The portion of the heat production due to normal voluntary activity was found to vary in a reciprocal manner with the heat increment—the lower heat increment of the high fat diets being associated with more activity.

A study was made of the variations in heat production and activity throughout the day.

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Some Physical and Chemical Properties of Extraction Naphthas[*]

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ALTHOUGH the physical and chemical properties of extraction naphthas have been covered in considerable detail in previous papers (1, 2), the question of evaporation losses, per cent oil remaining in the meal, and other plant performances as related to the solvent are being discussed rather frequently by both technical and non-technical personnel in an effort to account for extraction plant results. Accordingly, the following data are being presented with the view toward providing information on several of the commercially available light petroleum naphthas of the hexane type in order that the characteristics of this type extraction solvent can be better understood.

It has been known for many years that the various petroleum naphthas, including even the highly refined and comparatively narrow boiling range pentane, hexane, and heptane fractions that were introduced to the oil and fat industry in 1930, were composed of a number of different chemical compounds. Also, it long has been known that each of these hydrocarbon compounds, even though closely related to the others, has a somewhat different boiling point, specific gravity, solvent action, and other properties. Furthermore, it long has been known in the petroleum industry that it is difficult to assign percentage figures for the several naphtha constituents even though many of the naphtha fractions are composed of a half dozen or more different saturated hydrocarbon compounds as well as small amounts of unsaturated hydrocarbon and sulphur compounds. In fact, it only has been in comparatively recent years that laboratory analytical procedures have been devised which permit the assignment of fairly accurate figures to percentage composition of light petroleum naphtha fractions; that is, separating the several naphtha constituents one from the other is still a difficult feat to perform, not only from a manufacturing standpoint but also from a laboratory analytical standpoint. Based on past experience, different data for percentage composition of the commercial hexane type naphthas in Table I probably would be reported if they were analyzed some six months from now when using a modification of the presently employed method or some other method. These things should be kept in mind constantly by anyone attempting to correlate extraction plant results with any given naphtha.

An extensive investigation into the matter of pure hydrocarbons from petroleum was conducted in 1943 by John Griswold, C. V. Van Berg, and J. E. Kasch (3) of the University of Texas, who utilized selective solvents and chemical reactions as well as effective fractionation in their analytical technique for determining the composition of a commercial hexane fraction, namely Skellysolve-B. However, the data shown in Table I for chemical composition of several commercial hexane type naphthas were obtained (4) by the method developed by Gooding, Adams, and Rall and described in U. S. Bureau of Mines "Report PCR 44-009." In this method of analysis use is made of densities and refractive indices for the mercury "g" line and the sodium "D" line, which are determined at 68°F. for the various effectively fractionated portions of the hydrocarbon mixture. A reflux ratio of 30 to 1 was used in a perforated-plate type glass column having 55 theoretical and 80 actual plates in order to obtain the narrow boiling range fractions for the various measurements.

Although the A.S.T.M. D.86-46 method ordinarily is used for determining boiling range of rubber solvent naphtha, mineral spirits, motor gasoline, and other comparatively wide boiling range naphtha fractions, the A.S.T.M. D.216-40 method for distillation of natural gasoline was used for determining the data in Table II, since it has been found to be more satisfactory for analyzing the rather volatile narrow boiling range fractions of the pentane, hexane, and heptane type. Volumetric "recovery, residue, and loss" data in these distillations are not shown since it is considered that they have little if any meaning from a practical standpoint in extraction plant operations. For example, during the last stages of distillation, the compounds that make up the solvent are subjected to higher temperatures than those encountered in a typical extraction plant operation—local temperatures that perhaps go as high as 900°F., because of super heating—with the result that cracking and general decomposition take place with formation of compounds that did not exist in the original solvent.

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TABLE I

Chemical Composition of Various Commercial Hexane Type Naphthas (4)

Hydrocarbon and its boiling point		Naphtha "A"	Naphtha "B"	Naphtha "C"	Naphtha "D"	Naphtha "E"	Naphtha "F"
	°F.	%	%	%	%	%	%
n-Pentane	96.8	1.6	......	......	......	......	......
Cyclopentane	121.1	1.1	......	......	......	0.1	......
2-2-Di-methyl butane	121.5	3.8	......	......	......	3.2	......
2-3-Di-methyl butane	136.4	4.0	1.9	5.1	......	3.2	......
2-Methyl pentane	140.5	14.4	25.5	23.3	......	35.6	......
3-Methyl pentane	145.9	11.2	11.7	10.6	......	8.9	......
n-Hexane	155.7	41.7	40.9	47.4	92.0	36.3	76.0[2]
Benzene	176.2	0.5	1.4	1.5	3.2	2.2	7.0
Methyl cyclopentane	161.2	16.6	17.3	10.6	1.7	4.9	......
Cyclohexane	177.4	4.0	1.3	......	......	3.2	17.0[3]
Heptanes	174 to 209	......	......	......	......	2.4	......
Miscellaneous	....	1.0[1]	......	1.5[1]	3.1[1]	......	......

[1] Low boiling fractions not further identified.

[2] Paraffins and iso-paraffins, mostly n-hexane.

[3] Naphthenes, mostly methyl cyclopentane and cyclohexane.

Numerous methods have been employed to determine evaporation rates of petroleum naphthas and other solvents, but the data shown in Table III was determined by the procedure outlined by L. A. Wetlaufer and J. B. Gregor (5), with some modifications (6) to make easier the assembly of the apparatus and to enable more trouble-free operation. In this method 2 cubic centimeters of the naphtha are evaporated at a temperature of 77°F. with a measured air flow of 0.1 cubic foot per minute to the tube containing the sample. When used in connection with generally similar solvents, this method yields data that is useful in comparing volatility or drying time of two or more solvents and gives an indication of the distillation or condensation behavior of the solvent as well as possible odor, taste, and unsaponifiable troubles that may be encountered in extracted meals or oils.

TABLE II

Distillation Range of Various Commercial Hexane Type Naphthas (4)

	Naphtha "A"	Naphtha "B"	Naphtha "C"	Naphtha "D"	Naphtha "E"	Naphtha "F"
	°F.	°F.	°F.	°F.	°F.	°F.
I.B.P.	142	146	142	148	134	154
5%	146	148	146	152	143	155
10%	146	148	147	152	144	156
20%	147	148	148	153	146	156
30%	148	148	148	153	148	157
40%	148	149	148	153	148	157
50%	149	149	148	154	148	157
60%	150	150	149	154	149	157
70%	151	150	150	154	150	158
80%	152	151	150	154	150	158
90%	154	152	152	154	152	158
95%	156	153	154	154	154	159
Dry point	159	156	157	155	156	161

Table IV shows gravity, sulphur, bromine number, evaporation residue, flash, and vapor pressure data (6) for the same six commercial hexane type naphthas whose other properties are outlined in Tables I, II, and III. Evaporation residue was determined by evaporating 200 cubic centimeters of the naphtha at an oven temperature of 200°F., data thus obtained being valuable as an indicator of possible odor and taste trouble that might be encountered in extracted meals and oils. The other data were determined by the methods in general use in the petroleum industry. In this connection, it might be mentioned that, even though the data is not listed in table form, each of these six commercial hexane type naphthas was sweet to the Doctor test, was water white or 30 plus color on the Saybolt Chromometer, and was OK to the copper strip corrosion test for 3 hours at 122°F.

In general, high A.P.I. gravity or low specific gravity values for a similar type petroleum naphtha indicate a high percentage of paraffin type compounds and a low percentage of naphthene and aromatic type compounds while low A.P.I. gravity or high specific gravity indicate comparatively small percentages of paraffin type compounds and large percentages of naphthene and aromatic type compounds. However, since either paraffin or naphthene hydrocarbons are quite desirable as constituents of extraction naphthas for most purposes, gravity figures are of but little value in judging the quality of a solvent. Therefore the principal significance of gravity is that it serves as an easily determined value to use in quickly checking shipments of naphtha for conformance to type or previous shipments. It practically goes without saying that benzene and other aromatic hydrocarbons are less desirable from a health hazard standpoint than either paraffin or naphthene hydrocarbons.

TABLE III

Evaporation Rate of Various Commercial Hexane Type Naphthas (6)

	25% Evaporated	50% Evaporated	75% Evaporated	100% Evaporated
	min.	*min.*	*min.*	*min.*
Naphtha "A"	1.5	3.5	5.9	8.6
Naphtha "B"	1.8	3.9	6.1	8.8
Naphtha "C"	1.5	3.4	5.8	8.7
Naphtha "D"	2.1	4.2	6.6	9.5
Naphtha "E"	1.2	3.3	5.8	8.8
Naphtha "F"	2.3	4.5	6.9	9.9

TABLE IV

Some Physical Properties of Various Commercial Hexane Type Naphthas (6)

	A.P.I. gravity at 60°F.	Specific gravity at 60°F.	Sulphur (lamp) by weight	Bromine number 100 gram naphtha	Evaporation residue by weight	Flash point closed cup	Reid vapor pressure psi @ 100°F.
			%	*gr.*	%	°F.	*lb.*
Naphtha "A"	76.0	.6819	.004	.16	.0001	—25	5.3
Naphtha "B"	75.2	.6846	.004	.34[1]	.0003	—20	5.1
Naphtha "C"	77.0	.6787	.004	.04	.0011	—20	5.3
Naphtha "D"	81.2	.6653	.004	.33	.0013	—20	4.9
Naphtha "E"	78.7	.6732	.005	.05	.0008	—30	5.5
Naphtha "F"	68.5	.7075	.007	.30	.0010	—15	4.8

[1] Unsaturates or olefins content 0.18% by volume as calculated from Bromine Number of 0.34.

As in the case of gravity, the total sulphur content of a naphtha is of no great consequence in itself. Extraction naphthas and other special industrial naphthas, for that matter, ordinarily are given refinery treatment to the end that deleterious sulphur compounds either are removed or are converted into an inert form. Hydrogen sulphide, mercaptans, and dispersed sulphur are particularly objectionable from odor and corrosion standpoints; their presence, even in very small amounts, in an extraction naphtha is undesirable and will manifest itself in the Doctor and corrosion tests. Although the sulphur content of good motor gasolines may run as high as 0.15%, the sulphur content of the highly refined naphthas of the hexane type ordinarly will not be over about 0.01% by the lamp method, which tends to give high results. However, very little significance from an extraction plant performance standpoint can be assigned to the sulphur content of a naphtha provided, as already indicated, that it does not exist in corrosive or odorous form.

Since the evaporation residue results from suspended solid matter, greasy residues, gum forming compounds, and comparatively high boiling compounds, it is obvious that this value should be as low as possible in an extraction naphtha because it may result in deodorization trouble if not in meals and extracted oils with a foreign odor and taste. Experience has shown that an extraction naphtha for processing edible oils and meals should have an evaporation residue of not over 0.0016% by weight.

Flash point, vapor pressure, and distillation range of naphthas have some significance from a fire hazard standpoint, a matter that has been discussed in detail in a previous article (7). However, it might be mentioned that, with properties so closely related, there is little, if any, choice between the several commercial hexane type naphthas from a safety standpoint under ordinary conditions of use in an extraction plant.

Vapor pressure data, just as in the case of gravity, distillation, and most other data on naphthas, represents composite values of all of the chemical compounds that make up the particular fraction. Accordingly, one may reach erroneous conclusions by considering this one property of an extraction naphtha. However, vapor pressure is a measure of volatility and, in the absence of actual evaporation rate data, serves to indicate the drying time or ease with which a solvent may be evaporated from extracted meals and oils. A comparatively high vapor pressure, such as 6.0 pounds at 100°F. for example, of a commercial hexane type naphtha might indicate the presence of considerable amounts of excessively volatile compounds, such as butanes and pentanes, or perhaps an exceptionally large proportion of isohexanes with correspondingly smaller amounts of n-hexane and cyclo-hexanes. A comparatively high vapor pressure may foretell somewhat larger evaporation losses than usual, particularly if condenser capacity is inadequate or condenser water is fairly warm, and it may interfere with maintenance of some fixed extraction temperature without increase in pressure.

Distillation range, as determined by either the A.S.T.M. D.216-40 or A.S.T.M. D.86-46 method, is comparatively easy and quick to determine and is useful as a test to indicate whether an incoming shipment of extraction naphtha is of the type and quality previously furnished. In this connection, it should be pointed out that, unless the official apparatus is used and the official test procedure is followed in detail, widely varying results may be obtained which can lead to a distorted opinion of the quality of the naphtha. In fact, with the possible exception of odor, distillation range figures have caused more misunderstandings and have led to more erroneous conclusions than any other property of industrial naphthas, the result in the majority of cases of the use of homemade distillation equipment or the failure to rigidly adhere to the official procedure when using the proper equipment. Thus, distillation is a quick and convenient test to make for checking incoming naphtha shipments, but makeshift distillation equipment and haphazard test procedures should not be employed except with due regard for discrepancies that surely will result in the data thus obtained.

Distillation data shows the closeness of boiling range and therefore serves as an indication of general naphtha quality and, in the absence of definite evaporation rate data, gives a fair estimate of the drying time of the naphtha and the ease with which it can be vaporized from the extracted meals and oils. Furthermore, it indicates possible odor, taste, and unsaponifiable troubles that may be encountered in the extracted meals or oils. Also, distillation range, in the absence of definite chemical composition data, gives some indication of the presence of comparatively large amounts of relatively volatile compounds as well as relatively nonvolatile compounds, this being particularly true if the compounds are the excessively volatile butanes and pentanes and the difficultly vaporizable octanes and heavier. However, the importance of this matter from an evaporation loss standpoint frequently is over-emphasized in attempting to explain unusual performances of an extraction plant, as can be seen from the following example. Assume that a plant processes 150 tons of soybeans per day with a solvent loss of 1.0% when using a solvent with no compounds that cannot be recovered. Thus, in a 30-day period, the plant would process 9,000,000 pounds of soybeans and lose 90,000 pounds or approximately 15,789 gallons of solvent; that is, with a 1.0% solvent loss it would be necessary to add 15,789 gallons of solvent to the storage tank during the month in order to maintain the same solvent stock. Now, assume further that this same plant uses a second solvent which contains 5.0% of excessively volatile compounds that cannot be recovered at all—an extremely unlikely situation. Then, by the end of a 30-day period, it would be necessary to add 16,620 gallons of the second solvent in order to provide an equivalent 15,789 gallons of the first solvent; that is, 16,620 gallons or 94,733 pounds of the second solvent would be lost in processing 9,000,000 pounds of soybeans or a solvent loss of 1.05%—an increase that is well within the experimental error of a commercial extraction plant, namely, a negligible increase when consideration is given to the numerous things, such as valve leaks, pump shaft leaks, errors in gauging tanks, breathing losses, overflow water entrainment, speeded up operation, incomplete vaporization of solvent from meals, and so forth, which often are difficult to trace and which easily can account for much greater variations in solvent consumption. Even if the second solvent contained 20.0% of excessively volatile compounds or other compounds which were completely lost in the first passage through the extraction plant, the solvent loss would be only 1.25% as compared to the 1.0% loss assumed for the first solvent. Thus, the absurdity of blaming the extraction naphtha, when something in the plant operations suddenly results in a great increase of solvent loss, becomes apparent. This is especially true if the naphtha in the unusually high solvent loss period is the same as that used in the lower normal loss periods or at least is of the same type to such an extent that the most advanced and painstaking laboratory analytical technique is necessary to show the difference, if any, in chemical composition of the naphtha fraction in question.

Because of their ready chemical activity as compared to chemically inert paraffins and naphthenes, the olefins and other unsaturates are undesirable as constituents of extraction naphthas. As judged by the bromine number data in Table IV, which was determined by the A.S.T.M. D.875-46T method, each of the commercial hexane type naphthas is free from all except traces of olefins or unsaturates; in fact, the bromine number for each is in the range of the experimental error of the test procedure. By way of comparison with some other petroleum products, it might be mentioned that the bromide number of a good grade of cracked motor gasoline may be as high as 26.0 for an olefins or unsaturates content of about 14.3%; the highest of the bromine numbers in Table IV is 0.34 for an olefins or unsaturates content of only 0.18% by volume. It is considered that satisfactory operations can be obtained with an extraction naphtha which has a bromine number of 1.0 for an olefins or unsaturates content as high as 0.52% by volume, although lower values of course are desirable.

In conclusion, it might be mentioned that each of the commercially available naphthas of the hexane type possesses a mild-sweet odor, a very desirable feature from a safety standpoint since the presence of solvent liquid and vapor manifests itself through the workman's sense of smell.

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Annual Review of Literature on Fats, Oils, and Soaps. Part 1

Report of the Literature Review Committee*

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Introduction

In the broad field of fats, oils, and soaps, progress seemed steady with many papers of general interest, but it has been difficult to choose something for special emphasis. However, important disclosures attracted interest in the form of discussions, confirmations, and applications, thus reflecting the importance of the items.

STATISTICS AND OUTLOOK. Statistics and outlook on production, use, demand, and price were issued periodically by the Bureau of Agricultural Economics, U. S. Department of Agriculture (*Fats and Oil Situation Nos. 123-9*), and Office of Domestic Commerce, U. S. Department of Commerce (*Ind. Rept. — Fats and Oils, January 1949*). These seemed identical rather than supplementary along the lines of information that follow.

On the basis of statistics available, the yearly production of fats and oils from domestic materials beginning with crop year 1941-42, through estimates for 1948-49, were 9,625, 10,557, 10,989, 9,599, 8,827, 9,652, 9,838, and 10,515 million pounds, respectively. During 1948, the net imports were 300 million pounds less than in 1947 because of decreased receipts of Philippine copra, due to storm damage.

Domestic disappearance of fats and oils rose to 10.6 billion pounds as against 10.3 billion in 1947. This was exceeded once in our history when the all-time consumption record of 10.8 billion pounds was established in 1941.

The decline in the fats and oils market has brought most prices to the lowest levels since OPA ceilings.

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