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T.O.M. REEL 2

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TOM REEL 279

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1	Bureau of Mines Translations:*		
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	T-462	Ackermann, Dr. Latest German Developments on the Gas Phase. Gasoline Synthesis at Middle Pressures, 1942-1945. PB 82,060. Translation of a document found on FIAT Reel X-116, Frames 1717-1787.	0009-0018
	T-463	Duftschmid. Three Papers on the Duftschmid Oil Circulation Process. I. July 25, 1941. 4 pp. II. Brief Report on the Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen by the Oil Circulation Process. Oct. 9, 1939. 3 pp. III. State of Experiments on Alcohol Synthesis by the Oil Circulation Process. August 11, 1941. 11 pp. Translation of documents found on TOM Reel 134, Items I(b) 11; I(b) 12; I(b) 13.	0019-0035
	T-464	Michael, Dr. The Status of Hydrocarbon Synthesis from CO-H_2 Mixtures. July 24, 1941. Translation of a document found on TOM Reel 164, Frames 143-153.	0036-0048
	T-465	Boente. Solid Aromatics in the HOLD of Pitch Hydrogenation, Poelitz. July 15, 1941. Translation of a document found on TOM Reel 164, Frames 190-192.	0049-0051

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T-466	The Koppers-Totzek Powdered Coal Gasification. (A paper read by Friedrich Totzek, July 2, 1947, in Essen). Umschau, Vol. 66/67, p. 363.	0052-0056
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T-474	Three Papers on the Aromatics-Naphthenes Equilibrium. I. Aromatics-Naphthenes Equilibria Curves. May 22, 1943. Peters. II. The Production of Aromatics-Naphthenes Equilibria on the Nickel-Tungsten Catalyst 6718. Feb. 1940. 5 pp. and 4 curves. Peters. III. The Aromatics-Naphthenes Equilibrium on the Tungsten Sulfide Catalyst 5058. May 25, 1943. 1 p. and 1 curve. Peters and Trofimow. Translation of documents which appear on TOM Reel 173, Frames 699-702.	0181-0192
T-475	Brief Summaries of Three Papers on Splitting Hydrogenation. I. Splitting Hydrogenation Catalysts with HF Treated Alumina as Carriers. June 12, 1941. Rotter. Document appears on TOM Reel 173, Frames 483-488. II. Tungsten-Free Splitting Catalysts of the SiO_2-Al_2O_3-Fe_2O_3 Mixtures Treated with HF. May 1944. Günther. Document appears on TOM Reel 173, Frames 401-408. III. The Splitting Hydrogenation of DHD Residues. Feb. 1, 1943. Gieg and Simon. Document appears on TOM Reel 173, Frames 366-392.	0193-0199
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T-484	Refining Catalysts 7525, 7675, 7360, 7846. Nov. 1940. Translation of a document which appears on TOM Reel 173, Frames 198-199.	0238-0239
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SR-5	Translation Book 211. Cracking and Hydrogenation of Esthonian and Kashpirian Shale Tars. N.D. Tilicheyev and G.N. Sledzhiev. Translation of a document found on TOM Reel 255, *Chemistry of Solid Fuels*, Vol. 2, No. 2 (1931), pp. 3-15. (Sinclair translated only part of the article).	0375-0384
SR-6	Translation Book 210. Thermal Decomposition of Gdov Shales Under Hydrogen Pressure. By V.P. Tsybasov, S.A. Dymshits and I.S. Levit. Translation of a document found on TOM Reel 255, *Combustible Shales*, No. 4 (1935), pp. 82-87.	0385-0394
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SR-16	Translation Book 241. Hydrogenation of the Neutral Kerosene Fraction of Gdov Shale Tar. By Klukvin, N.A., Polozov, R. Ph., and Pheophilov, E.E. Translation of a document found on TOM Reel 255, Chemistry of Solid Fuels, Vol. 6, No. 4 (1935), pp. 340-347.	0526-0535

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3	Detection of Iso- and Alicyclic Compounds in Saturated Hydrocarbon Mixtures. By Dr. Dornow. Petroleum Institute of Hannover Technical School, July 7, 1944. (Translation by Standard Oil Development Co., from a document found on TOM Reel 73, Item 5, Frames 587-607.)	0605-0610
4	Refining of Light Oil from Low Temperature Carbonization of Coal. By W. H. Oppelt.	0611-0619
5	Azienda Carboni Italiani. Description of the Plant. (Translation of an Italian document).	0620-0653
6	A Chronological Summary of and Comments on Dr. Michael's Liquid Phase Process. (Schaumfahrweise). By L. W. Alberts.	0654-0662
7	Report of "Fouchers" on $CO+H_2$ Synthesis. (I.G. Farben), October 1947. Section II of Part I. Oil Recycle Process. Comments by L.W. Alberts.	0663-0666
8	Report for the FIAT consisting of a letter and drawing by Dr. Winkler on the subject of "Vergasung von feiner Kohle nach dem Verfahren von Dr. Winkler". (Carburation of Coal Dust According to the Winkler Process).	0667-0668
9	Report by Dr. Fr. Winkler entitled: "Historische Entwichlung der Vergasung von feinkörnigen Kohlen nach dem Verfahren von Fritz Winkler." (Historical Development of the Gasification of Fine Coal According to a Process Developed by Fr. Winkler.) Part I.	0669-0720
10	Report by F. Halle, L. Lorenz and G. Wietzel entitled: "Röntgenographische Untersuchung der Carbidierung von Nickelpräparaten im CO-Strom zwischen 140 and 250°." (X-Ray Examination of the Carbidization Process of Nickel Preparations in CO Current between 140° and 450°.) Part II.	0721-0739
11	A group of German memos relating to the above report. Included are memos: 70, 71, 72, 73, 74, 75, 78, 84, 93, 94, 103, 104, 105 and 114.	0740-0753

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12. "La Synthese CO+H_2 a l'I.G. Farben. 3^e Partie. Les Essences de Polymerisation". (The Synthesis of CO+H_2 at I.G. Farben. Part III. Polymer Gasolines.) Included in this paper are the following reports: 0754-0788

    1. "Magnesiumphosphatkontakt." (Magnesium phosphate catalyst.) 4 pp. By Dr. Schütze. 7/14/47.

    2. "Versuche zur technischen Herstellung des Polymerbenzinkontaktes." (Investigations on the technical production of polymeric gasoline catalysts.) 1 p. By Dr. Schütze. 7/14/47.

    3. "Polymerbenzinkontakt." (Polymeric gasoline catalyst.) 1 p. By Dr. Rabe. 8/28/47.

    4. "Polymerisationsanlage Schwarzheide. I. Mitteldruckanlage. II. Hochdruckanlage." (Polymerisation installations at Schwarzheide. I. Middle pressure installation. II. High pressure installation.) 4 pp. and 1 diagr. By Dr. Haubach. 7/15/47.

    5. "Versuche zur homogen Verteilung von Phosphorsäure auf aktivierten Holzkohlen." (Investigations on the homogeneous distribution of phosphoric acid on activated charcoal.) 9 pp. incl. 2 tables and 1 diagr. By Dr. Münch. 4/11/38.

    6. "Über das Klopverhalten von Fischergas-Polymerbenzin." (The Knock Behavior of Fischer Gas Polymeric Gasoline.) 11 pp. incl. 4 tables. By Dr. Münch. 4/14/1938.

13. Report entitled: "Die Isosynthese" (Isosynthese) by Helmut Pichler and Karl-Heinz Ziesecke from the Kaiser-Wilhelm Institut für Kohlenforschung, Mulheim. 0789-0931

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Bureau of Mines Translations

T-460 to K-6

(Not included: T-461, T-471,
T-477, T-481, T-483, K-1, K-2)

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

T-460
TOM Reel No. 238, Part 4 W. M. Sternberg
[redacted]

REPLY OF MR. TOTZEK OF THE HEINRICH KOPPERS COMPANY OF ESSEN, GERMANY TO A LETTER BY THE NORTH GERMAN COAL CONTROL, MAY 2, 1947

I will explain the points 10, 23 and 26 of your questionnaire by giving you an example of computation of the results. The example is based on a sample of soft coal which was used in a large number of the experiments and had the following ultimate analysis:

Water	1.95%
Ash	8.75%
H_2	4.27%
Pure carbon	80.5 %
Sulfur by combustion	1.80%
N_2	1.19%
O_2	1.46%
	100.00%

Compositions of the Gas

Gas was produced of the approximately following compositions:

CO_2	15.00%
CO	42.00%
H_2	42.00%
N_2	1.00%

According to these figures the proportion of CO : H_2 is 1 to 1, and they form together 84% of the gas. This has been the result of the test. We will show below the possibility of obtaining a gas of such composition.

Carbon Balance

Introduced, in powdered coal: 0.805 kg

Carried out in the gases formed:

(For the composition of the gas produced, see above)

Amount of gas measured 2.3 ncbm

$(0.42 + 0.15) \times 0.536 = 0.306$ kg/ncbm

$2.3 + 0.306$ = 0.705 kg of C/kg coal introduced

Carbon loss and difference in measurements

$0.805 - 0.705$ = 0.100 kg = 12%

Losses of coal amounting to 8 - 14% have been found during the course of the tests. These amounts depend very greatly on the uniformity of the powdered coal supply. Operations showed that we had to consider as normal a loss of carbon amounting to 10%. Our computations are based on the 12% loss found above.

Hydrogen Balance

Hydrogen in gas:

2.3×0.42 = 0.97 ncbm

Hydrogen from coal:

$\frac{0.0427}{0.09}$ = 0.47 ncbm

Hydrogen from decomposed steam:

$0.97 - 0.47$ = 0.50 ncbm

Accordingly 0.50 ncbm of steam have been decomposed with carbon.

Oxygen Balance

Oxygen in gas:

$(0.15 + \frac{0.42}{2}) \times 2.3$ = 0.83 ncbm

Oxygen from decomposed steam

$\frac{0.50}{2}$ = 0.25 ncbm

Oxygen supplied from the outside = 0.58 ncbm

The oxygen, nitrogen and sulfur present in the coal will be neglected because of the small amounts in which they are present.

Steam

Steam Requirements

The steam necessary to carry out the gasification process is composed from the steam decomposed and from the excess of steam necessary to maintain the process. The value is obtained from the water gas equilibrium.

Neither the equilibrium for water gas obtained in the presence of carbon, nor that in its absence can be used as a basis for computations of the powdered coal gas producer. (We refer here to the water gas equilibrium constant as given in literature). The results obtained are explained by graphic method of interpretation of water gas equilibrium constant for the two cases.

In the powdered coal producer a value will have to be used which will be an intermediate between these above equilibria. For the sake of safety we have based our computations on the equilibrium constant obtained in the absence of carbon, because we have found that the equilibrium approaches this constant. This produces a certain assurance about the maximum required amount of steam.

We calculate the volume of steam vH_2O from the graphical presentation of our numerical example as follows:

$$vH_2O = \frac{K_W \times vCO_2 \times vH_2}{vCO}$$

The values for CO_2, H_2 and CO are known from the composition of the gas given above. The value of vH_2O is unknown. According to our experience, the water gas equilibrium must be produced in the powdered gas producer at 1200°C when using soft coal of the composition given above. The curve shown in the appendix gives a value of 2.5 for K_W at 1200°C. The value of vH_2O is obtained from these figures:

$$vH_2O = \frac{2.5 \times 0.15 \times 0.42}{0.42}$$

$vH_2O = 0.375$ ncbm steam per ncbm gas

Total steam: $vH_2O = 0.375 \times 2.3 = 0.86$ ncbm steam/kg of coal used

Total steam requirements:

$0.86 + 0.5 = 1.36$ ncbm/kg of the coal used

Steam requirements in kg:

$1.36 \times 0.804 = 1.09$ kg

Steam from the moisture in the coal = 0.02 kg

Required from an outside supply of steam

$1.09 - 0.02 = 1.07$ kg

This sample computation shows that the calculated amount is dependent on certain experimental values. Tests have shown that the proportion of CO : H_2 always varies between the limits of 1 : 1.5 to 2 : 1, and that the corresponding CO_2 value varies between 18 and 8%. Experiments have also shown that the outlet temperature is approximately equal to 1200°C.

In addition to the material balance, we have to calculate the heat values. They can be computed as follows:

<u>Heat Balance</u>

Introduced:

1 kg of powdered coal u.h.v.		= 7700 kcal
Preheating of steam to 1200°C 1.07 x 0.524 x 1200		= 684 kcal
	Total	8384 kcal

Heat in the Products:

The l.h.v. of the gas produced = 2347 kcal/ncbm

Kcal in the gas produced:

2.3 x 2347		= 5400 kcal	= 64.5%
Losses of C			
0.12 x 0.805 x 8000		= 770 kcal	= 9.2%
Sensible heat in the gas produced (moist)			
Gas: 2.3 x 0.37 x 1200 = 1020 kcal			
Steam 0.86 x 0.42 x 1200 = 430 kcal		1450 kcal	= 17.2%
Balance: (Radiation and Convection Losses)		764 kcal	= 9.1%
	Total	8384 kcal	= 100.0%

We may state that the last item in the balance, the radiation and convection losses will be considerably lower on a larger scale installation because this factor is relatively high in experimental installation because of the size and the length of operations, and will be greatly reduced in operating units.

We may add the following:

Should a high CO concentration be required, it is obtained according to the equation:

$$2C + O_2 = 2CO$$

This reaction is strongly exothermic. CO_2 is added to reduce the temperature, with the following results:

$$C + CO_2 = 2CO$$

The amount of CO_2 necessary is determined by the temperature of the outlet gas, which is always computed to be equal to 1200°C.

The material and heat balance of such a gas will follow exactly the example cited above, i.e. after repeating computations using data obtained in experiments.

Amount of Steam Produced

As stated above, the heat contents manifested in the sensible heat of the gases can be readily increased. The temperature of 1200°C is very high and its utilization in steam boilers is economical. It permits obtaining high pressure steam which can be used as a source of energy for the production of oxygen.

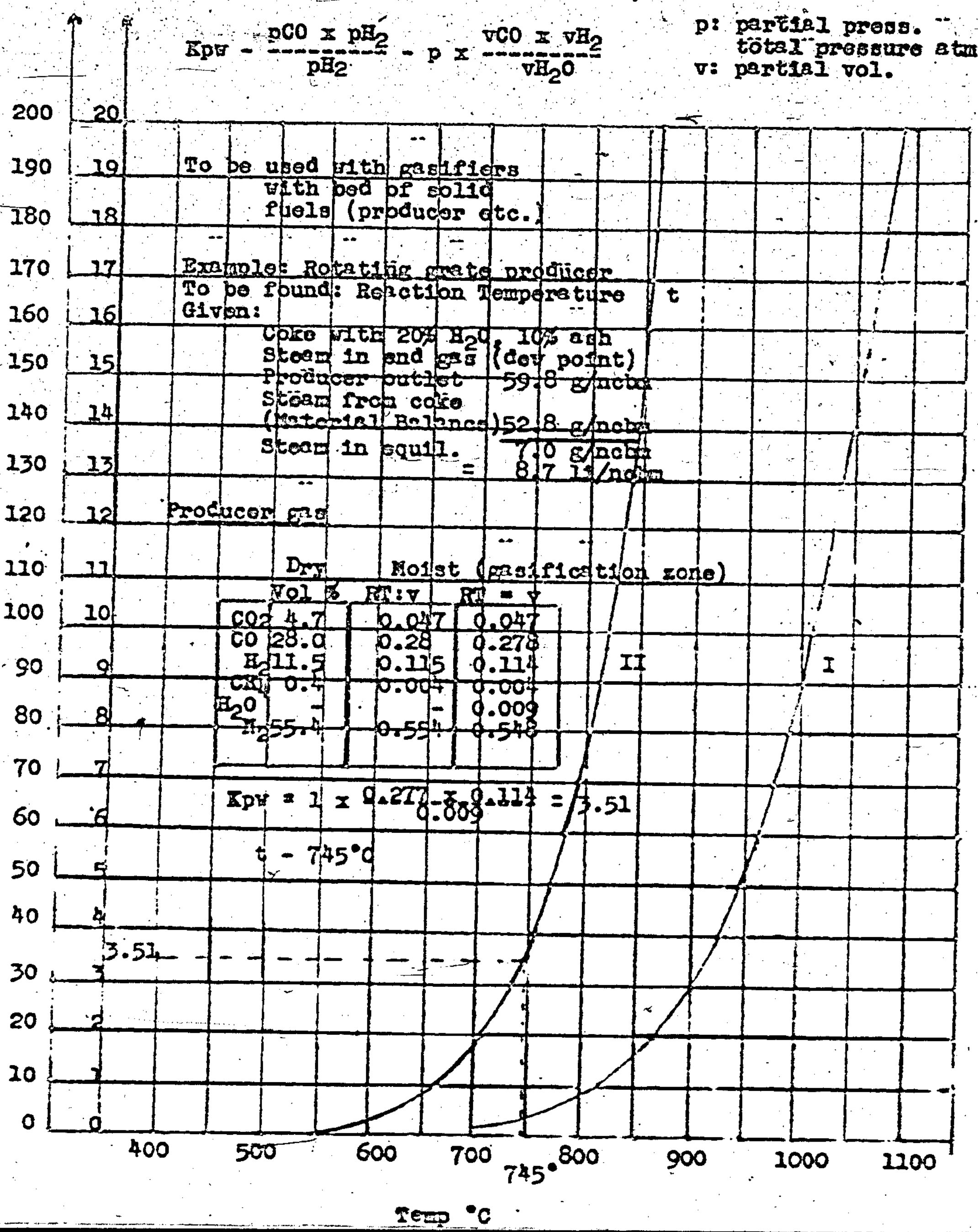
/s/ Heinrich Koppers
G.m.b.H.
Operations Section/Totzek

Changes in the Water Gas Equilibrium Constant KpW with the temperature (In Presence of Carbon)

T-460

$$K_{pw} = \frac{pCO \times pH_2}{pH_2} = p \times \frac{vCO \times vH_2}{vH_2O}$$

p: partial press.
total pressure atm.
v: partial vol.



To be used with gasifiers
with bed of solid
fuels (producer etc.)

Example: Rotating grate producer
To be found: Reaction Temperature t
Given:

Coke with 20% H_2O, 10% ash
Steam in end gas (dew point)
Producer outlet 59.8 g/ncbm
Steam from coke
(Material Balance) 52.8 g/ncbm
Steam in equil. 7.0 g/ncbm
= 8.7 lt/ncbm

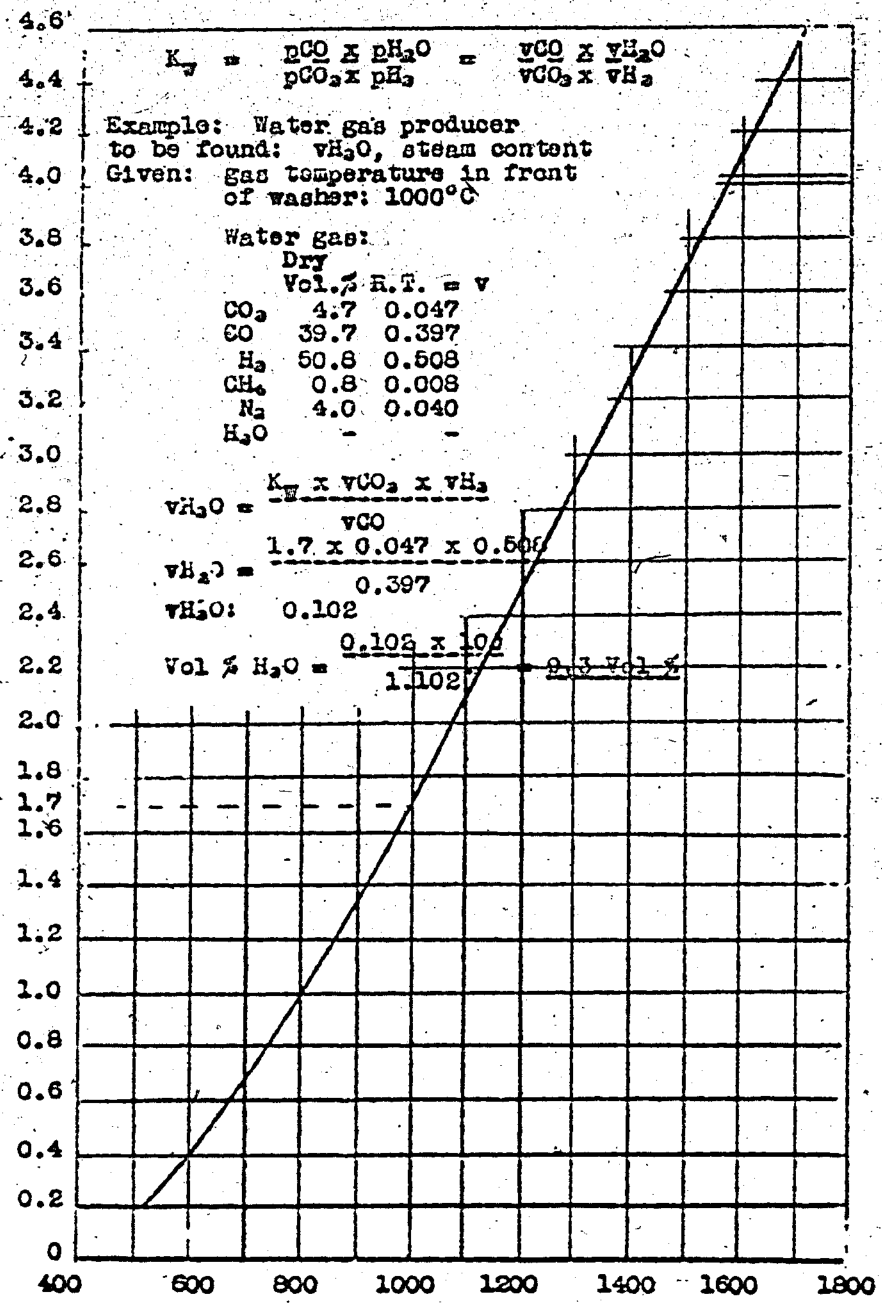
Producer gas

	Dry Vol %	Moist (gasification zone) RT:v	RT = v
CO_2	4.7	0.047	0.047
CO	28.0	0.28	0.278
H_2	11.5	0.115	0.114
CH_4	0.4	0.004	0.004
H_2O	-	-	0.009
N_2	55.4	0.554	0.548

$$K_{pw} = 1 \times \frac{0.277 \times 0.114}{0.009} = 3.51$$

t = 745°C

Changes in Water Gas Equilibrium Constant K_w
with the Temperature
(Only in the Gas Phase in the Absence of Carbon)



$$K_w = \frac{pCO \times pH_2O}{pCO_2 \times pH_2} = \frac{vCO \times vH_2O}{vCO_2 \times vH_2}$$

Example: Water gas producer
to be found: vH_2O, steam content
Given: gas temperature in front
of washer: 1000°C

Water gas:

	Dry Vol.%	R.T. = v
CO_2	4.7	0.047
CO	39.7	0.397
H_2	50.8	0.508
CH_4	0.8	0.008
N_2	4.0	0.040
H_2O	-	-

$$vH_2O = \frac{K_w \times vCO_2 \times vH_2}{vCO}$$

$$vH_2O = \frac{1.7 \times 0.047 \times 0.508}{0.397}$$

vH_2O: 0.102

$$\text{Vol \% } H_2O = \frac{0.102 \times 100}{1.102} = 9.3 \text{ Vol \%}$$

T - 462

0009

LATEST GERMAN DEVELOPMENTS ON THE GAS PHASE GASOLINE SYNTHESIS AT MIDDLE PRESSURES, 1942 - 1945

by Dr. Ackermann

FIAT Reel X-116, Frames 1717 - 1787

PB 82060

Summary of Results

In the middle pressure synthesis with iron catalysts of different origin, using CO-rich gas,

1) either the Louta or the Lux gas purification masses are suitable for use as catalysts in the synthesis after some preliminary treatment. The temperature required is higher than with actual catalysts, but appears to be capable of being lowered by a suitable reduction (forming methods) of the catalyst.

As an example, the preliminary gas purification Lux mass prepared by washing, drying and alkalization, operated for 3,000 hours with a CO-rich synthesis gas at 10 atm pressure and 248° with a normal load, producing 180 g hydrocarbons, of which 154 gram were the higher hydrocarbon (propane and up).

2) The effect of alkali content on the life, olefin, paraffin and alcohol formation of the carrier-free catalysts was reinvestigated.

A liquid phase synthesis catalyst, 2500 hours old and containing 2% K_2CO_3 produced an 87% CO conversion with 175 gr higher hydrocarbons, with no methane production.

The proportion of oxygenated compounds is only about 1/2 of that produced in the liquid phase.

A comparison of precipitated ferric nitrate catalysts with 0.25 to 10% K_2CO_3 showed that 1% K_2CO_3 produced the best results. The methane production is reduced from 18 to 3 g/ncbm CO + H_2 in comparison with the usual alkalization of 0.25% K_2CO_3. The proportion of paraffin formed has not been determined. Higher alkalization than 1% yields products richer in paraffin, but the life of the catalyst is proportionately reduced. The effect of alkalization on the production of oxygenated products is but slight in comparison to the effect in the liquid phase.

3) Efforts to apply the process of reduction under pressure, which has been found successful in the liquid phase, to operation~~s~~ in the gas phase was not successful.

4) Powdered iron, activated with copper and alkalies, can be used for gas phase hydrogenation. Activity is not satisfactory (80% conversion of CO at 260° C.). Surprisingly, no methane was formed with a high thruput.

5) The substitution of potassium silicate for potassium carbonate in catalysts deposited upon carriers and in carrier-free catalyst, as protected by a patent, has not been found to affect the direction of the CO:H_2 consumption, nor the paraffin production. It is possible to introduce a larger amount of K_2SiO_3 than of K_2CO_3 into

the catalyst without harming the catalyst, but no effect upon the proportion of the $CO:H_2$ consumption, nor on the paraffin production could be observed. Blue water gas has been used in these tests.

II. Middle pressure synthesis experiments with circulation of the tail gas with a low proportion of make-up gas to circulation gas and using either a CO-rich synthesis gas or an H_2-rich synthesis gas showed that:

1) with CO-rich gas (and a carrier-free catalyst) the proportion of circulation gas (between 0.6 and 3 p./1 part of make-up gas) did not affect the consumption proportion of CO to H_2, as could have been expected. The effect was great on the conversion, increase in yield from 170 to 190 g/ncbm CO + H_2 and the olefin proportion increased from 65% to 78%.

2) No solution of the problems was found in the circulation tests with dolomite carrier catalysts and a 2 H_2:1 CO with a circulation proportion of 1:1 because of deposition on the catalysts.

III. Circulation experiments at middle pressure with catalysts reduced by the manufacturer with either water gas or with hydrogen-rich synthesis gas for the increase of the CO conversion, and through that to increase the yield and the proportion of olefines, produced the following information:

1) The H_2:CO consumption proportion was increased from 0.63 with direct pass of the gas to 0.84 with a 1:1 circulation

and a colomite catalyst using water gas with 1.05 H_2:1 CO. This is the first indication that iron catalyst can convert even a high-hydrogen gas with optimum gas utilization and yields.

2) The H_2 + CO consumption increases from 80% with 1.20 H_2: 1 CO water gas, in a single pass and a dolomite catalyst to 85% in a two stage process and to 0.96% with a 1:1 and 1:1.02 gas in the first stage and 1:2 in the second stage. The methane formation still remains very high, forming 11 to 17% of the products formed, depending on the method of operation. The proportion of olefines is slightly increased by circulation, from 43.5 to 48.5%.

III b. Circulation tests with water gas or hydrogen-rich gas on dolomite catalysts reduced with CO at 0.1 atm resulted in satisfactory gas utilization under suitable operating conditions.

1) Preliminary tests under a great variety of operating conditions permitted us to select operating conditions suitable to any H_2:CO ratio.

2) The following circulation proportion (vol. circulating gas:volumes make-up gas) with a normal load of make-up gas (100 n.li. make-up gas/h, 1l catalyst volume) were adapted to properly utilize the make-up gas used:

Synthesis gas H_2:CO	Circulation ratio about
1.18	6
1.37	7
1.56	8
1.84	10
1.90	11
1.93	13

In this way 180 g hydrocarbons, (and over/nobm CO + H_2 were obtained by using the above method of synthesis, which has never been produced heretofore by others, as far as we know.)

These circulation proportions appear, however, undesirably high for industrial operations. Experimental runs with water gas and a circulation proportion down to 3:1 produced acceptable yields of 160 - 165 g with 86% CO conversion.

The effectiveness of the process even at atmospheric pressure has been discovered at a lower excess pressure with circulation, by showing that the H_2 + CO consumption at 2 atm gauge was but slightly less than at 10 atm.

3) When the middle pressure circulation synthesis with water gas is used immediately after reduction of the catalysts, without first operating with no circulation of the gas, the synthesis temperature can be reduced by about 5° to 210-212°C. With water gas of the composition of 1.28 H_2:1 CO and a circulation proportion of 5, 175 g of hydrocarbons are obtained on the average, although the H_2:CO consumption is not entirely in the same proportion as in the water gas.

4) Even with a circulation proportion of 1:2.5, 167 g hydrocarbons are obtained from water gas with an 88% CO conversion. The formation of methane is greater with higher circulation proportion, than with lower, and with a circulation of 1:2.5 it still equals 19-21 g.

5) The effect of higher (210°C.) or lower (190°C.) starting temperatures cannot be definitely stated when starting the circulation operations after reduction with CO under reduced pressure. Higher starting temperatures seem to require slower temperature increases.

6) Special tests were performed to lower the methane formation during circulation water gas synthesis on dolomite carrier catalysts, after having definitely established the satisfactory yield of total CH_3:

> With very low starting temperatures and very slight temperature increases, with a very low CO conversion of below 70%, the CH_4 formation is reduced from the normal 14% to 5% of the liquid products.

Increased alkalization has also a favorable effect, but not as much as expected.

It appears that the tendency for methane production is a peculiar property of the dolomite carrier catalyst used. The methane formation could not be kept below 10% in long time operations with a 90% CO conversion even with strong alkalization.

III c. Middle pressure circulation synthesis with kieselguhr-magnesia catalyst using water gas indicated that this catalyst behaved exactly like the dolomite catalyst with respect to H_2:CO consumption, permissible load, CO conversion, synthesis temperature and methane formation.

IV. Testing the applicability of the various processes for the reduction of the catalysts for the middle pressure synthesis gave the following results:

1) A synthesis temperature lowering by 10° was brought about by the carbon monoxide + hydrogen reduction of carrier-free catalysts for the middle pressure synthesis with CO-rich synthesis gas, in comparison to the usual reduction process.

2) A 10° lowering of the temperature results also with the reduced pressure CO-reduction of carrier-free catalysts for middle pressure synthesis with water gas. Similar synthesis temperatures seem to be well suited for the same space velocities as in the carrier catalysts. For equally high CO conversion the H_2:CO consumption is equally high, i.e. 0.9 with water gas. Appreciably more methane was formed (17 g) with low alkalinity catalysts (0.25% K_2CO_3).

3) Only negative results were obtained in the experiments for the direct pressure reduction of the dolomite catalysts with hydrogen-rich CO-free synthesis gas.

4) A repeated reduction of a dolomite catalyst reduced with hydrogen, for synthesis with water gas at 250°, has been found to have no effect upon the activity in the middle pressure synthesis.

5) When testing the reduction method used by Lurgi, in which the reduction was done for a short while at 250° and later at 225°, a less active catalyst was produced than in our original simple reduction.

V. "Taifun Reduction".

Reduction at very high space velocities with hydrogen-rich synthesis gas at atmospheric pressure in the temperatures of 280-320°C. has produced the most favorable results so far. The simplest process to be carried out industrially produces especially high activity state for the middle pressure synthesis, which manifests itself in lower synthesis temperature and greatly reduced tendency of methane formation.

Special tests have shown that:

1. Dolomite catalysts with 1% K_2CO_3.

Re-reduction by the Taifun Process of the catalyst already reduced with hydrogen was successful.

Still better results are obtained when green corn is reduced by the Taifun Process.

The carbon dioxide which used to be removed from reduction gases for the sake of safety, can be left in it.

The effect of space velocity is slight, as long as kept above 2000.

No preheating of the reduction gas is necessary.

The reduction temperature should mostly be kept between 300 and 350°C. with thick layers of catalyst.

The considerable heating up of the catalyst must be watched.

The methane formation with a 90% CO conversion amounts to 4-5% of the liquid products.

2) Use of more strongly alkalized dolomite catalyst did not lower any more the formation of methane during the middle pressure synthesis with a direct gas thruput. One might possibly detect disadvantages of the increased alkalization in a lower catalyst life and a reduced consumption ratio of H_2:CO.

3) Taifun-reduced lime catalysts excelled by a complete absence of methane formation. Their life was not, however, satisfactory.

4) Carrier-free catalysts showed the same advantages for water gas middle pressure synthesis after Taifun reduction as do catalysts upon carriers. The methane formation is again reduced to a minimum.

5) A cobalt catalyst reduced by the Taifun process for experimental reasons was almost inactive.

6) The connection has been investigated between carbide formation and free carbon.

VI. Experimental atmospheric pressure reduction under special operating conditions.

1) The carrier-free catalyst can also be used with satisfactory CO conversion at temperatures below 225°C., if operated at space velocities commonly used in large scale

operations. With an 85% CO conversion, 105 g. CH_4 was formed during the first 1000 hours.

2) The recirculation of the tail gas permitted operating with a proper H_2:CO consumption with iron catalysts at atmospheric pressure with yields similar to the cobalt catalysts.

For a proper consumption proportion H_2:CO, the circulation proportion of H_2-rich gas must be very high, about 12-14. The H_2:CO consumption is less satisfactory with a lower circulation proportion, but economical conversions are still obtainable with it. Harmful effects of the water gas reaction are reduced by having the synthesis gas as dry as possible during synthesis. The synthesis temperature is between 205 and 225°C.

3) Brief preliminary experiments at increased space velocities (excessive loads). The catalyst life and the H_2:CO consumption appeared less promising with a straight pass than the recirculation process.

UNITED STATES
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Items I(b)11 - I(b)13.

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T-463
W. M. Sternberg
November 10, 1948

THREE PAPERS ON THE DUFTSCHMID OIL CIRCULATION PROCESS

I

July 25, 1941

CATALYST

The process is based on the use of fused iron catalysts, which was developed by Dr. Linckh in 1927-1936 who also found the best methods of using it. The principal constituent of the catalyst is iron with small amounts of readily available and cheap addition substances. It can be repeatedly regenerated for use in a very simple manner by roasting it in air and re-fusing to form a new catalyst.

SYNTHESIS GAS

The synthesis gas is high in CO and has a proportion of $CO:H_2 = 1:0.7-0.85$. This makes the synthesis particularly economical if combined with a water gas producer, e.g., a Winkler generator, in which CO-rich gas is produced directly. All conversion becomes, in this case, unnecessary. The gas must, of course, be purified from sulfur and from organic sulfur, and if the CO_2 contents are high must also be passed through CO_2 scrubbers.

PRESSURE

The synthesis is best carried out at 25 atm pressure and is therefore a middle pressure synthesis.

OIL CIRCULATION PROCESS

The process carried out on a pilot plant scale in 1934-1938, had the liquid products obtained, as well as the synthesis gas, led over a fixed bed of granular catalysts in the reactor. The oil produced is recirculated. The synthesis of motor fuels is done in two stages, without the use of an intermediate CO_2 scrubbing. The fixed bed catalyst overcomes any difficulties in separation of the oil produced from the catalysts, as well as the non-uniform distribution of the catalyst in the oil occuring in the processes with finely divided suspended catalysts.

ADVANTAGES OF THE OIL CIRCUIT

The heat of the reaction in the oil circulation system is carried away from the catalyst by the oil circuit itself. A uniform temperature is produced throughout the whole bed of the catalyst, without overheating even the most active centers. The wetting reduces the formation of the undesirable products which might form as the results or an excessive conversion. The formation of gaseous products is lower than in the gas circulation process.

Unlike the processes with indirect heat removal, the catalyst is not distributed in thin layers. The reactors used have no insets in them. The process may well develop into one involving the construction of large synthesis units, with the resulting constructional advantages.

HYDROCARBON SYNTHESIS

Eighty-seven percent conversion in the two stages were obtained/1 cbm synthesis gas with a space/time yield of 0.72 kg of production/li catalysts, day, and with a total production of 150 g products/cbm gas. The products consisted of:

- 40% primary gasoline (50-55% olefines, 2% oxygen, o.n. 65)
- 20% gas oil (40-45% olefines, 0.6-1% oxygen, o.n. 78)
- 20% hard paraffin wax (m.p. 95°C)
- 15% gasol (about 75% olefines)
- 5% alcohols (chiefly ethanol)

ALCOHOL SYNTHESIS

The oil circulation process can be changed over to the synthesis of oxygenated compounds. With a pressure of 180 atm and with only 25-30% conversion of the synthesis gas in a single stage, and with a proportion of $CO:H_2 = 1:1$, 50% and over of alcohols were produced in all the fractions. The high pressure and the higher temperatures used reduce the size of the molecules, and as a result a relatively larger amount of lower and middle alcohols is produced. The oil circulation can, nevertheless, be also adopted to the alcohol synthesis, and one doubtlessly may expect to produce also the higher alcohols when using catalysts treated by the Merseburg method. One may even expect that the above mentioned favorable affect of the catalyst wetting with a corresponding weakening of the active centers of the catalysts will suppress a further conversion to olefines of the alcohols formed as a primary product.

5,000 TE/ANN PROJECT OPPAU

The plant designed for 5,000 te/ann production and laid out to permit enlarging it to 15,000 te/ann, is to be operated with off gases of the butanol and ammonia synthesis. The products formed are intended to be hydrogenated in the existing units and the gasoline and gasoil used as motor fuels. The paraffin wax will be used as a raw material for the production of detergents, for which it is well suited.

Operating under such conditions, the experimental production will be operated without additional costs.

PATENT SITUATION

The process is protected by the German and foreign patent applications as follows:

J 53,688, 11-18-35 (O.Z. 9,104)
J 57,290, 11-3-36 (O.Z. 9,635)
J 11,461, 3-21-39 (O.Z. 11,461)

In addition, the iron catalyst which so far has been found best, is protected by DRP 708,512, 11-14-35 (O.Z. 9,099).

/s/ Duftschmid

II

October 9, 1942

BRIEF REPORT ON THE HYDROCARBON SYNTHESIS FROM CARBON MONOXIDE AND HYDROGEN BY THE OIL CIRCULATION PROCESS

The data required for the calculation and design have been obtained in the 9 te/mo pilot plant for the development of synthesis of motor fuels and paraffin from water gas by the oil circulation process.

The oil circulation process is characterized by:

(1) The heat of the reaction is absorbed by the circulating oil from the catalyst and carried away. The

problem of heat removal and the safety of the process of the reaction is therefore solved with the simplest possible reactor construction (towers without insets).

(2) The iron catalyst to be used differs from the ammonia catalyst only by small additions.

(3) From construction standpoint the synthesis plant is similar to the usual pressure water scrubbers. The synthesis is performed at 20-25 atm. Ten thousand te/ann installation will consist of 22 towers, filled with the catalyst without any insets.

(4) The synthesis plant proper has the advantage over the Ruhrchemie-Fischer plants by requiring less than one-half the costs, and about one-third of the requirements for materials (iron and steel).

The cost of a 100,000 te/ann plant (synthesis plant without gas production and without the usual auxiliary units) will amount, according to the estimates of the M.T.A., Ludwigshafen, to RM 4,700,000, with an additional RM 1,020,000 for the catalyst production.

(5) The synthesis requires a CO-rich gas in proportion of: 50:50-56:44, produced directly in the Winkler gas generators. No conversion is necessary.

(6) The primary products are: 40% primary gasoline with an o.n. 62-68 (with 0.1 TEL - 81-85). The 2% oxygen content can be removed by treating with alumina which will increase the o.n. to 70-75 (with o.1 TEL - 85-87).

20% paraffin, m.p. around 90°C

15% gasol consisting of
12% propane
42% propylene
7% butane
26% butylene
5% isobutylene

5% alcohols consisting of
50% ethanol
25% methanol
25% higher alcohols, acetaldehyde, acetone, etc.

The proportion of the products can be altered within certain limits.

(7) One hundred and fifty g of the above products/ncbm CO + H_2 have been obtained so far in the pilot plant.

Further development possibilities are presumably still present in the process (variation in the catalyst, omission of the final purification of the synthesis gas, etc.).

It is therefore suggested that a production unit for 5,000 - 10,000 te/ann be installed in some already existing or projected plant with an available suitable gas supply. The cost of such a plant, including the cost of the catalysts, will amount to RM 522,000, for the 5,000 te/ann unit, or RM 809,000 for the 10,000 te/ann unit. The construction of a 10,000 te/ann unit would require 350 te iron and 0.8 te copper.

/s/ Duftschmid

III

August 11, 1941

STATE OF EXPERIMENTS ON ALCOHOL SYNTHESIS BY THE OIL CIRCULATION PROCESS

Dr. Muller-Cunradi has ordered in February 1940, to change over the oil circulation process to the production of higher alcohols and to conduct the proper experiments; this was done from February to May 1940, in a 160 li reactor, in which the earlier hydrocarbon synthesis experiments have been run.

In line with the then existing information on the hydrocarbon synthesis obtained in our own experiments, the following operating conditions were supposed to result in the increased formation of oxygenated products:

(1) The use of hydrogen-rich synthesis gas.
(2) Use of higher pressures.
(3) Incomplete conversion.
(4) The use of special catalysts.

The catalysts favoring the formation of oxygenated compounds had first to be prepared, and moreover the effect of operating conditions had yet to be determined, and the first series of experiments was therefore run with the catalyst 997 previously used for the synthesis of hydrocarbons (reduction temperature 500°C). Experiments were run with hydrogen-rich synthesis gas $CO:H_2 = 1:3$, with a conversion of 30-40% instead of the 50% commonly used in the synthesis of hydrocarbons.

The operating pressure was varied during the course of the experiments. The following pressures were used:

100 atm

20 atm

150 atm

180 atm

The pressure of 20 atm was also used because of the advantages of having a process using the same kind of equipment for the synthesis of hydrocarbons and of alcohols. The hydrocarbon synthesis was supposed to operate at 25 atm, and carrying out the alcohol synthesis in the same middle pressure equipment would naturally offer some advantages.

The experiments led to the following results, which agreed with our earlier observations.

The oxygen content of the products increased with increased pressure. The average oxygen content of the total product, including the gasol, calculated from analysis of the different products was as follows:

Pressure	Average Oxygen Content
20 atm	3.5%
100 atm	7.5%
150 atm	11.4%
180 atm	11.5%

The formation of water-soluble alcohols ran parallel with the above:

Pressure	Proportion of C_1-C_4 Alcohols in the Total Product
20 atm	18.4%
100 atm	24.7%
150 atm	40.5%
180 atm	36.1%

The large excess of hydrogen results in a high proportion of the low molecular weight alcohols (chiefly C_2H_5OH, with some C_1, C_3 and C_5 alcohols).

The increased pressure also results in an additional increase in the proportion of the lower alcohols.*

The above results show that:

> The increased hydrogen content of the synthesis gas raises the oxygen content of the total products.** The lower alcohols participate preferentially in this increased production of oxygenated compounds.
>
> The increase in pressure affects the increased total oxygen content as well as the formation of the lower alcohols in the same way as an increased hydrogen content of the synthesis gas.

The following may be stated with regard to the formation of hydrocarbons which proceeds side by side with the production of oxygenated compounds:

* The present results merely confirm the earlier ones previously obtained: thus in experiments with an operating pressure of 100 atm, other conditions remaining the same, 5.5% of water soluble alcohols were obtained when the proportion of $CO:H_2 = 1:1$, and 15.7% of water soluble alcohols were obtained with $CO:H_2 = 1:3$.

An examination of earlier tests for the synthesis of hydrocarbons with the synthesis gas in proportion $CO:H_2 = 1:1$ shows furthermore that the increase in pressure favors the formation of the C_1-C_2 alcohols:

Oppau 100 atm test, alcohols 6-8% of the total product.
Merseburg 200 atm, alcohols 12-14% of total products.

** We understand in this case by total products all the products with the exception of CH_4, C_2F_6, C_2H_4, CO_2 and H_2O.

The increased hydrogen content lowers the percent of the oxygen-free products in the total products. This is merely another statement of the fact that the oxygen derivatives have increased. It results, however, in a striking lowering of the molecular weight of the hydrocarbons, so that much gasol (C_3 and C_4) and light oils are formed. The rise in pressure affects in this respect the process in the same way as the increase of hydrogen in the synthesis gas.

The experiments were run with the purpose of producing synthetically primarily the higher alcohols, and the above results could not be considered very satisfactory in this respect.

The tendency to produce chiefly low mol. wt. products is affected greatly by the temperature of the synthesis. This viewpoint has, however, been taken into consideration right from the start in this series of experiments, and the catalyst was reduced at as low a temperature as possible (500°C); no improvements could however be observed with the catalyst 997. A second possibility might have been offered by a change of the $CO:H_2$ ratio, because the CO-rich gas produces more high-boiling oils. This measure was then used as shown below.

The higher alcohols (C_{12}-C_{20}) were particularly desired for the production of detergents, and would be contained in the higher fractions of the oils produced.

	100 atm	150 atm	180 atm
Water soluble oil, 150-250°C	9.2%	9.4%	6.7%
Water soluble oil, + 250°C	6.8%	4.6%	2.8%
Vacuum fraction (1mm 100-200°C)	5.4%	4.5%	2%

The above summary shows that the $C_{13}-C_{20}$ alcohols in the 100-200°C fraction (1mm Hg) formed but a small part of the total products, which agreed with the results given above that the hydrogen-rich synthesis gas and high pressure favored the formation of only a very small amount of high boiling oil constituents.

The average molecular weight of the alcohols in this fraction was assumed to be C_{14}, and the alcohol value was obtained from the saponification and hydroxyl numbers.*

The fraction consisted therefore of 30-40% alcohols. One could observe here no clear relationship between this value and pressure, and the important question of whether the higher alcohol content increases with increasing pressure must be still considered unanswered. We cannot evaluate in this respect the test at 20 atm becuase it failed to fit into the picture and produced hardly any high boiling oil.**

One may notice the relationship between the experimental temperature and the space/time yield.

20	100	150	180
200-286°C	236-278°C	220-270°C	235-260°C
0.43	1.00	0.80	0.95 kg/li,day

We may summarize these tests as follows:

> The process may perhaps prove of interest in the production of lower alcohols when operating with a large excess of hydrogen and at high pressures

* This method leads to high alcohol results, as has been shown by more accurate analysis.

** Experience has shown that after catalysts are operated under more extreme conditions, they no longer give normal values when changed over to milder reaction conditions. The order in which the tests were run were - first operating at 100 atm, and only then at 20 atm.

(50atm and over). Appreciable amounts of the C_3 and C_4 hydrocarbons are still formed in that way, and the process could be run in connection with the oxo process. In this way additional amounts of butanol, amyl alcohol, also aldehydes and ketones could be obtained.

Experiments with the synthesis gas $CO:H_2 = 1:1$ have been run after completing the tests with hydrogen-rich synthesis gas; the pressure was 120 atm and the conversion 30%.

As expected, the amount of the higher boiling constituents was increased with the higher carbon monoxide content. We obtained

24.0%	gasol
21.6%	oil - 150°
12.7%	oil 150-250°
9%	oil + 250°
32.7%	lower alcohols

The C_{12}-C_{20} fraction now amounted to 7.2% of the total product. We were, however, surprised to find that the proportion of oxygenated compounds has actually increased in this higher fraction.

Pressure	180	180 atm
$CO:H_2$	1:3	1:1
Hydroxyl number	45-50	60-65
Saponification number	40-50	89-95

The analysis of the products gave the following composition of the liquid fractions:

8.5%	methanol
21.0%	ethanol
10.0%	propanol
6.5%	alcohols C_4-C_{11}
2.5%	alcohols C_{12}-C_{20}
11.5%	water soluble fatty acids
5.0%	fatty acids C_5-C_{11}
1.5%	fatty acids C_{12}-C_{20}

26.5% hydrocarbon - 200°C)
3.5% hydrocarbon 200-300°C)1/2 of them
3.5% hydrocarbon + 300°C) olefines

Additional experimental data:

Space/time yield: 1 kg total product/li,h

Yield: 170g/cbm converted CO + H_2

Reactor temperature

Bottom	236°C
Top	260°C

Conversion 32.5% of CO + H_2

In our later work we retained the following operating conditions:

(1) Incomplete conversion, with the degree of conversion reduced to 20-30%

(2) CO-rich synthesis gas, CO:H_2 = 1:1

(3) Pressure 180 atm

The increased yield of high molecular weight alcohols was to be favored:

(4) By using oxygen-combining catalysts

(5) By selection of catalysts operating at lower temperatures.

Dr. Linckh has accordingly selected the following catalysts:

Catalyst 1227, especially active in forming O_2

Catalyst 1374, especially active, operates well even at 1 atm

ALCOHOLS

Test number	GV26	GV27
Catalyst number	1227	1374
Degree of conversion, % of CO + H_2	30.4	21.7
Pressure, atm	180	180
Space/time yield, kg/li,h	1.04	1.10
Yield g/cbm CO + H_2 conversion	177	226
Cold catchpot oil, % by weight of total production	8.7	27.5

Tail gasoil, % of weight of total production	31.5	21.1
Activated charcoal oils, % of weight by total production	16.5	12.3
Water soluble alcohols, % of weight by total production	11.8	8.9
Gasol, % of weight by total production	31.5	30.2
Reactor temperature, bottom °C	250-260	196-264
Reactor temperature, top °C	270-280	224-274
Percent C_{12}-C_{20} fraction in total production	20	40
Saponification number of C_{12}-C_{20} fraction	77	56
Hydroxyl number of C_{12}-C_{20} fraction	45	58

Date May 31, 1940 - September 18, 1940

The two tests have not indicated progress in the desired direction.

The catalyst 1227 did not produce the desired increase in alcohol formation.

The catalyst 1374 does begin work at 196-224°, but requires a gradual rise in temperature in order to maintain conversion. It does, however, definitely produce some iron carbonyl at the lower temperatures, which caused us to suspect that the formation of the carbonyl reduced the activity of the catalyst.

We intended to repeat the test with catalyst 1374 at lower pressures to reduce the formation of the carbonyl.

In the meantime, a smaller circulation unit had been completed in July, 1940. The synthesis reactor had a capacity of only 15 li, permitting work with smaller amounts of catalysts, while still accurately maintaining the proper conditions of operations.

A number of catalysts have been studied which have been especially developed by Dr. Linckh for the ethanol synthesis. We selected catalysts which gave the best results under conditions of ethanol synthesis, with a good alcohol and oil yield. We based our choice on the assumption that the catalysts which give high yields in lower alcohols will produce high molecular weight alcohols under other operating conditions.

These experiments have not, however, brought us much closer to the solution of the problem, because the results obtained with most of these catalysts were very similar to those obtained with the catalyst 997 in the large unit. Catalyst 997 was also used in the new unit for purpose of comparison and proved, in many respects, the best. The hydroxyl numbers of the C_{12}-C_{20} fraction exceeded slightly those obtained previously, and this catalyst excelled especially in the uniformity of operating conditions when compared with the newer catalyst, which gave fluctuations in the course of the synthesis.

The new unit also laid at rest some of the uncertainties about the irregularities in the operation of the larger unit. In the larger unit the preheating of oil was done by direct gas firing, so that any possible small difficulties in the circulation could have resulted in a harmful overheating of the oil, with a splitting of the higher alcohols. No gas firing was used in the new unit where it was replaced with steam heating with a temperature control. The large unit also will later have this source of danger excluded.

The next experiment was run with catalyst 1432 which was recommended by Dr. Müller as being oxygen-active as a conclusion from work in the larger unit. The catalyst operated throughout very uniformly. The circulation oil which contained the higher fractions was of an exceptional purity, without any trace of rust color. However, the alcohol formation was in general entirely similar to that in the other preliminary experiments. None of these experiments have been successful in increasing the absolute amounts of the higher boiling fractions. No catalysts have been found which permitted lowering the synthesis temperature and thereby overcoming the effect of pressure on reducing the size of molecules.

We learned at that time the results on synol process obtained in Merseburg:

> They found that special conditions of reduction of the catalysts (with a large amount of hydrogen) permitted using the fused iron catalyst at 195-220°C. With these catalysts an alcohol concentration at 50% in the middle and upper oil fractions could be obtained at an operating pressure of 20 atm.

Merseburg/has found, in this way, a solution for the problem of production of higher alcohols from CO + H_2 using iron catalysts.

The above work in the oil circulation process should leave no doubt about the applicability of the Merseburg results to work with the oil circuit. Their work permitted changing from the high pressure synthesis field to the middle pressure synthesis.

We are getting ready for runs using catalysts activated by the Merseburg method. The operating conditions will be 25 atm pressure, at synthesis temperature as close as possible to 195-225°C, the conversion kept low, with a temperature possibly selected somewhat higher if required by the oil phase.

. . . .

/s/ Duftschmid

UNITED STATES
DEPARTMENT OF THE INTERIOR
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LOUISIANA, MISSOURI

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W. M. Sternberg
December 15, 1948

THE STATUS OF HYDROCARBON SYNTHESIS FROM CO-H_2 MIXTURES

By Dr. Michael

TOM Reel 164, Frames 143-153 July 24, 1941

Gas Circulation Process
(For Gasoline Production)

The gas circulation process was developed to overcome the peculiar difficulties of the CO-H_2 synthesis with iron catalysts which requires a very careful heat regulation. Temperatures of 300° and above, which must be used for the production of high anti-knock gasolines, can no longer be obtained in tubular or plate reactors.

In the gas circulation the heat of the reaction is not led away through the wall but by the reaction gas itself and led to a waste heat boiler outside the reactor where it is cooled to 50° below the reaction temperature; the waste heat boiler can be maintained relatively small in size because of the large difference in temperature. No complicated insets have to be built inside the reactor. The temperature interval inside the reaction space is limited to 10° by the absorption by the gases of the heat of the reaction, and the makeup gas must be circulated about 100 times between the reaction space and the waste heat boiler in order to leave the circuit with a 75-80% conversion. In addition to the above hot circuit, there is a cold circuit with a circulation inside the cold circuit of about three times. Its purpose is the removal of water by cooling to the temperature of the cooling water and the deposition of the high molecular weight reaction products which would otherwise clog the catalysts. The gas which finally leaves the system is cooled to about +40°C, and the light gasoline and the greater part of the gasol are also condensed.

The carbon dioxide is now removed and the gas led through a second stage which is about four times smaller, and the total conversion is increased to over 90%.

Catalysts

A catalyst of very high mechanical strength is required because of the great gas velocity (the time of residence of the gas in the catalyst bed is less than one second). Operations up to 300° with sintered carbonyl iron and a small amount of borax have been found satisfactory. This catalyst shows no tendency for "going through". Its heat conductivity is so good that no local temperature rises develop due to overheating. The life of this catalyst has been found to be around 4 1/2 months in small scale tests.

The pressing of the catalyst powders must be done with very vigorous shaking, since only in that way can a homogeneous catalyst grain be obtained, and the catalyst would otherwise show a tendency to scale during operation.

Operating Conditions

High-test gasoline is obtained by operating at a temperature of 300°C or over. The breaking down of CO to carbon is prevented by not permitting the temperature to exceed 330°C. A pressure of 20 atm has been selected. The efficiency at smaller pressures is lower, while at higher pressures the C content is higher. The space/time velocity in the first stage is 0.8 and 0.6 in the second stage. The gas mixture has the same proportion of $CO:H_2$ as in water gas, namely 4:5 and even closer to 1:1. A high content in inerts slows down the production. The gas production with oxygen is therefore recommended. The sulfur content must be below 2mg S per cubic meter.

				Finished Products
Gases (except methane and ethane)	30%	(ethylene 8%) (propylene 9%) (propane 3% (butylene 8% (butane 2%	15 polymers gasoline or 35 alk. benz. (5% iso butane)	7% ethylene lubricant 8% propylene lubricant 7% iso octane
Gasoline, -200°C	47%,	refined 44%, o.n. 84		44% motor gasoline
Middle oil, 200-350°C	15%,	cetane number about 50		15% Diesel oil

			Finished Products
Paraffin, +350°	1-2%		1% paraffin
Alcohols in water of reaction	7%	(55% ethanol (20% propanol (Balance: butanol, acetaldehyde, acetone and acids	7% alcohols
	100%		

18-20% gasification (methane + ethane) to 80-82 parts of the above products

Refining of Gasoline

The crude gasoline contains 3-4% O and must be refined. This is done by passing at atmospheric pressure over alumina at 380° and finally over bleaching earth at 200°C. The loss of material amounts to 5-6%. The octane number of the crude gasoline is thereby increased from 70-79 to 84 (research method), with 50-55% boiling below 100°C after refining. The refined gasoline is stabilized with alpha naphthol, and has shown a storage stability of 2 1/2 years in a special storage test.

The Unsaturated Gases

The olefines can be used in a variety of ways; the butylene fraction contains 62% iso-compounds and can be used for the production of technical grade iso-octane; propylene and ethylene can be used for the production of alkylbenzols as well as for the production of aviation lubricants.

Diesel Oils.

The middle oil, 200-350°C, contains 1-1 1/2% oxygen and can be used as a Diesel oil without any pretreatment. The cetane number is 50, the pour point -28°C.

Lubricants from Middle Oil

The middle oil produces with SO_2 66% of refined products which will form 60% motor oil obtained by polymerization with $AlCl_3$.

Yields

Two stage operations with a total conversion of 91-92% of liquid products (after polymerization of the gasol) will produce 133 g without ethylene recovery, and 142 g with ethylene recovery, (which requires a Linde plant), per ncbm of pure gas. About 80% of the production is gasoline and 20% Diesel oil.

Large Scale Tests

A circulation reactor which was originally planned for 800-1000 te/ann of crude products and had a layer of catalysts 60 cm deep has been used at 325°C for a long time with an inert-rich off-gas of the butyl plant, with an adjusted CO content.

The reactor operated as expected. It indicated the desirability of improvements in one respect only. The cross section of the gas circuit changed up to 1:10, and the velocities of the gas stream could change correspondingly. They originated in the turns in the gas path. Gas eddies were locally produced which interfered with the passing through the catalyst bed. Dividing the catalyst bed into several intermediate spaces on different levels and with small intermediate spaces was an improvement. The new constructions are made with this in mind.

Foam Process

This is a process in the liquid phase with the finest dispersion of a floating catalyst, and the gas must in this process be distributed throughout the liquid in the form of the minutest bubbles. Such a fine subdivision is obtained by either intensive stirring or by using fine-pored foam plates. This method of operation offers the advantages of avoiding any local overheating of the catalyst which may lead to a high methane production and to a deposition of carbon, and the gasification is lowered to an insignificant amount. In addition, the catalyst is used in its simplest form and can be renewed without interruption of operations. High boiling products of the reaction are used as the suspension medium, and principally the paraffins.

The foam process was developed for the production of an olefinic middle oil. The amount of higher boiling constituents in the liquid phase is increased in this process, and when operating for the production of gasoline at 300°C and over, the high boiling products are distilled over and must be returned. The preferred pressure is 20 atm, like in the gas circulation process.

The foam is produced by means of stirring with a vertical shaft mixer a short distance above the bottom of the vessel. This arrangement has been found satisfactory in small scale runs, but still offers certain technical difficulties in large scale operations.

The use of a foam plate in place of a mixer is technically simpler and may be readily incorporated into large scale operations.

The catalyst sinks in the liquid phase in the course of time, and the total liquid must be slowly moved upwards. The gas and the liquid are separated above in a catchpot and the liquid again returned from below to the reactor. The cooling can be done during the return of the liquid to remove the heat of the reaction.

Catalyst and Reaction Conditions

A finely divided highly active iron catalyst is well adopted for the process, e.g. a finely ground reduced precipitation oxide catalyst. Oxygen is excluded by grinding the catalyst in oil.

The space/time efficiency increases with the pressure, better efficiency results in a saving of reaction space, and the equipment costs are kept low by operating at 20 atm pressure.

When operating for the production of middle oil and paraffin the synthesis is done in the temperature range of 200-250°C, while in the processes for gasoline the temperature range is around 300°C in order to obtain high octane numbers.

More CO than H_2 is consumed in the reaction gas. A proportion of $CO:H_2$ between 55:45 and 60:40 is recommended.

Middle Oil Process

The purpose of the middle oil process was the production of a maximum amount of olefines. Iron obtained from red iron oxide, finely ground with a small amount of potassium carbonate or potassium borate was used as a catalyst.

The operating temperature was 240-250°C. The space/time yield of the stirred reactors was 0.4, in the foam plate reactors 0.2, calculated to the volume of the liquid phase. A certain choice is left in the product distribution by the proper selection of catalysts. The preferred proportion of products was:

Gasoline, -200°C		31%
Middle oil, 200-350°C		30%
Paraffin, +350°C		39%
		100%

In addition:

Gasol		2-4%
C_3, C_4 alcohols in the water of reaction		4%
Gasification	less than	5%

When operations are run in more stages, e.g. in three stages, it is recommended to convert 50-60% of the CO-H_2 mixture present in every stage, with an intermediate removal of CO_2. When the contents of the inerts in the makeup gas are low, operations can also be conducted in one stage by returning the gas to the circuit after washing out the carbon dioxide.

Quality of the Products

The gasoline obtained in the process for middle oils has an octane number (R.M.) of 72 after refining.

The olefine content of the middle oil has been obtained by hydrogenation measurements to be:

Fraction	Olefine Content
200-230°C	70%
230-300°C	56%
300-350°C	44%

The olefine content of a 230-350°C fraction of one run was found to be 60% average in spite of the low olefine content of the higher fractions as found by the determination of the hydrogenation number.

The straight chain compounds of the individual fractions have been found to be:

200-230°C	69%
230-300°C	70%
300-350°C	74%

The amount of products is distributed approximately similarly to that in the individual middle oil fractions.

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A careful cracking of the paraffin at 400-420°C gave

		Olefine Content
Gasoline, -200°C	15%	-
Middle oil, 200-250°C	15%	69%
Middle oil, 250-350°C	55%	51%
Residue, 350°C	8%	-
Coke	5%	-
Gas	1-2%	-

Only about one-third of the paraffin is of sufficiently low molecular weight to permit its direct use for paraffin oxidation.

Uses for Middle Oil

Detergents

A direct addition of H_2SO_4 to the olefines of the middle oil of the 230-350°C fraction produces sulfonates according to the work done at the main laboratory of Ludwigshafen, and they may be considered very high-grade detergents. The balance of the neutral oil, unless used as Diesel oil, can be converted into Mersol, an excellent detergent, by sulfochlorination, or into aryl sulfonates by condensation with benzol and sulfonation.

Turkey red oils, or leather oils, can be produced by sulfonation of the unsaturated constituents (230-350°C) with emulsification of the saturated constituents.

Leather oils can also be made by oxidation of the middle oil fraction 270-350°, and leather fats can be obtained by oxidation of paraffins (Dr. Pfirrmann).

Fatty acids and soaps can be produced by the addition of carbon monoxide and water to olefines (230-350°C, Reppe process).

Aldehydes and alcohols can be obtained by the addition of carbon monoxide and hydrogenation to the olefines (oxo process of the Ruhrchemie).

Lubricants and Fuels

The more strongly branched middle oil of the gasoline process can produce lubricants with viscosity number of 105 which will meet all the specifications by polymerizing with aluminum chloride after purification with sulfurous acid. The middle oil from the middle oil process is still better suited for the production of lubricants because of the larger proportion of straight chain compounds. The heavy naphtha, +100°C, can be polymerized together with the middle oil. A lubricant with the viscosity number of 114, and a viscosity of 2.0°E at 100° can be obtained with a 47% yield. It meets all the requirements. The middle oil fraction 200-320°C has a cetane number of 60 when used as Diesel oil. Its pour point is -10° and is therefore not entirely satisfactory. It can, however, be made to meet the standards by lower cut and by a light cracking of the higher constituents.

Gasoline Process

Increasing the temperature to 310°C and returning the distillate to the liquid phase, produces the following products:

Gasoline, -200°C	60%
Middle oil, 200-350°C	30%
Paraffin	10%
	100%
Gasol	6%
Alcohols	6%
Gasification	about 5%

The enriched gasoline so obtained has an octane number (R.M.) of 78, after refining - 90.

The gasoline process has not yet been tested experimentally over a longer period of time.

The Yield in Liquid and Solid Products is Higher Because of the Lower Gasification

160-170 grams of liquid products can be readily obtained per normal cubic meter of the pure gas, to which gasol will have to be added. It is expected that yields of over 170 g will be obtained in the future.

Test for the Application of the Gas Circulation and the Foam Process for the Production of Synol Products

Tests with the synol catalysts of different size of particles have been run in the 4-liter gas circulation reactor.

Operations were conducted for five weeks at 195°C with a 3-5 mm particle size and the space/time yield of 0.4-0.5. After five weeks the space/time yield decreases suddenly. The catalyst was plugged up with the products, some of the catalysts became soft and could be ground up between the fingers. Recirculation of the products with a 30% conversion produced only one-half the alcohol yields against the Leuna synol process. Olefines replaced the mixed alcohols. Conversion was then further reduced in order to reduce to one-third the residence time with the catalyst. The products have not yet been studied any closer.

Coarser particle of catalyst (12-15 mm) had a longer life, but the space/time yield obtained with them was only 0.2.

Operations could not yet be conducted by the foam process at 195°C with the finest size of catalyst, because the space/time yield was too low. At 210° the space/time yield of 0.12-0.15 has been reached. Investigations showed the products to contain 75-80% of the alcohol contents of the Leuna products. The experiments are being continued.

/s/ Michael

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W. M. Sternberg
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SOLID AROMATICS IN THE HOLD OF PITCH HYDROGENATION, POELITZ

By Boente

TOM Reel 164, Frames 190-192 July 15, 1941

The sample consisted of 100 kg liquid phase HOLD obtained in the hydrogenation of pitch at higher concentrations of pitch.

The pitch contained

49.6% solids (benzene insolubles)
50.4% oil
14.6% ash in the solids
8.8% soluble asphalt in oil

Oil: specific gravity 1.096/50°C

Determination of Solid Aromatics

Summary

No special enrichment of any definite solid aromatics has been found in the HOLD, not even of hydrocarbons like carbasol, pyrene and coronene which have been found to be particularly stable in the industrial hydrogenation processes. Carbasol is present in only slightly higher concentration than in the other liquefaction oils, pyrene is almost absent, and coronene in only slightly higher concentration.

Tests have shown:

1) Carbasol - about 0.2% (of the total weight of HOLD).

This is approximately the same amount as is usually found in the liquefaction oil from bituminous coal tar pitch. The presence of carbasol in HOLD is explained by the presence of carbasol in bituminous coal tar pitch.

2) Pyrene

Pyrene is occasionally present to the extent of 10-15% in the coal liquefaction products (especially of l.t.c. oil) and is deposited in the crystalline form during the fractionating vacuum distillation of the l.t.c. oils, but none has been found in the pitch hydrogenation products.

The formation of pyrene in the coal liquefaction products is probably to be explained in the preformation of the pyrene molecules in the starting products.

3) Coronene - about 1.5% (to total weight of HOLD)

About 0.25% coronene is originally produced in the vacuum distillation (1-2 mm) of the HOLD. When the residue is again reheated (a process similar to l.t.c.), additional 1.25% coronene is obtained. Part of this hydrocarbon is therefore probably present as such in the HOLD. The remainder is probably newly formed during the high heating of the residue. It is already known that during the l.t.c. of Hydrogenation residues the solid aromatics become enriched in the l.t.c. oil.

The melting point of coronene is 432°C (corr.) and the boiling point 525°C at 760mm. The hydrocarbon, however, sublimes readily, and usually goes over during the l.t.c. of the hydrogenation residues together with the gum-like fraction with a boiling point at 760mm of 400-500°, and the gum-like oil holds coronene more or less in solution.

The proportion of the gum-like fraction, b.p. 400-500°C, is relatively small comparing to coronene in the HOLD, and coronene crystallizes relatively easily during the l.t.c. of the hydrocarbons and may easily cause the plugging up of the outlet.

A study of deposits from the precooler of the Poelitz l.t.c. kiln indicated the following composition:

20-25% coronene
75-80% high-boiling gum

Should the separation of coronene from the reaction products offer no particular difficulties, the production of this hydrocarbon would prove advantageous.

/s/ Boente

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Umschau
Volume 66/67, Page 363

THE KOPPERS-TOTZEK POWDERED COAL GASIFICATION*

The classical gasification technique depends very largely on the physical makeup of the fuel, so that essentially only lumps and non-baking fuels can be gasified.

Technical progress demands the development of a universal gasification process, which would permit the complete conversion of fuels of any kind into gas. We must then select a physical state of the fuel in which all solid fuels can be obtained. This leads to powder gasification which, however, can be successfully performed only in suspension. Powdered fuel gasification is as old as the gasification technique. The theoretical processes have been understood and systematized and the experimental work performed. According to the earlier conception, an effective interchange of heat and material is brought about chiefly by the relative motion, convection and diffusion between the gas envelope of the particles of coal dust and the reacting agents, analogously to the gasification processes in quiet bed of the fuel.

*A paper read by Friedrich Totzek, July 2, 1947, in Essen.

These points have been considered in the structural form and the operating conditions of the first experimental generators built, which permitted a maximum relative motion between the coal dust particles and the reaction agent. The reaction consisted at first in combustion with a steam-carbon dioxide mixture at temperatures up to 1600°. The results were disappointing. Only 20-25% of the carbon introduced was gasified. The coarser particles of coal dust precipitated in the generator, the ash was bared and slagged. The finest coal particles were carried out in the gas stream ungasified. The different series of experiments have brought exhaustive proof that no satisfactory gasification by purely endothermally acting reagents could be brought by contact of carbon with carbon dioxide or steam, and that the relative motion was insufficient to bring about a satisfactory gasification.

The following experiments were carried out with an air-steam mixture at a temperature of 1200°C. When strongly reactive fuels, like brown coal dust and brown coal l.t. coke dust were used, the gasification results changed suddenly. The slag still was produced in the liquid form. The gas outlet temperature was 1500°C.

These results lead to the realization that the principal importance was not in the relative motion of the fuel but in the kinetic energy of the gasification reaction, (i.e. the material and heat exchange). These, however, received complete play only when the particle of the dust was very finely ground and the coal dust and the reagent were perfectly mixed. This will make the gasification process almost independent of time, and the melting of the ash will be prevented by the reformation of carbon monoxide and hydrogen.

The final form of the generator took into consideration these facts based on natural laws. The results of the tests furnished a proof of the accuracy of the theory and construction.

In the different experimental series, brown coal dust, brown coal l.t. coke dust, and bituminous coal dust from the gas flame coal to the lean coal and even to coke dust have been gasified perfectly. The degree of gasification $\left(\frac{\text{gasified C}}{\text{C introduced}}\right)$ amounted to about 95%. The ash was carried out dry with the gas stream.

The gasifying means were air-steam and oxygen-steam with a preheating temperature of around 1200°C. The gas outlet temperature was between 900 and 1200°C depending on the reactivity of the fuel.

The gasification process and the gas obtained are characterized by the following data: a high concentration of $CO + H_2$; regulable proportion of $CO:H_2$, depending on the preheater temperature and the steam addition; simple sulfur compounds; no gum formers; a practically complete gasification of the fuel introduced; a possibility of gasifying any solid fuels; relatively small consumption of energy or oxygen.

When oxygen is used, a fuel of any kind, including waste fuel, can be used for the production of gas for the following industries: The Fischer-Tropsch synthesis, high pressure synthesis, ammonia synthesis, city gas production, fuel gas of every kind. All these industries can now be built around any desired fuel and operated with it.

The above properties of the gases, and in particular the concentration of CO + H_2 of up to 95%, the regulable ratio of CO:H_2, and the temperature at which the gas leaves the producer, and finally a BTU heating value of 2,000 to 2,400 k calories/cbm permit application of the process for the iron works:

The blast furnaces follow the rules of gasification of solid fuels by producing a gas of the highest carbon monoxide concentration. This gas is the reduction agent of the ore. The "blast furnace curve" gives information about the concentrations in the different temperature zones of the blast furnace shaft. It is further known, that the reducing ability of the gas is considerably increased in the presence of a certain proportion of hydrogen, e.g. 75% CO and 25% H_2. The gas produced in powdered fuel gasifiers is ideally suited with respect to temperature and concentration to meet these requirements and may be used for the reduction of ores, e.g. for the production of sponge iron. The gas escaping from the blast furnace after the reduction of the ore will have a heating value of around 2,000 k calories/cbm and can be used as a fuel gas for the hearth furnaces, if necessary, with carburization.

The powdered fuel gasifier offers a further possibility to produce a gas of the higher carbon monoxide and hydrogen concentration at such a high temperature to permit smelting operations in suitable equipment, and to reduce countercurrently the ore with the off-gases from the first unit.

The design shows that coke in the iron smelting processes could be replaced by other fuels, which follows from the above considerations. Experiments and proposals to eliminate coke from blast furnaces have been known (Wiberg et al).

The opinions of F. Wuest* on the Basset process are based on the above. Their principal points consist in that, were it possible to gasify coal dust at high temperature with a production of a gas of high concentration, the possibility would be offered to utilize completely the heat of the reaction of the combustion of carbon in purely metallurgical processes.

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*Stahl und Eisen, Volume 41 (1921), Pages 1841/48.

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Main Laboratory of Ruhroel
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T-467
Hugo Stinnes Works
December, 1944

HYDROGENATION OF BITUMINOUS COAL LTC PITCH

I. Introduction

The hydrogenation of bituminous coal high temperature pitch has been performed on an industrial scale for many years, in particular by the Ruhroel GmbH. The coke pitch has been found entirely satisfactory as a raw material for hydrogenation, so that today the principal amounts of the pitch produced in coking plants is used up in this way. The bituminous coal high temperature pitch offers advantages over bituminous coal as a raw material for hydrogenation because of its aromatic basic structure and its low ash content.

High temperature pitch is a pyrogenic decomposition product of coal, is low in hydrogen and has an aromatic structure because of secondary cracking reactions on the highly heated furnace walls. It is the hydrogen-poorest raw product of hydrogenation, and requires therefore higher temperatures and pressures for its hydrogenation than does bituminous coal. The reaction products of hydrogenation are also poorer in hydrogen and richer in aromatic hydrocarbons, than all other hydrogenation products. These properties are very desirable. The fuel oils obtained from coking pitch possess higher solvent action for asphaltic materials and are especially suited as solvating agents. The middle oil and the crude gasoline can be converted by suitable operations into a gasoline with an aromatic content of 40-50%. The hydrogenation of the coke pitch middle oil by the Ruhroel process (single stage vapor phase hydrogenation at 600 atm with predominatingly splitting conditions) produces an aviation gasoline which can be equal in quality to the products of bituminous coal hydrogenation only when the gasoline obtained in the latter is afterwards dehydrogenated.

The low ash content of coking pitch is an advantage during hydrogenation because no erosion of the equipment, such as occurs with bituminous coal, can happen.

The hydrogenating conditions for coking pitch are the same as in the hydrogenation of bituminous coal. Pitch is dissolved in its own heavy oil or in high boiling tar oils, pitch distillates, etc. A portion of the return HOLD is added to this solution. The catalyst is added in powdered form and pumped through the converters with the solution. About 65% of the injection feed is converted to distillable oils; the rest is withdrawn as HOLD. Part of the latter is again returned, while the rest is broken down into heavy oil and l.t.c. residue by the working up of the residues.

The large industrial scale l.t.c. of bituminous coal has made a great progress within the last years in Germany, and the question arises whether the l.t.c. pitch obtained in the distillation of the l.t.c. tar will also be suited for hydrogenation. We were commissioned by the Reichsamt fur Wirtschaftsausbau in December 1942 to study this problem, principally from the standpoint of primary importance to the Reichsamt, namely to determine whether the heavy oil obtained during the hydrogenation of the l.t.c. pitch would meet the requirements for marine fuel oil. We performed preliminary tests in January and February 1943 using an l.t.c. pitch of the Byk-Gulden Works. This was hydrogenated in the liquid phase for comparison with the high temperature hydrogenation. The amount of the sample was only 500 kg, and the tests could only be extended over six days. Preliminary experiments with the l.t.c. tar of the Upper Silesian hydrogenation works were run in April 1943, and with the l.t.c. pitch samples from the Fuel Investigation Institute of the Technische Hochschule in Darmstadt (under the leadership of Prof. Agde) in May 1943. We obtained two tons of l.t.c. pitch in November from the Gesellschaft für Teerverwertung, Duisburg-Meiderich, obtained by this firm by gas distillation of l.t.c. tar in tubular still. The l.t.c. tar was derived from a Koppers flushing gas installation at the Oheim mine of the Reichswerke Hermann Goehring in Kattowitz. We obtained one additional ton of l.t.c. pitch in January 1944, and ten tons in March 1944, from the l.t.c. tar of a Krupp-Lurgi plant of the von Velsen mine of the Saargruben-A.G. We have made large numbers of tests with the Oheim and later with the von Velsen pitch, testing the hydrogenating properties of bituminous coal l.t.c. pitch as commissioned by the Reichsamt, and the results obtained are recorded in this present paper.

Tests were conducted up to the end of July, and had to be frequently discontinued because of the disturbances arising from special conditions.

II. Raw Materials

Analyses of several bituminous coal l.t.c. pitches are summarized in Table 1, with an average analysis of bituminous coal high temperature pitch for purpose of comparison. The following principal differences can be seen between the two kinds of pitch:

1). The l.t.c. pitch is appreciably higher in hydrogen than coking pitch. Its hydrogen content is even way above that of the coking tar. The oxygen content of the l.t.c. pitch is also much higher. The carbon content is correspondingly appreciably lower than of the coking pitch. Nitrogen, sulfur and chlorine contents do not differ appreciably.

The ultimate analysis permits one to realize the far reaching difference in the basic structures of the two kinds of pitch, which leads one to suspect a different behavior during hydrogenation.

2). A fractionating extraction of the pitch substance with different solvents shows that the solubility in the non-polar solvents is much greater for the l.t.c. pitch than for the coking pitch. The high molecular weight constituents, insoluble even in the boiling mixture of tetraline and cresol (80:20) which have the highest solvent properties for pitch, are only present in very small amounts in the l.t.c. pitch. These compounds which were formerly erroneously called "free carbon" are just the ones to offer difficulties in hydrogenation and result in depositions in the pipelines and converters. They are therefore enriched in the HOLD and their amount is directly proportional to the amount of tetraline-cresol solids present in the raw materials. It has been found in practice that the hydrogenation of coking pitch is economical only when the tetraline-cresol solids in the pitch do not exceed 10%.

Fractionating extraction shows already, that the l.t.c. pitch will be more readily hydrogenated because of its low tetraline-cresol solids and its higher proportion of benzene and gasoline, than coking pitch.

3). The inorganic contaminations in l.t.c. pitch are present in a different form than in the high temperature pitch. If the solids insoluble in a solution of pitch in tetraline-cresol or in the middle oil of the pitch hydrogenation are filtered, almost 90% of the total ash of the coking pitch remains with the solids upon the filter, which permits one to conclude that the ash in the coking pitch is mostly present as an inorganic mixture. In l.t.c. pitch only 20-30% of the total ash can be removed by filtration. The principal amount is soluble in oil and therefore cannot be separated by filtration. The inorganic elements find themselves in chemical combination, presumably, with the oxygen compounds of l.t.c. pitch. These metallo-organic compounds are extraordinarily stable and are only decomposed at temperatures over 300°C. This behavior of the l.t.c. pitch ash leads to difficulties during hydrogenation, which have never been observed with high temperature pitch. The temperature range of 300-400° is reached in the preheater, and the decomposition of the metallo-organic compounds takes place in the preheater during the hydrogenation of the l.t.c. pitch. This results in very hard depositions in the preheater, which becomes completely plugged up in a short while. The deposits consist only of inorganic constituents, principally of iron.

The ash of the two kinds of pitch differ quite appreciably in their composition. The analysis of the total ash is shown in Table 2. One may see there that the l.t.c. pitch ash consists mostly of iron oxide. One may draw the conclusion that iron is the substance which interacts with the acid oxygen compounds in pitch, and occurs in an oil soluble form in the pitch. One cannot yet decide at present whether the iron is obtained from the ash constituents of the bituminous coal, or from the iron walls of the l.t.c. equipment, which appears more probable.

III. Hydrogenation in the Liquid Phase

The first experiments on hydrogenation of l.t.c. tar were run in hydrogenating exactly like the coking pitch in the liquid phase. The experimental conditions and results are summarized in Table 3.

The first test, S 35, shows that l.t.c. pitch behaves very differently in hydrogenation than does high temperature pitch. (Test S 34-2). The pitch concentration of the paste was 5% higher and the reaction conditions were unchanged, but the l.t.c. pitch nevertheless gave a clear reaction product, free from solids and asphalt, while the product from coking pitch was brown-black in coal and contained 7% solids in addition to 4.5% asphalt.

42% gasoline and middle oil could be distilled off the l.t.c. pitch reaction product. The residual heavy oil is greenish-brown and has a viscosity of about 3.5° on the Engler viscosimeter (2.8 mm capillary) at 50°C. Only 37% gasoline and middle oil are distilled over from the reaction product from the coking pitch up to 325°. The heavy oil is usually a black, very viscous oil, with over 10% solids and 7% asphalt. Its viscosity is too high to be determined in the Engler viscosimeter. A measure of the viscosity was obtained in a bitumen viscosimeter (5 mm capillary) at 100°C, and found to be 2.2°.

The l.t.c. pitch, unlike high temperature pitch, is downgraded completely under the above reaction conditions into asphalt-free products, forming vapors at the reaction temperature. This very gratifying fact nevertheless introduces great difficulties in the hydrogenation in the liquid phase. The reaction products are mostly in a vapor form in the upper part of the converter, and they no longer possess the ability to carry out the powdered catalyst from the converter. The latter sinks, therefore, and is collected in the bottom part of the converter. The high concentration of the catalyst in the lower part of the converter causes the formation of reaction centers there, the temperature of which can no longer be mastered after a few days of operation. The converter operates very unevenly at first, and exhibits, even after a few days, a strong tendency to sudden temperature rises, which makes the whole process entirely impossible industrially (personal notation by Dr. Frese: Use Lower Temperatures or Lower Pressures).

A more quiet operation was anticipated by continuously draining the deposited catalyst from the converter HOLD. This measure has not led to the desired results, because the catalyst apparently becomes firmly adherent to the walls, and cannot be completely withdrawn.

Test S 35 had to be discontinued, because after five days of operations the preheater no longer passed any material through it. The reason for it was the fact mentioned above, that the inorganic constituents, in particular iron, which are in organic combination in the pitch, are decomposed in the temperature range of the preheater and deposited in a very solid form.

The temperature was lowered 20° in Test S 36 and the gas thruput increased. These measures were, however, insufficient to carry the catalyst out of the converter and produce a more quiet operation. Moreover, depositions in the preheater continued to form and caused a complete plugging up after eight days of test.

The two series of tests have shown the practical impossibility of hydrogenating l.t.c. pitch by itself in the liquid phase, and a mixture of l.t.c. pitch and coke pitch in proportion 1:1 was used in Test S 37. The reaction temperature could now be safely maintained and the preheater had only insignificant constriction after ten hours of operation. The reaction product again contained high molecular weight asphaltic constituents which failed to vaporize at the reaction temperature, and the catalyst was carried out of the converter. The properties of the reaction product were those of a mixture of the products in S 34 and S 35. The addition of l.t.c. pitch to coking pitch increased the yield in gasoline and middle oil and reduced the viscosity and the asphalt content of the heavy oil. The products were richer in hydrogen and the phenol content rose.

Efforts were made in Test S 40 to reduce the addition of coking pitch to a minimum without making the converter operations difficult. The purpose of these experiments was to maintain the asphalt contents of the reaction products as low as possible by minimum additions of coking pitch and to still permit the direct use of the heavy oil as a fuel oil, though of a lower worth. The coking pitch proportion in the total pitch varied between 20 and 27%. The heavy oil obtained satisfied, in most cases, the requirements for fuel oil, after the solids had been removed by filtration. The temperatures in the converters, however, again became unmanageable with these mixtures of pitch, so that the coking pitch additions did not appear to be satisfactory for the hydrogenation on an industrial scale. There was also the usual plugging up of the preheater, although only after a longer time of operation.

We may summarize the results of our study of the hydrogenation of l.t.c. pitch in the liquid phase as follows:

1). L.t.c. pitch is more readily hydrogenated than the high temperature pitch or than the bituminous coal itself. It is completely downgraded at 450°C with 700 atm hydrogen partial pressure.

2). The hydrogenation of l.t.c. pitch alone is impossible in the liquid phase under conditions commonly used for coking pitch or for bituminous coal. L.t.c. pitch is downgraded so far in the course of the reaction, that all the reaction products are in the vapor form at the reaction temperature. The liquid phase is absent and cannot remove the catalyst from the reaction space. The catalyst is collected in the converter, and reaction centers are formed in which the temperature will rise suddenly, so that the whole reaction can no longer be mastered chemically.

The removal of the deposited catalyst through a converter HOLD did not seem possible with the equipment used.

When solutions of l.t.c. pitch in heavy oil are heated to over 300°C, a temperature reached in the preheater, the metallo-organic compounds are decomposed. This brings about a very solid inorganic deposition which completely plugs up the preheater after some time.

A reduction of the time of residence of the paste in the preheater by increasing the gas thruput brought no help.

The mixtures of equal parts of l.t.c. pitch and coking pitch produced no deposits in the preheater because the ash constituents were apparently carried out with the mixture. When the proportion of coking pitch in the total pitch is lowered to less than 30%, deposits are again formed in the preheater.

3). Mixtures of l.t.c. pitch and high temperature pitch can be readily hydrogenated in the liquid phase, when the coking pitch proportion is not under 35-40%. The catalyst no longer remains in the converter and the temperature can be readily maintained.

The addition of l.t.c. pitch to coking pitch increases somewhat the gasoline and middle oil yield. The heavy oil becomes thinner and contains less solids and asphalt. With coking pitch concentration in the total pitch less than 30%, the same difficulties are experienced as during the hydrogenation of l.t.c. pitch alone.

4). The l.t.c. pitch products are richer in hydrogen and contain more oxygenated compounds, in particular phenols (see Section VI).

IV. Hydrogenation with Fixed Bed Catalyst

Our tests on hydrogenation of l.t.c. pitch in the liquid phase showed the basic differences in the hydrogenation properties of l.t.c. pitch and high temperature pitch, and we attempted to hydrogenate l.t.c. pitch over fixed bed catalysts in the converter. The hydrogenation with fixed bed catalysts has so far been possible only with middle oils. Higher molecular weight raw materials, in particular those containing asphaltic materials, harmed the catalyst in a very short time, making it inactive and requiring its replacement. Our efforts to work the coking pitch paste over fixed bed catalysts, even after removing the solids by filtration, caused the complete coking up of the converter after a few days. We have, however, been successful in hydrogenating the asphalt-free heavy oil of the coking pitch liquefaction at 700 atm over catalysts developed here with the production of gasoline and middle oil, and without damaging the catalysts.

Our experiments have been summarized in detail in Table 4 and showed that l.t.c. pitch can be hydrogenated over fixed bed catalysts in continuous operations without damaging the catalyst, in spite of its high content in substances insoluble in standard gasoline (asphalt) because of its peculiar constitution. The insoluble constituents of the l.t.c. pitch, the amount of which corresponds to that of the tetraline-cresol solids, must, however, be previously removed by filtration, because they are not downgraded during the hydrogenation and are deposited upon the catalysts. The inorganic contaminations also which are formed by the decomposition of the originally organic combinations of the metals and could not be removed by filtration in the past, cause not merely deposition in the preheater, but also a settling out on the catalyst. Experiments for the removal of the total ash from the l.t.c. pitch had therefore to be carried out concurrently with the study of the hydrogenation of l.t.c. pitch, and the results are reported in the following section.

Hydrogenation was carried out at a pressure of 700 atm. A high partial pressure of hydrogen of at least 500 atm is indispencable for the downgrading of the high molecular weight constituents of pitch. The catalyst used was similar to the one developed previously for the splitting hydrogenation of middle oil to high aromatic gasoline. Its characteristic feature is the very small amount of the heavy metals. It consists essentially of activated aluminum hydrosilicates upon which less than 1% molybdenum and 2-5% chromium are deposited. The catalyst is shaped in a process developed here and produces a very abrasion-resistent pill. The experiments were first performed in the usual vapor phase equipment. The volume of the catalyst amounted to 5-7 li. In the Test G.S. 13 and the subsequent ones, the converter was provided with a HOLD drain at the bottom part. 2-6% of the amount injected was periodically drained through that line. In this way, 20-30% of the ash introduced was withdrawn from the reaction space. The pase withdrawn was again returned to the injection product before filtration.

Even with deashing performed very carefully, as in Test G.S. 15, the preheater was plugged up with inorganic depositions after longer operation, and the unit was equipped with two preheaters in the Test G.S. 17. In the first preheater the paste is heated to a temperature of not over 300°C, while the hydrogen is heated so high in the second preheater that in the bottom part of the converter where the liquid and the gas join, a temperature of 440-460°C is reached. The amount of hydrogen was increased and the preheater heated so high, that the gas temperature at the outlet was 520-530°C. This unit, shown in Fig. 1, has been found very satisfactory. The determination of the volume of the first preheater before the test and after twenty-eight days of operation showed no reduction.

The pressure filtration of the solution of l.t.c. pitch through ceramic filter material was done by using middle oil as a solvent. The middle oil of the coking pitch hydrogenation was used in Tests G.S. 12 and G.S. 17-1, in the other tests the middle oil separated in the l.t.c. pitch hydrogenation itself. With a pitch concentration of 60% the solution still could be filtered with high efficiency. As the solution is treated thermally for deashing, the pitch content of the mixture can be increased to 70% because of the ready filterability. In the experiment G.S. 13 an unfiltered mixture was added and the pitch concentration reached 80%.

The reaction temperature for the process with fixed bed catalysts was 440-460°C. Practically solid and asphalt-free reaction products were obtained in every one of our tests. These products were distilled in all the tests, with the exception of G.S. 17-3, with the production of a heavy oil with a viscosity of 5-6°E at 50° required for the marine fuel oil (Engler viscosimeter with 2.8 mm capillary). The middle oil and fuel oil cut was at about 300°C.

In the reaction product G.S. 17-3 the middle oil was cut at 325°C. The viscosity of the heavy oil at 50°C was 15°E. However, as described in Section VIII, it had already been found that a thermal after-treatment can readily reduce the viscosity of the heavy oil down to the required value, with a simultaneous desirable increase in gravity.

The properties of the reaction products obtained in these tests are discussed more fully in Section VI.

To summarize, our tests of hydrogenation of l.t.c. pitch over fixed bed catalyst have shown that:

1). Bituminous coal l.t.c. pitch can be hydrogenated over a fixed bed catalyst without having the catalyst damaged during continuous operations. This process is practically the only possible one for hydrogenation of unmixed l.t.c. pitch. It possesses a number of additional advantages, such as a high space/time velocity of 0.5 kg new oil/li of the reaction space and hour, and the complete downgrading of all asphaltic materials. Pitch is completely broken down in a single passage through the hydrogenation unit with the production of the valuable gasoline, middle oil and heavy oil. The properties of the heavy oil correspond immediately to the requirements of the marine fuel oil (see Sections VI and VIII). The crude gasoline and the middle oil can be converted into high-test aviation gasoline (see Section VII). No HOLD is produced, which eliminates the working up of the residues.

2). The complete elimination of the constituents in pitch, insoluble in middle oil and the practically complete elimination of the organically combined ash are the preliminary requirements for operations over fixed bed catalysts. This problem was solved in G.S. 17 by a thermal pretreatment of the mixture in the presence of 0.5% S, followed by filtration (see Section V).

3). The amount of ash of the order of magnitude of 0.005% is still present in spite of the deashing of the material, which may lead in a settling out in the preheater or upon the catalyst during continued operations, and 2 construction modifications were used which have been found satisfactory in G.S. 17.

a). The material and the hydrogen were heated in two different preheaters. The material then is not heated to a temperature higher than 300°C, so that no decomposition of the metallo-organic compounds takes place in the preheater. The required heat is introduced with the hydrogen.

b). Breaking down of the organically combined ash is postponed to the bottom part of the converter, and the raw material enriched with ash is drained through a HOLD line in the bottom part of the converter, to the amount of 2-6% of the material. In this way 20-30% of the small amount of ash still introduced can be removed before it can damage the catalyst.

4). The reaction product of the l.t.c. pitch hydrogenation over fixed bed catalysts is a yellow-brown oil, which is practically free from solids and asphalt.

5-6% water, 8-10% gaseous hydrocarbons, H_2S and NH_3 and about 85% liquid products are formed, referred to pitch. 8-10% of the liquid products is crude gasoline. The proportion of middle oil and heavy oil depends on the cut. With the cut at 300°C (viscosity of the heavy oil 5-6°E/50°C), 0-20% middle oil and 50-75% heavy oil are formed, depending on the reaction conditions. If the middle oil is distilled to 325°, 22% middle oil is obtained and 55% heavy oil of a viscosity of 15°E/50°C.

5). The thermal pretreatment of the raw products for deashing causes the products of the reaction to be lower in hydrogen. The aniline point of the crude gasoline drops by 15°C, the gravity of gasoline middle oil and heavy oil are increased.

V. Deashing of LTC Pitch

Table 4 shows that the total ash content of the feed consisting of 80% l.t.c. pitch of the Oheim mine in G.S. 13 amounted to 0.30%. Simple filtration, such as done in G.S. 12 permits lowering the ash content of the 60% feed to only 0.18%, because, as already mentioned, 70-80% of the total ash of l.t.c. pitch is in organic combination and therefore in a soluble form.

We have first of all found that part of this ash can be precipitated and filtered off, when the feed is heated with a small addition of sulfur for about one hour to a temperature of 100-150°C. In this way, the ash content of the 60% feed could be reduced to 0.04% in G.S. 15. The addition of sulfur has, however, the disadvantage that the filterability of the pitch feed is greatly reduced due to polymerization. The sulfur additions should therefore not exceed 0.1%.

The deashing achieved in Test G.S. 15 is yet insufficient, because it has led to a plugging up of the preheater after seventeen days of operation. We have succeeded, however, in discovering a process which not merely permits a sufficient removal of the ash, but also improves the filterability of the feed and of the original material to such an extent as to introduce desirable changes in the properties of the reaction products.

The feed is led with the addition of flower of sulfur at about 400°C through a system of pipes. No hydrogen is added. Small amounts of gas are nevertheless formed through splitting off of hydrogen and gaseous hydrocarbons, in particular methane, ethane and propane. The reaction is to a great extent independent of pressure. Operations are conveniently done under a pressure which forms in the unit through the solubility of gases in the products at the temperature of the deposition vessel. This pressure fluctuates between 50 and 60 atm.

The equipment used by us is shown in Fig. 2. This is by no means an ideal form and will have to be redesigned for an industrial installation.

The individual results are shown in Table 5. In the series of experiments C 4, the conditions in C 4-3 were found to be the most favorable. The series of test C 5 shows that when these conditions are maintained the space/time efficiency can be increased to 1.5 kg/li/h. With conditions such as in C 5-4, which may be considered the optimum conditions for the von Velsen pitch study, the ash content after the filtration, referred to pitch, was lowered from 0.3 to 0.006%. The filterability of the solution is of prime importance for the removal of the solids and the ash from the pitch solution, especially for industrial operations. In this respect l.t.c. pitch is also far superior to the coking pitch. Table 6 shows the times required by the different pitch feeds to pass through an experimental pressure filter under identical conditions. The time of filtration of bituminous coal crude solution is given for comparison. This was a reaction product of the coal extraction process of Pott-Broche, and the Ruhroel filters them in industrial filters. If we take the filter time of the crude solution as a standard for the industrial filtration operations, we will find that a solution of 50% of coke pitch in middle oil of the high temperature hydrogenation can no longer be filtered industrially. L.t.c. pitch on the other hand still produces technically filterable solution at the same concentration and with the same solvent. The favorable effect of the addition of a small amount of kieselgur upon the filtration time may be noted. Even with the concentration of 70% l.t.c. pitch in the feed, the time of filtration after the addition of 1% of kieselgur is the same as for the crude solution.

Determinations 7-9 show the above mentioned increase in the filtration time resulting from the addition of small amounts of sulfur. The feed is entirely unfilterable without the addition of kieselgur. Determinations 10 and 11 deal with the reaction products of the deashing experiments C 4-3 and C 5-4. One can see that with the thermal pretreatment the filtration time is good even without the addition of kieselgur, in spite of the high sulfur addition. The feed deashed by our process is considerably more readily filterable than the crude extract.

We have been able to completely confirm on a semitechnical filter plant the result found with the experimental filter, and we are of the opinion, that the industrial filtration will encounter no difficulties. In the industrial deashing troubles can be possibly met in the equipment by an incomplete removal of the ash which will slowly plug up the tubes. We have always found sediment in our equipment in the first bend of the first tube coil. In the dry state it was loose and could be readily removed mechanically. The industrial equipment should be constructed with a readily accessible catchpot in front.

We may summarize that we have found it possible to attain a practically complete deashing of the l.t.c. pitch by a novel process. In this treatment, as already has been shown in Section IV, the constitution of the pitch is changed by the splitting off of hydrogen and hydrocarbons. These changes are in a desirable direction, because the products of the subsequent hydrogenation are also poorer in hydrogen, i.e. strongly aromatic.

The deashing effect of the process is so thorough that the l.t.c. pitch feed can be hydrogenated over fixed bed catalyst without harming it during continuous operations by depositions of the ash.

VI. Primary Products of Hydrogenation

Table 7 shows the composition of the gaseous hydrocarbons produced in Test G.S. 13. The determination was done in the regular Leuna equipment. The analysis of the off-gases was not done in the other tests, but it may be assumed that the composition of the gases is practically unchanged.

The analytical data for crude gasoline from the l.t.c. pitch hydrogenation over fixed bed catalysts in Tests G.S. 15

and G.S. 17-1 are shown in Table 8. It may be seen that the thermal pretreatment of the feed in Test G.S. 17-1 caused the reaction products to be considerably more aromatic. The crude gasoline is equal by comparison to the crude gasoline of the high temperature pitch hydrogenation.

The same relationships exist for middle oil as shown in Table 9.

The effect of the thermal pretreatment of the pitch solutions is particularly great in the heavy oil produced in the hydrogenation, as shown in Table 10. Not only is there a much desired increase of the gravity, but the pour point and viscosity at 20° are considerably lower. For that reason, materials crystallizing out at room temperature (paraffin deposition) must make the heavy oil of G.S. 15 relatively more viscous, and they are not formed in the thermally preheated feed in G.S. 17. These small deposits dissolve at higher temperatures, and the viscosity of the two oils at 50°C is practically the same. The thermal pretreatment of the pitch solution has, therefore, the same effect as a subsequent temperature treatment (cracking). See Section VIII.

The heavy oils of the l.t.c. pitch hydrogenation over fixed bed catalysts produce high-grade fuel oils. However, the oil from G.S. 17 must be given a higher rating because of its aromatic basic structure, and the better solvent actions upon asphaltic foreign oils produced thereby.

We may summarize about the properties of the primary reaction products of the l.t.c. hydrogenation that, in line with the composition of the original feed, they are richer in hydrogen than the corresponding products of hydrogenation of high temperature pitch. When the l.t.c. pitch is pretreated thermally for deashing prior to hydrogenation, the reaction products become significantly lower in hydrogen, and become similar to those from coking pitch.

The crude gasoline and middle oil produced cannot be used as such. However, as shown in Section VII, they can be used as feed for the production of high-test aviation gasoline.

The heavy oil produces, directly, a high-grade fuel oil, which can, however, be still further improved by cracking, as shown in Section VIII.

VII. Aviation Gasoline from Crude Gasoline and Middle Oil

The crude gasoline and the middle oil from the l.t.c. pitch hydrogenation cannot be used as such. They are, however, raw products for the production of high-test aviation gasoline. It must be predicated upon the use of a suitable operating process and of catalysts with primarily a splitting action. We have worked up crude gasoline and middle oil from l.t.c. pitch (from S 40) by the Ruhroel process in one stage at 600 atm pressure over one of the catalyst prepared by us. We first operated with the crude gasoline and middle oil of the hydrogenation of l.t.c pitch (A-product) then with the mixture of the A-product with middle oil returned from the circuit (B-middle oil) and finally with middle oil B alone.

The analytical data on the feed oils, the reaction conditions, the yields and the reaction products are shown in Table 11. The table gives also the corresponding values for the vapor phase hydrogenation of crude gasoline and middle oil from the high temperature pitch hydrogenation. Comparison of the principal data, such as gasification and space/time yield, showed that the l.t.c. middle oil is converted into gasoline exactly like the middle oil from the coking pitch. It is most remarkable moreover, that the quality of the gasoline produced is practically the same. The gasoline from the l.t.c. pitch is somewhat higher in hydrogen, but this plays no role for the deciding factors of gasoline evaluation, namely the octane number and the overload curve shown in Fig. 3. The aviation gasoline obtained from coking pitch (type V.T. 330) is considered today one of the best gasolines. An aviation gasoline of the C 3 quality is obtained by the addition of technical iso-octane. The study of the overload curves shows that practically the same high quality gasoline is also obtained from the l.t.c. pitch.

Table 11 shows also that from the pure B-middle oil a gasoline of exceptional quality is obtained, with, however, a very high gasification. This fact was already known to us from the coking pitch B-middle oil.

To summarize, our results have shown that crude gasoline + middle oil of the l.t.c. hydrogenation can be converted into high-grade gasoline, and that by using a suitable method of operation such as the Ruhroel process, a gasoline of the same peculiar qualities can be obtained as from the coking pitch middle oil. The production of C 3 quality aviation gasoline is also possible from the l.t.c. pitch.

The space/time yield of the stall is 0.5 and therefore very high and corresponds to that from coking pitch middle oil. The gasification of about 20% referred to the feed is the same as in the vapor phase hydrogenation of middle oil from coking pitch. The one stage vapor phase hydrogenation of middle oil at 600 atm has been done for several years by the Ruhroel, and the conversion of l.t.c. middle oil to high-test motor fuel should offer no difficulties industrially.

VIII. Improvement in the Quality of Fuel Oil

Good quality fuel oil, especially such as required by the Navy, demands a minimum viscosity with a maximum gravity. This means that oils on an aromatic base are desired. The reason for it is a desire to fill the tanks at the home harbor with a fuel to which later foreign oils, including such of high asphalt content, can be added without deposition or flocculation which would lead to the plugging up of the pipelines and orifices. The coking pitch hydrogenation heavy oil (Welheim fuel oil) used as fuel oil represented so far the best quality, and was used primarily as a solvent to mix with such oil which alone would lead to depositions.

The heavy oil obtained from a thermally pretreated l.t.c. pitch (Table 10, experiment G.S. 15) has the required viscosity of 5-6°E/50°C but somewhat too low a gravity, because the latter should be an excess of 1.050. Nor are the pour point and the viscosity at 20° satisfactory.

Following the request of Director Dr. Moehrle, we have subjected this fuel oil to a simple temperature treatment without addition of hydrogen. We did this in the same equipment as for the deashing of l.t.c. pitch (Fig. 2). The optimum reaction conditions had been previously found in autoclave tests.

One may see from Table 12 that our tests have led to the desired results. The oil cracks at about 470°C with the splitting off of hydrogen and gaseous hydrocarbons, the gravity is increased and the viscosity and the pour point are considerably lowered. Unfortunately a small increase in the asphalt content and the Conradson test can not be here avoided. It can, however, be kept within permissible limits. The formation of the lower-boiling constituents of cracking causes the flash point to be no longer satisfactory. For this reason topping of the fuel oil becomes necessary. The sample shown in Table 12 was obtained by distilling off about 5% gasoline and middle oil to obtain again the flash point of over 100°C (open cup).

As already discussed in Section VI and as may be seen from Table 10, the thermally preheated hydrogenation heavy oil possesses the desired analytical values. The process suggested by us for a complete deashing of l.t.c. pitch made the subsequent cracking of the heavy oil unnecessary. It may, however, be economical to do it. The cut between middle oil and heavy oil could then be made so high that a maximum middle oil yield is obtained. The heavy oil thus obtained would have a high viscosity. Our tests have shown, however, that this can be reduced to the required level by a subsequent cracking. The gasoline and middle oil formed in that way will carry an appreciable part of the cost of this simple process. We operated at a pressure of 125 atm which formed in autoclaves under the selected conditions for the reaction. The reaction is, however, largely independent of pressure, and a lower pressure would be satisfactory.

We may summarize by stating that we can change the heavy oil from the thermally unpretreated pitch by a cracking process at 470° and about 100 atm pressure into a fuel oil which will completely satisfy the requirements of the Navy. The asphalt content will then be slightly increased. The 5-10% gasoline and middle oil must be later distilled off to obtain the required flash point. The gasification losses of the process amount to 5-10%.

The thermally pretreated l.t.c. pitch produces a heavy oil which meets the Navy requirements for fuel oil.

The increased yield of middle oil may in this case, however, make it advisable to first conduct distillation to the production of a heavy oil of high viscosity and then convert it subsequently by a cracking process into fuel oil which would meet the requirements. It would be but little inferior to the Welheim fuel oil with regard to its solvent properties for high asphaltic fuel oils.

IX. Summary and Critical Evaluation of the Results

Our tests extended over 1 1/2 years and have brought us to a solution of the problem of hydrogenation of bituminous coal l.t.c. pitch which could not be anticipated and which has caused us to evaluate the l.t.c. pitch as an outstandingly high-grade raw material for high pressure hydrogenation. Naturally, the assumption must be made here that the quality of the l.t.c. pitch is the same as was available to us in our tests.

In the course of our investigation we could prove the highly surprising fact that a solution of 60 parts l.t.c. pitch and 40 parts middle oil, freed from solids and ash, could be hydrogenated over fixed bed catalyst without damaging it, in continuous operations in spite of the 20% standard gasoline-insolubles present in the solution. Considering the well-known sensitivity to asphaltic materials of the catalyst used, this result is extraordinarily surprising. It can only be explained by the considerable differences in the average constitution of of l.t.c. pitch from the coking pitch. This difference may be seen from the analytical data; however, such a difference in behavior could not have been predicted.

The hydrogenation of the l.t.c. pitch over a fixed bed catalyst is carried out with a very much higher concentration of the catalyst than in the hydrogenation of coking pitch in the liquid phase, and as a result a complete downgrading of the l.t.c. pitch is obtained to asphalt-free liquid reaction products. The hydrogenation equipment is similar to a vapor phase stall, operations are done without HOLD and only a yellow-brown oil is obtained as a product. The liquid phase hydrogenation of high temperature pitch produces, on the other hand, only some 65% asphalt-free oil, while the rest forms the HOLD which is high in asphalt and is a highly viscous paste.

The complicated and costly working up of this HOLD is one of the most unattractive tasks of hydrogenation, and is completely eliminated in the working of the l.t.c. pitch. It requires, however, an elimination prior to the hydrogenation of the middle oil-insoluble constituents and of the total ash, including that organically bound. This problem was originally difficult but could be solved satisfactorily. The deashing process developed by us has the additional advantage that the basic structure of the l.t.c. pitch is altered, which results in the reaction products of the subsequent hydrogenation to be poorer in hydrogen and therefore more valuable.

The deashing process is exceedingly simple and should offer no difficulties even in its industrial realization. The costs of the process, compared to the working up of the HOLD, should be very slight.

The feed of the hydrogenation units is a filtered, solid-free feed, and all the technical difficulties met in the liquid phase hydrogenation of coking pitch are avoided, as well as the settling out and coking up inside the preheater, the pipelines and the converter and in particular the hot catchpot. As any practical man knows, this alone offers a great advantage.

A further advantage of the process for the hydrogenation of l.t.c. pitch over fixed bed catalyst developed by us consists in almost double space/time yield of the stall in comparison with the usual coking pitch hydrogenation. This means that the same high pressure equipment will work up in the same time double the amount of pitch producing correspondingly greater amounts of gasoline and fuel oil.

It is particularly surprising, and could not be anticipated, that we succeeded in obtaining reaction products of a quality which are practically as high as those obtained from high temperature pitch. The primary crude gasoline and middle oil can be converted to an aviation gasoline of the same quality by motor tests as the middle oil from coking pitch, using the Ruhroel process of the single stage vapor phase hydrogenation which has been used industrially by the Ruhroel for several years. The l.t.c. pitch produces aviation gasoline of C 3 quality.

The heavy oil from the thermally pretreated l.t.c. pitch is immediately produced of a quality to meet the very strict requirements for Navy fuel oil. A simple cracking process permits still further improvement in its quality.

The hydrogenation process for the l.t.c. developed and proposed by us can be represented by a flow sheet shown in Fig. 4. It shows the three principal paths of operation:

1). Deashing of the l.t.c. pitch solution by a temperature pretreatment at 410° and 50 atm, and followed by filtration.

2). Hydrogenation of the solid and asphalt-free solution at 450° and 700 atm.

3). Hydrogenation of the crude gasoline and middle oil, using the Ruhroel vapor phase process at 485° and 550 atm.

We may add to this a fourth step:

4). Cracking of the fuel oil at 475° at about 100 atm.

The flow sheet shows the following balance of the reaction products:

100 kg of l.t.c. pitch produced

Soluble products

44.5 kg Navy fuel oil
26 kg aviation gasoline

70.5

By-products

22 kg gaseous hydrocarbons and
NH_3, H_2S, which give about
10 kg of l.p.g. (propane-butane)

<u>Waste products</u>

6.5 kg H_2O
<u>1</u> kg solids

7.5

We have applied for two patents on the strength of the results of our investigation.

Circumstances have unfortunately forced us to discontinue our tests sooner than we wished. We regret in particular that the continuous test (G.S. 17) could not be continued for several months as we planned, but had to be interrupted after twenty-eight days of operation. The intended tests of direct use of l.t.c. tar had to be postponed to some later date. In spite of all that, we have been able to solve the problem set to us by the Reichsamt, and to furnish a definite proof for the exception suitability of bituminous coal l.t.c. pitch to hydrogenation.

/s/ Frese

Table 1

ANALYSIS OF VARIOUS LTC PITCHES AND THEIR COMPARISON WITH HIGH TEMPERATURE COKING PITCH

	Bituminous Coal LTC Pitch				
			Saargruben A.G.		
	Byk-Guldenwerke	Reichswerke	10 te sample	1 te sample	Bituminous Coal Coking Pitch
Soft. point	85°	68°	75°	71°	65°
Tetraline-Cresol (80:20) Solids	1.1 %	0.50 %	0.65 %	0.32 %	10 %
Ash: total	-	0.33 %	0.20 %	0.15 %	0.4 %
Ash: in solids	-	0.12 %	-	0.035%	0.35 %
Ash: org. combined	-	0.21 %	-	0.115%	0.05 %
Fractional Extraction:					
Tetraline-Cresol-Insolubles (80:20)	1.0 %	0.5 %	0.5 %	0.5 %	15.0 %
Benzol Insolubles	12.0 %	5.5 %	5.0 %	5.0 %	10.0 %
Standard Gasoline Insolubles	26.0 %	30.5 %	28.5 %	32.0 %	20.0 %
Standard Gasoline Solubles	61.0 %	63.5 %	66.0 %	62.5 %	55.0 %
Ultimate Analysis					
C	85.9 %	84.7 %	85.2 %	85.5 %	91.5 %
H	6.9	6.9 %	6.6 %	6.8 %	4.5 %
S	0.4 %	0.4 %	0.3 %	0.4 %	0.8 %
Cl	0.05%	0.02%	-	-	0.05 %
N	0.9 %	-	-	-	1.5 %
O (by difference)	about 5.0 %	-	-	-	about 1.5 %

Table 2

COMPOSITION OF TOTAL ASH IN LTC AND IN COKING PITCH

	Total Ash %	Fe_2O_3	SiO_2	Al_2O_3	CaO	AgO	Water Soluble*	Total
LTC ash of the v. Velsen - Grube (Saar)	0.15	80.0	6.5	6.0	2.0	0	7	101.5
LTC ash of the Oheim - Grube (Upper Silesian)	0.33	72.0	5.0	6.5	2.0	0	16	101.5
Coking pitch (Ruhr)	0.18	16.5	5.5	4.0	7.5	0	54	87.5

* The principal constituent of water solubles is NaCl.

Table 3

HYDROGENATION OF LTC AND COKING PITCH IN THE LIQUID PHASE

Constant Reaction Conditions: Pressure 700 atm. Gas: 98% Hydrogen, Load: 1 kg/1/Std.

Catalyst: Iron Oxide Upon LTC Coke, 2%
Of The Weight Of The Paste

Pitch	LTC Pitch									Coking Pitch
Origin	Upper Silesian – Mine Oheim			Saar – Mine von Velsen						Ruhr
Test Number	S 35	S 36	S 37	S 40						S 34-2
				1	2	3	4	5	6	
Pasting Oil	Product Heavy Oil	Product Heavy Oil	Heavy Oil from Coking Pitch	Heavy Oil from Coking Pitch	Product Heavy Oil, Filtered					Heavy Oil from Coking Pitch
Pitch in the Paste:										
LTC Pitch %	75	75	35	52.5	52	50	47.5	50	52	–
Coking Pitch %	–	–	35	17.5	13	15	17.5	15	13	70
Temperature °C	460-470	440-450	460	460	460	460	450	440	440	460
Proportion of Gas in the Feed	1:4.5	1:5.5	1:4.5	1:4.5	1:4.5	1:4.5	1:4.5	1:4.5	1:4.5	1:4.0
Duration of Test	5	8	10	11	5	7	2	11	3	5
Reaction Products, Referred to Pitch:										
Water	2.5	5	3	3.5	4	4	4	4	3.5	1
Gas	9.5	9	9	10.5	10.5	13	10	7	7.5	11
Gasoline	6	4.5								
Middle Oil	31	15.5	39	43	47.5	43	35	32	37.5	33
Heavy Oil	51	66	49	43	38	40	51	57	51.5	55
Heavy Oil										
Viscosity °E 2.8 mm capillary/50°	8.5	6.5								
5 mm capillary/100°	–	–	$\bar{1}.5$	$\bar{1}.4$	$\bar{1}.4$	$\bar{1}.3$	$\bar{1}.4$	$\bar{1}.7$	$\bar{1}.6$	$\bar{2}.2$
Asphalt	Free	Free	4.5	1.8	0.7	0.8	1.3	1.4	1.4	7
Remarks:	Operations Irregular Preheater Plugged Up	Operations Irregular Preheater Plugged Up	Quiet Operations Preheater Clean	Operations Irregular, Preheater Plugged Up After Tests S 40-2 and S 40-6						Operations Regular Preheater Free

0083 **Table 4** T-467

HYDROGENATION OF LTC PITCH OVER FIXED BED CATALYST

Constant Reaction Conditions: Pressure: 700 atm, Gas: 98% Hydrogen, Load, About 10 kg/li/h
Catalyst: <1% Mo, 2-5% Cr On Aluminum Hydrosilicate Carrier, In 4 mm Pills

	Test Number	G.S. 12	G.S. 13	G.S. 15	G.S. 17	
					1	3
Injection	Origin of Pitch	Mine Oheim	Mine Oheim	Mine Oheim	Mine von Velsen	Mine von Velsen
	Pasting Oil	Coking Pitch Middle Oil	Product Middle Oil	Product Middle Oil	Coking Pitch Middle Oil	Product Middle Oil
	LTC Pitch in Paste %	60	80	60	60 - 70	60 -
	Deashing Process	Paste Filtered, No Additions	Paste Not Filtered, No Deashing	Paste Filtered With Addition of 0.1% S	Paste Thermally In C 4, With Addition of 0.3 - 0.6% S, Then Filtered	Paste Thermally Pretreated In C 5 With Addition of 0.5% S Then Filtered
Test Conditions	Ash Content of Paste after Deashing. % by Weight	0.15	0.30	0.04	0.003	0.006
	Temperature °C	440	450	440	440 - 460	460
	Ratio: Feed-Gas x 1,000	1:3.5	1:4	1:4	1:5	1:5
	Duration of Test, Days	9	7	17	14	14
Reaction Products	% of Water Referred to Pitch	6	5	6	5	5
	% of Gas Referred to Pitch	8	8	8	10	10
	% of Gasoline Referred to Pitch	10	10 - 7	9	8	8
	% of Middle Oil Referred to Pitch	17	30 - 10	17 - 2	0	22
	% of Heavy Oil Referred to Pitch	59	45 - 62	60 - 75	77	55
	Space/time eff. 1 kg New Oil/li/h	0.5	0.65	0.5	0.5	0.5
Analysis	Gasoline, D^{15}_{4}	0.775	0.775	0.775	0.797	0.797
	Aniline Point °C	+ 31	+ 29	+ 29	+ 16	+ 15
	Middle Oil, D^{15}_{4}	0.958	0.940	0.955	0.980	0.980
	Phenol, % by Weight	6	9	7	7	9
	Heavy Oil, D^{15}_{4}	1.035	1.035	1.035	1.056	1.065
	Viscosity °E/50°C	5.5	6	6	5.0	15
	Asphalt, % by Weight	<0.5	<0.5	<0.5	0.25	0.35
	Remarks:	Regular Vapor Phase Equipment. Plugged Up In 5 Days.	Converter Let Down; Preheater Plugged Up In 7 Days. Strong Sedimentation in the Oil.	Converter Let Down; Preheater Plugged Up After 17 Days.	Unit with 2 Preheaters and Converter Let Down; After 28 Days Run, the Feed Preheater Remained Unobstructed.	

Table 5

DEASHING OF LTC PITCH BY THERMAL TREATMENT OF THE SOLUTION OF PITCH IN MIDDLE OIL

Pressure: 50-60 atm, Pitch from v. Velsen Mine, Time of Test: C 4; 21 days
C 5; 15 days

	Test Number	C 4								C 5				
		1	2	3	4	5	6	7	8	1	2	3	4	5
Test Conditions	Temperature °C	410	410	410	410	410	410	420	425	410	410	410	410	410
	Load kg/li/h	0.65	0.65	0.65	0.65	0.65	0.7	0.65	0.65	0.65	1.0	1.2	1.5	1.8
Injection Feed	Pasting Oil	Middle Oil from Hydrogenation of Coking Pitch								Product Middle Oil from C.S. 17				
	LTC Pitch in Paste, %	60	60	60	60	65	70	70	70	60	60	60	60	60
	Addition of % S	0.3	0.4	0.5	0.6	0.55	0.58	0.58	0.58	0.5	0.5	0.5	0.5	0.5
	Viscosity °E/50°C, 5 mm Capillary	18	20	20	26	62	>100	>100	>100	14	19	19	20	19
	Total Ash Referred to Pitch, %	0.40	0.35	0.40	0.30	0.50	0.60	0.60	0.35	0.25	0.30	0.30	0.30	0.25
Products of Reaction	Filtrate:													
	Total Ash Referred to Pitch, %	0.020	0.003	0.005	0.007	[illegible]	0.007	0.006	0.010	0.009	0.006	0.003	0.005	0.010
	Viscosity °E/50°C Referred to Pitch	5	5	5	6	9	23	27	31	5.5	5.0	5.5	5.5	5.5
	Filter Residue % Referred to Pitch	0.33	1.0	1.0	0.9	1.0	1.1	1.4	1.9	0.3	0.6	0.7	0.75	0.8
	Gas:													
	Weight % of Gas Referred to Injection Feed	1.2	1.2	1.1	1.0	1.0	0.95	1.1	1.5	1.4	1.4	1.4	0.9	0.8
	li H_2/kg Injection	2.2	1.3	1.4	1.0	0.9	0.8	0.5	0.9	0.8	1.1	1.0	0.7	0.7
	li Hydrocarbons/kg Injection	9.1	9.1	9.1	7.6	8.3	7.5	8.9	13.8	12.3	11.5	11.0	7.0	6.5
	C No. of Hydrocarbons	1.95	1.81	1.73	1.80	1.72	1.79	1.79	1.60	1.64	1.75	1.80	1.80	1.75

Table 6

Comparative Filtration of Crude Solution of L.T.C. Pitch, Coking Pitch and L.T.C. Pitch Paste in Experimental Filter Presses.

Filter Press with Ceramic Filters, Made by the Schumacher Factory, "brown-yellow, Graded 30". Apparent surface: 130 sq.cm.

Operating Conditions: temperature of paste, 150°C
operating pressure, 4.5-5.0 atm

Load: 1 kg. The filter time required for 1 kg was measured, and then, without renewing the filter, it was twice refilled with 1 kg and filtered. The residue was removed from the filter only after the three passes.

Test No.		Filtration time, min/kg, at 150°C and 5 atm gauge 1st kg	2nd kg	3rd kg	Total Filtration Time of 3 kg
1	Crude solution	1.5	4	7	12.5
2	50% coking pitch 50% pitch m.o.	11	53	105	169
3	50% l.t.c. pitch 50% pitch m.o.	1.5	6.0	9.0	16.5
4	50% l.t.c. pitch 50% pitch m.o. 1% kiselgur	0.2	0.8	2.0	3.0
5	60% l.t.c. pitch 40% pitch m.o. 1% kiselgur	0.5	1.5	4.0	6.0
6	70% l.t.c. pitch 30% pitch m.o. 1% kiselgur	0.5	3.0	9.0	12.5
7	60% l.t.c. pitch 40% pitch m.o. 0.1% sulfur 1% kieselgur	2	7	11	20
8	60% l.t.c. pitch 40% pitch m.o. 0.2% sulfur 1% kieselgur	3	10	15	28
9	60% l.t.c. pitch 40% pitch m.o. 0.2% sulfur 2% kieselgur	2	7	13	22
10	60% l.t.c. pitch 40% pitch m.o. 0.5% S pretreated thermally in C-4-3	1	3	4	8
11	60% l.t.c. pitch 40% pitch m.o. 0.5% S pretreated thermally in C-5-4	1	3	5	9

Table 7

Summary of the Gaseous Hydrocarbons Produced in G.S. 13.

Referred to Injection Feed:

CH_4 = 2.33 % by weight

C_2H_6 = 1.04 % by weight

C_3H_8 = 2.30 % by weight

iso - C_4H_{10} = 0.08 % by weight

n - C_4H_{10} = 0.52 % by weight

Total Gas Hydrocarbons 6.27 % by weight

Gasification Referred to Pitch: 7.3 %

Table 8

Crude gasoline in l.t.c. pitch hydrogenation over fixed bed catalyst. Effect of thermal pretreatment of pitch paste before hydrogenation. Comparison with crude gasoline from coking pitch hydrogenation.

	LTC Pitch Hydrogenation		
	G.S. 15	G.S. 17	
	Pitch Paste, Not Thermally Pretreated	Thermally Pretreated Pitch Paste	Coking Pitch Hydrogenation
Gravity, 15°C	0.779	0.797	0.850
Engler Distillation			
b.p.	35°	35°	33°
100° Vol. %	33	35	22
95 Vol. % °C	165°	167°	200°
Aniline Point °C	+ 28	+16.2	- 22.5
Phenol Wt. %	3.5	-	10.5
Bases Wt. %	0.5	-	2.0
Ultimate Analysis			
C %	85.3	-	87.0
H %	12.8	-	10.8
S %	0.05	-	0.035
Cl %	< 0.01	-	-

Table 9

Middle oil of the l.t.c. pitch hydrogenation over fixed bed catalyst. Effect of thermal pretreatment of the pitch paste before hydrogenation and comparison with hydrogenation products of coking pitch.

	LTC Pitch Hydrogenation		
	G.S. 15	G.S. 17-1	
	Paste Not Pretreated Thermally	Paste Thermally Pretreated	Hydrogenation of Coking Pitch
Gravity, 15°C	0.955	0.980	0.997
Engler Distillation			
b.p.	182°	183°	215°
250° % by Vol.	48	41	30
95 Vol. % °C	315	314	315
Aniline Point °C	$<-25°$	$<-25°$	$<-25°$
Phenol % by Wt.	6.6	6.6	2.1
Bases % by Wt.	1.7	-	3.8
Ultimate Analysis			
C	88.0	-	89.6
H	9.7	-	8.6
S	0.015	-	0.07
Cl	<0.01	-	-

Table 10

Heavy oil (fuel oil) from l.t.c. pitch hydrogenation over fixed bed catalyst; comparison with fuel oil from hydrogenation of coking pitch.

	LTC Pitch Hydrogenation		
	G.S. 15	G.S. 17-1	
	Paste Thermally Not Pretreated	Paste Pretreated Thermally	Coking Pitch Hydrogenation
Gravity, 15°C	1.030	1.057	1.105
Engler Distillation			
b.p. °C	343	320	342
360° Vol. %	25	40	25
Viscosity, °E/20°C	216	60	75
Viscosity, °E/50°C	5.8	3.0	5.2
Pour Point °C	- 1	- 12	- 13
Flash Point °C	181	175	183
Conradson-Test % by Wt.	0.3	1.3	1.3
Asphalt % by Wt.	0.2	0.9	-
Ash % by Wt.	0.001	0.01	0.002
Ultimate Analysis			
C % by Wt.	89.0	-	91.0
H % by Wt.	9.1	-	7.0
S % by Wt.	0.39	-	0.520
Cl % by Wt.	0.0005	-	0.030
Heating Value			
Upper Kcal/kg	9940	-	9570
Lower Kcal/kg	9460	-	9210

Table 11

Hydrogenation of crude gasoline and middle oil from the hydrogenation of l.t.c. and coking pitch in the vapor phase, by the Ruhroel process.

Reaction conditions: Pressure 550 atm, gas: 98% H_2, temp. 485°C, Ration, feed: gas = 1:3, load 1.0 kg/li/h.

Catalyst: < 1% Mo, 2-5% Cr, upon an aluminum hydrosilicate carrier.

		Oil from low temp. carboniz. pitch			Oil from coking pitch
		A-Product	B-Middle Oil	75% A-Product 25% B-M.O.	75% A-Product 25% B-M.O.
Injection Feed	Gravity, 15°C	0.965	0.903	0.943	0.936
	-170°, % by vol.	6.5	0	5.5	11
	Phenols, % by vol.	11.7	0.12	9.2	2.1
	H_2, % by vol.	9.6	10.6	10.1	9.4
Reaction Products	Water, %	4	0.5	3	1
	Gaseous hydrocarbons, %	13	37.5	15	12.5
	Gasoline, %	57	62	52	53
	B-middle oil, %	26	0	30	33.5
	Gasification % feed	19	38	22	19
	Staal space-time yield kg gas/li/h	0.57	0.6	0.52	0.52
Analysis of Gasoline	Gravity, 15°C	0.789	0.764	0.792	0.791
	Engler Distillation:				
	b.p., °C	51	32	51	47
	100 °C, % by vol.	33	64	33	47
	95% by vol., °C	164	143	164	166
	Vapor pressure, atm	0.3	0.54	0.3	0.34
	Aniline point, °C	+ 12.3	+ 12.1	+ 11.3	+ 7.2
	% aromatics	41	43	41	43
	Iodine number, %	2.7	1.2	2.4	1.3
	Ultimate analysis:				
	% C	87.8	87.5	87.6	88.0
	% H	12.2	12.5	12.4	12.0
	Octane number. M.M.				
	Not leaded	79.4	83.4	79.3	80.4
	0.09% TEL	90.6	95.0	91.2	90.8
	0.12% TEL	91.7	96.1	92.4	91.6

Table 12

IMPROVEMENT IN THE QUALITY OF HEAVY OIL FROM THE HYDROGENATION OF LOW TEMPERATURE CARBONIZATION PITCH BY A SUBSEQUENT CRACKING

Reaction conditions: Temperature 470°C, pressure 125 atm, load 1.0 kg/li/h

Gaseous reaction products: Gasification, % of injection feed
H_2 " " "
Total gas/kg injection feed: 50 li
H_2 " " " 5 li
Hydrocarbons 45 li
C-number of hydrocarbons 2.02

Liquid products of reaction:

	Injection Feed H.O. from G.S. 15	Products of Reaction after Distilling off 5% Gasoline and M.O.
Gravity, 15°C	1.036	1.057
Engler Distillation:		
b.p. °C	312	175
% by vol., 350°C	13.5	36
Viscosity, °E/20°C	96	14
°E/50°C	5.7	2.5
Pour point, °C	+8°	-28
Flash point, °C	184	101
Asphalt, %	0.23	0.54
Conradson Test, % C	0.85	2.9
Ultimate analysis:		
% C	89.3	89.5
% H	9.1	7.9
% S	0.24	0.21

Fig. 1 Arrangement for Hydrogenation of LTC pitch over fixed bed catalyst
(Experiment G.S. 17)

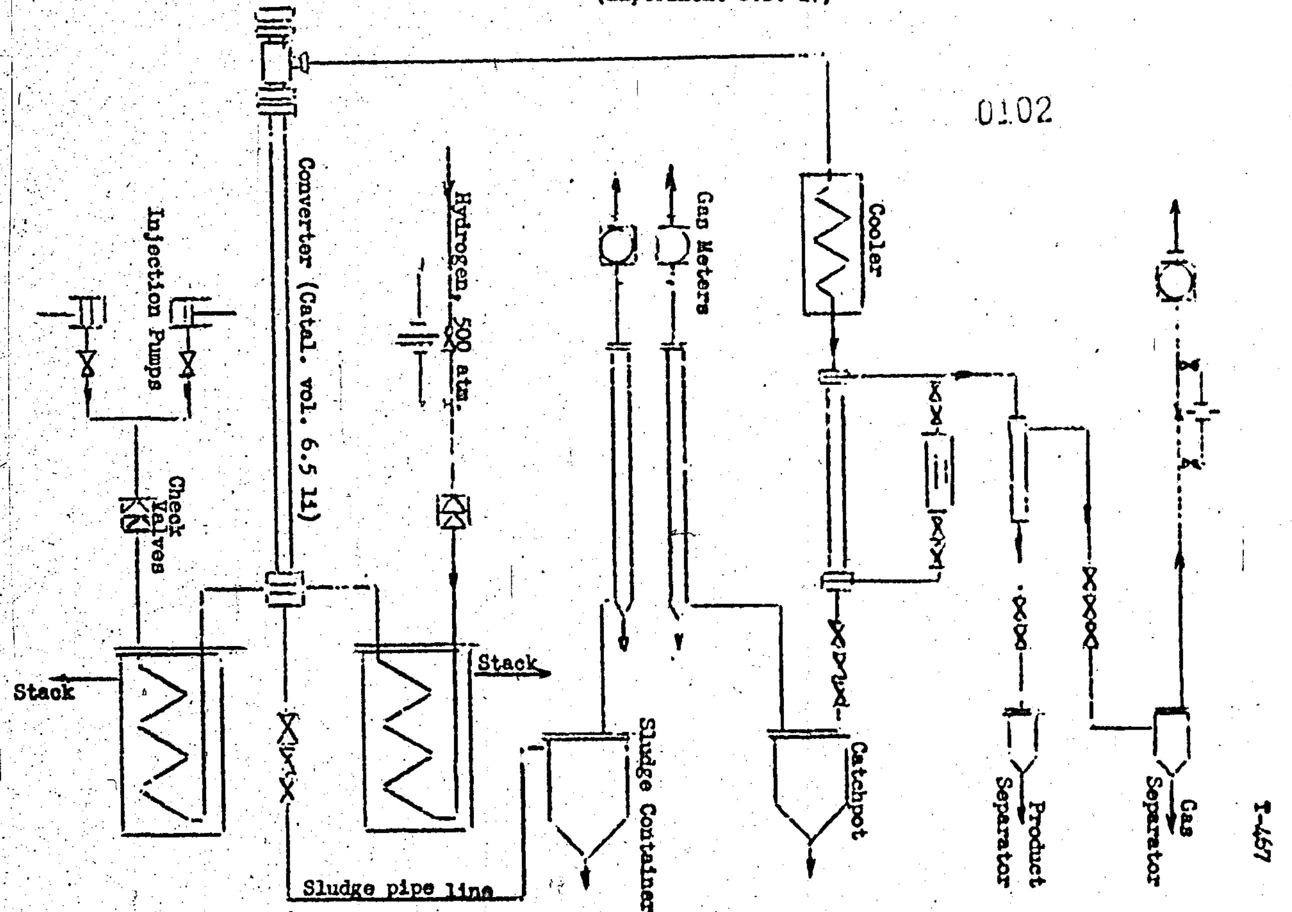
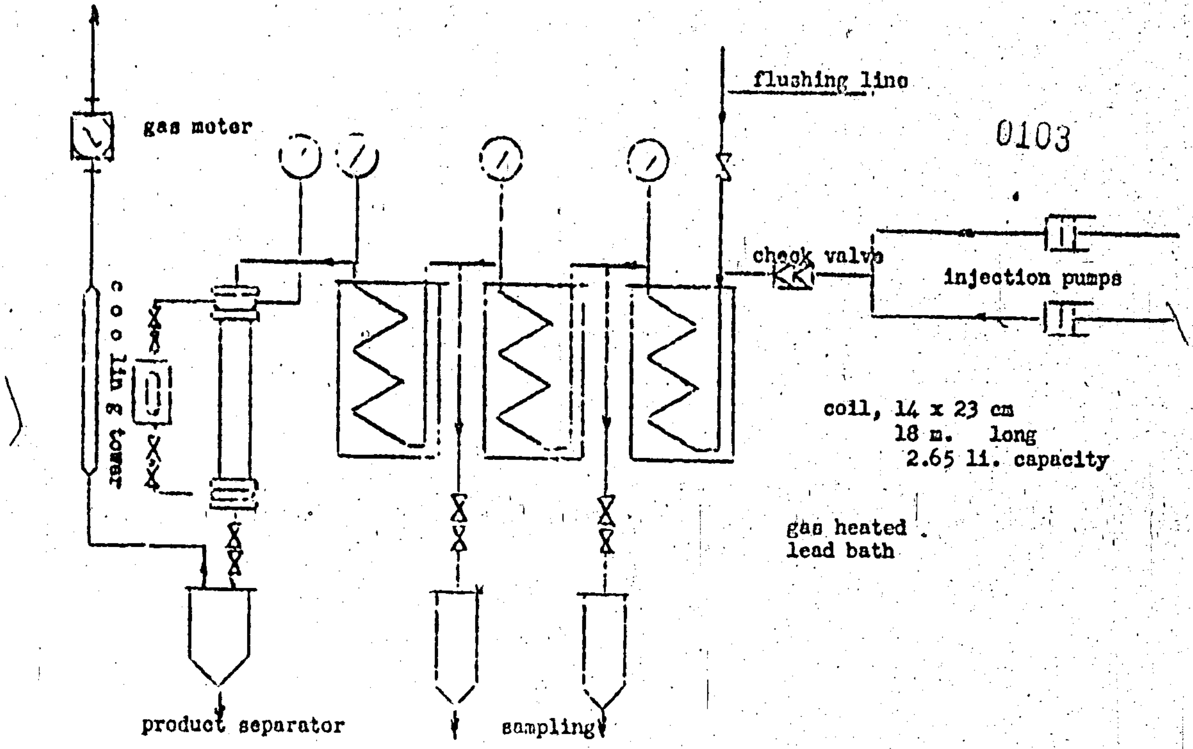


FIG. 2. FLOW SHEET FOR DEASHING OF LOW TEMPERATURE CARBONIZATION PITCH

0103



0104

F IG. 3

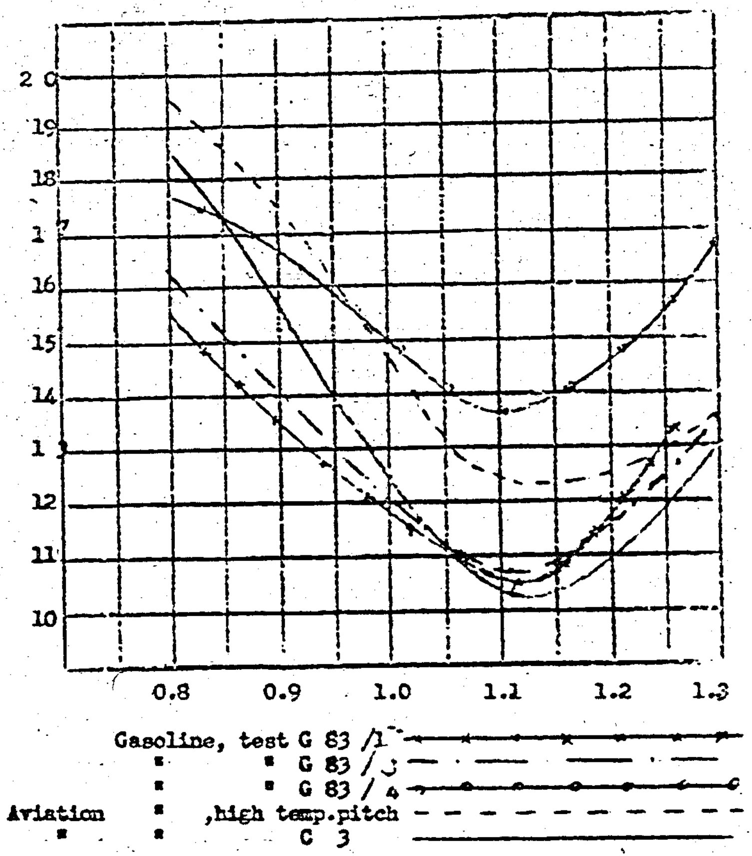

20
19
18
17
16
15
14
13
12
11
10
0.8
0.9
1.0
1.1
1.2
1.3
Gasoline, test G 83 /1
" " G 83 / 3
" " G 83 / 4
Aviation " ,high temp.pitch
" " C 3

FIG. 4 0105

T- 467

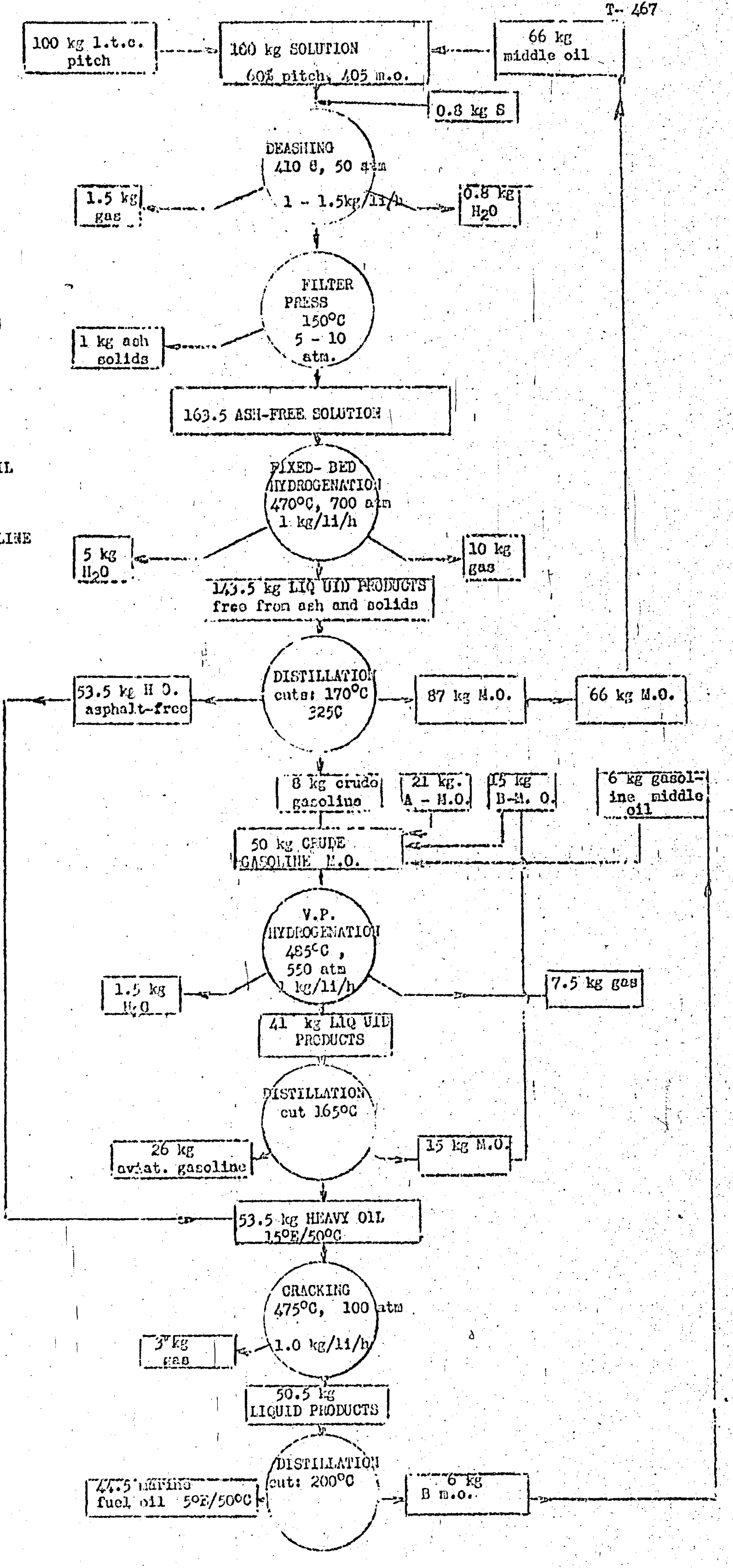
FLOW
SHEET
HYDROGENATION
BITUMINOUS
COAL
L.T.C.
PITCH

TO

MARINE FUEL OIL

AND

AVIATION GASOLINE



UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

0106

T-468
W. M. Sternberg
December 28, 1948

HYDROCARBON SYNTHESIS WITH AN IRON CATALYST

By Kölbel

TOM Reel 178, Frames 2627-2642 September 13, 1940

Introduction

It is hardly necessary for me to explain to my audience the importance of this topic, nor the intensive work and the great interest which has been created since the gasoline synthesis by Franz Fischer and Hans Tropsch has resulted in a successful industrial application. The excessively rapid scientific and industrial development of the cobalt catalyst has not made us forged that the use of cobalt as a catalyst makes us dependent on its importation from abroad or the colonies, and is uneconomical. I don't know whether the 10% loss of cobalt used as a catalyst in a single circuit is covered by the German production, but it is certain that the total German cobalt requirements go principally in the steel industry, and are in no way covered by domestic production. As long as this is the case, dependence on cobalt is a handicap and the further development of the Fischer-Tropsch synthesis, which is a key process, and a starting point for an entirely new organic chemical industry, the development which we may be able to measure by the immense development of the industry in America based on a further applications of petroleum for the production of the greatest variety of products. A further danger, caused by war conditions, consists in the necessity of centralization of the manufacture of the catalyst because of the high value of cobalt and of thorium, which also will be eliminated by changing to iron. The catalyst developed by us is simple to prepare with simple equipment and can be done in the future at the synthesis works.

It must further be remembered that changing the catalyst from cobalt to iron will greatly reduce the cost of the catalyst. These are not the only reasons for the trend of the development of the gasoline synthesis catalyst in the direction of the application of iron. The greatest attraction does not consist in the simple substitution of cobalt but rather in the possibility of synthesizing more readily convertible and cheaper products than can be done with cobalt. This applies also to the gasoline synthesized with iron, which can be considered as being useful as such, unlike the cobalt gasoline.

The problem of synthesis of hydrocarbons with iron catalyst is by no means as novel as it is assumed by many. Franz Fischer himself has continued the development of iron catalyst with his characteristic stubbornness ever since his conception of the idea of preparation of oil from coal by synthesis of CO and H_2-containing gases. In fact he was first to produce in 1925 at atmospheric pressure the homologs of methane from carbon monoxide and hydrogen using iron catalyst. The work with the iron catalyst has been continued even today, in spite of the high stage of development of the cobalt-thorium catalysts, and without regard to the existence of fundamental disadvantages of iron catalyst against cobalt and nickel catalyst which were believed to exist. The efforts were continuously started anew, because of the realization that iron plays in nature as well as in the arts a more important role as a catalyst, than cobalt and nickel. Finally, many industrial catalytic processes involving the use of costly metals have been changed over in the course of the development to the use of iron. Numerous patents of the I. G. Farbenindustrie lead one to assume that they have worked for a long time on the use of iron catalyst for the reduction of carbon monoxide and the formation of hydrocarbons. The results there recorded can, however, not be experimentally substantiated in spite of the many earnest efforts, nor do they equal as far as is known to the results obtained by Fischer and his students. We further are familiar with different work in Japan which consisted in almost painfully accurate reproduction of the principal features of Fischer's publications, but which have brought out nothing new beyond the results obtained by KWI. French scientists have occupied themselves intensively with the physical investigation of iron catalyst. The X-ray and thermo-magnetic methods used by them are highly original and very interesting, but they must be used with the greatest circumspection according to the results of our experimental work in this field.

Fundamental Problems with the Iron Catalyst

The reason for the slower development of the iron catalyst in comparison to the nickel and cobalt catalyst is found basically in specific problems and difficulties offered by iron in comparison with the other two metals when used as catalysts. We know that in the series iron-cobalt-nickel, the activity increases with respect to reduction of CO to hydrocarbons. Of these three elements, when considered for the technical hydrocarbon synthesis, iron offers the greatest attraction, but also fundamentally presents the greatest difficulties because it has the least activity. This finds its expression in the reaction temperatures with the different catalyst metals: at atmospheric pressure, the hydrocarbon synthesis can be carried out at 160°C with nickel, at 170-180°C with cobalt, and only at 225-250°C with the iron catalysts known today. The necessity of using higher temperatures with iron introduces a multitude of difficulties and problems:

1) The formation of gaseous products is greatly favored by rising temperatures, i.e., the liquefaction becomes poorer.

2) The formation of secondary products, e.g., through the decomposition of the high molecular weight primary paraffins, is greatly favored by rising temperatures. The types of secondary products, e.g., from the high decomposition molecular weight primary paraffins affect very unfavorably the life of the catalyst.

3) The separation of carbon from the carbon monoxide, the so-called carbon deposition, becomes greatly increased at higher reaction temperatures, which will threaten great technical difficulties, especially in the synthesis in the middle pressure range.

4) The synthesis equipment is the more difficult to construct and is the more expensive, the higher the reaction temperature. Were we to persist in leading away the heat of the reaction

with water, definite technical limitations will be imposed by the reaction temperatures. The empirical experience accumulated with cobalt and nickel as catalysts, cannot be used for the solution of these basic problems, because iron catalyst differs from the two brother elements by special conversion properties during the reaction.

The cobalt and nickel can cause two kinds of reduction on carbon monoxide:

1) Oxygen of the carbon monoxide may be split off as water during the formation of hydrocarbons. ($CO + 2\ H_2 = CH_2 + H_2O$).

2) The oxygen in the carbon monoxide can be used for the production of carbon dioxide with the formation of the unwanted methane. ($2\ CO + 2\ H_2 = CH_4 + CO_2$).

Iron, however, offers a third and principal kind of reaction, in which oxygen is used in the formation of carbon dioxide, with the simultaneous formation however of hydrocarbons ($2\ CO + H_2 = CH_2 + CO_2$). We might mention here in parenthesis that Fischer and Tropsch's statement in their collected work on the study of coal, that the iron and copper catalyst always cause the reaction to proceed by way of formation of carbon dioxide, and without formation of water, does not agree with our observations. We have developed iron catalyst in which there was a considerable amount of water formed during the carbon monoxide reduction, which therefore approached quite closely to the ideal case already stated by Fischer and Tropsch in 1926 of the use of water gas products, using equal parts of carbon monoxide and water according to the equation $3\ CO + 3\ H_2 = CO_2 + H_2O + CH_2$. We do not wish to discuss this any closer at the present, because our work in this direction has not yet been completed.

The composition of the gas must always correspond to the reaction; when water is formed, the proportion of $CO:H_2$ must be 1:2; 2:1 when carbon dioxide is formed, and when both reactions occur the proportion should be 1:1, i.e. the proportion such as exists in the usual water gas (blue gas). Naturally the nature of the hydrocarbons formed will be different depending on the operation. When an iron catalyst is used with carbon monoxide - rich gas, with the production carbon dioxide, products very high in olefines are obtained; when water is formed with hydrogen-rich gas, the products assume a more saturated character. These possibilities of variations differentiate iron synthesis from the cobalt and nickel catalyst, and are in themselves exceedingly desirable, but require overcoming considerable difficulties.

After having briefly discussed the problems met during the development of the iron catalyst, I will proceed with communicating some results of our own work in this field, carried out in Rheinpreussen with Dr. Ackermann and later with Dr. Ruschenburg. I will not overload you with details of the work which has lasted for nearly four years, and will limit myself for the sake of brevity principally to the communication of the results.

Investigation

The purpose of our work did not consist merely in finding a substitute of iron for cobalt, but to develop the hydrocarbon synthesis with iron to such an extent that it would no longer be a mere substitution for the synthesis with cobalt, but would represent actual technical and economic improvements. Our work began in Rheinpreussen in the spring of 1937, initially in two directions, in the continuation of the work begun at KWI at atmospheric pressure, and connecting it to the "synthol" work of Franz Fischer done in 1922 to 1924, using higher pressures for the production of anti-knock gasoline. The resumption of the work with iron catalyst appeared to us very promising because in the past ten years of development of synthol, considerable progress had been made with iron catalyst, which had not yet been used at increased pressures.

At the time we started our work, the status of development was given in the publications of Franz Fischer and in the work of K. Meyer with an iron - copper catalyst containing 25% copper, using a synthesis gas containing 28% CO and 56% H_2, and who obtained 55 g liquid hydrocarbons/nobm during 4 - 6 weeks' operation. The conversion without exception proceeded by way of carbon dioxide formation, the temperatures were 220-235°C. The $CO:H_2$ proportion of 1:2 used in these tests was the most unfavorable imaginable for work with this catalyst, and the reaction by way of carbon dioxide required the reciprocal proportion of 2 CO to 1 H_2. 95 g/cbm was the theoretical maximum yield with the gas of composition selected, $CO:H_2 = 1:2$. No success was obtained working with carbon monoxide-richer gas, because the action of the catalyst dropped off very rapidly after an initial high yield at normal pressures. Attempts to conduct the atmospheric pressures synthesis by way of water formation were also unsuccessful in the tests performed at the KWI.

Our results with the atmospheric pressure synthesis with iron catalyst consisted at that time in attempts to increase its life and accordingly also the yield over longer periods, using a catalyst of much simpler composition, and accordingly also much cheaper. We were also successful in working with a gas containing more carbon monoxide, without harming the catalyst. This success was achieved by avoiding side reactions, with the production of substances which caused a gradual poisoning of the catalyst. However, even in spite of the appreciably higher yields we obtained in our work at atmospheric pressure, it still remained much below the liquid product yield of the catalyst. This stage of development of the atmospheric pressure synthesis with the iron catalyst is of little interest to the outsider, and I will refrain from giving any details. The work was continued and no detailed information was given when positive results were obtained.

We considered at the beginning of our investigation that the iron catalyst could become of practical interest only after the yields could compete with the yields obtained with cobalt catalyst. This, however, was again possible only if the CO:H_2 ratio was selected to correspond to the operation of the iron catalyst, or conversely when the work of the iron catalyst was adapted to the hydrogen-rich synthesis gas. I.e., our task became to find an iron catalyst with which operations with carbon monoxide - rich gas became possible, or else operating conditions in which the iron catalyst operated like the cobalt and nickel catalyst, i.e. by way of water formation.

The very first pressure experiments with our own iron catalyst, which we began in the spring of 1937 and were admittedly based upon Fischer's synthol work, showed two striking results, which opened the possibilities of satisfying both requirements when working under pressure. With an appreciably less active catalyst we found during these first tests that when operating with water gas (1 CO:H_2) a surprisingly large amount of water was formed at pressures of 7-9 atmg and a temperature of 210°, with an almost complete utilization of the carbon monoxide. The amount of water formed was up to 40 g/cbm, and the drop in efficiency of the catalyst was barely perceptible in spite of using water gas. The higher pressure apparently overcame the harmful influence of higher concentration of CO and the hope seemed justified that water formation will be considerably increased when water gas was used under pressure. On the strength of this experience, we continued our experiments within the pressure range between 5 and 100 atmg using high-carbon monoxide as well as high-hydrogen gases. We would obtain up to 80 g of water per cbm synthesis gas with hydrogen-rich gases at medium pressures of 7-15 atmospheres with a formation of 85 g of liquid and solid products, almost 30% of which consisted of paraffin. Up to 1/3 of the conversion proceeded by way of water formation. We have got still better results using other catalysts. I would, however, not like to talk about it at present, because the work has not been completed.

The work with carbon monoxide-rich gases was appreciably more successful. We have succeeded right from the start in obtaining yields which were throughout equivalent to the cobalt yields, by changing over from atmospheric pressure to middle pressure and using a simple metal iron catalyst and a gas consisting of three parts CO to two parts H_2. The life of these catalysts seemed almost unlimited, and appeared even inconveniently long for a rapid development. Damage to the catalyst by the high carbon monoxide content was therefore overcome by the use of pressure. The products were water clear, colored slightly yellow and, always entirely free from crystallized paraffin. Franz Fischer made a report in December 1937 on the middle pressure synthesis which was the first preliminary communication on the iron catalyst pressure synthesis and which was in a surprisingly good agreement with our results.

We developed the following hypothesis from the unexpected fact that the harm done by the catalyst at high carbon monoxide concentrations and at atmospheric pressure disappears when the pressure is increased. The formation of hydrocarbons on the catalyst metal of the eighth group of the periodic system was caused according to Franz Fischer on two competing reactions of carbide hydrogenation. The carbide formation at atmospheric pressure is apparently easier with iron catalyst than the hydrogenation.

A minimum partial pressure of hydrogen seems to be required for a successful operation of the synthesis in order to hydrogenate the carbides formed from carbon monoxide and to re-form sufficiently rapidly the active centers of the catalyst through the re-formation of carbides. If the absolute hydrogen pressure, i.e., the hydrogen concentration, is below the minimum, all the active centers of the catalyst will become blocked by the carbide formation, and the activity will quickly drop. The minimum pressure of hydrogen is 0.5 atm abs when working at atmospheric pressure. When water gas is used, with 60% CO conversion, the pressure in the tail gas is already too low.

While using gas with still higher CO content the concentration is too low even in the synthesis gas, the catalyst becomes "carbided" or carbonized, and its activity drops rapidly. When operation at higher pressure, e.g., at 10 atmg, and with a 60% conversion of CO, the hydrogen pressure using water gas remains 3 atms abs. When the starting gas contains 3 CO:2 H_2, 1 atm abs will still be present with a CO conversion of 91%, or with a gas of 2 CO:1 H_2, 0.5 atm abs will remain with 81% conversion. When operating with a hydrogen pressure or about 1 atm abs, as happens with a gas which consists of 3 CO:2 H_2 at a pressure at 10 atmg, we may expect not merely a high conversion, a high amount of liquefaction, but also a long life of the catalyst. This hypothesis presupposes that the ability to form carbides does not increase to the same extent at increased pressure, as the hydrogenation ability. Such is the case when the iron catalyst is reduced (formed) at atmospheric pressure before operations at increased pressures. According to experience a maximum activity may also be attained under such conditions. If the catalyst is immediately started under full middle pressure, it hardly reaches full activity, and the carbide formation exceeds the hydrogenation. We realize that our hypothesis is not entirely free from contradictions, but it permitted us to explain the surprising differences in the behavior of the catalysts at atmospheric and under middle pressures, and we owe to it many instances when using it resulted in a practical success.

Results

I. Catalyst

Our principal work naturally consisted in the development of a suitable catalyst, of which we have brought out several types suitable for different purposes. For the sake of brevity I will report here only on the single-substance catalyst with which we operated the longest. As the name implies, the catalyst contains none of the usual additions, such as copper, manganese, aluminum, etc. It consists essentially of iron, and its activity is the result of a special method of preparation which causes the formation of a definite modification of iron oxide. The discovery of this catalyst which excelled in simplicity and operation was the result of our application of the most modern methods of catalytic chemistry, which has to our knowledge not yet been applied to the study of the catalytic processes of gasoline synthesis.

Ia. Mechanical Properties

Purely in outward appearance the catalyst looks somewhat like the silica gel in structure, and has the same extraordinary hardness and mechanical strength. The catalyst does not lose this strength during operations. The iron catalyst offers advantages over the present cobalt catalyst in its mechanical properties. Its filling weight is exceptionally large, and the reactor efficiency, referred to space, is 2 1/2-3 times as large with this iron single substance catalyst than with the present cobalt catalyst.

Preparation

The preparation of our iron catalyst is equally surprisingly simple as its composition. We already have prepared it on a semi-technical scale in batches of 10 kg and over and obtained reproducible highly active catalysts for several years. It is obvious that with such cheap starting material and simple method of preparation the catalyst costs play a very subordinate role. Their importance sinks still further when considering the life and the yields obtained with it. At the very start the reproducibility of the iron catalyst offered great difficulties, which as far as we know have not yet been overcome in KWI for Coal Studies. They depend on apparent accidents in the preparation of the catalyst, which makes the work much more difficult and its technical realization still questionable. We have realized the cause of these difficulties and eliminated them a long time ago. The reproducibility of good iron catalysts is no longer any problem to us.

Yields and Life

Other standards must be used when indicating the yield and the life of our iron catalyst than with the atmospheric pressure cobalt catalyst, because the life of our iron catalyst is not measured in weeks and months but in years. Referred to active gas ingredients the total yield in gasol, liquid and solid products is on an average 145 g/ncbm during the first one-half year. After one year's operation this total yield dropped on the average to 143 g. After one and one-half year's operation 132 g total products were still obtained per ncbm of active gas ingredients.

These data refer to a one stage process without circulation and without intermediate regeneration. When several stages are used, or the gas circulated, these yields can be still further increased according to our experience. The final life of our iron catalyst cannot yet be indicated, because our first catalysts have been seriously damaged in their activity after 15 months of operation by outside influence - failure of the temperature regulator, freezing of the gas line, etc. The catalyst with the longest operating time is still in use although it also has been damaged, and gives today after 19 months of operation a water clear liquid product including gasol of a total amount of 130 g/cbm active ingredients. The data on peak production have no meaning with the iron catalyst, but under special conditions a greater yield up to 160 g/cbm active gas ingredients can be obtained.

Degree of Liquefaction

Formation of Methane and CO Conversion

The carbon monoxide conversion could be maintained during the first 6 months of operation at 92%, with a degree of liquefaction of 73% and methane formation of 9% of the carbon monoxide converted. With increasing operating time the products formed by the iron catalyst are changed in the direction of formation of lighter boiling and gasol hydrocarbons. All these data are given for a single stage process.

Space Utilization or Space Velocity

A space velocity of up to 270 is obtained because of the great density of our iron catalyst with a normal gas load, i.e.

in one hour the gas volume is 270 times greater than the reactor volume. We may give for purpose of comparison the space velocity during the atmospheric pressure cobalt synthesis which reaches a maximum of only 150 with the single stage process, i.e. the gas volume is 150 times that of the reactor volume. The two stage process commonly used at present industrially reduces the space velocity to only 70 if the total gas converted is referred to all the reactors used. The space utilization is 3.5 to 3.8 times as high with the iron catalyst as with the cobalt catalyst at atmospheric pressure. This peak load is usually reduced in the course of operation, and the average space velocity is only equal to 170-190.

Synthesis and Operation Conditions

One great advantage of the iron catalyst in comparison with the cobalt catalyst is found in that it need not be reduced with hydrogen, which offered very great difficulties at first and can only be done today at a great expense. The starting of the iron single substance catalyst, as well as our other iron catalyst is done under certain readily re-producible conditions with the synthesis gas to be used in the synthesis. This "forming", as we call our starting, is very important for the activity of the catalyst. A perfectly definite carburization condition is important for the proper operation of the iron catalyst, and it differs quite considerably from that required for the atmospheric pressure synthesis.

The recognization of the proper degree of carburization is, however, very simple. I will emphasize here that we are not forced to forming at low pressure with carbon monoxide and at high temperatures for the production of our better catalyst, as is done at the KWI.

Depending on the operating conditions, the synthesis temperature of the catalyst varies between 210 and 260°, the synthesis pressure between 5 and 20 atms, normally in a much narrower range of between 9 and 15 atms. The optimum gas composition, when operating with the iron catalyst by way of carbon dioxide formation, is approximately 3 parts CO:2 parts H_2.

I am giving here analyses of the starting gas and tail gas with a single substance catalyst when operating by way of formation of carbon dioxide.

	Starting Gas	Tail Gas
CO_2	4.5	64.2
Hydrocarbons	0.10	3.6
O_2	0.0	0.0
CO	54.6	6.2
H_2	35.4	6.5
CH_4	0.6	9.7
C-number	1.0	1.78
N_2	4.8	9.8

Properties of the Products

In my discussions of the products formed with the single substance catalyst I will limit myself to such which are formed in the operations by way of carbon dioxide formation. The data referred to the average product of a one year operating period. The specific gravity of the total yield of the liquid products was 0.710 to 0.715.

The boiling range was as follows:

54%	by weight of liquid products	-120°C
63%	" " " " "	-150°C
67%	" " " " "	-165°C
73-75%	" " " " "	-195°C

The olefine content of the fractions vary with the decreasing boiling point between 45 to over 70%. Up to 7% alcohol-like substances are found in the fractions to 150°C. The motor properties, as expressed by the octane number of the stabilized fractions, are:

-120°C	o.n. 85
-150°C	" 76
-165°C	" 73
-195°C	" 66

These figures show that the gasoline with the iron catalyst may justly be called that, unlike the cobalt gasoline the octane number of which is incomparably lower. No cracking of the hydrocarbons obtained with the iron catalyst is required. We attribute these high octane numbers to the relatively low boiling point, to the higher iso-hydrocarbon content, to the presence of alcohol-like substances and to the high olefine content. The iron gasoline fulfills all requirements on purity as well as the cobalt gasoline. The gasoline olefines are as harmless with reference to gum formation when formed with the iron catalyst as the cobalt olefines. The motor behavior is perfect, I have used the gasoline obtained with iron catalyst for many months. The diesel fuels show good inflammability which varies depending on the boiling point of the fraction between 55 and 72 cetane number, which corresponds to 71 to over 100 cetene.

The gasol which comes over with the above products contains over 50% of C_4 hydrocarbons and is composed of 60-75% of olefines.

Equipment

The results communicated here were obtained in laboratory as well as on a pilot plant scale. The pilot plant tests have been emphasized right from the very start, because the difference between the laboratory synthesis and large scale equipment is too great, according to the experience with cobalt synthesis, to permit drawing any conclusions. Our pilot plant equipment has an hourly production of around 10 cbm gas thruput, and offers therefore, already, the possibility to appreciate the technical difficulties to be experienced in large scale operations, if the construction of the pilot plant reactors is to be retained in industrial equipment. This experimental installation has now been used without interruption for over two years. The individual catalysts have not been used for longer than seven months to save time. During that time the results obtained were similar to those obtained in the laboratory. Moreover, the pilot plant tests gave us a better insight into the course of the reaction, in particular with respect to the heat effects. We have paid particular attention to the reactor construction in the development of our synthesis, because the technical ripeness of the iron catalyst synthesis is merely a question of the proper reactor construction. We have already mentioned that the high reaction temperature offers one of the principal problems in the synthesis with iron catalysts. Mastery of these temperatures introduces difficulties which are aggravated by the high space velocity and the high catalyst thickness, making sufficiently rapid elimination of the heat of the reaction a very serious problem. This rapid leading away of the heat of the reaction is far more important with the iron catalyst than with the cobalt catalyst because the dangers of carbon deposition and of the reactor plugging up is here much greater. Were one to retain the usually used removal of the heat of the reaction by means of water, pressures of up to 50 atms gauge are to be expected in the cooling part of the reactors when using the same reactors as heretofore, which can be overcome industrially but will greatly increase the cost of the reactors. On the other hand it had been suggested to substitute oil cooling for the high cooling water pressures, as has been done by Franz Fischer in his first gasoline synthesis reactors. This does not appear a satisfactory solution to us, because a heat exchange system outside the reactor cannot materially reduce its costs in comparison to direct water cooling at high pressures; we were also afraid that even with high circulation velocities of the cooling oil its heat absorption properties would be insufficient to produce satisfactory and sufficient heat removal. We started out with the idea that water was the ideal cooling agent in every respect, particularly for the gasoline synthesis reactors, and we have developed a reactor in which the heat of the reaction is taken away only by the evaporation of water, but in which the pressure of the synthesis reactor steam boiler system exceeds

10 atms gauge with a synthesis temperature of 210-260°. This type of reactor is still in the process of development, and I must therefore omit giving more detailed information on it.

Entirely independently from the above we have also tried another method which seems to be suitable to overcome the danger of the carbon deposition or reactor plugging up as well as for the mastering of the high temperature and high heats of the reaction. This method consists in using the iron catalyst synthesis in the liquid phase, i.e. in a sludge or emulsion of the catalyst in the synthesis oil. This process offers advantages both with respect to operations and other construction of the reactor: the intimate contact of the cooling medium with the catalyst with the complete elimination of the wall separating the two produces ideal heat exchange conditions, under which the overheating or the carbon deposition, as well as the plugging up are almost completely excluded. The suggestions for carrying out gasoline synthesis in the liquid phase made by the KWI in Muelheim which are known to me, appear little promising at least from the standpoint of construction. We believe to have achieved important progress particularly in the construction of our liquid phase reactor because of its exceptional simplicity. Naturally, the synthesis in the liquid phase introduces numerous new problems, so that we cannot as yet make any definite reports on it, particularly because carrying out of these tests will require very much time with the exceptionally long life of our catalysts. We can, however, already say today that we have reached practically the same conversion in a liquid phase synthesis in our reactors, as in the vapor phase synthesis.

I have already mentioned that hydrocarbon synthesis with iron catalysts offers a few additional problems in gas production, purification, scrubbing, reintroduction of the off-gas carbon dioxide, etc. However, I seem to have used up too much time for discussion of these problems and must therefore come to a close.

I have already emphasized that the importance of hydrocarbon synthesis need no longer be discussed. The rapid development of gasoline synthesis by the Fischer-Tropsch methods, especially in the direction of working up of the primary product which may produce shortly gasoline as a by-product, deserves particular attention with the iron catalyst, because the products obtained from it are high in unsaturated compounds even in the high boiling fractions, which offer new possibilities in their working up in comparison with the cobalt products. I would not like to conclude my communication without acknowledging the support of our work by Director Kost or without expressing thanks to my collaborators, in particular to Dr. Ackermann.

/s/ Kölbel

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HYDROCARBON SYNTHESIS WITH IRON CATALYSTS

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The use of iron as a catalyst for the hydrogenation of carbon monoxide to higher hydrocarbons dates far back. The Badische Anilin und Sodafabrik has published already in 1913 information on the production of higher hydrocarbons from carbon monoxide under pressure using iron catalysts.

Franz Fischer and co-workers have carried out extensive experiments in that field at a later date, between 1921 and 1924, in the KWI in Muelheim-Ruhr. We may consider the characteristics of this experimental period to consist in the activation of iron by means of alkalies. The methods of preparation of catalysts at that time were still very imperfect and the activity was relatively low. Iron was used in a compact form, e.g. as iron filings coated with potassium carbonate. Such masses were naturally but little active. Work had to be done under such physical conditions which forced conversion to the limit, namely at high pressures and high temperatures, e.g. at 150 atm gauge and 400-450°C. Liquid products were then obtained, but no hydrocarbons, namely only oxygen-containing substances. This mixture was called synthol. It is of interest to know in this connection, that the synthol tests were not further continued, because of the impossibility of obtaining catalysts of long life. The masses became hard and plugged up after a short time and could be removed from the reaction space only with great difficulty.

We learned at that time to improve the catalyst production by finer subdivision of the active metal, and the temperature and pressure could be then lowered. The first production of higher hydrocarbons at atmospheric pressure was successfully done in 1925 using catalysts prepared by mechanical mixing of iron oxide and zinc oxide. The reaction temperature still was at 365-380°C, i.e. still relatively high.

It had been recognized already in 1925, that cobalt was also capable of forming higher hydrocarbons. The tests with cobalt were not, however, at first continued, in part because they were not very successful, in part also because of the high cost of cobalt. Thus, during the first four years of the development of gasoline synthesis work was done almost exclusively with iron catalysts. At that time chiefly decomposition catalysts were made obtained by roasting of nitrate mixtures. The yields obtained with that type of catalyst were rather small. Even in 1929 the maximum yield did not exceed 11 mls of liquid products per cbm water gas. The revaluation of the English pound sterling to one-half its former value happened in that year. This reduced the purchase cost of cobalt to about one-half. The experiments with the cobalt catalysts were started afresh. The introduction to cobalt of the improved production methods already developed for iron resulted immediately in appreciable progress, and two years later a yield of 100 g/cbm could be reached. Since that time, i.e. since 1930, the development went almost exclusively by way of the cobalt catalyst, and the iron catalysts have not been studied to any extent for ten years.

A particular inducement to start anew the tests with iron has been produced some time ago after the development of the cobalt catalyst had reached a certain limit. Experiments with iron catalysts were taken up in Germany again in at least six different places, independently from each other.

Franz Fischer has communicated in a closed meeting of the KWI his new experimental results with the iron catalysts. A second such meeting has taken place last Tuesday, September 10, 1940. The principal points from H. Pichler's report are here repeated:

1) Catalysts were used containing only iron or ~~at most~~ also alkalies, and formed by precipitation with soda or ammonia.

2) "Forming" is required prior to starting. This consists in a pretreatment with carbon monoxide or carbon monoxide-rich gases at higher temperatures but lower pressures than the synthesis pressure.

3) The preferred synthesis conditions are 15 atms, 220-250°C, CO-rich gas.

4) The yields obtained were 5-50% paraffins or 40-80% gasoline. The stabilized and washed gasoline contained 64%

olefines, 90% came over -145°C and had an octane number of 61.

5) It was particularly important, that the volume of the catalyst mass increased during operations, and that the catalysts had a tendency for deposition of elementary carbon. As a result these catalysts could best be used in a horizontal layer. With a vertical layer, difficulties arose in the gas passing through the catalysts and much effort had to be used for overcoming them, and the investigations in that field are still in progress.

The patent applications of the I.G. between 1935 and 1937 have, in the meantime, become known and included a new type of iron catalyst obtained by sintering of mixtures of finely divided iron with other substances. This type of sintered catalysts is naturally considerably less active than precipitation catalysts and require relatively high reaction temperatures, e.g. 320-380°C.

The Lurgi Company, Frankfort/Main has developed an iron precipitation catalyst which operates at about 250°C with rather good results.

Synthesis experiments with iron catalysts have also been carried out in the meantime in the laboratories of the Brabag Company in Schwarzheide. They also obtained good results using precipitation iron catalysts.

Dr. Kölbel has already reported on the results of the experiments in Rheinpreussen.

As far as our experiments in Holten are concerned, we have not limited ourselves to prepare a single catalyst which would give optimum results but have tried rather to apply the experience gained in the meantime with cobalt to carry out the work on a broad basis. As a result we are now in a position to produce individual catalysts for a great variety of purposes, as I will show you later on a few examples.

We have investigated the preparation of the catalysts by roasting of nitrates and particularly the preparation of the precipitation catalysts of the most diversified kind. Without giving details on the preparation of catalysts proper, we may say the following about the general experience with our iron catalysts. We may consider the low hydrogenation property of iron as being in several respects the principal difference from cobalt. The liquefaction is throughout more favorable than with the cobalt, in spite of the fact that all iron catalysts known heretofore operated at higher temperatures than cobalt. In addition, the saturation state of the liquid products is considerably lower, permitting the production of large yields of the valuable olefines. The lower tendency for methane formation in comparison with cobalt permitted operations with a much wider range of synthesis conditions, without causing either excessive gasification or too low conversion. This offers greater possibilities to affect the course of the synthesis by changing operating conditions, and in particular to change the boiling point range.

Iron differs appreciably from cobalt also in one other respect, namely with respect to the proportion of carbon monoxide and hydrogen used up. This proportion of consumption of CO and H_2

is not constant with cobalt and may be changed with the composition of the gas or by pressure. However, these changes of the gas or of the pressure are very slight with cobalt and permit the variation between 1 CO:1.9-2.1 H_2. On the other hand, with iron the proportion may be varied much more depending on the mixture, the form of the catalyst and the experimental conditions, producing the greatest variety of consumption proportion.

We have investigated this in detail and can today indicate to a certain extent the proportion of carbon monoxide to hydrogen between the limits 0.6-1.4 H_2:1 CO, which can be set at will by proper choice of the iron catalyst. We can in particular prepare such iron catalysts which consume carbon monoxide and hydrogen in the exact proportion in which they exist in the water gas. We can in this way overcome the difficulties of having to produce gases with appreciably more carbon monoxide than in the water gas.

It has been necessary so far to use a composition of a gas with cobalt catalysts which corresponded to the definite consumption proportion. This required the preparation of a special synthesis gas. Dr. Kölbel has just now stated that the gas composition had to be adjusted to the catalyst. We can, on the other hand, produce iron catalysts of such composition that it will be suitable with the gas most easily produced, the water gas.

You might state that carbon monoxide-rich gases may be necessary for the production of definite products, such as a high olefine or high paraffin content. Such is, however, not the case.

We shall show below the possibility of production of any desired products from water gas.

Changing over to water gas introduces a further advantage. The carbon monoxide-rich gases favor the deposition of elementary carbon, which may lead to notable difficulties in operations. We have completely overcome this danger by using our new catalysts.

The iron catalysts developed by us can be started in a variety of ways. We may subject them to a pretreatment at atmospheric pressure at temperatures reached in the synthesis and using water gas. It is remarkable that water gas may also be replaced by other gases, such as nitrogen, carbon dioxide, or even air. We have found that starting with water gas at high pressure is disadvantageous and in many cases results in failures. Unlike Fischer and his collaborators we have had good results with reduction with hydrogen, which was much easier with our iron catalysts than with the usual cobalt catalysts. Such iron catalysts can be reduced and made ready for operations in the reactors, without any loss of time for "forming", as is also the case with cobalt catalysts. Fischer has furthermore suggested to carry out the pretreatment of the catalysts with carbon monoxide in vacuum. This, however, offers no particular advantages nor experience.

We have found that with iron catalysts, predictions of their activity at higher pressures could not be made from behavior at atmospheric pressure. One is therefore forced to carry out all middle pressure catalyst tests at elevated temperatures. Pressure resisting experimental reactors are not as readily obtained as for atmospheric pressure reactors, and we had to use short tests of the different catalysts instead of the long duration tests. Nevertheless, we may consider the life of our iron catalyst to be at least as great as that of the present cobalt catalyst, basing it on semi-technical tests. We have succeeded in raising the activity of the iron catalysts to such an extent, that the reaction temperature could be used close to that used with cobalt catalysts, namely 220-230°C. These temperatures are still too high to permit the use of iron catalysts in the large industrial reactors at present available. We therefore make the efforts to further improve the catalyst preparation to permit a further lowering of the reaction temperature. We also are working on a new type of reactor construction and the practical results obtained with them will be presently reported.

We have carried out our pilot plant tests in pressure water cooled tubular reactors of known construction, e.g. in reactors with a gas thruput of 12 cbm/h. We duplicated the best results of our laboratory tests in a pilot plant - produced iron catalysts making long term tests. Our pilot plant tests have shown that the iron catalysts differ favorably with respect to hardness of the particles from the cobalt catalysts. As a result, our iron catalysts have a very high abrasion resistance. One sample, which has been used for two months in the pilot plant reactor, showed no carbon deposition nor increase in volume. The emptying of the reactors offers no difficulties.

It is well known that all products of the catalytic hydrogenation of carbon monoxide contain more or less of oxygen-containing compounds, and the more the higher the reaction pressure. The middle pressure products obtained with the iron catalysts contained correspondingly variable amounts of oxygen-containing materials, depending upon operating conditions and the catalysts used. We have even found that relatively large amounts of oxygen-containing primary products can be readily produced. This direction of the synthesis appears, however, in many respects less promising:

1) The oxygen-containing products are non-uniform, and consist by no means of alcohols only.

2) The lower molecular weights are mostly present, rather than the more valuable higher molecular weight compounds.

3) The oxygen-containing constituents cannot be separated by available means from the hydrocarbons.

4) We have found in the meantime other ways to produce oxygen-containing products in the pure state, such as alcohols, acids, esters, ketones, aldehydes, etc.

I will now tell you the numerical data obtained in our experiments, starting with the dependence of the course of the synthesis from the catalysts, then from the operating conditions and finally the summarized results.

Table 1 shows that we can produce with this catalyst either more gasoline or more paraffin (20-58% gasoline or 50-3% paraffin) with the same operating conditions.

The maintenance of the most favorable metal concentration has been of prime importance for the activity of the cobalt catalysts. The large number of tests performed have caused the adoption of the lower cobalt mixtures. This is the reason why, unlike the KWI and Rheinpreussen, we have not yet reached the conclusion that the question of the addition of carriers to iron catalysts has been definitely solved in favor of the carrier-free catalysts. We have instead studied carefully the proportions for iron.

Table 2 shows an illustration of the changes in the course of synthesis with the metal concentration. Higher boiling products are obtained with iron with increasing metal concentration, other conditions being left the same and vice versa. The preparation of catalysts involves a number of operations which may be changed. Table 3 shows changes in the course of synthesis produced by varying the operations during the catalyst production, while retaining the composition of the mass. This measure alone has been found sufficient to affect appreciably the liquefaction and the boiling point range.

Table 4 shows the same thing for a second variation of a single operation in the preparation of the catalysts of the same composition. This again permitted changing the boiling point curve as well as degree of saturation (10-25% gasol, 16-45% gasoline, 35-66% paraffin, 54-75% olefines).

Table 5 shows the possibility of affecting the boiling points and degrees of saturation by a third variation in the preparation of the catalysts of the same composition (16-52% gasoline or 66-22% paraffin).

We have verified the fact that such variations in the preparation can be equally successfully carried out on a pilot plant scale, as can be seen from Table 6.

The subsequent tables show the possibilities of changing the course of the synthesis with the same catalysts by using different synthesis conditions. Table 7 shows the effect of increase in pressure. In agreement with the results obtained elsewhere, the conversion at atmospheric pressure was considerably less than at higher pressure. We were forced to operate at the 75% CO conversion at an elevated pressure to obtain the same yields as are obtained at atmospheric pressure with a 95% conversion of CO. Obviously under such conditions the liquefaction is correspondingly poorer. For the same CO conversion, the yield increased with increasing pressure up to 10 atms gauge, and was no longer appreciably higher at 20 atms gauge. The boiling point curve changes in the well known way in producing less gasoline and more paraffin with increased pressure. The degree of saturation is not appreciably affected by increasing the pressure.

Table 8 shows the effect of the method of operation from the composition of the gas. We mean specifically under operating conditions the details of gas supply, as e.g. the flow velocity, etc. The more carbon monoxide and the less hydrogen is present in the tail gas, the less gasoline and the more paraffin is obtained. The amount of unsaturated hydrocarbons increases simultaneously with increasing carbon monoxide content.

We have found that with the iron catalyst the dilution of gases or increasing the flow velocity operated in the same way, namely by increasing the gasoline yield and the olefine content, while the paraffin formation was lowered, as can be seen in Table 9.

The individual examples cited above show that the boiling points and degree of saturation of the liquid products can be affected by a whole number of different measures. Were we to utilize all these possibilities simultaneously, i.e. were we to select the catalyst and the method of operation for the optimum conditions, one could easily get up the desired highest gasoline or paraffin yield or else the highest yields in unsaturated hydrocarbons. Table 10 shows a few examples. The first method of operation produced 81% gasoline and 6% paraffin. The paraffin contained 70% sulfuric acid-solubles and had an octane number of 69, or when leaded - 81 (boiling -200°C). We obtained only 14% gasoline and 64% paraffin yield in the third method of operation.

An improvement in the octane number of the primary product has heretofore been possible exclusively by increasing the proportion of unsaturated hydrocarbons. We know, however that there exists a further possibility by producing a strong branching of hydrocarbons in the primary products. We have made attempts to work in this direction, and have developed special catalysts for this purpose. The second column of Table 10 shows the results with such a catalyst (D). The olefine content of the gasoline is lower than in the preceeding one but its octane number is appreciably higher, namely 72 (b.p. -200°C). This shows that we have been successful in increasing the proportion of the iso hydrocarbons, as has also been confirmed by a boiling point analysis of the precision distillation fractions.

Table 11 shows numerical examples on the consumption proportion of $CO:H_2$ already discussed above. It may be seen that with seven catalysts of the same composition B, but prepared somewhat differently, the consumption proportion can be changed in relatively small steps over a wide range, keeping other synthesis conditions unchanged. A simultaneous change of the synthesis conditions permitted still further changing of the consumption proportion. A comparison shows further that with increasing carbon monoxide consumption the proportion of the unsaturated hydrocarbons increases. Table 11 shows further that the maximum paraffin yield is obtained when the carbon monoxide - hydrogen proportion in the synthesis gas was the same as in the off-gas.

Table 12 shows a pilot plant test, namely the paraffin synthesis from water gas, with all the important data. The low methane formation of only 7% with a yield of 145 g/ncbm of the active gas is worthy of notice. The paraffin yield amounted to 64%.

Table 13 gives juxtaposition of the most favorable individual results so far obtained with the iron and the cobalt catalysts. They show that the iron catalysts do not merely reach the yields obtained with the cobalt catalysts, but even exceed them.

It must, in that connection, be considered that the development of the iron catalyst is by no means concluded, and is still being continued. Further improvements can therefore be anticipated with certainty.

In the discussions which followed, Kölbel has stated that his catalysts were less sensitive to sulfur poisoning but had no numerical data at that time to substantiate his opinion.

✓

HYDROCARBON SYNTHESIS WITH IRON CATALYSTS

Table 1: Changing the Course of the Synthesis by Changing the Catalysts

Fundamentally different methods of preparation and composition. The same synthesis conditions: 20 atm gauge, water gas, 245°C, operating method I.

Catalysts	Boiling Point Distribution in Percent by Weight of the Liquid Products: Gasoline -200°C	Heavy Oil 200-320°C	Soft Paraffin 320-460°C	Hard Paraffin 460°C
[illegible]	58.5	24	14	3.5
B	20.5	13	16.5	50

Table 2: Changing the Course of the Synthesis by Changing the Metal Concentration

Catalyst B, water gas, 20 atm gauge, operation I.

Metal Concentration	High	Middle	Low
CO conversion	80	75	75
Yield, g/ncbm of active gas	143	140	115
Gasol, % of the yield	10	17	24
Boiling range:			
Gasoline, % by weight of liquid products	16	27	26
Oil, % by weight of liquid products	18	17	21
Paraffin, % by weight of liquid products	66	56	53
Olefines: % by volume			
in gasoline	64	65	72
in oil	56	54	69

Table 3: Changing the Course of Synthesis by Changing the Preparation of the Catalyst, Variation I

20 atm gauge, water gas, operation I, the same catalyst composition.

Catalysts	B 1	B 2	B 3
Temperature	220	230	240
% CO conversion	75	77	76
% CO in CH_4	14	7	6
% CO in CO_2	35	27	25
Gasol, g/ncbm	23	11	13
Liquid products, g/ncbm	85	130	127
Boiling range:			
% gasoline by wt.	45	16	22
% oil " "	20	18	22
% paraffin " "	35	66	56
Olefines: % by vol.			
in gasoline	69	64	63
in oil	63	56	55

Table 4: Changing the Course of Synthesis (Variations in Catalyst Preparation; Variation II)

20 atm gauge, water gas, operation I, the same catalyst composition.

Catalysts	B 4	B 5	B 6	B 7	B 8
CO conversion	80	75	75	80	80
Gasol, % by wt. of yield	10	16	25	25	20
B.p. range:					
Gasoline, % of liquid products	16	22	33	45	25
Oil, % of liquid products	18	22	23	20	20
Paraffin, % of liquid products	66	56	44	35	55
Olefines: % by vol.					
in gasoline	64	63	65	69	79
in oil	56	55	54	63	75

Table 5: Changing the Course of the Synthesis by Changing the Method of Preparation of Catalysts; III Variation

20 atm gauge, water gas, operation I, same composition of catalysts.

Catalysts	B 9	B 10	B 11
CO conversion	75	75	80
B.p. range:			
Gasoline, % by wt.	52	45	16
Oil, % by wt.	26	28	18
Paraffin, % by wt.	22	27	66
Olefines: % by vol.			
in gasoline	52	54	64
in oil	46	48	56

Table 6: Variation IV in the Preparation of the Catalysts, Pilot Plant

20 atm gauge, water gas, operation I, the same catalyst composition.

Catalysts	B 12	B 13
CO conversion	75	75
B.p. range:		
Gasoline, % by wt.	23	17
Oil, % by wt.	16	16
Paraffin, % by wt.	61	67
Olefines:		
% by vol. in gasoline	58	79
% by vol. in oil	49	81

Table 7: Changing of the Course of the Synthesis by Pressure

Water gas, same catalyst, same method of operation.

Pressure, atm gauge	atm Pressure	3	5	10	20
CO conversion	95	75	70	75	75
Yield, g/cbm	90	98	86	118	120
B.p. range:					
% by wt. of gasoline	57	32	30	25	22
" " " " oil	24	30	25	20	22
" " " " paraffin	19	38	45	55	56
Olefines:					
" by vol. in gasoline	68	64	63	62	63
" " " " oil	41	48	49	47	46

Table 8: Changing the Course of Synthesis by Altering Method of Operation, Valiant I

20 atm gauge, 245°C, the same catalyst, operating procedure and composition vary.

	I			II	
Operating Procedure	Synthesis Gas	Water Gas	CO-Rich Gas	Water Gas	CO-Rich Gas
% of CO in gas	26.3	38.0	50.9	38.0	50.9
% H_2	52.6	48.9	38.1	48.9	38.1
CO conversion	70	70	60	75	62
B.p. range:					
% by wt. of gasoline	38	25	20	43	20
" " " " oil	20	24	30	20	13
" " " " paraffin	42	51	50	37	67
Olefines:					
% by vol. in gasoline	77	79	86	65	80
" " " " oil	68	76	82	56	74

Table 9: Changes in Course of Synthesis by Changing the Operating Procedure to Variation

20 atms, CO-rich gas with 51% CO, 38% H_3, 245-250°, same catalyst.

Gas Dilution Velocity of Flow	) Increasing ————			
Yield, g/ncbm of active constituents	125	85	95	90
% gasol in the yield	13	13	12	16
Boiling range:				
% by weight of gasoline	20	20	20	40
" " " " oil	13	30	40	38
" " " " paraffin	67	50	40	22
Olefines:				
% by volume in gasoline	80	86	88	87
" " " " oil	74	82	81	82

Table 10: Simultaneous Change of Catalyst in Method of Operation

Catalysts	C	D	E
Pressure, atm gauge	10	15	20
Gas	water gas	water gas	CO-rich gas
% CO	39	39	50
% H_2	48	48	38
% gasoline by weight	81	39	14
" oil " "	13	31	22
" paraffin " "	6	30	64
Olefines:			
% by volume in gasoline	70	67	80
" " " " oil	65	58	73
Octane number (Primary gasoline -200°C)	69	72	81 leaded

Table 11: Displacing the Consumption Proportion of $CO:H_2$

Catalyst	B9	B10	B4	B5	B6	B7	B8	C
Gas		→	→	Water gas		←	←	CO 50.9%
Pressure, atm gauge		→	→	20		←	←	H_2 38.1%
method of operation	→	→	→	I		←	←	II
Consumption proportion: $CO:xH_2$	158	151	125	117	105	0.97	0.88	0.71 (to 0.6)
Boiling range:								
gasoline	52	45	16	22	33	45	25	20
oil	26	28	18	22	23	20	20	13
paraffin	22	27	66	56	44	35	55	67
Olefines:								
in gasoline	52	54	64	63	65	69	79	80
in oil	46	48	56	55	54	63	75	74

Table 12: Paraffin Synthesis with Water Gas

Catalyst: B4
Gas: water gas with 38% CO and
48% H_2 (1:126)
Pressure: 15 atms
Temperature: 230°C
Contraction: 60%
CO conversion: 80%
CO as CO_2: 25.6
CO as CH_4: 7.0
CO gasification: 67.4
H_2 conversion: 80.0
CO + H_2 conversion: 80.0
Consumption Proportion:
$CO:H_2$ 1:1.24

Yield g/ncbm active gas ingredients

	1st stage experimental	2nd stage calculated	1st and 2nd stage calculated
Gasol	10	3	13
Liquid products	135	20	155
	145	23	168

(Cont'd. on following page)

Table 12: Paraffin Synthesis with Water Gas (Cont'd.)

	1st stage experimental	2nd stage calculated	1st and 2nd stage calculated
Boiling range:			
gasoline	-200°C	16% by wt.	about 70% olefines
oil	200-320°C	20% " "	" 70% olefines
soft paraffin	320-460°C	22% " ")	64%
hard paraffin	over 460°C	42% " ")	

Table 13: Comparison of the Most Favorable Single Results with the Iron and Cobalt Catalysts

Catalysts	Fe	Co
Yield, g/cbm, 1st stage	145	130
Yield, g/cbm, 1st and 2nd stage	168	155
Boiling range:		
gasoline -200°C by weight	60	60
oil 200-320°C	40	30
paraffin, over 320°C	70	70
Olefines:		
in gasoline	90	65
in oil	82	55
Octane number (primary gasoline -200°C)	72	57-65

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

TOM Reel 12
Item 33
Frames 20'77-20'81

0148

T-470
W. M. Sternberg
January 11, 1949

OPERATING DIRECTIONS FOR STARTING THE PRODUCER

November 7, 1941

The starting up of the producer must be under the responsible direction of the shift supervisor of the gas works, and the following directions must be followed:

A. Starting a Cold Producer

1). Check all the parts of the producer: the grate drive, the recirculation pumps, the skirt drive, and the scraper of the gas outlet elbow.

2). Check to make sure that the flare valve is closed. Separate the pressure release pipeline of the coal pit pocket by turning the elbow at the valve and put in a blind. Test to see that the slide is inserted in the gas outlet.

3). The generator is pressured up with air at 20 atm after each major repair. The pressure is next released.

4). Water is fed into the jacket until the level of the water can be seen in the sight glass.

5). Remove the blind from the steam pipe, start heating the ash pocket, test the condenser head.

6). Fill grate with dry, no longer glowing and burned out ash (about 2.5 cbm) through the poker hole lid, arrange four torches of excelsior and have additional wood within reach near the different poker hole lids.

7). Open the spray cooler circulation drain, while leaving the injection valves and the condensate delivery valves closed. Supply cooling water to the spray cooler jacket.

8). Check the differential pressure gauge for air, oxygen and steam.

9). Open the coal pocket and coal conical ring.

10). Start operating the oxygen compressor with air or else start later the pipeline with 4.5 atm air from the auxilliary compressor.

11). Light the lighting torches and throw them in simultaneously through all the poker holes (it is forbidden to saturate the torches with tar, middle oil, or even with light oil).

12). Supply some air (50 mm Hg) and put in all the wood simultaneously into the four poker openings.

13). Close the poker openings.

14). Open full the flare valve (no flare valve of any other producer must, however, be open at the same time).

15). Close the coal cone, fill the coal pocket bin and close the coal pocket lid.

16). Give 1/4 of a coal pocket-full of gasification coal after about 15 minutes (the coal cone is to be opened for about 12 seconds).

17). The water drain valve of the steam pipeline at the gasification inlet elbow must be opened, the remaining steam shut-off valves are opened, taking care not to permit any steam going through the differential pressure meter.

18). Increase the amount of air to 400 mm Hg and add steam (2 mm Hg).

19). Slowly throttle the flare valve. When the generator pressure begins to exceed 1 atm, close the drain valve of the steam pipeline. Increase the pressure in the generator to 4 atms by additional throttling; and keep this pressure as constant as possible by regulating the flare valve.

20). Regulate the amount of steam to agree with the starting diagram BCG K IV/40.

21). Fill the spray cooler circuit with water, open the suction valve under the spray cooler, start up the circulation pump and open the injection valve. Turn off the condensate drain valve and check the condensate trap. Then send cooling water through the heat exchanger.

22). Add 1/4 pocket-full of gasification coal in half hourly intervals after the first coal addition.

23). Observe the gas outlet temperature. When 150°C is reached, add one additional pocket-full of coal.

24). When the gas outlet temperature reaches at least 180°C again add 1 pocket-full; this is to be continued.

25). Test the gas for O_2 after adding the first pocket-full; with 2% O_2 or less, the gas is lit or else sent through the steam cooler to the pressure release line, while the valve to the flare is closed. Regulate the cooling water supply in the steam coolers. Unless there are some important reasons not to do so, the gas must be sent through the steam cooler.

26). Watch the CO_2 content of the raw gas. It must vary between 22 and 25% CO_2. The carbon monoxide must be determined by analysis.

27). Turn off again the producer about 20 hours after the addition of the first full coal pocket, and release the pressure (see operating directions for shutting down the producer).

28). Replace the blind disc in the gas outlet with an orifice.

29). Again increase the pressure in the producer to 4 atms and produce the same conditions as existed before shutting down.

30). After the producer is full, increase its pressure slowly by throttling the flare valve (during 2 hours), keeping the amount of air constant at 400 mm Hg and regulating the amount of steam in accordance with the diagram BCG K IV/40.

31). When the producer is full, increase slowly over a two hour period the pressure to the required level, maintaining the amount of air at 400 mm Hg and regulating the steam by the diagram BCG K IV/40.

32). Change over from air to oxygen after 18 atm gauge is reached in the producer (close the intermediate pressure release valve at the second oxygen compressor) and after the air has been turned off, steam is set at first at 25 mm and oxygen at 20 mm.

33). Watch the producer pressure after changing it over to oxygen and regulate the flare valve accurately. Slowly increase the pressure to 20 atm.

34). Connect the producer to the raw gas pipeline by slow opening of the main shut-off valve. Then slowly close the flare valve or the valve to the condensate cooler.

35). Regulate the cooling water of the heat exchanger and of the spray cooler.

36). Increase the load on the producer, while increasing every 10 minutes the oxygen addition by 10 mm differential pressure. The amount of steam is to be regulated correspondingly according to the curves on diagram BCG K IV/41.

B. Starting the Producer after Short Interruption of Operations

If the operation of the producer were interrupted for less than 8 hours, operations can be resumed directly with oxygen, keeping the following in mind:

1). Test whether water can be seen in the sight glass.

2). Check whether the ash pocket heating has been started and whether the condensation trap is in order.

3). Check to see that the poking holes are closed.

4). Check whether the coal cone is set and whether the ash pocket lid is closed according to directions.

5). Open the flare valve completely, but no second producer may be simultaneously pressure released through the flare pipeline.

6). Control the differential pressure meter for oxygen and steam.

7). Should any blinds have been inserted in the gas outlet, they must first be withdrawn. The upper steam shut-off valve is opened, watching that the steam does not go through the differential pressure meter. The steam pipe drain valves at the gasification agents intake must be opened.

8). Set the steam and oxygen valve in accordance with the curves, diagram BCG-K IV/41; the drain valve of the steam pipeline is again closed when no more water escapes.

9). The flare valve is again throttled until the producer has reached 4 atm gauge pressure.

10). Test gas for O_2. With 2% O_2 or less, the gas is lit or else sent to the pressure release pipeline over the steam cooler, while the valve to the flare is closed. The cooling water in the steam cooler is regulated.

11). The spray cooler circuit is filled with water, the suction valve in the spray cooler is open, the circulation pumps are connected in, and the injection orifices are opened, the condensate drain valve is turned off and the condenser trap is checked.

12). The gas outlet temperature must be watched. When the temperature reaches 180°C the coal may be added as needed. Is the generator full when the gas inlet temperature is 180°C, the heating up can proceed unchecked.

13). The flare valve or the valve to the vapor cooler is slowly throttled, increasing the producer pressure (see Section A, paragraph 32). Normally, the time required for reaching the required operating conditions should be one hour from this moment.

14). The CO_2 content of the gas should be 33-36%. The carbon monoxide is to be checked by analysis.

15). When 20 atm gauge pressure is reached, the main gas outlet valve is opened and the producer connected in parallel. The flare valve or the valve to the vapor cooler is slowly closed.

16). The amount of cooling water in the heat exchanger and the spray cooler are regulated.

17). Slowly bring the performance of the producer up to requirements.

/s/ Otto

OPERATING DIRECTIONS FOR THE PRODUCER PLANT

Boehlen, February 7, 1942

TOM Reel 12, Item 33
Frames 30'22-30'37

1). Askania Regulating Unit

The supervision and operation is not done by the operating crew of the gas works, but is done automatically. Accordingly, no employees of the BCG may be employed at these units.

a). Gas Pressure Regulator

The pressures in the generators depend on the setting of the Askania gas pressure regulator behind the desulfurization. The operating personnel may not make any important changes in the setting. Only the shift foreman is permitted to make any changes in pressure, and special attention must be paid to always have sufficiently high gas pressure in the pressure water scrubbers, which will prevent too great a strain on the drive motors of the pump - turbine units. Whenever irregularities in the regulator unit make it impossible to maintain a constant gas pressure, regulations must be done by hand by the regulator operators, and the gas pressure is to be observed after short time intervals (3 minutes). The gas volume recorder must be observed during the opening or closing of the regulation valves. The thruput must not exceed the capacity of the regulator even for a short while, because this causes troubles with the measuring unit, or else water can be readily entrained by the gas into the pressure scrubber.

b). Steam Pressure

The steam pressure as well must be kept constant at 23 atm gauge by using the Askania regulator. In case of trouble the regulator must be turned off and the hand regulator set to "open". When the steam pressure is insufficient an alarm is sounded. The purpose of this signal is discussed in another section.

c). Oxygen Pressure

The oxygen pressure is best coupled up with the steam pressure for greater safety of operations, and is also equal to 23 atm gauge. These mining low directions are intended to prevent feeding oxygen alone into the generator when steam is shut off. In spite of this safety measure, the oxygen pressure must be continuously watched. The lead seal tag on the bypass valve of the oxygen regulating valve may be broken only by the shift foreman in case of emergency, and the shift foreman must then describe in his log the urgent necessity for doing so.

When the alarm signal for insufficient steam pressure is sounded, the oxygen regulator must immediately be changed over to hand regulation and the supply turned off. In addition, the superheater is protected by immediately letting off steam and the gas burner is extinguished. All the oxygen supply valves to the individual generators must be immediately closed. Time losses are avoided by informing the oxygen plant only afterwards about the occurrence.

2). Operating the Producers

a). Setting the Producer Load and Fixing the Oxygen - Steam Proportion

The proper load upon the producer is created by the correct supply of oxygen and gasification steam.

The amounts are read off on the pressure difference meter on the diagram BCG K IV/41. When changing the load, the oxygen plant must be immediately notified under normal operations, to permit the plant to maintain a constant oxygen pressure. The oxygen:steam ratio must be set in accordance with BCG K IV/41. This set of curves contains different curves (A, B, C, D and E), with each curve representing an increased steam supply in the alphabetic order. The steam supply must be kept as low as possible to maintain a proper quality of the gas (sufficient formation of methane); it must, however, be set depending on the appearance of the ash, to prevent difficulties in ash removal. The producer operators must therefore continuously observe the appearance of the ash. Whenever hard sintered ash pieces are present, the producer must be operated cooler by increasing the steam addition. The producer then must be set to the next higher curve. The increased addition of steam causes a lowering of the temperature in the gasification zone, because the conversion process of the steam with coal to carbon monoxide consumes heat. Only after the ash has again become free of slag, operations can be changed over to a lower steam-oxygen proportion. Slagging may also manifest itself in other ways.

1). The fire zone can be displaced, which will be shown by variations in the jacket temperatures. For this reason the jacket temperatures of the slagged-up producer must be connected to the six-coil recorder, while normally the jacket temperatures of gas generators are only recorded every two hours.

2). The gas production does not correspond to the amount of oxygen introduced. We may make a preliminary assumption of an oxygen consumption of 0.15 cbm oxygen/cbm of pure gas produced.

3). The gas outlet temperature is above normal.

4). The power consumption of the ash removal unit is above normal.

All these points must therefore be continuously watched even when operations proceed free of trouble.

During operations the carbon monoxide content is continuously determined by analysis. Care must always be taken to have the gas samples drained free of water, i.e. kept clean.

b). Feeding Coal to the Producers

The regular supply can be checked by the producer operator by observation of the gas outlet temperature. Should the latter become higher than normal, the coal pocket operators must be informed to permit them to tell whether any irregularities have occurred in the coal supply (coal remaining by hanging). The upper units inside the producer are protected from any danger by reducing the load when the gas outlet temperature exceeds 400°C, and if necessary the producer may have to be shut down. If the coal is supplied normally and yet the gas outlet temperature rises, other causes must be found and the shift supervisor must be informed.

c). Ash Removal from the Producers

The ash to be removed from the producer depends on the producer load. As much ash must always be removed as is introduced in the gasification coal as non-combustibles. If too much ash is introduced, too much unburned material remains in the ash (uneconomical), while when too much is carried out, the gasification zone is shifted upwards, which may also be observed at the gas outlet temperature.

The amount of ash removed may be set by changing the number of teeth moved by the rack and pinion. The ash pocket is to be emptied after 8 tooth-hours (number of teeth pushed forward, multiplied by the number of hours of operation). This is done by the ash pocket operators who must work under special operating directions, while the setting of the ratchet and the starting and stopping of the starting motor must be done by the producer operator. The latter must also supervise the grate drive. The drive connection must be protected during the deashing by hanging out a notice to prevent any unwanted closing of the circuit.

Shear pins are used for the mechanical protection of the drive, and three different shear pins, numbered 1-3, are available. In the regular operation only the shear pin 1 is to be used. The putting in of the shear pins must be done carefully and the producer plant supervisors must check the correct setting in every case. Should these shear pins break because of the too hard operation of the grate, the man in charge of the operation must be notified, and he in turn must give new directions. It is entirely forbidden to use other shear pins or even steel pins without special directions.

d). The Jacket Feeding

The cooling water jackets of the producer must be steadily supplied with the condensate in amounts based on continuous observation of the water level in the steam collector. The water level may under no conditions drop below the minimum level, and on the other hand only enough must be fed to have the level visible (according to directions). Should the gasifier need to be overfed in order to fill the spray cooler circuit, this may only be done under special directions of the shift supervisor. The producer operator or else the especially responsible feed supervisors must be held responsible for it. The care and servicing of the feed pumps is also entrusted to them. Should the feed pumps get out of order, the emergency feed line from the pumps of the pressure water scrubbers may be put to use with a specific consent of the men in charge of the operations. This may, however, be only done in exceptional cases because of the unfavorable water supply. After the line had been used, it must be shut down and drained.

The producer jackets must be regularly flushed to remove the sludge accumulations and to prevent too great concentration of evaporation residues of the water in the cooling jacket. A rule must be established that each producer must be flushed at least once a week by the producer operator and later by the feed men, with at least 50 cms of water, measured on the sight glass, drained off. Should only 15 cms be drained, this must be done frequently in time intervals of about one hour. The time of the sludge removal and the amount of water drained is to be entered by the operating personnel into the operation log. In addition, after each draining the boiler water sample must be taken and tested by the main laboratory.

c). <u>Spray Cooler Circuit</u>

Perfect operation of the spray cooler circuit is a necessary prerequisite for trouble-free operations. The condensation traps must be continuously watched. They must be regularly checked by the producer operator. The circulation pumps must use 9-10 amp of current if the amount of water injected is sufficient for cooling of the gas. The heat is removed by the return cooling water in the heat exchanger. The maximum possible amount of water must always be supplied to insure sufficient water in the heat exchanger and must be established by observing the off-water temperature. Should it be necessary, the cooling water may be throttled down in that particular producer, on which the temperature of the water is the lowest. If the water supply is increased, the temperature of the water should be 45-50°C. The temperature must be lowered to prevent a too rapid destruction of the cooling tubes and corrosion. Should the circuit get out of commission, which is readily recognized by the low current consumption of the circulation pump or by the insufficient gas cooling, the producer load must be immediately reduced and the circuit again refilled by additional feed. This may be done by overfeeding the individual producers, or with a single producer out of operation and the heat exchanger must be strongly flushed under the supervision of the operation supervisor by opening the drain valve while the injection valves or the suction valve on the spray cooler are kept closed. Should this fail to bring about the desired results, the management must be notified. The producer operator is further entrusted with the care of the circulation pumps and with the proper maintenance of the tar draining.

f). Operation of the Skirts

Should the continuous electric drive for operating the skirts not be available in all the producers, the gas outlet space is kept clean by rodding out the skirt once every shift, which will require about 40 half-revolutions. The operation supervisors must pay particular attention to this task and enter the time in the log.

g). Scraper Servicing

The scrapers for the cleaning of the gas outlet bend must be hand operated twice in every shift. When doing this the spindle must be completely drawn up and down. The scraper must not, however, be left in the extreme location, because of the danger of the spindles becoming stuck during temperature variations in the gas. The supervisor must check during every shift the easy operation of the scrapers.

h). Setting of the Heating Value

The pure gas produced should have an average heat value of 4500 kcal/ncbm (± 100 kcal/nobm), and all variations must be avoided as much as possible. Experience has shown that the heat value is higher with smaller gas load than with larger loads. This may be compensated first of all by a different efficiency of removal of carbon dioxide in the pressure scrubbers, for which purpose the operators of the pressure scrubbers must be given more detailed information by the supervisor of the gas production on the operating conditions.

Efforts must be made to have the regulation as sensitive as possible and to avoid large variations. The density recorder gives good information on this point and must therefore be continuously observed. Changing the load of the gas works must always be followed by regulating the pressure water scrubbing. With very small gas load the heat value of the gases may exceed 4600 kcal/ncbm, in spite of a high CO_2 content. In such case, the producer load must be increased with a possible starting of a second oxygen compressor and feed the excess gas to the pack installation. Should this be impossible for operational reasons, the average heat value is obtained by a higher load of the producers, by non-uniform operations of the different producers, or occasionally by shutting one producer out of operation. Getting one of the producers out of operation must, however, only be done when one may anticipate more than 12 hours of excess capacity of the generators. One should avoid reducing the oxygen concentration because of the difficulties of the regulating and the undesirable effect upon the whole operation.

3). General Remarks

a). Protection Against Gas Leaks. Welding Operations.

The gas produced is combustible and explosive and harmful when breathed in. For this reason, any leaks must be continuously looked for, and the management must be notified in special cases, e.g. in case of breaks of the main packing.

When the gas odor becomes noticeable, good ventilation must be taken care of and any welding operations which are being performed must be immediately stopped. Open fire and welding must, as a general rule, be done only with a written permission of the management. The supervisor must ask for a written permission in all doubtful cases. When the gas odor becomes strong, the scene of the trouble must only be approached with gas masks, and a second man, also with a gas mask, must also be present, and if leaks become very large, efforts must be made to exclude the corresponding parts of the unit or the pipeline, or shutting them off.

The gas producer building must be always sufficiently ventilated. In particular, all the windows and doors of the ash removal and coal service stations must be always open on the windward side even during the coldest time of the year or during the black-out. The shift supervisor or foreman is made responsible for it.

b). Lubrication

All the lubricating places of the equipment and machinery must be regularly serviced. A special oiler is put in charge of this task. Should any lubrication places become plugged up, this must be notified in writing. The supervisors must continuously satisfy themselves that all the lubrication places are in order.

c). Measuring Instruments

The mechanical shops are entrusted with the maintenance and operation of the control instruments except the Junkers calorimeter. Should any instrument fail, a message should be sent by telephone to the shops. In case of minor trouble, such as sticking of the recording paper, this may be helped by the producer operator, or else when great difficulties are to be anticipated in operation and a rapid fixing of the instruments cannot be done by the mechanic, the shift supervisor may be requested to help (e.g. differential pressure gauge for gas and oxygen).

When the Junkers calorimeter breaks down the laboratory is to be informed, and the latter is held responsible for the operation of this instrument.

d). Shift Log and Operation Record

A shift log is provided for the gas production. All the important operation events must be noted in the log, to keep the new shifts informed of all that happens during the shift.

A number of operation records must be kept for the supervision of the machinery and equipment. This must be done with extreme care by the producer operator. The shift supervisor has to watch the entries, because irregularities in operation of the plant can be particularly readily recognized there. The shift foremen have to read the records and initial them at least once during the shift.

/s/ Otto

OPERATIONS FOR STOPPING THE GASIFIERS, SECOND EDITION

Boehlen, August 30, 1943

TOM Reel 12, Item 33
Frames 30'38-30'41

The shift supervisor is primarily responsible for the stopping of the producers.

A. Stopping of the Producers Without Pressure Release

1). Stopping the coal supply of the producer.

2). Regulating valve for oxygen is stopped. Warning sign is hung up.

3). The steam supply valve is strongly throttled reducing the steam supply to the producer to about 2-3 mm.

4). The second shut-down oxygen valve is closed, and the in-between piece is pressure released.

5). The steam regulating valve is entirely closed, the upper main steam valve is also closed. A warning sign is hung up.

6). The grate drive is stopped, the switch secured.

7). The two outlet valves for raw gas are closed after about 15 minutes. The intermediate piece is pressure released and the pressure release valve is left open.

8). The pressure in the producer is regulated by opening the flare valve.

9). The water level is watched and the water fed as during normal operations.

B. Shutting Down with Pressure Release

1-7). As before.

8). Flare valve is slightly opened and the producer pressure drops slowly.

9). The water level is watched and the feed continued. The pressure release may proceed only at a sufficient rate to keep the water level always visible.

10). When a pressure of 5 atm gauge is reached, the spray cooler circuit is taken out of operations, with the circulation pumps stopped, the injection valves and the condensate drain valve closed. The water in the circuit is then slowly let out until gas escapes. This is to be repeated at short intervals until the pressure in the producer permits a steady reduction of the condensate formed.

The switch for the circulation pump is secured.

11). The shut-off steam valve of the stuffing box of the gasifying agents intake and between the ash pocket pressure release valves are closed.

12). When the producer no longer stands under any pressure, the permanent emergency flare is opened. In the absence of a permanent emergency flare the poker hole closure is opened and the ventilating pipe is set up. The heating steam line, the filling line and the shut-off steam lines for the ash pocket are closed with blinds. A blind disc should be put in the gas outlet only in case of a longer stoppage of the producer (over 24 hours), if no work is to be done on the producer.

C. Turning Over the Gas-Producer to the Repair Gang

Work on the producer is permissible only with special precautions as long as there is fire in the producer.

1). Blind discs must be inserted into the gas outlet and into the flare pipeline before beginning of work.

2). It is important to introduce nitrogen for two hours after pressure release through the ash pocket and with the open ash cone.

3). During that time the bolts of the flange connections which may be loosened, i.e. not the ones between the producer and the ash outlet elbow, can be loosened down to the last four bolts.

4). The following work is permitted during this operation condition:

a). Exchanging the ash elbow closure lids.

b). Exchanging the ash cones including the drive shaft and the upper drive.

Attention must be paid while working on a and b that a temporary lid on the ash outlet elbow, sufficiently strongly fastened by bolts, is put on even during the short interruption of work.

c). Changing of the packing of the connecting pipelines. The packing between the ash outlet elbow and the producer can, however, under no conditions be replaced.

d). The packing of all the stuffing boxes, except the pyrometer stuffing box.

e). Exchanging the packing between the ash pocket and the ash outlet elbow with a set ash cone.

5). The producer is flushed for at least 24 hours with a very O_2-free nitrogen (1-1.5%), then the packing between the producer and the coal hopper can be renewed or work done on the coal cone and the scraper of the gas outlet elbow, after having taken care, however, of creating suction after opening the ash cone and the ash pocket lid after the oxygen was turned off. Attention must here be paid to have only one opening at a time in the upper part of the producer, to prevent sucking in any air. Moreover, the coal pocket pressure release pipeline must be blinded off.

6). No other repair work may be done in the producer before it is emptied.

D. Emptying the Producer

1). All the work described in Section B, 1-13, must be performed.

2). Inserting the blind into the gas outlet and into the flare line.

3). The grate drive is connected to discharge and the ash, and later coal, are emptied in a strong blast with nitrogen and with the maximum possible motion of the ratchet.

4). The emptying of the ash pocket proceeds in the same operation steps as in normal operations, without, however, first pressure releasing the ash pocket and instead blowing nitrogen during the ash removal. The emptying of the ash pocket must proceed with particular care. The production of much dust must be avoided because of the possibility of dust fires.

E. Flushing of the Producer

When the producer cannot be emptied by means of the grate drive, it must be flushed with water. This work requires the following precautionary measures:

1). First of all, the work described in Section B, 1-13, must be carried out.

2). The blinds in the gas outlet pipeline and the flare line are inserted.

3). The blind inserted into the coal hopper pressure release pipeline.

4). The producer is flushed with nitrogen for 24 hours by way of the ash pocket.

5). The coal pocket is kept closed and the coal cone is set. A poker hole is opened and the spraying tube is inserted. The annular space between the poker hole and the spray tube is tightened up by moist cleaning cloth or in other ways.

6). The ash cone is raised and furnace suspended, the ash bin lid is screwed up and swung out of the way.

7). The spray tube is introduced as deep into the ash bed as possible and the water slowly turned on. Only enough water is turned on, not to have the steam pressure great enough to throw out the packing around the spray tube. This work must, however, be done by at least two men. The flushing is continued until the producer is practically clean.

8). If, however, the producer cannot be emptied even in this manner, other methods must be used.

F. <u>Entering a Producer</u>

1). Should it become necessary to enter a producer, all the blinds must be in place and all the drives must be protected (by safety signs).

2). Blinds must be inserted in

a). Gas outlet
b). Ash pocket pressure release pipeline
c). Ash heating line
d). Sealing steam for the gasification
agent stuffing box
e). The flare valve
f). Coal hopper pressure release pipeline
g). Spray cooler drain line

Notice to b, c and d: it is sufficient for the use of the producers to insert a blind into the main pipeline.

3). Sufficient airing of the producer is provided for (natural draft or fresh air blower).

4). The first man entering a shut-down producer must have a second man present.

5). The fire sinders remaining in the producer are eliminated, and after that the repair on the producer work can be carried out without any interference, except for the constant adherence to directions regarding the use of open flames and carrying out of welding.

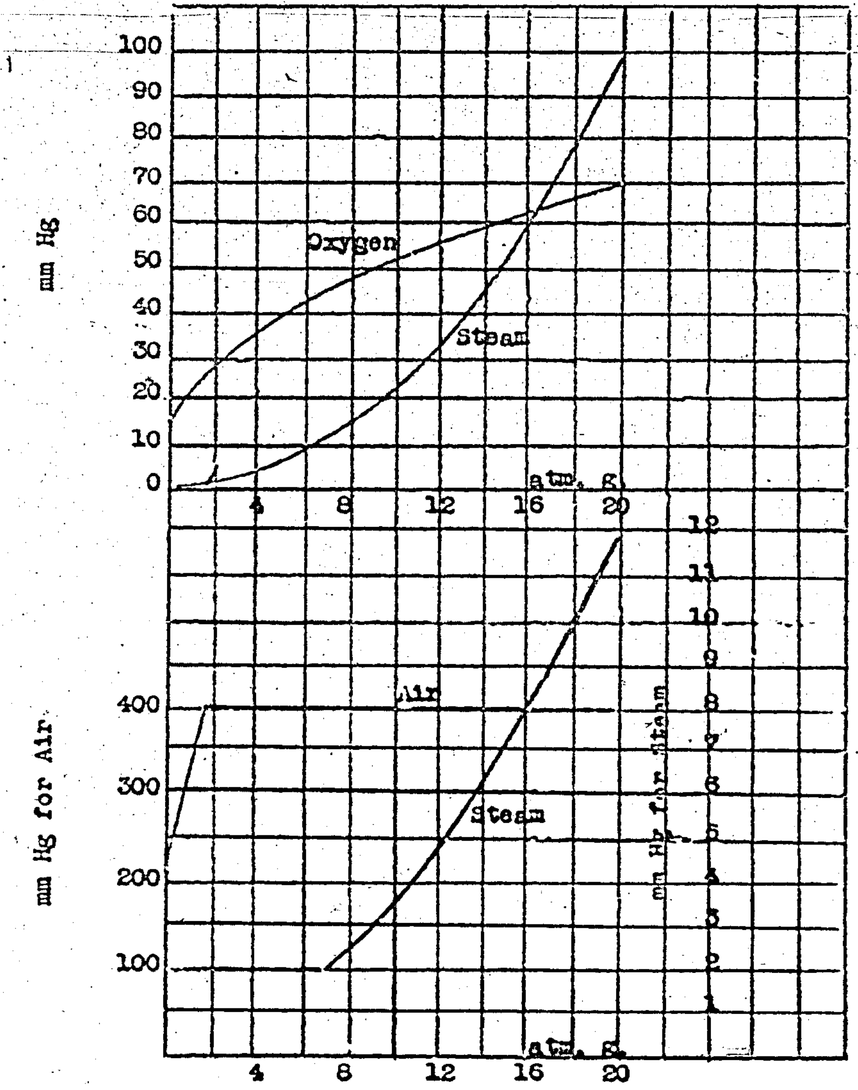
G. Miscellaneous

1). The jacket of the producer can be rinsed with cold water for rapid cooling of the producer after emptying it or after flushing it empty.

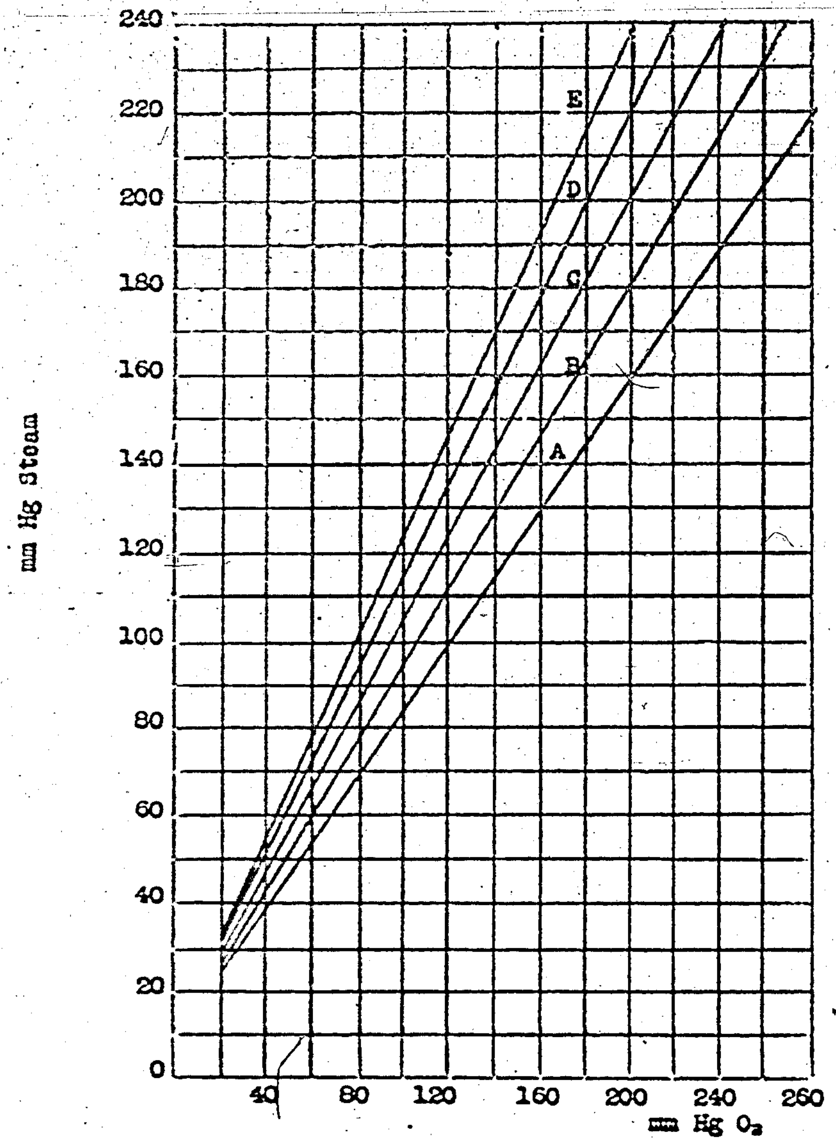
2). As long as there exists the possibility of fire in the producer, the jacket must never be empty, i.e. the water level must be visible.

3). As soon as the absence of a fire has been proven by entering the producer, the water jacket can be completely drained.

/s/ Otto



Starting Curves for Oxygen and Air. BCG K IV 40



Generator Operating Curves. BCG K IV 41

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
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High Pressure Experiments,
Ludwigshafen 558

0172

July 27, 1938

CALCULATION OF HYDROGENATION OF NAPHTHENES

By Dr. E. E. Donath

Summary

The assumption is made that the dehydrogenation equilibrium is reached during dehydrogenation of gasoline at 480°C and 50 atm, and that other temperatures and pressures, at which similar dehydrogenation could be expected, can be calculated (Figure 2).

It was further assumed that the diphenyl formation as condensation product results in the loss of activity of the catalyst and that other temperatures may be calculated for the same diphenyl formation as for 480°C and 50 atm H_2.

With these assumptions, the following series of temperatures, H_2 and gasoline vapor partial pressures can be calculated, at which the equilibria for the dehydrogenation and for condensation are equal:

	Temperature °C	Partial Pressure of H_2 atm	Partial Press. of Gasoline atm	Ltr. of H_2/100 g Gasoline
	580	200	0.88	3600
	525	100	0.77	2000
Starting Point of Experiments	480	50	0.67	1200
	425	20	0.55	900
	355	5	0.28	200
	290	1	0.2	70

Tests under these conditions were to be carried out.

Calculations

Tests (performed by Dr. Simon with 50 g gasoline and 600 li H_2) at 480°C, 50 atm H_2 partial pressure and 0.67 atm oil vapor partial pressure resulted in the formation of a product consisting of 20% naphthenes and 65% aromatics (maximum values).

We may assume that this value represents equilibrium, and will obtain then the following values for the equilibrium constants, making the simplifying assumption that the aromatics consist of benzene, and the naphthenes of cyclohexanes.

1.) $C_6H_6 + 3\ H_2 = C_6H_{12} + 46.5$ Cal.

$p_{C_6H_6} = 0.65 \times 0.67 = 0.43$ atm.

$p_{H_2} = 50$ atm.

$p_{C_6H_{12}} = 0.20 \times 0.67 = 0.13$ atm.

therefore:

2.) $$K_{p_1} = \frac{p_{C_6H_6} \times p^3_{H_2}}{p_{C_6H_{12}}} = \frac{0.43 \times 50^3}{0.13} = 4.1 \times 10^5 \text{ at } 480°C$$

$$\log.\ K_{p_1} = \log.\ 0.41 \times 10^6 = 5.6 \text{ at } 480°C$$

The Nernst approximation formula has been used for calculation of the temperature coefficients of these equilibrium constants, and the following expression was obtained:

3.) $$\log.\ K_{p_1} = \frac{-Q}{4.571 \times T} + \sum\gamma \times 1.75 \times \log T + \sum\gamma C$$

$$= \frac{46500}{4.571 \times T} + 3 \times 1.75 \times \log T + 4.8$$

from which we may calculate for temperatures between 200 and 600°C:

Temperature °C	200	300	400	500	600
$-\frac{Q}{4.571 \times T}$	-21.5	-17.8	-15.1	-13.2	-11.7
$- 3 \times 1.75 \times \log T$	14.1	14.5	14.8	15.2	15.4
$\sum \gamma C$	4.8	4.8	4.8	4.8	4.8
4.) $\log K_{p_1} =$	- 2.6	+ 1.5	4.5	6.8	8.5

The values in the equation 4) have been plotted as a curve in Figure 1, and the value K_{p_1} from the equation 2), i.e. direct experimental value is used. It may be seen that the two values differ by less than one-tenth of a percent, and it appears permissible to insert the K_p obtained from the temperature coefficients calculated by the approximation formula. In this way the broken line in Figure 1 for K_{p_1} has been obtained and marked "experimental".

A temperature can be found for any H_2 pressure by using the K_{p_1} "experimental" values of Figure 1 and these pressures will give the same dehydrogenation as is obtained at 480°C with 50 atm H_2. The following values are obtained:

5.) p_{H_2} = 50 atm. (starting point, according to definition)
$K_{p_1} = \frac{0.43}{0.13} \times 50^3 = 2.1 \times 10^5$; $\log K_{p_1} = 5.6$ for 480°C

5a) p_{H_2} = 200 atm.
$K_{p_1} = \frac{0.43}{0.13} \times 200^3 = 2.6 \times 10^7$; $\log K_{p_1} = 7.4$ for 580°C

5b) p_{H_2} = 20 atm.
$K_{p_1} = \frac{0.43}{0.13} \times 20^3 = 2.6 \times 10^4$; $\log K_{p_1} = 4.4$ for 430°C

5c) $p_{H_2} = 10$ atm.

$$K_{p_1} = \frac{0.43}{0.13} \times 10^3 = 3300; \log K_{p_1} = 3.5 \text{ for } 400°C$$

5d) $p_{H_2} = 1$ atm.

$$K_{p_1} = \frac{0.43}{0.13} \times 10^3 = 3.3; \log K_{p_1} = 0.5 \text{ for } 300°C$$

5e) $p_{H_2} = 0.1$ atm.

$$K_{p_1} = \frac{0.43}{0.13} \times 0.1^3 = 3.3 \times 10^{-3}; \log K_{p_1} = -2.5 \text{ for } 225°C$$

Figure 2 contains the values of the equations 5) to 5e), and shows therefore the relative changes of temperature with the H_2 pressure, with which the same dehydrogenation is obtained as at 480°C and 50 atm.

A supplementary assumption is made to permit one to get information on the deterioration of the catalyst using the equilibrium computations. It is assumed that the deterioration is caused by the formation of diphenyl, and that the concentration (partial pressure) of the diphenyl is no larger than in the test at 50 atm and 480°C. We get:

6.) $2\ C_6H_6 = C_{12}H_{10} + H_2 - 10$ Cal

from which we get from the Nernst approximation formula:

7.) $$\log K_{p_2} = \log \frac{p^2_{C_6H_6}}{p_{C_{12}H_{10}} \times p_{H_2}} = \frac{10\ 000}{4.571 \times T} + 1.4$$

For temperatures from 200 to 600°C the following values for K_{p_2} are obtained:

Temperature °C	200	300	400	500	600
$\frac{10\,000}{4.571 \times T}$	4.6	3.8	3.2	2.8	2.5
$\Sigma \gamma c$	1.4	1.4	1.4	1.4	1.4
8.) log K_{p_2}	6.0	5.2	4.6	4.2	3.9

These values for K_{p_2} are plotted in Figure 1. From this, and equation 7) we can obtain for 480°C and 50 atm hydrogen, 0.43 atm $p_{C_6H_6}$ and $K_{p_2} = 1.8 \times 10^4$ (log $K_{p_2} = 4.25$) which permits calculating the partial pressure of $C_{12}H_{10}$.

9.) $$p_{C_{10}H_{12}} = \frac{0.43^2}{1.8 \times 10^4 \times 50} = 2 \times 10^{-7}$$

This partial pressure for $p_{C_{10}H_{12}}$ and the equations 7) and 8) permits calculating the partial pressure of H_2, at which 0.43 atm C_6H_6 partial pressure and different temperatures and the $C_{12}H_{10}$ formation is as large as at 480°C, and a partial pressure of hydrogen at 50 atm and of C_6H_6 at 0.43 atm:

10.) from $$K_{p_2} = \frac{p^2_{C_6H_6}}{p_{C_{12}H_{10}} \times p_{H_2}} \; ; \; p_{H_2} = \frac{0.43^2}{2.10^{-7} \times K_{p_2}} = \frac{9.3 \times 10^5}{K_{p_2}}$$

10a) 200°C: log Kp = 6.0; Kp = 10^6; $p_{H_2} = \frac{9.3 \times 10^5}{10^6} = 0.9$

10b) 300°C: log Kp = 5.2; Kp = 1.6×10^5; $p_{H_2} = \frac{9.3 \times 10^5}{1.6 \times 10^5} = 5.8$

10c) 400°C: log Kp = 4.65; Kp = 4.5×10^4; $p_{H_2} = \frac{9.3 \times 10^5}{4.5 \times 10^4} = 21$

10d) 500°C: log Kp = 4.2; Kp = 1.6×10^4; $p_{H_2} = \frac{9.3 \times 10^5}{1.6 \times 10^4} = 58$

10e) 600°C: $\log K_p = 3.9;\ K_p = 8.10^3;\ p_{H_2} = \frac{9.3 \times 10^5}{8 \times 10^3} = 116$

The hydrogen partial pressures so calculated were plotted in Figure 2. It may be seen that the danger of formation of diphenyl (condensation product) is smaller during dehydrogenation at higher temperatures and higher pressures than at lower H_2 pressures and temperatures. The same partial pressure of the aromatic products of 0.67 atm and 0.43 atm is here presupposed, and no side reactions are assumed to take place.

One may compute the magnitude of the partial pressures of the aromatics and oil at different temperatures and H_2 pressures without any resulting strong condensation (diphenyl formation) as follows from the experimental conditions so far used.

11.) Computation for 580°C and 200 atm H_2.

$\log K_{p_2} = 3.9;\ K_{p_2} = 8 \times 10^3 : p_{C_{12}H_{10}} = 2 \times 10^{-7}$

$$p_{C_6H_6} = \sqrt{K_{p_2} \times p_{C_{12}H_{10}} \times p_{H_2}} = \sqrt{8 \times 10^3 \times 2 \times 10^{-7} \times 200}$$

$$= \sqrt{0.32} = 0.57 \text{ atm}$$

Gasoline partial pressure = 0.88 atm referred to 50 g gasoline and 1800 li H_2

11a) Calculation for 525°C and 100 atm H_2.

$\log K_{p_2} = 4.1;\ K_{p_2} = 1.25 \times 10^4;$

$$p_{C_6H_6} = \sqrt{1.25 \times 10^4 \times 2 \times 10^{-7} \times 100} = \sqrt{0.25} = 0.5 \text{ atm}$$

Partial pressure of gasoline 0.77 atm, referred to 50 g gasoline and 1800 li H_2

11b) Calculation for 425°C and 20 atm H_2.

log $K_{p_2} = 4.5$; $K_{p_2} = 3.2 \times 10^4$;

$$p_{C_6H_6} = \sqrt{3.2 \times 10^4 \times 2 \times 10^{-7} \times 20} = \sqrt{0.128} = 0.36 \text{ atm}$$

Partial pressure of gasoline 0.55 atm, referred to 50 g gasoline and 450 li H_2

11c) Calculation for 355°C and 5 atm H_2.

log $K_{p_2} = 4.9$; $K_{p_2} = 8 \times 10^4$;

$$p_{C_6H_6} = \sqrt{8 \times 10^4 \times 2 \times 10^{-7} \times 5} = \sqrt{0.08} = 0.28 \text{ atm}$$

Gasoline partial pressure 0.43 atm, referred to 50 g gasoline and 100 li H_2

11d) Calculation for 290°C and 1 atm H_2.

log $K_{p_2} = 5.3$; $K_{p_2} = 2 \times 10^5$

$$p_{C_6H_6} = \sqrt{2 \times 10^5 \times 2 \times 10^{-7} \times 1} = \sqrt{0.04} = 0.2 \text{ atm}$$

Gasoline partial pressure 0.31 atm, referred to 50 g gasoline and 35 li H_2

Tests according to conditions in the formulas 11) to 11d) are intended to be performed; larger amounts of H_2 result in a saving of the catalyst and are therefore advantageous, and have no effect on the dehydrogenation equilibrium.

/s/ Donath

Fig. 1

Hydrogenation and Condensation
Equilibrium

1. $C_6H_6 + 3\ H_2 = C_6H_{12} + 46.5$

$$K_{p_1} = \frac{p_{C_6H_6} \times p^3_{H_2}}{p_{C_6H_{12}}}$$

2. $2\ C_6H_6 = C_{12}H_{10} + H_2\ -10$

$$K_{p_2} = \frac{p_{C_6H_6}}{p_{C_{12}H_{10}} \times p_{H_2}}$$

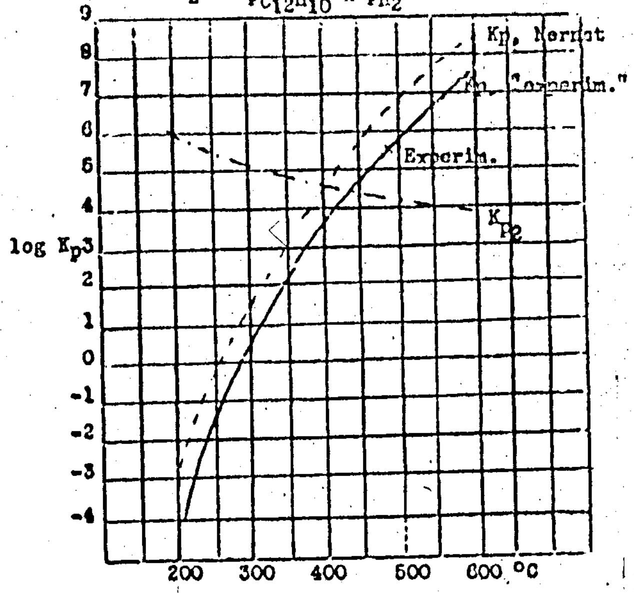
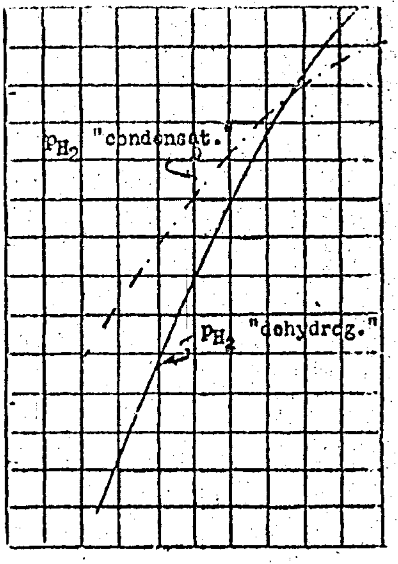


Fig. 2

Partial Pressure of Hydrogen and Temperature
for the Same Dehydrogenation and Condensation
(at $p_{C_6H_6}$ 0.43 atm)

1. p_{H_2} dehydrog. $= \sqrt[3]{K_{p_1} \times p_{C_6H_{12}}} = \sqrt[3]{\frac{0.43 \times K_{p_1}}{0.43}}$

2. p_{H_2} condens. $= \frac{p^2_{C_6H_6}}{p_{C_{12}H_{10}} \times K_{p_2}} = \frac{0.43^2}{2.5\ K_{p_2}}$



UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

T-473

High Pressure Experiments
Ludwigshafen, 558

0180

March 25, 1942
W. M. Sternberg

REFINING OF LIQUID PHASE GASOLINE FROM SCHOLVEN

Scholven liquid phase gasoline (P1305), end b.p. 165°C was refined with the catalysts 7360 and 8376. The conditions were:

Pressure	250 or 50 atm
Temperature	17 - 25.5 m.v.
Thruput	1.0 or 0.5 kg/li/h
Gas:oil	2.0 - 12.0 cbm/kg
CS_2 addition	0.75% to the weight of the feed

Details can be seen in the table.

Comparable tests with catalysts 7360 and 8376 showed the refining was no better with 8376, but the hydrogenation appreciably higher, which was unfavorably reflected in the o.n. The tests with 8376 were run at 250 atm only. At 18 mv, a thruput of 1.0, and 5 cbm gas/kg oil the tests and the iodine number of the product were good. Only 19% aromatics were retained from the original 23%. As a result, the o.n. was reduced by 2. The tests were not satisfactory with higher gasoline partial pressures (3 or 2.5 cbm gas/kg oil).

/s/ Günther

UNITED STATES
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LOUISIANA, MISSOURI

T-474

TOM Reel 173
Frames 699-702

0181

W. M. Sternberg
May 22, 1943

THREE PAPERS ON THE AROMATICS-NAPHTHENES EQUILIBRIUM

I

Dr. v. Muffling has calculated, several years ago, the equilibria for benzene-cyclohexane and for toluene-methyl cyclohexane and presented them graphically in the sheet of curves RSK 5731-16. The material is differently presented in the sheets of curves II and III.

a.) In the Sheet II the relationship between the concentration of the aromatics and the partial pressure of hydrogen in the different temperature ranges can be seen more readily.

b.) Sheet III illustrates the temperature and pressure relationship necessary to produce thermodynamic equilibria at definite concentration of aromatics.

/s/ Peters

0182

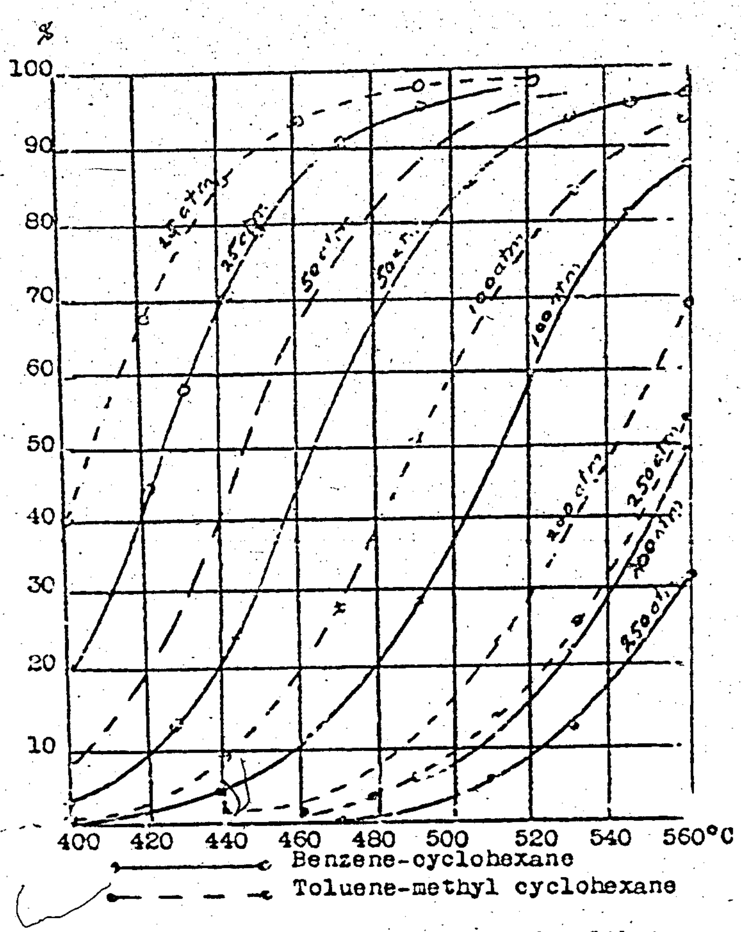

Fig. 1. Aromatics-Naphthenes Equilibria at Different Partial Pressures of H_2

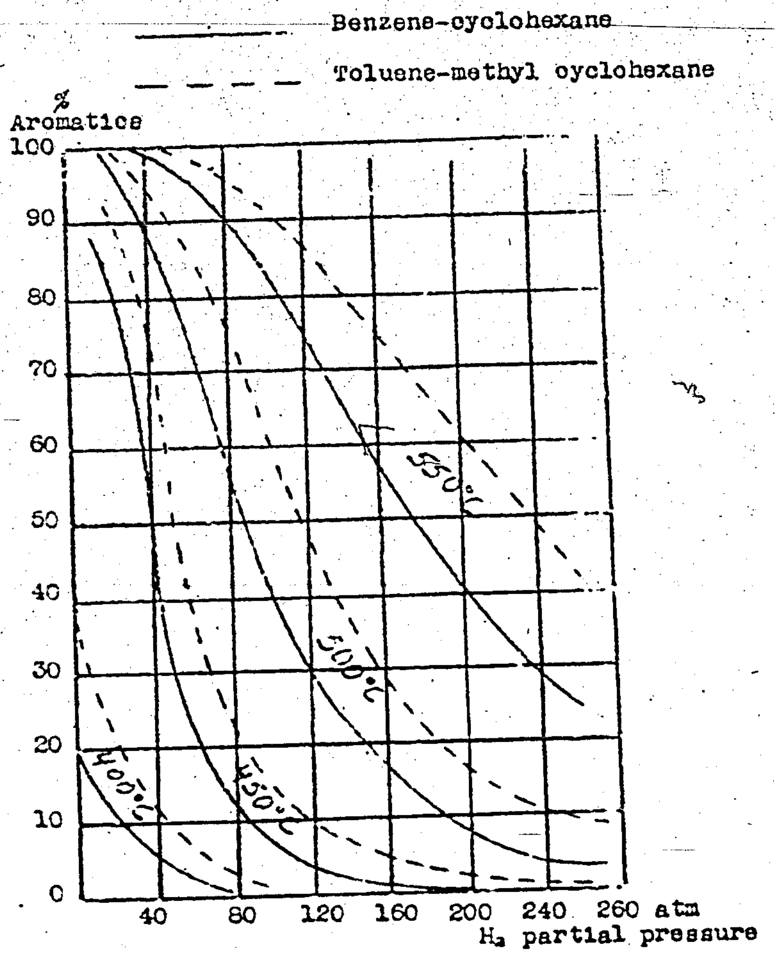

Fig. 2. Aromatics-Naphthenes Equilibria at Different Temperatures

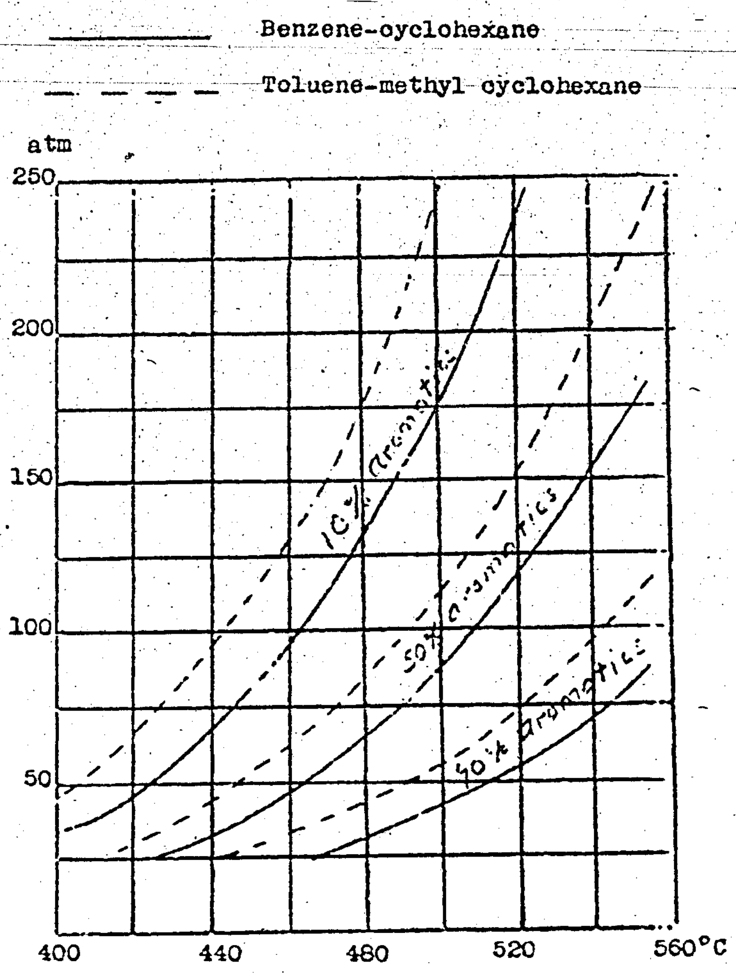

Fig. 3. Equilibria Conditions for Various Concentrations of Aromatics

February, 1940

II

THE PRODUCTION OF AROMATICS-NAPHTHENES EQUILIBRIA ON THE NICKEL-TUNGSTEN CATALYST 6718

Summary:

1.) An aromatics-naphthenes equilibrium is established inside a wide temperature interval upon the nickel-tungsten catalyst with a thruput of 0.5 and a total pressure of 50 atm, regardless of whether one starts with the pure aromatics, with the pure naphthenes, or with an aromatics-naphthenes mixture.

2.) With methyl cyclohexane at a temperature of 460°C an equilibrium becomes established with splitting as a side reaction, which produces at 510°C 2.5% gasification and the formation of benzene as well as toluene. With benzene cyclohexane, splitting has only been observed at temperatures above 500°C.

The production of equilibria of the aromatics and naphthenes on the catalyst 6718 were tested by conducting benzene-cyclohexane 1:1 mixture, or pure benzene, or pure cyclohexane, as well as pure toluene and pure methyl cyclohexane, and their 1:1 mixture. The tests were run at different temperatures and under the usual dehydrogenation conditions over 100 mls of the nickel-tungsten catalyst. The conditions were:

Total pressure	50 atm
Partial pressure of feed	6.5 or 5.5 atm
Hydrogen partial pressure	43.5 or 44.5 atm

Thruput — 0.5 kg feed/li catalyst/h
Gas thruput 2 cbm H_2/li catalyst/h

The products obtained at different operating temperatures were tested for their indices of refraction and the aniline point.

The results of the tests are shown in Tables I, Ia and II and compared with the theoretically calculated equilibria values. The computations were made on the strength of the results of Dr. v. Muffling of June 11, 1939.

Table I (cf. Curves I)

Benzene:Cyclohexane Mixtures (1:1)

Total pressure	50 atm
Partial pressure, feed	6.5 atm
Partial pressure, H_2	43.5 atm
Thruput	0.5 kg/li Cat/h
Hydrogen	200 li/kg feed

Days of Test	°C	Sp.Gr.	Refr. Index	% C_6H_6 by Wt.	% C_6H_6 by Wt. Theor.
1	235-270	0.780	1.4380	19.0	0
4	288	0.776	1.4282	4.0	
5	320	0.776	1.4270	0	
6	357	0.772	1.4240	neg.	
8	374	0.770	1.4248	neg.	
9	400	0.766	1.4242	neg.	4.5
10	425	0.776	1.4318	9	16.5
11	451	0.806	1.4512	39	45
13	467	0.826	1.4685	62	63.5
15	476	0.838	1.4750	70.5	72.5
18	500	0.852	1.4890	86.5	88
19	527	0.854	1.4923	90.2	96
21	552	0.852	1.493	91	98.5
23	400	0.790	1.4348	13.5	4.5
25	485	0.852	1.4822	79.0	80