Deacidification of a Synthetic Oil with an Anion Exchange Resin

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ABSTRACT: Esters of trimethylolpropane were prepared by reaction of trimethylolpropane with erucic acid. Unreacted erucic acid was eliminated by fixation on an anion exchange resin to produce an oil with a low free fatty acid content. The authors describe the deacidification of the reaction product by Lewatit MP500A and MP600 resins in a fixed-bed reactor or in a stirred reactor. The discontinuous process gave the best results with the Lewatit MP600 resin in a stirred reactor with a 99% yield. The acid value was below 0.1 after less than 1 h of contact.

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KEY WORDS: Anionic resins, deacidification, erucic acid, fatty acid, neopentylpolyol esters.

The acid value (AV) is an important criterion for synthetic oils used as lubricants (1,2); it should be low to reduce corrosion of metal components. After mineral or organic acid-catalyzed esterification, unreacted free fatty acid (FFA) and the catalyst must be removed to obtain a low AV for the ester product.

The more common methods to remove FFA are washing with alkali (3), treatment with alumina (4), or distillation under vacuum (5). Alkaline washing is generally carried out with sodium hydroxide to remove the fatty acids in the form of sodium salts. However, long-chain fatty acids form emulsions that are not readily removed. The alkaline adsorbent alumina has been used to remove C6–C18 fatty acids, but this material is not readily recycled. Distillation of long-chain fatty acids requires high temperatures and reduced pressures that increase the cost of processing.

In a previous study, the authors studied the deacidification of lipid mixtures by binding FFA onto anion exchange resins (6). For example, the binding of heptanoic, undecylenic, and oleic acids to the anion exchange resin Lewatit MP500, followed by recovery of the fatty acids, was determined. The aim of the present work was to prepare pure synthetic esters for subsequent evaluation of their properties (7, 8). The authors evaluated the deacidification of a mixture of synthetic neopentylpolyol esters by anionic resins in both fixed-bed and stirred reactors.

EXPERIMENTAL PROCEDURES

Materials. All reagents were commercially available and were used without further purification. The MP type resins (Bayer, Puteaux, France) are macroporous and strongly alkaline and were supplied as the chloride form.

Synthesis of trimethylolpropane ester. The oil used in these deacidification studies was obtained by esterification of trimethylopropane (TMP) and erucic acid ($C_{22:1}$) (Fig. 1). Trimethylolpropane (25 mmol) and erucic acid (75 mmol) were placed in a 250-mL glass reactor, which was fitted with a mechanical stirrer, a Dean-Stark trap with a condenser and nitrogen inlet. 4-Toluene sulfonic acid (*p*-TSA) (0.07 g) and 40 mL xylene were added to the reaction mixture. The mixture was heated in an oil bath at 170°C for 4 h. At the end of the reaction, the mixture was cooled and filtered. The oil was first diluted in diethyl ether for the deacidification tests. Chapelle *et al.* (6) reported that solvent is not required for deacidification, but the oil tested was extremely viscous, and a solvent was needed to aid percolation.

Resin pretreatment. The anionic resins supplied in the form of chlorides, were washed and permuted into the basic form with 2 N sodium hydroxide. At the end of the treatment, the resins were stored in diethyl ether.

Resin regeneration and FFA recovery. After deacidification, bound erucic acid was recovered by regeneration with an ethanolic solution of 2% acetic acid. After evaporation of the ethanol and distillation of the acetic acid, the recovered erucic acid could be reused.

Assay of resin capacity. The swollen OH^- form of the resin was percolated with a solution of 2 N NaCl until the eluant was neutral. The recovered solution was titrated with a standard NaOH solution.

Assay of AV. The AV was measured according to the French Standard method (AFNOR T 60-204) and corresponded to mg KOH/g oil.

Deacidification in a fixed-bed reactor. Deacidification was performed on a column (25 mm diameter, 200 mm high), filled with 30 mL anionic resin, at room temperature. The solute consisted of 40 g oil diluted in 40 mL diethyl ether at a flow rate of approximately 3 mL/min.

Deacidification in a stirred reactor. Deacidification was tested in a stirred reactor with increasing amounts of resin (5, 7, 10, and 14 g) and a fixed amount of oil (10 g) of initial AV = 30.5

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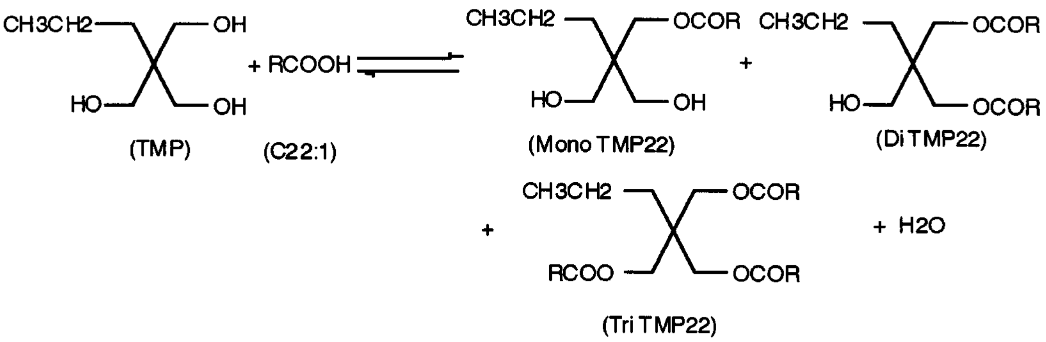

FIG. 1. Scheme of esterification between trimethylolpropane (TMP) and erucic acid. Mono TMP22, trimethylolpropane monoerucate; DiTMP22, trimethylolpropane dierucate; TriTMP22, trimethylolpropane trierucate.

(21.6% of the oil), diluted in 40 mL diethyl ether. The process was performed at 24°C in a 250-mL three-necked flask, equipped with a mechanical stirrer and a condenser.

Ethyl esters synthesis. Heptanoic acid and pelargonic acid were esterified with ethanol 99%. Cationic K2411 resin was used as catalyst. The resin was pretreated as described previously (9). The acid and ethanol in excess were refluxed for 8 h in a triple-necked flask, equipped with a mechanical stirrer and a condenser. At the end of the reaction, ethanol was evaporated, and the mixture was deacidified with MP600 resin.

RESULTS AND DISCUSSION

The highly alkaline type I or type II macroporous resins removed acid efficiently. Lewatit MP 600 and Lewatit MP 500A gave excellent results in both fixed-bed and stirred reactors. The macroporous ion exchange resins are characterized by a large internal surface area, good mechanical stability, high chemical resistance, and the ability to bind large organic ions.

Fixed-bed reactor. Table 1 lists the results for deacidification with anionic resins. Macroporous resins Lewatit MP 500A and Lewatit MP 600 were both efficient, with Lewatit MP 500A being the most efficient of the two. Lewatit MP 500A, apart from its ion exchange capacity, also has adsorbent properties. Its performance was therefore not related to the nature of its functional groups, particle size, or ion exchange capacity (MP500A, 0.33 meq/mL swollen resin; MP600, 0.77 meq/mL swollen resin), but appeared to derive more from its adsorbing capacity action. Adsorption was higher with the hydroxyl form, which is more swollen than the chloride form and thus has a higher contact surface area (in diethyl ether 20% of swelling from Cl^- to OH^- form for MP500A and 0% for MP600). Both resins were efficient for deacidification in columns, but the high viscosity of the oil made scale-up impractical. The authors were thus prompted to examine behavior in a stirred reactor to lower the need for solvent.

TABLE 1
Results of Deacidification in a Fixed-Bed Reactor with OH^- Form of Both Resins (initial AV = 15)[a]

	Column d = 25 mm, h = 200 mm		Column d = 30 mm, h = 450 mm	
	MP600	MP500A	MP600	MP500A
Measured capacity (meq/mL swollen resin)	0.77	0.3	0.77	0.3
Final AV	5.1	2	1.5	0.06
Yield (%)	66	87	90	99

[a]The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 − (final AV / initial AV) × 100. AV, acid value.

Stirred reactor. The best results were obtained in the stirred reactor. The four curves in Figure 2 show the progressive disappearance of acid for different amounts of the two resins. In contrast to that obtained in the column, Lewatit MP 600 was more efficient than Lewatit MP 500A. After contact for 3 h with 7 g Lewatit MP 600 resin, an acid content of 0.5% or a final acid index of 0.2 was obtained. A 99% deacidification was produced by this resin vs. only 51% for Lewatit MP 500A under identical conditions. With 10 g Lewatit MP 600, the acid index was reduced to 0.03 (99.9% deacidification). A similar level of deacidification was only obtained with 14 g of the Lewatit MP 500A resin.

Interestingly, between 60 and 90 min, acid levels rose in the presence of the Lewatit MP 500A resin. After an initial decline, acid levels rose, a phenomenon not observed with Lewatit MP 600. The effect was less noticeable with larger amounts of the Lewatit MP 500A resin. The equilibrium between the adsorbed and the free acid was altered. The partial desorption with Lewatit MP 500A was thought to stem from its high adsorbent activity. Adsorption involves interactions of low energy, and the presence of large amounts of residual acid in the medium may disrupt such interactions. The higher the amount of resin, the lower the residual acid; this leads to less desorption. Adsorption is thus essentially governed by the undissociated form. On the other hand, Lewatit MP 600 appeared to act essentially by ion exchange.

The two resins finally selected to deacidify the synthetic oil were thus shown to behave somewhat differently. Lewatit MP 500A led to deacidification by ion exchange and adsorption of erucic acid. Erucic acid adsorption is an equilibrium that is shifted at long contact durations, accounting for the re-

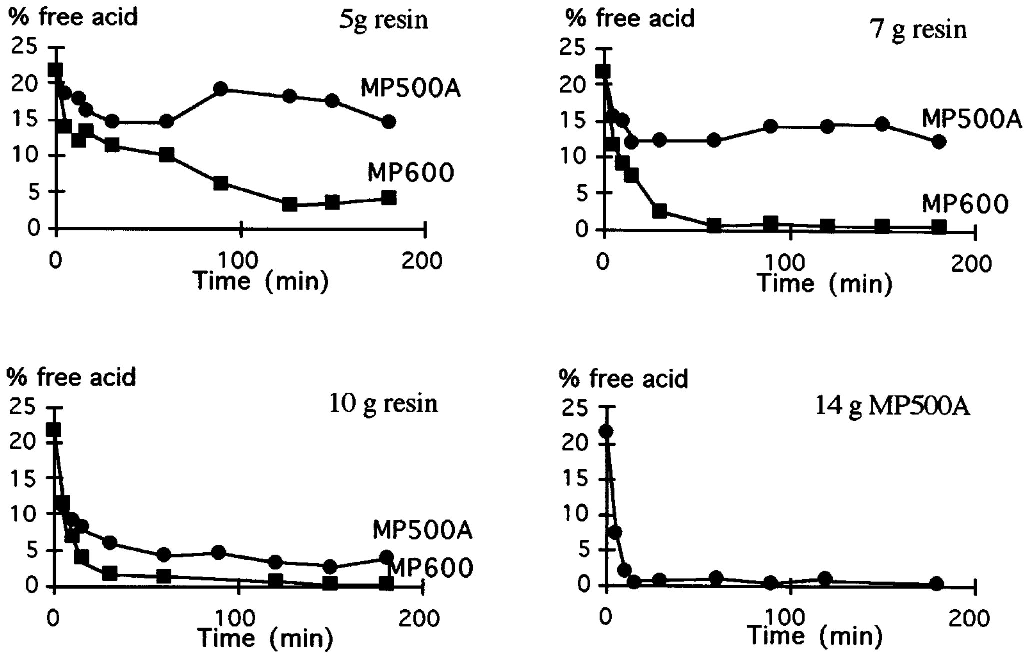

FIG. 2. Deacidification in stirred reactor: plot of acid content against time.

sults obtained in the stirred reactor. It was thus more suited for use in a fixed-bed reactor. Lewatit MP 600 on the other hand gave excellent results in the stirred reactor but poorer performance than Lewatit 500A in a fixed-bed reactor.

Overall, the authors recovered over 95% of a deacidified oil. After regeneration, the resin could be recycled, and the erucic acid recovered from the residual oil could be reused.

Study with new solvents. The experiments were performed with diethyl ether as the solvent, although others could be employed. However, because the mixture is highly lipophilic, solvents such as ethanol or acetone were not found to dilute the reaction mixture satisfactorily. Nontoxic lipophilic solvents, such as hexane, ethyl acetate, ethyl heptanoate, or ethyl pelargonate, might be suitable. They were as efficient as diethyl ether in the deacidification stage. At the end of the reaction, these solvents can be removed by distillation under reduced pressure at a suitable temperature. Table 2 lists some characteristics of these solvents including their boiling points and viscosities and log *P* (10,11). Log *P* is representative of the solvent lipophilicity. A lipophilic solvent is suitable to dilute the reaction mixture, while a hydrophilic one is not profitable. Although hexane and ethyl acetate (12) are commonly used to extract or dissolve oils, including culinary oils and those for pharmaceutical applications, the ethyl esters of pelargonic and heptanoic acids are now finding applications. The authors found that they lowered viscosity and improved fluidity. Therefore, the medium is suitable for deacidification because of increased diffusion into the polymer and consequently the accessibility of the active sites. In addition, ethyl esters are ecocompatible and work in a large temperature range.

Deacidification performed in a batch reactor is efficient with the anionic resin Lewatit MP600. The reactor can be improved by adding a filter system. After filtration of the deacidified oil, the reactor can be charged with more oil until the end of the resin activity. Then, the deacidification batch can be used as a regeneration reactor. Therefore, the batch reactor is as interesting as a column system. For viscous products, a solvent is necessary and the authors recommend new solvents, such as those named previously, to eliminate the problems from the use of diethyl ether. These solvents are characterized by a lipophilic nature with a low boiling point, suitable for fatty compounds.

TABLE 2
Characteristics of the Solvents Used

	Boiling point (°C)	log *P*		Viscosity (cSt) at		Pour point (°C)
		Alkane	Octanol	20°C	40°C	
Hexane	60	5.70	4	0.573	—	—
Ethyl heptanoate	189	—	—	—	1.1	<–70
Ethyl nonanoate	220	—	3.9	—	1.6	–42
Ethyl acetate	181	0.29	0.73	<1	—	—
Ethanol	80	–2.10	–0.25	—	—	—
Acetone	56	–0.92	–0.24	—	—	—

[a]Log *P* represents the solvent lipophilicity, where *P* is the partition factor between a solvent (alkane or octanol) and water. $P = [X]_{org}/[X]_{aq}$ where *X* is the molar concentration of the compound studied. —, no value available.

REFERENCES

1. Eychenne, V., Z. Mouloungui, and A. Gaset, Les lubrifiants à base d'esters de néopentypolyols, *Oléagineux Corps Gras Lipides 3*:57–63 (1996).
2. Eychenne, V., Z. Mouloungui, and A. Gaset, Total and Partial Erucate of Pentaerythritol. Infrared Spectroscopy Study of Re-

lationship Between Structure, Reactivity, and Thermal Properties, *J. Am. Oil Chem. Soc. 75:*293–299 (1998).

3. Nippon Oils and Fats, Neopentylpolyols Esters, Jpn. Kokai Tokkyo Koho 80,105,644 (1980).
4. Mancini, G., and L. Imparato, Polyester Lubricant, Ger. Offen. 2,432,680 (1975).
5. Cvengros, J., A. Tkac, M. Matas, and R. Lacko, Continuous Preparation of Neutral Oil, Czech. CS 222,059 (1981).
6. Chapelle, S., V. Baudrand, V. Rakotondrazafy, Z. Mouloungui, and A. Gaset, Desacidification des milieux lipochimiques par fixation des acides gras libres sur des résines échangeuses d'anions, *Riv. Ital. Sost. Gras 72:*153–157 (1995).
7. Eychenne, V., Synthèse des esters de néopentylpolyols. Corrélations structure/propriétés tribologiques/performances en lubrification, Ph.D. Thesis, Institut National Polytechnique de Toulouse, France, 1997.
8. Eychenne, V., and Z. Mouloungui, Relationship Between Structure and Lubricating Properties of Neopentylpolyol Esters, *Ind. Eng. Chem. Res.,* in press.
9. Vieville, C., Z. Mouloungui, and A. Gaset, C2–C18 Esters Synthesis and Analysis, *Chem. Phys. Lipids 75:*101–108 (1995).
10. El Tayar, N., B. Testa, and P.A. Carrupt, Polar Intermolecular Interactions Encoded in Partition Coefficients. An Indirect Estimation of Hydrogen-Bond Parameters of Polyfunctional Solutes, *J. Phys. Chem. 96:*1455–1459 (1992).
11. Hansch, C., and L. Albert, *Substituent Constants for Correlation Analysis in Chemistry and Biology,* John Wiley & Sons, New York, 1979.
12. Johnson, L.A., and E.W. Lusas, Comparison of Alternative Solvents for Oils Extraction, *J. Am. Oil Chem. Soc. 60:*229–242 (1983).

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