

**Chemistry.** — „*Decomposition of Paraffin Wax at 450° C. in Presence and in Absence of Hydrogen under High Pressure.*” By Prof. H. I. WATERMAN and J. N. J. PERQUIN, chem. eng. (Communicated by Prof. J. BÖESEKEN).

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Earlier investigations have shown the favourable influence of hydrogen under high pressure on the process of decomposition which occurs when paraffin wax is heated to 450° C. It was found that hydrogen under high pressure :

- a. Enters into combination, and forms part of the products, during the reactions which are proceeding.
- b. Causes the production of less unsaturated distillates (gasoline and kerosene).
- c. Lowers the specific gravity of the residue obtained on distillation of the reaction-product.

Notwithstanding the lack of experimental data and our imperfect knowledge of the reactions which occur, we have been successful in adding to our knowledge of the Berginisation process. We have reached this result by studying the influence of time on the decomposition at 450° C. of paraffin wax in the presence and in the absence of hydrogen under high pressure. The raw material which was used in these experiments was Rangoon paraffin, solidifying point (SHUKOFF) 58°, specific gravity 20°/4° : 0.913. Elementary analysis gave 84.6 per cent. C. and 14.8 per cent. H. The charge for each experiment was 200 grams ; this was heated at 450° C. in the autoclave already described by us <sup>1)</sup>. To promote mixing, three steel balls of a total weight of 79.5 grams were added. The chief results are shown in the appended table.

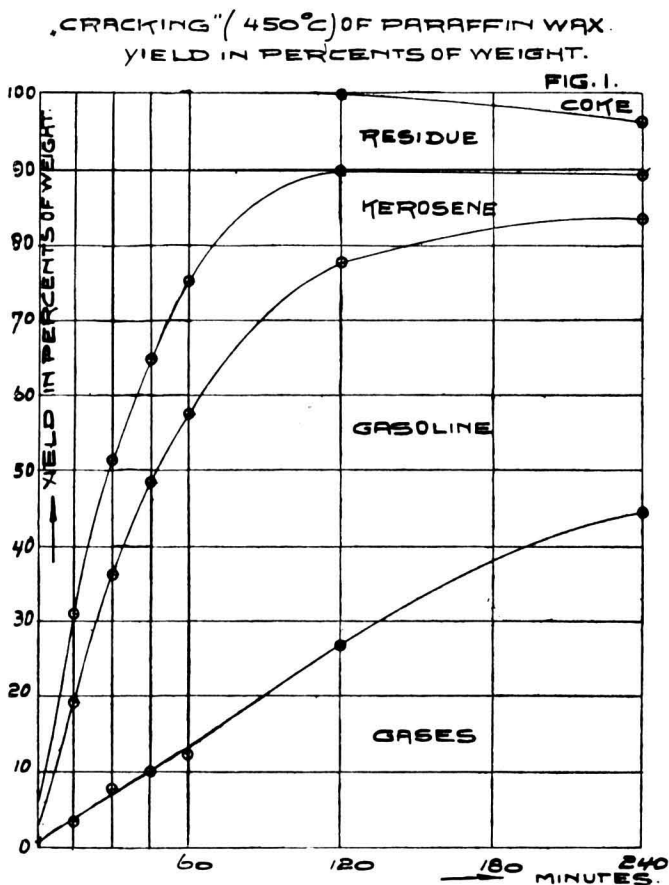
*The Influence of Time on the Decomposition of Paraffin Wax at 450° C. without the Addition of Hydrogen („Cracking”).*

The quantity of gas produced and the maximum pressure reached increase with time of heating ; the pressure after cooling and the volume of gas obtained likewise increase. The volume of „heavy hydrocarbons” also increases to a determined limit and in experiment 92 this maximum is reached. The quantity of hydrogen liberated increases regularly, while the average number of atoms of carbon per molecule of the methane hydrocarbons obtained does not show much variation ; it decreases from 2.4 to 2.1. Only traces of coke are formed at first. After two hours

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<sup>1)</sup> Journ. of the Institution of Petrol. Technologists, Vol. 10, N<sup>o</sup>. 45, Sept. 1924, p. 671—672. These Proceedings 27, p. 83 (1923—24).

(experiment 92) 0.3 per cent. of „carbon” is found ; but, after 4 hours, this has increased to 4.0 per cent. in the case of experiment 94. Our experiments indicate that the process is a normal one ; the paraffin hydrocarbons break down, immediately forming decomposition products such as the lower

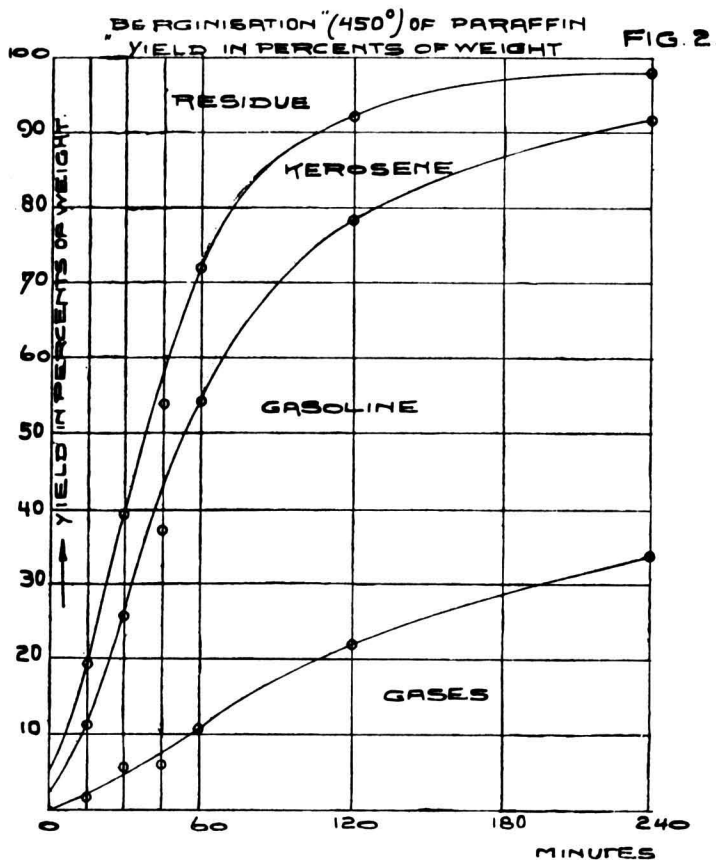


hydrocarbons (ethane and probably methane), and hydrogen. Since the liberation of „carbon” is not immediate, but takes place subsequently with great rapidity, it must do so at the expense of the products of decomposition, and not of the hydrocarbons present in the unaltered paraffin wax itself. The oil produced by short periods of heating solidifies completely at ordinary temperatures, while with longer periods the product becomes more liquid, notwithstanding the formation of considerable quantities of gas. At first the specific gravity diminishes rapidly, until after about one hour's heating the minimum is reached (No. 89, 0.767 ; No. 92, 0.766). Thereafter the liberation of „carbon” begins and at the same time the specific gravity of the oil rises (No. 94, 0.777).

The liquid product becomes progressively richer in gasoline although the absolute yield of gasoline (Fig. 1) after a rapid initial increase diminishes after two hours (after 2 hours, 50.6 per cent. ; after 4 hours, 38.9 per cent).

The percentage of kerosene in the liquid product diminishes after the first hour, as does the percentage yield (Fig. 1). The quantity of residue boiling above 300° C. diminishes continuously with the percentage yield (Fig. 1).

These facts show that at first gas, gasoline and kerosene increase at the



expense of the residue, but that subsequently the kerosene and gasoline at first formed diminish with the residue. As a result it is only the yield of gas which increases, with accompanying liberation of „carbon”. It must be understood that none of the fractions mentioned remains unaltered during the process. The whole system, excluding such constituents as hydrogen and methane, is in a condition of continual decomposition. This is proved by the decrease in the bromine values of the oil produced (7.5, 19.6, 25.1, 27.5, 27.4, 23.0, and 17.5 after 1, 15, 30, 45, 60, 120 and 240 minutes respectively). This decrease occurs after a preliminary increase (Fig. 3). The quantity of heavy hydrocarbons in the gas at first rises, but after two hours begins to fall, with an accompanying decline in the bromine value. The lowering of the bromine value is probably not due to the formation of gaseous unsaturated products such as ethylene, but rather to the occurrence of polymerisation. In this connection it is interesting to note that the specific gravity of the residue from the oil produced by cracking decreases

at first, and afterwards increases rapidly, finally becoming greater than unity (Fig. 4). It has already been mentioned that the specific gravity of the liquid product of the cracking experiments rises with prolonged treatment (Fig. 4).

*The Influence of Time on the Decomposition at 450° C. of Paraffin Wax in the Presence of Hydrogen under High Pressure (Bergius Process).*

In these experiments the autoclave was charged with hydrogen to 110 kg per sq. cm. before heating. The maximum pressures reached indicate a course of events different from that obtained in the cracking experiments. The maximum pressures 210.5 and 218 kg. per sq. cm. in experiments 99 and 106 are apparently caused merely by the rise in temperature, for decomposition and liberation of gas have hardly begun. Experiments 103,

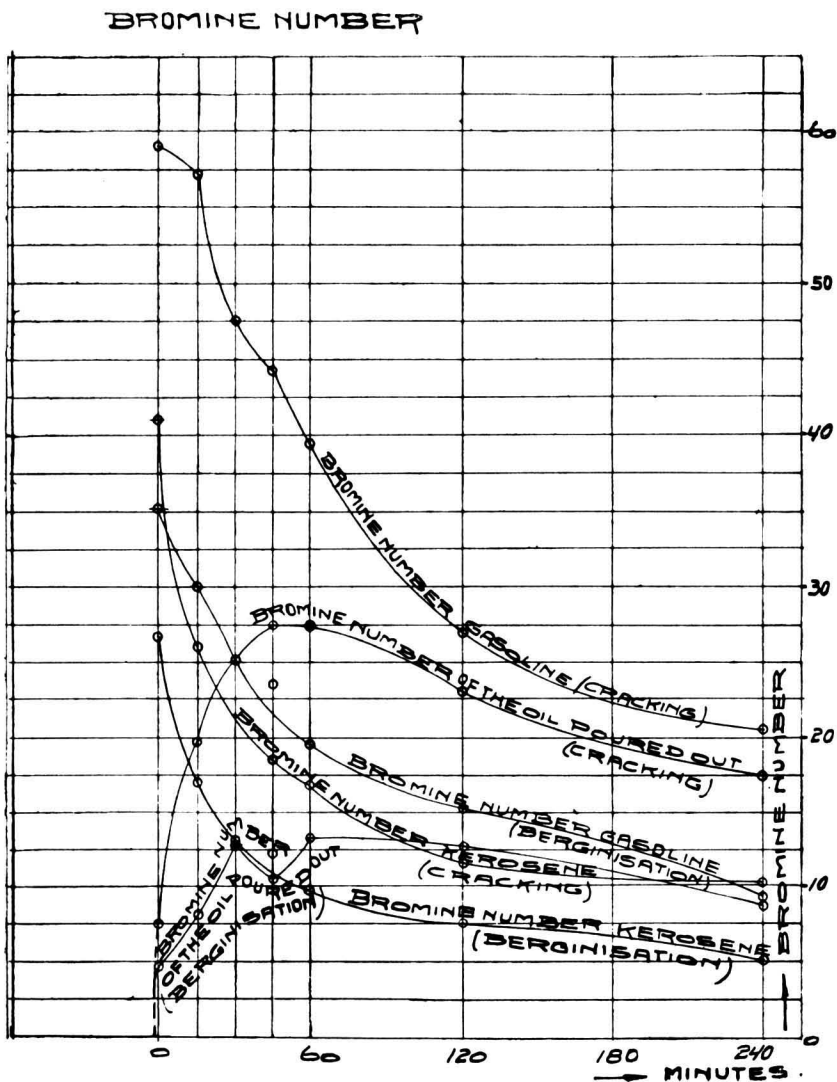


Fig. 3.

No.	Readings during the experiment						Ingoing Material			Product (per cent. on wax charged)				Analysis of the product				
	Time to reach reaction temp. (min.)	Time at reaction temp. (min.)	Initial pressure (kg. per sq. cm.)	Maximum pressure (kg. per sq. cm.)	Pressure cold (kg. per sq. cm.)	Temperature during reaction (° c.)	Wax (g.)	Gas (g.)	Gas (per cent. on wax).	Oil	Gas	"Carbon"	Loss (calculated)	Specific gravity	ENGLISH			
															Per cent. by weight on liquid product			
															Gasoline to 220° c.	Kerosene 220—300° c.	Residue above 300° c.	Loss
99	25	1	110	210.5	105	450°	200	11.4	5.7	99.7	6.1		—	—	—	—	—	
106	29	1	110	218		450°	200	12.7	6.3	99.7	6.6		—	2.3	2.4	94.8	0.5	
107	26	1	0	6.2	0.6	450°	200	0	0	99.3	0.7		0.884	2.5	2.9	94.2	0.4	
103	23	15	110	220	106.5	450°	200	12.4	6.2	98.5	7.7		—	9.3	8.4	81.7	0.6	
108	30	15	0	16.3	2.7	450°	200	0	0	96.8	2.2	0	1.0	0.831	15.1	12.2	71.4	1.3
104	30	30	110	223	104	450°	200	12.7	6.3	94.5	9.2		2.6	0.819	20.3	14.3	64.2	1.2
109	25	30	0	28.4	4.8	450°	200	0	0	92.5	4.3		3.2	0.781	28.2	16.3	52.8	2.7
102	26	45	110	219	100	450°	200	12.7	6.3	94.3	9.2		2.8	0.755	30.6	18.0	48.8	2.6
111	39	45	0	37	6.2	450°	200	0	0	90.0	6.7		3.3	0.771	38.5	18.3	39.2	4.0
74	28	60	110	224	95	450°	200	11.6	5.8	89.5	14.2		2.1	0.741	46.9	19.7	29.6	3.8
76	36	60	110	222	96	450°	200	11.5	5.8	89.5	13.1	0	3.2	0.746	44.5	19.8	33.5	2.2
89	28	60	0	48	8	450°	200	0	0	87.7	11.0		1.3	0.767	47.9	19.9	28.8	3.4
80	30	120	110	223	85.5	450°	200	11.6	5.8	78.0	22.2	0	5.6	0.718	67.8	17.5	10.0	4.7
78	32	60	110	228	85	460°	200	11.6	5.8	77.0	23.7	0	5.1	0.719	69.0	16.9	9.5	4.6
92	25	120	0	68	16	450°	200	0	0	73.0	21.9	0.3	4.8	0.766	65.8	16.6	14.0	3.6
87 <sup>1)</sup>	25+27	240	110	260 (220.5)	90.5 (82)	450°	200	15.2	7.6	65.7	35.5	0	6.4	0.703	83.0	9.5	2.5	5.0
94 <sup>1)</sup>	23+25	240	0	90 (70.2)	24.5 (15.8)	450°	200	0	0	51.5	37.8	4.0	6.7	0.777	71.9	11.3	13.1	3.7
72	20	60	110	222.5	102	450°	100	12.9	12.9	87.5	20.8	0	4.6	—	36.3	18.4	43.5	1.8
68	27	60	110	220	92.5	450°	300	9.7	3.2	93.3	7.7	0	2.2	0.753	36.6	19.7	39.6	4.1

<sup>1)</sup> In these experiments the heating was interrupted half way through, the autoclave was cooled (pressures 82 and 15.8 kg. per sq. cm. respectively), hydrogen was added, in the case of experiment 87, to 110 kg. per sq. cm. (none was added in the case of experiment 94) and the heating resumed. The maximum pressures then attained were 260 and 90 kg. per sq. cm. respectively; 220.5 and 70.2 kg. per sq. cm. had been reached in the first period of heating.

Liquid Product					Gas													Hydrogen fixed	
Distillation				Bromine value (addition)			Gas charged (litres)		Gas obtained (litres) <sup>3)</sup>										
Loss +	Per cent. by weight on wax charged						Liquid product	Gasoline	Kerosene	Hydrogen	Oxygen	Total	Heavy hydro-carbons	Oxygen	Carbonmonoxide	Hydrogen	Other hydro-carbons	Nitrogen	C-atoms (av.) in other hydro-carbons
	Gasoline + Loss	Kerosene	Residue																
—	—	—	—	—	—	—	105.2	1.4	106.8	—	1.0	0.0	104.5	0.3	0.6	—	—	—	
2.8	2.8	2.4	94.5	4.8	35.1	26.6	109.7	2.0	112.4	0	2.0	0.0	109.0	0.4	1.0	4.4	—	—	
2.9	2.9	2.9	93.6	7.5	59.2	41.0	0	0	1	0.1	0.0	0.0	0.2	0.2	0.4	2.4	—	—	
9.9	9.7	8.3	80.5	8.2	30.0	16.9	106.9	2.0	104.6	0	0.2	0.4	101.4	1.8	0.8	3.0	0.5	0.3	
6.4	15.9	11.8	69.1	19.6	57.4	26.0	0	0	3.2	0.6	0	0.0	0.3	1.3	0.8	2.3	—	—	
1.5	20.3	13.5	60.7	12.8	25.0	13.1	109.4	2.0	104.4	0	0.4	0.4	98.8	3.1	1.7	3.0	0.9	0.5	
0.9	28.6	15.1	48.8	25.1	47.6	20.8	0	0	5.8	1.3	0.0	0.1	0.7	3.9	0.7	2.2	—	—	
3.2	31.3	17.0	46.0	10.5	23.5	12.3	110.1	2.0	96.5	0.2	0.8	0.1	88.4	3.5	3.5	2.5	1.9	1.0	
2.5	38.2	16.5	35.2	27.5	44.3	18.5	0	0	10.4	2.4	0.1	0.1	1.0	5.7	1.0	2.2	—	—	
0.7	45.4	17.6	26.5	13.8	19.7	9.9	113.0	1.0	100.0	0.6	0.8	0.0	87.7	9.1	1.8	2.2	2.3	1.2	
6.7	41.8	17.7	30.0	12.8	19.2	9.8	112.1	1.0	98.5	0.8	0.4	0.6	87.0	8.4	1.5	2.2	2.2	1.1	
1.3	45.0	17.4	25.3	(27.4) <sup>2)</sup>	39.4	16.8	0	0	18.9	3.5	0.2	0.2	1.9	12.5	0.6	2.1	—	—	
2.5	56.6	13.7	7.8	12.8	15.3	7.6	113.8	1.0	101.0	1.0	0.4	0.7	77.0	20.4	1.5	2.5	3.3	1.6	
3.6	56.7	13.0	7.3	15.0	17.4	8.3	113.0	1.0	100.5	1.3	0.6	0.5	75.3	21.2	1.6	2.4	3.4	1.7	
9.4	50.6	12.1	10.2	(23.0) <sup>2)</sup>	27.7	11.7	0	0	32.5	4.3	0.5	0.4	2.3	23.7	1.3	2.2	—	—	
8.0	57.8	6.2	1.6	8.8	9.5	5.2	142.0	1.7	116.4	1.4	0.9	0.8	76.2	35.4	1.7	2.5	5.9	2.9	
75.6	38.9	5.8	6.7	(17.5) <sup>2)</sup>	20.5	10.3	0	0	55.6	3.2	0.4	0.4	3.4	47.8	0.4	2.1	—	—	
38.1	33.3	16.1	38.1	—	18.3	10.1	126.4	1.1	115.5	0.6	0.8	0.5	107.5	4.7	1.4	2.1	1.7	1.7	
40.7	38.0	18.4	36.9	14.3	22.1	11.3	103.1	0.3	86.5	0.9	0.5	0.3	74.5	7.8	2.4	2.4	2.6	0.9	

<sup>2)</sup> Approximate determinations.

<sup>3)</sup> CO<sub>2</sub> absent.

SPECIFIC WEIGHT (120°C) OF THE OIL POURED OUT  
AND OF THE RESIDUE OF ENGLER DISTILLATION

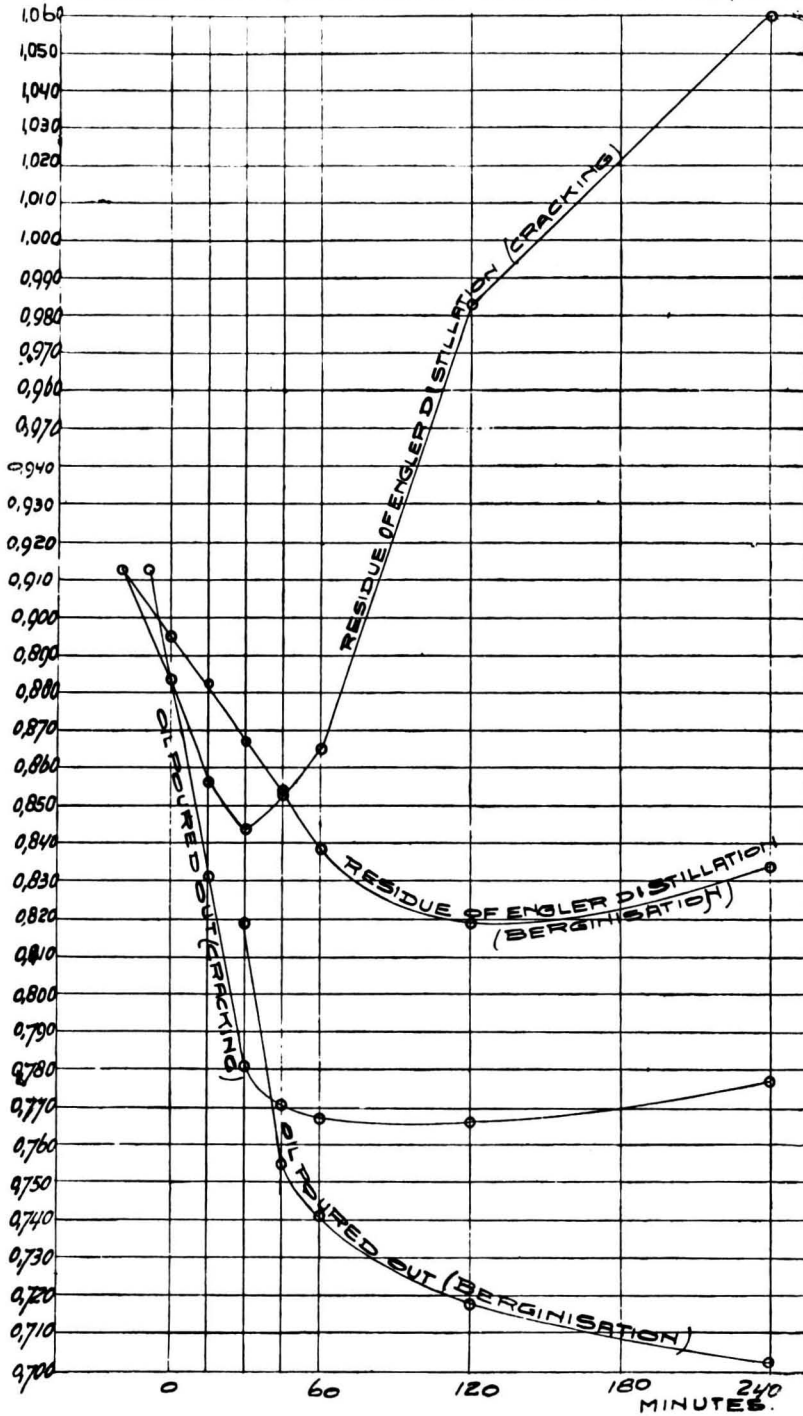


Fig. 4.

104, 102, 74, 76 and 80 after 15, 30, 45, 60, 60 and 120 minutes respectively, notwithstanding the decomposition which is taking place, give maximum pressures which are scarcely higher than those in experiments 99 and 106. This is doubtless because the effect of hydrogenation is becoming important. Confirmation is provided by the observed final pressures, which are smaller in proportion to the duration of the experiment. From the volume and composition of the gas obtained it follows that in experiments 103, 104, 102, 74, 76 and 80, and in 87 (where hydrogen was added twice), 0.3, 0.5, 1.0, 1.2, 1.1, 1.6 and 2.9 per cent. by weight of hydrogen respectively (calculated on the paraffin wax) are fixed. The bromine values of the original oil produced and of the corresponding gasoline and kerosene (Fig. 3) show that the bromine value is always lower than in the corresponding cracking experiments. A point of even greater importance is that after 60 and up to 120 minutes' Berginisation there is no decrease in the bromine value of the oil produced, as there is in the analogous cracking experiments. From this it may be concluded that probably polymerisation does not occur in these Berginisation experiments. It is only after further heating that the bromine value of the oil diminishes. Fig. 4 shows that after 120 minutes the specific gravity of the Engler distillation residue increases; up to 120 minutes' Berginisation this specific gravity diminishes.

The high hydrogen pressures used in Berginisation may be expected to modify the cracking process. A lower proportion of heavy hydrocarbons will be formed; in 99, 106, 103, 104, 102, 74, 76, 80 and 87, there are produced 0.0, 0.0, 0.0, 0.0, 0.2, 0.6, 0.8, 1.0 and 1.4 L. respectively. The longer the experiment lasts, the larger this quantity. This holds for the methane hydrocarbons also. In the Berginisation process there is less decomposition, for the average number of atoms of carbon per molecule, although it continuously diminishes, always remains greater than in the corresponding cracking experiments.

The change in the yields of gas, gasoline, kerosene and residue (Fig. 2) is an interesting result of Berginisation. The whole process is characterized by the formation of gas and gasoline and at first of kerosene, at the expense of the residue. Later, the percentage of kerosene diminishes. In our experiments the percentage of gasoline increased continuously. It is an important point that finally the residue almost wholly disappeared, so that only gases, gasoline and kerosene were left. The origin of the gasoline must be looked for in the cracking which is taking place.

These observations show that Berginisation results in a modification of the cracking process, gas and gasoline being formed initially in smaller quantity and of a less unsaturated character than the corresponding products of cracking. The falling off in the bromine value of the oil produced after a certain period of heating, and the continuous decline in the bromine value of the gasoline and kerosene, observed even more clearly in cracking than in Berginisation, must be attributed to the rupture of double bonds, followed by polymerisation in the case of cracking and, it may be



supposed, by hydrogenation of the portions of the molecule, so that polymerisation is prevented or modified, in the case of Berginisation. This must be in close connection with the fact that in our Berginisation experiments practically no carbon (coke) is formed. The breaking up of molecules must take place throughout Berginisation, as otherwise the increase in the yield of gasoline, which finally exceeds that in the corresponding cracking experiments, could not be explained.

The direct addition of hydrogen to unsaturated hydrocarbons already present is not probable, because no catalyst is added and because the temperature is so high that in many cases the tendency is towards a decomposition of the corresponding saturated hydrocarbon into hydrogen and the unsaturated hydrocarbon rather than towards a reaction in the reverse sense, although this decomposition will be modified by the presence of hydrogen under high pressure. We hope to deal with this subject in more detail at a later date.

The advantage of Berginisation as compared with cracking appears

Nature of the Product and of the Distillation Residue.

Experiment	Minutes heating after the reaction temperature has been reached	Product	Residue
106	1	S <sub>pw</sub>	S <sub>pw</sub>
<b>107</b>	<b>1</b>	<b>S<sub>pw</sub></b>	<b>S<sub>pw</sub></b>
103	15	S <sub>pw</sub>	S <sub>pw</sub>
<b>108</b>	<b>15</b>	<b>S<sub>pw</sub></b>	<b>S<sub>pw</sub></b>
104	30	S <sub>pw</sub>	S <sub>pw</sub>
<b>109</b>	<b>30</b>	<b>S<sub>v</sub></b>	<b>S<sub>v</sub></b>
102	45	S <sub>pw</sub>	S <sub>pw</sub>
<b>111</b>	<b>45</b>	<b>L (dark)</b>	<b>S<sub>v</sub></b>
74	60	S <sub>pw</sub>	S <sub>pw</sub>
<b>89</b>	<b>60</b>	<b>L (dark)</b>	<b>S<sub>v</sub></b>
80	120	L (clear)	S <sub>pw</sub>
78	60 (temp. 460°)	L (clear)	S <sub>pw</sub>
<b>92</b>	<b>120</b>	<b>L (dark)</b>	<b>L (dark)</b>
87	240	L (clear)	L (dark)
<b>94</b>	<b>240</b>	<b>L (dark)</b>	<b>L (dark)</b>

S<sub>pw</sub> = solid, like paraffin wax.

L (dark) = liquid, dark.

S<sub>v</sub> = consistency of vaseline.

L (clear) = liquid, clear.

distinctly from the elementary composition of the residue in the two processes. For instance, in experiment 87 the composition of the residue was 85.4 per cent. carbon and 13.8 per cent. hydrogen, in 94 91.8 per cent. of carbon and 8.2 per cent. of hydrogen, respectively ; in other words, Berginisation prevents loss of hydrogen from the residues. This is of considerable importance, the process of cracking always giving oils or residues which are poorer in hydrogen, because in the gases formed,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , etc., an excess of hydrogen is present. This loss of hydrogen to some extent takes place during Berginisation, but in this process the loss of hydrogen is supplied from outside. The advantage of Berginisation is, therefore, proved. It is true that the hydrogen introduced from the outside is later found wholly or partly in the gases, but this supply of hydrogen has prevented a too extensive removal of hydrogen from the hydrocarbons. The great influence of temperature is shown by a comparison of experiments 78 and 80. In experiment 78 the temperature was ten degrees higher, and the effect was that in half the time (60 minutes in 78 and 120 minutes in 80) nearly the same result was obtained. Analogous observations were made by Dr. A. E. DUNSTAN<sup>1</sup>). The ten degrees higher temperature has apparently doubled the velocity of the complex of reactions. This fact being mentioned it must be added that without a more detailed study of this subject there is not much matter for discussion on the theoretical significance of this observation. That the quantity of paraffin wax used has a great influence appears from experiments 72 and 68, in which the percentage of fixed hydrogen is quite different. It is necessary, therefore, always to work under completely comparable conditions.

*Summary.* Comparative experiments show that Berginisation has various advantages over heating in absence of hydrogen under high pressures (cracking). After some hours' Berginisation a larger percentage of gasoline and of kerosene is obtained, while less gas is produced. Coke has not been formed to any material extent. The liquid products of reaction are more saturated. The residue on distillation (boiling point exceeding  $300^\circ C.$ ) after 4 hours' Berginisation is but small. On the other hand, it must be observed that in Berginisation less gasoline and correspondingly less gas is formed initially than in the corresponding cracking experiments. In Berginisation cracking is restricted and the very reactive residues produced by cracking are converted into hydrocarbons of the gasoline and kerosene distillates. Polymerisation and the formation of coke from the unsaturated residues is thus prevented or diminished. While cracking gives rise to residue poor in hydrogen, Berginisation prevents the loss of hydrogen from residues. In one Berginisation experiment a residue was obtained which gave 13.8 per cent. of hydrogen, whereas the raw material contained 14.8 per cent. In a corresponding cracking experiment the residue contained only 8.2 per cent. of hydrogen.

<sup>1</sup>) Journ. Institution Petroleum technol. **10**, 728 (1924).

Berginisation must be considered as a combined cracking and hydrogenation process. The useful feature of cracking, the breaking down of hydrocarbon molecules, remains, but is made more regular, while the products are obtained in a more stable condition on account of the addition of hydrogen, so that extensive polymerisation and formation of coke are avoided. The main feature of Berginisation is, therefore, not the saturation of unsaturated hydrocarbons already present. In this respect it differs widely from the ordinary hydrogenation of vegetable or animal oils, which is conducted in the presence of catalysts.

This investigation clears up the scientific significance of the Bergius hydrogenation process.

In continuation of this research the isolation, as far as possible, of the chemical compounds formed will be attempted, while our results on the hydrogenation of coal by the Bergius method will be published shortly.

We wish to express our thanks to Mr. A. C. OUBORG, who assisted us during the course of these investigations.

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