Separation of Fatty Acid Methyl Esters from Tall Oil by Selective Adsorption

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ABSTRACT: Fatty acid methyl esters (FAME) and resin acids (RA) were separated from tall oil by selective adsorption. Commercial nonmodified molecular sieve 13X was used as adsorbent. The adsorption isotherms of fatty acids (FA), FAME, and RA on molecular sieve 13X at 25°C were determined using various solvents. The solvents were methanol, ethanol, isopropanol, acetone, benzene, hexane, isooctane, petroleum ether (40–60°C), and petroleum naphtha (80–180°C). With each solvent, FA and RA were adsorbed to a greater extent than FAME. Adsorption isotherms for RA and FAME in binary adsorption systems were also determined using petroleum ether, petroleum naphtha, benzene, and isopropanol. For each component in the binary adsorption, the equilibrium amounts are lower than the values for pure component adsorption. The adsorption of FAME decreased in the presence of RA markedly in petroleum ether and petroleum naphtha. This fact may be the indication of the phenomenon of selective adsorption. Separation was accomplished by adding a solution of esterified tall oil in solvents used in the binary adsorption systems, through a column packed with molecular sieve 13X. With petroleum naphtha, FAME and RA were recovered in yields of 93 and 94%, respectively, from esterified tall oil. Petroleum naphtha gave the best results. The effects of particle size of adsorbent and flow rate of solvent on the efficiency of the separation were also investigated in fixed-bed column studies. The particle size of adsorbent did not apparently alter the results. Changes in the particle size should not significantly change the number of available adsorption sites in a microporous molecular sieve.

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KEY WORDS: Fatty acid methyl esters, resin acids, selective adsorption, tall oil.

Fatty acid methyl esters (FAME) can be used as alternatives to fatty acids (FA) in the production of many oleochemicals (fatty alcohols, alkanolamides, α-sulfonated methyl esters, sucrose esters, and other fatty esters). Methyl esters are preferable to FA, as they yield higher purity finished products and require milder conditions during synthesis. Furthermore, the methyl esters also are easier to fractionate, are more stable, and are less corrosive than the corresponding FA (1,2). Resin acids (RA) are also valuable feedstocks to the chemical industry, as well as FAME. RA are monocarboxylic acids of alkylated hydrophenanthrene structures possessing an empirical formula of the $C_{19}H_{(27 + 0, 2, 4, \text{ or } 6)}COOH$ and generally classified into two main types, abietic (abietic, palustric, levopimaric, dehydroabietic) and pimaric (pimaric, isopimaric, sandaracopimaric) (3). They occur in nature as the major components in gum and wood rosin and are used in alkyd resins and ester gums for surface coatings, as well as in rubber polymerization, adhesives, paper-sizing agents, printing ink vehicles, and core oils (4).

FAME and RA could be prepared from tall oil, a by-product in the manufacture of pulp by the Kraft process (5). Tall oil consists mainly of free C_{18} unsaturated FA, RA, and relatively small amounts of unsaponifiables. The main components of tall oil RA are abietic and dehydroabietic acids, whereas the FA fraction of tall oil contains mainly oleic acid, linoleic acid, and its isomers (6). Tall oil FA are easily converted into their methyl esters by reaction with methanol in the presence of sulfuric acid, whereas the RA are virtually unesterified (7). This process is much more cost-effective than obtaining methyl esters by following alternative synthetic methods. The primary method of producing methyl esters is methanolysis of fats and oils in the presence of an alkaline catalyst, usually sodium methoxide (2). The alkali-catalyzed methanolysis method is successful only if the fat is almost neutral and the reaction mixture is substantially anhydrous. Failure to comply with these conditions causes soap formation, which leads the building up of a gel structure that prevents separation and settling of the glycerol. A second method of preparing methyl esters consists of a two-step process. The first step is splitting of fats or oils by the energy- and capital-intensive Colgate-Emery process (8). The resulting FA are then esterified with methanol. On the other hand, as a result of the increasing costs of harvesting, transportation, and producing, the production of gum and wood rosin has steadily decreased, and tall oil is accepted as the only source of RA in the past 20 yr.

Tall oil is one of the world's cheapest source of these organic acids, and much work has been done to separate FA and RA from tall oil (5). Some methods, i.e., fractional distillation, have been effective but have been too expensive to be commercially feasible for a low-cost material, such as tall oil. Few publications describing selective adsorption in FA and RA separations have been reported. Papps and Othmer (9) described the two components of hydrogenated tall oil, stearic and abietic acids, which were partly separated by selective adsorption using activated carbon. Koonce and Perry (10) showed that monohydric alcohol fatty esters can be recovered from a petroleum ether solution of tall oil after filtration through bleaching earth.

The use of molecular sieve as adsorbent in the field of fats and oils was first reported by Moreno and Ruiz (11). Selectivities of molecular sieve for FA esters have been later widely investigated and applied for the method of separation of saturated, monounsaturated, and diunsaturated FAME (12–15). Abe and Tanaka (16) have also mentioned that the molecular sieve column could be used for concentrating the ethyl icosapentaenoate in the mixed ethyl esters from sardine oil. Surprisingly, little attention has been directed to the use of molecular sieve for separating FA or fatty esters from tall oil. Only Cleary and Laughlin (17) have studied distillated tall oil, by which the content of RA was reduced to about 20–30 wt%. They have also prepared a special molecular sieve adsorbent comprising 23 wt% Ludox-bound silicalite in a SiO_2 matrix and achieved a filtrate rich in RA by passing a feed mixture containing 20 wt% distillated tall oil through a column packed with this molecular sieve. The FA were then recovered from the adsorbent by displacement with an organic acid which has higher affinity to the SiO_2 matrix than that of FA.

Because the primary use for fats and oils is the food market, a rapidly expanding world population drives up demand for fats and oils. This fact has also led to consideration of the use of tall oil FAME for industrial purposes. Therefore the objective of this study was to separate FAME from tall oil by selective adsorption. Commercial nonmodified molecular sieve 13X (Fluka Chemie AG, Buchs, Switzerland) was used as adsorbent. The effects of operational parameters (type of solvent, particle size of adsorbent, and flow rate of solvent) on the efficiency of the separation were investigated.

MATERIALS AND METHODS

Materials. Tall oil (SEKA Çaycuma Pulp and Paper Mill, Zonguldak, Turkey), molecular sieve 13X (Linde Union Carbide Type, 1/16-inch rods, pore diameter 10 Å) were used. The Linde 13X molecular sieve is a Faujasite-type zeolite containing 172 (Si, Al)O_4 tetrahedra, 86 Na^+ ions and an average of 230 H_2O molecules in a cell unit. The following high-performance liquid chromatography (HPLC) grade solvents were used: methanol, isopropanol, petroleum ether (b.p. 40–60°C), hexane, isooctane, petroleum naphtha (b.p. 80–180°C), benzene, and acetone with ethanol (96 wt%).

Analysis of tall oil and its fractions. The general characteristics of Çaycuma tall oil were determined according to the ASTM D 803-65 standard methods (18). Fractionation of the tall oil into their major components, FA and RA, and subsequent esterification of FA were carried out by the method of Kahila (19). For preparation of methyl esters, FA (10 g) were reacted with 200 mL of methanol containing 2 g of H_2SO_4 (specific gravity 1,82 to 1,84) at 60°C for 30 min in a nitrogen atmosphere. The reaction mixture was then mixed with 100 mL saturated salt (NaCl) solution and 50 mL diethyl ether, and the ether layer was separated. The lower layer was extracted two times with 50-mL portions of ether. The combined ether phases were washed free of acid, dried, and evaporated in a vacuum rotary evaporator (Büchi, Glasapparatefabrik, Flawil, Switzerland). Thus obtained, FAME were stored in nitrogen until use. The tall oil RA were converted to methyl esters with freshly prepared diazomethane (20). Both FA and RA methyl esters were analyzed by gas chromatography according to a method reported in our previous work (21). The general characteristics and compositions of Çaycuma tall oil and its FA and RA fractions are given in Table 1.

Determination of adsorption isotherms for single solute systems. For determining the adsorption isotherms, instead of standard compounds, the original FA and RA fractions of tall oil and FAME as prepared above were used as individual components. The molecular sieve 13X adsorbent in the form of 1/16-inch cylindrical rods was ground and screened into 35–50, 50–100, and 100–200 mesh fractions. The molecular sieve samples were dehydrated at 250°C for four hours for removal of water molecules which are located on Na^+ ions and surface oxygen atoms, therefore inhibiting the adsorption of other molecules. It is known that dehydration of X-type molecular sieves starts around 100°C, dehydration a maximum near 250°C, continuing until 350°C. However, complete dehydration is not required for chemical adsorption of molecular sieves, the usual dehydration temperature being around 250°C, which was the dehydration temperature selected for this study (22). The dehydrated molecular sieve samples were then kept in the desiccator for at least two hours before being used.

TABLE 1
The Main Characteristics of Çaycuma Tall Oil[a]

Oil characteristics	Value/amount
Acid value	148.5
Saponification value	161.4
Unsaponifiable matters (wt%)	5.0
Content of fatty acids (wt%)	37.0
Content of resin acids (wt%)	58.0
Composition of fatty acids	wt% of total fatty acids
Saturated acids	6.40
Oleic acid	46.64
Linoleic acid	25.87
Pinoleic acid (18:3-5, 9, 15)	4.56
Conjugated 18:2 acids	13.44
Conjugated 18:3 acids	2.68
Composition of resin acids	wt% of total resin acids
Pimaric acid	9.99
Sandaracopimaric acid	1.38
Levopimaric acid + palustric acid	7.29
Isopimaric acid	1.06
Abietic acid	57.67
Dehydroabietic acid	22.60

[a] SEKA Çaycuma Pulp and Paper Mill, Zonguldak, Turkey.

Adsorption isotherms for tall oil FA, RA, and FAME on molecular sieve 13X (35–50 mesh) were determined from a series of solvents according to the method of Evangelista *et al.* (23). The solvents were methanol, ethanol, isopropanol, petroleum ether (40–60°C), petroleum naphtha (80–180°C), hexane, isooctane, acetone, and benzene. Solutions with solute concentration (C_0) ranging from 20 to 150 mg/mL were prepared by dissolving solute in 25 mL of solvent in a sealed vessel, 5 g of molecular sieve 13X was added to each vessel. The vials containing adsorbent and solution were maintained at 25°C in a shaking water bath and were allowed to equilibrate for at least 24 h. Afterwards, they were allowed to stand. From each vessel, a sample of 5 mL supernatant liquid was pipetted off. The solvent was removed with a Büchi vacuum rotary evaporator. The residue was weighed. Thus solute concentration (C_e) at equilibrium was determined. Then the amount of solid adsorbed by the molecular sieve was calculated using Equation 1 (23):

$$q = \frac{(C_0 - C_e)V}{W} \qquad [1]$$

where q = amount of solute adsorbed by the molecular sieve (mg/g molecular sieve), C_0 = initial concentration of solute (mg/mL), C_e = concentration of solute at equilibrium (mg/mL), V = initial volume of solute solution (mL), and W = weight of molecular sieve (g).

Determination of adsorption isotherms for binary solute systems. For developing of simultaneous adsorption curves for RA and FAME in binary adsorption systems (RA/FAME/solvent), in starting solutions initial ratio of RA to FAME was adjusted to 60:40 (w/w), which is the original weight ratio of cited components in selectively esterified Çaycuma tall oil. The procedure was exactly as that just described for single solute systems, except for the determination of equilibrium concentrations of solutes, C_e (RA) and C_e (FAME). A sample of 5 mL was pipetted off from each flask; the solvent was removed with a Büchi vacuum rotary evaporator; the residue was weighed and analyzed for RA by direct titration with ethanolic 0.05 N KOH (ASTM D 803-65; Ref. 18); content of FAME was determined by weight difference and q (RA) and q (FAME) were calculated using Equation 1.

Column separation studies. A glass column (40 × 2.0 cm i.d.) was packed with 55 g of molecular sieve 13X (35–50, or 50–100, or 100–200 mesh) in petroleum ether. The column was fitted with an outer jacket, through which water having temperature of 25°C (or 50°C) was circulated to maintain the column at 25°C (or 50°C). Feed esterified tall oil (5.5 grams) was dissolved in 50 mL of investigated solvent and was run through the column; then the column was continuously eluted with the same solvent at a flow rate of 0.54 mL/min (or 1.2 mL/min). Fractions of 25–100 mL were collected from the column. A sample of 5 µL was taken from each fraction and was subjected to thin-layer chromatography (TLC) for rapid qualitative analysis of fractions. Each fraction was then evaporated to remove the solvent; the residue was weighed; the residue was further analyzed for RA, and FAME content was determined by weight difference.

In column separation studies conducted with direct tall oil samples, experiments were done under the same working conditions, except for analysis of eluants. In this case, residues were analyzed for RA according to the method of McNicoll (9), and FA contents of fractions were calculated by difference.

TLC analysis of eluants. TLC was performed on 20 × 20-cm glass plates coated with a 250 µm layer of Silica Gel G (Merck, Darmstadt, Germany). For RA/FAME systems, plates were developed in a solvent system of petroleum ether/diethyl ether/acetic acid (70:30:1, vol/vol/vol) (24). For RA/FA systems, Silica Gel G-coated glass plates were first impregnated by dipping in a 15 wt% etherical solution of undecane; after application, samples on plates were developed in acetic acid/water (96:4, vol/vol) solvent system (24). For both systems, studied spots on the plates were detected by iodine vapors (24).

RESULTS AND DISCUSSION

Figures 1–3 show adsorption isotherms of FA, FAME, and RA on molecular sieve 13X at 25°C using various solvents. Solvents had nearly the same effect on the adsorption of FA and RA, because of a close similarity between FA and RA in adsorbed amounts per gram of molecular sieve. However, with each solvent, FA and RA were adsorbed to a greater extent than FAME.

The experimental results showed that the molecular sieve 13X adsorbed more acids and esters in alcoholic media as compared to alkanes. This may be explained by the structural change occurring in clays under organic solvents. It has been previously shown that when clays (especially montmorillonite clays) are treated with polar organic solvents, i.e., alcohols, glycols, and amines, the organic molecules penetrate between the unit layers and displace the interlayer water, thus

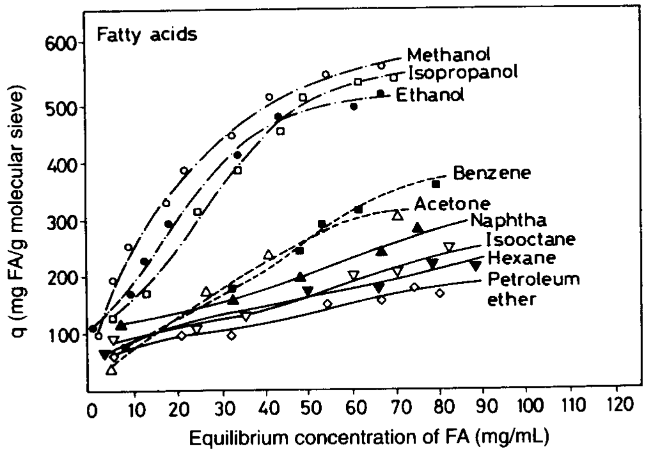

FIG. 1. Adsorption isotherms of tall oil fatty acids (FA) in various solvents. q, Amount of solute adsorbed by the molecular sieve (mg/g molecular sieve); see Equation 1.

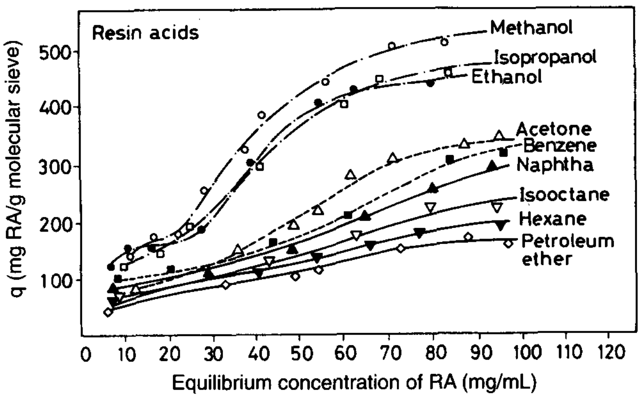

FIG. 2. Adsorption isotherms of tall oil resin acids (RA) in various solvents. Abbreviation as in Figure 1.

leading to increased basal spacing among clay layers (25). Molecular sieve 13X samples used in this study are partially dehydrated and still contain a number of water molecules associated with the Na$^+$ ions and/or framework oxygen atoms in cavities and on the channel walls. Therefore, it can be deduced that the alcohols have probably formed alcohol–water complexes with water molecules blocked on Na$^+$ ions and surface oxygen atoms, thus leading to removal of water molecules and freeing adsorption sites for acids and esters. Even though no scientific study was found explaining the adsorption mechanism of FA, RA, and fatty esters on molecular sieves, the mechanism theorized for adsorption of oleic acid on rice hull ash (26) and triglycerides on silicic acid (27) might also be valid for molecular sieves. Similarly, the FA and RA could have been adsorbed by hydrogen bonding to surface oxygen atoms (attached to Si and Al atoms) mainly through carboxylate ions. The adsorption of fatty esters should have been by hydrogen bonding to oxygen atoms through the ester carbonyl group.

Adsorption isotherms for RA and FAME in binary adsorption systems (RA/FAME/solvent) were also determined using petroleum ether, petroleum naphtha, benzene, and isopropanol. The selection of solvents for the binary systems was made taking into consideration that isopropanol was a representative alcohol; benzene, a typical aromatic hydrocarbon; and petroleum ether and petroleum naphtha, being aliphatic hydrocarbons with differing boiling points. In Figures 4 through 7, adsorption curves for pure RA and pure FAME

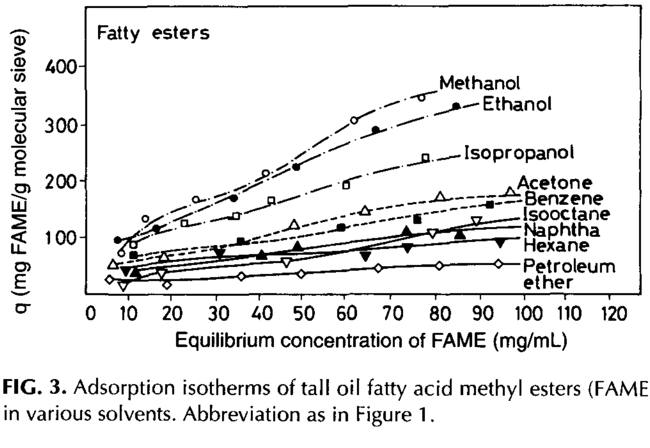

FIG. 3. Adsorption isotherms of tall oil fatty acid methyl esters (FAME) in various solvents. Abbreviation as in Figure 1.

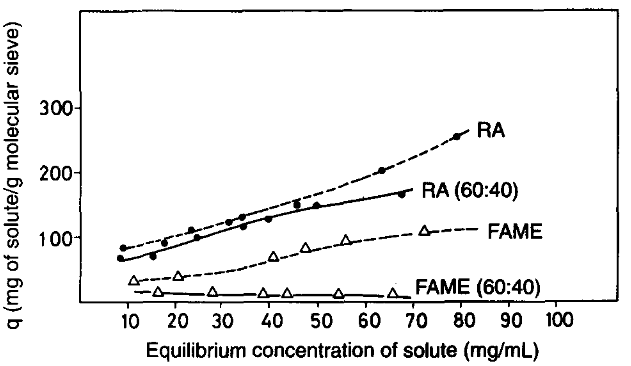

FIG. 4. Simultaneous adsorption of RA and FAME from petroleum naphtha, solvent, solutions at 25°C; mol., molecular. See Figures 1–3 for abbreviations. Figures in parentheses refer to initial RA/FAME weight ratio in starting solution.

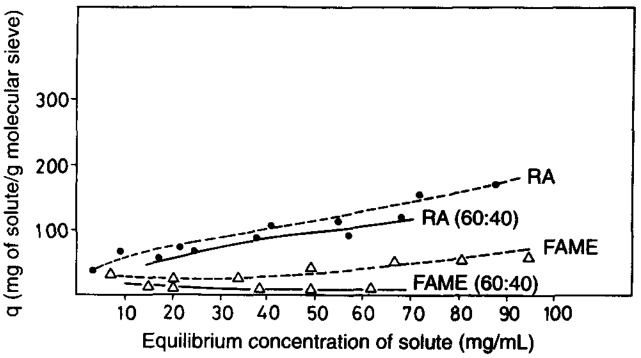

FIG. 5. Simultaneous adsorption of RA and FAME from petroleum ether, solvent, solutions at 25°C. See Figures 1–4 for abbreviations. See Figure 4 for weight ratio.

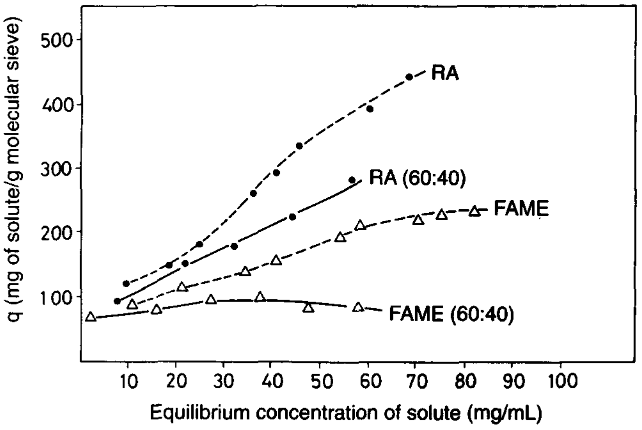

FIG. 6. Simultaneous adsorption of RA and FAME from isopropanol, solvent, solutions at 25°C. See Figures 1–4 for abbreviations. See Figure 4 for weight ratio.

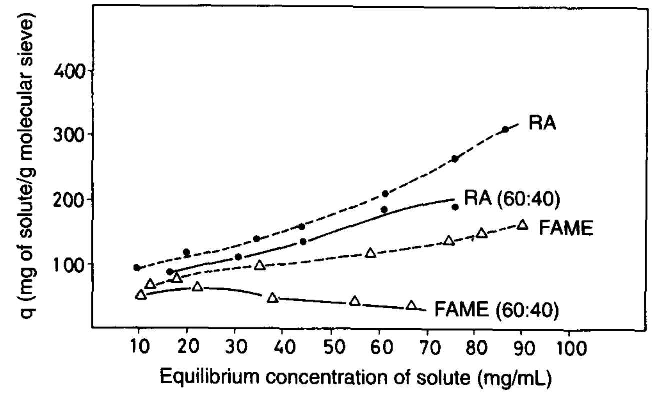

FIG. 7. Simultaneous adsorption of RA and FAME from benzene, solvent, solutions at 25°C. See Figures 1–4 for abbreviations. See Figure 4 for weight ratio.

were plotted along with the curves for the binary adsorption system of RA/FAME/solvent. For each component in the binary adsorption, the equilibrium amounts are lower than the values for pure component adsorption. It was also observed that the adsorption of FAME decreased in the presence of RA markedly in petroleum ether and petroleum naphtha solvents. This fact may be the indication of the phenomenon of selective adsorption. Taking this fact into consideration, these solvents were used in column separation runs.

The column operation conditions concerned with the fractionation of selectively esterified tall oil and tall oil are summarized in Table 2. Experimental results for one run was given in Table 3, as a representative example, and the elution curves obtained during the course of some selected runs were shown in Figures 8–11.

In the column experiment performed with petroleum ether, in the first 325 mL of eluate solvent, 74.6 wt% FAME left the column. The following 1250 mL removed the remaining FAME with some RA, to leave 66 wt% of total RA retained by the column. Then ethanol, having relatively strong eluting properties, was added through the column, and fractions of filtrate were again collected. Thus the remaining RA, 57 wt% of the total, were recovered by this manner (see Table 3 and Fig. 8).

Figure 9 shows the separation of FAME and RA in esterified tall oil from solution of isopropanol. Approximately 45 wt% of total FAME was removed in the 350 mL of eluent and was followed by mixtures of two components, leaving about 29 wt% of total RA in column. Thus the original charge was separated into three fractions as follows: first fraction containing 45 wt% of total FAME at a purity of 100%, and second fraction containing 71 wt% of total RA at a purity of 69%. Third fraction containing RA at a purity of 100% was obtained by further washing the column with isopropanol/ethanol (1:2, vol/vol) mixture. With isopropanol, the separation was not complete.

In the column separation experiment conducted with petroleum naphtha (Fig. 10), results indicated that 93 wt% of total FAME was recovered in the first 1450 mL wash solvent, 95.3% pure, leaving almost pure resin acids in the column. At 25°C, desorption of RA with ethanol was found to be incomplete. Ethanol at 50°C was then added, and eluates were again collected. Thus 95 wt% of total amount of RA was recovered. The separation of FAME and RA was almost complete with petroleum naphtha. Petroleum naphtha gave the best results among three solvents considered. If the column had been longer, a more efficient separation would probably have been obtained with petroleum ether and, to some extent, with isopropanol. The column separation results also confirmed the results obtained from the binary adsorption systems with same solvents.

Although the individual adsorption isotherms for pure FA and pure RA indicated that a good separation would not be obtained, some fractionation runs were also conducted with

TABLE 2
Summary of Column Separation Studies[a]

Run number	System	Solvent	Particle size of molecular sieve (mesh)	Flow rate of solvent (mL/min)
1	RA/FAME (60:40)	Petroleum ether	35–50	1.2
2	RA/FAME (60:40)	Petroleum ether	35–50	0.54
3	RA/FAME (60:40)	Petroleum ether	50–100	0.54
4	RA/FAME (60:40)	Petroleum ether	100–200	0.54
5	RA/FAME (60:40)	Petroleum naphtha	35–50	0.54
6	RA/FAME (60:40)	Petroleum naphtha	50–100	0.54
7	RA/FAME (60:40)	Petroleum naphtha	100–200	0.54
8	RA/FAME (60:40)	Petroleum naphtha	100–200	1.2
9	RA/FAME (60:40)	Isopropanol	35–50	0.54
10	RA/FAME (60:40)	Isopropanol	50–100	0.54
11	RA/FAME (60:40)	Isopropanol	100–200	0.54
12	RA/FA (60:40)	Petroleum ether	100–200	0.54
13	RA/FA (60:40)	Petroleum naphtha	100–200	0.54
14	RA/FA (60:40)	Isopropanol	100–200	0.54

[a] RA, resin acids; FAME, fatty acid methyl esters.

TABLE 3
Resin Acids–Fatty Acid Methyl Esters Fractionation on Molecular Sieve 13X[a]

	Eluants				Eluants		
Solvent	Volume (mL)	Content of FAME (mg)	Content of RA (mg)	Solvent	Volume (mL)	Content of FAME (mg)	Content of RA (mg)
Petroleum ether	25	53.2	—	Petroleum ether	100	6.7	35.4
Petroleum ether	25	74.5	—	Petroleum ether	100	—	33.4
Petroleum ether	25	138.4	—	Petroleum ether	100	—	27.0
Petroleum ether	25	160.4	—	Petroleum ether	100	—	19.3
Petroleum ether	25	158.3	—	Petroleum ether	100	—	6.8
Petroleum ether	25	165.4	—	Ethanol	50	—	37.8
Petroleum ether	25	149.0	—	Ethanol	50	—	84.3
Petroleum ether	25	159.1	—	Ethanol	50	—	147.9
Petroleum ether	25	149.7	—	Ethanol	50	—	168.9
Petroleum ether	25	127.1	—	Ethanol	50	—	198.0
Petroleum ether	25	132.3	—	Ethanol	50	—	219.7
Petroleum ether	25	83.7	—	Ethanol	50	—	217.0
Petroleum ether	25	84.2	—	Ethanol	50	—	195.3
Petroleum ether	25	75.8	6.4	Ethanol	50	—	119.1
Petroleum ether	25	58.4	18.0	Ethanol	50	—	93.7
Petroleum ether	50	51.3	25.7	Ethanol	50	—	89.8
Petroleum ether	50	47.9	33.4	Ethanol	50	—	50.5
Petroleum ether	50	33.2	45.1	Ethanol	50	—	48.3
Petroleum ether	50	37.8	35.4	Ethanol	50	—	47.9
Petroleum ether	50	16.8	47.6	Ethanol	50	—	55.8
Petroleum ether	50	13.7	55.3	Ethanol	50	—	39.4
Petroleum ether	50	11.2	39.9	Ethanol	50	—	28.8
Petroleum ether	50	17.9	51.4	Ethanol	50	—	17.7
Petroleum ether	100	10.2	54.7	Ethanol	50	—	25.1
Petroleum ether	100	14.7	50.8	Ethanol	50	—	5.9
Petroleum ether	100	8.1	43.7				

[a] Linde Union Carbide Type, Fluka Chemie AG, Buchs, Switzerland; molecular sieve = 55.0 g (100–200 mesh); esterified tall oil = 5.5071 g; flow rate of solvent = 0.54 mL/min. See Table 2 for abbreviations.

Çaycuma tall oil samples in the same solvents—petroleum ether, petroleum naphtha, and isopropanol. In these studies, the filtrates were found to be richer in RA to some extent; however, at no time was any fraction obtained containing pure RA or pure FA (see Fig. 11, as an example).

The effects of particle size of molecular sieve and flow rate of solvent on the efficiency of the separation of FAME and RA with petroleum naphtha are given in Table 4, a representative example. The particle size of adsorbent did not apparently alter the results. Changes in the particle size should not significantly change the number of available adsorption sites in a microporous molecular sieve. It is known that the external surface of the adsorbent particles contributes only a small amount of the total available surface area (22). As expected, the rate of solvent influenced the efficiency of the separation.

In conclusion, by selective adsorption using commercial molecular sieve 13X, FAME and RA could be directly obtained in yields of 93 and 94%, respectively, from esterified tall oil with petroleum naphtha. The proposed working conditions are moderate, relative to previous studies (9,17). In this

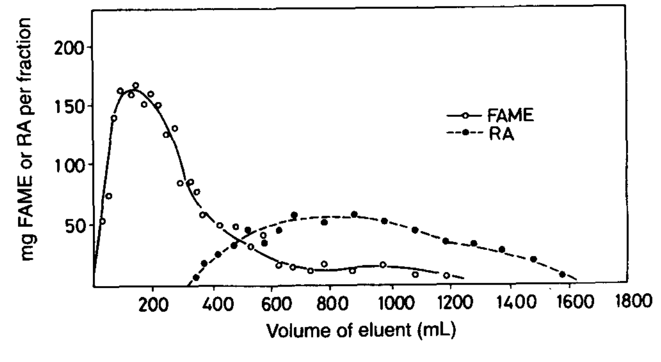

FIG. 8. Column separation of selectively esterified tall oil in the solvent petroleum ether. See Figures 2 and 3 for abbreviations.

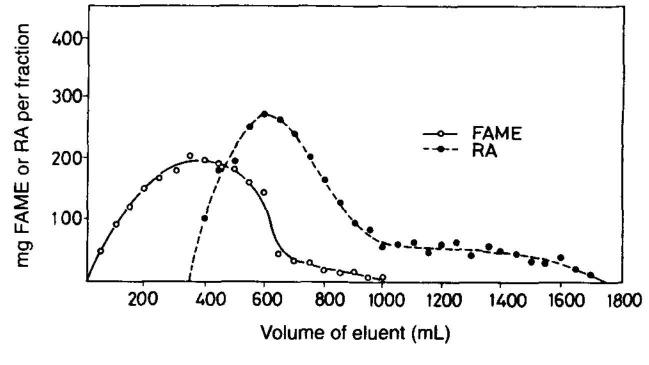

FIG. 9. Column separation of selectively esterified tall oil in the solvent isopropanol. See Figures 2 and 3 for abbreviations.

TABLE 4
The Effects of Particle Size of Adsorbent and Flow Rate of Solvent on the Separation of FAME and RA with Petroleum Naphtha

Run number	Particle size of molecular sieve (mesh)	Flow rate of solvent (mL/min)	Recovered FAME Yield (%)[a]	Recovered FAME Purity (%)	Recovered RA Yield (%)[b]	Recovered RA Purity (%)
5	35–50	0.54	93.9	94.1	92.8	100
6	50–100	0.54	93.4	94.6	93.7	100
7	100–200	0.54	93	95.3	94	100
8	100–200	1.20	95.4	88.6	89.4	100

[a] FAME content of esterified tall oil basis. See Table 2 for abbreviations.
[b] RA content of esterified tall oil basis.

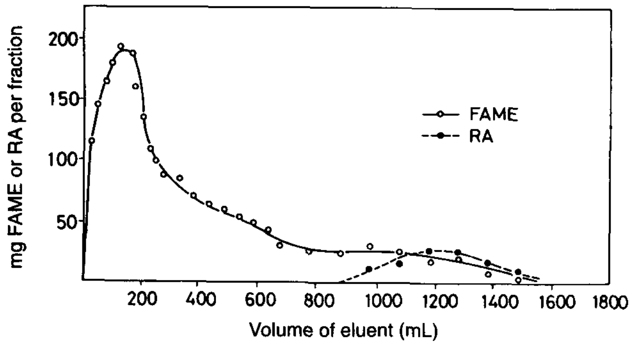

FIG. 10. Column separation of selectively esterified tall oil in the solvent petroleum naphtha. See Figures 2 and 3 for abbreviations.

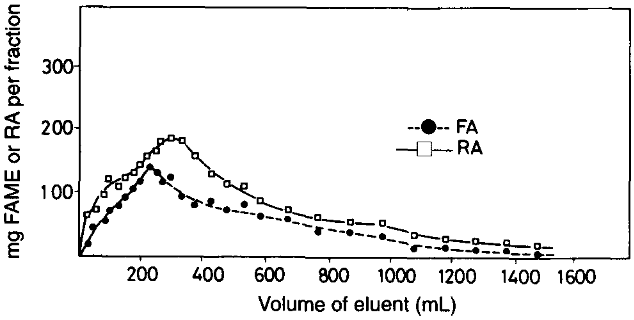

FIG. 11. Column separation of tall oil in the solvent petroleum naphtha. See Figures 1 and 2 for abbreviations.

study, commercial nonmodified molecular sieve was used. Experiments were conducted with tall oil in its original composition. Our process esterified tall oil FA with methanol with little RA esterification, conducting petroleum naphtha solution of esterified tall oil with molecular sieve 13X and washing the adsorbent with eluting solvents. The separation of these valuable products, FAME and RA, was found to be effective and almost complete.

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