Technical

Continuous Hydrogenation of Soybean Oil in a Trickle-Bed Reactor with Copper Catalyst

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ABSTRACT

Continuous hydrogenation of soybean oil with a stationary copper catalyst bed was performed at 110-180 C, 30-75 psig hydrogen and liquid hourly spaced velocities (LHSV) of 0.25-0.6 cc/hr/cc catalyst. In contrast to batch, continuous hydrogenation was achieved at a lower temperature with no need to postfilter the product. The soybean oil products from the continuous and batch processes hydrogenated to 0% triene were similar in fatty acid composition, *trans* content of 29% and linolenate selectivity of 5.

INTRODUCTION

Stationary bed or trickle-bed reactors have been developed extensively by the petroleum industry primarily for hydrocracking, hydrodesulfurization and hydrotreating of petroleum fractions of relatively high boiling points. Unlike a continuous slurry reactor in which oil containing suspended catalyst particles flows through the reactor, a trickle-bed reactor approaches plug flow behavior. Furthermore, the problem of separating catalyst from produce is eliminated.

Concurrent liquid and gas flowing continuously downward through a packed catalyst bed have been used in many chemical reactions. If the trickle-bed reactor diameter-to-catalyst diameter ratio is greater than 8 (generally, it is greater than 25 commercially), the nonuniformity of the flow and the wall effect is considered insignificant (1,2). As long as the initial distribution of the liquid on the top layer of packing is uniform, the flow through the catalyst bed is also uniform.

Continuous hydrogenation over a stationary catalyst bed is not new to fats and oil processing. Between 1922 and 1930, Bolton and Lush (3-6) reported their process for hydrogenating oils by passing the oil over nickel turnings in a tube reactor. Installations were very small, and the process apparently was used for production of stearine, where control of selectivity was not a factor (7). Recently, Mukherjee et al. (8) studied the activity and selectivity of several stationary catalysts for hydrogenating soybean oil, but they did not compare their results with batch hydrogenation nor optimize their conditions.

In this laboratory, Snyder et al. (9) reported the activity and selectivity for a copper chromite catalyst in a laboratory continuous slurry reactor. They postulated a hydrogenation scheme which closely simulated the experimental data when the triene and diene are reduced through a conjugated diene intermediate.

This paper reports on the continuous hydrogenation of soybean oil with a copper chromite catalyst (without binder) in a trickle-bed reactor, and the results are compared with those from a batch reactor using the same catalyst. Ordinarily, a binder is needed to hold the catalyst together and to give it mechanical strength when it is compressed into tablet form. However, binders may influence the catalyst and the resultant product, and this factor is considered in this work.

EXPERIMENTAL PROCEDURES

Materials

Alkali-refined and bleached soybean oil, obtained commercially, was used for all experiments. Fatty acid composition determined by gas-liquid chromatography (GLC) was: saturates, 16.1%; monoene, 24.3%; diene, 52.4%; triene, 7.2%; conjugated diene, 0.6%. Calculated iodine value (IV) was 130.

A commercial copper chromite catalyst (Cu 0203T, Harshaw Chemical Co., Cleveland, OH) containing 78% CuO, 20% Cr_2O_3, with a surface area of 8 m^2/g, total pore volume of 0.14 cc/g was used for all experimental runs. The pellets were broken with a mortar and pestle to give a 16-mesh catalyst. This catalyst, with relatively poor linolenate selectivity, was chosen for this study because it contained no binder, and products from both continuous hydrogenation and batch hydrogenation using it were similar.

Water-pumped hydrogen (99.99%) passed through an in-line Deoxo catalytic gas purifier (Englehard Industries, Newark, NJ) was the reducing gas. Water-pumped nitrogen was blended with hydrogen to condition the catalyst and to purge any contaminants from the system.

Hydrogenations

Continuous hydrogenations were done in a 1.0-in. IPS × 24-in. 316 stainless-steel reactor (Fig. 1) according to the flow diagram shown in Figure 2. Soybean oil was charged to the top of the reactor from a graduated vessel by a positive displacement laboratory Mini Pump (Milton Roy Co., Riviera Beach, FL) and a heat exchanger. The desired gas (H_2, N_2 or H_2/N_2 blend) was admitted to the top of the reactor just upstream to the catalyst bed. Catalyst volume in the reactor was 160 cc (320 g). The oil product/gas mixture flowing from the reactor to a degasser (Jerguson Gage and Valve Co., Burlington, MA) was continuously discharged (or sampled) through a liquid seal. Excess gas was continuously metered and vented. The oil product was analyzed as it came from the degasser.

The reactor and heat exchanger were heated to the desired catalyst bed temperatures by regulating steam pressure from 0-120 psig. Reaction temperatures were measured with a multipoint thermocouple inserted in the catalyst bed indicating the temperature at the top, middle and bottom

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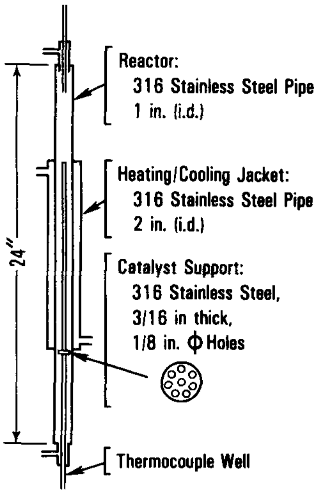

FIG. 1. Stationary bed reactor for continuous hydrogenation studies.

of the bed. Pressure was regulated at the gas cylinder and gas flow was controlled by throttling the exit gas.

Two precondition procedures were used to activate the catalyst. In one procedure, the catalyst was activated "dry," by first purging with N_2, raising the bed temperature to 170 C, and then introducing H_2. The H_2 content of the gas blend was raised in 10% increments while limiting the temperature to 190 C and maintaining the gas blend flow rate at 170 CC/min. After 100% H_2 was reached, the bed temperature was dropped to less than 100 C, the system was pressurized to at least 50 psig and the exotherm was monitored. Moisture formed during the catalyst reduction was collected and measured. The bed temperature was then raised to operating conditions and soybean oil was started through the bed at a rate to ensure even distribution over the catalyst bed surface and complete wetting of the catalyst. Additional moisture in the product was usually observed during this process. When the oil product was water-free, conditions to hydrogenate soybean oil were varied and data were collected. In another procedure, the catalyst was activated "wet," by first purging with N_2 at 170 C, and then introducing soybean oil through the catalyst bed at a rate slow enough to prevent channeling and excessive exotherm. A blend of 10% H_2 in N_2 was introduced at 170 cc/min, and the H_2 content in the blend was raised in 10% increments to avoid the exotherm from raising the temperature above 190 C. When the gas blend was 100% H_2, the pressure was increased in 10-psig increments to at least 50 psig. In this "wet" procedure, it was not necessary to reduce the temperature before pressurizing with H_2 because the exothermic heat was readily transferred to the flowing oil. Moisture formed during the catalyst reduction was collected and measured. When the oil product was water-free, conditions to hydrogenate soybean oil were varied and data were collected.

Batch hydrogenations were done in a Parr autoclave equipped with gas dispersion agitator (10) and internal heating/cooling coil (11). Soybean oil (440 g) and 1% pulverized Cu 0203T catalyst (4 g) were charged in the autoclave, degassed 3 times and heated under N_2 to the desired temperature. The autoclave was then evacuated, flushed and filled with H_2 to the desired pressure. The reaction began when agitation (1,700 rpm) started. At the end of the reaction, the oil/catalyst mixture was cooled to room temperature, filtered through filter aid to remove the catalyst and analyzed.

Methyl esters were prepared by transesterification with methanolic BF_3 reagent (12). GLC analyses were carried out at 200 C with an F&M Model 720 instrument and a 9-ft x ¼-in. stainless-steel column packed with 20% diethylene glycol succinate (Hi Eff 1 BP) on 80-100 mesh Gas Chrom P (Applied Science Laboratories, Inc., State College, PA). The thermal conductivity detector was operated at 280 C

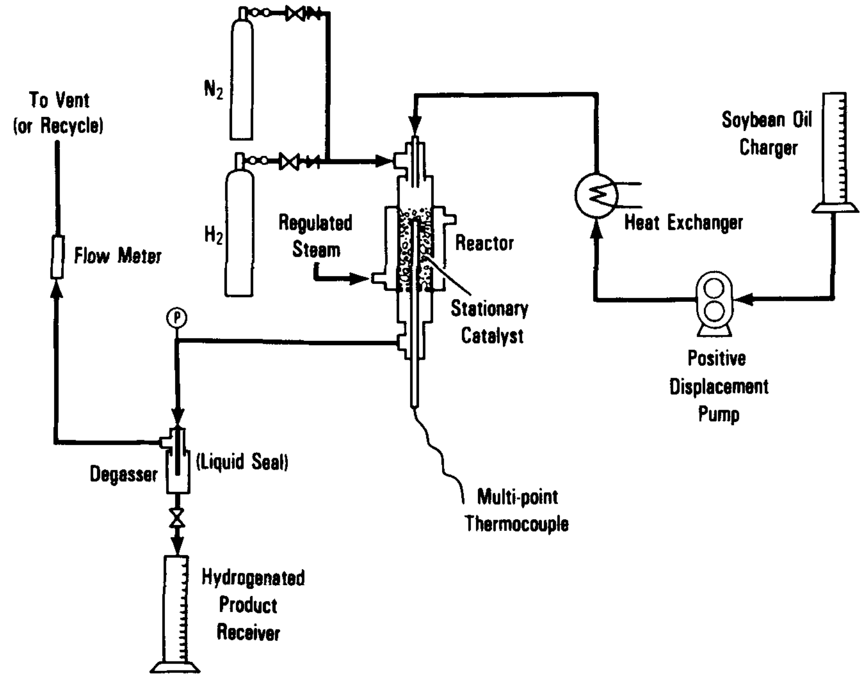

FIG. 2. Typical trickle-bed hydrogenation flow diagram.

TABLE I

Effect of Parameter on Triene and Iodine Value (IV)

Parameters	Pressure (psig)	Temp. (C)	LHSV	Triene	IV
Oil/H_2 down-flow	50	180	0.5	0.6	89
Oil/H_2 up-flow	75	180	0.6	1.3	102
Excess H_2	50	170	0.4	2.7	106
No excess H_2	50	170	0.4	4.9	116
Dry preconditioning[a]	50	180	0.25	1.1	96
Wet preconditioning[b]	50	180	0.25	0.3	92
16 Mesh catalyst	50	180	0.25	0.3	92
1/8 in. tablet	75	180	0.25	1.5	92
No binder (Cu 0203T)	30	180	0.25	2.2	99
Binder (Cu 1107T)	50	180	0.50	7.1	128

[a] Required <16 hr at 180 C, atmos. pressure to precondition catalyst.

[b] Required >29 hr at 180 C, 50 psig H_2 pressure, 0.6 LHSV to precondition catalyst.

and the injection port was at 240 C. the helium carrier gas rate was 75 cc/min.

Percentage *trans* isomer was measured by IR with a Perkin-Elmer Model 337 spectrophotometer (12).

Percentage linolenate was measured by alkali isomerization and determination of UV absorption with a Beckman DV-2 spectrophotometer (12).

RESULTS AND DISCUSSION

Exploratory runs were made with a stationary catalyst bed reactor as a basis for a statistical design study of hydrogenation parameters. Variables included: (a) oil and hydrogen up-flow through the reactor (flooded flow operation) compared to oil and hydrogen down-flow through the reactor (trickle-flow operation); (b) the effect of a large hydrogen excess compared to little or no hydrogen excess; (c) "dry" catalyst preconditioning (reduction of the catalyst in a dry state) compared to "wet" catalyst preconditioning (reduction of the catalyst wet with soybean oil); (d) catalyst size (16-mesh compared to 1/8-in. tablet) and (e) the effect of a catalyst binder. The effectiveness of the process was evaluated by determining the amount of triene and IV reduction (Table I). Although hydrogenation conditions were not identical for comparing trickle flow with flooded flow, trickle flow appeared better than flood flow; a large hydrogen excess (250:1 H_2-to-oil ratio) was better than little or no excess. Wet preconditioning of the catalyst was better than dry preconditioning, but by the dry method the time to precondition was less, there was no waste of oil and the catalyst exotherm was easier to recognize. Smaller catalyst particles were better than larger particles, and a catalyst without a binder was much better than one of similar composition with an alkaline binder (Table I). The decision to use trickle-flow for this study was made also on the basis of ease of operation, less back mixing and adequate triene reduction.

A statistical design with 17 hydrogenations was used to evaluate temperature effects under the best exploratory conditions, with additional independent variables of pressure (psig) and liquid hourly space velocity (LHSV, cc oil/hr/cc catalyst). A general quadratic equation was used to model data from these hydrogenations. A general quadratic equation of the form

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_1^2 + b_4 X_2^2 + b_5 X_1 X_2$$

was used to model data from these hydrogenations, where Y is the dependent variable and X_1 and X_2 are independent variables (temperature, pressure, LHSV). LHSV was the most important variable, because the multiple correlation coefficient (R) (13) between predicted and observed decreased from 0.92 to 0.54 for diene and from 0.90 to 0.71 for triene, when LHSV was deleted from the prediction equation. R is a measure of the association between observed and predicted fatty acid values. For runs at lower temperatures, there was little pressure effect.

An additional 14 hydrogenations were made at 30 psig while varying the temperature and the LHSV (Table II). Data from this series of hydrogenations were used to compute response surfaces (13) for monoene, diene and triene (Fig. 3). The respective multiple correlations, R, for monoene, diene and triene were 0.94, 0.94 and 0.96. The triene content between 0 and 3% in the hydrogenated product peaked between temperatures 132 and 135 C and decreased with decreasing LHSV. The diene content reached a maximum between 137 and 140 C and decreased with increasing LHSV. The monoene content reached a maximum between 136 and 138 C, but increased with decreasing LHSV. At a given LHSV rate, the fatty acid composition in the oil varies with increasing temperature. This phenomenon covering temperatures from 110 to 160 C is different from reported Arrhenius relationships for hydrogenations at 150 to 200 C (8,11,14,15). To obtain a 3% triene oil with an IV of 112, the LHSV could be increased to 0.59 at 135 C without an appreciable drop in diene or an increase in oleate. Thus, for a stationary Cu 0203T bed, H_2 pressure of 30 psig, temperature of 132 C and LHSV of 0.25, the fatty acid composition of the hydrogenated product would be triene 0.2%, diene 30.4%, monoene 53.7%, the calculated IV 99 and selectivity 5.

To compare continuous hydrogenations with batch hydrogenations, 2 runs were made in the Parr autoclave at 130 and 170 C. The hydrogenation at 170 C was carried out at the conditions of choice for a copper chromite catalyst (11,14). The low-temperature batch hydrogenation conducted at the optimal conditions for a continuous trickle-bed hydrogenation (135 C, 30 psig) showed no reduction in triene even after 225 min. However, at the favorable conditions for a batch hydrogenation (170 C, 30 psig), the triene content was effectively reduced (Fig. 4). A linolenate selectivity ratio (K_{Ln}/K_{Lo}) of 5 was calculated for both batch (170 C, 30 psig) and continuous (135 C, 30 psig) hydrogenations using Cu 0203T catalyst.

The analyses of products from the continuous hydrogenations fall close to the curve of values for the effective batch hydrogenation. For faster space velocities (0.3 and 0.5 LHSV) the values for diene and monoene in a continuous hydrogenated products fall very close to those of a

TABLE II

Fatty Acid Composition of Continuous Hydrogenated Oils (Stationary Catalyst Bed)

Run	Temp (C)	LHSV	Saturates	Monoene	Diene + CD[a]	Triene (AI)[a]	Conj. diene	*trans*	IV (Calc)[b]	SR (Ln)
1	110	0.4	15.9	33.3	47.7	3.7	0.7	8	121	4
2	115	0.3	15.6	38.1	44.0	2.3	0.6	13	115	4
3	115	0.5	15.6	33.9	46.6	3.9	0.7	8	119	3
4	120	0.25	16.1	46.4	36.7	0.8	0.5	18	106	4
5	120	0.5	16.3	37.2	43.6	2.9	0.7	10	115	3
6	125	0.25	16.1	49.2	34.4	0.3	0.5	20	103	6
7	125	0.4	16.5	41.2	41.0	2.3	0.6	14	112	3
8	125	0.55	15.9	36.6	44.1	3.4	0.8	9	117	3
9	135	0.25	15.8	60.4	23.2	0.1	0.5	26	93	5
10	135	0.3	16.0	51.1	32.3	0.6	0.6	19	101	4
11	135	0.5	15.3	41.8	40.6	2.3	0.8	14	112	3
12	140	0.4	15.3	49.0	34.7	1.0	0.7	18	105	4
13	153	0.3	16.7	42.9	37.8	2.6	0.4	15	109	3
14	153	0.6	17.3	33.8	44.5	4.4	0.5	8	118	3

[a] CD - conjugated diene; AI = linolenate content by alkali isomerization method.

[b] Iodine values (IV) calculated from fatty acid composition, determined by GLC and adjusted for certain conjugated dienes with came retention time as linolenate.

batch hydrogenation at identical iodine values, but the values for triene indicate that the higher LHSV yields a lower linolenate selectivity (Table II, Fig. 4).

Both Snyder et al. (9,15) and Mukherjee et al. (8) effectively hydrogenated soybean oil with copper chromite catalyst at temperatures above 180 C. At 190 C, 175 psig and 1% copper chromite in a slurry, Snyder reduced the triene in soybean oil to 1.2% with a selectivity of 10, equal to that reported for a batch system. Mukherjee et al. hydrogenated soybean oil with a stationary copper chromite catalyst and reduced the triene to 1.7% with a "linolenate selectivity" of 10. However, by recalculating their data by the same method used by Butterfield et al. (16), the selectivity is only 6. At a temperature of 155 C, both groups of workers found the degree of hydrogenation to be minimal and greater pressure was required to improve the catalytic action.

Both Snyder and Mukherjee reported a larger amount of conjugated diene formed during hydrogenation than was found in this work. The lower values may result from hydrogenating soybean oil at a lower temperature or with a different catalyst.

The results of this work demonstrate that continuous trickle-bed hydrogenation with a copper catalyst is capable of reducing the unsaturates in soybean oil to the same degree as a batch hydrogenation, providing the continuous reaction temperature is lowered. Although the equipment used for this study was not capable of delivering a product with zero triene, a pump with lower rate, a longer catalyst bed, or a more selective catalyst would be expected to improve the extent of triene hydrogenation.

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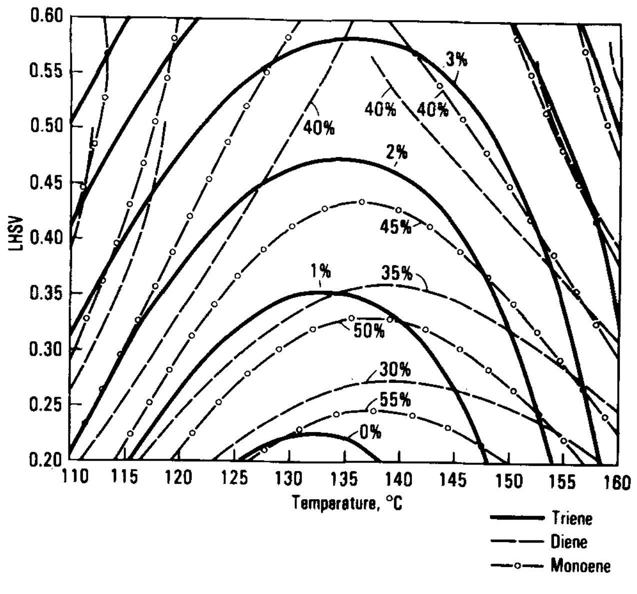

FIG. 3. Predicted contours at constant triene ——, diene ----, and monoene — o —. Independent variables–temperature and liquid hourly space velocity (LHSV). Pressure–30 psig.

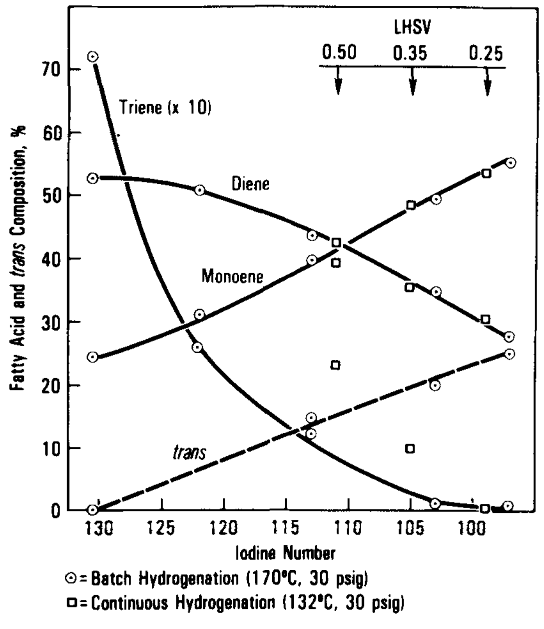

FIG. 4. Batch hydrogenation of SBO with Cu 0203T catalyst ⊙ ; continuous stationary catalyst hydrogenation at 0.25, 0.35 and 0.50 LHSV □.

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Evaluation of the Turbidity and Thin Layer Chromatographic Tests for Detection of Castor Oil

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ABSTRACT

Detection procedures for castor oil in genuine and treated groundnut oils were screened and false turbidity was noticed when ammonium molybdate/sulfuric acid reagents were added to rancid groundnut oil. Successively bleached and neutralized rancid groundnut oil samples do not respond to the tests. Turbidity did not appear for groundnut oils containing 10 and 20% castor oil and even for pure castor oil sample. Thin layer chromatography (TLC) was found to be quite effective for most of the treated, adulterated, genuine, old and fresh oil and fat samples, but showed a streaking, when applied to rancid groundnut oil. However, streaking could be greatly reduced and TLC could be successfully performed with bleached and neutralized, rancid groundnut oil samples.

INTRODUCTION

Castor (*Ricinus cummunis* L. Euphorbiaceae) is a widely cultivated oilseed crop in India. Castor oil is cheaply priced and is used as an adulterant for many common edible oils. Research on detection of castor oil started as early as 1951 (1) by estimating the hydroxyl value and refractive index of acetylated oils (quite low in the presence of castor oil). Colorimetric testing as reported by Auselmi et al. (2) was found unsuitable. Rajnish (3) has developed a turbidity (ammonium molybdate in sulfuric acid) method which also is said (4,5) to be unsatisfactory as it fails even with pure castor oil. A thin layer chromatographic (TLC) technique was developed by Lakshminarayana and Mani (5) for detection of castor oil which is quite effective in most cases. It is of less use (6), however, when the oil under investigation is highly oxidized.

Work has been done to evaluate molybdic acid, sulfuric acid and TLC methods for detection of castor oil. Effort has been made to verify the reported (6) interference due to high free fatty acid (FFA) content and autoxidation of edible oils using the characteristic triricinolein spot of castor oil on thin layer chromatoplates. Effects of oxidation, neutralization and bleaching have also been studied.

EXPERIMENTAL PROCEDURES

Castor and other oilseeds for the experiments were procured from seed suppliers and local markets. Oils were extracted using hexane in a Soxhlet apparatus. The extract was filtered and the solvent was removed under vacuum. Oils thus free from residual solvent were used for detection and chromatographic determinations. Samples with high FFA contents (sesame, groundnut and safflower oils) were procured from the old stocks of a local oil firm. Palmolein, RBD palm oil and rice bran oil were supplied by CFTRI Employees Consumers' Cooperative Society, pure ghee was from the Mysore dairy and vanaspati (Dalda) was manufactured by Hindustan Lever Ltd. in India.

Ammonium Molybdate Test

One mL of filtered oil sample dissolved in 10 mL of petroleum ether (bp 40-60 C), acidified with (2% v/v) conc. hydrochloric acid in a clean dry test tube. To this, one drop of reagent (1.25 g ammonium molybdate in 100 mL of sulfuric acid, sp. grav. 1.84) was added down the side of the test tube, and turbidity was observed instantaneously.

Thin Layer Chromatography

Thin layer chromatoplates (20 × 20 and 40 × 20 cm) coated with Silica Gel G (BDH grade, 0.25 mm thickness) were prepared following the procedure of Kirchner (7). A 1% chloroform solution of samples (5-10 μL) was spotted onto preactivated plates. Chromatographic grade petroleum ether (bp 40-60 C), ether and benzene were used as developing solvents. Spots were visualized in an iodine chamber and confirmed by charring the components after spraying the plates with 5% aq perchloric acid.

Oxidation

Oil was placed into a round-bottomed flask (500-mL capacity) provided with 2 side tubes. The flask was connected via a suction pump and air was allowed to bubble through the inlet into the oil. The contents were heated at 90 C on a steam water bath and then aerated for 10 hr (6).

Bleaching

Oil that was free from moisture was placed into a round-bottomed flask (500-mL capacity) fitted with an electric stirrer. Activated carbon (J.T. Baker Chem. Co., 10% w/w)