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In-situ epoxidation of linseed oil in the presence of ion-exchange resins

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Summary

Linseed oil has been epoxidised *in situ* with hydrogen peroxide and acetic acid in the presence of ion-exchange resins (Zeo-Karb 225 and modified Lignosite) as catalysts. Alkali-refined oil was used. The parameters studied were time, temperature, the amount of catalyst, and the hydrogen peroxide and acetic acid concentrations. The maximum oxirane content was 8.8 per cent when Zeo-Karb 225 was used, and 5.6 per cent in case of modified Lignosite.

Keywords

Raw materials: oils
linseed oil

Raw materials: plasticisers
epoxidised oil

L'époxydation in situ de l'huile de lin en présence de résines échangeuses d'ions

Résumé

L'huile de lin a été époxydisée *in situ* avec le peroxyde d'hydrogène et l'acide acétique en présence de certaines résines échangeuses d'ions (Zéo-Karb 225 et Lignosite modifié) en tant que catalysateurs. On a utilisé l'huile de lin raffinée par traitement avec alcali. Les paramètres étudiés furent, la durée et la température de la réaction, la teneur en catalysateur, et les concentrations de peroxyde d'hydrogène et d'acide acétique. En utilisant la Zéo-karb 225 on a obtenu une teneur maximale en oxirane de 8,8% et de 5,6% dans le cas de Lignosite modifiée.

In-situ Epoxidierung von Leinöl in Gegenwart von Jonenaustauschharzen

Zusammenfassung

Leinöl wurde in-situ mit Wasserstoffsuperoxid und Essigsäure in Gegenwart von Jonenaustauschharzen (Zeo-Karb 225 und modifiziertem Lignosite) als Katalysatoren epoxidiert. Es wurde alkali-raffiniertes Leinöl benutzt. Die untersuchten Parameter waren Zeit, Temperatur, Katalysatorenmenge und die Wasserstoffsuperoxid-sowie Essigsäurekonzentration. Wenn Zeo-Karb 225 benutzt wurde, war der Höchstgehalt an Oxiran 8,8% und mit modifiziertem Lignosite 5,6%.

Introduction

Refs. 1-6

The catalysts used in the epoxidation of oils are of two main types: the first includes aqueous catalysts or solids dissolved in the reaction medium (homogeneous phase reaction); the second comprises solid catalysts, usually ion-exchange resins, which do not dissolve in the reaction medium during the course of reaction, so that a two-phase (solid : liquid) reaction takes place. In general, insoluble solid catalysts are more desirable, because they minimise epoxide ring opening[1]; are easy to separate from the reaction medium; and can be regenerated for repeated use. Special resins crosslinked only to a small extent yield mostly by-products, whilst resins with a low metal content give the best results[2].

Epoxidised linseed oil of 9.1 per cent oxirane content has been prepared by Rheineck and Wako[3], by de Clerck's technique[4], using 23 per cent Dowex 50W-X8 as catalyst. Nagiah[5] has prepared epoxidised linseed oil of 8.7 per cent oxirane content in the presence of 15 per cent Amberlite CG-[illegible] as catalyst.

To the best of the authors' knowledge, modified Lignosite (a formaldehyde-treated lignin calcium sulfonate) has not previously been used as an epoxidation catalyst for linseed oil. It was used in their previous work for the epoxidation of dehydrated castor oil[6].

Experimental

Refs. 7-9

Materials used were as follows:

Linseed oil Alkali refined; iodine value (IV) 173.

Hydrogen peroxide Chemically pure. Strength determined precisely by the thiosulfate method[7] and found to be 32 per cent.

Zeo-Karb 225 A crosslinked polystyrene sulfonic acid (product of the Permutit Co.) with a dark yellow colour and rather coarse average particle size: granules passed through a 14 mesh but were retained by a 52 mesh sieve (—14—52). Sulfur content approximately 17 per cent, sulfonyl group content approximately 44 per cent.

Lignosite This is a fine, tan coloured powder, obtained from Georgia-Pacific, Bellingham Division, USA. Total sulfur content approximately 6.6 per cent, sulfonyl-group content approximately 14 per cent.

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Preparation of modified Lignosite

Refs. 8-13

The Lignosite was modified by heating with a mixture of concentrated sulfuric acid and formaldehyde at 140°C for 24 hours[8,9]. The product was a very hard, black, solid resin, which was insoluble in water. This was crushed and sieved to the mesh number (—20 – 50) and the sieved resin particles were washed with dilute hydrochloric acid until calcium free[10], and then with distilled water to remove the acidity. They were then washed with ethyl alcohol and dried under reduced pressure at 50°C.

Epoxidation

The oil was mixed with the required amount of acetic acid, and the required percentage of catalyst added, together with benzene, which served as the reaction medium. Continual moderate stirring of the mixture during the run is very important. With the reaction mixture at the correct temperature, hydrogen peroxide was added dropwise for a period of two hours*. The reaction was considered to begin when the first drop of hydrogen peroxide was added. At the end of the experiment the mixture was poured on to ice and immediately filtered. The residue was transferred to a separating funnel, the water layer was separated, and the oily layer was washed with warm distilled water until acid free, and then centrifuged and finally dried under vacuum at 40°C.

Oxirane content

The oxirane content was determined volumetrically by titrating the sample dissolved in benzene directly with 0.1 N hydrogen bromide in acetic acid (Durbetaki's reagent) using Crystal Violet as indicator[11,12].

Iodine value

The Woburn[13] method of determining the IV was employed.

Results and discussion

The *in situ* epoxidation of linseed oil was fully investigated using as catalysts: lignosulfonic acid polymer (modified Lignosite); a natural polymer sulfonic acid, and Zeo-Karb 225; a synthetic polymer sulfonic acid. Test runs were carried out to determine the conditions which give the highest oxirane content. The parameters studied were the reaction time and temperature, the amount of catalyst and the concentration of the epoxidation reagents (hydrogen peroxide and acetic acid).

Effect of time

Two series of experiments were performed to find out the effect of time on the process of epoxidation of linseed oil. The first series of reactions was catalysed by modified-Lignosite, the second by Zeo-Karb 225. The reaction conditions were the same in the two series, except that the amount of catalyst was 25 per cent in the first and 15 per cent the second. The temperature was fixed at 50°C, and the molar ratio of oil: acetic acid: hydrogen peroxide was 1:6:6 in all experiments. The results obtained are shown graphically in Fig. 1.

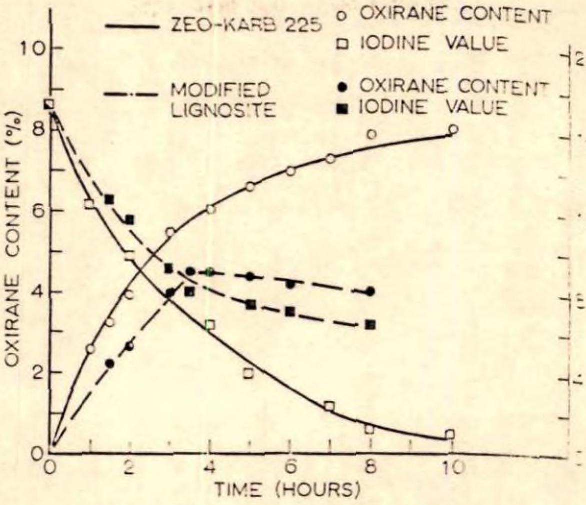

Fig. 1. Effect of time on the epoxidation process

Fig. 1 shows that modified Lignosite produces maximum epoxidation in a reaction time of 3.5 hours, after which the oxirane content decreases. On the other hand, the IV decreases with time, indicating that the double-bonds are opened in spite of the decrease in oxirane content. This means that fission of epoxide rings occurs with time; thus an acetoxy-hydroxy compound is formed as a byproduct.

It is also clear that using Zeo-Karb 225, no depression of oxirane content is evident up to a reaction time of 10 hours.

Effect of temperature

Two other series of experiments were performed to find the effect of temperature on epoxidation. The molar ratio of oil : acetic acid : hydrogen peroxide in all experiments was 1 : 6 : 6. The reaction time was 3.5 hours, and the amount of catalyst was 25 per cent for the modified Lignosite series; for the Zeo-Karb 225 series, the reaction time was four hours and the amount of catalyst was 15 per cent.

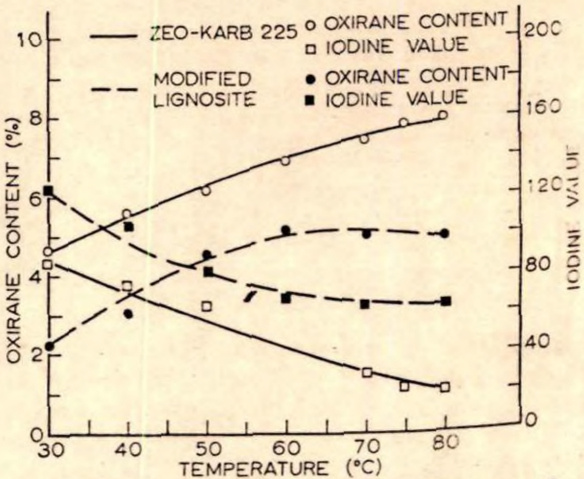

Fig. 2. Effect of temperature on the epoxidation process

Fig. 2 illustrates the effect of reaction temperature on IV and the oxirane content. Whilst modified Lignosite produces maximum oxirane content at 60°C, Zeo-Karb 225 catalyses the epoxidation progressively as the reaction temperature increases. On the other hand, the iodine value decreases gradually in both cases; this means that the small depression

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*In the experiments with reaction time of one hour, the hydrogen peroxide was added over a period of half an hour; in those of 1.5 hours reaction time, the hydrogen peroxide was added over a period of one hour.

observed in oxirane content at above 60°C with modified Lignosite may be due to fission of the epoxy groups to give saturated products.

Effect of catalyst

In view of the above results, the reaction time was fixed at 3.5 hours and the temperature at 60°C for the modified Lignosite series, and for Zeo-Karb 225 the corresponding figures were four hours and 75°C. The molar ratio of oil : acetic acid : hydrogen peroxide was 1:6:6 in all experiments.

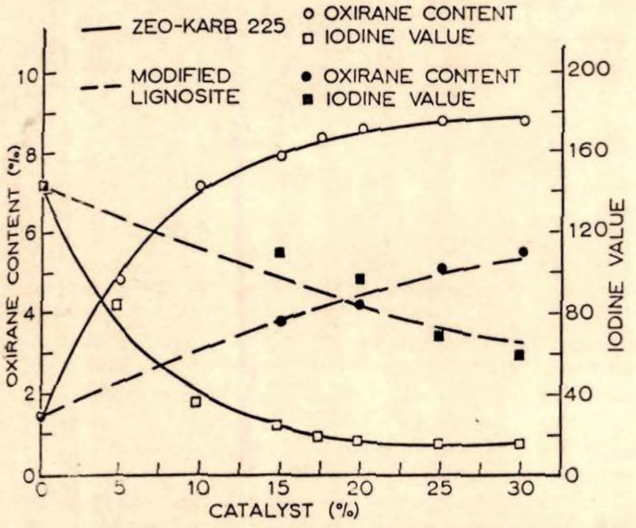

Fig. 3. Effect of choice of catalyst on the epoxidation process

The two oxirane curves in Fig. 3 show that the oxirane content increases with increasing amounts of catalyst. With modified Lignosite, the oxirane content is always lower, and 25 per cent catalyst is needed to produce an oxirane content of 5.10 per cent. With Zeo-Karb 225, 17.5 per cent catalyst is sufficient to produce an oxirane content of 8.30 per cent.

Effect of acetic acid

The effect of acetic acid was studied in two series of experiments to select the most suitable amount of acetic acid, which gives the highest oxirane content using both modified Lignosite and Zeo-Karb 225. The reaction conditions in the first series were reaction time 3.5 hours, reaction temperature 60°C, modified Lignosite catalyst concentration 25 per cent; and in the second series, the reaction time was four hours, reaction temperature 75°C, Zeo-Karb 225 content 17.5 per cent. The concentration of hydrogen peroxide in the two series was fixed at six moles/mole of oil.

The curves *showing the influence* of acetic acid concentration in the epoxidation reaction are given in Fig. 4.

With modified Lignosite, *there is a small increase in oxirane* content with an increase in acetic acid content until a value of about 5.10 per cent is reached at six moles of acetic acid per mole of oil. Using Zeo-Karb 225, the oxirane content is always higher; the maximum (8.40 per cent) is reached when between 5.5 and 6.0 moles of acetic acid per mole oil are used.

Effect of hydrogen peroxide

Finally, the effect of hydrogen peroxide concentration was studied in two series. The reaction conditions selected were 3.5 hours reaction time, at 60°C and with 25 per cent modified Lignosite in the first series, and four hours reaction time, 75°C, and 17.5 per cent Zeo-Karb 225 catalyst in the second. The amount of acetic acid in the two series was fixed at 5.5 moles/mole of oil. The changes of oxirane content and IV with hydrogen peroxide content are shown in Fig. 5.

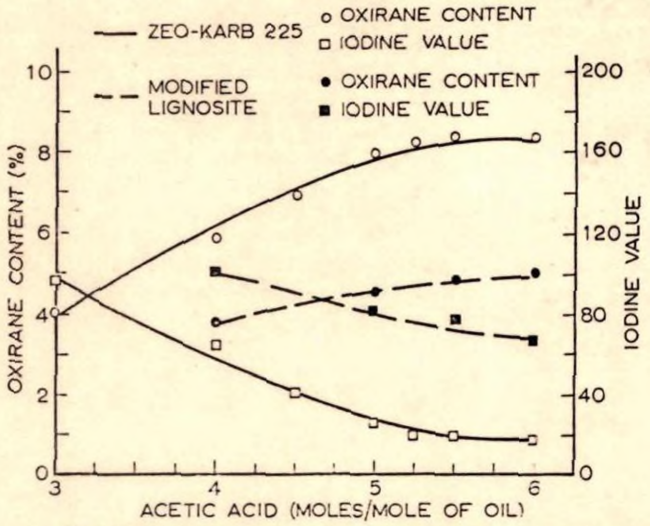

Fig. 4. Effect of acetic acid on the epoxidation process

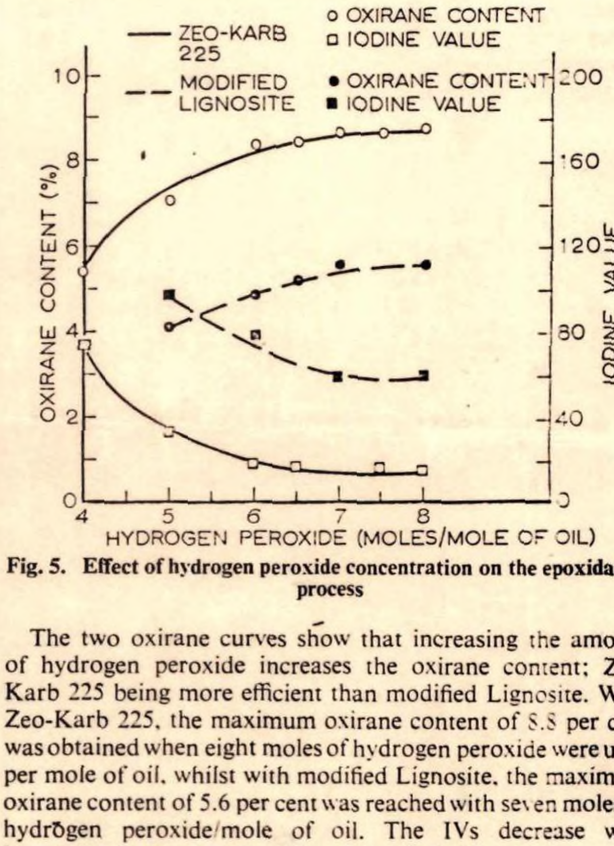

Fig. 5. Effect of hydrogen peroxide concentration on the epoxidation process

The two oxirane curves show that increasing the amount of hydrogen peroxide increases the oxirane content; Zeo-Karb 225 being more efficient than modified Lignosite. With Zeo-Karb 225, the maximum oxirane content of 8.8 per cent was obtained when eight moles of hydrogen peroxide were used per mole of oil, whilst with modified Lignosite, the maximum oxirane content of 5.6 per cent was reached with seven moles of hydrogen peroxide/mole of oil. The IVs decrease with increasing hydrogen peroxide content in both cases.

Conclusions

The optimum conditions for the *in situ* epoxidation of linseed oil, using solid sulfonated synthetic and modified, naturally occurring polymers as catalysts, have been obtained. Zeo-Karb 225 is found to be more efficient than modified Lignosite, which may be attributed to the higher $—SO_3H$ content of the former and its attachment to an aromatic residue.

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References

1. Daroowala, F. E., and Desikasher, N., *Indian Oil J.*, 1965, **31,** (3), 51.
2. Chadwick, A. F., Barlow, D. O., D'Addieco, A. A., and Wallace, J. G., *J. Am. Oil Chemists' Soc.*, 1958, **35,** 355.
3. Rheineck, A. E., and Wako, S., *J. Paint Techn.*, 1973, **45** (582), 66.
4. de Clerck, D., US Patent 3,242,196 (1966).
5. Nagiah, V., Dakshinamurthy, H., and Aggrawal, J. S., *Indian J. Techn.*, 1966, **4** (9), 280.
6. Ghanem, N. A., Moustafa, A. B., and Badran, B. M., *Chem. and Ind.*, 1973, 900.
7. Vogel, A. I., "Quantitative inorganic analysis", 3rd Edn., London: Longmans, p. 363.
8. Kin, Z., *Prace Inst. Cellulz. Papier*, 1953, **2,** 14.
9. Kin, Z., *Prezglad Papier Niczy*, 1953, **9,** 113.
10. Fiegel, F., "Spot test in inorganic analysis", 1958, New York Elsevier Publishing Co., p. 220.
11. Durbetaki, A. J., *Anal. Chem.*, 1956, **28,** 2000.
12. *Am. Oil Chem. Soc.*, "Tentative methods", 2nd Edn., Chicago.
13. *Ind. Eng. Chem.*, Analytical Edition, 1941, **13,** 787.

Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the September issue of the *Journal:*

Kinetics of film formation of alkyl silicate zinc-rich coatings *by T. Ginsberg*

Paint disfiguration by migration of antioxidant from wall board adhesive *by D. A. St. John and K. R. Markham*

Polyester resins and glass reinforced polyesters (GRPs) with particular emphasis on chemical plant *by J. A. Raymond*

Prospects for surface coating resins in the European market *by Ch. P. Martin*

The Health and Safety Act *by D. M. Wilson* (*Student Review*)