Chemistry. — *"The decomposition of Cottonseed-Oil in a Closed Vessel at* 450° *Compared with the Hydrogenation of this Oil by the Method of* Bergius *with Hydrogen under High Pressure."* By Prof. H. 1. Waterman and J. N. J. Perquin. (Communicated by Prof. J. Böeseken.)

(Communicated at the meeting of September 29, 1923).

A. Mailhe recently carried out some experiments on the preparation of mixtures of hydrocarbons from fats.[1] Mailhe made use of catalysts and from different kinds of vegetable oils he obtained at 600°—650° gases of high calorific value, which contained H_2, CO, and CO_2 and lower hydrocarbons, a liquid of low boiling-point, and a distillation residue. By subjecting the latter once more to the same treatment, he finally obtained only gases and a low-boiling liquid as a final-product. This liquid still contained some acid; it was neutralized with lye, and then hydrogenated over metal at 180°—200°. Thus Mailhe obtained hydrocarbon mixtures, consisting of saturated and aromatic hydrocarbons, and also of naphthenes. This treatment was applied to different vegetable oils. For the way in which the reaction takes place, as Mailhe imagines it, we may refer to his publication[2]).

Industrially these researches are of no importance excepted of course under abnormal conditions which may possible arise in different countries from time to time. Formerly Engler[3]) has prepared during his classical research these hydrocarbon mixtures in a still simpler way. He obtained by distillation of fish oil at 300°—400° and 4—10 atmospheres about 75 %, of a liquid mixture of hydrocarbons.

In this investigation of Engler's it was particularly of great importance that the process of conversion takes place almost quantitatively. Here too there were formed besides the *liquid* hydrocarbons, also *gaseous* ones, chiefly CH_4, but further also CO, CO_2, and water.

Investigations made by us of late concerning Bergius' hydrogenation process induced us to extend this research also to fats.

[1]) Préparation de pétrole à l'aide d'huiles végétales et animales, Bulletin de la Société de Chimie Industrielle **4**, 40 (Octobre 1922); La pyrogénation catalytique des huiles animales, La revue pétrolifère, **1**, N⁰. 17. Mars 17, 1923.

[2]) Compare also Katalyse und Erdölbildung, C. Engler, Chemie und Physik des Erdöls, Leipzig 1913, p. 412 et seq.

[3]) C. Engler—H. Höfer, Das Erdöl II, 110 (1909).

In the berginisation of products containing carbon and hydrogen one has only to deal with two processes, the process of cracking and the process of hydrogenation; in this case, however, the matter was still somewhat more complicated, because here the hydrocarbons must first be formed from fats. It is self-evident that here the berginisation experiment proper had to be compared with the cracking experiment.[1] Where in his distillation experiments ENGLER worked at 300° and 400° and under a comparatively low pressure, this experiment was carried out at much higher temperature (450°) and very high pressure.

For the rest the way of experimenting was analogous to that followed by us with paraffine as experimental material[2]. Only with this difference that here a high-pressure apparatus constructed for the purpose was used (see figure 1)[3]. Besides, the temperature in the metal wall of the autoclave was measured, by which it was ascertained during the experiments that there was no question of any overheating of the walls. The capacity of the autoclave was ± 1.000 cm³. In the experiments described here no use was made of the condenser.

Both experiments are recorded in table A.

It has been proved by the experiments that also under these circumstances the fatty oils are converted into mineral oil to a very great percentage, just as this is the case in ENGLER's experiments.

It is clear from the graphical representations fig. 2, in which the change of pressure and temperature is given, how very sensitive the apparatus used is, and how accurate the results obtained are. Even very small variations of temperature are immediately expressed in the pressure-curve. The change of the pressure during the berginisation is essentially different from that in the cracking experiment. The rise of the pressure is considerably smaller in the berginisation than in the cracking.

Furthermore it appears from the gas-analysis that the oxygen of the cottonseed oil is driven out in both cases almost quantitatively as CO, CO_2, and H_2O. Smaller quantities of acids (compare acid percentage) and ketones may still be present in the oil obtained. The

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[1] The decomposition when cottonseed oil is heated in a closed vessel is always called "cracking" in what follows.

[2] H. I. WATERMAN and J. N. J. PERQUIN, Hydrogenation of paraffin by the BERGIUS's Method; Proceedings Kon. Akad. v. Wetensch., Amsterdam, Vol. XXVI, 226 (1923).

[3] In the construction of this apparatus we had the assistance of Prof. J. C. ANDRIESSEN, for which we express our thanks to him here.
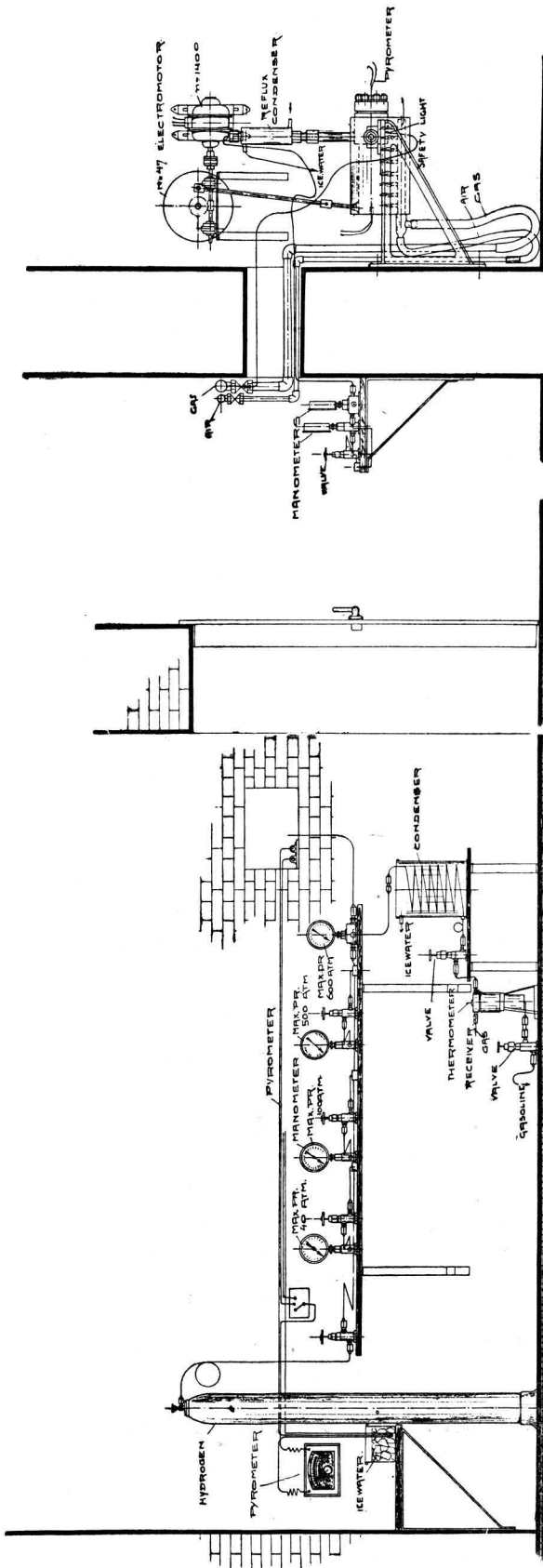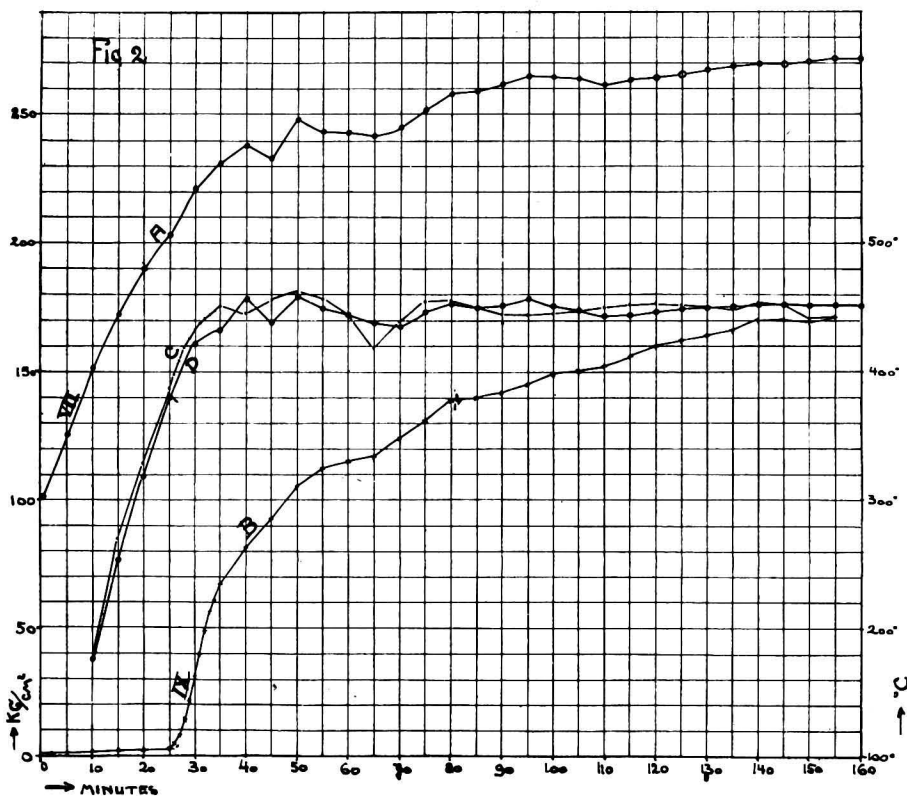
Fig. 1.

expulsion of the oxygen from the oil is very clearly shown by the oxygen balance.

If it was already very probable from the shape of the pressure curve that hydrogenation really took place in the berginisation, this appeared with certainty from the gas analysis. Considerable quanities of hydrogen have been consumed.

A and B: PRESSURE CURVES   C: TEMPERATURE CURVE IX

D: TEMPERATURE CURVE VII

Oxygen balance
Experiment N⁰. VII

Before the experiment		After the experiment	
In cottonseed oil	32.4 gr.	In gases: [1] CO_2 CO O_2	20.5 gr.
In hydrogen (0₂ content: 2.0 %)	2.2 gr.	In water (10 gr.)	8.9 gr.
	34.6 gr.	Total	29.4 gr.

[1] Leaving water vapour out of consideration.

Oxygen balance
Experiment N⁰. IX

Before the experiment	After the experiment
In cottonseed oil 32.4 gr.	In gases: [1] $\begin{matrix} CO_2 \\ CO \\ O_2 \end{matrix}$ } 22 gr. In water (2 gr.) 1.8 gr. Total 23.8 gr.

[1] Leaving water vapour out of consideration.

We have set ourselves the question already before [1]), in how far, also in the ordinary cracking experiments the hydrogenation in BERGIUS' sense may take place to a smaller or greater degree. This hydrogenation is called by us internal hydrogenation in contrast with that which is brought about by the hydrogen supplied from the outside. It might be possible that also in this cracking experiment internal hydrogenation has taken place. In this case there is, however, another way possible, namely that in which the CO formed during the process by the action on water, might yield hydrogen in statu nascendi:
$$CO + H_2O \rightleftarrows CO_2 + H_2.$$
At the time ENGLER and GRIMM already drew attention to the hydrogenation by means of carbon monoxide [2]), FISCHER and SCHRADER have systematically investigated the hydrogenation of coal with carbon monoxide [3]). Whether the internal hydrogenation and the indirect hydrogenation by CO in such experiments as performed by us, actually takes place, and if so to what degree, will have to appear in a separate investigation.

The indirect hydrogenation by CO can, indeed, also have taken place in the berginisation experiment, though there, in consequence of the excess of hydrogen, the watergas equilibrium will shift to the side of the CO.

In both experiments the losses were important, the loss being greatest in the cracking experiment. This is perhaps partly caused by condensation of hydrocarbons and water in the tubes between the manometers and the autoclave; there were also losses during

[1]) Congrès international des combustibles liquides. Paris 9⁻—15 Octobre 1922, Chimie et Industrie, Mai 1923, p. 200—207.

[2]) Compare ENGLER und J. GRIMM, Ueber direkte Abspaltung von Kohlenoxyd und die Umsetzung desselben mit Wasser. Berichte 30, 2925—26 (1897).

[3]) Compare FR. FISCHER und H. SCHRADER, Hydrierung von Kohlen durch Kohlenoxyd. Brennstoffchemie 2, 257 (1921).

CRACKING AND BERGINISATION OF COTTONSEED OIL AT 450°.

TABLE A.

No. of the experiment	Time of heating to the required temperature (in minutes)	Duration of the experiment proper (in minutes)	Initial pressure in atmospheres	Maximumpressure in atmospheres	Final pressure in atmospheres	298 gr. cottonseed oil used obtained in gr. resp. in percentage of weight — oil	water	gas	coke	loss	Oil obtained Sp. gr. at ± 15°	Acid value	Distill. according to ENGLER (yield in percentages of weight) — Gasoline to 220°	Kerosene 220—300°	Residue > 300°	Loss	Bromine value (addition) of the — Gasoline	Kerosene	Acid value of the — Gasoline	Kerosene	Gases obtained: Quantity in litres	Density compared with air	Analysis — CO₂	Heavy hydrocarbons	O₂	CO	H₂	Other hydrocarbons	(rest) Nitrogen	Number of litres of supplied hydrogen	Number of litres of hydrogen still present	Number of litres of hydrogen consumed	Absorbed hydrogen in grammes	Percentages of weight of hydrogen absorbed
VII	40	120	101	272	47,7	203 (66,0 %)	10 (3,3)	68 (22,3)	5,5 (1,8)	20,3 (6,6)	0,793	5,1	60.6 (44,2)[4]	17,7 (11,7)	15,5 (10,5)	6,2	14.5	6,5	3,2	0,9	63	0,877	18,8 (24,4)	1,1 (1,4)	0,4 (0,5)	7,3 (9,5)	23,0	44.2	5,2	± 75 L. (8.8 Gr.)	14,5	60,5	5,4	1,8
IX	35	120	0 atmospheric pressure	171	32,0	169 (56,7 %)	2 (0,7)	64 (21,5)	15 (5,0)	48 (16,1)	0,818	1,0	57,1 (35,2)[4]	17,1 (9,7)	20,8 (11,8)	5,0	16,8	8.5	0,3	1,8	51	1,022	23,8 (25,9)	2,8 (3,0)	0,9 (1,0)	10,9 (11,8)	8,0	49,9	3,7					

TABLE B.

No. of the experiment	Time of heating (min)	Duration (min)	Initial pressure	Maximumpressure	Final pressure	Used ± 200 Gr. cottonseedoil (XXII: 200 Gr., XXIII: 204 Gr., XXIV: 200 Gr., XXV: 198 Gr., XXVI: 202 Gr., XXVII: 201 Gr.); obtained from this in gr. — oil	water	gas	coke	loss	Sp. gr. at ± 15°	Acid value	Gasoline to 220°	Kerosene 220—300°	Residue > 300°	Loss	Bromine Gasoline	Bromine Kerosene	Acid Gasoline	Acid Kerosene	Quantity in litres	Density compared with air	CO₂	Heavy hydrocarbons	O₂	CO	H₂	Other hydrocarbons	(rest) Nitrogen	Number of litres of supplied hydrogen	Number of litres of hydrogen still present	Number of litres of hydrogen consumed	Absorbed hydrogen in grammes	Percentages of weight of hydrogen absorbed
XXII[1]	35	60	110	270	79	126 (59,3 %)	8,5 (3,9)	69 (32,4)	1 (0,5)	8,9 (3,9)	0,774	0,3	67,1 (43,7)[4]	14,9 (8,8)	11,6 (6,9)	6,4	17,2	5,2	0,3	0,1	95	0,582	8.5 (18,4)	0,4 (0,9)	0,4 (0,9)	6,2 (13,4)	53,9	27,1	3,5	108 L.[6] (13,4 Gr.)	51,2	56,8	5,1	2,5
XXIII	35	60	110	251	85	146 (67,2 %)	8,5 (3,9)	58 (26,7)	0,6 (0,3)	4,3 (1,9)	0,790	7,6	59,3 (43,4)[4]	20,8 (14,0)	15,1 (10,2)	4,8	17,0	5,0	6,3	1,2	92	0,512	9,3 (24.3)	1,0 (2,6)	0,5 (1.3)	3,7 (9,7)	61,8	20,0	3,7	108 L.[6] (13,4 Gr.)	57,0	51	4,6	2,3
XXIV[2]	35	60	0	79,5	22	124 (62 %)	1 (0,5)	42 (21)	14 (7)	19 (9,5)	0,817	1,3	52,9 (35,0)[4]	22,3 (13,8)	21,2 (13,1)	3,6	24,3	7,9	1,0	0,2	31	1,094	27.9 (31.2)	4,8 (5,4)	0,9 (1,0)	10,0 (11,1)	10,5	45,8						
XXV	33	60	0	81,5	21,6	132 (66,6 %)	3,5 (1,7)	44 (22,2)	14 (7,1)	4,5 (2,3)	0,812	1,9	55,5 (38,5)[4]	21,0 (14,0)	21,2 (14,2)	2,3	24,0	7,9	1,9	0,3	32,5	1,077	26,4 (29,4)	4,6 (5,1)	1,1 (1,2)	12,8 (14,2)	10,3	38,2	6,6					
XXVI	40	60	0	81,5	21,5	127 (63 %)	3,5 (1,7)	46 (22,8)	14.5 (7,2)	11 (5,5)	0,816	2,3	55,3 (37,4)[4]	20,7 (13,0)	20,0 (12,6)	4,0	24,0	7,6	2,4	0,4	33,5	1,093	25,4 (28,2)	4,2 (4,7)	0,8 (0,9)	13,4 (14 9)	10,0	40,8	5,4					
XXVII	36	5	110	222	96,5	172 (81,4 %)	9,5 (4,5)	30,8 (14,6)	0,6 (0,3)	—	0,847	36,4	19,3 (17,1)[4]	22,4 (18,2)	56 6 (46,1)	1,7	42,0	15,6	22,7	7,6	103	0,239	5,0 (33,3)	0,4 (2,7)	0,3 (2,0)	2,9 (19,3)	85,0	6,4		111,4 L.[6] (10.0 Gr.)	87,5	23,9	2,1	1,0

[1]) The thermo-couple having been slid from the tube, the temperature rose in this experiment during the last 10 minutes to ± 500°.
[2]) Just before the termination of this experiment there arose a small leakage, which could soon be repaired by screwing on the reflux cooler.
[3]) The figures placed between brackets indicate the yield in percentages of weight of the initial product.
[4]) Gasoline inclusive the loss in the distillation by ENGLER's method.
[5]) The percentages placed between brackets have been calculated on gas free from hydrogen.
[6]) Determined experimentally.

the opening and pouring out. In a series of observations made later (berginisation experiments XXII and XXIII and cracking experiments XXIV, XXV and XXVI) the results of which are likewise recorded in table B, we have succeeded in reducing these losses greatly by placing a reflux cooler on the autoclave. The oxygen balances are in still better harmony there.

Oxygen balance		
Experiment N⁰. XXII		
Before the experiment	After the experiment	
In cottonseed oil 21.7 Gr.	In gases: ¹) CO_2 CO O_2	16.3 Gr.
In supplied hydrogen (O_2 content 2.5 %) 3.9 Gr.	In water	7.5 Gr.
Total 25.6 Gr.	Total 23.8 Gr.	

¹) Leaving watervapour out of consideration.

| Oxygen balance		
Experiment N⁰. XXV		
Before the experiment	After the experiment	
In cottonseed oil 21.5 Gr.	In gases: ¹) CO_2 CO O_2	15.7 Gr.
	In water	3.1 Gr.
	Total 18.8 Gr.	

¹) Leaving watervapour out of consideration.

Fig. 3 represents the change of pressure and temperature in these experiments. The experiments were always made with about 200 gr. of cottonseed oil. For the rest the circumstances were analogous to those of nrs. VII and IX.

It may be a drawback for the technical execution of these experiments that the iron of the apparatus is pretty quickly attacked through the formation of organic acids.

It appears from the experiments described that both by cracking and by berginisation, cottonseed oil can very efficiently be converted into hydrocarbon mixtures with high gasoline percentage. It appears from experiment XXVII, which was heated for 36 minutes, and was kept at a temperature of 450° for only 5 minutes, that even after this short period of heating a considerable part of the oxygen of the fat had been

expelled, while the hydrocarbons formed also had been partially decomposed, so that a considerable yield of gasoline and kerosene had been obtained already.

The conversion is not yet complete here, as appears among other things from the high acid value (36,4) of the oil.

TIME IN MINUTES.

A PRESSURE CURVES

B MEAN TEMP. CURVE
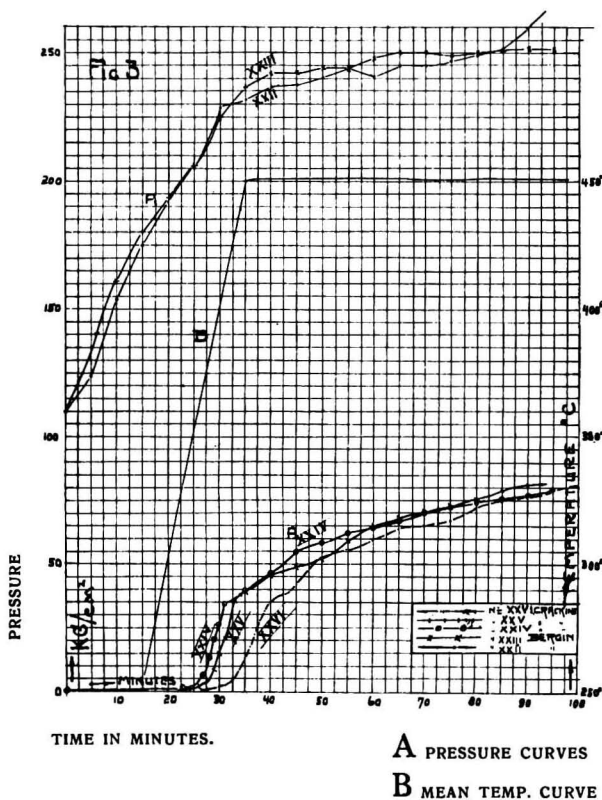
The value of unsaturation (bromine value) of the gasoline and kerosene formed is greater in **XXVII** than in the other berginisation experiments. In all these experiments the behaviour of the cottonseed oil is not very different from that of a hydrocarbon mixture, as the oxygen can easily be eliminated from it. In the berginisation of the cottonseed oil very much hydrogen is consumed, among others directly or indirectly for the formation of water. In both processes formation of coke takes place, this being considerably less in the berginisation experiments. We have been struck with the fact that also in other berginisation experiments with paraffine, formation of small quantities of "carbon" takes place. It will be of great importance to perform a berginisation experiment in which this separation of carbon is entirely absent. If this does not succeed, it will have to be examined

in how far this carbon, which has been formed during the process, and which will be active according to Chaney [1]), at least if it is formed at low temperature (below 500°—600° C.), may act as a catalyst [2]).

In conclusion we express our thanks to Mr. J. A. Beukers, who has assisted us in the execution of an important part of these observations.

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[1]) N. K. Chaney, The activation of carbon, Transactions of the American electrochemical Society, **36**, (1920).

[2]) A similar investigation should also be carried out with regard to metals that are accidentally present, as nickel, vanadium etc. Compare Ramsay, J. of the Soc. of Chem. Ind. **42**, p. 287 T. (1923).