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Rapeseed Oil Transesterification By Heterogeneous Catalysis

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ABSTRACT

Methyl fatty esters derived from vegetable oils are a promising fuel for direct injection diesel engines. This study's purpose was to identify a heterogeneous catalyst to selectively produce methyl fatty esters from low erucic rapeseed oil. Most experiments were at atmospheric pressure and approximately the corresponding boiling point temperature of the mixture, 60-63 C. However, the catalytic activity of an anion exchange resin was tested at 200 C and 68 atm (1000 psig) and at 91 C and 9.2 atm (135 psig). All samples were analyzed by thin layer chromatography with samples from the elevated temperature and pressure experiments also analyzed by mass spectroscopy. The most promising catalyst examined was CaO•MgO. The activities of the catalysts CaO and ZnO appear to be enhanced with the addition of MgO, therefore the transesterification reaction mechanism may be, in this instance, bifunctional. The anion exchange resin catalyst at 200 C and 68 atm generated substantial amounts of both methyl fatty esters and straight-chain hydrocarbons, even though these reactions did not go to completion. At 91 C and 9.2 atm the cracking also occurred but at a substantially reduced rate, and no transesterification was noted.

INTRODUCTION

Vegetable oils have long been considered a potential diesel fuel, although their use has been hindered by economic and technical difficulties. High viscosity and other physical properties of neat vegetable oils promote incomplete combustion in conventional direct injection diesel engines (1). Recently, considerable research has been conducted on identifying and solving these problems to provide a viable diesel fuel.

Vegetable oil transesterification via alcoholysis into methyl or ethyl esters is one approach to a viable vegetable oil-based diesel fuel. Transesterification significantly reduces vegetable oil viscosity, thereby improving fuel atomization and consequently fuel combustion characteristics (2). Short- and long-term engine testing indicates that fatty ester fuels may perform well in both indirect (3) and direct injection diesel engines (2,4,5,6).

A number of excellent homogeneous catalysts exist for transesterification. Freedman and Pryde (7) and Kusy (8) report 95% fatty ester yields in one hr using sodium hydroxide, sodium methoxide and sodium ethoxide catalysts. Fuls and Hugo (9) also report good methyl ester yields using sulfuric acid and para-toluene sulfonic acid homogeneous catalysts. An interesting variation on the transesterification scheme by homogeneous catalysis is the successful attempt of Nye et al. (10) to produce methyl fatty esters from used frying oil. Homogeneous catalysts cause one primary problem; they must be neutralized and removed from the reaction products. A heterogeneous catalyst would greatly simplify and economize the catalyst removal step. This study's purpose was to identify a heterogeneous catalyst to selectively produce methyl esters from rapeseed oil.

MATERIALS AND METHODS

The quantities of reactants used in all experiments were 0.25 gmoles of crude low erucic rapeseed oil and 1.5 gmoles of methanol. The literature (7,11) demonstrates that the optimal molar ratio of alcohol to triglycerides is 6:1, i.e., twice the stoichiometric. The catalyst concentration suggested is 1 molar per cent (7) or 0.3-0.5% based on the weight of the vegetable oil (8). These concentrations reduce to approximately 0.02 gmoles at the reactant quantities used in this research. The actual catalyst amount used in each batch varied from 0.0055 to 0.82 gmoles.

The allotted reaction time was arbitrarily set at 12 hr for each batch with samples collected at the 6-, 9- and 12-hr marks. Freedman and Pryde (7) report that equilibrium was essentially reached in one hr with sodium hydroxide and sodium methoxide catalysts. The 12-hr reaction time was chosen to accommodate potential catalysts that might have been limited by slow reaction kinetics and to minimize the effects of any potential mass transfer resistance.

The reaction vessel was a 500 ml glass batch reactor with a water-cooled condenser and thermometer. The reactor temperature was generally maintained at 60-63 C, slightly under the mixture's boiling point. With an excellent catalyst, the reaction can proceed at room temperature (11). Groggins (12) states as a rule of thumb that the kinetics of a transesterification reaction approximately double with every 10 C incremental rise in temperature. Although perhaps true in general, Sridharan and Mathai (13) state that alcoholysis with basic catalysts at temperatures above 16 C (60 F) causes various side reactions, particularly saponification, to predominate. The reaction mixture was kept as moisture-free as possible to minimize the hydrolysis of the fatty acids into the fatty acid salts. As little as 0.3% water causes some fatty acid salt formation.

Because transesterification rates are a strong function of temperature, the reaction was attempted at an elevated temperature and pressure with an anion exchange resin catalyst. The purpose of the elevated pressure was to maintain the reactants in the liquid phase at the elevated temperature. The reactants and catalyst were placed in a 500 ml stainless steel container. The air was flushed from the system and replaced with nitrogen to prevent oxidation. The container was placed in a mechanical rocker with heating element, and the mixture was allowed to react for the usual 12-hr period.

The collected samples were analyzed by thin layer chromatography (TLC). To provide a qualitative batch comparison of the catalytic activity, the size of each circular area on the TLC sheet, representing an individual compound, was measured. The area representing the methyl fatty ester of each sample was converted to a percentage of the total areas of all compounds in that sample. The largest number from all TLC analyses was assigned the value of 10 and all other TLC results expressed proportionally. The TLC results from the experiment with the upper assigned limit, 10, appear comparable to $NaOCH_3$ catalyzed reactions which produce yields in excess of 95% (7,8). However, TLC is a qualitative method. Therefore the numbers assigned to the TLC results are for a qualitative comparison of catalytic activity and should not be confused with per cent yield.

A double focusing gas chromatograph-mass spectrometer (GC-MS) analyzed the products from the elevated temperature and pressure experiments. The equipment collected the spectra at 70EV at a 0.5 sec per decade scan rate and operated in the positive ion mode with electron impact. The mass range was 500-20 amu with a mass resolution of 1000. The chromatographic column was a 30 m long and had an inside diameter of 0.25 mm with a 0.25 micron phase coating thickness. The gas chromatograph temperature program was initially 50 C for 3 min, then raised 5 C/min to 280 C and held at that temperature for 10 min.

Table I lists the three catalyst supports used in this research. Using MgO, Al_2O_3, and SiO_2 catalyst supports allowed the examination of the effects of strong basic, weak basic and acidic supports, respectively, on the selected catalysts. Table II lists the catalysts examined in this investigation including the base-line batch runs of the catalyst supports.

It was speculated that a successful catalyst will be basic, possibly strongly basic. The CaO, K_2CO_3, and Na_2CO_3 experimental series were selected because Tanabe (14) identified them as having basic characteristics. These three catalysts also were tested without supports to compare their relative performance and the support effects. The 7% $CaO \cdot Al_2O_3$ catalyst is a support from United Catalyst Inc. It was tested as received because of the CaO content. The activated carbon and Fe_2O_3-on-MgO-crush catalysts were suggested by Rindt (15) as being basic catalysts. The Fe_2O_3-on-MgO-crush catalyst was tested in powder rather than in pellet form because of ease of preparation. The

TABLE I

Catalyst Supports

Name	Supplier	Form	Surface area (m^2/gm)	Average pore diameter (Å)	Composition
1. MG-0601	Harshaw Chem. Co.	0.318 cm tablets	17	635	98% MgO
2. AL-0104	Harshaw Chem. Co.	0.318 cm tablets	80-100	136	97% Al_2O_3
3. T-1517	United Catalysts Inc.	0.476 cm spheres	131	180	93% SiO_2, 3% Al_2O_3

TABLE II

Catalysts Examined

Catalyst	Composition	Catalyst	Composition
1. MgO support	98% MgO	15. Na_2CO_3 powder	–
2. Al_2O_3 support	97% Al_2O_3	16. Activated carbon	–
3. SiO_2 support	93% SiO_2, 3% Al_2O_3	17. Fe_2O_3 on MgO support crush	2.73% Fe_2O_3, 97.3% MgO crush
4. $CaO \cdot Al_2O_3$ support	7% CaO, 92% Al_2O_3	18. $CH_3ONa \cdot SiO_2$	1.5-3.6% CH_3ONa, 98.5-96.5% SiO_2 support
5. $CaO \cdot MgO$	9.22% CaO, 91.8% MgO support	19. $NaAlO_2 \cdot MgO$	3.32% $NaAlO_2$, 96.8% MgO support
6. $CaO \cdot Al_2O_3$	14.8% CaO, 85.2% Al_2O_3 support	20. $NaAlO_2 \cdot Al_2O_3$	6.83% $NaAlO_2$, 93.2% Al_2O_3 support
7. $CaO \cdot SiO_2$	12.6% CaO, 87.4% SiO_2 support	21. Zn metal	–
8. CaO powder	–	22. Cu metal	–
9. $CaO \cdot MgO \cdot Al_2O_3$	8.34% CaO, 5.64% MgO, 86.0% Al_2O_3 support	23. Sn metal	–
10. $K_2CO_3 \cdot MgO$	4.76% K_2CO_3, 95.2% MgO support	24. Pb metal	–
11. $K_2CO_3 \cdot Al_2O_3$	14.2% K_2CO_3, 85% Al_2O_3 support	25. $ZnO \cdot MgO$	7.39% ZnO, 92.6% MgO support
12. K_2CO_3 powder	–	26. $ZnO \circ Al_2O_3$	26.2% ZnO, 73.8% Al_2O_3 support
13. $Na_2CO_3 \cdot MgO$	0.77% Na_2CO_3, 99.2% MgO support	27. $ZnO \cdot SiO_2$	13.0% ZnO, 87.0% SiO_2 support
14. $Na_2CO_3 \circ Al_2O_3$	4.6% Na_2CO_3, 95.3% Al_2O_3 support	28. Anion Exchange Exchange	–

$CH_3ONa \cdot SiO_2$ catalyst is an attempt to select an outstanding homogeneous catalyst and bond it to a solid support with sufficient strength to prevent the catalyst from going into solution but not to inhibit its catalytic properties. Perhaps the CH_3O^- anion causes the catalytic activity and, therefore, this anion may bond with an acidic catalyst support. Whether this bond has sufficient strength can be determined only empirically. The $NaAlO_2$ catalysts were examined because of hopes that these catalysts would perform similarly to NaOH. The metals examined, Zn, Cu, Sn, and Pb, were suggested as potential transesterification catalysts by Groggins (12).

The acidic catalyst $ZnO \cdot SiO_2$ was tested because two publications indicated that it may be potentially successful. Wu and Storch (16) state, "An acid carrier with a combination of weakly hydrogenating components such as zinc, magnesium, and chromium oxides behaved like a basic carrier." Furthermore, Sridharan and Mathai (13) list a zinc silicate catalyst as promoting 85% fatty ester yield in a coconut oil and methanol system. The $ZnO \cdot MgO$ and $ZnO \cdot Al_2O_3$ catalysts were tested to determine the activity of ZnO with all supports used in this study. The $CaO \cdot MgO \cdot Al_2O_3$ catalyst was selected on the basis of prior experimental results from this study. The catalyst used in the elevated temperature and pressure experiments was a 20-50 mesh Dowex 2-X8 anion exchange resin in the hydroxide form.

Most heterogeneous catalysts investigated were prepared by impregnation, either directly without subsequent calcination, or a salt of the catalyst was impregnated on the support and calcined to form the desired catalyst. The preparation procedure involved immersing the support in an aqueous solution of the catalyst or catalyst salt, air-drying at elevated temperature and, when necessary, calcining at sufficient temperatures in the presence of oxygen to decompose the salt to the oxide. Frequently, the aqueous solution was saturated. However, when it was speculated that a lower catalyst loading was desirable, the solution concentration was reduced accordingly. To reduce the moisture in the reaction, the catalysts were, after preparation, dried at a temperature above the boiling point of water. The catalysts were then held in a desiccator until placed into the reaction.

The acid/base strength and the relative quantity of acid/base sites were measured for each catalyst.

RESULTS AND DISCUSSION

Table III lists the test results. The relative methyl fatty ester values, as previously described, provide a qualitative comparison of catalytic activity. The catalyst supports were tested to detect any favorable catalytic activity and to establish baseline results. The two basic supports, MgO and Al_2O_3, produced a substantial amount of soaps, i.e., the salts of the free fatty acids, with the more concentrated basic support, MgO, producing the greater abundance of soaps.

The CaO catalytic series presented a fascinating variety of results. The $CaO \cdot MgO$ catalyst provides the best activity but also produced a prodigious quantity of soaps thereby rendering this catalyst, as constituted in this study, unsuitable for commercial applications. The TLC results appear, however, comparable to $NaOCH_3$-catalyzed reactions which produce yields in excess of 95% (7,8). The $CaO \cdot Al_2O_3$ and $CaO \cdot SiO_2$ catalysts produced no detectable methyl fatty esters. The apparent discrepancy between the relative ester values of the $CaO \cdot MgO$ heterogeneous catalyst and the CaO homogeneous catalyst may be partially because the $CaO \cdot MgO$ product sample did not reflect the quantity of soaps in the mixture. It also may be that the $CaO \cdot MgO$ catalyst has a higher activity than the CaO powder. From this initial experimental series, it was speculated that the CaO and MgO may function as a bifunctional catalyst and, therefore, a $CaO \cdot MgO \cdot Al_2O_3$ catalyst could prove interesting. Impregnating the MgO on the alumina support decreases the number of MgO sites and may result in a decrease in soap production without inhibiting the catalytic activity for tranesterification. However, this catalyst produced substantially less quantities of both the methyl fatty ester and the soaps. Comparison of the experimental $CaO \cdot MgO \cdot Al_2O_3$ catalyst results with the $CaO \cdot Al_2O_3$ and $CaO \cdot SiO_2$ results provides supporting data for the hypothesis that one mechanism for the transesterification of triglycerides is bifunctional in nature. A bifunctional catalyst is defined in this study as a catalyst requiring two different molecular species to activate the desired reaction. The actual catalysis may or may not occur on both sites.

The three K_2CO_3 catalysts produced good methyl fatty ester yields, with $K_2CO_3 \cdot MgO$ appearing somewhat superior to $K_2CO_3 \cdot Al_2O_3$. Unfortunately, the K_2CO_3 catalyst disassociated from the support and went into solution. It

TABLE III

Catalyst Results

Catalyst	Relative methyl fatty ester production[a]	Catalyst	Relative methyl fatty ester production[a]
1. MgO support	None detected	15. Na_2CO_3 powder	0.8
2. Al_2O_3 support	None detected	16. Activated Carbon	None detected
3. SiO_2 support	None detected	17. Fe_2O_3 on MgO support crush	None detected
4. $CaO \cdot Al_2O_3$ support	None detected	18. $CH_3ONa \cdot SiO_2$	2
5. $CaO \cdot MgO$	10	19. $NaAlO_2 \cdot MgO$	None detected
6. $CaO \cdot Al_2O_3$	None detected	20. $NaAlO_2 \cdot Al_2O_3$	None detected
7. $CaO \cdot SiO_2$	None detected	21. Zn metal	Trace
8. CaO powder	3	22. Cu metal	None detected
9. $CaO \cdot MgO \cdot Al_2O_3$	0.5	23. Sn metal	Trace
10. $K_2CO_3 \cdot MgO$	5	24. Pb metal	Trace
11. $K_2CO_3 \cdot Al_2O_3$	4	25. $ZnO \cdot MgO$	0.5
12. K_2CO_3 powder	6	26. $ZnO \cdot Al_2O_3$	Trace
13. $Na_2CO_3 \cdot MgO$	Trace	27. $ZnO \cdot SiO_2$	Trace
14. $Na_2CO_3 \cdot Al_2O_3$	Trace	28. Anion Exchange Resin	a 2[b] b Trace[c]

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[a] The relative methyl fatty ester production is a qualitative guide to catalytic activity.

[b] The experiment was conducted at 200 C and 68 atm (1000 psig).

[c] The experiment was conducted at 91 C and 9.2 atm (135 psig).

TABLE IV

Product Component Concentrations from the Elevated Temperature and Pressure Experiments with the Anion Exchange Resin Catalyst

Experiment A: 200 C and 68 atm (1000 psig)		Experiment B: 91 C and 9.2 atm (135 psig)	
Component	Analyzed sample percentage	Component	Analyzed sample percentage
1. $C_{21}H_{44}$ $C_{21}H_{42}$ $C_{19}H_{36}O_2$	50	1. $C_{22}H_{46}$	2
2. $C_{20}H_{42}$	3	2. $C_{21}H_{44}$	4
3. $C_{19}H_{40}$	3	3. $C_{20}H_{42}$	4
4. $C_{18}H_{38}$	4	4. $C_{19}H_{40}$	4
5. $C_{17}H_{36}$	4	5. $C_{18}H_{38}$	7
6. $C_{16}H_{34}$	7	6. $C_{17}H_{36}$	4
7. $C_{15}H_{32}$	7	7. $C_{16}H_{34}$	7
8. $C_{14}H_{30}$	6	8. $C_{15}H_{32}$	13
9. $C_{13}H_{28}$	7	9. $C_{14}H_{30}$	7
10. $C_{12}H_{26}$	6	10. $C_{13}H_{28}$	14
11. $C_{11}H_{24}$	3	11. $C_{12}H_{26}$	13
12. $C_{10}H_{22}$	2	12. $C_{11}H_{24}$	16
		13. $C_{10}H_{22}$	5

was hoped that the Na_2CO_3 catalyst might bond to the support with greater strength but still have activity similar to the K_2CO_3. However, the $Na_2CO_3{\cdot}MgO$ and $Na_2CO_3{\cdot}Al_2O_3$ catalysts generated only trace ester concentrations. The Na_2CO_3 homogeneous catalyst produced considerably smaller ester yields than the K_2CO_3 homogeneous catalyst, indicating that catalytic activity in this reaction is not just a function of the anion.

The $CH_3ONa{\cdot}SiO_2$ catalyst generated small ester concentrations because the catalyst dissolved about 20% of the support. A subsequent test with used catalyst was conducted to determine if a sufficient catalyst quantity remained on the support to produce esters. No esters were detected, indicating that the CH_3ONa went into solution and/or the dissolution of the support clogged the pores. The granular metals tested, Zn, Cu, Sn and Pb, produced, at best, only trace methyl fatty ester concentrations.

The ZnO catalyst series appeared promising from the literature (13,16) but yielded disappointing results. The $ZnO{\cdot}MgO$ catalyst generated small ester concentrations, while $ZnO{\cdot}Al_2O_3$ and $ZnO{\cdot}SiO_2$ produced only trace yields. That the $ZnO{\cdot}MgO$ catalyst produced slightly greater amounts of methyl esters than the $ZnO{\cdot}Al_2O_3$ and $ZnO{\cdot}SiO_2$ catalysts reinforces the bifunctional catalysis hypothesis.

The elevated temperature and pressure effects were examined in the two anion exchange resin catalyzed experiments. The first run, conducted for 12 hr at 200 C and 68 atm (1000 psig), yielded a dark-brown, odoriferous, oily, single-phase liquid. Results from the GC-MS are given in Table IV. Roughly half of the sample analyzed appeared in three MS peaks in the C_{21} range. One peak was $C_{21}H_{44}$, a straight-chain unsaturated hydrocarbon, and another of the peaks indicated $C_{19}H_{36}O_2$, a methyl oleic ester. The third peak in this range could not be resolved but may be a C_{21} mono-unsaturated straight-chain hydrocarbon. The remaining half of the sample analyzed was straight-chain hydrocarbons (C_{10} through C_{20}) with the individual component concentrations ranging from 2 to 7%. This GC-MS is accurate to ±15% of the concentration measurement and 0.5 amu of the mass measurement. Not included in Table IV are the unreacted triglycerides, free fatty acids and other miscellaneous compounds. This reaction did not go to completion but did produce substantial amounts of products. Rapeseed oil can be cracked thermally without a catalyst at 540 C (1000 F) (17).

The second anion exchange resin catalyst experiment (91 C and 9.2 atm) was executed at a more moderate temperature to reduce triglyceride cracking without hindering the transesterification mechanism. At the conclusion of the allotted reaction time the mixture settled into two liquid layers: a yellow-light brown layer on top and a brown layer on the bottom. The mixture was slightly odoriferous. MS results indicate only traces of methyl ester formation at best, whereas some of the triglycerides pyrolyzed to straight-chain hydrocarbons. Sizable amounts of triglycerides remained unreacted.

The most promising catalyst examined in this investigation was $CaO{\cdot}MgO$. This catalyst, as prepared in this study, also produces liberal quantities of free fatty acid salts as unwanted by-products. The results of the CaO and ZnO experimental catalyst series suggest that the transesterification reaction mechanism is bifunctional.

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*Total Phospholipids in Crude Palm Oil: Quantitative Analysis and Correlations with Oil Quality Parameters.

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ABSTRACT

Phospholipids, selectively extracted from crude palm oil and free of colored carotenoids, can be quantitatively determined by the phospholipid-molybdenum blue complex in hexane. A study of the phospholipid in crude palm oil in relationship to other components affecting oil quality shows that they have a beneficial effect while any detrimental effect may be of an indirect nature.

INTRODUCTION

Phosphorus constituents in edible oils generally are considered as undesirable impurities causing refining problems and oil losses (1,2). In commercial crude palm oil, phospholipids and total phosphorus are reported present at 0.8-3.3 ppm (as P) and ca. 20 ppm (as P) respectively (3). Although the two sources of phosphorus (inorganic phosphates and phospholipids) are chemically distinct, usually only the total phosphorus content is determined and then converted to equivalent phospholipid value. This is because simple, reliable methods of phospholipid quantitation are not generally available at present for routine quality control analyses. Furthermore, phospholipids seldom are differentiated from other phosphorus compounds. Recently we have described a thin layer chromatographic (TLC) procedure for palm oil phospholipids (3). More recently a Iatroscan-Chromarod method also has been reported (4) for some oils. For other edible oils colorimetric methods (5-7) based on molybdenum blue complexes have been tried with varying degrees of success, while a gravimetric method is possible when large amounts of phospholipids are present as in rapeseed oil (8). In this paper we describe a simple analytical method for the determination of total phospholipids in crude palm oil. Correlations of phospholipid values with other quality parameters of palm oil are studied, and the effect of phospholipids on palm oil quality is discussed.

EXPERIMENTAL

Materials

Crude palm oil samples were obtained from a few palm oil mills in West Malaysia. Dipalmitoylphosphatidylcholine and dipalmitoylphosphatidylethanolamine were purchased from Sigma (St. Louis, Missouri), whereas phosphatidic acid was from General Biochemicals (Chagrin Falls, Ohio). All other chemicals were of analytical or reagent grades and were used without further purification. Solvents were redistilled before use. Modified Zinzadze's reagent was as described previously (3).

Visible absorption spectra were recorded on a Beckman DU-7 spectrometer in a 10 mm cell. Mechanical vessel shaking was carried out by an electric flask shaker (Griffin and George, Great Britain).

Procedure

Crude palm oil (10.0 g) was stirred magnetically and refluxed with methanol-acetic acid (95:5, v/v, 20 ml) for 20 min. After cooling, the methanolic layer was separated and the oil was washed once with methanol (10 ml). The combined methanolic portion was rotary-evaporated to dryness, and chloroform (3 ml) was added immediately to redissolve the extract. The extract was then purified through a short column of acid-treated Florisil (2.5 g, 10 cm × 0.8 cm) by eluting with chloroform (10 ml), acetone (10 ml) and finally with methanol-acetic acid (98:2, v/v, 15 ml). The methanolic eluant was collected and rotary-evaporated to dryness in a 20 cm × 2 cm boiling tube. The purified phospholipids were determined by a procedure similar to those reported (6,7,9), but with modifications. Modified Zinzadze's reagent (4 ml) was added and the contents were well-shaken for 30 min. The blue complexes formed were extracted by shaking with hexane (5 ml) for 1 min. A visible spectrum was recorded and absorbance was read at 711 nm, λ_{max} for crude palm oil phospholipids. A sample reagent blank was found to be negligible. Hence, hexane can be used as blank.

The complex formation and extraction procedure was tested using both synthetic phosphatidylcholine and purified crude palm oil phospholipids for different time periods. Recovery of phospholipids by extraction was studied using a standard addition technique by spiking 5.0 g aliquots of crude palm oil sample with 100, 200 and 500 μg of synthetic dipalmitoylphosphatidylcholine in methanol. The phospholipids were then extracted and purified as described above.

The determinations of inorganic phosphates and total phosphorus are described in detail in the accompanying paper (10).

Phosphoric Acid Degumming of Crude Palm Oil

A sample of crude palm oil (100 g) was treated with 85% phosphoric acid (0.1 ml) at 90 C under argon for 20 min with magnetic stirring. Tonsil Optimum FF bleaching earth (2 g) was then added and further stirred at 90 C for 30 min. The hot oil was filtered through a sintered glass funnel (fine porosity) under partial vacuum. Ten g of the degummed oil were then analyzed for phospholipid content using the procedure described.

RESULTS AND DISCUSSION

The low levels of phospholipids in palm oil preclude the use of gravimetric methods for their determination. The thin layer chromatographic method (3) previously used by us is suitable but suffers from the disadvantage that relatively skillful techniques are required in order to obtain quantitative and reproducible results. The Iatroscan chromato-

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