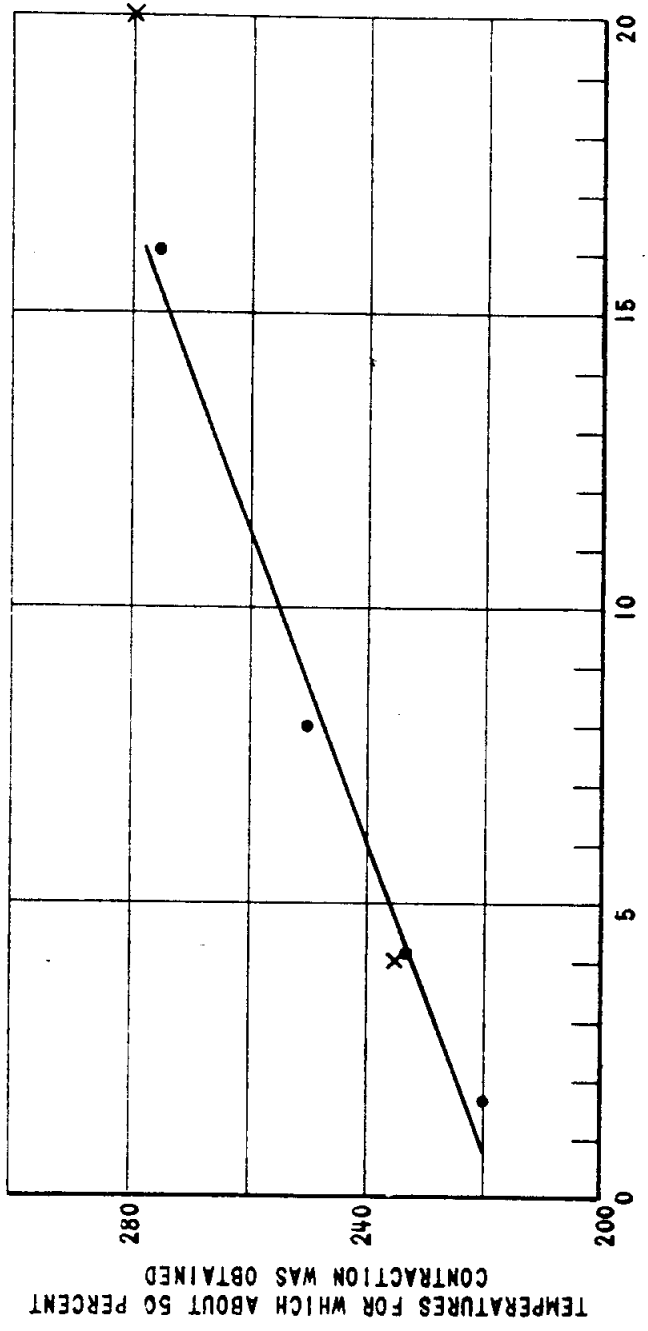
Figure 20. - Relationship between reaction temperature and gas throughput (for constant 50 percent conversion).

We want to mention here that the disturbing influence of the volume increase of the catalyst observed in experiments 2 to 4 was not observed in all cases. Thus a catalyst which was precipitated by ammonia and inducted with mixed gas at one atmosphere yielded good conversions for three months in vertical position at temperatures of between 240 and 260°C. Experiments to clarify the situation are still in progress.

It can be mentioned here that the space-time yields observed with the iron-kieselguhr catalysts approximately correspond to that of the cobalt catalysts. If the iron-kieselguhr catalysts should be used on an industrial scale, similar pieces of apparatus as are used in the case of cobalt should be satisfactory for the iron-kieselguhr catalysts. In the laboratory, we worked with water-cooled tubes. The steam pressures of course are higher corresponding to the increased reaction temperatures. They vary between 30 to 50 atmospheres, all according to the duration of the test.

C. Pelleting of the Catalyst.

The catalyst described earlier and produced from ferric nitrate solutions with sodium carbonate as well as the iron catalysts which were precipitated with ammonia (also ferri catalysts) were solid after having been dried and broke with a glassy fracture. Their rigidity should be sufficient for industrial application.

Nevertheless experiments were carried out the object of which was to grind the iron catalysts and put them into shape of pellets. The blackish-brown color of the granular original catalyst changes over to reddish-brown when it is ground. The pellets which are formed from the powder retain this brown color. We have discovered that the pellets not always retain the original activity of the catalyst. It might be that the cause for this activity decrease has something to do with the overheating through which the catalyst goes when it is pressed into pellets.

We were in a position to produce iron catalyst pellets of very good activity and high lifetime when we mixed paraffin to the catalyst powder prior to pelleting. For this we used synthetic paraffin which had been made into fine scales.

Table XXIV, Experiment 1, gives the results of an experiment conducted with pellets. They contained 25 percent paraffin as referred to the iron. Experiment 2 brings a comparative experiment where no paraffin was added. The paraffin does influence the process of induction and may be regained practically all. The pellets retained their shape even after a long time of the synthesis.

At the beginning of the reaction period, the conversion obtained was practically the same in both cases (this is also brought out in the table with the respective gas analyses). After several weeks of operation, however, the temperature had to be raised more rapidly for case 2 where no paraffin had been used in the preparation of the catalyst. The activity of the catalyst of Experiment 1, after 50 days of operation corresponds to the activity of the catalyst of Experiment 2 after 25 days of operation.

Even with the addition of only 5 to 10 percent of paraffin, a favorable result upon the activity of the pelleted catalyst was observed.

Table XXV
Experiments with a Catalyst Which was Pelleted

Days of operation	Experiment 1		Experiment 2	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
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	sKW	O_2	CO	H_2	KW	cX	N_2
Experiment 1	Initial Gas:	2.1	0.0	0.2	53.8	35.7	0.2	1.0	8.0
	Final Gas:	59.7	3.9	0.1	1.1	10.2	7.6	1.9	17.4
Experiment 2	Initial Gas:	2.1	0.0	0.1	53.7	38.0	0.4	1.0	5.7
	Final Gas:	61.5	3.5	0.0	1.8	13.2	7.2	1.8	13.0

D. Some Details on the Further Processing of the Primary Products.

In the middle-pressure synthesis with iron catalysts, various types of reaction products are obtained as will be shown in another chapter. They may be utilized in a similar manner as the products obtained during the synthesis with cobalt catalysts. It is superfluous here to mention the various usages of these products. In some points, however, there are some fundamental differences between the products of the iron synthesis, and the cobalt synthesis. First, there is the appearance of synthol-like byproducts as for instance various alcohols, and secondly, there is also the appearance of more unsaturated hydrocarbons. The oxygen-containing as well as the unsaturated compounds give the iron benzene higher anti-knock properties. These compounds have no tendency toward resin formation. The benzene which is produced with iron catalysts remains entirely colorless and water-clear after months of storage.

The middle-pressure synthesis with the iron catalyst gives a greater amount of unsaturated gasol hydrocarbons. These may be polymerized and form liquid hydrocarbons of high octane numbers. Therefore, the synthesis with iron catalysts seems to be especially adapted for the production of high quality benzene.

The catalytic polymerization of olefin hydrocarbons has been investigated by Ipatieff and co-workers (23) of the Universal Oil Products Co. We carried out some similar investigations which had to do with synthesis and polymerization taking place concurrently.

The catalyst which we used consisted of $Cd(PO_4)_2 \cdot 4 H_3PO_4$. As a carrier we used cadmium phosphate $Cd_3(PO_4)_2$ which was produced from cadmium nitrate solutions with a calculated quantity of Na_2HPO_4 and NaOH. The precipitation was carried out at the boiling point. It was washed with hot water and 98 percent phosphoric acid was added, evaporated, dried, and pelleted.

When gasol containing 35 to 40 percent of unsaturated hydrocarbons was passed over this catalyst, (one liter of gaseous gasol per hour per 10 g. of catalyst) at a pressure of 7 atmospheres and 140°C., 40 percent of the unsaturated hydrocarbons were converted, at 160°C., 60 percent, and at 130°C., 70-80 percent was converted. A polymerized benzene was obtained which split off 10 to 20 percent of the compounds boiling above 180-200°C. The residue was hydrogenated and had an octane number of 97 to 99. Next we carried out a series of experiments where we passed the total reaction gas from the iron middle-pressure synthesis at the synthesis pressure over the phosphoric acid catalyst (after precipitation of the condensible products at room temperature). Approximately the same catalyst volumes were used both in the synthesis and the polymerization. The synthesis was in progress already for two months before we started polymerizing. We used an iron catalyst precipitated with ammonia and containing 1/4 percent K_2CO_3. It had been inducted with mixed gas at atmospheric pressure. The yields of solid, liquid, and gasol hydrocarbons amounted to 140 g. per normal cubic meter of ideal gas. Table XXXVI shows some analyses of the reaction gases after the synthesis (a). Under (b) analyses of the reaction gases after the polymerization are given. The series of experiments was carried out at 15 atmospheres. The temperature and the syntheses were near 250°C., and for the polymerization near 200-220°C.

Table XXXVI
Composition of Reaction Gases After Synthesis and Polymerization

	CO_2	sKW	O_2	CO	H_2	KW	c/γko.	N_2
a	58.3	3.7	0.2	8.7	12.8	6.7	1.6	9.5
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	1.3	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

The analyses show that 2/3 to 3/4 of the volume of the hydrocarbons disappeared during the polymerization.

Table XXXVII shows the quantities expressed as g. per cubic meter of ideal gas of solid, liquid, and gasol hydrocarbons formed during the synthesis with, and during the synthesis without polymerization. The first values correspond to approximately 3 weeks of operation. The latter correspond approximately to an additional week of operation, for which the polymerization step was omitted. The activated-carbon-benzene was only recovered once at the end of the conversion (that is, in between the synthesis and polymerization).

Table XXXVII
Coupling of Synthesis and Polymerization

Polymerization	Yields, g./Normal cu. meter		Weight Percent of Liquid Hydrocarbons		
	Liquid hydrocarbons including paraffin	Gasol	Behind synthesis	Behind polymerization	After activated-carbon-benzene
with	125	14	70	20	10
without	105	30	85	0	15

During the first period, 139 g. of liquid hydrocarbons (including paraffins) and gasol hydrocarbons were produced by the synthesis. During the second period (without polymerization) 135 g. per normal cubic meter were produced. The synthesis, therefore, furnished approximately 3 percent more products during the first period, the amount of liquid hydrocarbons formed, however, was 19 percent greater, mostly at the expense of the gasol converted by the polymerization. In the case of the polymerization experiment, 70 percent of the liquid products after the synthesis apparatus precipitated in the receivers working at room temperature. 20 percent of the products obtained therein originated from the polymerization apparatus and 10 percent consisted of activated-carbon-benzene. Some of the activated-carbon-benzene was not condensed in the first receiver and it was carried over the phosphoric acid catalyst. Consequently part of this activated-carbon-benzene polymerized and formed unsaturated benzene hydrocarbons. The gasol hydrocarbons during the polymerization decreased from 30 to 14 g. per normal cubic meter, the quantity of the activated-carbon-benzene only decreased from 16 to 13 g. per normal cubic meter. This may be explained by the fact that the C_4 hydrocarbons polymerize most readily. Whereas, molecules having either more or less carbon atoms polymerize more slowly. Therefore, over the phosphoric acid, esters chiefly only the dimeres of the olefins are obtained.

It is advantageous to remove the synthetic benzene from the reaction gas before the polymerization step. Therefore, it is possible to further process the reaction gas obtained through the middle-pressure synthesis with iron catalysts and obtain polymer benzene. This may be done in one step. It has to be found out in actual practice whether it is more economical to proceed in such a manner or whether it is better to carry out a separate polymerization of the various constituents.

Experiments which have used acid iron phosphate instead of cadmium phosphate have shown similar results.

The benzenes reported in Table XXXVII were stabilized and washed with sodium hydroxide and tested for the octane number in a motor. Approximately 2/3 of the total liquid products of this experiment boiled in a range of 30-180°C.

Table XXXVIII shows the properties of a benzene without following polymerization, of a benzene boiling up to 180°C, which was produced by a synthesis and polymerization, and of a benzene which boiled up to 150°C, with following polymerization. Of all three products, Table XXXVIII shows the density, the olefin content, the boiling point characteristics, and the vapor pressure at 37.8°C. as well as the octane number.

Table XXXVIII
Influence of an Additional Polymerization Upon the Properties of Benzene Obtained in the Middle-Pressure Synthesis with Iron Catalysts

No.	$d_{15°}$	Boiling Point Characteristics					$P_{37.8°}$	Octane No.
		Olefin percent	Beginning °C.	10% °C.	50% °C.	90% °C.		
1	0.696	64	30	46	83	145	0.54	61
2	0.705	65	32	53	100	150	0.48	67
3	0.700	65	34	60	95	130	0.55	71

With the additional polymerization of the olefins (Table XLVIII No. 1) an octane number of 61 was obtained, with polymerization, the octane number was 67 (No. 2). When the benzene was cut off at 150°C, (No. 3), then it had an octane number of 71.

When 0.7 cc. of lead tetra-ethyl was added to each liter of benzene (No. 2), the octane number could be raised to 79, when the same amount of lead tetra-ethyl was added to the benzene (No. 3), the octane number was 80.

Conclusion

A survey was made of the work carried out on the middle-pressure synthesis with iron catalysts. First we discussed the precipitation, alkalization, and induction of the catalyst. Secondly, we were concerned with finding the most favorable synthesis conditions (gas composition, pressure, temperature, additions, regeneration, etc.). Thirdly, we discussed the reaction products and lastly, we discussed the general problem of synthesis gas production, apparatus constructions, pelleting of the catalyst, and further processing of the primary products.

The most important results of all the investigations are as follows:

1. Precipitation of the Iron Catalyst. Generally, the catalysts were precipitated by treating ferric nitrate solutions with sodium carbonate or ammonia. The ferric nitrate solutions were separated by dissolving technical iron in dilute nitric acid. The catalysts which were prepared from ferric solutions were superior to those prepared from ferrous solutions.

2. Alkalization of the Catalysts. The presence of alkali is not required for the synthesis, and is of no importance to the yield. The addition of alkali in increased quantities, however, causes the formation of higher molecular weight hydrocarbons. In the production of paraffins, therefore, the addition of alkali is important. In general, we used potassium carbonate. However, other alkali salts produced the same effects.

3. Induction of the Catalyst. In order to produce an active catalyst it is necessary to carry out an induction with CO-rich gases or better still with pure CO. The induction is carried out at pressures which are below those of the synthesis, as for example, atmospheric pressure. It was found, however, that reduced pressures are still more favorable.

The gas used for the induction, in order to get the best results, should be conducted over the catalyst surface at a high velocity and at temperatures of over 250°C., preferably between 300 and 350°C. This should be continued up to a point where the formed CO_2 reaches a more or less constant minimum value.

4. The Synthesis. The optimum ratio of CO-H_2 in the synthesis gas was found to be 3:2. The optimum synthesis pressure was found to be between 10 to 20 atmospheres. The optimum synthesis temperatures were found to be between 230 and 240°C. The catalysts are able to convert the synthesis gas at considerably

lower temperatures already from the very beginning. However, this is unfavorable for the lifetime of the catalyst. Neither are temperatures above 280°C, recommended for the beginning (on account of carbon formation).

The addition of kieselguhr (after alkalization) causes a considerable increase in catalyst activity.

Hydrogen treatment of the catalyst prior to the synthesis shows no advantages. However, a hydrogen treatment given repeatedly between syntheses causes a regeneration and reactivation of the iron catalyst.

5. Optimum Yields. The best solid, liquid, and gasol hydrocarbons were found to be somewhere near 150 g. per normal cubic meter of ideal gas. The longest lifetime was found with a catalyst which still gave 140 g. per normal cubic meter after 1-1/2 years of operation at a temperature of 260°C, without any kind of regeneration.

6. Reaction Products. The nature of the reaction product can be varied within wide limits according to the working conditions.

Five to 50 percent of the total solid and liquid hydrocarbons consisted of paraffins. Not only low-melting paraffins are obtained, but especially high-melting ones with a melting point above 125°C, were discovered.

The liquid reaction products differ from those of the cobalt catalysts in that they contain a greater percentage of unsaturated hydrocarbons as well as a greater quantity of synthol-like products. These, for example, contain alcohols and esters of various size molecular weight.

The octane number of the stabilized benzene cut off at 180°C, is 60 to 63. When the synthesis is coupled with the following polymerization, the unsaturated gasol hydrocarbons may be polymerized and the octane number may be raised by 10 points, and by the addition of 0.7 cc. of lead tetra-ethyl per liter of benzene, an additional increase of 10 points can be obtained.

Ten to 30 percent of the solid, liquid, and gasol hydrocarbons consist of gasol. Its contents of olefins amounts up to 80 percent. Increase in temperature or catalyst activity causes an increase in total gasol yield, also a lowering in their olefin content, however.

Furthermore, we found that the iron catalysts are capable of producing an acceptable city gas at 10 atmospheres working pressure.

7. Synthesis Gas Production. The production of a synthesis gas containing CO and H_2 in the ratio of 7:2 may be accomplished by the interaction of CO_2 and steam in the water-gas generator. The necessary CO_2 is furnished by the synthesis itself. Furthermore, it is possible to produce a useful synthesis gas by gasification of coke or coal with oxygen.

8. Apparatus Details. We discussed the relationships between apparatus details and the lifetime and effectiveness of the catalyst. The best results are obtained in horizontal respectively slightly inclined reaction tubes. If it is desired to cool the reaction vessels with water, they have to be strong enough to withstand a steam pressure of 30 to 50 atmospheres.

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