Changes in Composition of the Fatty Phase During the Twitchell Splitting of Coconut Oil

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THE mechanism of the reaction by which fats and oils are hydrolyzed into fatty acids and glycerol has intrigued investigators for many years. The hydrolysis of the monohydric alcohol esters in a single phase is a well known simple reaction compared to the complex hydrolysis of the trihydric alcohol esters, such as oils and fats in a system of two liquid phases. The published literature is quite extensive and reflects the many efforts that have been made to explain the kinetics of hydrolysis of fats and oils either by the autoclave process, with and without catalysts, or the Twitchell process.

Research on this subject in the past has been handicapped by the lack of analytical methods which could be used to determine the amounts of fatty acids, glycerol, mono-, di-, and triglycerides in the presence of one another—all of which are products of the reaction. Today, methods are available which make these analyses possible (1, 2). In this investigation, confined to a study of the changes in composition of the fatty phase during the Twitchell splitting of coconut oil, these new analytical methods were used.

The course of the reaction was established by the analyses of a series of samples taken from a 15,000-pound batch of crude coconut oil during a normal, three-boil Twitchell splitting operation. In all 45 samples were taken, from which 14 were selected for complete analyses. An abstract of the operating log is given in Table I, which also indicates when the samples analyzed were taken.

All samples were immediately centrifuged to separate the fatty from the aqueous phase, clear portions of the fatty phase being set aside for analyses. The first of these 14 samples had a moisture content of 0.1% and unsaponifiable matter of 0.5%. These results were then applied to the remaining 13 samples in calculating the complete composition of the fatty phase in order to reduce the amount of analytical work inasmuch as the possible error resulting from this procedure was regarded as being beyond the limits of accuracy of the other analytical methods used.

From the saponification value the mean molecular weight of the coconut fatty acids was found to be 207.71, from which the theoretical mean molecular weight, the combined glycerol, and the total fatty-acid content of the corresponding mono-, di-, and triglycerides were calculated.

	Mean Molecular Weight	Per Cent Glycerol	Per Cent Total Fatty Acids
Monoglycerides	281.79	32.68	73.71
Diglycerides	471.48	19.53	88.11
Triglycerides	661.18	13.93	94.25

The centrifuged samples were found to contain some free glycerol in solution in amounts up to a maximum of 0.5%. Since the monoglyceride determinations were made according to the procedure of Handschumaker and Linteris (1), the calculations automatically include any free glycerol present as though it were monoglycerides. Hence monoglyceride determinations were made both on the centrifuged samples and on the same samples washed with a saturated solution of sodium sulphate to remove any free glycerol. The amount of glycerol so removed was calculated from the difference in the two monoglyceride determinations as follows:

TABLE I

Twitchell Splitting of Coconut Oil—Operating Log

	Elapsed Time Hours	Sample Taken No.
First Boil		
Coconut oil charged—15,000 lb. Sap. Value = 254.3, Acid Value = 17.7	0.00	....
Steam on	.25	1
Coconut oil boiling	.50	....
Water charged—40% on fat basis	2.00	....
30% sulfuric acid charged—0.5% on fat basis as 100% sulfuric acid	2.50	....
Splitting agent charged—0.7% on fat basis, Acto 500, Atlantic Refining Co	2.58	10
First boil began	2.67	....
	2.83	13
	3.25	17
	3.91	20
	4.75	22
	6.75	24
	8.75	26
	10.75	28
	13.75	31
Steam off—first boil ended after 15.78 hours boiling	17.75	35
Sweetwater drawn off	20.75	....
Second Boil		
Steam on	20.75	....
Fatty acids boiling	21.58	....
Water charged—25% on original fat basis	22.50	....
30% sulfuric acid charged—0.25% on original fat basis as 100% sulfuric acid	22.58	....
Second boil began	22.58	....
	23.58	37
Steam off—second boil ended after 5 hours boiling	27.58	41
Sweetwater drawn off	30.17	....
Third Boil		
Steam on	30.17	....
Fatty acids boiling	30.42	....
Water charged—25% on original fat basis	30.50	....
30% sulfuric acid charged—0.25% on original fat basis as 100% sulfuric acid	30.75	....
Third boil began	30.83	....
Steam off—third boil ended after 6 hours boiling	36.83	45
Sweetwater drawn off	39.42	....

If m_1 = monoglyceride determination on the unwashed sample in per cent

m_2 = monoglyceride determination on the washed sample in per cent

g = free glycerol in the unwashed sample in per cent

mw_1 = molecular weight of glycerol

mmw_2 = mean molecular weight of monoglycerides

then

$$g = \left\{ \frac{m_1}{100}(100) - \frac{m_2}{100}(100 - g) \right\} \times \frac{\frac{mw_1}{4}}{\frac{mmw_2}{2}}$$

$$= \left(m_1 - m_2 + \frac{m_2 g}{100} \right) \times \frac{\frac{92.09}{4}}{\frac{281.79}{2}}$$

$$= \left(m_1 - m_2 + \frac{m_2 g}{100} \right) \times 0.1634$$

The total combined glycerol in the samples was determined by a modification of the analytical procedure by Troy and Bell (2) in which the oxidant was a mixture of periodic acid and 80% acetic acid instead of a mixture of periodic acid and sulphuric acids. The free fatty acid content was calculated from the acid value and the mean molecular weight of the fatty acids. The di- and triglycerides were determined by calculations based on two algebraic equations, one of these being a total glycerol balance of all glycerol containing components, the other representing a material balance of all components.

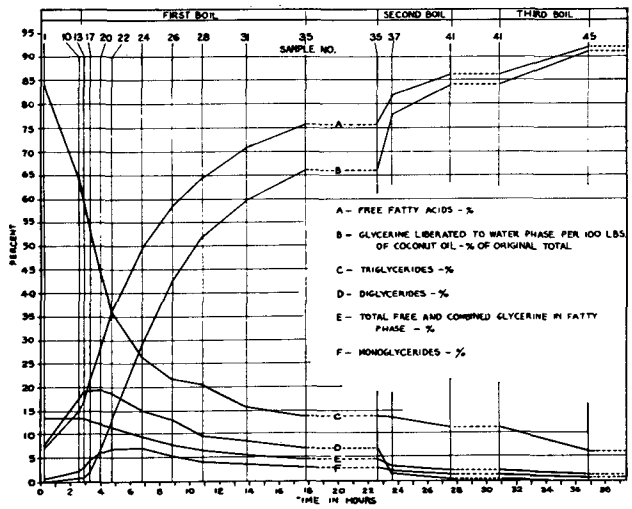
Since all these analyses were made on the washed samples, the results were recalculated to adjust for the free glycerol present so that they would all be on the basis of the unwashed centrifuged samples. The final results are shown in the upper section of Table II. The accompanying chart is a graphic representation of the same results plotted against time as abcissae, thus correlating the data with respect to both the operating log in Table I and the time at which samples were taken.

Curve A shows the free fatty acid content of the various samples. The rate at which fatty acids were liberated increased rapidly during the first 3.25 hours, gradually decreasing after another 1.50 hours until the end of the first boil. During the beginning of the second boil the rate increased again, as would be expected, due to the water change, followed by another decrease in rate. The third boil reflected similar changes but with somewhat less activity.

Curve C shows the corresponding changes in the triglyceride content, the decomposition rate increasing rapidly during the first 3.25 hours, gradually decreasing after another 1.50 hours to the end of the first boil, following more or less an inverted pattern of Curve A. During the second and third boils, however, the rate of decomposition did not reflect sudden changes as shown on Curve A, merely decreasing steadily to the end of the reaction. The reaction pattern shown by curves A and C is well known and quite normal.

Curve E represents the total free and combined glycerol in the fatty phase. From the analytical data given in Table II the amount of free glycerol in the fatty phase is relatively small, varying only from 0.01% in sample 1 to a maximum of 0.52% in sample 24 taken after 6.75 hours, decreasing thereafter to

TWITCHELL SPLITTING OF COCONUT OIL — CHARACTERISTICS OF THE FATTY PHASE



0.10% in the last sample taken at the end of the reaction. These small amounts are not significant to curve E, which, for all practical purposes, represents the changes taking place in the combined glycerol content of the fatty phase during the reaction. It will be observed that there is no change in the combined glycerol content in samples 1, 10, and 13 for the first 2.83 hours and that thereafter the amount of combined glycerol falls at a decreasing rate to the end of the reaction. The fact that the combined glycerol did not change during this early period might be interpreted by itself as indicating that hydrolysis had not yet taken place. However, when considered along with the increase in free fatty acid content and the decrease in triglycerides, it is evident that hydrolysis had set in at a considerable rate but only with respect to the decomposition of triglycerides into di- and monoglycerides and fatty acids without liberating any glycerol.

This is shown by both curves F and D, which represent respectively the mono- and diglycerides present. It will be seen that the original diglyceride content increased sharply from 7.6 to a maximum of 19.5% in the short time of 3.9 hours, falling off at a gradually declining rate to the end of the first boil after 17.75 hours to 7.08%. After changing the water,

TABLE II

Twitchell Splitting of Coconut Oil—Characteristics of the Fatty Phase

	Sample No.													
	1	10	13	17	20	22	24	26	28	31	35	37	41	45
Composition	Per cent													
Free fatty acids	7.11	15.09	16.94	21.62	28.48	36.47	49.76	58.61	64.42	70.69	75.08	81.90	86.22	92.20
Free glycerine	.01	.08	.11	.20	.35	.49	.52	.42	.45	.40	.39	.22	.17	.10
Monoglycerides	.58	2.22	3.00	4.55	6.02	6.97	7.04	5.40	4.11	3.72	2.99	2.07	1.35	.80
Diglycerides	7.60	17.51	19.14	19.35	19.49	18.92	15.15	13.11	9.67	8.69	7.08	1.59	.22	.00
Triglycerides	84.10	64.50	60.21	53.68	45.06	36.55	26.93	21.86	20.75	15.90	13.86	13.62	11.44	6.30
Unsaponifiable	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50
Moisture	.10	.10	.10	.10	.10	.10	.10	.10	.10	.10	.10	.10	.10	.10
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total free and combined glycerine in fatty phase—%	13.39	13.21	13.21	12.94	12.41	11.55	9.54	7.79	6.58	5.53	4.68	3.12	2.24	1.24
Calculated weight of fatty phase per 100 lb. coconut oil—lb.	100.00	100.59	100.79	100.95	101.01	100.83	99.80	98.68	97.87	97.32	96.80	95.73	95.22	94.70
Calculated weight of glycerine in fatty phase per 100 lb. coconut oil—lb.	13.39	13.29	13.32	13.07	12.54	11.65	9.52	7.69	6.44	5.38	4.53	3.00	2.14	1.17
Calculated weight of glycerine liberated to water phase per 100 lb. coconut oil—lb.	0.00	0.10	0.07	0.32	0.85	1.74	3.87	5.78	6.95	8.01	8.86	10.39	11.25	12.22
Glycerine liberated to water phase per 100 lb. coconut oil—% of total	0.00	0.81	0.57	2.45	6.41	13.02	28.94	42.62	51.94	59.81	66.17	77.68	84.06	91.26

the diglycerides fell sharply during the second boil within an hour to 1.59%, disappearing completely in the third boil.

The behavior of the monoglycerides was somewhat different. With only 0.58% originally present, the monoglyceride content increased during the early stages at a slower rate than the diglycerides, with a much more rapid increase beginning after the diglycerides reached a maximum. The monoglycerides reached their maximum of 7.04% after 6.75 hours, after which the amounts present gradually decreased to 0.8% in the last sample.

These results appear to confirm the theories of the earlier investigators that the reaction proceeds stepwise from the triglyceride to the diglyceride with the liberation of one mol of fatty acid, then from the diglyceride to the monoglyceride with the liberation of a second mol of fatty acid, and finally from the monoglyceride with the simultaneous liberation of the third mol of fatty acid and one mol of glycerol. It seems that in the early stages of hydrolysis only the the first two of these reactions occur, after which all three reactions take place simultaneously. From the results it is not possible to calculate the various rates of reaction because of the simultaneous formation and decomposition of both mono- and diglycerides. The results do show, however, that the three reaction rates vary with respect to one another due to the continuously changing equilibrium conditions effected by the changes in composition of both fatty and aqueous phases.

In the lower section of Table II some further calculated results are given. The first of these shows the theoretical weight of the fatty phase per 100 pounds of original coconut oil calculated on the basis of an invariant total fatty-acid content throughout. The corresponding weights of total free and combined glycerol present in the fatty phase per 100 pounds of original coconut oil were then also calculated. From these figures it was then possible to determine for each stage during the hydrolysis the weight of glycerol which had been liberated to the aqueous phase per 100 pounds of original coconut oil. Recalculating these on a percentage basis of the original amount of glycerol present resulted in the figures shown on the last line of Table II, which, in turn, are shown graphically in the chart as curve B.

By comparing curve A and B it will be observed that the amount of glycerol split off to the water phase in general follows the amount of free fatty acids liberated, as would be expected, but with a considerable lag in the early stages of hydrolysis. During the balance of the first boil the rates parallel one another quite closely. In the second boil, the rate at which glycerol was liberated increased substantially, much more so than the rate at which free fatty acids were set free. The changes during the third boil are similar, but not so marked.

Finally, the analysis of the last sample showed it to contain 92.2% free fatty acids, 0.10% free glycerol, 0.8% monoglycerides, 6.30% triglycerides, with no diglycerides, 0.5% unsaponifiable, and 0.1% moisture. Based on the original amounts present, further calculations indicate that 92.7% of the total fatty acids were liberated in the fatty phase and that 91.3% of the total available glycerol was set free in the aqueous phase.

In conclusion, it is pointed out that in the subsequent distillation of such crude split fatty acids, the presence of free glycerol, mono-, or diglycerides can result in reesterification of some of the free fatty acids to triglycerides. For example, fatty acids of the composition indicated could readily increase in triglyceride content by about 40%, resulting in a substantial increase in distillation residues with a reduction in yield of distilled fatty acids. Thorough washing of the stock with water before distillation to remove any free glycerol will, in part, minimize this possibility. However, the best solution to this problem is to carry out the hydrolysis as far as possible beyond the point where either mono- or diglycerides are likely to be present followed by a thorough water wash.

In the Twitchell hydrolysis of fats and oils this is not so readily accomplished because the various impurities occurring, particularly in the lower grade stocks, reduce the rate of reaction, necessitating prolonged boiling, thus making the achievement of high splits much more difficult. The removal of these impurities, by pretreating the stock before Twitchelling, will greatly improve conditions and give better results. Stocks like coconut oil, admittedly respond much easier to Twitchell splitting than the low grade tallows and greases, or some of the acid oils, such as cottonseed and soybean.

The high pressure continuous fat splitting process has the advantage of overcoming these difficulties. This process can hydrolyze any of the above-mentioned stocks to 98% or more without any pretreatment. In this process the fatty phase is continuously washed with fresh water to remove any free glycerol, and the presence of mono- and diglycerides in the fatty acids produced is virtually eliminated because of the high degree of hydrolysis obtained (3, 4).

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