

Mr. H. E. Potts asked whether soda had a more penetrating effect on the fibre than lime, and might not the difference be due to the difference in the surface tension induced by the lime or soda used.

Mr. CLAYTON BEADLE replied that the alkali was washed out of the beaten stuff. After beating, the fibre was able to retain a far larger quantity of water than when unbeaten. Whether that was a chemical or physical phenomenon it was difficult to say. Eighteen years ago he had made some experiments on the rates at which desiccated cotton wool and other forms of cellulose took up water on exposure to the air. He believed that he was the first to observe that this absorption gave rise to an increase in temperature and that the two, namely the temperature rise and moisture absorption, bore some relation to one another (Beadle and Dahl, *Chem. News*, **73**, April 17, 1896). Subsequently, without any knowledge of these observations, Professor Orme Masson measured the actual heat evolved per gram of water absorbed (*Proc. Roy. Soc.*, 1904, **74**, 230—254). Up to the time of the publication of Masson's researches he (Mr. Beadle) had been inclined to regard the rise of temperature as evidence of chemical changes, but Masson's conclusions were that the amount of heat was approximately that calculated for the quantity of vapour absorbed, and that the water condensed on the cotton did not combine chemically with it. That, however, still left the explanation of "wetting" by prolonged beating or "ageing" an open question. Some regarded it as real hydration, but others thought that it was purely mechanical.

The beaten *Hedychium* became more wet and slimy to the feel, absorbed water and became more gelatinous as the result of ageing, and simultaneously the bursting strain of the paper produced therefrom increased. As the material increased in wetness or hydration it became more susceptible to putrefactive changes, resulting in the destruction of just that portion of the material which had given increased strength, hence the undoing of the initial effects of ageing.

With regard to the use of soda or lime, the relative amounts required to be used in practice was not a matter of molecular ratios. In practice it was found that 10 per cent. of lime would bring about a somewhat similar result to 5 per cent. of caustic soda. In the case of soda, soluble salts were obtained, whilst with lime the salts were insoluble. Furthermore, the amount of lime in solution at any one time was small as compared with soda, and boiling with

lime was a longer operation in consequence. The hydration effect was greater in the case of soda, as would be observed on comparing the two curves.

THE CHEMICAL EXAMINATION OF LIQUID FUELS.

BY W. HAMILTON PATTERSON, M.Sc.

In comparison with the enormous advances made in the mechanical application of oil as a source of power, the chemical side of the question has been somewhat neglected, and there is much room for scientific research and investigation in the preparation and utilisation of fuels. There is also much overlapping and ambiguity in the nomenclature of the various technical products which are put on the market as liquid fuels. There should be some distinction between "oil fuels" and "fuel oils." In this paper the term "fuel oil" will be reserved for oils burnt in external combustion, *e.g.*, under a boiler for the purpose of raising steam; "oil fuels," on the other hand, will mean oils utilised for the production of power in internal combustion engines. The term liquid fuel may be applied in either case.

Although many fuel oils may often be equally well utilised as oil fuels, there is a difference in the requirements. In oil fuels volatility is of greater importance, and the obtaining of oils which will neither corrode nor give trouble in the cylinders of internal combustion engines on explosion or burning. In fuel oils more vital factors are cheapness, a fairly high flash point, and high calorific value. The various liquid fuels and their allied products derived either from petroleum or coal tars are not definite compounds; it is therefore impossible to assign to these varying mixtures scientific names. It is, however, greatly to be deplored that, in technical usage, the same name is not applied in different parts of the world to denote what is essentially one and the same product. What confusion occurs, for example, in the meaning of the words, paraffin, benzine, solar oil, naphtha, etc. To add still further to the chaos which already exists we find specially coined trade names. Of oil fuels the only variety widely used for certain kinds of motor engines is petrol, but alcohol might be used instead with equal efficiency, provided it could be obtained cheaply enough, and also benzol, or even better, a mixture of the two.

TABLE I.

No.	Description.	Sp. gr. at 15-0° C.	Carbon.	Hydrogen.	Sulphur.	Oxygen and nitrogen.	Net calorific value in calories.	Net calorific value in B.Th.U.
1.	Fuel oil used on trial of a torpedo destroyer . .	0.921	85.28	11.03	0.55	2.24	9,086	17,975
2.	Petroleum product sold at a little over £2 per ton	(0.888) at 18° C.	80.20	12.57	0.31	0.02	10,097	18,175
3.	Ordinary crude petroleum	0.923	—	—	0.45	—	9,956 (Hydrogen assumed 12.0%).	17,021
4.	"Light fuel oil"	(0.900) at 18° C.	88.58	10.81	0.43	0.18	10,113	18,405
5.	"Admiralty fuel oil"	0.928	86.40	11.55	0.34	1.71	9,961	17,930
6.	"Residuum"	(0.943) at 18° C.	86.44	11.23	0.30	2.03	10,065	18,117
7.	"Black oil"	0.928	86.44	11.83	0.51	1.22	9,977	17,950
8.	A refined oil	(0.904) at 18° C.	85.05	12.15	0.37	2.43	9,998	17,996
9.	A Roumanian crude oil	0.825	—	—	0.20	—	9,024 (H assumed 13.0%).	17,863
10.	do.	0.830	83.77	12.08	0.20	2.06	10,012	18,022
11.	Solar oil (Texas)	(0.862) at 18° C.	85.35	12.02	0.17	1.50	10,191	18,344
12.	Scottish shale oil	0.855 (at 18.0°C.)	86.16	12.37	0.20	1.21	10,138	18,248
13.	do.	0.862	85.35	12.44	0.20	1.74	10,176	18,317
14.	do.	0.867	—	—	0.33	—	9,961 (H assumed 12.5%).	17,930
15.	A coal tar oil (?)	0.958	86.16	9.05	0.80	3.00	9,422	16,960
16.	A gas oil	1.067	87.62	5.98	0.07	5.73	8,974	16,153
17.	do.	1.004	83.72	7.20	0.82	8.17	8,876	15,977

When, however, liquid fuels have to compete with coal for the production of power, only crude products, by-products, or residues can be considered. The available sources of such liquid fuels may be divided as follows:—

(1) Crude petroleum or residues and products from petroleum.

(2) Tar oils from coal distillation, coking or producer plants, especially from bituminous coal producers.

(3) Liquids or oils from vegetable or animal sources including alcohol and nut oils (at the present time of little importance).

(4) Oils from lignite, peat, wood, or shale.

The last class is not very important as far as this country is concerned, except as regards the Scottish oil production from shale, which amounts to about 70 million gallons per annum. This figure includes, however, a large percentage of constituents too valuable to be utilised as ordinary liquid fuel. The following results have been obtained in the examination of various liquid fuels, most of which are available in this country and obtainable at the cheapest price; the highest price (i.e., at the time of the experiments) in any case in this country being a little over £3 per ton, most of them, however, being considerably cheaper. They have been examined more particularly with reference to their use as oil fuels. The calorific values were determined by the Mahler bomb calorimeter, a method which gives absolutely reliable results when worked under proper conditions. The sulphur was determined by titration of the bomb liquid, allowance being made for the nitric acid produced in each case. Carbon and hydrogen were determined by the ordinary combustion method of elementary organic analysis.

Open tests were made of flashing and burning points, while viscosity was determined in a special viscometer. The main figures are tabulated in Table I.

Of these oils, Nos. 3, 11 and 14 have been found to work well on Diesel engines, and there is good reason to suppose that Nos. 1, 2, 5, 7, 8, 12, 13 and 14 would work equally well.

Nos. 16 and 17 have been found to give trouble with Diesel engines. As fuel oils probably all the oils tabulated would give an efficiency proportional to their net calorific value. It will further be seen that the sulphur content is in no case excessive. The much lower calorific values of oils Nos. 16 and 17 may account in some measure for the trouble they give in Diesel engines, but there are other factors which are brought out in the tables below. In combustion of fuels in the bomb calorimeter, the products of combustion are cooled to the ordinary temperature of the calorimeter; the hydrogen of the fuel is oxidised to water which gives up its latent heat on condensation. There is also a small amount of sulphuric and nitric acids produced which must be allowed for. The heat value actually obtained in the bomb calorimeter is the gross value, while that corrected for hydrogen and acid formation is the net value, and corresponds to the maximum energy of the fuel which is available for the production of work in ordinary practice. It is astonishing how in ordinary commercial practice the two values are confused. To apply the right correction for the water condensed, it is necessary to know the hydrogen in the oil (also the free water if there is any present). To ascertain the correction due to the former cause, the only absolutely reliable means is to determine the hydrogen by making an elementary analysis of the oil. This is, however, a tedious process and in most cases, as will be shown below, the hydrogen content may be assumed with an accuracy sufficient for the purpose of applying this correction in technical work.

TABLE II.

No.	Open flash point, °C.	Burning point, °C.	Hydrogen.	Gross calorific value (in calories).	Hydrogen correction.	Acid correction.	Net calorific value.
1.	133°	164°	11.03	10,644	644	14 (total)	9,986
2.	125°	147°	12.57	10,798	679	15 + 7	10,097
3.	125°	155°	(12% assumed)	10,622	(648 assumed)	8 + 10	9,956
4.	187°	220°	10.81	10,720	584	13 + 0	10,114
5.	138°	163°	11.55	10,606	624	13 + 8	9,981
6.	166°	197°	11.23	10,690	606	12 + 7	10,065
7.	144°	172°	11.83	10,640	639	12 + 12	9,977
8.	122°	135°	12.15	10,672	656	10 + 8	9,998
9.	Ordinary temp.	Ordinary temp.	(13.0% assumed)	10,642	(702 assumed)	12 + 4	9,924
10.	Ordinary temp.	Ordinary temp.	12.08	10,731	702	11 + 6	10,012
11.	92°	07°	12.02	10,905	697	13 + 4	10,191
12.	129°	158°	12.37	10,825	668	13 + 6	10,138
13.	130°	150°	12.44	10,868	672	13 + 7	10,176
14.	130°	146°	(12.5% assumed)	10,646	(675 assumed)	3 + 7	9,961
15.	77°	106°	9.05	9,944	489	9 + 24	9,422
16.	90°	109°	5.08	9,322	324	8 + 16	8,974
17.	77°	86°	7.29	9,295	394	7 + 18	8,870

TABLE III.

No.	Net calorific value.	Calculated value.	Difference.	Percentage fractionated.							
				80° C.	120°	160°	200°	240°	280°	320°	360°
1.	9,986	10,300	+344	—	—	—	0	3	15	34	54
2.	10,138	10,520	+391	—	—	0	8	10	20	—	—
4.	10,114	10,315	+201	—	—	—	—	—	0	12	50
5.	9,981	10,295	+334	—	—	—	—	—	14	40	76
6.	10,065	10,193	+128	—	—	—	—	—	16	20	68
7.	9,977	10,401	+424	—	—	—	—	4	11	31	—
8.	9,998	10,335	+337	—	—	—	—	11	58	—	—
10.	10,012	10,450	+438	0	17	31	41	49	57	—	—
11.	10,191	10,608	+417	—	—	0	11	32	64	—	—
12.	10,138	10,529	+391	—	—	—	0	0	10	70	—
13.	10,176	10,479	+303	—	—	—	0	7	28	—	—
15.	9,422	9,479	+ 57	—	0	4	8	29	—	—	—
16.	8,974	8,630	—345	—	—	—	6	40	55	—	—
17.	8,876	8,620	—256	—	—	{ 180° 13 }	48	{ 220° 86 }	—	—	—

In Table II., the figures are given for the open flash points, burning points, hydrogen contents, gross calorific value given by the bomb calorimeter determination, the water correction for the hydrogen, the acid correction in the order nitric acid+sulphuric acid, and the corrected or net calorific value.

In low boiling fractions of petroleum products, the hydrogen content may reach 16 per cent. or more.

It is of interest to calculate the calorific values from the results of analysis and to compare them with those actually obtained by the calorimeter. For this purpose, the German modification of the Dulong formula is used,

i.e., $81C + 290(H - \frac{O+N}{8}) + 25S - 6W$, a formula which gives results in the case of ordinary coal, within 1 per cent. of the actual. It is not meant to be implied that this formula is strictly applicable to oils, but if it is applied, the differences are instructive. Applying this to the oils above, figures are given in Table III.

Figures for fractionation are also appended.

Curves plotted to show the change of viscosity with temperature show very sudden rises in viscosity at the low temperature end of the curve. For instance, viscosity figures for No. 2 are:—

15° C.	18° C.	25° C.	50° C.	75° C.	
68-67	31-71	15-57	5-55	2-70	(Water = 1.)

At the low temperature end of the curve, 0-1° C. makes a very marked difference in the time of flow. This is of importance when oils are to be used on internal combustion engines. The Diesel engine can take an oil which will not visibly flow at ordinary temperature, if the oil has been subjected to a preliminary heating. On the other hand, it is possible to have an oil too mobile, which gives trouble by leaking through the valves. If an engine is taking feed at a temperature where the viscosity curve for the particular oil used is steep, trouble will probably be caused by the slight temperature variations making such a marked difference in the rate of flow of the oil.

A curve plotted to show the percentage fractionated at various temperatures shows a steep initial rise in No. 2 and a wave surface with two crests in the cases of Nos. 9 and 10, but the rest do not differ widely from straight lines of varying inclinations to the ordinates.

The tables above bring out in sharp contrast the distinction between products which have petroleum for their origin and those which have coal. This is especially noticeable in the case of the differences between actual and calculated calorific values which are negative in the latter case.

The two products are entirely different in all their properties, typical mainly of the differences between saturated and cyclic hydrocarbons.

No. 1 fractionated gave the following results:—

	Carbon.	Hydrogen
	per cent.	per cent.
1st Fraction 13 per cent., b.pt. 235°—275° C.	84-04	12-16
4th Fraction 32 per cent., b.pt. above 385° C. (or residue)	87-74	10-45

In the latter case there was some free carbon.

Taking petroleum products by themselves, there is a general relationship between low specific gravity, low flash point, high hydrogen content, low boiling point, and conversely between high specific gravity, high flash point, low hydrogen content and high boiling point; but, as is to be expected in such a complex and varying substance, a mixture of many distinct chemical compounds, no absolute relationship can be traced.

DISCUSSION.

Mr. J. TWOMEY asked if the author could recommend a satisfactory empirical formula for the estimation of the hydrogen in coal.

Mr. CLAYTON BEADLE asked if the author could explain the fact that the differences between the calculated and experimental values were positive in all cases of the oils, except the last two on the table.

PROFESSOR DONNAN asked what was the trouble in the Diesel engine referred to. Was it due to formation of carbon? What oils, other than petrol, could be used in engines of the motor-car type; also how far could the coal-tar oils referred to compare with petrol?

Mr. H. E. POTTS asked how the sulphur was estimated in the various oils. Personally he found that the addition of alkali chloride to four times the amount of the nitrate present was advisable to give accurate results.

PROFESSOR BALY asked whether any work had been done with the use of "cracked oils" in engines of the Diesel type. Would it not be possible to carry such oils in cylinders and use them in internal combustion engines? He imagined that those oils were very cheap, and they burnt very easily.

Dr. J. HARGER asked if the author had had any experience with coal tar oils distilled from coal at low temperatures, such as 400° C. It seems as if the supply of fuel for motor-car engines, etc., in the future must lie in this direction.

Mr. PATTERSON, in reply, said he only knew of one formula for estimating hydrogen in oils, and that connected specific gravity with hydrogen content. The figures he had given showed what very false results that would lead to. The trouble referred to in internal combustion engines was generally due to deposition of carbon. Sulphur was estimated by double titration of the bomb liquid by barium hydroxide and sodium carbonate; this method only occupied about ten minutes. He did not think that the "cracking process" was carried out to any great extent. Either the lowering of boiling point was not greatly altered thereby, or else, if it were so, the quantity of oil so transformed was relatively small. He had no experience with oils made by distillation of coals at low temperatures.

Journal and Patent Literature.

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German.—1 mark each (with full particulars) to Kaiserlich Patentamt, Berlin, Germany.

I.—GENERAL PLANT; MACHINERY.

PATENTS.

Drying apparatus. C. Wille, Tempelhof, Germany. U.S. Pat. 1,051,359, Jan. 21, 1913.

The apparatus consists of a double-walled drying drum mounted to rotate horizontally within a trough, the whole

being enclosed in a chamber provided with heaters. Conveyor-devices are mounted on the exterior of the drum—which, if not of polygonal cross-section, is provided internally with chains extending along its whole length for the purpose of bringing the charge into intimate contact with the heated air—and suitable provision is made for the circulation of heated air through and around the drum.—W. E. F. P.