beaker, the weight obtained being used in determining the refining loss of this oil.

The above method has proven satisfactory for use in our laboratory in determining the refining characteristics of our extracted degummed soybean oil. However, in consideration of an extracted oil of the non-degummed type, it was found that such an oil, when put through the above procedure, introduced difficulties in the form of persistent emulsions which did not allow an efficient separation of the oil and soap layers. Consequently it was decided to treat this oil as if it were an expeller type oil, and it was found that the oil responded nicely to the official procedure now in the books for expeller soybean oil.

At the present time and with due consideration for the results obtained in the work described above, it is our recommendation that the refining of extracted soybean oil be carried out according to the two methods outlined above, namely, the water-wash separatory funnel method for extracted oil of the degummed type, and the official expeller procedure for extracted oil of the non-degummed type. It seems to us at the present time that such distinction must be made and that satisfactory evaluation of these two types of extracted oil can be arrived at through the use of the procedures outlined.

S. O. SORENSEN

Thermal Properties of Fats and Oils

V. The Heat Capacity and Heat of Fusion of Highly Hydrogenated Cottonseed Oil

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IN AN earlier paper (4) of this series thermal data were reported for cottonseed oil (I.V. = 108.3), partially hydrogenated cottonseed oil (I.V. = 59.5) and a mixture of cottonseed oil and petroleum naphtha. This work on highly hydrogenated cottonseed oil (I.V. = 0.85) completes the present calorimetric investigation of this oil.

The calorimetric apparatus and the general procedure followed in making the measurements were described in the first paper (2) of this series. However, before the present work was initiated, an additional calibration of the calorimeter was made, in the course of which the determination of its heat capacity was extended to 340° K. Also, the calorimeter thermocouple was calibrated against a platinum-resistance thermometer from 90° to 400° K. The calibrated thermocouple was checked to within an accuracy of 0.02° at several fixed temperatures used for thermometer calibration.

Composition and Characteristics of the Oil

The composition and characteristics of the oil have been recorded in detail in a previous communication (1). The oil exhibited polymorphism, solidifying in four different forms, which had melting points of 62.3°, 61.0°, 58.5°, and 50.5° C. Following the nomenclature adopted in the preceding paper, the four forms corresponding to these temperatures are referred to as Forms I, II, III, and IV, respectively.

Heat Content of the Oil

A SAMPLE of the liquefied oil, weighing 35.341 g., was placed in the calorimeter and quickly solidified by immersing the calorimeter in a bath of liquid nitrogen. The temperature of the calorimeter and contents appeared to approach that of the bath within about 40 seconds. The calorimeter was then assembled within the complete apparatus in the usual way. After the necessary heat capacity and heat of fusion runs on the quickly chilled sample, heat capacity measurements were made on the liquefied oil. The apparatus being left unchanged, the same sample of oil was slowly chilled, tempered at 1° to 1.5° C. below its melting point (i.e., at about 61° C.) for about 36 hours, and similarly tested for heat capacity and heat of fusion.

The accumulated heat content of each sample between 200.0° and 373.1° K. (—73.1° to 100.0° C.) are presented in tabular form in Table I and in graphic form in Figure 1. Over the range of temperatures in which melting occurred, the values for the heat content were determined during continuous heating of the samples from the lowest temperature

TABLE 1

Accumulated Heat Contents Above 200° K. of Samples of Highly Hydrogenated Cottonseed Oil.

Quickly solidified sample		Tempered sample	
Temp. °K.	cal./g.	Temp. °K.	cal./g.
200.0	0.0	200.0	0.0
225.0	7.44	230.0	8.57
250.7	16.00	259.4	18.14
260.5	19.73	269.2	21.79
266.8	22.14	275.5	24.16
272.8	24.50	281.4	26.47
278.4	26.82	286.9	28.75
283.8	29.09	291.9	30.99
289.0	31.31	296.4	33.22
293.9	33.49	300.8	35.39
298.5	35.63	305.2	37.49
302.9	37.74	309.4	39.55
307.0	39.81	313.4	41.56
310.9	41.84	317.2	43.52
315.1	43.80	320.3	45.49
320.1	45.63	323.0	47.44
324.7	47.42	325.2	49.39
327.3	49.33	326.9	51.36
329.5	53.00	328.4	53.30
330.9	57.35	329.7	55.25
331.8	61.38	331.2	59.18
332.5	65.40	332.5	63.08
333.1	69.42	333.5	66.96
333.6	73.43	334.1	70.85
334.0	77.44	334.6	74.73
334.4	81.45	335.1	78.60
334.8	85.44	335.5	82.45
335.3	89.42	335.9	86.29
336.3	93.34	336.2	90.13
339.2	95.09	336.8	93.93
350.0	100.80	339.4	95.04
360.0	106.17	350.0	100.64
373.1	113.35	360.0	106.10
....	....	373.1	113.19

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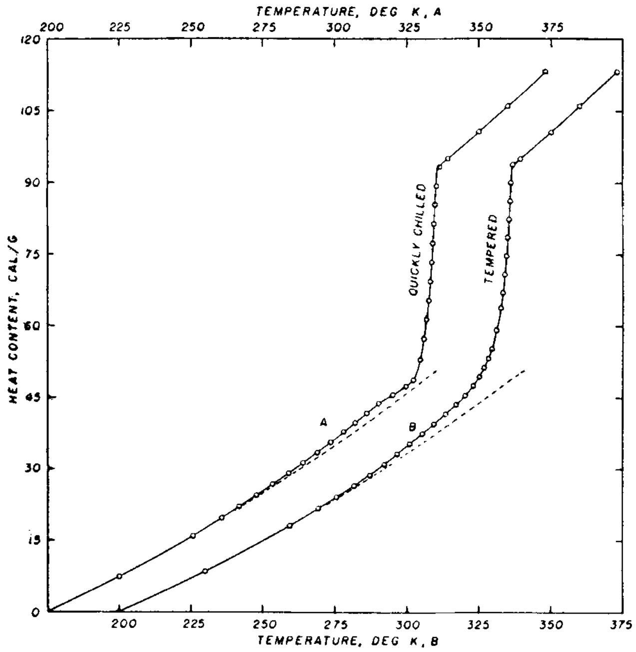

FIG. 1. Accumulated heat contents of highly hydrogenated cottonseed oil, quickly chilled, and tempered, above 200° K. (cal./g.).

employed, that is, from temperatures representing a completely solid state to those in which the oil was completely liquid. Since the rate of melting was very slow (about 8 hours required), it may be assumed that a state of near-equilibrium existed between the liquid and solid phases during the fusion of the oil.

The regular increase in the slope of the heat content curve (Figure 1) for the tempered sample indicates that in this sample the oil was, as expected, in its highest melting form (Form I). However, the plateau, beginning at about 308° K. (35° C.), in the heat content curve for the quickly chilled sample is evidence of a polymorphic transformation. The broken lines in Figure 1 represent the accumulated heat capacities of the solid oils, calculated from the heat capacity equations for the solid and liquid oils, as given below. Unfortunately, it was not possible to carry out the calorimetric examination of the quickly chilled sample immediately after it was solidified, because of the time (about 2 days) required to set up and evacuate the calorimetric apparatus after introduction of the sample. During this time the sample warmed to room temperature. Since polymorphic transformations occur readily in the hydrogenated oil at room temperature, the quickly solidified sample undoubtedly consisted of a mixture of polymorphic forms. The data on the quickly chilled sample depend on its previous history and are only to be taken as an indication of possible variations in the solidified material.

Heat Capacity of the Solid and Liquid Oil

THE values for the heat capacity determined with the tempered and quickly chilled solid oils, as well as those for the liquid oil at different temperatures, are assembled in Table 2.

The following equations for expressing the changes in heat capacity, c_p, in calories per gram, with temperature, t, °C., were calculated from the experimental data of Table 2.

For the liquid oil, 60° to 80° C.:

$$c_p = 0.458 + 0.00097t$$

For the solid oil, tempered, —80° to —10° C.:

$$c_p = 0.364 + 0.00135t$$

For the solid oil, quickly chilled, —80° to —20° C.:

$$c_p = 0.383 + 0.00141t$$

Deviations of the observed values from the calculated values, obtained by using these heat-capacity equations, are shown in columns 3, 6, and 9 of Table 2.

An extrapolation of the present data on the solid oil to high temperatures would yield heat-capacity values somewhat higher than the values for hardened cottonseed oil reported previously by Gudheim (3).

A correlation of the heat capacity data for unhydrogenated cottonseed oil (4), partially hydrogenated cottonseed oil (4), and the substantially completed hydrogenated cottonseed oil is shown in Figure 2. In the liquid phase, the highly hydrogenated oil has the highest heat capacity over the measured temperature range; whereas, in the solid phase, the unhydrogenated cottonseed oil has the highest heat capacity. Within the experimental temperature range, the heat capacity of the quickly chilled solid oil is approximately 5 percent higher than that of the tempered solid oil at any given temperature.

Heat of Fusion of the Oil

HEAT of fusion measurements were made on both the tempered and quickly chilled oil. The heat of fusion, calculated at the point of half-fusion, for the tempered sample was 44.3 cal./g. at 334.6° K. (61.5° C.), and that for the quickly chilled sample was 41.9 cal./g. at 333.5° K. (60.4° C.). The differences between these values and similar values calculated at the conventionally extrapolated melting points of the oils were less than the probable experimental errors in making the determinations. The extrapolated melting point of the tempered oil was 336.5° K. (63.4° C.), and that of the quickly chilled oil was 335.9° K. (62.8° C.). Melting of the solid oil

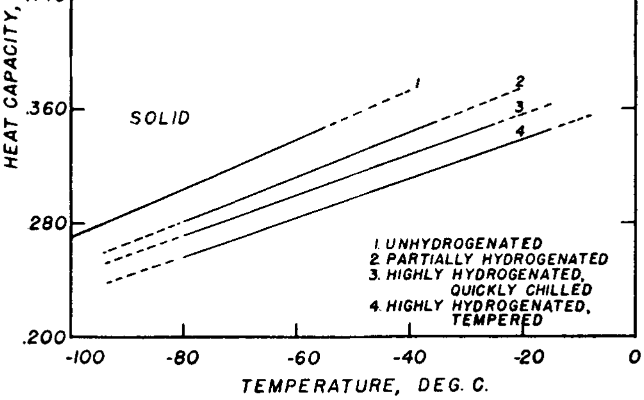

FIG. 2. Comparison of heat capacities of unhydrogenated, partially hydrogenated, and highly hydrogenated cottonseed oils, in the solid and liquid states.

TABLE 2

Heat Capacity, c_p, of Highly Hydrogenated Cottonseed Oil in Solid and Liquid States at Various Temperatures.

Solid oil, tempered			Solid oil, quickly chilled			Liquid oil		
Temp. °K.	Observed c_p	Deviation of obs. from calc. value	Temp. °K.	Observed c_p	Deviation of obs. from calc. value	Temp. °K.	Observed c_p	Deviation of obs. from calc. value
	cal./g.	*cal./g.*		*cal./g.*	*cal./g.*		*cal./g.*	*cal./g.*
203.3	0.270	0	196.2	0.275	0	340.1	0.524	0.001
210.9	0.281	0.001	203.4	0.284	0.001	344.1	0.526	—0.001
218.4	0.291	0.001	211.3	0.296	0	347.6	0.530	0
226.5	0.300	—0.001	218.6	0.306	0	351.5	0.535	0.001
233.8	0.310	—0.001	225.4	0.315	—0.001	355.1	0.537	—0.001
241.6	0.321	0	232.3	0.326	0.001	....	....	....
248.4	0.332	0.001	240.8	0.338	0.001	....	....	....
255.6	0.342	0.002	....	....	....	....	....	....

was first detected in the tempered sample at 258° K., ±1° (—15° C.) and in the quickly chilled sample at 247° K., ±1° (—26° C.).

Previously reported heat of fusion values for highly hydrogenated cottonseed oil (3) are slightly higher than the present value for the tempered sample.

The difference in the heat of fusion of the two samples, amounting to 2.4 calories per gram, cannot be considered a true heat of transition, in view of the probable heterogeneity of the rapidly solidified sample. The heat of fusion of commercially prepared lots of hydrogenated oil of this approximate iodine value should generally lie between the two experimentally determined values.

Summary

1. The heat content of a quickly chilled sample, and that of a slowly chilled and tempered sample, of almost completely hydrogenated cottonseed oil, has been measured over a temperature range within which there is in each case complete transformation of the oil from a solid to a liquid form.

2. Heat capacity data have been calculated for the liquid oil and for the quickly chilled and the tempered solid oil. Equations expressing the changes in heat capacity with temperature have been derived. A correlation of the heat capacity data on highly hydrogenated cottonseed oil and similar data previously obtained on unhydrogenated cottonseed oil, and on partially hydrogenated oil, in both liquid and solid states, is presented.

3. The heat of fusion calculated for the quickly chilled and for the tempered solid oil is given.

LITERATURE CITED

1. Bailey, A. E., Jefferson, M. E., Kreeger, Florence B., and Bauer, S. T., Oil & Soap 22, 10-13 (1945).
2. Bailey, A. E., Todd, S. S., Singleton, W. S., and Oliver, G. D., Oil & Soap 21, 293-97 (1944).
3. Gudheim, A. R., Oil & Soap, 21, 129-33 (1944).
4. Oliver, G. D., Singleton, W. S., Todd, S. S., and Bailey, A. E., Oil & Soap 21, 297-300 (1944).

Precise Laboratory Fractional Distillation of Fatty Acid Esters

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SINCE the first attempts, over 65 years ago, to utilize fractional distillation to separate individual fatty acids, the art has gradually improved until today this process is a common commercial operation. On a laboratory scale Professor Hilditch and his coworkers have been the foremost proponents of this technique, which has been extended and amplified by Dr. H. E. Longenecker in this country. The latter has recently reviewed this field (1).

The more widespread use of fractional distillation in the fatty acid field, however, has been hampered by an incomplete understanding of basic principles on the part of many investigators. Frequently this has resulted in the use of inefficient fractionating equipment and consequent unsatisfactory results. It is the purpose of this paper to review, in the light of our experience, the more important features of fractional distillation technique as applied to fatty acid esters.

Fractional distillation may be looked upon as a process in which vapors leaving the liquid in the still pot are allowed to pass upwards through a column at the top of which they are condensed. A portion of the condensate is returned as "reflux" downwards through the column where it is brought into more or less intimate contact with the ascending vapors. Here a heat interchange takes place between the relatively cooler liquid and the warmer vapors so that the more volatile part of the liquid is vaporized while the more easily condensible part of the vapors is condensed. Under ideal conditions the heat lost by the rising vapors is gained by the descending liquid, there being no loss or gain of heat from the outside. The net result is a concentration of the more volatile material in the top of the column with increasing concentration of less volatile material as the bottom of the column is approached.

A pictorial representation of the process is seen in Fig. 1 which shows a so-called vapor-liquid equilibrium curve. As a hypothetical case, a liquid of x_1 mole % of B at t_1 will give rise to vapor which when

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