

Hydrolysis During Deodorization of Fatty Oils.

Catalytic Action of Fatty Acids

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THE DEVIATIONS of steam deodorization curves from theoretical calculations have been attributed by Bailey (1) to two possible factors: a) hydrolysis of the oil by steam stripping; b) a negative deviation of the oil/fatty acid system from ideality.

In a former work (2) the existence of a negative deviation, because of molecular association, has been demonstrated, and the true vapor pressures have been determined. In the present work the hydrolysis of oil has been studied, and experiments have shown that the extent to which it occurs may be sufficiently great to cause serious errors when the vaporization efficiency is calculated on the basis of the free fatty acid reduction. Fatty acids have catalytic action on hydrolysis, which may be attributed to the nonassociated acid molecules.

Experimental

Investigations were carried out into the hydrolysis of peanut oil a) during steam deodorization and b) in a static system, under specific absolute vapor pressures. The experimental conditions were as follows:

- 75-g. samples of peanut oil, containing various amounts of fatty acid, were deodorized at a specific absolute pressure in a condensation-free deodorizer (3), in which steam-condensation was avoided by heating the upper part of the apparatus. The fatty acids formed by hydrolytic splitting were determined by titration of both the oil and the contents of the condenser.
- 60-g. samples were heated in flasks under various specific absolute water vapor pressures (removal of air by evacuation); and the increases in the free fatty acid contents were ultimately determined by titration. Throughout a given experiment the water vapor pressure was kept constant by the thermostatic control of a water supply reservoir, connected to the reaction vessel by a capillary. In this method therefore steam is not led through the oil, nor is stirring applied.

In both methods the fatty acid content of an oil sample during the experiment was taken as the mean of the initial and final concentrations since the reaction is autocatalytic and the difference between the concentrations is small.

The first method was used for oils of low free fatty acid content; the second method is more suitable for higher free fatty acid contents. In comparative experiments the two methods yielded practically the same results; thus with the relatively shallow oil

layers of method b) it is not necessary to employ blowing steam.

The increase in free fatty acid content observed when oil is deodorized, for 4½ hr., with steam at a pressure of 400 mm. and a temperature of 180°C., is shown in Figure 1. The two lower points on each curve were obtained by method a), the others by method b). Using method a), the amounts of free fatty acid found in the flask and in the receiver were added together. The results are plotted as a function of the free fatty acid content of the oil, for which, as stated above, the average of the initial and final contents is taken. The increase is small in comparison with the initial content; however, in view of the fact that the formation of free fatty acid is accelerated catalytically by the free fatty acid originally present, it was considered advisable to plot the amount of free fatty acid formed as a function of the average amount present.

The catalytic effect is clearly indicated by the trend of the resulting curve since the amount of hydrolytically formed free fatty acid increases sharply with the amount of free fatty acid present, despite the fact that the amount of dissolved water increases only very slightly with the amount of free fatty acid available. The concentration of dissolved water was measured, at 105°C., as a function of the stearic acid content, by passing through steam, at a pressure of 1 atm. The water content was determined by means of the Karl Fischer method. The resulting curve is also shown in Figure 1. The increase in free fatty acid content found on deodorizing oil that contained 1% stearic acid with steam at various pressures and 180°C., for 4 hr., is shown in Figure 2. The three lower points were obtained by method a), the remaining three by method b).

It will be seen that at pressures between 0 and 600 mm. and in the presence of a constant amount of free fatty acid (1% stearic acid) the rate of hydrolysis is directly proportional to the pressure. From these data it is therefore possible to calculate the influence of hydrolysis in factory deodorizations. It is found that with a factory oil column (3 m. in

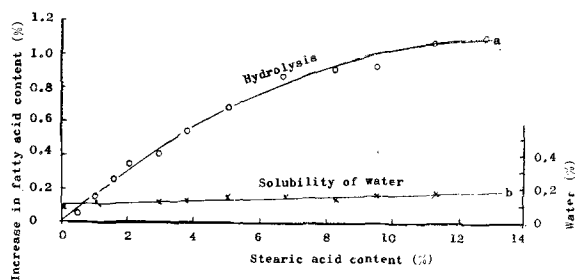


Fig. 1. Hydrolysis of peanut oil containing stearic acid.

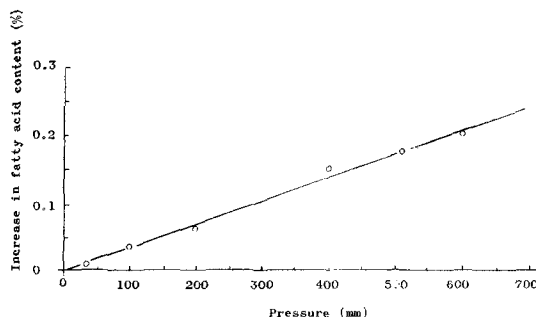


Fig. 2. Effect of pressure on the hydrolysis of a peanut oil containing 1% stearic acid.

height) and using a pressure of 122 mm. Hg (*i.e.*, average pressure exerted by a steam pressure of 20 mm. abs., above the column), the free fatty acid concentration increases from the initial 1% to 1.042%, in 4 hr. (*i.e.*, by 4.2% of the initial concentration). On using a pressure of 20 mm. in the laboratory deodorizer, on the other hand, the increase obtained is only 0.007%, that is, 0.7% of the initial concentration.

Efficiency measurements made in laboratory deodorizers are generally completed in less than 4 hr., and as a result the increase in the free fatty acid content, because of hydrolysis, is small. Although the error from this source is insignificant, even after 4 hr. of deodorization, it must nevertheless be taken into account in accurate measurements, as is evidenced by Figures 1 and 2. An example will demonstrate the effect of hydrolysis upon deodorization efficiency, as determined by fatty acid steaming at higher absolute pressures. A sample of refined peanut oil containing stearic acid was deodorized under the following conditions:

Weight of sample (g.).....	75
Duration of steaming (hr.).....	4
Temperature (°C.)	180
Absolute pressure (mm. Hg).....	390
Amount of steam (g.).....	201
Initial percentage F.F.A.	0.827
Final percentage F.F.A.	0.707
Percentage F.A. in condenser.....	0.265

The reduction in the percentage of free fatty acid was therefore 0.120% while 0.265% fatty acid was found in the condenser, giving an over-all increase in fatty acid of 0.145%, calculated as stearic acid.

The vaporization efficiency may be calculated from Bailey's equation (1)

$$\left(S = \frac{PO}{EP_v} \ln \frac{V_1}{V_2} \right)$$

where the value corresponding to the vapor pressure of the pure acid is in this case 1.14 mm. (2).

Calculation of vaporization efficiency on the basis of the reduction in free fatty acid in the sample gives

$$E = \frac{390 \times 0.08}{1.14 \times 11.18} \times 2.3 \log \frac{0.827}{0.707} = 0.41$$

while calculation from the steam-distilled fatty acids gives an efficiency of

$$E = \frac{390 \times 0.08}{1.14 \times 11.18} \times 2.3 \log \frac{0.827}{0.562} = 1.0$$

It will be seen that the influence of hydrolysis on the vaporization efficiency, as determined from the amount of fatty acids distilled with the steam, is slight (in the absence of hydrolysis, the efficiency would be $1.0 \pm 1\%$), whereas the calculation based upon the reduction in free fatty acid content of the oil gives rise to serious errors.

Mechanism of the Catalytic Action

The relationship established between the catalytic action and the concentration of stearic acid is expressed in curve a of Figure 1. The nonlinearity of this curve is surprising as it might have been expected that, with homogeneous catalysis, the catalytic action would be directly proportional to the concentration,

thus giving a straight line. The explanation for this can be found in the association of the fatty acids.

The catalytic action can originate only from the $-\text{COOH}$ group which acts as a H^+ -ion donor. Since association of the molecules results from the formation of a hydrogen bridge, dimeric molecules cannot release H^+ -ions. The catalytic action is determined therefore not by the total concentration of acid (as plotted in curve a, Figure 1) but solely by the concentration of monomeric acid.

Recently the degree of association of chemically pure stearic acid (4), in paraffin solutions at various temperatures, has been determined by infrared, spectrometric measurements. It has been shown that, at higher temperatures, the degree of association varies greatly with variations in concentration. At the reaction temperature of the hydrolysis measurements (180°C.) the following values were found:

Concentration		Degree of association
Moles/kg.	% by weight	α
0.007	0.20	0.09
0.02	0.57	0.19
0.10	2.8	0.45
0.50	14.2	0.70
2.0	56.9	0.85

The concentration of the monomer does not therefore increase proportionally with the total concentration of acid. If the above-mentioned considerations are correct, a straight line should be obtained when the increase in the fatty acid concentration resulting from hydrolysis is plotted against the concentration of the monomeric acid content (calculated from the degree of association). It will be seen from Figure 3 (line c) that this is, in fact, true. At higher concentrations however, deviations occur (dotted line d).

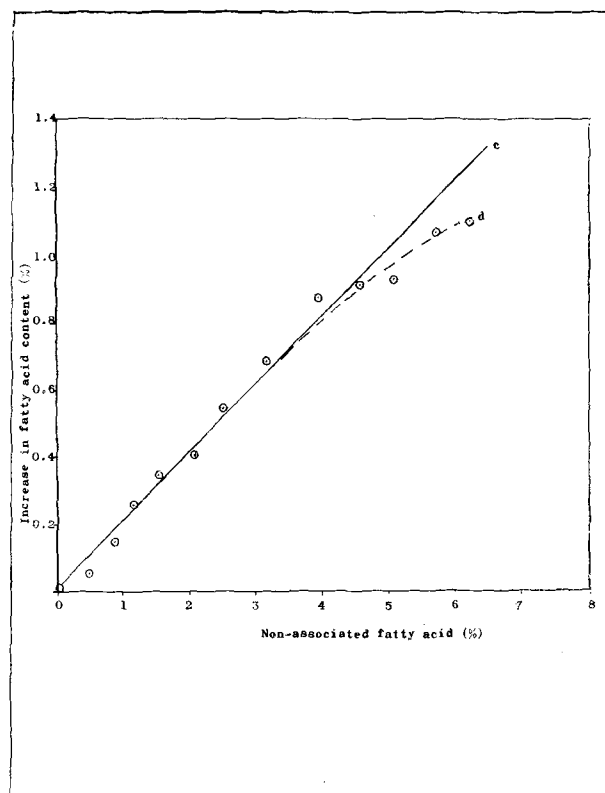


FIG. 3. Relationship between monomeric fatty acid content and catalytic action.

This is to be expected since, during the measurements, no attempt was made to remove the mono- and diglycerides formed as a result of hydrolysis; as their concentrations increase, the shifting of the hydrolysis equilibrium in the opposite direction becomes progressively more pronounced. It is seen however that, up to a total concentration of 8% fatty acid, the rate of hydrolysis is directly proportional to the monomer concentration.

The effect of the dissolved water and of the solvation by the oil was not taken into account. The latter effect reduces the number of free $-COOH$ groups while the former plays a role in the splitting off of H^+ -ions, which results in the shifting of the monomer/dimer equilibrium in the direction of the dissociation. Neither effect is apparently very great, and one may be expected to counterbalance the other.

Summary

The hydrolysis of peanut oil at subatmospheric pressures and $180^\circ C$. has been studied, using both a static and a dynamic method. The conditions applied to the latter method are identical with those used in the current steam deodorization process.

It has been found that, as a result of catalytic action, the rate of hydrolysis is a function of the free fatty acid content and moreover increases in direct proportion with the absolute pressure.

From data of the degree of association it has been shown that only the monomeric acid has catalytic action. It is clear therefore that acid catalysis by H^+ ions must also be involved.

It was further established that when the calculation of vaporization efficiency is based upon the reduction in free fatty acid content, hydrolysis may give rise to serious errors.

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Solubility and Fractionation of Lipides in Sulfur Dioxide¹

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LIQUID SO_2 is recognized as an important solvent in petroleum refining (9) and in certain areas of chemical research (1) but seems to have received little attention as a solvent for lipides. The first application of SO_2 to lipides was probably that of Grillo and Schröder (10), who used it for extracting oils from seeds and other materials. The development of the Edeleanu process (9) for fractionating hydrocarbons in liquefied SO_2 did not promote equally intense studies of this solvent with lipides. Zerner, Weiss, and Opalski (21), determining the mutual solubilities of SO_2 and castor, rapeseed, olive, and other oils at different temperatures, found that solubility is higher when double bonds or hydroxyl groups are present in the fats. Several patents suggest the use of SO_2 for fractionating lipides, but few fundamental data on the solvent properties of this compound are given (8). In the course of studies on cetene and diolefins Seyer and Ball (18) determined the solubility of cetyl alcohol in liquefied SO_2 . Cox and Reid (5) fractionated unsaponifiable lipides of marine source into saturated and unsaturated portions by Soxhlet extraction with SO_2 at atmospheric pressure. These authors indicate that, when the same procedure is applied to fatty acids, considerable amounts of saturated material are extracted along with the unsaturated components. DeCarli (6) had reported however that palmitic, stearic, and oleic acids are insoluble in liquid SO_2 . These scattered observations apparently have not been reinvestigated or supplemented even though extensive

studies on the solubility of lipides in organic solvents have been published (3, 4).

We report the solubilities of some long-chain fatty acids and methyl esters in SO_2 at temperatures between -50 and 25° . Methyl esters of unsaturated fatty acids are highly soluble in this solvent, and no detailed measurements have been made with them. Using the solubility data as a guide, mixtures of lipides were fractionated in SO_2 , at atmospheric pressure, below the boiling point of SO_2 (-10°).

Solutions of saturated acids and esters in SO_2 are colorless while those of unsaturated lipides are yellowish. The intensity of color depends greatly upon impurities in the materials. When SO_2 is evaporated to recover the solutes, unsaturated lipides are obtained as yellow oils, which are difficult to decolor under high vacuum. The last traces of SO_2 are held rather tightly but may be easily removed by washing the solutions of such lipides in an inert solvent with water or dilute alkali (recoveries 95-99%). Neither UV and IR spectra nor iodine values were changed when linoleic and linolenic acids were dissolved and stored in SO_2 for a day or longer at -20 to -30° . Storage at room temperature causes slow darkening to a brown oil, which is partly insoluble in petroleum ether. The soluble fraction can be decolorized by washing, as above, after which the lipides appear unchanged. Normal yields of the characteristic polybromides were obtained from the unsaturated acids recovered from SO_2 , providing further proof that they had not been changed by the procedures. The solubilities of saturated esters remained unchanged after storage for one to three days in SO_2

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