THESIS

THE LIQUEFACTION OF CARBONACEOUS MATERIALS BY HYDROGENATION.

Part I: The Hydrogenation of Thirteen Representative Alberta Coals of Various Rank.

Part II: The Action of Tetrahydronaphthalene as a Hydrogenating Agent.

Part III: On the Continuous Hydrogenation of Bitumen from the Bituminous Sands of Alberta.

Presented in fulfilment of the requirements for the degree of Master of Science.

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GENERAL INTRODUCTION

In the Province of Alberta there exist vast deposits of coal, bitumen, and natural gas (2, 3, 13, 34), the development of which has been restricted up to the present time to a few coal mining areas and to three gas fields. Exploitation of the resources of the Turner Valley in particular has attracted much attention in recent years. The extraction of naphtha from the "wet" gas has resulted in wholesale wastage through the practice of burning all excess stripped gases in the field. That such a practice is to be condemned has been realized and efforts have been made recently to minimize loss through conservation restrictions.

Although complete conservation of the Turner Valley gases with the object of their ultimate utilization as fuel would be the ideal solution of this problem, it appears highly improbable that such will be practiced. The Province is plentifully supplied with natural gas elsewhere, which fact creates considerable opposition to conservation, and it is likely that in excess of 100,000,000 cu. ft. will be wasted daily for some time to come.

From the viewpoint of a chemist these wasted or other natural gases offer a cheap source of raw material for a variety of proven and possible processes;

particularly so when the other carbonaceous materials available, coal and bitumen, are considered. As illustrative of the possibilities inherent in the hydrocarbon compounds available the production of carbon black (16), methanol and other solvents, the pyrolysis of natural gases to produce aromatics and olefines, and the hydrogenation-cracking of bitumens and coals to produce motor fuels may be mentioned. In this last-named process the preparation of hydrogen may be readily achieved through pyrolytic decomposition of natural gas. The impure hydrogen thus formed may be readily purified by preferential absorption of the unchanged hydrocarbons on activated charcoal, as suggested by Frolich (23), or by taking advantage of the greater solubility of hydrocarbon gases in gas oils, kerosene, etc., at high pressure. This latter method is practiced by the Standard Oil Development Co. (29) and by the I. G. Farbenindustrie (28).

The lack of adequate petroleum resources in Alberta and the increasing demand for motor spirits suggests the utilization of hydrogen from natural gas as an agent in the liquefaction of coal and bitumen. The purpose of this investigation has been to determine the susceptibility to hydrogenation of various Alberta coals, and to determine the optimum conditions under which reaction takes place between hydrogen and bitumen on a con-

tinuous basis. Experiments carried out in the first part of the investigation showed the exceptionally beneficial effect of one of the suspending agents employed. A further study of the action of this substance was made, in which various carbonaceous materials were used.

For the sake of convenience the report has been divided into three parts. Part I presents the work carried out on the coals, part II deals with the hydrogenating action of tetrahydronaphthalene, and the preliminary investigation on the continous hydrogenation of bitumen from the Fort McMurray bituminous sand deposits has been discussed in part III.

PART I

ON THE HYDROGENATION OF THIRTEEN REPRESENTATIVE ALBERTA COALS OF VARIOUS RANK.

PART I

INTRODUCTION.

In recent years the hopes of those interested in the economic utilization of coal, and of those primarily interested in the production of liquid fuels in countries lacking adequate supplies of petroleum have been raised by the development of various processes for the "liquefaction" of coal.

Of these processes perhaps the most promising, and certainly the most unique, is the possibility of reaction between hydrogen and coal. The process as developed by Bergius requires the reaction to take place at temperatures from 430 °C to 480 °C, depending on the coal employed, and under pressures of hydrogen varying from 50 to 200 atmospheres. Use is made of ferric oxide, or "lux masse", to act as a desulfurizing agent. This process is known as "berginization", or the non-catalytic hydrogenation of coal.

In the more recent methods of procedure, use has been made of a line of sulfur-resistant catalysts developed by the I. G. Farbenindustrie. These catalysts materially decrease the necessary operating temperature, and this results in a lower formation of coke. Such catalytic methods are termed "hydrogenation", or "catalytic hydrogenation" of coal. Either process is often referred to as a "hydrogenation-cracking" process.

LITERATURE REVIEW

The first attempt to liquefy coal with hydrogen was made by Berthelot (8) as early as 1870. A French coal was mixed with a saturated hydriodic acid solution and the mixture sealed in a glass tube. By heating the tube to 270 °C, the hydriodic acid was decomposed, and a sufficient thermal pressure produced for the hydrogen to react with the coal. Using reaction periods up to twenty-four hours, Berthelot was able to convert as high as 60% of the coal to liquid products.

Fischer and Tropsch (21) in 1917-20, were unable to confirm these results using hydriodic acid alone, but a modified procedure involving the additional use of red phosphorous enabled them to successfully carry out the reaction. An extensive research followed which resulted in a fairly complete tabulation of the susceptibility to hydrogenation of coals of various ages. In general it was found that the chloroform-soluble reaction products increased with decreasing age of the coal.

In a later paper (22) Fischer was able to confirm the earlier results using sodium formate in the presence of water as the reducing agent. Pressures as high as fifty atmospheres were developed and the conversion to liquid products amounted to approximately 44%

by weight of the coal.

In 1913 Bergius (6) reported that cellulose, when heated to a temperature of 340 °C in the presence of hydrogen under a pressure of 100 atmospheres, was decomposed to a black powder similar in many respects to a soft bituminous coal. Under a pressure of 500 atmospheres a much more drastic decomposition took place, resulting in the evolution of a large amount of hydrocarbon gases, and a residue containing over 88% carbon. Bergius was thus led (7) to compare the action of hydrogen on coal to the action on cellulose. In the preliminary experiments conversions to oils amounted to over 70% of the dry, ash-free coal. Attempts to carry out the reaction on a larger scale resulted in the formation of excessive amounts of coke, because of superheating due to the poor conductivity of the dry charge. In order to minimize coke formation by elimination of superheating, the coal was mixed previous to treatment with hydrogen, with sufficient mineral oil or coal tar to maintain a fluid charge.

The reaction was considered by Bergius to require no catalytic aid, but later developments led to the addition of ferric oxide as a desulfurizing agent. A recent investigation by Skinner and Graham (54), however, shows that besides desulfurizing action, ferric

oxide is definitely catalytic in its action in the hydrogenation process.

Owing to the war, little progress was made by Bergius in the development of a process for continuous hydrogenation on a commercial scale, but by 1921 a renewed activity in this field resulted in the installation of a plant capable of treating one ton of coal per day. The development of a line of sulfur-resistant catalysts by the I. G. Farbenindustrie (28) soon led to the hydrogenation of coal and coal tars on a very much larger scale.

Since 1923 a considerable amount of experimental work on the hydrogenation of British coals by the Bergius process has been carried out in the Mining Research laboratory at Birmingham University, and later at H. M. Fuel Research Station at London. Shatwell and Graham (52) investigated the susceptibility to hydrogenation of the fractions obtained by extraction methods of coal. In general it was found that hydrogenation of immature coals resulted in larger yields of solid products and lower gas yields than encountered with normal bituminous coals and the oil yields were much the same in each case. In a later paper (44) Shatwell showed that the view held by Bergius, that coals containing over 85% carbon were not amenable to hydrogenation, was incorrect.

Subsequent investigations by Graham and co-workers (25, 26) involved the use of phenol as a suspension agent for the coal. This choice was made on account of the ease with which phenol may be removed from the reaction products. The technique employed may be briefly summarized as follows: a 200 gram sample of the finely ground coal was mixed with 100 grams of phenol and a small amount of catalyst. The reaction mixture was transferred to a three litre rotating autoclave and hydrogen led in to the desired initial pressure. The autoclave was then heated to 430 °C and held at this temperature for a period of eight hours. In this manner yields of refined gasoline amounting to twenty-five gallons per ton of dry ash-free coal were obtained.

Lush (40) comments on these investigations with regard to the choice of phenol as the medium, since at 250 °C this substance is readily reduced at pressures as low as 15 atmospheres, the final product being cyclohexane. Lush also suggests that the low yields of phenolic bodies (4%) encountered by Graham, in comparison with the 18 - 20% yields reported by Bergius may be accounted for by the mass-action effect of using phenol.

In addition to these investigations, a con-

siderable amount of experimental work has been done in other European countries. For example, Waterman and others of Delft, Holland, have reported the hydrogenation of Emma coal, asphalt, paraffin wax, and cottonseed oil by the Bergius process, and a comparison has been made between the reaction with hydrogen and the well-known cracking reaction (59, 60, 61). In hydrogenating coal cresol was used as the suspending agent and a large conversion to liquid products was obtained, even when the carbon content of the coal was over 88%. From the large consumption of hydrogen (over 4% by weight of the coal) Waterman concluded that an appreciable amount of the hydrogen appeared in the liquid products.

From an exhaustive comparison of the behaviour of paraffin wax upon hydrogenation and on cracking Waterman postulated that the function of hydrogen in hydrogenation of this type is to prevent dehydrogenation in cracking. Whether Waterman is willing to extend this theory to the hydrogenation of coal is not certain. The theory may be better expressed by saying that the hydrogen does not cause saturation of double bonds, but causes a more regular decomposition than occurs in the cracking reaction, and hence diminishes polymerization with resultant coke formation.

In contrast to the views held by Waterman,

Kling and Florentin (37) state that the hydrogenation reaction is characterized by rupture in the molecule which results in the formation of nascent double bonds, making the addition of hydrogen possible.

Tropsch (58) supports this view. Two reactions are postulated for hydrocarbons and three for phenolic compounds. For the latter:

(1). $ROH + H_2 \;\text{——}\; H_2O + RH$

(2). $RH \longrightarrow$ unsaturated fragments.

(3). The fragments from (2) are saturated by hydrogen.

In other words the function of the hydrogen is to diminish coke and gas formation by stabilizing unsaturated fragments which would otherwise further decompose to gases, or would polymerize to coke. Tropsch and Kling both consider that the function of the catalyst is to lower the decomposition temperature of the molecules, promoting rupture, and the subsequent reaction of hydrogen addition is better able to comp~~l~~ete with the polymerization reaction. With no catalyst, higher temperatures must be used to produce cracking, and at the high temperatures employed, the polymerization reaction moves forward at a sufficiently high rate to produce large amounts of coke, notwithstanding the presence of hydrogen in high concentrations.

Spilker (55, 56) has also demonstrated that the hydrogenation reaction probably takes place in a manner similar to that suggested by Kling. The experimental procedure adopted by Spilker involved the use of catalysts such as ferric chloride, long known for their drastic cracking action, together with substances containing iodine, such as sodium iodide.

Wilson (63, 64) has demonstrated mathematically on consideration of the kinetics of the reaction that cracking has a true end point only when the liquid phase has completely disappeared, whereas this is not true of the hydrogenation reaction. In support of this view Kiss (36) has derived formulae for the two reactions, showing that:

(1). Cracking is a monomolecular decomposition reaction characterized by polymerization.

(2). Hydrogenation is a cracking reaction in which polymerization is prevented by the stabilization of cracked fragments.

Whether no polymerization takes place in the latter reaction due to prevention of dehydrogenation, as suggested by Waterman, or whether this is due to the stabilization by actual hydrogenation of unsaturated linkages is difficult to say. The actual results found by Waterman are in perfect agreement with the theoretical

data presented by Kiss.

Besides the more widely-known investigations mentioned above, interest in the Bergius process has been shown in many other countries. For example Arend (4) has hydrogenated a few French coals, Hlavica (30) and co-workers have studied the possibility of liquefaction of some typical German coals by hydrogenation, Tashiro (57) has reported the hydrogenation of coal and low-temperature tars in Japan, and Beuschlein (9) has adapted the technique of Graham and Skinner to a study of the liquefaction of some American coals.

The behaviour of Canadian coals on hydrogenation has received little attention. Graham (27) conducted a few experiments in which six typical Alberta coals supplied by Prof. E. Stansfield were studied. A preliminary investigation of Alberta coals has been carried out by Boomer and Saddington (51) at the University of Alberta. Comparisons between these results and those obtained by Graham are difficult to make, due primarily to the great differences in technique employed. In this preliminary report a suitable procedure has been adopted, and has the advantage of not being dependent for success upon the medium used. A study of various catalytic agents and of various suspension media was made and attention was drawn to the highly

beneficial effect of tetrahydronaphthalene, commonly termed tetralin.

The literature on the subject of destructive hydrogenation of coal and of related materials is characterized throughout by a lack of experimental detail. The large number of patents that have appeared in recent years dealing with this process are obscure and entirely unilluminating. The review presented above cannot be considered as a complete treatment of the literature for this reason, but it is felt that little of importance has been omitted. An exhaustive treatment of the whole subject up to the year 1930 has been presented by Ellis (15).

EXPERIMENTAL PART

MATERIALS

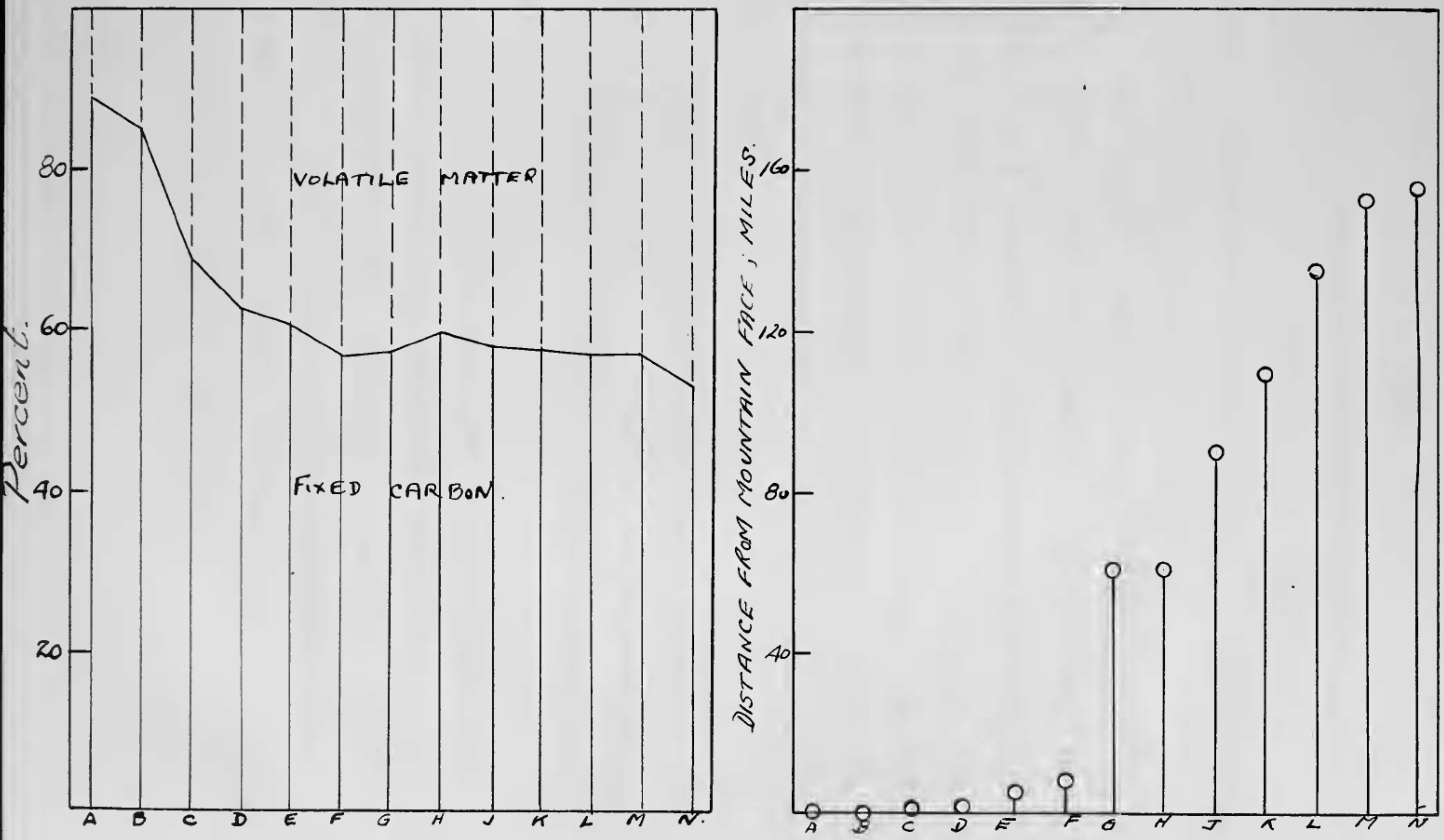
The series of thirteen coals studied was obtained through the courtesy of Prof. E. Stansfield of the Research Council of Alberta. A complete description and analysis is given in Table 1A and 1B, and in figure 1. The coals are representative samples taken during the 1930 field work of the Alberta coal survey. They are arranged in order of their maturity starting from A, an anthracite - semianthracite coal, and ending at N, of lignitic character. The following typical characteristic variations will be noticed as the coals decrease in age.

(1). Increase in moisture.

(2). Decrease in calorific value.

(3). Decrease, in general, in $^{C}/_{H}$, or carbon hydrogen ratio.

Figure I has been inserted with table 1A and 1B which illustrates the interesting change in location of the samples. Samples A and B were taken on the mountain face, C. and D in the foothills immediately east, E and F a distance of some sixty miles east of the mountain face, and a more or less regular increase in distance from the mountain face will be noted to N, located one hundred and sixty miles east of the



PROXIMATE ANALYSIS. DRY ASH-FREE COAL

face.

With the above chart is given the proximate analysis on the dry ash-free coals. This data was supplied through the courtesy of Prof. E. Stansfield of the Research Council of Alberta.

The samples, stored under water when received, were filtered, ground to somewhat less than pea size, and dried in a current of Viking natural gas at 110 °C and at a pressure of 25 mm. mercury. This gas, largely methane, is dry and free of sulfur. The coal was immediately transferred, after drying, to a ball mill where it was ground to pass 100 mesh, and was then ready for use.

Commercial electrolytic hydrogen was used. The catalyst was in every case molybdic oxide prepared by the dehydration of molybdic acid just below dull-red heat.

Two suspension media were used, tetralin and a paraffin oil fraction of medicinal grade known as liquid petrolatum B.P. The tetralin was the 1, 2, 3, 4 isomer and of the grade supplied by Eastman. (B.Pt. 202 - 204 °C. The A.S.T.M. distillation of the liquid petrolatum used is given in Table II.

TABLE IA. COALS OF 1930 ALBERTA SURVEY.

Coal	Geological Horizon	Canadian Classification	Pure dry coal S etc. omitted C	H	O+N	SEYLER'S Classification	Calorific value B. T. U. Pure Moist Coal	Ulmin's soluble in potash. % of pure dry coal.	Fuel Ratio FC/VM as received.
A	Kootenay	Anthracite[1]	93.05	4.05	2.90	Ortho-carbonaceous	15,380	0.05	7.5
B	"	Bituminous[2]	91.40	4.40	4.20	ortho-carbonaceous	15,560	0.0	5.4
C	"	Bituminous	88.7	5.20	6.10	Ortho-bituminous	15,380	0.0	2.25
D	"	Bituminous	87.65	5.60	6.75	Ortho-bituminous	15,490	0.02	1.75
E	"	Bituminous	85.10	5.55	9.35	Para-bituminous	14,610	0.16	1.70
F	Belly River	Sub-bituminous	83.80	6.05	10.15	Meta-per-lignitous	14,240	1.9	1.19
G	"	Domestic	79.5	5.4	15.1	Ortho-lignitous	12,580	11.5	1.35
H	Edmonton	"	78.95	5.30	15.75	Orth-lignitous	11,880	47.1	1.32
J	Belly River	"	77.9	5.2	16.9	Orth-lignitous	11,320	13.6	1.40
K	"	"	77.40	5.15	17.45	Ortho-lignitous	10,370	39.5	1.36
L	"	"	75.40	5.25	19.35	Orth-lignitous	9.940	49.7	1.50
M	"	"	73.5	5.2	21.3	Lignite	9,250	54.1	1.45
N	Edmonton or younger	"	71.95	5.15	22.9	Lignite	8,420	60.2	1.12

More correctly: 1-semi-anthracite; 2-semi-bituminous.

TABLE IB. COALS OF ALBERTA 1930 SURVEY.

Sample	Location	H_2O A.R.	Ultimate Analysis			1 - Dry Basis, 2 - Pure Coal basis.			
			C	H	Ash	S	N	O	C/H
A,306/30	Anthracite	2.2	80.50	3.50	12.0	1.00	1.1	1.9	23.0
			92.45	4.00	-	0.65	1.3	1.6	23.1
B,307/30	Canmore	1.4	85.10	4.05	6.0	0.75	1.5	2.6	21.0
			90.65	4.35	-	0.80	1.7	2.5	20.8
C,303/30	Coleman	1.4	81.35	4.70	7.3	0.45	1.2	5.0	17.3
			88.30	5.15	-	0.45	1.3	4.8	17.1
D,302/30	Bellevue	1.2	73.45	5.55	15.1	0.60	1.3	5.0	16.1
			87.25	5.60	-	0.45	1.5	5.2	15.6
E,305/30	Pincher Creek	3.3	76.10	4.75	10.1	1.15	0.7	7.2	16.0
			84.7	5.55	-	0.45	1.2	8.1	15.3
F,304/30	Lundbreck	4.9	70.55	5.00	13.9	0.85	1.9	7.8	14.1
			83.30	6.00	-	0.60	2.3	7.8	13.9
G,301/30	Lethbridge	9.8	70.15	4.80	10.8	0.75	1.8	11.7	14.6
			79.1	5.35	-	0.55	1.9	13.1	14.8
H,308/30	Champion	12.9	70.90	4.80	7.7	0.40	1.3	14.9	14.8
			78.65	5.30	-	0.35	1.3	14.4	14.8
J,309/30	Taber	15.0	69.95	4.75	8.8	1.10	1.7	13.7	14.7
			77.40	5.15	-	0.65	2.0	14.8	15.0
K,310/30	Grassy Lake	18.8	67.85	4.65	10.6	1.20	1.4	14.3	14.6
			76.70	5.10	-	0.90	1.9	15.4	15.0
L,311/30	Winnifred	22.6	68.30	4.40	10.0	0.60	1.3	15.4	15.5
			74.90	5.20	-	0.70	1.4	17.8	14.4
M,313/30	Redcliff	26.6	67.65	4.35	10.4	0.50	0.8	16.3	15.6
			73.10	5.15	-	0.55	1.1	20.1	14.2
N,312/30	Eagle Butte	30.3	60.70	3.95	12.2	0.35	1.2	21.6	15.4
			71.65	5.15	-	0.40	1.1	21.7	13.9

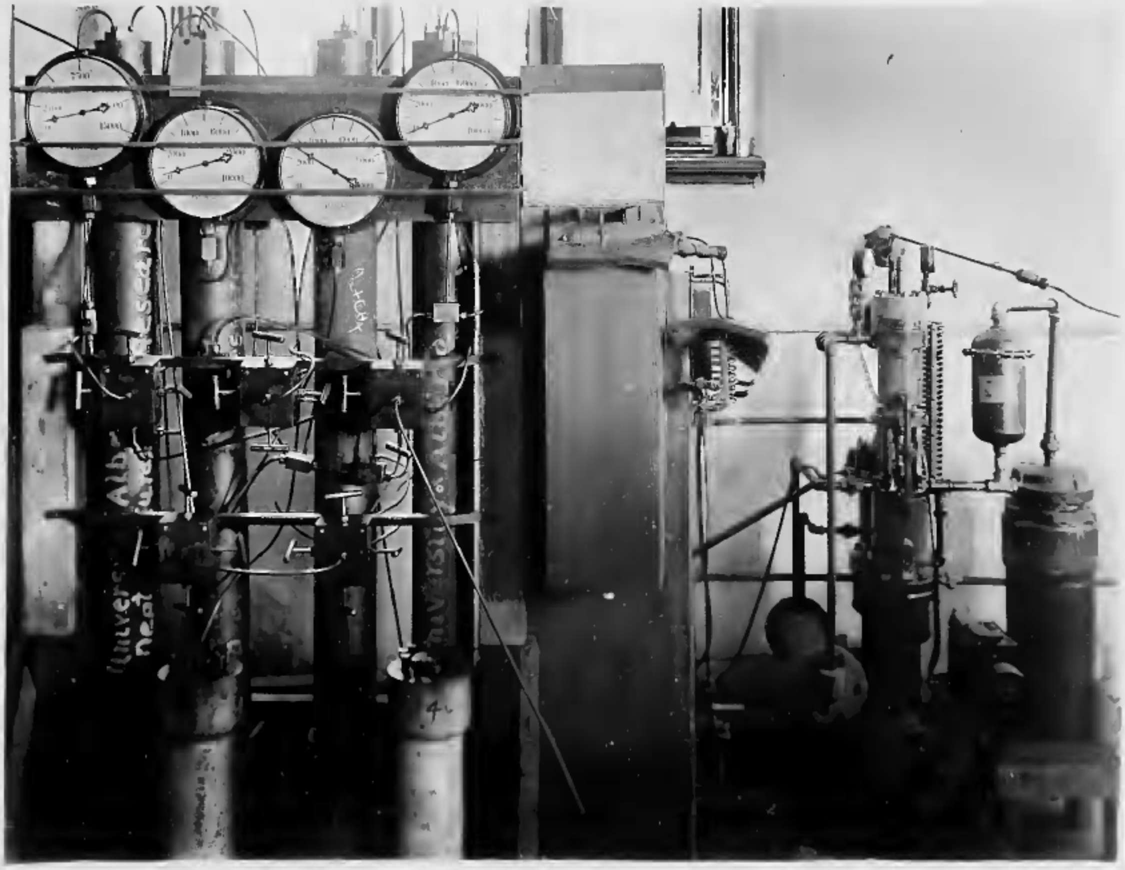
N. B. Pure coal analyses taken from curves.

TABLE II

L.B.P. 152 °C.

10% - 327 °C 40% - 365 ° 70% - 380 °
20% - 345 ° 50% - 371 ° 80% - 385 °
30% - 357 ° 60% - 376 ° 90% - 395 °

3½% at 300 °C
91½% at 400 °C



Compressor and Gas Storage System.

The Rix three stage compressor is shown in the right background, and the storage cylinders in the left foreground.

APPARATUS

The compression and gas storage system consisted of a compressor and auxiliary equipment designed for operation to 5000 lbs. per sq. inch pressure. Standard types of joints and valves were used (19) in which all seals were metal to metal. Pressure measurements were recorded continuously on a Bourdon tube gauge calibrated at intervals by comparison with a standard dead weight piston gauge or a Bourdon tube test gauge. Temperature measurements, made with a calibrated iron-constantan thermocouple, were recorded on a Leeds and Northrup recording potentiometer controller. The instrument enabled control to ± 5 °C.

The autoclave and its supporting parts is illustrated in Figure 2. The arrangement is similar to that described by Peters and Stanger (49). The autoclave, machined from 511 - K A 2 chromium nickel steel bar and designed for service to 7500 lbs. per sq. inch pressure at 500 °C, was closed at each end by six bolts in compression bearing on end plates B which seated on a confined annealed copper gasket. A ring nut C, screwed into the shell by buttress threads, transmitted the stress from the end plates to the autoclave body. One end plate carried a thermocouple

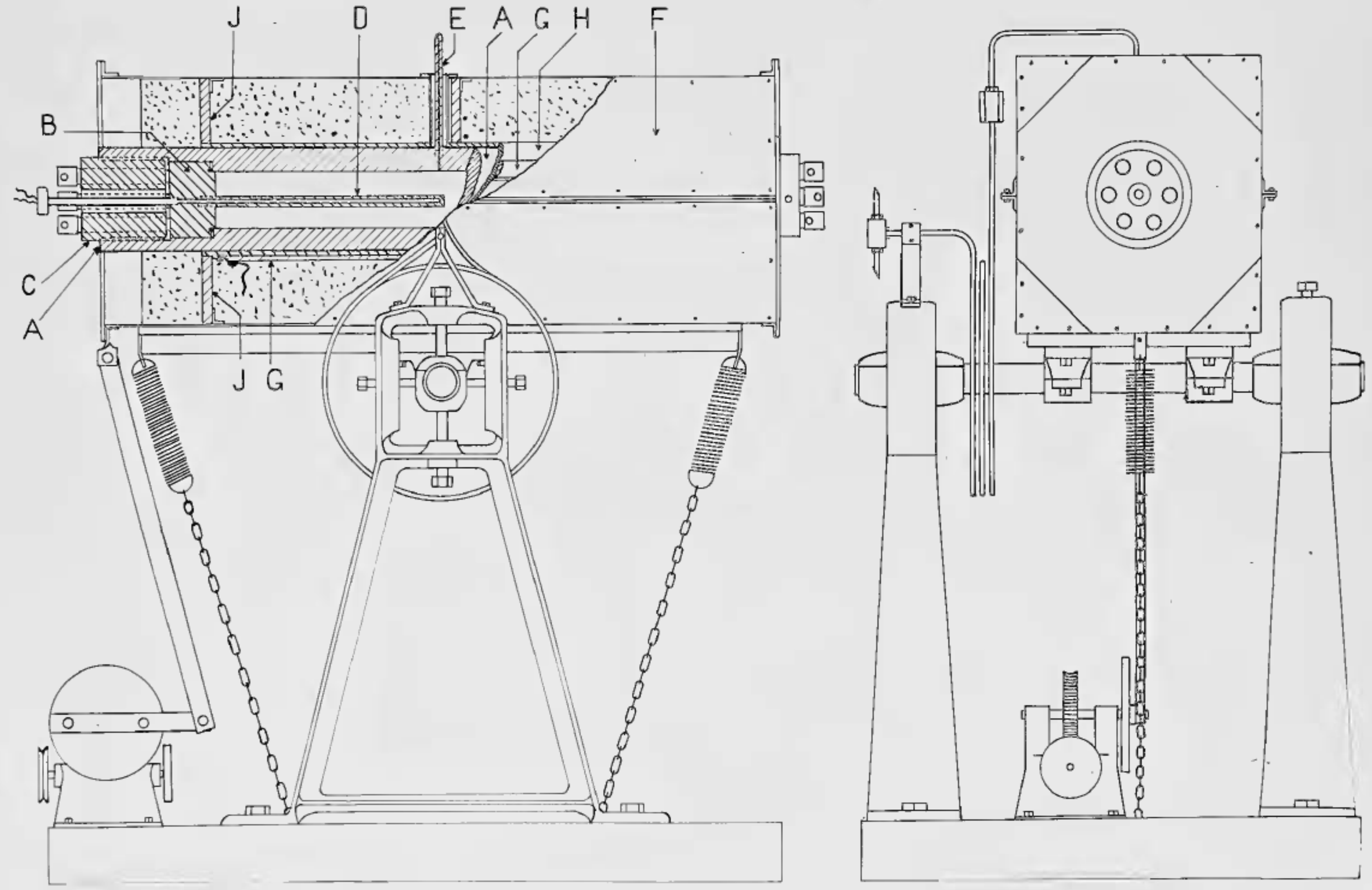


Figure 2. 1800 c.cm. Oscillating Autoclave.

well D which extended coaxially inside the shell to its centre. The gas connection E was made to the reaction chamber at its midpoint to allow charging and removing gases. The capacity of the autoclave was 1800 c. cm. when assembled.

The autoclave was heated by five strip heaters attached to the outside of a split cylindrical casing made from the longitudinal halves of a 5 inch steel pipe, in which the autoclave was directly enclosed.

The outer furnace casing of sheet metal on a light angle iron frame carried the weight of the insulation only. The split inner casing H, which carried the heaters, was bolted to steel cross-members J, supported by the base plate of the furnace. Both halves of the furnace were identical in design, the upper half being bolted to the lower along an outside longitudinal flange.

The autoclave fitted snugly in the two halves of the inner casing, rotation being prevented by two lugs fitting recesses in the pipe. A uniform temperature was maintained at the autoclave surface by heat conduction ar~~r~~ound the casing which was 1/4" thick.

Examination of the autoclave was readily accomplished by dismantling the furnace and removing the autoclave. In a similar manner the installation

of new heaters was readily effected by the removal of the split inner casing to which the heaters were bolted.

The base of the furnace was attached to two flat box journals fitted on a shaft which was supported at each end by pillow blocks on inverted shaft hangers. A motor operating a reducing gear equipped with a crank and connecting rod mechanism produced the oscillating motion. Springs stretched from each end of the furnace base to chains of adjustable length attached to the floor insured a smooth oscillating motion.

Gas connection was made to the inlet E through a flexible 1/8 x 5/8" copper coil consisting of three turns of 12" diameter attached to the bearing shaft. The outer end of this coil was attached to a standard T connection, one line from which led to the pressure gauge, the other line terminating in a second T connection, from which one line led to the gas storage system, the second leading to an expansion valve, through which it was possible to bleed the autogenous gases.

Heat control on the autoclave was maintained by adjustment of master rheostats placed in series with the heaters. A magnetic switch, operated by the controller through a relay, cut in or out one of the rheostats in accordance with temperature fluctuations.

PROCEDURE

Approximately 200 gram samples of the dry powdered coal were intimately mixed with the desired quantity of suspending agent, and 5% by weight of molybdic oxide thoroughly incorporated with the mixture. One hundred and fifty gram samples of tetralin were found to produce a sufficiently fluid charge, while 200 grams of liquid petrolatum were required. The resulting paste was transferred to the autoclave, the weight added being accurately determined, the apparatus sealed gas-tight, and after washing out the air with Viking natural gas, hydrogen was added to the desired initial pressure. Oscillation was commenced when the autoclave reached a temperature in the neighborhood of 100 °C. The reaction chamber was maintained at the desired operating temperature for a period of four hours, during which time a steady decrease in pressure indicated a corresponding absorption of hydrogen. No attempt was made to counteract the possible catalytic effect of the steel walls of the autoclave.

At the end of the four hour interval heating was discontinued and the autoclave allowed to cool overnight. The residual gases were bled through the expansion valve the following morning and led through activated charcoal absorbers, after which they were

measured in an oil-filled wet test meter before storage in a water-sealed gas holder.

The gas was allowed to stand until of uniform composition and a sample drawn off for analysis. The increase in weight of the charcoal absorbers was noted and the spent absorbent revivified by steam distillation, the yield of condensable products being noted.

The autoclave was recharged with hydrogen and a second cycle completed in a manner identical with that described above. The reaction chamber was then opened and the contents withdrawn as rapidly as possible, weighed, and transferred to a glass-stoppered vessel. In spite of the precautions taken the volatile nature of some of the constituents of this mixture resulted in high evaporative losses. The reported oil yield is consequently low by this amount. In those experiments using liquid petrolatum a hard brittle coke adhering to the walls of the autoclave was often encountered and was removed with difficulty. The estimated loss of solid products in such cases was ten grams.

The determination of the yield of solid and liquid products did not prove difficult. The oily mass from the autoclave was filtered by suction and

the residual solids thoroughly washed with ether and subsequently dried and weighed. The weight of dried coke, less the weight of catalyst used thus represented the solid residue from the coal, together with any coke formed in the decomposition of the medium. In this way the oil yield was determined as the difference between the total weight of reaction products extracted from the autoclave and the dried solid residue.

The filtrate from the ether washing was distilled to recover the ether, the bottoms being added to the oil obtained by filtration. The combined oils were then subjected to distillation analysis. The first fraction, boiling below 175 °C, usually contained a large amount of water and consequently divided into two layers on condensing. The yields of oil and water were recorded separately. The second or middle fraction included that portion of the oil which distilled between 175 °C and 225 °C and in those experiments in which tetralin was used included all the recovered tetralin and decalin as well as any naphthalene formed. The final fraction, boiling between 225 °C and 300 °C, was usually small and included a viscous red oil of evident lubricating value. On occasion wax-like crystals were obtained in the neighborhood of 280 °C. The residue from the

distillation was a stable pitch boiling to 450 °C without decomposition and usually melting in the neighborhood of 40 °C. The pitch was of particular interest in its close resemblance to the residues obtained from distillation analysis of the products of hydrogenation of bitumen from the Athabasca bituminous sand deposits (10).

The distillation of oils in those experiments using liquid petrolatum was carried out more readily than in the tetralin series. The water content was usually quite low and an even distillation curve to 300 °C was obtained. The yield of pitch was considerably higher than in the tetralin series and the pitch was quite soft..

The calculation of the yield of gaseous products was accomplished by use of the data procured on gas analyses and total gas volumes. In estimating the amount of hydrogen absorbed, two procedures were adopted. In the petrolatum series it was assumed that both the medium and the coal were reduced and hence the total decrease in hydrogen was attributed to absorption by the total charge, less catalyst. It will be seen that the actual absorption of hydrogen by the coal alone cannot be estimated. In those experiments in which tetralin was used however, it is

safe to assume that no hydrogen was absorbed by the tetralin, for though saturation of the double bonds would lead to the formation of decalin, with consequent hydrogen absorption, distillation analyses showed no constant-boiling fraction corresponding to decalin. In this regard it has been demonstrated by Spilker (55, 56), Hugel (32) and Lush (41) that tetralin is the final reduction product of naphthalene under comparable operating conditions. Hence the total decrease in hydrogen could be attributed to absorption by the coal without serious error.

RESULTS AND DISCUSSION

For the sake of convenience the results have been classified under two main headings:

1. The hydrogenation of coal in the presence of tetralin.
2. The hydrogenation of coal in the presence of liquid petrolatum.

In a similar manner the discussion has been split up into parts so as to more conveniently assemble the required results.

A. Hydrogenation in the Presence of Tetralin.

The results obtained upon the hydrogenation of thirteen representative Alberta coals, using tetralin as medium have been presented in tabular form in Table III. For the most part the data presented will need no interpretation, but it will be advantageous to more clearly define a few of the rows included.

The % hydrogen absorbed is given in % by weight of the total charge, less the catalyst. The gas yield in litres per kilogram charge is also calculated on the basis of the total carbonaceous charge and is derived from the gas volumes, less hydrogen, removed from the autoclave.

The conversions to liquid, gases and solid

Table III
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TABLE III - Hydrogenation of Alberta Coals in the Presence of Tetralin.

Experiment Number	ANTHRACITE					Sub-Bituminous		Domestic					
	146	148	151	171	155	144	157	159	161	163	165	167	169
	Semibituminous												
Sample Number	A-306	B-307	C-303	D-302	E-305	F-304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of Coal in grams	186	195	185	194	191	200	204	200	189	193	194	195	199
Weight of Tetralin in grams	144	146	138	146	144	132	149	148	144	145	146	151	147
Catalyst, % by weight	5	5	5	5	5	5	5	5	5	5	5	5	5
Number of cycles	2	2	2	2	2	2	2	2	2	2	2	2	2
Time per cycle in hours	4	4	4	4	4	4	4	4	4	4	4	4	4
Average temperature, ° C.	450	450	450	450	450	450	450	450	450	450	450	450	450
Average Initial Pressure, 161 sq.in.	960	940	995	1015	1000	920	1000	990	1045	1000	790	970	1030
Average maximum pressure	2545	2500	2595	2620	2570	2525	2665	2855	2950	2785	2570	2715	3195
Average final pressure	660	595	525	530	510	450	475	505	585	485	410	510	545
Average pressure drop	300	345	470	385	490	470	525	485	460	515	380	460	485
% Hydrogen absorbed	3.9	4.4	6.0	5.7	5.3	5.5	5.8	5.6	5.5	6.2	4.5	5.6	5.9
Gas yield, less H, in litres per kg. charge	76.8	74.8	110.8	98.8	75.7	117.0	100.0	111.0	85.3	113.8	96.0	105.6	119.0
% charge to liquids	35.5	46.8	69.0	69.5	67.7	60.2	65.5	61.2	65.4	66.0	64.5	65.0	64.3
% charge to solid residue	52.4	41.3	23.5	18.6	16.9	15.7	14.7	14.4	11.5	11.6	13.2	10.8	10.8
% charge to gas (including from charcoal)	6.0	6.7	8.5	8.4	7.8	9.9	9.4	11.2	12.3	11.0	9.6	10.2	10.8
% charge to loss	6.1	5.2	9.0	3.5	7.6	14.2	10.4	13.2	10.8	11.4	12.3	14.0	14.1
Gas Analysis, %													
CO_2	0.2	0.2	2.2	1.0	0.4	1.3	2.9	4.4	3.9	4.2	7.3	7.2	8.8
C_2H_2n	0.4	0.4	0.4	0.5	0.5	0.6	0.7	0.2	0.1	0.1	0.3	0.1	0.3
H_2	77.3	74.5	60.9	63.4	72.0	52.4	56.5	57.5	71.5	54.5	56.2	57.5	56.6
CO	0.6	0.6	1.7	0.7	1.0	1.4	1.9	1.1	1.2	3.2	1.6	2.0	2.1
C_2H_6	4.5	5.5	8.7	9.7	7.2	13.1	14.7	12.0	9.0	24.8	10.8	10.9	11.3
CH_4	9.9	12.1	16.0	12.7	11.0	25.2	14.3	27.7	25.8	16.1	19.0	21.0	20.2
% Coal converted. Coal as received.	10.8	32.3	64.6	73.5	77.0	80.0	80.5	81.3	86.4	86.3	83.0	87.7	88.0
% " " . Dry ash-free coal.	12.2	34.9	72.3	85.0	87.0	92.0	90.7	89.3	95.1	95.7	91.2	96.7	96.2
% charge to volatile products absorbed in charcoal.	2.3	2.8	3.0	3.4	3.7	2.6	3.3	3.3	3.8	3.7	3.7	3.3	3.1
% Charge to Oil. (1) Oil to 175°C.	3.6	3.6	5.4	6.1	3.6	10.8	7.3	6.8	6.7	7.9	7.2	7.1	7.4
(2) Oil to 225°C.	27.7	30.4	41.9	43.1	37.6	37.9	34.7	36.0	39.1	36.7	36.6	37.5	37.0
(3) Oil to 300°C.	30.0	32.3	45.0	49.5	45.4	44.5	43.2	42.7	46.6	46.5	43.8	46.5	44.8
(4) Pitch.	5.5	14.5	23.7	19.4	20.7	14.2	15.9	13.2	14.6	10.6	12.0	12.3	9.6
(5) Water	0.0	0.0	0.3	trace	1.3	0.6	6.3	5.0	4.2	7.9	8.7	5.6	8.7
(6) Loss	0.0	0.0	0.0	0.6	0.3	0.9	0.0	0.3	0.0	0.0	0.0	0.6	1.2

residue is calculated on the total charge, including the catalyst, and for this reason the figures given on solid residue recovered include the catalyst. The % of charge to loss is thus the difference between 100 and the sum of the recovered products.

The gas analysis figures are an average of each cycle, account being taken of the gas volumes in each case.

The figures on total conversions are obtained from the coal charged less the solid organic residue removed from the autoclave. This figure thus represents the weight of coal converted to gas, oil and water. The conversion to a percentage basis has been made in each case. To calculate the conversion of the coal on the basis of the ash-free coal, it is only necessary to add to the non-organic solid residue (catalyst) the weight of ash in the amount of coal charged. In this way the carbonaceous solid residue decreases, with consequent higher values for coal conversion.

The distillation analyses have been entered to show the percent conversion of the total charge to the respective boiling ranges cited. Water has been included in a separate section and the true oil yield computed. The loss presented at the end of this section of the table represents distillation losses only. The

total oil and water distillate to 300 °C plus the yield of residual pitch plus the distillation loss will thus in all cases add up to the total conversion of the charge to liquid products.

The results in Table III indicate clearly the definite progression in susceptibility to hydrogenation from old to young coals. Numerous small discrepancies will be noted but for the most part these are within experimental error. The hydrogen absorption increases roughly from 3.9 to 4.4% for anthracite coals to an average value of 6.0% for domestic coals. In this respect Exp. 165 on coal L - 311 represents an interesting departure from the normal value. It will be noted however that the initial pressure of hydrogen was extremely low. Hence it may be suggested that the extent of reaction is to a large degree dependent upon the concentration of hydrogen.

The discrepancy in Exp. 161 on coal J - 309 is not large and probably within experimental error. The absorption of hydrogen is slightly lower than the normal value but this may be attributed to the shorter period of operation. The remaining experiments fall into a fairly normal progression from the point of view of hydrogen absorption. They may be averaged as follows:

Coal	Hydrogen Absorption
Anthracite - (semi anthracite)	3.9%
Semi anthracite (semi bituminous)	4.4%
Bituminous	5.6%
Sub bituminous	5.6%
Domestic	5.9%

In agreement with this tendency to increased hydrogen absorption, an inspection of the pressure-time and pressure-temperature relations indicates that the rate as well as the amount of hydrogen absorption also increases as the age of the coal decreases. In this regard figures 3 and 4 represent the pressure-time and pressure temperature relations of the first cycle of experiments conducted with representative coals of various rank. In figure 3 the rate of reaction at constant temperature, sometime after hydrogenation has commenced, is indicated by the downward slope of the curve, while the total decrease in pressure is a rough measure of the extent to which hydrogenation has taken place. Thus for an anthracite coal the rate of reaction is low and the total absorption is small. For bituminous and sub-bituminous coals the rate of reaction is much the same, although the younger coal exhibits a much greater absorption. The extremely rapid and large absorption of hydrogen by domestic coals is clearly illustrated in the fourth curve.

Pressure-Time Relations---First Cycle.

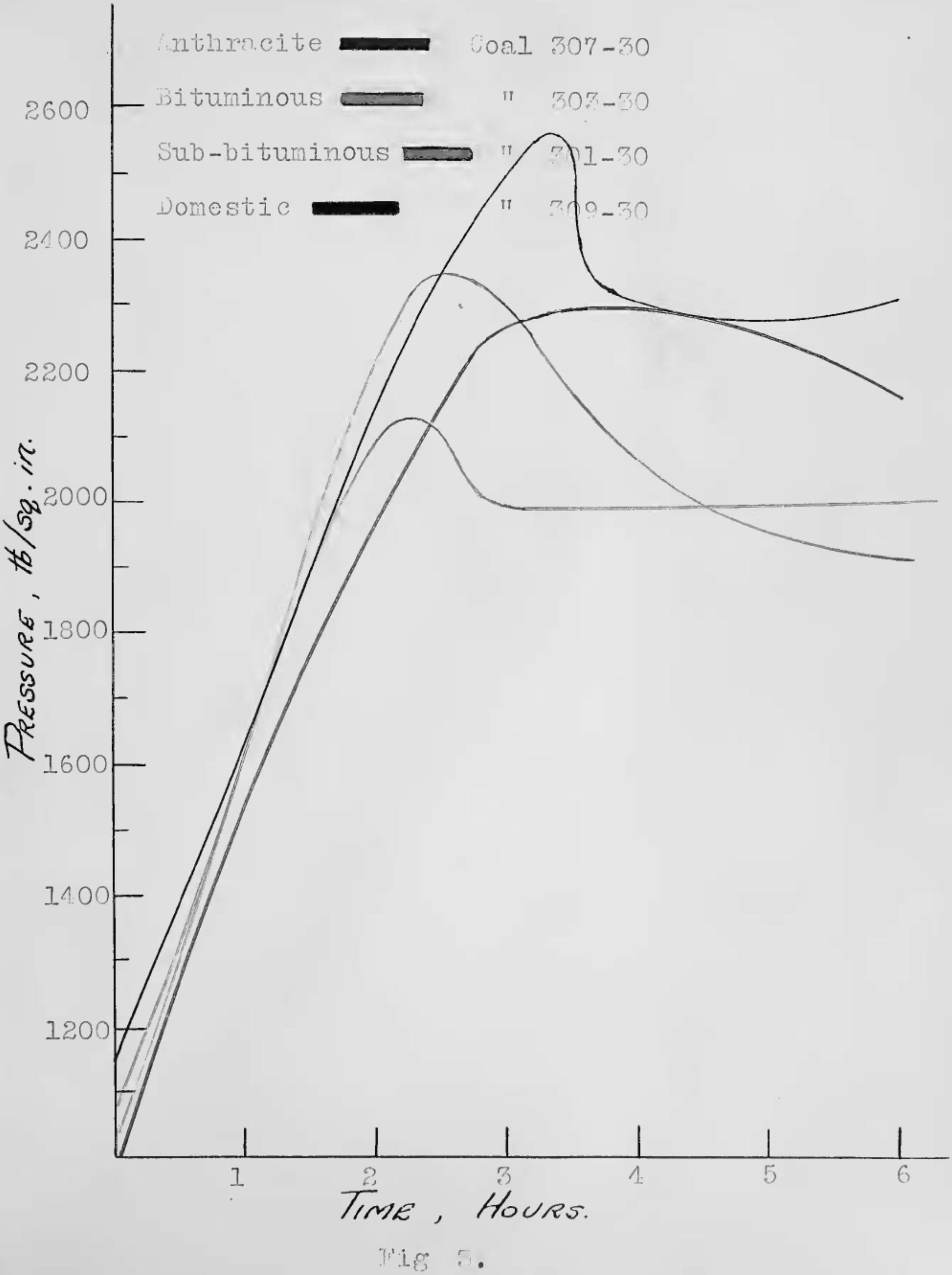

Fig 5.

Pressure-Temperature Relations--- First Cycle.

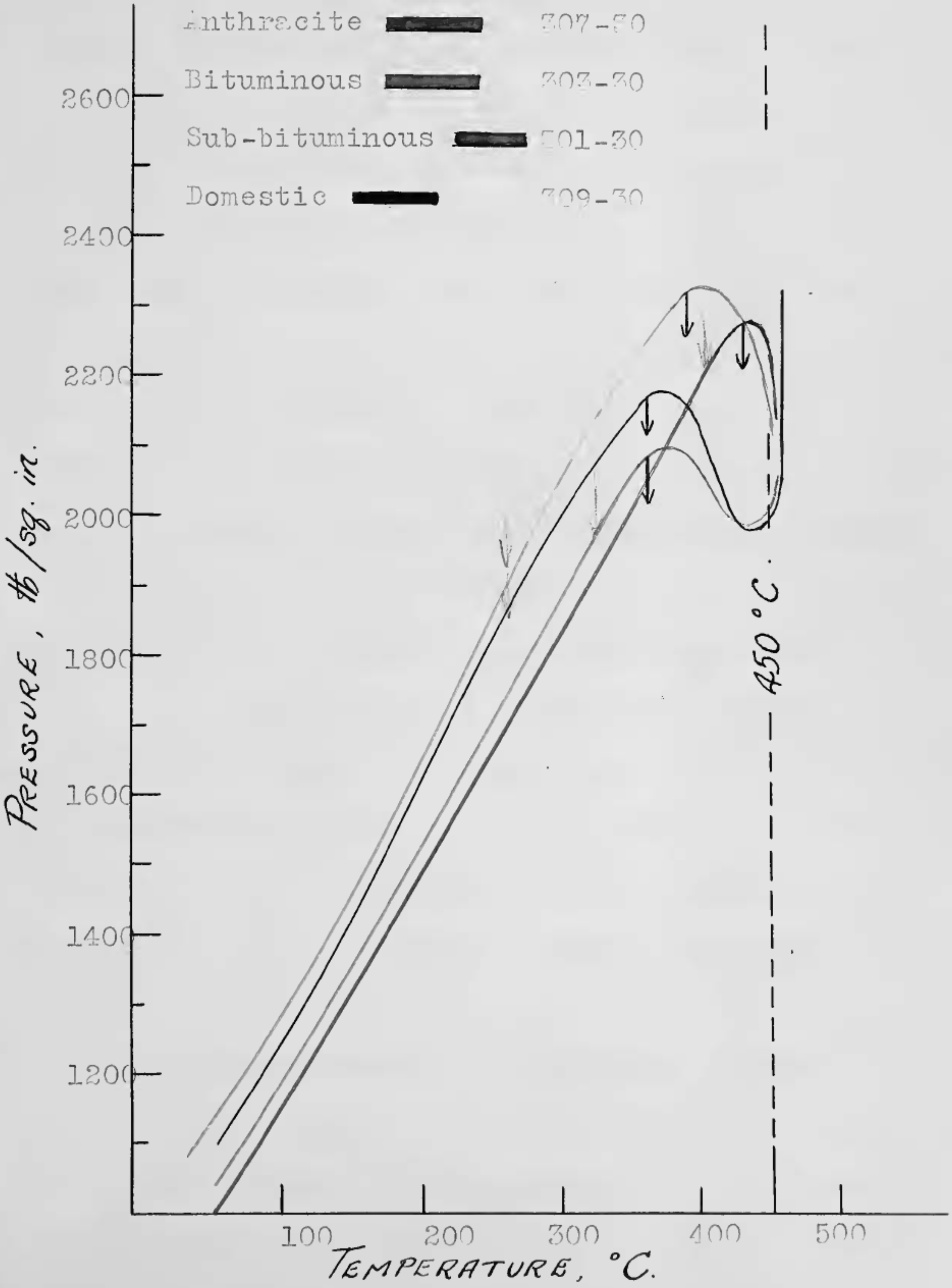

Fig 4.

A similar analysis may be made by inspection of figure 4, in which the pressure-temperature relations of the four coals are illustrated. It will be noted that the temperature at which hydrogenation commences, indicated by a change in sign of the slope in the rising portion of the curve, and marked approximately by arrows, decreases regularly with decreasing age of the coals. Layng (39) has pointed out that a decrease in the temperature of plasticity of coals becomes apparent when the coals are arranged in descending order of their maturity. The exact correlation of the "rest" temperature and initial decomposition temperature in hydrogenation has received the attention of Arend (4), who has shown that a very definite relationship does exist.

Figures 5 and 6 present the pressure-time and pressure-temperature relations of the second cycle of experiments on the same four coals illustrated in figures 3 and 4. An examination of figures 5 and 6 reveals that an appreciably higher temperature is required for hydrogenation to take place when a coal has been previously attacked by hydrogen. Apparently the more unstable constituents become completely hydrogenated in the first cycle. This evidence is of extreme importance when the possibility of operation on a continuous basis is considered. The evidence shows that under the

Pressure-Time Relations---Cycle 2.

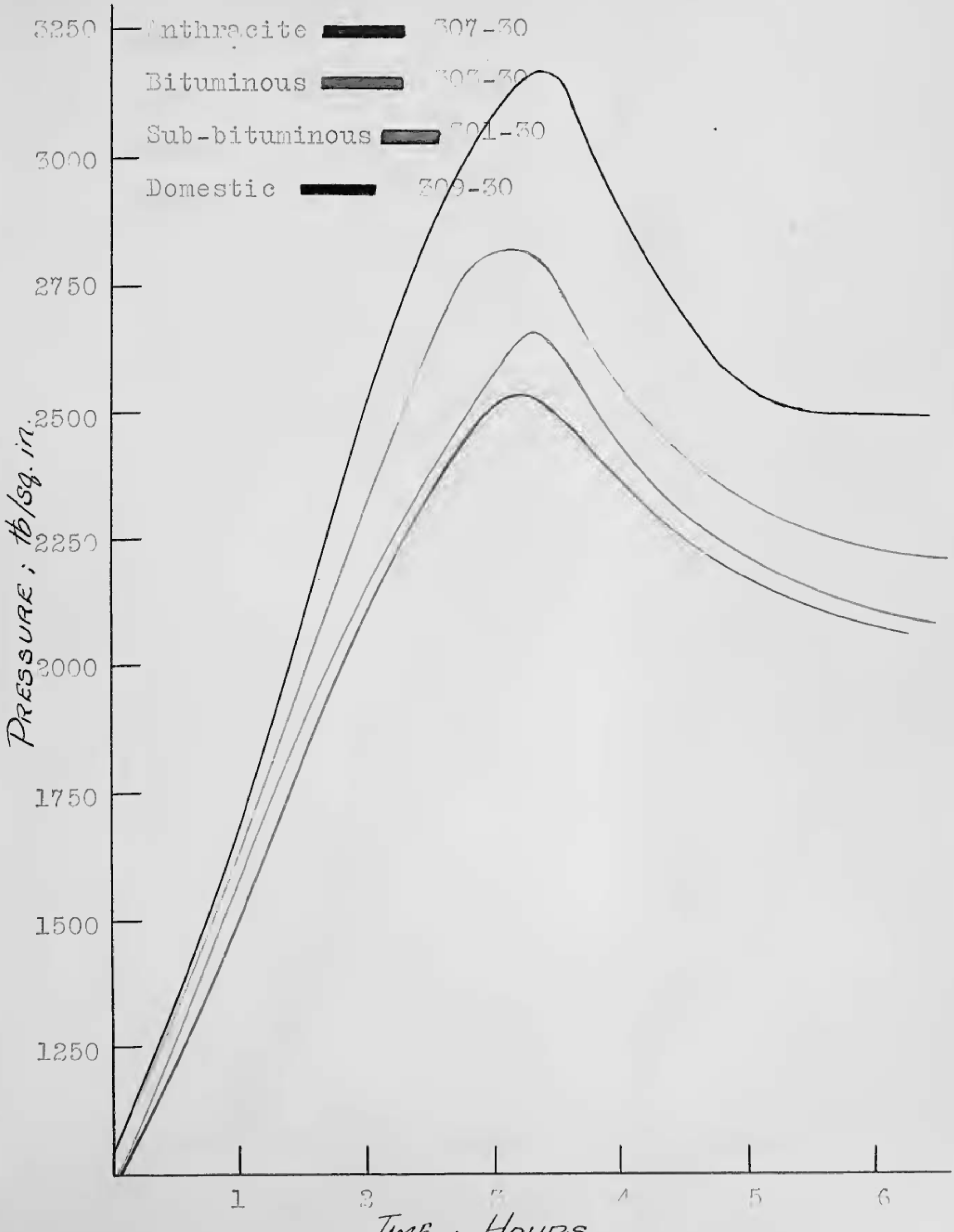

Fig. 5.

Pressure-Temperature Relations---Second Cycle.

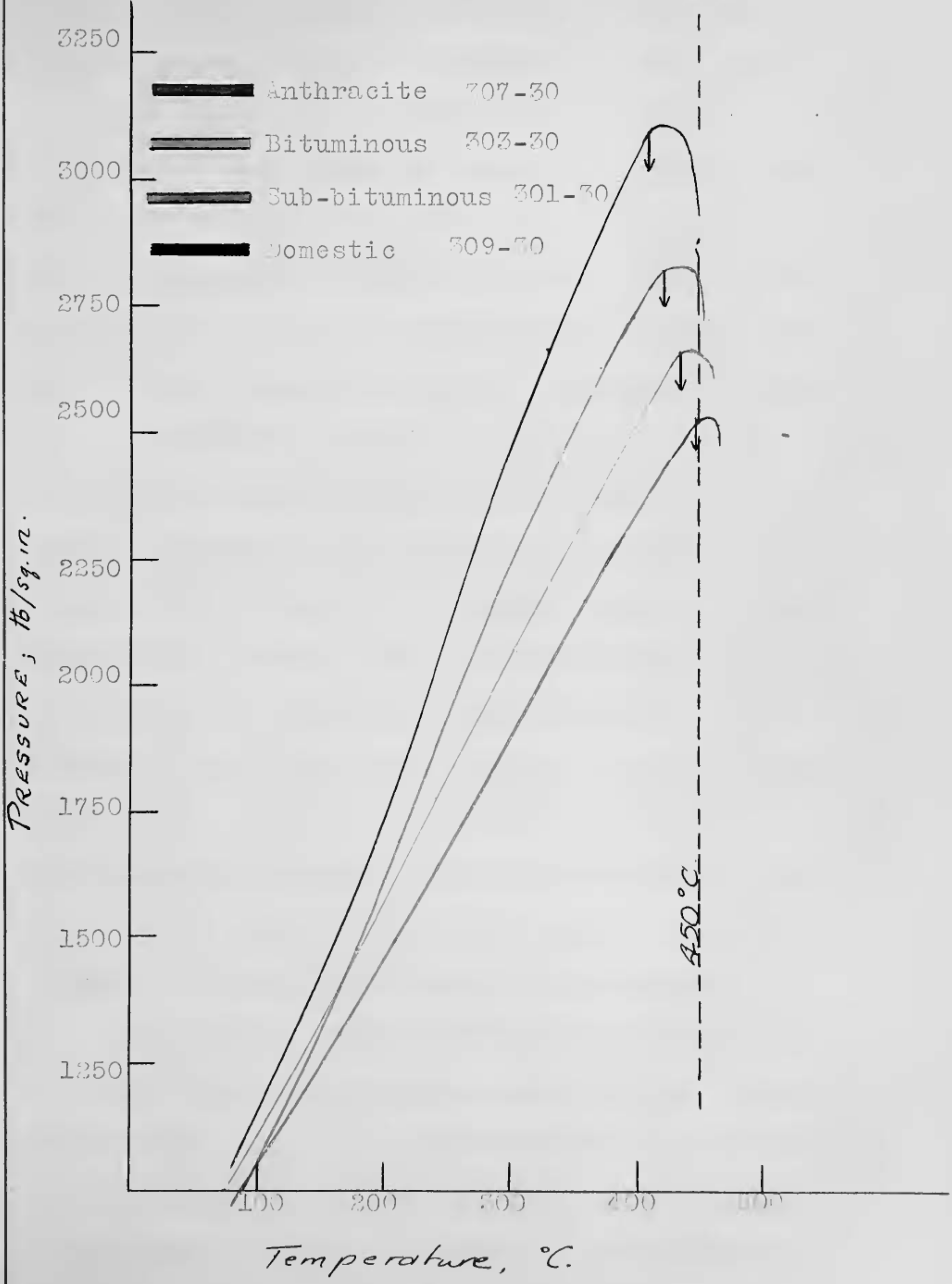

Fig. 6.

conditions most suitable for partial hydrogenation of fresh material the reaction is not complete and more drastic conditions are necessary to obtain further reduction. This would suggest that satisfactory results, with particular regard to speed of reaction, would be obtained in continuous operation when apparatus designed for a multi-stage process was used. This fact has been recognized by the I. G. Farbenindustrie (28) who have carried out extensive research along these lines.

A further inspection of Table III shows a definite increase in gas production as the coals decrease in rank. Coincident with this is the expected tendency toward the development of higher maximum pressures. Analysis of the exit gases shows a pronounced increase in the carbon dioxide and carbon monoxide yields. The extent to which the coals became oxidized during milling and storing is difficult to estimate, and the susceptibility to oxidation that is characteristic of young coals may account in some measure for the increased production of oxygenated compounds.

Paralleling this tendency for increased yields of carbon dioxide and carbon monoxide, the formation of water takes place to a greater extent in younger coals. It is assumed that water is formed upon the reduction of hydroxyl groups in the coal and hydrogenation of oxidation products formed during exposure of the coal

to the air, together with the possible reduction of more complex oxygenated compounds originating in the coal. The fate of the oxygen in the coal upon hydrogenation will be more fully discussed later.

From Table III it is further apparent that there is a general tendency toward increased mechanical losses with decrease in age of the coals. This may be taken as indicating an increasing conversion to low-boiling oils. Appreciable amounts of propane, butane and other volatile hydrocarbons appeared in the charcoal absorbers and this, with the excessive amounts of carbon dioxide formed in the combustion analyses of the residual gases further support this view.

Though numerous small discrepancies are apparent there is a tendency toward a decrease in residual hydrogen with decreasing maturity of the coals. From the theoretical point of view this fact is of great interest. It has been earlier stated that there are two conflicting theories regarding the mechanism of the hydrogenation reaction. Waterman (59, 60, 61, 62) based his theory that the function of the hydrogen was to prevent dehydrogenation in cracking upon evidence that the hydrogen absorbed could be accounted for in the gaseous products produced, and also that the amount of hydrogen absorbed was to some extent independent

of the extent to which hydrogenation took place. The theories of Kling (37) and of Tropsch (58), on the other hand, are based on experimental evidence in agreement with the data given in this investigation.

Further inspection of Table III shows that in general the relative conversions of light oil, gas and water increase at the expense of pitch formation. That is, the ratio of low boiling oils, gas and water to pitch increases with decreasing maturity of the coals.

Two experiments on domestic coals (exp. 165 on L - 311 and 167 on M - 313) were characterized by the appearance of considerable naphthalene in the reaction products. This would suggest that the reaction was incomplete after eight hours of operation. As has been previously mentioned, the initial pressure in exp. 165 was extremely low. Since the pressure-time charts indicated that the reaction was incomplete, and since naphthalene was produced in large quantities, in spite of a high concentration of hydrogen in the residual gases, these experiments are of interest in that they illustrate the extremely efficient "carrier" action of tetralin.

Assuming that the distillation products between 175 °C and 225 °C may be attributed directly to the tetralin (i.e. as decalin, unchanged tetralin, and

naphthalene), then the average recovery of the tetralin charged was 80%. The 20% loss was in all probability due to the decomposition of some of the tetralin, with the formation of benzene, cyclohexane and other volatile liquids.

B. Hydrogenation in the Presence of Liquid Petrolatum

Though the behaviour of the coals upon hydrogenation follows in general the same trend as in the experiments in which tetralin was employed, the efficacy of liquid petrolatum as a suspending agent for coal will be seen to be definitely lower than tetralin. A more complete comparison of the two media will be made later.

The results of this series of experiments have been set forth in Table IV. In this table the rows have the same significance as in Table III. It will be noted however that a larger sample of medium has been used in this series and that the hydrogen absorption is much lower than in the tetralin series, due in some part to the method of calculation, in which the whole charge was considered. Furthermore these experiments were run at 425 °C as against 450 °C in the presence of tetralin. The reason for this lies in the greater stability of tetralin toward heat. Extensive decomposition of liquid petrolatum takes place at 450 °C with the formation of gas and coke.

An inspection of the table shows the expected increase in gas production and in maximum reaction pressures with decrease in maturity of the coal. The

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TABLE IV. - Hydrogenation of Alberta Coals in the Presence of Liquid Petrolatum.

Experiment Number	Anthracite-Semi-bituminous		Bituminous		Bituminous	Sub-Bituminous		Domestic						
	147	149	152	154	156	145	158	160	162	164	166	168	170
Sample Number	A-306	B-307	C-303	D-302	E-305	F-304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of coal in grams	197	194	191	195	190	179	193	194	188	189	195	193	196
Weight of Solvent in grams	197	204	191	205	201	179	195	200	193	189	195	194	199
Catalyst, %	5	5	5	5	5	5	5	5	5	5	5	5	5
Number of Cycles	2	2	2	2	2	2	2	2	2	2	2	2	2
Time per cycle in hours	4	4	4	4	4	4	4	4	4	4	4	4	4
Average temperature, °C.	425	425	425	425	425	425	425	425	425	425	425	425	425
Average initial pressure	920	880	990	1030	1015	985	970	985	1015	1005	970	995	970
Average maximum pressure	2195	2080	2380	2405	2480	2525	2500	2480	2645	2670	3050	2740	2950
Average final pressure	725	660	570	645	610	570	510	605	555	565	610	565	575
Average pressure drop	195	220	420	385	405	415	460	380	460	440	360	430	395
% Hydrogen Absorbed	1.0	1.4	2.6	2.1	2.2	2.5	2.5	2.5	2.6	2.6	2.4	2.5	2.4
Gas yield, less H_2, in litres per kg. charge	37.5	40.4	116.2	45.2	65.0	71.5	79.5	82.5	66.0	92.5	137.0	78.3	87.0
% Charge to liquids	38.5	44.6	49.5	54.0	57.2	59.6	53.2	56.8	57.8	59.8	41.3	56.7	64.3
% Charge to solid residue	48.5	46.8	33.0	33.7	28.8	28.5	25.8	23.0	22.8	22.4	30.0	25.1	16.7
% charge to gas & charcoal	5.4	5.7	9.1	4.9	7.6	7.8	8.8	10.1	7.3	10.2	16.0	8.6	9.0
% charge as loss	7.6	2.9	8.4	7.4	6.4	4.1	12.2	10.1	12.1	7.6	12.7	9.6	10.0
Gas Analysis, %													
CO_2	0.2	0.3	6.3	0.3	0.4	0.6	2.7	4.3	3.6	4.8	7.6	6.5	9.0
C_nH_{2n}	0.3	0.3	0.2	0.4	0.3	0.5	0.5	0.5	0.1	0.2	nil	0.3	0.2
H_2	87.0	83.5	52.8	81.5	74.8	73.7	65.4	63.5	71.8	62.5	53.7	67.6	62.8
CO	0.4	0.2	2.9	0.4	1.4	1.3	1.0	1.6	1.2	3.0	2.7	2.3	2.0
C_2H_6	3.8	1.6	6.7	3.3	3.7	6.8	11.3	13.7	7.8	12.1	27.8	9.3	10.4
CH_4	2.4	8.7	15.7	7.3	12.0	11.9	10.0	13.2	14.4	18.8	11.5	10.8	13.5
% Coal converted (dry coal)	7.1	9.3	40.8	37.7	47.9	50.3	55.6	61.0	61.8	63.0	46.9	57.5	74.6
% Coal converted (dry ash-free basis)	8.0	10.1	45.6	43.6	54.2	57.7	62.6	66.9	68.1	69.9	51.4	63.4	81.6
% Charge to volatile products absorbed in charcoal	3.7	3.8	4.0	2.9	4.6	3.2	4.2	4.4	3.0	4.3	3.7	3.7	3.4
% Charge to oil. (1) Oil to 175°C.	6.6	7.8	12.8	9.1	8.2	11.7	9.9	13.0	9.4	12.6	11.8	9.4	10.7
(2) Oil to 225°C.	12.6	12.0	21.0	15.0	15.9	20.7	19.2	22.5	17.0	22.1	19.2	16.3	17.5
(3) Oil to 300°C.	20.2	20.1	32.7	25.4	26.7	34.0	29.3	33.0	28.7	32.5	26.9	29.3	30.5
(4) Pitch	18.3	23.9	15.4	28.6	28.1	23.4	20.0	20.0	25.2	22.4	9.1	23.8	24.6
(5) Water	0.0	0.0	1.4	0.0	1.9	2.2	3.9	3.5	3.6	4.6	5.0	3.3	7.1
(6) Loss	0.0	0.6	0.0	0.0	0.5	0.0	0.0	0.3	0.3	0.3	0.3	0.3	2.0

exception to this statement obtained in exp. 152 on coal C - 303 cannot be explained on the grounds of technique. The exit gas was unusually low in hydrogen. The excessive gas yields in exp. 164 on K - 310 and in exp. 166 on L - 311 may be attributed to a higher temperature of operation. The former experiment was out of control and the temperature rose to 440 °C for a short time. The latter, also out of control, rose to 470 °C and the temperature was over 430 °C for 45 minutes. The excessive coke yield and low conversion to liquids that occurred in this experiment may also be attributed to the high operating temperature. Hence the coal cannot be accurately judged from this experiment. More reliable data on the relative behaviour of these coals may be obtained from experiments 163 and 165 of the tetralin series. It is interesting to note the low gas formation in exp. 154 on D - 302 in spite of a maximum reaction temperature of 442 °C, the temperature remaining above 430 °C for one hour.

Table IV again shows the increased yields of low-boiling oils with decreasing maturity of the coal, characterized by high evaporative losses, that was found in the tetralin series. The same comparison to Table III may be successfully made with regard to relative yields of low-boiling oils, gas and water to

high-boiling oils or pitch.

It is to be noted that the formation of water in this series of experiments is not as great in general as was found in the tetralin series, while the carbon dioxide production compares favorably in amount with the data in Table III. A more complete discussion of the water and carbon dioxide yields in the two series will be given later.

Figures 7 and 8 represent the pressure-time relations of the first and second cycles of experiments conducted on the same four coals discussed in figures 3, 4, and 5 and 6 in the tetralin series. From an inspection of figures 7 and 8 it will be seen that again hydrogen absorption is greatest and most rapid with domestic coals. Sub-bituminous and bituminous coals exhibit appreciable absorption, though the reaction rate is lower than for domestic coals, while the slight effect of hydrogen on anthracite coal is again brought out.

Yields as high as 75% of a domestic coal to oil, gas and water under the conditions employed indicate that heavy petroleum oils such as liquid petrolatum may be suitable vehicles for suspending the coal. It is to be expected that conditions, varying for each coal, could be found such that higher conversions would

Pressure-Time Relations---First Cycle.

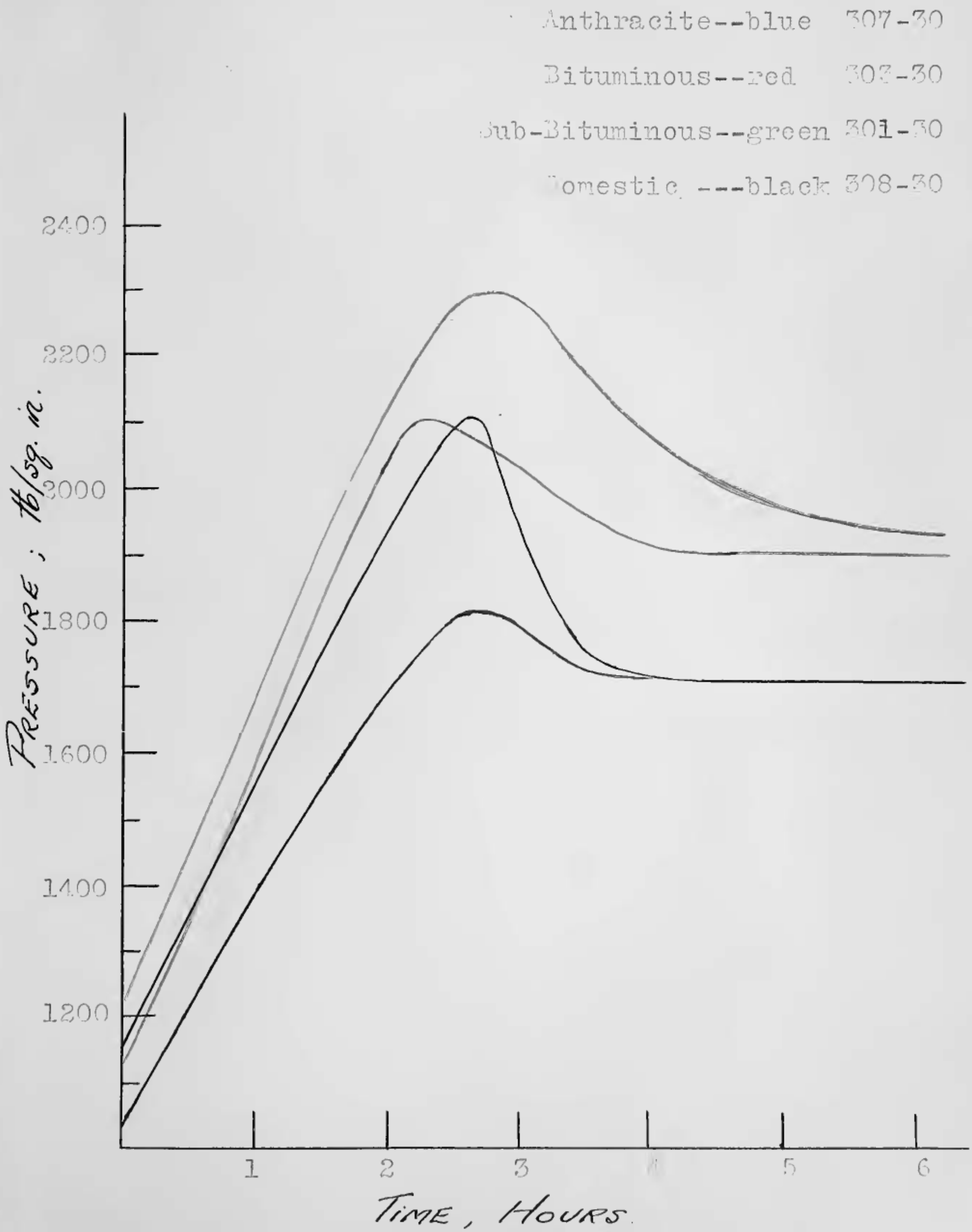


Fig 7.

Pressure-Time Relations---Second Cycle

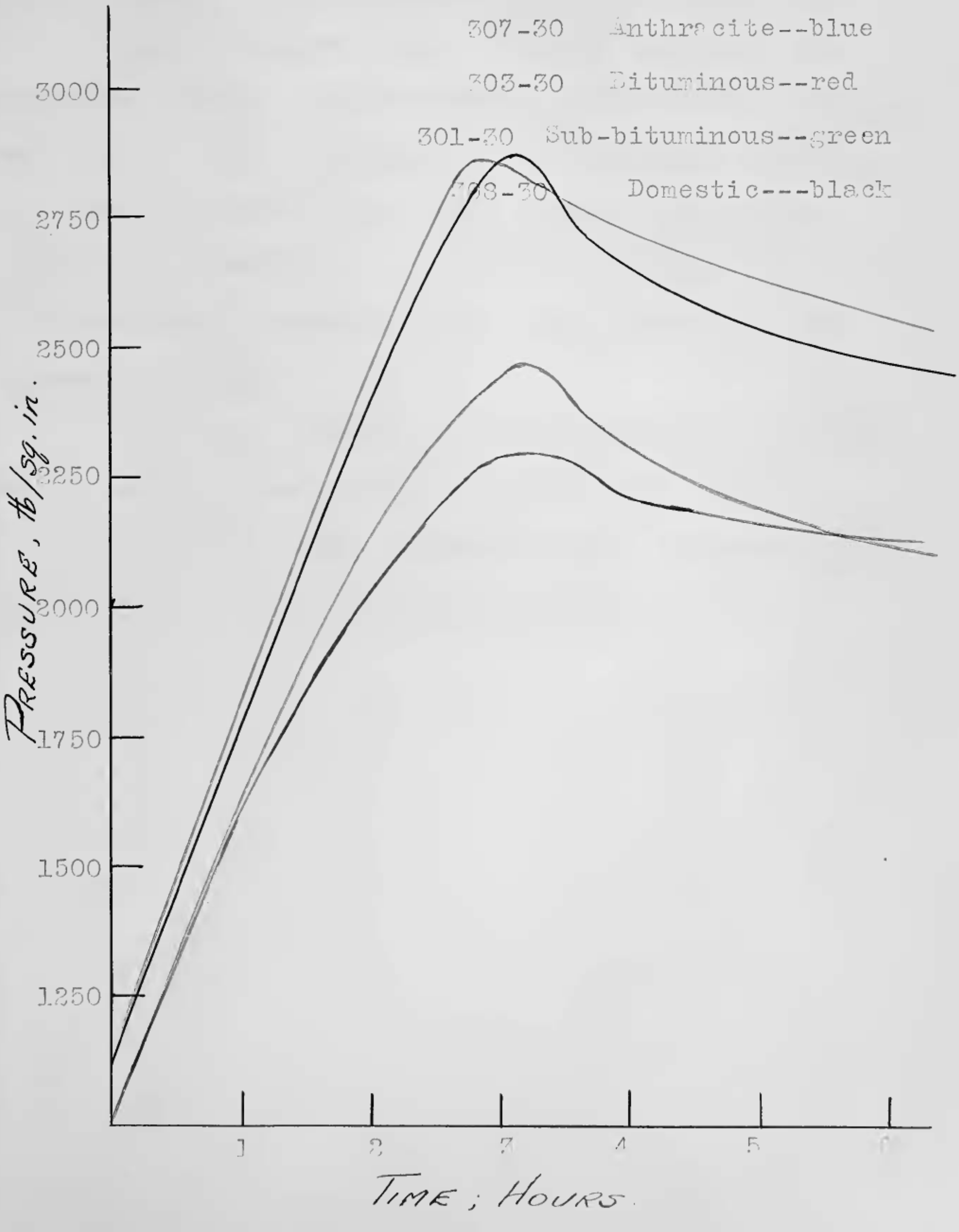


Fig. 3.

take place, but the procedure in this investigation was standardized so as to form a basis for comparison of the coals studied. This procedure was, of course, based on the preliminary experiments conducted by Boomer and Saddington (51). A preliminary treatment with water gas was shown in that investigation to materially decrease the oxygen content of the coal, saving materially on hydrogen consumption. Hence there is possibility of a technique being developed which could operate on a commercial scale.

It is not possible to determine what fractions of the coke and gas produced in this series are assignable to the coals themselves since decomposition of the liquid petrolatum occurs to some extent.

C. Comparison of Tetralin and Liquid Petrolatum as Suspending Agents.

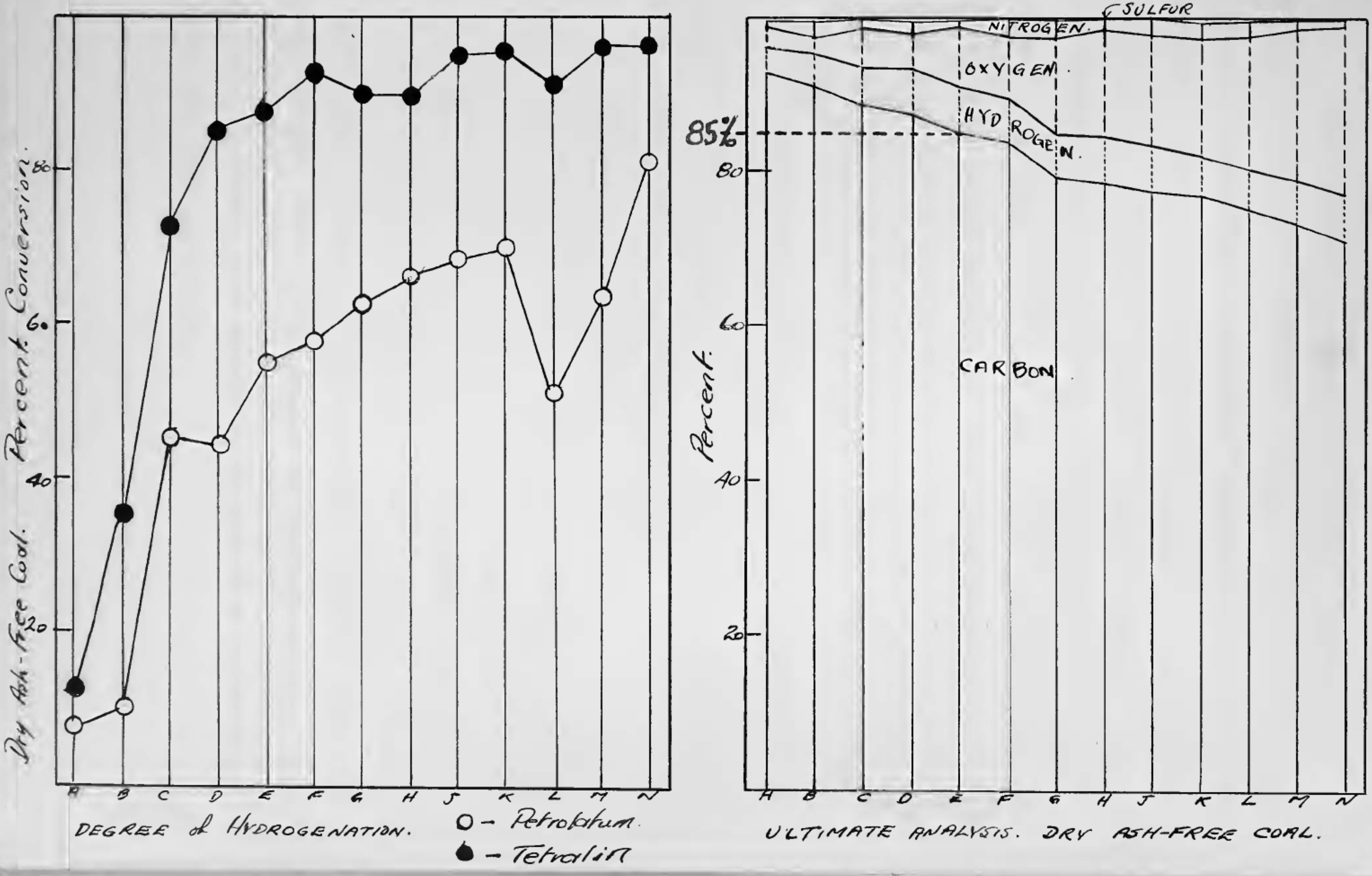
The definite superiority of tetralin as a suspending agent for coal is most readily shown by higher hydrogen absorption and lower coke formation than occurs in the petrolatum series. This superiority is attributed to the carrier action of tetralin and to its solvent power on coal.

Carbon dioxide production is much the same with both solvents, indicating no special tendency of tetralin to aid in the decomposition of carboxyl groups in the coal. Water formation is definitely greater in the tetralin series and indicates reduction of oxygenated compounds, probably those containing hydroxyl groups, which are not otherwise changed.

The formation of ammonia in certain experiments using tetralin indicates the reduction of nitrogenous materials, whereas the absence of ammonia as a product of reaction in any of the experiments of the liquid petrolatum series shows that a milder reduction has taken place. Ammonia formation in the tetralin series may, however, be attributed to the higher operating temperature employed. A clear comparison of the two media may be drawn from the following table:

TABLE V.

	Petrolatum			Tetralin		
Coal	Oil & Gas	Water	Total	Oils & Gas	Water	Total
Conversions on Basis of Dry Coal.						
A	7.1	0.0	7.1	10.8	0.0	10.8
B	9.3	0.0	9.3	32.3	0.0	32.3
C	38.0	2.8	40.8	64.1	0.5	64.6
D	37.7	0.0	37.7	73.4	0.1	73.5
E	44.1	3.8	47.9	74.7	2.3	77.0
F	45.9	4.4	50.3	79.0	1.0	80.0
G	47.8	7.8	55.6	69.7	10.8	80.5
H	53.9	7.1	61.0	72.6	8.7	81.3
J	54.5	7.3	61.8	79.0	7.4	86.4
K	53.8	9.2	63.0	72.9	13.4	86.3
L	36.9	10.0	46.9	67.8	15.2	83.0
M	50.9	6.6	57.5	77.7	10.0	87.7
N	60.3	14.3	74.6	72.9	15.1	88.0
Conversions on Basis of Dry, Ash-free Coal.						
A	8.0	0.0	8.0	12.2	0.0	12.2
B	10.1	0.0	10.1	34.9	0.0	34.9
C	42.5	3.1	45.6	71.7	0.6	72.3
D	43.6	0.0	43.6	84.9	0.1	85.0
E	49.9	4.3	54.2	84.1	2.9	87.0
F	52.7	5.0	57.7	90.9	1.1	92.0
G	53.8	8.8	62.6	78.6	12.1	90.7
H	59.1	7.8	66.9	79.7	9.6	89.3
J	60.1	8.0	68.1	86.9	8.2	95.1
K	59.9	10.0	69.9	80.5	15.2	95.7
L	40.4	11.0	51.4	74.5	16.7	91.2
M	56.1	7.3	63.4	85.7	11.0	96.7
N	66.0	15.6	81.6	79.9	16.3	96.2



DEGREE of HYDROGENATION.

ULTIMATE ANALYSIS. DRY ASH-FREE COAL.

Fig 9.

The columns in table V are self-explanatory and the figures serve to show the relative effect of the two media quite clearly. A rapid comparison may be made by consulting figure 9, in which the degree of hydrogenation is given on a thumb-nail chart. In this diagram, the percent conversion of coal in all cases represents total conversion to gas, oil, and water, and is calculated from the residual solid material. The large discrepancy on L in the petrolatum series has been mentioned earlier, and is due to the high temperatures at which hydrogenation took place.

For the sake of convenience the ultimate analyses of the dry ash-free coals has been recorded in figure 8 with the above-mentioned chart. It will be seen that in general hydrogenation is proportional to the oxygen content of the coal, and is inversely proportional to the carbon content. This fact was early recognized by Bergius (7), and in this connection Bergius postulated that coals containing higher than 85% were not amenable to hydrogenation. Thus, of this series, coals A - E inclusive would not be susceptible to hydrogenation. It is seen that at least with coals C, D, and E a large conversion has been obtained.

D. Conclusions.

Thirteen Alberta coals of graded rank have been hydrogenated in the presence of tetralin at 450 °C and in the presence of liquid petrolatum at 425 °C. The definite superiority of tetralin as a suspending agent has been shown, and it is believed that this superiority is due to the efficient manner in which tetralin acts as a hydrogen carrier and to its powerful solvent action on coal. Hence the use of tetralin or materials of similar chemical constitution is indicated in a commercial process as being promising, and it is possible that the greater cost of the medium would be more than made up by its increased efficiency over the ordinary heavy oils.

A definite progression from old to young coals has been shown by increasing yields of volatile oil, gas and water, with decreasing yields of pitch and coke.

Coal conversions as high as 94% with tetralin and 75% with liquid petrolatum have been reported.

E. The Fate of Oxygenated Compounds in the Hydrogenation of Coal.

Parr and Hadley (48) investigated the oxidation of coal and found that the combined oxygen was liberated as carbon dioxide upon thermal decomposition of the coal. It is reasonable to suppose, therefore, that carbon dioxide is a product, to some extent, of thermal decomposition, rather than of the specific action of hydrogen. This would account for the production of carbon dioxide in comparable amounts in the two series of experiments.

The formation of water is due in a large measure to hydrogenation of phenolic bodies in the coal (58). Examination of table V reveals that in general water is produced to a greater extent in the tetralin series. Two theories may be proposed to account for this.

(1). Increased water formation in the tetralin series may be attributed to the higher temperature of operation throughout, resulting in a decreased stability of the phenolic substances. This theory is substantiated by the excessive water yields reported in those experiments of the petrolatum series in which the temperature of the reaction chamber rose above 430 °C. For example, exp. 164 on coal K - 310 was out of control and the

temperature rose to 440 °C. The water yield in this case was 4.6%. In exp. 166 on L - 311 the temperature rose to 470 °C and the yield of water was 5.0%. Experiments on other domestic coals resulted in water yields averaging 3.5% (neglecting coal N - 312, of lignitic character). In these experiments the temperature did not rise above 430 °C

(2). The alternative theory may be stated with some evidence in its favor. It is the view that excessive water yields are produced by hydrogenation of phenolic bodies which would otherwise remain unattacked, the action being attributed to the efficient manner in which tetralin itself will act as a hydrogenating agent. In view of the fact that eight hours of operation at a temperature of 450 °C produced a water yield of 8.7% in exp. 165 on coal L - 311 of the tetralin series, a yield much higher than the excessive yield of 5.0% on the same coal with petrolatum, in which experiment the temperature rose to 470 °C, it may be reasonably concluded that the higher yield of water was due to either the specific action of tetralin or to the longer period of operation at the high temperature. It is probable that both of these proposed causes affect the water yields. Unfortunately, definite information requires experiments that have not

been made - i.e. equal temperatures of operation for the two media, and ultimate analyses.

The mechanism of reactions involving the production of carbon monoxide is more obscure and no justifiable conclusions may be drawn from the data presented. It may be remarked, however, that reduction of carboxyl groups by successive stages would produce aldehydes which, according to Hurd (35), decompose readily to give carbon monoxide and a hydrocarbon. Such a source is not improbable and will fit the observed facts.

PART II.

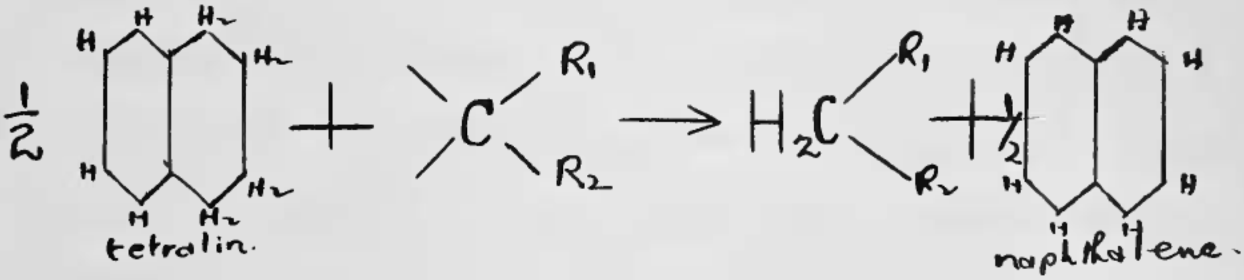
ON THE ACTION OF TETRAHYDRONAPHTHALENE AS A HYDROGENATING AGENT.

PART II

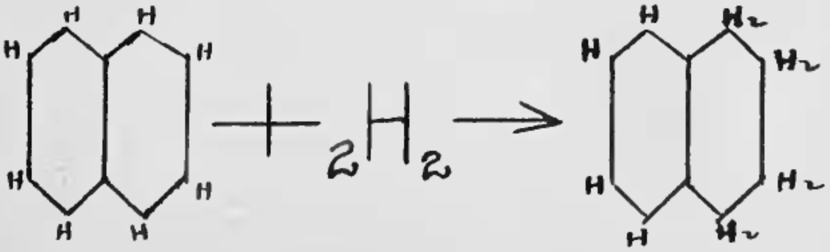
The Action of Tetralin as a Hydrogenating Catalyst

Introduction:

The action of tetralin as a suspending agent in the hydrogenation of coal has been discussed in Part I and the most striking results obtained in that investigation were in regard to the use of this substance. The superiority of tetralin to other media used and, it is believed, to other media reported elsewhere is due to the hydrogen carrier action of the tetralin, a property which it possesses to a remarkable degree. By hydrogen carrier action is meant the ability of a substance to undergo such changes as are represented in the following equations:



This reaction is followed by hydrogenation of the naphthalene to reform tetralin. i.e.



According to these equations tetralin acts as a hydrogenating catalyst according to the accepted intermediate com-

pound theory (71). The reaction is analogous to the formation of a hydride of nickel in the hydrogenation of organic compounds in the presence of an active form of this metal.

In order to study further the hydrogenating action of tetralin the behaviour of a number of carbonaceous materials in the presence of tetralin and under hydrogenating conditions has been investigated. The materials used were bitumen, pitch residues from the hydrogenation of bitumen and of coal, and two types of cellulosive materials, namely grain screenings and wood.

On account of the high content of polynuclear aromatic compounds similar in constitution and properties to naphthalene present in the aromatic tar obtained by the pyrolysis of hydrocarbon gases, the action of this tar as a hydrogenating agent has been also studied in a few experiments.

Literature Review:

The properties of tetralin as a hydrogenating catalyst have in only one instance been reported in the literature. Akabori and Suzuki (1) found tetralin to possess an efficient promotor action in the hydrogenation of cinnamic acid, linoleic acid, and other similar compounds, using palladium black as a catalyst.

A thorough investigation of the hydrogenation of naphthalene has been made by Hall (33). In this investigation it was shown that in the presence of molybdic oxide naphthalene may be hydrogenated at 450 °C, the reaction products containing 68% tetralin. At temperatures in excess of 460 °C however, marked decomposition occurs with the formation of gas, coke, and low-boiling oils. The earlier researches of Spilker (55, 56) and of Kling (37) were in agreement with the results obtained by Hall, though in general the lower temperatures used resulted in an appreciable reduction in the yield of hydronaphthalenes.

With regard to the hydrogenation of such materials as have been studied in this investigation, much has been reported from those countries lacking adequate deposits of carbonaceous materials suitable for motor fuels. The hydrogenation of bitumen, asphalt, and shale oil has been studied to a considerable extent and

a complete review of this field of investigation will be presented in Part III.

The hydrogenation of residual pitch obtained from the hydrogenation of coal has been exhaustively studied by the I. G. Farbenindustrie and by other concerns practicing the hydrogenation of coal and coal tars on a commercial scale. The literature is thus composed largely of patents so that little has been presented in the way of experimental data. It is apparent, however, from the specifications listed that arrangements in technique must be so made as to operate under more strenuous conditions of temperature and catalyst than are required for the hydrogenation of coal. The most reliable experimental data on the hydrogenation of stable tars from coal has been presented by King and Mathews (66) and by Morgan and Veryard (65). According to Morgan the hydrogenation of otherwise resistant residues may be brought about by the use of molybdic oxide and sulfur as catalytic agents in a very high concentration of hydrogen. The effectiveness of this catalyst was also demonstrated by King in an investigation of the continuous hydrogenation of coal tars and their residues from previous hydrogenation. The most effective means of obtaining rapid and complete decomposition was found to be vapor phase hydrogenation at temperatures as high as 500 °C.

The hydrogenation of cellulose has attracted the attention of many investigators. Bergius (6) decomposed cellulose thermally in a closed vessel under the pressure of the autogenous gases. The coal-like substance obtained was later hydrogenated to produce a small quantity of oil resembling a crude petroleum. Bowen (11) found that cellulose did not undergo any appreciable change under berginization conditions at 440 °C, but using nickel as a catalyst a 3 to 4% decrease in hydrogen pressure was recorded and water, tar, and a small amount of a light oil was obtained. The exit gas contained 85% hydrogen, the remainder consisting of approximately 8% carbon dioxide, 2% carbon monoxide, and 5% hydrocarbon gases, largely methane.

Frolich and Spalding (68) compared the decomposition of cellulose in the presence of a methanol catalyst in atmospheres of hydrogen and nitrogen. The similarity in the products obtained led these workers to the belief that the decomposition was thermal only.

Waterman (67), using cotton wool pellets, studied the decomposition of cellulose under pressure, with and without hydrogen, at a temperature of 450 °C. The reaction products were found to contain carbon monoxide, carbon dioxide, methane, water, and a solid residue. The hydrocarbon gas yield appeared to be

slightly increased by the addition of hydrogen, but no other difference was noted.

Fierz-David (20) has reported the hydrogenation of cellulose and wood in the presence of ferrous oxide, cupric oxide, and nickel oxide as catalysts. In the presence of cupric oxide a 38% conversion of cellulose to a sticky tar was obtained, while the use of nickel oxide resulted in the complete conversion of wood pulp to water and a clear mobile oil. Ferrous oxid appeared to exert no influence in the reaction.

In an attempt to increase the yield of methanol from wood distillation, Frolich and Spalding (68) conducted an investigation of the high pressure distillation of wood. In the presence of hydrogen at 10 atmospheres pressure and at temperatures from 280 to 370 °C, yields of methanol as high as 3.1% of the wood were obtained, an increase of 100% over the amounts obtained at atmospheric pressure. The presence of methano catalysts appeared to favor the formation of tar with a reduction in the yield of methanol.

An extensive research program on the hydrogenation of wood has been carried out by Lindblad (70). Operation at 250 °C with nickel or cobalt catalys resulted in the formation of a thick tar, while at higher temperatures gas formation became extensive. Wit

cobaltous sulfide impregnated on sawdust yields of oils amounting to 40% of the wood by operation at 350 °C were obtained. In these experiments sulfite liquor was used as the suspending agent for the wood. Yields as high as 56% of the carbonized charge to oils were obtained using ferrous hydroxide with ferrous sulfide as catalyst.

A preliminary investigation of the behaviour of wood and cellulose under hydrogenating conditions in the presence of tetralin has been made by Boomer and Argue (5). With regard to the hydrogenation of cellulose it was found that (1) the beneficial effect of tetralin was shown by more complete decomposition of the cellulose than was obtained in experiments in which tetralin was not used, and (2) the hydrogenating action of tetralin was demonstrated by the formation of naphthalene in those experiments conducted under high pressure of an inert gas. In these cases the decomposition of the cellulose was as complete as in experiments in which hydrogen was used.

Tetralin was shown to act as a very efficient catalyst in the hydrogenation of wood, promoting the formation of large amounts of carbon dioxide, carbon monoxide, methane, water, and oils. With hydrogen also present increased conversions to liquid and gaseous products were obtained. The nearly complete dissolution of wood occurring in these experiments was in sharp contrast

to the results of other investigators, and the highly efficient manner in which tetralin promoted gas and oil formation suggested the attempt to hydrogenate grain screenings.

Materials:

The bitumen used was obtained from Dr. K. A. Clark of the Research Council of Alberta, and was prepared by the hot water separation process from McMurray bituminous sands (13). The large amounts of water present in the crude bitumen tar made prolonged heating at 110 °C a necessary step in purification. The pitches used in this investigation were composite samples of distillation residues obtained from the ether-soluble oil from the hydrogenation of coal and bitumen. The history of each pitch used will be given later. The screenings were supplied by Dr. Robert Newton of the Department of Field Crops and were representative samples of elevator screenings, being largely weed seeds with some chaff. Their description and analysis will be discussed later. The samples of wood used were in all cases firwood sawdust.

Apparatus:

The apparatus and procedure employed was identical with that used in the investigation on coal. The second series of experiments on weed seeds was conducted in a small autoclave designed for continuous gas circulation. This apparatus has been described in connection with the experiments for which it was used.

Experimental Results and Discussion.

1. The Hydrogenation of Bitumen.

A determination of the effect of tetralin on the hydrogenation of bitumen at 400 °C was made using approximately 400 gram samples in the 1800 c.cm. oscillating autoclave described in Part I. The results of three experiments with bitumen have been presented in Table VI. In these experiments bitumen has been hydrogenated with and without tetralin, and one experiment on bitumen with tetralin in the absence of hydrogen has been recorded to offer data regarding the extent to which tetralin may be expected to act as a hydrogenating agent for bitumen.

In Table VI the titles on the left margin have the same significance as in the similar tables drawn up in connection with the experiments on coal in Part I. The conversions to gas, oils, and solid residue have again been calculated on the basis of the total charge, so that the reported solid residue includes the recovered catalyst. Insofar as hydrogen absorption is concerned, the figure in experiment 179 is given by calculation on the basis of total bitumen charged, it being assumed that tetralin does not absorb hydrogen under the operating conditions employed.

An analysis of the results of experiments 178

5% MoO_3
2 cycles
4 hrs each

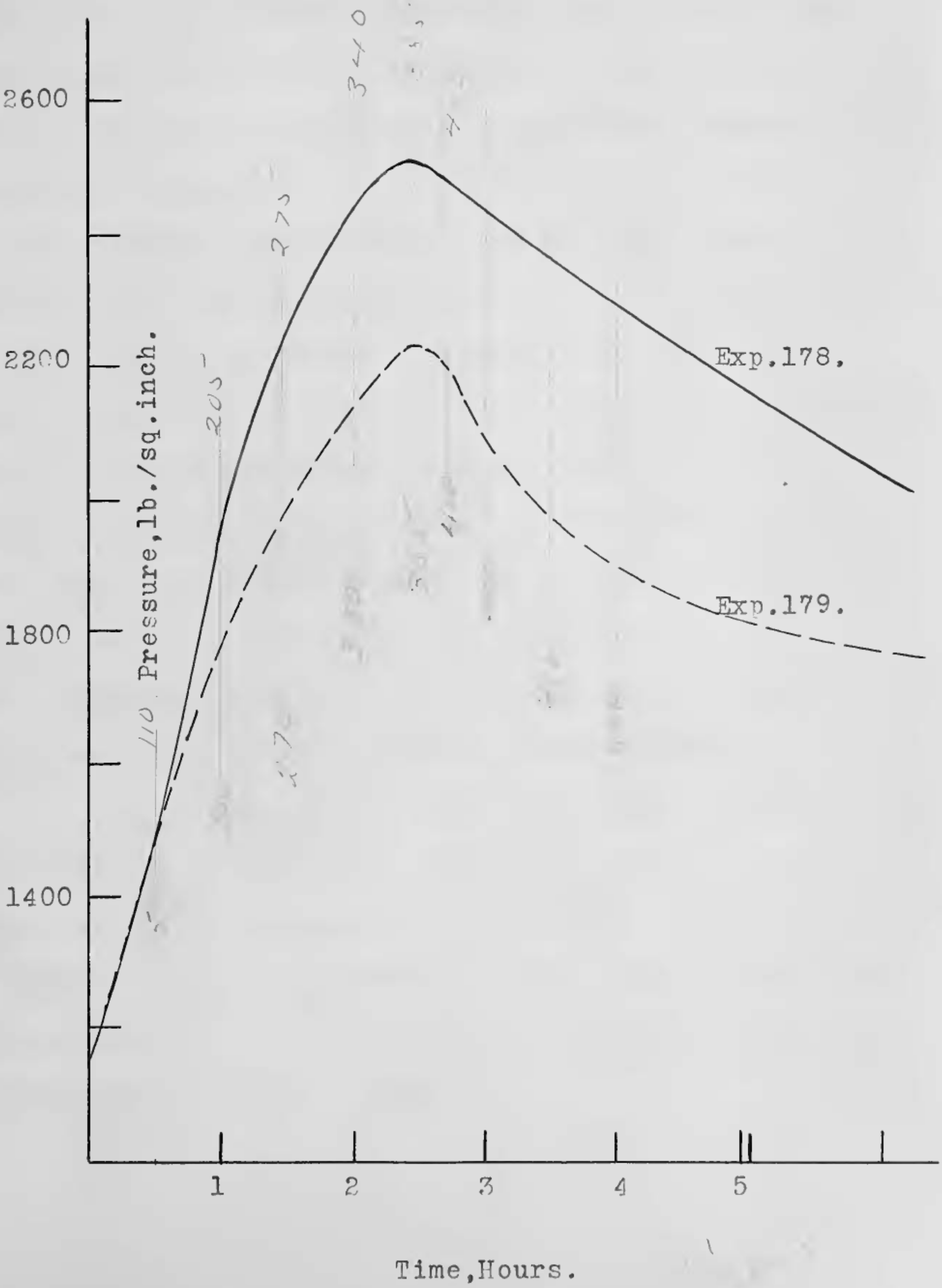
TABLE VI

Material	Bitumen		
Experiment Number	178	179	180
Tetralin, grams	0.0	110	104
Material, grams	391	294	302
Temperature, °C.	400	400	400
Average pressure, lb/sq.in.			(CH_4)
Initial, cold	1115	1060	1035
Maximum, hot	2575	2450	3510
Final, cold	770	795	1105
Hydrogen absorbed, % by wt.	2.0	2.3	
Gas produced, L/kg. charge	54.8	56.9	131.0
Hydrogen in gas, %	81.6	80.2	3.4
Yields, based on init. charge:			
Charcoal absorber	2.0	1.9	4.5
Oil, %	80.7	80.0	33.7
Solid residue, %	10.6	9.4	20.5
Gas, %	4.0	3.3	14.5
Naphthalene, %	0	0	16.8
Loss, %	4.7	7.3	14.5
Conversion of charge to fractions, based on oil distillation yields			
over at 175°C., %	8.5	7.6	3.2
" " 225°C., %	13.3	33.0	5.3
" " 300°C., %	26.6	41.6	12.4
Pitch, %	54.1	38.4	21.3
Loss, %	0.0	0.0	0.0

and 179 in Table VI shows that tetralin was of little benefit as regards yields of oils, but a slight decrease in coke and gas formation was evident. That a more extensive decomposition of bitumen occurred in experiment 179 with tetralin is shown by higher absorption of hydrogen and more complete removal of sulfur as hydrogen sulfide. The low conradson carbon value for the oil from experiment 179 may be in part due to the low viscosity of the oil, with consequent ease of settling of suspended matter rather than to a lower conversion to finely divided carbon.

Whereas it has just been demonstrated that the conversion to liquids, etc. was not materially affected by the addition of tetralin, there was, nevertheless, a large increase in the rate of reaction using this agent. Figure 10 presents the pressure-time record of the first cycle of experiments 178 and 179. Inspection of figure 10 reveals that the rate of reaction at constant temperature, and sometime after hydrogenation has commenced, showed by the downward slope of the curve, was approximately doubled in the case where tetralin was used. It will be noted that the total decrease in pressure was much the same in each case, showing, roughly, that the extent of reaction in the two experiments was comparable.

Figure 10.


2600
2200
1800
1400
Pressure,lb./sq.inch.
1
2
3
4
5
Time,Hours.
Exp.178.
Exp.179.
340
270
205
110

With regard to experiment 180, in which tetralin was used as a hydrogenating agent in the absence of hydrogen 173 litres of methane was charged to the autoclave and approximately 180 litres recovered. Approximately 2% of the oil recovered was tetralin, and 5% was naphthalene. The tabled recovery of naphthalene, entered as % of initial charge, was obtained from the solid material extracted from the autoclave as crystalline naphthalene. Roughly 70% of the tetralin charged was converted to naphthalene, and on this basis the absorption of hydrogen by the bitumen was between 0.7 and 0.8%. The result clearly demonstrates the powerful hydrogenating action of tetralin. The high yields of gas and solid residue reported for this experiment may be attributed to an insufficient concentration of tetralin to give complete hydrogenation, so that cracking became extensive.

In conclusion it may be said that tetralin possesses to a remarkable degree the ability to act as a catalyst in the hydrogenation of bitumen. The presence of tetralin under hydrogenating conditions is beneficial from the point of view of rate of reaction rather than of conversion to volatile oils.

2. The Hydrogenation of Pitch Residues.

The hydrogenation of pitch residues obtained from the A.S.T.M. distillation to 300 °C of the oily reaction products from the hydrogenation of bitumen was carried out at 420 °C and the effect of the addition of tetralin determined by comparative experiment. In the presence of metallic catalysts only, Boomer and Saddington (10) showed that the residues were remarkably stable and resistant to hydrogenation, but operation at a high temperature (460-500 °C) in the presence of a cracking catalyst such as aluminium chloride resulted in a high conversion of the pitch. In the light of the probable reactions involved in hydrogenation by tetralin it would appear improbable that the decomposition or cracking temperature would be appreciably lowered by the presence of tetralin, but an increase in the rate of hydrogenation with a subsequent decrease in coke and gas formation would be a likely consequence of the use of this substance. From the point of view of continuous operation the reduction of these pitch residues is of extreme importance and any method by which the rate of reaction may be increased is worthy of investigation.

The results of two experiments with the above mentioned pitches have been shown in Table VII. In experiment 176 the hydrogenation of the pitch was undertaken

TABLE VII

Material	Residue Oil	
Experiment Number	176	177
Tetralin, grams	0.0	98
Material, grams	399	293
Temperature, °C.	420	420
Average pressure, lb/sq.in.		
Initial, cold	1100	1060
Maximum, hot	2360	2500
Final, cold	640	750
Hydrogen absorbed, % by wt.	2.4	2.3
Gas produced, L/kg.charge	72.0	43.7
Hydrogen in gas, %	71.7	82.3
Yields, based on init. charge:		
Charcoal absorber	2.6	1.7
Oil, %	80.3	91.4
Solid residue, %	10.3	7.3
Gas, %	6.5	4.5
Naphthalene, %	0 9	0
Loss, %	~~2.9~~ .3	3.2
Conversion of charge to fractions, based on oil distillation yields		
over at 175°C., %	2.5	2.1
" " 225°C., %	5.3	20.4
" " 300°C., %	13.8	33.5
Pitch, %	64.7	57.8
Loss, %	1.8	0.0

without tetralin, and in experiment 177 the pitch was mixed with approximately 1/3 of its weight of tetralin before treatment with hydrogen. An inspection of Table VII reveals that the only noticeable effect of tetralin has been to reduce the coke and gas yields. The pressure-time and pressure-temperature charts for these experiments failed to show any difference in the rate of reaction.

No appreciable benefits are to be expected from the use of tetralin with these substances under the conditions employed. Further experiments with tetralin under more strenuous temperature conditions and with an active destructive catalyst such as aluminium chloride, which has been shown (10) to decompose these pitches are indicated.

The hydrogenation of pitches from coal hydrogenation was conducted in a similar manner to that described above. Two samples of pitch were used:

(1) Composite pitches from the hydrogenation of coal with tetralin as a hydrogenating and suspending agent. These pitches were remarkably stable, and at room temperature were solid.

(2) Composite pitches from the hydrogenation of coal in the presence of liquid petrolatum. These pitches were less stable than the tetralin samples, and at room temperature were quite soft.

A more complete description of the samples used has been given in Part I.

TABLE VIII

Experiment No.		From Petrolatum 172	175	From Tetralin 173	174
Wt. of pitch in grams		390	356	268	387
Wt. of medium in grams (Tetralin)		-	42	129	-
Catalyst, MoO_3		5	5	5	5
Number of cycles		2	2	2	2
Time per cycle in hours		4	4	4	4
Temperature, average °C.		450	450	450	450
Pressure, average init., lb/sq.in.		930	1135	1035	1065
" " max. "		2245	2740	2360	2495
" " final "		670	820	610	555
" " drop "		260	315	425	510
H_2 absorbed	%	1,6	2,3	3,4	2.8
Gas yield, less H_2, in l./kg. charge		46.3	80.8	100.5	86.3
Yields based on init. charge					
Charcoal absorber		1.2	3.3	2.9	2.0
Oil recovered	%	85,2	84.3	76.8	64.0
Solid residue recovered	%	3,9	5.5	8.2	18.0
Gas	%	3.1	8.2	7.3	8.9
Loss	%	~~7.7~~ 6.6	1.4	7.7	9.1
Gas Analysis:					
CO_2	%	0.3	0.1	0.0	0.2
C_nH_{2n}	%	0.1	0.0	0.0	0.1
H_2	%	83.0	72.8	71.8	62.2
CO	%	1.2	0.8	1.1	0.6
C_2H_6	%	2.1	11.5	12.6	21.6
CH_4	%	7.7	8.1	9.7	15.2
Pitch converted (based on pich fraction found by distillation)	%	32.0	52.4	40.7	51.6
Distillation yields, based on initial charge (Water)		0.2	0.0	0.0	0.0
Oil over at 175°C.	%	3.8	11.4	5.1	1.0
" " " 225°C.	%	6.8	23.8	23.6	5.5
" " " 300°C.	%	18.0	42.1	33.2	14.4
Residue (pitch)	%	67.2	41.8	40.6	49.1
Loss	%	0.0	0.4	3.0	0.5

The results of this series of experiments have been presented in the usual manner in Table VIII. In experiments 172 and 175 the pitch from the petrolatum series (Part I) was hydrogenated with and without tetralin at 450 °C. From an examination of Table VIII it is apparent that a more drastic action occurred in exp. 175 with tetralin than in exp. 172 in which no tetralin was used. This is borne out by conversions of 52.4% of pitch to oil, gas and water as against a 32% conversion, and also by the higher hydrogen absorption of 2.3% as compared with 1.6%. It will be noted that the increased formation of gas and solid residue with tetralin present is extremely unusual.

With regard to experiments 173 and 174, in which hydrogenation of the pitch from the tetralin series (Part I) was undertaken, the results obtained offer better evidence of the beneficial effect of tetralin. From an examination of Table VIII it is evident that the presence of tetralin has materially decreased coke formation (exp. 173). The higher absorption of hydrogen that occurred in this experiment indicates a more complete reaction in the presence of tetralin.

Inspection of the pressure-time and pressure-temperature curves for this series of experiments failed to reveal any increased rate of reaction using tetralin.

The results indicate that the pitches under dis-

cussion are extremely stable and resistant to hydrogenation, but their decomposition is materially increased by the addition of tetralin, as shown by higher absorption of hydrogen and decreased coke formation.

3. Hydrogenation with Aromatic Tar.

On account of the similarity in constitution between naphthalene and many constituents of the aromatic tar from the pyrolysis of natural gas, the effect of this material as a suspending agent for coal has been studied in the following series of experiments.

The tar used was a product of the pyrolysis plant at Calgary, in which a separate investigation on natural gas was in progress. Distillation analysis of the tar has been given in Table IX.

TABLE IX

I.B.P. - 90 $^{\circ}$C
10% - 208 $^{\circ}$
20% - 225
30% - 244
40% - 269 $^{\circ}$
50% - 309
60% - 325
70% - 386
73.5% - 390 $^{\circ}$C.
Barometric pressure
67 cm. Hg.

Constant boiling fractions: 20% at 225 $^{\circ}$C - naphthalene
5% at 290 $^{\circ}$C
10% at 345 $^{\circ}$C.

The material was largely composed of polynuclear aromatic compounds, and contained a few percent of free carbon in suspension.

The preliminary experiments of this series were conducted using the tar as received as the suspending agent, but the abnormal hydrogen absorptions encountered indicated that this material was extremely unsaturated, and partial hydrogenation of the tar itself resulted in the formation of a material more suitable for suspending

TABLE X

Charge	Pyrolysis tar	Bituminous coal No. 305-30 (1)	(2)	(3)	Domestic coal No. 309-30 (1)	(2)	(3)
Experiment No.	186	155	183	189	161	188	187
Medium, grams	505	150	204	190	150	182	199
Coal, grams		200	191	195	200	182	199
Temperature, °C	425	450	450	450	450	450	450
Average Pressures lb./sq.in.							
Init., cold	1120	1000	1090	1120	1045	1115	1130
Maximum, hot	2425	2570	2720	2740	2950	3080	3340
Final, cold	480	510	435	505	585	500	500
Hydrogen absorbed, % by weight	2.1	3.0	3.7	3.4	3.1	3.8	3.4
Gas produced, L/Kg.charge	44.6	76	107	104	85	93	112
Hydrogen in gas, %	70.0	72	44.3	54.3	71.5	53.9	48.2
Yields based on initial charge:							
Charcoal absorber	0.8	3.7	2.9	2.5	3.8	2.6	2.9
Oil, %	81.6	67.7	55.4	70.2	65.4	64.9	62.7
Solid residue, %	13.6	16.9	27.5	15.5	11.5	18.5	16.5
Gas, %	3.1	7.8	9.3	9.8	12.3	9.5	11.4
Loss, %	~~1.7~~ 99.1 .9	~~7.6~~ 96.1 3.9	~~7.8~~ 95.1 4.9	~~4.5~~ 98.0 2.0	~~10.8~~ 93.0 7.0	~~7.1~~ 95.5 4.5	~~9.4~~ 93.5 6.5
Conversion of dry coal to oil and gas		77.0	50.8	77.8	86.4	71.8	75.2
Conversion of charge to fractions based on distillation yields							
Oil over at 175°C. %	1.6	3.6	2.5	5.9	6.7	6.2	7.0
" " " 225°C. %	22.3	37.6	16.2	23.1	39.1	20.9	21.0
" " " 300°C. %	41.2	45.4	27.6	34.4	46.6	32.0	33.2
Pitch, %	39.5	20.7	27.2	34.0	14.6	29.2	23.7
Water, %	0.0	1.3	0.6	1.8	4.2	3.7	5.2
Loss, %	0.9	0.3	0.0	0.0	0.0	0.0	0.6

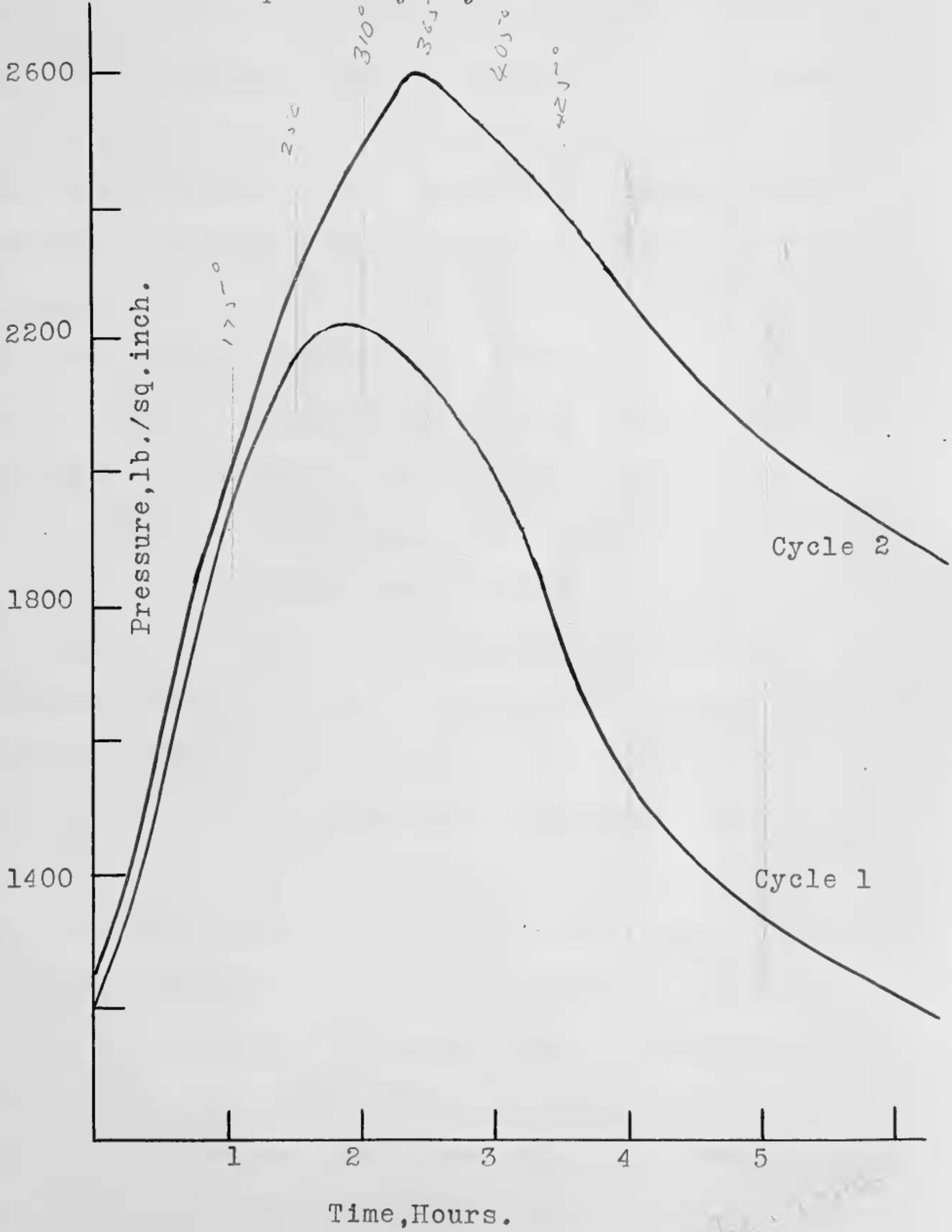
coal. Hydrogenation resulted in the formation of tetralin and other polynuclear naphthenes similarly constituted. These compounds would be expected to exert a definite catalytic action in hydrogenation.

The results of experiments using the tar and the hydrogenated tar as media for coal hydrogenation have been presented in Table X. Two coals were used, E - 305 classified as a bituminous coal in Table I and J - 309, a domestic coal. For the purpose of comparison the results of experiments 155 and 161 of the tetralin series (Table III) on these coals have been recopied. The hydrogen absorption in each case was recalculated to conform with the method adopted for the pyrolysis tar, i.e. absorption by the total carbonaceous charge.

Experiment 186, in which the tar itself was hydrogenated with 5% molybdic oxide at 425 °C has been included in Table X. The hydrogen absorbed is fairly large, being 2.1% by weight of the tar. The high yield of solid material in this experiment is deceptive as it includes 5% of the charge as catalyst, together with at least 5% of free suspended carbon present in the original tar. Hence the coke formed during hydrogenation was extremely small. The ether-soluble oil obtained from this experiment was used as the suspending agent in experiments 187 and 189.

Figure 11.

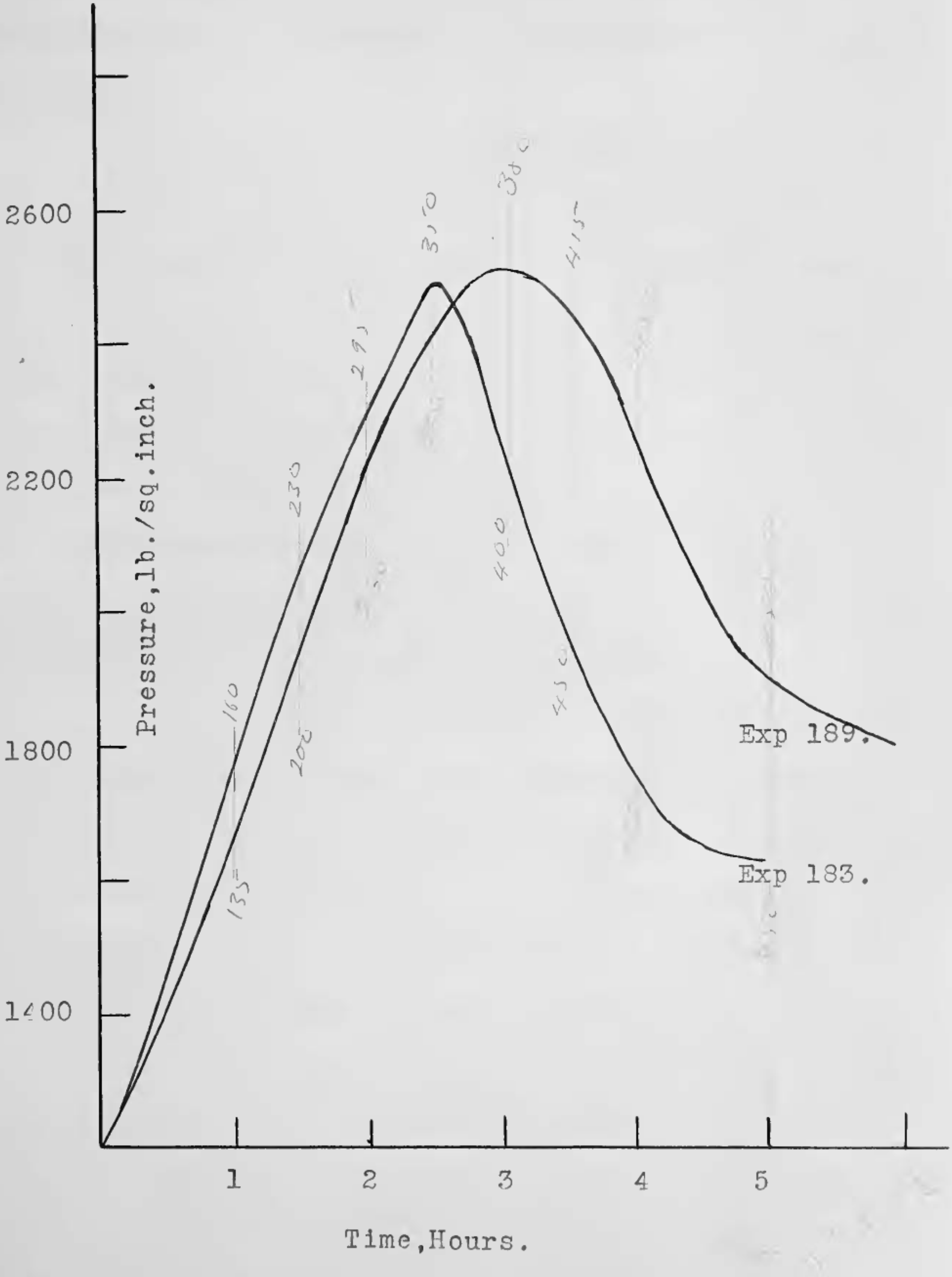
Exp.186--Pyrolysis Tar.



That enormous hydrogen absorption with low gas formation occurred in the hydrogenation of the tar is shown in figure 11, in which the pressure-time curves of the two cycles of experiment 186 are illustrated. The continuous downward slope of the curve in the second cycle indicates that hydrogenation of the tar was incomplete. The oil recovered in this experiment contained 14% of tetralin, as compared with 20% of naphthalene in the original tar, so that on this basis 70% of the naphthalene was hydrogenated to tetralin. This fact is of interest in that the above figure agrees closely with the 68% conversion to tetralin obtained by Hall (33) in the hydrogenation of naphthalene with molybdic oxide at 450 °C.

In experiment 183 the untreated tar was used as the suspending agent in the hydrogenation of the bituminous coal E - 305. In experiment 189 the same coal was hydrogenated using the partially hydrogenated tar as the medium for coal suspension. From the data in Table X it will be seen that the hydrogenation of bituminous coal has been accomplished with a fair degree of success using the pyrolysis tar, a 50% conversion of the dried coal being obtained, as compared with a 48% conversion using liquid petrolatum (Table V, exp. 156). The conversion obtained was much lower than with tetralin, due probably to the inability of the coal to successfully com-

Figure 12.


2600
2200
1800
1400
Pressure,lb./sq.inch.
1
2
3
4
5
Time,Hours.
Exp 189.
Exp 183.
160
135
230
200
295
310
380
415
400
450

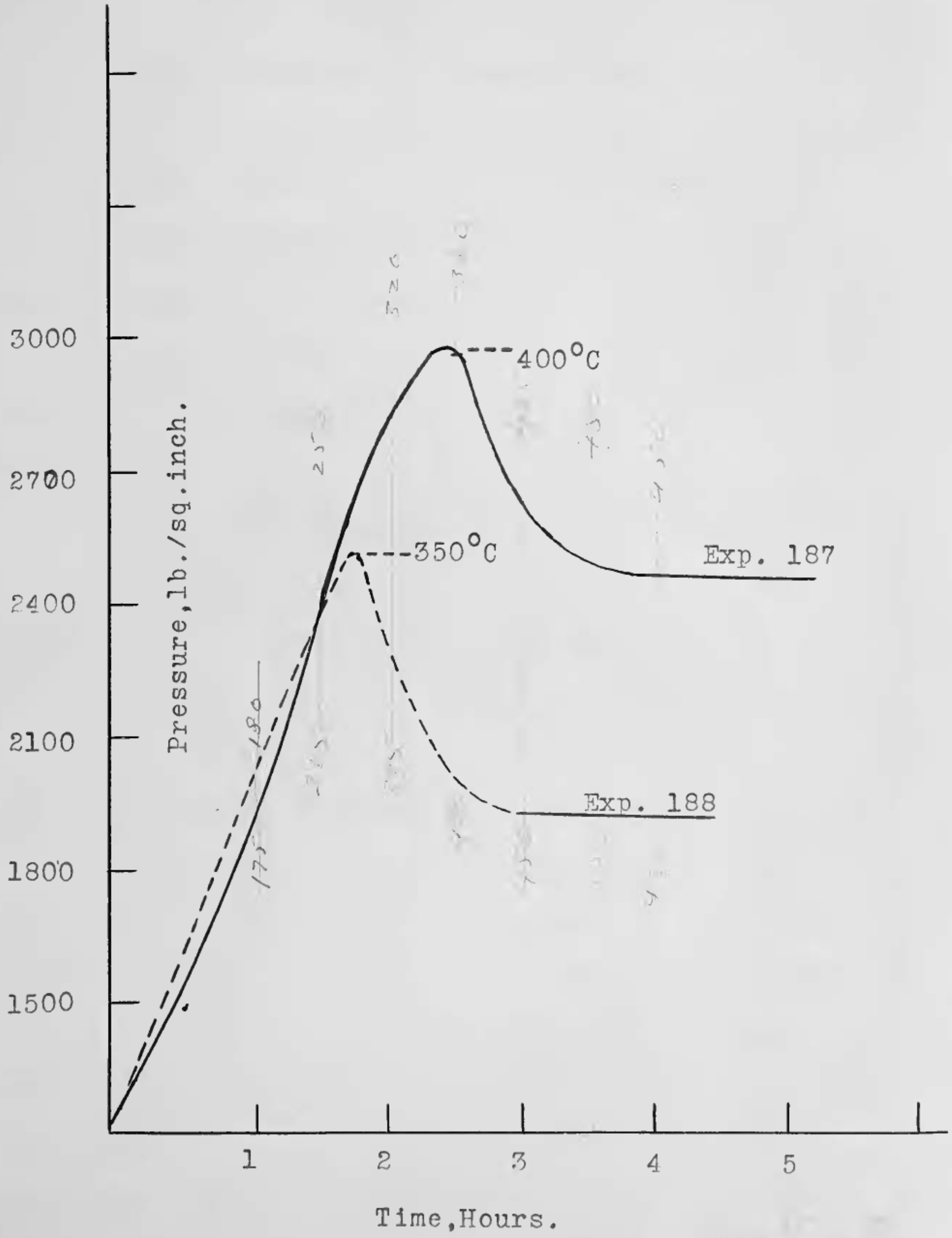
pete with the tar for the hydrogen available. In contrast to this result the remarkably high conversion of the coal obtained with the hydrogenated tar indicates that this material acts as a hydrogen carrier quite as efficiently as tetralin.

In figure 12 the pressure-time curves of the first cycles of experiments 183 and 189 are illustrated. It will be noted that the extremely unsaturated nature of the untreated tar is reflected in an exceptionally low maximum pressure attained in experiment 183, and in a fast absorption of hydrogen at a temperature of 350 °C, the pressure decreasing with increasing temperature from this temperature onward. The more normal absorption in experiment 189 indicates a lesser tendency on the part of the hydrogenated tar to take up hydrogen.

The behaviour of a domestic coal under similar conditions (exp. 187 and 188) indicates again that the pyrolysis tar is a satisfactory medium for the hydrogenation of coal, a conversion of the dry coal amounting to 71.8% being obtained as compared with a 61.8% conversion using liquid petrolatum (Table V, exp. 162).

The definite superiority of tetralin to the tar is again illustrated by higher conversion of the coal, while the beneficial effect of hydrogenated tar as a suspending agent is brought out by the high yields of gas,

Figure 13.


3000
2700
2400
2100
1800
1500
Pressure, lb./sq.inch.
400°C
350°C
Exp. 187
Exp. 188
1
2
3
4
5
Time, Hours.

oil, and water obtained. A definite lower conversion has been obtained than with tetralin, however, and this may be due, in part at least, to the incomplete reduction of the tar previous to use as a suspending agent.

Figure 13 shows the pressure-time record of the first cycles of experiments 187 and 188. An inspection of this chart again shows the extreme rapidity with which hydrogen is absorbed in exp. 188, in which the unhydrogenated tar was used. A more normal curve resulted using the hydrogenated tar, indicating a slower absorption of hydrogen.

Conclusions:

The effect of pyrolysis tar as a hydrogenating agent for coal has been studied and comparisons with tetralin made. The pyrolysis tar shows a great affinity for hydrogen and for this reason the hydrogenation of coal is partially depressed. The hydrogenated tar acts as an efficient suspending agent for coal, as shown by high conversions of coal to gas, oil, and water. The beneficial action of this tar is attributed to its similarity in constitution to tetralin, the polynuclear compounds present acting as hydrogen carriers for the coal. The results are of some practical value in connection with the whole problem of utilization of natural gas in that a successful pyrolysis process would result in a supply of

tar of low cost and excellent properties for the hydrogenation of coal.

4. Hydrogenation of Grain Screenings.

The investigation on the hydrogenating action of tetralin was extended to a study of its ability to assist in the reduction of cellulosic materials of which the first example is grain screenings. Many suggestions have been offered for the economic disposal of the tremendous quantities of screenings which result each year from the cleaning of grain in the elevators at Fort William and Port Arthur, so that a twofold purpose was served by the following study.

The samples were obtained from Dr. Robert Newton of the department of Field Crops. A description of their moisture content and appearance has been given in Table XI.

TABLE XI

Exp. No.	Sample No.	Description	Dry matter as % of wet weight
194	1	Black seeds, Lambs quarter, etc.	90.8
193	2	Very fine material. Refuse screenings, seed coats and chaff	91.4
192	3	Ragweed screenings, seeds largely	91.5
191	4	Slightly coarser than number 2. Refuse screenings	91.3
190	5	Mixture of 1,2,3 and 4	91.4
195		Equal parts of hydrogenated No. 4 and No. 3	

TABLE XII. HYDROGENATION OF SCREENINGS IN THE PRESENCE OF TETRALIN.

	1	4	5	3	2	6
Experiment Number	190	191	192	193	194a	195
Sample Number	5	4	3	2	1	4 3
Weight of seed in grams	367	295	311	267	345	245
Previous treatment of seed	none	none	dried @110°C	dried @110°C	Dried @110°C	Hydrogenated
Weight of Tetralin in grams	236	211	244	200	210	196
Time in hours	2	2	2	2	3	1.5
Temperature, °C.	350	300	325	325	250-350	350
Initial pressure, lb/sq.in.	1110	990	1115	935	990	1095
Maximum pressure	4920	2560	4040	3420	3290	2390
Final pressure, cold	1235	755	1205	1035	1085	785
% charge to liquids	58.3	54.3	48.6	54.2	51.1	53.5
% charge to solids	24.0	36.2	38.9	32.0	32.0	40.8
% charge to gases	4.2	2.7	2.8	2.7	2.6	0.4
% charge as loss	13.5	6.8	9.7	11.1	14.3	5.3
% seeds to liquids (1)	33.6	26.5	36.1	35.1	38.4	22.1
% seeds to liquids (2)	53.6	33.4	25.5	39.3	44.3	25.9
Gas Analysis, % CO_2	26.2	27.6	20.2	21.7	15.7	4.6
C_nH_{2n}	0.0	0.2	0.0	0.0	0.0	0.0
H_2	60.5	64.3	73.9	72.0	79.3	91.2
CO	1.0	1.0	0.5	1.2	0.5	0.5
C_2H_6	1.3	0.9	0.0	0.0	0.0	0.0
CH_4	10.5	4.8	5.2	5.3	3.3	3.6
Structure of seeds in solid residue.	destroyed	well preserved	part destroyed	part destroyed	destroyed	destroyed
Distillation of oil, I.B.Pt.	80°C.	80°C.	76°C.	80°C.	78°C.	79°C.
% Water	9.6	3.9	9.9	9.0	13.7	0.9
% oil to 175°C.	1.9	0.4	4.0	0.9	2.1	1.7
% oil (less tetralin) to 225°C.	5.3	5.7	10.3	6.3	6.6	4.7
% oil (less tetralin) to 300°C.	8.9	10.5	13.9	12.4	13.3	11.1
% pitch	18.1	12.7	21.1	14.9	19.9	12.0
% loss	0.7	1.3	0.0	0.4	0.0	0.0
Fractionation on 14" column (200-206°C.) tetralin recovered, entered as % of tetralin charged.	97.0	97.5	64.3	80.2	71.3	98.3

(a) Experiment in two cycles, the first at 250°C., the second at 350°C., both of 1.5 hrs. duration.

The apparatus and procedure was identical with that previously described. The results obtained using the 1800 c.cm. oscillating autoclave have been given in Table XII. With regard to the data presented in this Table, two values have been given for the % conversion of seeds to liquids.

(1) was calculated on the basis of recovered liquid and tetralin as tabled and is subject to errors due to mechanical and evaporative losses.

(2) was calculated from the mass of solid residue and the mass of gas formed and may be the more precise value.

The oil distillation analysis has been entered as % of the total oil used for distillation and bears no direct relation to the yield of liquid products extracted from the autoclave. The tetralin recovered, entered as % of tetralin charged, was calculated from the distillation fraction between 200 and 206 °C and from the total material extracted from the autoclave less the solid residue. An attempt has been made to record the extent to which destruction of the original physical characteristics of the seeds took place since this probably indicates roughly the extent to which reaction occurred.

Inspection of Table XII shows that the structure of the seeds was completely destroyed at 350 °C. With

operation at 300 °C the seeds remained well preserved, while at 325 °C partial decomposition occurred. In this regard the small black seeds appeared more resistant to hydrogenation than did the other types of seeds and screenings.

The formation of gases was extremely low in all cases. In this connection the relatively high conversion to gas may be attributed to the high operating temperature used. That high gas yields were not encountered in the second cycle of exp. 194 is probably due to the high partial pressure of hydrogen present by reason of the earlier removal of carbon dioxide. The low gas formation in exp. 195 may be due to the small amount of reaction which occurred on account of previous hydrogenation of the screenings. This was borne out by the high concentration of hydrogen in the exit gas.

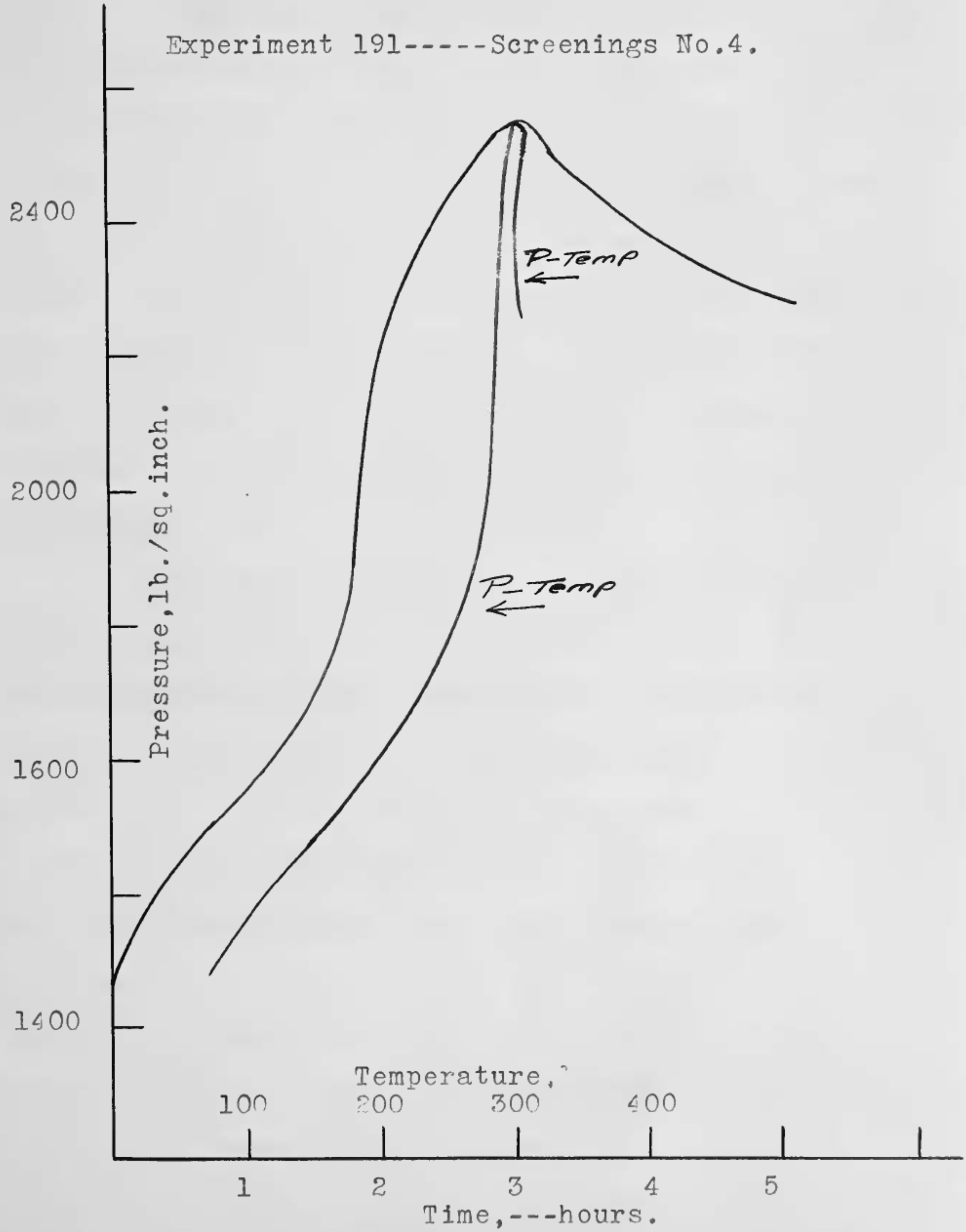
The formation of water was extensive in nearly all of the experiments. In this regard the relatively low yield reported in exp. 191 may be attributed to the low temperature of operation, and the low yield in 195 is undoubtedly due to previous hydrogenation of the seeds, during which treatment the elimination of water was normal. The water was acidic in every case.

The light oils obtained upon distillation of the liquid reaction products possessed a faint yellow color

which darkened on standing. The extremely sour odor common to all the distillates was readily removed by washing with 65% sulfuric acid. The pitches obtained by distillation were similar in all cases in that they possessed a high melting point, being extremely hard and brittle at room temperature. The stability of the pitches was not great, cracking occurring below 300 °C. In those experiments in which the structure of the screenings was not completely destroyed, the hydrogenated seeds were carefully removed from adhering carbon and thoroughly washed with ether. The dried seeds were then heated at atmospheric pressure. In all cases a heavy yellowish oil with a pungent odor distilled out of the seeds. On account of this fact a second treatment with hydrogen was given the seeds at 350 °C (exp. 195) and resulted in a high conversion to liquid products.

With the exception of exp. 195 the gas analyses showed high concentrations of carbon dioxide in the autogenous gases. From the low water and carbon dioxide yields encountered in exp. 195 it may be concluded that these compounds were almost entirely eliminated in the first treatment with hydrogen. The formation of carbon dioxide may be explained from the data presented, since the high concentration of carbon dioxide in the exit gases in exp. 191 suggests that this substance is for the most

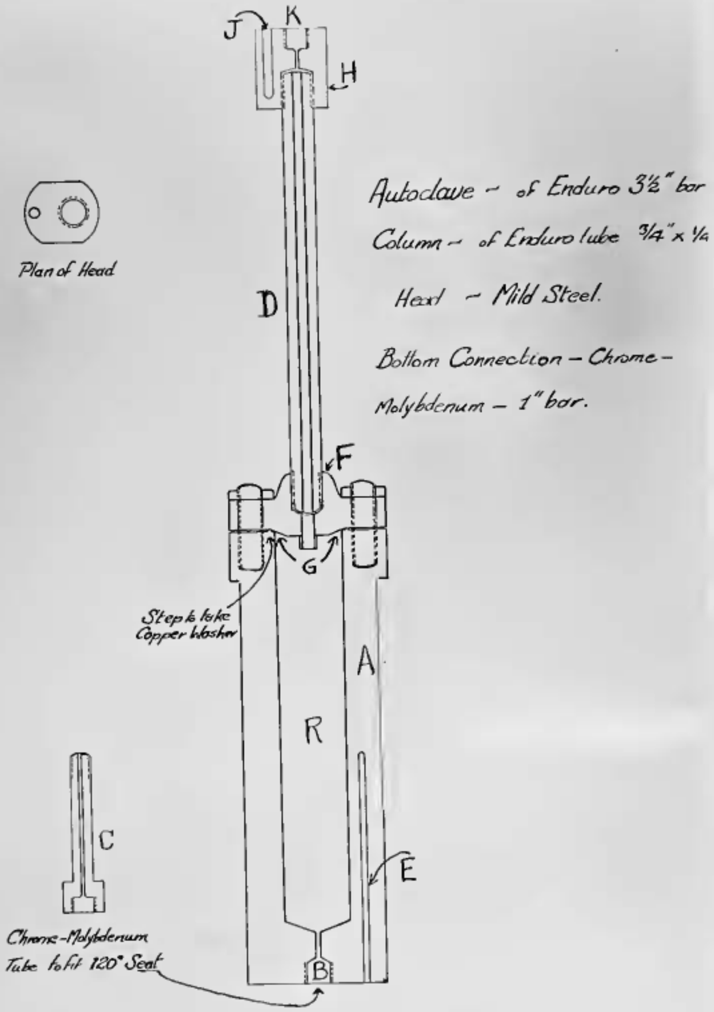
Figure 14.



Experiment 191-----Screenings No.4.
2400
2000
1600
1400
Pressure,lb./sq.inch.
P-Temp
P-Temp
Temperature,°
100
200
300
400
1
2
3
4
5
Time,---hours.

part eliminated below 300 °C. An inspection of figure 14, in which the pressure-time and pressure-temperature relations in exp. 191 are illustrated, reveals that after heating for approximately one hour, when the autoclave temperature reached 250 °C, a rapid increase in the slope of the curve occurred. Since carbon dioxide was evolved below 300 °C it is reasonable to assume that the rapid increase in pressure at 250 °C was due to the formation of large amounts of carbon dioxide. On this evidence it may be suggested that carbon dioxide was formed through a thermal decomposition of the screenings occurring at approximately 250 °C.

The elimination of water cannot be explained from the data available, and whether the formation of water occurred through thermal decomposition or whether by hydrogenation of alcoholic hydroxyl groups can only be determined by an investigation of the cracking of grain screenings under high pressure of an inert gas. In any event the elimination of water (and carbon dioxide) does not account for a great deal of the oxygen in the original charge. In general less than 20% of the oxygen content, about 3.5% of the carbon, and 10% of the hydrogen of the original cellulosic material appeared as water, carbon monoxide, and carbon dioxide, the oxygen eliminated appearing in approximately equal amounts as water and carbon



Autoclave – of Enduro 3½" bar

Column – of Enduro tube 3/4" x 1/4

Head – Mild Steel.

Bottom Connection – Chrome-Molybdenum – 1" bar.

Fig. 15.

Small Autoclave for Hydrogenation of Weed Seeds.

dioxide, and the hydrogen as water. It is evident that the oils produced must contain a considerable amount of oxygenated compounds.

The tetralin is seen to behave as an efficient catalyst by reason of relatively high conversions of seeds. The medium may be recovered almost quantitatively from the reaction products, the decomposition of tetralin during hydrogenation being negligible under the temperature conditions used.

In view of the high yields of oil obtained in the above investigation on screenings, work was extended to operation on a semi-continuous scale,using sample 5 of the screenings as received. The apparatus used was such as would allow a continuous flow of hydrogen through the reaction chamber, sweeping out any gases and volatile oils as formed. The autoclave used for this purpose has been illustrated in figure 15. The autoclave body A was machined from Enduro 3½" bar. A gas entrance to the reaction chamber R was made through a chrome-molybdenum tube C machined to fit a 120 ° seat B drilled in the centre of the base of the autoclave. The thermocouple well E extended as illustrated to a point midway along the autoclave body A. The reaction chamber was closed by the head F held in place by six ½" bolts of hardened drill steel screwed into the autoclave body. The gas-tight joint was made at G by a step carrying an annealed copper gasket.

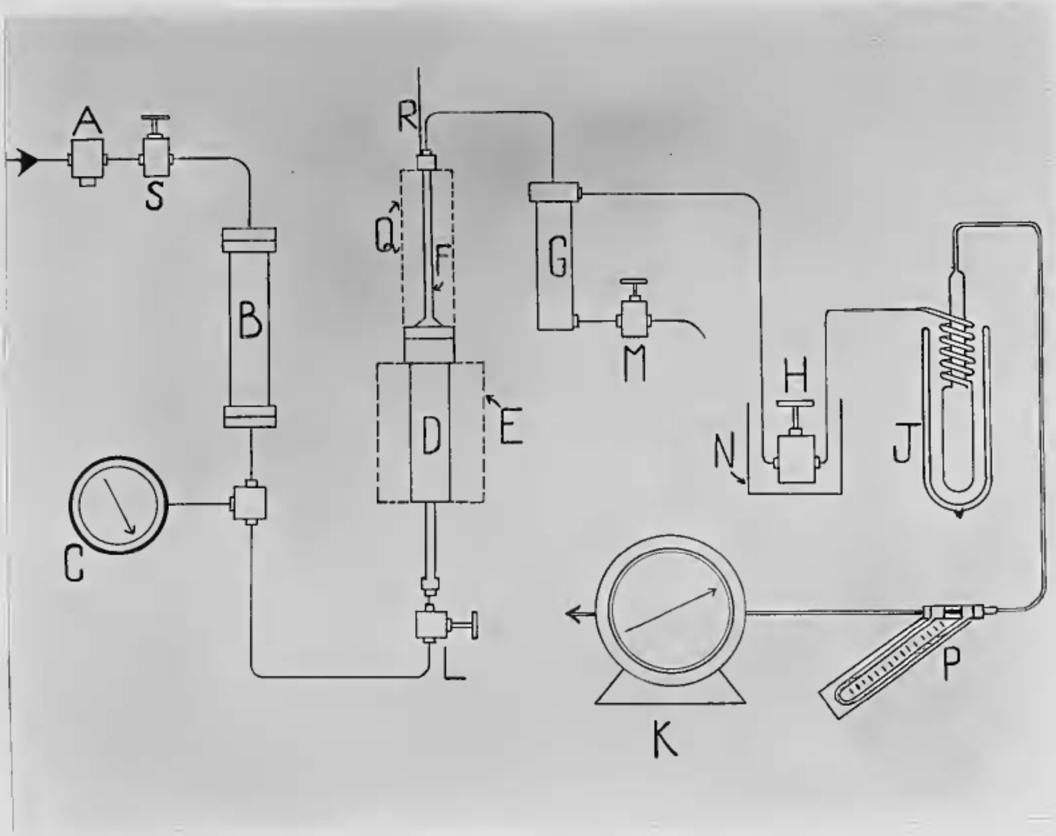


Fig. 16.

Flow Diagram for the Hydrogenation of Weed Seeds.

The column D of 1/4 x 3/4" Enduro tube was designed with smoothly finished ball ends of 1" radius to fit 120 ° seats. Connection was made with the autoclave cover at F. The column head H was fitted to the upper end of the column D by a connection similar to that at F. The exit gas connection was made at K, the temperature of the exit gases being measured by a thermometer inserted in the head at J. The assembled autoclave fitted snugly into a split electric furnace.

The termperature measurements of the reaction chamber were made by an iron-constantan thermocouple and recorded on a Leeds and Northrup recording potentiometer controller. The adjustment of a series resistance by the controller operating through a relay maintained the autoclave at the desired operating temperature, the maximum deviation being 5 °C.

A convential drawing of the complete setup is given in figure 16. The hydrogen from storage was led through the check valve A to the small storage cylinder B, installed to prevent sudden pressure changes weakening the Bourdon tube of the pressure gauge C. By opening the valve L the gas passed into the reaction chamber D, incased in the split electric furnace E, and through the heated column F to the water-cooled pressure condenser G. From the condenser the gas passed to the expansion valve

H maintained in a heated oil bath N to avoid freezing of the valve tip. From the expansion valve the gas was then led at atmospheric pressure through the ice-cooled condenser J to the differential flowmeter P and then to the oil-filled wet test meter K. The gas,collected in a water-sealed gas holder, was sampled for analysis after standing 3 or 4 hours.

The desired quantities of screenings and tetralin were transferred to the reaction chamber and the column bolted in place. The autoclave was placed in the split electric furnace and gas-tight connection made at the upper and lower ends. Hydrogen was led in to the desired initial pressure and heating of the autoclave commenced. Gas flow was started at a temperature in the neighborhood of 200 °C, on account of the possibility of a back pressure developing through the rapid evolution of carbon dioxide, in which event the tubing and valve L would become plugged with screenings. The column F was heated by a bunsen burner directed upon an asbestos sheet Q surrounding the column, the temperature at the head being measured by the thermometer T. At the end of an experiment the valves S and L were closed and the autoclave allowed to cool, the pressure slowly decreasing as the gases passed through H. When the autoclave was cold and the pressure was in the neighborhood of 500 lb/sq.inch the liquid condensate was blown through M and the remaining gas in the system released

through H. By disconnecting the tubing at the lower side of the valve L and at the head of the column it was possible to remove the autoclave from the furnace, the column being subsequently removed and the contents of the reaction chamber noted. The products were weighed and transferred to a glass-stoppered vessel.

The solid residue was removed by filtration of the total mass extracted from the autoclave, removal of adhering oil being effected by washing with ether. After the treatment with ether the solid material was dried and weighed. The filtrate from the ether washing was topped to remove the ether and the bottoms combined with the original oil. The combined oil was placed in a separatory funnel and the water drained off, after which the oil was distilled through a 14" fractionating column equipped with a device for maintaining a constant reflux ratio. The water was tested for acidity and distilled through a Cooper and Fasce (72) column to recover any low-boiling constituents soluble in water.

Experimental Results and Discussion.

The results obtained from this series of experiments are entered in Table XIII. The two temperatures recorded are:

(1) The autoclave temperature, or the temperature at which the reaction chamber was maintained during

TABLE XIII - Hydrogenation of Grain Screenings.- 2.

Experiment Number	5-1	5-2	5-3	5-4	5-5	5-6	5-7	5-8	Combined Pitch 5-9
Weight of Seeds, grams	91	45	50	50	50	50	50	50	60
Weight of Tetralin, grams	57	60	148	150	150	150	150	150	150
Catalyst, (5% by weight)	-	-	-	-	-	-	Zn[1], Cu[1], Al[1]	M_oO_3	M_oO_3
Temperature (Autoclave), °C.	330	350	350	375	400	400	400	400	425
Stillhead Temperature, °C.	62	64	-	67	220	215	215	220	235
Hydrogen Flow, c.c. per min.	120	130	120	130	125	180	180	180	185
Hydrogen Flow Commenced, °C.	210	-	225	175	225	175	200	200	165
Total Gas to Holder, cu.ft.	1.562	1.895	0.560	1.670	0.931	1.630	0.811	0.885	0.672
Initial Pressure, lbs/ sq.in.	1100	1150	-	800	800	800	750	750	1100
Operating Pressure, lbs/ sq.in.	2750	2600	2450	2300	2150	2850	2650	2300	3150
Time in operation, minutes	40	40	20	60	60	120	60	60	40
% Charge to liquids (Less Catalyst)	58.5	69.8	83.8	83.0	83.5	84.5	81.5	83.5	92.5
% " " Solids	26.4	23.8	12.1	8.0	6.0	4.0	3.5	4.0	0.5
% " " Gases	0.6	0.7	0.5	0.8	1.1	1.1	0.7	0.7	0.2
% " " Loss	14.5	5.7	3.4	8.3	9.4	10.4	14.3	11.5	6.8
% Screenings to Solids	42.8	55.6	48.0	32.0	24.0	16.0	14.0	16.0	1.7
% " " Water	18.0	18.5	23.0	24.0	20.0	24.0	24.0	24.0	3.3
% " " Oils, ~~less Water~~	23.0	30.0	53.0	44.0	50.4	46.0	50.0	46.7	78.5
Gas Analysis, % CO_2	1.9	2.5	2.8	3.0	3.3	4.8	2.6	2.5	0.0
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H_2	97.0	96.8	94.7	91.3	92.7	90.7	88.3	93.4	93.5
CO	0.2	0.1	0.4	0.5	0.4	0.6	1.3	1.0	0.2
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.5
CH_4	0.4	0.5	1.2	2.4	3.5	2.9	3.9	3.0	5.4
Structure of Seeds in Coke	fairly well preserved	about 60% destroyed	about 50% destroyed	about 80% destroyed	about 90% destroyed	completely destroyed	completely destroyed	completely destroyed	-
Distillation of Oil. I.B.Pt. °C.	-	54	57	62	52	62	63	82	89°C
% Oil and water to 175°C.	-	8.5	8.0	9.7	9.4	10.3	11.0	9.8	1.6
Oil and Water to 225°C.%(Less Tetralin).	no distillation	13.4	14.0	12.3	12.0	12.9	12.0	12.6	4.2
Tetralin, 200-206°C., %		76.3	76.8	78.7	78.7	77.0	77.3	77.8	74.4
Pitch, %		7.3	6.8	9.4	9.4	10.1	11.0	9.8	21.4
% Loss		3.0	2.9	0.0	0.0	0.0	0.0	0.0	0.0
Recovered tetralin, as % of tetralin charged		84.4	82.8	84.3	83.3	89.3	83.8	86.3	96.3
Nature of Water. Acidity — omit to state in 1T		acidic	acidic	acidic	acidic	acidic	acidic	acidic	neutral
% Boiling below 9.5°C. 95.0°C		22.5	25.6	24.0	28.0	30.0	18	23	-

operation.

(2) The stillhead temperature, or the temperature at which the exit gases from the autoclave left the head of the column.

The row titled "Gas flow commenced, °C" records the temperature of the reaction chamber at which the circulation of hydrogen was started. In those experiments in which a metallic catalyst was used the conversions were based on total organic charge so as to conform with the other calculations.

From an examination of Table XIII it will be seen that for reaction periods of one hour complete destruction of the seeds occurred only when an operating temperature of 400 °C or higher was used. The results in experiments 5-5, 5-6, 5-7, and 5-8, all at 400 °C indicate that the solid material may be reduced to 4% of the original charge, or to 15% of the weight of the screenings used. This represents an exceptionally high conversion to oil and water. Gas production was uniformly small representing only a small part of the screenings charged. While reaction appears almost complete at 400 °C, a high yield of liquid products was obtained by operation at 375 °C, lower temperatures resulting in only partial decomposition of the seeds. In this connection the low yield of unchanged solid material reported in 5-1 at 330

°C may be explained on the grounds of faulty technique, the abnormally high loss entered in the table consisting for the most part of solid material lost in handling.

The beneficial effect of the longer period of operation used in exp. 5-6 at 400 °C is revealed by a decreased amount of the seeds remaining in the solid residue compared with the amount obtained in exp. 5-5. In this regard the effect of the two metallic catalysts employed, Zn: Cu: Al (1:1:1) in exp. 5-7 and molybdic oxide in exp. 5-8 was to decrease the solid residue in an experiment of one hour duration the same amount as obtained in two hours without a catalyst (exp. 5-6).

In contrast to the earlier results (presented in Table XII) heat treatment of the solid residues obtained from hydrogenation at 400 °C did not result in the distillation of any oil from the recovered coke.

Gas formation was low in all the experiments, the carbonaceous gases consisting for the most part of carbon dioxide and methane, with small amounts of carbon monoxide. The formation of water in large amounts is unavoidable, and it may be that appreciable amounts of hydrogen are used in the elimination of oxygen as water. Distillation analysis of the water showed a content of up to 30% of substances boiling below 95 °C.

On the basis of the oxygenated compounds carbon

dioxide, carbon monoxide, and water formed in hydrogenation, then in those experiments conducted at 400 °C approximately 50% of the oxygen, 2% of the carbon, and 35% of the hydrogen of the original cellulosic materials was removed as water and these gases. Hence a considerable amount of oxygen remained in the recovered oils.

Experiment 5-9 was conducted on the hydrogenation of a composite sample of pitches obtained in previous runs. A higher operating temperature was used, and molybdic oxide employed as a catalyst. In spite of the strenuous conditions imposed the pitch remained resistant to complete decomposition. The unusual stability of this pitch, showed by negligible coke and gas formation, is in sharp contrast to the unstable nature of the residual pitches obtained by hydrogenation of screenings at lower temperatures for a longer time (discussion following Table XII).

The rate of hydrogen flow in all cases appeared insufficient for distillation of the light oils as formed. It was necessary to keep the stillhead temperature as low as possible to avoid distillation of the tetralin, and attempts to secure fractionation of the light ends was only partially successful. This is borne out by the initial boiling point reported for the oily reaction products.

Further examination of Table XIII reveals that

the losses in general increase with increase in operating temperature, indicating a higher conversion to volatile oils. (Exp. 5-1 must be excepted on account of the faulty technique previously described).

Conclusions:

From the point of view of conversion to oils, gas, and water good results have been obtained by the hydrogenation of grain screenings at 400 °C in the presence of tetralin.

The beneficial effect of metallic catalysts has been demonstrated by an increased rate of reaction, though higher conversions have not been obtained.

The residual pitches obtained have been shown to be remarkably stable and fairly resistant to hydrogenation, though appreciable decomposition does occur at 425 °C.

5. The Hydrogenation of Wood.

A short investigation of the behaviour of firwood sawdust in the presence of tetralin was conducted in the 1800 c.cm. oscillating autoclave previously described. The results of this study have been presented in Table XIV.

From an examination of the Table it will be seen that the wood underwent a considerable decomposition in the presence of tetralin, hydrogen absorptions as high as 3.7% by weight of the wood being obtained. In exp. 197 the low temperature of operation accounts for the slight reaction taking place, whereas at 350 °C in exp. 196 the pressure-temperature record indicated that extensive cracking occurred. It was thus attempted in exp. 198 to hydrogenate wood in two cycles, the first cycle being operated at 325 °C and the second at 375 °C. The result was highly satisfactory, the total conversion of wood to oil, gas, and water being 58% by weight of the wood, and it is highly probable that higher conversions could be obtained by using more suitable operating conditions. Nevertheless the beneficial effect of tetralin is shown by comparison with the maximum conversion of 56% of wood reported by Lindblad (70) in an extensive study of the effect of a great number of metallic catalysts and suspending agents on the hydrogenation of wood.

TABLE XIV - Hydrogenation of Wood in the Presence of Tetralin, ~~and the effect of Additional Catalysts~~, over a limited Temperature Range.

Experiment Number	196	197	198
	17	12	
Weight of Wood in grams	163	152	149
Weight of Tetralin in grams	198	180	148
Number of Cycles	1	1	2
Average Time per Cycle, hours	2	1	1
Average Maximum Temp., °C.	350°C	325°C	325-375°
Average Initial Pressure	1220	1200	1140
Average Maximum Pressure	3740	3435	3475
Average Final Pressure	1205	1175	1140
Average Pressure Drop	15	25	0
Hydrogen Absorbed, % by Wt.	3.3	2.5	3.7
Gas yield, less H_2, in litres /kg.chge.	26.7	15.9	36.7
% Charge to Liquids	68.7	56.9	65.0
% Charge to Solids	20.2	34.3	23.9
% Charge to Gas	1.2	1.1	1.3
% Wood to Oils	33.6	13.6	37.2
% Wood to Water	9.2	8.5	10.1
% Loss	9.9	7.7	9.8
Gas Analysis, % CO_2	8.0	7.0	4.3
C_nH_{2n}	0.4	0.0	0.0
H_2	81.3	89.3	87.8
CO	1.3	0.9	0.6
C_2H_6	0.6	0.0	0.5
CH_4	6.0	2.9	2.2
Distillation of Oil in 14" column			
I.B.Pt.	43°C.	62°C.	54°C
% H_2O	8.7	6.9	7.8
% Oil to 175°C.	2.3	1.7	1.7
% Oil to 225°C. (less tetralin)	12.7	5.8	13.1
% Oil to 300°C. (less tetralin)	no dist. (crack)	crack no dist.	crack no dist.
% Tetralin in Oil	68.4	80.4	64.3
Recovered Tetralin, %	92.3	84.4	83.8

Summary.

The action of tetralin as a hydrogenating agent has been studied with various carbonaceous materials under a variety of operating conditions.

The beneficial effect of tetralin in the reduction of residues from bitumen hydrogenation has been shown by increased rate of reaction and lower coke and gas formation.

The hydrogenating power of tetralin alone has been demonstrated by hydrogenation reactions carried out in an inert atmosphere.

That materials containing large amounts of polynuclear aromatic compounds may act as hydrogenating agents in a manner similar to tetralin has been demonstrated in an investigation of the influence of aromatic tar from the pyrolysis of natural gas as a suspending agent for coal.

The action of tetralin as a hydrogenating agent in the reduction of cellulosic materials has been studied in an investigation of the hydrogenation of grain screenings and wood, and high conversions of these materials to gas, oil, and water have been reported.

It is suggested that the tetralin owes its efficiency to the "hydrogen carrier" action possible with polynuclear aromatic hydrocarbons in the presence of

hydrogen. The action may be compared to that of a solvent and a catalyst in that it is believed that tetralin hydrogenates unsaturated fragments resulting from the cracking of carbonaceous materials. In this reaction tetralin is dehydrogenated to naphthalene, but in the presence of catalysts, and at temperatures in excess of 300 °C, the naphthalene is readily reduced again to tetralin in high concentrations of hydrogen (33). Tetralin is an excellent solvent for carbonaceous materials (15), thus insuring the necessary close contact at high temperatures of the hydrogen donator and the hydrogen acceptor.

PART III

ON THE CONTINUOUS HYDROGENATION OF BITUMEN FROM THE BITUMINOUS SANDS OF ALBERTA.

PART III

Continuous Hydrogenation of McMurray Bitumen.

Introduction.

It has been demonstrated in an earlier investigation (10) that the hydrogenation under pressure of bitumen on a batch scale may be accomplished under severe enough conditions of temperature and with a catalyst to insure a rapid reaction without coke formation. The results obtained pointed to an extension to operation on a continuous basis in a reaction chamber designed so that hydrogenation could occur in the gas and liquid phases.

In what follows the susceptibility of bitumen to hydrogenation on a continuous scale has been investigated, and equipment has been devised whereby a satisfactory operative technique may be used.

Literature Review.

While the hydrogenation of bitumen has not received a great deal of attention in the past, investigations on the hydrogenation of allied substances such as gas oils, pitch, coal tars, and petroleum residues have been extensively carried out.

The hydrogenation of coal tars and pitches yields products similar in nature to those obtained from asphalts. In this regard the researches of Hugel (31), Morgan (63) and Tropsch (58) have been mentioned previously. The hydrogenation of gas oil was studied by Dunstan (43) and Shatwell (53) and the results obtained in these investigations indicated that higher yields of gasoline could be obtained than by the cracking process. The hydrogenated product was of higher quality, and the refining losses sustained were very low. An investigation of the susceptibility to hydrogenation of asphaltic oils has been carried out by Roberti (50), and high yields of volatile oils of good quality were obtained. In this regard it was demonstrated that molybdic sulfide supported on pumice or charcoal was a highly beneficial catalyst. Bruylants (12) working in the Bergius laboratory at Mannheim, has studied the hydrogenation of bitumen and petroleum residues on a continuous scale. By virtue of higher gasoline yields and

superior qualities of the gasoline it was shown that hydrogenation offered more satisfactory results than were obtained by the cracking process. In support of the theory of the mechanism of hydrogenation proposed by Waterman (60) Buylants concluded from his results that the function of the hydrogen in hydrogenation was to prevent dehydrogenation in cracking. Hence no hydrogen was absorbed by the oil. The evidence for this proposed mechanism was extremely scanty. In contrast to the higher yields obtained by Roberti and Bruylants, Waterman (60) found that Mexican and Borneo asphalts were no more susceptible to hydrogenation than to cracking. It may be suggested here in this regard that the high temperatures and low hydrogen pressures used in these experiments accounted to some extent for the low oil yields obtained.

The hydrogenation of petroleum oils and residues was first undertaken by the Standard Oil Development Co. and the highly satisfactory experimental results obtained led to the installation of hydrogenation plants capable of treating several thousand barrels of crude oil daily. A description of the methods of operation used and the products obtained has been given by Haslam (29) and McKee (42). In all of the processes used operation may be continued for months at a time without either deactivation of catalyst or coke formation.

The susceptibility to hydrogenation of McMurray bitumen has been exhaustively studied in batch scale operation by Boomer and Saddington (10, 51). It was found that in the presence of hydrogen under a pressure of approximately 200 atmospheres bitumen was hydrogenated at 425 °C without appreciable coke formation, provided a suitable catalyst such as molybdic oxide was used. The refined gasoline yields of approximately 35% of the bitumen did not represent an increase over the yields obtained by cracking (17), but the negligible coke formation in hydrogenation both of the bitumen and of the heavy oil residues from previous hydrogenations suggested the use of continuous operation with recycling of the heavy oils. It was shown that only about 15% of the bitumen was highly resistant to hydrogenation. Continuous operation with recycling has also been suggested by Sachauen (73) from a consideration of the kinetics of the reaction, and this experimental results, as a means of obtaining high yields of gasoline. According to Nash (46) the oil yield obtained upon berginization of McMurray bitumen amounted to 50% of the charge as compared to a 41% yield obtained by cracking. Direct retorting of the bitumen yielded 62% of oils. The high coke formation reported for the berginization experiments may be attributed to the high temperature used (450 °C.) in the absence of a catalyst.

Besides the results mentioned above, the specifications described in the large patent literature indicate that more satisfactory results may be expected in continuous operation than by batch treatment. A full review may be found in Ellis (15).

Materials;

The bitumen was supplied by Dr. K. A. Clark of the Research Council of Alberta and was prepared by the hot water extraction process from Fort McMurray bituminous sands (13). An extensive analysis of the bitumen has been given by Nash (46), from whose paper the following properties have been reproduced below.

Sp. Gr. 1.02 - 1.03
I.B.P. 60 °C.
Englar distillation, standard
I.P.T., given as % by volume.
Distillate to 175 °C - 7%
175 - 225 °C - 9%
225 - 300 °C - 18
Above 300 °C - 66

Sulfur content.
Crude distillate - 2.68%
Fraction to 175°C- 1.64%
175 - 225° - 2.61
225 - 300° - 2.75
Above 300° - 3.38

Saponifiable matter - 2%
Asphaltenes - 22.5%
Resins - 24%
Oily constituents - 51.5%

Ultimate Analyses.
S, 2.73%. C, 84.49
H, 11.23. N, 0.04.

After separation from the sand the tar, freed from asphaltenes and petroleum resins by Marcusson's method, was found to have the following characteristics:

d^{20} 0.927
n^{20} 1.500
Optical activity dextro 1.5-1.6.
Viscosity @ 25 °C - 20.0
Mol. weight - 350.

S - 1.87
C - 85.76
H - 12.19
Iodine No. 2.1.

This data by Nash while probably indicative of the general nature of McMurray bitumen and of value in showing the relative amounts of various fractions and constituents, cannot be taken for other samples, especially with regard to the ultimate analyses. Below is given some

analytical data on the bitumen used in the early stages of this work.

Carbon - 82.3%
Hydrogen - 10.2%
Nitrogen - 0.37%
Sulphur - 4.2%

Initial b.p. - 175 °C
Carbon residue - 14.2%
Density at 25°C - 0.998

The above data differs widely from that given by Nash and is probably approximately true of all the bitumen used in this work. The later samples of bitumen differ from the above principally in regard to density which is higher, 1.02 to 1.03 gr. per ccm. at 25 °C.

The behaviour of the bitumen toward hydrogenation cracking and direct retorting as reported by Nash has been previously discussed in the literature review.

The crude bitumen as received contained a large amount of water and prolonged heating at 110 °C was a necessary operation in purification. All large particles of suspended matter were removed by filtration of the hot tar through a 100 mesh sieve.

The hydrogen used was prepared by electrolysis of 15% H_2SO_4 using lead electrodes. The hydrogen was purified by passage through a glass tube packed with copper gauze and maintained at a temperature of 400 °C. In this manner any oxygen present was removed as water.

The catalyst used was in all cases molybdic oxide. In those experiments in which the catalyst was

introduced into the autoclave in the powdered form and maintained in suspension by agitation of the charge, the molybdic oxide was prepared by dehydration of molybdic acid below dull red heat. In some experiments the catalyst was supported on inert carriers and in these cases was prepared by impregnating the carrier with a saturated solution of ammonium molybdate with subsequent heating to give the oxide; the process being repeated a number of times so that as large an amount of catalyst as possible was obtained.

The supports used were unglazed porcelain and pumice. Attempts to prepare a suitable inert alumina catalyst proved unsuccessful, the final product being in all cases too friable for use. Silica gel supports were not prepared on account of the possibility of glazing occurring at the high temperatures used on ignition.

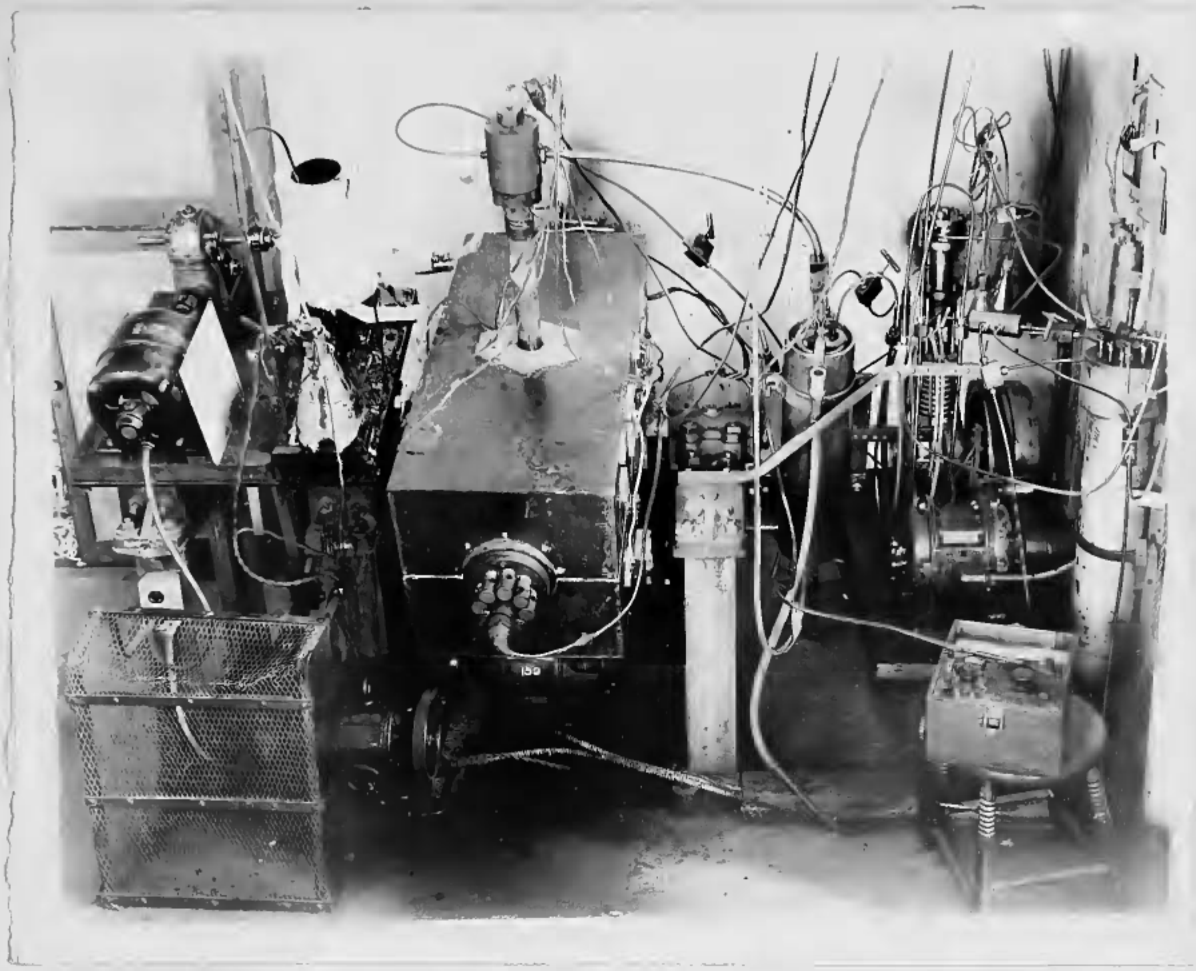


Fig. 17.

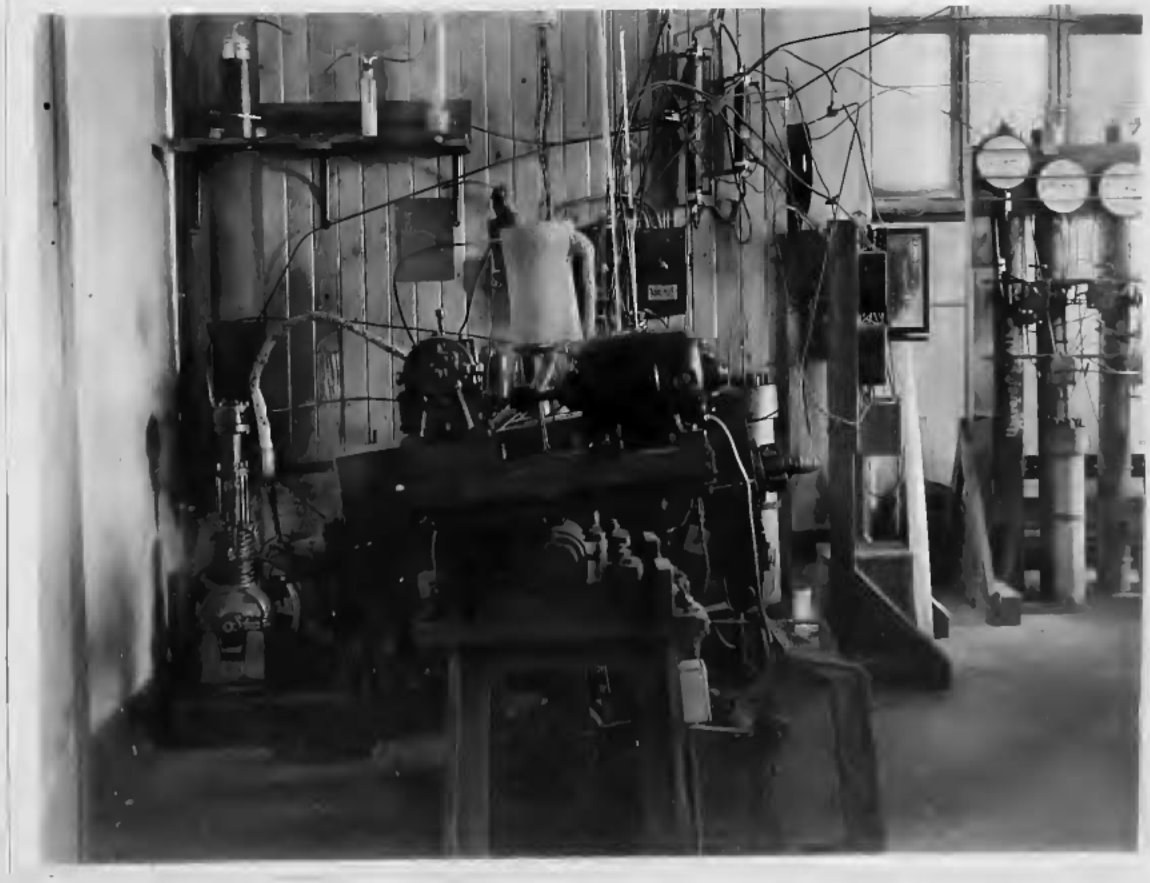


Fig. 1

Apparatus:

The compression and gas storage system was the same as that used in the other parts of this work and has been described briefly.

On account of the multiplicity of parts, the apparatus used for semi-continuous and continuous-batch hydrogenation of bitumen has not been represented by a detailed drawing, but two photographs, figures 17 and 18, and a flow sheet, figure 19, have been shown.

The autoclave is shown in an inclined position in figure 17, centre foreground, and denoted M in figure 19. The reaction chamber was in some respects similar in design to the 1800 c.cm. oscillating autoclave previously described, particularly with regard to the end plates, ring nuts, etc. Its inside dimensions were 9 cm. diameter by 66 cm. long, a volume of 4100 c.cms.

Leading from the autoclave chamber, and bolted to its midpoint by six 5/8" studs screwed into the autoclave body, was a high pressure distilling column A, 2.8 cm. diameter and 45 cm. long terminating in a distilling head carrying a coaxial thermocouple well and a gas connection and a lead off to the condenser. The gas-tight connections to the autoclave and head were made at the ends of the column by annealed copper gaskets. The autoclave body, end plates, and the distilling column

were made of a high chromium nickel steel. From the distilling column the autogenous gases and oils could be led via a 5/16" I.D. chrome-vanadium tube to a coil of the same material terminating in a receiver D, figure 19, both of which were immersed in a water cooler, shown in the right centre of figure 17.

One end plate of the autoclave carried a thermocouple well extending to the centre inside of the reaction chamber. A 1/2" I.D. tube equipped with an electric heater, led to the other end plate and served as a preheater for the gas and tar entering the autoclave through this tube.

The autoclave fitted snugly in a semi-circular trough made by splitting longitudinally the appropriate size of pipe. Heat transmission occurred from the heaters through this trough to the autoclave. The trough was screwed to three cast iron pedestals, one of which at each end carried the weight of the autoclave. These end pedestals fitted over the large end portion of the autoclave and prevented sliding motion. The pedestals were bolted to a longitudinal H beam which also carried the lower half of the sheet iron furnace casing B, figure 19, and shown also in the centre foreground of figure 17 as a box-shaped structure. The top half of the furnace casing was made in two parts and was bolted to the lower half.

The design of the uppoer part of the furnace was such that the part of 1/4" steel in contact with the autoclave fitted snugly and served as a means of producing uniform heat conduction to the autoclave from the upper heaters.

Heating was produced by nichrome windings supported on transite sheets bolted around the autoclave casing which heated this casing by radiation and conduction through the small air space present. Sil-O-Cel insulating powder was packed in the space between the transite sheets and the outer sheet iron casing, bolted to the longitudinal girder mentioned previously to a cradle supported on the main shaft, the end of which may be seen in the centre foreground of figure 18. The shaft was held in place by three adjustable pillow blocks attached to three inverted shaft hangers, one of which may be seen in the centre foreground of figure 18, the other two being on either side of the autoclave, figure 17. The shaft hangers were bolted to a heavy cast iron base. Attached to the main shaft between and above the two left hangers, figure 17, was a table supporting a steam generator, a tar reservoir, and a hydraulic pump operated through a reducing gear by a small electric motor. The table and contents are shown in figure 17, left foreground, and in figure 18, centre foregound. Bolted to the opposite end of the main shaft was a steel bar to which was attached the condenser re-

ceiver and surrounding water cooler. A second receiver not visible in the photographs but shown as E on figure 19 was connected to the first receiver through valve 8, to the atmosphere through valve 9, and to the atmospheric pressure collecting system by a small expansion valve in its lower end.

The main shaft carrying the autoclave in its cradle, the tar supply system and the condensing system was connected through a jointed connecting rod to a rotating crank on the slow speed shaft of a reducing gear as may be seen at the lower foreground in figure 18 and left foreground of figure 17. A motor resting beneath the autoclave cradle on the base casting was used to drive the high speed shaft of the reducing gear.

Gas connections from the moving parts to the rigid auxiliary equipment were made by the two copper coils coaxial with the main shaft, and visible in the right foregound of figure 17. They are indicated diagramatically at the right and left sides of figure 19. The coil supports may be seen attached to the right end shaft hanger (figure 17). These coils of 1/8 x 5/8" copper tubing consisted of three turns of about 12" diameter.

One end of each coil was bent in to the centre of the coil and attached to a bar bolted to the main shaft

while the other or fixed end at the circumference was attached to a bar bolted to the end shaft hanger.

Two chrome-vanadium cylinders of 5 litres capacity each, front end of figure 17, right, were used as gas purifiers, one fitted with baffles and 4 litres of gas oil acting as a scrubber and the other as a spray trap and gas reservoir. These are visible in figure 17 at the extreme right. Above and behind the second purifier may be seen the safety valve inserted to protect the equipment against high pressures developed in the event of a plugged gas line.

The gas circulating pump may be seen in figure 17, right background, or in figure 18, left background, and is shown at J, figure 19. The cylinder carrying the head, in which was cut two poppet valves, was bolted to the cylinder of a small air compressor whose piston was modified to act as a crosshead for the circulator piston. The dimensions of the circulator were 7/16" bore x 3 1/2" stroke and it was driven at about 180 r.p.m. The gland was of the double type designed to recover from the space between the glands any gas that leaked from the cylinder, which gas could be sent to the atmospheric storage system as is shown in figure 19.

The temperature of the reaction chamber was

measured by an iron-constantan thermocouple inserted in a thermocouple well extending to the middle of the autoclave and was recorded by a two point Leeds and Northrup potentiometer controller. Heat control was accomplished by the adjustment of series resistances by a magnetic switch operated by the controller through a relay. Temperature measurements of the stillhead were made with an iron-constantan thermocouple and a portable potentiometer shown in figure 17, at the lower right foreground. Temperature measurements and control of the preheater to the autoclave, visible in figure 18, left background, where the asbestos covered tar supply line terminates were made by an iron-constantan thermocouple connected to the controller, the adjustment of resistances being effected in a manner similar to that described for temperature control of the reaction chamber.

Pressure measurements were made by a Bourdon tube recording gauge calibrated by comparison with a standard dead weight piston gauge.

The atmospheric-pressure part of the equipment can best be seen in the flow diagram (dotted lines in figure 19). This apparatus consisted of a separator, K, for separating the oil from dissolved and entrained gas and an absorption train for these gases. The circulating pump leak was also connected to this separating system.

The absorbers used were an ice condenser and a charcoal absorber for volatile ends, a calcium chloride tube for water, and a soda-lime tower for hydrogen sulfide. From the absorbers the gas passed through an oil-filled wet-test meter and to storage in a water-filled gas holder. Upon the completion of a run the residual gas in the autoclave was liberated through a heated expansion valve to a similar absorption train to storage in a gas holder.

The apparatus as described above represents the final development of considerable experimentation and was used only in the later experiments carried out in the manner described in what follows as Procedure B. The earlier work was carried out without a gas circulator, a preheater for the gas and tar entering the autoclave or a high pressure scrubber for the gas and in other details was less satisfactory. The methods followed are described below under Procedure B and A.

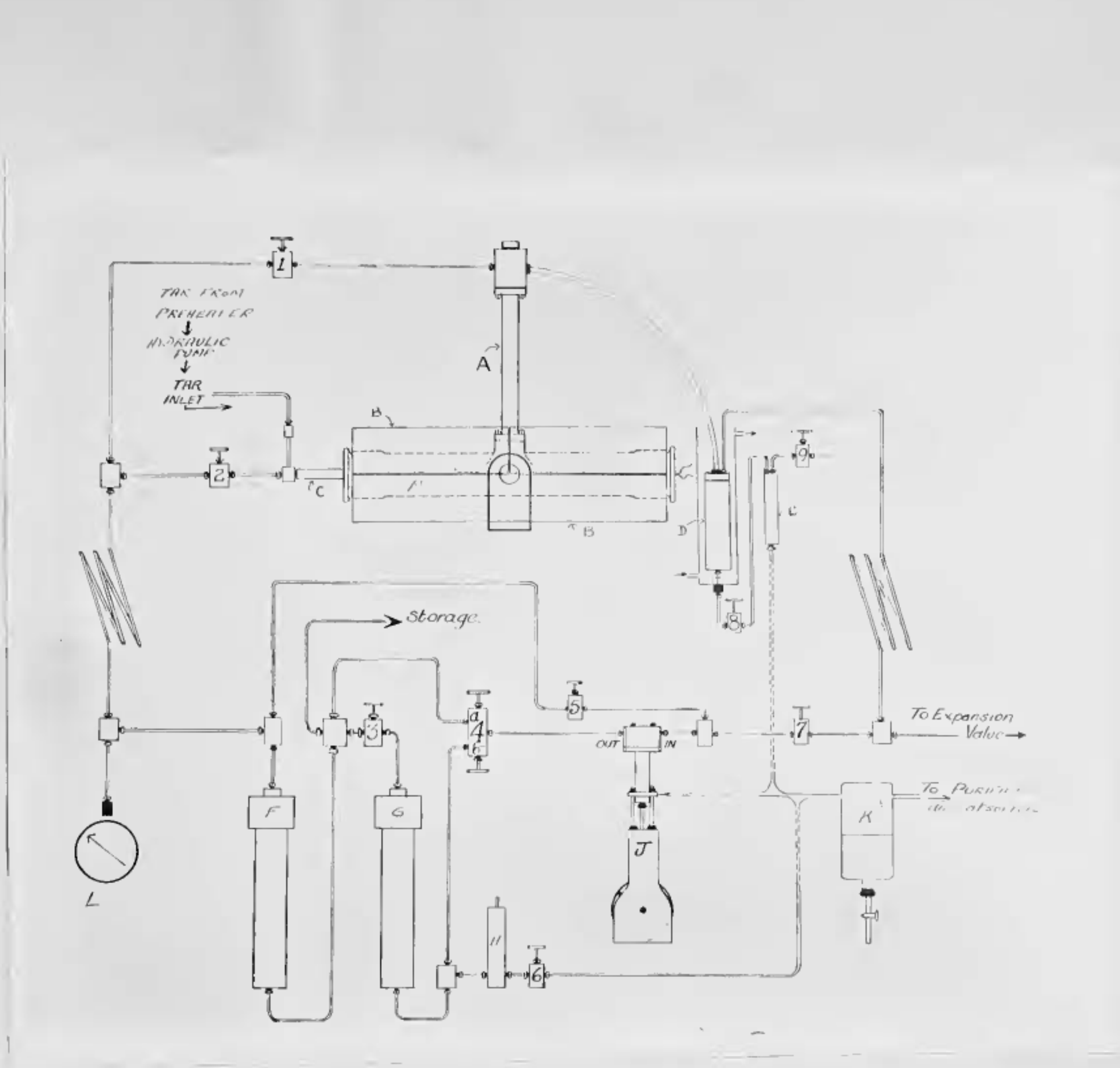


Fig. 19. Flow Diagram.

Procedure.

The installation of improved equipment from time to time necessitated changes in procedure, but in general two distinct methods of operation were adopted; the first, termed a continuous-batch procedure, has been outlined below in A. Of the second procedure, a more satisfactory technique termed semi-continuous hydrogenation, has been described at some length in B.

Procedure A.

Although figure 19 illustrates a great deal more equipment than was used in the early experiments for which procedure A was adopted, it will be advantageous to refer to this diagram in the following outline. Pending the installation of a gas-circulating pump, the distillation of hydrogenated oils through the column A under pressure was promoted by the use of a gas-bleeding operation conducted as follows: The apparatus was charged with hydrogen to the desired initial pressure and approximately two litres of tar pumped into the heating autoclave. When the autoclave had remained at the operating temperature for a length of time sufficient to produce an extensive conversion of bitumen, valve 2 was opened. On opening valve 8 the pressure in the autoclave was released, and the gas at higher pressure in F passed through valve 2 into the autoclave. In this manner a

flow of gas through the reaction chamber and out by the column A occurred, which resulted in the distillation of appreciable amounts of oil. The oil was condensed in D and forced through 8 into a separator at atmospheric pressure. The reduction in pressure throughout the system which resulted from this bleeding operation was compensated for by recharging the auxiliary storage cylinder F with fresh hydrogen to the original pressure, the gas passing from F through 2 to the reaction chamber. When an amount of pressure distillate corresponding to a 50% conversion of the bitumen had been collected a fresh supply of tar was pumped to the autoclave and the whole process repeated. This operation was continued until the end of the experiment, in general one complete cycle taking two hours to perform.

The analytical procedure adopted with regard to the products will be described following procedure B.

Procedure B.

The large losses sustained by removal of the pressure distillate in the manner described above and the poor conversion results obtained made the installation of improved handling equipment necessary for accurate work.

The difficulties involved in promoting distillation by bleeding the autogenous gases, as well as the unsatisfactory yields obtained with such a procedure pointed to the use of a gas-circulating system by means of which a continuous distillation of hydrogenated oils could be obtained. The installation of such a system would also allow purification of the hydrogen under pressure by passage through absorbers wherein hydrogen sulfide, hydrocarbon gases and oil vapours would be absorbed.

The complete equipment devised to offer the most suitable results has been indicated in the flow diagram (figure 19).

Hydrogen was passed in to the desired initial pressure and approximately two litres of tar pumped into the autoclave. During the time the autoclave was heating to the operating temperature valve 1 was open and valve 2 closed so that the pressure would remain equal inside and outside the converter, thus removing any possibility of the inlet tubing becoming plugged with tar through the development of a back pressure. As a precautionary measure this valve arrangement was always used when the circulating pump was not in use. When the autoclave reached the desired temperature the gas circulating pump was put in operation.

Under normal operation the gas was pumped by J

to the two-way valve 4, through the "b" end of which it was forced to the oil scrubber G, where hydrogen sulfide and hydrocarbons were partly removed and the hydrogen concentration raised. From G the gas passed through valve 3 to the four-way connection illustrated. Valve 4 "a" and the line to the storage system being closed, the gas passed to the spray trap or auxiliary storage F, from which it proceeded via the copper coil (illustrated by means of staggered gas lines) to the valve 2, valve 1 being closed. From 2 the gas passed through the preheater C to the reaction chamber M where some gas was absorbed in reaction. The remainder, together with hydrocarbon gases and hydrogen sulfide, promoted, by rapid circulation, the distillation of gasoline through A. From A the mixture passed to D, where the oil was condensed. The gases passed on to the valve 7 via the second copper coil, and from valve 7 returned to the circulating pump J.

If at any time the formation of a high-boiling distillate indicated a too-rapid circulation of gas, opening valve 5 resulted in a by-pass of gas from F through valve 5 to the pump J. The extent to which valve 5 was open as compared to the opening of valve 2 naturally determined the fraction of gas which would bypass the autoclave. Moreover, when it was necessary to replace the oil in scrubber G with fresh oil, operation was not dis-

continued. At such times valve 4b was closed, valve 3 closed, and valve 4a opened, the cylinder G thus being completely bypassed while the second bypass using valve 5 remained unaffected. The oil was removed from G whenever desired by opening 6, the pressure of gas above the oil in G forcing the material through the safety valve H to the atmospheric pressure separator K, the accompanying gas passing through the absorbers to the meter and gas holder.

The pressure distillate collected in D was removed by opening valve 8, which let it into E, from which an expansion tip allowed its removal to K, the gases passing again to the meter and holder via the absorption train.

The amount of tar pumped to the autoclave was kept as close as possible to 50% more than the amount of pressure distillate removed, experience having shown this to be a good approximation of the ratio to be used to allow a balance. The process has been termed semi-continuous because it has been found advantageous to pump the tar into the autoclave in batch lots, during which time the circulating system was shut down and all valves except 1 closed. In this manner the possibility of distillation of cracked fragments before stabilization had occured by hydrogenation was precluded.

By adjusting the resistances so that the autoclave temperature fell to 200 °C, the apparatus could be safely left overnight with all valves shut except 1. Operation could be continued on the following day. At the end of an experiment the circulating pump was stopped, all valves closed, and the heat shut off. When the autoclave was cold valve 7 was opened and the autogenous gases bled through the expansion valve to an absorption train, meter, and gas holder. The autoclave was opened and the contents removed. The coke and the catalytic mass remaining from filtration of the autoclave material was washed with ether, dried, and weighed. The ash content of the coke was usually determined.

The oil from the scrubber G was removed in the manner previously described and stripped of dissolved gases and volatile oils by distillation. The increase in weight of the charcoal, calcium chloride, and soda-lime absorbers was noted, and the charcoal revivified by distillation with steam superheated to 150 - 175 °C, the recovered oil yield being tabled.

Analysis of the pressure distillate usually consisted of distillations, density and sulfur determinations, olefine content measurement, and analysis of the constitution of the gasoline fraction by the Egloff-Morrell method (18). Refining data was usually obtained.

in those experiments in which a suitable grade of heavy oil was secured as a product of reaction vacuum distillation followed by viscosity measurements of the lubricating oil fractions were made.

The calculation of gas yields offered considerable difficulty and in most of the experiments the figures presented may be in error by 1-2% by reason of the large volumes under consideration and the losses sustained from time to time.

RESULTS AND DISCUSSION

A. Continuous-Batch Hydrogenation of Fort McMurray Bitumen

The results obtained in three experiments which were operated under the conditions described in procedure A are presented below. As a foreword it may be stated that experiment 2-3 was carried out under berginization conditions, i.e., no catalyst was used. Experiments 2-4 and 2-5, in which the catalyst, molybdic oxide, was used, offer comparative data on the effect of time of operation on coke formation as well as data on the effect of improved handling conditions on the losses sustained. On account of unavoidable gas losses occasioned by leakage in the compression system and occasionaly in the hydrogenation equipment, the values given for conversion to gaseous hydrocarbons and for hydrogen absorption are not very reliable. The experimental data in these experiments will be considered separately.

Experiment #2-3.

The results obtained in this experiment were extremely unsatisfactory on account of extensive coke formation. The following table describes the operating conditions employed and the yields of oil, gas and coke obtained..

TABLE XV

Experiment number	2-3
Time, hours at temperature	19
Operating temperature, °C	425
Average of maximum pressures, hot	1950 lb/sq. inch.
Average pressure drop during absorptions	50 " "

Materials recovered, % by weight of bitumen.	
Residual oils, from autoclave	15.6%
Pressure distillate	9.4
Coke	40.8
Gas	7.5
Loss	26.7

Fractionation Data.	Press. Dist.	Residual Oil
- to 225 °C	83%	47%
225 - 260 °C	4%	9%
260 -	2%	42%
Loss	11%	2%

Yields:	
Bitumen to gasoline	16.9%
" " kerosene	1.8%
" " fuel oil	6.4%

The low I.b.p. of the pressure distillate, namely 25 °C, may account to some extent for the large losses tabled, though it is believed that these losses are for the most part due to mechanical difficulties in handling the distillate with the apparatus in use.

The low pressure drop accompanying each absorption is misleading unless it be remembered that the total volume of the gas phase was in excess of 8 litres as compared with a liquid phase volume of about one litre. Consequently these small pressure drops represent a normal hydrogen absorption.

The large coke production is very unfavorable and particularly so as the coke was hard and solidly attached

to the walls of the autoclave. The results obtained indicate that the hydrogenation of bitumen cannot be satisfactorily carried out under continuous operation without the aid of a catalytic agent.

Experiment 2-4.

Following the experiment discussed above a determination was made of the effect of a catalytic agent. The run was of short duration due to failure of the hydraulic pump. The results obtained are presented below.

The operating conditions under which this experiment was carried out are given in Table XVI.

TABLE XVI

Operating conditions

Time, hours operation at temperature	12
Temperature, °C	425
Total bitumen added, grams	2650
Catalyst, MoO_3, grams	100
Initial hydrogen pressure, cold	1800 #/sq. in.
Average of maximum pressures, hot	2700 #/sq. in.
Average pressure drop during absorption	250 "

The yields of products obtained and preliminary distillation analysis of the oil produced are shown in table XVII.

TABLE XVII

Materials recovered, % by weight of bitumen.

Residual oil from autoclave	39.5%
Pressure distillate	29.8%
Coke	7.0%
Gas	4.1%
Loss	19.6

Fractionation Data

	Press. dist.	Residual Oil
to 225 °C	74%	23%
225 to 260 °C	7	9
above 260 °C	12	64
loss	7	4

Yields:		
	Bitumen to gasoline	37.8%
	" to kerosene	5.6%
	" to fuel oil	26.1%

The small amount of coke formed in this experiment appeared in a finely divided form suspended in the oil, a most favorable condition from the point of view of handling the material in continuous operation. When it is considered that the mineral matter of the original bitumen runs as high as 2% the yield of coke actually formed in hydrogenation will be seen to be 5-6% of the charge. This figure is a very favorable value.

The pressure distillate again had an I.B.P. of 25 °C and hence a large loss has been recorded due to evaporation of volatile constituents during handling of the distillate.

The properties of the various fractions are illustrated by the analytical tables given below.

1. Crude Gasoline, 225 °C end point.

density at 20 °C - 0.7526
solubility in 91% H_2SO_4 - 7.0%
sulfur, % - 0.30

The % solubility in the 91% H_2SO_4 is a measure of the olefine content of the oil, though the figure is not an exact value due to solubility of sulfur compounds in the acid. The sulfur value was obtained by the lamp method according to A.S.T.M. specifications.

Upon refining with 23 ° Baume (= 13%) sodium hydroxide, followed by two treatments with 10% by volume

of 93% H_2SO_4, the gasoline was found to have the following properties:

density at 20 °C - 0.7446
solubility in 91% H_2SO_4 - $< 1\%$
sulfur, % - 0.098

The refining loss was 12% by volume, made up for the most part by evaporation of light ends during agitation. The figure is very much higher than would be obtained in refinery practice. The odor of the finished product was sweet, the corrosion good, and the color water white, and the gasoline remained unchanged in color after standing for several months. During this time no gum formed. As would be expected from the refining method employed, the stock was doctor pass.

2. Kerosene. The total oil distilling between 225 °C and 260 °C was collected and samples taken for analysis. The more important data is given below.

Crude Kerosene,
Density at 20 °C - 0.8920
solubility in 91% H_2SO_4 - 21%
sulfur, lamp method, % 1.32

Refining by repeated treatment with 93% H_2SO_4 yielded a water white product with the following properties:

Density @ 20 °C	0.8904
solubility in 91% H_2SO_4	$<1\%$
sulfur, %	0.34%

A large refining loss of 20% was encountered. This was to be expected from the high solubility of the

unrefined stock in 91% H_2SO_4. The value given, 21%, consists to a large extent of sulfur compounds.

Experiment 2-5.

From the results obtained in the two experiments above it became apparent that an improved method of handling the pressure distillate was necessary in order to curtail losses. This was accomplished by the use of a second condenser in series with the first, a valve connecting the two being opened when it was desired to draw off a sample. The closed system at atmospheric pressure used in conjunction with the second condenser is shown in the flow diagram (figure 20). The semi-continuous hydrogenation of McMurray bitumen carried out in experiment 2-5 under these improved handling conditions is described below.

TABLE XVIII

Operating conditions

Experiment number	2-5
Time, hours in operation at temperature	32
Initial pressure, cold. lb/sq. inch	1800
Average of maximum pressures, hot	2750
Charge (bitumen) to autoclave, grams	5130
Catalyst, molybdic oxide, grams	100
H_2 absorbed, % by weight of bitumen	2.1

The conversions of bitumen to various products that were obtained under the above conditions are presented in table XIX.

TABLE XIX

Materials recovered, % by weight of charge

(1) to hydrocarbon gases	5.8%
(2) to hydrogen sulfide	1.1
(3) to water	0.6
(4) to pressure distillate	49.2
(5) to coke	26.8
(6) to residual tar (in autoclave)	4.3
(7) loss	12.2

From the above data it may be seen that the tabled loss is a decided decrease over the values recorded in previous experiments. The corresponding increase in yield of light oils (pressure distillate) is readily seen. The formation of coke, considerably higher than recorded in the previous experiment, has been attributed to the longer time of operation. That a shorter period of operation must be used is not a necessary conclusion, and attempts must be made to hydrogenate bitumen without serious formation of coke in runs considerably longer than 32 hours to obtain a process suitable for commercial application. Two remedies immediately suggest themselves, and later experimentation will be seen to have developed along these lines. The remedies suggested are

1. Gas circulation, resulting in immediate distillation of stabilized volatile oils before further cracking occurs with the formation of coke by polymerization.

2. Supported catalysts whereby the possibility of settling out will be precluded.

Analytical data on the recovered products from experiment 2-5 are given below.

1. Crude pressure distillate.

In this experiment two procedures were resorted to in obtaining the distillate. By the first method the autoclave temperature was reduced to 275 °C and the autogenous gases completely removed, the stillhead temperature being maintained at 225 °C. Under these conditions distillation of the autoclave oil through the vertical column resulted in the collection of gasoline in the condenser having an end point of approximately 250 °C. This practice is common in refinery technique, where a similar procedure, known as "flashing" is used. The crude distillate obtained was found to have the following properties:

Density at 20 °C	- 0.7766
solubility in 91% H_2SO_4	- 9%
sulfur, %	0.72
% distillate to 225 °C	81.1

The second method of obtaining low-boiling oils was the usual high-pressure practice described in procedure A, whereby a sudden bleeding of the autoclave gases resulted in a pressure drop of 3000 #/sq. inch to 2000 #/sq. inch accompanied by rapid distillation of oil. By this method a straw colored distillate having the

following properties was obtained:

Density @ 20 °C	- 0.8250
solubility in 91% H_2SO_4	18%
sulfur, %	1.10
% distillate to 225 °C	72.3%

The combined distillates to 225 °C end point were refined by the usual treatment. Refining data is presented below.

Refined gasoline stock.

Density at 20 °C	- 0.7608
solubility in 91% H_2SO_4	1%
sulfur, %	0.088
refining losses	12%

No gum tests were carried out. The stock was water white, color stable, doctor pass, and sweet in odor. No color developed after standing for one month. The total refined gasoline represented a yield of 33.8% of the bitumen charged.

An Egloff-Morrell (18) analysis of the refined gasoline showed the following:

Unsaturated	hydrocarbons	7.5%
Aromatic	"	14.7
Naphthene	"	47.5
Parraffin	"	30.3

On this basis the gasoline had an aromatic equivalent of 28.5.

i.e. the antiknock value was equal to that of a paraffinic mixture containing 28.5% of aromatics (18).

Conclusions.

From the results obtained in semi-continuous

hydrogenation of bitumen it may be concluded that

(1) The formation of excessive amounts of coke in experiment 2-3 is an unfavorable result of operation in the absence of a catalytic agent.

(2) The difficulties involved in obtaining a continuous distillation of volatile oils under pressure point to the installation of a gas circulating pump which would allow a rapid current of hydrogen to pass through the autoclave without the drop in pressure consequent to the bleeding operation employed in experiments to this point. At the same time a smaller coke production would occur due to a continous maintenance of a sufficiently high partial pressure of hydrogen to preclude the polymerization reaction which would otherwise follow cracking. The use of a gas circulating pump would also make possible the installation of a suitable oil scrubber to remove gaseous or volatile hydrocarbons from the autogenous gases under pressure.

(3) The appearance of a high coke yield in experiment 2-5 points to the use of supported catalysts in order that settling out of the catalytic mass may be precluded in experiments of long duration.

B. Continuous Hydrogenation of McMurray Bitumen

As suggested in the conclusions drawn from the preceding investigation a gas circulating system and a

high-pressure oil scrubber were added to the equipment and used for all following experiments. The arrangement of apparatus and the methods of manipulation from this point onward coincide with the flow diagram (figure 20) and the procedure outlined as method B.

In the three experiments discussed together in what follows, the effect of rate of gas flow and the effect of a suitably supported catalytic mass upon the yields of gasoline and coke have been determined.

In experiment 2-6 the effects of the use of an unsupported catalyst and of a high rate of gas flow have been studied, while in experiment 2-7 a lower rate of gas flow under the same catalytic conditions was used. In an attempt to increase the throughput the temperature was raised to 435 °C, and it will be seen later that the large amount of hard coke formed indicated the use of more moderate temperatures.

In these experiments the stillhead temperature was found to vary directly with the gas-flow rate, so that this temperature has been recorded in all of the experiments. The actual flow rates are not obtainable from the equipment in use and only a rough idea of the change in rate of gas flow was possible by observation of the stillhead temperature.

With the data furnished by these two experiments

at hand, experiment 2-8 was carried out under immensely improved operating conditions. A comparison of the three experiments is given in the following tables.

TABLES XX

Operating Conditions for Continuous Hydrogenation

Experiment number	2-6	2-7	2-8
Time, hours in operation at temperature	4+7	13.5	26
Autoclave temperature, °C	425	435	425
Stillhead temperature, °C	300	260	210
Rate of gas flow (approximate)	Max.	¾ Max.	2/3 Max.
Average operating pressure, hot	1900#/sq. in.	2000	2300
Charge (bitumen) to autoclave	3050	5575	4832
Catalyst, MoO_3, grams	100	125	31 on porcelain

The effect of the variation of these conditions upon the products formed is difficult to accurately judge. As an example the coke produced (Table XXI) in 2-7 may be attributed to one or both of

(1) A higher operating temperature

(2) An unsupported catalyst.

Nevertheless an attempt can be made to trace the reasons for coke formation and various other phenomena which took place, from the relations between the operating conditions and the yields of products as tabulated in the following table.

TABLE XXI

The Effect of Autoclave Temperature

Experiment number	2-6	2-7	2-8
Autoclave temperature, °C	425°C	435°C	425

% bitumen to oil	36.4	45.2	66.4
% bitumen to coke	19.0	12.1	6.0
% bitumen to gas		11.1	8.6

The figure on gas formation in experiment 2-6 is not available. The cause of high coke formation in 2-6 in spite of the moderate temperature may be traced to operation in two stages. It is probable that the coke formed in the first stage settled in the bottom of the autoclave during the quiescent period between stages, carrying the catalyst with it and caking to a hard mass. As a result coke formation became excessive in the second stage of operation because of the absence of a catalyst. A comparison of the coke yields in 2-7 and 2-8 shows the beneficial effects of the lower temperature and the supported catalyst. The high yield of oil reported in 2-8 is considered due to the use of a supported catalyst and a moderate gas-flow rate.

The effect of the rate of gas flow and stillhead temperature is shown in Table XXII.

TABLE XXII

2. The Effect of Stillhead Temperature and Rate of Gas Flow

Experiment number		2-6	2-7	2-8
Stillhead temperature, °C		300	260	210
Rate of gas flow (approximate)		max.	3/4 max.	2/3 max.
% total distillate boiling below 225°C		13%	43.6%	55.9%
Egloff-Morrell Analysis of distillate boiling below 225 °C	unsaturates		6.7	8.0
	Aromatics		12.5	11.1

naphthenes		30.4	24.9
paraffins		50.4	56.0
Viscosity of lubricating oils from higher boiling pressure distillate			
Saybolt (Universal Tip) at 100 °F	371"	98"	298"
@ 130 °F	218"	61"	127
210 °F	68"	36	47.5
Carbon residue of bottoms from vacuum distillation	0.68%	3.51%	1.04%
Crude distillate, solubility in 91% H_2SO_4	33%	20%	16%

The above table shows that a marked decrease in low-boiling distillates results from an increase in stillhead temperature which, as mentioned before, is partially controlled by the rate of gas flow. The Egloff-Morrell analysis of the 225 °C end point fraction does not offer any conclusive evidence regarding the unsaturated content of the gasoline, but the figures on solubility in 91% sulfuric acid show that compounds rich in sulfur as well as large amounts of unsaturates are distilled through the column at high stillhead temperatures and with rapid gas circulation. This fact was evidence of incomplete reaction as operation under satisfactory conditions results in the gasification of the greater part of the combined sulfur as hydrogen sulfide.

The viscosities of the lubricating oils obtained by vacuum distillation of the high-boiling ends of the pressure distillate have been entered in the above table since the quality of the gasolines obtained should bear

some relationship to the lubricating value of the heavier oils. The evidence is not conclusive, however. The oil obtained in exp. 2-6 corresponds to an exceptionally high grade lubricating oil of viscosity S.A.E. 20. The oil was straw-colored, the good color reflecting the low conradson carbon value found to be less than 0.05%. The oil obtained in exp. 2-8 was also of a very high grade, and corresponded to an S.A.E. 10-20 lubricating oil.

The high gas rate and high temperature used in exp. 2-7 resulted in the rapid distillation of an oil which had probably not become completely stabilized or hydrogenated, since the viscosity measurements on the oil bore evidence of a distinctly inferior lubricating value. This inferiority in grade was borne out by the dark color that developed after standing for a short time.

The high quality of the oil obtained in exp. 2-6 may be explained on the grounds of technique, since the stillhead temperature was on two occasions raised to higher than 325 °C. This resulted in the rapid distillation of high-boiling oils which had probably remained in the autoclave for a sufficient length of time to become completely stabilized.

The effect of an increase in pressure is not readily determined on account of the large number of variable conditions employed. In the light of the ex-

perimental evidence obtained by Boomer and Saddington (10) in a preliminary investigation on a batch scale it is reasonable to suppose that the yield of oils would in general vary directly as the partial hydrogen pressure.

The greater part of the analytical data obtained regarding the products from these experiments has been reserved for individual study. The results are given below.

Experiment 2-6.

This experiment was commenced with a view to at least twelve to twenty-four hours operation continuously but after four hours treatment hydrogenation was suspended due to failure of the electric heaters. The second attempt at operation met with little success because of excessive coking due no doubt to caking of the catalyst with coke during the time required for repairs. The data regarding yields has been presented in Table XXIII. With regard to the figure on coke production, a rapid combustion developing within the autoclave when it was opened while hot to remove the contents resulted in a substantial loss. The tabled conversion, based on the weighed solid residue recovered, is consequently low by this amount.

TABLE XXIII

Conversion of Bitumen, % of charge.

(1) to oils	36.4%
(2) to water	1.2
(3) to coke	19.0 approximately
(4) to hydrocarbon gases	10.0 approximately
(5) to hydrogen sulfide	3.6
(6) Loss	not available

The residual tar in the autoclave showed the following properties:

(1) Conradson carbon	17.1%
(2) percent asphaltenes	15.0%

The crude oil had a density at 20 °C of 0.9194 and the solubility in 91% H_2SO_4 was 33%. Distillation analyses of the crude distillate is given in Table XXIV.

TABLE XXIV

Distillation Data

Distillation in a 27" air jacketed fractionation column packed with spiral stainless steel turnings, with crude pressure distillate.

I.B.P.	28 °C
10%	- 92 °C
20%	- 136 °
30%	- 160 °
40%	- 180 °
50%	- 192°
60%	- 211 °
70%	- 228 °
Bottoms	- 28%
Loss	- 2%

Crude gasoline fraction to 225 °C had

density @ 20 °C	- 0.7544
solubility in 91% H_2SO_4	- 8%
Sulfur, %	0.44

Refined to give a stable doctor pass, water white, gasoline, S - 0.076%

Refining loss - 13%

Vacuum distillation of bottoms from crude pressure distillate at 12 mm. Hg. pressure.

Charge - 350 c.c.
I.B.P. - 124 °C.
to 190 °C - 115 c.c - fraction A
190 - 225 °C - 111 c.c. - fraction B
225 - 250 °C - 58 c.c.)
250 - 275 °C - 34 c.c.) - fraction C
275 - 300 ° - 17 c.c.)
Bottoms - 14 c.c.
Loss - 1 c.c.

Fraction A was a high grade spindle oil. Fractions B and C were combined and a light acid treatment was sufficient refining treatment. The resulting oil was a high grade lubricating oil corresponding to S.A.E. 20. Viscosity measurements have been presented earlier (Table XXII).

Experiment 2-7.

A successful experiment carried out at 435 °C for 13.5 hours continuous operation resulted in the following conversions.

TABLE XXV

Conversion of Bitumen, % of Charge.

(1)	Conversion to oils, %	45.2
(2)	to water, %	2.7
(3)	to hydrogen sulfide	4.1
(4)	to hydrocarbon gases	11.1
(5)	to coke	12.1
(6)	Residual tar in autoclave	1.5
(7)	Losses	13.3

A relatively high coke yield indicates that the temperature used, 435 °C, allowed a rapid cracking reaction with consequent excessive polymerization to coke. Analytical data on the constitution of the gasoline by

Egloff-Morrell analysis and on the lubricating value of the heavy oils have been presented in Table XXII. Further data on the properties of the crude pressure distillate are given below in Table XXVI. A characteristic property of natural and cracked gasolines is a lowering in anti-detonation value with increase in molecular weight. It has been found, however, that gasolines produced by the hydrogenation of crude petroleum, asphalt, etc., offers an interesting exception to this tendency, and it has been stated (29) that the anti-knock value of the higher boiling constituents of gasoline produced by hydrogenation is greater than that of the more volatile ends. To determine whether this important characteristic is possessed by gasoline produced by bitumen hydrogenation a sample of crude gasoline with a 225 °C end point was fractionated to produce the following cuts:

Fraction A. I.B.P. 28 °C to 125 °C E.P.
Fraction B. 125 °-175 °C.
Fraction C. 175 -225 °C.

The Egloff-Morrell analyses and aromatic equivalents of these fractions are given below.

	Fraction A.	Fraction B.	Fraction C.
Unsaturates	6%	7%	7%
Aromatics	2.0	13.6	22.0
Naphthenes	39.6	30.8	20.8
Paraffins	52.4	48.6	50.2
Aromatic equivalent	13.1	22.7	28.6

The aromatic equivalent varies directly as the anti-knock value. Hence it may be concluded that the

less volatile fractions of gasoline produced by hydrogenation of McMurray bitumen have an appreciably higher value as antidetonants than have the lower fractions and offer possibilities as "safety" fuels.

Distillation analyses similar to those presented for experiment 2-6 have been carried out and the results given in Table XXVI.

TABLE XXVI

Distillation Data

Distillation in a 27" air jacketed fractionation column packed with spiral stainless steel turnings with crude pressure distillate.

I.B.P. 24 °C.
10% - 83 °
20% - 122 °
30% - 143 °
40% - 164 °
50% - 190 °
60% - 210 °
70% - 225 °
Bottoms - 27%
Loss - 3%

The crude distillate to 225 °C had the following properties: Density at 20 °C - 0.7481
solubility in 91% H_2SO_4 - 7%
sulfur, % 0.28%
On refining a water white gasoline was prepared with a sulfur content of 0.086%. The refining loss was 9% by volume.

The bottoms from the above fractionation were distilled in vacuo through the 27" column under a pressure of 2-4 mm. Hg.

Charge to still 260 c.c.
I.B.P. 103 °C.
103-175 °C 108 c.c.
175-265 °C 146 c.c. - lubricating oil.
Bottoms 6 c.c.

The lubricating oil obtained was of very low grade and of high color. A large amount of decomposition occurred

in distillation. The viscosity measurement (Saybolt, Universal Tip) are given as follows:

98" at 100 °F.
61" at 130 °F.
36" at 210 °F.

Experiment 2-8.

This was a satisfactory experiment upon the continuous hydrogenation of McMurray bitumen at 425 °C in the presence of ~~a~~ MoO_3 supported on unglazed porcelain as catalyst. The high oil conversions, with low gas and coke yields show that more suitable operating conditions have been employed in this experiment. The conversions obtained have been recorded below in Table XXVII.

TABLE XXVII

Conversion of Bitumen, % of charge.

(1)	to oils	66.4%
(2)	to water	1.55
(3)	to hydrogen sulfide	4.0
(4)	to coke	6.0
(5)	to hydrocarbon gases	8.55
(6)	Residual tar in autoclave	5.4
(7)	losses	8.1

Hydrogen absorption, % by weight: 2.94%.

An inspection of Table XXVII reveals that a considerably higher oil yield has been recovered than has been previously reported. Along with this high yield is tabled the low value for losses. With regard to the coke yield, it has been previously stated that the mineral content of the bitumen is as high as

2%, so that the recovered solid residue consists largely of inorganic material. By ashing a representative sample it was found that a mineral residue amounting to 76.8% of the coke remained.

The conversion to hydrogen sulfide agrees closely with the previously tabled value of 4.1% in experiment 2-7, and considering the total sulfur content of the original bitumen was between 4 and 5% this figure represents an almost complete gasification of the combined sulfur.

The more accurate data available in this experiment allowed a calculation of the hydrogen absorption. The tabled value of 2.94% was determined from the total hydrogen charged less the hydrogen recovered from all the waste gases and the residual gases remaining at the end of the experiment, and represents a fairly complete absorption according to the data presented by Boomer and Saddington (10).

Distillation analyses of the pressure distillate have been tabled below. The gasoline fraction was refined to a stable water white oil whose properties have also been presented in the following table.

TABLE XXVIII

Pressure Distillate. Fractionation and refining data.

I.B.P.	27 °C	140 °C	35.2	225 °C	84.8
over at	40 °C - 2%	160	45.8	Bottoms	15.0
	60 - 6%	175	54.0	Loss	0.2
	80 - 11.4	190	62.4		
	100 - 17.6	200	68.6		
	120 - 25.4	210	73.8		

Properties of crude distillate to 225 °C.

Density @ 20 °C	0.7718
Solubility in 91% H_2SO_4	10%
Sulfur, %	

The oil, on refining, gave the following tests as carried out in the Imperial Oil Inspections Laboratory, Calgary, Alberta.

AP.I Gravity	53.4
Sulfur	trace.
Doctor	pass.
Acid Heat	7 °F.
Corrosion, Hg.	O.K.
Gum	41.2 mg.
Octane No.	61.0
Initial B.P.	122 °F

A.S.T.M. distillation

over at 60 °C	1.5%
70	3
100	18
105	21
140	50
177	82
190	89
200	93
204	93½
210	94½
225	95½
238	96½
F.B.P.	464 °F

The bottoms from the distillation to 225 °C were distilled through the 27" column under 2-4 mm. Hg. pressure.

I.B.P.	102 °C.		
to 140 °C	4.8%	200-225°C	14.3%
140-175°C	20.4	225-240°C	9.0
175-188°C	21.9	Bottoms	1.2
188-195°C	18.5	Loss	1%
195-200°C	9.9		

Fraction from 200-225 °C taken as lubricating oil, light grade. The viscosity measurements given below

show this oil to possess high qualities in this regard.

Saybolt viscosity (Universal Tip) at	100 °F	- 298"
	130 °F	- 127"
	210 °F	- 47.5"

The relatively high yield of crude kerosene and fuel oil obtained from the pressure distillate in the above experiments suggested the possibility of increasing the gasoline yield by recycling the heavier oil. In order to determine approximately the extent to which decomposition of this oil would occur under the operating conditions employed, an experiment was carried out in the 1800 c.cm. autoclave using bottoms from the distillations to 225 °C of pressure distillates as the charge. The result of this treatment has been given below. It will be noted that hydrogenation has taken place without any coke formation whatsoever. The low yield of light oil obtained shows that the material hydrogenated was exceedingly stable, and that more strenuous temperature conditions must be employed.

TABLE XXIX

Batch Hydrogenation of Middle Oil and Heavy Oil from continuous hydrogenation of Bitumen.

Experiment No. 199	
Temperature of operation, °C	425.
Catalyst, MoO_3	5%
Hours in operation at temperature	2
Initial pressure, cold	1000 #/sq. inch
Max. pressure, hot	2100 #/sq. inch
Hydrogen absorbed, % by weight of oil charged	0.9%
Conversion of oil to gas	2.53%

Conversion of oil	to coke	0.0%
	to light oil (FBP 225°C)	12.8
	to heavy oil (IBP.225°C)	83.4
	loss	1.3

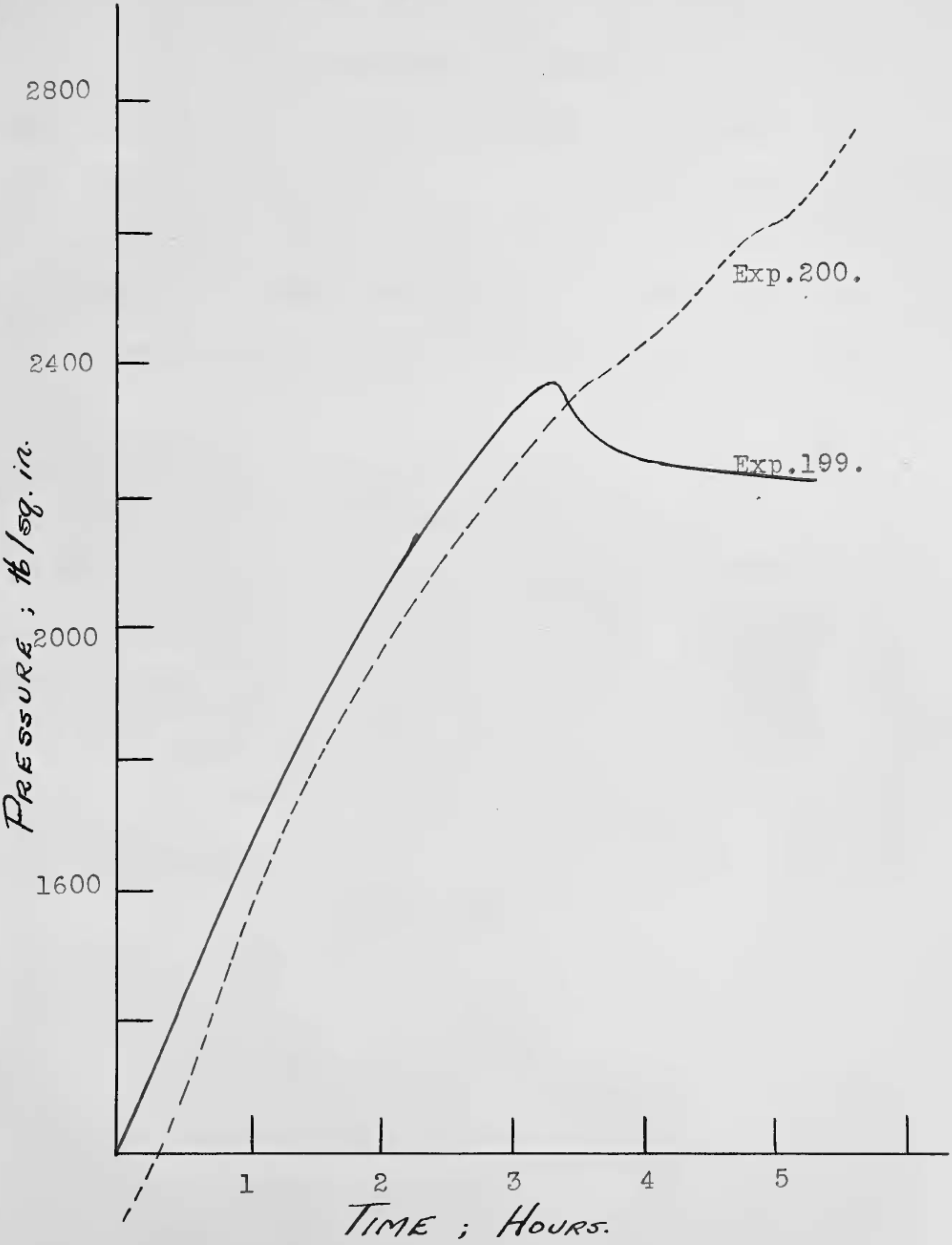
Hence it may be concluded that at 425 °C the recycling of heavy oil would not result in coke formation, but the stability of the oil would be such as to make conversion to light oil very slow. In order to determine the effect of more strenuous operating conditions on the susceptibility of this material to hydrogenation, an experiment similar to 199 was carried out at 470 °C. The yields obtained were:

Experiment 200	
(1) Conversion to gas	20.51%
(2) Conversion to coke	0.93%
(3) Light oil (F.B.P. 225 °C)	38.37%
(4) Heavy oil (I.B.P. 225 °C)	36.74%
(5) Loss	3.45%
Hydrogen absorption, %	1.4

Thus it is seen that recycling at the higher temperature would result in the formation of large amounts of volatile oils, as well as a considerable yield of gas. The coke yield shows that continuous operation at 470 °C is feasible.

The pressure-time charts of exp's. 199 and 200 have been shown in figure 2D. The drop in pressure in exp. 199 is roughly equivalent to the hydrogen absorption, the extent of gas formation being small. In exp. 200 a continued rise in pressure at constant temperature is a result of the high gas formation that occurred.

Figure 20.



2800
2400
2000
1600
1
2
3
4
5
Exp.200.
Exp.199.
Pressure ; lb/sq. in.
Time ; Hours.

On account of the possibility of recycling heavy oil at 425 °C without coke formation, and with partial conversion to more volatile oils, the following three experiments on the continuous hydrogenation of bitumen have been carried out. In these experiments the heavy oils from fractionation to 225 °C of pressure distillates have been recharged to the autoclave. The low viscosities of the oils made a more easily handled charge when mixed with fresh bitumen than was obtained with the bitumen alone.

Experiment 2-9.

In this experiment the catalyst used was molybdic oxide supported on pumice. The extremely active nature of this material was shown by excessive coke formation. The run was of short duration on account of plugging of one of the gas lines with tar and coke. Pressure measurements became erratic and gas circulation was impossible. The yields obtained have been given in Table XXX below.

TABLE XXX

Experiment number 2-9		
Temperature, °C	425.	
Hours at temperature	13.	
Bitumen to autoclave, grams	3835	
Conversion of bitumen, as % of charge.		
(1) 220 °End Point Gasoline		19.7%
(2) Heavy oil and unchanged tar		11.0%
(3) Coke		50.3%
(4) Hydrogen sulfide (approx)		2%
(5) Hydrocarbon gases (approx.)		6.3%
(6) Losses (approx.)		11 %

The gas and hydrogen sulfide yields were difficult to estimate on account of the gas lines being plugged, resulting in incomplete removal of gaseous products through the absorbers and meter. The tabled values were estimated from the data available.

Experiment 2-10.

The effect of recycling heavy oils using molybdic oxide supported on porcelain at 425 °C was studied in exp. 2-10. The catalyst was placed in a steel tray held immovable in the autoclave, so that catalytic hydrogenation was possible in both the liquid and vapor phase. The results of operation for twenty hours have been presented in Table XXXI.

TABLE XXXI

Experiment number	2-10
Temperature, oC	425
Catalyst, MoO_3 on porcelain Vapor and liquid phase hydrogenation possible.	
Hours in operation at 425 °C	20.
Bitumen to autoclave, gms.	4560.
Conversion of bitumen, as % of charge.	
(1) to 220 °C end point gasoline	48.3%
(2) to heavy oil and unchanged tar	28.1%
(3) to water	2.8%
(4) to hydrogen sulfide	4.0%
(5) to coke	6.8%
(6) to hydrocarbon gases (approx.)	6.0%
(7) Loss	4.0%

The extremely low loss recorded in Table XXXI was due to operation without leaks occurring. The beneficial effect of preheating the tar and hydrogen to 350 °C has been demonstrated by a low coke and gas yield.

The extremely unstable constituents probably decomposed at a slow rate so that hydrogenation was complete before excessive cracking occurred with consequent coke formation. The total recovery of liquid products, 76.4% of the charge, represents a high value in comparison to earlier results.

Experiment 2-11.

The hydrogenation of bitumen under experimental conditions similar to 2-10 has been undertaken in a thirty hour experiment. In this experiment the large amounts of stable middle oil which accumulated in the autoclave during the first twenty hours operation made further reaction difficult, so that the temperature of the reaction chamber was raised to 435 °C in order to promote decomposition of these oils. The high yield of pressure distillate obtained by this means, together with the low coke formation which resulted illustrates the advantage of higher temperatures in the decomposition of stable middle oil. The yields of products obtained in this experiment have been recorded below in TableXXXII.

TABLE XXXII

Experiment number	2-11
Temperature, °C	425-435
Hours in operation at 425°C	22
" " " " 435°C	8
Bitumen to autoclave, grams	3330.
Heavy oil from previous hydrogenation of bitumen, grams	585.

Total charge to autoclave, grams	3915.
Conversions of bitumen, % of charge.	
(1) 220°C E.P. gasoline.	53.5%
(2) to heavy oil (I.B.P. 225°)	22.0%
(3) to mineral matter from bitumen	2.3%
(4) to coke	1.9%
(5) to H_2S	3.2%
(6) to water	0.7%
(7) to hydrocarbon gases (approx.)	6.5%
Losses (approx.)	10.0%

It may be seen from an examination of the above Table that a decided increase in the yield of pressure distillate has been obtained, while the very small value given for coke formation is evidence of a very favorable reaction. The exact figures on gas formation are not available, so that the tabled losses may be in error by the same amount as the error in the gas calculations. The total bitumen and heavy oil to the autoclave, as given in the above table, represents the fresh bitumen charged plus heavy oil obtained from previous experiments. Hence the actual material charged to the autoclave was much greater in amount than has been tabled, heavy oil from the tabled charge having been added for recycling from time to time. The yield of hydrogen sulfide tabled is in fair agreement with the values obtained in former experiments. The fresh bitumen had an ash content of 2.9% and on this basis the actual coke formation was calculated by difference between total recovered solid residue (less

the catalytic mass) and the known mineral content of the bitumen charge. It will be seen that roughly 60% of the solid residue obtained is comprised of mineral matter and this material is unavoidably present.

Summary.

The hydrogenation of McMurray bitumen has been studied under continuous-batch and semi-continuous operating conditions and yields of gasoline amounting to over 50% of the bitumen have been obtained without the formation of appreciable amounts of coke. It has been demonstrated that the gasoline yield may be materially increased by recycling the heavy oils formed upon hydrogenation.

A considerable amount of equipment has been devised, by means of which a suitable operating technique may be used.

The beneficial effect of catalyst supports, by means of which hydrogenation may be promoted in both the vapor and liquid phases, has been shown by the use of a suitable tray carrying the catalytic mass.

The oils obtained have been, for the most part, unusually low in sulfur content, considering the high concentration of sulfur in the original tar, extensive elimination of sulfur occurring as hydrogen sulfide. The more volatile oils formed may be refined to high quality gasolines low in sulfur, water white and stable in color, and high in anti-knock value. Lubricating oils of exceptionally low carbon residue and extremely satisfactory viscosity properties have been obtained.

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