SUMMARY

These experiments have established the following facts:

1—That a satisfactory naphtha may be obtained by means of this process wherein the oil is cracked in the presence of nascent hydrogen.

2—That superheating the oil vapors is desirable for "cracking."

3—That pressure is necessary for "cracking."

4—That a combination of pressure and superheat is essential.

5—That the presence of a refractory material in the "cracking chamber" acts as a catalyzer, aids the "cracking," and increases the yield of naphtha obtained.

6—That hydrogen is formed in the manner described, and that it evidently does unite with a greater portion of the unsaturated decomposition products formed, producing saturated compounds.

7—That iron or steel shavings in the cracking chamber constitute a satisfactory catalyzer.

8—That the catalyzer should be frequently renewed.

9—That the yields of naphtha obtained increase as the pressure is increased up to 100 lbs.; above that pressure we have no data.

10—The best results were obtained when using about 10 lbs. of steam per gallon of oil.

11—That the steam should be superheated to at least 600° C. before mixing with the oil vapors.

12—That the mixture of superheated steam and oil vapors should be heated to 650° to 675° in the "cracking chamber."

13—That the residue, obtained by distilling off the naphtha formed, is worth just as much as the original "raw" oil.

14—That carbonization takes place in the retort and more or less gas is formed in the process.

15—Oils having higher boiling points are "cracked" easier than those having lower boiling points, but the quantity of gas formed is greater.

16—That the cost of naphtha produced by this process may be approximately expressed by the equation

$$C = 1.33x + 0.9,$$

where

C = the cost of the naphtha in cents per gallon,

x = the cost of the starting oil in cents per gallon.

As to future work on the problem, we have considered the following:

I—More careful study of the temperature to which the steam should be superheated before mixing with the oil. This might lead, in the construction of a commercial plant, to placing the steam superheater next to the fire and utilizing the heat for cracking, after it leaves this superheater.

II—A study of spraying the cold oil into the superheated steam in a mixing and vaporizing chamber, which later might or might not have to be heated.

III—A more careful study of the construction of the cracking chamber, and the method of passing the vapors through the same, with the idea of determining whether it is not better to heat the vapors to the desired temperature as quickly as possible.

In conclusion, the writer desires to express his thanks to Mr. W. W. Sanders and to Mr. L. M. Bourne, under whose supervision these experiments were performed, for their interest and suggestions.

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REFINING VEGETABLE OILS¹

By CHARLES BASKERVILLE

Crude vegetable and animal oils contain a variety of impurities traceable to a great variety of causes. The character of the crude oil depends not only upon the kind and part of the vegetable (wood, nut, seed, etc.) or animal (fish, whale, etc.) used, but the quality of the raw material at the time of expressage or extraction (rusting, rotting, fermentation, sprouting, heating, etc.), the method followed, the care exercised in the process, and the conditions to which the oil is subjected prior to its refining. It is not proposed to discuss these matters in detail, as this communication deals more specifically with certain of the vegetable oils.

A distinguished oil chemist in a recent interesting summary of the "Contributions of the Chemist to the Cottonseed Oil Industry,"² has said, "the chemist

* * * found that the quality of the oil closely followed the free fatty acid present"³ and "The chemist's greatest service to the industry has been in the refining of the oil, * * * and finally bringing into use the tintometer for measuring the color against standard glasses * * * ."⁴

The present customary practice for refining vegetable oils referred to depends upon neutralizing the free fatty acids in the crude oil, usually by agitating the oil with an aqueous solution of an alkali, the strength and the amount having been previously determined by laboratory tests, agreed upon as a standard, and then heating the mixture during agitation to a suitable temperature until the oil "breaks." The mass is then allowed to stand until the "foots" settle to the bottom of the kettle, when the supernatant oil is drawn off by means of a swivel siphon. Invariably some "dreg" floats on top of the oil. If this be very great, its settling is sometimes facilitated by throwing salt on top of the oil in the kettle. In any event, the oil drawn off is clouded, perhaps on account of the presence of some dissolved soap, globulated moisture and suspended matter, doubtless colloidal in nature. This oil is then "brightened" after drawing off, by throwing in small amounts of fuller's earth, heating again, and passing through a filter press.

The time-factor in settling (6 to 12 hours) of the "foots" materially affects the completeness of the separation referred to above, but in any event the "foots" is wet with oil. The "foots" also entrains oil. Consequently, during the rush season, the effi-

¹Read before the New York Section, American Chemical Society, April 9, 1915, and the Inter-State Cottonseed Crushers' Association, Birmingham, Ala., May 18, 1915. Since brought up-to-date, Jan., 1916.

²Wesson, *THIS JOURNAL*, 7 (1915), 277.

³I have determined that this is true only in a general way, as was no doubt meant by the writer quoted.

⁴One familiar with the color changes in glass may question the real accuracy attainable in the use of such standards. However, it is the best now available.

ciency of yield of refined oil must be sacrificed for speed and quantity refined; in other words, more speed in refining, more loss of refined oil, whatever the analysis upon which purchase and sale are based, may indicate. Coconut oil sometimes requires forty-eight hours to settle.

A process which would reduce the amount of oil entrained in the "foots" to a minimum, thus increasing the yield of a refining, and one which would not be dependent upon the slow subsidence of the "foots,"

FIG. 1—COMPARATIVE LOSSES IN REFINING COTTONSEED OIL BY OLD PRACTICE AND NEW PROCESS

i. e., admit of rapid separation with consequent increase in capacity of a refinery, therefore, seemed not only to be desirable, but, if secured, would approximate the highest efficiency one might hope for in such an industrial operation.

I have succeeded in working out such a process, and shall now proceed to describe the principles involved. The technical laboratory tests with batches of 12 to 20 lbs. have been verified in the factory on the commercial scale.

The aims to be accomplished are:

1—To reduce the amount of oil entrained in the "foots," thus increasing the yield of "whole oil."

2—To reduce the time of contact of the excess alkali (necessary for the "break" and to secure the best "color") to the minimum.

3—A technological corollary calls for the utilization of any by-products.

It is assumed that all oils, good, bad and indifferent, are to be treated. However, this may not be necessary, as in some cases only the good, and perhaps the indifferent oils are refined at some places.

In my investigations, lasting through several years, I have taken various kinds of crude vegetable oils from various sources with various (extreme) conditions and refined them. In many cases I have been told that no attempt would ordinarily be made to refine a particular oil, as it should be sent to the soap kettle, the corresponding price only being expected. Such oils would have presented much better values if they could have been refined by the present practice. These oils have yielded to my process and have been refined.

If we can get the "foots" into such a condition that it may be filtered and then squeezed, we may reduce the amount of whole oil entrained. If we can do this immediately after the "break" and while the oil is still hot, we shall be able to reduce the time the "whole oil" is exposed to the saponifying action of the excess alkali necessary.

There are present in oils groups of bodies which in general terms are called colloids. These colloids may or may not be colored; may or may not make the oil turbid, for colloids are of such a state of subdivision that they remain suspended in the liquid, where they may be, for a long period of time. Some colloids may be and are coagulated by heat, some by acids, some by alkalies, some by salts, or electrolytes, and in time will settle out. For example, linseed oil may be and is refined by adding lime and allowing the mixture to stand for several months, during which time the colloids settle out. Colloids that have been coagulated, or lumped, may be filtered out. Some coagulated colloids in their formation absorb coloring matter.

Suitably prepared cellulose fiber will absorb some coloring matter. It will bring out an agglomeration of the material precipitated from oils by treating the oil with alkalies and heating, and it will bind the particles together so that they lose their somewhat slimy character and may be filtered away from the oil in which they were produced. I have also found short-fibered "linters" is a suitable form of cellulose for some oils.

Therefore, I add cellulose suitably prepared along with the caustic to the oil to be refined. The "break" takes place normally on heating as in the ordinary process, but the precipitated mass is in such a physical condition that it may be separated from the oil immediately by filtration.

As mentioned above, some colloids, perhaps colored, are thrown down by salts, so in certain cases some salt (1 per cent of sodium chloride) may be added

If there be a slight excess of water present, the sodium chloride serves also to "salt out" any soap in that water. The addition of salt, however, is not necessary in all cases.

I have also discovered that the tendency of the soaps formed by the caustic alkali treatment to emulsify with the oil, or so to distribute themselves through the oil as to render their separation difficult, may be overcome by subjecting the oil, at a suitable stage of the treatment, to the action of an anhydrous salt which is capable of taking up water of crystallization, the preferred salt being dry sodium carbonate (soda

which it is filtered. At first some soap may pass through the filter cloths. In that event, the first filtered oil may be run directly back into the refining kettle, and pumped through the press until the oil is "bright." This usually occurs within a few minutes. In fact the speed of filtration is directly dependent upon the speed of the pumps. This re-filtration also improves the color. This oil is neutral and can be bleached and deodorized, or both at once, or it may be stored safely. If "linters" is used, $\frac{1}{4}$ to $\frac{1}{2}$ per cent of the dry cellulose is added.

The danger of making a whole kettle into soap-stock through failure of the refiner to be "on the job" is reduced to a minimum, as in several thousand trials this has not occurred, the trials having been made by different people with various grades of oils of different character. In other words, the process is nearly "fool-proof." Any man of fair intelligence can operate the process and the air of mystery surrounding the professional refiner is dissipated. The superintendent has a double check on the refinery by weighing the finished oil and cake. The daily reports when summed up should coincide with the annual inventory. I have known of cases where as much as 100,000 lbs. of oil have failed to appear in the inventory, but were reported daily and had to be charged to profit and loss when the operation was under the usual process.

The curves in Fig. I have been made from a series of cottonseed oils very variable in character, to show the comparative losses by the normal, present practice and my process. Fig. II shows the comparative saving with several other oils.

I have also been able to secure a farther 1-3 per cent. saving by subjecting the "cake" to hydraulic pressure. This extra saving is not shown in the charts.

The process is very rapid, the controlling factor being filter-press capacity. A study of plate filter-presses has indicated a preference for a center feed press making $1\frac{1}{2}$ - to 2-in. cakes. The filter press problem in connection with the process is not one of filtering area but cake capacity. Presses, as the Kelly or Sweetland, which are dumped mechanically, meet the conditions better than plate presses. A new Sweetland press recently devised for this process promises the best results. It is provided with bottom exits and the under bivalve swings through an arc of 165° . Monel metal filter cloth makes the machine practically permanent. By a slight increase in filter press capacity the output of a refinery may be doubled or even tripled.

UTILIZATION OF BY-PRODUCT

The cake may be converted directly into soap, the cellulose becoming very finely comminuted. It forms an unobjectionable filler for some grades of soap, especially soap powders. The cake may be "cut" with acid directly. The cellulose settles quickly in the aqueous layer from the black oils, which latter may be drawn off ready for market or use. When the cake is to be converted into black grease, I use anhydrous sodium sulfate "salt cake" in place of soda ash as the "agglomerator." Printed instructions for the use of

FIG. II—COMPARATIVE LOSSES WITH VARIOUS OILS

ash) which, as is well known, is capable of taking up one, seven, or ten molecules of water of crystallization, according to temperature conditions. By such treatment, the soaps which have already been formed by the treatment with caustic alkali, and which have become so incorporated with the oil as to be incapable of complete separation by ordinary filtration, are hardened, presumably by dehydration, and are so modified that they are readily separated by simple filtration. Sodium sulfate, which acts in the same way, may be used instead of the soda ash.¹

The process is carried out by adding ordinarily 2 per cent of prepared cellulose (less than 1 per cent real cellulose), a suitable amount of caustic soda (usually much stronger than commonly used), and a determined amount of soda ash. The whole is thoroughly agitated by mechanical means while it is being heated (45° – 65° C.) to produce the "break," after

¹ These ideas are covered by U. S. Patents Nos. 1,105,744; 1,105,743; 1,130,698; 1,114,095.

the method as an analytical procedure or working the process on a commercial scale may be had on application to the author.

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THE THERMAL VALUES OF THE FATS AND OILS I—THE HEAT OF BROMINATION

By J. W. MARDEN

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INTRODUCTORY AND HISTORICAL

According to H_{ehner} and M_{itchell},¹ "the action of bromine upon unsaturated bodies is instantaneous and is attended with a considerable evolution of heat. It is complete and quantitative. * * * It is not complicated to any extent by secondary reactions. The amount of hydrogen bromide formed measures the substitution, and is very small in most cases." H_{ehner}² found this value, when a number of fats and oils were mixed with bromine, to be as follows:

FAT OR OIL	Olive	Castor	Butter	Boiled Linseed
Per cent free HBr.....	1.5 to 2.7	2.7	0.9	8.8

It has been found more recently by M_{ellhiney}'s method,³ however, that there are a few fats and oils where the substitution is very large.

H_{ehner} and M_{itchell} also showed that each oil, when treated with an excess of bromine, gave a characteristic temperature rise and that the quantitative data obtained by this temperature change, when the fats and oils were mixed with bromine in a suitable tube, furnished more reliable data on their purity than the Maumené sulfuric acid test. They expressed the opinion that a method worked out on this basis could well replace the longer method for the iodine number as a test for the purity of a fat or oil. In their method 1 gram of oil, dissolved in 10 cc. of chloroform, is placed in a Dewar vacuum test tube and exactly 1 cc. of bromine, previously brought to the same temperature as the oil solution, is added. The rise in temperature is measured by an accurate thermometer graduated to one-fifth of one degree. A test tube packed in cotton was first used but later replaced by a Dewar tube. As one would expect, the test tube packed in cotton gives lower results. The whole operation takes only a few minutes.

Table I gives the results obtained by H_{ehner} and

TABLE I—RESULTS BY HEHNER AND MITCHELL(a)

OIL OR FAT	Rise in temperature	IODINE NUMBER		DEVIATION	
		Experimental	Calculated	Absolute	Per cent
Lard.....	10.6° C.	57.15	58.3	1.15	2.0
Butter.....	6.6	37.07	36.3	-0.77	-2.1
Almond.....	17.6	96.64	96.68	0.04	0.04
Olive.....	15.0	80.76	82.50	1.74	2.1
Maize.....	21.5	122.0	118.2	-3.80	-3.2
Cottonseed.....	19.4	107.13	106.7	-0.43	-0.4
Castor.....	15.0	83.77	82.5	-1.27	-1.5
Linseed.....	30.4	160.7	167.2	6.5	3.9
Rape 1.....	18.4	88.33	101.2	12.87	12.7
Rape 2.....	17.6	77.2	96.8	19.6	20.0
Cod Liver.....	28.0	144.03	140.0	-4.03	-3.8

(a) Abbreviated from Lewkowitsch's "Chemical Technology and Analysis of the Oils, Fats and Waxes," Vol. I, Macmillan & Co. (1909).

M_{itchell}. The rise in temperature due to the bromination of each oil multiplied by the factor 5.5 very nearly gives the same value for the iodine number as H_{ehner} and M_{itchell} obtained experimentally. The factor

¹ H_{ehner} and M_{itchell}, *Analyst*, **1895**, p. 148.

² H_{ehner}, *Analyst*, **1895**, pp. 20, 49.

³ M_{ellhiney}, *J. Am. Chem. Soc.*, **21** (1899), 1084.

must be determined, of course, with each individual apparatus, because of its heat capacity.

Wiley¹ has proposed a more convenient method of

TABLE II—RESULTS BY WILSON (HEHNER-MITCHELL METHOD)

OIL OR FAT	Rise in temperature	IODINE NUMBER		DEVIATION	
		Experimental	Calculated	Absolute	Per cent
Cocoonut.....	1.4° C.	8.4	8.2	-0.2	-2.4
S. A. Tallow.....	7.3	44.0	43.2	-0.8	-1.8
Olive, pure.....	14.0	82.0	82.5	0.5	0.6
Rape.....	18.0	103.4	104.5	1.1	1.06

handling the oil and bromine which he uses in somewhat the same way as H_{ehner} and M_{itchell}.

Table II gives a few of the results obtained by Wilson,² using the original H_{ehner} and M_{itchell} method, which show very good agreement between the calculated value and the iodine number found by analysis.

The work of J_{enkins}³ does not show such good concordance when an attempt is made to obtain the iodine number from the temperature rise by multiplication with a factor.

TABLE III—RESULTS BY JENKINS

OIL	IODINE NUMBER		DEVIATION	
	Experimental	Calculated	Absolute	Per cent
Blown Rape.....	55.3	74.1	18.8	34.0
Blown Cottonseed.....	62.2	78.1	15.9	25.6
Neat's Foot.....	71.6	72.4	0.8	1.1
Olive.....	80.1	81.5	1.4	1.7
Castor.....	84.1	83.8	-0.3	-0.36
Japanese Wood.....	165.7	133.4	-32.3	-19.5
Raw Linseed.....	174.3	173.9	-0.04	-0.02

Since there are many discrepancies between the two iodine values, it is suggested⁴ that each individual oil be given a constant to suit the apparatus in which the work is done. This would, of course, make this method too cumbersome for practical use in replacing the method for the determination of the H_{übl} iodine number.

Gill and Hatch⁵ have tried the method with about the same degree of success. More recently S_{teipel}⁶ has published several contributions on the determination of the iodine number of the fats and oils by means of the bromine thermal test. He has repeated practically all of the previous work and his results agree well with former determinations. He finds that he is unable to calculate the iodine number from the bromine thermal value with accuracy but that he must have a constant for each individual oil and each apparatus.

An attempt has been made also to throw some light on the structure of certain unsaturated compounds when they combine with bromine. L_{ouguine} and K_{oblukoff}⁷ have measured the heat produced when various compounds dissolved in carbon tetrachloride react with bromine, also dissolved in carbon tetrachloride. They found that the heat of solution of most fats and oils in carbon tetrachloride is very small and that the heat produced per gram molecule of bromine, when accurately determined, varies considerably with each individual compound. In spite of these tests, however, there has been no technical attempt to measure the heat of bromination of the fats and oils by a rapid calorimetric method and to put this de-

¹ *J. Am. Chem. Soc.*, **18** (1896), 378.

² *Chem. News*, **1896**, p. 87.

³ *J. Soc. Chem. Ind.*, **16** (1897), 194.

⁴ Archbutt, *J. Soc. Chem. Ind.*, **1897**, p. 310.

⁵ *J. Am. Chem. Soc.*, **21** (1899), 27.

⁶ S_{teipel}, *Seifenfabrikant*, **31** (1911), 349, 393, 421, 445, 473, 501, 525.

⁷ L_{ouguine} and K_{oblukoff}, *J. Chem. Phys.*, **4** (1906), 209 and 489; **5** (1907), 186; *Compt. rend.*, **150** (1910), 915.