Acetalization of Aldehyde Oils by Catalysis with Cation-Exchange Resins[1]

R. E. BEAL, D. E. ANDERS and L. T. BLACK,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Aldehyde oils produced on a pilot-plant scale gradually polymerized at room temperature and became extremely viscous or solidified in a few weeks. Initial viscosity level was maintained by converting the oils to acetals by use of a strong cation resin catalyst which, it was found, does not cause appreciable transesterification. Aldehyde conversion was determined by infrared absorbance at 2720 cm^{-1}. The effects of amount of alcohol and resin on degree of conversion were studied. Storage studies indicate that the acetal oils must be protected from oxidation.

Introduction

INTRODUCTION OF ALDEHYDE groups into soybean and linseed oils is one means for obtaining new products of potential industrial value. Ozonization and reduction reactions used to convert unsaturated oils to what are termed "aldehyde oils" having various degrees of aldehyde functionality have been described (9,10). Because of their high degree of reactivity, aldehydes tend to undergo various side reactions. Consequently, aldehyde oils undergo self-polymerization at room temperature and gradually increase in viscosity and then solidify within a few weeks if sufficient aldehyde functionality is present. Of various methods to stabilize aldehyde oils, conversion to acetal products offers several advantages. These acetals undergo little or no viscosity increase during room temperature storage and have a more pleasant odor than the aldehyde oil product. For some reactions, such as conversion to other acetals or to oximes, the acetal and aldehyde oils may be used interchangeably.

Conversion of aldehydes to acetals is usually catalyzed by strong acids. When a strong acid catalyst is used for converting aldehyde oils to the corresponding acetals however, the triglyceride structure is lost (Fig. 1) due to transesterification. Partial random ozonization is illustrated here, although the exact location of partial ozone attack on the triglyceride double bonds is not known. The typical molecule of aldehyde oil would not be as highly unsaturated as shown when the ozonization is carried to 90% completion as described in the experimental procedure.

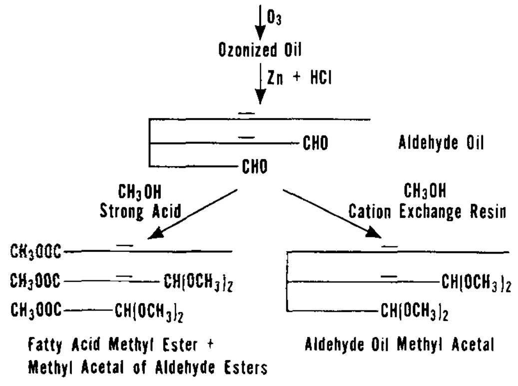

FIG. 1. Flow sheet for aldehyde oil acetal preparation, starting with partial random ozonization of the triglyceride. The unsaturation positions shown are illustrative only.

Weakly acidic salts have been used as catalysts to form acetals without transesterification (11), but metallic ions introduced with the salts catalyze polymerization of aldehydes on heating, and the salts are difficult to remove and recover (4).

Sussman (12) showed that a strong cation-exchange resin may be used to catalyze esterification, acetalization and other reactions. We find that by use of strong cation resins as catalysts, aldehyde oil acetals can be obtained without appreciable transesterification and that the resin may be reused several times.

Procedures

The apparatus shown in Figure 2 was used to study the conversion of aldehyde oils to methyl or butyl acetals. Initially, reactions were conducted with a Teflon-coated (13) magnetic stirrer revolving on the bottom of the reaction flask. This action caused appreciable attrition of the resin used as catalyst, and a method of suspending the stirrer in a Teflon sling which revolved in a Teflon bearing was devised. Reactions were conducted with dry soybean aldehyde oil, alcohol and cation-exchange resin, at reflux, with stirring to keep the resin suspended and to prevent bumping and with a drying tube to exclude atmospheric moisture.

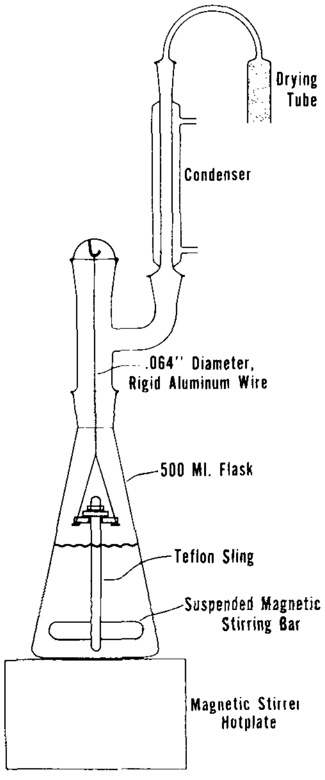

FIG. 2. Apparatus for acetal reaction.

---

[1] Presented at AOCS Meeting in Cincinnati 1965.

[2] No. Utiliz. Res. Dev. Div.,. ARS, USDA.

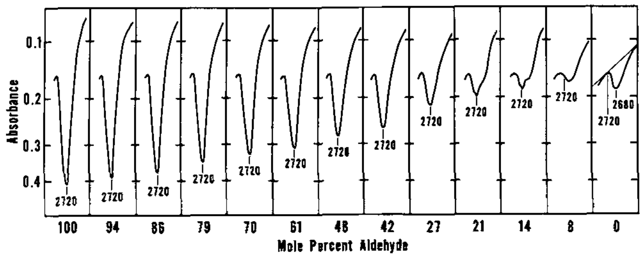

FIG. 3. Determination of residual aldehyde content by infrared absorbance at 2720 cm^{-1}.

Aldehyde oil was prepared by dissolving one part refined, bleached soybean oil in 1.5 parts methanol and 3 parts ethyl acetate and bubbling an ozone-oxygen mixture from an ozone generator through the solution at 5 to 10C until ozonization of the oil was about 90% complete. The ozonized solution was reduced in a glass-lined vessel by adding powdered zinc and acetic acid alternately at a rate slow enough to prevent the temperature from exceeding about 40C and with stirring and external cooling, until a peroxide test was negative. The reduced solution was filtered, washed with water three times, centrifuged to remove water and dried and stripped to remove volatile aldehyde by-products by passing once through a glass falling-film evaporator under vacuum (0.1 mm) at 100C. Aldehyde oil was stored at −18C in 100-g bottles.

Acetal reactions were conducted on samples from the same batch of soybean aldehyde oil with Dowex 50W X-4, 20–50 mesh, as the cation-exchange resin catalyst. Cation resins of other degrees of crosslinking gave comparable results. The resin was prepared by washing on a Buchner funnel with dilute (1–5) hydrochloric acid and then with distilled water until the effluent was neutral to indicator paper. The wet resin was then dried by adding toluene and refluxing to a Stark and Dean distilling trap until no more water was collected; the resin was then filtered and exposed to air until the toluene odor disappeared. A second method used to dry the resin was to wash it several times with methanol until the effluent methanol showed essentially no water pickup when tested by the Karl Fischer method. Ten grams of water-free resin immersed in methanol occupied a volume of 29 ml. Resin amount for a reaction was determined volumetrically. In reactions where the resin was reused without regeneration, it was washed with methanol between uses. The resin gradually darkens with use, possibly due to adsorption of aldehydes or by-products, but this discoloration did not prevent its reactivation and reuse. When dimethoxypropane (DMP) was the dehydrating agent in preparing the methyl acetals, the resin darkened rapidly but did not become inactive. DMP normally undergoes polymerization and darkening when heated under acidic conditions (7).

During each reaction, samples were removed at intervals, with care to prevent the introduction of moisture, filtered and stripped of solvent on a water bath at about 80C under a slow stream of nitrogen and high vacuum (<1 mm Hg absolute). Molecular weights were determined by the vapor-pressure method in a Mechrolab, Model 301A, osmometer with acetone solvent. Conversion of aldehyde to acetal was determined by infrared absorption at 2720 cm^{-1} in an Infracord, Model 337, spectrophotometer and KBr cells as described by Anders and Pryde (1). Figure 3 shows the relation of absorbance to mole percent aldehyde. Carbonyl analyses were by the hydroxylamine-hydrochloride method (2). Unsaturation was determined by the method of Brown et al. (6), modified by Miwa et al. (8) and correction for aldehyde reduction was made graphically (5).

Results

Cation-exchange resin concentration affects the rate of conversion of aldehyde oil to the dimethyl acetal. With DMP added to remove water of reaction (Table I, Series A), an acetal conversion of nearly 95% was obtained in ½ hr with 8.7% catalyst (% dry wt resin based on aldehyde oil wt) and only 80.5% with 3.5% catalyst. Substantially maximum yield was reached in ¾ hr at the higher catalyst level and 1¼ hr at the lower level. At 1.75% catalyst, the rate was appreciably less, but after 4 hr about the same degree of conversion, more than 97%, was reached. At all catalyst concentrations, the molecular weight of the product increases during the first 2 hr and then decreases somewhat. The increase is due both to acetal formation and to polymerization. Theoretical molecular weight of the dimethyl acetal based on molecular weight and carbonyl content of the original aldehyde was 625.

At the low resin concentration, the higher molecular weight is believed caused by greater polymerization of aldehyde because of slower conversion to acetal. After about 2 hr reaction time, when acetal formation is essentially complete, the molecular weight decreases somewhat, probably because of slow alcoholysis of triglycerides. Both acetal formation and ester alcoholysis occur with strong cation-exchange resins, under reflux conditions, but acetal formation proceeds so

TABLE I
Effect of Reaction Conditions on Aldehyde Conversion to Acetal

Reaction time, hr	Acetal conversion, %				Molecular weight			
	½	1	2	4	0	1	2	4
Cation exchange resin, wt %				Series A				
1.75	34.5	50.0	73.0	97.5	550	750	745	715
3.5	80.5	96.5	98.0	97.5	550	700	710	690
8.7	94.5	97.5	98.5	98.5	550	665	685	625
				Series B				
1.75	71.0	87.5	92.5	94.5	550	735	730	705
8.7	95.5	96.5	97.5	97.5	550	615	590	585
				Series C				
8.7								
1st use	95.5	97.0	97.5	98.5	550	615	590	585
2nd use	81.0	88.0	97.0	97.5	550	600	570	555
3rd use	65.0	78.5	94.5	97.0	550	600	570	555

	Series A		Series B		Series C	
Reactants	Weight	Molar	Weight	Molar	Weight	Molar
Aldehyde oil	100	1	100	1	100	1
Methanol	32	3.1	128	12.3	128	12.3
Dimethyoxypropane (DMP)	52	1.67	......	......	......	......

much faster that the amount of alcoholysis is slight at normal reaction times.

Further reactions were conducted with reduced amounts of methanol. With 8 parts methanol and 60 parts DMP per 100 parts aldehyde oil, the degree of conversion was the same as shown in Series A, but the reaction rate was lower. The methanol added is only 40% of the theoretical amount required to form dimethyl acetal, the rest being provided by hydrolysis of DMP.

A large excess of methanol gave acetal conversion as high as 98% without DMP. The effect of catalyst concentration on acetal conversion rate and molecular weight is given in Table I, Series B when 12.6 moles (6.3 equivalents) of methanol per mole of aldehyde were used without DMP. With a 3.0 mole equivalent excess (not shown), 95% conversion was reached after 2 hr. At 8.7% catalyst concentration, the rate of acetal formation is practically identical to that in Series A with DMP present. At the 1.75% level, the reaction was faster than that in the presence of DMP. Molecular weight increase was lower than with DMP.

When the acetal reaction was conducted with 1% sulfuric acid as catalyst, the molecular weight decreased to 395 after 2 hr at reflux and to 320 after 4 hr. The latter molecular weight indicates that conversion of triglycerides to methyl esters was nearly complete in 4 hr.

The data shown in Table I, Series A and B were obtained with new resin. When the resin was reused without reactivation, the reaction rate and the molecular weight of the acetal oil changed as shown in Table I, Series C. Reaction equilibrium was reached in less than 1 hr with fresh resin, about 2 hr with once-used resin and about 2½ hr with twice-used resin. The resin was washed with methanol and kept under methanol overnight between runs. Decrease in catalytic activtiy may have been caused by adsorption of a thin layer of material on the resin. The resin could be restored substantially to its original activity by treatment with acid. Differences in molecular weight of the product between the first, second and third uses were small and suggest that the resin may be used several times at least before it needs to be regenerated.

To test azeotropic distillation for making acetals, butyl acetals of the aldehyde oil were prepared by refluxing *n*-butanol (100% molar equivalent) and toluene with the aldehyde oil and cation-exchange resin (8.6%). Water from the reaction was collected from the azeotrope in a moisture trap. At 99C the resin, originally amber, darkened quickly and became black, whereas in forming the methyl acetal at 68C the resin darkened slowly and did not become dark until used a number of times. Although the reaction was continued several hours until water formation reached a constant value, only 92.3% of the aldehyde was converted to the butyl acetal and molecular weight increased to 860 (theory for the butyl acetal equals 770).

Changes in properties that resulted when an aldehyde oil made from soybean oil and the corresponding methyl acetal oil were stored at 75–80F are summarized in Table II. The aldehyde oil was made as previously described and converted to the methyl acetal with about 300% excess methanol and used cation-exchange resin (Dowex 50W). To determine if storage stability is adequate without complete conversion to the acetal, the reaction was discontinued after 89% acetal conversion. The aldehyde and acetal oils were analyzed for carbonyl content, molecular weight and infrared absorption (Table II) and were put in Gardner tubes. The headspace in the tubes was flushed with nitrogen, and the tubes were stoppered with cork stoppers and sealed with cellophane adhesive tape. The headspace between the surface of the oil and the stopper was about ⅜ in. for each tube. Gardner color and viscosity of the aldehyde and acetal oils were determined by comparison with standard Gardner tubes. The sample tubes stored at room temperature (ca. 25C) were exposed to light from north windows, and Gardner viscosities determined periodically. These were converted to poises from a conversion chart. The viscosity of the acetal oil increased slightly during the first 25 days and then remained constant, whereas the aldehyde oil showed a continuous nearly linear increase in viscosity poises until the test was terminated after 90 days. Thus, even at 89% conversion the acetal oil had adequate viscosity stability for extended storage.

TABLE II
Storage Stability of Aldehyde and Acetal Oils

Properties	Aldehyde oil storage time 0 Days	Aldehyde oil storage time 90 Days	Acetal oil storage time 0 Days	Acetal oil storage time 90 Days
Viscosity, Gardner	H-I	Z-1+	F	G-H
Viscosity, poise	2.1	27.0	1.5	1.8
Infrared absorbance, 2720 cm^{-1}	0.405	0.290	0.044[a]	0.036
Carbonyl, meq/g	2.55	2.52	2.36	2.05
Molecular weight	895	1195	930	840
Hydrogen iodine value	.....	40	......	45
Color, Gardner	8	8–9	8	8–9

[a] 89% conversion to the acetal.

Infrared absorption at 2720 cm^{-1} decreased nearly 30% for the aldehyde oil during storage. This change indicated that aldol condensation accounted for the viscosity and molecular weight increases observed. The carbonyl content of the aldehyde oil as determined by wet analysis decreased little. This slight variation in carbonyl analysis does not rule out aldol condensation. Since this reaction is reversible, the aldol product could be converted back to the aldehyde and then to the oxime under the conditions used to determine carbonyl. Although the acetal oil increased little in viscosity, it showed a marked decrease in carbonyl content. An even more rapid decrease in carbonyl occurred after a Gardner tube was opened and the acetal oil was exposed to the air. After 25 days, carbonyl content fell to 1.84 meq/g and after 31 days, to 1.71. Further tests indicate that acetal oils are more stable when stored in the dark.

The hydrogen iodine values were not determined on the original oils, but values after 91 days' storage were typical for unstored oils of comparable aldehyde content. This similarity indicates that unsaturated centers were probably not involved in reactions occurring during storage. The colors of the oils underwent no appreciable change during room temperature storage in clear glass bottles.

According to Austerweil and Palland (3) catalysis of acetalization with a cation-exchange resin causes a reaction, slowed by solvents, that results in formation of the olefinic ether when the aldehyde molecule is larger than C_4. However, examination of some of our acetal oil products by infrared in the range of 934 to 1667 cm^{-1} did not reveal any olefinic ether (11).

Conditions producing 95% conversion of aldehyde oils to methyl acetals include use of dry materials, at least 300% excess of alcohol and a maximum reaction temperature of about 70C. Although a dehydrating agent, such as 2,2-dimethoxypropane, was not necessary, its use substantially decreased the amount of methanol required to obtain good acetal conversion and increased acetal conversion slightly. The optimum economic catalyst level will depend on reaction rates obtainable in relation to the number of reuses of catalyst. The cation-exchange resin can be reused several times without reactivation. Costs of new catalyst, catalyst regeneration and equipment and processing all have to be balanced to determine the most economic process. The acetal oil did not increase much in vicosity during storage but did require protection against oxidation.

In addition to the soybean oil studies, aldehyde oils made from refined linseed and *Crambe abyssinica* oils have also been satisfactorily converted to acetal oils by the procedure described.

ACKNOWLEDGMENT

Assistance in experimental work by Lloyd Carlson and Gary Spyres. Robert Bates, University of Arizona, gave valuable advice.

REFERENCES

1. Anders, D. E., and E. H. Pryde, JAOCS *43*, 305–306 (1966).
2. Anders, D. E., E. H. Pryde and J. C. Cowan, *Ibid. 42*, 236–243 (1965).
3. Austerweil, G. V., and R. Palland, Bull. Soc. Chim., France 1164–1167 (1954).
4. Beal, R. E., JAOCS *43*, 122–124 (1966).
5. Black, L. T., and R. E. Beal, to be submitted for publication.
6. Brown, H. C., K. Sivasankaran and C. A. Brown, J. Org. Chem. *28*, 214–215 (1963).
7. Dow Chemical Co. Bulletin, 2.2-Dimethoxypropane (1956).
8. Miwa, T. K., W. F. Kwolek and I. A. Wolff, Lipids *1*, 152–157 (1966).
9. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, JAOCS *38*, 375–379 (1961).
10. Pryde, E. H., and J. C. Cowan, Ibid. *39*, 496–500 (1962).
11. Pryde, E. H., D. J. Moore, H. M. Teeter and J. C. Cowan, J. Org. Chem. *29*, 2083 (1964).
12. Sussman, S., Ind. Eng. Chem. *38*, 1228 (1946).

[Received August 23, 1966]