

FILM STUDY GROUP  
SUBJECT INDEX AND REPORT

T. O. M. REEL NO. 66

Prepared by

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Pittsburgh, Pennsylvania

ABSTRACT AND INDEX OF TECHNICAL OIL MISSION

MICROFILM

REEL NO. 66

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U. S. GOVERNMENT TECHNICAL OIL MISSION

NOTE: The pages in this reel are numbered consecutively. The item numbers are those listed in the T.A.C. Index.

BAG 3445 TARGET 30/5.01

RUHRCHEMIE A.G. STERKRADE-HOLTEN

Frame  
No.

ITEM 9: Oven 11, Filling 13 Complete Records (Cont.)

1

Data sheets for 13th filling of Oven 11, pressure experimental plant using iron catalyst at 20 atm. pressure and a temperature of 200-225°C.

- a) Percentages of benzine, oil and paraffin, specific weight, boiling ranges and olefin content.
- b) Production reports giving gas analyses and amounts of rest gas, synthesis gas, water gas and recycle gas used, conversion and liquefaction figures, yields of products.
- c) Gasol yields and analyses.

Graphical records of % CO and % H<sub>2</sub> conversion and % CO<sub>2</sub> and % CH<sub>4</sub> calculated on CO conversion. Ordinates are temperature and %, abscissas are dates and catalyst hours.

372

Graphical records of rest gas, recycle gas, water gas and consumption, ordinates are temperature and H<sub>2</sub>/CO, abscissas are date and catalyst hours.

Graphical records of % olefins in benzine to 200°C. and oil 200-320°C. Ordinates are % paraffin and % olefin, abscissas are date and catalyst hours.

Percentages of benzine, oil and paraffin, specific weight, boiling ranges and olefin content.

ITEM 10: Graphical Records, January to August, 1944 - Refining

431

Analyses of cuts, light benzine and gas oil, alkazid plant, Diesel oil-caustic, gas oil-caustic.

ITEM 11: Official Test of Iron Catalysts, Data Sheets from 1944

440

Giving gas analysis, total product, olefins, paraffin, alcohols, esters, acids, aldehydes and ketones, yields/m.<sup>3</sup> without and with methane.

<u>ITEM 12:</u>	<u>Data Sheets for Ovens 33 and 34</u>	445
	Days, temperature, m. <sup>3</sup> /h., % contraction, % CO + H <sub>2</sub> conversion, % CO <sub>2</sub> , % CH <sub>4</sub> , % C <sub>2</sub> , g. gasol/m. <sup>3</sup> end gas, g. liquid products/m. <sup>3</sup> gas.	
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	Names of analysts and time required for analyses.	
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	A short report on sulfur removal "Feinreinigung" regarding use of a heat exchanger.	
<u>ITEM 16:</u>	<u>General Synthesis Operation</u>	457
	1. Memorandum of May 22, 1940	
	a) A discussion concerning calculation of yields from analytical data for licensees.	
	b) Quality of catalysts. Complaints regarding catalyst quality may be on account of the quality of kieselguhr used in making the catalysts. Discussion about reduction of the catalyst temperature of reduction should be as low as possible. Care must be taken that containers are closed tightly so that no air may get to the catalyst.	
	c) Short discussion about damages due to the quality of the water used in the medium pressure synthesis plant.	
	2. Memorandum of November 23, 1940	
	a) Discussion regarding supply of rest gas, steam, water gas and coke.	
	b) The "Feinreinigung" (S removal) has to purify <u>75000 m.<sup>3</sup> water/gas/h.</u>	
	c) Conversion plant. Bacteria form H <sub>2</sub> S in the cooling water. This can be inhibited by addition of zinc chloride. Cl <sub>2</sub> is not suitable because it is used up completely in the upper water layers.	
	d) Discussion on poor performances of compressors due to corrosion, especially of packings.	
	e) Data about synthesis: During October 5055 tons liquid products were produced (including gasol 5669 tons). In normal pressure	

synthesis-gasol production was 19-25 g./m.<sup>3</sup> ideal gas, that is 17 per cent, in the pressure synthesis 14-16 g./m.<sup>3</sup> ideal gas, that is 11 per cent calculated for liquid products. This compares favorably with results of other synthesis plants. The ideal gas yields in normal pressure synthesis are 124.9/144.1 g./Nm.<sup>3</sup> and in pressure synthesis 134.6/147.7 g./Nm.<sup>3</sup>; the average for both is 130.2/146.1 g./Nm.<sup>3</sup>. The space velocities are 656 and 586 Nm.<sup>3</sup> synthesis gas/h., respectively, and in medium pressure plants the H<sub>2</sub>/CO is 1.8.

- f) A heater was installed for synthesis gas II. The hot synthesis gas II gives better conversion. The same is intended for the normal pressure plant and for the new recycle project.
- g) Difficulties of emptying the oven in medium pressure synthesis were overcome. These difficulties were due to improper starting and damages by water.
- h) The so-called "wet recycle with injectors" is a success. It consists in starting with the end-gases from the ovens, which contain all reaction products.
- i) Corrosion in the end gas pipes of the pressure plant may be due to electrical corrosion by cobalt dust which deposits in the fine fissures of the pipe. The corrosion was observed only on the bends of the pipe.

ITEM 17: Comparison of Operation Methods at Rheinpreussen,  
Essener Steinkohle and Ruhrbenzin

470

Remarks concerning a lecture of March 11, especially about operation and defects in the synthesis at Ruhrbenzin.

Gas flow. The water gas from the generators flow first into a gasometer; from here it flows through two parallel crude purifiers and then part of the gas goes through the fine purifier and another part directly to the medium pressure plant. Part of the gas coming from the fine purifier is taken off for conversion. Steam injectors are used for conveying the gas. The water gas and conversion gas are blended to a CO/H<sub>2</sub> ratio of 1:1.8.

Of the products obtained, only the paraffin of the medium pressure synthesis is collected separately. The oil and benzine from both plants are collected together and fractionated.

The defects are as follows: Comparing the gas flow of the three plants, it was pointed out that gas mixing at Ruhrbenzin is not intensive because the setting of the CO/H<sub>2</sub> ratio is made directly at the synthesis installation.

In the water gas plant there are several defects, mainly difficulties with the grades and irregularities in the size of coke and its water content.

Due to the lack of Theisen washers, dust and soot are deposited in the crude purification. Furthermore, as soon as the gas from the crude purification contains more than 0.3 per cent oxygen, sulfur precipitates in the fine purification and a long time is necessary before satisfactory operation is again obtained.

Conversion. The variations in steam pressure which occurred rather often are responsible for many variations in the conversion and deficiencies of the synthesis. The bacteria which reduce sulfate to sulfide in the cooling water is controlled by an addition of  $ZnCl_2$ .

The salt entrained with the steam is deposited in the uppermost catalyst layers which gives higher resistance and lower performance. In order to keep these deposits away from the catalyst a coke layer was added but this was not successful. A layer of crushed bricks was better.

Operation. At present an oven is started at  $150^{\circ}C$ . with  $500 \text{ m.}^3/\text{hr.}$  synthesis gas II. Until March of last year an oven was started with  $500 \text{ m.}^3/\text{hr.}$  synthesis gas I and the temperature was increased in such a way that a CO contraction of 60 to 65 per cent occurred. This was maintained for about 36 hours. Then, when the contraction decreased, the amount of gas was increased and the temperature increased until the previous contraction was obtained. The defect of this operation was that during the first 36 hours, the synthesis gas was converted almost completely to methane and appreciable carbon deposition occurred in the upper part of the oven. This upper layer was then unsuitable for further action. In order to avoid these defects, the oven was started with recycling in such a way that at first  $1,000 \text{ m.}^3/\text{hr.}$  end gas II were used and in addition  $500 \text{ m.}^3/\text{hr.}$  synthesis gas I. Contraction was then kept to 45 to 50 per cent for about 1-1/2 to 2 days. It could be observed that methane formation decreased appreciably. After two days the end gas II was reduced to  $503 \text{ m.}^3/\text{hr.}$  and the synthesis gas was increased to  $1003 \text{ m.}^3/\text{hr.}$  After one more day, recycling was stopped and the oven was charged only with synthesis gas. This method had the defect that the amount of gas could not be kept constant and therefore differences resulted in the composition of the synthesis gas. The oven was therefore started as previously in the second stage which avoids larger differences in the composition of the starting gas and makes the control of the oven more simple. Similar to Rheinpreussen, the oven is operated for a few days with  $500 \text{ m.}^3/\text{hr.}$  synthesis gas II, and then increased to as large an amount of gas as possible.

Changing from the first stage to the second stage could not always be done according to plan because the ovens in the second stage did not keep the desired temperature due to low space velocity. This difficulty, however, was not serious because the first stage off-gases are mixed and the ovens for the second stage being new, work at a comparatively low temperature.

Until March 1st, 1940, Ruhrbenzin operated in the same manner as other licensees, namely that the synthesis gas was converted mostly in the first stage (with approximately 60 per cent CO contraction) and only a small part in the second stage (25 to 30 per cent contraction). Considering that this requires using high temperatures in the second stage in order to convert the remaining small amounts of the synthesis gas which causes considerable gasification, the operation was changed to more conversion in the second stage (40 to 50%), similar to operation at Essener Steinkohle. Lowering of the contraction in the first stage could be achieved by increasing the amount of gas or by lowering the temperature. Both methods are milder and therefore decrease  $\text{CO}_2$  and  $\text{CH}_4$  formation. This leaves an end gas richer in CO and  $\text{H}_2$  for the second stage which could be worked up at lower temperature and gave better liquefaction without the danger of too much gasification.

As no conclusive results were obtained by the method, it was discontinued and the old method used again. Temporarily the  $\text{CO}_2$  was washed out of the synthesis gas but the duration of the experiments was very short and did not permit a definite conclusion.

Between September and November, 1939, the CO contraction (rest gas) in the first stage was 58 to 59 per cent; in the second stage, 28 to 30 per cent; a total of 70 to 71 per cent. For the same months of 1940 they were 52 to 54 per cent, 35 to 38 per cent and 70 to 71 per cent, respectively. The CO conversion for these periods is 88 to 90 per cent and 88 to 91 per cent, respectively.

Defects in the synthesis are due to the bad mechanical condition of the ovens (lamella ovens). The defects of these ovens and repairing of the ovens are described extensively.

ITEM 18: Operation Methods at Essen Steinkohle, November, 1940

482

Synthesis gas was produced by adding converted coke oven gas to water gas. Purification was carried out through crude and fine purification and an after purification. Part of the synthesis gas leaving the after purification was taken for conversion and exact setting of the  $\text{CO}/\text{H}_2$  ratio. Another part of the gas was used for pressure conversion and the hydrogen obtained used for hydrogenation in the synthesis ovens (the  $\text{CO}_2$  was first washed out by alkazid). The gas leaving the first stage passed through activated carbon and then into the second stage. The rest gas from the second stage was passed through activated carbon and then to a rest gas gasometer. The oil obtained was separated from water and then sent either to the fractionation or the cracking plant. The AK benzine together with the gasol passed to the stabilizer.

The water gas plant consisted of 10 Koppers generators. The average capacity of 1 generator was  $9000 \text{ m}^3/\text{hr}$ . synthesis gas. The coke used, 40 to 90 mm., had 8 to 10 per cent ash and 5 to 7 per cent water (values up to 17 per cent water occur). Coke consumption was  $0.46 \text{ kg./m}^3$  synthesis gas and  $4.44 \text{ kg./kg.}$  liquid products. Steam consumption was



0.8 to 0.9 kg./m.<sup>3</sup> water gas. The generator was operated for six months.

Operation of the purifier and the difficulties encountered are described. The gas leaving the "Feinreinigung" has 0.5 to 0.8 g. sulfur/100 m<sup>3</sup>.

The conversion plant is from Bamag with a guaranteed performance of a CO conversion to 12 per cent at 7200 m.<sup>3</sup>/hr. and for 4 per cent CO at 6000 m.<sup>3</sup>/hr. The plant was operated with 1000 m.<sup>3</sup>/hr. synthesis gas with a CO conversion to 1 to 2 per cent. The gases leaving the plant had 0.5 g./100 m.<sup>3</sup> H<sub>2</sub>S corresponding to the organic sulfur in the gas.

Hydrogen plant. Data for this plant which was furnished by Bamag are given. The CO<sub>2</sub> and the remaining H<sub>2</sub>S are removed by the alkazid method type "N".

Synthesis. The average period in the first stage was 90 days and the 2nd stage 150 days. Emptying of the oven was carried out not only according to the age but according to the quality of the catalyst. Catalysts of different size (1 to 2 to 3 mm.) and even catalysts with normal and roasted kieselguhr are in the same oven. Ovens which have only normal and only roasted kieselguhr did not show differences. The catalysts are made from Oberohé and AKW kieselguhr and have a cobalt kieselguhr ratio of 1:5.5 and 1:1.7 to 1.8.

Regeneration of the catalyst is carried out at present with hydrogen but should be changed to intermediate extraction. Hydrogenation is carried out at 200°C. with 1000 m.<sup>3</sup>/hr. fresh hydrogen + 3000 m.<sup>3</sup>/hr. recycle hydrogen. The operation takes about 12 hours, of which 4 hours are used for heating and cooling of the oven. Four to five hydrogenations are carried out during the catalyst life; the temperature increase for the first period is a maximum of 192°C., the second period 196°C., the third period 198°C. and the fourth period 200°C.

Extractions prior to emptying the oven are carried out with a heavy benzine fraction at about 90-100°C. and with about 120 m.<sup>3</sup>/oven (5 m.<sup>3</sup>/hr). The extract is distilled at 160°C. and 400 mm. pressure to yield paraffin with a solidification point of 85-90°C. which at 450°C. still contains 4 per cent oil. After the extraction the ovens are dried at 200°C. with hydrogen and emptied.

Operation. Operations are started with about 400 to 500 m.<sup>3</sup>/hr. of off-gas and in the first and second stages sufficient synthesis gas I and synthesis gas II are added so that the gas contains 12% CO<sub>2</sub>. Synthesis gas I contains 4-4 1/2% CO<sub>2</sub>, synthesis gas II 9% and the off-gas 19-20% CO<sub>2</sub>. The starting temperature in the first stage is 150 to 152°C. and in the second stage 160 to 163°C. During the starting period (1st stage 3 days; 2nd stage 2 days) the temperature is raised to 170°C. During this period the amount of off-gas is continually decreased until only synthesis gas flows through the oven. Control is by recording instruments and continuous CO<sub>2</sub> analysis. During starting the CO<sub>2</sub> contraction is kept at 45 to 50%; the first stage then is increased to 53 to 55% and the 2nd stage to 55 to 56%.

Activated carbon plant - size and operation of the plant described.

Further processing: The plant consists of a Carburol unit, a cracking unit, a fractionation plant of Still and the stabilizing plant of Lurgi. The cracking plant is operated at a temperature of 510°C. to yield 25 to 30% Diesel oil, 50 to 55% gasoline and 14 to 15% crack gas. The crack gas contains 50 per cent C<sub>3</sub> + C<sub>4</sub> and 10% gasoline. This gasoline mixed with the activated carbon gasoline has an octane number of 60; the activated carbon gasoline alone has an octane number of 62. The stabilizing plant gives a gasoline boiling from 28°C. to 165°C., 95% to 150°C. It contains 38 to 40% olefins; the C<sub>3</sub>-C<sub>4</sub> contains up to 50% olefins. Losses in stabilizing are 4 to 7%.

ITEM 19: Determination of Branched Chains in Mixtures of Paraffin

494

The report is dated July 11, 1944. The method is based on the fact that isomers boil approximately 5°C. lower than the normal components. The so-called branching number indicates how much branching is present. For instance, normal heptane has a branching number  $z = 0$ ; 2,4,4-trimethylpentane has a branching number of 3; and a mixture of these two compounds of 50 mol % has a branching number  $z = 1.5$ .

The branching number is determined by fractional distillation of a sample in a column of 10 theoretical plates with a reflux ratio of 1:10. The individual cuts are taken at temperatures which are 5°C. higher than the boiling points of the normal paraffin. The amount,  $H_n$ , the molecular weight,  $M_n$ , and the boiling point,  $K_{pn}$ , are measured. A curve is plotted with the temperature as abscissa and molecular weight as ordinate. The temperatures corresponding to the boiling points of the normal paraffins are connected with straight lines and give the so-called zero curve. The branching number  $Z_n$  of the individual cuts is found by subtracting the boiling point  $K_{pn}$  from the temperature  $T_0$  which corresponds to the molecular weight  $M_n$  on the zero curve and the difference is divided by 7.

$$Z_n = \frac{T_0 - K_{pn}}{7}$$

ITEM 20: Standardization of Lubricating Oil Specifications

501

This is a collection of minutes of the Committee to standardize lubricating oils. An extensive index is given for practically every machine, which gives the lubricating oil recommended. The following table shows the eight types of lubricating oils with specifications.

Designation	TYPE							
	2.1E20	3.5E20	2.5E50	4.1E50	6.5E50	9E50	12E50	15E50
Properties								
Viscosity	at 20°				at 50°			
Engler Degrees (E)	2.1	3.5	2.5	4.1	6.5	9.0	12.0	15.0
Tolerance	±0.5	±0.5	±0.5	±0.5	±0.1	±0.1	±0.1	±0.1
Centistokes (CST)	12.8	25.4	16.7	30.2	49.0	68.2	91.1	114.0
Tolerance from	7.4	21.2	11.8	26.2	45.2	60.6	83.5	106.3
to	17.6	29.5	21.1	34.2	52.7	75.9	98.8	121.6
Flash Point, °C.	above 100°	at least 125°	at least 150°		at least 175°		at least 200°	
Behavior in the Cold in U tube		at 0° at least 10 mm. rise in 1 minute				at 5°		
Reaction	neutral							
Neutralization No.	maximum 0.3							
Ash Content	maximum 0.02%							
Hard Paraffin Content	0%							
Water Content	maximum 0.1%							
Solid Impurities	0%							

ITEM 21: A Brief Description of the OXO Process

544

This is a one page description of the processes for reacting unsaturated hydrocarbons with CO and H<sub>2</sub> to form aldehydes using a cobalt thoria catalyst and the reduction of the aldehydes to fatty alcohols.

ITEM 22: Cobalt and Thorium Recovery

546

This paper describes the cobalt recovery from spent catalyst. Investigations have shown that neutralizing the solution with sodium carbonate does not precipitate all cobalt and that it is necessary to increase the alkalinity to a pH of 10 to 11 with potash hydroxide to precipitate the last traces of cobalt. The paper on thorium recovery describes only the separation of iron and thorium from the spent catalyst.

ITEM 23: Joint Investigation of "Abreisstemperatur" of Synthetic Spirits

582

No explanation of the expression "Abreisstemperatur" is given. So-called "ring" tests were made at five different laboratories for four different gasoline qualities. Tables and many graphs are given. The graphs show throughput of the gasoline in liter per hour as abscissa and the "Abreisstemperatur" in degree Centigrade as ordinate. These temperatures are all between approximately 60 and 90°C.

ITEM 24: Synthetic Fuels - Octane Number and Peroxide Formation - Joint Reports

601

This is a report of investigation on synthetic gasoline made by seven companies: Brabag Schwarzheide, Essener Steinkohle, Hoesch, Krupp, Rheinpreussen, RCH and Victor during December 1943.

1. Peroxide formation in synthesis gasoline. No description of the method is given (titanium chloride was used). The peroxide formation is different in the individual plants for the olefins vary as the CO/H<sub>2</sub> ratio. The gasolines from plants which operate their activated carbon units in two stages show the greatest tendency to peroxide formation. There is no connection between the olefin or iodine number and the tendency to peroxide formation.

A gasoline which was investigated several years ago and since that time stored in a closed drum had decreased in peroxide number appreciably; resin had been formed and the octane number had increased again.

2. Relation of octane number and peroxide number. Investigations were made which show the decrease of the octane number with increase of the peroxide number. In medium pressure gasolines, increase of peroxide gives a greater decrease of the octane number than in low pressure gasolines.

An extensive discussion about a "true" method of octane number determination is given. Many tables and graphs are included. A program

of sampling, storage and analysis of synthesis gasolines discussed and agreed upon.

ITEM 25: Monthly Reports of Pressure Experimental Plants 702

These reports summarize the data given in Item 9.

ITEMS 26 and 27: Weekly and Fortnightly Reports 887

Short reports summarizing data from Item 9.

ITEM 28: S.I.C.S. Plant - Wax Production and Recovery 1008

A record giving quantities of the oil condensate and crude paraffin with fresh catalyst and with old catalyst at the plant Arezzo.

Summary:

	Fresh Catalyst	Old Catalyst	
		A	B
Age of the Oven, Days	23-32	118	120
AK Benzine, wt.%	8.5	25.1	25.5
Oil Condensate, wt.%	51.5	71.0	64.3
Crude Paraffin, wt.%	40.0	3.9	10.2
Total Liquid Products	100.0	100.0	100.0
Liquid Product, wt.% of total	92	80	85
C <sub>3</sub> and C <sub>4</sub> , wt.% of total	8	20	15

It was pointed out that these figures are extremes and that current production is intermediate.

A report about operation of the extraction plant "Arezzo" is illegible.

ITEM 29: Details of M. P. Experimental Ovens 1019

Details of medium pressure experimental reactors.

Oven No.	Type Designation
12	Pressure water
12A	Water tube
2	Tube, star inserts
8	Double tube
13	Double tube
14	Pressure Lamella
3	Double tube
3A	Double tube

Oven No. 13, used for runs mentioned in Items 9, 25, 26 and 27.

Manufacturer: Krupp Delivered - Beginning of June, 1940

Weight 750 kg.

Oven Measurements:

Total diameter 320 mm.

Inner diameter 300 mm.

Wall thickness 10 mm.

Maximum pressure:	Working pressure	Testing pressure
On the water side	65	100
On the gas side	20	?

Tubes:

Number: 7

Length: 4200 mm.

Wall thickness: 2.5 mm.

Diameter - inner 74 mm.

outer 79 mm.

Heat conducting inserts:

Heat conducting plates.

Tube volume 14.8 lt.

Catalyst volume 104 lt.

ITEM 30: Views on Theoretical Aspects of Synthesis 1941

1035

Formulas are developed for calculating the analysis of synthesis gas prepared by blending water gas and converted water gas.

This theory attempts to oppose the conception of intermediary  $\text{CH}_2$  formation which has been considered valid but in no way proven. Instead a theory formulating the synthesis of hydrocarbon by means of addition and condensation reaction is proposed. The reactions participating in the synthesis are dependent on the specific state of the catalyst and on certain external conditions of the experiment.

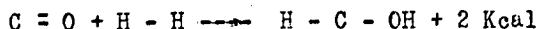
Theoretically, the hydrocarbon formation takes place with a considerable positive heat effect. The heat evolved operates against further maintenance of the synthesis but, on the other hand, reaction may take place in various directions with different heat effects. The synthesis will, therefore, come to equilibrium in the state of minimum heat effect. This is, however, only possible so far as the particular condition of the catalyst permits a thermally favorable reaction.

The conversion of carbon monoxide to methane is accompanied by heat evolution of 76.7 K cal/g. mol. In the formation of ethane, however, less than  $2 \times 76.7$  K cal will result; in formation of 2 mols of propane still less than in 3 mols ethane, etc. Thus, thermally the formation of higher hydrocarbons is favored against the formation of methane.

After the starting period is over, the temperature of the contact is increased very slowly in the region of 180-200°C. This gradual temperature

rise does not have a great influence on the quality and composition of the reaction products. The reason for the temperature increase is only to provide the higher activation energy necessary to equalize the small decrease in catalyst activity. Only at temperatures of 200°C. and higher does a gradually different course of the synthesis start.

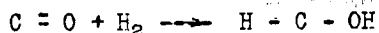
As the fundamental reaction of the Fischer synthesis (of which all other individual reactions are derived), the addition of hydrogen to carbon monoxide is assumed with formation of iso-formaldehyde (hydroxy methylene).



The catalyst can bring about this slightly exothermic primary reaction if the system is supplied with the necessary heat energy. This is done by heating to about 140°C. The catalyst acts here purely as a hydrogenating catalyst due to its fine cobalt dispersion.

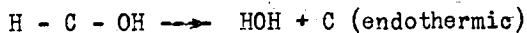
Starting with the primary iso-formaldehyde, hydrocarbon formation is characterized during the starting period by a gradually increasing formation of methane which may be accompanied by a more or less heavy carbon deposit (during this period no liquid products are formed). Therefore, it must be assumed that because of its original state the catalyst prevents the formation of higher hydrocarbons or permits it only in an exceedingly small degree. The changes which take place in the catalyst itself may be a consequence of carbide formation. Unfavorable to the carbide theory is the fact that catalysts do not work satisfactorily with heavy carbon deposits, but this does not mean that slight carbide formation may not have favorable effects. The concentration of the reactants in the synthesis gas and the linear velocity are of special importance in connection with the chemical changes of the catalyst during the development period. During the starting period, the changes of the properties of the catalyst consist in considerable loss of hydrating activity in favor of pronounced dehydrating activity. Parallel to this change in properties, the catalyst decreases in hydrogenating activity with a corresponding increase of dehydrogenating activity.

Based on the primary reaction:



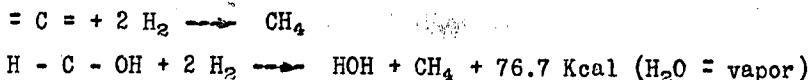
the following individual reactions are developed:

1. During the start, the catalyst activity may be so great that the kinetic energy of the primary products is sufficient to start a spontaneous decomposition reaction:

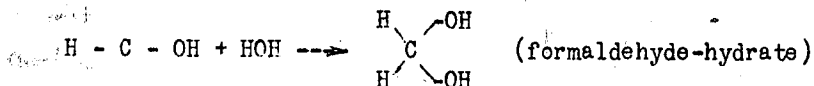


Carbide or carbon formation takes place especially at the first impact of the synthesis gas on the catalyst, and this dehydration is probably due to the dryness of the fresh catalyst.

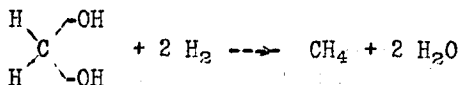
2. The high hydrogen concentration results in hydrogenation of either carbon in statu nascendi or H - C - OH particles to methane.



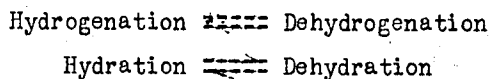
3. After a starting time which leads to the formation of a small amount of water, the catalyst starts to act purely due to its hydrating properties which can be observed by much higher formation of methane. Water addition to one molecule iso-formaldehyde takes place with formation of its hydrate.



This hydrate cannot form higher hydrocarbons but is subject to the strong hydrogenating influence of the system and, therefore, through simultaneous attack of hydrogen on both OH groups, saturation to methane takes place without methanol as an intermediary stage.



The methane formation process is apparently favored by high linear velocities (1) because hydrogenation is accelerated by the kinetic energy of the hydrogen particles and (2) the decomposition of the hydrate to normal formaldehyde is suppressed (short contact time). By continued temperature and chemical influences in the system, changes in the catalyst structure take place which promote the equilibriums:



The changed course of the reaction may be recognized by a decrease in methane formation. At the same time, the synthesis starts to take place in the direction of higher hydrocarbons. Formaldehyde hydrate is dehydrogenated to a peroxidic structure which decomposes to CO<sub>2</sub> and H<sub>2</sub> or rearranges to formic acid. The hydrate may react with CO to yield H<sub>2</sub>, CO<sub>2</sub> and isoformaldehyde or with isoformaldehyde to produce methyl alcohol, CO<sub>2</sub> and H<sub>2</sub>. The acid-forming reaction is the main hindering factor for a successful synthesis because the stable fatty acids formed by secondary reactions act against the desirable producing and maintaining of dehydrating activity in the catalyst.

4. After sufficient formation of the dehydrating activity, the catalyst starts to direct the synthesis to higher hydrocarbons.



The original formation of formaldehyde hydrate is excluded to a large degree (catalyst now dehydrates). Instead, the reaction is started by the direct conversion of the HC - OH moles. At higher linear velocities the HC - OH moles have too high a kinetic energy and change to the normal form. The normal formaldehyde now starts an acyloin condensation. The length of the chain grows, in the reverse ratio of the linear velocity of the  $H_2CO$  particles. This reaction is limited by the secondary dehydrating reactions which cause an increasingly higher strain on the condensing molecule and finally causes breaking of the chain which leads to almost exclusive formation of gaseous hydrocarbons.

5. If aggregation of the HC - OH molecules takes place, then the ideal operation condition for exclusive formation of higher hydrocarbon is attained. All three partial processes (condensation, dehydration and hydrogenation) during chain formation are considered to be simultaneous but taking place with different velocity. If the hydrogenation reaction overtakes the condensation, then chain formation is stopped by saturation. If hydrogenation lags behind condensation, then the increasing strain of the long molecules causes interruption of chain. This second case may be abnormal because then the unsaturated part of two adjacent chains would give branching which is found to only a very small degree in the reaction products. The water from the reaction is proposed to condense in the capillaries of the catalyst. After a certain pH in the capillary water of the catalyst system has adjusted itself, the commencement of orderly chain condensations can probably be started only when the primary product gets on the surface of the water.
6. Through reaction a decrease of linear velocity takes place through contraction in the last part of the reaction tube, even considering all vaporized reaction products. This, in connection with the decrease of CO and  $H_2$ , is the reason for certain "end reactions" which take place parallel to the main reaction. These side reactions are similar in character to the reactions previously mentioned.
7. In the end zone of the reaction system, a limited conversion of  $CO_2$  to methane, or higher hydrocarbons, may take place.
8. Conclusions:
  - a. High linear velocities and high temperatures act favorably for a shortening of the starting time.
  - b. The metallic cobalt must be influenced by a carbide formation.
  - c. Carbonyl formation is considered abnormal and as having a poisoning influence on the catalyst.

ITEM 31: Papers Relating to Erection of Medium and High Pressure Experimental Plants by Lurgi

1067

This item consists of correspondence with details regarding the delivery dates, erection, etc., of a high pressure experimental plant using CO rich gas. Drawings are included for a condenser cooled by ammonia, an experimental generator, heated receiver for paraffins and flow sheet.

Several plot plans and drawings appear at the conclusion of this reel:

BAG 2288 TARGET 30/5.01  
STERKRADE-HOLTEN

- |                                       |      |
|---------------------------------------|------|
| 1. Plan of Works                      | 1102 |
| 2. Apparatus Scheme OXO Plant         | 1104 |
| 3. M. D. Benzine Synthesis Project 22 | 1106 |

BAG 2288 TARGET 30/5.04  
HOESCH BENZIN GmbH

- |                 |      |
|-----------------|------|
| 1. Map of Plant | 1108 |
|-----------------|------|