

Cyclic Fatty Acid Yields from Linseed Oil¹

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Abstract

Increased yields of saturated cyclic fatty acids which are fluid at -50°C have been obtained from linseed oil. Depending on reaction conditions, yields varied from 20–42 g of cyclic acids per 100 g of linseed oil. Solvent ratios of 6, 3, and 1.5:1; catalyst concentrations of 10, 30, 60, and 100%; and reaction temps of 225, 275, 295, and 325°C were evaluated. Ethylene glycol and diethylene glycol were compared as reaction solvents.

In general, high solvent ratios favored high cyclic acid yields at the lower reaction temperature, but as the temperature increased the effect of solvent ratio decreased. Increasing the percentage excess of sodium hydroxide increased the cyclic acid yield. Diethylene glycol gave higher yields than ethylene glycol at comparable conditions.

Introduction

SCHOLFIELD AND COWAN (6) demonstrated that the S triene system in linolenic acid can be partially converted to a cyclized structure by prolonged heating with excess alkali in a suitable solvent. Distillation of the cyclized mixture gives monomeric and polymeric fractions with cyclic and unconverted straight chain acids in the monomeric fraction. Further work by Friedrich et al. (3) on linseed oil, linolenic acid, and tung oil produced evidence that the cyclic monomers are, at least in part, vicinal disubstituted cyclohexadienes. The saturated acids in linseed oil appear to be unchanged, but linoleic acid is conjugated. Polymeric acids are probably formed by the Diels-Alder reaction of conjugated linolenic and/or linoleic acids (4).

Cyclic acids or their derivatives may be utilized in the preparation of alkyd resins, plasticizers, and lubricants (1,5). This paper illustrates the relation of solvent ratio, catalyst concentration, reaction temperature, and type of solvent to yields of cyclic acid from linseed oil.

Experimental

Reactions were conducted in a 2-liter Parr autoclave with refined linseed oil containing 54.3% linolenic acid (fatty acid basis), glycol solvent, and sodium hydroxide as catalyst (Fig. 1). The amount of sodium hydroxide used was that required to saponify the oil plus a percentage excess. Tests were made at several solvent ratios (6, 3, 1.5:1), reaction temperatures (225, 275, 295, and 325°C) and catalyst amounts (10, 30, 60, and 100%). Except for two tests in which diethylene glycol was used, ethylene glycol was the solvent. Figure 1 is a flowsheet showing the cyclization reaction and analytical procedure.

Before each test the reactants and solvent were placed in the reaction vessel and it was evacuated and flushed with high-purity nitrogen several times. After heating the reaction mixture to the desired temperature, samples for analysis were removed at intervals through a water-cooled tube into a receiver flushed

with inert gas. The samples were diluted with approximately 10 volumes of water and acidified with 25% sulfuric acid to free the fatty acids. The fatty acid phase was removed by several hexane extractions, dried over sodium sulfate, and filtered.

The fatty acids were esterified with 0.7 vol of dimethoxypropane, 0.2 vol of methanol, and 1% sulfuric acid (based on the weight of fatty acid). The purpose of converting the acids to esters was to block the formation of undistillable polyesters during subsequent distillation by the reaction of carboxyl groups with hydroxyl groups previously shown by Friedrich et al. (3) to be present on some of the acids.

The esters were distilled in glass to a pot temp of 225°C at 0.25 to 0.50 mm Hg absolute pressure. The distilled monomeric esters were hydrogenated to below 3 iodine value (I.V.) at 200°C , 600 psi hydrogen pressure, by using 0.1% palladium catalyst in the form of 10% palladium on carbon. The filtered, hydrogenated esters were dissolved in 20 vol of acetone, the solution was cooled to -50°C , and then it was filtered to remove the saturated straight chain esters. This procedure was repeated on the saturates to insure maximum recovery of the cyclic esters. The crystallizer used has been described by Friedrich (2). After removal of the solvent from the filtrate by evaporation on a steam bath under a stream of air, the esters were then tested for the presence of straight chain saturates by cooling to -50°C and if clouding was evident, the crystallization step was repeated.

Yields of polymeric and cyclic acids were calculated on the basis of 100 g of linseed oil. Four samples were removed during each test and the yields of cyclic and polymeric acids were plotted against reaction time.

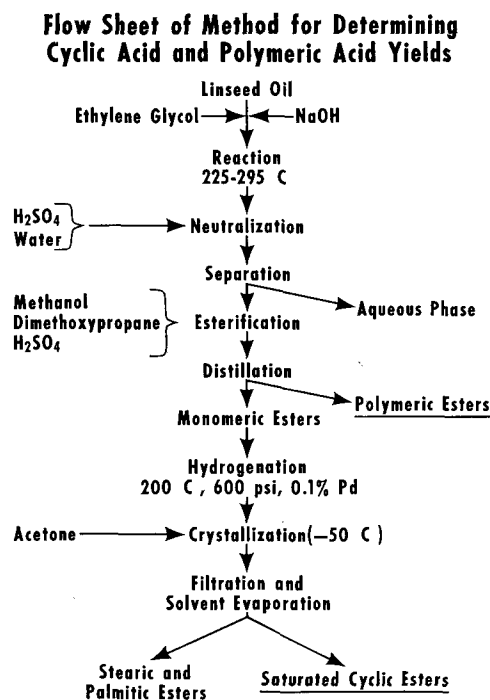


FIG. 1. Flowsheet of method for determining cyclic acid and polymeric acid yields.

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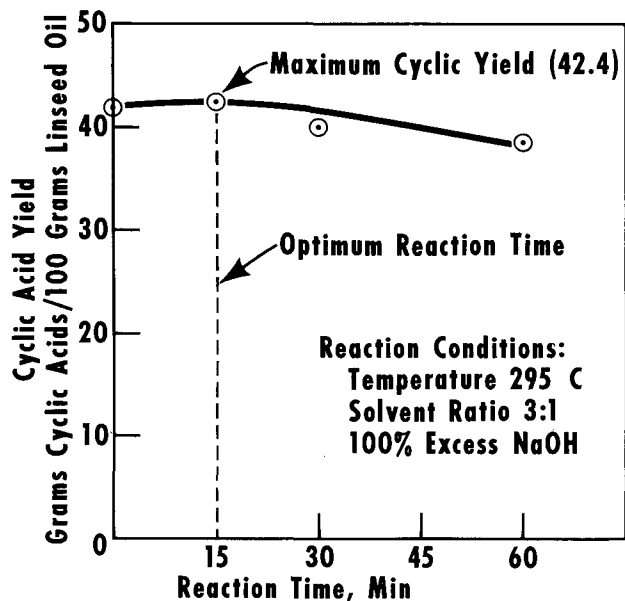


FIG. 2. Determination of maximum cyclic acid yield and optimum reaction time.

These samples were plotted on a graph, such as Figure 2, and the point of maximum cyclic acid yield and optimum reaction time was determined. This procedure was repeated for every run, and data from these graphs were used to prepare subsequent graphs. Yield of cyclic acids reached a maximum then declined slightly as the reaction was continued while yield of polymeric acids increased continuously. Evidently cyclic acids are slowly converted to polymeric acids as the reaction continues.

Results and Discussion

In Table I, ethylene glycol and diethylene glycol are compared as solvents. At a solvent ratio of 3:1, 30% excess NaOH, reaction temp of 295C, the yield of cyclic acids was 36.0 g per 100 g of linseed oil with ethylene glycol and 38.8 with diethylene glycol. A longer time was required to obtain maximum cyclization with ethylene glycol as the reaction solvent. Longer heating gave a high polymer yield and this probably accounts for the slightly higher cyclic acid yields with diethylene glycol as solvent. At a solvent ratio of 6:1, yield of cyclic acid was also higher with diethylene glycol than with ethylene glycol.

The effect of excess NaOH catalyst on yield is shown in Figure 3. All tests of this series were made at a solvent ratio of 3:1 and 295C reaction temperature. As the percentage excess alkali was increased from 10 to 100, cyclic acid yield increased from 28 to 42 g per 100 g of linseed oil, a 50% increase. Apparently little increase in yield occurs when NaOH amounts to over 100% excess, as noted by the nearly flat trajectory of the curve at this point.

TABLE I
Effect of Solvent on Cyclic Acid Yield at a Reaction Temperature of 295C and 30% Excess NaOH

Solvent ratio glycol/oil	Reaction ^a time, hr	Cyclic acid ^a in monomer, %	Product yield, g	
			Polymeric ^a acids	Cyclic acids
3	Ethylene glycol			
	1	45.9	17.5	36.0
6	2	48.4	19.4	37.0
	Diethylene glycol			
3	½	48.5	15.0	38.8
	½	46.5	13.0	38.1

^aAt maximum cyclic acid yield.

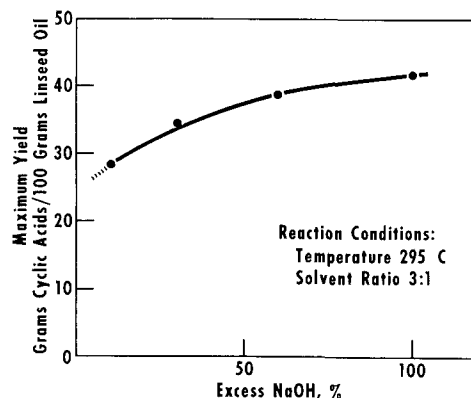


FIG. 3. Effect of catalyst concentration on cyclic acid yield.

Figure 4 shows the effect of reaction temperature and solvent ratio on cyclic acid yield at two levels of NaOH catalyst. Since the formation of cyclic acids is a monomolecular reaction, whereas polymerization involves two or more molecules, one would expect that dilution of the reaction by using a high solvent ratio would favor the monomolecular cyclization reaction. At both catalyst concentrations (10% and 30%) dilution does appear to favor cyclic acid formation at the lower reaction temperatures. However, at temps of about 300C and above, the effect of solvent ratio is small. Two factors may account for this small ratio. One is that dilution not only results in a greater average distance between molecules to favor the monomolecular reaction, but conversely results in reducing the catalyst concentration at the reaction site. The other factor is that the reaction rate for cyclization may increase to a greater extent with an increase in both temperature and catalyst concentration than does the reaction rate for polymerization. Since cyclization and polymerization are essentially competitive reactions, conditions which favor one should reduce the other.

At two reaction conditions with diethylene glycol as the reaction solvent, 1-2% higher cyclic acid yields were obtained than with ethylene glycol. A 50% increase in yield was obtained when the amount of

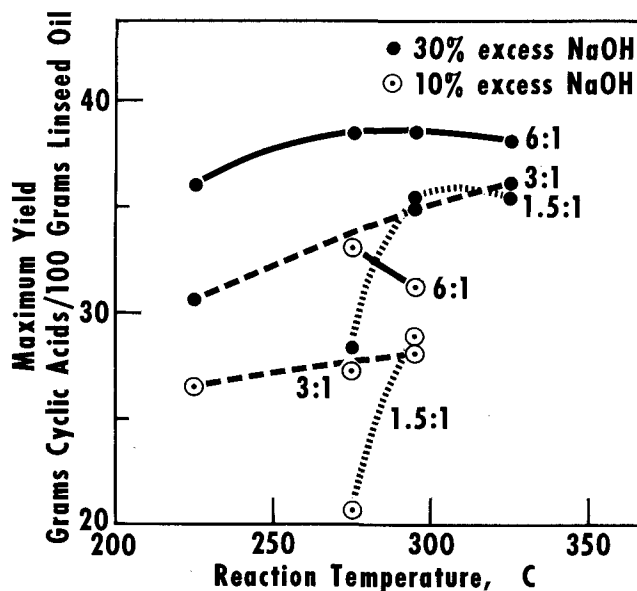


FIG. 4. Effect of reaction temperature and solvent ratio on cyclic acid yield at two catalyst concentrations.

excess NaOH catalyst was increased from 10 to 100%. At a reaction temperature of about 300C nearly comparable yields of cyclic acids were obtained at solvent ratios of 6, 3, and 1.5:1. At all temperatures, the best yields occurred at the highest solvent ratio.

ACKNOWLEDGMENT

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Reactivity of Zinc Oxide and Titanium Dioxide in the Presence of Dispersing Agents¹

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Abstract

The effect of various dispersing agents on the interaction between zinc oxide and titanium dioxide in water was investigated. Addition of conventional dispersing agents to suspensions of zinc oxide and titanium dioxide reduces initial viscosities but increases the rate of interaction; however, ethylene glycol reduced interaction. Higher concentrations of dispersing agents caused foaming of the suspensions and caking of the pigments. If organic dispersing agents are replaced by inorganic phosphates, pigment interactions, foaming, and caking can be prevented in suspensions containing as much as 61% solids by weight.

Introduction

MIXTURES of zinc oxide and titanium dioxide show a rapid increase in pH and viscosity when dispersed in water without dispersing agents or other chemicals. These increases are due to a chemical interaction causing the formation of tridimensional structures (2). In 35% suspensions the interaction is most pronounced when the weight ratio of ZnO and TiO₂ is in the order of 1:2. This pigment ratio coincides with that in practical paint formulations. The pH shifts from near neutral to an equilibrium value of 9.2, and the viscosity increases by a factor of 10 in a period of 1 month after preparation.

In many emulsion paint formulations pigment interactions have been avoided by eliminating zinc oxide and using mercury compounds or other chemicals to obtain mildewcidal properties. However, other advantages obtained from the use of zinc oxide, such as better through-dry of the paint film, reduction of film degradation by U.V. absorption, and low cost, are lost.

Preliminary experiments showed that the addition of conventional organic dispersing agents did not prevent pigment interactions. Therefore a detailed study of pigment suspensions in a variety of dispersing agents was undertaken to obtain more information on the reactivities of the various components. This work showed that inorganic phosphates prevent the interaction between ZnO and TiO₂.

Experimental

Suspensions with 35 and 50% solids were prepared by weighing dry pigments into glass jars. Dispersing

agents were dissolved in distilled water to the highest concentration used in a particular series of suspensions. The solution and additional water were added to the dry pigment in the right proportions necessary to obtain the desired percentage solids and dispersing agent concentration. This procedure was not successful at the 61% solids level because the dry pigment volume was too large for the containers used. Therefore, the pigments were added slowly to the dispersing agent solutions.

All suspensions were shaken for 1½ hr at 25C in a Gump shaker, and pH and viscosity measurements were carried out as described previously (2). For viscosities between 1,000 and 5,000 cp spindle No. 3 was used exclusively with the Brookfield RVF viscometer at 20 r.p.m. Below 1,000 cp spindle No. 2 was used for better precision, and spindle No. 4 was used for values above 5,000 cp only.

In the series containing ethylene glycol the pigments were shaken in the water solution before the ethylene glycol was added to prevent the formation of a stable foam.

The titrations were performed by adding a 25% commercial stock solution of dispersing agent from a micro-burette to the pigment slurry, which was stirred continuously with a Premier DD Dispersator. The Dispersator was stopped during the actual pH measurements, and more dispersing agent was added only after the pH value had become constant. The specific pigment grades and the particular dispersing agents used are given although this naming should not be construed as an endorsement over similar materials from other manufacturers:

Azo ZZZ-55 zinc oxide (American Zinc Sales Co.) and Ti-Pure R-510 titanium dioxide (Pigments Department, E. I. duPont de Nemours & Co.) were used exclusively.

Tamol 731 (sodium salt of carboxylated polyelectrolyte) and Acrysol A-1, A-3, and A-5 (polyacrylic acid with varying molecular weight) are products of Rohm & Haas Co.

The modified dialdehyde starch used was prepared at the Northern Laboratory by oxidation of dialdehyde starch with chlorine in methanol solution (3). The sodium salt was obtained by titration of an aqueous solution of the product with sodium hydroxide to pH = 9.0, and subsequent evaporation of the water at 100C.

The poly-itaconate was prepared by polymerization of itaconic acid. Itaconic acid (20 g) was dissolved in a mixture of 25 ml dioxane and 25 ml of 0.5 N hydrochloric acid, and 0.25 g potassium persulfate

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