

Report 5. Interrogation of Director Alberts.

Date of Interrogation : April 13, 1945

Location : Herr Alberts' house, "An der Muhle",
Waltrop, nr. Castrop-Rauxel.

Personnel conducting Interrogation :

Dr. V. Haensel, U.S., Petroleum Administration for
War.

Capt. C.C. Hall, British, Ministry of Fuel and Power

Reported by : Capt. C.C. Hall.

Object of Interrogation

Herr Alberts' present position is that of Director of the Castrop-Rauxel plant (Target 30/5.03), but up to late in 1943, he had been manager at Sterkrade-Holten, and the object of the interrogation was to obtain information concerning this latter plant and the work of Ruhrchemie.

The Synthesis Cycle at Sterkrade. According to Herr Alberts, the system employed by Ruhrbenzin during recent years is as outlined in the flow scheme Fig. 13. It comprises two independent systems, one operating in two stages at normal pressure and using $H_2 : CO = 2 : 1$ as raw material and the other operating in three stages at 11 atmospheres pressure, the $H_2 : CO$ ratio of the inlet gas to the three stages being adjusted to 1.4 : 1, 1.6 : 1 and 1.8 : 1 respectively, by introducing the requisite amount of "converted" water-gas before each stage.

For Stage 1 on the medium-pressure side the inlet gas rate is 1000 m³/oven/hour, the temperature 180-200°C. and the gas contraction, 50%. Similar conditions obtain for Stage 2. In Stage 3, where all newly-charged ovens are started, higher rates (2,000 m³/oven/hour) and lower temperatures (165-185°C.) can be employed. The overall contraction is about 75% and the yield, 150 gm. C₃ and higher hydrocarbons/m³ ideal gas.

The history of a freshly-charged oven was as follows. It is started in Stage 3 and run for 10-14 days. It is then put on Stage 2 where it may remain for the rest of the catalyst's life or it may be transferred

after a period to Stage 1. Alternatively it may go direct from Stage 3 to Stage 1. The precise history depends on the demands of Stages 1 and 2 for new ovens but the charge of catalyst always remains on stream for approximately the same total time i.e. 9 to 11 months, depending on smoothness of operation, lack of interruptions etc. No solvent-extractions or other reactivation treatments are carried out in the medium pressure section.

The advantage of the scheme of commencing with a gas relatively deficient in hydrogen and then increasing the proportion of hydrogen in later stages lies in combining the beneficial effects of low hydrogen proportion on olefine content and methane production with the efficient utilisation of the carbon monoxide achieved with normal synthesis gas ($H_2 : CO = 2:1$).

Using normal synthesis gas throughout, 14% of the total hydrocarbons produced is methane but with the above scheme the proportion is reduced to 10%.

The products produced by this method of working are as follows :-

| | |
|----------------------|---|
| $C_3 + C_4$ | : 10% (Olefines 40%) (13% of C_4H_8 is iso) |
| $C_5-170^\circ C.$ | : 25% (" 24%) O.N. (Motor) ca. 45. |
| $170 - 280^\circ C.$ | : 30% (" 9%) |
| $280 - 340^\circ C.$ | : 20% Soft Wax |
| Residue* | : 15% Hard Wax M.P. ca. $90^\circ C.$ |

(*This includes 3% of wax extracted from the catalyst at the end of its life.)

It would appear that the total annual output of primary products from the whole system was of the order of 70,000 tonnes.

The Water-Gas Recycle Project. One of the reasons why it was found difficult, from an inspection of the contact oven house and the adjacent plant, to determine the nature of the cycle employed was that although the scheme outlined above was actually being used, most of the plant and pipe connections necessary for an entirely different scheme had been installed. This scheme involved the use of all the medium-pressure ovens in one stage with water-gas as the feed material and a 3:1 recycle gas-fresh gas ratio, the unrecycled residual gas being passed to a

normal 2-stage atmospheric-pressure section after adjustment of the $H_2:CO$ ratio to 2:1 in a CO-conversion unit. The system is illustrated by the flow diagram, Fig. 14. It had only been tried out on an experimental scale, the full-scale trials having been held up due to difficulties in obtaining certain items of equipment such as heat exchangers and expansion joints. As stated above most of the equipment was already installed, and a series of towers found at Sterkrade were identified by Alberts as the system of heat exchangers, direct condensers and charcoal absorbers for the recycle gas stream.

The object of this method of working was the production of olefines by maintaining a high concentration of CO in the gas mixture. If this is attempted by, for example, using an undiluted synthesis gas of composition $2CO + H_2$ there is a tendency to get carbon deposition. Alberts stated that the use of water gas with recycling was the best method of achieving the desirable effects of high CO concentration while avoiding carbon deposition. The principle of the process was illustrated by Alberts as follows :-

| | <u>Parts H_2</u> | <u>Parts CO</u> |
|-------------------------|-------------------------------|-----------------|
| Fresh water gas | 1.25 | 1.00 |
| Consumed in reaction .. | <u>1.00</u> | <u>0.50</u> |
| Residual gas | <u>0.25</u> | <u>0.5</u> |
| 3 volumes recycle gas . | 0.75 | 1.5 |
| 1 " fresh water gas | <u>1.25</u> | <u>1.0</u> |
| Total | <u>2.0</u> | <u>2.5</u> |

i.e. total inlet gas has the inverse $H_2 : CO$ ratio to that of water gas.

The reaction temperature for the process was higher than usual viz. $220-225^\circ C$. The gas contraction in the process was 50% and the yield 100-110 gm. C_3 and higher hydrocarbons/ m^3 ideal gas. In the pilot plant experiments a catalyst life of 6-7 months had been obtained. The products were as follows :-

| | | |
|---------------------------------|---|----------------------|
| $C_3 + C_4$ | = | 8% (olefines 60-65%) |
| Benzin $C_5 - C_{10}$ | = | 30% (" 60 ") |
| Middle oil $C_{10} - C_{17/18}$ | = | 28% (" 40 ") |
| Wax $> C_{18}$ | = | 34% (" small %) |

The gasol fraction formed an excellent raw material for polymer gasoline production. The benzin had an octane of 50-55 but this could be increased to 70 by an isomerisation process involving no gas formation or change in boiling range and olefine content. It consisted of treatment at atmospheric pressure and 300°C. in the vapour phase over Floridin activated by treatment with HCl. The space velocity and clay life were the same as for normal clay refining. Alternatively the benzin could be polymerised with aluminium chloride to give a lubricating oil of viscosity-pole-height 1.7.

The unsaturated middle oil would have formed the main raw material for the OXO plant. The paraffinic residue, after the latter process had removed the olefines, would be sold as diesel oil.

Alberts considered that this recycle process was the best method of conducting the synthesis with a cobalt catalyst.

Composition of Cobalt Catalysts

Alberts stated that in his view the most important effect of replacing thoria with magnesia was the increased hardness of the resulting catalyst and consequent reduction of dust formation in the ovens which causes bad gas distribution leading to "hot spots". Other advantages were ease of initiating synthesis, less tendency to form methane and carbon and increased life. It was only since magnesia-containing catalysts had come into use that lives up to 8 months had been achieved at normal pressure.

Alberts stressed very strongly the necessity for trials on the full-scale as early as possible in the development of new catalysts. On the laboratory scale, comparatively small differences were detected between ThO_2 , MgO , and $\text{ThO}_2 + \text{MgO}$ promoted catalysts. In the full-scale ovens, however, very important differences appeared. He considered that Co-MgO-Ksgr. catalysts were best for large-scale operation. The most suitable catalyst for normal-pressure operation is also most suitable for medium-pressure operation.

Oven Charge. Originally the charge per N.P. oven was 1000 kg. Co but in the last few years the charge had been successively reduced to 900, 850 and 820 kg. without reduction in the gas throughput or yield. The oven charge used in the normal-pressure oven in the cycle

shown in Fig. 13 was 820-850 kg., and for the medium-pressure ovens about 10% less. Alberts stressed that the maximum gas rate which could safely be employed in Stage 1 was 1000 m³/oven/hour.

Iron Catalysts. There had been no full-scale trial of iron catalysts but a considerable number of tests on a 1/10th full scale (100 m³/hr.). Ruhrchemie, Rheinpreussen, Ruhland and Lurgi had all developed iron catalysts and a trial of all four types had been staged at Ruhland on the 100 m³/hr. scale. The results were inconclusive. Alberts claimed to have no information about the Kaiser Wilhelm Institute iron catalyst.

Concerning the work of RCH on iron catalysts, Alberts said that further progress had been made since the S.I.C.S. contract. At the time of this contract the development was in quite an early stage. There were difficulties in reproducing batches of catalyst and the trials had not reached the 100 m³/hr. scale. The yields guaranteed to S.I.C.S. were calculated from small-scale single-stage results! It was anticipated that it would take 2 years to build the S.I.C.S. plant and that during this period RCH would be able to straighten-out all the difficulties.

When Alberts left Sterkrade in 1943, the proved life of the iron catalyst was only 3 months. On this basis, in a period of 1½ years the cost of replacement would be greater than that of cobalt. He believed that the RCH catalyst contained copper but no alkali and was prepared by precipitation from the nitrates on to kieselguhr. The catalyst was designed to give a balance between CO₂ and H₂O as oxygen end-products. The temperatures and pressures employed in the synthesis control the proportion of organic oxygen compounds formed. Alberts believes that iron is the catalyst of the future.

Alberts was then questioned on a number of miscellaneous topics :-

The Fischer Iso-Synthesis. He believed that it operates at temperatures in the region of 400°C. and pressures of the order of 150 atmospheres with catalysts other than Ni, CO or Fe. He doubted whether it had any practical value; it was probably cheaper to use catalytic cracking.

Nickel synthesis catalysts were of no value; they produced excessive methane.

I.G. Developments. I.G. were supposed to have three lines of development :-

1. Use of sintered iron catalysts in a fixed bed.
2. Use of other types of iron catalysts in the liquid phase.
3. Use of iron catalysts with a high rate of recirculation.

All three processes gave low yields and gave rise to complex mixtures of hydrocarbons and oxygen compounds which were only of value as fuel. The octane number of the benzine produced was in the region of 70. So far as he knew none of the processes had been applied on the large scale.

New Types of Synthesis Ovens. Alberts did not believe that cobalt catalysts could be operated successfully other than in the conventional German type of oven. Iron catalysts might possibly be employed in other types of apparatus. Their own experience with liquid-phase operation, which had been tried out several times at different plants, was most discouraging.

The experimental oven at Sterkrade had been constructed for the S.I.C.S. project. It was not a success.

Cobalt-Silver Catalysts. These had not been tested outside the laboratory. The catalysts were soft and of short life.

Cobalt Catalyst Reduction. The optimum conditions were very difficult to establish. Generally speaking, the lower the reduction temperature, the better, but lower temperatures required longer times. A 10°C. difference in the temperature of reduction made an important difference in the activity and life of the catalyst in the oven - a difference visible during the first three days of operation.

The Slow Precipitation of Cobalt Catalysts was dismissed as a 'patent racket'.

Metallgesellschaft developments such as the use of diluted catalysts and of 'porous rods' in the catalyst space were dismissed as 'patent rackets'.

Reactivation of Cobalt Catalysts. Reactivation with solvent or hydrogen is never used in medium-pressure synthesis and only in the first stage of atmospheric-pressure synthesis. In the second stage it is unnecessary as little or no wax is formed. Originally hydrogen was used, for the first time after 4 weeks operation then at 14-day intervals. Then, to save hydrogen, solvent treatment was substituted, but this was not so effective as hydrogen treatment. Finally solvent treatment followed by hydrogen treatment was used and this was the most successful method of all. The time intervals used are the same as those given above.

The high-temperature re-reduction treatment was a Roelen invention. It has never been tried on the full-scale but Alberts is convinced it will work and was preparing to try it at Castrop-Rauxel just before the bombing started. The process consists in treating the oven contents at 400°C. for 3 hours in pure hydrogen at 2000 m³/hour. The object of the treatment is the removal of persistent carbonaceous deposits.

Kieselguhr for Cobalt Catalyst Preparation. Iron and calcium should be as low as possible. Physical structure is of particular importance and there is a risk of ruining this by acid treatment. The only real test is to "try it and see".

Total Recycle of Products. This had been tried-out on the full scale, but was found to lead to lower conversions and an increase in saturated hydrocarbons.

Catalyst density. Use of dense catalysts (i.e. weighing more than 350 gm./litre) led to excessive reaction in the top layers of catalyst with formation of methane and carbon.

Synthesis of Lubricating Oils. The best oils were obtained by aluminium chloride polymerisation of cracked primary product. The normal procedure was to crack the total primary product after removal of benzin (e.p. 170°) in a Dubbs unit operated at as low a pressure as possible in order to ensure reaction in the vapour phase. The pressure was ca. 8-10 ats. and the temperature 480-500°C. The yields were as follows :-

| | | | |
|------------------|-----|-----|--|
| Spirit to 180°C. | : | 70% | (olefines 70-75%) |
| Gas | : | 30% | (C ₃ + C ₄ : 25% |
| | | | C ₂ H ₄ : 14% |
| | | | C ₂ H ₆ : 12% |
| | | | Rest: H ₂ , CH ₄ , etc.) |
| Residue | ca. | 1% | |

The soft wax fraction alone forms a better cracking stock giving 80% yields of benzin to 180° containing 80% olefines.

The polymerisation is carried out in batches in vessels 3 m. in diameter and 6 m. high fitted with agitators and heating and cooling coils. The charge is 24-30 m³ stock + 1.5% AlCl₃. At the start the temperature is maintained at 40°C. and is subsequently raised to 80° and finally to 100°C. The total reaction time is 6 hours. The sludge settles to the bottom and the upper layer still containing sludge in suspension is run into a settling tank. The sludge remaining in the polymeriser is used for the subsequent batch. After settling the clear upper layer is mixed with clay and zinc oxide and then passed through a filter press. The filtrate is topped at atmospheric pressure and then distilled in vacuum, 5 cuts being made. The viscosity pole height of the best cut is 1.85.

Using soft wax as cracking stock an oil of v.p.h. 1.6 can be prepared. In this case the olefines boiling up to 250°C. can be polymerised.

When using primary product (less benzin) as raw material, the over 180° portion can either be recycled or disposed of as diesel oil.

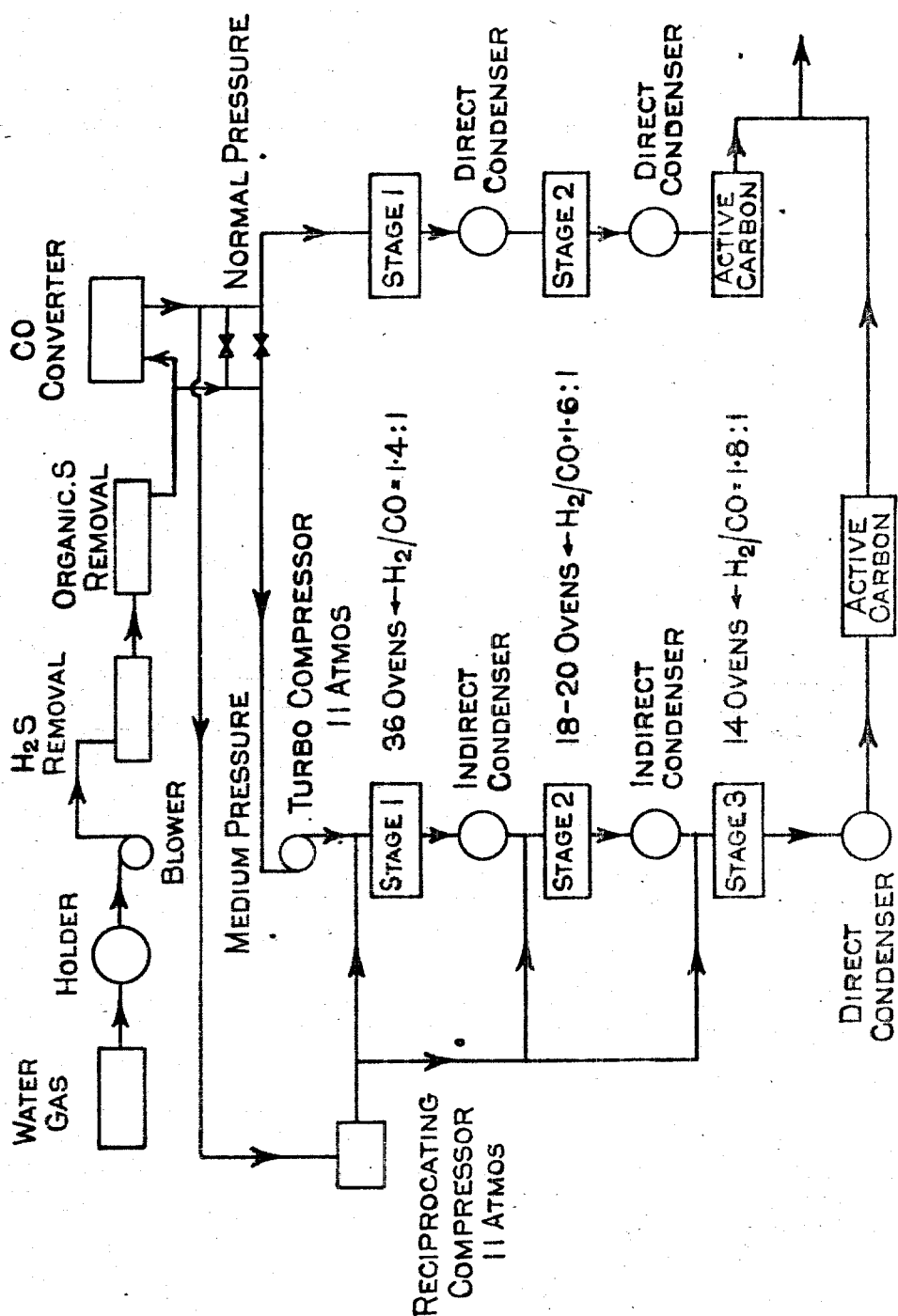


FIGURE 13. FLOW SCHEME FOR SYNTHESIS CYCLE USED AT STERKRADE
(C.I.O.S. 30/501, 502, RUHRCHEMIE AG - RUHRBENZIN AG, STERKRADE)

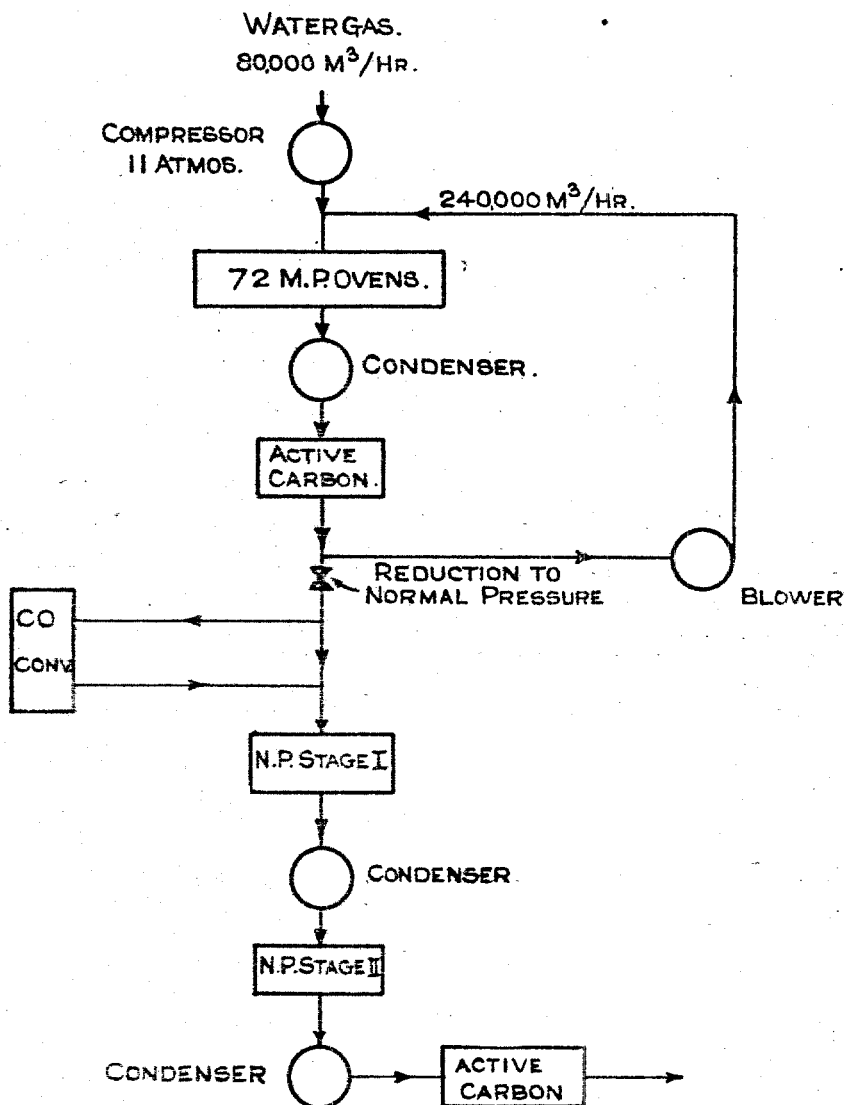


FIG.14. FLOW SCHEME FOR RECYCLE PROJECT.

(C.I.O.S. 30/5-01,5-02 RUHRCHEMIE A.G.

-RUHRBENZIN A.G. STERKRADE.)