Polyglycerol Esters: Optimization and Techno-Economic Evaluation

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ABSTRACT

Optimization of the two-step reaction for preparation of polyglycerol esters of fatty acids from the industrial point of view has been studied. Parameters such as nature of the alkaline catalyst, temperature and time of the reaction have been examined. It was found that the polymerization process needs 260-280 C in the presence of inert gas and 2.5 mol % of NaOH as catalyst. The esterification can be accomplished in the absence of additional catalyst and temperatures as low as 230 C. A simulation model of a chemical plant has been used for evaluation of cost of the production of such emulsifiers.

INTRODUCTION

Polyglycerol esters of fatty acids have been available for about 20 years and are produced by several companies in the U.S. and Europe. Several patents and papers have been published describing the general methods of manufacture as well as some of their properties and applications (1-6).

Polyglycerol esters are generally prepared in two-step reactions, alkaline polymerization of glycerol at elevated temperatures followed by an esterification reaction with fatty acids.

The purpose of this paper is to reevaluate those two reactions from the point of view of the industrial chemist and to consider the role of the catalysts (type and concentration), the need for inert gas, and of temperature on the rate of the reaction.

The parameters affecting the rate and yield of the reactions have been tested using a model of an economic evaluation to optimize reaction conditions and to estimate production costs.

EXPERIMENTAL

Materials and Instrumentation

The polymerization of glycerol has been carried out using anhydrous extra pure glycerol purchased from E. Merck, Darmstadt (99% pure by GLC), as well as commercially available food-grade glycerol. The catalysts were all A.R. grade, commercially available from BDH and Baker and were used without further purification.

The esterification process was accomplished without additional catalysts and with commercially available fatty acids; stearic (50% C_{18} and 48% C_{16}); oleic (85% pure); palmitic (84% pure); myristic (90% pure) and lauric (90% pure).

Analyses of the products were done using: RVO-Brookfield viscometer; Lovibond Colour Comparator (SETA Model ASTM D 1500-IP-196); Perkin Elmer (Model 720) infrared spectrophotometer; Hilger and Watts refractometer (at 60 C); DuPont 21-490 B, chemical ionization mass spectrometer. Product composition was determined using HPLC from Spectra Physics (SP-8000) equipped with a variable UV detector (detection done at 220 nm), SP-8000 data system and 10 μL loop autoinjector. The column was 250 × 4.1 mm Lichrosorb diol, 10 μm (for details, see ref. 7).

PROCEDURE

Polymerization

Extra dry glycerol was heated in a regular esterification vessel to 120-150 C for 10-30 min. A measured amount of powdered catalyst was added and vigorously stirred. The temperature was then raised to 220-280 C and the volatilized water from the reaction was trapped and measured. Samples were withdrawn and their viscosity, refractive index, density and composition were determined. Variations in the type of catalyst and its percentage, temperature and time were examined.

Esterification

The polyglycerol obtained from the previous reaction was further esterified with various molar ratios of fatty acids (stearic, palmitic, myristic, lauric and oleic) at elevated temp. (160-230 C) without or in the presence of basic catalysts. The reaction was quenched when the acid value of the product was close to zero.

RESULTS

Glycerol Polymerization

The polymerization of glycerol involves the α-hydroxyl groups of two glycerol molecules to form an ether linkage with release of a water molecule. Care must be taken during the reaction to exclude air from the system. Traces of acid or oxygen forms acrolein and other condensation products which darken the final product. A search for a reducing agent to be present during the polymerization process in the vessel and to minimize formation of colored materials led us to add catalytic amounts of Al or Mg metals to the glycerol before heating. In addition, exclusion of air has been achieved by bubbling CO_2 or nitrogen during the condensation process. The results are summarized in Table I for the preparation of trigycerol.

A typical rate of reaction in which glycerol was polymerized under alkaline catalysis is demonstrated in Figure 1. The reaction was done at 260 C in the presence of 2.5 mol % of NaOH and under nitrogen atmosphere. The conversion of glycerol was estimated by determining the hydroxyl value of the product together with its refractive index, viscosity and the amount of water distilled out during the process. The figure indicates that the amount of water evolved in the early stages of the reaction is significantly higher than at the later stages, which makes the evaluation of the degree of polymerization and molecular weight of the long polymers more difficult and less accurate.

TABLE I

Use of Reducing Agents and Inert Gases in the Polymerization Process of Glycerol (catalyst 2.5 mol % NaOH; 4 hr at 260 C)

Additives	Water evolved/mol glycerol (mL)	Viscosity (CP, 65 C)	Color (Gardner Standards, 1933 scale)	Product
Control[a]	14.10	1490	12+	tetra-penta
N_2 (750 cc/min)	14.10	1500	12-	tetra-penta
CO_2 (750 cc/min)	14.00	1520	12-	tetra-penta
Mg[b] + CO_2	14.20	1540	4.5	tetra-penta
Al[b] + CO_2	14.00	1500	4.5	tetra-penta

[a] Since, in the absence of inert gas the reaction was slower, it was carried out for 5 hr to accomplish formation of tetra-penta glycerol.

[b] 2.5 mol %.

The effect of the temperature on the yield of polymerization has been examined using a similar procedure and the results are presented in Figure 2. It can be seen that the reaction proceeds at temperatures as low as 240 C (reactions done at temperatures lower than 220 C were slow and only minor conversions of glycerol have been detected). The rate of the polymerization increases significantly with temperature; 270 C seems to be a suitable temperature for such condensation. Temperatures higher than 280 C are impossible since glycerol starts to decompose and the amount of acrolein increases significantly.

The optimal amount of the catalyst (NaOH) was examined (Fig. 3) and it is obvious that increasing catalyst amount speeds up the polymerization process. High catalyst concentrations accelerated the reaction to rates from which there was almost no control on the polymer length chain (10% mol catalyst). If short-chain polymers are needed, only 0.5 to 1% mol catalyst is sufficient. For a higher degree of polymerization, 4-6% mol of catalyst will be preferred.

Since it is obvious that alkaline conditions are needed for catalysis, several bases have been tested as catalysts including hydroxides, carbonates and oxides of several metals. Figure 4 presents results of rate of polymerization for some hydroxides and oxides and Figure 5 illustrates the results obtained from several carbonates. The comparison has been done on the molar basis and not on weight percentage. In each experiment, 2.5 mol % catalyst was introduced. The following order of activity has been achieved in 4 hr polymerization reaction:

$$K_2CO_3 > Li_2CO_3 > Na_2CO_3 > KOH > NaOH > CH_3ONa > Ca(OH)_2 > LiOH > MgCO_3 > MgO > CaO > CaCO_3 = ZnO$$

The order of the activity did not change significantly when the reaction was quenched after 2 hr.

It is notable that, although hydroxides are better bases than carbonates, K_2CO_3 was a better catalyst than KOH. From the solubility measurements and observations, it was noticed that the carbonate had better solubility in the glycerol and in the polymeric product at elevated temperatures than the KOH and thus it is believed that both solubility and basicity influence the rate of reaction, and their interplay is most significant for the reaction rate.

The oxides are very weak catalysts mainly because of a lack of solubility. Nucleophiles or weak bases had no catalytic effect on the reaction.

Esterification Process

The esterification process needs lower temperatures and thus the second-step reaction is done after cooling the polymer to as low as 160 C. Lower temperatures also guarantee that further polymerization of glycerol will be avoided. Since the esterification can be done either at alkaline or neutral conditions, no additional catalyst was needed.

The polyglycerol has significantly higher specific gravity and did not dissolve at room temperature in the polyglycerol esters. Thus, any excess of unreacted polyglycerol can be separated from the product by simple decantation. The rate of the reaction was determined either by measuring the volatilized water evolved from the reaction or by determining the acid value of the product from which the amount of free fatty acid can be calculated. In addition, product composition was determined from product analyses using high performance liquid chromatography (HPLC) (7).

It is worth noticing that the sodium hydroxide that was used as a catalyst has an additional, important role in the esterification process. It transforms part of the fatty acid into its sodium salt which helps to solubilize the polyglycerol at high temperatures in the product. The role of NaOH was demonstrated in three consecutive experiments in which hexaglycerol was esterified with 1 mol of oleic acid for 2 hr in the absence of additional NaOH (the catalyst from the polymerization reaction was not excluded) and in the presence of 0.85 and 1.5 mol %. The results showed 35, 20 and less than 5% of unreacted hexaglycerol, respectively, at the end of the reaction. The NaOH added in the third experiment transformed 28% (by calculation) of the oleic acid into sodium oleate.

Table II summarizes, in part, the results from the esteri-

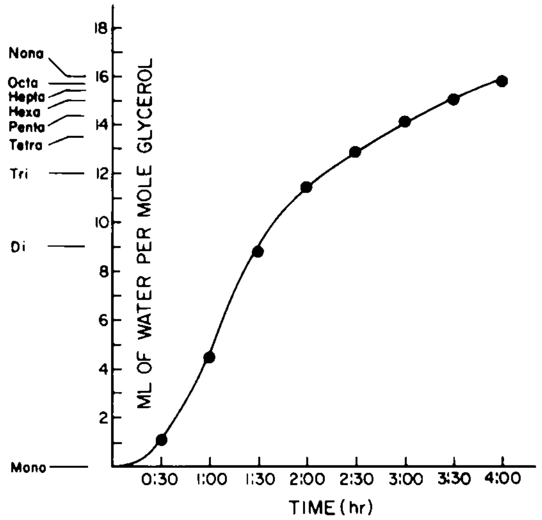

FIG. 1. Typical proceeding of polymerization of glycerol under alkaline catalysis. 2.5 mol % NaOH, 260 C under nitrogenic atmosphere.

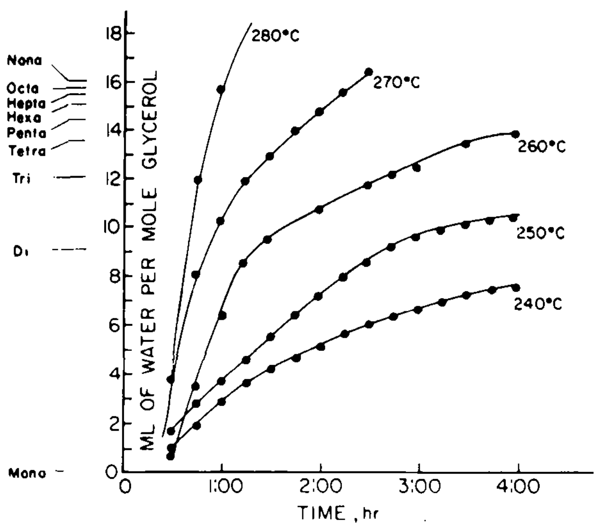

FIG. 2. The effect of the temperature on the yield of polymerization using 2.5 mol % NaOH under nitrogen.

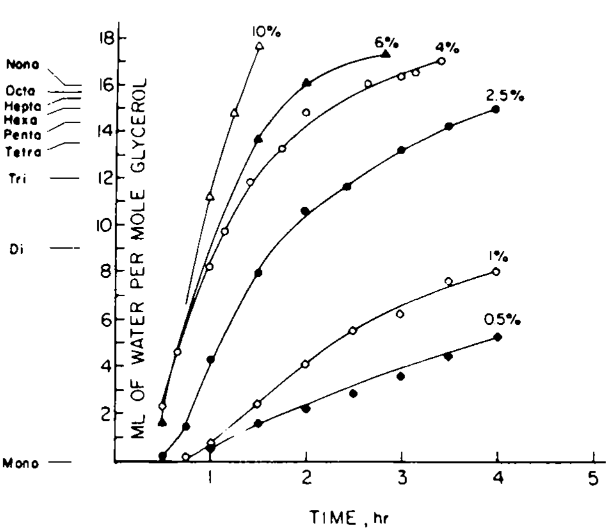

FIG. 3. The effect of catalyst (NaOH) concentration on the polymerization reaction rate: 260 C; under nitrogen atmosphere.

fication process. The reaction was done at 230 C for 1-2 hr until most of the fatty acid was consumed (acid number of 0.5-2). The formed ester was named according to the fatty acid/polyglycerol ratio when the reagents were charged into the reactor, even though the internal product composition might be different (see separate report on polyglycerol fatty acid ester composition [7]).

The main conclusions from this study are that: (a) for higher fatty acid/polyglycerol ratios (higher esterification) longer reaction time is needed to complete the process (see expt. 1, 6 and 7); (b) stearic, palmitic, myristic, lauric and oleic acids react in almost the same rate (see expt. 1, 6 and 7) and the amount of the catalyst used (see expt. 8, 9 and 10); (c) the color of the product is not affected by the esterification process but only by the polymerization process; (d) excess of catalyst can speed up the reaction and does not affect the color of the final material.

The results obtained from the chemical experimental part are the basis for the economical evaluation which was the main aim of this work.

ECONOMIC EVALUATION

An economic evaluation of the polyglycerol esters production has been made, using a simulation model of a chemical plant that was established at the Casali Institute (8).

The evaluation has been performed in two steps: (a) optimization of the polymerization reaction, and (b) evaluation of polyglycerol ester production costs.

Polymerization

Preparation of three polymers has been checked: triglycerol, hexaglycerol and decaglycerol. For each of these, the economic influence of three reaction parameters: type of catalyst, concentration of catalyst, and reaction temperature, have been tested. The results are presented in Table III, expressed as production costs.

A production cost of $2.90-3.06/kg has been calculated for the polyglycerol production, based on the following data: glycerol price—$1,490/ton; yearly production of polyglycerol ester—500 tons; different cost components are as presented in Table IV (as per Nov. 1980).

From Table III, it can be seen that the differences found in the production costs for different polyglycerols and various reaction conditions are of little significance, i.e.,

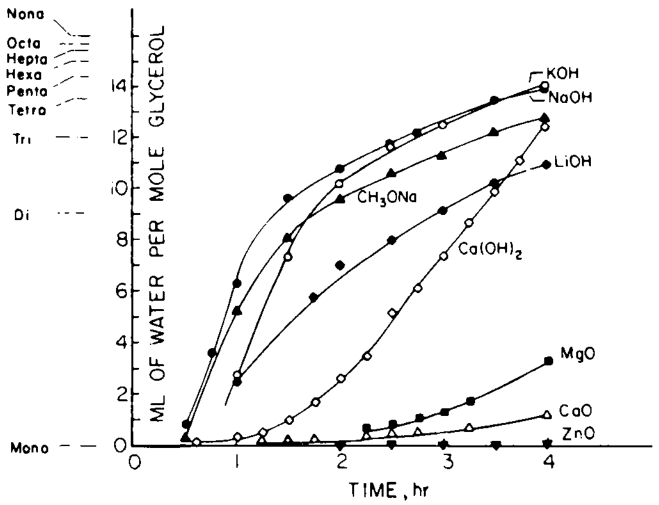

FIG. 4. The rate of the polymerization reaction using several oxides and hydroxides as catalysts.

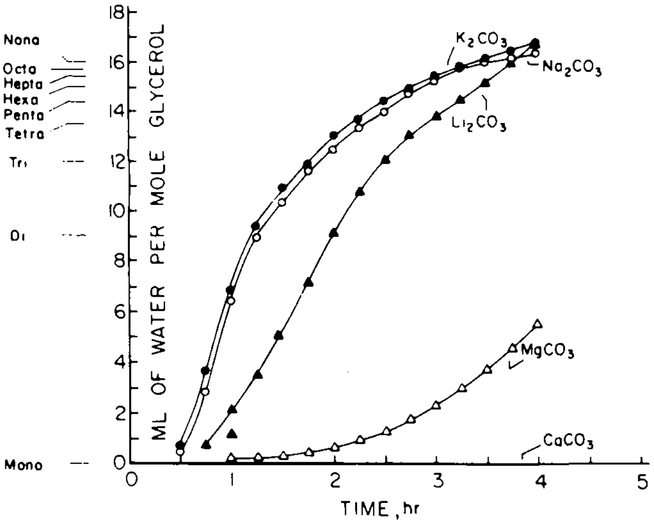

FIG. 5. The rate of the polymerization reaction using carbonates as catalysts.

TABLE II

Conditions of the Esterification Reaction and Properties of the Products

Exp. no.	Product[a]	Color (Gardner Standards, 1933 scale)	Unreacted polyglycerol (wt %)	Added catalyst (NaOH) (wt %)	Time (hr)	Temperature (C)	Acid number
1	3.G.1.O	4	20	0	1:00	233	1.7
2	3.G.1.S	4	18	0	1:00	233	1.8
3	3.G.1.P	4	21	0	1:00	232	2.0
4	3.G.1.M	4	20	0	1:00	232	1.9
5	3.G.1.L	4	18	0	1:00	233	1.9
6	3.G.2.O	4	5	0	1:30	231	1.9
7	3.G.4.O	4	0	0	2:15	232	1.8
8	6.G.1.O	11-	38	0	1:00	233	2.0
9	6.G.1.O	11-	15	0.85	1:00	233	0.4
10	6.G.1.O	11-	0	1.50	1:00	233	0.7
11	10.G.1.O	12-	41	0	1:00	234	1.0
12	10.G.1.S	12-	42	0	1:00	231	1.8
13	10.G.1.P	12-	42	0	1:00	233	0.8
14	10.G.1.L	12-	42	0	1:00	233	1.1
15	10.G.10.O	9	0	0	2:30	233	1.6

[a] G-glycerol; O-oleate; S-stearate; M-myristate; L-laurate; P-palmitate. It should read, e.g., 3.G.4.O = triglycerol-tetraoleate.

TABLE III

Cost Optimization of the Polyglycerol Process

Parameter checked	Possible cost of polyglycerol ($/ton)		
	Triglycerol	Hexaglycerol	Decaglycerol
Type of catalyst[a]			
NaOH	2966	3059	3060
Ca(OH)$_2$	2964	–	–
Li$_2$CO$_3$	2975	–	–
Na$_2$CO$_3$	2965	3031	3086
Concentration of catalyst (%)[b]			
10.0	2943	3034	3061
4.0	2966	–	3060
2.5	2940	3059	3060
Temperature of reaction (C)[c]			
260	2940	3059	3060
270	2940	3032	3059
280	2935	3032	3032

[a] Concentration of catalyst, 2.5%; temperature, 260 C.

[b] Catalyst, NaOH; temperature, 260 C.

[c] Catalyst, NaOH; concentration of catalyst, 2.5%.

TABLE IV

Triglycerol Cost Components

	Thousand $/year	$/Ton	Percent cost
Direct mfg. cost	241.1	2402.8	
Raw materials cost	172.0	1720.0	58.5
Direct labor	36.0	360.0	12.2
Indirect labor	14.4	144.0	4.9
Maintenance	5.4	54.0	1.8
Supplies	.8	.0	0.0
Utilities	9.5	94.9	3.2
Packaging	3.0	30.0	1.0
Sales expense	15.0	150.0	5.1
Depreciation	10.8	107.9	3.6
General and administrative	5.3	52.5	1.7
Factory administration	14.4	144.0	4.9
Taxes and insurance	2.2	21.6	0.7
Research and development	6.0	60.0	2.0
Total product cost	294.7	2938.8	100.0

TABLE V

Hexaglycerol Cost of Raw Materials Components[a]

Reactant name	Glycerol	NaOH
Reactant mol wt	92.0	40.0
No. mol charged	6.0	.1
No. mol reacted	6.0	.1
Reactant price ($/ton)	1490.0	350.0
Reactant quant. (T/T int)	1.2	.01
Reactant cost ($/T int)	1780.3	3.0
Total cost reactants		1783.3 $/ton hexaglycerol
Auxiliaries name	Nitrogen	
Auxiliaries charged (T/T)	.0	
Auxiliaries recovered (T/T)	0	
Auxiliaries price ($/T)	250	
Auxiliaries cost ($/T int)	5.0	
Total cost auxiliaries		5.0 $/ton hexaglycerol
Total cost chemicals		1788.3 $/ton hexaglycerol

[a] Reaction conditions: 260 C; 100% yield.

2-4%. One can explain the results by examining the raw materials economics file for a typical case as presented in Table V. It can be seen that the cost of the catalyst represents (for all the cases) less than 1% of the cost of the raw materials. From this point of view, the type and concentration of the reaction catalyst have no significant economic importance.

Since the reaction yield is 100%, the effect of different catalyst types and concentration is expressed only by the different time periods needed to attain the desired degree of polymerization. The same situation is valid for the different reaction temperatures.

Table VI presents the extreme times of reaction needed to obtain a practical total polymerization, using different catalysts and concentrations. From Table VI, it is clear that, although the differences in the relative reaction time are significant, the absolute values are small.

TABLE VI

Minimal and Maximal Periods of Time Needed in the Plant to Produce Several Polyglycerol Chains

Polymer produced	Time of reaction (hr)	
	Minimum	Maximum
Triglycerol	0.5	3.8
Hexaglycerol	1.4	4.0
Decaglycerol	1.0	4.0

It is obvious that a shorter reaction time can influence the product's economic value by the equipment dimension and, consequently, the equipment cost, as well as by the energy cost.

From the profit and loss account (Table IV) it appears that the cost components connected with the equipment cost (as depreciation, maintenance and supplies) are representing only a small part of the total costs—ca. 6-8%. A similar conclusion can be drawn when the energy costs are considered (ca. 5-6% of the total costs) although our method of assessing this item is less precise. A reduction in the equipment size, by a shorter time of reaction, significant as it can be, will not change substantially the economic picture of the process. In this situation, the reaction conditions which are more favorable to the quality of the product must be chosen.

As optimal reaction conditions, the following have been chosen: (a) catalyst NaOH at a concentration of 2.5% molar; (b) temperature of reaction, 280 C.

Esterification

In the second stage of the project evaluation, the production of a number of polyesters has been simulated within conditions of the polymerization as just recommended. The conversions and yields previously quoted for the esterification process have been considered. A production of 500 T/year has been assessed. The possible costs and prices

TABLE VII

Polyglycerol Esters' Costs and Prices

Product	Costs ($/ton)			Possible price
	Raw materials[a]	Capital related[b]	Total	$/ton[c]
Triglycerol monooleate	1373	231	2291	2436
Triglycerol dioleate	1264	–	–	–
Triglycerol trioleate	1211	106	1873	1940
Hexaglycerol monooleate	1521	154	2334	2431
Hexaglycerol trioleate	1325	120	2037	2114
Hexaglycerol hexaoleate	1222	112	1896	1967
Decaglycerol monooleate	1618	330	2761	2968
Decaglycerol dioleate	1503	265	2507	2672
Decaglycerol decaoleate	1226	–	–	–
Decaglycerol monostearate	1590	330	2727	2933
Decaglycerol monolaurate	1625	175	2500	2611

[a] At a cost of $1490 for glycerol and $990 for a ton of oleic.
[b] Depreciation (10 years, straight line); maintenance and supplies.
[c] At an imposed return on investment of 15%.

TABLE VIII

Profit and Loss Account for Triglycerol Trioleate for 500 Tons Production per Year

	Thousand $/yr	$/ton	Gross sales prc.
Gross sales	970.2	1940.5	100
Direct mfg. cost	707.1	1410.9	72.9
Raw materials cost	605.8	1211.6	62.4
Direct labor	36.0	72.0	3.7
Indirect labor	14.4	28.8	1.5
Maintenance	10.7	21.3	1.1
Supplies	1.6	.0	.2
Utilities	23.6	47.2	2.4
Packaging	15.0	30.0	1.5
Gross margin	263.1	529.4	27.1
Sales expense	97.0	194.0	10.0
Merchandising margin	166.1	335.4	17.1
Overhead costs	134.1	268.2	13.8
Depreciation	42.7	85.3	4.4
General and admin.	34.0	67.9	3.5
Factory admin.	14.4	28.8	1.5
Taxes and insurance	4.3	8.5	.4
Research and development	38.8	77.6	4.0
Total product cost	938.2	1873.2	96.7

calculated according to our model (8) are presented in Table VII.

The total costs presented are in the range of $1.9-2.8/kg polyglycerol fatty acid ester with a possible range of prices at $2.0-3.0/kg (for a return on investment equal to 15%). These values, together with the known qualities of the polyglycerol esters, permit, in our opinion, the penetration of the food emulsifier market by this category of products.

From a closer examination of the production costs of the polyglycerol esters, (Table VIII presents cost calculation for the triglycerol trioleate), it is evident that the raw materials costs are representing a high part of the total costs, about 65-70% and, therefore, are the parameters that must be tackled in order to optimize the product. The ratio between the polyglycerol and the fatty acids in the polyester is the determining factor in the raw materials cost: the lower the ratio, the lower the cost, as presented in Table VII.

Using the economic information presented in connection with the surface-activity efficiency, it is possible to choose the most suitable product from the polyglycerol esters family for a given task and to establish the best trade-off between the different esters.

REFERENCES

1. Babayan, V.K., Food Prod. Dev. 2:58 (1968).
2. Babayan, V.K., JAOCS 51:260 (1974).
3. Babayan, V.K., and R.T. McIntyre, Ibid. 48:307 (1971).
4. Babayan, V.K., and H. Lehman, U.S. Patent 3,637,774 (1972).
5. Seiden, P., and B.M. Martin, U.S. Patent 3,968,169 (1976).
6. McIntyre, R.T., JAOCS 56:835A (1979).
7. Garti, N., and A. Aserin, J. Liqu. Chrom. (in press).
8. Cevidalli, G., and B. Zaidman, Chem. Eng. (July 14, 1980) 145.

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