limited both by degree of resolution and by the diffuseness of the spots, especially at low R_f values. With natural mixed triglycerides there is much overlapping and the separations achieved do not become apparent until the second dimensional separation of the fatty acids is done. However, since any given fatty acid can be present in several different triglycerides the methyl ester appears as a streak elongated in the first dimension. The major triglycerides can be estimated from the relative density of the fatty acids at any given first dimension R_f zone. The analysis of triglycerides presented here is less exact than that of Privett and Blank (4); however, it is a simpler procedure in that it is all done on a single chromatogram.

Incomplete transesterification of fatty acids may be caused by a high relative humidity, drying of the chromatogram in the methanol vapor, or excess sodium methoxide. Cholesteryl esters incompletely transesterify. Spreading or unwanted migration can be caused by too heavy spraying or condensation of the methanol vapor.

The total length of time to complete a two dimensional chromatogram is 7 hr for the triglycerides and 4 hr for the mixed lipids.

The transesterification by elatography has been very useful in our hands, particularly with mixed lipids. It is also useful with column chromatography for quickly determining the fatty acids in fractions; in which case different fractions are spotted on a single chromatogram, transesterified, and the methyl esters separated.

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Catalysts for Selective Hydrogenation of Soybean Oil.[1] I. An Experimental Method for Evaluating Selectivity

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Abstract

The undesirable flavor reversion properties of soybean oils may be counteracted by selective hydrogenation of the linolenate components. Screening of catalysts for this purpose was accomplished by a standardized laboratory hydrogenation of a refined, bleached soybean oil under atmospheric pressure. A mathematical derivation utilizes analytical chromatographic data to determine linolenate/linoleate reaction rates as a selectivity index S_L for a given catalyst.

Introduction

THE VALUE of soybean oil as an edible product has long been recognized. However, the formation of flavors is an undesirable aspect which has received considerable attention. It is rather generally accepted that the linolenic acid constituents are a primary precursor of flavors (1). Thus, if linolenic constituents can be selectively hydrogenated, improved soybean oil could find expanded use both as a cooking and a salad oil. A major problem is to evaluate whether present catalysts are sufficiently selective to accomplish the specified hydrogenation and if not, to develop heterogeneous catalysts which can achieve the desired goals.

In order to obtain such information, the conventional approach would involve periodic sampling of an experimental reaction, plotting concn of components against time or percentage converted and then empirically adjusting constants for specific reaction rate (2). This approach would not be useful for a screening program where many catalysts would require evaluation. Dutton (3) has developed a procedure based on the kinetic equations for consecutive first order reactions which determines the ratio of reaction rate constants of linolenate and linoleate carbon-carbon double bond hydrogenation. The method requires that the test mixture be comprised of equal amounts of linolenate and linoleate components, either triglycerides or monoesters. Then a single experimental hydrogenation (with 0.5 mole hydrogen/mole mixture) and analytical determination of the triene, diene, and monene components provides all the information needed to give the ratio of the linolenate/linoleate reaction rates.

While Dutton's method is precise and useful, it does not evaluate catalyst selectivity for the oil product of immediate interest, i.e., soybean oil. Therefore, it was deemed more direct to use a typical soybean oil in a standard hydrogenation experiment and employ the analytical data to provide similar kinetic information for evaluating a wide variety of catalysts.

Criteria for Selectivity

The maximum selectivity would occur if hydrogenation would reduce only the linolenic component of soybean oil without appreciably changing any other constituent. This result would provide an equivalent increase in linoleic concn, but no change in oleic or stearic concn. Thus, a cursory examination of a hydrogenated product by gas chromatography would reveal many catalysts which had little or no selectivity. Such an approach does not take full advantage of the available data nor does it permit relative ratings where differences are small.

Assume that the rate of hydrogenation of each component is given by a relation

$$-dA/dt = k' A(H_2) F(C) \qquad [1]$$

where A is Ln, Lo, O (linolenic, linoleic, oleic) concn
H_2 is hydrogen concn
F(C) is a function of catalyst concn.

If all experiments are performed at constant pres-

[1] Presented at the AOCS Meeting, Toronto, 1962.

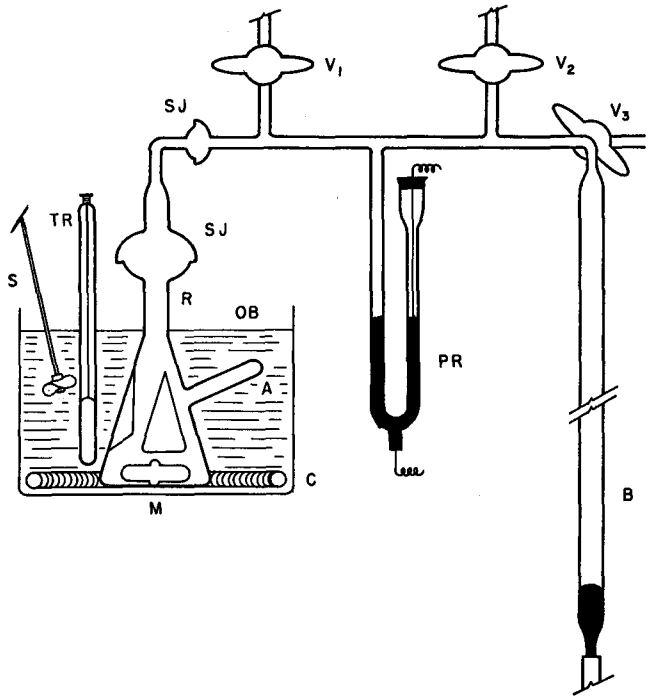

FIG. 1. Catalytic hydrogenation apparatus.

an electrical circuit. Interruption of this circuit by absorption of hydrogen within the reactor activated a solenoid value to force hydrogen from buret B through stopcock V_3 until the pressure was again balanced at PR.

Principal features of the hydrogenation system are shown in Figure 2. The oil bath OB was positioned by means of a laboratory jack LJ stationed on a platform. The driving force for the mercury in buret B was obtained by elevating the leveling bulb LB. Oil vapors from the vacuum pump VP or the system were trapped by cold trap T_1. Hydrogen from a cylinder was passed through a Deoxo unit to remove oxygen and then through cold trap T_2 containing activated charcoal to remove moisture and any adsorbable impurities.

The procedure for performing experiments varied slightly with different catalysts. Catalysts which were already in a reduced form ready for use were entered directly into the oil (normally 15 g). Where the catalyst was in an unreduced form, the catalyst was placed in the side arm while oil was added to the bottom of the reactor flask. Air was removed by alternate evacuation and flushing with hydrogen several times. Then the system was filled with hydrogen and the catalyst was heated in the side arm at reducing temp as desired or until hydrogen reduction ceased. The excess hydrogen was pumped off and the catalyst was added to the oil by rotating the reactor flask. The reactor was brought to temp under vacuum and hydrogen was entered into the system. No hydrogen absorption occurred until the magnetic stirrer bar was activated. The total hydrogen was equivalent to an excess of 200% above that needed to saturate one double bond of the linolenic component present. Various reaction temp were used, mainly 35,50,65,80, 100, and 150C. Following an experiment, the stirring was stopped and the excess hydrogen was immediately pumped off. The oil was separated from the catalyst by filtration through a Gooch crucible. If oil holdup in the catalyst appeared appreciable, the catalyst was washed with thiophene-free benzene. The excess benzene was boiled off on a water bath.

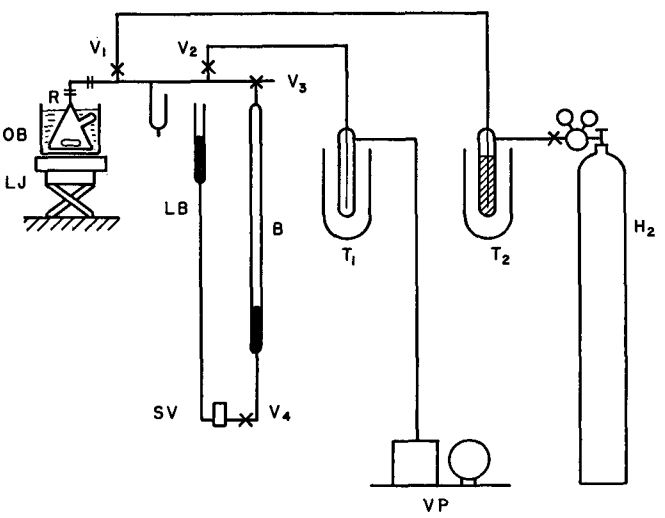

FIG. 2. Flow diagram of hydrogenation apparatus.

A 1-g sample of the product was added to 300 ml absolute methyl alcohol and anhydrous hydrogen chloride was added until the solution was saturated. The esters were refluxed overnight and then were recovered by water washing and extraction with ethyl ether. The methyl ester product (3–4 μl) was then injected into a 8-ft gas chromatographic column packed with 20% of polyethylene glycol succinate on 60- to 80-mesh chromosorb (acid-washed). Either a Barber-Coleman or an Aerograph A-90C instrument was used. The peak areas recorded were calibrated with known standards. Since palmitic acid would be presumably unaffected, it served as an internal standard and confirmation of the analytical results. Isolated *trans*-double bonds were determined by IR spectroscopy (4).

The soybean oil used was obtained from Swift & Co., Chicago, Ill., through K. F. Mattil. The sample is described as refined in the plant with caustic, water-washed twice and bleached in vacuo with a mixture of neutral and activated earths. The sample was then washed in the laboratory with dilute phosphoric acid and rebleached with neutral clay. The sample was stored at −10 to −20C until used.

Discussion

The method outlined has proved useful in providing a rapid evaluation of catalysts. As Bailey (2) indicated, the ratio of reaction rates of linolenate to linoleate in triglyceride oils containing linolenic ester is ca. 2. If under specific conditions the catalyst provides a lower ratio, e.g., 1.7, the hydrogenation is considered non-selective. On the other hand, any values of S_L over 2.0 indicate a selective catalyst. On such a basis, it becomes meaningful to rate catalysts on the basis of a limited number of experiments. However, since slight errors in gas chromatography analysis could provide erroneous S_L values, it is well to consider any specific experiment within a framework of related experiments. With this viewpoint, useful conclusions can be drawn with a limited number of experiments. Confirmation by other methods, such as that of Dutton (3), and through use of radioisotopic tracers (5), would be valuable. Also, other analytical determinations such as *trans*-ester formation by IR spectrophotometry, conjugation of double bonds by ultraviolet spectrophotometry, as well as position of double bond by nuclear magnetic resonance (NMR) or by oxidative cleavage and characterization

sure and if hydrogen diffuses rapidly enough to the catalyst surface so that depletion does not occur, then (H_2) can be considered constant. Since the catalyst remains uniform in a given experiment, F(C) remains constant [although slight changes due to reduction during reaction, competition by reacting species for active surface sites, specific poisoning, etc., might change the function, F(C)].

Thus, we can write

$$-dA/dt = kA \quad [2]$$

where $k = k'(H_2)F(C) =$ a constant.

Upon integration, we get

$$\log A/A_o = -kt \quad [3]$$

where A_o is the concn of A at $t = O$.

Let the concn of the reactive species at any time x be written as:

$$Ln_x, Lo_x, O_x$$

and at $x = O$

$$Ln_o, Lo_o, O_o.$$

We can define selectivity in terms of the solution to the above rate equation as:

$$S_L = \log(Ln_x/Ln_o)/\log(Lo_x/Lo_o) \quad [4]$$

and

$$S_o = \log(Ln_x/Ln_o)/\log(O_x/O_o) \quad [5]$$

where S_L represents the selectivity of linolenic relative to linoleic component and S_O represents the selectivity of linolenic relative to oleic component.

It is evident that S_O and S_L represent the relative reaction rates since

$$S_L = -k_{Ln}\,t/(-k_{Lo}\,t) = k_{Ln}/(k_{Lo}) \quad [6]$$

$$S_o = -k_{Ln}\,t/(-k_O\,t) = k_{Ln}/(k_O) \quad [7]$$

The time term (t) can be cancelled since the components are all exposed to the catalyst for the same time period.

Calculation Procedure

To calculate the values of S_L and S_O for each experiment performed in an identical manner, the amount of each component hydrogenated must be determined. These quantities can be deduced from the analytical data for the initial removal; it is a negative quantity of each component.

Thus, the stearic component can increase in concn only by hydrogenation of the oleic component. Therefore, the actual hydrogenation of oleic component is equal to the increase in stearic; since hydrogenation represents removal, it is a negative quantity in terms of oleic concn.

$$\Delta O = -(S_f - S_i) \quad [8]$$

where ΔO is the concn increment due to hydrogenation of oleic component
S_i is the initial stearic concn
S_f is the final stearic concn.

Similarly, the decrease in linolenic component can be due only to hydrogenation of linolenic. Hence

$$\Delta Ln = (Ln_f - Ln_i) \quad [9]$$

where ΔLn is the incremental change in concn due to hydrogenation
Ln_i is the initial concn of linolenic
Ln_f is the final concn of linolenic.

The linoleic component increases in concn because of linolenic hydrogenation but decreases from its own hydrogenation. This may be expressed as

$$Lo_f - Lo_i = \Delta Lo - \Delta Ln \quad [10]$$

where ΔLo is the incremental change in linoleic component due to hydrogenation
Lo_i is the initial concn of linoleic
Lo_f is the final concn of linoleic.

Equation [10] can be solved for ΔLo in terms of known quantities, i.e.,

$$\Delta Lo = Lo_f - Lo_i + Ln_f - Ln_i \quad [10a]$$

It is possible to derive one more equation which can be used to check the results given in equations [8] and [10a]. Thus, the oleic component concn decreases due to hydrogenation of oleic and increases from linoleic hydrogenation. This may be written similar to equation [10], or

$$O_f - O_i = \Delta O - \Delta Lo \quad [11]$$

where ΔO is the incremental change in oleic component due to hydrogenation
O_i is the initial oleic concn
O_f is the final oleic concn.

This equation may be solved for ΔO and ΔLo as follows,

$$\Delta O = O_f - O_i + \Delta Lo \quad [11a]$$

$$\Delta Lo = \Delta O - (O_f - O_i) \quad [11b]$$

Thus, to find ΔO from equation [11a], the value of ΔLo obtained in equation [10a] is used. To find ΔLo from equation [11b], the value of ΔO from equation [8] is used. Equations [8] and [11a] are hence separate methods of determining oleic component hydrogenation and similarly, equations [10a] and [11b] are separate solutions for ΔLo. If the analyses are precise, these solutions should agree. In application to a large number of experimental determinations, the two equations gave values within the range of accuracy of gas chromatography (i.e., within $\pm 0.2\%$) and accordingly, the average values of ΔO and ΔLo were used in calculating S_L and S_O.

Apparatus and Procedure

The nature of the equipment has no bearing on the proposed evaluation method since it is general in scope and applicable to any repetitive hydrogenation experiment in which access of hydrogen to the catalyst surface is not a controlling factor. However, the equipment which was used is believed to have certain novel features which made its application of particular value and convenience.

The apparatus is shown in Figures 1 and 2. The main features are shown in Figure 1. The reaction vessel (R) comprised a 125 ml flat-bottom flask which had three indentations to destroy the vortex action of the Telfon-encased magnet bar (M). The stirrer bar was actuated by a 1140 rpm rotating magnet (not shown). The reaction flask was maintained in an oil bath (OB) heated by an internal coil (C) of nichrome wire. The oil bath was agitated by stirrer S and its temp controlled by the mercury thermoregulator (TR). The temp control was generally within ± 0.1C.

Another feature of the reactor flask was the side arm for use in activating catalysts. Here, up to 550C could be attained for reduction with oil present in the flask. Complete freedom in manipulating the catalyst was derived from the two spherical joints SJ.

Prior to any experiment, the oil and catalyst were degassed by evacuation through stopcock V_2. Hydrogen was entered through stopcock V_1. In conducting either reduction of catalyst or hydrogenation of oil, the pressure of hydrogen was maintained at atmospheric pressure by pressure regulator PR. This comprised a mercury manometer which maintained

of fragments would also provide insight in the performance of heterogeneous catalysts. Obviously, a pre-screening survey must be made before such detailed investigations are made. The proposed method has proved exceedingly useful in this respect.

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Analysis of Fatty Acid-Ethylene Oxide Adducts by Countercurrent Distribution[1]

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Abstract

Countercurrent distribution (CCD) has been found to be a very satisfactory means for the direct determination of free polyol, monoester and diester in a wide range of fatty acid-ethylene oxide adducts in which the average polyoxyethylene (POE) chain length varies from 1–40 ethylene oxide units. A suggested procedure with three solvent systems, providing optimum separation over the entire scope of products, is presented in this paper.

Several fatty acid-ethylene oxide derivatives were analyzed and good separations were obtained as indicated by well-defined wt distribution curves. The results on POE-8-stearate verify earlier conclusions that the product consists of unesterified POE glycols and POE glycol mono- and diesters in the approximate molar proportions of 1:2:1.

CCD was also used to effect partial fractionation of the monoester according to POE chain length. The fractionation, although incomplete, is sufficient to permit estimation of polymer distribution.

Introduction

THE LITERATURE (1,2,3) reports several methods for the analysis of the products resulting from the reaction of long-chain fatty acids with ethylene oxide or POE glycols. The overall reaction results in an equilibrium mixture of free POE glycols, monoesters and diesters of the fatty acid as discussed by Birkmeier and Brandner (2).

Malkemus and Swan (1) developed a method for the analysis of POE glycol esters which they applied both to products made by esterifying POE glycol with fatty acid and to adducts of fatty acid and ethylene oxide. The free POE glycol is extracted from the product and discarded. The remaining ester portion is analyzed for saponification and hydroxyl numbers. From these constants and those of the original material, the quantities of free polyol, monoester and diester are calculated. The procedure is quite simple, but requires great accuracy in the determination of the analytical constants.

Birkmeier and Brandner (2) reported a procedure for the analysis of POE-8-stearate (Myrj® 45, Atlas Chemical Industries, Inc.). This method requires recovery and analysis of both the unesterified POE glycols and the mixed esters. The relative amounts of monoester and diester are calculated from the saponification and hydroxyl numbers of the mixed ester portion after correcting for the small amounts of free fatty acid, ash and water which are present.

There is disagreement among the several investigators on the mole ratios of free polyol, monoester and diester in the products. Malkemus and Swan and Wrigley, Smith and Stirton (1,4,5) reported mole ratios of monoester to diester varying from 1:1–2:1. In the previously mentioned paper (2) the authors determined the mole ratio of free polyols to monoesters to diester to be ca. 1:2:1, and pointed out that this is the mole ratio expected if ester interchange is established during the ethylene oxide addition.

Since all of the foregoing estimates of composition were indirect, and, at most, involved separation of free polyol from the ester portion, but not of monoester from diester, a search for a more satisfactory separation procedure appeared desirable. Some trial was made of column chromatography which had been reported to be applicable (3), but incomplete separations were observed in our laboratory. Attention was then directed to the CCD technique developed by Craig (6).

The present paper describes the application of the CCD technique for the direct determination of free polyol, mono- and diesters in long chain fatty acid-ethylene oxide adducts. A solvent system, which had been reported by Drew and Schaefer (7) for the separation of reaction products resulting from the addition of ethylene oxide to long-chain alcohols, was found satisfactory for the analysis of products prepared with 1–8 moles of ethylene oxide/mole fatty acid. Modifications of the system were necessary for satisfactory separations of similar derivatives in which 20 and 40 moles ethylene oxide were added.

Experimental

Apparatus and Solvent Systems. The CCD apparatus employed is the Model No. 5-B (H. O. Post Scientific Instrument Co., Inc.). It has 100 cells with a capacity of 40 ml in either phase. Flasks for the evaporation of extract are extraction type, flat bottom, wide neck and 150 ml capacity.

The solvent systems used are as follows:

Solvent System Composition, % (V/V)			
System	A	B	C
Solvent			
Hexane	35	34	32
Chloroform	15	16	18
Absolute ethanol	40	....	....
3-A denatured ethanol	....	40	40
Water	10	10	10

[1] Presented in part at the AOCS meeting in St. Louis, 1961.