TENDENCY TO SMOKE OF ORGANIC SUBSTANCES ON BURNING. PART II.—SMOKE PRODUCTION AND BURNING CHARACTERISTICS OF HYDROCARBON GELS.

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Summary.

In a previous paper a description has been given of the tendency of organic substances to smoke on burning and in the present paper the smoke production during the burning of hydrocarbon gels has been investigated. The weight of smoke formed has been determined and the obscuring power of the smoke cloud measured by an optical density method. The burning characteristics of the gels were also examined. These burning characteristics have been assessed by determining the unburned residue resulting from the combustion of a constant weight of gel with a constant burning area exposed, together with the time of burning and maximum and mean flame heights.

The effect of the following variables on the above measurements has been investigated and discussed in detail :

    (i) Chemical composition of the hydrocarbon base.
    (ii) Volatility of the hydrocarbon base.
    (iii) Viscosity of the gel.

For reduction of smoke formation, the composition of the hydrocarbon base was found to be most important, while the volatility was equally important in controlling the burning characteristics. The viscosity of the gel had no apparent effect on smoke production.

Introduction.

Solid fuels consisting of hardened or thickened liquids have long been used for small-scale heating processes such as curling-tong heaters, laundry irons, portable spirit stoves, and firelighters. The earliest thickened liquid employed for such processes was a soap-solidified alcohol, but the use of this product is no longer extensive, as it tended to liquefy on burning, hence giving rise to serious fire risk to the user. Incrustation, excessive inorganic residues, and unsatisfactory burning, especially when most of the alcohol had been burnt, were other objections, so that the soap-thickened product was eventually replaced by an alcohol–nitro-cotton gel which did not have this disadvantage.

The so-called " Meta " made from compressed metaldehyde has been marketed and used extensively for this purpose, and paraformaldehyde and hexamethylenetetramine, both in compressed form, have also been proposed in this connexion.

In the United States a gel manufactured by thickening kerosine has been in use as a beacon, flare, or source of emergency heat. During the war similar hydrocarbon gels have been widely used as filling materials for fougasses and incendiary bombs.

The smoke production from various hydrocarbon gels has been measured, and the methods employed and results obtained are described in this paper. The burning characteristics—namely, time of burning, maximum recorded flame height, mean flame height, unburned carbon, and unburned residue —have also been determined for all thickened fuels investigated.

3 A

APPARATUS.

The various gels examined were burned, under standard conditions, in a metre-cube box provided with glass panels for observation. One side formed a door which could be clamped to render the cube air-tight. An air-blower was fitted by means of which a smoke cloud could be cleared from the box in about five minutes. The box contained a thermometer, an electric spark device by which the gels were ignited, a metre rule fixed in a vertical position for flame-height measurements, and a fan for rendering the smoke clouds homogeneous. For the purpose of estimating the amount of smoke produced by the combustion, a filter was attached (externally) to the cube by which a measured volume of air charged with smoke could be drawn through a filter-paper on which the carbon was deposited.

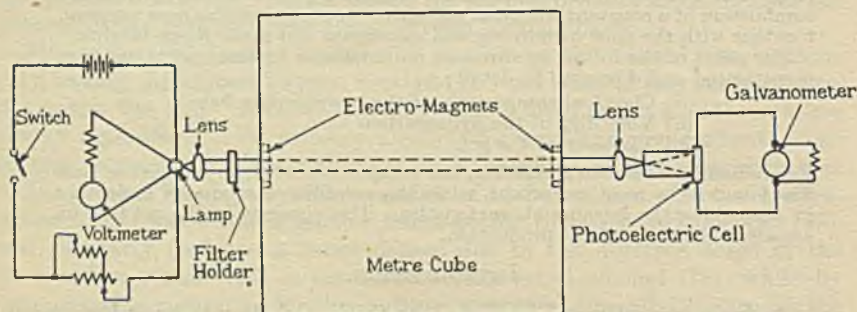The obscuring effect of the smoke was measured optically using the

FIG. 1.

METRE CUBE OPTICAL SYSTEM.

system shown diagramatically in Fig. 1. A six-watt bulb, run at constant voltage to give a uniform source of light, was set at the focus of a convex lens. The parallel beam thus produced passed horizontally through the metre-cube box to a second convex lens on the other side, by which it was focused on to an aperture. The light passing through the aperture then passed on to the surface of a rectifier photo-electric cell, the temperature of which was controlled at $25.0°$ C by a constant-temperature water-jacket. The current from the cell passed to a galvanometer and its deflections were indicated by the use of a lamp and scale. Thus the galvanometer deflection gave a measure of the quantity of light incident on the cell.

During an experiment, smoke tended to deposit on the glass in the path of the light beam, giving a very slightly lower galvanometer deflection. It was shown, however, that if no smoke were deposited before the gel ceased burning, then no correction was necessary. To eliminate the necessity of any correction, circular electro-magnets were attached to the inside of the glass of the cube, to hold metallic covers over the glass in the path of the beam during the burning of the gel; these covers were released by breaking the electric circuit when combustion ceased and before measurements were made.

PROCEDURE.

1·50 grams of gel were weighed in the apparatus, illustrated in Fig. 2, and designed to prevent evaporation. Slightly more than 1·50 grams were introduced into the brass dish (1 in diameter, $\frac{3}{8}$ in deep, approximate weight 34 grams) and the lid screwed tightly in position, a fibre packer making an air-tight joint. Slight air pressure was then applied through the tap in the lid by means of a hand bellows and a thread of gel ejected through a small hole in the base of the dish. This thread was cut away with the
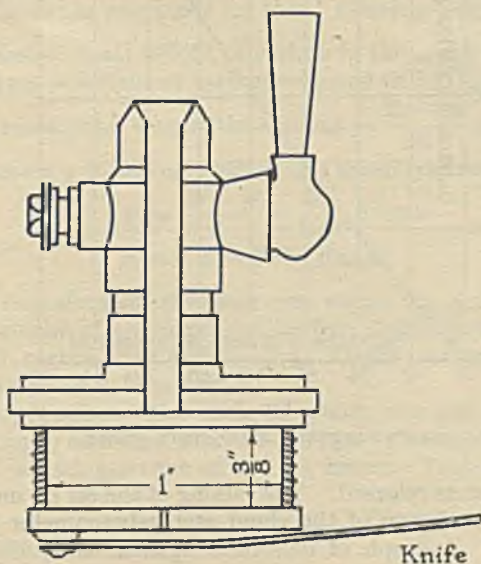

FIG. 2.

cutter attached to the bottom of the dish and arranged to swivel over the hole. The apparatus was then re-weighed and this process repeated until exactly 1·50 grams remained in the dish. The top was left in position until immediately before ignition, which was initiated by the passage of a spark.

The following data were measured.

1. *Optical Density.*

Optical density for one metre was used as a measure of the obscuring power of the smoke produced and may be defined as :

$$\text{Optical density} = \log_{10} \frac{1}{\text{decimal fraction of the incident light transmitted}}.$$

The galvanometer was first calibrated with the cube empty, by interposing neutral light filters of known percentage transmission into the beam and observing corresponding deflections. A calibration curve of

galvanometer deflection against percentage of incident light transmitted
was plotted and a typical curve is shown in Fig. 3.

The gel was ignited and when burning ceased (" zero-time ") the fan was
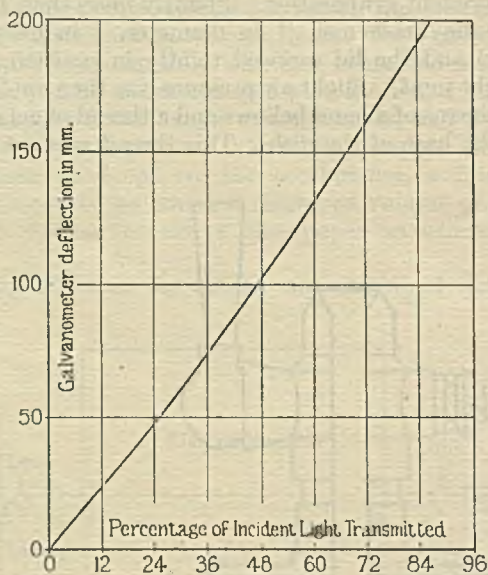

FIG. 3.

GALVANOMETER CALIBRATION CURVE.

started and the covers released.   The mixing of the air by means of the fan
caused partial coagulation of the cloud and galvanometer deflection was
noted with time.   A graph of deflection against time, Fig. 4, gave the
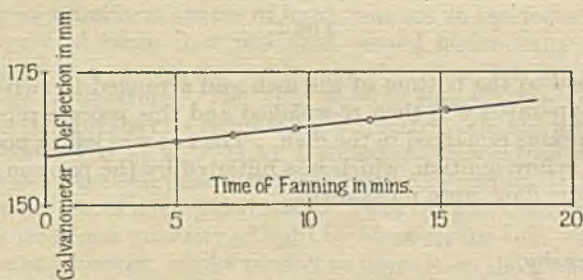

FIG. 4.

GRAPH TO OBTAIN GALVANOMETER DEFLECTION AT " ZERO " TIME.

" zero-time " deflection by extrapolation and the corresponding trans-
mission was obtained from the calibration curve.   Hence the optical
density at " zero-time " was obtained.   The lower the optical density, the
lower the smoke-producing property of the gel.   Precision estimated as ±5
per cent.

2. *Wastage.*

(*a*) *Unburned Carbon.*—The particle size of the cloud from these gels varies over a wide range and, whilst some of the smoke remains in the air, the larger particles are deposited on the floor of the cube. These quantities were measured separately, the amount in the air being estimated after 20 min air mixing by the fan.

The weight of carbon in the air was obtained by drawing 100 litres of the cloud through a weighed dry filter-paper, drying the filter-paper and carbon and reweighing. A small aperture was left in the side of the cube so that the volume of cloud removed was replaced by fresh air and approximate allowance was made for this " dilution " as follows :

If x grams = total weight of carbon in the cloud (1000 litres)
and y grams = weight of carbon removed in 100 litres

$$\therefore \quad \text{mean total weight throughout} = \frac{2x - y}{2} \text{ grams.}$$

Assuming y to be removed at this mean concentration

$$\therefore \quad y = \frac{2x - y}{2} \times \frac{100}{1000} \text{ grams}$$

Hence $x = 10 \cdot 5 y$ grams.

The carbon deposited on the floor was swept up, dried, weighed, and added to the weight of air-suspended carbon determined as above. The total unburned carbon was expressed as weight per cent of gel taken. Precision estimated as ± 15 per cent.

(*b*) *Unburned Residue.*—The dish in which the gel was burned was weighed, first empty and then with the residue. The unburned residue was expressed as a weight per cent of the gel taken. Precision estimated as ± 10 per cent.

3. *Burning Characteristics.*

(*a*) *Time of burning.*—This is observed from the first ignition until the flame was completely out and measured in seconds. Precision estimated as ± 10 per cent.

(*b*) *Mean flame-height.*—The flame height in centimetres was observed after each 30 sec during burning and the mean value taken. Precision estimated as ± 10 per cent.

(*c*) *Maximum flame-height recorded.*—This was obtained from the mean flame height records. Precision estimated as ± 10 per cent.

All the data given in the following pages for each individual gel are, unless otherwise stated, the average of six different determinations.

A relationship between optical density and unburned carbon, which, of course, appears as smoke, obviously exists and is plotted in Fig. 5.

EFFECT OF HYDROCARBON BASE.

Variation of the composition of the hydrocarbon base has a great influence on smoke formation. It is, of course, well known that among hydrocarbons an increase in C/H ratio increases smoke formation on burning and it has already been shown in a previous publication that decreasing smoke

tendency is in the order aromatics, unsaturateds, naphthenes, and paraffins. The selection of a suitable hydrocarbon base should materially decrease
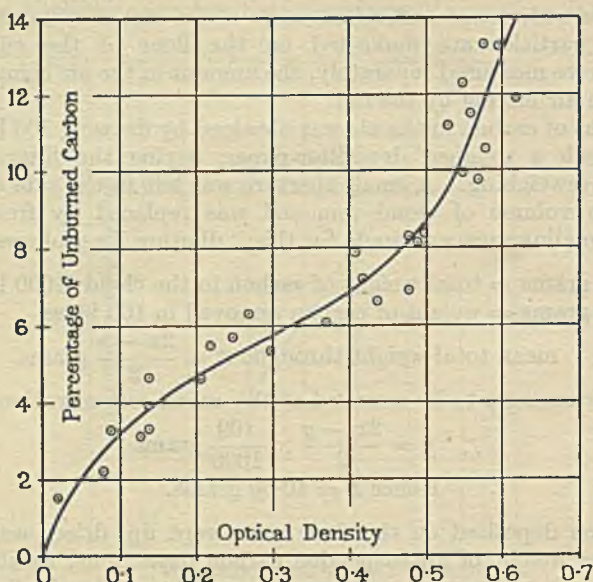

FIG. 5.

RELATIONS BETWEEN UNBURNED CARBON AND OPTICAL DENSITY.

smoke formation. The quantitative effect of such selection was, therefore, investigated, employing the hydrocarbon material listed together with its approximate chemical composition in Table I.

TABLE I.

Hydrocarbon Material Used for Making the Gels Investigated.

Hydrocarbon base.	Aniline point, ° C.	Approximate chemical composition.	Smoke-point flame height, cm.
Benzole	—	Largely aromatic	0·9
Pool motor spirit	30·9	Aromatic content 25%	5·1
S.B.P.1	59·7	Aromatics 3%, unsaturateds 0·5%, naphthenes 18%, paraffins 75·5%.	9·0
S.B.P.1, aromatic free	62·9	18·6% naphthenes, 81·4% paraffins	10·3
60–80°C, petroleum ether, aromatic free	58·0	—	8·9
n-Heptane	70·1	Nearly pure n-paraffin	15·9

The smoke-point data were determined in the special smoke-point lamp previously described. The aniline point has been appended as an indication of the degree of paraffinicity.

Employing the above hydrocarbon materials as the solvent with 5 to 7 per cent thickener the following data were obtained (Table II).

It is at once obvious from Tables I and II that the more paraffinic in chemical composition the hydrocarbon base the less the smoke generation. In addition to the reduction of smoke by the increase in paraffin content,

TABLE II.

Variation of Hydrocarbon Base.

Gel.		Burning characteristics.			Wastage.		
Hydrocarbon base.	Thick-ener, % by weight.	Time of burning, sec.	Mean flame height, cm.	Max. flame height, cm.	Un-burned carbon, % gel.	Total wastage, % gel.	Optical density.
Benzole	7	189 .	14·3	22·2	13·3	22·9	0·58
Pool motor spirit . .	7	439	9·7	15·4	7·9	15·6	0·41
60–80° C, petroleum ether, aromatic free . .	5	225	13·8	23·3	3·0	9·2	0·14
S.B.P.1	5	241	14·2	22·8	4·7	9·6	0·14
S.B.P.1, aromatic free .	5	252	12·2	23·4	3·3	9·2	0·09
n-Heptane * . . .	5	305	10·2	23·5	1·5	6·2	0·02

* Average of four determinations.

the total percentage of the gel wasted is materially decreased owing to more complete combustion. As shown by the optical density and percentage of gel lost as unburned carbon, the replacement of an aromatic hydrocarbon base such as benzole by an aromatic free saturated hydrocarbon base results in a very marked decrease in smoke production.

A further series of experiments was carried out to determine the relation-

TABLE III.

Variation of the Aromatic Content of Gels Containing Thickener.

Percentage by volume of aromatics in S.B.P.1–benzene mixtures.	Burning characteristics.			Wastage.					Optical density.
	Time of burning, sec.	Mean flame-height, cm.	Max. flame-height, cm.	Air sus-pended unburned carbon, % gel.	Un-burned carbon on floor, % gel.	Total unburned carbon, % gel.	Un-burned residue, % gel.	Total wastage, % gel.	
0 *	252	12·2	22·4	3·3	—	3·3	5·9	9·2	0·09
3 *	241	14·2	22·8	4·7	—	4·7	4·9	9·6	0·14
6	248	15·6	21·1	4·5	0·1	4·6	6·2	10·8	0·21
9	248	15·4	20·9	5·6	0·1	5·7	6·2	11·9	0·25
12	250	15·5	21·3	5·2	0·1	5·3	6·1	11·4	0·30
25	238	15·7	22·0	6·3	0·9	7·2	5·9	13·1	0·42
50	209	14·4	23·5	7·6	2·2	9·8	5·5	15·3	0·57
100	194	14·7	23·7	7·0	4·9	11·9	4·5	16·4	0·62

* Results from earlier experiments using a different sample of S.B.P.1, with and without the normal aromatic content.

ship between the aromatic content of the hydrocarbon base and the burning characteristics, wastage, and optical density. For this purpose gels were prepared from various mixtures of S.B.P.1 and A.R. benzene containing 5 per cent thickener. The results are shown in Table III.

The results for the hydrocarbons containing 0 and 3 per cent aromatics were obtained from earlier experiments using a different sample of S.B.P.1.

Thus, while they are included in the table for the sake of completeness, the general discussion applies to aromatic contents of 6 to 100 per cent.

It is apparent that the time of burning of the gels remains constant up to 25 per cent aromatics, after which the rate of burning increases. Again the mean flame-height and maximum flame-height are fairly constant up to 25 per cent aromatics, when the former begins to decrease and the latter to increase. An indication that the benzene flame may be hotter than a paraffin flame is given by the percentage of unburned residue, since this shows a decrease after 25 per cent aromatics.

As would be expected, the unburned carbon and optical density show a general increase with aromatic content, and the relationship between
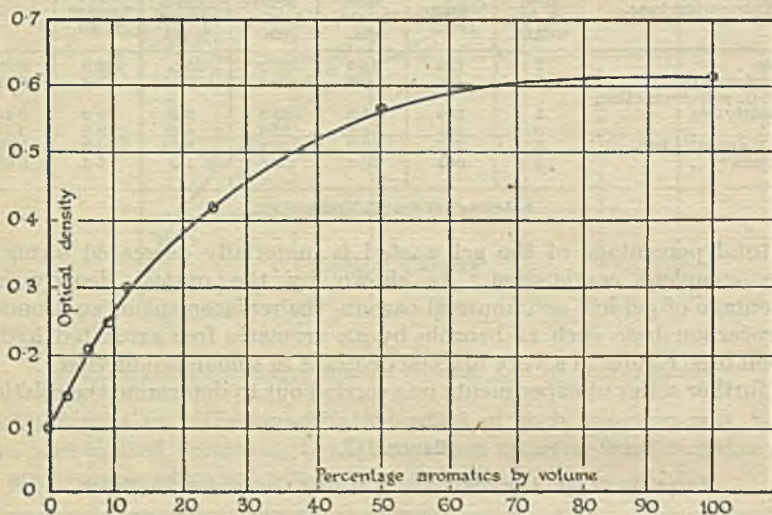

FIG. 6.

RELATIONS BETWEEN OPTICAL DENSITY AND AROMATIC CONTENT FOR BENZENE–S.B.P. 1 MIXTURES.

percentage aromatics and optical density is shown in Fig. 6. It has been observed that a benzene flame gives much larger carbon particle size than a paraffin flame, and this is indicated by the increase in the percentage unburned carbon deposited on the floor of the cube with increasing aromatic content. Such carbon, of course, is not included in the optical density measurement, and this explains the asymptotic nature of the optical density–aromatics curve. For the range of 0 to 12 per cent aromatics, the relationship between the optical density and percentage aromatics by volume is expressed with fair accuracy by the equation :

$$D = 0{\cdot}018A + 0{\cdot}09$$
$$\text{where } D = \text{Optical density}$$
$$A = \text{Percentage aromatics by volume.}$$

The total wastage increases with the aromatic content, since the decrease in unburned residue is offset by the increased unburned carbon.

A comparison of the results for the type of gel investigated suggests that

25 per cent is a critical aromatic content and is probably a rough division between a " paraffinic " type and an " aromatic " type of gel.

EFFECT OF VISCOSITY OF THE GEL.

The effect of gel viscosity on the smoking tendency was investigated by burning a number of gels prepared from the same components but of different viscosities, owing to the presence of different proportions of

TABLE IV.

Variation of Viscosity.

| Gel.			Burning characteristics.			Wastage.		Optical density.
Solvent base.	Thickener, % by weight.	Viscosity, sec.	Time of burning, sec.	Mean flame height, cm.	Max. flame height, cm.	Unburned carbon, % gel.	Total wastage, % gel.	
60–80°C, petroleum ether, aromatic free* .	7·5	3,021	226	12·9	22·1	3·4	11·9	0·14
60–80°C, petroleum ether, aromatic free .	5·0	608	225	13·8	23·3	3·9	9·2	0·14
60–80°C, petroleum ether, aromatic free .	3·0	118	218	14·2	26·4	3·9	7·2	0·14

* Average of four determinations.
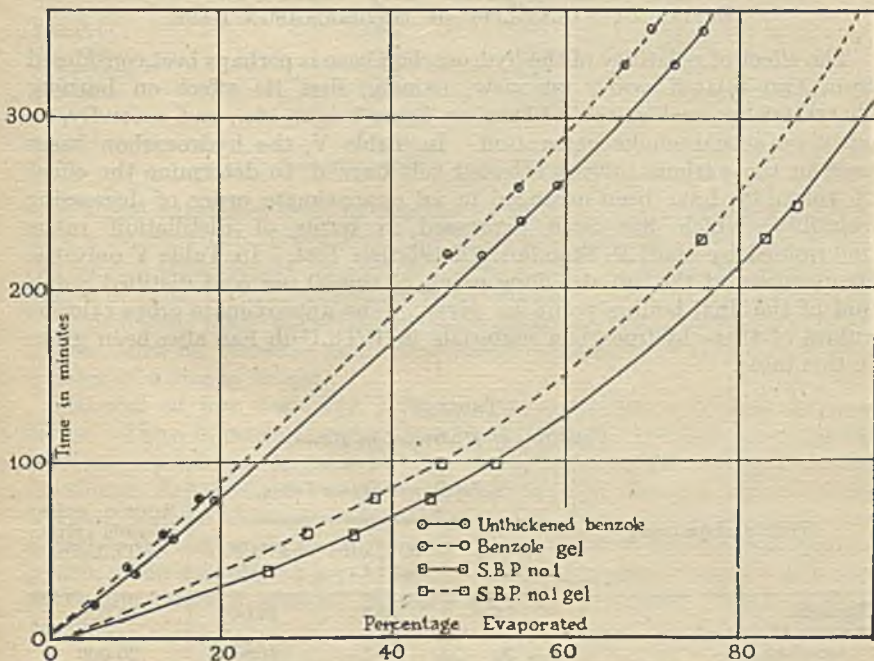
FIG. 7.

RATE OF EVAPORATION OF GELS AND THE CORRESPONDING UNTHICKENED LIQUID MIXTURES.

thickener.   As a comparative measure of gel viscosity, the time of fall in seconds of a steel ball 3/16 in in diameter through 10 cm of gel at 20° C was used.   The results of this series of experiments are given in Table IV.

Although the viscosity was varied over a very considerable range the smoke formation, as shown by the optical density and percentage lost as carbon, was not affected.

The burning characteristics have been slightly modified by changes in viscosity, a decrease in viscosity increasing flame-height.   The rate of burning, as indicated by the constant time of burning, has, however, not been affected (Col. 4).

Data on the relative rates of evaporation, under the same conditions, of gels and the unthickened hydrocarbon–peptiser mixtures give some support for the above conclusions.   The gels and liquid mixtures were allowed to evaporate, at air temperature under a draught shield, from similar containing vessels.   The vessels and contents were weighed at frequent intervals and curves were plotted of percentage evaporated against time.   The results are shown in Fig. 7.

It would appear that, even for the great difference in viscosity between a gel and the unthickened liquid, the rate of evaporation is not greatly modified.   Assuming this to apply under conditions of combustion, then no great change in burning characteristics with varying viscosity would be anticipated.

EFFECT OF VOLATILITY OF HYDROCARBON BASE.

The effect of volatility of the hydrocarbon base is perhaps best considered from two related points of view, namely, first its effect on burning characteristics such as rate of burning, flame-height, etc., and, secondly, its effect on actual smoke generation.   In Table V, the hydrocarbon bases used in the various solvent selected gels burned, to determine the effect of volatility, have been arranged in an approximate order of decreasing volatility, which has been expressed in terms of distillation range determined by the I.P. Standard Distillation Test.   In Table V only the temperature of the initial boiling point, of the 50 per cent distilled point, and of the final boiling point are given.   The approximate gross calorific values of these hydrocarbon materials in B.Th.U/lb has also been given in this table.

TABLE V.

Volatility of Hydrocarbon Bases.

Hydrocarbon base.	Volatility characteristics.			Approx. gross calorific value, B.Th.U/lb.
	I.P.B., ° C.	50% off at ° C.	F.B.P., ° C.	
Benzole	75	79·5	141·0	18,050
60–80° C, petroleum ether, aromatic free	50	68·5	109·5	20,000
S.B.P.1	43	67·5	139·5	20,200
n-Heptane	Boiling point 98·4° C.			20,800
Kerosine	180	216·0	260·5	20,000

EFFECT OF VOLATILITY ON BURNING CHARACTERISTICS.

In Table VI the composition of the gels made up with these hydrocarbon bases is given, and as far as possible the same thickener in as nearly as possible the same concentration has been employed, with the exception of the kerosine gel, which was a trade composition, where the thickener and its concentration were unknown.   As before, the gels have been arranged in approximate order of decreasing volatility.

It will be seen from the above table that under the conditions employed, namely, the burning of a constant weight of gel (1·5 g) with an exposed surface of constant area, that volatility profoundly affects the burning characteristics.   Any decrease in volatility decreases the rate of burning along with decrease of flame height.

TABLE VI.

Effect of Volatility on Burning Characteristics.

Gel.		Burning characteristics.		
Hydrocarbon base.	Thickener, % by weight.	Time of burning, sec.	Mean flame height, cm.	Max. flame height, cm.
Benzole	7·0	189	14·3	22·2
60–80° C, petroleum ether, aromatic-free * . .	7·5	226	12·9	22·1
S.B.P.1	5·0	241	14·2	22·8
Benzole	6·0	271	9·4	20·1
n-Heptane * . . .	5·0	305	10·2	23·5
Kerosine . . .	Trade composition	699	7·4	8·9

* Average of four determinations.

A single substance such as benzole or heptane, when burned, tends to give a flame which slowly increases in height to a maximum for a short period and then rapidly dies down.   The relative volatility determines the length of time to reach maximum flame-height.

Wide boiling range material showing a steady increase in the boiling point curves, such as kerosine, and, to a certain extent, S.B.P.1, tends to give a flame of a steady height.

Material of low volatility gives low flame-heights and long burning times.   Thus, in general, under these conditions of burning, a hydrocarbon mixture containing appreciable low boiling-point fractions reaches its maximum flame-height rapidly and maintains it through much of the burning period.   A single hydrocarbon on the other hand appears to reach a higher maximum flame-height more slowly and to fall off quickly.   A hydrocarbon mixture of low volatility shows a gradual increase to a low maximum, then a gradual decrease with a consequent longer time of burning.

VOLATILITY AND SMOKE PRODUCTION.

The effect of volatility on smoke generation is markedly affected by chemical composition; it was therefore determined by tests on the same

gel at different temperatures. This has been done for the kerosine gel at gel temperatures of approximately 20° C and 100° C. The data obtained are tabulated in Table VII.

Increasing the volatility of this gel by increasing the gel temperature has considerably altered the burning characteristics, namely, increased greatly the rate of burning and increased the flame-height.

TABLE VII.

Volatility Effect Produced by Temperature Variation.

Gel.	Approx. gel temp., ° C.	Burning characteristics.			Un-burned carbon, % gel.	Optical density.
		Time of burning, sec.	Mean flame height, cm.	Max. flame height, cm.		
Kerosine .	20	699	7·4	8·9	5·9	0·22
Kerosine * .	100	105	23·0	34·0	12·3	0·55

* One determination only.

With the lower temperature and hence lower volatility the mean flame-height of 7·4 cm is only a few cm above the smoke-point of 4·7 cm ; the amount of smoke formed for the hydrocarbon base in this gel is comparatively low, as shown by the unburned carbon and optical density data. With higher volatility at the higher temperature the mean flame-height of 23·0 cm is well above the smoke-point flame-height, and hence smoke

TABLE VIII.

Volatility Effect Produced by Variation of Boiling Range.

Boiling range, ° C.	Mean flame height, cm.	Max. flame height, cm.	Time of burning, sec.	Un-burned carbon, % gel.	Un-burned residue, % gel.	Total wastage, % gel.	Optical density.
48– 82	13·2	22·1	221	2·2	5·9	8·1	0·08
55– 99	12·8	21·3	279	3·2	5·5	8·7	0·14
58–120	12·3	18·8	319	2·9	5·1	8·0	0·14
60–141	12·2	19·2	329	3·1	5·1	8·2	0·13
70– 99	11·7	20·2	276	3·0	5·4	8·4	0·13
86–103	11·6	20·6	312	3·1	5·1	8·2	0·16

formation is comparatively heavy. An increase in volatility, therefore, tends to increase flame-height and increase smoke formation.

The effect on smoke formation of hydrocarbon base volatility, when fractions of various boiling ranges were prepared from the same petroleum starting material, was examined. This should indicate the loss or gain in smoke formation given by the selection, from a petroleum material, of a particular fraction of most suitable volatility.

The source material (benzene I), from which the various S.B.P. fractions were prepared, was freed from aromatic hydrocarbons and distilled to give

the required boiling ranges.   Gels prepared from these fractions containing 5 per cent thickener were burned and the smoke formation investigated. The results are shown in Table VIII.

It will be observed that the smallest amount of smoke is given by the fraction of boiling range 48 to 82° C.   The smoke formation for the other fractions of lower volatility, although somewhat higher, is fairly constant over the boiling ranges examined.   Thus, although the 48 to 82° C fraction is best, no great increase in smoke would result from the use of any of these higher boiling fractions.

To sum up, an increase in volatility of the hydrocarbon base decreases the time of burning, increases the flame-height and increases smoke formation.   In the selection of a suitable smokeless gel it is essential that a correct balance must be maintained between chemical composition and volatility to obtain the necessary burning characteristics with relative absence of smoke.

Conclusion.

Hydrocarbon Base.

The more saturated or paraffinic in chemical composition the hydrocarbon base the less the smoke generation.   The use of a gel prepared from an aromatic-free saturated hydrocarbon base results in a very marked reduction in smoke formation.   Benzole is particularly potent as a smoke producer.

Viscosity.

In the burning of a constant weight of gel with a constant area of exposed surface, the viscosity of the gel has no effect either on the rate of burning or on smoke formation.   Under the same conditions, however, an increase in viscosity decreases flame height.

Volatility.

In the burning of a constant weight of gel with a constant area of exposed surface an increase in volatility increases both rate of burning, flame-height, and smoke formation.

ON THE COURSE OF THE REACTION AT 100° C IN THE SYSTEM PARAFFIN/OXYGEN.

By D. J. W. KREULEN (Fellow).

SUMMARY.

The oxidation of solid paraffin has been investigated. The quantities of peroxides and aldehydes formed are proportional to time, while the quantity of acids is a quadratical function of time.

If copper is present the peroxides are destroyed and an increase if the quantity of aldehydes is observed. In conclusion, the results obtained with white oils, xylene, and solid paraffin are compared.

IN sequel to preceding studies * we have now investigated the course of the reaction during the oxidation of solid paraffin.

The paraffin chosen for this investigation had the following constants :— mol. weight, 418; melting point, 57° C; aromatic rings, 0 per cent; naphthenic rings, 0 per cent, and paraffins 100 per cent. Small quantities of peroxides ($1 \cdot 6$ mg O_2/100 g) and aldehydes ($0 \cdot 3$ mg KOH/g) were present in it.

225 g of this paraffin were oxidized at 100° C with oxygen in our standard apparatus. The stirring velocity was 1500 r.p.m. During the oxidation samples were taken and the increase in peroxide number, carbonyl number, and acid value was determined.

The test was discontinued during the night. The oxygen was then replaced by CO_2 and the flask was kept at 60° C in order to prevent solidification of the paraffin.

It appeared to be rather difficult to get reliable results. So the results of two separate experiments are recorded in Fig. 1 and the most probable average lines are drawn. As usual for this purpose Fig. 1 is drawn on a logarithmic scale.

Although the results show a rather large dispersion around the average lines, it is evident that we have to regard both peroxides and aldehydes as primary reaction products, since the tangent of the angle of slope is unity.

The acids, however, are formed quadratically (via one intermediate stage), since the tangent of the angle of slope is 2.

In Table I the peroxides, aldehydes, and acids which were read from the average lines of the graph are expressed on a comparable base, viz., millimol/100 g paraffin.

Apparently the reaction of solid paraffin with oxygen follows the same course as that of xylene with oxygen. However, while during the oxidation of xylene about equal quantities of peroxides and aldehydes are formed, the oxidation of paraffin results in quantities of aldehydes which are about twice that of the peroxides.

The conformity of the course of the two reactions induced us to investigate whether, during the oxidation of paraffin, there exists the same copper susceptibility with regard to the destruction of peroxides as in the case of xylene.

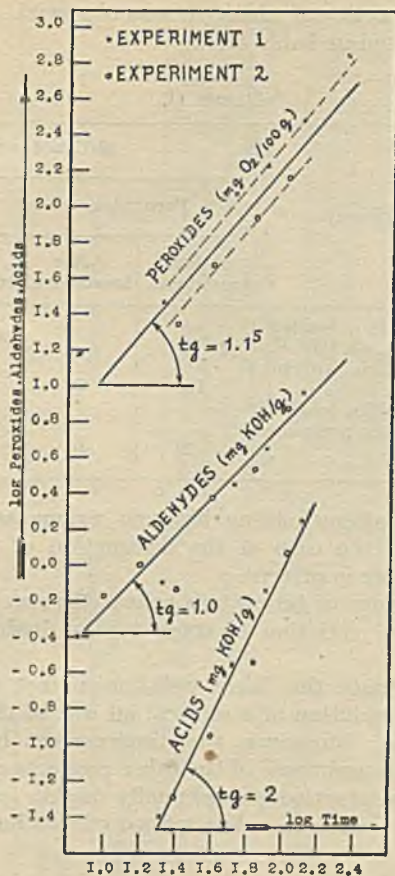* *J. Inst. Petrol.*, 1946, **32**, 515, 525.

FIG. 1.

INCREASE OF PEROXIDE NUMBER, CARBONYL NUMBER AND ACID VALUE (ON A
LOGARITHMIC SCALE) DURING THE OXIDATION OF PARAFFIN.

For that purpose two samples of oxidized paraffin were treated at 100° C
with oxygen and air respectively in the presence of electrolytic copper.
The paraffin coloured green and the peroxides were destroyed.   Moreover

TABLE I.

Oxidation time, hrs.	Millimol per 100 g.		
	Peroxides.	Aldehydes.	Acids.
10	0·38	1·00	—
16	0·63	1·59	0·04
25	1·06	2·64	0·09
40	1·81	4·18	0·25
63	3·12	6·79	0·66
100	5·44	11·27	1·79

an increase in the quantity of aldehyde was observed.   The figures which
were found are collected in Table II.

TABLE II.

Condition of experiment.	Millimol per 100 g.			
	Peroxides.		Aldehydes.	
	Before treatment.	After treatment.	Before treatment.	After treatment.
25 c.c. of oxidized paraffin, treated for 6 hrs with oxygen at 100° C. in the presence of electrolytic copper	18	2	83	121
125 c.c. of oxidized paraffin treated for 13 hrs with air in the presence of electrolytic copper . .	2½	0	12	18

Apparently the analogy holding between xylene and paraffin during
oxidation extends to the case of the destruction of peroxides in these
substances when copper is present.

In conclusion it seems of interest to collect the results obtained in our
investigations on the oxidation of some typical hydrocarbons.   This is
done in Table III.

The results accentuate the fairly well-known fact that the course of
reaction during the oxidation of a mineral oil will be closely related to its
chemical constitution.   Moreover, the disagreement between the results
obtained for white oils and those of the other products accentuate the well-
known fact that in practice exceptionally highly refined oils behave
differently during oxidation than less refined oils; * but obviously further
research is required.

Rotterdam,
   Laboratory for Coal and Oil Chemistry.

TABLE III.

Liquid.	Constitution.	Reaction stage in which are formed :			Ratio peroxides : aldehydes.	Influence of copper.
		Per-oxides.	Alde-hydes.	Acids.		
White oils	Naphthenic rings coupled with paraffinic side chains.	1st	2nd	3rd	Initially 1 : 2 decreasing to 1 : 3	With small quantities of copper (up to 10 grm of filings/250 c.c. of oil) both the rate of reaction and the formation of peroxides, aldehydes, and acids are unaffected by its presence. With large quantities of copper an increase in the rate of reaction is observed.
Xylene	Aromatic ring coupled with paraffinic side chains.	1st	1st	2nd	1 : 1	When copper is present peroxides are destroyed and the quantity of aldehydes very probably increases. An insoluble cuprous-salt of toluic acid settles from the reacting liquid.
Paraffin	100% paraffin	1st	1st	2nd	1 : 2	When copper is present peroxides are destroyed and the quantity of aldehydes increases.

EXPERIMENTS ON THE PRODUCTION OF TOLUENE FROM COAL TAR PRODUCTS AND OTHER SOURCES.

By C. M. Cawley, J. H. G. Carlile, H. E. Newall, and
F. E. T. Kingman.

Precis.

Great Britain's large toluene requirements during the war were met by increased production from coke-oven and gas-works benzole and by importation from the United States, where production from petroleum was carried out on a large scale. At the beginning of the war, however, it was uncertain whether sufficient toluene would be available, and a study was made of some of the ways of making this substance from coal-tar products—benzene, xylene, cresol, and naphthalene. Particular attention was given to the possibility of preparing toluene by the hydrogenation of cresol, and a continuous process working at a pressure of 10 to 20 atm and a temperature of 430–440° C was developed to a semi-technical scale (120 gal per day). A laboratory examination was also made of the cyclization of n-heptane.

During 1939, it was anticipated that, in the event of a prolonged war, the supply of toluene in Great Britain might become inadequate. At the request of the War Office, and later the Ministry of Supply, certain researches were accordingly undertaken at the Fuel Research Station in connexion with the development of processes for the production of toluene from indigenous materials. The work was supported by additional studies for which no special remit was given. The results of the whole investigation are given in outline in the present paper.

The chief sources of aromatic hydrocarbons in this country are the coal tar and benzole which are obtained as by-products from the coal carbonization industries, and it seemed likely that these products would provide the most suitable raw materials for processes for the production of toluene. Attention was therefore directed chiefly to the reactions of benzene, xylene, cresol, and naphthalene, but a study of the cyclization of n-heptane was also made, since there was just a possibility that supplies of this hydro-carbon might be made available by the operation of the Fischer–Tropsch process.

Toluene from Benzene.

The preparation of toluene from benzene via the formation of benzaldehyde appeared to be an attractive method of synthesis, and following the publication of the results of work showing that yields of 94 per cent could be obtained,[1] the War Office requested the Department of Scientific and Industrial Research to undertake an investigation of the possibilities of producing toluene in this way. The synthesis is carried out in two stages, namely :

    (1) the preparation of benzaldehyde from benzene and carbon monoxide in the presence of aluminium chloride; and
    (2) the hydrogenation of benzaldehyde to toluene.

The first stage, investigated at the Chemical Research Laboratory, Teddington, will form the subject of an independent publication in which it will be shown that although an excellent conversion to benzaldehyde may be attained, the reaction is commercially impracticable because aluminium chloride functions as a reactant rather than as a catalyst.

The experiments were carried out in a continuous, laboratory-scale, hydrogenation apparatus, which consisted essentially of a vertical cylindrical reaction chamber (10 in long by 0·5 in int dia) which was charged with 25 ml of catalyst and heated externally by means of an electric furnace. Benzaldehyde with hydrogen was pumped upwards through a preheater to the catalyst bed, and the products issued to a condensing and collecting system. A full description of the apparatus, designated No. 10 Converter, has been given elsewhere.[2]

The catalyst used was pelleted molybdenum disulphide as prepared for the hydrogenation of cresol to toluene (described below). The benzaldehyde was a commercial sample containing 90 per cent boiling from 180·5 to 181·5° C and having an estimated purity of 95 per cent.

As the result of a few preliminary experiments, it was found that the following conditions were suitable : temperature, 430° C; pressure, 5 atm; input of benzaldehyde, 12 ml per hour; input of hydrogen, 50 litres per hour. An experiment to ascertain the " life " of the catalyst under these conditions was carried out, and towards the end of the experiment the input of benzaldehyde was increased to 24, 36, 48, and finally 96 ml per hour, and the rate of hydrogen was increased proportionally. The duration of the experiment was 423 hours, which included 346 hours at an input of benzaldehyde of 12 ml per hour, 6 hours at 24 ml per hour, 17 hours at 36 ml per hour, 50 hours at 48 ml per hour, and 4 hours at 96 ml per hour. The total amount of benzaldehyde treated was therefore 7692 ml, or 308 volumes per volume of catalyst.

Throughout the whole experiment, the liquid product consisted of water and a colourless mixture of hydrocarbons, the yields being :

Water	16·5 per cent by wt
Liquid hydrocarbons . . .	83·6 per cent by wt

The specific gravity of the hydrocarbons at 15° C varied from 0·872 to 0·874. There was only a very small amount of destructive hydrogenation and the yield of gaseous hydrocarbons amounted to only 1 or 2 per cent. The amount of hydrogen consumed was that required by the reaction :

$$C_6H_5CHO + 2H_2 = C_6H_5CH_3 + H_2O$$

The liquid hydrocarbons were distilled and the yield of the fraction boiling from 105 to 115° C was found to be 94·6 per cent by wt of the hydrocarbons or 79 per cent by wt of the benzaldehyde treated (96 per cent of the theoretical). This fraction was analysed by the Manning method [3] and found to contain less than 1 per cent of saturated hydrocarbons; physical properties of the fraction (compared with those of pure toluene) were :

	Fraction.	Pure toluene.[3a]
d_4^{20}	0·8670	0·8670
n_D^{20}	1·4962	1·4969

No deterioration of the activity of the catalyst was detected, since complete conversion of the benzaldehyde to a product of constant quality was maintained throughout the experiment. A satisfactory basis for a process for the continuous conversion of benzaldehyde to toluene was therefore demonstrated.

TOLUENE FROM XYLENE.

The production of toluene by the pyrolysis of xylene was investigated during the war by the South Metropolitan Gas Company and the Department of the Government Chemist. South Metropolitan Gas Company obtained a patent [4] for the process as conducted at a temperature of 700 to 850° C in the presence of hydrogen or a gas rich in hydrogen.

An extensive investigation of the production of toluene by cracking of solvent naphthas and xyloles in hydrogen was also carried out at the Chemical Research Laboratory, Teddington, for the Directorate of Scientific Research, Ministry of Supply. The results have been embodied in two papers * now awaiting publication by the Society of Chemical Industry. This work showed that when the cracking was carried out in hydrogen over silver gauze at 750° C a yield of toluene equal to over 38 per cent of the raw material consumed was obtained in one stage. In an extension of this investigation in which hydrogen and pressures above atmospheric were employed, it was found that the conversion of crude xyloles to toluene reached 40 to 50 per cent.

Small-scale experiments, in the Department of the Government Chemist, showed that the cracking of heavy coal-tar naphtha at 800° C in the presence of coal gas yielded 13 to 23 per cent of toluene and 3 to 8 per cent of benzene, the exact amounts varying with the composition of the naphtha; this procedure has been patented.[4a] These results were encouraging, but before proceeding to the development of the process on a large scale the Assistant Director of Chemical Research of the Ministry of Supply wished to determine whether similar results would be obtained on an intermediate scale. At his request, therefore, an experiment on a semi-technical scale was carried out at the Fuel Research Station.

The plant used for this experiment consisted essentially of two similar vessels, serving as the preheater and reaction chamber, which were supported in a brick setting heated by means of water gas. The vessels were vertical, cylindrical steel tubes (5 ft long by 6 in int. dia) filled with broken brick (graded ¾ to 1½ in) and connected base to base. The naphtha to be cracked was delivered by means of an oil pump to the top of the preheater, where it was joined by a stream of carrier gas, and the products issuing from the top of the reaction chamber were passed to a condensing and collecting system.

The naphtha treated was an acid-washed heavy coal-tar naphtha, 90 per cent of which distilled between 158° and 186° C. The carrier gas was coal gas from the mains of the South Metropolitan Gas Company,

* " The Production of Toluene by the Cracking of Solvent Naphtha and Xyloles in Hydrogen. Part I. Experiments at Atmospheric Pressure," by E. A. Coulson, R. Handley, E. C. Holt, and (the late) D. A. Stonestreet.
" The Production of Toluene by the Cracking of Solvent Naphtha and Xyloles in Hydrogen. Part II. Experiments in Metal Reaction Tubes, and with Increase of Pressure above Atmospheric," by E. A. Coulson and R. Handley.

Limited. The hourly throughputs of naphtha and coal gas were one gallon and 300 cu.ft. A length of 1·8 ft of the reaction chamber was held at 790 to 800° C, and the time of contact at this temperature was 0·56 sec; the total time of contact in the preheater and reaction chamber was 5 sec.

In the first treatment, or cycle, 120 gallons of naphtha were pyrolyzed. The liquid product was distilled to remove benzene, toluene, and polymerized products, and the intermediate fractions were re-cracked in a second cycle under the same conditions. This process was twice repeated, making a total of four cycles in all. The final product was analysed by fractional distillation under the direction of Mr. S. A. Ashmore of the Department of the Government Chemist.

The overall yields of all products (per cent by weight of the original naphtha) for the whole experiment were as follows :

	Wt per cent.
Oil boiling up to 95° C (benzene) .	5·3
Oil boiling 95–125° C (toluene) .	19·9
Oil boiling 125–175° C (xylenes and trimethylbenzenes) .	11·4
Residue boiling above 175° C (polymerized material) .	31·3
Gas, pitch, carbon, and loss .	32·1
	100·0

The high-boiling residue consisted to a large extent of polymerized material including some naphthalene. The calorific value of the residual gas during the first cycle was 100 B.Th.U per cu.ft higher than that of the original coal gas; in the later cycles there was practically no difference between the calorific values of the two gases.

There was some formation of pitchy material which was deposited in the outlet pipe from the reaction chamber and in the water-cooled condenser, and it was found advisable to steam out the pipelines on the outlet side of the plant periodically. Before this was done, trouble was experienced with the formation of blockages. At the end of the experiments, it was found that there was some deposition of carbon on the refractory brick in the preheater and reaction chamber. The deposit was heaviest at the inlet to the preheater and gradually diminished in the direction of flow.

The yields of toluene in the four cycles were respectively 12·1, 4·8, 1·8, and 1·2 per cent. In practice, the process would not be operated in separate cycles, but a mixture of fresh naphtha and recycle oil would be treated continuously. With this raw material, the yields of benzene and toluene would be respectively 6 per cent and 22 to 23 per cent by weight of the naphtha. The increase in the calorific value of the gas would be about 50 B.Th.U per cu.ft.

The large loss of material due to polymerization can be reduced by increasing the concentration of hydrogen. Thus it was shown in earlier work at the Fuel Research Station [5] that o-xylene (100 g) when heated in a two-litre autoclave under an initial pressure of hydrogen of 100 atm for two hours at 480° C yielded :

Benzene .	2 per cent
Toluene .	47 per cent
Unchanged xylene .	36·5 per cent
Gas and loss .	14·5 per cent

Further experiments were accordingly made during the present investigation; xylene was treated with hydrogen under pressure in a continuously operated plant where the time of contact was necessarily relatively small in comparison with that in the autoclave, and it was found that suitable conditions were a temperature of 600° C and a total pressure of 50 atm. The apparatus used consisted essentially of an electrically heated, vertical, cylindrical reaction tube ($\frac{5}{8}$ in int dia).   The tube was packed with silica chips or other contact material occupying a space of 60 ml, of which 40 ml were at a temperature of 550 to 600° C.   The throughputs used in the experiments for which results are quoted in Table I were 20 ml per hour of commercial xylene and 15 litres per hour of hydrogen.   The partial pressure of hydrogen under those conditions was 38 atm and the time of contact, 1·2 min.

TABLE I.

Results of the Hydrogen-Cracking of Xylene at 600° *C and* 50 *atm.*
(Yields expressed as percentages by weight of xylene treated.)

Experiment.	I:	II.	III.	IV.	V.
Contact material used.	Silica chips.	Silica gel.	Silica gel impregnated with alumina.	Mixed alumina and silica gel.	Active carbon.
Yield of oil product	94·0	92·0	95·0	79·2	92·0
Sp. gr. of oil product at 15° C	0·865	0·866	0·865	0·872	0·870
Fractionation of oil product :					
Up to 78° C	0·9	0·6	3·1	2·0	1·3
78–81° C	1·4	3·4	1·2	12·8	13·6
81–108° C	1·8	2·2	2·9	2·5	4·6
108–111° C	16·9	24·2	25·2	31·8	36·8
Above 111° C	70·5	59·1	60·0	24·0	30·3
Loss	2·5	2·5	2·6	6·1	5·4
Total	94·0	92·0	95·0	79·2	92·0
Properties of fractions :					
78–81° C					
n_D^{20}	1·4895	1·4928	1·4995	1·4995	1·5000
d_4^{20}	0·8731	—	—	0·8759	—
108–111° C					
n_D^{20}	1·4953	1·4960	1·4965	1·4966	1·4968
d_4^{20}	0·8661	—	—	0·8670	—

The main reaction under the conditions of the experiment was demethylation to toluene; a smaller proportion of benzene was also produced, and there was extremely little nuclear hydrogenation.   The yields and proportions of toluene and benzene were influenced to a marked extent by the contact material, the yields of toluene ranging from 16·9 to 36·8 while those of benzene ranged from 1·4 to 13·6.   The cracking activity of silica gel (freshly prepared [6]), as used in Experiment II, was increased by the incorporation of alumina, either by impregnation with aluminium nitrate to yield the contact material [6] used in Experiment III, or by mixing silica and alumina gel during preparation, as in the case of the catalyst [7] used

in Experiment IV.   All these active silica and alumina gel catalysts, and the active carbon used in Experiment V, showed a rapid loss of activity, probably owing to the deposition of carbon.   Thus in Experiment III, after the treatment of 600 ml of xylene, the used catalyst (33·6 g) was found to contain 26·3 per cent of carbon.

In a continuous process for the hydrogenation-cracking of xylene, therefore, a yield of toluene of about 20 per cent per pass, or 50 per cent by complete conversion, might be expected, although these yields could almost certainly be increased.

Toluene from Naphthalene.

A possible synthesis was indicated by earlier work at the Fuel Research Station on the high-pressure hydrogenation of phthalic anhydride,[8] which was found to give a yield of toluene of 35 to 45 per cent by wt; this corresponds to 40 to 50 per cent by wt calculated on naphthalene, or 55 to 70 per cent of the theoretical yield.   The synthesis is interesting from the chemical point of view, but it was not thought to provide a satisfactory basis for a practical process.

Previous work [9] had also shown that the hydrogenation-cracking of tetralin at high pressures in batch-operated autoclaves yielded successively n-butyl benzene, ethyl benzene, toluene, and benzene.   The yield of toluene was not high (about 15 per cent by wt), but since the other aromatic hydrocarbons in the product were also of considerable value, the results were thought to be of some promise for the development of a process. Experiments were accordingly undertaken with this object in view, and it was found that the hydrogenation-cracking reaction could be operated continuously at a temperature of 600° C and a pressure of 200 atm in an apparatus similar to that already described for the hydrogenation-cracking of xylene.   The reaction tube was packed with silica chips occupying a reaction space of 40 ml at a temperature of 550 to 600° C, and it was found that tetralin could be suitably treated at a throughput of 40 ml per hour with hydrogen passing at the rate of 30 litres per hour.   Under these conditions the time of contact of the tetralin at 550 to 600° C was two to three minutes as compared with two hours at 500° C in the batch experiments.   The yields of products, calculated as percentages by weight of the tetralin treated, were approximately as follows :

Benzene .	10
Toluene .	9
Ethyl benzene .	14
Other hydrocarbons, b. pt <200° C .	13
Tetralin and naphthalene .	28
Gas and loss .	26

The extent of nuclear hydrogenation in the aromatic hydrocarbons was of the order of 1 per cent.   These results were of considerable promise, but further development was abandoned, since more attractive processes were available.

Toluene from Cresol.

A process for the production of toluene by the hydrogenation of cresol at atmospheric pressure was developed at the Fuel Research Station during 1932–34.[10]   A supported molybdenum catalyst was used and at a reaction

temperature of 450° C and a throughput of cresol of 0·2 vol per vol catalyst per hour, the conversion to toluene was initially complete, but the catalyst deteriorated rapidly and the conversion fell to 60 per cent in five hours. The catalyst was then reactivated with air at 500° C during a further five-hour period.

The process constituted a practical method for the reduction of cresol to toluene, but was not considered suitable for application on a large scale, particularly owing to its discontinuity and low throughput in relation to the amount of catalyst employed.

At the request of the War Office and later the Ministry of Supply, an investigation was accordingly undertaken to devise a continuous process using a higher space velocity of cresol. In order to achieve this a more active catalyst was used with a slightly elevated pressure of hydrogen.

The danger of using an elevated pressure was that methyl *cyclo*hexane would be formed by nuclear hydrogenation. Some equilibrium data for this reaction for conditions in the region of those employed for the reduction of cresol are given in Table II.[10a]

TABLE II.

Equilibrium Data for the Hydrogenation of Toluene.

Reaction temperature.	Amount of methyl *cyclo*hexane in equilibrium mixture, per cent by wt.	
	5 atm H_2.	10 atm H_2.
350° C	16·3	60·9
400° C	0·9	6·8
430° C	0·2	1·5

It was thought that it might be possible to obtain substantially pure toluene by using a very short time of contact, although employing conditions under which the product would contain an appreciable proportion of methyl *cyclo*hexane if equilibrium were reached. It was, however, found impossible to do this with the catalysts examined using times of contact that gave a reasonable conversion; although equilibrium was not attained, a sufficient proportion of methyl *cyclo*hexane appeared in the products to render the conditions unsuitable.

The pressure which may be used without giving rise to substantial nuclear hydrogenation increases with increase in reaction temperature, but since the rate of deterioration of the catalyst also increases as the temperature is raised, it was desirable to use the lowest possible temperature. With the catalyst finally chosen—pelleted molybdenum disulphide—it was known that temperatures much in excess of 430° C should not be used if a long-catalyst " life " was to be obtained. It therefore appeared that an upper limit of ten atmospheres was imposed on the working pressure. Subsequent work showed that this was in fact the case with a fresh, active catalyst, but that as the catalyst deteriorated, it was possible to maintain complete conversion of the cresol to hydrocarbons, without increasing the yield of methyl *cyclo*hexane, by gradually increasing the pressure.

A continuous process based on these principles was worked out on a small scale, and was then transferred to a semi-technical scale in which 5 gal cresylic acid per hour were treated. The Department of Scientific and Industrial Research was requested by the War Office to carry out a trial on this scale for a period of 30 days. The present account is largely concerned with the results of this semi-technical-scale experiment, which fully illustrates the process.
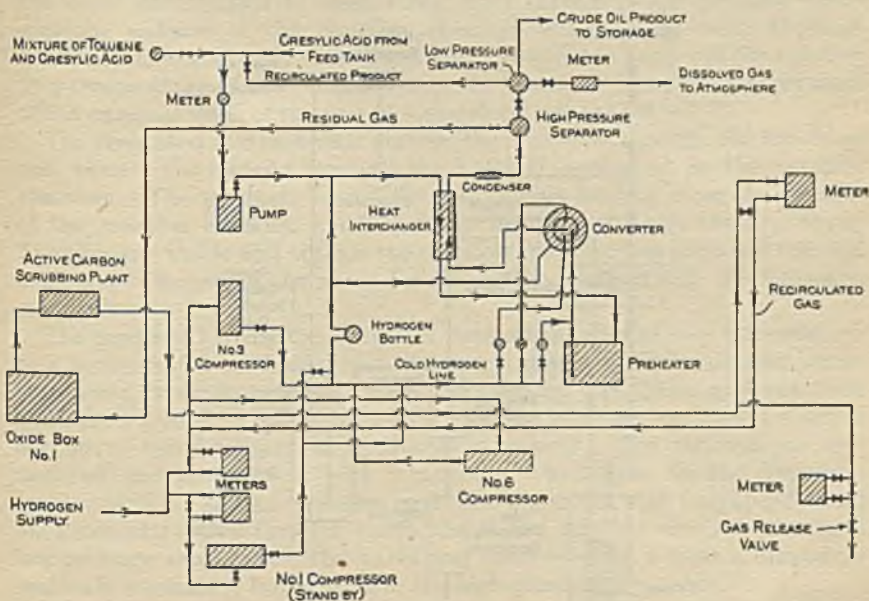

Fig. 1.
LAYOUT OF SEMI-TECHNICAL SCALE PLANT.

Apparatus and Plant.

The exploratory experimental work was carried out in a laboratory-scale apparatus (already described as No. 10 Converter [11]) designed for the hydrogenation of oils at pressures up to 400 atm. It consisted essentially of a cylindrical reaction chamber (10 in long by 0·5 in dia), which was filled to a height of 8 in with 24 ml of catalyst, and heated to the required temperature by means of an external electric furnace. Cresol and hydrogen at the required pressure were pumped downwards through the catalyst bed, and the products issued to a condensing system.

The plant used for the semi-technical-scale experiment was that originally designed for the hydrogenation of tars and oils at throughputs up to 400 gal per day and at pressures up to 400 atm. A description of this plant has already been published.[12] Owing to the lower reaction pressure required by the present process, a certain number of modifications in the plant were necessary, but the minimum amount of alteration was made. The plant was not, therefore, entirely suited to the examination of the present process; in particular the bore of all the pipelines was too narrow

to enable the designed throughput to be obtained at the relatively low pressures used. The actual throughput was 120 gal of cresylic acid per day.

The arrangement of the plant, as used in the present experiment, is shown diagrammatically in Fig. 1, and the operation of the plant is illustrated by the simplified flow diagram shown in Fig. 2.

Cresylic acid was stored in a 3000-gal tank from which it flowed by gravity into a 500-gal mixing tank, in which 1 per cent of carbon disulphide
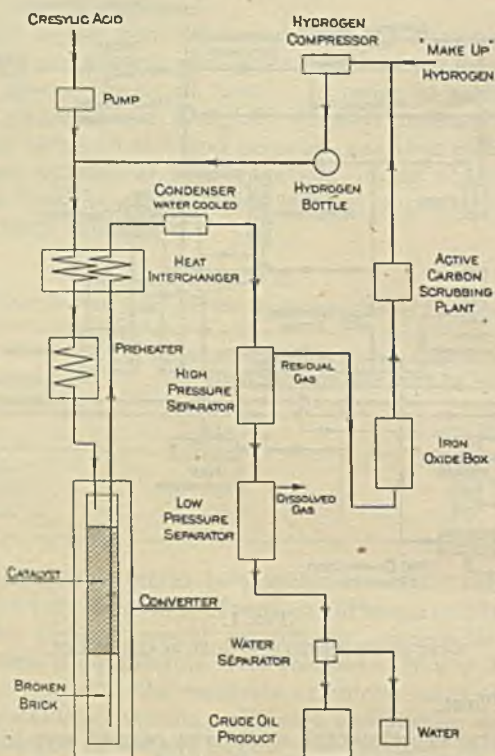

FIG. 2.

FLOW DIAGRAM OF SEMI-TECHNICAL SCALE PLANT.

was added to the cresylic acid. (Under the reaction conditions the carbon disulphide yields hydrogen sulphide in sufficient amount to maintain the activity of the catalyst.) The treated cresylic acid was then blown by means of compressed air to two calibrated 700-gal feed tanks, from which it passed through a meter to a cresylic acid pump which delivered it at the required pressure into a high-pressure line. Here it was mixed with hydrogen from the compressors, and the mixture passed through a heat interchanger and preheater to the converter.

The heat interchanger consisted of 170 ft of " twin " high-pressure tubing—*i.e.*, two lengths of tubing welded together and bent to form a coil—through which the raw materials and products flowed counter-

current. The coil was housed in a rectangular box lined with insulating material. The preheater was a gas-fired coil 250 ft in length.

The converter consisted of a pressure vessel with an internal reaction chamber. The former was a vertical cylindrical steel vessel, 13 ft in length by 16 in in int dia. The reaction chamber, suspended concentrically within the pressure vessel, was 11 ft in length by 8 in in int dia. The chamber was fitted with internal radial metal strips to assist the rapid distribution of heat. The inner surface of the pressure vessel and the outside of the reaction chamber were coated with thermal-insulation material. By this means it was possible to carry out the reaction at a temperature of 430° C in the reaction chamber, while the temperature of the external walls of the pressure vessel did not exceed 90° C.

The preheated raw materials entered the converter through the top cover and passed downwards through the catalyst contained in the reaction chamber. The products issued through a pipe leading from the bottom of the reaction chamber and extending upwards through the top cover. The pressure inside and outside the reaction chamber was balanced through a pipeline connecting the space for thermal insulation with the hydrogen supply.

The products leaving the converter passed through the heat interchanger to a water-cooled condenser, and thence to a high-pressure separator where the liquid product separated from the residual gas. The gas was then freed from hydrogen sulphide in an iron-oxide box and scrubbed by active carbon in order to remove hydrocarbon vapour. The purified gas was metered and recirculated with "make-up" hydrogen by the hydrogen compressors. The high-pressure separator was fitted with a sight glass and an automatic valve through which the liquid product was released to a low-pressure separator. The valve was controlled by a float arranged to maintain a constant liquid level in the high-pressure separator.

When the liquid product was released to atmospheric pressure, a small quantity of dissolved gas was evolved and passed through a meter to atmosphere. The liquid flowed through a water separator, and the oil flowed to two 700-gal calibrated tanks and thence to a plant in which it was washed with caustic soda for the removal of cresylic acid and hydrogen sulphide.

In order to assist in temperature control, in the event of any sudden increases of temperature, connexions were fitted for the supply of " cold " hydrogen, i.e., hydrogen which entered the reaction chamber at atmospheric temperature. Lines were fitted so that cold hydrogen could be supplied at the top, centre, or bottom of the catalyst bed. It was found in practice that the reaction temperature could be very readily controlled without the use of any cold hydrogen.

Raw Materials.

It was found that the grades of commercial cresylic acid which could be made available were suitable for the process, provided that they consisted of freshly distilled material, free from high-boiling residues and readily oxidizable compounds. The grades must of course contain a high proportion of cresol to ensure a good yield of toluene.

The cresylic acid treated in the semi-technical-scale experiment was

supplied by Messrs Yorkshire Tar Distillers, Limited; it was delivered in four batches at successive stages during the experiment, so that the freshly distilled material was not stored for a long period before use. The first batch was used in the preliminary experiments, which were carried out to determine what modifications to the plant were necessary in order to make it suitable for the present experiment. The properties of the other three batches are shown in Table III. Material for a small-scale control experiment was all taken from Batch 2, as it was expected that the quality of the cresylic acid would not vary appreciably from batch to batch. Actually it was found that variations did occur in the phenol and cresol content and that these were considerable. Batch 3 was especially high in phenol and

<div align="center">TABLE III.</div>
<div align="center">Properties of Cresylic Acid.</div>

Batch number.							2.	3.	4.
Experimental period in which used (inclusive)						.	1 to 10	11 to 23	24 to 32
Quantity used, gal	.	.	.	.	.	.	1100	1520	1050
Density, d_4^{20}	.	.	.	.	.	.	1·0371	1·0397	1·0373
Phenol content, % by wt	.	.	.	.	.	4·2	9·0	4·0
Cresol content, % by wt	.	.	.	.	.	89	82	86
Distillation range, per cent by wt :									
Up to 189° C.	.	.	.	.	.	.	0·5	0·4	0·5
189–192° C	.	.	.	.	.	.	0·2	0·2	0·2
192–197° C	.	.	.	.	.	.	12·3	25·7	6·0
197–200° C	.	.	.	.	.	.	59·3	45·6	46·5
200° C—F.B.P.	.	.	.	.	.	.	26·1	25·9	43·7
F.B.P.	.	.	.	.	.	.	202·7° C	202·9° C	204·2° C
Residue	.	.	.	.	.	.	1·0	1·6	1·9
Loss	.	.	.	.	.	.	0·6	0·6	1·2
Total	.	.	.	.	.	.	100·0	100·0	100·0

low in cresol content. The average phenol and cresol contents of the whole of the cresylic acid used in the semi-technical-scale experiment were 6·1 and 85·5 per cent respectively.

The make-up hydrogen used was made by the Lane process and had the following composition : CO_2, 0·4; CO, 1·2; H_2, 98·4 per cent.

Catalyst.

The catalyst used consisted of molybdenum disulphide which was prepared by a patented procedure [13] in two stages, namely (1) the preparation of molybdenum trisulphide by precipitation with mineral acid from an aqueous solution of ammonium thiomolybdate, and (2) the decomposition of molybdenum trisulphide to molybdenum disulphide. The manufacture of pelleted molybdenum trisulphide in quantity for the semi-technical-scale experiments was undertaken by Messrs Hopkin and Williams, Limited.
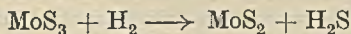
The decomposition or reduction of the trisulphide, which was carried out in a stream of hydrogen sulphide or a mixture of hydrogen sulphide and hydrogen, was attended by a vigorous evolution of heat. Thus, in an experiment with 100 g of molybdenum trisulphide, heated in a horizontal cylindrical silica tube of 1¼-in bore in a stream of hydrogen sulphide, a sudden evolution of heat occurred at about 360° C, which raised the

temperature of the material by 80° to 100° C. The nature of this exothermic reaction is not known since it seems to be fairly well established that the reaction

$$MoS_3 \longrightarrow MoS_2 + S$$
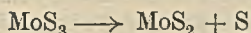
is actually endothermic.

It was found that the activity of the resulting molybdenum disulphide depended to a large extent upon the rate of rise of temperature during the decomposition of the trisulphide. For a high activity, it was found to be essential to heat the trisulphide in thin layers, using a low rate of rise of temperature, and ensuring the continuous passage of a stream of gas through the material during its decomposition. Smooth temperature control was obtained by the use of a mixture of two volumes of hydrogen and one volume of hydrogen sulphide, since the reaction

$$MoS_3 + H_2 \longrightarrow MoS_2 + H_2S$$

starts at a lower temperature than the decomposition reaction. The production of molybdenum disulphide for the semi-technical-scale experiment was carried out with 30 kg batches of the trisulphide in an electrically heated annular vessel formed by two co-axial cylinders 6 ft in length by 3 in and 6 in in int dia respectively. With this apparatus, the most active catalyst was made when the rate of heating was 0·5 to 1·5° C per min.

During the decomposition of the molybdenum trisulphide, which was in the form of cylindrical pellets, 3/16 in dia by 5/64 in thick, some physical disintegration occurred. The product was a granular material, of size 1/32 to 3/16 in, having a bulk density of 1·25 g/ml, and was used as a catalyst in this form. It was stored before use in an atmosphere of nitrogen to prevent loss of activity by oxidation.

Effect of Other Variables.

The results of the examination of the effect of other variables in the small-scale apparatus may be summarized as follows :

    1. In order to obtain the highest activity of the catalyst, it is necessary to maintain hydrogen sulphide in the reactants at the concentration given by the addition of 1 per cent of carbon disulphide to the cresylic acid ;

    2. The hourly throughputs of cresylic acid and hydrogen suited to the catalyst and the reaction conditions are respectively 0·5 vols, and 4700 vols, per vol of catalyst ;

    3. The initial temperature and pressure should be 430° C and 10 atm respectively. A greater pressure cannot be used at first without giving rise to the formation of excessive quantities of methyl *cyclo*hexane. It was found that the activity of the catalyst in promoting nuclear hydrogenation is reduced more rapidly than its activity in promoting deoxygenation. As the catalyst deteriorates, therefore, it is possible to maintain complete conversion of the cresol to hydrocarbons, without increasing the yield of methyl *cyclo*hexane, by gradually increasing the pressure. The limit to such an increase in

pressure is imposed only by the plant, but if a limit of 30 atm is taken, a " life " of two months should be obtained and a further extension to about three months should be possible by raising the reaction temperature progressively to a maximum of about 480° C;

4. Under these conditions the average degree of conversion of the cresylic acid into hydrocarbons amounts to 99·6 per cent and the average yields of toluene and methyl *cyclo*hexane, respectively, to 89 per cent and 6 per cent of the theoretical.

Results of the Semi-Technical-Scale Experiment.

Throughput of Raw Materials.   While maintaining the required conditions of pressure in the reaction chamber, it was not possible, owing to the narrow bore of the pipelines, to obtain the full throughput for which the plant was designed.   The maximum throughput obtainable with a pressure of 10 atm in the reaction chamber was 5·0 gal of cresylic acid per hour (*i.e.*, 0·55 tons per day) and 3600 cu.ft of hydrogen per hour.   This throughput was accordingly adopted for the experiment, and represented an increase in scale from the small-scale experiments of 2000 times.   The time of contact of the reactants in the catalyst bed, when working at this throughput and at a temperature and pressure of 430° C and 10 atm respectively, was approximately 2·5 sec;   the corresponding time of contact in the preheater was approximately 1·5 sec.

The reaction chamber was too large for the permissible throughput, and in order to work at the required hourly throughput of 0·5 vol cresylic acid per vol catalyst, the chamber was only half filled with catalyst.   The volume used was 1·68 cu.ft (*i.e.*, 47 litres or 127 lb).   The catalyst bed was 5 ft 6 in in depth and occupied the position shown in Fig. 2.   The space (4 ft in length) below the catalyst bed was filled with broken brick.   The gas space (1 ft 6 in in length) was left above the catalyst bed to improve the distribution of the reactants throughout the catalyst bed.

Owing to the design of the reaction chamber, it was found that the reactants were not uniformly distributed in the catalyst bed.   The catalyst was therefore not used to the best advantage, and a higher throughout per unit volume of catalyst would certainly be obtained in a reaction vessel of suitable design, *e.g.*, a vertical cylindrical vessel built up from a number of trays, the catalyst bed consisting of a series of layers separated by gas spaces.

Conditions of operation.   In starting the experiment, a mixture of toluene (70 per cent) and cresylic acid (30 per cent) was circulated until a temperature of 200° C was reached in the catalyst bed.   Cresylic acid containing 1 per cent of carbon disulphide was then charged to the reaction chamber.

It was decided that the initial temperature and pressure to be used at the hourly throughput of 5·0 gal of cresylic acid should be 430° C and 10 atm respectively, but that these conditions should be approached gradually to ensure good temperature control.   The actual conditions during the first day were an average maximum reaction temperature of 395° C with a pressure of 8 atm and a throughput of 3·8 gal per hour.   The throughput was gradually increased to the desired value during the next two days, and on the fourth day the conditions were :   Average maximum temperature

433° C; pressure, 9·4 atm; throughput, 5·0 gal per hour. The pressure was raised to 10 atm on the fifth day.

The performance of the plant was entirely satisfactory from the engineering standpoint throughout the experiment. The plant was still working well and the conversion was being maintained when the plant was shut down after 32 days running.

During this period, it was necessary to raise the temperature and pressure gradually as the catalyst deteriorated in order to maintain the plant output. At the beginning, the desired temperature was 430° C, but since this could not be maintained uniformly, it was decided to raise the maximum temperature to 433° C, in order that as much as possible of the catalyst should be in the neighbourhood of 430° C. It was found that the temperature of only 40 to 45 per cent of the length of the catalyst at the centre was within 10° C of the maximum. Since the temperature also varied across the catalyst bed to the extent of 25 to 30° C from centre to circumference it follows that the proportion of catalyst maintained at the desired temperature was a great deal less than 40 per cent.

Owing to the poor temperature distribution, the general level of temperature was too low, and a rather high proportion of methyl *cyclo*hexane in the product was a direct consequence of this. It was not, however, possible to increase the general temperature level appreciably without raising the maximum temperature excessively and so increasing the rate of deterioration of the catalyst.

A maximum reaction temperature of 433° C and a pressure of 10 atm were maintained, from the 5th to the 14th day. Owing to the deterioration of the catalyst it was necessary to raise the pressure and temperature gradually, and a pressure of 17 atm and a temperature of 439° C were reached on the thirty-second day. For the same reason it was also found necessary to increase the temperature of the feed material required to maintain a given reaction temperature. Thus, during the period from the fifth to the thirteenth day, while the reaction conditions were unchanged, the feed temperature had to be raised from 357 to 374° C.

Thermal Data. Since the plant was not designed for the production of toluene from cresol, the heat flow data calculated for the present experiment are not truly representative of the process. For example, since the catalyst chamber was only half filled with catalyst, the heat losses from the converter were much greater, in proportion to the total amount of heat involved, than they would have been in a suitably designed plant. The heat data obtained in the present experiment are still, however, of interest in providing a rough guide to the distribution of heat in a full-scale plant.

The essential thermal data are given in Table IV and are illustrated diagrammatically in Fig. 3. In calculating the data, the heat in the raw materials entering the heat interchanger was regarded as zero.

The relative importance of the various quantities of heat is more readily seen if their proportions are reduced to the basis of 100 units for the heat supplied in the preheater. The heat lost from the walls of the converter is a very large part of the total heat required by the process, but, as already explained, the proportion would be very much less in a plant designed for toluene production.

The heat of reaction corresponded to a value of 68 cal per g (7340 cal

per gm mol) of cresylic acid. This is about the same as the value which may be calculated from the heats of combustion of cresylic acid, hydrogen, and toluene, but it must be remembered that the probable error is very high in both cases.

TABLE IV.

Hydrogenation of Cresylic Acid : Heat Balance.

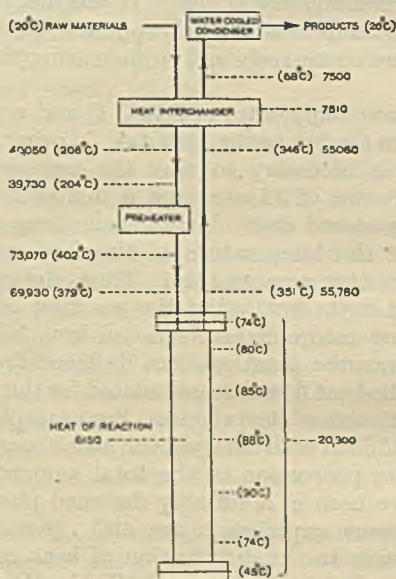|	B.Th.U per hour.	Arbitrary units.
Heat supplied in preheater	33,340	100
Heat of reaction (by diff.)	6,150	18
Total heat supplied to process . . .	39,490	118
Heat lost from converter	20,300	61
Heat lost from heat interchanger	7,510	22
Heat lost in product leaving heat interchanger .	7,500	22
Heat lost from pipelines	4,180	13
Total heat loss	39,490	118

FIG. 3.

HEAT FLOW DIAGRAM.

Gas Data. The composition of the make-up of hydrogen has already been given. The oxides of carbon (1·6 per cent) which it contained were hydrogenated to methane under the conditions of the reaction, and methane thus tended to accumulate in the residual gas (*i.e.*, gas remaining after removal of the condensable product). A proportion of the residual gas (3 per cent) was accordingly released to the atmosphere, and the composition

of the process gas was : CO_2, 0·4; CO, 0·4; H_2, 95·7; CH_4, 2·3 per cent. There was no evidence that any gaseous hydrocarbons were formed from the cresylic acid.

The average rate of flow of process gas per gallon of cresylic acid was 749 cu.ft (at S.T.P.), or 4670 vol per vol of cresylic acid. The actual consumption of pure hydrogen, after deducting (1) hydrogen released to atmosphere and (2) hydrogen used in converting oxides of carbon to methane and water, amounted to 46 cu.ft (at S.T.P.) per gallon of cresylic acid treated; this corresponds to 2·3 per cent by weight.

Yields. During the experiment 3670 gal (17·07 tons) of cresylic acid were treated, and 3730 gal (14·41 tons) of oil product were obtained. This corresponds to an average yield of 84·4 per cent by weight.

The oil product was obtained partly as a condensate and partly from the gas by scrubbing with active carbon. As the reaction pressure was raised the pressure of the gas leaving the high-pressure separator was increased; the proportion of the scrubber spirit accordingly decreased while that of the condensate increased. Thus the spirit from the scrubber decreased from 17·0 per cent by weight of the cresylic acid treated on the fourth day to about 4 per cent at the end of the experiment. The average yields expressed as per cent by weight of the cresylic acid treated during the period from the fourth day to the end of the run were as follows :

Spirit from scrubber			6·6
Oil condensate			78·3
Water			16·3
Loss			1·1
Total			102·3

The proportion of unchanged cresylic acid in the total oil product was 0·4 per cent.

The oil products were analysed as follows. The product was extracted with sodium hydroxide solution, and the unchanged cresylic acid recovered and weighed. The hydrocarbons were dried, and 100 g were fractionated from a 250-ml flask fitted with a 30-in fractionating column containing a closely fitting steel helix. The hydrocarbons boiling above 95° C were collected in a series of 10° fractions. The fraction 95 to 105° C was refractionated into fractions boiling up to 95° C, 95 to 105° C, 105 to 115° C, and residue above 115° C. The final fraction boiling from 95 to 105° C was assumed to consist entirely of methyl *cyclo*hexane; this was certainly not correct, but since the fraction was small the error involved was not large, and the assumption gave a maximum figure for the yield of methyl *cyclo*hexane, and hence a minimum figure for the yield of toluene. The fraction of 105 to 115° C (of which a very large proportion distilled between 109 and 111° C) amounted to about 80 per cent by weight of the total hydrocarbons, and consisted mainly of toluene with a very small proportion of methyl *cyclo*hexane. The proportions of these two constituents were calculated from determinations of density (d_4^{20}) and refractive index (n_D^{20}).

The results and the method of analysis are illustrated by the results for some of the liquid condensates recorded in Table V. The yields for the

3 c

whole experiment, per cent by weight of the cresylic acid converted, were as follows :

Benzene and *cyclo*hexane	6·4
Methyl *cyclo*hexane	5·6
Toluene	63·2
Xylenes	8·3

The yields of toluene and methyl *cyclo*hexane corresponded respectively to 87·3 and 7·3 per cent of the theoretical. Of the cresols in the cresylic acid 94·6 per cent was therefore accounted for; the remainder was partly

TABLE V.

Analysis of Oil Product (Condensate) from Hydrogenation of Cresylic Acid.

Period (24 hr).	2.	7.	14.	22.	28.	Fraction 95–105° C r. 1–12.	Fraction 95–105° C r. 20–31.
Yield of liquid product, % by wt of cresylic acid treated	62·4	76·1	78·7	80·5	82·0	—	—
Cresylic acid in liquid product, % by wt	nil	nil	0·8	0·5	0·4	—	—
Fractionation of hydrocarbons, % by wt :							
Up to 95° C	4·0	4·3	6·8	8·0	4·0	20·1	20·8
95–105° C	2·0	3·2	4·8	3·5	3·2	46·2	35·5
105–115° C	82·0	81·4	77·3	75·0	81·3	23·4	39·1
115–125° C	—	—	—	1·0	0·9	—	—
125–135° C	—	—	—	2·2	1·5	—	—
135° C—F.B.P.	—	—	—	—	1·1	—	—
F.B.P.	115° C	115° C	115° C	135° C	136° C	110° C	115° C
Residue	9·6	9·3	10·2	6·8	6·3	} 10·3	4·6
Loss	1·8	1·8	0·9	2·3	1·7		
Properties of fractions :							
1. 95–105° C—							
Density, $d_4^?$	—	0·8268	0·8394	0·8336	0·8193	0·7972	0·7976
Refractive index, $n_D^?$	1·4640	1·4679	1·4770	1·4698	1·4017	1·4432	1·4465
2. 105–115° C—							
Density, $d_7^?$	0·8609	0·8604	0·8610	0·8610	0·8610	0·8582	0·8576
Refractive index, $n_D^?$	1·4928	1·4928	1·4930	1·4920	1·4922	1·4895	1·4924
Amount of methyl cyclohexane in fraction 105–115° C by wt :							
(i) From density	6·5	6·4	5·8	6·0	6·0	8·8	9·5
(ii) From refractive index	5·3	5·3	5·0	6·4	6·0	9·8	6·0
(iii) Mean	5·9	5·9	5·4	6·2	6·0	9·3	7·8

a true loss and partly an analytical error, since some methyl *cyclo*hexane and toluene was almost certainly left in the fractions recorded as benzene and xylenes. With improved fractionation, therefore, the yields of toluene and methyl *cyclo*hexane would probably be increased.

Comparison with Small-Scale Experiment. In order to establish an accurate comparison between the laboratory investigations and the semi-technical-scale trial, a continuous experiment on a small scale (12 ml cresylic acid per hour) was carried out concurrently. Very similar results were obtained in this experiment, the yields of the various products being almost identical with those obtained on the larger scale. Conversion of the cresylic acid was again maintained by gradually raising the temperature and pressure, values of 440° C and 18 atm respectively being reached on the thirty-second day.

TOLUENE FROM n-HEPTANE.

It was well known that paraffinic or mono-olefinic hydrocarbons with chains of more than six carbon atoms may be converted to aromatic hydrocarbons by a cyclization reaction over suitable catalysts at temperatures from 400 to 600° C. A study was therefore made of the possibility of utilizing this process for the production of toluene from n-heptane obtained by the Fischer–Tropsch synthesis.

Fischer–Tropsch oil was prepared from water gas by passage at atmospheric pressure over a cobalt–thoria–kieselguhr catalyst at 180 to 190° C. n-Heptane was separated by fractionation from the paraffinic residue from the fraction boiling from 40 to 140° C after this had been used for the preparation of lubricating oil by polymerization with aluminium chloride. The yield of n-heptane amounted to about 5 per cent by weight of the total Fischer–Tropsch product. The physical properties of the n-heptane separated in this way are compared with published data in Table VI.

TABLE VI.

Properties of n-*Heptane.*

	Pure heptane.	Heptane prepared from Fischer–Tropsch oil.
Boiling point	98·4° C	98–99° C
Density, d_4^{20}	0·6838	0·6834
Refractive index, n_D^{20} . .	1·3877	1·3870

The apparatus used for cyclization consisted of a Pyrex reaction tube, 20 in long by $\frac{5}{8}$ in int dia. On the top of the tube was a cup and mercury seal into which fitted a calibrated dropping funnel. The top seven inches of the tube were filled with broken silica, and the next eight inches contained the catalyst. The reaction tube was held inside a vertical electrically heated, aluminium-block furnace, 18 in long. The aluminium block, 11 in long, was placed at the bottom of the furnace and gave a uniform temperature throughout the catalyst. The throughput of heptane was 10 ml per hour, or 0·25 vol per vol catalyst per hour.

The Effect of Various Catalysts on the Cyclization of n-Heptane.

The following catalysts were the most active of those examined :

(1) Molybdenum trioxide (20 per cent) on alumina gel, prepared by impregnating the gel with the requisite quantity of ammonium molybdate in aqueous solution, drying and igniting at 500° C ;

(2) Molybdenum trioxide–alumina, containing 20 per cent molybdenum trioxide, prepared by adding ammonia to a solution of ammonium molybdate and aluminium nitrate, filtering, washing, drying, and igniting at 500° C ;

(3) Ammonium chromo-molybdate, prepared by adding ammonium molybdate in aqueous solution to chromium nitrate, and filtering, washing, and drying the precipitate ;

(The catalytic activities of heteropoly acids of molybdenum for the

aromatization of n-heptane–n-heptene feed have already been reported (Herington & Rideal. *Proc. Roy. Soc.*, 1945, **A 184**, 425) and the activity of ammonium chromo-molybdate, prepared as described above, compared with that of the other catalysts for a n-heptane feed.)

(4) Chromic oxide–alumina (20 per cent Cr_2O_2), prepared by precipitating the hydroxides with ammonia from a solution containing the nitrates, and filtering, washing, drying, and igniting the hydroxides;

(5) Chromium oxide, prepared by the reduction of chromic acid with alcohol, followed by precipitation with ammonia. (Various methods of preparation of chromium oxide for hydrogenation and dehydrogenation reactions have been described; the preparation used in the present investigation had been found to give an active catalyst for another purpose [14]);

(6) Chromic oxide on activated alumina, prepared by impregnating granules of activated alumina (10 to 12-mesh) with an aqueous solution of chromium nitrate or ammonium dichromate. (This catalyst was used for cyclization by Grosse, Morrell, and Mattox [15]);

All the catalysts were heated in hydrogen for 1 hour at the reaction temperature before the flow of heptane was started.

The results obtained with these catalysts are given in Table VII. The supported molybdenum trioxide (1) and molybdenum trioxide–alumina (2) catalysts were more active than the chromic oxide–alumina catalyst (4) and the heteropoly compound, ammonium chromo-molybdate (3). The rate of deterioration of the molybdenum oxide catalyst (1) at 470° C was, however, very high, the proportion of aromatic hydrocarbons in the product falling from 42·5 per cent in the first period of 40 min to 17·0 per cent in the fourth period of 40 min.

Chromium oxide (5) showed a higher conversion and a slower rate of deterioration than the molybdenum-oxide catalyst (1), the yield of aromatic hydrocarbons falling from 43 per cent in the first period of 40 min to 31 per cent in the fourth period of 40 min.

The reaction temperature of 550° C recommended by Grosse, Morrell, and Mattox, for cyclization with their catalyst (6), consisting of chromic oxide on activated alumina, was higher than the temperature previously used for this reaction (normally 470° C). At 550° C it was found that this catalyst gave a higher conversion to aromatic hydrocarbons than the other catalysts and its activity increased during the experiment from the first to the fourth period of 40 min. The overall conversion (39 per cent) was lower than that obtained by Grosse and his co-workers (66 per cent), but the catalyst appeared to be the most suitable for use in large-scale operation.

A catalyst containing 8 per cent of chromic oxide was used for the experiment (catalyst No. 6, Table VII). Further experiments were made to determine the effect of varying the amount of chromic oxide from 4 to 15 per cent. Variation from 4 to 10 per cent was found to be without much influence, but the catalyst containing 12 per cent was markedly more active. Further increase in the proportion of chromic oxide was not beneficial. The catalyst containing 12 per cent of chromic oxide was therefore used in all subsequent experiments.

TABLE VII.

Effect of Various Catalysts on the Cyclization of n-*Heptane.*

Catalyst.	1.	2.	3.	4.	5.	6.
Reaction temperature, ° C	470	470	470	470	470	550
Duration of experiment, hr	2·7	1·3	1·3	1·3	2·7	2·7
Yields, per cent by wt of original heptane :						
Liquid product	70·9	58·8	82·8	78·2	77·4	62·6
Gas	15·5	17·3	8·6	8·5	14·4	30·9
Loss	13·6	23·9	8·6	13·3	8·2	6·5
Total	100·0	100·0	100·0	100·0	100·0	100·0
Analysis of total liquid product, per cent by wt of original heptane :						
Aromatic hydrocarbons	17·0	16·4	14·9	11·1	28·0	39·0
Unsaturated hydrocarbons	5·3	0·7	5·5	5·1	6·2	8·2
Saturated hydrocarbons	46·3	40·5	61·4	61·0	43·2	14·7
Residue	2·3	1·2	1·0	1·0	nil	0·7
Aromatic hydrocarbons in product, per cent by wt of product :						
First period of 40 min	42·5	—	—	—	43·0	55·5
Fourth period of 40 min	17·0	—	—	—	31·0	62·7

The Effect of Temperature and Catalyst Pretreatment.

The effect of temperature on the cyclization of *n*-heptane using the catalyst containing 12 per cent of chromic oxide is shown in Table VIII. The conversion to aromatic hydrocarbons was practically the same at 540° C and 550° C, and decreased above 550° and below 540° C. All the subsequent experiments were carried out at a temperature of 550° C.

TABLE VIII.

Effect of the Temperature of Reaction.

Catalyst : 12 per cent chromic oxide on activated alumina.
Duration of experiment : 6 hours.

Temperature, ° C.	520.	530.	540.	550.	560.
Yields, per cent by wt of original heptane :					
Liquid product	70·2	63·8	63·6	63·4	59·2
Gas	22·3	28·2	27·1	28·3	32·2
Loss	7·5	8·0	9·3	8·3	8·6
Total	100·0	100·0	100·0	100·0	100·0
Analysis of total liquid product, per cent by wt of original heptane :					
Aromatic hydrocarbons	43·5	47·5	48·9	50·4	46·2
Unsaturated hydrocarbons	4·3	3·9	4·2	4·7	9·3
Saturated hydrocarbons	20·9	9·6	8·1	6·7	2·1
Residue	1·5	2·8	2·4	1·6	1·6
Aromatic hydrocarbons in product, per cent by wt of product :					
First 2 hours	65·2	79·0	80·0	82·0	81·0
Third 2 hours	59·1	72·0	76·7	74·0	79·4

In most of the experiments at 550° C, the yield of aromatic hydrocarbons amounted to about 50 per cent of the heptane treated, whereas Grosse [15] reported a yield of 66 per cent.   Some experiments were made to determine whether various heat treatments of the catalyst would improve its activity. In three experiments, the supported catalyst was heated to temperatures of 550°, 600°, and 650° C respectively, but there was practically no difference in the activities of the three catalysts.   When, however, the support (activated alumina) was heated in hydrogen to a temperature of 900° C before impregnation with ammonium dichromate, a more active catalyst was obtained.   This catalyst gave a yield of 56·8 per cent of aromatic hydrocarbons in a run of six hours duration.   During the first two hours, the product contained 91·2 per cent of aromatic hydrocarbons, and during the last two hours, 85·1·per cent.

The Rate of Deterioration of the Catalyst.

A deterioration experiment of 70 hours total running time was then carried out, the catalyst being revivified after each run of 2 or 6 hours by the passage of air at the rate of 0·5 cu.ft per hour.   The time required to burn off the carbon deposited on the catalyst was approximately 6 hours after a run of 6 hours, and 1 hour 20 minutes after a run of 2 hours duration. After revivification the catalyst was reduced with hydrogen.   The results of the " odd-number " runs are given in Table IX.

There was a slow deterioration in the activity of the catalyst, shown by the decrease in the yield of aromatic hydrocarbons, from about 57 per cent to 51 per cent after 70 hours.   This represented by far the best performance of any of the catalysts studied, and was considered to provide the basis of a satisfactory process.

The mechanism for the deterioration of these catalysts has been worked out by Herington and Rideal (*loc. cit.*).

SUMMARY.

Investigation of various processes for the production of toluene was undertaken at the Fuel Research Station, largely on behalf of the War Office and the Ministry of Supply.   Attention was mainly directed to the treatment of coal products, but a brief study was also made of the cyclization of *n*-heptane.   The raw materials examined and the essential results obtained were as follows :

Benzene.

One method for the production of toluene from benzene is carried out in two stages, namely (1) the preparation of benzaldehyde from benzene and carbon monoxide in the presence of aluminium chloride, and (2) the hydrogenation of benzaldehyde to toluene.

The first stage, investigated at the Chemical Research Laboratory, Teddington, was deemed impracticable, but it was shown that the second could be carried out as a continuous process over molybdenum disulphide at 430° C and 5 atm to give a yield almost equal to the theoretical.

TABLE IX.

Experiment Showing the Rate of Deterioration of the Catalyst.

Catalyst : 12 per cent chromic oxide on activated alumina.
Alumina preheated in hydrogen to 900° C before impregnation.
Reaction temperature : 550° C.

Number of run.	1.	3.	5.	7.	9.	11.	13.	15.	17.	19.	21.	23.	25.	27.
Duration of run, hr.	6	6	2	2	6	2	2	2	2	2	2	2	2	2
Total time of running at end of run, hr.	6	18	22	26	34	38	42	46	50	54	58	62	66	70
Yields, per cent by wt of original heptane :														
Aromatic hydrocarbons	56·8	52·6	58·6	60·3	53·5	52·4	53·2	53·0	55·0	51·2	50·3	50·9	51·8	50·7
Unsaturated hydrocarbons	4·8	3·9	4·0	3·8	5·0	—	4·5	2·9	2·8	2·8	4·2	4·8	4·2	3·1
Saturated hydrocarbons	2·3	6·5	2·6	1·6	5·3	—	4·6	5·9	2·6	6·9	6·4	8·1	7·1	7·0
Residue	0·7	1·2	0·8	1·0	1·2	—	1·5	0·8	1·2	1·1	0·9	0·8	1·7	1·8
Total liquid product.	64·6	64·2	66·0	66·7	65·0	66·0	63·8	62·6	61·6.	62·0	61·8	64·6	64·8	62·6
Aromatic hydrocarbons in product, per cent by wt of product:														
First 2 hours	91·2	89·3	88·9	91·6	89·3	79·5	83·4	84·6	89·1	82·5	81·3	78·8	80·0	81·0
Third 2 hours	85·1	74·5	—	—	76·4	—	—	—	—	—	—	—	—	—

Xylene.

The cracking of coal-tar naphtha at 790 to 800° C in a continuous process on a scale of 1 gal per hour, gave yields of benzene and toluene of 6 per cent and 22 to 23 per cent respectively.

It was found that the yields could be greatly improved by cracking in the presence of hydrogen under pressure. Thus the continuous hydrogenation-cracking of xylene on a scale of 40 ml per hour at 550 to 600° C, under a total pressure of 50 atm, gave a yield of about 50 per cent of toluene.

Naphthalene.

The hydrogenation-cracking of tetrahydronaphthalene was successfully carried out as a continuously operated process on a scale of 40 ml per hour over silica chips at 550 to 600° C and 200 atm. The yields of benzene, toluene, and ethyl benzene were respectively 14, 12, and 19 per cent of the tetralin converted.

Cresol.

A process for the hydrogenation of cresol to toluene was developed to a semi-technical scale for the treatment of 120 gal of cresylic acid per day.

The catalyst used consisted of molybdenum disulphide made by the reduction of the trisulphide in an atmosphere of hydrogen and hydrogen sulphide under carefully controlled conditions of temperature. The hourly throughputs of cresylic acid and hydrogen were respectively 0·5 vols, and 4700 vols per vol of catalyst. The initial maximum reaction temperature and pressure employed in the semi-technical-scale experiment were 433° C and 10 atm respectively. Conversion to hydrocarbons was complete. As the catalyst deteriorated, the conversion was maintained by raising the temperature and pressure, values of 439° C and 17 atm respectively being reached on the thirty-second day.

During the experiment, 3670 gal (17·07 tons) of cresylic acid were treated and 3730 gal (14·41 tons) of oil product were made. This corresponds to an average yield of 84·4 per cent by weight. The proportion of unchanged cresylic acid in the total oil product was 0·4 per cent. The yields of toluene and methyl *cyclo*hexane corresponded respectively to 87·3 and 7·3 per cent of the theoretical.

n-*Heptane.*

It was concluded that the most suitable catalyst for the cyclization of *n*-heptane (derived from Fischer–Tropsch oil) on a large scale would be chromic oxide supported on activated alumina. At a reaction temperature of 550° C, the yields of aromatic hydrocarbons amounted to about 57 per cent of the heptane treated (or 62 per cent of the theoretical yield) over a period of 6 hours.

A run of 70 hours was carried out in which the catalyst was regenerated by oxidation with air after 6 hours running or in some cases after 2 hours running. The conversion decreased from 57 per cent of aromatic hydrocarbons with the fresh catalyst to about 51 per cent after 70 hours running.

ACKNOWLEDGMENTS.

References.

[1] Demann, Krebs, and Borchers. *Tech. Mitt. Krupp. Tech. Berichte*, 1938, **6**, 59.
[2] Report of the Fuel Research Board for the Year ended 31st March, 1939, p. 132.
[3] Manning and Shepherd. Fuel Research Technical Paper No. 28, 1930.
[3a] Egloff and Grosse. U.O.P. Booklet No. 217.
[4] South Metropolitan Gas Company. B.P. 569,035 (1945).
[4a] Roffey, Ashmore, and Penny. B.P. 574,549 (1946).
[5] Cawley and Hall. *J. Soc. chem. Ind.*, 1934, **53**, 810.
[6] Standard Oil Development Co. B.P. 526,355 (1940).
[7] Standard Oil Development Co. B.P. 525,981 (1940).
[8] Cawley. *Fuel*, 1933, **12**, 366.
[9] Hall. *Fuel*, 1933, **12**, 76.
[10] Newall. Fuel Research Technical Paper No. 48, 1938.
[10a] Francis. "Thermochemistry of Petroleum Hydrocarbons," *The Science of Petroleum*, 1938, p. 2088.
[11] Cawley and King. Fuel Research Technical Paper No. 45, 1937.
[12] Cawley and King. Fuel Research Technical Paper No. 51, 1939.
[13] International Hydrogenation Patents Co., Ltd. B.P. 455,313 (1936).
[14] Lazier and Vaughan. *J. Amer. chem. Soc.*, 1932, **54**, 3080.
[15] Grosse, Morrell, and Mattox. *Industr. Engng. Chem.*, 1940, **32**, 528.

OBITUARY.

JOHN FALCONER TAYLOR.

IT is with regret that we record the death on September 16, 1946, of John F. Taylor who, only in December last, retired after a long association with the Burmah Oil Company and its chief engineer since 1928.

Born in 1872 he was apprenticed to the Barrowfield Iron Works Ltd., Glasgow, in 1888, subsequently taking charge of outside erection work and later becoming chief draughtsman. In 1910 he joined the staff of Messrs. A. Gillespie and Son, Consulting Engineers, and, under the direction of the late Mr. John Gillespie, was actively engaged in the design and lay-out of all the extension schemes in Iran up to about 1916, including the famous Admiralty extension. He also carried out similar duties in con-nexion with the original layout at Llandarcy.

When, in 1919, Mr. John Gillespie became Chief Engineer of the Burmah Oil Company, Mr. Taylor came to London with him and subsequently succeeded him as Chief Engineer on his retirement in 1928. Mr. Taylor had thus been directly associated with the two companies (Burmah Oil Company and Anglo-Iranian Oil Company) for thirty-five years.

Among the many projects with which Mr. Taylor was concerned, his work on the Singu Reclamation Scheme, involving the building of the Training Wall along the bank of the Irrawaddy at Singu, will long be re-membered. He was elected a Member of the Institute in 1929.

His passing will be deeply regretted by his many friends in Britannic House, as well as those in the East.

W. W.