Soybean Soapstock Utilization: Fatty Acid Adducts with Ethylene and 1-Butene

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ABSTRACT

The relation of certain reaction variables to yield was investigated in the preparation of ethylene and 1-butene Diels-Alder adducts with alkali conjugated linoleic and linolenic acid soaps derived from soybean oil soapstock. Adduct yields generally increased with pressure at the 295 C reaction temperature. Maximum yields obtained with fatty acids derived from soapstock were ca. 80% of theory with ethylene and 40% of theory with 1-butene. Purification of adduct methyl esters by vacuum fractional distillation gave adducts with >95% purity. Ethylene adduct amides showed promise as antiblock agents for plastic film.

INTRODUCTION

Since ancient times, drying and semidrying vegetable oils such as linseed and soybean oils have been cooked or heat bodied to increase their viscosity and improve the properties of surface coatings prepared from them. The chemical nature of the changes accompanying the viscosity increase was not understood entirely until Bradley and Johnston (1) and Wheeler (2) assembled convincing evidence that the principal reaction involved a Diels-Alder addition mechanism. At the elevated temperatures used for heat bodying oils, methylene-interrupted diene and triene systems of linoleic and linolenic acid groups shift to conjugated forms. Then, these groups combine with other unsaturated fatty acid groups in the same and other glyceride molecules to form a Diels-Alder ring structure, giving crosslinked polymeric products of increased viscosity. Under the same conditions, conjugated triene formed from linolenate undergoes ring closure to form monomeric cyclic fatty acids by a similar mechanism (3).

When linoleic and linolenic acid soaps were heated under alkali conjugation conditions, the Diels-Alder reactions also occurred, and gave higher yield of polymeric fatty soaps and monomeric cyclic fatty soaps than thermal treatment alone (4). From a consideration of these reactions, an investigation was made in 1959 of the reaction of ethylene, the simplest dienophile, with the conjugated triene system formed by alkali treatment at elevated temperatures of linolenic acid in linseed oil (5). Analysis by gas liquid chromatography (GLC) of completely hydrogenated monomeric fatty esters prepared from these reaction products indicated that ethylene reacted by the Diels-Alder mechanism to yield an adduct with 20 carbon atoms in the fatty acid chain, i.e., a new, single peak appeared in the GLC curve with a retention time appreciably greater than that of methyl stearate and of the methyl ester of the C-18 cyclic acid. The same peak was found when the reaction was carried out with safflower fatty acids, showing that conjugated linoleic acid reacted similarly. In later studies, ethylene was reacted with a model compound, 9,11,-*trans,trans*-octadecadienoic acid, and analysis of the resultant product confirmed the proposed Diels-Alder reaction (6). Kaufmann and Buescher later reported the reaction of ethylene, propylene, and 1-butene with the model conjugated diene and triene systems, i.e., sorbic acid, 9,11-octadecadienoic acid, and *beta*-eleostearic acid, by the same mechanism (7).

The present report describes the reactions of soybean oil soapstock and derived fatty acids, a byproduct of alkali refining, with ethylene or 1-butene to form Diels-Alder adducts. Dry soybean soapstock consisted of ca. 70% total fatty acids which had about the same content of linoleic and linolenic acids as the oil. Soapstock was, therefore, a relatively low cost source of these polyunsaturated acids and a practical starting material for preparing the proposed adducts.

PROCEDURES AND ANALYSES

Soapstock obtained from a commercial refinery contained 41.2% moisture, 65.3% total fatty acids on a dry basis, and a fatty acid composition of: palmitic, 17.0%; stearic, 2.8%; oleic, 16.8%; linoleic, 57.3%; and linolenic, 6.2%. One series of reactions was made with ethylene (technical grade, Matheson Chemical Co., (Joliet, IL) or 1-butene (chemically pure, Matheson Chemical Co.) and untreated soapstock; another series was made with fatty acids. These fatty acids were prepared by saponifying the soapstock with excess alkali, reacidifying to pH 1 at 80-100 C, and extracting with hexane. The recovered dark colored fatty acids were reacted without being distilled.

Reactions to prepare ethylene and 1-butene adducts were conducted in a 1-liter Magna Dash Autoclave (Autoclave Engineers, Erie, PA) designed for a maximum working pressure of 5000 psi. A stainless steel reactor such as this was not recommended for extended use with high pressure caustic reactions with water was the solvent. Repeated reactions done at this laboratory showed that use of glycol as a solvent did not cause stress cracking. The autoclave was charged with wet soapstock or crude fatty acids, sodium hydroxide, 1 mole in excess of saponification per mole fatty acids, and ethylene glycol or diethylene glycol as solvent, usually 3 parts by wt per part soapstock or fatty acid.

For ethylene reactions, the autoclave was evacuated, pressurized with nitrogen, evacuated, and pressurized with ethylene at room temperature to the desired level. The pressure in the autoclave increased when heated to the reaction temperature. For example, when the initial ethylene pressure was 400 psi, the pressure was ca. 1000 psi at reaction temperature.

When reactions were conducted with 1-butene, the soapstock or fatty acids, solvent, and alkali were added to the autoclave which was evacuated and cooled to ca. -20 C. 1-Butene was passed from a cylinder through a coil immersed in a dry ice bath and collected as liquid in a graduate cylinder. This liquefied 1-butene was drawn into the autoclave in an amount sufficient to give the desired pressure at the reaction temperature.

In preliminary studies, reaction temperatures of 275 C, 300 C, and 325 C were investigated. Subsequently, a temperature of 290-295 C was used.

Following a reaction, the autoclave was cooled to room temperature and excess pressure was vented. Reaction products issued from the vent as a thick foam. The products were combined with hexane and centrifuged to remove small amounts of hexane soluble polyolefin from ethylene or butene polymerization. The aqueous layer containing the glycol soap was acidified to ca. pH 1.5 with dilute sulfuric acid to convert soaps to fatty acids. The fatty acid layer was washed, dried, and converted to methyl esters by refluxings4 hr with ca. 5 moles methanol per mole fatty acid and 1% sulfuric acid. Crude esters were washed with water, dried, and steam distilled to 250 C pot temperature and

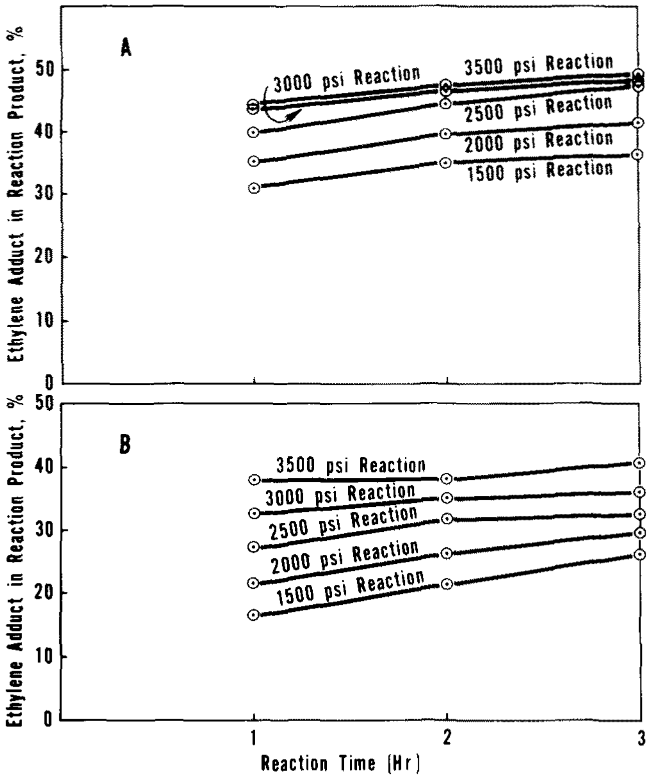

FIG. 1. (A) Relation of reaction pressure and time on yields of ethylene adduct from soapstock fatty acids. (B) Relation of reaction pressure and time on yields of ethylene adduct from raw soy soapstock.

<0.1 mm Hg absolute, and distilled monomer and undistilled polymer fractions were weighed.

Ethylene and 1-butene adducts of ca. 98% purity were recovered by steam fractional distillation at ca. 0.05 mm Hg of monomeric fatty acid methyl esters from the respective reactions. A 3 ft x 1 in. glass Vigreaux column with a 2 in. diameter glass jacket wound with heating wire and insulated was used for batch fractional distillation.

To obtain saturated adducts, purified unsaturated adducts were hydrogenated at 200 C, 1000 psi, 0.2% of 5% palladium-on-carbon catalyst, 2 hr, to final iodine value (IV) of 3 or lower. Amides were prepared both from hydrogenated and unhydrogenated ethylene adduct methyl esters by the method of Kohlhase, et al., (8) with ammonium acetate catalyst. Unreacted esters were recovered from amides by several recrystallizations from acetone.

Products were analyzed for saponification value (9) and IV (10) by standard AOCS methods. Amide melting points were determined with a Fisher-Johns apparatus.

Ethylene adduct monomers were analyzed by GLC on an F&M 720 chromatograph with a 6 ft x 4 mm stainless steel column with 10% SE 30 on 80-100 mesh Chromosorb LAW using helium carrier gas with thermal detector at 320 C and column temperature of 250 C; 1-butene adduct monomers were analyzed similarly on a column packed with diethylene glycol succinate (DEGS).

RESULTS AND DISCUSSION

Yields of adduct from the reaction of alkali isomerized polyunsaturated fatty acid soaps with ethylene and 1-butene were related to several factors, including the amounts of solvent and excess alkali used, the temperature and time of reaction, the type and amount of agitation, the ratio of monoene to diene, and the reaction pressure. After brief experimental tests of these factors, major variables affecting adduct yields were estimated to be reaction time, temperature, and pressure with constant head space. A reaction temperature of 290-295 C was used in reported reactions because polymer yield was greater at higher temperatures and reaction time was prolonged at lower temperatures. Conditions which favored the formation of monomeric adducts also minimized dimer and high polymeric adducts because both were products of the polyunsaturated fatty acids. A diethylene glycol fatty acid ratio of 3 and 1 mole excess NaOH over saponification were used in the reported tests although they were not necessarily the economic optimum if all factors were considered in a cost estimate.

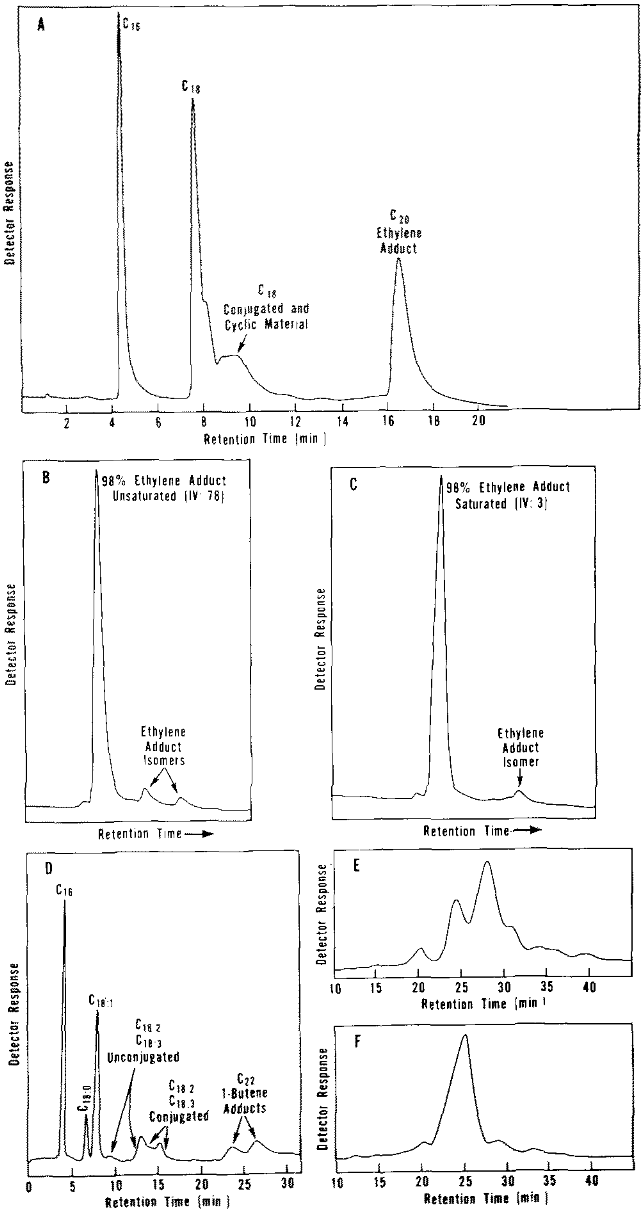

FIG. 2. Gas liquid chromatography (GLC) of distilled monomeric methyl esters from an ethylene adduct reaction; column packed with 10% SE 30 on 80-100 mesh Chromosorb LAW. (B) GLC of C-20 ethylene adduct methyl ester; column packed with 10% SE 30 on 80-100 mesh Chromosorb LAW. (C) GLC of hydrogenated C-20 ethylene adduct (iodine value [IV] = 3) methyl ester; column packed with 10% SE 30 on 80-100 mesh Chromosorb LAW. (D) GLC of monomeric methyl esters from a 1-butene adduct reaction; column packed with 20% diethylene glycol succinate (DEGS). (E) GLC of purified 1-butene adduct; column packed with 20% DEGS. (F) GLC of purified, hydrogenated 1-butene adduct; column packed with 20% DEGS.

The relation of reaction pressure and time on yields of ethylene adduct from soapstock fatty acids is given in Figure 1A. Separate reactions were made to obtain points

TABLE I

Some Properties of Ethylene and 1-Butene Adduct Fatty Acid Methyl Esters

Adduct	Refractive index (20 C)	Wijs iodine value	Saponification equivalent[a]	Boiling point (C)[b]	Melting point (C)[e]	Amide melting point (C)
Ethylene						
Unsaturated	1.4698	77.5	320.4 (322)	$\frac{168\text{-}173}{193\text{-}200}$	8-15	90.5- 91.5[c]
Saturated	1.4617	3.0	319.5 (324)	$\frac{170\text{-}175}{193\text{-}200}$	10-15	119.5-123.5[d]
1-Butene						
Unsaturated	1.4705	75.6	350.8 (350)	185-190	8-15	--
Saturated	1.4650	2.3	355.7 (352)	--	10-15	--

[a] Theory value in parentheses.

[b] Absolute pressure measured after receiver and between dry ice trap and vacuum pump was 0.035 mm Hg; $\frac{\text{vapor temperature}}{\text{boiling liquid temperature}}$ while ca. 90% of esters steam distilled.

[c] Purity; 97% C-20, 97% amide, according to gas liquid chromatography (GLC) and %N.

[d] Purity; 95% C-20, 93% amide, according to GLC and %N.

[e] Point where esters become completely fluid.

on the curves, because conditions did not permit taking samples of sufficient size for distillation and accurate analysis for polymer and monomer during a reaction. Adduct yields, based on GLC analysis of vacuum distilled monomeric acid methyl esters, were calculated as a percentage of total monomeric and polymeric acid esters obtained from reaction products. Because of the difficulty of adding the exact amount of monoene to produce the desired pressure for each reaction at reaction temperature, some extrapolation of data was necessary to obtain the data given in Figures 1A and 1B.

In the maximum yield of ethylene adduct from soapstock fatty acids shown in Figure 1A, 50% represented almost 80% of theory, because the soapstock acids contained 63.5% polyunsaturates. On a wet soapstock basis, the yield was 19.5%. The data indicated that reaction times longer than 3 hr at 290 C, and pressures higher than 3500 psi produced only small increases in adduct yield.

The data given in Figure 1B indicated that conducting the reaction with raw soapstock instead of soapstock fatty acids resulted in a somewhat lower yield of adduct based on total fatty acids recovered from the reaction. In these reactions, most of the nonfatty acid material, exclusive of glycerine and other water solubles, was recovered in the distillation residue along with polymeric fatty acid esters as a dark viscous material. After 3 hr reaction at 3500 psi, the yield of adduct was ca. 65% of theory, or a maximum yield of 15.8% on a wet soapstock basis.

In reactions with 1-butene, the adduct failed to form readily. Significant yields were obtained only by preconjugation of the linolenate and linoleate with 1 mole excess NaOH at 180 C for 1 hr prior to the addition of 1-butene to the reactor. Yields with wet soapstock at 3800 psi of 1-butene and 5 hr reaction were 28.5% of theory and 6.9% on a wet soapstock basis.

By comparison, refined soybean oil was preconjugated in this manner with 1 mole excess NaOH at 180 C for 45 min, then reacted with 2800 psi of 1-butene at 305 C for 5 hr. The reaction product showed a 39.1% yield of theory which was 9.5% on a wet soapstock basis.

The GLC of distilled monomeric methyl esters from an ethylene adduct reaction is shown in Figure 2A. Relative retention time for the C-20 ethylene adduct peak from the air injection peak was 3.54 compared to palmitic. For unreacted soybean esters, the C-18 esters were eluted in a single peak. The shoulder and flat peak following the C-18 peak in Figure 2A were believed to be conjugated C-18 isomers of linoleate and linolenate and C-18 cyclic esters derived from linolenic acid during the reaction. Mixed esters shown in Figure 2A were fractionally steam distilled to yield the C-20 ethylene adduct ca. 98% pure (Fig. 2B). The main peak was believed to include all ethylene adduct isomers derived from linoleic acid, while the 2 following peaks probably were derived from linolenic acid, and had a double bond outside the cyclohexene ring. Hydrogenation of this distilled unsaturated adduct to an IV equal to 3 gave the saturated adduct (Fig. 2C). It was evident that hydrogenation removed one of the after peaks shown in Figure 2B, and this material probably was part of the main adduct peak.

The monomeric fatty methyl esters from the 1-butene adduct reaction gave the GLC in Figure 2D. Two major and about equal adduct peaks were obtained, apparently corresponding to the possible orientations of the cyclohexene side chains, axial or equatorial. Figure 2E illustrates a GLC curve for the 1-butene adduct esters after purification by fractional distillation. There were indications here of a number of isomeric butene adducts in the small flat peaks eluted both before and after the main peaks, which may have been formed with linolenic acid judging from the amounts indicated. Figure 2F was purified 1-butene adduct after hydrogenation. Many of the isomers had disappeared.

Some properties of the adduct fatty methyl esters (Fig. 2B) are presented in Table I. Despite the low estimated melting point of the unsaturated adduct methyl esters, the amide melting points were higher than expected from comparison with stearamide, oleamide, and erucamide. Although the amides were recrystallized from acetone several times, there were indications from Kjeldahl nitrogen analyses of some ester contamination of amides which would have been expected to lower the melting points. Mass spectra gave major peaks at 352 for saturate 1-butene adduct and 322 for unsaturated ethylene adduct. Ions of mass 81 and 80 indicated the presence of a cyclohexane or cyclohexene ring in the 2 1-butene adduct samples. A 2 carbon side chain was shown for 1-butene adduct by an ion with 29 less mass units than the base ion.

The properties of the ethylene and butene adducts suggested they may have applications where readily available natural fatty acids and their derivatives do not have optimum properties for certain industrial uses. For example, the saturated and unsaturated C-20 adduct amides were tested as additives for polyethylene film by a commercial company. In comparison with commercial erucamide they gave slightly better film clarity, but showed slightly less effectiveness in preventing blocking.

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