Cyclic Fatty Acids: Removal of Aromatic Acids Formed During Hydrogenation[1]

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Abstract

Monomeric fatty acids derived from the alkali treatment of linseed oil at temperatures above 200C contain cyclic (1,2-disubstituted cyclohexadiene) and straight-chain fatty acids. Hydrogenation converts cyclic to liquid, saturated cyclic acids that can be recovered in a pure state by crystallization. During hydrogenation (palladium catalyst) some of the unsaturated cyclic acids form aromatic fatty acids by loss of hydrogen and under some conditions are not subsequently hydrogenated. It was necessary to establish conditions for complete hydrogenation since color and oxidative stability at high temperature are inversely related to aromatic content. Previously, the preparation of cyclic acids free of aromatic acids was by hydrogenation in the presence of a high concentration of acetic acid. A further study of reaction variables established conditions to make saturated cyclic fatty acids free of aromatic without acetic acid. Factors favoring the elimination of aromatic acids include a high catalyst concentration, high temperature and pressure, good hydrogen dispersion in the liquid and good agitation.

Introduction

Extensive research has been conducted at the Northern Regional Research Laboratory on the preparation and properties of monocarboxylic C-18 disubstituted cyclohexadienoic acids, called cyclic fatty acids (CAL, cyclic acids from linseed oil) (1,3–5,7,8,10–15). Monomeric fatty acids, derived from alkali treatment of linseed oil in a suitable solvent at temperatures above 200C, contain unsaturated cyclic and saturated and unsaturated straight-chain fatty acids. Hydrogenation of the unsaturated monomeric acids followed by solvent crystallization is used to separate pure saturated cyclic fatty acids (HCAL, hydrogenated cyclic acids from linseed oil) from saturated straight-chain acids. The hydrogenation of unsaturated cyclic acids proceeds as shown in Figure 1. While the CAL sample is being heated with palladium-on-powdered-carbon (Pd-C) catalyst in the presence of hydrogen, some of the CAL lose hydrogen to form ortho-disubstituted aromatic fatty acids (ACAL, aromatic cyclic acids from linseed oil), and the remainder of the CAL add hydrogen to form HCAL. The percentages of ACAL and HCAL formed depend on several reaction variables. Separation of the HCAL and ACAL from stearic and palmitic acids can be accomplished either by crystallization at low temperatures (−40C) (6) or by the urea adduct method or by a combination of the two.

Previously Friedrich et al. (9) described the preparation of pure 18 carbon ACAL by hydrogen transfer when unsaturated cyclic and straight-chain acids are heated with Pd-C in the absence of hydrogen. He also reported that following complete hydrogenation of CAL with Pd-C and a large excess of acetic acid, ACAL were not present although they may have formed and then became hydrogenated. The presence of ACAL is undesirable because they impart color and oxidative instability to the HCAL. Further studies of reaction variables were made to produce ACAL-free HCAL without the addition of acetic acid. Because one potential use of HCAL is in lubricants, stability tests were made with various mixtures of the 2-ethyl hexyl esters of HCAL and ACAL. After controlled oxidation, the viscosity and acid number increase were determined as measures of stability.

Procedure

Hydrogenation reactions were carried out in a 1-liter Magne-Dash high-pressure autoclave. A second autoclave was also used which had a 300 cc capacity with a variable-speed agitator of a type that draws gas from the head space and redisperses it in the substrate. The autoclave was charged with unsaturated monomeric fatty acids (46.2% cyclic and 53.8% straight chain), pressured with hydrogen several times to remove air and then heated under about 500 psi hydrogen pressure to the desired temperature. The pressure was increased to the desired level when operating temperature was reached. Tests conducted in the Magne-Dash were sampled at several time intervals to determine the amount of ACAL present, whereas tests conducted in the 300-cc autoclave were hydrogenated until no further hydrogen uptake was observed, plus an additional hour. Hydrogenated monomeric fatty acids were filtered on a steam-jacketed Buchner funnel to remove the catalyst. The catalyst was washed with warm hexane to prepare it for reuse. Approximately 20-g samples of the hydrogenated monomeric acids were diluted 1:1 with hexane and esterified about 16 hr at room temperature with 0.7 vol dimethoxy propane, 0.2 vol methanol and 1% sulfuric acid per volume of fatty acids. After washing with aqueous potassium carbonate to neutralize the catalyst and remove any unconverted fatty acids, and then washing twice with water, the methyl esters were subjected to a GLC analysis and percentages of HCAL and ACAL were calculated.

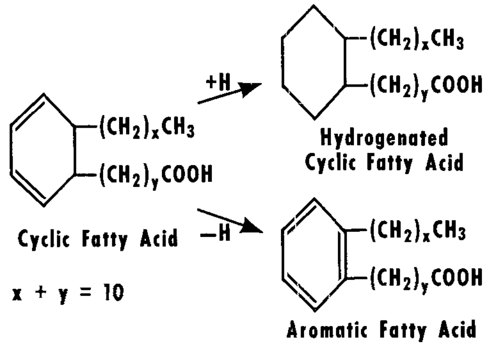

FIG. 1. Formation of aromatic and hydrogenated cyclic fatty acids during hydrogenation of cyclic fatty acids.

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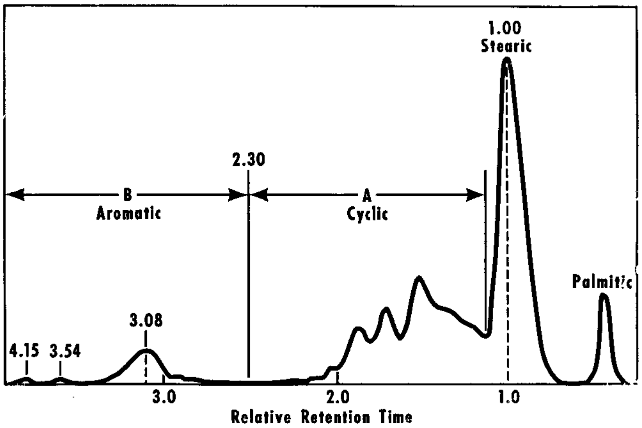

FIG. 2. Typical gas-liquid chromatogram of hydrogenated monomeric fatty acid methyl esters.

Hydrogenated monomeric methyl esters free of ACAL, as shown by ultraviolet analysis, were subjected to a GLC analysis as were other samples shown to contain ACAL. A cutoff point on the chromatogram was then determined to calculate ACAL content of the hydrogenated monomer. A typical chromatogram is shown in Figure 2. The region marked "A" represents HCAL isomers and the region marked "B," ACAL isomers. Material eluting after a relative retention time of 2.30 (based on stearic acid as 1.00) was calculated as ACAL since in the absence of ACAL (by UV) no material was eluted beyond this point. If the sample contained considerable ACAL, three peaks appeared on the chromatogram: a large peak at a relative retention of 3.08 and two smaller ones at 3.54 and 4.15. Some of the results obtained by GLC analysis were checked by UV to substantiate the accuracy of the GLC calculations in determining ACAL content of the hydrogenated monomer. The extinction coefficient (1.095) used in the UV calculations was determined by averaging a large number of known coefficients for orthodisubstituted aromatic compounds. There was close agreement between the two methods. A method for determining total nonstraight-chain content of the hydrogenated monomer has been described by Black and Eisenhauer (2).

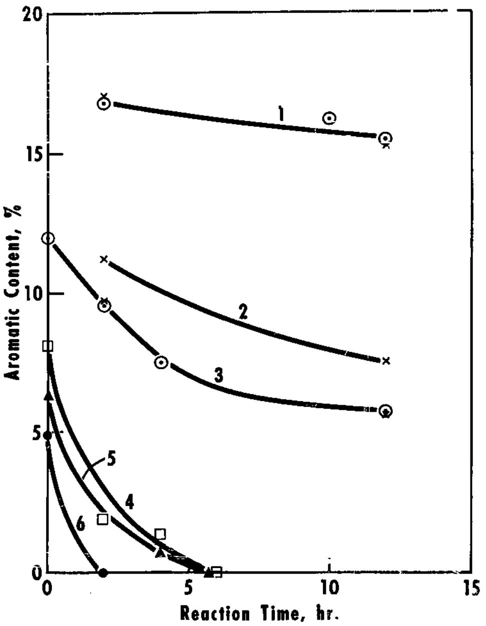

FIG. 3. Effect of hydrogenation pressure and catalyst concentration on aromatic fatty acid content of hydrogenated cyclic acids (1-liter Magne-Dash).

Curve	Hydrogenation conditions		Catalyst amount % Pd	Type of catalyst
	Pressure psi	Temp. C		
1. ⊙	600	200	0.025	Used 5% Pd-C
×	600	150	0.041	Used 5% Pd-C
2. ×	1500	150	0.041	Used 5% Pd-C
3. ⊕	2000	200	0.025	Used 5% Pd-C
+	2000	150	0.041	Used 5% Pd-C
4. □	2000	200	0.025	New 5% Pd-C (catalyst A)
5. ▲	2000	200	0.025	New 5% Pd-C (catalyst B)
6. ●	600	200	0.25	Used 5% Pd-C

To determine the relation of ACAL content to high-temperature oxidative stability, mixtures containing various ACAL-HCAL ratios were converted to their 2-ethyl hexyl esters. Ten-gram samples of esters containing 1 cm of copper foil and 1% phenothiazine stabilizer were aerated 72 hr at 175C by bubbling filtered, dry air through the heated sample at the rate of 500 ml/hr. The viscosity increase and acid number were then determined. Viscosity was measured at 100F (37.8C) in a Cannon-Fenske viscometer.

Results and Discussion

The effects of hydrogen pressure and catalyst concentration on the rate of reduction of ACAL to HCAL are illustrated in Figure 3. These data, obtained from tests conducted in a Magne-Dash hydrogenator, indicate that the rate of reduction is slow at the lowest catalyst concentration and hydrogen pressure used but is rapid at the highest concentration. It is evident from examination of all the curves that during the period when the unsaturated monomeric acids and catalyst are being heated under hydrogen to the desired reaction temperature (about 15–20 min), conditions exist which are more favorable to ACAL formation than to its reduction. This effect is due to the presence in the original monomeric fatty acids of both unsaturated cyclic and unsaturated and saturated straight-chain fatty acids. In the presence of Pd catalyst straight-chain unsaturates act as hydrogen acceptors to promote the dehydrogenation of CAL to ACAL (9). By the time the temperature has reached 150C (at 500 psi) substantially all the straight-chain acids have completely hydrogenated and the formation of ACAL is also virtually complete according to our data. We are concerned here only with subsequent reduction of the preformed ACAL to HCAL and conditions of operation which allow complete or essentially complete reduction in a reasonable time.

Comparison of curves 1, 2 and 3 in Figure 3 shows that increasing the hydrogenation pressure from 600 to 1,500 or to 2,000 psi significantly increases the rate of ACAL reduction. Data from tests made at 150C with 0.041% Pd catalyst and tests at 200C with 0.025% Pd fall essentially on the same curves at 600 psi and 2,000 psi operating pressure. Evidently the effect of higher catalyst concentration in the first series, to increase the rate of reaction, was exactly canceled by using a lower reaction temperature. New, unused 5% palladium-on-carbon catalyst was much more active than used catalyst (curves 3, 4 and 5). The reduced activity of the used catalyst, however, may be readily compensated by increasing the amount used (curves 1 and 6). Although there is a reduction in catalyst activity after the first use, no appreciable reduction in activity has been noted in subsequent reuse, i.e. when the catalyst has been recovered and reused several times.

In addition to tests made in the Magne-Dash autoclave, others were conducted in the 300-ml autoclave. This was equipped with a variable-speed gas-dispersion agitator and with vertical baffles, to assist gas dispersion and to prevent liquid swirling. This autoclave had no provision for sampling during operation and so hydrogenation reactions were continued until hydrogen uptake as shown on a 2,000-psi gauge with 20 psi graduations had apparently stopped, and then an additional hour. The data (Fig. 3) indicate that the hydrogenation of ACAL to HCAL probably continues under all conditions tested but at low catalyst concentrations particularly (curves 1, 2 and 3), the rate is so slow as to be almost negligible. The data of Figures 4 and 5 are therefore treated as endpoint results although the reaction may not have reached an absolute endpoint.

The relation of hydrogenation temperature to final ACAL content is shown (Fig. 4) from tests made at 600 psi, 900 rpm agitator speed with 0.041% Pd in the form of 5% Pd-C. ACAL content decreased linearly from 10% to about 3% when the reaction temperature increased from 150C to 250C.

Agitation has a significant effect on ACAL content. Two measures of agitation were studied: the relation of increased agitator speed to ACAL content under otherwise constant conditions, and the relation of increased volume of CAL hydrogenated to ACAL content at a constant agitator speed. For the agitator speed tests, conditions of operation were as shown (Fig. 5) for all tests. Increasing the speed from 500 to 1,400 rpm decreased ACAL from 24% to about 4%. With the type of gas-dispersion agitator used in these tests, increased speed causes not only more liquid mixing but also a higher rate of recirculation of hydrogen from the reactor headspace into the liquid in the form of fine bubbles. Therefore, at high speeds the liquid is kept more nearly saturated during a period of rapid hydrogen uptake, a condition which is less conducive to dehydrogenation during the initial stages of the reaction when both unsaturated cyclic and unsaturated straight-chain acids are being hydrogenated. Therefore, at high speeds we should expect a lower amount of ACAL to be formed and a higher rate of reduction of those formed. The effect of increasing the volume of CAL hydrogenated under fixed operation conditions is the same as that of reducing agitator speed, i.e. increased ACAL. Increasing the volume of liquid in the hydrogenator does two things: it causes less hydrogen to be recirculated from the headspace due to increased liquid head on the agitator, and it disperses that hydrogen in a larger volume of liquid and apparently causes a lesser degree of saturation of the liquid with hydrogen, a situation more conducive to dehydrogenation and the formation of ACAL.

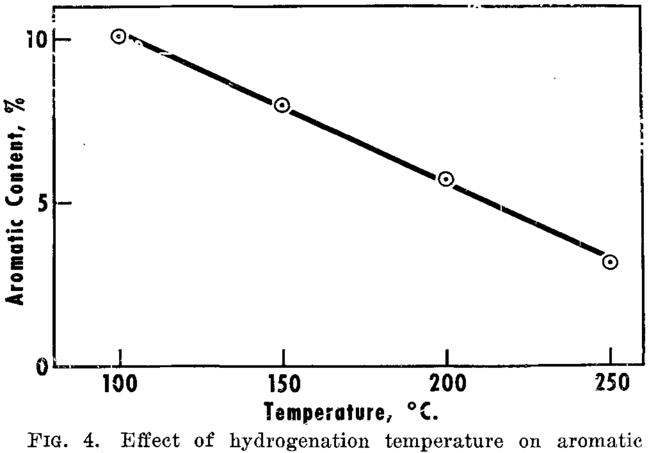

FIG. 4. Effect of hydrogenation temperature on aromatic fatty acid content of hydrogenated cyclic acids. Conditions: 300-ml autoclave, 600 psi, 0.041% Pd, 100-ml batch size.

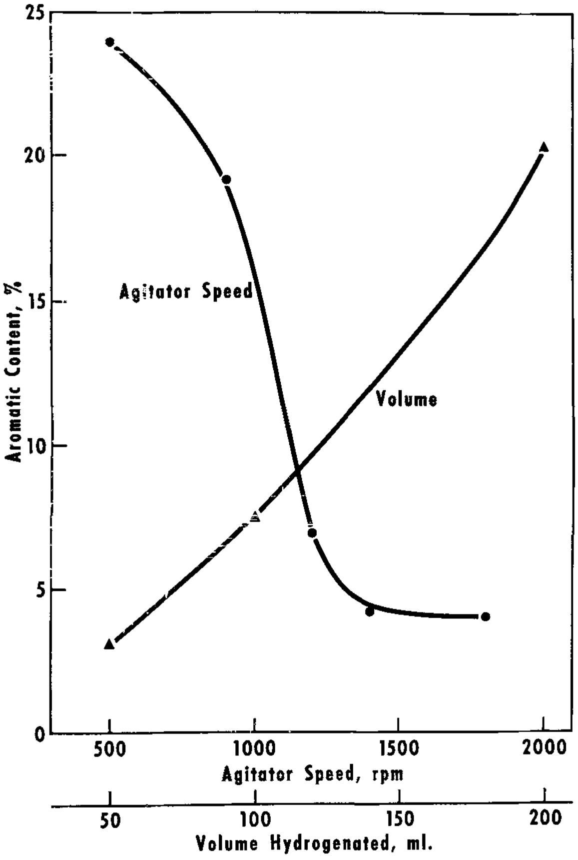

FIG. 5. Effect of agitation on aromatic fatty acid content of hydrogenated cyclic acids. Conditions for agitator speed tests: 300-cc autoclave, 200-ml batch 0.009% Pd (new 5% Pd-C catalyst), 150C, 600 psi; for volume hydrogenated tests: 300-ml autoclave, 0.041% Pd (new 5% Pd-C catalyst), 150C, 600 psi, 900 rpm agitator speed.

Increased pressure, temperature, agitator speed and catalyst concentration all favor a reduction in ACAL content of HCAL, but catalyst concentration is the most important factor for eliminating ACAL in a reasonable reaction time.

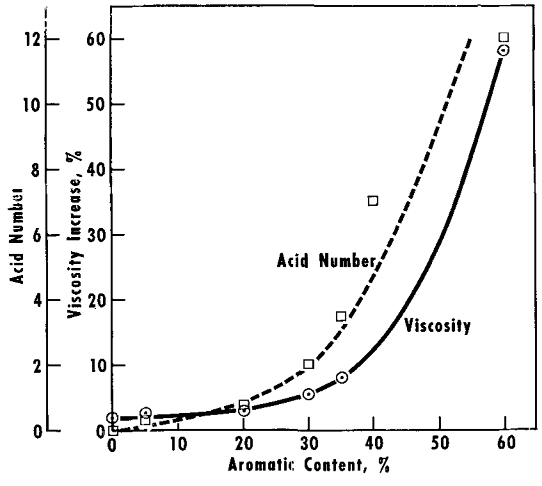

FIG. 6. Relation of aromatic fatty acid ester content to oxidative stability for aromatic-saturated cyclic acid ester mixtures. Increase in viscosity and acid number after 72 hr of oxidation at 175C.

The relation of ACAL ester content to high-temperature oxidative stability is shown in Figure 6. Military Specification 7808 for jet aircraft lubricants requires a maximum acid number of 2 and a viscosity change within limits of −5 to +15% after the 72-hr oxidation test. Therefore, the ACAL content of HCAL esters must not exceed 30% to meet these specifications. Color stability at 100C is also adversely affected by ACAL although quantitative data were not obtained. For uses other than jet lubricant, color stability may be more important than other considerations. Consequently, practical conditions of hydrogenation to minimize or eliminate ACAL are a major factor in HCAL utilization.

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