the oil was completely miscible with the solvent, but selectivity was the same, contrary to our original hypothesis of two-phase hydrogenation. Thus a polar solvent does not need to form a two-phase system to improve selectivity. Though this observation refutes our earlier hypothesis, the experimental application of this concept remains unaffected.

Table III lists the selectivities at various catalyst concentrations. Within experimental error, selectivity remained constant over a wide range of catalyst concentrations.

In an effort to find other solvents useful for selective hydrogenation, a survey was made; the results are shown in Table IV. All solvents were tested with 5% palladium-on-alumina catalyst at room temperature and atmospheric pressure, except for trimethyl phosphate which was used with a commercial nickel catalyst at 100C. Hydrogenation with methyl formate was performed at 0C. As can be seen from Table IV, highly polar solvents like DMF, furfural and tetramethyl urea improved selectivity, whereas less polar and nonpolar solvents were not beneficial despite an increase in hydrogenation rates. Furfural and trimethyl phosphate produced large amounts of *trans* isomers possibly because of the presence of catalyst poisons in the solvents. If 1,2-dimethoxyethane containing peroxides was used, a high selectivity of 4.0 was obtained. A high *trans* content was also produced, which is probably indicative of the peroxides acting as selective poisons (13). After removal of peroxides from the solvent, selectivity dropped to a nearly normal value. The *trans* was still slightly higher possibly due to traces of peroxides which are removed with difficulty. With acetone, the high *trans* content also indicates poisons; but selectivity is not improved. It appears that selectivity can often be improved by poisoning the catalyst. However, since the *trans* content did not increase with DMF or tetramethyl urea, it might be inferred that these two solvents act by a process other than catalyst poisoning. The two-phase hydrogenation hypothesis proposed earlier is not a necessary prerequisite for improving selectivity since the same high selectivity was obtained even when there is only one phase. A more likely explanation is that of McQuillin et al. (14), namely, the solvent influences the polarity of the catalyst surface so that the highly unsaturated molecules are adsorbed on the catalyst surface in preference to the less unsaturated triglycerides.

A technical grade DMF gave a selectivity of 3.6; a chemical grade, 3.0. The spectro grade DMF used gave higher values than either of the other two samples. These differences may reflect the extent of impurities present in the solvent.

Selectivities achieved, when applied to soybean oil, should produce a liquid oil of greater flavor stability. Since hydrogenations are carried out at low temperatures, the flavor stability may further be improved by the suppression of many side reactions that normally accompany a high-temperature hydrogenation.

ACKNOWLEDGMENT

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Effect of Internal Distributors in a Packed Column on the Steam Stripping of Hexane from Soybean Oil

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Abstract

Internal distributors were designed and installed in a 6-in. diameter column with an 8-ft bed of ½-in. berl saddles. The distribution pattern of a liquid (water) flowing down the column was first determined. The distributors picked up the water from the wall of the column and redistributed it towards the center producing definitely better distribution across the column than obtained without them. Steam stripping of hexane from soybean oil was next carried out in the column both with and without the distributors. The residual hexane in the oil varied exponentially with the steam-oil ratio. Under the experimental conditions 18% less steam was required for comparable stripping with the distributors in the column than without them.

Introduction

PACKED COLUMNS have had considerable use in stream-stripping the residual solvent from oil miscellas following the initial separation of most of the solvent in an evaporator. Dumped packings such as raschig rings and berl saddles, are usually used in preference to stacked packings because of lower cost and higher capacities. A major problem in the efficient use of packed columns for either stripping or absorption is that of securing uniform distribution of the liquid over the surface of the packing. When the falling liquid is applied uniformly to the top surface of the packing, the uniform distribution exists only momentarily. As the liquid moves downward it spreads outward accumulating on the column wall. When the liquid is applied by a center feed it distributes outwardly as it moves down. Uniform distribution exists only as a flat plane theoretically

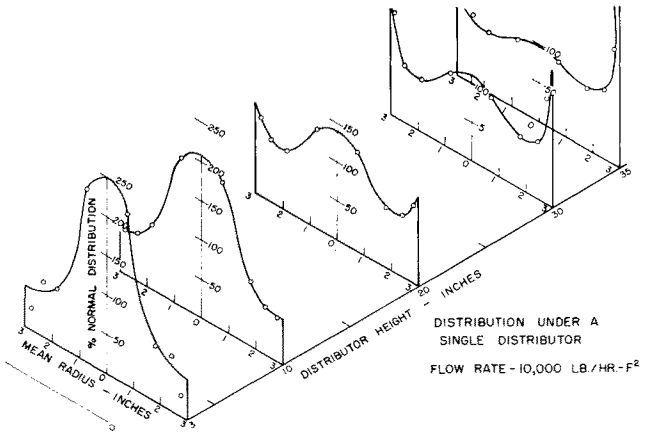

FIG. 1. Typical flow distribution with center feed.

of zero thickness after which the movement toward the wall begins.

Leva (4) and Eckert (2) recommend the use of the distributor plates to reestablish uniform distribution. Kirschbaum (3) used an inverted perforated cone as a distributor. Arnold and Ingebo (1) used a special packing of spaced wire cloth. Distributor plates and cones even though perforated interfere with free movement of steam up the column. The wire cloth packing was expensive.

Flow Distribution Studies

The first part of the present study was on the distribution down a packed column with special distributors for redistributing the water as it flowed down the column. The column was an 8-ft length of 6-in. glass pipe packed with a 7-ft height of ½-in. berl saddles and fitted with a radial trough collector similar to that used in previous studies by Ingebo (1). This collector consisted of four concentric brass rings soldered to a brass plate forming four compartments each having a cross sectional area of 0.0492 sq. ft. The water which flowed out through tubes in the bottom was weighed to obtain the amounts per time intervals.

The distributors used for picking up the water on the column wall and conveying it back to the center of the column were short sheet metal cylinders 5 9/16 in. in diameter by 2 ¼ in. high and equipped with two ⅜-in. copper tubes extending to the center of the column. They were inserted in the column where they were held in place by ⅜ Tygon tubing forming an O-ring around the outside near the bottom and acting as a seal.

Water was fed to the center of the top of the column through a rotameter and controlled by a globe valve and a needle valve connected in parallel. Flow rates varied from 2,000 to 20,000 lb/hr/sq ft which covered the practical flow range for this type of bed. A series of 24 runs were made to determine the distribution of the water down the column both with and without the special distributor to observe the flow patterns.

Without distributors the high flow from the center feed moved outward towards the wall as the water moved down the column. This is shown in Figure 1.

When a distributor was inserted in the column the pattern of distribution under it was practically that obtained under the initial feed as shown in the figure. The best distribution under the distributor was obtained at a depth of 18 in.

TABLE I

Stripping Results

Feed			Stripped oil		
% Solvent	lb/hr	Steam/oil Ratio	Temp., °F	%	Residual solvent
Without distributors					
3.77	150.1	0.553	250		0.31
3.77	183.8	0.428	240		0.52
4.03	193.8	0.330	245		0.98
4.03	207.3	0.303	252		0.84
4.03	228.4	0.275	238		1.25
6.20	217.6	0.411	244		0.47
6.20	238.3	0.382	244		0.75
2.75	234.4	0.375	250		0.66
2.75	235.3	0.272	250		1.48
2.75	235.3	0.222	250		2.49
With distributors					
8.95	153.9	0.570	240		0.10
8.95	207.7	0.420	235		0.19
8.15	214.4	0.261	275		0.73
8.15	202.1	0.334	273		0.47
8.15	202.1	0.433	245		0.22
7.64	171.8	0.520	248		0.14
7.64	181.0	0.540	240		0.14
6.15	228.5	0.266	260		0.75
6.15	226.1	0.345	270		0.38
4.38	168.3	0.451	275		0.15
4.38	178.8	0.425	295		0.17
4.38	229.5	0.209	285		1.82

Steam Stripping Studies

In the second part of the study soybean oil containing from 2.75 to 8.5% commercial hexane was steam stripped to determine the effectiveness of the column with and without distributors.

The column used in the distribution studies was packed with 8 ft of ½-in. berl saddles. It was provided with a stainless steel column head with a spray head at the top of the column. This head was twice the diameter of the column to aid any entrained oil to settle. The column was insulated with a 3-in. layer of glass wool.

The miscella was heated to 250F by steam jacketed heat exchangers and measured to the column by an orifice meter. The stripping steam at 90 psi was first superheated 68F by passing it adiabatically through an expansion valve to atmospheric pressure. It was then metered with an orifice meter to the bottom of the column. Pressure in the column was held slightly below atmospheric to prevent escape of hexane vapors to the outside air. The hexane content of the miscella and stripped oil were determined by gas-liquid chromatography using a ¼-in. O.D. copper column 10 ft long packed with Fluoropak with a substrate of 10 di-*n*-butyl sebacate per 100 g of packing.

Ten stripping runs were made without distributors in the bed and 12 runs were made using seven of the distributors used in the distribution studies spaced 10 in. apart. Oil flow rates ranged from approximately 150 to 235 lb/hr with steam flow rates 50 to 105 lb/hr and steam-oil ratios from 0.21 to 0.57. Residual solvent in the stripped oil varied from 0.31 to 2.49% without distributors and 0.10 to 1.82% with the distributors. The relationship between the logarithms of the reciprocals of the residual solvent percentages and the steam-oil ratios for each series approximates a straight line. The slopes of the lines, which are functions of the liquid distribution, are 3.80 for the column without distributors and 4.73 for the column with the distributors. Detailed data are given in Table I.

The addition of the distributors decreased the residual hexane concentration by 46% at a constant steam-oil ratio. At a constant residual percentage the steam consumption was decreased 18% with a

constant oil rate. The addition of the distributors produced no noticeable pressure drop in the column.

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• *Letters to the Editor*

Direct Application of Serum to Thin-Layer Plates for Rapid Determination of Serum Lipids[1]

IN THIS LABORATORY it has been found in confirmation of earlier studies with silicic acid impregnated paper (1) and observations with thin-layer systems (2) that lipid chromatography may be carried out on thin-layer plates to which serum is applied directly. This direct application of serum to thin-layer plates is a useful technique for rapid qualitative and quantitative evaluation of serum lipids.

As a screening procedure for cholesterol and triglyceride, 20 μl of serum are applied to thin-layer plates coated with a 0.125 mm layer of silica gel. The serum spots are dried 3 to 4 min under an infrared lamp. The plates then are developed in n-hexane/diethyl ether/acetic acid (80:20:1.5 v/v/v) (3) and the separated lipid components charred with 0.6% $K_2Cr_2O_7$ in 55% H_2SO_4 (w/v) (4) at 180–190C for 40 to 60 min. There is excellent correlation between the spot size of the triglyceride fractions of serum samples chromatographed in this manner and the concentration of triglyceride as determined by a modified Carlson procedure (5). Total cholesterol levels (6) correlate with the spot size and intensity of the sum of the cholesterol ester and cholesterol fractions. Differences in the ratio of cholesterol to cholesterol esters are readily discernible on such thin-layer chromatograms.

Free cholesterol and the other slower moving lipids are not clearly separated by this screening technique. However, as illustrated in Figure 1, these constituents can be resolved by using a thicker layer, 0.25 mm, of adsorbent and developing three times to the same point (F), 5 or 6 cm from the starting line, with chloroform/methanol (2:1 v/v), prior to final development in the solvent system. The resulting chromatograms are virtually indistinguishable from those obtained when lipid extracts of the same sera are chromatographed.

Both screening techniques are particularly useful in fat tolerance tests to estimate the level of serum triglyceride and the time at which the concentration reaches a maximum. In addition, the procedures are helpful in selecting the size aliquot to be used in quantitative procedures for triglyceride and cholesterol.

For quantitative analysis of triglyceride an aliquot of serum containing from 25 to 75 μg of triglyceride is applied. The lipids are extracted and the chromatogram developed as previously described. After the lipid components are visualized with Rhodamine 6G, the areas of Silica Gel G containing triglyceride are extracted at room temperature with n-hexane/diethyl ether (50:50 v/v). Then the extracts are saponified, and the original triglyceride

TABLE 1

Mean Serum Triglyceride Concentrations by Thin-Layer and Modified Carlson Procedures [a]

Serum sample No.	Thin-layer[b] mg%	Modified[c] Carlson mg%
1	50	73
2	78	96
3	113	141
4	157	185
5	224	259
6	509	597

[a] Six serum samples analyzed on two occasions by both procedures. Standard error of the sample mean was 4 mg%.
[b] Eight analyses for each serum sample.
[c] Four analyses for each serum sample.

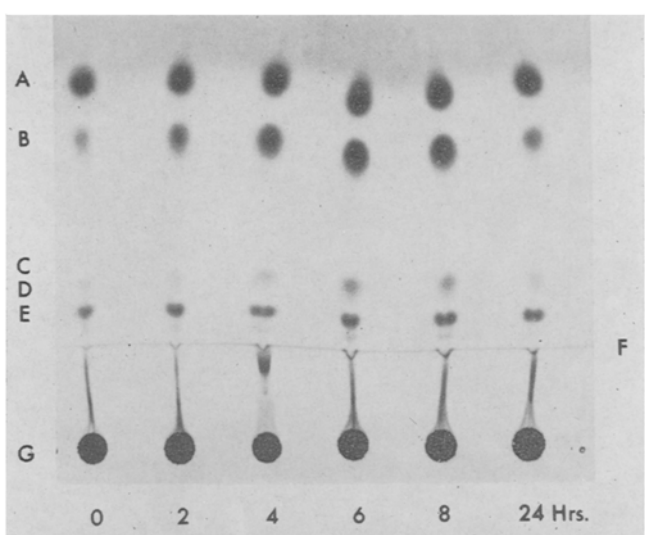

FIG. 1. Chromatogram of serum samples from a fat tolerance test: Samples were drawn at 0 (fasting sample), 2, 4, 6, 8, and 24 hr after ingestion of 100 g of corn oil. A, cholesterol ester; B, triglyceride; C, fatty acid; D, free cholesterol; E, diglyceride; F, front to which the chromatoplate was developed with chloroform/methanol; G, serum samples, 20 μl spotted. Serum triglyceride (5) concentrations, left to right: 209, 289, 566, 691, 587, 162 mg %.

[1] Based on results presented at the 56th Annual Meeting of The American Oil Chemists' Society, Houston, Texas, 1965.