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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,

* 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 V.

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 V

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

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 ³ /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

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.

Pressure
Drop

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 3.0 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 23,000 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 23,000 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 230°F. (110°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.

The curve in Figure VI was a plot of temperature, gas throughput and catalyst life versus time for the life period of the catalyst. At the start, the chamber was used in the first-stage for a period of about 75 hours and was then switched to the first-stage and used uninterruptedly for 100 hours. It was then regenerated by treatment with hydrogen for 12 hours and used again in the first-stage for an additional 100 hours. It was regenerated with hydrogen for 12 hours and again used in the first-stage for an additional 100 hours. It was regenerated with hydrogen a third time for 12 hours, used in the first-stage for 100 hours, regenerated with hydrogen for 12 hours, and used 100 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 VI
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 taken from operation at one time and four new ovens put in operation.

The spent catalyst contained large quantities of solid paraffins. 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 40% 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 410°F. (210°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". The catalyst was still pyrophoric after the solvent treatment and had to be deactivated before digestion.

Solvent
Treatment

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.

Catalyst
Removal
from
Chamber

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.

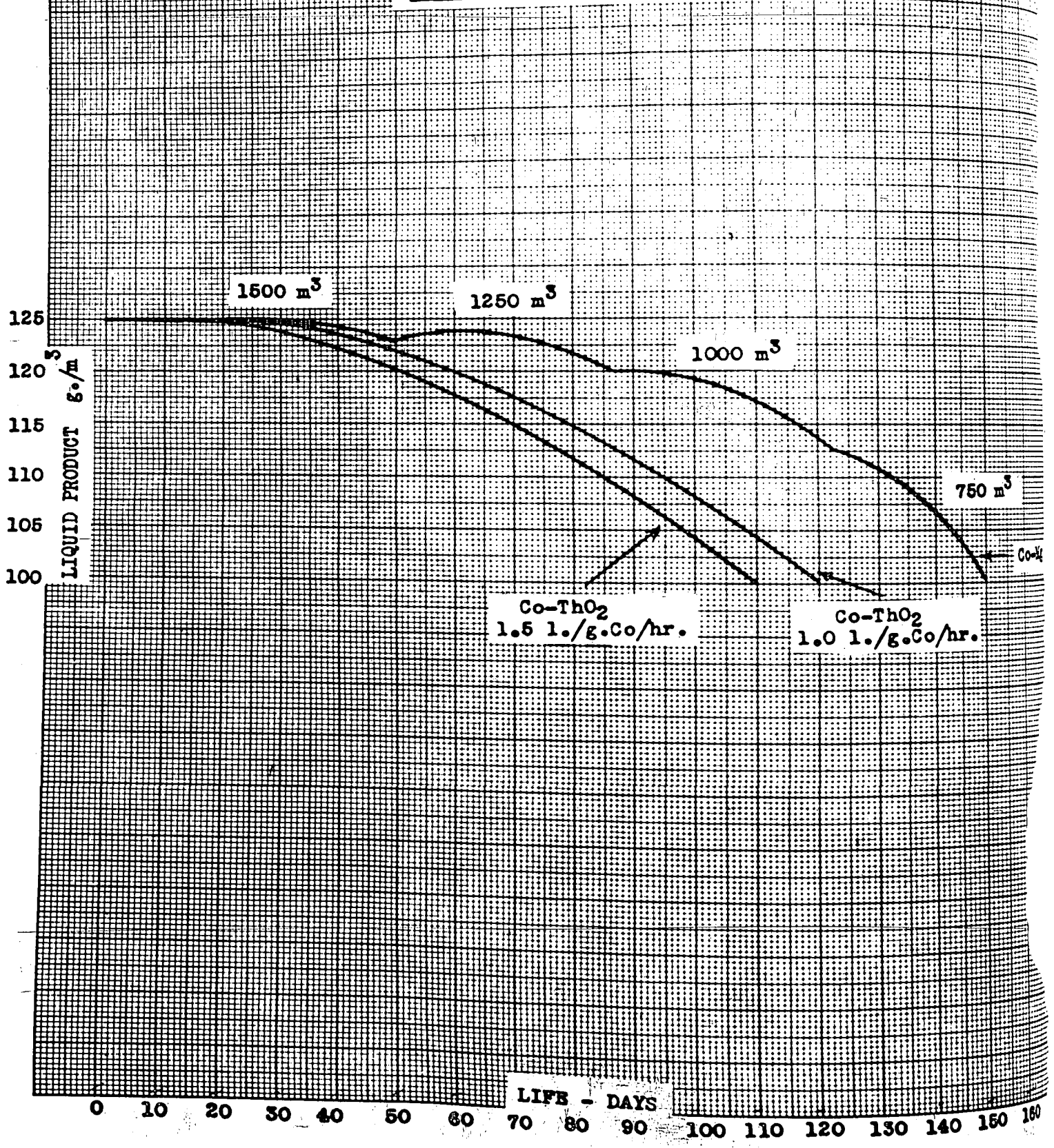
A chamber was out of use for 3.5 days for each four month period, inclusive of solid paraffin extraction, cooling, opening, dumping the catalyst, refilling and returning to production. The solid paraffins were removed, on the average, 2-1/2 times in a four month period, 10-12 hours required for each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

Chamber
Off-Time
Period

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FIGURE VII

OIL YIELDS versus TIME for
VARIOUS INLET GAS RATES.



Holten, for one reason or another, off-time averaged 7-8%.

The catalyst life was also dependent upon the inlet gas rate as shown on Figure VII. The lower two curves of Figure VII indicate a shorter life for the higher gas rate over the cobalt-thoria catalyst, measuring the life in terms of time. If the catalyst life were measured in terms of oil produced, it would appear from the relative position of the two curves that the life of the catalyst with the higher gas rate was greater. The upper curve on Figure VII was obtained by varying the gas rate in accordance with the activity of the catalyst rather than the usual procedure of varying the temperature in accordance with the activity of the catalyst. There seemed to be some advantage to decreasing the gas rate rather than increasing the temperature as the catalyst became inactivated.

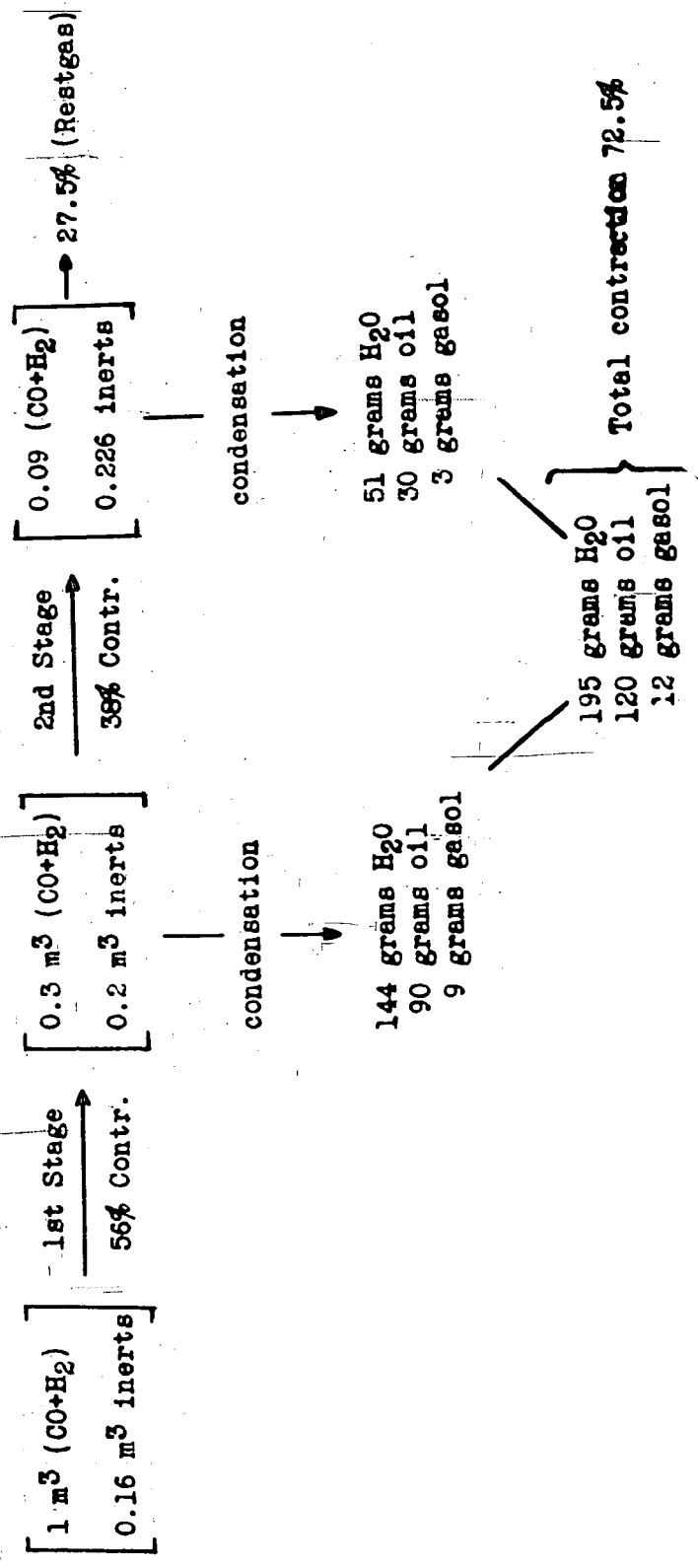
The total conversion of carbon monoxide, regardless of the pressure under which the synthesis was carried out, was of the order of 90% for the two-stage operation. This conversion corresponded to a tail gas amounting to about 30% of the original synthesis gas charged. The tail gas was composed of about 6% carbon monoxide, 10% hydrogen and 18% methane, and had a calorific value of

Atmospheric
Pressure
Yields

FIGURE VIII

SCHEMATIC 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 (C₃ and C₄ 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 VIII opposite.

Figure VIII

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 25,000 cubic feet (725 cubic meters). This throughput together with the above yield would correspond to a production of 45 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_3 and C_4 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 (C₃ and C₄ hydrocarbons) was about 90%. The

Charcoal
Absorption

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TABLE III

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% C₃ - 60% C₄

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 III, 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.

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.

Table III
Atmospheric
Pressure
Product
Characteristics

154002176

FIGURE IX

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

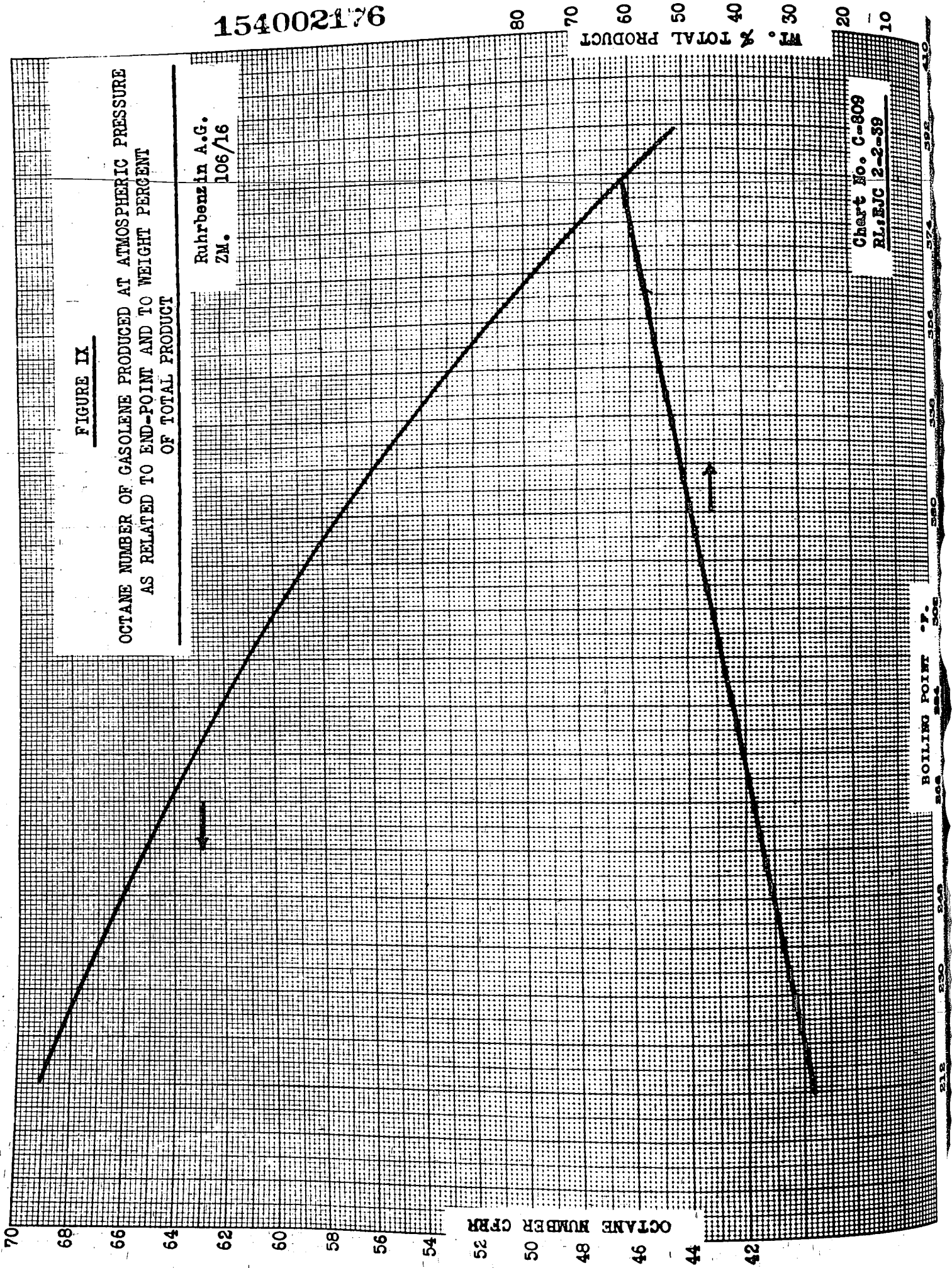


Chart No. C-809
RL,EJC 2-2-59

BOILING POINT °F.

OCTANE NUMBER CPR

WT. % TOTAL PRODUCT

20
10

574 572 570 568 566 564 562 560 558 556 554 552 550 548 546 544 542 540 538 536 534 532 530 528 526 524 522 520 518 516 514 512 510 508 506 504 502 500 498 496 494 492 490 488 486 484 482 480 478 476 474 472 470 468 466 464 462 460 458 456 454 452 450 448 446 444 442 440 438 436 434 432 430 428 426 424 422 420 418 416 414 412 410 408 406 404 402 400 398 396 394 392 390 388 386 384 382 380 378 376 374 372 370 368 366 364 362 360 358 356 354 352 350 348 346 344 342 340 338 336 334 332 330 328 326 324 322 320 318 316 314 312 310 308 306 304 302 300 298 296 294 292 290 288 286 284 282 280 278 276 274 272 270 268 266 264 262 260 258 256 254 252 250 248 246 244 242 240 238 236 234 232 230 228 226 224 222 220 218 216 214 212 210

The relation of the octane number to the end point of naphtha produced at atmospheric pressure is shown on Figure IX opposite. A second curve on Figure IX 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.

Figure IX

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 (C₃ and C₄ 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.

154002178

(133)

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 ₂	55.0	32.5	10.0
CH ₄	0.4	8.0	17.8
CO ₂	13.5	35.5	55.0
N ₂	3.1	6.5	10.0
Olefins	-	0.5	1.2

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

Normal-Pressure Synthesis

Summary

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

Average Hydrogen Content of Liquid Primary Products 15.2%.

154002130

(135)

~~(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 ₂	29.8	60
	<u>44.7</u>	<u>477</u>

<u>Products:</u>		
Liquid (excl. C ₃ and C ₄)	= 120 grams	(15.2% hydrogen)
C ₃ and C ₄	= 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 ₃ and C ₄	1.05	12.6
In CO ₂	0.46	5.5
In CH ₄	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 ₂	59.6	59.6
<u>Output</u>		
In Liquid	18.25	18.25
In C ₃ and C ₄	2.15	2.15
In CH ₄	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 ₂	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>

154002181

(136)

(Basis: 1 cubic meter of ideal synthesis gas)

Heat
Balance

<u>Heat Input:</u>	<u>Kg. Cal.</u>	<u>%</u>
Ht. of Combustion of CO	1,010	33.3
Ht. of Combustion H ₂	<u>2,032</u>	<u>66.7</u>
Total	3,042	100.0
<u>Heat Output:</u>		
120 g liquid products/10 900 cal.	1308.0	43.0
15 g C ₃ + C ₄ Hydrocarbons	177.0	5.8
Tail Gas: CO:59.3 1.:151.6		
H ₂ :84.7 1.:298.0		
CH ₄ :49.5 1.:472.0	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.

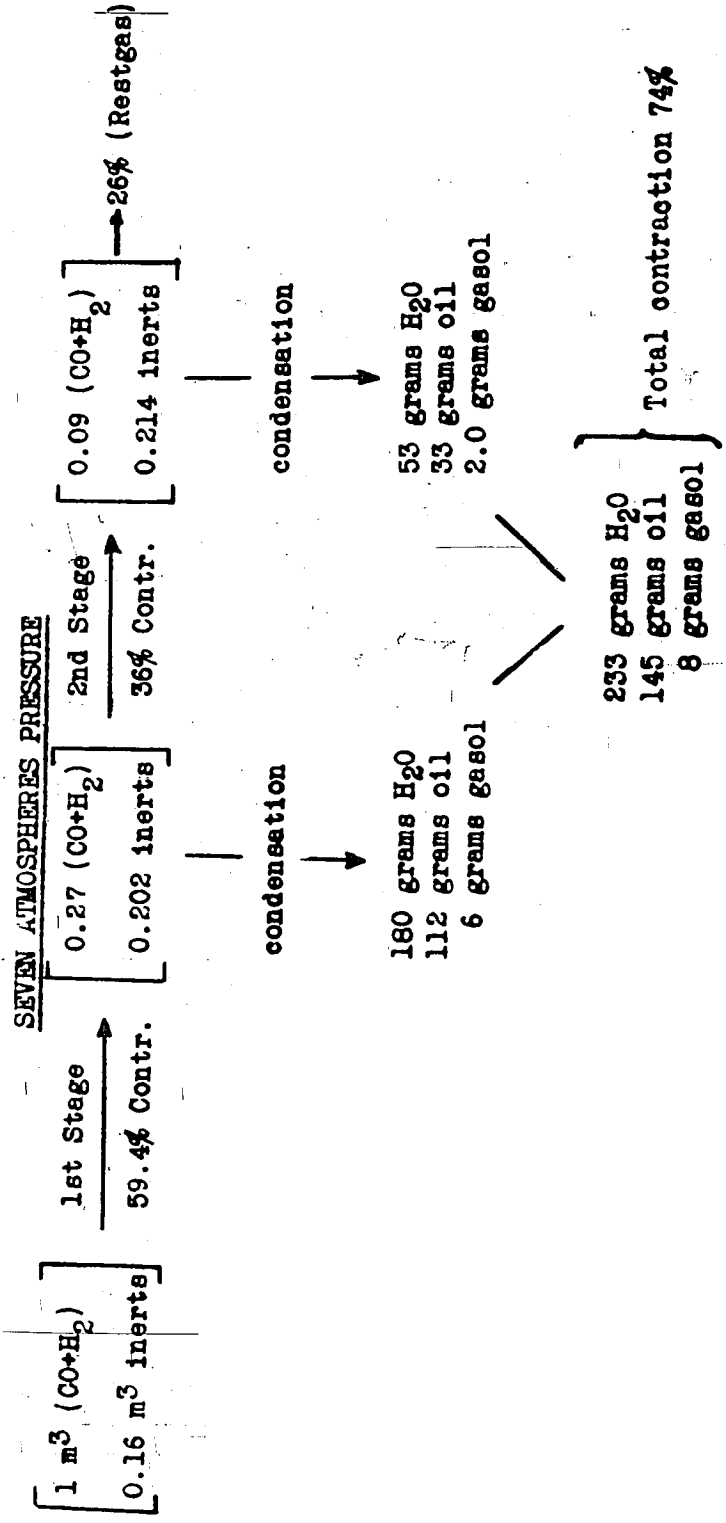
Ruhrchemie had 16 of these high pressure chambers in operation at the first of December, 1938. They had in the process of construction about 56 additional high pressure chambers for the Heltten plant. A more detailed description of these chambers together with drawings will be found in the section dealing 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 (C₃ and C₄ 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 X

SCHEMATIC FLOW SHEET FOR SYNTHESIS AT



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

Figure X

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

154002186

TABLE IV

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% C₃ - 60% C₄

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 IV 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 IV

154002188

TABLE V

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

Pressure - atmospheres	1	7
H ₂ : CO Ratio	2 : 1	2 : 1
Operating Temperature - °F.	364-388	356-392
Operating Period - months	4	At least 6
<u>Products in grams/m³ of (CO+2H₂)</u>		
CH ₄	32	25-27
CO ₂	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 V 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 V

154002190

FIGURE XI

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

Ruhrbenzin A.G.
ZM. 106/17

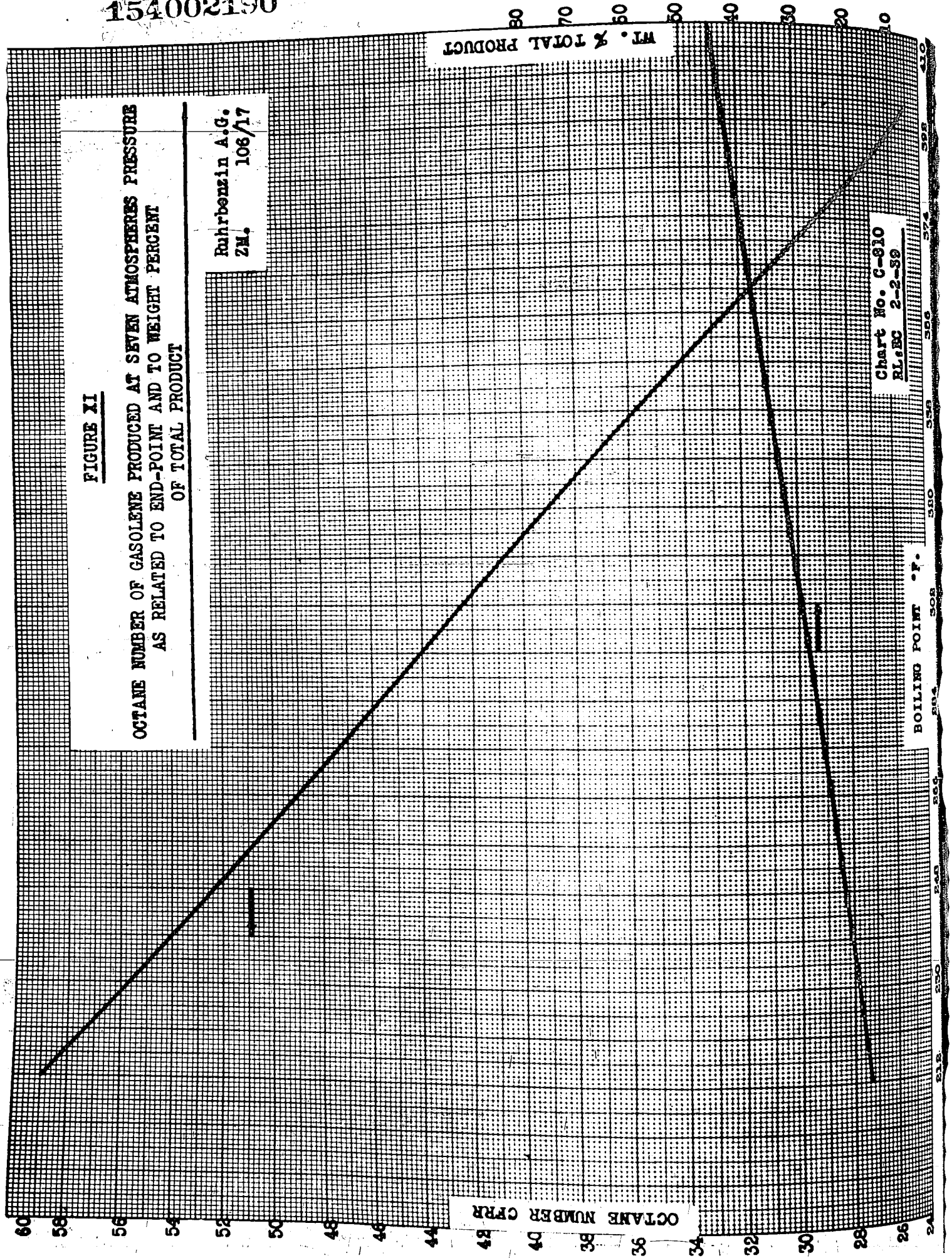


Chart No. C-810
PL:EC 2-2-38

OCTANE NUMBER CPR

WT. % TOTAL PRODUCT

BOILING POINT °F.

The relation between octane number and the end point of the naphtha is shown on Figure XI 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 XI

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 ³
C ₃ + C ₄ Hydrocarbons	10 g./Nm ³
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%.

154002193

(144)

(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 ₂	29.8	60
	<u>44.7</u>	<u>477</u>

Products:

Liquid (excl. C ₃ and C ₄)	= 145 grams (15% hydrogen)
C ₃ and C ₄	= 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 ₃ and C ₄	0.70	8.4
In CO ₂	0.27	3.3
In CH ₄	1.84	22.1
In Rest of Gas	1.78	21.4
	<u>14.84</u>	<u>178.7</u>

Hydrogen Balance:

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

Oxygen Balance:

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

154002194

(145)

(Basis: 1 cubic meter of ideal synthesis gas)

Heat
Balance

<u>Heat Input</u>	<u>Kg. Cal.</u>	<u>%</u>
Ht. of Combustion of CO	1,010.0	33.3
Ht. of Combustion of H ₂	<u>2,032.3</u>	<u>66.7</u>
Total	3,042.3	100.0
<u>Heat Output:</u>		
145 g liquid products/10 900 cal.	1581.0	52.0
5 g C ₃ + C ₄ unsaturated hydrocarbons/11 700 cal.	58.8	1.9
5 g C ₃ + C ₄ 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	<u>99.0</u>	<u>3.3</u>
	3042.3	100.0

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 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.

Operating Variables

The usual operating range of the cobalt catalyst was 356-390°F. (180-198°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. (198°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	37%	30%
Old	37%	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 differ-
 ent. Between five and ten atmospheres, the relative
 production of olefins and paraffins may be altered--
 the higher the pressure, the higher the paraffin con-
 tent 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 gasolene 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-
ation in the carbon monoxide to hydrogen ratio did not
affect the ratio of light to heavy liquids.

Effect of
Hydrogen to
Carbon
Monoxide
Ratio

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 cata-
lyst 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 40-60%. 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 gasolene, 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 55,000 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	350 kg. Co.		340 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		

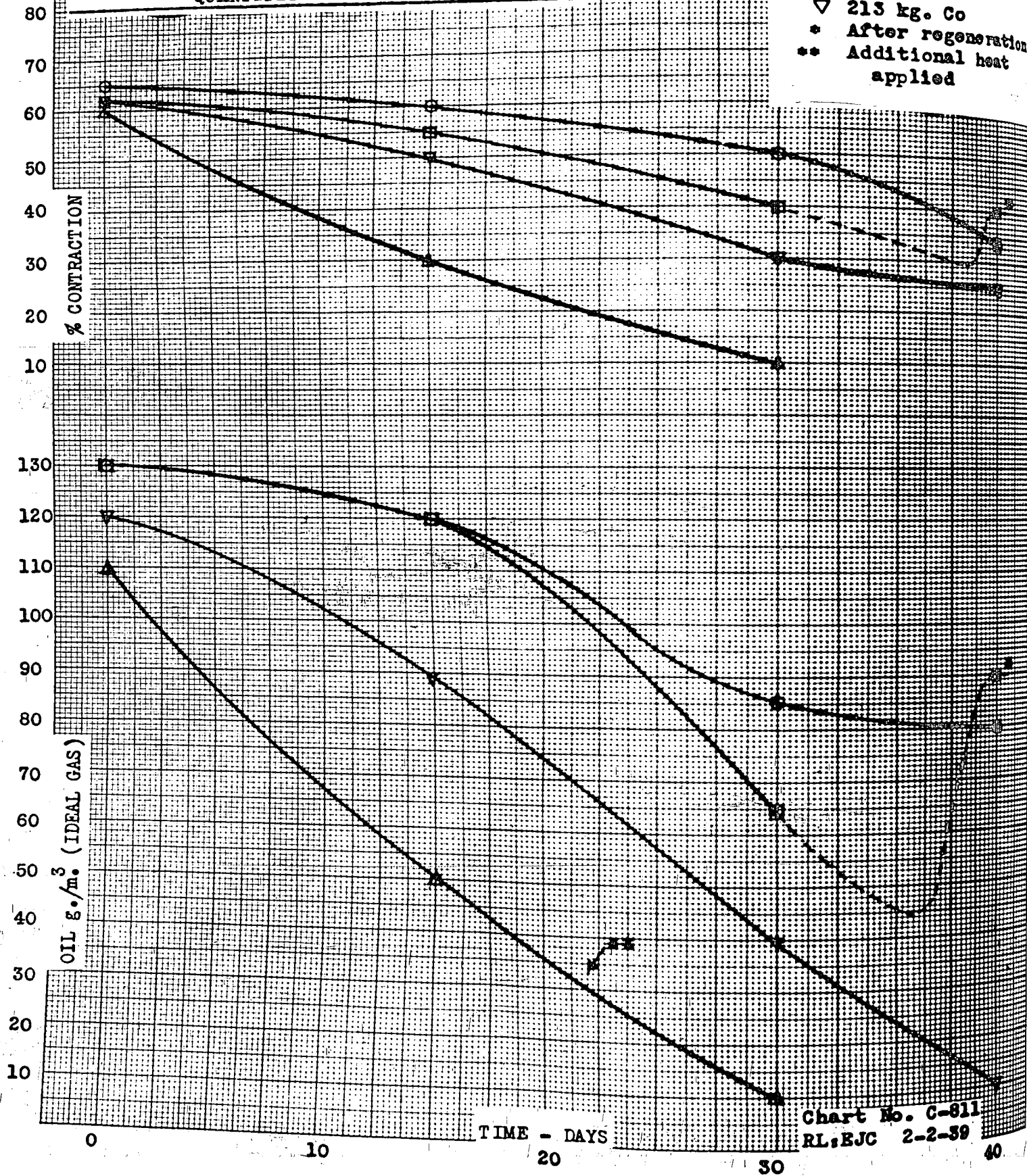
* After 23 days it was necessary to supply heat to chamber.

** Immediately after regeneration

FIGURE XII

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

Gas Rate - 1000 l./m.³ Chamber
Temperature - 190-195°C.
○ 850 kg. Co
□ 640 kg. Co
△ 425 kg. Co
▽ 213 kg. Co
* After regeneration
** Additional heat applied



The results given on the preceding page are shown plotted in Figure XII 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.

FIGURE XIII

OIL PRODUCTION VERSUS INLET GAS RATE

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

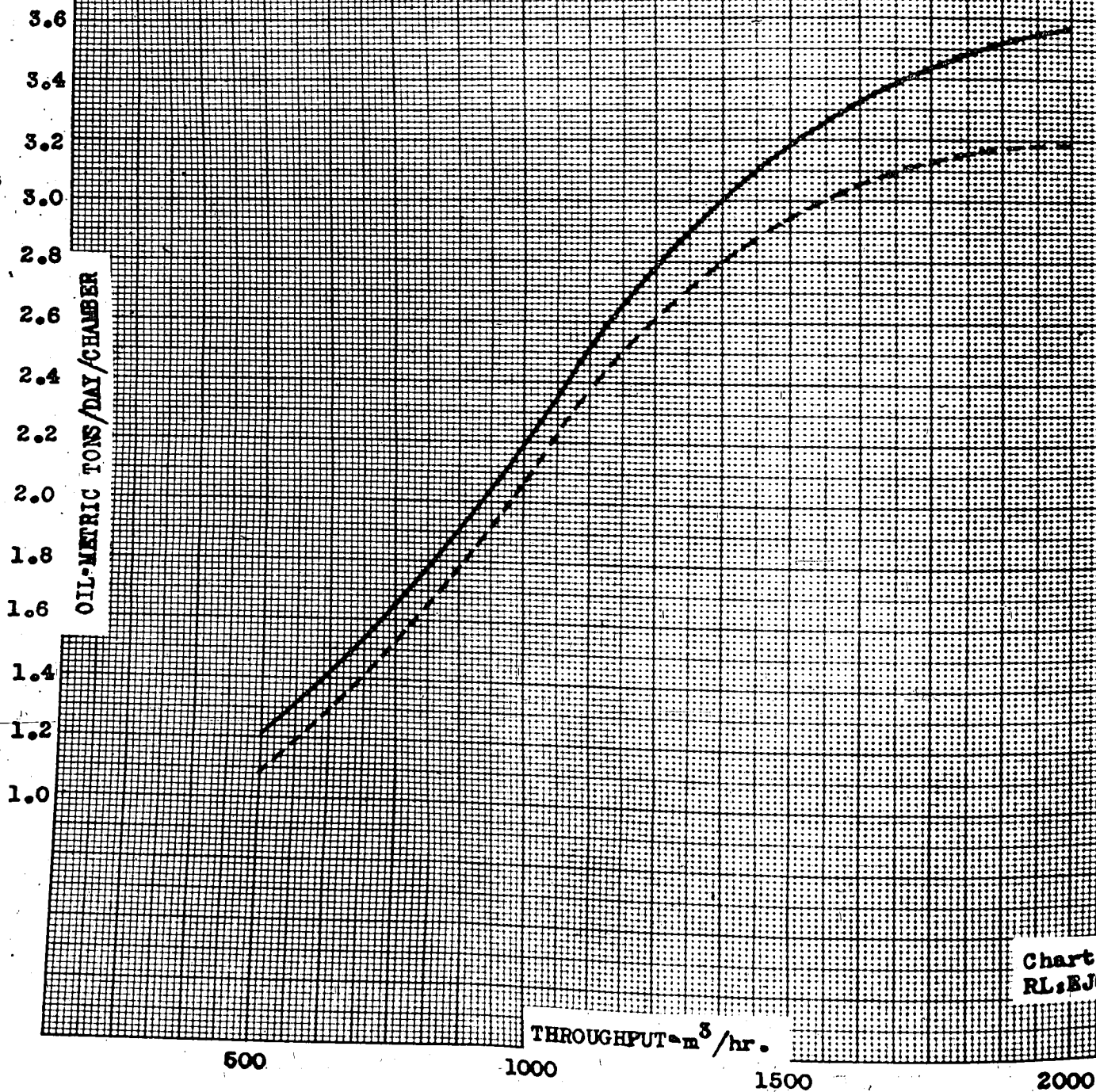


Chart No. C-812
RL:EJC 2-2-39

Figure XIII 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 XIII 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 XIII

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>m³/Chamber/hr.</u>	<u>Oil Yields</u> <u>Tons/Chamber/Day</u>	<u>g./m³</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.

Pelleted
Catalysts

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

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.

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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.

I.G. FARBENINDUSTRIE SYNTHESIS PROCESSES

The material presented in this section has been divided into two groups:

1. The use of iron catalysts
2. The use of cobalt catalysts

The work upon the iron catalyst has been further subdivided according to the method employed to remove the heat of reaction:

1. By circulation of oil
2. By circulation of gas

The iron catalysts, which had been employed for the synthesis of ammonia from nitrogen and hydrogen, also were found to catalyze the reduction of carbon monoxide to hydrocarbons. The catalysis of the latter reaction occurred most favorably under pressures from 200-1500 pounds per square inch (15-100 atmospheres) and at temperatures from 500-700°F. (270-360°C.). This type of iron catalyst was very inactive at atmospheric pressure and differed from the precipitated catalysts further in that a much higher temperature was required.

Iron
Catalysts

With the precipitated nickel and cobalt catalysts, the upper temperature limit at which oil could be produced was determined by the point at which the methane synthesis became predominant, which was in the neighborhood of 400°F. (200°C.). The upper temperature limit with the iron catalysts, however, was determined by the point at which carbon formation began to blanket the catalyst, which was around 700°F. (360°C.). The iron catalysts formed some methane but the methane formation never became the limiting factor with these catalysts.

Due to the necessity of high temperature operation, on the verge of temperatures that would initiate carbon formation, special care had to be taken to remove the heat of reaction when using iron catalysts. If one particle of catalyst became overheated, carbon was deposited around it and the carbon acted as thermal insulation which caused even greater overheating and more extensive carbon formation, and so on until the catalyst was covered with carbon. In an effort to minimize the danger of overheating, catalysts were developed which in themselves were good thermal conductors and the synthesis reaction was carried out over such catalysts in the presence of inert materials, either gases or liquids. The gaseous or liquid inert materials were circulated through the reactor, absorbed the heat of reaction in the reactor and carried it to the outside where it was removed, the cooled inert material being recirculated.

The use of gaseous and liquid heat absorption systems has been separately studied and each found to be readily operable. The one has certain advantages over the other as will be evident from the subsequent discussions.

The process of carrying out the synthesis reaction with iron catalysts embodying the removal of the heat of reaction with the circulation of oil had been developed on the basis of a stationary bed of catalyst. This method was chosen because certain simplifications were possible in comparison with the alternative method of circulation of the catalyst as a suspension in the oil. The essential technical details for operation at pressures of 1500 pounds per square inch (100 atmospheres) or higher have been worked out on a semi-commercial scale, capacity of about two barrels (0.25 tons) of oil per day. It appeared that the process could be used at moderate pressures--200-300 pounds per square inch (15-20 atmospheres)--without appreciable changes.

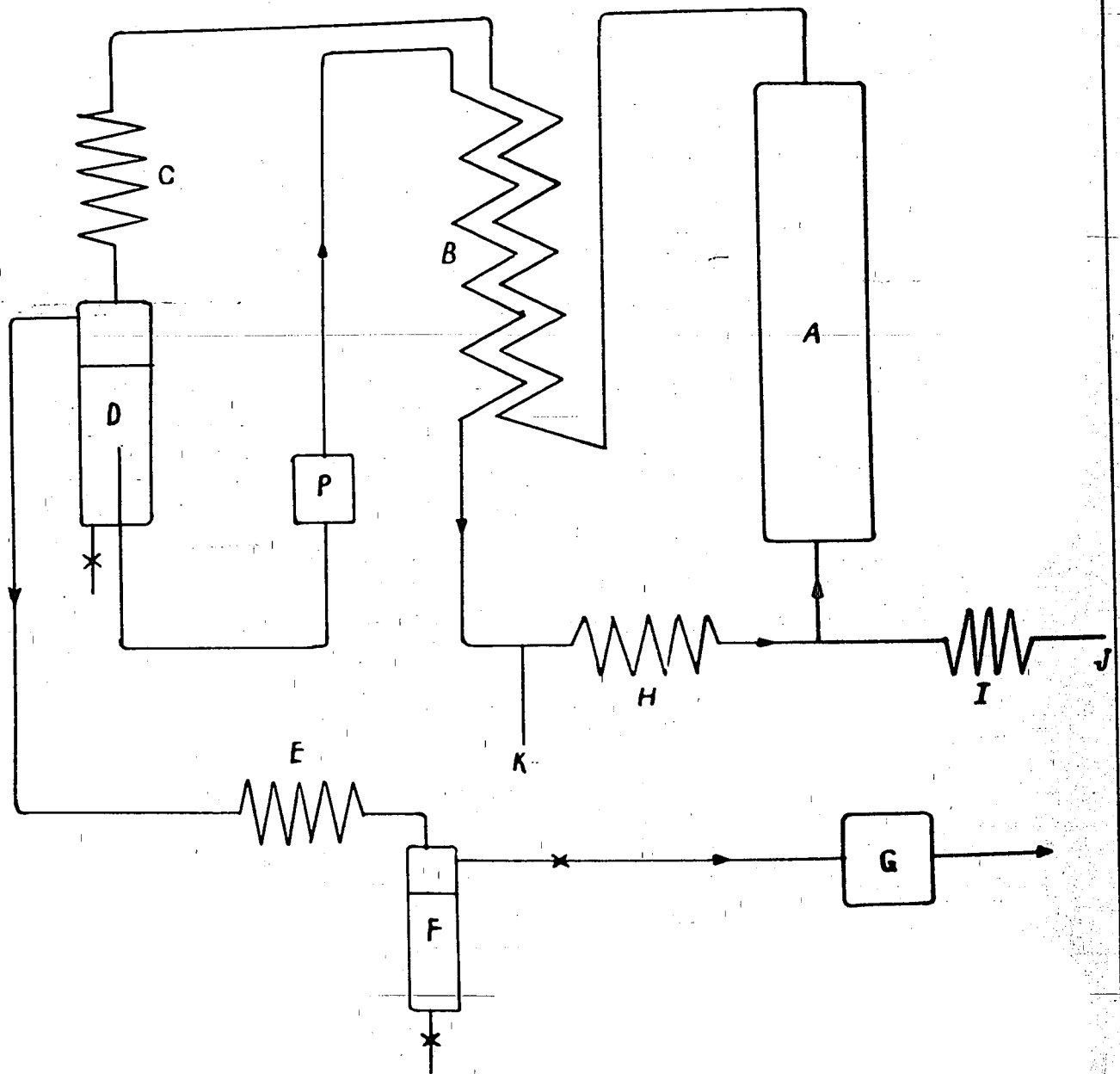
The synthesis on the semi-commercial scale was carried out in a vertically mounted reactor, with an

Heat Removal
by Oil
Circulation

Apparatus

154002223

FIGURE XIV
SYNTHESIS REACTION WITH OIL CIRCULATION



inside diameter of 4-3/4 inches (120 millimeters) and a height of 20 feet (6 meters). The reactor was an open tube except for a small centrally located tube which contained the thermocouples. The free space in the reactor amounted to about two cubic feet (60 liters) and this space was completely filled with catalyst, which has been described in a preceding section.

A diagrammatic sketch of the apparatus assembly is shown in Figure XIV opposite. The fresh synthesis gas and oil entered Reactor A, from the bottom, passed through the reactor and was taken overhead through a heat exchanger B, where the cold recirculated oil stream was reheated. The product stream was passed through an additional cooler C, where it was cooled to 140-250°F. (60-120°C.), and thence to liquid separator D. The gases and vapors were taken from the separator through a second cooler E, where the temperature was lowered to about 70°F. (20°C.), into a second separator F. The gases and vapors from F were passed through the charcoal absorber G. A constant oil level was maintained in separator D, by recirculating oil through pump P, and by drawing off any excess. From the pump, the recirculated oil stream passed through the preheater B,

Figure XIV

through a supplementary heater H, and back through the reactor. Fresh synthesis gas could be introduced at point J, and preheated in the heater I; or could be introduced at point K, and preheated in the heater I; or could be introduced at point K, and preheated together with the recirculated oil in heater H. Heavy naphtha was withdrawn from separator F.

The recirculated oil used was that produced in the synthesis itself. The boiling range of the oil could be regulated as desired by control of the condensing temperature in the separator D. The boiling range of a typical cycle oil was as follows:

Circulating
Oil

<u>Volume Per Cent</u>	<u>Temperature</u>
5	212°F. (100°C.)
10	240°F. (115°C.)
20	295°F. (146°C.)
30	350°F. (177°C.)
40	408°F. (209°C.)
50	470°F. (243°C.)
60	535°F. (280°C.)
65	572°F. (300°C.)

The amount of oil circulated was varied with the throughput to the reactor; the greater the throughput,

the greater the quantity of oil circulated. The rate of oil circulation for the experiments reported here was 40-50 volumes per volume of oil produced. This rate of oil circulation was sufficient to maintain the desired temperature and conversion.

The reaction temperature was dependent upon the composition of the synthesis gas, the degree of conversion desired, and the activity of the catalyst. The synthesis could be carried out over a wide temperature range, the upper temperature limit being around 750°F. (400°C.). Above this temperature the circulated oil began to crack and the yield of liquid products was decreased. Experiments reported here were in the temperature range of 520-680°F. (270-360°C.).

The life of the catalyst was not known at the time the installation was visited, but the experiment then being made had been in progress for 1500 hours.

Life of
Catalyst

154002227

(175)

The following tabulation gives a summary of the operation: Operation Summary

Catalyst

Type	Iron
Volume	2.1 cubic feet (60 liters)
Weight	264 pounds (120 kilograms)

Synthesis Gas: 55%CO:45%H₂

Conditions

Temperature	660°F. (350°C.)
Pressure	1500 pounds per square inch (100 atmospheres)

Throughput

Synthesis Gas - per hour	4600 cu.ft. (130 cu. meters)
Circulating Oil - per hour	150-200 gals. (550-750 liters)

Yields - per hour:

Unconverted Synthesis Gas	2340 cu.ft. (66 cu. meters)
Methane	88 cu.ft. (2.5 cu. meters)
Gasol	0.72 gals. (2.7 liters)
Gasolene	1.42 gals. (5.4 liters)
Oil and Wax	1.14 gals. (4.3 liters)
Alcohol	0.19 gals. (0.7 liters)
Water	1.25 gals. (4.7 liters)
Carbon Dioxide	470 cu.ft. (13.3 cu. meters)

Yields per cubic meter H₂ + CO

Methane	28 g.	25 g. (42 cc.)
Gasol	12 g. (21cc)	59 g. (84 cc)
Gasolene	29 g. (42cc)	52 g. (68 cc)
Oil and Wax	26 g. (33cc)	9 g.
Alcohol	4 g.	74 g.
Water	37 g.	409 g.
Carbon Dioxide	202 g.	136 g. (194 cc)
Total Liquid Hydrocarbons	67 g. (96cc)	

On Inlet Gas

On H₂ + CO Converted

Yields based on catalyst:

Oil - gallons per day per pound catalyst	0.30
gallons per day per cubic foot catalyst	37.5
kilograms per day per kilogram catalyst	1.74
kilograms per day per liter catalyst	3.48

Gas Contraction
Gas Analysis:

	37.5%
	<u>Volume %</u>
H ₂	37
CO	44
CH ₄	3
CO ₂	16

154002228

(176)

<u>Conversion of CO to:</u>	<u>% on Inlet CO</u>	<u>% on CO Converted</u>
Methane	3	7
Gasol	3	7
Gasolene	8	17
Oil and Wax	8	15
Alcohol	1	2
Carbon Dioxide	19	38
Unaccounted for	7	14
Total	49	100
Liquid Hydrocarbons	19	39

<u>Material Balance:</u>	<u>Inlet Grams</u>			<u>Outlet Grams</u>		
	C	H ₂	O ₂	C	H ₂	O ₂
Carbon Monoxide	295	--	393	149	--	198
Hydrogen	--	40.2	--	--	20.4	--
Methane	--	--	--	10	3.5	--
Gasol	--	--	--	10	2.3	--
Gasolene	--	--	--	25	4.7	--
Oil and Wax	--	--	--	22	3.9	--
Alcohol	--	--	--	2	0.6	2
Water	--	--	--	--	4.1	33
Carbon Dioxide	--	--	--	55	--	147
Total	295	40.2	393	273	39.5	380
% Recovered				93	98	97

Liquid Products:

<u>Analysis:</u>	
Gasol	16-18%
Gasolene	42%
Diesel Oil	20-27%
Lubricants	7-8%
Soft Wax	5-6%
Oxygenated Products	6%

Gasolene: boiling to 392°F. (200°C.)

Paraffins	53%
Olefins	42%
Aromatics	3% (?)
Octane Number - C.F.R.R.	68

Diesel Oil: boiling range 392-752°F. (200-400°C.)

Cetane Number	78
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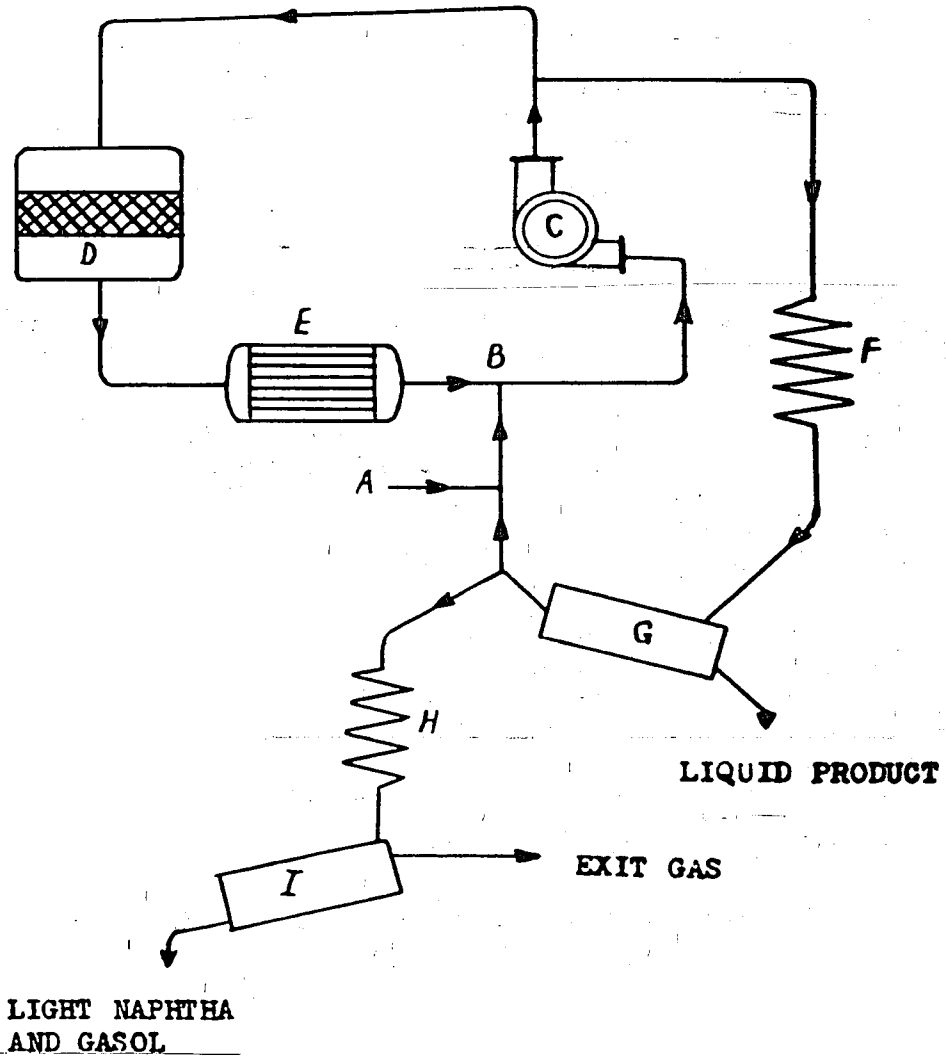
The iron catalysts were insensitive to temperature changes of 18-36°F. (10-20°C.) and would withstand greater temperature increases for short periods. Calculations showed that the temperature increase resulting from the reaction of 75% of synthesis gas could be limited to 18°F. (10°C.) by a hundredfold dilution and to 36°F. (20°C.) by a fiftyfold dilution. The dilution could be made with synthesis gas (that is, limiting the conversion to about 1 or 2%), but the dilution was preferably done with the heavier since they apparently exerted a "quieting" effect upon the catalyst. It was found feasible to use the tail gases from the synthesis reaction, after removal of the heavier synthesis products.

Heat Removal
by Gas
Circulation

A pressure of 300 pounds per square inch (20 atmospheres) was found optimum with the particular catalyst employed, although it was emphasized that the optimum pressure would vary with the activity of the catalyst. With the iron catalyst, pressures in excess of 20 atmospheres caused the production of larger quantities of oxygenated organic compounds at the expense of the hydrocarbons, while at pressures lower than 20 atmospheres, the conversion was much lower.

Pressure

FIGURE XV

SYNTHESIS REACTION WITH GAS CIRCULATION

The temperatures employed were in the range of 575 to 650°F. (300 to 350°C.), the results to be presented here being obtained at 608-626°F. (320-330°C.). The hundredfold diluted synthesis gas entered the reactor at 608°F. (320°C.) and after undergoing reaction left the reactor at 626°F. (320°C.).

Temperature

A schematic flow sheet of the apparatus is shown in Figure XV opposite. Fresh synthesis gas entered at point A, joined the recycle gas stream at B, passed through the blower C, and into the reactor D, which was a circular vessel 2.5 feet (77 centimeters) inside diameter, containing catalyst at a depth of 2.8 feet (85 centimeters). From the reactor the gas stream was cooled in E, which generated high pressure steam, and again sent to the blower. A portion of the gas stream from the blower was passed through a water cooler F, and into a gas-liquid separator G, from the bottom of which a heavy liquid product was drawn. The gas from the separator G was largely returned to the main stream, but a portion was passed through the liquid ammonia cooler H, and into liquid-gas separator I, from the bottom of which light naphtha and gasol were withdrawn. The gases from separator I, were

ApparatusFlow SheetFigure XV

discarded as tail gas.

The summary of results on the following pages has been made from the information supplied. It should be mentioned that these results, to a large extent, represent calculations from the original data.

Catalyst:

Type
Volume
Weight

Iron
14 cu.ft. (400 liters)
2200 pounds (1 ton)

Summary
of
Results

Synthesis Gas:

H₂ 56%
CO 44%

Conditions:

Temperature

608-626°F. (320-330°C.)

Pressure

300 lbs./sq.in. (20 atmospheres)

Throughput:

Synthesis gas - per hour

3,800 cu.ft. (107 cu. meters)

Recycle gas - per hour

380,000 cu.ft. (10700 cu. meters)

Total - per hour

383,800 cu.ft. (10807 cu. meters)

Yields - per hour:

Methane
Ethylene
Propylene
Butylene
Gasolene
Diesel Oil
Paraffin
Alcohol
Water
Carbon Dioxide
Total Liquid Hydrocarbons

164 cu.ft. (4.6 cu. meters)
45 cu.ft. (1.3 cu. meters)
0.6 gallons (2.3 liters)
0.5 gallons (2.0 liters)
2.3 gallons (8.5 liters)
0.6 gallons (2.2 liters)
0.1 gallons (0.3 liters)
0.4 gallons (1.7 liters)
3.0 gallons (11.3 liters)
363 cu.ft. (10.3 cu. meters)
4.1 gallons (15.3 liters)

Yields - per cubic meter (H₂ + CO):

Methane
Ethylene
Propylene
Butylene
Gasolene
Diesel Oil
Paraffin
Alcohol
Water
Carbon Dioxide
Total Liquid Hydrocarbons

31 grams
15 grams
11 grams (21 cc.)
11 grams (18 cc.)
56 grams (80 cc.)
16 grams (21 cc.)
2 grams (3 cc.)
12 grams (16 cc.)
106 grams (106 cc.)
189 grams
96 grams (143 cc.)

Yields based on catalyst:

Liquid Hydrocarbons

0.04 gallons per day per pound of catalyst

6.9 gallons per day per cubic foot of catalyst

0.4 liters per day per kilogram of catalyst

0.9 liters per day per liter of catalyst

Gas Contraction:

60%

Gas Analysis - Volume %

	<u>Exit Gas</u>	<u>Recycle Gas</u>
Methane	11	8
Ethylene	3	2
Propylene	--	1
Butylene	--	1
Water	--	24
Carbon Dioxide	24	18
Carbon Monoxide	27	20
Hydrogen	<u>35</u>	<u>26</u>
	100	100

Conversion of CO to %:

	<u>On Inlet</u>	<u>On CO Converted</u>
Methane	10	13
Ethylene	5	7
Propylene	4	5
Butylene	4	5
Gasolene	20	27
Diesel Oil	6	8
Paraffin	1	1
Alcohol	3	4
Carbon Dioxide	<u>22</u>	<u>30</u>
Total	75	100
Liquid Hydrocarbons	35	46

Material Balance:

	<u>Inlet-grams</u>			<u>Outlet-grams</u>		
	<u>C</u>	<u>H₂</u>	<u>O₂</u>	<u>C</u>	<u>H₂</u>	<u>O₂</u>
Carbon Monoxide	25130	--	33500	6240	--	8320
Hydrogen	--	5330	--	2480	830	--
Methane	--	--	--	1360	225	--
Ethylene	--	--	--	1010	180	--
Propylene	--	--	--	1010	175	--
Butylene	--	--	--	5100	870	--
Gasolene	--	--	--	1470	250	--
Diesel Oil	--	--	--	230	40	--
Paraffin	--	--	--	740	170	410
Alcohol	--	--	--	--	1260	10080
Water	--	--	--	<u>5500</u>	--	<u>14700</u>
Carbon Dioxide	--	--	--	25140	5340	33510
Total	25130	5330	33500	100	100	100
% Recovered						

Liquid Products:

Weight Analysis:

Gasol	21%
Gasolene	51%
Diesel Oil	15%
Paraffins	2%
Alcohol	11%

Gasolene:

Octane Number	-	straight	
	-	treated method	A (50% at 212°F. (100°C.) 80 CFRR)
	-	treated method	B (50% at 212°F. (100°C.) 84 CFRR)
	-	treated method	B 88 CFRR
	-	blend 10% in 60	O.N. Fuel 107 CFRR
	-	blend 50% in 60	O.N. Fuel 95 CFRR

Olefins:

approximately 80%

Oxygen Content:

raw	3.0-3.5%
treated	0.5%

Gum:

2.5 milligrams per 100 grams after storage

Diesel Oil:

Cetene Number	53
Pour Point	-11°F. (-24°C.)
Oxygen Content	1.5-2.0%
Olefin Content	80% (approximately)

Alcohols:

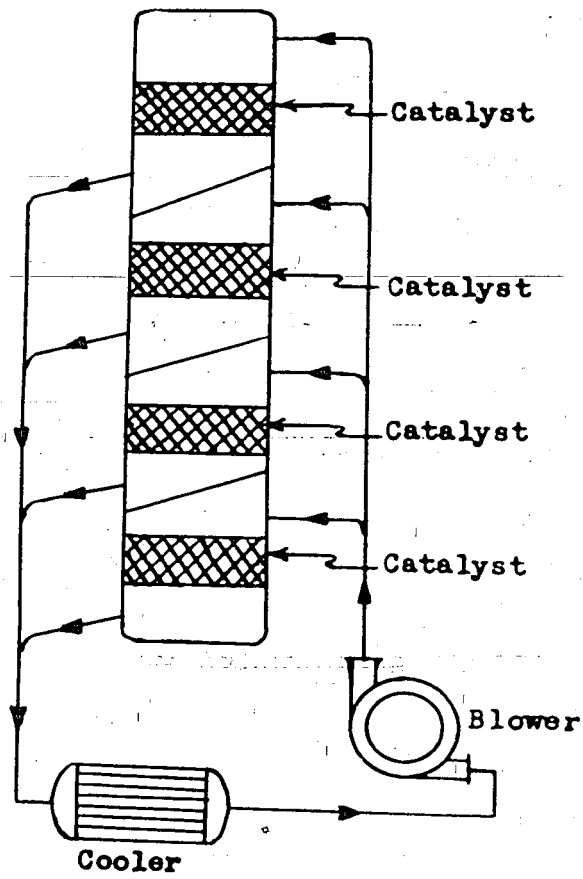
Weight Analysis:

Acetaldehyde	5%
Acetone	11%
Ethyl Alcohol	57%
Propyl Alcohol	25%
Heavier Alcohols	2%

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FIGURE XVI

REACTOR WITH PARALLEL GAS FLOW FOR
IRON CATALYST WITH GAS CIRCULATION



The energy required for circulation of the gas stream increased as the third power of the catalyst depth and it was therefore advantageous to use shallow beds. The above described operation with an 85 centimeter depth of catalyst required an energy consumption of about 1.25 kwh per gallon (0.5 kwh per kilogram) of liquid product for the gas circulation. It was thought that the above figure could be at least halved by use of shallower beds in a parallel flow, as indicated in Figure XVI opposite. A proposal had been submitted for the erection of such a reactor large enough to produce about 120 barrels of liquid products per day (5000 tons per year).

The life of the catalyst was not accurately known. A batch of the catalyst had been in continuous use on a laboratory scale for 2.5 months before an accidental temperature increase led to pulverization of the catalyst. The semi-commercial plant, the results from which have been given earlier, had been in operation only about one month. It was thought that in large-scale operation the catalyst would have a very long life, since relatively large amounts of sulfur in the synthesis gas were without effect upon the catalyst activity. The catalyst

Energy for
Gas
Circulation

Flow Sheet

Figure XVI

Catalyst
Life

could be very simply regenerated by roasting and reducing; the regenerated catalyst frequently showing greater activity than the original catalyst.

The investigations of the precipitated cobalt catalysts were carried out in two separate laboratories, and since the method of attack was different in the two instances the work in the two laboratories will be presented separately.

Cobalt
Catalysts

The research at Leuna was directed primarily towards the development of catalysts for the production of liquid hydrocarbons and the work consisted largely of the manufacture and testing of catalysts. The catalysts were first tested in the conventional laboratory equipment and those catalysts which produced 110 grams or more of primary product per cubic meter of synthesis gas for a period of two to three weeks in the laboratory were further investigated in the pilot plants.

Leuna
Investigation

At the time the Leuna laboratory was visited, it was stated that 600-800 catalysts were under test in the laboratory and that an average of 100 such catalysts were discarded each week as being unworthy of further

Laboratory

study. The laboratory reactors were horizontally mounted, ~~since it had been found that appreciably better yields~~ were thus obtained as compared to a vertically mounted reactor. The explanation of the better yields from the horizontal tubes was that more uniform temperatures were obtained due to convection currents.

The pilot plant experiments were carried out in two types of reactors:

Pilot Plant
Work

1. Catalyst outside horizontal cooling tubes which were closely fitted to vertical metal plates
2. Catalyst in tubes inside a water bath

Average catalysts gave hydrocarbon yields per cubic meter of ideal synthesis gas of 110-115 grams at atmospheric pressure and 140 grams at eight atmospheres pressure; two-stage operation in each instance. The characteristics of the products were about the same as those reported by Ruhrchemie, except that a smaller methane production was obtained.

The reactors in which the catalyst was placed outside cooling tubes, closely resembled the Ruhrchemie atmospheric pressure reactors in construction. The larger reactor, which held 18 cubic feet (500 liters)

Catalyst
Outside Tubes

of catalyst, was used exclusively at atmospheric pressure.

This chamber was giving a yield of 70 grams of liquid hydrocarbons per cubic meter of synthesis gas at the time of the visit and had been in operation with the same catalyst for over nine months.

A similarly constructed reactor, which held five cubic feet (150 liters) of catalyst, had been used at higher pressures, but proved inoperable at pressures above 60 pounds per square inch (4 atmospheres). The cause of the failure of this reactor under pressure was lack of temperature control.

The tubular reactors consisted of various sized smooth tubes welded into a cylindrical shell containing water under pressure. Twelve reactors were in use which were 5 feet (1.5 meters) long. Each of these reactors contained three liters of catalyst when filled to a 3 foot (90 centimeters) depth. The remainder of 2 linear feet of reactor was utilized to preheat the incoming gases. The tubular reactors contained 119 tubes of 6 millimeter size or 43 tubes of 10 millimeter size or 19 tubes of 15 millimeter size. Two reactors, each containing 19 tubes of the 15 millimeter size, were 15 feet (4.5 meters) high and held 12 liters of

Tubular
Reactors

catalyst when filled to a depth of 12 feet (3.6 meters).

~~A tubular reactor was being constructed to accommodate a 33 foot (10 meter) depth of catalyst.~~

Each of the tubular reactors was provided with condensing and charcoal adsorption equipment and could be operated at any pressure up to 375 pounds per square inch (25 atmospheres). The inlet gas quantities were measured in the usual type dry gas meters; those for reactors operating under pressure being enclosed in steel spheres provided with sight glasses. The "temperature" in the reactors was measured by the methane formation. The latter, in turn, was estimated from the specific gravity of the tail gas, a special meter having been developed to record the specific gravity continuously in terms of methane content.

The results from the pilot plant work had indicated some advantages of the cobalt-magnesia catalyst over the cobalt-thoria catalyst. The magnesia catalyst was more rugged and more easily reproduced than the thoria catalyst. The thoria catalysts gave slightly better oil yields and were subject to less temperature fluctuation upon starting synthesis gas over a new catalyst.

Results

Catalyst

The apparent density of the catalyst had no effect upon the activity when the activity was expressed as oil produced per unit of synthesis gas per volume of catalyst. The apparent density was varied from 0.3 for the filter cake fragments to 1.0 for hard pellets. An interesting result, in this connection, was a yield of 130-135 grams of liquid hydrocarbons per cubic meter of synthesis gas when operating a reactor with 6 millimeter tubes into which 5 millimeter catalyst pellets had been carefully stacked one on top of the other. The gas stream flowed downward through the annular space between the catalyst pellets and the walls of the tube.

Catalyst
Density

The practice was to reduce the catalysts in the reactors themselves and no difference could be detected in the activity of a catalyst reduced in a shallow layer (10 centimeters) at 650-750°F. (350-400°C.) and that reduced in a deeper bed (4,500 centimeters) at temperatures of 390-570°F. (200-300°C.).

Reduction

The partially deactivated catalyst could be Revivification
equally well revived by:

1. Treatment with hydrogen at 390-750°F.
(200-400°C.), or
2. Extraction with pylol at 260°F. (125°C.).

The solvent extracted catalyst could be put back into operation more quickly than the hydrogen treated catalyst, due to a lower temperature sensitivity of the former.

The depth of catalyst was found to be without appreciable effect upon the oil yield in the range of depths from three to twelve feet (1-4 meters), the greater depth appearing to give slightly higher yields. It was thought that possibly the catalyst depth could be increased to as much as 30 feet (10 meters) without seriously affecting the oil yields. It was thought unlikely that greater depths could be used, since at 30 feet (10 meters) the head of water in the cooling system was sufficient to cause the temperature to be 6°F. (3.5°C.) higher at the bottom than at the top of the reactor.

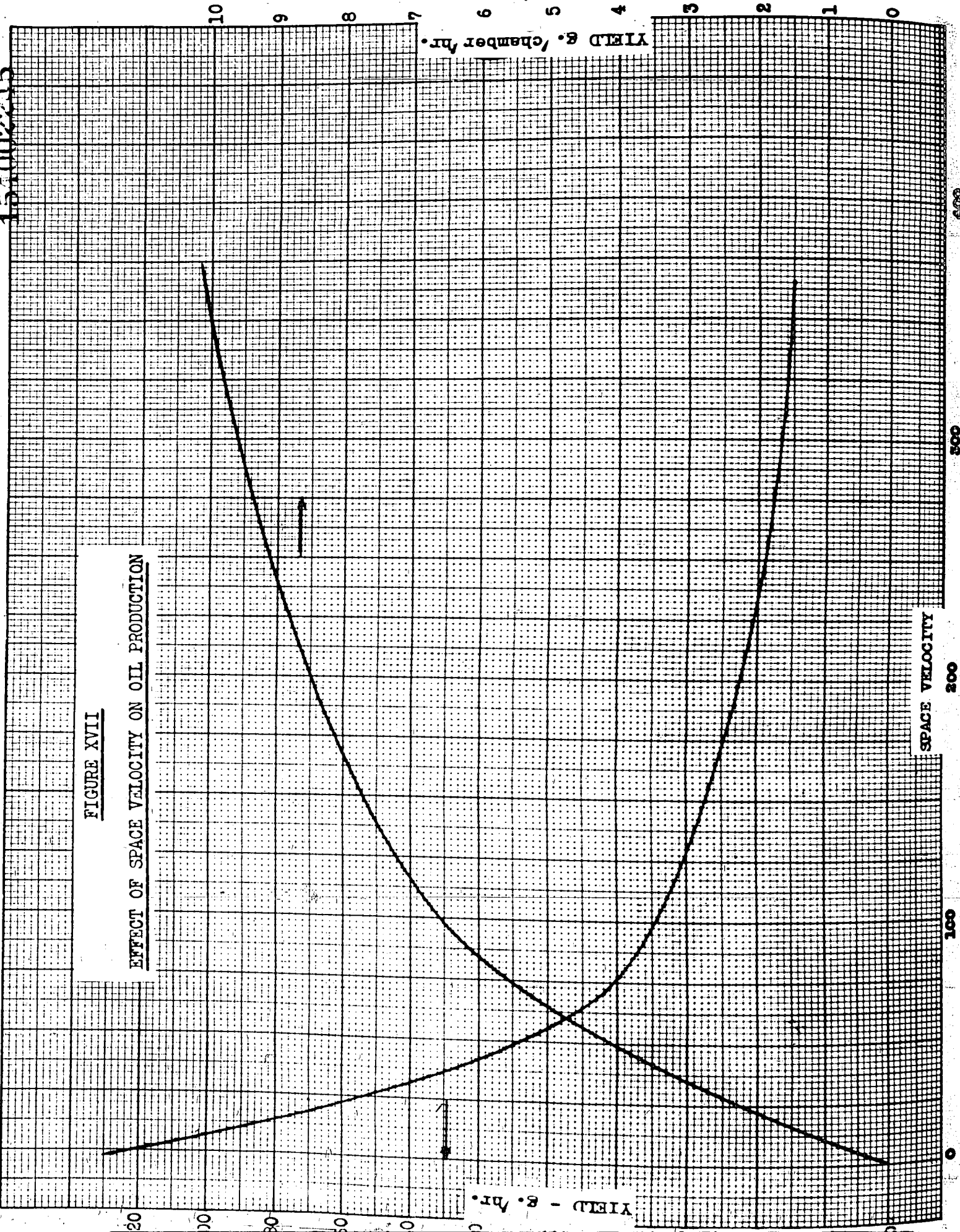
Catalyst
Depth

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FIGURE XVII

EFFECT OF SPACE VELOCITY ON OIL PRODUCTION



Gas
Velocity

The fact that the depth of bed had no effect upon the oil yields indicated the desirability of investigating the influence of gas velocity, since in the deeper beds the gas velocity over the top section was much higher than that over the top section of a shallow bed. When the gas velocity was varied over a fourfold range with a constant depth of catalyst, it was found that as the gas velocity was increased the oil yield per reactor increased to a maximum and then appeared to remain stationary. The oil yield per unit of gas, however, decreased as the gas velocity increased. The results of this investigation are shown graphically in Figure XVII. From the trend of the curve for oil production per chamber versus gas rate, the desirability of higher gas velocities was indicated. The effect of the higher velocities upon the life of the catalyst was not known, although, from the fact that lighter hydrocarbon products were obtained at the higher rates, it might be concluded that less heavy hydrocarbons would be retained on the catalyst and that this would increase the life.

Figure XVII

Recirculation
of Tail Gas

The effects of recirculation of the product gases from the synthesis reaction were being

determined at the time the laboratory was visited. Preliminary indications were that higher oil yields would be obtained per unit of synthesis gas and per unit of catalyst volume. In addition, the hydrocarbon product was of lower molecular weight--65-70% boiling up to 356°F. (180°C.) in product from recirculation experiments as compared with 40-50% in the same range for the normal product.

A tubular reactor was constructed in five serial sections, with provision for sampling from each section. Analysis of samples from each section indicated that one-fifth of the total reaction was occurring in each section of the catalyst. Samples of catalyst were taken from each section of the reactor after six weeks use, tested in the laboratory and found to have identical activities. These results tended to disprove the theory that the upper portions of the catalyst were responsible for the production of the greater part of the oil. It is difficult to reconcile the identical activities of the catalyst from the top and bottom sections of the reactor with the well established fact that the temperature is much higher in the top section of a catalyst bed.

Sectional
Reactor

Oppau
Investigation

The experimentation at Oppau was originally directed towards development of a catalyst that would convert carbon monoxide and hydrogen largely to solid paraffin. As a first step in the investigation, an attempt was made to determine the contribution of each of the main components in an active catalyst, taking the cobalt-thoria-kieselguhr catalyst ($\text{Co}:0.18\text{ThO}_2:1.0\text{SiO}_2$) as a standard. The life and activity of each catalyst preparation was compared to that of the cobalt-thoria standard catalyst, the experiments being conducted on a laboratory scale, single-stage in glass reactors at atmospheric pressure.

The catalyst of cobalt alone (no support and no promoter) was investigated, since cobalt was thought to be the main catalytical material in the standard catalyst. This catalyst was prepared by the slow addition (over a period of 8 hours) of a cold dilute cobalt solution (12 grams cobalt per 8 cc. of water) to a cold solution of sodium carbonate. This catalyst gave an oil yield of about 110 grams per cubic meter for a period of about 24 hours at atmospheric pressure and a gas rate of one liter per hour per gram of cobalt. The short life was attributed to the sintering of the cobalt lattice, since a very small amount

of paraffin was produced.

The catalyst was then prepared in which magnesia was incorporated with the cobalt, since magnesia and cobalt oxide were known to form mixed crystals. It was thought that the magnesia would prevent the destruction of the cobalt lattice and thus prolong the life of the catalyst. At a gas rate of one liter per hour per gram of cobalt, the oil yields were 80-85 grams per cubic meter when magnesia had been added to the extent of 2-15% on the cobalt. This catalyst had a very high apparent density (1.2) and occupied a volume only 1/4 that of the normal content. An oil yield of 100 grams per cubic meter was obtained for a period of two months when a normal rate of gas per unit volume of catalyst (1/4 the normal weight) was used.

Cobalt-
Magnesia
Catalyst

When the cobalt-magnesia catalyst was supported upon kieselguhr, the oil yield was about 103 grams per cubic meter at a gas rate of one liter per hour per gram of cobalt.

Cobalt-
Magnesia-
Kieselguhr
Catalyst

A catalyst of cobalt supported on kieselguhr was prepared in the same manner as the previously mentioned pure cobalt catalyst. This catalyst gave an oil yield of about 105 grams per cubic meter at a gas rate of one liter per hour per gram of cobalt over a period of about four months. The oil yield was somewhat lower than that from the normal contact (105 grams versus 115 grams per cubic meter) but the catalyst showed a remarkable life in that it could be used for four months without regeneration. The exceptional life was attributed to the fact that solid paraffin was formed only during the first 14 days.

Cobalt-
Kieselguhr
Catalyst

When this catalyst was tested under 12 atmospheres pressure, more paraffin was produced than with the standard cobalt-thoria catalyst, although the reverse had been true at atmospheric pressure. The gas velocity was increased over this catalyst, giving the following results:

<u>Gas Rate</u> <u>Liters/hr./g. of Co</u>	<u>Oil Yield</u> <u>Grams/cu. meter</u>
1	140-150
2	120
4	90

The temperature was increased 18°F. (10°C.) when the gas rate was doubled, and was increased another 18°F. (10°C.) when the gas rate was quadrupled.

From the above investigations of the role of the three components, that of thorium oxide appeared to be two-fold. On the one hand it stabilized the cobalt lattice and on the other hand it directed the reaction towards the production of higher boiling products. From the latter conclusion, it appeared that the greater amounts of solid paraffins would be obtained with catalysts containing a higher percentage of thoria and tests of such catalysts confirmed the conclusion.

KELLOGG SYNTHESIS PROCESS

The first experimentation in the Kellogg laboratory upon the synthesis of hydrocarbons from carbon monoxide and hydrogen involved the use of nickel catalysts; more particularly, the nickel-manganese-alumina-kieselguhr catalyst. This catalyst was investigated on a small scale in glass reactors and on a larger scale in a steel reactor. Cobalt catalysts, containing various materials as promoters, have been studied on a small scale in glass reaction tubes. The thorium-promoted cobalt catalyst has been tested on a small scale in both glass and steel reactors.

Scope
of Work

The apparatus and technique employed for the small-scale experiments were, in general, similar to those reported in the literature upon the synthesis reaction. The glass reactors were 16 mm. inside diameter and were mounted vertically in an aluminum block furnace. The steel reactors for the small-scale experiments were of various inside diameters from 14-51 mm. Temperatures were measured in the furnace and in the top half-inch of the catalyst bed, the latter temperature being that referred to in the

Small Scale
Experiments

Apparatus

following description of results. The gas quantities in and out of the reactor and the volumes of oil and water produced were measured hourly. The exit gases were analyzed periodically.

The experiments upon the nickel catalyst:

Ni:0.20 MnO:0.09 Al₂O₃:1.2 SiO₂ covered the effect of variables in the catalyst preparation, such as extent of washing, addition of potassium carbonate, catalyst density, addition of graphite and variation in manganese content.

The use of 150 cc. of wash water per gram of nickel gave the most active catalyst and the indications were that the use of larger quantities of wash water would not increase the oil-producing properties of the catalyst. It appeared, however, that the use of larger quantities of wash water would decrease the extent of the undesirable side reactions.

The addition of potassium carbonate to the catalyst, in amounts up to 1% of the metallic nickel content, had no significant effect upon either the direction or the extent of the synthesis reaction. Rewetting and/or redrying the catalyst caused the

Nickel
Catalysts

Ni-MnO-
Al₂O₃-SiO₂

Extent of
Washing

Addition of
Potassium
Carbonate

(198)

production of slightly less oil per unit of synthesis gas and a decrease in the yield of oil per unit amount of carbon monoxide consumed. This was true whether the rewetting was done with pure water or with potassium carbonate solutions.

At a given temperature, the oil production was greater, the lower the apparent density of the catalyst. This was probably due to the fact that the facility with which the temperature in the catalyst bed could be controlled, increased with a decrease in the apparent density of the catalyst. The fraction of the total reacted carbon monoxide recovered as oil was higher when filter-cake fragments were used than when pellets were used.

The addition of graphite to the catalyst, up to about 9% of the metallic nickel content, was apparently without effect upon the activity of the catalyst.

The use of more than 20% manganous oxide (based on the nickel content) did not increase the activity of the catalyst.

Tests made upon two preparations of nickel molybdate showed them to be completely inactive as

Density of
Catalyst

Addition of
Graphite

Manganese
Content

Nickel
Molybdate

regarded oil production.

Cobalt-base catalysts have been prepared and tested which contained thoria, manganese, alumina, manganese-alumina, ceria or magnesia as promoter. In comparison with the nickel catalysts, cobalt catalysts were found to have a higher initial oil-producing activity, longer active life, and less tendency to sinter at higher temperatures. In addition, it appeared that reproducible catalytic activity was more easily obtained with the cobalt catalysts than with the nickel catalysts.

Cobalt
Catalysts

The cobalt-thoria-kieselguhr catalyst has been found to be about the best synthesis catalyst tested. The experimental work upon this catalyst has been more extensive than upon any other individual catalyst and has included determination of: conditions for optimum oil yields, optimum amount of support, effect of dilution of the catalyst, effect of electro-washing the precipitated catalyst, effect of reactor sizes and materials, effect of inlet gas velocity, and the effect of pressure.

Cobalt-
Thoria
Catalysts

Conditions

The optimum oil production per normal cubic meter of synthesis gas--160-170 cc.--was obtained at about 420°F. (215°C.) at an inlet gas rate of one liter per hour per gram of cobalt, when the catalyst was used in the form of filter-cake screenings with an apparent density of about 0.2. The use of the catalyst in the form of pellets--higher apparent density and therefore a smaller reaction volume per unit weight of cobalt and therefore more heat of reaction liberated for a given cooling surface--gave lower oil yields than were obtained from the filter-cake screenings.

The optimum oil production per unit weight of cobalt in unit time, within the range of the experiments, was 270 cc. per pound of cobalt per hour, at 438°F. (225°C.), an inlet gas rate of four liters per hour per gram of cobalt, through a catalyst bed depth of 3 feet (90 centimeters), in a reactor with an inside diameter of 0.5 inches (14 millimeters). The life of the catalyst under these conditions has not been determined, but if the life be assumed to be four months, the above yield would correspond to a production of five barrels of oil per pound of cobalt (1200 tons of oil per ton of cobalt) per life period of the catalyst.

A few preliminary experiments under a pressure of 100 pounds per square inch (8 atmospheres) indicated that somewhat higher oil yields were obtained at the higher pressure than at atmospheric pressure. The products from the pressure operation contained larger amounts of high-boiling hydrocarbons, with only traces of oxygen-containing organic compounds.

Pressure
Operation

The quantity of support (kieselguhr) has been varied from zero to seven times the weight of the metallic cobalt. The unsupported catalyst was not very active towards oil production and tended to produce chiefly solid hydrocarbons. An amount of support equivalent to the weight of metallic cobalt gave the most active catalyst of those tested. An increase in the amount of support above that equivalent to the weight of cobalt decreased the catalytic activity towards oil production, although the decrease was not appreciable until the amount of support was about four times the weight of the cobalt. There was no significant effect of additional support upon the temperature difference existing between the furnace and the catalyst bed and no observable increase in the efficiency with which the carbon monoxide was converted into oil.

Amount of
Support

Within the range of experimentation, there was but little difference whether the support was incorporated before precipitation or added after precipitation as a dry powder.

The distribution of catalyst pellets among inert porcelain beads, to obtain a larger reaction volume, did not affect the oil yields.

"Dilution"
of Catalyst

A catalyst prepared in the usual manner, except that it was electrolyzed for a short time after washing the precipitate, showed extraordinary activity--193 cc. of oil per normal cubic meter of pure synthesis gas over the temperature range 400-420°F. (204-216°C.)

Electrowashed
Catalyst

Comparative experiments with reactors of glass, brass and steel of the same dimensions indicated that the optimum oil yields were not affected by the material of which the reactor was made. The temperature difference between the catalyst and furnace was about 40°F. (22°C.) less in the metal reactors than in the glass reactor.

Reactor
Materials

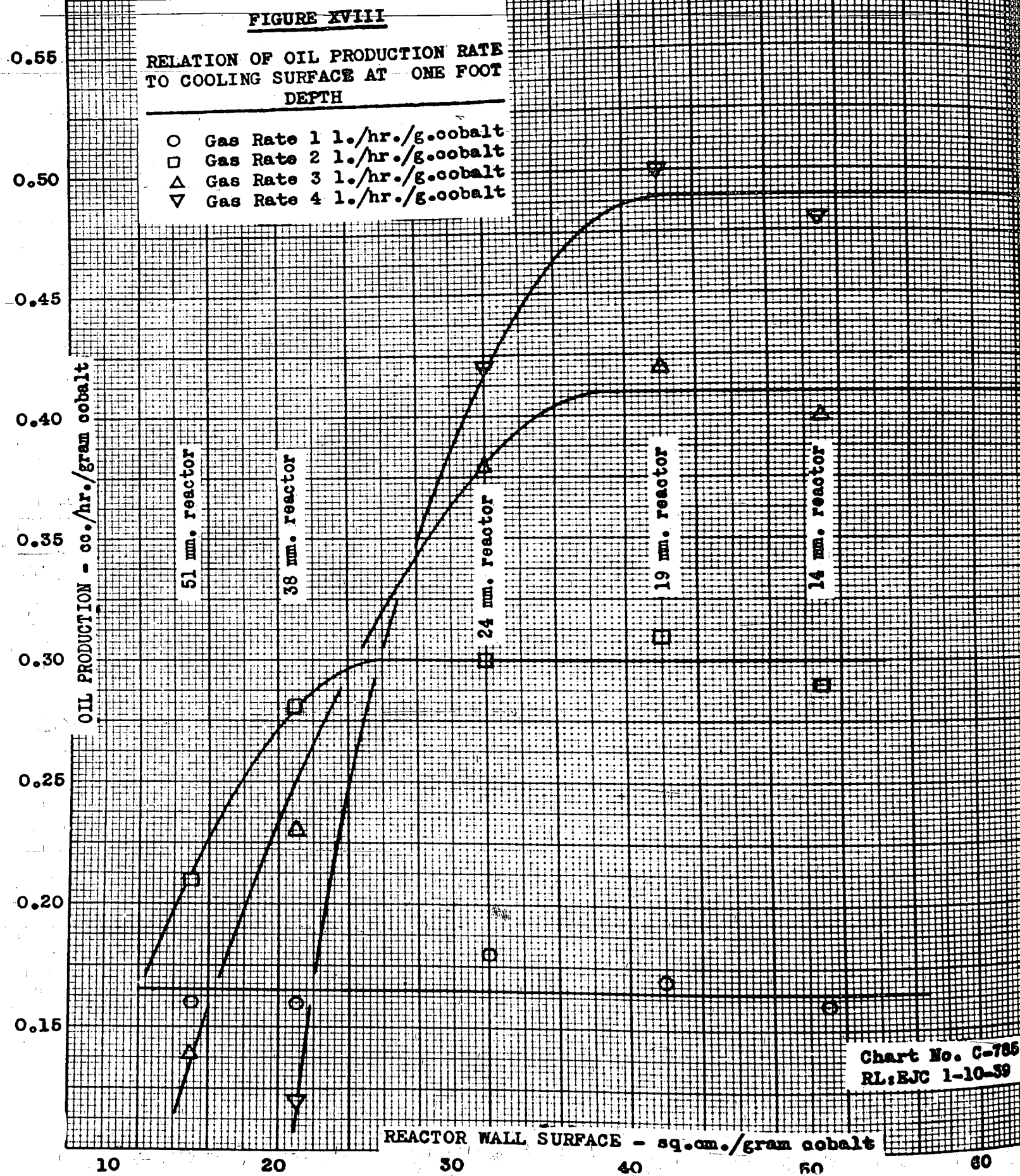
Experiments were made with a steel reactor with an inside diameter of two inches (51 millimeters).

Reactor
Diameters

When the same amount of heat of reaction was liberated in unit time, the oil yields were about the same for the same depth of catalyst bed regardless of the dimensions of the reactor. At the same gas rate per unit of catalyst, the two inch (51 millimeter) reactor was much inferior to the three-fourths inch (16 millimeter) reactor for the same depth of catalyst. At the same gas rate and with the same amount of catalyst (different depth of catalyst bed) the larger reactor was again inferior to the smaller reactor. At very low gas rates per unit weight of catalyst--as low as 100 cc. of gas per hour per gram of cobalt--the excess catalyst did not affect the oil yield.

The above comparison of the usual size reactor with the wider reactor indicated that any investigation of the optimum reactor diameter would be intimately connected with the gas rate through the reactor, probably due to changes in the amount of heat of reaction to be dissipated per unit of reactor wall surface. Therefore, the continuation of the study of the effect of reactor diameter was made at various inlet gas rates.

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The results of the study of inlet gas rates in reactors of various diameters probably can be presented most clearly in the form of graphs. Figure XVIII opposite is a plot of oil production versus the amount of reactor wall surface available for dissipation of the heat of reaction. A series of experiments were made at gas rates of from one to four liters per hour per gram of cobalt and each curve on the graph represents the results from a given gas rate, all the curves having been obtained at a catalyst depth of one foot (31 centimeters).

Inlet
Gas Rates

Figure XVIII

It was evident that at one liter per hour per gram of cobalt the oil production was not affected by change in the reactor diameter from one-half inch to two inches (14 mm. to 51 mm.). At two liters of gas per hour per gram of cobalt, the oil production was much less in the two-inch (51 millimeter) reactor and was slightly less in the one and one-half inch (38 millimeter) reactor than in the reactors with a smaller diameter. At three liters of gas per hour per gram of cobalt, the oil production from the two larger diameter reactors (two-inch (51 millimeter) and one and one-half inch (38 millimeter)) was much

lower than from the smaller reactors. The oil production from the one-inch (24 millimeter) reactor was slightly lower than that from the smaller reactors. At four liters of gas per hour per gram of cobalt, only the two reactors with the smaller diameters gave similar yields. Thus, at a catalyst depth of one foot, the allowable diameter of the reactor decreased with an increased gas rate, until at four liters of gas per hour per gram of cobalt, the largest diameter reactor that would give optimum oil production was three-fourths inch (19 millimeter).

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FIGURE 22A

RELATION OF OIL
RATE TO COOLING
TWO REACTORS

○ 1930 Series
□ 1931 Series
△ 1932 Series

14 mm. Reactor

24 mm. Reactor

38 mm. Reactor

OIL PRODUCTION - cc./hr./gram cobalt

REACTOR WALL SURFACE - sq. cm./gram cobalt

10 20 30

0.55

0.50

0.45

0.40

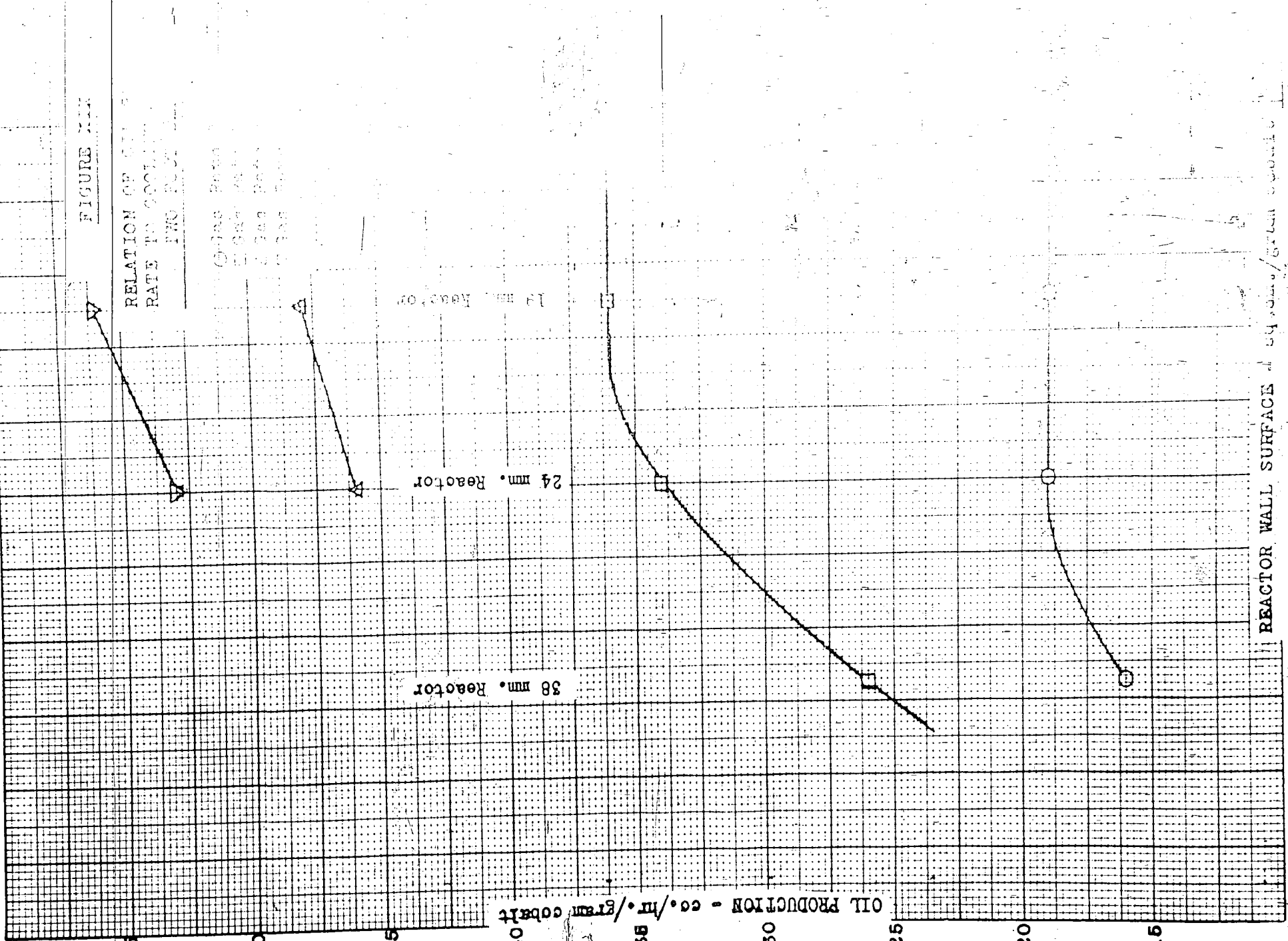
0.35

0.30

0.25

0.20

0.15



The results obtained at a catalyst depth of two feet (61 centimeters) are shown in Figure XIX. The curves on this chart are similar to those previously shown, except that their position has been moved towards the right on the bottom axis. The experimentation was not sufficiently extensive to accurately locate the break in the two upper curves.

Figure XIX

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FIGURE XX

RELATION OF OIL PRODUCTION RATE
TO COOLING SURFACE AT THREE FOOT
DEPTH

- Gas Rate 1 1./hr./g.cobalt
- Gas Rate 2 1./hr./g.cobalt
- △ Gas Rate 3 1./hr./g.cobalt
- ▽ Gas Rate 4 1./hr./g.cobalt

OIL PRODUCTION - cc./hr./gram cobalt

24 mm. Reactor

19 mm. Reactor

14 mm. Reactor

REACTOR WALL SURFACE - sq.cm./gram cobalt

10

20

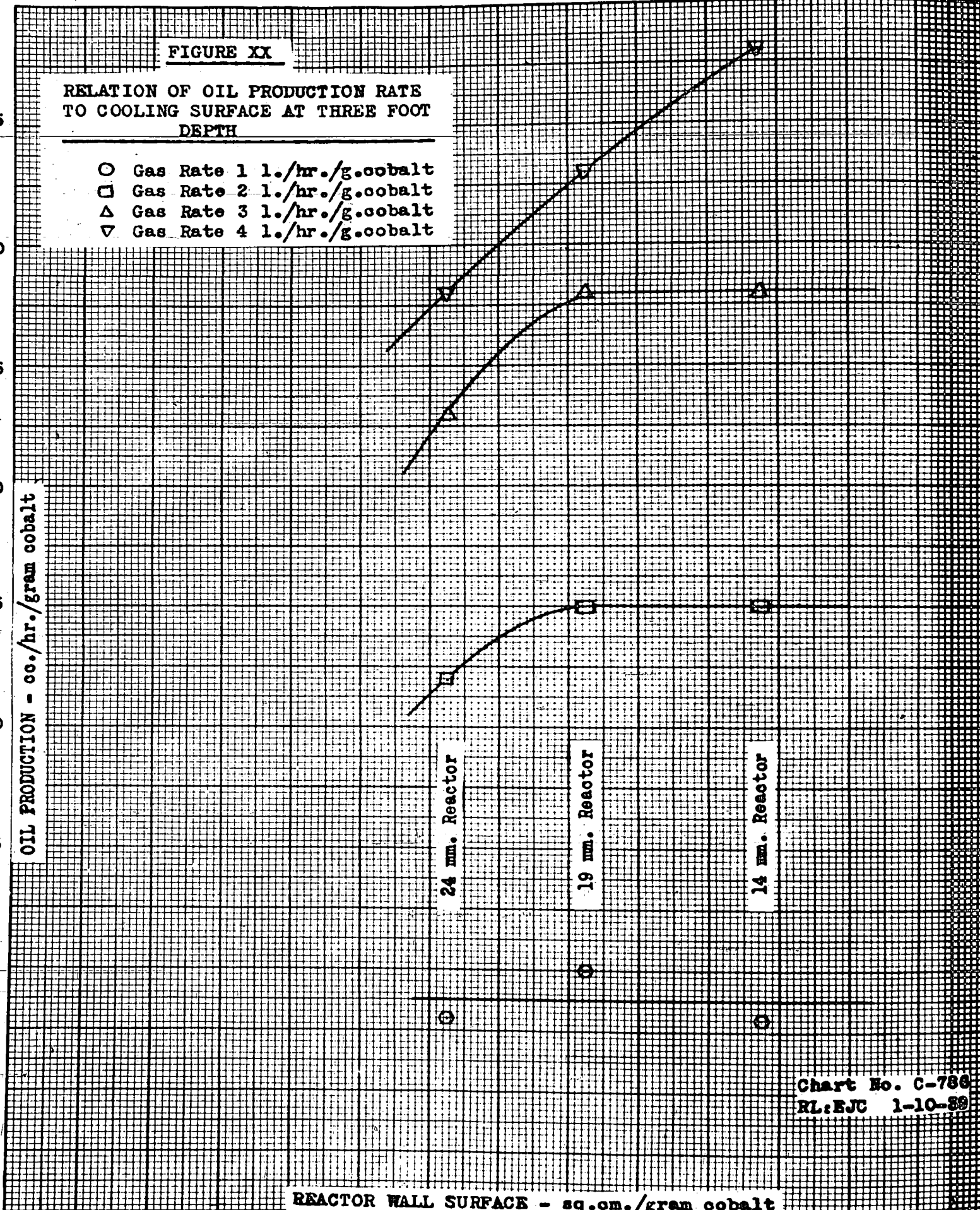
30

40

50

60

Chart No. C-786
RL:EJC 1-10-39



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(207)

Figure XX opposite shows the results obtained with a catalyst depth of three feet (92 centimeters). It is evident that the break in the curves has moved still further to the right along the bottom axis, although the data were insufficient to locate the break in the curve for four liters of synthesis gas per hour per gram of cobalt.

Figure XX

FIGURE XXI

RELATION OF OIL PRODUCTION TO DEPTH OF CATALYST BED

- 14 mm. Reactor
- 19 mm. Reactor
- △ 24 mm. Reactor
- ▽ 38 mm. Reactor

4 l./hr./g.Co.

3 l./hr./g.Co.

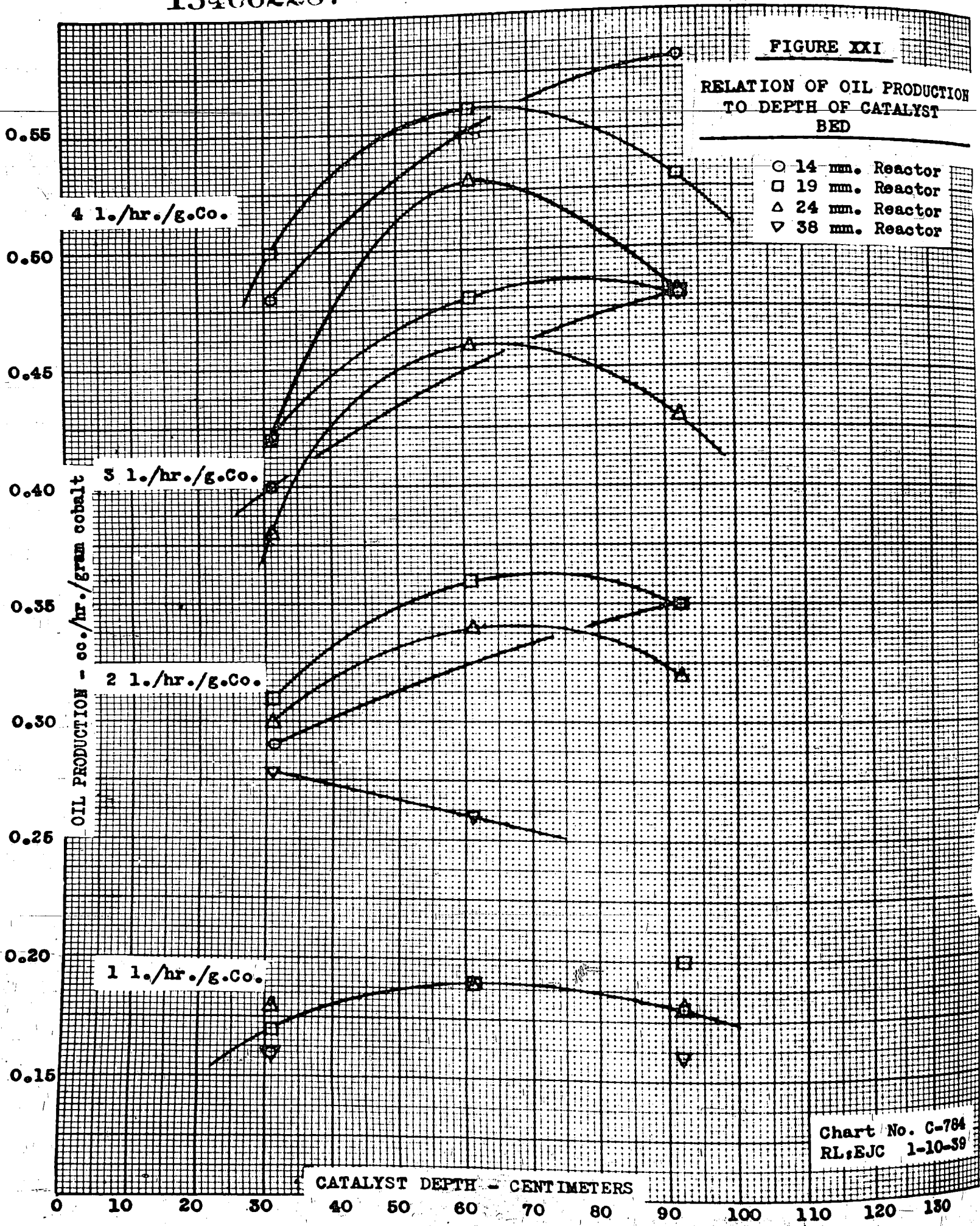
2 l./hr./g.Co.

1 l./hr./g.Co.

OIL PRODUCTION - cc./hr./gram cobalt

CATALYST DEPTH - CENTIMETERS

Chart No. C-784
RL:EJC 1-10-39



The data have been replotted in Figure XXI, which Figure XXI relates the oil production to the depth of catalyst bed. Within the precision of the data, it appeared that there was but little effect of catalyst depth upon the oil production in the range of depths from one to three feet at an inlet gas rate of one liter per hour per gram of cobalt. Likewise, the diameter of the reactor--from one-half to one and one-half inches (14 to 38 millimeters)--had no effect upon the oil yields. At a gas rate of two liters of synthesis gas per hour per gram of cobalt, the results varied with the diameter of the reactor. The one and one-half inch (38 millimeter) reactor gave a decreased oil production with increased catalyst depth. The one-inch and the three-fourths inch reactors showed a small maximum oil yield at a depth of about two feet. The one-half inch (14 millimeter) reactor was not used at a catalyst depth of two feet and consequently it is not definitely known if a maximum existed. As the gas rate was increased the maxima became sharper but remained at a catalyst depth of about two feet. Higher yields of oil and flatter maxima were obtained with the three-quarter inch (19 millimeter) reactor than with the one-inch (24 millimeter) reactor.

~~As before, the one-half inch (14 millimeter) reactor~~
was not tested at a catalyst depth of two feet, but the results from a three-foot catalyst depth at an inlet gas rate of four liters per hour per gram of cobalt indicated that the oil production had not been as much affected by the depth of catalyst bed in the smaller tube as it had been in the larger tubes.

Cobalt-manganese catalysts were found to produce almost as much oil as cobalt-thoria catalysts, but at a somewhat higher optimum temperature--445°F. (230°C.).

The hydrocarbon product from the cobalt-manganese catalysts had a higher average molecular weight and it contained a greater proportion of solid paraaffins than that from the cobalt-thoria catalysts.

The oil-producing properties of cobalt-manganese catalysts were not affected by:

1. Substitution of sodium carbonate for potassium carbonate as the precipitant.
2. Precipitation from a cold rather than a hot solution.
3. Washing the precipitated catalyst with more than 150 cc. of wash water per gram of cobalt.

Cobalt-
Manganese
Catalysts

Catalyst
Preparation
Variables

~~4. Washing the support (kieselguhr) successively with hydrochloric and nitric acid.~~

The best oil yields were obtained with catalysts containing 35-50% manganous oxide. The curve of oil yield versus per cent manganous oxide appeared to flatten out above 35% manganous oxide at about 150 cc. of oil per cubic meter of synthesis gas.

Quantity of Promoter

The cobalt-manganese catalysts were about as active after 90 hours use as at the start.

Experiments of Longer Duration

Decreasing the amount of support below that equivalent to twice the weight of cobalt did not decrease the efficiency of catalysts containing 15 or 20% manganous oxide.

Amount of Support

Alumina and alumina plus manganese were found to promote the oil-producing properties of the cobalt-kieselguhr catalyst, the combination of promoters having a greater effect than either used alone.

Cobalt-Alumina and Cobalt-Manganese Alumina Catalysts

The average molecular weight of the hydrocarbon product from the cobalt-alumina catalyst was much lower than that from any other catalyst studied. The products from the cobalt-manganese-alumina

catalyst resembled those from the cobalt-manganese catalyst, in that solid hydrocarbons were precipitated at room temperature.

Small amounts of alumina, around 2%, increased the activity of the cobalt-kieselguhr catalyst about 40%, but amounts above 4% decreased the activity. The pellets of the cobalt-alumina catalyst had a remarkably lower activity than the filter-cake screenings.

The optimum amount of alumina was apparently greater, around 8%, when the cobalt was precipitated upon the aluminum hydroxide-kieselguhr mixture than when cobalt and alumina were coprecipitated upon the kieselguhr. The cobalt-alumina catalysts were characterized by a high sensitivity of very small changes in the alumina content.

The coprecipitated cobalt-manganese-alumina catalyst gave an oil yield about 18% greater than that from the cobalt-manganese catalyst and over 100% greater than that from the cobalt-alumina catalyst. The best preparation showed a yield of over 150 cc. of oil per cubic meter of synthesis gas, which was about the same as the yield from the cobalt-thoria catalyst.

Coprecipitated
Cobalt-Alumina
Catalysts

Cobalt
Precipitated
in Aluminum
Hydroxide

Cobalt-Manga-
nese-Alumina
Catalysts

Coprecipitated
Catalyst

The oil yields from catalysts made by mixing as dried powder, cobalt-alumina catalyst with cobalt-manganese catalyst, were intermediate between those from cobalt-alumina catalyst and those from cobalt-manganese catalyst.

Dry Mixed
Catalyst

Cobalt-ceria catalyst, prepared in the same way as the previously described cobalt-thoria-kieselguhr preparations, could not be made to give reproducible results and therefore could not be compared with certainty with other cobalt catalysts. In some instances, the activity of the ceria-promoted catalysts approached that of the thoria-promoted catalysts, but in general the activity was somewhat lower.

Cobalt-Ceria
Catalyst

Attempts were made to prepare cobalt catalysts by the coprecipitation of cobalt and magnesia, the magnesia serving as the support in place of the ordinarily used kieselguhr. It was thought that a greater dispersion of the cobalt might be obtained in this method of preparation and that the activity would consequently be enhanced.

Cobalt-
Magnesia
Catalyst

The coprecipitation of cobalt and magnesia did not result in very active catalysts due to the

difficulty encountered in reducing such catalysts. The experiments were not of sufficient extent to indicate results that could be expected from a greater dispersion of the cobalt.

The nickel-manganese-alumina catalyst was used in a reactor three inches (75 millimeters) in diameter, fitted with a corrugated sheet which made close contact with the walls of the reactor. Experiments were made on this reactor at catalyst bed depths of 16-23 feet (5-7 meters). At a catalyst depth of 16 feet (5 meters), it was found impossible to obtain the anticipated oil yields, a part of the failure being attributable to the high density of the catalyst pellets. At a catalyst depth of 23 feet (7 meters), much lower yields of oil were obtained than at the lower depth, which indicated that the depth of the catalyst bed may have been too great in either instance. However, it was subsequently determined that this catalyst was very difficult to use even on a small scale, due to the impossibility of close temperature control.

Nickel-Manga-
nese-Alumina
Catalyst In a
20-Liter
Reactor