

FILM STUDY GROUP
SUBJECT INDEX AND REPORT

T.O.M. REEL NO. 65

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ABSTRACT AND INDEX OF TECHNICAL OIL MISSION

MICROFILM

REEL NO. 65

INDEX OF REEL NO. 65

NOTE: The frames of each of the ten sections of this reel start with page 1 and therefore, to avoid confusion, the location of items is indicated by prefixing a Roman numeral to the frame number. Thus I 1 refers to Section I, Frame 1.

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U. S. GOVERNMENT TECHNICAL OIL MISSION

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SECTION IBAG 2708Metallgesellschaft Lurgi, FrankfurtITEM 1:Frame No.

Report from Lurgi on a gasification test with Concordia lean coal for the Lurgi pressure gasification process, operating at 20 atm. pressure.

I 1

The coal size was 5-10 mm and had properties as follows:

H ₂ O	2.66%
Ash	4.05%
Gross heating value	8042 Cal/Kg
Net heating value	7774 Cal/Kg

The gasification was conducted with gas containing 84% oxygen. The purified gas contained CO₂ 1.5%, CO 21%, H₂ 56%, CH₄ 18.6%.

ITEM 2:

Report of test on Wiesche lean coal regarding suitability for use in the Lurgi pressure gasification process.

I 3

Coal analysis

Size	3-10 mm
Fixed C	81.24%
Volatile matter	7.10%
Ash	5.04%
Moisture	6.56%

The gasification was conducted with gas containing 84.7% oxygen. Analysis is given for the gas produced at 10, 15 and 21 atm. and extrapolated values for 30 atm. CO₂ remains practically constant at about 27%; CO increases with increase in pressure from 17.5 to 22.2%; H₂ decreases from 43.8 to 33.3; CH₄ increases from 9.1% to 13.9% and the ratio H₂/CO decreases from 2.49 to 1.5.

The test was successful; the ash was fine-grained and not sintered; the yield of gas was favorable: 1690 Nm³ purified gas per ton of coal with an oxygen consumption of 198 Nm³. Steam consumption was 1.4 Kg per Nm³ of purified gas. These figures are higher than with brown coal, probably due partly to the low volatile content and the somewhat low reactivity of the coal.

Graphs are given for temperature, % CO and H₂ in the crack gas and purified gas, and net heating value.

ITEM 3: Report of test on Upper Silesian coal (bituminous coal) to determine whether the coal is suitable for the Lurgi pressure gasification process and whether a synthesis gas of a CO/H₂ ratio of 1:2 can be made directly. I 11

Analysis of coal:

Size	3-10 mm
Ash	6.4%
Fixed C	54.1%
Moisture	7.2%
Volatile matter	32.3%

The generator was operated at a pressure of 5 atm. with a mixture of oxygen and steam. The consumption of 83.2% oxygen was 0.186 Nm³ and 465° C. steam consumption was 0.975 Kg. per Nm³ of purified gas.

Data on purified gas:

CO ₂	1.0%
CO	30.3%
H ₂	60.6%
CH ₄	5.5%
Gross heating value	3370 K Cal/Nm ³
Efficiency (gas and tar)	85%

The figures show that the coal is very useable for the production of synthesis gas and that a ratio of CO/H₂ of 1:2 can be obtained. The economic aspects are good, because the mining costs for Upper Silesian coal are low and a high grade, low temperature tar is obtained as by-product.

Handwritten sheet in English: The bituminous coal described contained 32.3% volatile matter. It was used to produce synthesis gas, and an oxygen pressure of only 5 atm. was used in consequence. It might be possible to use the process, fluxing the ash from bituminous coals by introducing the steam for the methane process above the introduction of the oxygen, which would be supplied with only part of the steam. Steam/O₂ ratio in the 5 atm. process is much higher than in normal operation, the methane content being reduced to 5% approximately.

ITEMS 4 & 5:

assembly of pressure generator, two drawings.

I 17

SECTION II

BAG 1481A

Thyssen Galocsy Slagging Gas Producer

ITEM 1:

Report by Thyssensche Gas & Wasser Werke describing the process (in English): II 1

The application of an oxygen instead of an air-blast for the gasification of solid fuel has become economically interesting since the Linde-Frankl process has made possible cheap oxygen production when large quantities are required. Lignite has already been gasified on a large scale with oxygen in Winkler gas producers. Technical difficulties, especially insufficient durability of refractory materials at the high temperatures attained, have prevented until now similar large plants for non-caking bituminous coal.

The T.-G. process overcomes this difficulty by conducting the combustion with oxygen in two steps, either of which can be easily controlled. In the first step a mixture of oxygen and steam is blown into an entrance-chamber of the producer where a quantity of any combustible matter is ignited so that the resulting gas mixture is heated up to the temperature at which steam and carbon dioxide are able to react rapidly with hot carbon. In the second step this hot mixture is admitted to the solid fuel in the shaft of the producer with such a content of superfluous oxygen, that the heat produced by the combustion of carbon to carbon monoxide exactly supplies the demand of heat for the decomposition of steam and carbon dioxide, the smelting of slack, and, if desired, the reduction of ore. Any excess of temperature, which could destroy the refractory shaft lining, is however avoided.

The industrial producer is similar to a blast-furnace. The lower part has several burners, each having an entrance-chamber for the above-mentioned primary combustion. Preferably auxiliary-gas is ignited therein. If no cheap gas or other combustible material is available for this purpose, a part of the produced gas is used. By such means no surplus of fuel is consumed because the products of combustion are reduced in the second step to carbon-monoxide and hydrogen, consuming thereby exactly the heat gained by the combustion in the first step.

After having studied the process for several years in a semi-industrial producer, consuming 2 tons of bituminous coal daily, a producer of industrial scale with complete testing facilities was erected during the war. This plant used surplus oxygen from a synthetic ammonia plant and produced gas for hydrocarbon synthesis. An existing shaft-furnace, 12 m. high, 28m³. volume and with an internal diameter of 1.35 m. at the burners, was adapted to test the system.

With the maximum available quantity of 29,800 Nm³. of 85.5% oxygen or 20,300 Nm³. of pure oxygen a day, the producer consumed 47 tns. of metallurgical coke, thus producing 105,400 Nm³. of gas of 2,600 kcal heating value, that is, 274 x 10⁶ kcal/day. A three day test at the above consumption, using only 4 of the 5 installed burners, demonstrated that the maximum output was not reached with the available quantity of oxygen. The producer was in satisfactory operation for several months in spite of many war-time interruptions. The producer itself has never been damaged and can start operation if the synthetic ammonia plant is able to supply oxygen.

Technical advantages.

Continuous working, simple construction, no change of valves during the run, no mechanical device or operation except charging fuel and tapping of slag (and iron, if desired). Application of approved procedure and methods of gas-producers and blast-furnaces greatly increased output in comparison with existing plants, highest thermal efficiency on account of low nitrogen content, total gasification without any loss of combustible in the slag. Recovery of by-products of the low-temperature-distillation type. Immediate adaptability of the output to the consumption. From cold start to full run in 12 hours.

Economical advantages.

Utilization of nearly all available and cheaper combustibles for total gasification instead of classified coke or producer-coal. Thus, coal with a high ash content or not suitable for coke-production may be used. If required, ashes may be mixed with the coal to prevent caking in the shaft. Cheaper gas for industrial heating and synthetic processes. Production of large quantities of low-temperature tar as by-product.

Applications

Production of large quantities of gas, from 100,000 to 1,000,000 Nm³/day in a single unit, with a low content of carbon dioxide and nitrogen, and consequently of high combustion temperature with a calorific value of 2,700 to 3,100 kcal/Nm³ depending on the combustible gasified. Especially suitable for 1. Heating-gas for industrial plants. 2. Gas for synthesis of hydrocarbons, securing nearly the theoretical amount of liquid products. Since the waste gas of the synthesis is poor in nitrogen, it can be returned almost totally as auxiliary gas to the burners. Methane and other undesirable hydrocarbons thereby become regenerated to gas for the synthesis. 3. Gas for hydrogenation processes, the conversion of carbon monoxide with steam to hydrogen and carbon dioxide being performed in the upper part of the shaft. 4. Gas for the supply of towns and industries, either indirectly by heating coke-ovens, setting free an equivalent quantity of distillation gas, or directly by converting part of the produced gas to methane for enriching the calorific value. 5. In blast-furnaces for the reduction of iron ore. The process decreases the costs of plant and operation. Air heaters are not needed, since preheating takes place in the entrance-chambers of the burners; smaller furnaces and blowers are required on account of low nitrogen content.

ITEM 2:

Operating report of the Thyssen-Galocsy Producer

II 5

Four runs were made but the results are not very significant because every run was interrupted either by attack from Allied planes or because of a shutdown in a plant supplying oxygen, etc.

The results showed, however, that the arrangement of the burners should be changed and that the temperature of the slag should be kept higher than in blast-furnace operation. Tuyeres were arranged in a manner similar to a blast furnace, and the temperatures could be kept constant at the tuyeres, between 1400 and 2000°C. as desired. The slag ran off smoothly.

Some results:

Oxygen:	CO ₂	2.8%	Net heating value	2735 Kcal/Nm ³
	CO	70.4%	Steam decomposition	90%
	H ₂	23.1%	Total Gas Calorific Value	= 85.2
	CH ₄	0.2%	Fuel Calorific Value	

Oxygen used was 90% purity.

Consumption per 1 Nm³ Oxygen:

Oxygen (100% purity)	.29 Nm ³
Steam	.21 Kg
Coke (6865 K Cal/Kg)	.46 Kg

ITEM 3:

Plan of site of Generator - 4 prints. Plans of generator with arrangement of burners and cooling boxes. II 8

ITEM 4:

Estimation of cost for 1 generator of 12000 m³/hour gas output, including buildings but excluding railway siding, pipe lines outside, gasometer and cooling tower, giving a total of 875,000 RM. II 12

SECTION III

BAG 1928a

Material from Dr. Sachsse's Office

Ludwigshafen-Oppau

Index to Section III

III 1

Production of synthesis gas and acetylene by partial combustion of methane and other processes.

ITEM 1.

Report in which Dr. Sachsse criticizes an offer of Linde for a two-chamber generator process for synthesis gas. Linde's data are considered to be an optimistic estimate and to be inaccurate. III 3

ITEM 2: Calculations for the Ferngas (gas obtained from a distant place) splitting plant N Oppau III 6

Heat calculations for cooling and heating with flow sheet, indicating the temperatures of a cooling-evaporating system N3155-16 and a flow sheet N3156-16 stating volumes and percentages of 7000 m³/h of gas for Saar gas splitting plant N Oppau 631 through the CH₄ and CO converters to the high pressure apparatus.

ITEM 3: Detailed cost estimate for new Oppau plant III 18

Request for appropriation of 1,900,000 RM. to enlarge a plant for the production of synthesis gas and acetylene from methane and oxygen. 8 sheets give itemized cost estimates.

ITEMS 4 & 5: Request of Saar Ferngas Co. for price increase III 27

Detailed criticism with cost calculation for converting 14,000 m³ Ferngas to 26,580 m³ split gas (54% H₂, 20% CO, 1.9% CO₂) to converter gas (60% H₂, 3.5% CO, 16% CO₂) equivalent to 19,400 m³ H₂ + CO using oxygen, steam and catalyst. Total 7.27 RM/1000 m³ H₂ + CO.

ITEM 6: Supplement to 4 III 34

ITEM 7: First production of new Oppau plant III 35

The value of the synthesis off gas (CO 24.6%, H₂ 45.7%) is taken equal to the value of the waste gas from the butyl plant (CO 39.2%, H₂ 35.2%) with which it is mixed.

ITEM 8: Calculation for enlarging the coke oven gas splitting plant in Linz (N plant) III 36

Calculations of heat of reaction, heat balances and cooling of gas in heat exchangers. Graph for heat balance of water in a cooling-moistening cycle. Flow sheet for converting 7000 m³ coke oven gas + 3770 m³ air + 441 m³ O₂ in CH₄ and CO converters to 16,200 m³ split gas containing 10350 m³ CO + H₂ (with gas analyses).

ITEM 9: > Calculations for a coke oven gas splitting plant K Oppau III 53

Calculation of operating expenses for a plant for converting 7000 m³/h coke oven gas in one unit. No figures for labor are included.

Discussion of Brabag with I. G. concerning acquisition of the gas splitting plant Schlesien Benzin which was started but will not be finished. I. G. gives data on cost and possible use of the plant for Brabag, where 8000-10000 m³/h of Hy waste gas of the following composition is available:

CH ₄	31%
C ₂ H ₆	19%
CO	2.5%
C ₃ H ₈	2.4%
C ₄ H ₁₀	0.25%
C ₅ H ₁₂	0.08%
H ₂	38%
N ₂	5%
Net heating value	6534 K Cal/m ³
Organic sulfur (as COS)	50 mg/m ³
H ₂ S	None
Gas at 5 atm. pressure	

ITEM 11: Comparison of composition and cost of gases from various sources.

III 69

Shown in table form.

ITEM 12: Comparison of Koppers and I.G. Röhrenofen (tube oven) process May, 1941, (D.R.P. 570026)

III 70

Letter of I.G. to Brabag giving comparative figures for cost and operation of a Hy-gas split gas plant, in which it is shown that the I.G. process is by far better and cheaper than the Koppers process.

ITEM 13: Calculations for coke oven gas splitting plant N Heydebreck

III 79

Calculations same as in Item 8.

ITEM 14: Supplementary Material to Item 12, September 1941

III 90

The Koppers Company has reduced the cost for the plant which is now practically the same as for the I.G. Röhrenprocess. In addition the Koppers Company offers to guarantee every item in their proposal and to make all repairs for 2% of the cost of the plant (as estimated in their offer) for ten years. I.G. assumes Koppers makes these favorable conditions to get the business and to collect data and experience on their process in operation.

ITEM 15: Supplementary Material to Item 12

III 92

Letter I.G. to Brabag of October, 1941, indicating that the 5% cost for repairs in the offer includes everything, but I.G. refuses to give guarantees.

ITEM 16: Supplementary Material to Item 12, October, 1941

III 93

Calculation of cost of operation for the I.G. process. Labor given as 5 man hours for processing 1000 m³ gas.

ITEM 17: Supplementary Material to Item 7

III 95

Data are given for the value of the butyl waste gas used in the Oppau plant from September, 1940 to September, 1941. An average of 12 million m³/quarter was processed.

ITEM 18: Heat balance of I.G. Röhrenofen process

III 97

Calculated from operations on two different days in Pölitz. Comparison is made between the efficiency of splitting of 79.7% with the gasification efficiency of a watergas generator with steam production of maximum 67% efficiency.

ITEM 19: Calculation of heat balances for the methane splitting plant in K plant - Heydebreck

III 103

Heat balance calculations for converter, heat exchanger and cooler are given. Handwritten note in English: Calculation relating to production of CO and H₂ according to $2\text{CH}_4 + \text{O}_2 \longrightarrow 2\text{CO} + 4\text{H}_2$ in the presence of steam including calculated heat balances for two systems. The calculations suggest that the CO + H₂O reaction takes place to some extent as the calculated product is CO₂ 7%, CO 23.8%, H₂ 69%, CH₄ 0.2%.

ITEM 20: Comparison of Röhrenofen and Partial Combustion Process for Production of hydrogen from natural gas.

III 114

Comparison of the I.G. Röhren process (Schiller) with the Sachsse process for conversion of Bentheim natural gas at Huels. Available are 150,000 to 200,000 Nm³/day natural gas of the following composition:

O ₂	.08%	CH ₄	94.7%
CO	.23%	C ₂ H ₆	0.35%
N ₂	4.63%	CO ₂ + H ₂ S	200 mg/Nm ³ (??)

1. Röhrenprocess (Schiller)

The methane is freed from H₂S and organic sulfur, preheated in a recuperator and led into the so-called Röhrenofen in which the conversion $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{H}_2$ takes place. The contact (catalyst) of the oven is marked BZZ041. It

consists of 20% nickel on alumina cement and is in NCT₃ tubes, which are heated from outside. During operation the temperature of the catalyst is 750°C, the temperature of the walls of the tubes is 900°. The split gases leaving the oven have approximately the following composition:

CO ₂	8%	N ₂	2%
CO	13%	CH ₄	1%
H ₂	76%		

The gases are led through a recuperator in which they preheat the gases going to the oven and then are led to the CO conversion. The flue gases from the Röhren oven go to a waste heat boiler in which steam of 20 atm. is produced. The waste heat from the CO converter may be used to preheat the Röhren oven fuel gas. The hydrogen coming from the CO converter has the following composition:

C Hy	1%	N ₂	2%
CO	3% (min. 1.5%)	H ₂	94%

One Röhren oven contains 66 NCT₃ tubes and has an output of 15000 m³/h split gas. Calculated for natural gas, the increase in volume during methane conversion is 3.7 times the entering gas or calculated for methane 3.9 times. Each unit may be operated, therefore, with 4000 m³/h methane. The requirement on fuel gas for heating the ovens is 1050 heat units/m³ CO + H₂ and 4.5 tons/h of 20 atm. steam are produced in the waste heat boiler. For the methane conversion there is used 1.72 Kg steam/m³ methane.

It is possible to produce in the Röhren oven a CO-H₂ mixture suitable for methanol synthesis, by adding some CO₂ to the gases entering the oven.

The investment for 3 Röhren ovens, fuel gas production and CO conversion amounts to 4.8 mill. R.M.

Instead of NCT tubes, CMT tubes may be used.

2. Sachsse-Process

Methane is converted to a CO + H₂ mixture by partial combustion with oxygen. The largest type of oven, operated with coke oven gas, has a capacity of 15000 m³ CO + H₂ mixture per hour. The volume increases threefold, and the unit may be operated with 5000 m³/h methane. A maximum of 1 mg(?) sulfur/m³ of entering gases is permissible. Therefore the gas after passing the alkacid purification must be

purified further. Two + one units are necessary, and the gas leaving the ovens has the following composition:

CO ₂	5%
N ₂	2.3%
CO	26.0%
H ₂	66.0%
CH ₄	0.2 - .3%

The highest temperature in the partial combustion zone is 1200°C. After the combustion zone, a catalyst (magnesite) is contacted to obtain practically total conversion of methane. In order to activate the catalyst, 1 mg nickel/m³ is added to the gas entering the oven. The temperature of the gas leaving the oven is 700°C.

Methane and oxygen are preheated separately in heat exchangers with Sichromal tubes through which pass the exit gases from the oven. The preheated gases pass through the combustion oven and the contact and are then freed from soot in the so-called Sachsse filter. The gases then pass to a CO converter. In a pilot plant 2000 m³ methane/h have been converted by this process. The investment for three ovens with a CO conversion unit and "Linde" plant for making 5000 m³ O₂/h would be 4.2 million R.M.

A table is shown comparing both processes regarding amounts of raw materials, fuel gas, steam and investment costs.

ITEM 21: Patent on partial combustion process for ammonia synthesis gas. III 119

O.Z. 14396 September 10, 1943 I.G. Farbenindustrie

Process for the production of a gas for the ammonia synthesis by splitting the off-gas from the Fischer-Tropsch process with steam and/or oxygen or oxygen containing gases, and under certain circumstances carbon dioxide.

ITEM 22: Patent on acetylene production by partial combustion III 128

O.Z. 12010 February 12, 1940 I.G. Farbenindustrie

A device for producing acetylene by partial combustion of hydrocarbons with oxygen in a flame reaction, characterized by using a practically empty reaction chamber in which the dimension in the direction of flow does not exceed 200 mm., this being the largest dimension. A parallel tube distributor precedes the reaction chamber and a water quench is used at the exit.

ITEM 23: Cost estimate for production of 70% acetylene and synthesis gas by partial combustion III 134

This cost estimate is based on converting hydrocarbons to acetylene (9.3%) by the oxygen process, followed by concentration of the acetylene by washing with water under pressure. There is obtained acetylene of 70% concentration, the remainder being carbon dioxide.

1. Calculation for processing 3070 m³/h C₂H₆ and producing 1000 m³ split gas containing 9.3% acetylene (low pressure)

Fuel gas	4.5 million heat units
KWH	120
Labor	5 men
Water	160 m ³

2. Calculation for concentrating acetylene including compression to 30 at. Incoming gas 10000 m³ split gas.

KWH	2250
Water	300 m ³
Labor	3 men

ITEM 24: How to operate the acetylene burner

III 165

1. Detailed instructions on how to operate the acetylene burner. (October 1, 1942)
2. Detailed instructions on how to operate the acetone oven. (October 1, 1942)
3. Drawings
 - a. Burning chamber of splitting oven.
 - b. Acetylene burner.
 - c. Determination of flame velocity by the Bunsen method.
 - d. Arrangement for determination of flame velocities of motor fuels.
 - e. Schematic representation of temperature increase of the flame front.
 - f. Flame velocities of propane-oxygen mixtures at different temperatures.
 - g. Flame velocity of methane with 37% oxygen at variable temperatures.
 - h. Flame velocity with change of air number.
 - i. Flame velocity with change of temperature of flame.

- k. Velocity of extinguishing as a function of diameter of burner tube.
- l. Distance of base of flame from burner tube. Methane and ethane.
- m. Same for propane.
- n. Velocity of extinguishing for different forms of nozzles.
- o. Schematic representation of the concentration and velocity at the outlet of the gas jet.
- p. Distance of base of flame from the tip of the burner as a function of throughput.

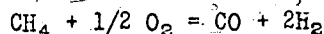
ITEM 25: Paper on Burning Velocity by Dr. Sachsse

III 196

A. Processes in which the Flame Velocity is Important

1. The Oppau-oxygen Process for producing synthesis gas.

This process concerns the conversion of hydrocarbon containing gases, such as coke oven gas, with oxygen to a mixture of CO and H₂ according to the equation:



This equation is only a general equation for the total conversion. Actually, two steps are involved. The coke oven gas, pre-heated to 600°C, is reacted with oxygen or air-oxygen mixtures. Part of the hydrocarbons is converted, and the temperature of the gas mixture increases to 1300°C. These gases are led over a nickel-magnesia catalyst on which the remaining hydrocarbons are converted to CO and H₂ with consumption of heat. The temperature falls to about 950°C. The latest oven has a burning chamber attached to the side and a tangential inlet for gas. This oven is used in several installations, and at the present time 13 units with a total gas production of more than 200,000 cubic meters per hour are in operation in Waldenburg, Linz, Hydebreck, and Oppau.

The Oxygen is introduced centrally to the burning chamber in the same direction as the gas, but flowing with a greater velocity. The object is to have as uniform and complete a combustion as possible in the burning chamber. In order to improve mixing, the oxygen stream is given a vigorous spin by inserting guiding plates into the nozzles. In this way mixing is obtained after traveling 1-1/2 diameters of the outer burning tube. This amounts to 100 centimeters. This mixing, however, can be carried too far in which case the flame pulls off and extinguishes because a

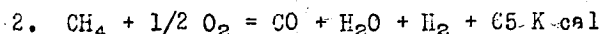
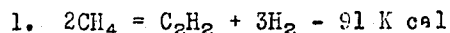
great deficiency of oxygen is employed. Only a small part of the gases should be burned and, therefore, the flame velocity is less than in complete combustion. If mixing is too extensive the regions of high oxygen content, and thereby high flame velocities, are eliminated. Such conditions are always present when using an air number which is much different from $\lambda=1$. This is, for instance, the case with rotary furnaces which have an excess of air or flue gas.

For a burner tube of 700 mm, diameter, a throughput of approximately 23,000 cubic meters per hour is used at a velocity of 85 meters per second. Furnace engineers predicted such an oven would be unable to withstand this load but up to the present no difficulties have been experienced probably because the gases are clean and free of dust.

2. The Acetylene Process

In the process described above the flame velocity was important, but in the acetylene process the flame velocity is of decisive influence; in fact, so decisive, that it is one of the claims of the patent.

The energy consumption is of great importance in acetylene production and, therefore, attempts were made to conduct the reaction in such a way that the heat produced by burning part of the methane converted the remaining methane to acetylene. The following equations describe the reaction:



The time is of the order of .01 of a second, and the temperatures lie between 1400 and 1600°C. At lower temperatures no acetylene is formed, and at higher temperatures it decomposes very rapidly into hydrogen and carbon black. Methane and oxygen are pre-heated separately to the ignition temperature which lies between 400 and 600°C and then led into the mixing chamber. Here the gases are mixed to obtain a mixture of, for instance, 63% methane and 37% oxygen at 500°C. This mixture is within the ignition limits and could react, but it does not react because it does not stay in the mixing chamber long enough and there is no motive for ignition. This gas mixture flows through canals into the burning chamber and burns stationary after ignition. The mixture has a certain flame velocity, corresponding to its composition and temperature. The dimensions of the oven are such that

the gas velocity in the feeding canals is greater than the flame velocity, and the gas velocity in the burning chamber is smaller than the flame velocity. At the spot at which the gas leaves the feeding canals and the flame burns, it always progresses against the gas stream but cannot enter the feeding canals because the gas velocity is too great. The gas is cooled suddenly when leaving the burning chamber by spraying with water. It is thereby possible to keep very exact reaction conditions with suitable dimensions and loads of the burners, and the yield of acetylene from methane is almost quantitative. The part of methane which is converted into carbon monoxide and hydrogen according to reaction 2, amounts to approximately one-third of the total methane. The process, therefore, is a combined procedure for the simultaneous production of acetylene and synthesis gas. The production of synthesis gas from methane is interesting as such and, therefore, it is possible to produce acetylene especially advantageously where synthesis gas is required. The process is technically carried out in Oppau. One burner processes 1000 m³ per hour, and a plant for large output is under construction in Hydebreck.

B. General Investigations of Flame Velocities

1. Flame Velocity in Mixtures

Flame velocities as a function of reaction velocity of combustion, transfer of energy to the fresh gas, and final temperature of the flame are discussed.

2. Flames of not Pre-mixed Gases

Flame velocities when gas mixing and combustion occur together are discussed.

ITEM 25: Calculations on production of acetylene and acetone.

III 205

(a) Calculation for conversion of 4140 m³/h methane to 670 kg acetone.

(b) Calculation of heat balance of acetylene burner, in acetone oven and for catalyst regeneration.

Extensive calculations of heat balances are given.

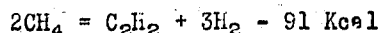
ITEM 26: Short Memo on Production of Acetylene and Acetone.

III 215

The Incomplete Combustion of Methane with Oxygen.

Methane and oxygen are pre-heated separately, mixed and subjected to a flame reaction. In the flame, which has a temperature of 1300-1400°, part of the methane burns according to $\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2 + \text{H}_2\text{O} + 65 \text{ kcal}$ while another part is converted by endothermic reaction to

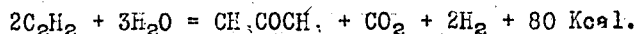
acetylene.



From 100 m³ CH₄ and 57 m³ O₂, about 190 m³ of gas is produced containing 8-9% C₂H₂, 3-4% CO₂, 24-25% CO, 55-58% H₂ and 4-7% CH₄. The time of contact with the flame is of the magnitude of .01 second. After passing the flame, water is sprayed into the gas stream to suppress further decomposition of acetylene. Split gas of the above-mentioned analysis leaves the burner saturated with steam at approximately 85°C.

Acetone from Acetylene

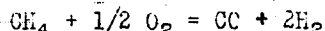
Split gas, while still hot, is freed from carbon black and after passing a heat exchanger, is converted to acetone at 400° with a zinc oxide catalyst.



For chemical reasons the reaction needs a very large excess of steam (C₂H₂ to H₂O = 1:10) and it is conducted on a dilute gas in order to better control the heat of reaction. The split gas retains 0.2-.4 acetylene.

The gas containing the acetone is washed with water, to obtain a 2% acetone solution which can be concentrated by distillation to pure acetone.

In the residual gas, the 4-7% residual methane is converted by combustion,



to yield a synthesis gas which is free of nitrogen and sulfur.

Procedure for Concentrated Pure Acetylene

Experiments to obtain concentrated pure acetylene by washing of the split gases with an organic solvent (butyrolactone) have been made.

ITEM 27: Report on Production of Acetone

III 217

A survey concerning the various methods of acetone production.

(a) Wood distillation; (b) Fermentation; (c) Propylene hydration and dehydrogenation; (d) Acetylene hydration followed by oxidation to acetic acid and then conversion to acetone. Discussion of the use of ZnO in a single stage process.

ITEM 28: Short Memo on Development of Diacetylene Chemistry at Huels, April 29, 1943.

III 227

In the production of acetylene by the arc process in Huels, considerable amounts of diacetylene, vinylacetylene, methyl and

phenylacetylene accumulate as by-products. The separation and use of these higher acetylenes are discussed.

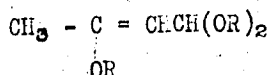
ITEM 29: Memo on Addition of Alcohol to Diacetylene.

III 229

Methanol containing alkali (1%) was diluted with about twice the amount of dioxane and reacted with diacetylene or the mixture of diacetylene and methanol at 75°C. Methoxy vinylacetylene, b.p. (760) 116-120° C was formed.

If the concentration of alkali and the temperature are raised, 2 moles of alcohol can be added. The addition takes place in 1-4 position and gives butynacetals of the type formula $\text{CH}_2\text{C} \equiv \text{C} - \text{CH}(\text{OR})_2$.

These butynals add a further molecule of alcohol to the triple bond and give alcoxycrotonaldehydeacetals, in which the alcoxy group is in β position:



ITEM 30: Patent Application on Solvents for Acetylene.

III 231

O.Z. 14333 July 22, 1943 I.G. Farbenindustrie

It was found that lactones, especially γ -butyrolactone, have good solvent action for acetylene. The lactones are superior to acetone because they have a high boiling point (e.g. butyrolactone boils at 204° and solidifies at -40°) and much purer acetylene can be obtained from solutions because only small amounts of solvent escapes with the acetylene.

Due to their high boiling point and good solvent power, lactones may be used for washing out acetylene from gas mixtures, such as gases from treatment of saturated hydrocarbons in the electric arc.

ITEM 31: New facts from the acetylene and carbon monoxide chemistry.

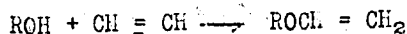
III 234

Lecture Dr. Reppe, June, 1944

Dr. Reppe gave a review on his extensive research work on reactions with acetylene or carbon monoxide, which he carried out in Ludwigshafen during the last years, showing many formulas and samples.

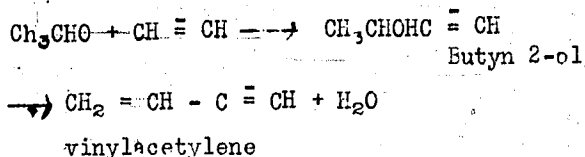
(a) acetylene chemistry

Starting point of the work was the problem of introduction of the vinyl group in suitable organic compounds, e.g. the synthesis of vinyl ethers according to



The reaction between acetylene and ammonia does not give the vinylamine as expected, but 2 methyl 5 ethylpyridine. By

suitable oxidation, this can be converted to nicotinic acid, which may be used for synthesis in the nicotinic acid series. The second group of reactions comprises the introduction of the $\text{CH}\equiv\text{C}$ group into organic compounds. It is applicable to many classes of compounds with reactive hydrogen and opened the way for the synthesis of countless new compounds. Farthest advanced technically is the action of acetylene on aldehydes and ketones (alkynol synthesis). It is used on a large scale for the butadiene synthesis by way of butyndiol. The alkynol synthesis permits the synthesis of complicated compounds with several double or triple bonds, e.g. vinyl acetylene by way of butyn 2-ol.



The third group of acetylene reactions concerns cyclo-octatetraene. This eight-membered ring with 4 double bonds can be synthesized catalytically by polymerization of acetylene, and up to now it was known only as a laboratory curiosity. The study of cyclo-octatetraene and its reactions has shown that its behavior is not uniform and that it can react according to several structural formulæ.

(b) Carbon monoxide chemistry.

A systematic study of the reaction of carbon monoxide with unsaturated aliphatic compounds showed that probably cyclic intermediates are formed and these are split by water, hydrogen, alcohols, acids and other compounds and are converted to the respective acids, aldehydes, esters or anhydrides. The condition for the addition of carbon monoxide to acetylenes and ethylenes is the presence of carbonyls, e.g. nickel carbonyl. A special case of this general reaction is the oxosynthesis of Ruhrchemie in which aldehydes are formed by the reaction of carbon monoxide and hydrogen with olefins, and these aldehydes are then either reduced with hydrogen to aliphatic alcohols or oxidized with oxygen to aliphatic acids.

Acrylic acid or acrylic esters may be formed from acetylene and the corresponding saturated compounds for ethylene. With higher olefins and water, aliphatic acids with one carbon more are formed. The reactions of carbon monoxide may be applied as well to derivatives of furan. Introduction of 2 moles carbon monoxide and water gives adipic acid in good yield.

In connection with the catalysis of carbon monoxide reactions, experiments were carried out with carbonyl hydrogens, e.g. iron carbonyl hydrogen and cobalt carbonyl hydrogen.

Acetylene preparation
 Acetone synthesis
 Acetone scrubber flow scheme
 Acetone recovery flow scheme
 Acetone scrubbers and recovery system
 General flow sheet
 Layout of combustion stage (Nachbrenner) for synthesis
 gas preparation
 Surrounding plants - building layout on site
 Heat exchanger
 Photographs
 Linz Plant - Flow sheet of NH₃ synthesis gas production
 Heydebreck plant - Heat exchanger

ITEM 44: Material for Butyl and Methanol Synthesis

III 256

Comprehensive tests on attack of 50% each H₂ and CO and 72% H₂ + 28% CO on various steels at 200° and 400-450°C. The attack is probably due, at least in part, to carbonyl formation. This could be avoided by powder galvanizing of the steels. Galvanizing was carried out in the following way with a mixture of 16% zinc dust and 84% alumina. Within 48 hours the temperature was raised to 200° and then kept at this temperature for 10 hours. The temperature was then raised within 102 hours to 730° and kept there for 20 hours, cooling within 2-3 days.

The temperature stability of the galvanized steel is good. The outermost layer consists of mixed crystals containing 92.75% Zn and having a melting point of 730°C (melting point of pure zinc 429°C). The next layer still has 83% zinc and an even higher melting point of 765°C.

Steel N5 was attacked by the gas, but powder galvanized steel has given very satisfactory results up to this time. A table is included showing results of the tests with N5, N5 powder galvanized and V2AE. To avoid corrosion, it is recommended that oxygen be removed from the fresh gas or, better still, that pure methanol be used. Materials should be tested first as to whether they are stable to methanol, and only when this test is good should mixtures be tested as to stability to CO + H₂.

ITEM 45: Behavior of Various Materials Exposed to Synthesis Gas.

III 267

A comprehensive report on behavior of various steels, especially Sichromel 85A, V2AE, K4Ms, NCT5, Chromfer, N5A "inkromiert", N8A "inkromiert", N9A "inkromiert", FF30P, V17F, N10, N9, N8, N8A, and N8V. Many metallographic tests and illustrations of microscopic sections are given.

Summary: No attack was found with V2AE, Sichromel 85A, NCT5 and FF30.

V17F steel (17% Cr) shows slight CO attack and is said to become brittle.

On N steels a layer richer in Cr is formed, but no damage to lower layers resulted.

Perfect vapor galvanizing of N steels was successful in tests.

ITEM 46: Damage to Heat Exchangers

III 275

An extensive survey (22 pages) on damage to air or gas heat exchangers made from seamless and welded tubes.

It is recommended:

1. Welding for connections should be avoided.
2. Seamless tubes are to be preferred.
3. Care should be taken in making weld connections to the headers. Heat treatment after welding should be carried out very carefully.
4. No objection is to be made against material of increased scale resistance provided that the sensitivity of the alloy used is not unduly increased. The use of steels with increased scale resistance is not justified by experiments.

ITEM 47: Production of Mischkybol

April 14, 1944

III 301

Mischkybol is a mixture of 70% VT702, 15% Diethylbenzene and 15% isopropylbenzene. This mixture shows better supercharging performance than C3II gasoline. Similar favorable results were obtained with a mixture of 30% isopropylbenzene and 70% VT702.

The report discusses the amount to be produced from ethylene or propylene and the location of the future plant.

ITEM 48: Report on Ignition of Gas Mixtures by Grinding Wheel Sparks.

III 304

An arrangement of an apparatus, which was used to determine the explosibility of several gas mixtures by sparks, is discussed and illustrated.

It was found that the gas mixtures have to be tested throughout the explosive limits, for instance, with ethylene and carbon monoxide, ignition occurs at a ratio of gas to air which is below the ratio with the highest flame velocity.

A summary of test with grinding wheel sparks and electric sparks is included.

SECTION IV
BAQ 1677A TARGET 30/4.10

ITEM 1: Coal Hydrogenation Plant, Wesseling

IV 1

Operating Report

Many parts of this report are directly translated in T.A.C. Report ZGC-2 (TOF-17). Many interesting illustrations and flow sheets are missing. The following tables, which are not included in the T.A.C. report show the steels used in this plant.

Steels Used in Hydrogenation. I. G. Qualities

No.	Quality	Alloying	Treatment	Analysis							Strength, Kg/mm ²	
				C	Mn	Si	Cr	W	Mo	V		
1	S1	C	Normal	.28-.36	.60-.80	.20-.35	-	-	-	-	-	50-60
2	S2	C	"	.16-.25	.45-.60	.20-.35	-	-	-	-	-	40-48
3	S3	Cr	"	.20-.25	.85-.95	max .30	.30-.50	-	-	-	-	50-60
4	S3K	C	"	.18-.25	1.10-1.30	.20-.40	-	-	-	-	-	50-60
5	S3H	Cr	"	.23-.28	.85-.95	max .30	.30-.50	-	-	-	-	50-60
6	S3HK	C	"	.23-.28	.85-.95	max .30	-	-	-	-	-	50-60
7	M1	CrMo	Oil improved	.20-.30	.40-.60	.25-.35	2.5-3.0	-	.20-.25	-	-	65-77
8	N5	CrMo	Air improved	max .12	.30-.50	.20-.40	2.5-3.0	-	.20-.30	-	-	50-60
9	N5A	Cr V	Air improved	max .12	.40-.60	.25-.35	2.5-3.0	-	-	.10-.20	-	50-60
10	N5B	Cr	Air improved	max .12	.30-.50	.25-.35	2.5-3.0	-	-	-	-	50-60
11	N5C	Cr V	Air improved	.15-.20	.30-.50	.25-.35	2.5-3.0	-	.35-.45	.10-.20	-	50-60/55-65
12	N6	CrMoV	Air improved	.15-.20	.30-.50	.25-.35	min 5.5	.40-.60	.40-.60	.10-.20	-	60-75
13	N8	CrMoV	Oil improved	.15-.20	.30-.40	.25-.35	2.5-3.0	-	.40-.60	.05-.15	-	55-80
14	N8A	Cr V	Oil improved	.20-.25	.60-.80	.25-.35	2.5-3.0	-	-	.25-.35	-	70-85
15	N8V	CrMoV	Oil improved	.18-.23	.40-.60	.25-.35	2.5-3.0	-	.40-.60	.40-.50	-	80-95
16	N9	CrMoV	Air & oil "	.19-.26	.40-.60	.25-.35	2.5-3.0	-	.20-.30	.45-.55	-	80-95/75-90
17	N10	CrMoV	Air & oil "	.19-.26	.30-.40	.25-.35	2.5-3.0	.35-.45	.35-.45	.70-.85	-	80-95/70-85
18	N10A	CrMoV	Air & oil "	.19-.26	.30-.40	.25-.35	2.5-3.0	.20-.30	.25-.35	.80-.90	-	80-95/70-85
19	K1	Cr	Water improved	.25-.33	1.00-1.30	.50-.80	1.0-1.3	-	-	-	-	70-80
20	K1GV	Cr	Improved	.2	-	-	1.0	-	-	.2	-	70-85
21	K1MS	MnSi	Improved	.35	1.2	1	-	-	-	-	-	70-85
22	K2	CrMo	Oil & air "	.23-.28	.60-.90	max .40	.9-1.1	-	.20-.25	-	-	60-70
23	K2A	Cr	Oil & air "	.23-.28	.60-.80	.20-.30	.9-1.1	-	-	-	-	60-70
24	K2M	Mn	Improved	.23-.28	1.2-1.5	.6	-	-	-	-	-	55-60
25	K3	CrMo	Water improved	.25-.30	.50-.70	.20-.30	1.0-1.2	-	.14-.20	-	-	70-80
26	K3CV	Cr	Improved	.2	.7	-	1.2	-	-	.25	-	70-80
27	K4MS	MnSi	Improved	.33-.40	1.1-1.6	1.1-1.6	-	-	-	-	-	80-90
28	K5	CrMoV	Water & oil "	.20-.25	.60-.80	.25-.40	1.3-.6	-	.50-.60	.30-.40	-	80-95
29	K6			.4-.5	1	-	1	-	-	.2	-	90
30	K7	CrMo	Improved	.3	1.0	-	1.5	-	-	1.2	-	80-95

Steels Used in Hydrogenation. I. G. Qualities (Cont'd)

No.	Yield point; min. Elastic limit Kg/mm ² at °C		Notch Tenacity m Kg/cm ²	Min. Flongation 1-5-d %	Min. lasting Stability * Kg/mm ² at °C				Heat Treatment				Temper °C		
	20	300			350	400	450	500	550	600	Forging °C	Annealing °C		Hardening °C	Cooling medium
	20	300			350	400	450	500	550	600					
1	27	-	-	-	> 6	22	-	-	-	1050-850	700	870	Air	-	
2	-	-	-	-	> 10	26	-	-	-	1100-850	690	900	Air	600-650	
3	30	-	-	-	> 8	24	-	-	-	1100-850	690	850	Air	600-650	
4	30	-	-	-	> 6	24	-	-	-	1100-850	650-700	850	Air	600-650	
5	30	-	-	-	> 6	26	-	-	-	1150-800	650-700	850	Air	600-650	
6	30	-	-	-	> 6	24	-	-	-	1050-800	650-700	850	Air	600-650	
7	45	35	-	-	> 4	15	-	-	-	1100-850	700-750	900-950	Air	650-700	
8	30	-	-	-	On edge	22 lg	-	-	-	1050-850	750	900-950	Air	700-730	
9	(25)	-	-	-	> 10	22 lg	-	-	-	1100-850	750	980-1000	Air/oil	700-730	
10	-	-	-	-	On edge	22 lg	-	-	-	1050-850	750	920-950	Air/oil	700-730	
11	30-35	-	-	-	> 8-6	20-17-18	-	-	-	1100-850	750	980-1000	Air/oil	700-730	
12	35	-	-	-	On edge	18	-	-	-	1100-850	750	950-970	Air	680-750	
13	45	-	-	-	> 81	18	33	20	10	1100-900	700-720	950-970	Oil	680-730	
14	50	-	-	-	> 81/5 qu	16	33	-	-	1100-900	700-720	950-980	Oil	680-700	
15	55oil	-	-	-	10.6-8.5	16	-	-	-	1050-850	700-720	1000-1030	Oil	660-680	
16	50	-	-	-	10.6-8.5	16	-	-	-	1050-850	700-720	1000-1030	Air or oil	660-680	
17	55-50	-	-	-	10.6-8.5	14	-	25	20	1100-900	700-740	1020-1050	Air or oil	690-730	
18	55-50	-	-	-	10.6-8.5	14	-	25	20	1100-900	700-740	1020-1050	Air or oil	690-730	
19	50	-	-	-	> 7lg	6qu 16 lg 13qu	-	-	-	1050-850	700-720	830-850	Water	620-660	
20	50	38	34	-	8	17	22	15	8	1050-850	700-730	950	Oil	600-650	
21	50	-	-	-	6	16	-	-	-	1050-850	700-730	950	Oil	600-650	
22	38	-	-	-	On edge	15	-	-	-	1100-850	700-730	920	Oil or air	600-650	
23	38	-	-	-	On edge	15	-	-	-	1100-850	700-720	920	Oil or air	600-650	
24	> 40	-	-	-	On edge	18	-	-	-	1100-850	700-720	920	Oil	600-650	
25	> 50	-	-	-	> 8	16	-	-	-	1100-850	700-720	930-950	Water	640-680	
26	> 50	-	-	-	8	17	30	20	10	1050-850	700-730	950	Oil	600-650	
27	60	45	-	-	6	14	15	10	5	1100-850	680-720	850	Oil	620	
28	65	60	55	-	> 8	16	45	34	26	1100-900	700-750	980-1000	Oil or water	650-680	
29	60	45	-	-	6	14	-	-	-	1050-850	700-720	950	Oil	600-650	
30	60	-	-	-	8-6	16	40	30	20	1050-850	700-720	1000-1030	Oil or air	660-680	

HIGH PRESSURE 325 AT. Useable Material for

Temperature Step	Operating Temp. °C.	Nominal Width	Pipe	Template Pipe	Blank Flange	Screw Flange	Screws	Nuts	Lenses
I	0-200	6-16	St 45.29				S3		
		16-160		S2	S2	S1	K4MS	S3	S2
II now (200-400°C)	200-400	200	St 35.29				K1 K1MS		
		6-200	N8A	N8A	N8A	K4MS K1 K1MS	K4MS K1 K1V K1CV K1MS	S3	N5A
II hitherto (200-480°C)	200-480	6-200	N8	N8	N8	N8	K3 K3CV	S3	N5
		6-200	N9	N9	N9	N9	K3 K3	S3	N5
III now 400-510°C	400-510	6-45	N8	N8	N8	N8	K3 K3CV	S3	N5A
		58-200	N8V N10	N8V N10	N8V N10	N8V N10	K3 K3CV K5 K3CV K5	K3 K3CV K5 K3 K5V K1MS K3 K1V	N5 N5A
III hitherto 480-510	480-510	58-200	N8V N10	N8V N10	N8V N10	N8V N10	K3 K3CV K5 K3CV K5	K3 K3CV K5 K3 K5V K1MS K3 K1V	N5 N5A

HIGH PRESSURE 700 AT.

Useable Material for

Temperature Step	Operating Temp. °C.	Nominal Width	Pipe	Template Pipe	Blank Flange	Screw Flange	Screws	Nuts	Lenses
I	0-200	6-16		S3	S3	S1	S3		S2
		24-160 except 135	K2M		K4MS	K4MS	K4MS K1	S3	
		135	K2	S3	K1 K1MS	K1 K1MS	K4MS K6	S3 K1 K1V K1CV	S3
II now 200-400°C	200-400	6-45				K4MS K1	K4MS K1 K1V		
		58-160 except 135				K1MS K4MS	K1MS K4MS K1 K1V	S3	N5A
		135	N8A	N8A	N8A	K1 K3	K4MS K6	S3 K1 K1V K1CV	N8 N8A
III hitherto 200-420°C now 400-510°C	200-420 400-510°	6-160	N8	N8	N8	K3 K3CV	K3 K3CV	S3	
		6-16	N9	N9	N9	K3CV K5 K5V	K3CV K5 K5V	S3 K3 K1V K1CV	N5A
		24-45	N10	N8V N10	N8V N10	N8V N10	K7 K5	K7 K5	K1MS K3
III hitherto 420-510°C	420-510°	58-160	N9 N10W	N9 N10	N9 N10	K5V	K5V	K1CV	
		6-160						K5V	

SURVEY OF MATERIALS FOR HIGH PRESSURE 325 AND 700 AT.

Operating Pressure	Temperature Step	Operating Temp. °C.	Nominal Width	Pipe	Template Pipe	Article				
						Blank Flange	Screw Flange	Screws	Nuts	Lenses
325	I	0-200	6-10	St 45.29	S2	S2	S1	S3	S3	S2
			16-160	St 35.29	S2	S1	S3	S3	S3	S2
			200	St 35.29	S2	S1	K4MS	S3	S3	S2
	II	200-400	6-200	N8A	N8A	N8A	K4MS	K4MS	S3	N5A
			6-200	N9	N9	N9	K3CV	K3CV	S3	N5A
					S3	S3	S3	S3	S2	
700	I	0-200	6-16	K2M	S3	S3	S1	S3	S3	S2
			24-160	K2M	S3	K4MS	K4MS	K4MS	S3	S3
					N8A	N8A	K4MS	K4MS	S3	N5A
	II	200-400	6-16	N9	N9	N9	K3CV	K3CV	S3	N5A
			24-45	N10	N9	N9	K3CV	K3CV	S3	N5A
			58-160	N10	N9	N9	K7	K7	K1MS	RL 1.7%

ITEM 2: Process of recovering oil from shale at Schoenberg, Wuerttemberg.

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The oil shale contains approximately 5% oil. It is up to 9 meters thick in places and covered only by a thin layer of clay. Processing is done in circular piles, the arrangement of which is described. On the bottom of each pile is a system of pipes which are connected to a main. The main leads to an electric precipitator and a blower.

The pile is covered with a 10 cm thick layer of peat and wood shavings (approximately 10 Kg/m²), and this layer is ignited. The blower is started, and as soon as the O₂ content falls below 8% the gas is put into the main. At the start the temperature of the gas is 20°C, and increases to 200°C at the run conclusion. The combustion zone has a temperature of 1000-1100°C. From each pile 12,500 m³/h gas are collected, the oil is separated in electro-filters, and the gases from the filter have the following composition:

0.5 - 1.2%	-	H ₂ S
1-9 g/m ³	-	SO ₂
7%	-	CO
1.2%	-	H ₂
1.6%	-	CH ₄
1.5%	-	C H n m
0.02 - .1 g/m ³	-	NH ₃
1 - 8%	-	O ₂
Remainder	-	N ₂

The gas has only 600 heat units and, as gases below 1000 heat units do not burn with air, a new oven construction had to be used. A burning chamber is heated with oil to 1200°C. and the gas, preheated to 600°C. is then burned in this hot chamber. Drawing of the oven and flow sheet are given.

The oil from the filter is led into concrete tanks in which the water is separated. If an emulsion forms, it is broken by adding "Dismulgen" to the oil in separatory tanks of 80 m³. The water contains 0.5 - 5 g phenol.

The oil is useable for tractors, as diesel oil, and is very suitable for hydrogenation.

SECTION V

BAG 3028 TARGET 30/OPPORTUNITY

KLÖNNE, DORTMUND.

Fine Purification Plant with Drawings

V 1

Specification of fine purification plant.

Drawing 3834 - Gas heater.

- 70156 - CS₂ purification plant. Plan.
- 71614 - Assembly of fine purifier.
- 71668 - Oxide Tray.
- 525283 - Carrier for purifier.
- 525136 - Section of purifier.
- 711236 - Cover of purifier
- 711261 - Arrangement of fine purification plant.
- 711274 - Purifier shell.
- 711279 - Assembly of fine purifier.
- 721445 - Upper and lower trays for purifier.
- 722615 - Carrier for fine purifier.
- 732424 - Gas-tight packings for trays.

SECTION VI

BAG 1928 TARGET 30/4.03

I.G. FARBENINDUSTRIE, LUDWIGSHAFEN.

ITEM 1: File on Estonian shale oil - March-October, 1943. VI 1

(a) Preliminary Hydrogenation Results with Concentrates of Estonian Shale. VI 2

Hydrogenation was carried out at 300 and 600 atm. The concentrate used had 79% Kerogen (organic substance), 17.5% ash and 4-6% water.

Results are shown in a table. Apparently the conversion of Kerogen decreases as the temperature increases at 300 atm. Working at 600 atm. gives better reduction of asphalt.

Comparison of hydrogenation of shale with lignite from Sudetenland shows that with lignite, asphalt, and gasification is twice as high and conversion is much lower. Sudeten lignite had 13% ash, 87% organic matter (74.9% C, 6% H₂, 17.1% O₂, 1.1% S, and 19.3% tar by retorting).

(b) Preparation of ash-free bitumen from Estonian shale concentrate. VI 7

Optimum conditions were 8-10 hours at temperatures of 20.5-21 MV and a dilution of 1:1 with aromatic coal tar middle oil. However, the yield of pure bitumen was not very satisfactory.

Conversion of shale calculated on raw concentrate is 84.4% of Kerogen.

(c) Alkylation of gasoline from Estonian shale and of some VI 9 unsaturated gasolines of other origin.

On carbonization of Estonian shale 20-25% oil is obtained, containing about 20-22% boiling within the gasoline range. This gasoline is 80-85% olefinic (Iodine number 225) and has 0.5-1% S as mercaptans. The smell is, therefore, exceedingly unpleasant and makes the gasoline unuseable. Sweetening with sodium plumbite and with H_2SO_4 causes losses of 22% on a laboratory scale. On a large scale, losses are stated to be 10-12%. The odor is improved but not satisfactory because the purified product still contains 0.2% S. Experiments were attempted to improve the smell and octane number by H_2SO_4 alkylation with excess isobutane.

The yield of alkylate was rather unsatisfactory, especially compared with other gasolines of high olefin content (e.g. Michael gasoline). It seems as if the poor yield was due to high losses in purification, only to a small part to polymerization and ester formation.

A table is included for alkylation of Rumanian gasoline and "Staub-Kt" (fluid catalyst) dehydrogenated gasoline.

(d) Concentrate from Estonian shale.

VI 13

A mixture of "Flotol" and petroleum 1:1 was used as flotation agent for wet ground shale (70% 60M). Flotol consists of alcohols of the terpene series. Tar and shale oils were not selective.

Extraction has no advantage over carbonization. Experiments showed that the same is true for hydrogenation of flotated or carbonized shale.

Refining of gasoline from Estonian shale with H_2 at 3 at., catalyst $Al_2O_3 + MoO_3$ gave good results. S 0.08%, odor good, lowering of iodine number, octane number poor at 18 MV, but good (77) at higher temperatures.

Without H_2 , catalyst $Al_2O_3 + Fe + Cu$, atmospheric pressure, the S content is higher (.3 - .5%); octane number is good but still better at higher temperature. In both cases the gum test is high and inhibitors should be used.

ITEM 2-3: Polycyclic Aromatics from Hydrogenation Products

VI 40

The paper deals with polycyclic aromatic compounds from coal hydrogenation, especially from oils produced in carbonization of the hydrogenation slurry or from high temperature hydrogenation oils.

The compounds were separated by vacuum fractionation. Cuts of 2° range were obtained, from which crystallized separately carbazole pyrene, methyl and dimethyl pyrene. Dihydropyrene was separated from the pyrene which accompanies it by separating the pyrene as the picrate in carbon tetrachloride.




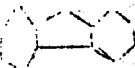
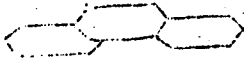

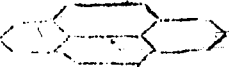
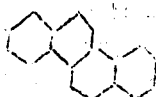



Benzperylene and coronene distill at 4mm at about 340°C. and are contaminated by resin, which can be removed by washing with acetone or benzene. They are separated by fractional crystallization from xylene or dichlorobenzene.

Other compounds such as fluorene, anthracene, and chrysene are present only in very small amounts because these compounds are not stable under hydrogenation conditions and are decomposed to methylated benzenes and naphthalenes. The reason is that these compounds have four adjacent CH groups while compounds such as perylene or coronene have three or less adjacent CH groups.

The heats of combustion were determined in the I.G. laboratories and the heats of formation calculated, as shown in the following tables:

Heat of Combustion					
Compound	Formula	Molec. Weight	Heat of Combustion		
			Q_v at const. volume	Q_v at const. volume	Q_p at const. pressure
			cal/gr	Kcal/Mol	Kcal/Mol
Pyrene	C ₁₆ H ₁₀	202.1	9294	1878.3	1879.8
1,2 Dihydropyrene	C ₁₆ H ₁₂	204.1	9466	1932.0	1933.8
Sym. Hexahydropyrene	C ₁₆ H ₁₆	208.1	9771	2033.3	2035.7
Perhydropyrene	C ₁₆ H ₂₆	218.2	10553	2302.7	2306.6
1,12 Benzperylene	C ₂₂ H ₁₂	276.1	9124	2519.1	2520.9
Coronene	C ₂₄ H ₁₂	300.1	8957	2688.0	2689.8
Perhydrocoronene	C ₂₄ H ₃₆	324.3	10359	3359.4	3364.8
Perhydrocoronene(isomers)	C ₂₄ H ₃₆	324.3	10374	3364.3	3369.7

Heat of Formation

Compound		Crystal form	Heat of formation Kcal	
			per Mol	per gram
Benzene (solid) C_6H_6		rhombic	-11.3	-.145
Naphthalene $C_{10}H_8$		monoclinic plates	-16.0	-.125
Acenaphthene $C_{12}H_{10}$	$H_2C - CH_2$ 	rhombic needles	-19.9	-.129
Fluorene $C_{13}H_{10}$	CH_2 	leaflets	-19.3	-.116
Phenanthrene $C_{14}H_{10}$		monoclinic plates	-23.1	-.13
Anthracene $C_{14}H_{10}$		monoclinic plates	-27.6	-.155
Pyrene $C_{16}H_{10}$		monoclinic plates leaflets	-29.8	-.148
Chrysenē $C_{18}H_{12}$		rhombic plates	-34.6	-.152
Perylene $C_{20}H_{12}$		leaflets	-39.4	-.156
Benzperylene $C_{22}H_{12}$		plates	-37.1	-.134
Coronene $C_{24}H_{12}$		<u>long, thin</u> <u>needles!</u>	-17.4	-.058

Heats of hydrogenation are briefly discussed. The average heat of hydrogenation of all double bonds in coronene is exceptionally low: 12 Kcal/Mol.

ITEM 2-b: Coronene

VI 58

Coronene crystallizes as yellowish, very fine long needles, m.p. (corr.) 432°C. b.p. 525°C. at 760 mm, distilling without decomposition. Very slightly soluble in organic solvents such as toluene, xylene, etc. (about 0.1%). Fluorescence is very strong: in ultra-violet light yellowish green, in solution blue.

Coronene may be sulfonated and halogenated; oxidizing compounds give quinonoid products. Dyestuffs made from Coronene show very good fastness.

Hydrogenation easily leads to perhydrocoronene, probably because of several resonating structures.

Perhydrocoronene crystallizes from benzene in long, fine white needles, m.p. 370°C, b.p. 430°C; heating with selenium at 360°C. gives coronene. Many isomers of perhydrocoronene are possible; an isomer, with m.p. 203°C, dull white needles, much more soluble in benzene than the higher melting compound, was isolated.

Partial hydrogenation is not possible with nickel or tungsten sulfide; with a mixed sulfidic catalyst it was possible to obtain dodecahydrocoronene, crystallizing in small, yellow, square plates, m.p. (corr.) 353° C. It forms no picrate and shows blood red fluorescence in hot H₂SO₄ (coronene-green).

Perhydrocoronene and coronene form a very stable molecular complex in the ratio 1:1. This complex crystallizes from xylene in coarse needles, m.p. (uncorr.) 406-408°C. This complex is so stable that coronene cannot be separated from it by picric acid.

Perhydrocoronene, containing 2% coronene, shows strong phosphorescence. After irradiation of the crystals with ultra-violet, ordinary or artificial light, an orange phosphorescence is observed. Irradiation with light of short wave lengths gives blue fluorescence and orange phosphorescence. On heating the crystals to 74°C, a change of modification takes place and the color changes reversibly to blue for 1-2 minutes.

Hydrogen bridging between the inner ring of perhydrocoronene and coronene may be responsible for the phosphorescence.

SECTION VII

BAG 3041 TARGET 30/4.02

I.G. FARBENINDUSTRIE, LEUNA

ITEM 1: Determination of Methanol in Aqueous solutions of Fatty Alcohol Sulfates.

VII 1

Two determinations of methanol are described extensively. The best is the nitrite method, in which the CH_3OH is converted to methylnitrite, an insoluble gas b.p. -12°C . The gas is decomposed in a receiver with HCl and KI and the iodine determined in the usual way. The fatty alcohol sulfate solutions foam very much; for this reason the sulfates are precipitated first with barium acetate. An improved apparatus is used, an illustration and description of which are given. The nitrite method is based on W. M. Fischer and A. Schmidt, Berichte 57, 694 (1924) and Ender, Z. ang. Ch. 1934, 227.

The second method consists of oxidizing the methanol with KMnO_4 in alkaline solution and titrating with oxalic acid. A blank must be run. The method is not quite as good as the first one but is used to save iodine.

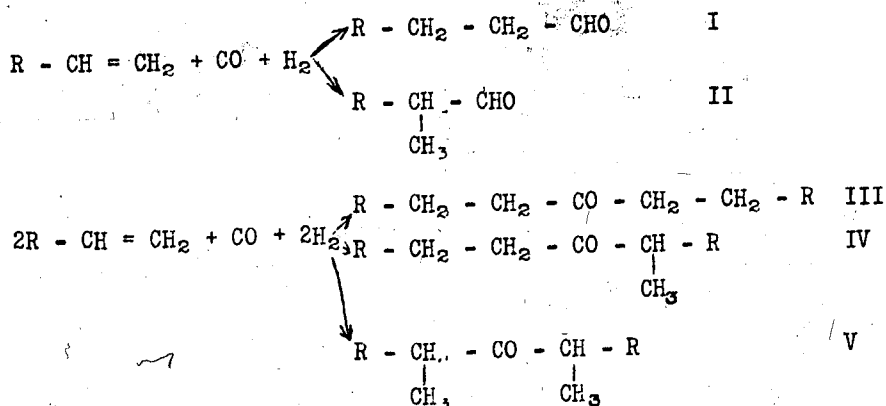
ITEM 2: On the Reaction Products of the Oxo Process

VII 15

To obtain a more exact knowledge of the course of the Oxo Process, studies were undertaken to investigate the reaction with some individual olefins.

Theoretically, the following reactions are possible:

(a) Primary Reaction Products - Aldehydes and Ketones.



(b) Secondary Reaction Products

The aldehydes can be converted further into acids, alcohols and esters (Cannizzaro rearrangement). In addition, polymerization and condensation products are possible.

The products derived from isohexylene, dodecylene and cyclohexene are described, analyzed and characterized by derivatives. Aldehydes and ketones could be ascertained as primary compounds, and as secondary compounds acids, alcohols, esters, and polymerization and condensation products of aldehydes. The experiments were extended to technical olefins (cracked olefins and KWSy olefins) and the products converted to alcohols. Reaction with chlorosulfonic acid gave sulfuric esters, the detergent properties of which were compared with other sulfonates.

ITEM 3: Production of Mersol and Mersolate on the Basis of Petroleum Products. VII 33

For a long time it was the object of experiments at Leuna to produce capillary-active compounds from products of tar and coal hydrogenation. Since 1936, the action of sulfur dioxide and chlorine on hydrocarbons has been investigated. Systematic experiments showed that aliphatic saturated hydrocarbons were best suited for the reaction and, therefore, the product of the Fischer synthesis, Kogasine II was investigated as charge stock in place of the gas phase B hydrogenation product. In the dark, chlorine and SO_2 did not react at all with hydrocarbons, and only by irradiation with light of wave length 3000-4500 μ were hydrocarbon sulfochlorides produced. Based on this knowledge, the products Mersol and Mersolate were developed starting from Kogasine II. These products, together with the fatty acids from paraffin oxidation, are the main source of washing agents for Germany and other European countries. The demand was so tremendous that the available Kogasine was insufficient and it was therefore necessary to find other raw materials for sulfochlorination. Kogasine being a synthesis product, costs .31M/Kg. and, therefore, the cheaper Rumanian and Hungarian mineral oils were investigated.

The reactions which take place when chlorine and SO_2 react with hydrocarbons are discussed. As an example, an aliphatic hydrocarbon, C_{15} was assumed which corresponds to the average carbon number of Mepasine (hydrogenated Kogasine II fraction). The ideal reaction gives the desired alkyl monosulfochloride. A consecutive reaction which takes place when the concentration of the monosulfochloride has reached a certain amount yields the disulfochloride. This reaction is not desired and can be suppressed if the conversion of the hydrocarbon mixture is low. Chlorine substitution reactions in which the chlorine is bound directly to carbon also take place. These reactions are undesirable because they consume unnecessary chlorine. Only the chlorine bound to sulfur is desired because only the sulfochloride group converts the hydrocarbon after saponification into a water soluble product. The chlorosubstitution takes place at higher temperatures, for instance, above 100°C. substitution is the main reaction and sulfochlorination is negligible. Sulfochlorination is, therefore, usually carried out at temperatures between 20 and 30°C, but chlorination of the chain cannot be completely avoided. With Mepasine it amounts to approximately 10%.

Sulfochlorination of Oil Fractions

According to recent results, it seems that fractions boiling between 230-340°C. are best suited. The oil must first be hydrogenated to a mixture of saturated hydrocarbons. In contrast to Kogasine, which is hydrogenated at 320°C. and 200 atms over a sulfidic catalyst, the oil must be hydrogenated at about 350°C. Furthermore, the hourly space velocity with oil is only about one whereas the space velocity with Kogasine may be up to eight. The consumption of hydrogen is several times more with oil than with Kogasine. For this reason, the extraction of the oil with selective solvents before hydrogenation to remove the compounds containing oxygen, sulfur and nitrogen and hydrocarbons deficient in hydrogen was attempted. This pre-extraction was carried out to remove 50% of the original hydrocarbon mixture and thereby paraffinic oils were obtained. These refined products may be hydrogenated with ease, similar to Kogasine. The products are water-white oils having a specific gravity of 0.81 when using paraffin base oils and a specific gravity of 0.835 when using naphthenic oils, compared with Kogasine which has a specific gravity of 0.766 after hydrogenation.

Sulfochlorination of Hydrogenated Oils

In order to get a conversion of 40% with Mepasine, 10 hours are necessary; with hydrogenated oil, 17 hours; and with an extensively refined and hydrogenated oil, 13 hours. This decrease in reaction velocity is not considered serious. The reaction velocity compared with Kogasine decreases very appreciably if one attempts to obtain sulfochlorination of more than 50%, in addition, much substitution by chlorine takes place. Conditions are somewhat more favorable if the oil is extensively refined by extraction, but still the chlorine substitution may reach 25% with hydrogenated oil compared with about 10% with Kogasine. The reason for the difference lies in the higher amount of cyclic hydrocarbons in hydrogenated oils. This detrimental influence of cyclic hydrocarbons is perceptible even in high dilution.

The procedure is to sulfochlorinate the hydrocarbon mixture only to 50 or 33%. The reaction product is saponified with 10% sodium hydroxide and the unchanged hydrocarbons, after separating from the sulfonate solution, are used again for sulfochlorination. These recycle oils could be sulfochlorinated without difficulty in the case of Mepasine, however with oil, the recycle obtained after the first 50% sulfochlorination is dark colored and does not undergo sulfochlorination. The failure with recycle oil is due to the presence of small amounts of compounds which stop the reaction initiated by light. The nature of these substances is yet unknown, but it is possible to remove them in a very simple way by hydrogenating the oils under similar conditions of pressure and temperature as initially used. The recycle oils were dechlorinated before hydrogenation by passing the vapors over lumpy bauxite at 360°C.

Converting Oil Sulfochlorides to Mersolate

The oil sulfochlorides are worked up to sulfonates in the same way as the Mepasine, i.e. saponification with 10% sodium hydroxide, separating the neutral oils and then drying the solution on drum driers. The dry sulfonates are plastic masses which may be worked up on a flaker to give flakes.

ITEM 4: Flow diagram of DHD process, Leuna

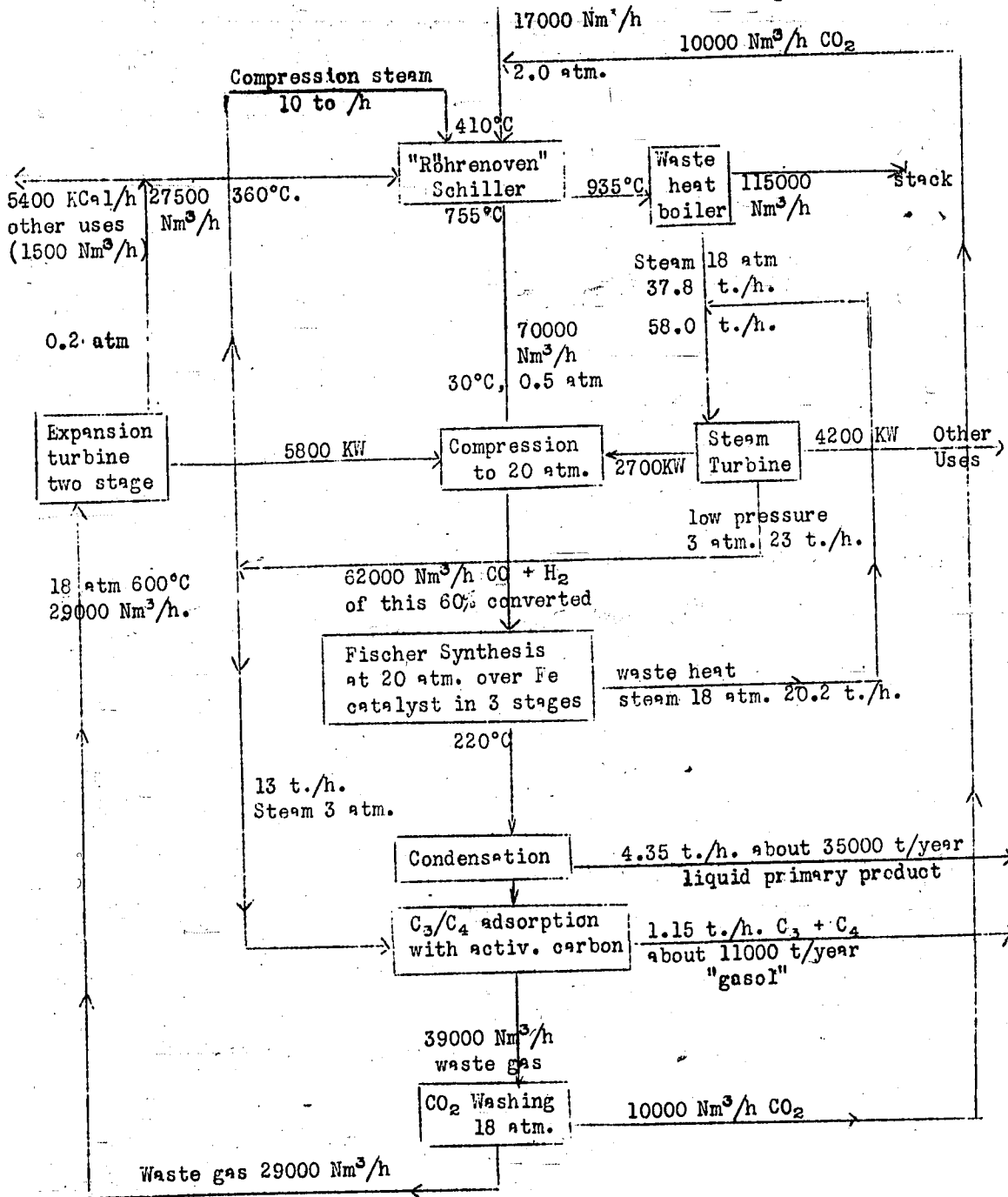
VII 44

ITEM 5: Production of Fischer gasline from natural gas

VII 45

Production of Fischer gasline from natural gas. Cracking in "Röhrenoven" with steam and CO₂. Synthesis at 20 at. over iron catalyst (see flow sheet). A very brief cost estimate is shown. The attached table compares several processes.

Natural Gas 97% CH₄, 3% N₂



Process	Pressure atm	Temp. °C.	Yields g/Nm ³										Catalyst	Syn-thesis Gas ¹ CO:H ₂	Stages
			Total	"Gasol"	Gasoline		Diesel Oil	Paraffin	Alcohols	Ethylene	CH ₄ + C ₂ H ₆				
					1-2	25-30%									
Fischer Tropsch (1)	0	200°	155	38	69	38	10						Co	1:2	1
Fischer Pichler (1)	10-20	200°	178	33	39	36	70						Fe	1:2	1
Ammonia Laboratory Scheuermann	12		130- 140	1-2 (25-30% olefins)	14	25	90-100						Special cat- alyst (Co- Kieselgur) for straight chain paraffins, espec. suitable for oxidation	1:2	1
Oil circulation (2)	100	270-360	147	25	61	52	-						Stationary (fixed) Fe sintered catalyst	45:55 to 55:45	2
Hot Gas Circula- tion (3)	20	320-330	160	35	83	21	1-2 8-10						Sintered Fe catalyst Suspended	4:5 to 9:10	-
process Michael	20	300	177	21	64	37	10								
Synol process (4) (Me)	20	190-200	130										Up to 60%	Fe	-

(1) Heat removal through tubes or chambers (steam production).
(2) Heat removal through circulation of oil produced. Changing for olefins gives 48% alcohols, 18% fatty acids, 34% hydrocarbons with 50% olefins.
(3) Heat removal through reaction gases.
(4) Gas phase, later liquid phase with finely divided catalyst. 30-40% hydrocarbons with up to 60% olefins.

ITEM 6: Questionnaire of November 13, 1944, concerning important foreign motor fuel processes-for use in prisoner of war interrogations (?)

VII 48

Questions on design and operations, especially for:

- (a) Adiabatic cracking (new Houdry process)
- (b) Thermoform cracking process (TCC process) developed by Socony Vacuum Oil Company.
- (c) Fluid catalyst (F.C.) process of Standard-Shell-Texas group.
- (d) Hydrofluoric acid alkylation.
- (e) Processes for new special motor fuels. Triptane, Dynafuel.

ITEM 7: Patent on Condensation Products of Oil Fractions by Treatment with Metal Halides

VII 59

Patent disclosure dated Leuna, December 30, 1944, Process for Preparing Technically Valuable Materials by condensation of gasoline, middle oil, Diesel oil and heavy oil fractions containing aliphatic and cyclic compounds (especially aromatic) in the presence of metallic halides and other condensing agents or polybasic mineral acids and their derivatives, at concentrations at which predominately condensation and only to a very small degree substitution takes place.

Example

A fraction of oil (185-225°C.) from low temperature carbonization of Central German lignite was treated first with sulfuric acid (10 per cent) to remove organic bases; then with sodium hydroxide solution (10 per cent) to remove acidic components (phenols, cresols). The refined product obtained showed the following boiling range:

185 - 200°C.	40 per cent
200 - 210°C.	43 per cent
210 - 220°C.	10 per cent
220 - 225°C.	7 per cent
Residue	3 per cent

Five hundred pounds by weight of this material were run into boron fluoride-phosphoric acid, which was prepared by passing 106 parts by weight boron fluoride into 134 lb. by weight of phosphoric acid (85 per cent). The temperature was kept at 10-20° by cooling. After addition the mixture was kept at 50-60° for five hours. The boron fluoride-phosphoric acid was then separated and the oil was washed free of acid with a salt solution. There were obtained 380 parts by weight of a raw condensation product, the boiling ranges of which were determined by vacuum distillation.

Forerun to 185°C.	3.7 per cent
185°C - 225°C.	62.61 per cent
225°C - 240°C.	6.32 per cent
High boiling residue	26.00 per cent

The 26 per cent high boiling residue (20 per cent yield calculated on the starting material) is light brown oil of high viscosity which is very suitable for lubricating purposes and which may be decolorized if desired.

ITEM 8: Patent on removal of non-alcohols from mixtures with alcohols of more than 8 C atoms by azeotropic distillation. VII 63

Patent disclosure dated Leuna, January 26, 1945

Mixtures of higher alcohols and hydrocarbons, boiling above 200°C. are separated by azeotropic distillation with polyhydric alcohols. These form azeotropes with the hydrocarbons which boil lower than the azeotropes of the alcohols. The following polyhydric alcohols form azeotropes with hydrocarbons, but not with the alcohols, and are therefore especially suitable: butenediol 1,3, hexanediol 1,6, and pinacone. Separation is stated to be better in vacuum distillation.

Enrichment of the alcohol may be effected by extracting with aqueous methanol, and the enriched mixture then separated by azeotropic distillation.

ITEM 9: Recipe for K.K. catalyst. VII 71

$Al_2O_3 : SiO_2 = 1 : 9$

Yellowish round molded body of bulk weight 0.7, resistance to compression 10 to 30 Kg and high elasticity.

(a) Preparation of alumina:

Sodium aluminate solution : commercial alumina is dissolved in hot 25% NaOH, using 1.5 mol Na_2O per mol Al_2O_3 . The aluminate solution contains 200 g Al_2O_3 per liter. Nitric acid (45 per cent) at pH 6 (antimony electrode) is added to a precipitation temperature not higher than about 50°C. Water in an amount of one-third of the final volume is added to the precipitation chamber before the two solutions are run together. The filter cake is pressed and washed with water either on the filter or by decanting until the washwater shows no NO_3 reaction, and dried at 120°C. until the residue on ignition is approximately 70 per cent.

(b) Preparation of the silica gel

Sodium silicate solution (spec. grav. 1.333, 27 per cent SiO_2) and 2 n sulfuric acid are run together at a pH of 3-4 and a temperature of 10-15°C. The clear solution is coagulated by heating to 70-80°C, broken into pieces of 3-5 cm and washed by decantation until the wash water shows no SO_4 reaction. Distilled or purified condensation water may be used for washing. One hundred kg. of SiO_2 require about 40 m³ of wash water. The washed silica gel is dried at 120°C. to a residue on ignition of 70 per cent and ground ("vibrom") until 90 per cent passes 200-300 mesh.

(c) Preparation of catalyst from the gels.

The alumina is converted in a kneading machine with water into a plastic mass (containing 50-60 per cent solid material) and peptized by addition of 45 per cent nitric acid. Ten per cent of the theoretical amount, calculated for $Al(NO_3)_3$, is used; the alumina swells considerably. Then the silica gel (with additional water to make it a plastic mass) is added with constant kneading in a ratio $Al_2O_3 : SiO_2 = 1 : 9$. The mass is then further kneaded for 6 - 10 hours.

Another way of preparing the catalyst is mixing the dry gels and kneading with addition of water in a kneading machine for only 1 - 3 hours (no nitric acid necessary!).

The kneaded mass is pressed in an extruder and then made into balls in a machine ("Frankoma"), used in making candy. The balls are dried at 120° and then calcined at $450^\circ C$. for 4 hours.

X-ray spectrograms of the catalyst show few faint lines of aluminum oxide; the catalyst is therefore amorphous. If the catalyst is heated over $550^\circ C$. for some time, the X-ray spectrogram shows sharp but not well defined lines (recrystallization).

ITEM 10: Propane peroxide. Dutch report on pilot plant and late I.G. research.

VII 72

(a) Report on Dutch patents 5252 (1941) and 155,114 (1943) from laboratory of N. V. De Bataafsche Petroleum Maatschappij, Professor Zerbe, April 21, 1944.

Description of patents and semi-commercial plant. Propane and insufficient oxygen are reacted at $465^\circ C$. in a spherical chamber, in order to get maximum volume with minimum wall surface. The chamber is lined with V2A steel and the walls are air cooled. The reaction is started by ignition, and the necessary temperature maintained by adjusting the amount of oxygen.

The exit gas is cooled to $0^\circ C$. The condensate contains organic peroxides which are "selectively converted into formic acid and hydrogen".

Yield is stated to be 5.2 Kg of 30% hydrogen peroxide and 2.5 Kg. formic acid from $100 m^3$ propane.

(b) Novotny: preparation of H_2O_2 by oxidation of organic compounds. Experiments on propane oxidation under pressure were conducted. The product contained only about 3-4% H_2O_2 and 35-50% aldehydes.

(c) Report Eckoldt, April 8, 1945.

1. Preparation of aceto-peracid by oxidation of acetaldehyde

a. Experiments with flowing oxygen. The oxygen used as

an oxidizing agent was taken from a cylinder and dried by passing it through concentrated sulfuric acid. It then passed a flow meter (containing concentrated sulfuric acid), next a tower with soda-lime, and then led into the cylindrical reaction vessel through a porous plate which insured fine dispersion. The effluent gas passed a reflux condenser (held at $-10^{\circ}\text{C}.$), then a cooling vessel ($-60^{\circ}\text{C}.$), a wash bottle with water, and finally a flow meter. The results were not uniform, however, about 64% of the oxygen used was present in the product as peroxide.

b. Experiments with Stagnant Oxygen. The reaction was carried out in a shaking cylinder (about $3/4$ l.), cooled with ice. The vessel was connected through a tower filled with phosphorus pentoxide to a graduated vessel containing oxygen with water as sealing liquid. From acetaldehyde 68% of the oxygen consumed was obtained as peroxide.

2. Hydrolysis of acetoperoxide to hydrogen peroxide and acetic acid.

Only preliminary experiments were made with acetoperoxide made from 100% hydrogen peroxide and acetic anhydride. The hydrolysis was slow and accompanied by a loss of active oxygen.

SECTION VIII

BAG 3413

Deutsche Gold & Silberscheideanstalt

ITEM 1: Methanol Synthesis with Ternary Zn Mn Cr catalyst (Mn2)

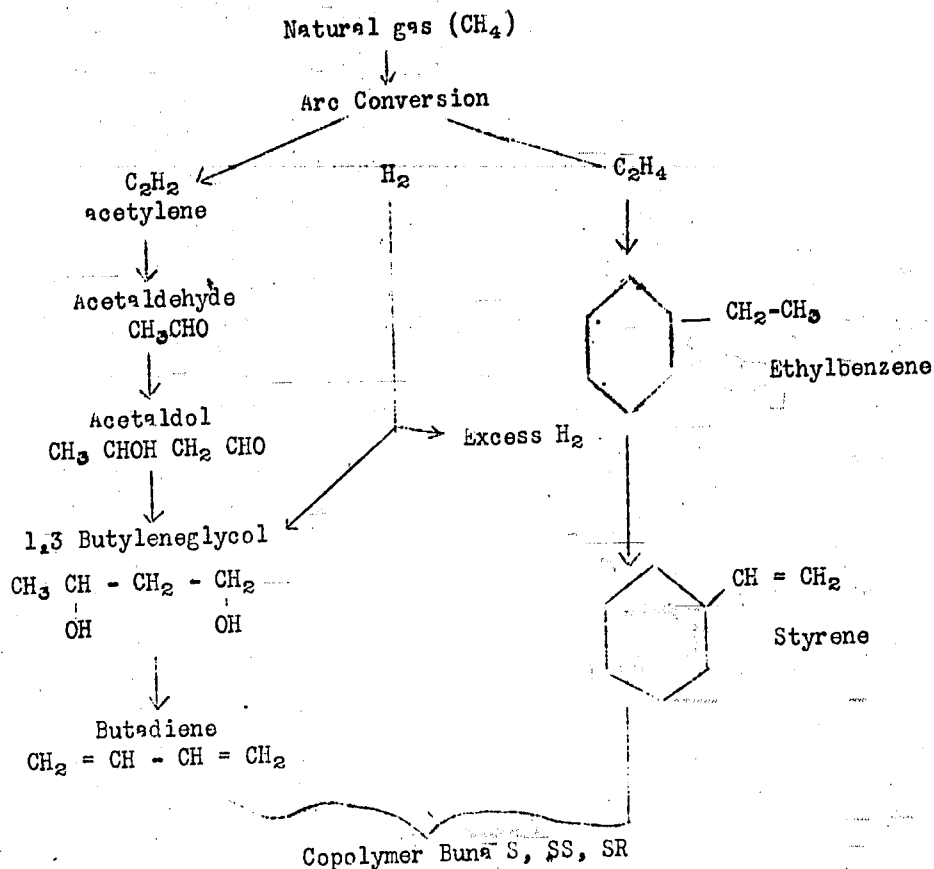
VIII 1

Preparation of catalyst: 392 g zinc acetate, 62.5 g CrO_3 and 143 g manganous nitrate are dissolved, precipitated with ammonia, washed, dried, and formed. (60.6% ZnO , 21.9% MnO , 16.2% CrO_3).

The activity surpasses the binary Zn-Cr catalyst "Stal" which gives at a S.V. of 10000 and $375^{\circ}\text{C}.$ about 720 g. of $\text{CH}_3\text{OH}/\text{h}/\text{liter}$, while Mn_2 gives 850 g/h/liter (estimated).

The high yield of isobutyl alcohol (3.2%) with a non-alkalized catalyst, which was precipitated with NH_3 , is considered remarkable.

ITEM 2: Pencil sketch of process by Dir. Baumann.



ITEM 3: Diacetylene absorption curve (infra-red)

VIII 5

ITEM 4: Miscellaneous analytical processes

VIII 7

(a) Analysis of a gas mixture with the Leuna column

Mixtures of close boiling hydrocarbons can be separated by fractionation in the Leuna column which appears to consist of sections of spiral made from 1.8 m of glass tubing, inner diameter 2-3 mm. Between the sections reflux dropping tips show both whether the reflux is satisfactory and whether the column is working properly.

About 1000 cc of gas are sufficient for the analysis. Operation is as follows: The pressure throughout the distillation is kept constant by means of a regulator (30 mm, to 100 mm). The condensing head is cooled to a low temperature, and the temperature of the stillpot is raised slowly until the reflux is uniform (1 drop in 2-5 seconds). Then the head temperature is allowed to rise

until the prescribed vapor pressure in the column is reached. During distillation the temperature of the bath liquid around the stillpot is raised slowly, and the temperature of the condenser is kept constant to $+1^{\circ}\text{C}$. for each cut. The end of the cut is reached when no further gas is pumped off. Then the temperature of the condenser is raised until the next fraction distills.

(b) Determination of hydrocarbon mixtures with fractional condensation (Stock)

The determination of hydrocarbon mixtures of 1 to 5 C atoms is carried out by the condensation method according to Stock. For separation of hydrocarbon mixtures, five different cooling baths are used.

- I. liquid nitrogen (-193°C .)
- II. pentane + liquid nitrogen (-150°C .)
- III. alcohol-ether + liquid nitrogen (-125°C .)
- IV. alcohol-ether + liquid nitrogen (-105°C .)
- V. acetone + solid CO_2 (-80°C .)

Under the conditions of the experiment, i.e. high vacuum, the C_4 and C_5 hydrocarbons condense in receiver V and IV; C_3 hydrocarbons condense mostly in receivers III and II, and in II the C_2 hydrocarbons. The CH_4 escapes with inert gases, is pumped off with a "Toepler" pump, measured, and analyzed.

The individual fractions are warmed and measured gasvolumetrically. For determination of small amounts of lower or higher hydrocarbons present, a molecular weight determination is carried out. The content of olefin can be determined by bromination.

With this method it is possible to separate a mixture of low boiling paraffins and olefins with inert gases into individual components.

(c) Determination of higher acetylenes with silver nitrate method.

The gas to be analyzed is drawn into a "Bunte" burette with mercury. About 10 cc of acetone is drawn in and the burette rotated to dissolve the gas in the acetone. Then a measured volume of 0.1 n AgNO_3 + 2% NH_3 (25%) is drawn in (avoid air) and the burette shaken for about 10 minutes. The contents of the burette are rinsed into a 250 cc volumetric flask, filtered + through a dry filter into a dry vessel, and the excess of Ag titrated with NH_4CNS .

$$\text{Calculation: } A = 2G - 2.24 V$$

$$B = G - A$$

$$A = \text{vol \% RC} \equiv \text{CH}$$

$$B = \text{vol \% HC} \equiv \text{C} - \text{R} - \text{C} \equiv \text{CH}$$

$$G = \text{vol \% Total acetylene (Hg(CN)}_2)$$

$$V = \text{cc } 0.1 \text{ n } \text{AgNO}_3 / 100 \text{ cc gas.}$$

(d) Determination of butadiene in the presence of paraffins and olefins.

1. The butadiene determination is carried out according to the maleic anhydride method, described in literature.

A 100 cc gas mixture is passed several times through molten maleic anhydride at 100°C. The decrease in volume corresponds to the content of butadiene. Paraffins and olefins with 1 to 4 C atoms are not dissolved to any appreciable amount.

2. If butadiene should be determined in the presence of paraffins and olefins, a combined method may be used advantageously. About 90 cc of the gas mixture is drawn into a "Bunte" burette and 40 cc n/2 bromide-bromate solution added to the mixture, acidified with a mixture of K₂SO₄ + H₂SO₄. The burette is shaken to constant volume and the decrease in volume determined. Then about 10 cc of n KI solution are added, shaken, and after a short time the contents discharged into a flask and the excess iodine back titrated with n/10 Na₂S₂O₃.

Assuming ideal gases, the content of butadiene and olefin, is calculated by the formula:

$$X = \frac{B - 0.883s}{.903}$$

$$Y = s - X$$

X = cc butadiene in 100 cc gas used (760 mm, 0°C)

Y = cc olefins in 100 cc gas used

B = cc 0.1 n bromide solution/100 cc gas used

s = cc contraction (bromine)/100 cc gas used

SECTION IX

BAG 5 TARGET 30/4.13

Politz

Table on Catalyst Composition

IX 1

<u>Symbol</u>	<u>Composition</u>
<u>Hydrogenation gas phase</u>	
5058	100 % WS ₂
7846 W250 (substitute for 5058)	10 % WO ₃ + 3% NiO + act. alumina
6434	10 % WS ₂ + terrana
<u>Hydrogenation-Dehydrogenation</u>	
7360 (1. Raff. catalyst)	6% MO ₃ + alumina
6108 (2. Raff. catalyst)	Terrana

Hydrogenation CV2b (aromatization)

7019

Hydrogenation T52 - Kala

3076

Hydrogenation, liquid phase (tar)

1102 Me = Lu 5475

6612

10927 Me

Hydrogenation, liquid phase (coal)

iron sulphate

"sulfigram"

Bayer mass dried-not formed
(used gas purification mass)

T 52 plant

5063 (Dehydrogenation)

4821 (Polymerization)

Splitting

2041 BZ catalyst

"Braunoxyd" - catalyst

Zinc oxide

"Bayer" mass (in pills)

"Lux" mass

In its place is used "Lauts" mass with about 45% water, 53.7% Fe₂O₃
(+ Ti), 10.1% sand and clay, 14% hydrate mass, 22.2% alkali.

TG Claus contact (2 kinds: soft and hard) Claus plant

15% CrO₃ + 5% V₂O₅ + act. carbon

2 mols. NiS + 1 mol WS₂

2% MO₃ - lignite coke (Grude)

10% FeSO₄

10% FeSO₄ + 5% NaOH

FeSO₄ · 7H₂O

Na₂S

7.6% SiO₂, 7.7% TiO₂, 46% Fe₂O₃,
12.7% Al₂O₃, 6.5% Na₂O, 17.6% CaO,
0.7% MgO, 0.9% SO₃

Al₂O₃ + Cr₂O₃

H₃PO₄ on ?

Hy gas splitting-containing Ni
(conversion)

Organic sulfur purification

Organic sulfur purification
tower purification

SECTION X

BAG 1477 TARGET 30/5.01

Ruhrchemie, A.G.

ITEM 1: Treatment of foreign workers

X 1

Instructions, etc.

END OF REEL