

Chemistry. — “*Conversion of paraffin by heating under pressure in the presence of hydrogen, methane and other gases*”¹⁾. By Prof. H. I. WATERMAN and J. N. J. PERQUIN, Chem. eng. (Communicated by Prof. J. BÖESEKEN).

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The research taken up by us concerning *the scientific and technical significance of Bergius' hydrogenation process* is going to ask still many years of study, while a thorough experimental ability and a highly specialised knowledge of the different kinds of apparatus are necessary. Meanwhile we are already able to give some of the most important results.

Material and working scheme.

The research concerns this time the same kind of paraffin while the scheme of working and the apparatus used have been described in an earlier communication on the decomposition of cottonseed oil²⁾. With the exception of a couple of experiments, where we distilled during the heating, also now no condensor was used.

Excepted in the two experiments just mentioned the heating was done in a closed vessel and consequently no gases were added or blown off during the experiment.

As characteristics for the judgment of the oil we used:

1. *The appearance of the oil, as well as the yield and distillation limits.* Already before we have communicated that by the berginisation of paraffin the oil obtained was clear and light in colour.

2. *The spec. gravity of the oil or of the residue* resulting after the distillation according to ENGLER. In case of hydrogenation the spec. gravity is lower.

3. *The bromine value of the oil or of the fractions* obtained from ENGLER'S distillation. Here we want to lay stress upon the fact that

¹⁾ This research is a continuation of a former publication: “The hydrogenation of paraffin by the BERGIUS' Method”. Proceedings Koninklijke Akademie van Wetenschappen, Amsterdam, Vol. XXVI, p. 226 (1923), see also *ibid* Vol. XXVII p. 83. (1924). *Chimie et Industrie*, numéro spécial Mai 1923, p. 200–207.

²⁾ These Proceedings, Vol. XXVII, p. 83 (1924).

the hydrogen consumed is not used in the first place for the elimination of the unsaturation of the gasoline and kerosene formed but probably to improve the residue. An analytical research of this residue (elementary analysis) combined with a determination of the molecular weight, has to bring light into this matter.

4. *The amount of hydrogen consumed.*

This appears entirely from the gasanalysis.

Experimentally it was proved that the apparent consumption of hydrogen, caused by hydrogen dissolving in the oil, was practically of no account.

5. *The quantity of heavy hydrocarbons in the reaction gases.*

In general the lower this quantity the better in technical sense the results are.

6. *The change in pressure during the heating.*

Though the significance of the change in pressure, after the temperature has become constant, has not been definitely settled, a consideration of the pressure curves can give some understanding whether or not we have to do with analogous processes.

A difficulty with this is however that e.g. a relative pressure lowering may be caused by the addition of hydrogen (hydrogenation) or by polymerisation in the gaseous phase¹⁾.

Review of the experiments.

In the table one finds a review of the most important results.

The two experiments in which during the heating gas was blown off were the numbers 58 and 59.

In 58 the reflux cooler was not provided with cooling water while the autoclave was kept closed until the pressure amounted to seven atmospheres²⁾.

Hereafter gas was blown off continuously and the pressure kept constant at seven atmospheres.

Whereas in 59 the autoclave was filled with nitrogen up to seven atmospheres before the beginning of the experiment, therefore the gases could be blown off directly from the beginning of the heating. The conditions in 58 and 59 have some resemblance with those that occur in cracking processes such as the BURTON process³⁾.

¹⁾ N. IPATIEW, Polymerisation der Äthylen-Kohlenwasserstoffe bei hohen Temperaturen und Drucken, Berichte 44, 2978 (1912).

²⁾ A clogging of the tubing caused the pressure to rise to 14 atmospheres during about 10 minutes.

³⁾ H. I. WATERMAN and H. J. W. REUS, The cracking process of BURTON, Rec. Trav. chim. des Pays-Bas 43, (1924), 87.

Of all in the table mentioned experiments only in 58 and 59 a distillate was obtained during the experiment. In 58 the distillate became solid at 0° C., the bromine value being very high 76.5, while the residue in the autoclave was liquid and had a bromine value of 24.6.

In 59 the bromine value of the distillate was 82.7 and of the residue 39.7. The residue contained gum-like constituents. For further research a portion of the distillate and residue of 58 and 59 were mixed in the proportion by weight as they were formed in the experiments.

Although also in 58 and 59, as well as in all other experiments little or no cokeformation occurred, the oils of experiment 58 and 59, as far as their bromine value was concerned, and the gases on account of their great percentage of heavy hydrocarbons, stood far back by all other experiments.

Especially the difference was great with those experiments, where, according to BERGIUS, was heated with hydrogen under high pressure, namely in 55 and 57 but especially with experiment 52 where a very high hydrogen pressure was reached.

In 52 not less than at least 34 Liters of hydrogen have been consumed, in 55 and 57 more than 20 Liters. If we compare this with experiment 60 and 61, then it appears that in this connection *a high hydrogen pressure was indeed necessary*. For the oils of experiment 60 and 61 have a higher bromine value and a higher spec. gravity, while it appears from the gasanalysis of experiment 61 (the gas of experiment 60 was lost) that practically no hydrogen had been consumed; 7.6 Liters hydrogen were added and 7.7 Liters were recovered. In cracking experiment 56 which can be compared with these 1.3 Liters hydrogen were formed. *Neither does hydrogen in status nascens offer any improvements* in this respect as appears from experiments 62 and 63 where mixtures of CO and H₂O were used ¹⁾.

In these experiments the CO₂ and hydrogen, formed according to the equation. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, were present in the reaction gases in nearly equivalent quantities, namely 6.6 and 7.1 Liters CO₂ with respectively 6.4 and 7.6 Liters hydrogen.

In the corresponding experiment 56, already mentioned, 1.3 Liters hydrogen were formed.

¹⁾ This confirms a research by H. I. WATERMAN and F. KORTLANDT: "The treatment of Mexican asphalt and paraffin wax by heating under high pressure with sodiumformate and with carbonmonoxide and water respectively, Rec. trav. chim. des Pays-Bas 43 p. 249, (1924).

As in 60 and 61, it appears that in 62 and 63 no important hydrogen consumption took place. In this respect there is no difference for paraffin between hydrogen under low pressure and hydrogen formed during the experiment by the reduction of water by CO.

An indifferent gas under high pressure, such as nitrogen (64) and high pressure technical methane (53 and 54) neither has a favourable influence.

We find that in 64 the amount of nitrogen added remained unchanged, while in 54 the total volume of hydrocarbons in the reaction gases was only slightly changed. Experiment 53 seems to point to a, may be slightly pronounced, decrease. The results of the gasanalysis (percentage N₂), the low pressure after complete cooling and the low yield of gas, however, point to a small leak that probably arose during the cooling. Furthermore one sees that in 54 the hydrogen present in the methane as an impurity is recovered after the experiment.

If we compare the experiments with hydrogen under high pressure (52, 55 and 57), hydrogen under low pressure (60 and 61), methane under high pressure (54), hydrogen in status nascens (CO + H₂O, 62 and 63) nitrogen under high pressure (64) and simple heating in a closed autoclave only under the pressure of the gases that develop during the heating (56) then it appears that:

1. *The yield of oil, resp. gasoline, kerosene and residue is practically the same in all these experiments.*

From this appears that the yield of gas ought to be practically the same too.

2. *Experiment 52, 55, and 57 with hydrogen under high pressure distinguish themselves in a favourable sense, namely:*

A. a better appearance and a lower spec. gravity of the oil.

B. a lower bromine value (addition) of the gasoline and kerosene.

If we compare 60 and 61, 53 and 54, 62 and 63, 64 and 56 on the one side, with 58 and 59 on the other, in the latter two experiments distillation took place during the heating while the pressure was kept constant at seven atmospheres, then it appears that:

a. the yield of gas was greater in 58 and 59. The yield of oil is consequently lower, even if (in 58 and 59) there had not been any losses ¹⁾.

b. The gas of 58 and 59 contained much heavy hydrocarbons.

¹⁾ One has to reckon with the fact that in 58 the experiment was started without any pressure while experiment 59 was started after the nitrogen pressure amounted seven atmospheres.

CRACKING OF

No.	Time required to reach the temp (min.)	Duration of the exp. after the reaction temp. has been reached (min.)	Reaction temperature (average)	Pressure at the beginning of the experiment KG/cm ²	Max. pressure during the experiment	Pressure after complete cooling	Products obtained			Spec. grav. of the oil at 15°	Distillation of the oil poured out (ENGLER)			
							In Grammes		Liters		Gasoline ³⁾ (up to 220°) Gr.	Kerosene 220–300° Gr.	Residue > 300° Gr.	Sp. grav. residue 15°/15°
							Oil	Gas	Gas					
52	35	60	450°	110	219	87	177	27.5	93	0.735	98.2	35.0	43.8	0.837
55	40	60	450°	60	142	50	172	33.8	61	0.745	109.2	31.8	31.0	0.846
57	25	60	452°	60	140	50	173	32.4	60.5	0.744	104.4	34.2	34.4	0.841
60	30	60	451°	7	65.5	—	173	—	—	0.769	100.2	33.6	39.2	—
61	29	60	450°	7	59	13	177	17.5	19.5	0.769	92.0	35.6	49.4	—
53	40	60	450°	75	189.5	59	174	75.2	87	0.769	97.8	34.2	42.0	0.883
54	48	60	451°	60	162	61	174	77.4	91	0.772	99.1	35.0	39.9	0.883
62	31	60	451°	23	117	32	176 ¹⁾	47.5	41	0.767	96.1	36.6	43.3	—
63	40	60	450°	23	116	31.5	180 ¹⁾	51.4	43.8	0.765	97.7	35.9	46.4	—
64	33	60	451°	60	172.5	66	176	96.7	80	0.768	98.3	34.7	43.1	—
56	32	60	449°	0	49.5	8.8	171	23.2	18	0.763	95.6	32.0	43.4	0.875
58	30	60	450°	0	7	0	133 ²⁾	30	19.5	0.750	85.3	23.0	24.7	0.866
59	31	60	450°	7	7	0	161 ²⁾	44.6	29.5	0.773	77.2	27.1	56.9	0.850

1) Saturated with water.

2) In these experiment oil losses were great.

3) Including losses caused by evaporation during the distillation.

4) The oil obtained is here a mixture of distillate and oil poured out of the autoclave in the true proportion by weight.

PARAFFIN (200 Gr.).

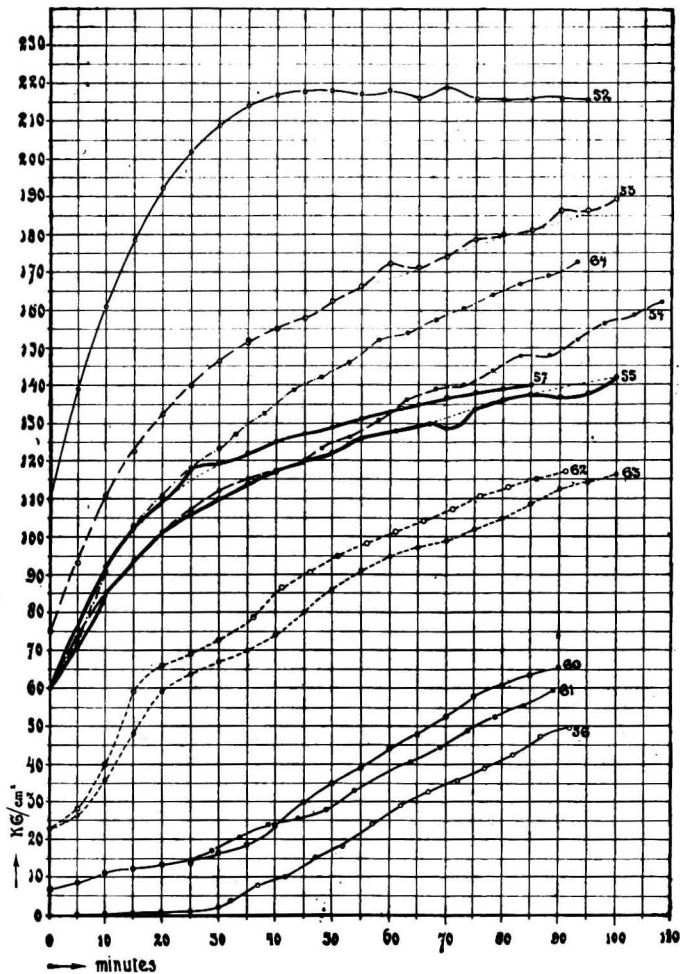
Bromine value (addition).			Liters of gas added before the beginning of the experiment 5)							Liters of gas recovered after the experiment 5)							
Oil obtained	Gasoline	Kerosene	CO ₂	Heavy hydrocarbons.	O ₂	CO	H ₂	Other hydrocarbons (CH ₄ a.o.)	N ₂ (rest)	CO ₂	Heavy hydrocarbons	O ₂	CO	H ₂	Other hydrocarbons (CH ₄ a.o.)		N ₂ (rest)
14.5	19.3	9.5	—	—	0.3	—	113.2	—	—	—	0.9	—	—	79.3	9.3	3.5	Hydrogen under high pressure
22.1	28.4	13.7	—	—	0.1	—	63.9	—	—	—	1.3	0.6	—	40.4	16.4	2.3	
21.1	28.9	13.6	—	—	0.1	—	63.9	—	—	—	1.6	0.2	—	41.3	15.7	1.7	
23.8	34.5	15.7	—	—	—	—	7.6	—	—	The gas of this experiment was lost							Hydrogen under low pressure
25.0	38.3	16.8	—	—	—	—	7.6	—	—	—	1.4	0.2	—	7.7	9.3	0.9	
26.4	35.9	15.9	0.6	3.5	1.2	1.0	4.0	77.3	9.0	1.3	2.5	0.3	0.8	5.1	74.6	2.4	Methane under high pressure
23.6	35.6	14.4	0.4	2.6	1.0	0.8	3.0	58.9	6.8	—	2.1	0.8	1.0	2.8	77.0	7.3	
24.9	37.8	16.5	—	—	0.1	23.5	0.4	not determined	not determined	6.6	1.3	0.3	14.5	6.4	10.3	1.6	CO + H ₂ O in equivalent quantities
25.1	37.9	16.5	—	—	0.1	23.0	0.4	not determined	not determined	7.1	1.3	0.2	15.8	7.6	10.7	0.9	
23.7	35.4	16.1	—	—	1.9	—	—	—	65.1	1.0	0.8	0.3	—	1.4	11.0	65.5	Nitrogen under high pressure
28.7	41.5	16.9	—	—	—	—	—	—	—	—	3.6	0.2	—	1.3	11.7	1.3	Cracking under its own pressure
63.2 4)	86.4	29.7	—	—	—	—	—	—	—	0.2	6.8	0.3	0.1	1.2	8.0	2.9	Cracking under constant pressure (7 atm.)
45 9 4)	78.0	26.5	—	—	—	—	—	—	14.0	0.1	5.9	0.2	—	1.0	6.8	15.5	

Heating in a closed vessel

5) Here has not been reckoned with the gas present in the autoclave before and after the experiment (about 1 Liter). In all experiments excepted in 56 the autoclave was forced up first and then blown off and the gas measured after which the autoclave was forced up again, consequently practically no air is present. In 58 the air was driven out by nitrogen before the experiment.

c. The bromine value of the oil of 58 and 59 is extraordinary high.

The heating in a closed autoclave or the heating in one which has been filled before with a little hydrogen, methane or nitrogen under high pressure or with CO (+H₂O), and by which pressures of 50 atmospheres and higher were reached during the heating, is consequently better than a heating by which one keeps the pressure constant at 7 atmospheres and one distills in the meantime.



A consideration of the graphical representation of the change in pressure in 52, 55 and 57, 60, 61, 53, 54, 62, 63, 64 and 56 shows that, with the exception of the three berginisation experiments 52, 55 and 57, the pressure increases considerably even after the temperature has become constant.

There were hydrogen has been consumed (52, 55 and 57) the

curve is absolutely different, the pressure curve becomes nearly horizontal in 52 where most hydrogen has been consumed.

As explained before, we cannot enter into an explanation of the course of the pressure curves because a clear understanding of the kind of reaction products and of the chemical reactions taking place during the process fails at present. Finally we wish to express our thanks to Mr. J. A. BEUKERS, chemical engineer, for his assistance during the course of this research.

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