Removal of Metal Catalysts from Aldehyde Oils[1]

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Abstract

Aldehydes made from soybean or linseed oils, or their methyl esters, darkened and polymerized following preparation by ozonolysis and catalytic or chemical reduction in stainless-steel pilot-plant equipment. Treatment with a cation exchange resin in the hydrogen form substantially reduced the amount of color formed and the polymerization.

When conducted prior to removal of volatiles by stripping the resin treatment of soybean aldehyde oil decreased final color from Gardner 17 to 10 with a concomitant decrease in molecular weight and viscosity due to decreased polymerization. Resin pretreatment of methyl azelaaldehydate (MAZ) increased distillation yields. Since addition of several metal salts to MAZ reduced distillation yield to varying degrees, metal-catalyzed polymerization must occur.

Introduction

PREPARATION OF NEW ALDEHYDE products from soybean and linseed oils, or their methyl esters, on a laboratory scale by treatment with ozone followed by reduction of the ozonized material has been reported (9–11). Translated to a larger scale in stainless-steel pilot-plant equipment the process gave aldehyde products which, contrary to our experience in laboratory preparation, were now extremely dark in color and partially polymerized because of metallic contamination and therefore generally unsuited for further derivative studies. Treating aldehydes with a cation exchange resin for the removal of metals before polymerization occurred and preventing further metallic contamination largely overcame the problem of metal-catalyzed polymerization and discoloration.

The catalytic effect of certain metallic compounds for promoting the polymerization or oxidation of aldehydes has been the subject of a number of investigations. Shoruigin and co-workers (12) described the conversion of certain aromatic and aliphatic aldehydes to dimeric products by the action of mixed aluminum and magnesium filings, but iron and copper were said to be without effect. Wieland and Richter (15) reported that certain heavy metals accelerated the autoxidation of some aromatic aldehydes but that aliphatic aldehydes were not affected. The metal catalysis of aldehyde polymerization to obtain useful polymers has been the subject of a number of patents in which alkali metal alkoxides, N-metal compounds or organometallic derivatives were added to obtain faster reaction, improved properties, or both (1,4–7,14). The effect of iron in causing aldehydes to darken has also been noted (13).

Two types of aldehyde products have been prepared and examined in the present studies—one made from soybean and linseed oils by complete or partial ozonization followed by reduction of the ozonized product, and the other by similar treatment of the fatty acid methyl esters derived from soybean oil. Splitting of unsaturated fatty acids at double bonds by the action of ozone with subsequent oxidation to produce dibasic acids is a well-known commercial process. However, ozonization followed by reduction to make aldehydes has apparently been used only on a laboratory scale.

Figure 1 shows the method used for preparing aldehyde oils in these studies. Refined soybean oil dissolved in methanol and ethyl acetate in the ratio 1:1.5:3 parts by weight was cooled to 10C and stirred while oxygen containing about 1.5% ozone was bubbled through the solution. Ozonization of C=C in the presence of methanol is reported to give the methoxy hydroperoxide structure shown (3). Only one third of the triglyceride molecule is shown. Cleavage of the fatty acid chain is not selective, so that each fragment has a 50:50 probability of forming the hydroperoxide or the carbonyl compound. The reaction was conducted in a stainless-steel vessel equipped with stainless-steel agitator and sparge coil. Unabsorbed oxygen was vented from the reactor through a refrigerated condenser. Venting through the condenser entails some loss of solvent, but this could probably be largely recovered by a suitable absorption system such as a glycol scrubber.

Following the ozone reaction, the solution was transferred to a stainless-steel hydrogenator where 0.15% of reduced palladium catalyst based on oil weight was added in the form of 10% palladium on carbon. The solution was reduced at 30–50C under 20–30 psi hydrogen pressure until the solution no longer gave a test for peroxides. After filtration to remove the catalyst, the preferred procedure was to evaporate to about one-fifth the original volume by a single pass through a falling film evaporator under vacuum while keeping the solution temperature below about 60C to minimize the formation of polymer. This procedure removed a substantial portion of the solvents and low-boiling aldehydes. Treatment with a cation exchange resin was then performed after which the resulting aldehyde oil was heated to 100–120C at about 0.1 mm abs with steam sparging to remove pelargonaldehyde, caproaldehyde and residual amounts of solvent. The aldehyde oil was analyzed for viscosity, color, molecular weight and carbonyl content.

Preparation of methyl azelaaldehydate (MAZ) from soybean oil methyl esters was conducted in a similar manner as shown in Figure 2, except that methanol was the only solvent used. After ozonization, reduction, filtration and solvent evaporation under vacuum at 60C max, the aldehydes were treated with cation resin and water at room temperature. The product was then fractionally distilled with steam sparging to 210C at 1 mm abs. MAZ contained methyl palmitate and the dimethyl ester of azelaic acid, a byproduct of the reaction. These were only partially separated by fractional distillation.

The cation exchange resin used in all the tests was Dowex 50W, X-4, 50–100 mesh. The resin was washed on a Buchner funnel with hydrochloric acid diluted about 1 to 10 with distilled water (based on 1 volume of diluted acid per volume of resin) and then was washed several times with distilled water to remove excess acid. Complete removal was not necessary. The first tests were made with resin dried by washing with methanol following the acid and washing treatments. However, better results were obtained if both water and resin were used for treating the aldehydes. The resin, water and aldehyde oil, or aldehyde ester,

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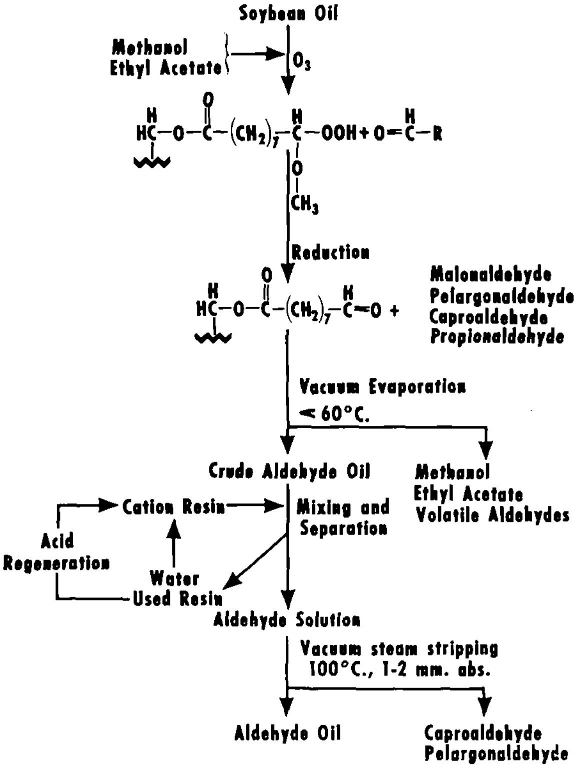

FIG. 1. Preparation and resin treatment of soybean aldehyde oil.

were agitated vigorously for about 20 min at room temperature, the mixture was allowed to separate, and the oil was decanted off and filtered to remove traces of resin. The resin may be regenerated by acid treatment and water washing and reused. It should be regenerated within a few hours after use since aldehydes are retained on it and cause it to darken gradually. Otherwise, if it is to be stored used resin should be washed with methanol to remove residual aldehydes.

Results and Discussion

Results obtained by treating an aldehyde oil with cation exchange resin are summarized in Table I. A quantity of aldehyde oil solution, taken after catalytic reduction and filtration but without evaporation to remove solvent, was stored at 0C for this series of tests. To remove the more volatile components, including pelargonaldehyde, the control sample was evaporated to 100C at 0.5 mm with steam sparging in a glass, round-bottom flask heated in a water bath; this test and all subsequent ones were made in the same apparatus under substantially the same stripping conditions. The second and third tests, in which the aldehyde solution was treated with different amounts of cation exchange resin dried with methanol, show the effects of this treatment in reducing the color. Since the solution contained methanol, the resin probably catalyzed some acetal formation. In the fourth test the aldehyde solution, which tested pH 4.7, was neutralized to pH 7.0 with alcoholic KOH before evaporation. This darkened the color. Treatment of the neutralized solution with the cation exchange resin, which had the effect of converting the salt of neutralization back to the acid, improved the color but less than did the same amount of resin without KOH being added. For the sixth test the solution was first concentrated to one-fifth the original volume by evaporation under vacuum below 60C to remove most of the solvents and the more volatile aldehydes.

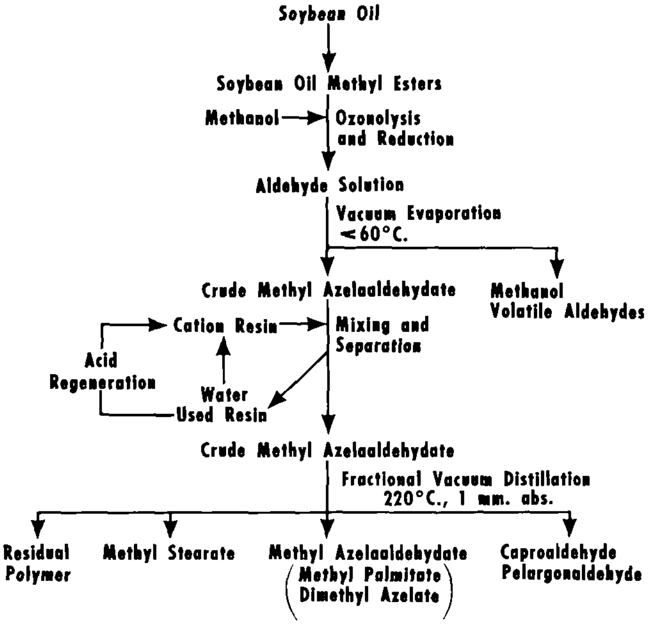

FIG. 2. Preparation and resin treatment of methyl azelaaldehydate.

The concentrated solution was then treated at room temperature with one-half volume of resin and one-half volume of water per volume of aldehyde oil. After stripping, the aldehyde oil product had a Gardner color of 10 and a considerably lower molecular weight than the oil in the first test showing that the resin treatment improved the color and decreased polymerization. The last procedure gave the best results. Water washing without resin, followed by stripping, gave an extremely dark oil. Pinns (8) reported that strongly acid exchange resins catalyze self-condensation and polymerization of aliphatic aldehydes, but addition of water or solvent hinders catalysis. Apparently little or no polymerization due to the resin treatment occurred in the tests we report by virtue of the substantial amount of water used.

In Figure 3 the effects of cation exchange resin

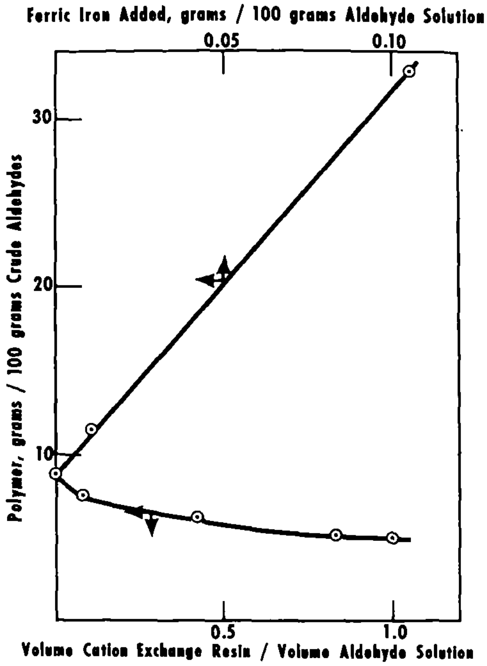

FIG. 3. Effect of ferric salt addition (upper curve) and resin treatment (lower curve) on distillation yields of methyl azelaaldehydate.

TABLE I

Effect of Cation Exchange Resin Treatment on the Color of Aldehyde Oil

Treatment	Proportions of aldehyde/resin/water by vol	Properties of aldehyde oil	
		Gardner color:	Molecular weight
Control	....	17	1145
Dry resin [a]	8/1/0	14	....
Dry resin	2/1/0	12	....
Aldehyde solution neutralized to pH 7.0	....	18+	....
Aldehyde solution neutralized to pH 7.0 and treated with dry resin	2/1/0	14	....
Aldehyde solution concentrated to one-sixth the original volume and treated with resin and water	2/1/1	10	760

[a] Dowex 50W, X-4, 50–100 mesh, acid-activated, washed and dried with methanol.

treatment for reducing the amount of undistilled polymer obtained on vacuum steam distillation of MAZ, and of added iron for increasing it are shown. With no resin treatment, 8.8% polymer was obtained, whereas treatment with increasing amounts of resin decreased the amount of polymer. One volume of resin per volume of crude aldehyde solution reduced the polymer to 5%. The addition of iron, as ferric chloride, to the aldehyde solution increased the polymer yield. At a level of 0.01% iron (ferric ion) the polymer was increased to 10.7% and at 0.1% iron, to 33%.

To determine the effects of a number of different metals for promoting polymer formation in aldehyde products from soybean oil, a quantity of MAZ was prepared from soybean methyl esters and steam distilled at 210C, 0.5 mm abs. No attempt was made to separate the various components by fractional distillation, and the distilled product contained not only the major constituent, MAZ, but also pelargonaldehyde, caproaldehyde, methyl stearate, methyl palmitate and small amounts of other aldehydes and esters. The acetate salts of 10 metals were either prepared from the hydroxides or obtained as reagent grade salts. Each of these was added in an amount sufficient to provide 0.1% of the metal ion, to 200-g portions of the distilled aldehydes. The aldehydes were then heated at 100C in a 500 ml round-bottom distilling flask for 1 hr while high-purity nitrogen was bubbled through the sample to prevent oxidation, provide agitation and evaporate the water added with the metallic salts. The aldehydes were then steam-distilled again to 210C at 0.5 mm abs and the amount of polymer was determined (Table II). No hydrolysis of aldehyde esters during steam distillation was observed. Control samples to which no metal was added gave an average of 2.5% polymer. Calcium, magnesium, nickel and chromium produced small increases in polymer, whereas lead, zinc, sodium and aluminum gave somewhat larger increases in polymer formation. Iron and copper gave the largest increases of the metals tested. In the final test of this series, an aldehyde sample to which 0.1% iron had been added as the acetate salt was treated with an equal volume of cation exchange resin and one volume of water by mixing together for 20 min at room temperature. The aldehyde sample was separated and heated 1 hr at 100C under nitrogen and then vacuum steam-distilled to give 3.4% polymer, only slightly more than the control.

The metals (salts) used in the tests were selected as the types which might be encountered in processing equipment or which might be introduced into the aldehyde product in some other manner. For example, chemical reduction with zinc and acetic acid may be used instead of catalytic reduction to reduce the ozonized solution and produce aldehydes. The reduced solution is then filtered to remove unreacted zinc and undissolved zinc acetate and washed with water to remove soluble materials. This treatment may allow calcium, magnesium and sodium from the water to be retained by the aldehydes. Washing the aldehyde with deionized water was not effective in removing metallic contaminants either at room temperature or when the aldehyde and water were heated and agitated at 200C under pressure (2). It appears that organic salts or complexes which are only slightly soluble in water are formed with the metals.

TABLE II

Effect of Metals on Polymer Formation from Distillation of Crude Methyl Azelaaldehydate

0.1% Metal added as acetate salt	Polymer,[a] % g/100 g aldehyde
Control	2.3, 2.7
Ca++	4.6
Mg++	4.1
Ni++	3.5
Cr+++	4.2
Pb++	7.4
Zn++	7.3
Na+	7.6
Al+++	6.9
Fe+++	12.9, 12.2
Cu++	14.3
Fe+++ added then removed by cation exchange resin treatment	3.4

[a] Crude aldehydes were vacuum-distilled before addition of metal. Redistillation was at 0.5 mm abs to 210C with steam sparging.

The aldehyde solutions used were protected from oxidation and were weakly acidic to prevent polymerization due to oxidation or to base-catalyzed aldol condensation. Therefore, it is demonstrated that polymerization was metal-catalyzed and that it may be minimized by adequate metal removal with a cation exchange resin treatment.

To prevent metals from becoming dissolved in the aldehydic products, and thus obviate or at least minimize purification, well-refined soybean or linseed oils should be used, and all operations should be conducted in glass- or plastic-coated equipment. Among the plastics, polyethylene and polytetrafluoroethylene have been used with satisfactory results. By using adequate precautions to minimize metal contamination, aldehyde oils of various degrees of functionality were prepared on a pilot-plant scale from soybean and linseed oils. These products were equal in color to the original oils and were of nearly theoretical molecular weight. No serious difficulties should be experienced in manufacturing such aldehydic materials on an industrial scale.

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