

Frames 65-71
72-82

Two copies of a paper by Michael on the contemporary status of hydrocarbon synthesis from a mixture of CO and H₂, dated July 24, 1941.

A comparison of gas recycling and foam processes.

Frames 83-84

Discussion of replacement of cobalt catalyst with iron. April 19, 1943.

The discussions were limited to the desirability of replacing cobalt with iron because of the scarcity.

Frames 85-87

Cobalt catalysts for Fischer Plants. April 19, 1943.

Discussion of available supplies of cobalt and losses during operations.

Frames 88-90

Discussions on the possibility of replacing cobalt catalysts with iron catalysts in the Fischer synthesis. February 3, 1943.

According to present information iron catalyst can replace cobalt only in pressure synthesis. No iron catalyst is known to replace cobalt under present operating conditions for cobalt catalyst.

All iron catalysts developed by the I.G. operate at temperatures exceeding 2200°, or above the maximum temperature used with cobalt.

Only the synol catalysts of the I.G., a fused iron catalyst, operating with high-CO gas between 185 and 210° could be used in the existing reactors. The reaction products are entirely different, and consist principally of oxygen-containing compounds with only 15% of a wax fraction 325-500° C. which still contains oxygen. According to Dr. Wenzel, at operating pressures 15-25 atm., 150 gm. liquid products are obtained in four stages per cubic meter of pure gas; the products contain 40-60% alcohols. The space-time yield is 0.35 kg./l., day, and was tested in a 750 l. reactor.

As with all iron catalysts, more CO₂ than H₂O is formed, while water is the only byproduct in the present reactors operating with cobalt. An additional CO₂ scrubbing would be required when changing over to iron catalysts.

Iron catalysts operating above 2200° C. are studied in three I.G. locations.

1. A fused iron catalyst prepared by Dr. Linckh's method operates at atmospheric pressure at 230-240°, with the production of 80 gm. liquid products per cubic meter, according to Dr. Duftschmidt.
2. Dr. Scheuermann uses an iron-copper precipitation catalyst at 12 atmospheres and 230° C. (220° minimum) producing 77 gm. liquid products per cubic meter in one stage; 78% solid wax is present in the fraction above 325°. Laboratory tests gave a space-time yield of 0.45 kg./l., day.
3. Dr. Michael uses a modified sintered iron catalyst in 5 l. reactors at 20 atm. and 250° C. with 0.5 kg./l., day space-time yield of liquid and solid products with 50-60% wax above 350° C. The gas conversion in a single stage is 70%. The catalyst could still be used at 230° with considerably smaller space-time yield.

Frames 91-93

Gas synthesis test as of June 10, 1941.

A report by Dr. Michael on the use of ground synol catalyst in a foam converter and a lump synol catalyst in recycle reactors.

Frames 94-97

Alcohol synthesis from CO-H₂ mixtures by the gas recycle process, September 13, 1941.

In the gas recycle process, the heat of the reaction is removed inside the reactor by the gas itself and transferred to a cooling system, from which the gas is returned to the reaction space. The recycled gas is about 100 times greater in amount of the make-up gas, if 80% of the latter is converted.

The methane-ethane gasification amounts to but a few percent, and the gas conversion is very high if carbon dioxide is scrubbed out from the recycle gas.

The products are separated at three temperatures, wax is removed in a hot separator maintained at about 100°, the intermediate boiling fractions are condensed in a water-cooled separator, and the light ends are condensed at -10- -40° C.

The products in the table on next page were obtained in the gas recycle reactor with a fused iron catalyst at 195° C., 20 atm. The distillation products were neutralized with 5% KOH and washed four times. The standard I.G. analytical methods were used in the determinations.

| Fraction | a | b | c | d | e | f | g | h |
|--|--------------|------------------|------------------|--------------------|---------------------|---------------------|--------------------|-------------|
| | | | | | | | | |
| Percentage | -100° 6.6 | 100-150° 22.6 | 150-200° 18.8 | -100/18 mm. 3.4 | -150/18 mm. 13.4 | -200/18 mm. 23.3 | -250/18 mm. 6.7 | 250° 5.2 |
| Gasoline 48% Middle oil 46.8% | | | | | | | | |
| Avg. molecular wt. | 95 | 108 | 121 | 131 | 162 | 216 | 291 | 460 |
| Free alcohols, % | 7.8 | 19.0 | 28.7 | 24.1 | 28.5 | 19.0 | 13.8 | 15.0 |
| Esterified alcohols | 0.4 | 0.8 | 2.3 | 2.7 | 3.2 | 3.8 | 5.2 | 16.2 |
| Total alcohols | 8.2 | 19.8 | 31.0 | 26.8 | 31.7 | 22.8 | 19.0 | 31.2 |
| Aldehydes + ketones | 5.7 | 6.7 | 9.0 | 7.6 | 6.5 | 4.2 | 7.8 | 92.0 |
| Free acids | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Olefins by hydro- genation, % | 65 | 59 | 46 | 46 | 38 | 23.5 | 46 | 17 |
| Olefins from iodine number (Hanus), % | 65 | 52 | 34.5 | 35.5 | 29 | 20 | 20 | 48 |
| Oxygen, % | 4.2 | 5.6 | 7.2 | 6.0 | 5.3 | 2.8 | 2.3 | 4.7 |

1/ This fraction, solid at room temperatures, cannot be analyzed by the methods used.

Frames 98-103

Status of gas synthesis tests. November 14, 1941.

Frames 104-105

Status of gas synthesis test. February 13, 1942.

A report on a large foam reactor started in 1/17/42. The reactor was operated for 20 days only and the test had to be stopped for reasons not connected with the method, but for want of proper oil cooling.

Frames 106-109

Discussion of CO-H₂ synthesis on 4/7/41.

Discussion of the Leuna synol process.

Frames 110-114

Discussions of testing of aviation gasoline. June 10, 1941.

Scattering of results of determination of olefins, aromatics and iodine number, using BVM directions of October, 1940.

1. Directions were not closely followed by a number of laboratories in the determination of olefins and aromatics. For instance, Eggertz tubes were substituted for the Kattwinkel shaking tube, the samples were not strongly shaken for 15 minutes with sulfuric acid as directed, the shaking out was not repeated with fresh acid when more than 10% aromatics were present.
2. The DVM directions for the determination of olefins and aromatics are generally not sufficiently precise. Factors which are known to affect results very strongly are either not at all defined or only inexactly defined: E.g., the temperature conditions, intensity of shaking, etc.
3. The olefin determinations following DVM directions frequently gives too high results. The aromatics are determined by subtraction of olefins from the sum of aromatics and olefins, and as a result aromatics are also inaccurate. As a result, only the sum of aromatics and olefins should be reported.
4. The DVM method generally gives too high results for the sum of aromatics and olefins, and the error is the greater the less aromatics are present in gasoline.

5. The iodine numbers determined by the DVM directions are generally much too high.

Frames 114-125

Knock limit curves.

January 10, 1941.

A number of curves are presented for the knock limit with three fuels with and without additions of ET 110. (isooctane)

Frames 126-128

Remarks on Fromherz paper on the calculation of supercharge curves, by Dane, Raichle, and Nonnenmacher. June 10, 1941.

Frames 129-134

Aviation gasoline discussion of July 16, 1941.

Discussion of the quality of C₃ aviation gasoline, its storage stability, the effects of light gasoline addition to CV₂b gasoline, alkylate addition, the DVL process of supercharge curve determinations with divided injection, valve overlapping, thermal stressing of motors, etc.

Frames 135-139

Report on a visit to the BMW Flugmotorenbau G.m.b.H. Berlin, February 6, 1942.

The purpose of the visit was to find the reason of lead separation from CV₂b gasoline, which was attributed to the presence of some poorer grade gasoline in the tank when CV₂b gasoline was pumped in.

Frames 140-141

Octane numbers of light gasoline fractions.

| | Research method | | Motor method | |
|---|-----------------|-----------|--------------|-----------|
| | No Tel | +0.12 Tel | No Tel | +0.12 Tel |
| Light gasoline - 110° C. from bit. coal hydrogenation | 82 | 96 | 77 | 93 |
| Light gasoline -110° C. from bit. coal tar m. oil | 83 | 98 | 78 | 92.5 |
| Light gasoline -110° C. from lignite hydrogenation | 88 | - | 78 | 92.5 |
| Alcohol gasoline -110° C. | - | - | 78 | 99 |

Frames 142-147

Evaluation of knock limit curves of alcohol-gasoline mixtures, February 8, 1941.

The knock limit curves of all the mixtures were different from expected and exceptionally poor, and the methods therefore were tested.

It was found that there either existed a constant source of error (in the motor) or else the samples tested were not as represented. A check against synthetic mixtures showed that the actual values should have been close to the expected values.

Frames 148-155

Comparability of knock limit curves by the Oppau process and the supercharge curves by the DVL process. September 1, 1941.

Summary

The testing office at Oppau has now developed a process based on the method of O.N. determinations and consisting in the determination of the knock limit curves of fuels in relation to the air excess λ at constant charging pressure by varying the compression. The critical compressions found were plotted against the corresponding O.N., giving the knock-pressure curve which is similar to that obtained by the DVL method plotted by variation in compression and called the supercharge curves. A comparison of conditions shows that the processes in both methods are not identical, because in the Oppau method the compression, temperature and pressure of the cylinder charge are changed, while in the DVL process only pressure is changed. The curves by the Oppau method are therefore expected to be somewhat different in character than those obtained by the supercharge method; aromatic fuels will cause a characteristic steeper rise in the supercharge curve than do paraffinic fuels, and this rise will be far less pronounced when measured by the Oppau method. It was, in addition, concluded that plotting knock limits in terms of octane numbers produces different curves than the supercharge curves, in that the less knock-resistant fuels give steeper curves than more knock-resistant, which is not true for supercharge curves. A better comparability with the supercharge curves is obtained by plotting the knock limit curves in terms of ξ , or better still by using performance terms instead of octane numbers.

Frames 156-157

Specifications for the Scholven aviation gasoline VT-345, May 25, 1944.

Frames 158-167

Knock testing with different mixtures of aromatics, November 19, 1942.

The results of tests of two deliveries of aromatics are presented in two tables and six graphs.

The octane numbers (M.M. and R.M.) of the mixtures of aromatics were determined with and without the addition of 0.12% by volume of Tel. The following substances affected knocking particularly strongly:

| | <u>Made with</u> | <u>Boiling range</u> |
|--------------------------|-------------------|----------------------|
| Tripropyl benzene | AlCl ₃ | 225-230° |
| Do. | do. | 230-240 |
| Propyl di n-butylbenzene | do. | 155-266 |
| Dipropyl n-butylbenzene | do. | 230-256 |
| Dipropyl benzene | do. | 225-230 |
| Tetrapropyl benzene | do. | 260-280 |
| Propyl n-butylbenzene | do. | 200-250 |
| Di n-butylbenzene | do. | 220-260 |
| Ethyl propyl benzene | do. | 150-230 |

The knock resistance of the following compounds is the lowest:

| | <u>Made with</u> | <u>Boiling range</u> |
|--------------------|--------------------------------|----------------------|
| Octyl benzene | AlCl ₃ | 230-250° |
| Do. | H ₂ SO ₄ | 210-250 |
| Hexyl benzene | AlCl ₃ | 200-220 |
| Do. | H ₂ SO ₄ | 210-215 |
| Tetraethyl benzene | AlCl ₃ | 220-260 |
| Do. | do. | 280-320 |
| Do. | do. | 190-320 |

Frames 168-172

Differences between bituminous coal upgrading processes, May 27, 1943.

The differences between specific requirements for iron and coal in various coal upgrading processes cannot be precisely evaluated because of the different products formed and different quality of the products.

Coal input and iron consumption are given in the appended tables for five typical coal upgrading processes. They were based on Upper Silesian conditions because local bituminous coal can be carbonized at low temperature and because of the scarcity of coking coals.

High pressure hydrogenation is represented in cases 1 and 2, and is characterized by its adaptability to the different raw materials, variation in products and quality requirements. The plants can produce aviation gasoline, motor gasoline, Diesel oil, or fuel oil, as required.

Bituminous coal l.t.car. and high temperature coking are tabulated in cases 4 and 5. Coke is the principal product in these processes, and the proportion of liquid fuels is relatively small.

Case 3 is a combination of l.t.car. with hydrogenation, in that the l.t.car. tar is further upgraded, while most of the coke is retained for solid fuel economies.

The hydrogenation basis (cases 1 and 2) was evaluated from data from the large existing plants or plants under construction. The single products of hydrogenation are high-grade fuel from coal. Case 1 is a pure aviation gasoline plant, while fuel oil and aviation gasoline are to be obtained in case 2 in the proportion 1:1. Both aviation gasoline and fuel oil meet the highest requirements of the aviation ministry and of the Navy. The unavoidably formed off gases--ethane, propane, butane--are used as power gas or else are the principal raw material for the production of i-octane and synthetic lubricants, and are necessities for high test fuels and lubricants.

A comparison of tonnage of mineral oil products in cases 1 and 2 shows that about 10 percent more mineral oils are produced with fuel oil production. The iron requirement for these plants is also smaller, corresponding to the lower power consumption in hydrogenation to fuel oil.

Phenols at present obtained in hydrogenation plants are derived from effluent waters; phenol production could be greatly increased at the cost of aviation gasoline production. Comparison of case 3, combination of bituminous coal l.t.car. and tar hydrogenation with regular coal hydrogenation (case 1) shows that the oil production is reduced to one-third for the same coal input, but that a large amount of coke is formed in its stead. A small part of the l.t.car. coke (8%) is used for the hydrogen production in tar hydrogenation. Most of the coke can be used for home heating or for transportation as producer coke, or is used in other ways industrially, such as creating the necessary coke basis for other hydrogenation plants. Thus, bituminous coal l.t.car. was necessary in Blechhammer in connection with hydrogenation, because insufficient coking coals are available in Upper Silesia.

The actual coal consumption in case 3 is found from the difference between the coal used locally and the l.t.car. coke returned to the coal industry. A considerable amount of coke is produced in the combination process in addition to oil, but the iron requirements for the installation of a plant for one million tonnes of coal per annum is only one-third of that of case 1.

In direct hydrogenation the actual coal consumption per tonne mineral oil and the iron requirements are about as high as in the combination l.t.car. with hydrogenation, in which large amounts of coke are produced in addition. This shows that the expenditure for end products of the same quality is of the same order of magnitude in different processes. This is true, however, only for the tar content of Upper Silesian coal of 10% on the average. The iron requirements would rise for the combination process with lower tar contents in the coal.

Case 4 is combination of l.t.car. of bituminous coal with distillation and processing of the l.t.car. tar. The hot surface process (BT process) was used in this combination as the most favorable l.t.car. process found experimentally. Tar was to be processed by the recently developed Byk Gulden process.

In this combination, l.t.coke is again the principal product, and fuel oil, phenol, motor gasoline, and pitch are produced from tar. The proportion of light fuels is relatively small.

L.t.car. fuel oil properties meet the requirements of the Navy, but are lower in value than the hydrogenation fuel oil. Recoverable phenols and the gas produced in charring which can be used as city gas, are important.

Case 5 brings out the analogy between low and High temperature coking of bituminous coal; coking is followed by tar distillation.

Iron requirements referred to coal throughput are in this case somewhat lower than in low temperature carbonization. Coking offers the advantages of producing better metallurgical coke and larger amounts of coke, but less tar, and advantages of l.t. coking consist in almost three times greater yield of liquid products. Coking coals will be naturally always coked because of the demands for metallurgical coke. The further development of l.t.car. will be in the direction of producing metallurgical coke from coal unsuitable to coking.

It follows readily from the above listing of characteristic differences of various processes of upgrading coal, that direct comparison between hydrogenation and l.t.car. is impossible: Hydrogenation produces chiefly high-test liquid fuels, while coke is the principal product of l.t.car.

TABLE - Differences between bituminous coal upgrading processes.

| Case | 1 | 2 | 3 | 4 | 5 | Remarks |
|---|---|------------------|-------------------|---------------------|--------------------|---|
| L.t.car. | Lurgi flushing gas | | | Combination process | Coking | Briquetting not required for l.t.car. |
| Input | | | | | | |
| Coal with 8% water, tonnes | 204,000 | 158,000 | 1,520,000 | 1,208,000 | 1,000,000 | |
| Power requirements | | | | | | |
| Coal for power, $H_u = 7,000$ kcal./kg., T. | 2,600 | 2,040 | 19,600 | 14,500* | 20,000* | *Coke breeze can be used for purpose. |
| Coal for gasification, $H_u = 7,000$ kcal./kg., T. | - | - | - | 102,000* | 130,000* | *The gas produced is used as city gas, and fuel gas for firing must be obtained in producers. |
| Products | | | | | | |
| Char, 5% H_2O , T. | 143,000 | 111,000 | 1,065,000 | 835,000 | 687,000 | |
| L.t.car. tar, T. | 18,950) | 14,700) | 142,000 | 91,500 | 37,000 | |
| L.t.car. gasoline, T. |) |) | | 8,300 | 9,200 | |
| Excess gas, kcal. | 102×10^9 | 79×10^9 | 760×10^9 | 560×10^9 | 1200×10^9 | |
| Hydrogenation or tar processing Process | | | | | | |
| | Coal hydr. Coal hydr. Tar hydr. Byk-Gulden Distillation | | | | | |
| Input | | | | | | |
| Hydrogenation coal | | | | | | |
| 8% water, 4% ash, T. | 205,000 | 205,000 | - | - | - | |
| L.t.car. tar, T. | 18,950 | 14,200 | 142,000 | 94,500 | 37,000 | |
| Tar from power production, T. | 6,650 | 5,900 | - | 8,150 | 10,500 | |
| Power requirements | | | | | | |
| Power coal in hydrogenation and tar processing, T. | 234,000 | 184,000 | - | 33,400 | Incl. above | |
| Power coal for tar hydrogenation, $H_u = 7,000$ kcal./kg., T. | 24,200 | 19,400 | 192,000 | - | - | |
| Coal for fuel gas, $H_u = 7,000$ kcal./kg., T. | 83,000* | 74,000* | - | - | 1,600 | *The excess gas from l.t.car. is insufficient and must be supplemented with producer gas. |

TABLE (cont'd.)

Assumed heat contents of
the products:

| | | | | |
|------------------------------|--------------------------------|---------------------------|---|--|
| Coke, $H_u = 7,000$ kcal/kg. | L.P. gasoline 10,500 kcal./kg. | Fuel oil, 9,150 kcal./kg. | L.O. benzene 9,600 kcal./kg. | C_3, C_4 , 11,000 kcal./kg. |
| C_2 , 11,300 kcal./kg. | Phenol, 7,800 kcal./kg. | Pitch, 8,600 kcal./kg. | City gas from BT car., 6,200 kcal./mm. ³ | City gas from coking, 4,400 kcal./mm. ³ |