# Preparation of Vinyl Ether Monomers from Conjugated Soybean Alcohol[1]

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Recent work at this laboratory on the polymerization of vinyl ether monomers derived from conjugated soybean fatty alcohol has stimulated considerable industrial interest. New processing studies on the preparation of the monomers are described in the present work, which was carried out in conjunction with a pilot-plant program to prepare samples of conjugated soybean-isobutyl vinyl ether copolymers for industrial evaluation.

Of the various methods reported in the literature for preparing vinyl ethers, one that appears well-suited to large-scale production consists of vinylation with acetylene in the presence of alkali catalysts. Such vinylations have been carried out previously under pressure with octadecyl and oleyl alcohols (1, 2). Reppe (3) has indicated that pressure is not required for the vinylation of high-boiling alcohols. Vinyl ethers of soybean and linseed fatty alcohols were prepared at atmospheric pressure and reported by coworkers, Teeter *et al.* (4). The present investigations include preparation of monomers by atmospheric reaction of acetylene with soybean fatty alcohol in the presence of potassium hydroxide catalyst and a study of purification of crude monomers by vacuum distillation.

Copolymers prepared from these fatty vinyl ether monomers have shown promise for industrial use as baked coatings for metal (5, 6). The films possess such properties as good adhesion to metals, flexibility, resistance to abrasion, and resistance to acids, alkalies, and solvents.

## Experimental

*Materials and Methods.* Unadol 40, a mixture of straight-chain, saturated and unsaturated, monohydric alcohols derived by the sodium reduction of soybean fatty esters was used. The approximate composition of the soybean fatty alcohols was 53% linoleyl, 8% linolenyl, 25% oleyl, 8% cetyl, 5% stearyl, and a trace of arachidyl alcohol.

The alcohol is available from commercial sources with the double bonds predominantly in either conjugated or nonconjugated positions. The conjugated form was used primarily although the nonconjugated form was employed in the first four vinylation runs.

Commercial "welding"-grade acetylene, analyzing 99.5% acetylene content on an acetone-free basis, was employed. No attempt was made to remove acetone vaporized with the acetylene from the cylinder.

Potassium hydroxide (C. P. pellets) was used as the catalyst. The pellets were either added directly to the fatty alcohol, or they were dissolved in absolute methanol or water prior to addition to the fatty alcohol.

Vinyl ether content was determined by the iodometric method as described by Teeter *et al.* (4).

Solid material in the vinylation mixture was determined by separating in an International centrifuge at 2,000 r.p.m.

*Apparatus and Procedure.* A sketch of the 8-liter reactor and the apparatus accessories used for the vinylation is shown in Figure 1. A series of experiments established that the highest degree of contact efficiency developed between acetylene and fatty alcohol when the acetylene was fed directly below a flat-blade turbine agitator placed in a baffled stainless-steel reactor.

The distillation apparatus consisted of a 5-liter flask, heating mantle, Vigreux distillation-column, condenser, receiver, carbon dioxide-acetone cold trap, vacuum gage, and vacuum pump. The Vigreux column, which was insulated with asbestos tape, functioned also as a foam and liquid entrainment separator. Controlled heat was applied to the Vigreux column by electrical resistance wire to regulate the reflux rate and product take-off rate.

In the vinylation procedure 4,200 g. of soybean fatty alcohol were charged to the reaction vessel and preheated in the oil bath. Nitrogen was fed to the surface of the alcohol mixture to inhibit surface oxidation. The catalyst (3 to 5 g. of KOH per 100 g. of fatty alcohol) was added during the heat-up period, and the acetylene feed was started slowly after the temperature had reached 150°C. When the vinylation control temperature was reached, the acetylene flow was increased to a rate of 10 liters/min. Exothermic heat was controlled by reducing the heat input and lowering a cooling coil into the reaction mixture as required. The progress of the reaction was followed by taking periodic samples for vinyl ether content. When maximum vinylation had been obtained, the acetylene feed was replaced with nitrogen and the mixture was cooled to room temperature. The crude vinylated mixture was purified by vacuum distillation in either one or two steps.

A sufficiently pure product was obtained by a single distillation if the fatty alcohol was heated, prior to the vinylation step, under vacuum to 175°C. to convert the catalyst to potassium alkoxide. Water or methanol used for solution of the catalyst was also removed in this step. During removal of the water formed in this reaction the fatty alcohol turned to a red-amber color. The hot solution was transferred to the reactor and vinylated. The crude vinylated mixture was then distilled at approximately 1–2 mm. Hg. pressure, using no reflux in the Vigreux column.

When no previnylation treatment was used, two successive distillations were required to purify the crude vinyl ether. The first was conducted rapidly without fractionation. Then the distillate was redistilled with fractionation while a forerun of about 6%

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[1] Presented at the fall meeting, American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.

[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

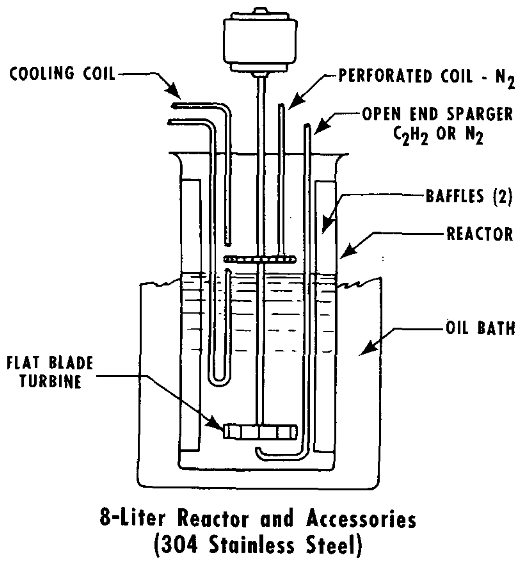

Fig. 1. Eight-liter reactor and accessories.

of the charge was removed. The remaining material was distilled without fractionation.

## Results and Discussion

*Monomer Preparation.* Vinylation reaction rate is controlled by the flow rate of acetylene. In Test No. 1, Figure 2, a relatively low acetylene flow rate was used, and a vinyl ether content of 70% was attained only after 4 hrs. of reaction. Further increases of acetylene to 2.4 liters/min./kg. resulted in a reduction of reaction time, high reaction rate, and high yield. Vinylation curves for five tests, showing the effect of increasing acetylene flow rate, are presented in Figure 2. In several of these runs the vinyl ether content of the reaction mixture reached 86–87%. The curve for Test No. 3 reflects the changes in slope when the acetylene flow rate is increased within the same run. The curvilinear relationship shown in Figure 3 is obtained when Figure 2 is replotted as the percentage of vinyl ether produced per minute *vs.* acetylene flow rate.

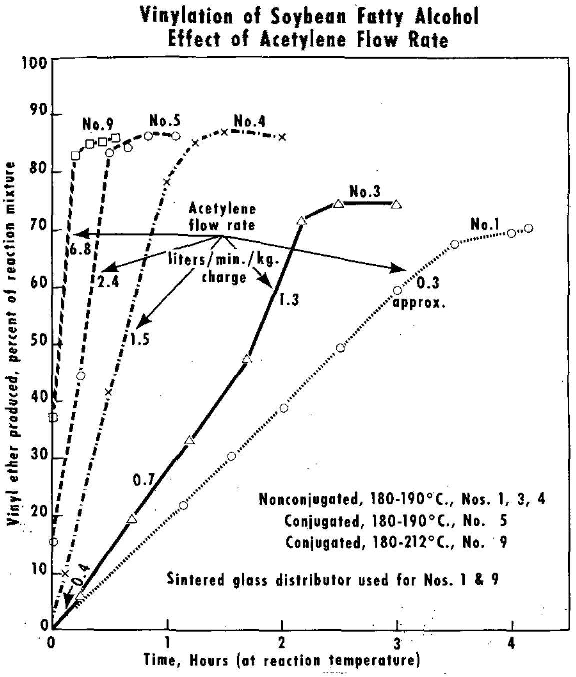

Fig. 2. Vinylation of soybean fatty alcohol. Effect of acetylene flow rate.

An exceedingly fast vinylation rate was achieved when the reaction was conducted in a simple column with a sintered glass ebullator. No attempt was made to control the temperature. A vinyl ether content of 82.3% was reached in 13 min. after the fatty alcohol charge had reached 180°C. The vinylation curve, No. 9, is shown in Figure 2 for comparison with previous controlled-temperature runs. Considerable heat was evolved and, although the heat source was removed, the temperature continued to rise to a maximum of 212°C. An abnormally high concentration of solids however was formed at these high temperatures. This situation offers additional purification problems and precludes the experiment as a recommended procedure.

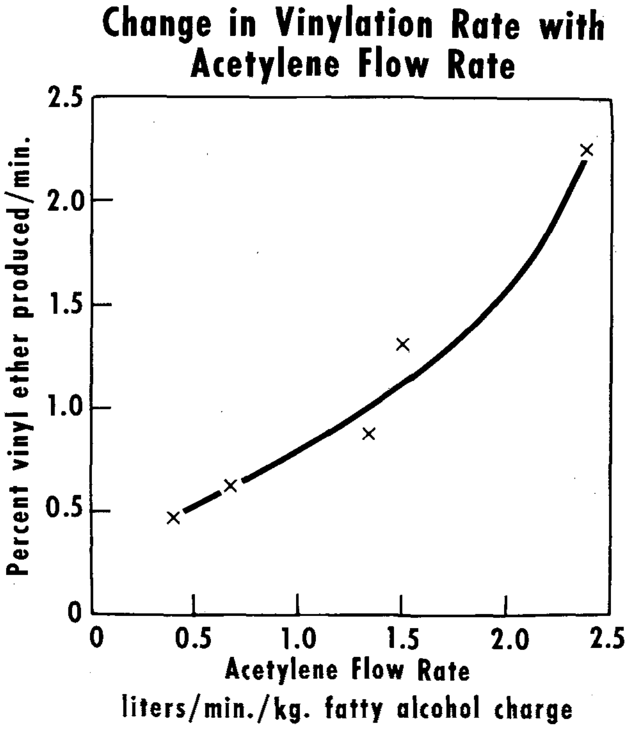

Fig. 3. Change in vinylation rate with acetylene flow rate.

Moderate foaming was experienced near the end of each vinylation run although little to no foaming occurred for rapid vinylations. When the reaction was continued for periods longer than 45–50 min. considerable foaming was encountered in the late vinylation stages.

Absorption of acetylene in the vinylation averaged 61% for three runs where high flow rates were used. This relatively low value would be expected without the re-use of acetylene. On a commercial scale the acetylene would be recycled for economic reasons.

Temperatures for the vinylation were studied over the range of 170–200°C. while acetylene flow rates at 2.4 liters/min./kg. charge were maintained. Vinylation curves for a series of runs at three temperature levels are shown in Figure 4. Control of the

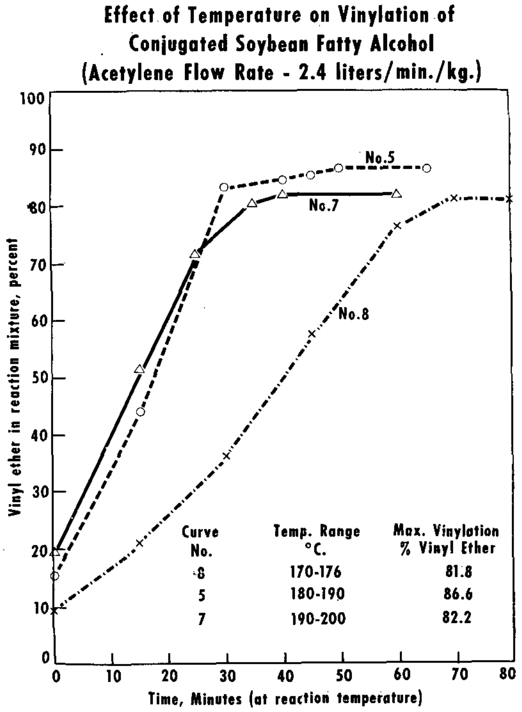

FIG. 4. Effect of temperature on vinylation of conjugated soybean fatty alcohol.

temperature between 180°–190°C. resulted in a high reaction rate with an optimum yield of 86.6% vinyl ether. Similar vinylation yields were obtained whether conjugated or nonconjugated fatty alcohols were used. Increases in conjugation during the vinylation reaction are represented by diene and triene values given in Table I.

The amount of KOH catalyst used was investigated over the range of 3–5%, based on the weight of fatty alcohol. The data presented in Table II indicate that higher yields are obtained at the 4 and 5% levels; however, at 4%, a smaller concentration of solids is produced in the reaction mixtures. Solids material in the reaction mixture was less with lower catalyst concentration. Test 17 shows that the reaction rate was significantly increased at the 3% level when the temperature was increased to 190°C.

While methods for simplifying catalyst introduction into the fatty alcohol were investigated, it was found that solid KOH pellets could be dissolved in the fatty alcohol during the heat-up period. This method gave the same yield as the former procedure of adding the catalyst as a solution in methanol. If the catalyst was introduced as a 48% aqueous solution, severe foaming, a darker product, and lower vinyl ether yields occurred.

TABLE I

Increased Conjugation of Soybean Fatty Alcohols After Atmospheric Vinylation at 180°–190°C.

| Material | Diene | Triene |
|---|---|---|
| | % | % |
| Nonconjugated soybean fatty alcohol[a] | 1.0 | 0.15 |
| Pure vinyl ether derived from [a] | 40.0 | 0.66 |
| Conjugated soybean fatty alcohol[b] | 20.7 | 0.80 |
| Pure vinyl ether derived from [b] | 37.6 | 0.30 |

[a] Used for tests 1–4.
[b] Used for tests 5–17.

*Monomer Purification.* Less than 98% vinyl ether content was realized from the first crude products, a result which was too low for successful polymerization. After the distillate was redistilled to yield a 98–99% vinyl ether product, an over-all average yield in five runs was obtained of 73%.

TABLE II

Effect of KOH Concentration Level on Vinyl Ether Yield and Solids Content of Vinylation Mixture

| Test No. | KOH level[a] | Temperature range | Time to reach max. vinylation | Solids materials in reaction mixture | Yield, % of theory |
|---|---|---|---|---|---|
| | % | °C. | min. | % | |
| 14 | 5 | 180–185 | 55 | 34.2 | 86.6 |
| 15 | 4 | 180–185 | 57 | 21.9 | 86.9 |
| 16 | 3 | 180–200 | 75 | 17.8 | 80.1 |
| 17 | 3 | 190–195 | 45 | 20.6 | 81.0 |

[a] Basis: g. of 86.4% KOH pellets per 100 g. of fatty alcohol.

The purification procedure was simplified when the catalyst was converted to potassium alkoxide before vinylation. As a result, only one distillation was required to produce monomer product containing 98–99% vinyl ether. The vinyl ether product was virtually colorless and was obtained with an average yield of 88.5%. Distillation data are given in Table III.

Approximately 10% of the vinyl ether remained in the pot residue after distillation. The residue generally hardened to a porous solid upon cooling; nitrogen was used to break the vacuum. No attempt was made to recover the vinyl ether in this fraction.

TABLE III

Purification of Crude Vinyl Ethers by Vacuum Distillation

| Test No. | First distillation | | Boiling-point range | Pressure range | Redistillation | | Over-all vinyl ether yield |
|---|---|---|---|---|---|---|---|
| | Vinyl ether content of | | | | Vinyl ether content of | | |
| | Charge | Product | | | Forerun | Product | |
| | % | % | °C. | microns | % | % | % |
| 2-Step distillation | | | | | | | |
| 6 | 86.8 | 98.8 | 165–192[c] | 580–1400[c] | 99.2 | 98.8 | 77.4 |
| 7 | 82.0 | 97.0[a] | 163–182 | 580–1500 | 100.0 | 99.5 | 82.5 |
| 8 | 78.8 | 96.1 | 156–190 | 440–600 | 91.1 | 96.8 | 62.4 |
| 12 | 82.5 | 97.2 | ...... | 580–1400 | 91.1 | 97.6 | 76.0 |
| 5 + 6 | 89.2[b] | 96.3 | 169–198 | 700–1600 | 95.1 | 99.4 | 66.7 |
| Average | ...... | ...... | ...... | ...... | ...... | 98.4 | 73.0 |
| 1-Step distillation | | | | | | | |
| 13 | 83.4 | 98.9 | ......[d] | 920–3700[d] | ...... | ...... | 89.5 |
| 15 | 86.8 | 98.1 | 172–199 | 1300–4200 | ...... | ...... | 84.5 |
| 16 | 82.1 | 99.5 | ...... | 400–1100 | ...... | ...... | 90.1 |
| 17 | 84.8 | 99.6 | 168–185 | 2200–2100 | ...... | ...... | 89.7 |
| Average | ...... | 99.0 | ...... | ...... | ...... | ...... | 88.5 |

[a] Estimate. [b] Value is high on account of solids removed by centrifuging. [c] Data for redistillation. [d] Data for first distillation.

Solids were separated by centrifugation in one experiment to study the over-all effect on distillation yield. Normally, solids from the vinylation reaction were included in the feed to the distillation flask. The centrifugate was separated and distilled, but a low yield resulted because the vinyl ether entrained in the centrifuged solids constituted a substantial loss. A method was developed for recovering the vinyl ether entrained in the centrifuged solids. Four volumes of water were used to disperse the solids, and the resulting mixture was neutralized to pH 7.0 with 5% aqueous $H_2SO_4$. Upon neutralization a 2-phase separation resulted. The lower layer of water analyzed 0.2% vinyl ether whereas the upper vinyl ether layer contained 73.8%. The upper layer was decanted and redistilled. Recovery of pure vinyl ether from both the centrifugate and the treated solids however did not result in total yield improvement.

*Product, Yield, and Quality.* Pure vinyl ether monomer was prepared with an average over-all weight yield of 80.2%, based on the weight of fatty alcohol. Yield and quality of vinyl ethers produced are presented in Table IV.

If the alkali is all converted to potassium alkoxide and the alkali-reacted alcohol is considered as not being available for vinylation, only a calculated yield of 79.4% of theory is possible. Because yields up to 89.9% were obtained in experimental work, the assumption appears invalid.

The purified vinyl ethers were successfully copolymerized with isobutyl vinyl ether by using $SnCl_4$ catalyst to produce copolymers in the molecular weight range of 4,000–9,500. The polymers were clear, viscous liquids that possessed Gardner-Holdt viscosities of Z—6+ and were in the range of Gardner color values from water white to No. 4. This work will be described in a subsequent publication.

TABLE IV

Soybean Vinyl Ether Yields and Quality

| Test No. | Crude-vinyl ether yield | | Distilled vinyl ether | | |
|---|---|---|---|---|---|
| | % of theory | G. vinyl ether 100 g. ROH[b] | Yield g. vinyl ether 100 g. ROH[b] | Gardner color | Vinyl ether content |
| | | | | | % |
| 4[a] | 89.9 | 97.3 | ...... | ...... | ...... |
| 5[a] | 88.5 | 96.9 | ...... | ...... | ...... |
| 6[a] | 88.8 | 97.1 | ...... | ...... | ...... |
| 13[a] | 83.6 | 91.5 | 81.9[c] | 1 | 98.9 |
| 15[a] | 86.9 | 95.1 | 80.4[c] | 1–2 | 98.1 |
| 16 | ...... | ...... | 78.9[c] | 1 | 99.5 |
| 17 | ...... | ...... | 79.5[c] | 1 | 99.6 |
| Average | 87.5 | 95.6 | 80.2 | ...... | 99.0 |

[a] Conducted at optimum vinylation conditions.

[b] ROH = fatty alcohol charge.

[c] Based on single distillation recovery.

## Summary

The atmospheric vinylation of conjugated or nonconjugated soybean fatty alcohols has been accomplished in reaction periods of less than 1 hr. with high flow rates of acetylene. Optimum vinylation conditions were maintained when solid KOH pellets were used at a concentration level of 4% and the reaction was conducted at 180°–190°C. Similar levels of conjugation in vinyl ethers were observed, using either nonconjugated or conjugated starting fatty alcohols. Crude vinyl ether yields averaged 87.5%.

Higher recovery of the purified vinyl ether resulted when a heat treatment was used to convert the catalyst to potassium alkoxide prior to vinylation. A product containing 98–99% vinyl ether was obtained by a single vacuum-distillation step with a yield increase of 15% over the 2-step distillation method. This process yielded 80.2 parts by weight of pure vinyl ether per 100 parts of fatty alcohol charge.

Fatty vinyl ether monomers produced by either of the two alternate purification methods were successfully copolymerized with isobutyl vinyl ethers.

## Acknowledgment

The authors wish to express their appreciation to L. E. Gast and E. J. Dufek for technical assistance, C. A. Glass for ultraviolet analyses, and A. Clark for vinyl ether analyses.

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[Received April 20, 1959]