apparently as reliable as when petroleum emulsions were tested.¹

The authors believe that the method herein described is applicable to a wide variety of organic emulsions, possibly solid as well as liquid, and recommend its trial in all laboratories not fully satisfied with the methods at present in use. While it is not believed that results may necessarily be more accurate than those now obtainable, an increase in convenience and rapidity is anticipated.

PREVIOUS WORK ALONG SIMILAR LINES

On account of the simplicity of the modified method the authors have found it difficult to believe that their work could be new. The literature has been searched diligently, however, and it has been found that practically all the distillation methods for water determination have involved the use of apparatus of the conventional type and arrangement. The methods of Besson and Gray approach most closely the procedure recommended in the present paper. The basic idea of the authors' method was conceived after reading a description of the apparatus of Besson. Neither his method nor that of Gray is, however, believed to be as practical as that of the authors. The apparatus is not as simple and convenient and no attempt is apparently made to make the distillation continuous by refluxing the solvent into the flask.

SUMMARY

General experience has indicated that the method of distilling in the presence of an immiscible solvent is the most reliable and most generally satisfactory scheme of estimating the water content of organic emulsions, particularly petroleum emulsions.

The Pittsburgh Petroleum Laboratory of the Bureau of Mines has developed modifications of this method that add considerably to its convenience.

A description of the apparatus and procedure employed by the Bureau appears in the present paper.

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HEAT BALANCE OF A DISTILLATION PLANT FOR THE RECOVERY OF FATTY ACIDS FROM COTTONSEED FOOTS

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Some years ago the writer was engaged in development work along lines of fatty acid distillation. Before this could be undertaken it was necessary to know the value of the heat of vaporization of fatty acids under operating conditions, *i. e.*, at the temperature and reduced pressure usually employed in distillation. A search of the literature of this subject failed to yield the desired information and the determination of these values was, therefore, undertaken by the writer. The results are given here in the hope that they may be of value to the profession.

The heat of vaporization can be calculated from the vapor pressure curve of the fatty acids, and the latter can be determined in the laboratory. As a commercial fatty acid distillation plant was available, however, advantage was taken of this fact to make a large-scale determination. This was preferred, as it was thought that it would not be possible to reproduce working conditions on a laboratory scale. One of the most important of these factors is the effect of the pitch in the still bottom. As it accumulates it becomes necessary to raise the distillation temperature sometimes

as much as seventy-five degrees or more. It was also believed that any variation in composition of the fatty acids or other factors would be averaged in a larger-scale determination.

The fatty acids were obtained from foots from the refining of crude cottonseed oil. The crude oil consists principally of a mixture of the glycerides of palmitic, linoleic and oleic acids containing also small quantities of glycerides of arachidic and possibly stearic acids.¹ In addition to these glycerides there are also present the glycerides of all these acids in various stages of decomposition.

Crude cottonseed oil is usually refined with caustic soda, whereby the partially and wholly decomposed glycerides are separated out as a soap (foots). This soap is only partially saponified and contains considerable quantities of neutral oil, together with most of the coloring, nitrogenous and mucilaginous matter that was present in the crude oil. The preponderant constituent of the foots is probably a soda soap of oleic acid, inasmuch as olein, the glyceride of oleic acid, is largely present in cottonseed oil and is most readily broken down. The composition of the foots will vary considerably, depending to a great extent on the amount of neutral oil retained in refining.

The foots may be killed and acidulated, *i. e.*, the saponification may be completed by boiling with sufficient alkali and the resulting soap treated with mineral acid to liberate the fatty acids; or the foots may be first treated with a mineral acid to free it from alkali, and then saponified by the Twitchell or

other process to remove the remaining glycerol radicals. In either case the end result is a mixture of free fatty acids ready for the distillation process.

Two distillations were run on entirely different lots of fatty acids, since several months elapsed before the distillation plant could be spared for the second determination, and it was not practical under the existing conditions to store a portion of the first lot of stock for use in the second determination.

METHOD

The method employed in making the determination was as follows: The distillation plant was operated on fresh fatty acid stock, with no fatty acid or pitch left in the still from previous distillations. Before starting the tests, distillation was carried on until conditions were constant. A flying start and stop of the tests were used in a manner similar to that employed in making evaporative boiler tests. Thus, without interruption or disturbance of the distillation, tests were started and stopped immediately after emptying the condenser drums.

Measurements of all such quantities as were required to write a heat balance of the plant were made. Assistants were stationed at points where manual control was necessary. All readings were taken at 5-min. intervals.

The accompanying diagram gives an outline of the distillation plant employed. It consisted of a coal-fired still, supplied with superheated steam through a reducing valve and a separately fired superheater. This still was fed continuously so that the volume in the still was constant, the level in a gauge glass being

¹ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 2, 5th Ed., p. 197.

carefully watched. The combined fatty acid vapor and superheated steam passed over from the still to a water-cooled tubular type of condenser. Here the fatty acids were condensed out and collected in a drum in the bottom of the condenser. At intervals the fatty acids were transferred to the separatory drums, whence, by means of compressed air, they were transferred to a scale tank for weighing. This scale tank is shown on the same floor level as the still. Actually, as a matter of convenience, it was placed on an upper floor, so that the fatty acid after weighing could be dropped into a storage tank on a lower level. Here entrained moisture was settled out and weighed. The distilled fatty acids were allowed to stand until laboratory tests showed that all the moisture had settled out.

The steam passed over to a barometric condenser, and the fixed gases were taken care of by a vacuum pump. The barometric condenser discharged into a separatory catch basin, where the small quantity of entrained fatty acid was recovered by skimming.

The cooling water was carefully weighed, allowance being made for surface evaporation from the top of the open condenser and the scale tanks. This allowance was based on actual loss in evaporation of an open vessel immersed in the top of the condenser.

EXPERIMENTAL DATA ON FATTY ACID RECOVERY

	TEST A MARCH 7 hrs.	TEST B MAY 7 hrs.
Length of test.....		
Average barometer corrected to 58.4° F.....	29.62 in. Hg	29.10 in. Hg
Vacuum condenser vapor inlet corrected to 58.4° F.....	24.13 in. Hg	24.24 in. Hg
Vacuum condenser vapor outlet corrected to 58.4° F.....	25.17 in. Hg	24.68 in. Hg
Average temperature at vapor inlet.....	433.8° F.	445.5° F.
Average temperature at vapor outlet.....	141.9° F.	134.0° F.
Average temperature of stock into separatory drums.....	136.8° F.	131.9° F.
Average temperature of condensing water into condenser.....	33.6° F.	52.6° F.
Average temperature of condensing water out of condenser.....	123.1° F.	178.0° F.
Average temperature of condensing water, bottom of condenser.....	116.0° F.	118.5° F.
Total steam consumed.....	7229.0 lbs.	5901.0 lbs.
Total stock into separatory drums (after deducting settled water and moisture).....	11077.0 lbs.	13091.0 lbs.
Total stock from 1st catch basin (after deducting moisture content).....	3176.0 lbs.	2839.0 lbs.
Total stock from 2nd catch basin (after deducting moisture content).....	286.0 lbs.	278.0 lbs.
Total stock (dry).....	14539.0 lbs.	16208.0 lbs.
Average moisture content of stock.....	0.713 per cent	0.4 per cent
Water carried with stock into separatory drums and settled out.....	538.0 lbs.	272.0 lbs.
Water present in stock into separatory drums as moisture.....	80.0 lbs.	53.0 lbs.
Water present in stock from catch basin.....	25.0 lbs.	12.0 lbs.
Total water carried over and present as moisture.....	643.0 lbs.	337.0 lbs.
Condensing water.....	57740.0 lbs.	36719.0 lbs.
Rate of evaporation of condensing water (lbs. per sq. ft. per hr.).....	0.54 lb.	1.46 lbs.
Area from which evaporation took place.....	31.0 sq. ft.	31.0 sq. ft.
Area from which radiation took place.....	357.9 sq. ft.	357.9 sq. ft.
CALCULATED RESULTS		
Total heat to raise 1 lb. of stock from 32° F. to vapor under the test conditions.....	315.3 B. t. u.	308.2 B. t. u.
Heat to vaporize 1 lb. of stock under test conditions.....	130.5 B. t. u.	118.0 B. t. u.

To measure the vacuum, mercury U-gauges were placed at the inlet to the surface condenser and in the vapor pipe outlet, as close to the water surface as possible.

Temperatures were taken at these two points, also at the following points: the surface of water in sur-

face condenser, water near bottom of condenser shell, cold water supply, and fatty acids at outlet of condenser drum. Wherever possible, thermometer wells were used, filled with appropriate liquids—at the vapor inlet, oil, on account of the high temperature, and elsewhere mercury.

The quantity of steam was determined by means of a specially calibrated Gebhart steam flow meter located between the reducing valve and the superheater. The quality of the steam was not determined. It was calculated that with a drop of pressure in the reducing valve, of some sixty odd pounds, the steam was practically dry and saturated.

With one exception, conditions were kept very close to the average, there being little or no variations. This exception was the temperature of the cooling water at the top of the condenser. This fluctuated somewhat more than was desirable, because of the difficulty in the water control and the large volume present in the condenser shell.

In the table are given the data of the two tests and the calculated results.

CALCULATION OF RESULTS

The method of arriving at the calculated results was as follows: A heat balance was struck. In this balance it was assumed that the steam as measured was dry and saturated. An error of perhaps one-half of one per cent enters here. It was further assumed that there was practically no condensation in the vapor pipe connecting the still with the condenser. As this pipe pitched toward the condenser, any condensation would be collected in the condenser drum. This pipe was 12 in. in diameter and 14 ft. long, and was insulated with very heavy magnesia covering. The heat loss was a negligible percentage of the total passing.

The temperature at the condenser inlet was assumed to be that of saturated fatty acid vapor, *i. e.*, it was assumed the fatty acid vapor carried no entrained liquid fatty acid and was not superheated. The very large diameter and height of the still precluded entrainment, and laboratory tests showed that at 28.25 in. to 29.5 in. of vacuum the boiling point is very close to 440° F. This checks very well with the actual large-scale tests where steam for distillation was used. As might be expected, somewhat lower temperatures were found.

The total heat in the superheated steam was obtained from the Molière chart and data published by Prof. C. C. Thomas.¹

The heat lost by radiation from the condenser shell was calculated from the values in Kent's "Mechanical Engineers' Handbook."² The value used for the mean specific heat of the fatty acids was 0.46.

The heat balance as struck is given at top of next page.

The close agreements of the results is rather astonishing. There is a difference of only about 2 per cent in the values for total heat per pound of stock. However, the values for heat of vaporization differ by about

¹ *Trans. Am. Soc. Mech. Eng.*, 29 (1907).

² 1898 Ed., p. 536.

$$\begin{array}{rclclcl}
 \text{Total heat above } 32^{\circ} \text{ F.} & & \text{Heat taken up by con-} & & \text{Heat lost by evaporation} & & \text{Heat lost by radiation} \\
 \text{in the fatty acid dis-} & = & \text{densing water} & + & \text{of condensing water} & + & \text{from condenser shell} \\
 \text{tilled} & & & & & & \\
 & & \left[\begin{array}{l} \text{Total heat above } 32^{\circ} \text{ F.} \\ \text{of steam entering con-} \\ \text{denser} \end{array} \right] & - & \left[\begin{array}{l} \text{Total heat above } 32^{\circ} \\ \text{F. in steam leaving} \\ \text{condenser} \end{array} \right] & - & \left[\begin{array}{l} \text{Heat above } 32^{\circ} \text{ in water} \\ \text{carried over with stock} \\ \text{into settling tank} \end{array} \right] \\
 & + & \text{Heat to raise stock in condenser drum from } 32^{\circ} \text{ F.} & + & \text{Heat to raise stock from catch basin from } 32^{\circ} \text{ F.} \\
 & & \text{to drum temperature} & & \text{to condenser temperature}
 \end{array}$$

Substituting the proper figures in this heat balance, and dividing by the quantity of fatty acid distilled, we find: Total heat above 32° F. per lb. of fatty acid distilled = 315.3 B. t. u. for Test A

Whence, on the assumptions before stated, we have: Heat of vaporization per lb. of fatty acid at 24.51 in. vacuum = $315.3 - 0.46(433.8 - 32) = 130.5$ B. t. u.

Similarly we find for Test B the values 308.2 B. t. u. and 118.0 B. t. u., but at 25.14 in. vacuum.

9 per cent. This discrepancy can be accounted for in two ways: Firstly, the stock was not the same in both cases. Undoubtedly, there was some difference in the mixtures being distilled, but unfortunately no chemical analyses were made to determine the difference; secondly, the two tests were made at somewhat different pressures and temperatures.

The heat of vaporization differs with temperature. If it did not the vapor pressure curve would be a straight line, and this we know is not the case. Probably the discrepancy is due to a combination of these two factors.

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NUMERICAL RELATION BETWEEN CELLS AND TREATMENTS IN EXTRACTION PROCESSES

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In a previous study of extraction processes¹ conducted at the U. S. Forest Products Laboratory, Madison, Wisconsin, it was found that no definite relation had ever been developed between the number of solvent treatments received by each charge of material and the number of cells or extractors required to furnish this number of treatments. It was also evident that the ideas in regard to such a relation were very much confused, and that the usual conception was the entirely unfounded one that for a certain number of treatments an equal number of cells was required or the same number plus one.² After it had been determined how many treatments in series were required for efficient extraction and how much time would be required for boiling, pumping, discharging, charging, etc., there was still no method by which it could be determined how many cells or extractors would be required by the process.

In the development of the numerical relation between the cells and the treatments it will be necessary to consider a general case covering all conditions; and this will require the use of terms and the assumption of conditions that may seem unusual or impractical to operators who have had experience with only one kind of extraction process and have used a peculiar

set of terms for describing the various operations. On this account indulgence is requested from the readers who find unusual processes described in unusual terms, and they are asked to overlook these until the general principles become clear.

There is, of course, a definite relation between the number of cells and the number of treatments. It varies with different methods of manipulation, however, and several conditions of treatment must be known accurately before the relation can be developed. It is necessary to know the amount of time required for the operations performed on each charge other than the typical extraction operations, and this time must be known in terms of the typical extraction operations. These latter operations are:

1—The movement of solvent from one charge to another, from the last charge to storage or from the solvent tank to the first charge, which movements will be called "pumping" and designated by *p*.

2—The period of the actual solution action of the solvent on the charge, whether by standing, boiling, or agitating, which will be called "boiling" and designated by *b*. These typical operations are necessary parts of every discontinuous extraction process and may vary only in the time required for their fulfillment.¹ While there are only these two kinds of extraction operations, each may take place a variable number of times in a complete cycle of extractions. The non-extraction operations may vary widely in number, kind, and time required, and include charging and discharging the cells, or any preliminary or after-treatment performed on the charge while in the cells.

SIMULTANEOUS PUMPING

The simplest way to determine the relation between the number of treatments and the number of cells in terms of the time required for the various operations seems to be to use cut and try methods under several different sets of conditions and then to find the complete mathematical relation by inspection. This can be readily done by representing a series of extractions graphically. The easiest system to start with is one in which the pumping of all cells in action is done simultaneously. A series of extractions in four cells by this system can be represented as in Fig. 1.

In this method of representation the arrows indicate movement of the solvent or pumping; for instance, the first line of the diagram indicates simultaneous move-

¹ THIS JOURNAL, 9 (1917), 866.

² Krüssmann, *Mel. & Chem. Eng.*, 15 (1916), 78.

¹ As will be seen later, *b* may equal zero in some cases.