

Fig. 5. Comparison of two absolute methods for relating reflectance to soil content of clay soiled cloth.

tivation and gravimetric analysis) for relating the percentage of reflectance to the soil content of clay soiled cloth is given in Figure 5. The soil content expressed as mg of clay/g cloth was determined from activity ratio data of clay soiled cloths and the known wt of the cloth disc used in the activation analysis method. The gravimetric analyses of the soil content

of clay soiled cloths are the data of Martin and Davis (5).

Fairly good agreement is obtained for the two absolute methods at high reflectance reading or low clay-soil content on the soiled cloth. The discrepancies noted between the two methods in the range of 50 reflectance units have not been completely resolved.

#### ACKNOWLEDGMENT

Assistance from Russell Mesler, University of Kansas, and G. J. Henon. This work carried out with the financial support of the Whirlpool Corp.

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[Received December 11, 1963—Accepted June 4, 1964]

## Continuous Production of Cyclic Fatty Acids<sup>1</sup>

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### Abstract

Kinetic studies of a batch treatment of linseed oil to produce cyclic acids indicated that of a continuous process conducted in a flow-through reactor and involving rapid heat-up of reactants, followed by a short reaction time, might be feasible. Tests were conducted in a continuous system to examine the effects of flow rate (retention time), reaction temp, reaction system pressure and reagents on product yields. The reactant solution (linseed oil-ethylene glycol-sodium hydroxide) was pumped through an externally heated tube and discharged through a back-pressure valve. Maximum cyclic acid yields based on wt of oil were 37% by the continuous method and 40.4% by the batch process when the feed was saturated with nitrogen, and 39.5% and 46.1% for the respective methods when the feed was saturated with ethylene. These differences may be offset by the advantages inherent in a continuous process.

### Introduction

THE CHEMISTRY of cyclic monomeric fatty acids prepared from linseed oil, and details of their production in batch reaction using the oil and an alkali catalyst in a suitable solvent system, have been described in previous papers from the Northern Laboratory (3,4,6,7).

Unsaturated cyclic acids have been given a pre-

liminary evaluation in alkyd resin formulations and found to impart good color stability properties to the resin with respect to yellowing tendency (6). The low-melting point of the completely saturated cyclic fatty acids suggests that other valuable uses also may be developed in the fields of lubricants, plasticizers and other products.

Extensive studies of the relation of processing conditions to yield of product suggested the production of these cyclic fatty acids by a continuous process. Details of such a process for producing cyclic fatty acids are described here, and a comparison is made of some product yields obtained by the batch and continuous methods.

### Equipment and Procedure

Figure 1 is a diagram of the continuous apparatus used. It consists of a supply container, positive displacement pump, steam preheater, both a preheater coil and a reactor coil immersed in a molten solder bath, an aftercooler, a variable back-pressure valve and a product collector. The entire flow system is constructed of 3/8-in. type 316 stainless-steel tubing. The internal volumes of the bath preheater coil (28 ml) and the reactor coil (136 ml) were determined by displacement measurements with water. The reactants consisting of linseed oil, sodium hydroxide and ethylene glycol were mixed and heated in another vessel, not shown, to effect saponification of the oil and solution of the soaps and excess sodium hydroxide in the solvent. This solution was deaerated under vacuum to

<sup>1</sup> Presented in part at the AOCS Meeting, New Orleans, 1962.

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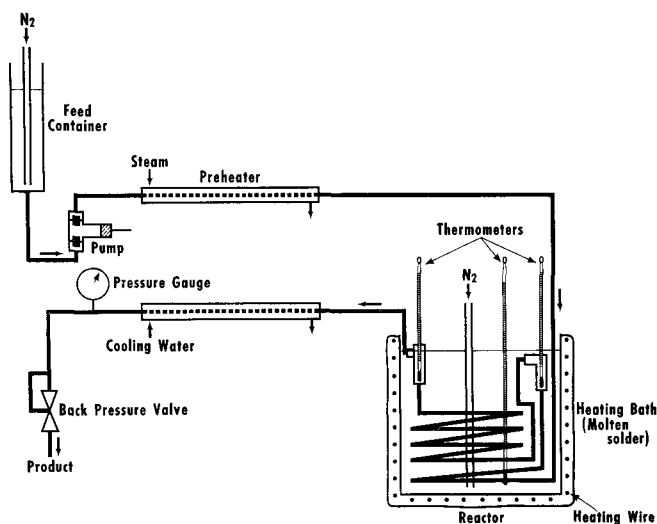


FIG. 1. Apparatus for continuous treatment of linseed oil to produce cyclic fatty acids.

remove dissolved oxygen and placed under nitrogen. The solution was then transferred to the feed container at a temp at which it is completely liquid and homogeneous and which depends on the solvent-to-oil ratio. When this ratio is 6, the solution is liquid and homogeneous at ca. 30C, but at lower ratios it must be maintained at higher temp. Ethylene was used in place of the nitrogen in many of the tests to obtain higher yields (1). It was dissolved in the de-aerated feed solution in an autoclave by evacuating and then pressurizing to ca. 200 psi with ethylene gas. The pressurized solution was pumped directly from the autoclave through the heated reaction coil.

The feed rate, controlled by adjusting the length of stroke of the positive displacement pump, was determined by weighing the product flowing from the reactor at regular time intervals. Molten solder was selected as the heating medium because it effects a good heat-transfer rate. By bubbling a slow stream of nitrogen through the molten solder, temp uniformity was obtained throughout the bath. The preheat section of the coil immersed in the bath was designed to

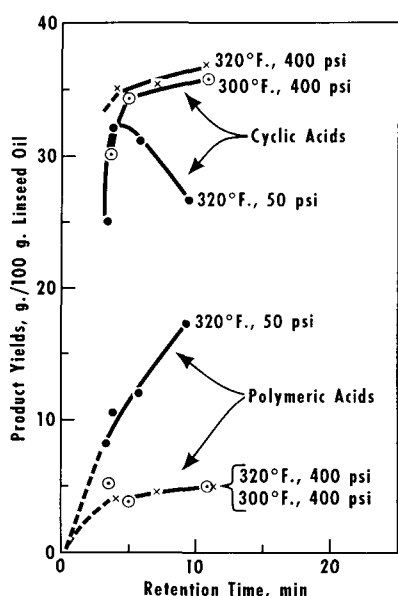


FIG. 2. Effect of retention time, temp and pressure on product yields from continuous cyclic acid reaction with nitrogen.

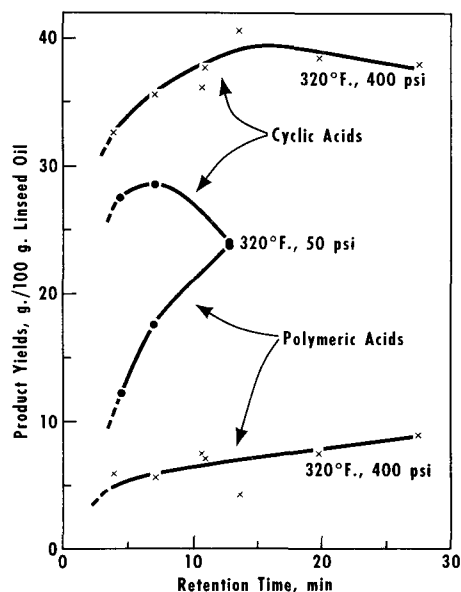


FIG. 3. Effect of retention time, temp and pressure on product yields from continuous cyclic acid reaction with ethylene.

heat the reactants to reaction temp. In actual tests the temp of the fluid leaving the preheater was only 5-6C below the temp of the bath.

Average retention time of the reactants in the reactor section was calculated from the measured internal displacement volume of the coil, the measured specific gravity of the reaction mixture at the reaction temp, and wt rate of flow of the reaction mixture. Owing to the possible formation of bubbles of gas or vapor within the reaction coil it is uncertain if the actual retention time in the reactor was always the same as the calculated time. The pressure on the system was regulated by operating manually the variable back-pressure valve at the discharge end of the reaction system.

In operation the system was held at the desired conditions for at least 10 min before 2 or 3 samples were collected. After acidification the fatty acids were recovered and converted to their methyl esters. These esters were quantitatively vacuum distilled to separate monomeric esters from polymeric esters and samples of the monomeric esters were completely hydrogenated and analyzed by GLC to determine the cyclic acid ester content. Details of the methods used are described in earlier publications (2,3). Results obtained with two samples prepared under the same conditions were averaged to obtain the data used in the subsequent tables.

### Results and Discussion

In Figure 2 is shown the relation between retention time of the reactants in the reactor section of the heated coil and yields of cyclic and polymeric fatty acids. The feed solution was saturated with nitrogen

TABLE I  
Conditions for a Continuous Cyclic Acid Reaction

Solvent-oil ratio	Excess NaOH %	Reaction pressure, psi	Reaction temp, °C	Retention time, min	Yield, g/100g linseed oil		
					Polymeric acids	Cyclic acids	Neutral equivalent of monomeric acids
3	25	260	310	7.2	8.2	27.8	286
3	100	500	340	6.4	4.6	37.5	285
6	100	50	320	5.8	12.0	31.1	288
3	25	275	358	4.0	27.0	20.8	328
3	25	275	351	11.3	40.5	22.3	331

TABLE II  
 Comparative Yields of Cyclic Acids from Batch and Continuous Reactions

Reaction	Solvent-oil ratio	Excess NaOH %	Reaction pressure, psi	Reaction temp, C	Reaction time, min <sup>a</sup>	Yield, g/100g linseed oil		
						Polymeric acids	Cyclic acids	Polymer and cyclic acids
Batch	3	30		With Nitrogen				
Continuous	3	25	300	295	30	11.2	35.3	46.5
Batch	3	100		335	7.2	5.1	28.8	33.9
Continuous	3	100	400	295	30	8.3	40.4	48.7
Batch	6	100		300	12	5.0	36.0	41.0
Continuous	6	100	400	320	12	5.0	37.0	42.0
Batch	6	100	300 <sup>b</sup>	With Ethylene				
Continuous	6	100	400	295	30	8.5	46.1	54.6
				320	15	7.1	39.5	46.6

<sup>a</sup> Heat-up time ca. 45 min for batch reaction; 1-5 min for continuous reactions.

<sup>b</sup> Initial ethylene pressure on autoclave before heating.

for these tests. With a reaction pressure of 400 psi, the cyclic acid yield at temp of 300C and 320C increased as retention time was increased up to 11 min. Although it is not evident that maximum yields were attained at this retention time, data presented in Figure 3 indicate that a maximum yield is reached between 10 and 15 min. As the cyclic acid yield increases with longer reaction time, polymer acid yield also increases at about the same rate at both temp. A pressure of 50 psi on the system favors the formation of polymer and yields of cyclic acid reach their maximum soon, then decrease rapidly. Since both cyclic acids and polymeric (dimer, trimer and higher) acids formed from conjugated linolenic acid, conditions favoring high yields of one obviously cause lower yields of the other. At low pressure probably ethylene glycol becomes vaporized in the heated coil, a condition apparently conducive to polymer formation. The disappearance of cyclic acid coupled with the increase in polymeric acids indicates that polymer formation may result in part from reaction of cyclic acid with conjugated linolenic or linoleic acid to form a bicyclic dimer acid.

In Figure 3, data are presented from tests made at 320C with ethylene in the feed solution. Comparing the curves in Figures 2 and 3 for tests at 320C and 400 psi indicates that the reaction with ethylene is initially slower than with nitrogen; at a 7-min retention time cyclic acid yields are about the same; thereafter higher yields are obtained with ethylene. Higher yields of polymeric acids are also obtained with ethylene. At retention times above 15 min cyclic acid yield declines, whereas the yield of polymer continues to increase.

At 50 psi pressure, polymer formation is again much higher and cyclic acid lower than at 400 psi. Also polymeric acid formation can be increased slightly at low pressure by using ethylene instead of nitrogen. For maximum cyclic acid yields the pressure on the reaction apparently should exceed the vapor pressure of the solvent at the reaction temperature, to prevent vaporization of the solvent.

Several tests were made above 350C to determine the upper limit of temperature. Results summarized in Table I show that some decomposition of fatty acid soaps occurred at 351 and 358C and pressures of 275 psi. Products of reactions at 310C, 260 psi; 320C, 50 psi; and 340C, 500 psi, had neutral equivalents comparable to those of monomeric acids (cyclic plus straight chain) prepared at 250C by the batch method. However, monomeric acids from tests made at 351 and 358C had high neutral equivalents indicative of the presence of unsaponifiable material resulting from decomposition of fatty acid soaps. Also, when the methyl esters of the crude fatty acids from these tests were vacuum distilled to separate monomeric from

polymeric acids, an appreciable quantity of material distilled ca. 50-75C below the distillation temp of the methyl esters. This material was evidently pyrolytic decomposition products. Possibly there would have been less decomposition if a higher pressure had been maintained on the system.

Comparative yields of cyclic fatty acids produced from linseed oil by the batch and continuous methods are summarized in Table II. Yields represent the maximum obtained at each operating condition by conducting reactions for optimum times. In all cases, the best batch yields were higher than the best continuous yields at comparable solvent-to-oil ratios and amt of catalyst. The sum of the yields of polymeric and cyclic fatty acids from a test is an indication of the extent of reaction (the linseed oil used contained 51% linolenic acid, triglyceride basis). Yields from continuous reactions with ethylene probably would have been higher if the feed solution had been held under higher pressure thereby dissolving more ethylene in the solution, but this aspect was not investigated because of equipment limitations. In batch reactions with ethylene cyclic acid, yields were increased by using an increased pressure. Ethylene is believed to form a 1,4-disubstituted cyclohexene by reaction with conjugated diene systems (5).

Generally, the advantages of conducting a reaction process by a continuous rather than by a batch treatment include greater ease of control adaptability to automatic handling, better uniformity of product and possibly lower labor, equipment and utilities costs/unit of production capacity. In view of these possible advantages a continuous process may be preferred even though the maximum yield of product is somewhat lower than by the batch method.

The equipment used in these tests is probably the simplest that could be employed in a continuous system. Although higher product yields might possibly be obtained if the apparatus were modified somewhat, the unit demonstrated the effects of pressure, temperature, reaction time and amt of reagent on yields of cyclic and polymeric fatty acids by a continuous process involving the treatment of linseed oil with excess alkali in a glycol solution.

#### ACKNOWLEDGMENTS

Assistance in constructing equipment and analyzing samples is appreciated from Lloyd Carlson, Sheldon Smith and Lynn Black.

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[Received May 27, 1964—Accepted July 6, 1964]