

Chemistry. — "*Hydrogenation of Paraffin by the BERGIUS' Method*".

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In a previous communication on the hydrogenation by BERGIUS' method of mineral oils or allied products, different experiments were discussed, which were carried out with heavy Borneo-asphalt-oil, distillation residue (pitch) of this oil, and with asphalt obtained by distillation of Mexican crude oil ¹⁾.

The experiments in question, comprising both cracking- and berginisation experiments, were executed in a vertical immovable autoclave.

That we have now chosen another material, technically perhaps of less importance for this purpose, is owing to the peculiar advantages which commercial paraffin offers for such experiments over other materials, as asphalt. Paraffin is much more easily analysed than asphalt, and this holds also for the products prepared out of paraffin, when they are compared with the corresponding substances formed in the treatment of asphalt. Thus paraffin yields products that are less strongly coloured than Mexican asphalt. For these experiments we had an autoclave at our disposal which could be shaken continuously ²⁾.

The way of procedure was for the rest quite analogous to the earlier experiments; the arrangement of the apparatus is represented in fig. 1. The capacity of the autoclave was about 2500 cm.³, the heating took place by means of gas, in such way that the temperature could be regulated accurately to a few degrees.

The paraffin had a Sp. Gr. (15°/15°) of 0,913, the solidifying point (SHUKOFF method) was 50,6°, the bromine-value, (addition) determined by MC. ILHINEY's method ³⁾, was 0,5.

¹⁾ Congrès international des combustibles liquides, Paris, 9—15 Octobre 1922; Chimie et Industrie, numéro spécial, Mai 1923, p. 200.

²⁾ Apparatus supplied by ANDREAS HOFER, chief instrument-maker at the laboratory of Prof. Dr. FRANZ FISCHER, Kaiser Wilhelm Institut für Kohlenforschung, Mülheim—Ruhr.

³⁾ Journ. Am. Chem. Soc. **16**, 275 (1894), **21**, 1084 (1899), Journ. Soc. Chem. Ind. **19**, 320 (1900); H. BECKURTS, Die Methoden der Massanalyse, Braunschweig 1913, p. 480.

Practically the bromine value of the paraffin may, therefore, be neglected. The bromine-value determined according to Mc. L. HINEY's method, is obtained by subtracting the substituted bromine from the

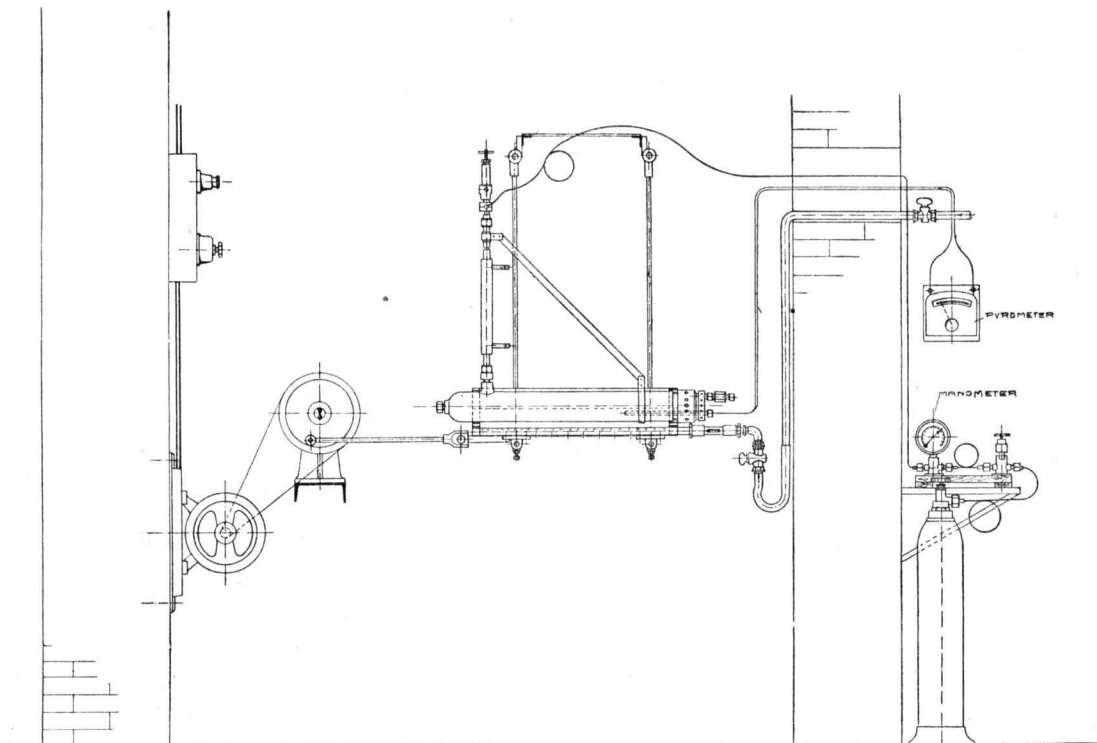
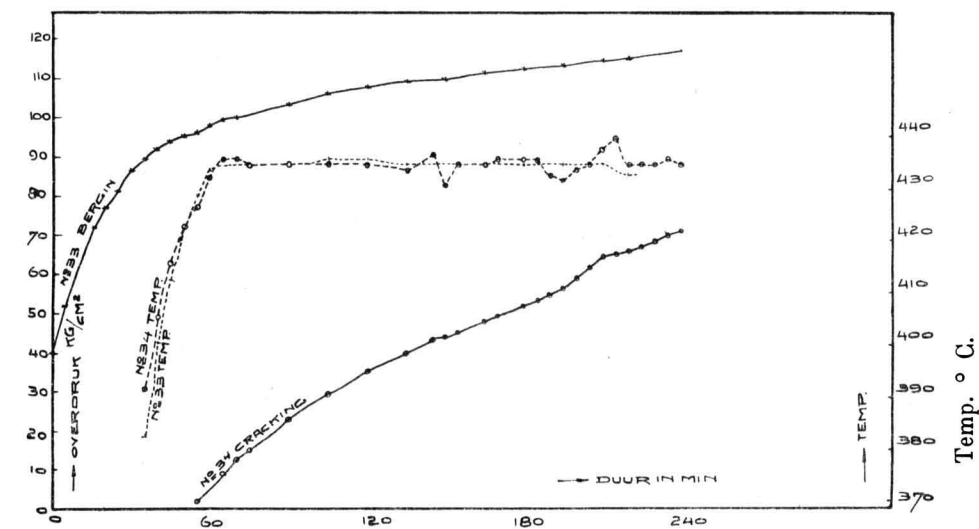


Fig. 1.



Overdruk = Pressure

Duur in min. = Time in minutes

Fig. 2.

total amount of the absorbed bromine. The remaining quantity gives a measure of the degree of unsaturation, and is expressed in percentages of weight of the weighed quantity.

In every experiment 300 gr. of paraffin was taken, an equal weight of stones being put in the autoclave to promote a thorough mixing; the temperature was always 435° . Some of the results obtained are recorded in the table, and in fig. 2 an illustration is given of the variation of the pressure in the course of experiments 33 and 34. Though in experiment 33 the typical pressure curve according to BERGIUS given in our preceding communication is not obtained, probably on account of the high temperature, the difference from the cracking-pressure curves is nevertheless very striking. In all the other experiments recorded in the table the pressure curves obtained are analogous to those of 33 and 34. The oils obtained by the BERGIUS' process were coloured from yellow to red, and perfectly transparent, a small quantity of "carbon" was deposited on the bottom. The oils obtained in cracking were very dark of colour and pretty well opaque. Here too separation of some carbon is found. The small quantity of carbon which is deposited on the bottom, when the weight of carbon which had already been deposited on the stones is added, is so small, both in the cracking and in the BERGIUS' method, that practically *the paraffin may be assumed to have been entirely converted into oil and gas in both processes.*

In this we leave out of consideration experiments 35, 37, and 40, where the duration of the processes was still so short that the reaction product had remained partially solid. Hence the product obtained had to be melted out in these experiments.

It appears from the experiments made that,

1. observations can be obtained which can be perfectly reproduced (compare 35 and 37, and 46 and 48).

2. if the duration of the experiments is long enough, the paraffin is practically quite converted into liquid oil and gas, both in the cracking and in the BERGIUS' process.

3. the yield of gasoline does not differ much in the two processes.

4. there is a great difference in the nature of the residues left in the distillation of the oil obtained according to ENGLER. Its specific gravity is always smaller in the Berginisation experiments than in the corresponding cracking experiments, which is a confirmation of corresponding experiments made by BERGIUS.

5. It appears from the final pressure, also in connection with the gas analysis (percentage of hydrogen), that actually considerable quantities of hydrogen are absorbed in the berginisation.

COMPARISON OF BERGINISATION AND CRACKING AT $\pm 435^{\circ}$ C.

N ^o . of the experiment	Time required to reach the temperature in minutes	Duration of the proper experiment in minutes	Initial pressure in atmospheres	Maximum pressure during the experiment	Final pressure after complete cooling	Obtained oils in grammes	Bromine content (addition)	Distillation of the obtained oil according to ENGLER					Gases.			
								Weight % of the distilled oil.				Sp. G. residue 15°/15°.	Quantity in Litres	Sp. Gr. compar- ed with air	Hydrogen percentage.	
								to 220°	to 300°	residue > 300°	Loss %)					
35	Berginisation	60	60	40	110.5	37.5	260 ¹⁾	16.4	24.9	41.0	56.3	2.7	0.846	—	0.24	85.8
37		60	60	40	108.5	37.5	272 ¹⁾	16.1	22.8	37.9	59.0	3.1	0.854	—	0.20	89.5
36		60	120	40	107	31	272	19.0	36.6	56.6	38.7	4.7	0.838	—	0.37	74.6
33		60	180	40	117	30	256	20.8	51.7	72.1	22.4	5.5	0.852	—	0.56	56.9
46		75	240	40	118	28	250	21.0	58.9	79.6	14.8	5.6	0.836	63	0.63	47.5
48		75	240	40	120	28	249	20.7	59.7	79.2	13.8	7.0	0.838	62.5	0.63	46.5
40	Cracking.	80	60	0	30	± 2	271 ¹⁾	21.6	23.0	39.0	60.1	0.9	0.854	—	0.99	—
45		70	120	0	51.5	< 4	270	27.6	41.9	63.7	32.0	4.3	0.855	—	0.80	—
34		60	180	0	71	5	246	26.1	56.1	76.5	17.5	6.0	0.900	—	1.10	2.3
49		75	240	0	72	7.5	238	23.9	56.8	76.9	16.2	6.9	0.902	29	0.94	3.7

¹⁾ The product obtained was still solid and had to be melted out, which gave rise to extra losses of weight.

²⁾ Belongs to the lowest fraction.

6. The bromine value caused by addition of the oils obtained by berginisation is lower than that of the corresponding cracking experiments. It is, however, very risky to draw general conclusions from this bromine value, for dissolved unsaturated gases can have a great influence on the halogen value.

The example given here proves convincingly that a determination of the yield of oil and gas from a solid substance does not suffice to enable us to form a correct opinion on the process of BERGIUS. A comparative cracking experiment is required for this. Possible results refer only to the procedure followed, in this case to the periodic process, the temperature at the experimenting etc.

It is self-evident that in practice processes that proceed continuously, will be preferred. It may, however, be considered to be an established fact that when BERGIUS' method of procedure is followed, important quantities of hydrogen added from the outside, are chemically bound. After the scientific researches of SABATIER c.s. concerning the hydrogenation of hydro carbonic vapours with catalyst and the technical hardening of fatty oils (NORMANN and others), this fact, combined with the absence of express addition of catalyst, may be considered as the third great discovery in the region of hydrogenation.

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