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III. SYNTHESIS REACTION

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RUHRCHEMIE SYNTHESIS PROCESS

The synthesis process has been carried out under:

Ruhrchemie  
Process

- (a) atmospheric pressure
- (b) under seven atmospheres

and the subsequent material in this section has been subdivided accordingly. The atmospheric pressure work represented by far the larger part of the commercial experience, and as a consequence the discussion of the atmospheric pressure work will be found to be much more complete than that of the seven atmospheres pressure work.

The synthesis gas was converted into hydrocarbons by passage over a catalyst at 350-400°F. (175-200°C.)\*, and under pressures from one to ten atmospheres. The synthesis step has been carried out in two stages, in order to obtain a sufficiently high conversion that the tail gases could be discarded without large losses of carbon monoxide. The catalyst used was cobalt precipitated upon kieselguhr together with a promoter. At first, thoria was used exclusively as the promoter,

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\* All temperatures given in this section refer to temperatures calculated from the steam pressure on the cooling system.



but later the thoria was gradually replaced by magnesia until it now appears that the thoria may be entirely eliminated.

The contact chambers for the synthesis reaction were equipped with water-cooled pipe systems for the purpose of removing the heat of reaction. The cooling system was under pressure and connected to a steam accumulator fitted with the auxiliary equipment of the ordinary steam boiler. The catalyst was charged through the top of the chamber and rested on hinged screens which could be lowered in order to remove the spent catalyst. Gas was supplied to the chamber from the top and flowed downward through the chamber. Details of the two types of chambers will be found in the Appendix.

The operations involved in carrying out the synthesis reaction at atmospheric pressure are schematically presented in the form of a flow sheet in Figure III. The various pieces of equipment have been labeled and all the available material quantities have been given on the flow sheet, starting with the raw materials--coke and water--and ending with the finished materials--oil and water. The drawing appears largely self-explanatory,

Flow Sheet  
Atmospheric  
Pressure  
Operation

Figure III

and consequently only a brief outline of the operations will be given here.

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Water gas was made from coke in the usual operating sets, was cooled in a water scrubber, passed through a blower and then through iron oxide (Luxmasse) towers to remove hydrogen sulfide. The gas was then preheated to 390-570°F. (200-300°C.) and passed through towers containing a contact (67% Luxmasse, 33% soda) to remove organic sulfur compounds. The purified gas was split into two streams, one of which was heated to 900°F. (490°C.) and passed over a catalyst, together with steam, to convert a part of the carbon monoxide into carbon dioxide and hydrogen. After the passage of one gas over the catalyst, the two streams were reunited. The hydrogen to carbon monoxide ratio in the original gas was 1.25:1.0 and this was changed to 2:1 by the above conversion.

The gas then passed to the first stage synthesis reaction chambers, in which a carbon monoxide conversion of about 70% and a gas contraction of about 60% were obtained. The products and unconverted synthesis gas were discharged from the reaction chamber to a direct contact water cooler and the gaseous material from the latter was passed through charcoal adsorbers. The gas from the charcoal adsorbers was sent through the second stage synthesis reaction chambers where an additional carbon monoxide conversion of

21% and gas contraction of 38% were obtained. The materials leaving the second stage chambers were given the same treatment as first described for those from the first stage chambers, with the difference that the hydrocarbon adsorption on the charcoal was much more nearly complete.

The cycles on the charcoal adsorbers were as follows:

<u>Operation</u>	<u>Time - Minutes</u>	
	<u>First Stage</u>	<u>Second Stage</u>
Adsorption	40	20-60
Steam purge	20	20
Drying (hot tail gas - 1500 m <sup>3</sup> /hr.)	20	20-40
Cooling (cold tail gas)	20	20-40
Total	100	120

The exit gas from the final charcoal adsorption was burned as fuel, since it contained only about 6% carbon monoxide and about 10% hydrogen.

The catalyst depth in the atmospheric pressure chambers was eight feet (2.5 meters). This depth was determined primarily by restrictions on the size of the chambers imposed by the profile of the German railways. It was thought, from an operational standpoint, that the depth could have been as much as 16 feet (5 meters) but not greater, since there then would have been an insufficiency in cooling surface in the top section of the chamber.

Catalyst  
Depth



Pressure  
Drop

The normal pressure drop through the atmospheric chamber amounted to 2-6 inches (50-150 mm.) of water when the chamber was filled with catalyst 2-3 mm. in size. The pressure drop was independent of the age of the catalyst and was not affected by solid paraffins on the catalyst. The greatest variation in pressure drop was caused by variation in the size of the catalyst particles. There was a very small difference in pressure drop from beginning to end of the operation due to the somewhat greater gas volume at the higher temperature used near the end of the operation.

Ruhrchemie had 52 atmospheric pressure contact chambers at Holten, 49 of which were in operation on the average. The number of ovens not in use therefore averaged three, which represented six per cent of the total. On the average, 36 ovens were used in the first-stage and 13 ovens used in the second-stage.

The usual commercial practice will be emphasized in this section, although variations from the normal practice will be mentioned. Each of the various steps involved in the procedure will be described individually, the order of discussion being that of a chronological history of a freshly reduced catalyst charge.

Atmospheric  
Pressure  
Procedure

A number of the individual operations were similarly performed regardless of the pressure. Others, more particularly the actual technique involved in carrying out the synthesis reaction, were carried out differently under pressure.

Ordinarily, four synthesis chambers were combined into a block fitted with a common steam accumulator. It was the usual custom at Holten to use three of the chambers in a block as first-stage chambers, that is, supplied with fresh synthesis gas; and in the fourth chamber to use gas from the three first-stage chambers. From an operational standpoint there was no preference whether two, four or six chambers were connected to one steam accumulator.

A thin metal frame was placed around the top of an open synthesis chamber and the air displaced from the

Charging  
of Catalyst

frame and chamber by carbon dioxide. The reduced catalyst was brought above the chamber in a transport vessel and allowed to flow out of the transport vessel onto the top of the chamber inside the frame. The catalyst flowed freely and readily filled the free space in the contact oven. When the chamber was almost filled, the final distribution of the catalyst was made by means of small rakes. Care was taken that none of the catalyst was above the cooling surface of the chamber. The cover was placed on the filled chamber and made gas-tight by means of bolts around the outer edges. The oven was then flushed with nitrogen and was ready for use. Five hours were required to fill the chamber with catalyst and replace the covering. Each chamber had a capacity of 350 cu.ft. (10 cu.m.).

The chamber was heated to the reaction temperature-- 320°F. (160°C.)--by the circulation of hot water through the cooling tubes of the chamber. This required from 2-3 hours. At 320°F. (160°C.), the synthesis gas was passed over the catalyst at a rate of 21,000 cubic feet (600 cubic meters) per hour. If reaction occurred, the gas rate was brought to 49,000 cubic feet (1400 cubic meters) per hour within a short time. If no reaction

Starting  
Synthesis  
Gas Over  
Fresh  
Catalyst

occurred, the hot water circulation was continued until such a temperature was reached that the reaction occurred.

The gas used for starting a fresh catalyst was tail gas from first-stage chambers. When it was necessary to start the new chamber with fresh synthesis gas, the initial gas rate was still 21,000 cubic feet (600 cubic meters) per hour, but subsequent increases in the gas rate were made much more slowly. Ordinarily the tail gas from the first-stage was used over a fresh catalyst for 2-3 days at the rate of 49,000 cubic feet per hour. At the end of this time the tail gas could be replaced by fresh synthesis gas at the rate of 42,000 cubic feet (1200 cubic meters) per hour. Tail gas was used to start the fresh catalyst because, being less reactive, sudden temperature increases were minimized. Another advantage in the use of tail gas with a fresh catalyst was that less sulfur was present than in the fresh synthesis gas. Apparently the fresh catalyst was much more susceptible to sulfur poisoning than the catalyst which had been in use for a few days.

A constant conversion of 65% of the carbon monoxide was maintained in the first-stage. This corresponded to a gas contraction of 57%, which was determined by measurement of the carbon dioxide concentration entering and

Operation  
Atmospheric  
Pressure

First-Stage  
Operation

leaving the chamber.

A throughput of 42,000 cubic feet (1200 cubic meters) per hour was maintained through a chamber for a total of about 1800-2000 hours. After a few days, the catalyst activity had decreased slightly and to compensate for this the temperature was raised one to two degrees in order to maintain constant the 65% conversion of carbon monoxide. The temperature was slowly increased with time to maintain the conversion until a temperature of 392°F. (200°C.) had been reached. This phase of the operation usually lasted about 1000 hours. When the maintenance of the 65% conversion of carbon monoxide would have required a temperature higher than 392°F. (200°C.), the synthesis gas was stopped and the catalyst treated with hydrogen for about ten hours at about 400°F. (205°C.). The hydrogen treatment partially restored the activity of the catalyst so that 42,000 cubic feet (1200 cubic meters) of synthesis gas per hour could be passed over the catalyst and the 65% conversion obtained at a temperature well below 392°F. (200°C.). The conversion was again held constant by increasing the temperature from time to time until a temperature of 392°F. (200°C.) was again reached. This second phase occupied about 800 hours. The hydrogen treatment was then repeated. Following the second hydrogen treatment, the conversion could be maintained at 65% for about 200 hours at a gas rate of 42,000 cubic feet (1200 cubic meters) per hour at temperatures not exceeding 392°F. (200°C.). When the conversion began to fall off at

392°F. (200°C.) at a gas throughput of 42,000 cubic feet (1200 cubic meters) per hour, the gas rate was gradually decreased at such a rate that the conversion of 65% was maintained at 392°F. (200°C.). When the gas rate had fallen to 28,000 cubic feet (800 cubic meters) per hour, the conversion was maintained at 65% by gradual increase in the temperature to 400°F. (205°C.).

When the carbon monoxide conversion fell below 65% at 400°F. (205°C.) at a gas rate of 28,000 cubic feet (800 cubic meters) per hour, the chamber was taken out of operation and the catalyst removed. The average gas rate over the whole catalyst life period was 35,000 cubic feet (1,000 cubic meters) per hour of ideal gas.

The life of the catalyst after the second hydrogen treatment averaged about 1000 hours, for a total life of 3000 hours. The yields of hydrocarbons could have been increased by more frequent hydrogen treatments, but the additional time lost would have offset the increase in yield.

A partial revivification of the catalyst could be accomplished in situ, by means of:

Intermediate  
Revivification

1. Treatment with hydrogen, or
2. Treatment with oil solvent

Ordinarily, the intermediate revivification of the catalyst was done with hydrogen at Holten, although experiments made there indicated some advantages to the use of the solvent treatment. It was planned in future installations to make provisions for solvent treating the catalyst. The lack of suitable equipment on the synthesis chambers at Holten was the reason given for not using the solvent method of revivification.

The chamber was heated to 400-410°F. (205-210°C.) and hydrogen passed over the catalyst at the rate of about 53,000 cubic feet (1500 cubic meters) per hour. The hydrogen was recirculated at the above rate, 5000-7000 cubic feet (150-200 cubic meters) per hour of fresh hydrogen being added.

Hydrogen  
Treatment

The hydrogen used at Holten was the exit gas from the catalyst reduction plant, although the hydrogen could be taken from the carbon monoxide conversion plant. In the latter instance it would have been

necessary to reduce the carbon monoxide conversion. This could be accomplished by passing the gas together with steam over nickel catalysts at a temperature of about 350°F. (175°C.).

The hydrogen revivification of the catalyst required 10-12 hours. About one-half of the wax contained on the catalyst was converted to methane by the hydrogen treatment. The hydrogen revivification was considered complete when the methane formation had ceased. The gas led off from the recycle stream in the hydrogen revivification was added to the synthesis tail gas.

It may be of interest to note in this connection that Ruhrchemie regard the synthesis catalyst as a cracking catalyst in the presence of hydrogen. Their conclusion was based on the following observations:

1. The carbon on the catalyst as carbides could account for only about 20% of the methane formed.
2. The yields of wax obtained when the catalyst was solvent treated were about twice those obtained when the catalyst was hydrogen treated.
3. Lower molecular weight oil products were obtained in the hydrogen treatment than in the solvent treatment.

In contradiction to the above conclusion, a temperature



increase was noticed when hydrogen was introduced, which indicated an exothermic reaction. The cracking reaction was endothermic and the only probable exothermic reaction was the hydrogenation of the carbides. Also, the formation of the methane took place at the same temperature at which the catalyst had previously been used for the production of oil. It is difficult to understand how the relatively slight change in the partial pressure of the hydrogen could have had such a profound effect upon the initiation of the cracking reaction.

The synthesis chamber to be revived was cooled down to 250°F. (120°C.) and light naphtha from the synthesis plant (endpoint 280°F. (140°C.)) was distilled into the oven. The naphtha condensed on the catalyst and dissolved and washed off the wax and a part of the resinous material. The overall yields of hydrocarbons could be increased from one to two grams per cubic meter of synthesis gas by using this solvent treatment in place of the hydrogen treatment.

Solvent  
Treatment

The gas throughputs to second-stage chambers were somewhat higher than those to the first-stage chambers, being on the average 50,000 cubic feet (1,400 cubic meters) per hour of gas from the first-stage chambers. The second-stage chambers were not given a hydrogen treatment during their four months use. The reason given for

Second-Stage  
Operation

omitting the hydrogen regeneration was that the large quantities of inert gases in the partially used synthesis gas served to keep the catalyst clean. An additional reason was that the passage of the gas through the first-stage chambers removed all sulfur compounds and probably a large part of the tar-forming compounds from the synthesis gas.

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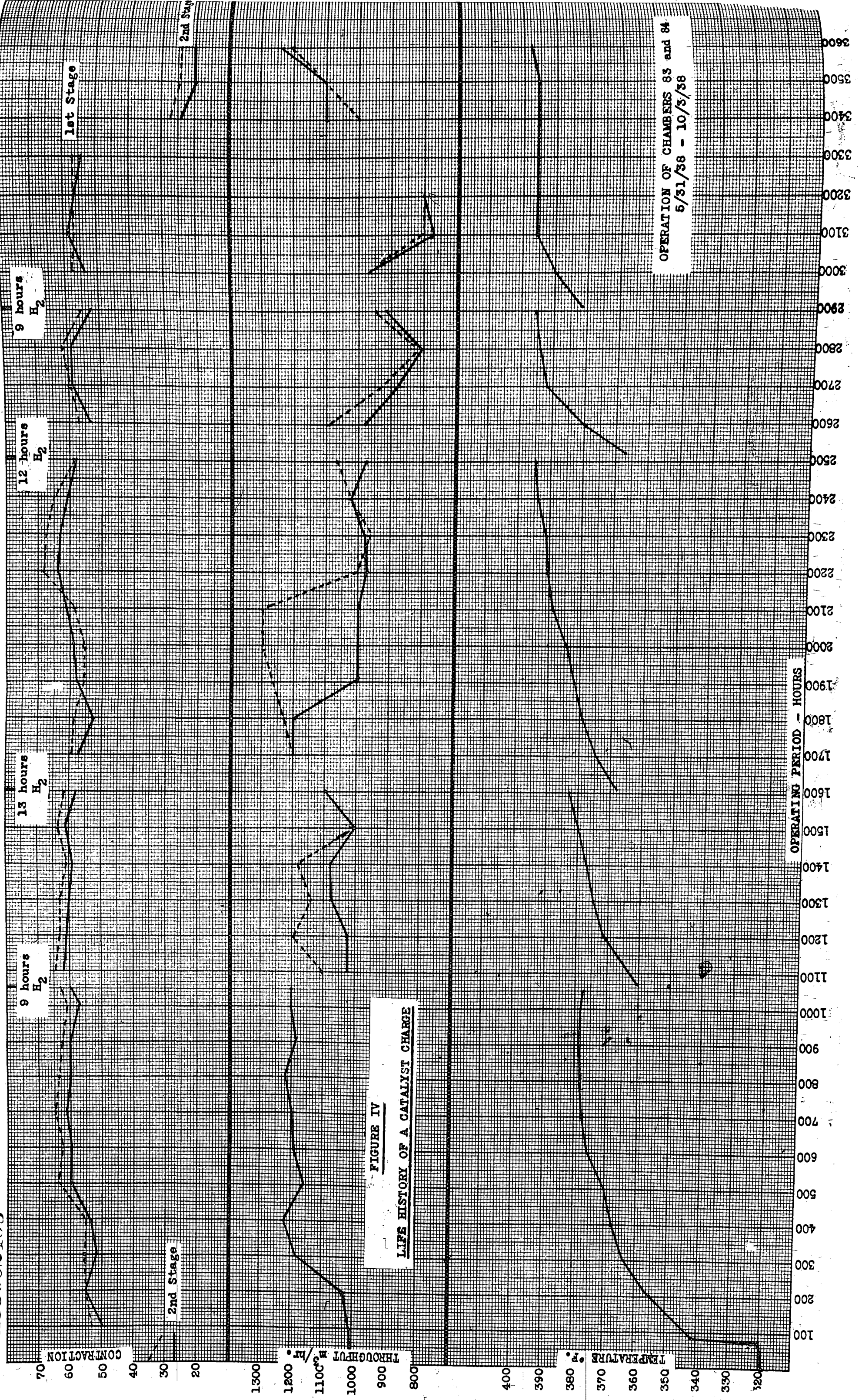


FIGURE IV  
LIFE HISTORY OF A CATALYST CHARGE

The curve opposite shows a plot of temperature, gas throughput and contraction versus time for the life period of the catalyst. At the start, the chamber was used in the second-stage for a period of about 75 hours and was then placed in the first-stage and used uninterruptedly for 975 hours. It was then regenerated by treatment with hydrogen for nine hours and used again in the first-stage for an additional 500 hours. It was regenerated again with hydrogen for 12 hours and again used in the first-stage for an additional 800 hours. It was treated with hydrogen a third time for 13 hours, used first-stage 300 hours, regenerated with hydrogen for nine hours, and used 300 hours first-stage. It was then transferred to the second-stage for 200 hours at the end of which time the catalyst was removed.

This particular example was switched to the second-stage much later than usual. The times that the chamber was used in the first or second stages, and the points at which the hydrogen treatments were made, were dependent upon the operational program of the plant as a whole rather than upon the requirements of a particular chamber. The object was to prevent interruptions in the quantity of gas

Figure IV

Life History  
of Catalyst  
Charge

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used and in the amount of oil produced in the entire plant. As a rule, four ovens were removed from operation at one time and four new ovens put in operation.

The spent catalyst contained large quantities of solid paraffins, up to amounts equivalent to the weight of the catalyst. It was not only economical to recover the solid paraffins for their own value, but the subsequent extraction of the catalytic metals from the kieselguhr was greatly facilitated by the removal of the solid paraffins. The weight of solid paraffins on the spent catalyst was always decreased from about 100% to at least 25% before the digestion of the catalytic materials was attempted. The solid paraffins could be removed from the catalyst by treatment in any of the following ways:

1. Hydrogen treatment at 410°F. (210°C.)
2. Treatment with synthesis gas at a temperature of 415°F. (213°C.)
3. Treatment with a mixture of synthesis gas and hydrogen at a temperature of 415°F. (213°C.)
4. Treatment with steam at 840°F. (450°C.)
5. Treatment with light naphtha at 250°F. (120°C.)

The hydrogen treatment has already been described in some detail under the heading intermediate re-vivification and will not be repeated here. This hydrogen treatment, of course, only removed the solid

Paraffin  
Removal  
from  
Spent  
Catalyst

Hydrogen  
Treatment

paraffins and left the catalyst still pyrophoric. The deactivation procedure depended upon the composition of the catalyst.

For synthesis gas treatment, the steam valves were closed while still passing synthesis gas over the catalyst and the chamber allowed to heat up until a temperature corresponding to a steam pressure of 19 atmospheres on the cooling system was reached. This temperature was maintained for about one day. This treatment simultaneously deactivated the catalyst and freed it largely from wax. Larger amounts of methane were produced than in the hydrogen treatment but the excess methane was produced from the synthesis gas so that no net loss of oil occurred. The exit gases from this treatment were added to the synthesis tail gas.

Synthesis  
Gas  
Treatment

The combined hydrogen and synthesis gas treatment was used for the thoria catalysts, since substantially complete removal of the solid paraffins could not be accomplished by either treatment alone. Only enough synthesis gas was added with the hydrogen to maintain a thermal balance at a temperature corresponding to 19 atmospheres steam pressure in the cooling system

Hydrogen and  
Synthesis  
Gas Treatment



The steam treatment had to be made at temperatures of 750-930°F. (400-500°C.) and was very effective, especially in the instance of the thoria catalyst. This treatment, however, was not generally used at Holten due to the fact that it could not be carried out in the synthesis chambers themselves, which would not withstand the high temperatures. The spent catalyst received from licensees, containing all the solid paraffins that were present on the catalyst at the time it was taken out of operation, was subjected to the steam treatment. The spent, waxy catalyst was pressed into egg-size pieces and charged to a tower where 840°F. (450°C.) steam could be passed over the catalyst. The steam treatment not only removed the solid paraffins from the catalyst but also deactivated the catalyst sufficiently to render it no longer pyrophoric.

Steam  
Treatment

The treatment with solvent was the same as that described under the heading, "Intermediate Revivification".

Solvent  
Treatment

The catalyst was still pyrophoric after the solvent treatment and had to be deactivated before digestion.



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Catalyst  
Removal  
from  
Chamber

After the removal of the solid paraffins by any of the various treatments described, the steam pressure on the cooling system of the chamber was reduced to atmospheric pressure and the chamber allowed to cool. The chamber was then flushed with nitrogen or carbon dioxide, the latter preferably, and the catalyst was removed. A screw-type conveyor was attached to the bottom trough of the chamber, and the chamber flaps lowered, whereupon the catalyst ran out of the chamber in about 90% of the instances. When the catalyst failed to run out, the chamber was reclosed and treated with hydrogen at a higher temperature, and then the dumping operation again attempted. A stream of carbon dioxide was directed onto the catalyst on the conveyor and into the transport vessel into which the catalyst was being transferred. When all the catalyst had been transferred, the transport vessel was closed and sent immediately to the catalyst factory.

The life of the catalyst was defined as that length of time over which an accumulative yield amounting to an average of 120 grams of oil per cubic meter of synthesis gas was obtained. At atmospheric pressure the catalyst had a life in the commercial plant of about four months.

Life of the Catalyst

The life of the catalyst was regarded as primarily a function of time and temperature and not of the liquid produced. Ruhrchemie regarded resin formation as being probably the chief limiting factor in the life of the catalyst. The resin formation was itself dependent upon the quantities of tar-forming substances in the synthesis gas. Consequently, the life of the catalyst would only be related to the quantity of liquid made insofar as the quantity of gas that passed over the catalyst was related to the liquid formed.

From analyses of the spent catalyst, it was evident that under the conditions used at Holten the sulfur in the synthesis gas was not responsible for the inactivation of the catalyst. The sulfur present on the spent catalyst depended upon the source of the synthesis gas:

Sulfur on Spent Catalyst

<u>Source of Synthesis Gas</u>	<u>% Sulfur in Spent Catalyst</u>
Cracked Gas	0.05
Coke	0.5
Brown Coal	3.0

The sulfur on the spent catalyst also varied with the catalyst composition. Using synthesis gas prepared from coke, a spent thoria catalyst contained 0.4% sulfur, while a mixed thoria-magnesia catalyst contained 0.08-0.1% sulfur. The sulfur in the spent catalyst was lost in the regeneration process as sodium sulfate, so that no special treatment was necessary for its removal.

It was thought that the life of the present catalyst was too short for the sulfur to have any bearing upon the life, but in the event that the tar-forming material in the synthesis gas could be entirely eliminated, it was thought that the life of the catalyst might be sufficiently prolonged that the sulfur deposition on the catalyst would become the controlling factor in the catalyst life.

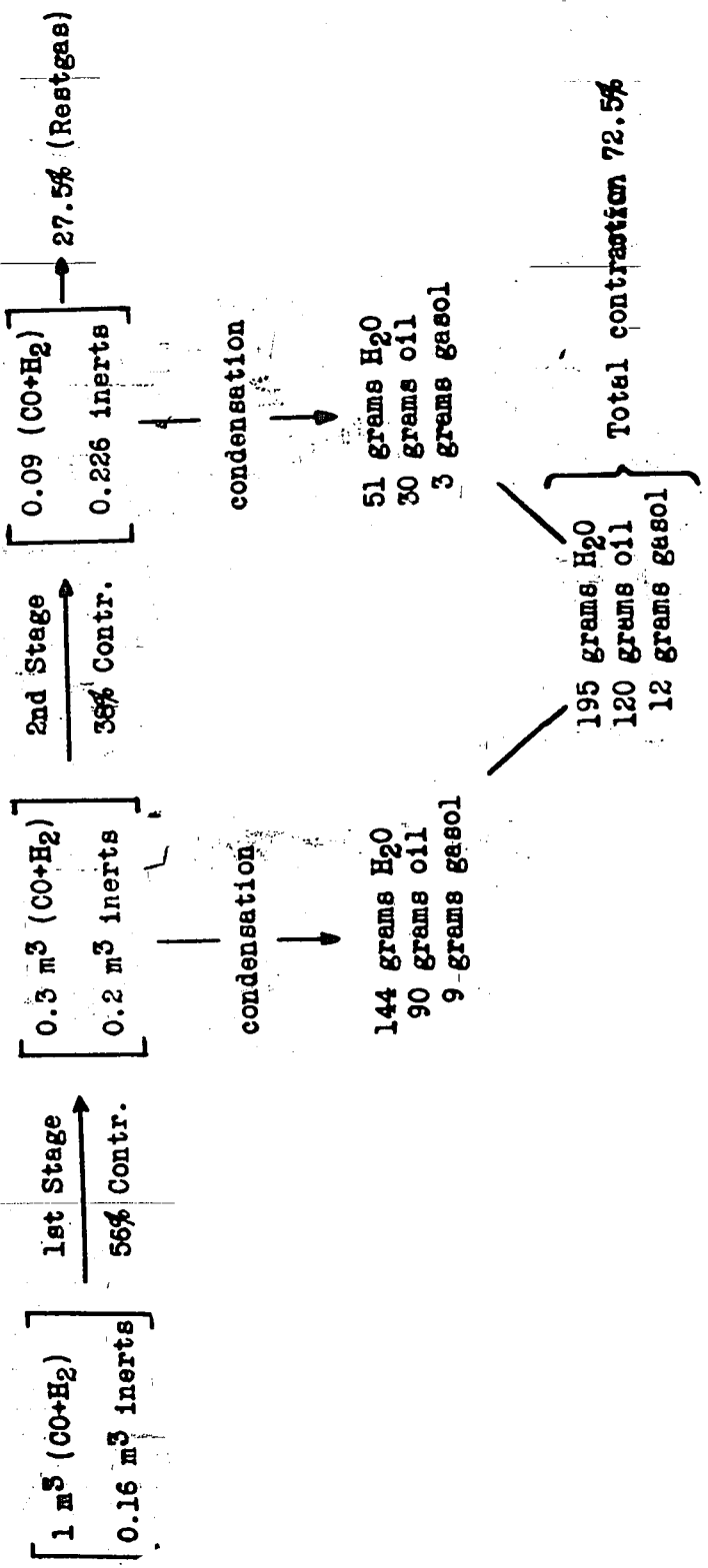
A chamber was out of use for 3.5 days for each four month period, inclusive of solid paraffin extraction, cooling, opening, dumping the catalyst, refilling and returning to production. The solid paraffins were removed, on the average, 2-1/2 times in a four month period, 10-12 hours required for each extraction. About 3% off-time was necessary but at

Chamber  
Off-Time  
Period

FIGURE VI

SCHMATIC FLOW SHEET FOR SYNTHESIS AT

ATMOSPHERIC PRESSURE



about 250 B.T.U. per cubic foot (2000 WE).

The overall yield of oil (two-stage operation) at atmospheric pressure averaged about 120 grams per cubic meter of synthesis gas. In addition, 12 grams per cubic meter of gasol ( $C_3$  and  $C_4$  hydrocarbons) were obtained. The yield of liquid hydrocarbons from the first-stage operation was about 90 grams per cubic meter together with about nine grams gasol per cubic meter. The yield of liquid hydrocarbons from the second-stage operation was about 30 grams per cubic meter, together with three grams of gasol per cubic meter, these yields being based on the ideal synthesis gas entering the first-stage. The yields are shown schematically in Figure VI opposite.

Figure VI

The oil production per ton of cobalt for the life of the catalyst was therefore the same for the first-stage chamber as for the second-stage chamber. At atmospheric pressure, the average gas throughput per chamber per hour was 25,600 cubic feet (725 cubic meters). This throughput together with the above yield would correspond to a production of 43 gallons of oil per pound of cobalt (255 tons of oil per ton of cobalt) per lifetime of the catalyst.

The hydrocarbon products were roughly separated into three groups:

Products

1. Methane
2. Gasol (C<sub>3</sub> and C<sub>4</sub> hydrocarbons)
3. Liquid products containing all material above pentane.

The liquid products were further separated into gasoline, kerosene, Diesel oil, gas oil and wax.

The hot synthesis products, together with the residual gases were discharged from the contact chambers to cooling washers, wherein the products were contacted directly with a spray of cooling water. The cooling washers were lined with acid-proof brickwork and packed with acid-resistant stoneware rings. The cooling water was recirculated, only enough fresh water being added to maintain the acidity of the stream below the point at which corrosion of pipe lines would set in. The acidity of the cooling water could also be regulated by the addition of alkali. The pumps, pipe lines and the cooling device for the recirculated cooling water were advisedly made from acid-resistant material.

Separation  
of Products  
Atmospheric  
Pressure

Water  
Cooler

About 70% of the acidic compounds in the cooling water was acetic acid, the remainder being organic acids of higher molecular weight.

The hot synthesis gases and products were cooled to about 75-85°F. (25-30°C.), whereby the heavy synthesis products were condensed. The condensed hydrocarbons had an initial boiling point of about 265°F. (130°C.) and included all the hydrocarbons with a boiling point higher than 340°F. (170°C.). This represented about one-half of the total hydrocarbon product.

The separation of cooling water from oil was accomplished in aluminum lined tanks or in pits lined with acid-resistant brickwork. The separation took place very quickly and consequently small vessels could be used.

The gases leaving the water coolers at about 75°F. (25°C.) were passed through towers of active charcoal to recover the lower boiling hydrocarbons. The recovery of the normally liquid hydrocarbons was substantially complete after passage of the gases over the active charcoal. In addition, the recovery of the gasol ( $C_3$  and  $C_4$  hydrocarbons) was about 90%. The

Charcoal  
Absorption

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TABLE II

PROPERTIES OF PRODUCTS FROM ATMOSPHERIC  
PRESSURE SYNTHESIS

Distillation of Total Product (except gasol):

I.B.P.	95-104°F.	(35-40°C.)
5% (by weight)	114	(46)
10	134	(57)
20	175	(80)
30	218	(103)
40	266	(130)
50	320	(160)
60	379	(193)
70	447	(231)
80	525	(274)
90	624	(329)
94	680	(360)

Gasol: About 12% of total liquid hydrocarbon product

40% C<sub>3</sub> - 60% C<sub>4</sub>

Properties of Individual Fractions:

	<u>Gasol</u>	<u>Gasolene</u>	<u>Diesel Oil</u>	<u>Paraffin</u>
Specific Gravity	-	0.693	0.765	0.90
Olefins - Vol. %	50	35	12	-
Iodine Number	-	-	-	2
Acid Number	-	0.005	0.02	-
Pour Point	-	-	48	-
Boiling Index	-	240	491	-
Octane Number-CFRR	-	44	-	-
Cetane Number	-	-	90	-
Cetene Number	-	-	103	-



operation of the charcoal absorption system will be described in connection with the apparatus.

The tabulation opposite, Table II, shows the distillation range of the total normally liquid hydrocarbon product from atmospheric pressure operation. As is evident from the tabulation, about 63% of the total oil boiled in the gasolene range, about 25% in the Diesel oil range and the remainder above 608°F. (320°C.). The properties of these fractions are given in the latter part of the tabulation opposite.

Table II  
Atmospheric  
Pressure  
Product  
Characteristics

Due to the low octane number of the 392°F. (200°C.) end point gasolene, this fraction was further divided into a light naphtha--60 octane number (CFRR) for end point of 293°F. (145°C.)--and a heavy naphtha with a very low octane number. The light naphtha had only to be stabilized and blended with cracked gasolene or other material with a high octane number. The heavy naphtha had to be reformed before it could be used as gasolene.

FIGURE VII

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OCTANE NUMBER OF GASOLENE PRODUCED AT ATMOSPHERIC PRESSURE  
AS RELATED TO END-POINT AND TO WEIGHT PERCENT  
OF TOTAL PRODUCT

Ruhrbenzin A.G.  
ZM. 106/16

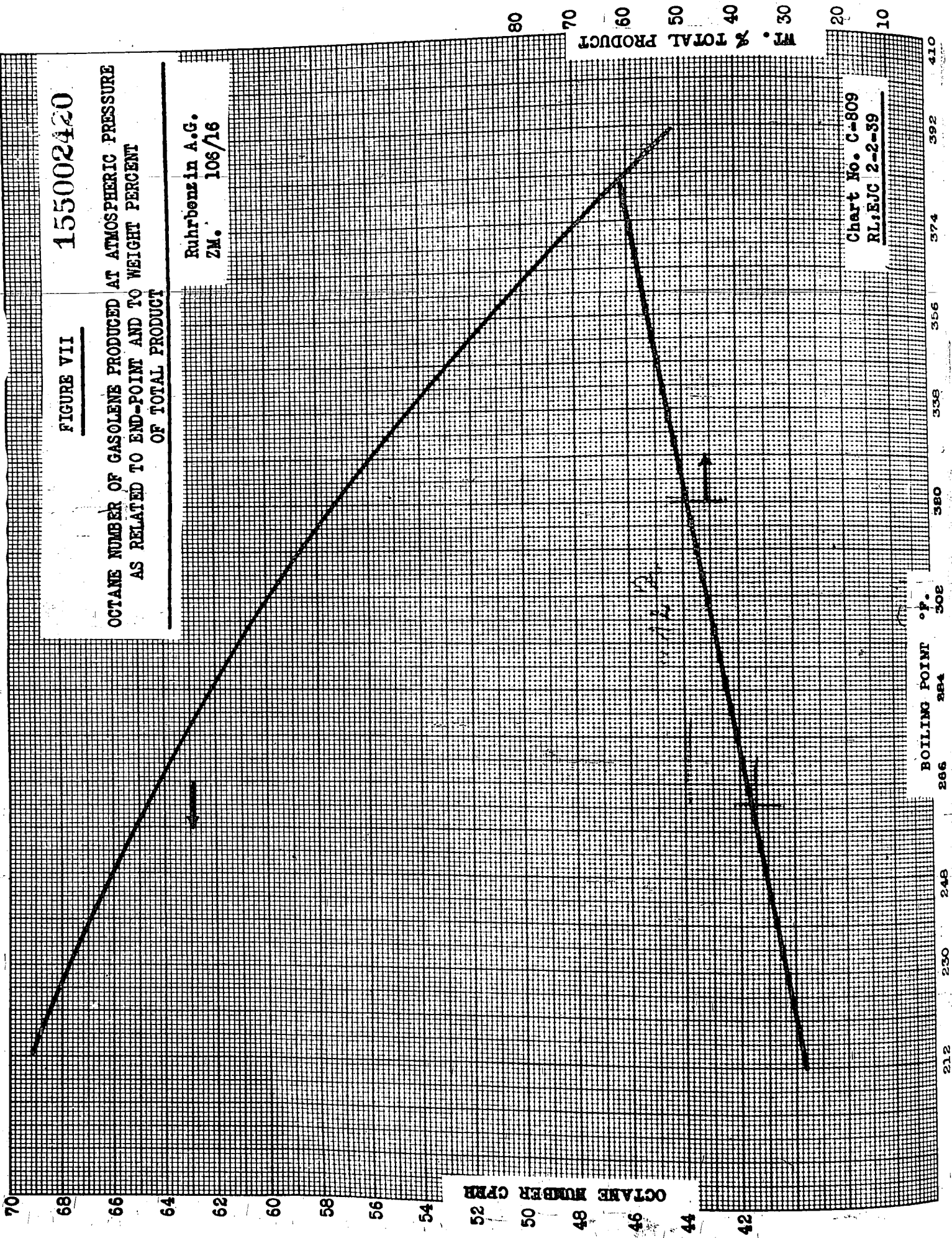


Chart No. C-809  
RL,EJC 2-2-39

The relation of the octane number to the end point of naphtha produced at atmospheric pressure is shown on Figure VII opposite. A second curve on Figure VII shows the relation of end point to weight per cent of the total hydrocarbon product. It can be seen that about 45% of the total product could be obtained as a light naphtha with an octane number of 60 CFRR.

The Diesel oil fraction had a cetene number from 90-100 and was thus superior to average gas oils. This fraction was used to blend with inferior Diesel oils or with coal tar oils to produce a marketable Diesel oil.

The material boiling above 608°F. (320°C.) was used as a raw material for manufacture of plate paraffin with a melting point of 126°F. (52°C.) and of hard paraffin with a melting point of 185-194°F. (85-90°C.).

The gasol fraction ( $C_3$  and  $C_4$  hydrocarbons) was composed of about equal amounts of olefins and paraffins. The olefins could be polymerized to high anti-knock material and in the same operation be separated from the paraffins. The latter were bottled under a pressure of 150 to 200 pounds per square inch (10 to 15 atmospheres) and sold as liquid motor fuels for lorries or for use as household gas supply.

The following gas analyses were given:

Gas  
Analyses

<u>Constituent</u>	<u>Volume %</u>		
	<u>Entering</u> <u>First-Stage</u>	<u>Leaving</u> <u>First-Stage</u> <u>75% Conversion</u>	<u>Leaving</u> <u>Second-Stage</u> <u>20% Conversion</u>
CO	28.0	17.0	6.0
H <sub>2</sub>	55.0	32.5	10.0
CH <sub>4</sub>	0.4	8.0	17.8
CO <sub>2</sub>	13.5	35.5	55.0
N <sub>2</sub>	3.1	6.5	10.0
Olefins		0.5	1.2

cont. 35.5 %  
69.9 "

A summary of the yields and conversions obtained at atmospheric pressure is shown in the following tabulation. Succeeding tabulations show material balances and what was termed a heat balance. No further information could be obtained regarding the latter item.

Normal-Pressure Synthesis

Summary

Liquid Primary Products	120 g./Nm <sup>3</sup>
C <sub>3</sub> + C <sub>4</sub> Hydrocarbons	15 g./Nm <sup>3</sup>
CO Conversion	93% on input
CO Liquification	57% on CO input (no C <sub>3</sub> , C <sub>4</sub> )
Degree of Liquification	69% (includes C <sub>3</sub> , C <sub>4</sub> ) of CO input, i.e., 69% of transformed CO was converted into liquid primary products.

Average Hydrogen Content of Liquid Primary Products 15.2%.

155002424

(105)

(Basis: 1 cubic meter of ideal synthesis gas)

Material  
Balance

<u>Input:</u>	<u>Gram Mols</u>	<u>Grams</u>
CO	14.9	417
H <sub>2</sub>	29.8	60
	<u>44.7</u>	<u>477</u>

Products:

Liquid (excl. C <sub>3</sub> and C <sub>4</sub> )	= 120 grams (15.2% hydrogen)
C <sub>3</sub> and C <sub>4</sub>	= 15 grams
Conversion of CO	= 83%

Carbon Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In CO	14.9	179
<u>Output</u>		
In Liquid	8.45	101.7
In C <sub>3</sub> and C <sub>4</sub>	1.05	12.6
In CO <sub>2</sub>	0.46	5.5
In CH <sub>4</sub>	2.22	26.6
In Rest of Gas	2.66	32.0
	<u>14.84</u>	<u>178.4</u>

Hydrogen Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In H <sub>2</sub>	59.6	59.6
<u>Output</u>		
In Liquid	18.25	18.25
In C <sub>3</sub> and C <sub>4</sub>	2.15	2.15
In CH <sub>4</sub>	8.80	8.80
In Rest of Gas	7.50	7.50
In Reaction Water	22.60	22.60
	<u>59.30</u>	<u>59.30</u>

Oxygen Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In CO	14.9	239
<u>Output</u>		
In CO <sub>2</sub>	0.91	14.6
In Rest of Gas	2.67	42.7
In Reaction Water	11.30	181.4
	<u>14.88</u>	<u>238.7</u>

(Basis: 1 cubic meter of ideal synthesis gas,

Heat  
BalanceHeat Input:

	<u>Kg. Cal.</u>	<u>%</u>
Ht. of Combustion of CO	1,010	33.3
Ht. of Combustion H <sub>2</sub>	<u>2,032</u>	<u>66.7</u>
Total	3,042	100.0

Heat Output:

120 g liquid products/10 900 cal.	1308.0	43.0
15 g C <sub>3</sub> + C <sub>4</sub> Hydrocarbons	177.0	5.8
Tail Gas: CO:59.3 l.:131.6		
H <sub>2</sub> :84.7 l.:298.0		
CH <sub>4</sub> :49.5 l.: <u>472.0</u>	951.6	31.3
Heat Content in Vaporized Reaction Water	120.5	4.0
Heat Content in Vaporized Hydrocarbons	20.0	0.6
Heat Content of the Led-Away Steam	356.0	11.7
Sensible Heat of Tail Gas	10.9	0.4
Losses by Radiation and Transmission	<u>98.0</u>	<u>3.2</u>
	3042.0	100.0

The filling of the chamber and the starting of synthesis gas over new catalyst was done in the same manner as that described for atmospheric pressure. The synthesis reaction occurred at about the same temperature under pressure as at atmospheric pressure. The increase of the temperature with the age of the catalyst was very much slower than for the corresponding atmospheric pressure operation.

Operation  
Under  
Pressure  
Procedure

Ruhrchemie have had synthesis chambers operating under pressure for something over six months; in this time it had not been necessary to revivify the catalyst, and the temperature had not reached 392°F. (200°C.). Consequently, the life of the catalyst under pressure was not known except that it was in excess of six months, and in the six-month period no intermediate revivifications had been necessary. The explanation of the longer life under pressure was that lighter oil products were liquified on the catalyst and washed off solid paraffins and some resins.

Life of  
Catalyst

The depth of the catalyst bed in the pressure reactor was usually about 15 feet (4.5 meters), the depth being chosen solely on the basis of capital cost. The pressure chamber filled in the ordinary way with

Depth of  
Catalyst Bed



catalyst, 2-3 mm. particle size, showed at atmospheric pressure a maximum variation in resistance to gas flow of 10% from tube to tube in the chamber. This 10% variation in pressure drop through the 2,000 annular spaces in the reactor was considered indicative of uniform filling of the chamber with catalyst.

Ruhrchemie had 16 of these high pressure chambers in operation at the first of December, 1938. They had in the process of construction about 56 additional high pressure chambers for the Holten plant. A more detailed description of these chambers together with drawings will be found in the section dealing specifically with equipment.

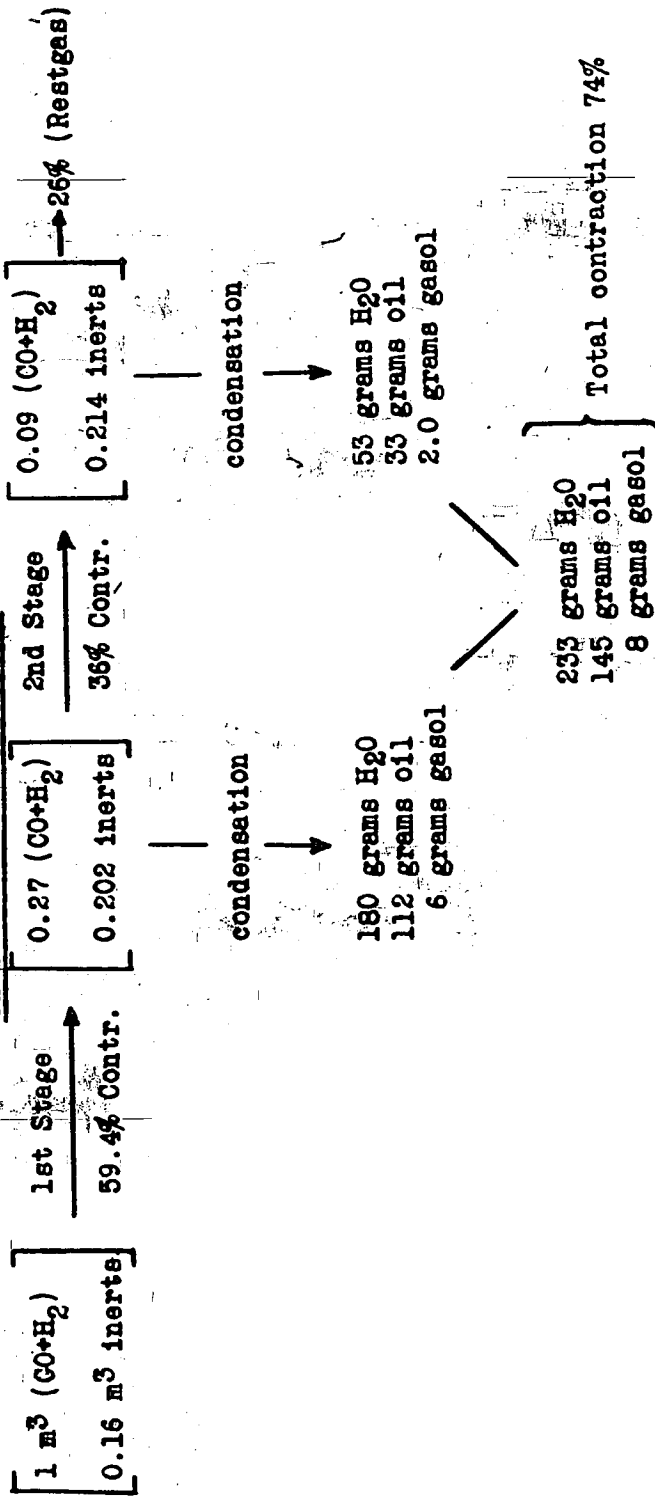
The overall yield of oil (two-stage operation) at seven atmospheres pressure was 145 grams per cubic meter of synthesis gas. In addition, eight grams of gasol ( $C_3$  and  $C_4$  hydrocarbons) per cubic meter were obtained. The yield of liquid hydrocarbons from the first-stage operation was about 112 grams per cubic meter together with about six grams of gasol per cubic meter. The yields from the second-stage under pressure were 33 grams of oil and two grams of gasol per cubic meter of synthesis gas entering the first-stage

Yields Under  
Seven  
Atmospheres  
Pressure

FIGURE VIII

SCHEMATIC FLOW SHEET FOR SYNTHESIS AT

SEVEN ATMOSPHERES PRESSURE



chamber. The yields from the pressure operation are shown schematically in Figure VIII opposite.

Figure VIII

The overall oil production under pressure per ton of cobalt may be calculated from the yield data preceding and the average inlet gas rate per chamber per hour of 26,800 cubic feet (760 cubic meters). This calculated oil production under pressure corresponded to 77 gallons of oil per pound of cobalt (484 tons of oil per ton of cobalt) per lifetime of six months. The oil production was somewhat different in the two stages, being 57 and 45 gallons per pound of cobalt (342 and 271 tons per ton of cobalt) respectively, in the first and second stages.

The products from operation at seven atmospheres pressure contained a high proportion of high boiling paraffins, so that under the influence of the pressure about 35% of the total hydrocarbon product condensed in the bottom of the reaction chamber, and was withdrawn therefrom as liquid. The fraction recovered from the bottom of the synthesis chambers had an initial boiling point of about 390°F. (200°C.).

Separation  
of Products

The hot gases and vapors from the synthesis chamber were passed through water-cooled tubular

155002430

TABLE III

PROPERTIES OF PRODUCTS FROM SYNTHESIS  
AT SEVEN ATMOSPHERES PRESSURE

Distillation of Total Product (except gasol):

I.B.P.	95-104° F.	(35-40°C.)
5% (by weight)	127	(53)
10	162	(72)
20	232	(111)
30	305	(152)
40	376	(191)
50	448	(231)
60	520	(271)
70	594	(312)
80	617	(325)
81.5	680	(360)

Gasol: About 5% of total liquid hydrocarbon product

40% C<sub>3</sub> - 60% C<sub>4</sub>

Properties of Individual Fractions:

	<u>Gasol</u>	<u>Gasolene</u>	<u>Diesel Oil</u>	<u>Paraffin</u>
Specific Gravity	-	0.690	0.765	0.90
Olefins - Vol. %	50	18	8	-
Iodine Number	-	-	-	2
Boiling Index	-	240	487	-
Pour Point	-	-	48	176
Octane Number -CFRR	-	26	-	-
Acid Number	-	0.005	0.02	1.5

condensers to separate out a middle fraction having an initial boiling point of about 280°F. (140°C.) and amounting to about 45% of the total production of liquid hydrocarbons. The products, as well as the gases, were acidic and care had to be taken to avoid corrosion. The condensing equipment could be made of alloy steel, or, more cheaply, alkali could be injected into the bottom of the reaction chamber. It was stated that 0.4 to 0.5 pounds of sodium hydroxide were required for the neutralization of one pound of reaction water (inclusive of carbon dioxide extraction).

The remainder of the normally liquid hydrocarbons, together with substantially all the gasol ( $C_3$  and  $C_4$  hydrocarbons), were recovered in an oil absorption system.

Table III opposite shows the distillation range of the total normally liquid hydrocarbon product

from the synthesis carried out at seven atmospheres pressure. It will be observed that a greater proportion of the hydrocarbons was in the higher boiling ranges when the synthesis was carried out under pressure. About 43% of the total oil boiled in the gasolene range, about 29% in the Diesel oil range,

Characteristics  
of Products  
from Pressure  
Synthesis

Table III

155002432

TABLE IV

SUMMARY OF CONDITIONS, YIELDS AND PRODUCT QUALITIES FOR THE  
COBALT-MAGNESIA-THORIA CATALYST

Pressure - atmospheres	1	7
H <sub>2</sub> : CO Ratio	2 : 1	2 : 1
Operating Temperature - °F.	364-388	356-392
Operating Period - months	4	At least 6
<u>Products in grams/m<sup>3</sup> of (CO+2H<sub>2</sub>)</u>		
CH <sub>4</sub>	32	25-27
CO <sub>2</sub>	3	1-2
Gasol	12	7-8
Oil	120	145
<u>Inspections on oil products</u>		
I.B.P. °F.	94	94
% off at 212°F.	28.5	17
392	61.5	42
608	88.5	72
<u>Fraction to 392°F.</u>		
Specific Gravity	0.693	0.69
Olefin Content - %	35.0	18
Acid Number - mg KOH/gram	0.005	0.005
Gum Content - mg/100 grams	1	less than 1

and the remaining 28% above the Diesel fraction. Thus only approximately two-thirds as much gasolene was produced as was made at atmospheric pressure, slightly more Diesel oil, and over twice as much material boiling above the Diesel oil fraction. Some of the properties of the individual fractions are shown in the latter part of the tabulation.

The actual conversion of carbon monoxide was the same regardless of the pressure under which the synthesis reaction was carried out, the difference in yields of oil being due to a greater methane production in the low pressure operation. A comparison of the conditions for, and the products from, atmospheric pressure operation and seven atmospheres pressure operation are given in Table IV opposite. In addition, the catalyst operated at atmospheric pressure contained appreciable quantities of solid paraffins. At the end of four months use, a cobalt-thoria catalyst would contain about 3300 pounds (1.5 tons) of wax per chamber, while a cobalt-magnesia catalyst would contain about 2200 pounds (one ton) of wax per chamber.

Table IV

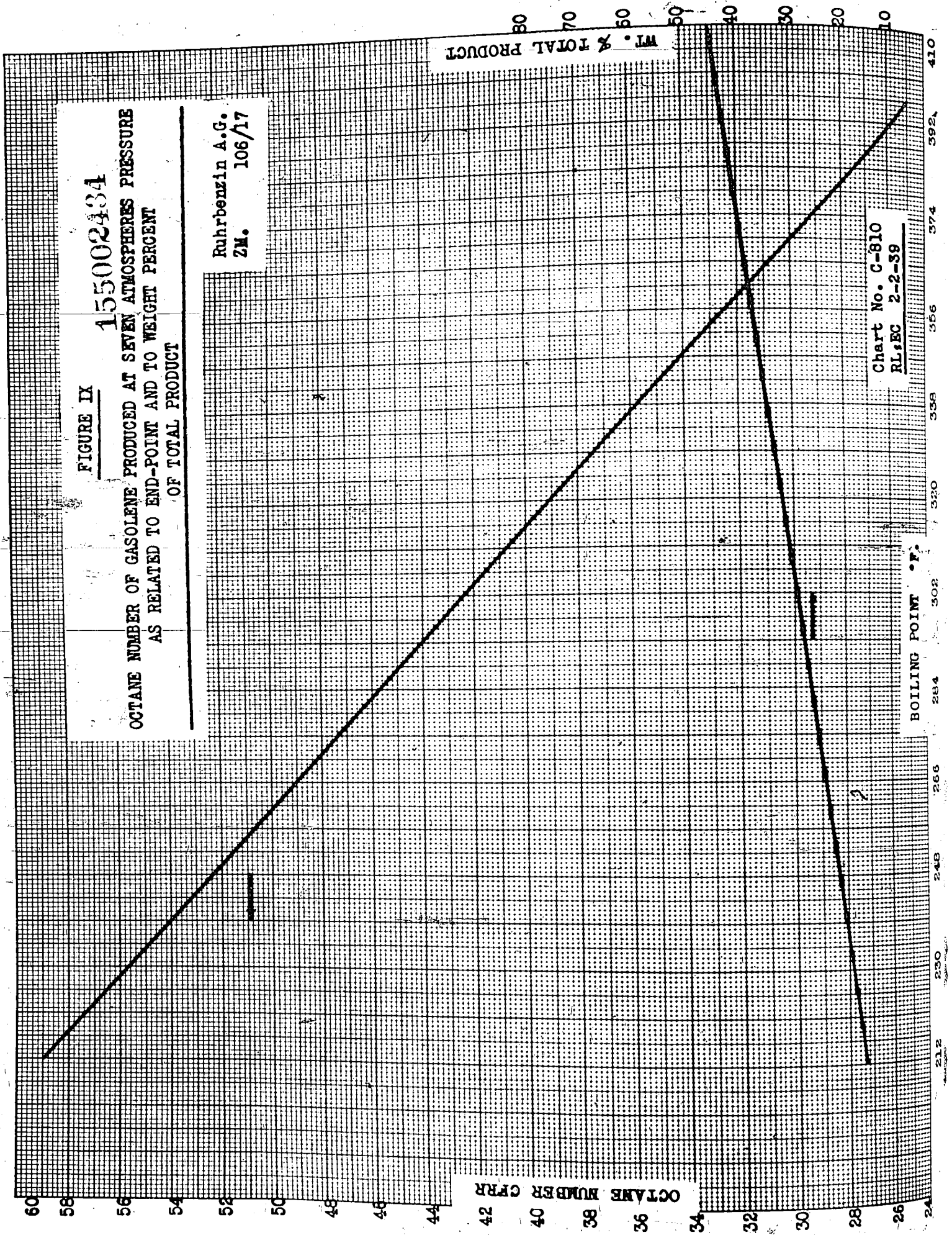
FIGURE IX

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OCTANE NUMBER OF GASOLINE PRODUCED AT SEVEN ATMOSPHERES PRESSURE  
AS RELATED TO END-POINT AND TO WEIGHT PERCENT  
OF TOTAL PRODUCT

Ruhrbenzin A.G.  
ZM. 106/17

Chart No. C-810  
RL,EC 2-2-39





The relation between octane number and the end point of the naphtha is shown on Figure IX opposite. It is readily apparent that to obtain directly a gasoline having an octane number of 60 CFRR, it would be necessary to cut to an end point of 210°F. (99°C.) and such a cut would represent only about 15% of the total hydrocarbons produced, which is to be compared with light naphtha of 300°F. (150°C.) end point representing 45% of the total liquid produced at atmospheric pressure.

Figure IX

As was previously mentioned, the production of Diesel oil was somewhat greater from operation under pressure than from the atmospheric synthesis. There is a possibility that even more Diesel oil could be made from the heavy products from pressure synthesis by a mild cracking operation.

The treatment of the products from the pressure synthesis was essentially the same as that given for the atmospheric pressure synthesis. The tabulation on the following page gives a summary of the yields and conversion, material balance and a heat balance for the synthesis under seven atmospheres pressure.

Synthesis Under Pressure

Liquid Primary Products	145 g./Nm <sup>3</sup>
C <sub>3</sub> + C <sub>4</sub> Hydrocarbons	10 g./Nm <sup>3</sup>
CO Conversion	88% on input
CO Conversion to Liquid	69% on input
Degree of Liquification	78.4% on CO input, i.e., 78.4% of the trans- formed CO was converted into liquid primary products.

Average Hydrogen Content of Liquid Primary Products -15%.

(basis: 1 cubic meter of ideal synthesis gas)

Material  
Balance

<u>Input:</u>	<u>Gram Mols</u>	<u>Grams</u>
CO	14.9	417
H <sub>2</sub>	29.8	60
	44.7	477

Products:

Liquid (excl. C <sub>3</sub> and C <sub>4</sub> )	= 145 grams (15% hydrogen)
C <sub>3</sub> and C <sub>4</sub>	= 10 grams
Conversion of CO	= 88%

Carbon Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In CO	14.9	179
<u>Output</u>		
In Liquid	10.25	123.5
In C <sub>3</sub> and C <sub>4</sub>	0.70	8.4
In CO <sub>2</sub>	0.27	3.3
In CH <sub>4</sub>	1.84	22.1
In Rest of Gas	1.78	21.4
	14.84	178.7

Hydrogen Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In H <sub>2</sub>	60.0	60.0
<u>Output</u>		
In Liquid	21.8	21.8
In C <sub>3</sub> and C <sub>4</sub>	1.6	1.6
In CH <sub>4</sub>	7.4	7.4
In Rest of Gas	3.6	3.6
In Reaction Water	25.1	25.1
	59.5	59.5

Oxygen Balance:

<u>Input</u>	<u>Gram Atoms</u>	<u>Grams</u>
In CO	14.9	239
<u>Output</u>		
In CO <sub>2</sub>	0.55	8.8
In Rest of Gas	1.77	28.5
In Reaction Water	12.50	200.7
	14.82	238.0

(Basis: 1 cubic meter of ideal synthesis gas)

Heat BalanceHeat Input

	<u>Kg. Cal.</u>	<u>%</u>
Ht. of Combustion of CO	1,010.0	33.3
Ht. of Combustion of H <sub>2</sub>	2,032.3	66.7
Total	3,042.3	100.0

Heat Output:

145 g liquid products/10 900 cal.	1581.0	52.0
5 g C <sub>3</sub> + C <sub>4</sub> unsaturated hydrocarbons/11 700 cal.	58.8	1.9
5 g C <sub>3</sub> + C <sub>4</sub> saturated hydrocarbons/11 630 cal.	58.2	1.9
Tail gas: 0.128 x 4 977 kcal.	637.0	21.0
Heat Content of Vaporized Reaction Water at 150°C.	150.3	4.9
Heat Content of Vaporized Hydrocarbons at 150°C.	21.8	0.7
Heat Content of the Dry Tail Gas at 150°C.	6.2	0.2
Heat Content of the Led-Away Steam - 0.145 x 5 kg x 593 kcal.	1430.0	14.1
Losses by Radiation and Transmission	99.0	3.3
	<u>3042.3</u>	<u>100.0</u>

This section contains material from the commercial plant, from the semi-plant scale equipment and from the laboratory. An effort has been made to emphasize the data from the commercial plant, but in numerous

Operating  
Variables

instances the latter did not have sufficient flexibility to permit an evaluation of a particular variable. The scale of the equipment in which the operation was carried out has been noted.

The usual operating range of the cobalt catalyst was 356-390°F. (130-193°C.) over a period of four months. The temperature used was dependent upon the activity of the catalyst as outlined in a previous section. If the reaction was started and maintained at 388°F. (193°C.), lighter liquid products, more gasol, and more methane were obtained. The catalyst life was considerably shortened at the higher temperature.

Temperature

The liquid products obtained from low temperatures operation contained a higher percentage of higher molecular weight products. As a consequence, the products from a fresh catalyst were heavier than those from an old catalyst, since the latter required a higher reaction temperature. The chambers were put in and taken out of operation on such a schedule as

to have the least overall variation in liquid products from the synthesis plant as a whole. The following tabulation gives an indication of the variation in products from old and new catalyst:

<u>Catalyst</u>	<u>Liquid Boiling at 300°F. (150°C.)</u>	<u>Olefins</u>
New	57%	30%
Old	57%	40%
Average	47%	35%

Methane production appeared to be entirely a function of temperature and did not vary with the age of the catalyst except insofar as different temperatures were used. There was no appreciable change in the octane number of the gasoline.

In the pressure range from 1-5 atmospheres, the directional change in products with alterations of the conditions was the same as for atmospheric pressure operations, but the changes were quantitatively different. Between five and ten atmospheres, the relative production of olefins and paraffins may be altered-- the higher the pressure, the higher the paraffin content and the lower the olefin content. From 10-15 atmospheres, there was a negligible increase in

Effect of  
Pressure  
Upon the  
Synthesis  
Reaction

paraffins with increased pressure. Above 15 atmospheres pressure, the total hydrocarbon yield decreased due to the formation of oxygenated organic compounds. The experiments were made in the semi-plant scale equipment. The following tabulation gives an indication of the effect of pressure upon the solid paraffins:

<u>Pressure Atmospheres</u>	<u>Solid Paraffin % of Total Oil</u>
1	5-10
6	15
11	25-28
16	32-35

It may be of interest to note here that the total gasoline with an octane number of 66 CFRR, which may be produced from the products from the pressure operation, was 120 grams per cubic meter of synthesis gas and had the following sources:

<u>Source</u>	<u>Grams/cubic meter</u>
Directly from Synthesis	29
Cracking of Heavier Products	85
Polymerization of all Olefins	6
Total	120

The octane number, motor method, was practically the same as the research method for this particular stock.

By using a hydrogen to carbon monoxide ratio of 1.8:1 instead of the usual 2:1, the octane number of the gasolene was increased 2-3 points, accompanied by an olefin increase of about 5%. Such a small vari-

Effect of  
Hydrogen to  
Carbon  
Monoxide  
Ratio

~~ation in the carbon monoxide to hydrogen ratio did not~~  
affect the ratio of light to heavy liquids.

Experiments have been made using gas directly from the generators in which the ratio of hydrogen to carbon monoxide was 1.25:1. At atmospheric pressure, the catalyst life with a gas with this ratio was much shorter than with the usual ratio, being about four weeks for the same yield on the basis of ideal gas present. More olefins were produced, the olefin content of the light gasolene going from 40-50%. The gasol fraction from the normal operation contained 50% olefins. With the lower hydrogen to carbon monoxide ratio, the percentage of unsaturates in the gasol fraction could be increased up to 73%. The octane number of gasolene made from this ratio of hydrogen to carbon monoxide was not available, but the CFRR of 300°F. (150°C.) end point material, made when using a hydrogen to carbon monoxide ratio of 1.5:1, was 67-68.



When operating under pressure with the ratio of hydrogen to carbon monoxide of 1.25:1, good results were obtained over a period of two months. The ultimate life of the catalyst with this mixture under pressure was not known except that it must have been greater than two months. The use of the lower hydrogen to carbon monoxide ratio under seven atmospheres pressure resulted in increasing the olefin content of the total liquid from 20-35% with scarcely any change in the relative quantities of gasoline, oil and wax. The same total yield of hydrocarbons was obtained from the first-stage operation. These results were of an experimental nature, obtained in the semi-commercial scale apparatus, and two-stage experiments had not been made.

The production of low boiling material was increased with an increase in the amount of inert gases in the synthesis gas. 15% inert gases were normally present in the synthesis gas used at atmospheric pressure. Since a large part of the inert gases consisted of carbon dioxide, a large part of the inert material could be removed by washing the synthesis gas with water under pressure.

Effect of  
Inert Gases

Effect of  
Gas Rates

The ordinary commercial practice with the atmospheric chambers was to pass into the first-stage chamber about 42,000 cubic feet (1200 cubic meters) per hour of synthesis gas containing in the neighborhood of 15% inert material. The inlet gas rates to the first-stage chambers were measured by an orifice meter, but the gas rates in the second-stage chambers were not directly measured. As stated previously, the practice was to maintain a gas contraction of 57% in the first-stage chambers and to use such a number of second-stage chambers as would correspond to about 10% greater throughput to the second-stage chambers than to the first-stage chambers. The gas throughput was dependent upon the amount of inert material in the gases so that when the inert material amounted to 50%, the throughput of ideal gas would be about 21,000 cubic feet (600 cubic meters) per hour. The throughput was also affected to some extent by the particular catalyst used and also by the pressure under which the synthesis reaction was carried out. Cobalt-thoria catalysts would operate efficiently at gas throughputs of 35-42 cubic feet (1-1.2 cubic meters) of synthesis gas per kilogram of cobalt per hour, while the cobalt-magnesia catalysts would accommodate gas throughputs of 53-60 cubic feet

(1.5-1.7 cubic meters) per kilogram of cobalt per hour.

The highest gas throughput tested commercially by Ruhrchemie was 60,000 cubic feet (1700 cubic meters) per ton of cobalt per hour. In the laboratory, experiments have been made at gas throughputs as high as 350,000 cubic feet (10,000 cubic meters) per ton of cobalt per hour. The higher rates gave lower yields, more olefins and more light liquid products. A change in space velocity from 1 to 1.5 caused an increase of from 2-3% in the low boiling fractions.

A figure for the liquid production per ton of cobalt for a catalyst life of four months was calculated upon the basis of the yield of 120 grams of oil per cubic meter of synthesis gas, namely, 760,000 pounds (345 tons) of oil per ton of cobalt.

This figure did not agree with later data submitted, which indicated a yield of 560,000 pounds (255 tons) of oil per ton of cobalt per life period of four months. No data were available for a flow rate of 50,000 cubic feet (1500 cubic meters) per ton of cobalt per hour for the life period of six months.

It was impossible to ascertain definitely if the production limits were solely dependent upon the catalyst or if they were not to some extent a reflection of the heat removal limitation of the synthesis chamber. The same chamber was used at the

same gas rate with the same yield of oil per chamber with catalysts containing varying amounts of cobalt and kieselguhr. The first catalyst used contained 3100-3300 pounds (1400-1500 kilograms) of cobalt per chamber filling. The catalyst in current use contained about 1900 pounds (850 kilograms) of cobalt per chamber filling. A new catalyst, which has not been extensively tested commercially, contained about 1,000 pounds (450 kilograms) of cobalt per chamber filling. It was thought possible that eventually a catalyst could be used which would contain only 220 pounds (100 kilograms) of cobalt per chamber filling. These results might be considered as indicating that the heat removal capacity of the chamber was a limiting factor in the ultimate oil production. However, they might also be regarded as indicating greater catalytic activity with greater dispersion of the cobalt.

One of the commercial chambers was half-filled with catalyst and operated at the rate of 42,000 cubic feet (1200 cubic meters) per hour. The life of the catalyst in this instance was only four weeks as compared to the normal life of four months. This was a catalyst in current use in the commercial plant, and, therefore, contained about 950 pounds (425 kilograms) cobalt for the half-filled chamber. The conclusion of Ruhrchemie was that this half-filled chamber should have been

operated at 21,000 cubic feet (600 cubic meters) per hour. The results, together with the conclusions, seem to indicate that the factor which chiefly limited the oil production was the heat removal capacity of the chamber.

The following data were obtained from the operation of commercial chambers at a practically constant temperature of 380°F. (190°C.) at a gas rate of 35,000 cubic feet (1,000 cubic meters) per hour per chamber. The oil yields were given in grams per normal cubic meter of ideal gas, while the gas rates were given in normal cubic meters of synthesis gas containing about 15% inert material. The chambers contained respectively, a whole charge, three-quarter charge, half charge, and one-quarter charge of the standard cobalt-magnesia catalyst.

Time Days	850 kg. Co.		640 kg. Co.		425 kg. Co.		213 kg. Co.	
	Contr.	Oil	Contr.	Oil	Contr.	Oil	Contr.	Oil
0	65	130	62	130	62	120	60	110
15	58	120	55	120	48	90	30	50
30	50	85	40	70	28	42	10	10*
40	42	80	40	90**	25	10		

\* After 23 days it was necessary to supply heat to chamber.  
\*\* Immediately after regeneration

155002448

FIGURE X

OIL YIELDS (AND GAS CONTRACTION) VERSUS TIME  
FOR CHAMBERS CONTAINING VARIOUS  
QUANTITIES OF CATALYST

Gas Rate - 1000 l./m.<sup>3</sup> Chamber  
Temperature - 190-195°C.

- 850 kg. Co
- 640 kg. Co
- △ 425 kg. Co
- ▽ 213 kg. Co
- \* After regeneration
- \*\* Additional heat applied

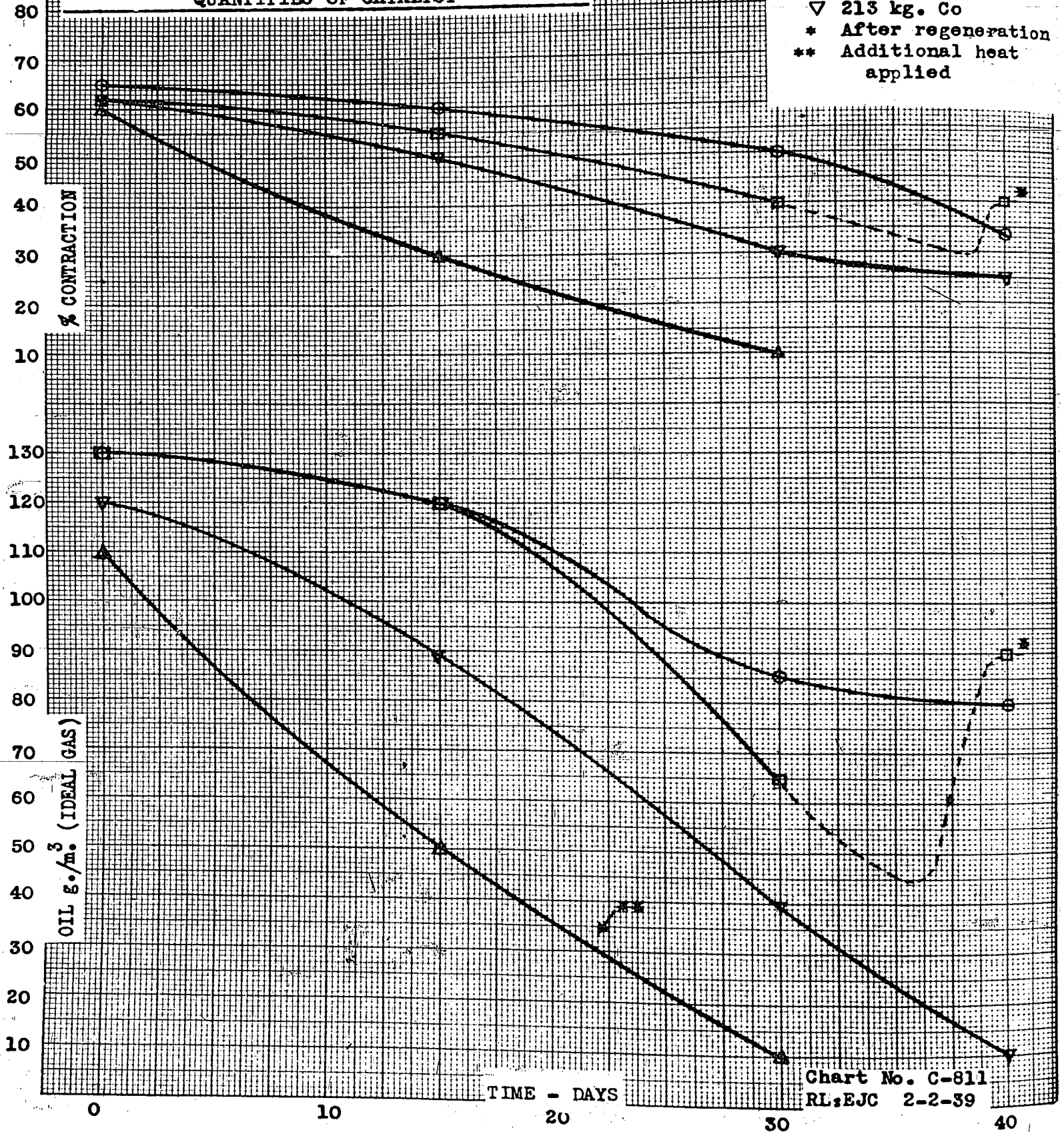


Chart No. C-811  
RL:EJC 2-2-39

The results given on the preceding page are shown plotted in Figure X opposite. From the lower set of curves it is clear that the oil production was less, the smaller the amount of catalyst in the chamber. However, it should be mentioned that the results obtained in the Kellogg laboratory would indicate that the comparison of yields from these catalyst quantities would better be made at the optimum temperature for each chamber rather than at a constant temperature. The higher the gas rate per unit of catalyst the higher the optimum reaction temperature should be.

155002450

FIGURE XI

OIL PRODUCTION VERSUS INLET GAS RATE

— 0 - 1500 hours operation  
- - - 500 - 1500 hours operation

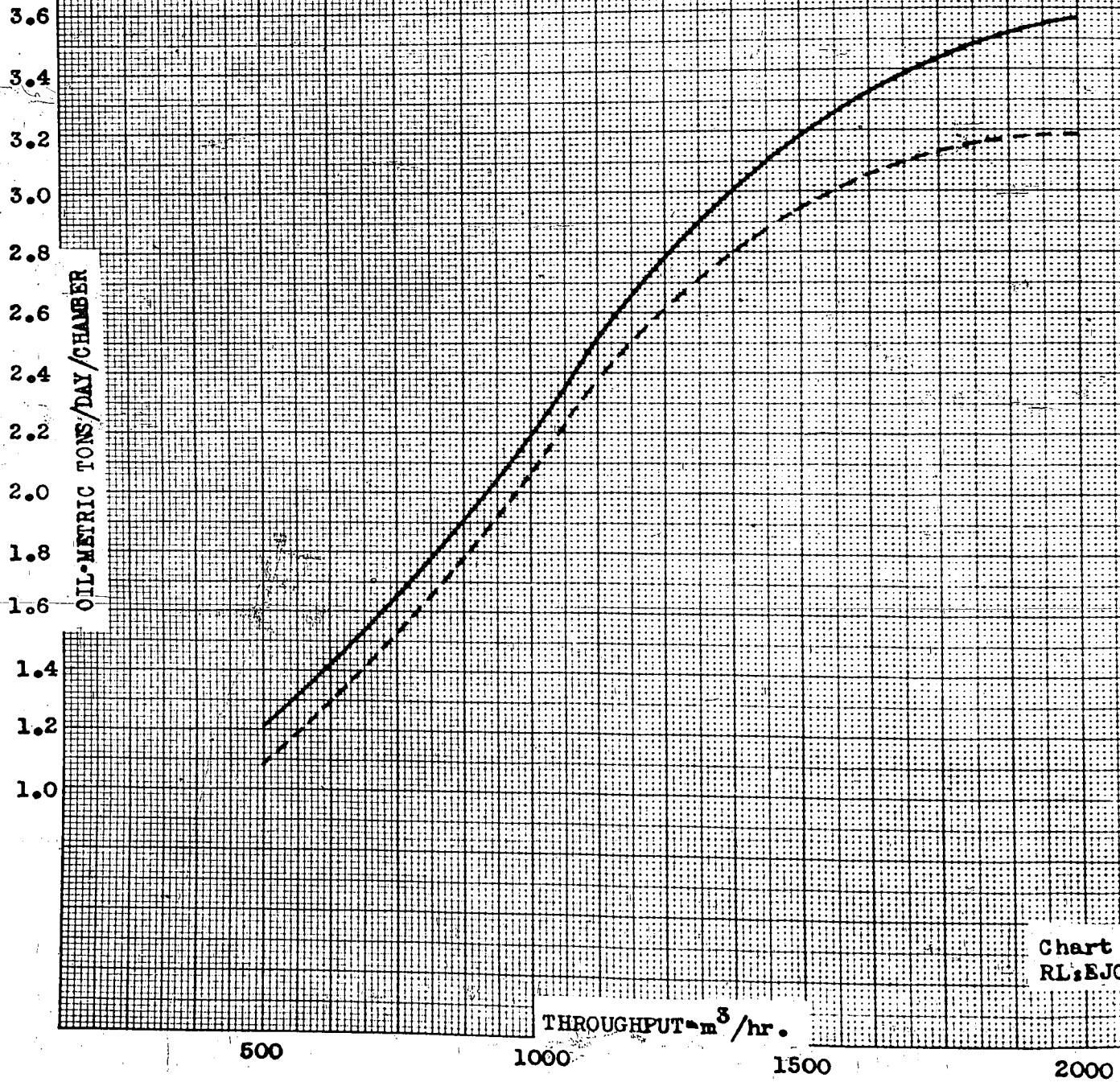


Chart No. C-812  
RL:EJC 2-2-39



Figure XI is a plot of the yields of oil per unit time per unit of catalyst as a function of the inlet gas rate. The data were taken from experiments in glass tubes in an aluminum block, the gas stream not being preheated. The data were calculated to correspond to the commercial size chamber and the ordinates on Figure XI were in the calculated units. The upper solid curve was obtained from starting with a new catalyst and using such a catalyst for 1500 hours. The lower broken curve was obtained from 1,000 hours operation of a catalyst which had previously been used for 500 hours. It was evident that the older catalyst gave somewhat lower results than the new catalyst. These results were obtained at atmospheric pressure. A similar but higher curve was obtained at seven atmospheres pressure in semi-commercial scale equipment. In every instance the oil yield dropped rapidly at rates beyond that corresponding to 2.3 liters of gas per hour per gram of cobalt. It should be mentioned that these experiments were made at the optimum temperature for the particular catalyst and gas rate, ranging from 365-392°F. (185-200°C.). Experiments at atmospheric pressure were being repeated on the semi-plant scale equipment whose construction was similar to the commercial high pressure chambers.

Figure XI

Ruhrchemie thought that there were two possible explanations of the optimum point on the curve:

1. Heat removal limitation of the equipment
2. Contact time limitation

They regarded the latter as the chief factor for two reasons:

1. The optimum point fell at the same gas rate in both the atmospheric and the high pressure chambers, although the cooling characteristics of the two chambers were quite different.

2. Experiments made in an apparatus where the cooling surface was relatively very much larger--one millimeter annular space between water-cooled tubes--showed no different results as regards oil production, although the methane formation was about 10% lower.

The experiments on this reactor (capacity about 175 cc. of catalyst) were being continued and the gas rates of 1, 2, 3, 4, 5 and 10 liters per hour per gram of cobalt would eventually be tested.

The synthesis reaction was regarded as being made up of three steps:

1. Adsorption
2. Reduction and Polymerization
3. Product Desorption

The first two steps were rapid in comparison with (3), and therefore the latter determined the speed of the overall reaction. Step (3) could be speeded up by the use of higher temperatures, but there was always the danger that the course of (2) would be altered too far in the direction of methane formation.

Some additional data were taken from experiments made in glass tubes and aluminum blocks for one-stage operation. Similar to the results previously mentioned, these data had been calculated to correspond to the commercial size chamber.

<u>Gas Rate</u> <u>l./Chamber/hr.</u>	<u>Oil Yields</u> <u>Tons/Chamber/Day</u>	<u>g./m<sup>3</sup></u>	<u>g./g.Co/hr.</u>
1000	2.33	114	0.13
1500	3.20	105	0.19
3000	4.17	68	0.24
6000	6.20	51	0.36

These data differ from the previously described results in that they are for one-stage operation and were taken over an operating period of only 200 hours. The indications were that for this relatively short time the yield of oil per gram of cobalt per hour increased with the gas rate, as far as the data went. These latter data are more nearly comparable to the data taken in the Kellogg laboratory and their difference from the long

period, two-stage operation would indicate the necessity of making life tests on catalysts operating at high gas rates.

Ruhrchemie had a commercial chamber at Ruhland, which had been in operation 100 days on the 22nd of November, 1938, at a gas rate of 60,000 cubic feet (1700 cubic meters) per hour per 1900 pounds (850 kg.) of cobalt. This chamber showed a contraction of 60% and a carbon monoxide conversion of 70-75% and had not been revived or regenerated at the end of 100 days operation. The exceptionally long life was attributed to improvement in the catalysts although no specific nor intentional change had been made in the catalyst or in its preparation. It was possible, therefore, that the longer life was due to the higher gas rate used.

The explanation of why operations at Holten and elsewhere were not carried out at the peak of the curves was:

1. The limited condensing equipment of the present commercial chambers
2. The necessity for high yields of oil per unit of synthesis gas.

In this connection it may be mentioned that the experiments

to be made at Holten by Ruhrchemie at the request of USAC cannot be made at rates higher than 71,000 cubic feet (2,000 cubic meters) per hour per chamber. This limitation was due to the previously mentioned limited condensation apparatus and further, to the fact that compression facilities were not available to overcome the greater pressure drop at higher gas rates. It was suggested to Ruhrchemie that for the experiments to be made for USAC:

1. A high pressure chamber be used at atmospheric pressure.

2. That the chamber be only half-filled with catalyst in order to raise the gas rate per unit of cobalt.

Objections to these suggestions were made as to the impracticability of either suggestion.

A commercial atmospheric pressure chamber was filled with catalyst in the form of pellets (about twice the normal apparent density and therefore with about twice the normal amount of cobalt in this chamber) and was operated at 42,000 cubic feet (1200 cubic meters) of synthesis gas per hour. The oil yields were practically the same as when operating such a chamber at this gas rate over the normal catalyst. In another instance, twice the usual amount of kieselguhr was added in the catalyst preparation and the resultant catalyst made into the form of pellets. A chamber filled with this pelleted catalyst (the normal amount of cobalt per chamber) likewise gave the same yield of oil at the gas rate of 42,000 cubic feet (1200 cubic meters) per hour. Ruhrchemie have always used light catalysts, since they believe that the high pressures necessary to form the pellets destroyed the structure of the kieselguhr and left the surface of the catalyst pellet with a much impaired porosity.

The use of such a variety of catalysts, i.e., catalysts containing cobalt and kieselguhr in varying proportions; pelleted catalysts; half-filled chamber; etc., without any effect upon the maximum oil production per chamber, was a strong indication that the oil production

Pelleted  
Catalysts

was limited by the heat-removal facilities of the atmospheric chamber. The use of higher gas velocities increased the oil production somewhat, but probably only insofar as the heat capacity of the additional gas quantities assisted in the removal of the heat of reaction. In this regard, it is interesting to note that the oil production per unit of cobalt was steadily rising at a gas rate equivalent to seven liters per hour per gram of cobalt when the reaction was carried out in laboratory equipment, whereas in the commercial, atmospheric pressure chambers the oil production per unit of cobalt began to fall off at gas rates above two liters per hour per gram of cobalt.

The gas throughput per unit of cobalt was about 20% greater at seven atmospheres than that used under atmospheric pressure. The most efficient space velocity for higher pressure operation had not been determined, although it was considered certain that it would be higher than for atmospheric pressure operation. It was regarded as certain that it would not be possible to increase the space velocity under pressure in direct proportion to the pressure due to the fact that while the rate of adsorption was

Gas Rates  
in Pressure  
Operation

increased the rate of desorption of the products was decreased by the application of pressure.

Using the cobalt-magnesia catalyst under pressure the usual custom at Holten was to start a new catalyst at the rate of 60,000 cubic feet (1700 cubic meters) of synthesis gas per chamber per hour. This rate was decreased somewhat as the catalyst lost activity, although the oldest catalyst in use--more than six months old--had not required even a partial revivification with hydrogen. No higher gas rates had been used in the high-pressure chambers.

The heat of the synthesis reaction was ordinarily removed from the synthesis chamber by the evaporation of water to form steam under pressure and subsequently leading the steam away. It was thought worthwhile to attempt to remove the heat of reaction by the recirculation of the gaseous products of the reaction. For this purpose a semi-commercial chamber having a capacity of 14 cubic feet (400 liters) of catalyst was used. This particular chamber had a construction similar to that of the commercial high-pressure chamber. Fresh synthesis gas was added to the recycle gas and the mixture passed

Heat Removal  
by Gas  
Recirculation



through a compressor into the chamber. The gases leaving the chamber were cooled and the liquid products condensed. A portion of the recycle gas was bled off, the amount being such as to hold the system around the chamber in thermal balance, that is, no steam generation but some heat loss by conduction and radiation.

The following tabulation gives the conditions and results:

Chamber capacity	14 cu.ft. catalyst (400 liters)
<u>Gas Rate</u>	
Fresh synthesis gas	1400 cu.ft./hr. (40 cu. meters)
Recycle gas	5700 cu.ft./hr. (160 cu. meters)
<u>Temperatures</u>	
Water jacket	374°F. (190°C.)
Inlet gas	122-140°F. (50-60°C.)
Contraction	30%
Conversion on the fresh carbon monoxide	90%

The above recycle ratio was probably specific to the particular equipment used, and would probably have been larger for a larger chamber and would have been affected directly by the chamber insulation.

The usual custom in the operation of the synthesis reaction has been to introduce the gas at the top of the reaction chamber and allow the gas to flow downward through

Reversal of  
Direction  
of Flow

the catalyst. Operation in which the gases entered the bottom of the chamber and flowed upward through the catalyst had been made, in the nature of experiments. Two atmospheric pressure commercial chambers were operated upflow for 16 days. Although the covers of the chambers were gas-tight, the upflow experiments were stopped because of paraffin leakage through the joints around the cover. There was no difficulty encountered in the operation in this manner and little if any difference noted in the results, that was attributed to the reversal of the direction of flow. These experiments will be repeated on chambers in which more care will be taken to insure a paraffin-tight cover.

Experiments were made in which the usual flow of gases were reversed in the high pressure chambers--about seven atmospheres pressure. Difficulties in operation were encountered due to the plugging of the annular spaces near the top of the chamber with solid paraffins. Not all of the annular spaces were plugged but those that were plugged caused an uneven distribution of the synthesis gas so that the annular spaces which would allow free passage of the gases were operating at too high gas velocity. No difference in the products was observed with the reversed synthesis gas flow.

Detailed information on individual experiments then being carried out on the semi-commercial scale in the pilot plant laboratory was not given. The following paragraphs summarize the information that was obtained. The types of equipment in use in the pilot plant laboratory were:

Pilot Plant  
Laboratory

1. Two flat sheets of iron, 8 feet (2.5 meters) wide, were welded together along the edges so that the distance between the sheets was one centimeter inside measurement. The welded sheets were then rolled into the form of a spiral so that there was about one centimeter clearance between laps. The spiral was in a cylindrical tube provided with a water jacket and the inside space of the spiral was connected to the water system. There were 17 annular spaces in the completed reactor.

2. A fluted star-shaped tube was placed inside a cylindrical tube 34 mm. inside diameter and about eight feet (2.5 meters) long. The fluted tube was spot welded to the cylindrical tube at each point of contact. The entire free space inside of the cylindrical tube was filled with catalyst.

3. A cylindrical tube two inches (54 mm.) outside diameter, four feet (1.2 meters) long was placed

inside another cylindrical tube 2.5 inches (65 mm.) inside diameter. The inside tube was filled with water and the outside tube placed in a water bath. Catalyst was placed in the annular space.

4. A tube 20 mm. inside diameter and four feet (1.2 meters) long was surrounded by a water bath and filled with catalyst.

5. A chamber was constructed in a manner exactly similar to the commercial high pressure reactors except that the length was eight feet (2.5 meters). The cross sectional area of each annular space was about 11 square centimeters.

In reactors of the type described under (5), experiments had been made under a pressure of seven atmospheres at various synthesis gas inlet rates. No preheating of the gases was done except that which occurred in the top part of the chamber itself. Such a chamber was said to be practically inoperable at a rate of ten liters of synthesis gas per hour per gram of cobalt, that is, practically no oil production. At a gas rate of two liters per hour per gram of cobalt, the temperature had to be raised 18°F. (10°C.) in order to obtain the same yield as that obtained at the gas rate of one liter per hour per gram of cobalt. The life of the catalyst at the doubled gas rate was only three months as compared to six months with the ordinary gas rate.

External heat had to be supplied to those chambers which contained less than 500 liters of catalyst. Chambers containing between 500-1000 liters of catalyst required no supplementary heating after the reaction had been started, and there was also no appreciable generation of steam. Chambers containing more than 1000 liters of catalyst had to be cooled by the evaporation of water under pressure. It was planned to investigate the effect of pressure systematically in a 1000-liter chamber by operation at 1, 2, 3, 4, 5, 7 and 10 atmospheres. Likewise, a systematic investigation of the effects of the increased gas rates was planned.