

Industrial Hydrogenation of Cottonseed Oil: A Compositional Study

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Abstract

Intermediate samples during a typical plant hydrogenation of cottonseed oil for vanaspati (shortening) manufacture have been examined for their fatty acid composition by gas-liquid chromatography and *trans* isomers content by infrared spectrophotometry. In the initial stages, hydrogenation of linoleate proceeds almost exclusively in preference to that of oleate. During this period, *trans* isomers are also formed at a rapid rate. It has been proposed that this high selectivity and high *trans* isomer formation are linked to the formation of conjugated diene from linoleate as a first step in the hydrogenation. It has been found that a linear relationship exists between the linoleate content and the *trans* isomers content or the $^{k}10.38 \mu$ values of the glycerides. The practical utility of this plot is that it can be employed as a guide to arrest the process at any desired linoleate level.

Introduction

COTTONSEED, GROUNDNUT and soybean oils are subjected to partial hydrogenation on a commercial basis to produce such edible products as margarines, shortenings and vanaspati. An added feature of cottonseed oil is its high content, 20–25% (1–3) of palmitic acid and as this is close to that of cocoa-butter, 26.2% (4–6) hydrogenation of this oil has assumed special importance to manufacture cocoa-butter substitutes and other confectionery fats (7–17). Of the oils mentioned above, cottonseed oil is the most extensively investigated on such aspects of hydrogenation as: *trans* and positional isomers formation (18–22); selectivity and kinetics (23–29,39) and effect of such variables as catalysts (30–36), temperature (19,26,28,37,41), pressure (26,28,37–41), speed of agitation (26,28,37,41) and solvents (38–42). Some studies of practical interest such as continuous hydrogenation (43), physical properties of products (18,44,45) and reuse of catalysts (46,47) have also been made. Very few of these studies, however, are related to the actual industrial practice of hydrogenation. It was felt that following the course of the process by examining intermediate products for their fatty acid composition by such an accurate and modern tool as gas-liquid chromatography (GLC) might not only provide a better control on the process

but also might lead to a better understanding of the nature of the reactions. This paper reports such a compositional study during a typical hydrogenation of cottonseed oil for vanaspati manufacture.

Experimental

Samples were drawn during the plant hydrogenation of refined cottonseed oil (I.V. 110.9, S.V. 197.5) with nickel catalyst (reused plus fresh Rufert catalyst equivalent to about 0.1% nickel on oil basis) at about 180C (starting temperature 140C, finishing temperature 180C) and at slightly above atmospheric pressure (5–15 psig). The zero hour sample corresponds to the time when the catalyst was well mixed with the oil after addition. The results are recorded in Table I.

Infrared analyses were carried out on the filtered samples as such and also on their corresponding methyl esters with a Perkin-Elmer Model 21 infrared spectrophotometer having sodium chloride optics. The *trans* peak for the oils or fats and their methyl esters occurred at 10.38μ and absorbance at this wavelength was used to calculate the specific absorption coefficient ($^{k}10.38 \mu$) for the hydrogenated samples and the *trans* isomer content of the methyl esters was calculated as methyl elaidate after correcting for *cis* absorption using pure methyl oleate and methyl elaidate as primary standards.

Gas-liquid chromatographic analyses were done with a Perkin-Elmer Model 800 gas chromatograph having a flame ionization detector, on a 2-meter butane-diol-succinate polyester column (8% on HMDS chromosorb 80–100 mesh) at 210C with nitrogen as carrier gas (45 ml/min measured at column).

Results and Discussion

The data in Table I show that in the first 2 hr hydrogenation of the linoleic portion of the glycerides is proceeding at a fast rate with the concurrent formation of large amounts of *trans* isomers accompanied by a sharp increase in melting point of the products. At these times hydrogenation of oleate occurs only to a small and limited extent as seen by a small increase in the stearate contents. If the actual amount of linoleate hydrogenated and the amounts of *trans* and stearate formed at particular times are related to each other, a better picture of the process emerges. This is done in Table II for the first 3 hr of hydrogenation.

TABLE I
Analysis and Fatty Acid Composition of Hydrogenated Cottonseed Oil

Time hours	Glycerides				Methyl esters				
	MP. C	I. V. Wijs 30 min	$^{k}10.38 \mu$	C ₁₄ ^a	C ₁₆ ^b	C ₁₈	C ₁₈ ¹⁼	C ₁₈ ²⁼	% <i>trans</i> ^c
0	20.5	104.6	0.0476	0.2	22.2	0.9	21.8	55.0	4.7
1	26.0	91.6	0.1237	0.2	22.2	1.2	46.1	30.3	22.8
2	35.0	71.7	0.2251	0.2	22.1	1.5	70.5	5.7	44.4
3	36.5	67.6	0.2296	0.2	22.2	1.7	72.3	3.7	46.1
4.75	37.5	66.4	0.2325	0.2	22.1	6.7	68.8	2.2	44.4

^a Traces of C₁₂ is also present in all samples.

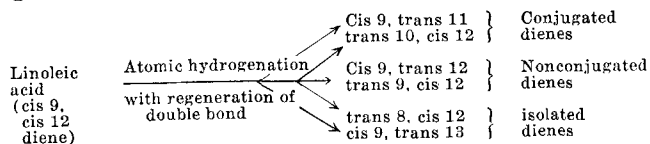
^b A little C₁₆¹⁼ is visible as shoulder in the first sample.

^c Calculated as methyl elaidate.

TABLE II
Hydrogenation Data

Duration	% Stearate formed	% Linoleate hydrogenated	Linoleate		(Hydrogenated)	% <i>trans</i> formed	<i>trans</i> linoleate
			Oleate				
1st hour	0.3	24.7	24.7	=	83	18.1	0.73
			0.3				
2nd hour	0.3	24.6	24.6	=	83	21.6	0.9
			0.3				
3rd hour	0.2	2.0	2.0	=	10	1.7	0.9
			0.2				

Under pressures employed in commercial hydrogenation, such as that of the present study it can be assumed that no linoleate is hydrogenated to stearate as supported by the C^{14} -tagged study of hydrogenation of methyl linoleate (48). Therefore the amount of stearate formed during a particular period can be taken to be due to the hydrogenation of oleate or monoene. The ratio of linoleate to oleate hydrogenated (column 4) is extremely high and thus denotes a high selectivity of the reaction in the first 2 hr. If *trans* and *cis* monoenes are formed in equal amounts by the hydrogenation of linoleate then the ratio of *trans* to linoleate hydrogenated (column 6) should be about 0.5 whereas it is higher in all cases. It is generally accepted that atomic hydrogenation (49) causes the formation of *trans* and positional isomers (50-51). Taking such observations as that conjugation (19) occurs during the hydrogenation of linoleic acid and positional isomers (52) with double bonds at 6 through 14 positions are formed, it was postulated (53) that the following intermediate dienes can be formed as a first step during the hydrogenation of this acid:



Of these it is reasonable to expect the conjugated dienes to be hydrogenated as soon they are formed and so will be the fastest to disappear, of the three types of dienes indicated above. It is also known that conjugated dienes, irrespective of their geometry, give rise to high proportion of *trans* isomers in the monoenes (54,55). It is therefore suggested that the high selectivity and high *trans* isomers formation as observed in the present study are linked to the occurrence of conjugation during the hydrogenation of linoleic acid. In the third hour the hydrogenation has almost come to a standstill, as only 2.0% of linoleate and 0.2% oleate have been hydrogenated. Thus the 5.7% of diene remaining at the end of 2 hr of hydrogenation are possibly the accumulated isomers of linoleate and not the *cis* 9, *cis* 12 diene. Since the nonconjugated diene (*cis* 9, *trans* 12 or *trans* 9, *cis* 12) isomerizes slowly even with alkali (56), it may not give rise to conjugated dienes readily under hydrogenation conditions and thus will hydrogenate slowly. Dienes with isolated double bonds have been shown by calculation (23,57) to have rates of hydrogenation closer to oleate. Further support to the point that such isomeric dienes are formed is given by the very slow disappearance (1.5%) of the diene in the last 1.75 hr of the reaction as compared to the monoene (5%). The larger amount of monoene hydrogenated is due to the mass-effect (72% monoene against 3.7% diene) and not to any greater reactivity.

Though some evidence (58) for the presence of such isomeric dienes in hydrogenated edible products exists, yet unequivocal evidence can be obtained only by isolating the residual dienes and establishing their structure. It may be mentioned here that hydrogenations of geometric isomers of linoleic acid and dienes with isolated double bonds still remain unstudied.

To ascertain the relationship between the *trans* isomers and linoleate, their contents at different stages were plotted. It is seen from Figure 1 that a straight line relationship (solid circles) exists between these. If instead of the methyl elaidate content of the methyl esters, the $k_{10.38}$ of the glycerides (open circles) are substituted still the straight line relationship prevails. The practical significance of this is that such a plot can be used to know the linoleate (diene) content at any stage of hydrogenation by just determining the infrared absorption at the *trans* peak wavelength directly on the sample drawn (10.38μ in the present study) calculating the $k_{10.38}$ and reading the linoleate content corresponding to this from the graph. Thus such a plot can be used as a guide to stop the hydrogenation at any desired linoleate level. It is known that for deep-fat frying such as frying potato chips lightly hydrogenated cottonseed oil (about 24-30% linoleate) is preferable (59) to the straight oil itself or the shortening derived from it. As can be seen from the Table I the first hour product comes closest to this. It should be mentioned that the literature (18,19,26,28,29,31,37,41,47) on hydrogenation is replete with such plots as relating time to refractive index, iodine value, *trans* content, linoleate content, etc., or iodine value to some of the above-mentioned variables, but this is the first time the relationship existing between linoleate to *trans* isomers or $k_{10.38}$ of the glycerides has been pointed out. It is realized that this plot represents only a single run and that its practical value will be enhanced by obtaining several such plots representing different conditions, particularly the catalyst composition and resultant activity, the other conditions such as temperature, pressure and speed of agitation being nearly constant for any unit.

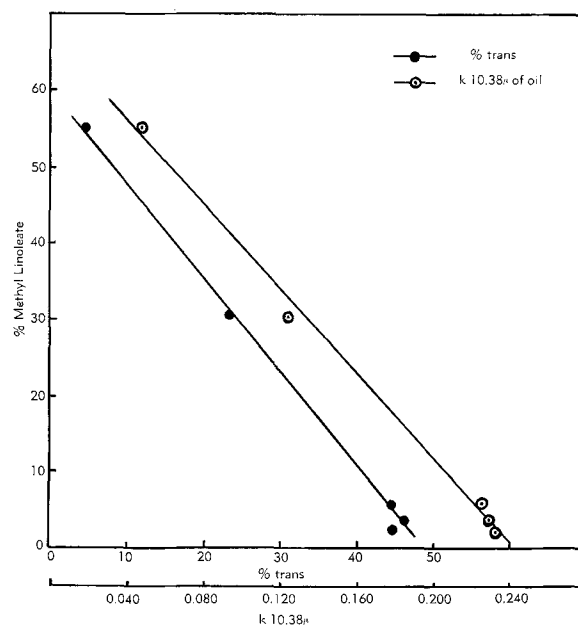


FIG. 1. Relationship between methyl linoleate (%) and *trans* isomers (%) and specific absorption coefficient ($k_{10.38}$) of the glycerides of hydrogenated cottonseed oil.

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