

similar to those obtained from other coniferous trees. The exact character of the terpenes present can not be determined from the data presented.

Sample No.	Boiling-point.	Sp. gr. at 15°.	Index of refraction at 15°.	Specific rotation.	Vapor-density.	Iodine absorption.
1	96°-97°	0.6863	1.3905	0	..	0
2	96°-97°	0.6840	1.3887	+2'	..	0
3	97°	0.6860	1.3902	+3'	3.54	0
4	158°-160°	0.8640	1.4765	-15° 23'	..	high
5	155°-160°	0.8578	1.4738	-7° 9'	..	very high
6	157°-160°	0.8583	1.4754	-41° 12'	..	high

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ON THE HEAT OF COMBUSTION AS A FACTOR IN THE ANALYTICAL EXAMINATION OF OILS; AND THE HEATS OF COMBUSTION OF SOME COMMERCIAL OILS.¹

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INTRODUCTION.

THE accuracy, the rapidity of manipulation, and the moderate cost of the bomb calorimeters now in use, have made it practicable for chemists to employ the determination of heat of combustion (or calorific power) not only for the valuation of fuels, but as an aid to, or check upon, the chemical analysis of other organic materials. The comparison of the values actually determined by the calorimeter with those calculated for the constituents found by analysis has been used for some years as a check upon the accuracy of the analyses of foods and physiological products, especially by Atwater and his associates at Middletown, Conn., and by Wiley and Bigelow in the U. S. Department of Agriculture.

It is evident that this method of checking the results of proximate analysis can be applied in any case in which the calorific values of the determined constituents are accurately known. The determination of heat of combustion may also give direct

¹ A considerable part of the work here recorded was carried out in the laboratories of Wesleyan University for the privileges of which, as well as for the use of the bomb calorimeter employed, we are greatly indebted to Prof. W. O. Atwater.

aid in distinguishing between similar materials. Butter, having a relatively high proportion of fatty acids of low molecular weight, has a lower heat of combustion than lard or margarine and this fact has been utilized by de Schweinitz and Emory in testing the purity of butterfat.¹ This principle would evidently find little application among the fatty oils since they show little variation as regards the mean molecular weights of the fatty acids present. Neither is the heat of combustion greatly affected by the presence of unsaturated acids. Stohmann (using the chlorate method) found only a small difference between stearic and oleic acids and almost no difference between olive oil and linseed oil.

However, it seemed likely, that, on the one hand, oils rich in hydroxy-acids like castor oil, and on the other hand, waxes like sperm oil or non-fatty oils like resin and petroleum oils, might differ sufficiently from the ordinary fatty oils to give some value to the determination of heat of combustion as one means of detecting mixtures of oils of these different classes.

It occurred to us, moreover, that the oxidation which takes place when an oil "dries" must result in a loss of calorific power and that a measure of this loss might often be of more value than the simple determination of increase in weight. A lubricant consisting of a mixture of semidrying fatty oil with petroleum might show little or no change in weight on heating in contact with the air, the oxidation of the former oil being obscured by the partial volatilization of the latter. Since, however, the volatilization of hydrocarbons by decreasing the amount of combustible matter would increase the loss of calorific power (calculated upon the original weight) it is probable that this determination would immediately indicate the objectionable nature of such a sample. Even in the absence of hydrocarbon oils, the information obtained by determining the loss of calorific power on exposure may sometimes be of value in judging the quality either of an oil intended to "dry" or of a lubricant in which any such tendency is highly objectionable.

In some drying experiments already made, in which oils were exposed at about 50° for forty hours, we have found a loss of calorific power amounting to over ten per cent. in the case of

¹ This Journal, 18, 174.

linseed oil, while lard oil subjected to the same treatment lost less than one per cent. The results, are, however, considerably affected by variations in the temperature employed and in the amount of surface over which the oil is spread. These conditions are still under investigation and the discussion of this subject will be left for a later paper.

We give below the heats of combustion of several samples of commercial oils with some consideration of the relation of this value to the analytical constants most commonly determined.

THE HEATS OF COMBUSTION OF SOME COMMERCIAL OILS.

With the exception of mineral oils intended for fuel,¹ few combustions of oils appear to have been recorded. Berthelot² quotes only the results obtained by Stohmann;³ *viz.*, two samples of linseed oil, 9488 and 9439 calories per gram; two of poppyseed oil, 9597 and 9562; two of rapeseed oil, 9627 and 9759; and three of olive, 9467, 9458, and 9608. The determinations were made by the chlorate method and afterward corrected by dividing by the empirical factor 0.9857, which was derived from a comparison of the results obtained on solid animal fats by the two methods. Gibson,⁴ who also used the chlorate method, found for olive oil 9471, and for sperm oil, 10001 calories per gram. Wiley and Bigelow,⁵ while studying the calories of combustion of the constituents of cereals, made the following determinations upon oils extracted and purified in the laboratory: wheat oil, 9359; rye oil, 9322; maize oil, 9280 calories per gram. Merrill⁶ found the heat of combustion of a sample of coconut oil pressed in the laboratory to be 9066 calories per gram.

In addition to these oils a considerable number of "ether extracts" have been examined by Stohmann,⁷ Wiley and Bigelow,⁸ Atwater and associates (unpublished) and by Merrill.⁹ The

¹ Poole, "Calorific Power of Fuels" (1898), pp. 238-240, quotes determinations of heat of combustion of several samples of mineral oils by various observers but without sufficient detail as to the methods by which they were obtained to enable us to compare them with those here recorded.

² "Thermochimie," Tome II, p. 565.

³ See review article in Experiment Station Record, VI, 601.

⁴ Report of the Storrs (Conn.) Experiment Station for 1890, p. 190.

⁵ This Journal, 20, 309.

⁶ Bull. 65, Maine Experiment Station, p. 111.

⁷ *Loc. cit.*

⁸ *Loc. cit.*

⁹ *Loc. cit.*

latter's work upon the oils extracted from nuts included the determination of the more important "constants" and these would indicate that the samples examined did not differ greatly from the corresponding oils obtained by commercial methods.

As a rule the heats of combustion of ether extracts have been found distinctly lower than those of the corresponding commercial oils, the difference being doubtless due to the presence of other ether-soluble substances.

Our own work has been done entirely upon commercial oils, some of the samples being fresh and presumably typical, while others are known to be more or less altered by age and exposure.

Apparatus and Methods Employed.—The heats of combustion were determined with a bomb-calorimeter of the Atwater-Blakeslee type.¹ Accordant results for the hydrothermal equivalent of the apparatus were obtained (1) by calculation from the weights and specific heats of the component materials; (2) by five combustions of cane-sugar, the quantity of heat liberated by the combustion being assumed to be 3959 calories per gram of substance burned;² (3) by three combustions of benzoic acid, the heat liberated being assumed to be 6322 calories per gram.³

The heats of combustion given in the table are the mean of two (or in some cases three or four) determinations. The average deviation of individual determinations from the mean was ± 0.12 per cent. of the value found (about 11 calories). In only three cases did the deviations exceed ± 0.25 per cent.; *viz.*, linseed oil III (No. 3), + 0.39 and - 0.31 per cent., petroleum III (No. 40) ± 0.38 per cent., and rape oil II (No. 18) ± 0.30 per cent.

The results obtained with the bomb-calorimeter are, of course, heats of combustion at constant volume. To reduce these to heats of combustion at constant pressure it is necessary in the case of solid or liquid compounds containing only carbon, hydrogen, and oxygen to add

$$\left(\frac{1}{2}p - q\right) \frac{T}{M} \text{ calories per gram,}$$

¹ W. O. Atwater and O. S. Blakeslee: "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," Storrs (Conn.) Experiment Station Report for 1897, p. 199.

² Average of the results of Berthelot and Vieille (three determinations): *Ann. chim. phys.*, [6], 10, 458 (1887); Stohmann and Langbein (four determinations): *J. prakt. Chem.*, [2], 45, 313 (1892); and Atwater and Tower (seven determinations): Unpublished.

³ Identical average of the results of Longuine (four determinations): *Ann. chim. phys.*, [6], 13, 330 (1888); and of those of Stohmann, Kleber, and Langbein (four determinations): *J. prakt. Chem.*, [2], 40, 128 (1889).

p being the number of atoms of hydrogen and q the number of atoms of oxygen in the molecule, M the molecular weight of the substance and T the absolute temperature of the calorimeter. The correcting terms for the principal constituents of oils at 20° C. were calculated from the elementary composition and from the results thus found we have estimated the following corrections for the oils included in this investigation: American petroleum, 22 calories; sperm oil, 18 calories; castor oil and rosin oil, 14 calories; all oils consisting essentially of glycerides of non-hydroxylated fatty acids, 15 calories.

Method of Kindling the Samples.—The device employed to insure the ignition of the oil in the bomb is one which we have not seen described. The oil was absorbed upon a small amount of fibrous asbestos, such as is used in Gooch crucibles, contained in the small platinum capsule ordinarily used in combustions of solids, and was ignited directly by the electrically fused iron wire. This method has proved perfectly satisfactory and is obviously more accurate than that of burning, with the oil, a quantity of kindling substance—such as a block of cellulose or a gelatine capsule.

Determination of "Constants."—The usual methods were followed. The specific gravity was determined by means of a carefully calibrated Westphal balance. Free acid was dissolved by vigorous shaking with alcohol, titrated with tenth-normal alkali and calculated as oleic. For the determination of the iodine absorption, the solutions of iodine and of mercuric chloride were prepared separately and mixed only about twenty-four hours before use. The flasks used were similar to those described by Vulté and Gibson.¹ About twice as much iodine was added as was expected to be absorbed and the whole allowed to stand in a dark closet at room temperature for eighteen to twenty hours. The determinations were usually made in sets of six to twelve, several "blanks" being run with each set.

Description of Samples Examined.—1. Linseed oil from seed grown in Dakota. Prepared by crushing the seeds between rollers and pressing in hydraulic presses. This sample was obtained directly from the manufacturers, and from the description given by them it must have been less than six months old when examined.

¹ This Journal, 22, 457.

2. Linseed oil purchased in open market. Origin unknown. Had been kept about two years in a dark closet in the laboratory.

3. Linseed oil several years old. This sample had been kept for a long time in a bottle only partly filled, and had frequently been opened and exposed to diffused sunlight.

4. Boiled linseed oil of unknown history.

5. Poppyseed oil. This sample was several years old, but had been fairly well protected from light and air.

6. Maize oil furnished by the Glucose Sugar Refining Company. This sample came directly from the factory with the statement that it had been pressed from cooked corn germs, and had gone through no refining process, except that it was allowed to settle in a large tank before shipment. It was examined soon after being received.

7. Maize oil purchased in open market and kept in a closed can for about three years.

8. Crude maize oil of unknown history.

9. Prime summer-yellow cottonseed oil.

10. Choice summer-yellow cottonseed oil.

11. Choice summer-white cottonseed oil.

Nos. 9, 10, and 11 were kindly furnished by the Southern Cotton Oil Company through the courtesy of their chemist, Mr. Geo. F. Tennille, to whom we are also indebted for the following statement: "These oils are of undoubted origin, and were refined to a yellow by caustic soda only. The white oil was made from a choice yellow by bleaching with fuller's earth and then deodorizing by a secret process."

12 and 13. Samples of crude cottonseed oil of unknown history.

14. Cottonseed oil which had been kept in a partly filled bottle for some time.

15. Very old sample of winter-yellow cottonseed oil, showing in marked degree the effects of oxidation, although, as its history is unknown, it may have been abnormal when fresh.

16. Commercial sesame oil, about one year old.

17. Commercial rape oil examined as soon as received.

18 and 19. Commercial rape oils which had been in the laboratory for some years.

20. Castor oil purchased from retail druggist.

21. Castor oil of unknown origin, at least a year old.

22. Commercial peanut (arachis) oil, about a year old.
23. Commercial almond oil, about a year old.
24. Commercial almond oil, several years old.
25. "Best" commercial olive oil, about a year old.
26. Olive oil of unknown origin, labeled "special."
27. Refined menhaden oil. This sample was several years old but had been kept air-tight in a full bottle.
28. Crude commercial menhaden oil, about a year old.
29. Fresh "Bergen" cod-liver oil.
30. Old sample of cod-liver oil; discolored; origin unknown.
31. Whale oil believed to be entirely pure. The sample was at least twenty years old but had been kept well corked in a full bottle.
32. Best commercial lard oil furnished us by Dr. A. G. Manns, chemist for Armour & Co. This sample was examined a few weeks after being received.
33. Lard oil "for lubricating," about a year old.
34. Commercial lard oil, four or five years old.
35. "Extra winter" lard oil which had been kept in a partly filled can for about three years.
36. Sperm oil obtained direct from makers. The sample was about ten years old but had been kept during most of the time in a well-stoppered bottle in a dark closet.
37. A rather heavy rosin oil of unknown history.
- 38, 39, and 40. Commercial petroleum oils intended for lubricating.

No.	Description of oil.	Specific gravity $\frac{15.5}{15.5}$	Iodine absorption. Per cent.	Free acid as oleic. Per cent.	Heat of combustion per gram.	
					Constant volume. Calories.	Constant pressure. Calories.
1.	Raw linseed, I—1900; fresh...	0.934	182.4	4.30	9364	9379
2.	Raw linseed, II—1898.....	0.938	175.9	1.22	9379	9394
3.	Raw linseed, III—old.....	0.947	156.7	5.30	9215	9230
4.	Boiled linseed.....	0.953	150.7	7.40	8810	8824
5.	Poppyseed.....	0.926	129.6	2.66	9382	9397
6.	Maize oil, I—1900.....	0.924	120.3	3.32	9413	9428
7.	Maize oil, II—1898.....	0.926	120.7	2.56	9436	9451
8.	Maize oil, III—crude.....	0.926	122.4	1.68	9419	9434
9.	Cottonseed, I—prime yellow..	0.920	102.5	0.20	9396	9411
10.	Cottonseed, II—choice yellow	0.921	106.4	0.32	9401	9416
11.	Cottonseed, III—choice white	0.923	105.5	0.08	9390	9405
12.	Cottonseed, IV—crude.....	0.927	103.2	2.28	9397	9412

No.	Description of oil.	Specific gravity 15.5 15.5	Iodine absorp- tion. Per cent.	Free acid as oleic. Per cent.	Heat of com- bustion per gram.	
					Constant volume. Calories.	Constant pressure. Calories.
13.	Cottonseed, V—crude.....	0.927	9336	9351
14.	Cottonseed, VI—rather old....	0.929	100.1	0.92	9323	9338
15.	Cottonseed, VII—old.....	0.941	93.7	2.03	9168	9183
16.	Sesame.....	0.924	105.3	1.65	9395	9410
17.	Rapeseed, I.....	0.922	107.4	0.82	9489	9504
18.	Rapeseed, II.....	0.920	108.6	0.68	9462	9477
19.	Rapeseed, III.....	0.926	99.3	2.94	9412	9427
20.	Castor, I.....	0.967	84.1	0.26	8863	8877
21.	Castor, II.....	0.964	86.9	2.18	8835	8849
22.	Peanut (arachis).....	0.917	105.9	0.16	9412	9427
23.	Almond, I.....	0.919	98.1	5.13	9454	9469
24.	Almond, II.....	0.931	89.8	7.00	9311	9326
25.	Olive, I.....	0.917	85.1	2.51	9457	9472
26.	Olive, II.....	0.916	78.8	0.40	9451	9466
27.	Menhaden, refined.....	0.935	..	0.36	9360	9375
28.	Menhaden, crude.....	0.934	..	1.92	9371	9386
29.	Cod-liver, fresh.....	0.927	165.6	0.56	9437	9452
30.	Cod-liver, old.....	0.938	137.3	1.50	9277	9292
31.	Whale.....	0.924	126.6	0.60	9473	9488
32.	Lard oil, I—1900.....	0.917	74.3	0.74	9451	9466
33.	Lard oil, II—1899.....	0.919	72.5	1.25	9447	9462
34.	Lard oil, III.....	0.922	72.9	2.64	9394	9409
35.	Lard oil, IV.....	0.924	69.3	2.34	9372	9387
36.	Sperm oil.....	0.886	78.7	0.78	9946	9964
37.	Rosin oil.....	0.989	76.9	14.40	10145	10159
38.	Lubricating petroleum, I.....	0.881	10797	10819
39.	Lubricating petroleum, II....	0.897	10753	10775
40.	Lubricating petroleum, III...	0.905	10682	10704

It will be seen that the sperm, rosin, and mineral oils are considerably higher in calorific value than the fatty oils and that among the latter the values are slightly higher for the non-drying than for the drying oils. Castor oil shows an exceptionally low value, due doubtless to the presence of ricinolein instead of olein as the principal constituent. Boiled linseed oil shows a similar low heat of combustion. The "choice summer-white" cottonseed oil does not seem to have been appreciably affected in iodine absorption or heat of combustion by the special refining process to which it has been subjected.

The samples which are known to be old and whose specific gravities are high and iodine figures low, have in all cases given

rather low heats of combustion. The variations of the latter value are evidently more closely related to those of specific gravity than to those of iodine absorption or acidity.

Oxidation induced by the action of light and air seems to have lowered the heat of combustion to almost the same extent that the specific gravity is raised, so that for oils of a given variety the product of these values is practically a constant unaffected by age and exposure. In the cases examined, this product is slightly higher for the drying than for the non-drying oils though the difference is necessarily less than that between the specific gravities. Among the ordinary fatty oils examined, the value of this product (large calories per gram \times specific gravity at 15.5°) ranged from 8.80 in the case of raw linseed oil, II, to 8.63 in the case of the peanut oil. Castor and boiled linseed oils show somewhat lower values.

As compared with the ordinary fatty oils, this product is slightly higher for the sperm oil and considerably higher for the mineral and rosin oils.

By dividing the heat of combustion by the specific gravity, a value is obtained which ranges from 10.0 to 10.3 in the fresh fatty oils examined (though lower in case oxidation has taken place) and is considerably higher in sperm oil and mineral oils (in the cases examined 11.2 for sperm oil and 11.8 to 12.3 for the mineral oils).

Thus, it would appear that a determination of heat of combustion (which can be accomplished in forty to fifty minutes), especially when considered in relation to the specific gravity, may be of value in the detection of mineral or rosin oils in fatty oils, or of fatty oils in sperm oil.

Further experiments are now being made upon the relation of the specific gravity and heat of combustion with special reference to the effects of exposure to light and air. We hope to discuss later the more detailed applications of this method of studying the fixed oils, and, if possible, to extend it to the examination of essential oils.