The transesterification by heterogeneous catalysis of rapeseed oil triglycerides to the methyl ester derivatives

by Gary Reed Peterson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

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 rapeseed oil.

The reaction was conducted in a 500 ml batch reactor with catalysts generally prepared by impregnation. Most experiments were at atmospheric pressure and approximately the corresponding boiling point temperature of the mixture, 140-145°F. The catalytic activity of an anion exchange resin was tested, however, at 200° C and 1000 psig and similarly at 91°C and 135 psig. The catalyst supports used, MgO, Al2O3, and SiO2, allowed the examination of the effects of strong basic, weak basic, and acidic supports, respectively, on the selected catalysts. All samples were analyzed by thin layer chromatography with samples from the elevated temperature and pressure experiments also analyzed by mass spectroscopy. The mass spectroscopy analyses were conducted by the Mass Spectrometer Facility, Chemistry Department, Montana State University.

The most promising catalyst examined was CaO MgO. This catalyst produced methyl fatty ester yields apparently comparable to those produced by a NaOCH3 catalyst, which is known to generate ester yields in excess of 95%. Many tested catalysts generated no detectable ester quantities. 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 1000 psig generated both methyl fatty esters and straight-chain hydrocarbons. Although this reaction did not go to completion, it appears to have produced substantial products. At 91°C and 135 psig cracking also occurred, but at a substantially reduced amount, and no transesterification was noted.

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

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Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1984

APPROVAL

of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ACKNOWLEDGMENTS

The author expresses his appreciation to Dr. J. E. Robbins and Ms. S. Gerhardt, Chemistry Department, Montana State University for their advice during the course of this investigation.

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ABSTRACT

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The reaction was conducted in a 500 ml batch reactor with catalysts generally prepared by impregnation. Most experiments were at atmospheric pressure and approximately the corresponding boiling point temperature of the mixture, 140-145°F. The catalytic activity of an anion exchange resin was tested, however, at 200°C and 1000 psig and similarly at 91°C and 135 psig. The catalyst supports used, MgO, Al_2O_3, and SiO_2, allowed the examination of the effects of strong basic, weak basic, and acidic supports, respectively, on the selected catalysts. All samples were analyzed by thin layer chromatography with samples from the elevated temperature and pressure experiments also analyzed by mass spectroscopy. The mass spectroscopy analyses were conducted by the Mass Spectrometer Facility, Chemistry Department, Montana State University.

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The anion exchange resin catalyst at 200°C and 1000 psig generated both methyl fatty esters and straight-chain hydrocarbons. Although this reaction did not go to completion, it appears to have produced substantial products. At 91°C and 135 psig cracking also occurred, but at a substantially reduced amount, and no transesterification was noted.

INTRODUCTION

Vegetable Oil Fuels

In 1911 Rudolf Diesel wrote:

> The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which will use it. This may appear a futuristic dream but I can predict with great conviction that this use of the diesel engine may in the future be of great importance [1].

A vegetable oil diesel fuel is particularly attractive, in theory, for agricultural machinery. If vegetable oil fuels become economically viable, a farmer could plant a fraction of his land in oil producing crops and use the fuel derived to power his entire operation. For example, Helgeson and Schaffner [2] estimate that if vegetable oil was a viable diesel engine fuel, the agricultural fuel needs of North Dakota, Minnesota, and South Dakota could be met by 6-9 million acres of sunflower or approximately 10% of the total cropland of those states. Additionally, vegetable oil production yields a high protein meal suitable for stock feed as a by-product [3]. Quick [3] states, "The overall efficiency, based on the ratio of fuel output to agricultural plus processing energy inputs, for the plant oils is the highest of all the farm fuel alternatives."

However, vegetable oil fuels are not economically viable at present. Collins' et al. [4] analysis indicates that diesel fuel prices would have to double or triple before vegetable oil fuels would become economically competitive. Furthermore, on-farm processing of plants to vegetable oils appears to be considerably more expensive than centralized industrial processing [5].

Vegetable oil fuels also pose a philosophical question. In a world where millions of people are starving, should agricultural produce be used as fuel instead of food? Bruwer and Hugo [6] argue that given the highly mechanized agriculture of the food-exporting nations, any disruption or hindrance in fuel procurement would retard food exports to a hungry world. A viable vegetable-oil agricultural fuel would eliminate this possibility.

The physical characteristics of vegetable oils pose several technical problems. Although indirect injection diesel engines have reportedly operated satisfactorily on crude de-gummed vegetable oil fuels [6,7], direct injection diesel engines, as are used in most agricultural machinery, only operate adequately for a brief duration on neat vegetable oil fuels. Long-term use results in injector coking, gum formation and lubricating oil thickening [8]. According to Pryde [9]:

> These problems are related to the high viscosity and non-volatility of the vegetable oils which result in inadequate fuel atomization and incomplete combustion . . . a number of secondary problems will [also] require attention such as the effects of free fatty acids, phosphatides, and degree of unsaturation. Also needed will be studies on additives to improve cylinder lubrication, fuel atomization, combustion, viscosity, and oxidative stability of the vegetable oil.

These complications may be partially alleviated in the future by plant breeding or genetic engineering [10].

Vegetable oils were tested as a diesel fuel extender in an effort to solve the problems given above. Cochran et al. [11] and Goodrum [12] conducted protracted engine tests using several vegetable oil-diesel fuel blends. Although the detrimental effects of neat vegetable oil fuels are mitigated, both groups report cylinder coking. In addition, Cochran reports a microbial growth in all soybean oil blends tested.

Vegetable oils have also been examined as components in other hybrid fuel mixtures. Goering and Fry [13] report considerable cylinder and injection coking after a 200 hour diesel engine test with Shipp Nonionic fuel. This microemulsion fuel consisted of 50% No. 2 diesel fuel, 25% degummed, alkali-refined soybean oil, 5% 190-proof ethanol, and 20% 1-butanol [13]. Ziejewski's et al. [14] study noted similar problems using a microemulsion fuel of 53.5% alkali-refined sunflower oil, 13.3% 190-proof ethanol and 33.4% n-butanol.

Chemical Modification of the Vegetable Oil

Vegetable oil transesterification via alcoholysis into the methyl or ethyl ester derivative is an alternative approach to a viable vegetable oil-based diesel fuel. Transesterification significantly reduces the vegetable oil viscosity thereby improving the fuel atomization and consequently the fuel combustion characteristics. The fatty ester possesses many similar physical characteristics to no. 2 diesel fuel as illustrated by Table 1, consisting of data primarily from Clark's et al. study [15]. Fuel filter plugging at temperatures near freezing are a problem of fatty ester fuels, as shown in Table 1, and may require a fuel heater [16].

Table 1. Properties of No. 2 Diesel Fuel, Neat Sunflower Oil, Methyl Soyate, and Ethyl Soyate.*

Test Property	ASTM Test No.	No. 2 Diesel Fuel	Neat Sunflower Oil	Methyl Soyate	Ethyl Soyate
Viscosity @ 40°C (cSt)	D-445	2.49	31.17**	4.05	4.41
Higher Heating Value (MJ/kg)	D-240	45.5	39.6 **	39.8	40.0
Cetane Rating	D-613	45.0	--	--	48.2
Cetane Rating	D-976	--	--	54.0	--
Pour Point (°C)	D-97	-6.7	-9 †	-3.9	-3.9
Cloud Point (°C)	D-2500	-18 ††	-7 ††	1.1	1.1
Flash Point (°C)	D-93	73.33	--	151.2	160.0

*Unless otherwise indicated the data is from Clark et al. [15].
**Data from Tahir et al. [17].
†Data from Kaufman et al. [18].
††Data from Baranescu and Lusco [19].

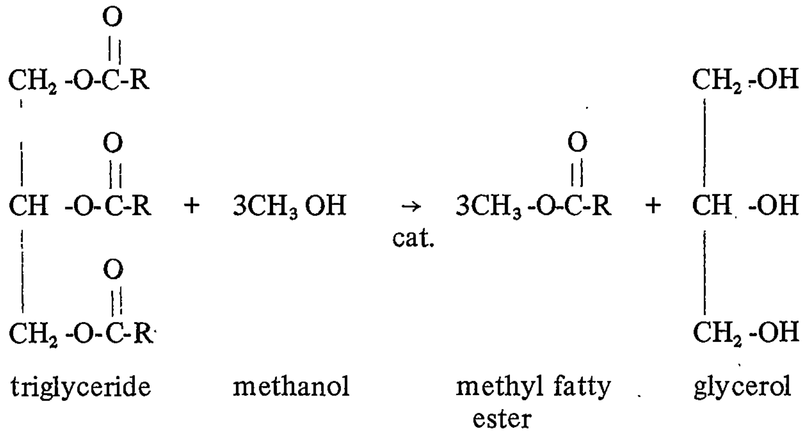
The cetane number is a measure of the fuel's self-ignition ability. Under given engine conditions the lower the cetane number, the longer the ignition delay and consequently the greater the amount of fuel injected until self ignition occurs [19]. Klopfenstein [20] provides a semi-empirical equation to estimate methyl fatty ester cetane numbers:

$$\text{cetane index} = 58.1 + 2.8\left(\frac{n-8}{2}\right) - 15.9\,D$$

where n is the number of carbon atoms and D is the number of double bonds. Using the analysis provided by Downey [21] of this study's rapeseed oil feedstock, the cetane number of the derived methyl esters can be expected to be 49.7.

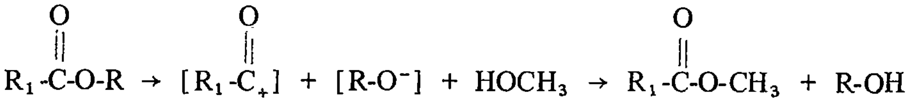
Short- and long-term engine testing indicates that fatty ester fuels can perform well in both indirect [22] and direct injection diesel engines [15,16,23,24]. Clark et al. [15] report fuel filter plugging caused by gum formation in the fuel. This problem was diminished, but not eliminated, by filtering the fuel prior to use. The gum formation may be related to the fatty ester's oxidative stability, a phenomenon studied by du Plessis and de Villiers [25]. Another potential problem of fatty ester fuels has been identified in several studies [26,27,28] which indicate that ester fuel dilution of the lubricating oil results in a decrease in the lubricating oil kinematic viscosity. Furthermore, the methyl fatty esters of canola oil may cause excessive engine wear [26].

The reaction to transesterify the vegetable oil triglyceride into the methyl ester derivative is [29]:



$$\begin{array}{l} CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} \\ | \\ CH\ \text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} \\ | \\ CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} \end{array} + 3CH_3OH \xrightarrow[\text{cat.}]{} 3CH_3\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} + \begin{array}{l} CH_2\text{-OH} \\ | \\ CH\ \text{-OH} \\ | \\ CH_2\text{-OH} \end{array}$$

The R groups are the various fatty acid components, which are a strong function of the growing environment [10]. A successful catalyst must selectively break the carbon-oxygen single bond and proceed with the following mechanism [30]:



$$R_1\text{-}\overset{\overset{O}{\|}}{C}\text{-O-R} \rightarrow [R_1\text{-}\overset{\overset{O}{\|}}{C}_+] + [R\text{-}O^-] + HOCH_3 \rightarrow R_1\text{-}\overset{\overset{O}{\|}}{C}\text{-O-}CH_3 + R\text{-}OH$$

with R_1 being the fatty acid component.

A number of excellent homogeneous catalysts exist for the above reaction. Both Freedman and Pryde [31] and Kusy [29] report over 95% fatty ester yields in one hour using sodium hydroxide, sodium methoxide, and sodium ethoxide catalysts. Fuls and Hugo [32] also report good methyl fatty ester yields using sulfuric acid and para-toluene sulphonic acid homogeneous catalysts. An interesting variation on the transesterification scheme by homogeneous catalysis is Nye's et al. [33] successful attempt 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. The subject transesterification reaction requires excess alcohol. However, excess free alcohol in the fatty ester fuel detrimentally effects the combustion properties and, from a safety standpoint, a 5% alcohol concentration in the fuel suppresses the flash point to room temperature [23]. Should the catalysts remain in solution, the reaction would proceed in reverse when the alcohol was recovered by distillation [34]. Another compelling reason for the catalyst's removal from the product is that a strong acid or base in a diesel fuel substitute would cause serious engine corrosion. The neutralized catalyst can be removed from the fatty ester by washing with water [29,35].

A heterogeneous catalyst would greatly simplify and economize the catalyst-removal step. However, a successful heterogenous catalyst should produce minimum ester yields in the order of 90% as suggested by Hawkins and Fuls [23]. Tests conducted with a 70% methyl fatty ester and 30% vegetable oil mixture revealed unacceptable coking within 50 hours [23].

The choice of vegetable oil will affect the combustion and oxidation properties of the resultant fatty ester. Klopfenstein and Walker [36] state:

> Among the methyl esters of the saturated acids, thermal efficiency was inversely related to the chain length of the fatty acid. Introduction of a double bond resulted in increased efficiency. Further increases in unsaturation had negligible effects on thermal efficiencies.

They conclude that an ester fuel derived from a vegetable oil with a high oleic acid content should be superior to an ester derived from an oil with longer constituent fatty acids. The methyl oleic ester oxidation rate, because of its one double bond, is approximately 10% that of a fatty ester containing two double bonds and about 7% that of a three double bond fatty ester. The fatty ester oxidation causes the polymerization resulting in gum formation according to Peterson et al. [37].

Rapeseed oil was selected as the vegetable oil feedstock for this study because of its suitability for the vigorous Montana climate [10]. An additional consideration was the cost and availability to the researcher.

RESEARCH OBJECTIVE

This study's purpose was to identify a heterogeneous catalyst to selectively produce methyl fatty esters from rapeseed oil.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Apparatus and Reaction Parameters

The reaction vessel was a 500 ml glass batch reactor, open to the atmosphere, with a water-cooled condenser and thermometer. A heating mantle maintained the reaction mixture at a constant temperature with the mixture being agitated with a magnetic stirrer.

The quantities of reactants used in all experiments were 0.25 gmoles of crude rapeseed oil and 1.5 gmoles of methanol. Experiments [31,38] demonstrate that the optimal molar ratio of alcohol to triglycerides is 6:1, i.e., twice the stoichiometric.

Crude rapeseed oil, instead of refined, was selected as the vegetable oil feedstock because, should this process prove practicable on an on-farm scale, the producer will be using crude, not refined, vegetable oil. Cost was an additional consideration. However, Freedman and Pryde [31] used refined soybean and sunflower oils because they believe that the acid number should be < 1 [38, 39]. This correlates to a free fatty acid content of < 0.5% [38]. The acid number is a measure of the free fatty acid content of a vegetable oil as measured by the American Oil Chemists Society Official Method Ca5a-40 [40]. Freedman et al. [38,39] successfully conducted experiments using crude vegetable oil with an acid number of 6. However, the reaction required additional catalyst and produced greater quantities of free fatty acid salts, i.e., soaps. Kusy [29] transesterified both crude and purified soybean and sunflower oils and noticed no significant difference in yields.

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 [39].

The catalyst concentration suggested is 1 molar % [31] or 0.3-0.5% based on the weight of the vegetable oil [29]. 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 hours for each batch, with samples collected at the 6, 9 and 12 hour marks. Freedman and Pryde [31] report the equilibrium was essentially reached in one hour with sodium hydroxide and sodium methoxide catalysts. The twelve-hour reaction time was chosen to accommodate potential catalysts that might have slower reaction kinetics and to minimize the effects of any potential mass transfer resistance.

The reactor temperature was generally maintained at 140-145°F, slightly under the mixture's boiling point. With an excellent catalyst the reaction can proceed at room temperature [38]. Groggins [41] 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 [42] state that alcoholysis with basic catalysts at temperatures above 60°F causes various side reactions, particularly saponification, to predominate.

Because the transesterification reaction kinetics may be a strong function of temperature, the reaction was attempted at elevated temperature and pressure using an anion exchange resin catalyst. The purpose of the elevated pressure is 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 serve as an inert. The container was placed in a mechanical rocker with heating element and the mixture was allowed to react for the usual 12 hour period.

Analytical Procedures

The collected samples were analyzed by thin layer chromatography (TLC). This method measures the relative chemical compositions in a sample by measuring the distance each compound travels up a silica gel sheet as compared to a known sample. 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 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% [29,31]. 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 percent yield.

A mass spectrometer analyzed the product from the elevated temperature and pressure experiments. The Mass Spectrometer Facility, Chemistry Department, Montana State University conducted the analyses.

Catalysts

Table 2 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. Because catalysts with an average pore diameter in the 80-100 Å range are effective in the catalytic hydrotreating of solvent refined coal, a molecule much larger than the triglyceride, it was assumed, therefore, that all supports used in this investigation had sufficient average pore diameter for triglyceride diffusion [43].

Table 2. Catalyst Supports.

Name	Supplier	Form	Surface Area (m^2/gm)	Average Pore Diameter (Å)	Composition
1. MG-0601	Harshaw Chem. Co.	1/8 in tablets	17	635	98% MgO
2. AL-0104	Harshaw Chem. Co.	1/8 in tablets	80-100	136	97% Al_2O_3
3. T-1571	United Catalysts, Inc.	3/16 in spheres	131	180	93% SiO_2, 3% Al_2O_3

Table 3 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 [30]. The CaO, K_2CO_3 and Na_2CO_3 experimental series were selected because Tanabe [44] identified them as having basic characteristics. These three catalysts were also 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 [45] as being basic catalysts. The Fe_3O_3-on-MgO-crush catalyst was tested in powder rather than pellet form because of ease of preparation. If this catalyst had shown promise, a more thorough investigation of its properties would have insued.

The $CH_3ONa\cdot SiO_2$ catalyst is an attempt to select an outstanding homogenous catalyst and bond it to a solid support with sufficient strength to prevent the catalyst from going into solution but not inhibiting its catalytic properties. Robbins [30] speculates that the CH_3ONa anion causes the catalytic activity and therefore this anion may bond with an acidic catalyst support. Whether this bond has sufficient strength can only be determined empirically.

The $NaAlO_2$ catalysts were examined because of hopes that these catalysts would perform similarly to NaOH.

Table 3. 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, 98.5-96.4% SiO_2 support
5. $CaO \cdot MgO$	8.22% CaO, 91.8% MgO support	19. $NaAlO_2 \cdot MgO$	3.23% $NaAlO_2$, 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, 85.8% Al_2O_3 support	25. $ZnO \cdot MgO$	7.39% ZnO, 92.6% MgO support
12. K_2CO_3 powder	——	26. $ZnO \cdot Al_2O_3$	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. $Na_2CO_3 \cdot Al_2O_3$	4.67% Na_2CO_3, 95.3% Al_2O_3 support	28. Anion Exchange Resin	——

The metals examined, Zn, Cu, Sn and Pb, were suggested as potential transesterification catalysts by Groggins [41].

The acidic catalyst $ZnO \cdot SiO_2$ was tested because two publications indicated that it may be potentially successful. Wu and Storch [46] 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 [42] 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. Other ion exchange resins were not examined in this study to avoid duplication of Robbins' current research [30].

Most heterogeneous catalysts investigated were prepared by impregnation, either directly with no 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, and, when necessary, calcining at sufficient temperatures (see Table 9, Appendix) 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.

The acid/base strength and the relative quantity of acid/base sites were measured for each catalyst. It was conjectured that the catalytic activity may be a strong function of these parameters.

Tanabe [44] provides the procedure for measuring the catalysts' acid/base strength, pK_a. The pK_a is defined as $-\log K_a$ where K_a is the thermodynamic acid dissociation equilibrium constant [47]. For acids the pK_a value is less than seven and for bases it is greater than seven [44]. The procedure involves mixing approximately 0.2 gm of the pulverized catalyst, 2 ml of benzene, and about 0.2 mg of the appropriate indicator and observing the color change. The appropriate indicators are listed by Tanabe [44,48] and are given in Table 4. Each catalyst and support actually contains sites of various acid/base strengths although this test only measures the most predominant strength.

The catalysts' relative quantity of acid/base sites were measured by placing approximately 0.5 gm of catalyst in 5 ml of solvent (water) and titrating basic catalysts with 0.1011 N aqueous H_2SO_4 and acidic catalysts with 0.1000 N aqueous NaOH until the phenolphthalein endpoint of the solution was reached. The solution was allowed to stand a minimum of one hour between each titrant addition to insure adequate titrant diffusion into the catalyst pellet interior.

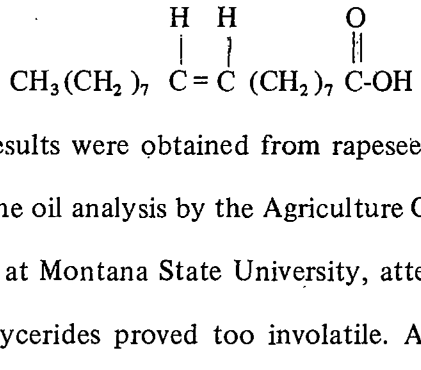
Table 4. Acid/Base Strength Indicators.

	Color		
Indicator	Base-Form	Acid-Form	pK_a
Crystal Violet	blue	yellow	0.8
Methyl Red	yellow	red	4.8
Bromothymol Blue	green	yellow	7.2
Phenolphthalein	red	colorless	9.3
2,4-Dinitroaniline	violet	yellow	15.0
4-Chloro-2-nitroaniline	orange	yellow	17.2
4-Nitroaniline	orange	yellow	18.4
4-Chloroaniline	pink	colorless	26.5

RESULTS AND DISCUSSION

Composition of the Crude Rapeseed Oil

Table 5 provides the composition of the crude rapeseed oil used in this investigation. The Agriculture Canada Research Station at Saskatoon, Saskatchewan provided the analysis [21] using gas-liquid chromatography. The free fatty acid content of the crude rapeseed oil was 0.245%, expressed as, by convention, oleic acid [40]. The various free fatty acids differ in the number of carbon atoms and the number of double bonds. For example, oleic acid is [10]:



$$CH_3(CH_2)_7\,\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}\,(CH_2)_7\,\overset{\overset{O}{\|}}{C}\text{-OH}$$

Interesting analytical results were obtained from rapeseed oil transesterification with CH_3ONa catalyst. Prior to the oil analysis by the Agriculture Canada Research Station, the Mass Spectrometer Facility, at Montana State University, attempted to analyze the crude oil. Unfortunately the triglycerides proved too involatile. An indirect approach was to transesterify the triglycerides with CH_3ONa, a reaction that goes virtually to completion [31,38,49], and by mass spectrometry determine the crude rapeseed oil composition. Table 6 provides these analytical results. There is a general qualitative agreement between these results and the Canadian results in Table 5. However, the quantitative difference in results indicates the potential error in using equipment that is not standardized to vegetable oil analyses. Mass spectrometer sample ionization may be the cause of the fatty acid cracking noticed in these results.

Table 5. Composition of the Crude Rapeseed Oil Used in This Study.

Fatty Acid		
Name	No. of C Atoms:No. of Double Bonds	Fatty Acid Percentages
Myristic	14:0	0.6
Palmitic	16:0	5.2
Palmitoleic	16:1	0.4
Stearic	18:0	1.8
Oleic	18:1	42.9
Linoleic	18:2	38.1
Linolenic	18:3	6.6
Arachidic	20:0	1.4
Eicosenoic	20:1	0.3
Behenic	22:0	0.6
Erucic	22:1	1.9
Lignoceric	24:0	0.3

Table 6. Mass Spectrometry Results of CH_3ONa Homogeneous Catalyst Experiment.

Compound	Analyzed Sample Percentage	Compound	Analyzed Sample Percentage
1. C_{23}, not a hydrocarbon, molecular wt = 292 gm/gmole	0.74	9. C_{16}, straight-chain hydrocarbon	2.1
2. C_{21}, not a hydrocarbon	1.3	10. C_{15}, straight-chain hydrocarbon	1.5
3. $C_{19}H_{36}O_2$ methyl oleic ester; $C_{18}H_{32}O$ fraction of methyl oleic ester	45	11. C_{14}, straight-chain hydrocarbon	2.2
4. $C_{19}H_{34}O_2$ methyl linoleic ester	31	12. C_{13}, straight-chain hydrocarbon	2.1
5. C_{20}; straight-chain hydrocarbon	0.92	13. C_{12}, may not be a hydrocarbon, may possibly contain oxygen	0.94
6. C_{19}, straight-chain hydrocarbon	1.1	14. C_{12}, straight-chain hydrocarbon	1.6
7. C_{18}, straight-chain hydrocarbon	1.5	15. C_{11}, straight-chain hydrocarbon	1.9
8. C_{17}, straight-chain hydrocarbon	1.8	16. C_{10}, straight-chain hydrocarbon	0.3

Experimental Heterogeneous Catalysis Results

Table 7 lists the test results. The relative methyl fatty ester values, as previously described, provide a qualitative comparison of catalytic activity.

Table 7. Catalyst Results.

Catalyst	Relative Methyl Fatty Ester Production*	Catalyst	Relative Methyl Fatty Ester Production*
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 – trace†

*The relative methyl fatty ester production is a qualitative guide to catalytic activity.
**The experiment was conducted at 200°C and 1000 psig.
†The experiment was conducted at 91°C and 135 psig.

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 acidic support, SiO_2, produced only a small amount of soaps.

The CaO catalytic series presented a fascinating variety of results. The $CaO \cdot MgO$ catalyst provides apparently outstanding methyl fatty ester yields, but also produces a prodigious quantity of soaps thereby rendering this catalyst, as constituted in this study, unsuitable for commercial applications. The TLC results appeared, however, comparable to $NaOCH_3$ catalyzed reactions. 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·MgO heterogeneous catalyst and the CaO homogeneous catalyst may be partially because the CaO·MgO product sample did not reflect the quantity of soaps in the mixture. It may also be that the CaO·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 would prove interesting. It was conjectured that by impregnating the MgO on the alumina support, the decrease in the number of MgO sites may result in a decrease in the soap production without inhibiting the catalytic activity for transesterification. However, this experiment produced substantially less quantities of both the methyl ester and the soaps. The contrasting experimental results from the $CaO{\cdot}MgO{\cdot}Al_2O_3$ catalyst as compared to the $CaO{\cdot}Al_2O_3$ and $CaO{\cdot}SiO_2$ catalysts provide 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. An additional deduction can be obtained from the $CaO{\cdot}MgO{\cdot}Al_2O_3$-catalyzed experiment. The Al_2O_3 support has the smallest average pore diameter of all supports used. Therefore, this catalyst's activity apparently indicates that the average pore diameter of all catalyst supports used are sufficient for triglyceride diffusion.

The K_2CO_3 and Na_2CO_3 experimental series produced some interesting results. 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 was hoped that the Na_2CO_3 catalyst might bond to the support with greater strength and still have a similar activity as 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 experiment was the empirical test of an interesting theory. Unfortunately, although small ester concentrations were generated, the test was unsuccessful as the CH_3ONa catalyst dissolved about 20% of the support. A subsequent test with the 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 but yielded indifferent results. The $ZnO \cdot MgO$ catalyst generated small ester concentrations, while the remaining catalysts, $ZnO \cdot Al_2O_3$ and $ZnO \cdot SiO_2$, produced only trace yields. The $ZnO \cdot MgO$ catalyst apparently produced slightly superior amounts of methyl fatty esters than the $ZnO \cdot Al_2O_3$ and $ZnO \cdot SiO_2$ catalysts, perhaps reinforcing the bifunctional hypothesis.

The $ZnO \cdot SiO_2$ catalyst was tested in three experiments. The first two catalyst batches were impregnated with $ZnCl_2$ with the first batch, based on information provided in Tanabe [44], being calcined for three hours. A mass balance after the first $ZnO \cdot SiO_2$ catalyst experiment indicated that some of the catalyst and/or support went into solution, implying that there was incomplete $ZnCl_2$ oxidation during calcination. Therefore a second $ZnO \cdot SiO_2$ batch was prepared and calcined for 18 hours. A significant difference in the number of the catalyst's acid sites was noted, indicating that the first batch was indeed insufficiently calcined. Whereas the $ZnCl_2$ in the first batch went into solution during the titration, with the second batch, presumably, some of the ZnO remained on the catalyst in multiple layers, reducing the number of acid sites. Nevertheless a mass balance after the second $ZnO \cdot SiO_2$ experiment indicated that a portion of the catalyst and/or support is going into solution. McCandless [50] hypothesized that perhaps the $ZnCl_2$ proved too stable to fully oxidize to ZnO and suggested impregnating the support with $Zn(NO_3)_2$ and calcining to ZnO. An experiment, in accordance with this advice, was conducted but yielded only trace ester concentrations. Furthermore, the catalyst supports degraded in all $ZnO \cdot SiO_2$ experiments. Metal oxide catalysts on SiO_2 support are listed in the literature [44,46, 51], therefore it seems unlikely that the ZnO is dissolving the SiO_2 support. It may be that the ZnO and SiO_2 chemical interaction weakens the support's structural strength, enabling the stirring mechanism to pulverize the support.

The elevated temperature and pressure effects were examined in the two anion exchange resin-catalyzed experiments. The first run, conducted for 12 hours at 1000 psig and 200°C, yielded a dark-brown odoriferous, oily, single-phase liquid.

The product appearance was sufficiently intriguing to warrant analysis by the MSU Mass Spectrometer Facility. The analytical mass spec results are given in Table 8. Roughly half of the sample analyzed was in three peaks in the C_{21} range. One peak was $C_{21}H_{44}$, a straight-chain, unsaturated hydrocarbon, and another peak 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%. The mass spectrometer used is accurate to ±15% of the concentration measurement and 0.5 atomic unit of the mass measurements [52]. This analysis does not include unreacted triglycerides, free fatty acids and other miscellaneous compounds that were excessively involatile for this analytical method. This reaction did not go to completion but nevertheless does appear, from the TLC results, to have produced substantial products. Rapeseed oil can be thermally cracked without a catalyst at 1000°F [53].

Table 8. Product Component Concentrations from the Elevated Temperature and Pressure Experiments with an Anion Exchange Resin Catalyst.

Experiment A: 200°C and 1000 psig		Experiment B: 91°C and 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}	1.7
2. C_{20}	3	2. C_{21}	4.1
3. C_{19}	3	3. C_{20}	4.3
4. C_{18}	4	4. C_{19}	4.0
5. C_{17}	4	5. C_{18}	7.1
6. C_{16}	7	6. C_{17}	4.0
7. C_{15}	7	7. C_{16}	6.6
8. C_{14}	6	8. C_{15}	13
9. C_{13}	7	9. C_{14}	7.2
10. C_{12}	6	10. C_{13}	14
11. C_{11}	3	11. C_{12}	13
12. C_{10}	2	12. C_{11}	16
		13. C_{10}	4.7

The second anion exchange resin-catalyzed experiment was attempted because of speculation that, at a more moderate temperature above the normal boiling point, the triglyceride cracking might be reduced without hindering the transesterification mechanism. A similar procedure was followed as with the previous experiment with the exception that the temperature and pressure were maintained at 91°C and 135 psig. 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, with the mass spectrometer sample being representative of both layers. The mixture was slightly odoriferous. Mass spectrometer results indicate only trace methyl fatty ester quantities at best, whereas, insofar as the triglycerides reacted, they pyrolyzed to straight-chain hydrocarbons. The TLC results indicate that sizable amounts of triglycerides remain unreacted.

The appendix presents the acid/base strength and the relative quantity of acid/base sites for each catalyst. No correlation between these results and the catalysts activity was noted in this data because numerous other factors affecting the catalytic mechanism were not held constant. For example, the catalyst's acid/base strength measurement revealed only the aqueous strength of the most prevalent site, but did not quantify the range of acid/base strengths for the range of sites. Furthermore, the measurement did not differentiate between Lewis and Bronsted acids and bases. Likewise, the measurement of the relative quantity of acid/base sites gave an indication of the total number of sites, but did not give a measure of the different catalytic sites.

CONCLUSIONS

1. The most promising catalyst examined in this investigation is CaO•MgO. This catalyst, as prepared in this study, also produces liberal quantities of free fatty acid salts as an unwanted by-product. The results of the CaO and ZnO experimental catalyst series suggest that the transesterification reaction mechanism is, in this instance, bifunctional.

2. There is no apparent correlation, from this investigation's data, between catalytic activity and the catalyst's acid/base strength or number of acid/base sites.

3. Catalytic transesterification at elevated temperatures and pressures may produce substantial amounts of cracked hydrocarbons as a by-product.

RECOMMENDATIONS FOR FURTHER STUDY

1. Further study of the CaO·MgO catalyst is warranted. Parameters that could be investigated include relative catalyst concentrations, impregnation order, calcination and impregnation techniques, and various types of catalyst supports. Refined vegetable oil reactants could probably reduce the CaO·MgO catalyst's free fatty acid salt production.

2. The stochastic approach to catalyst research should be continued with an emphasis on bifunctional metallic or metal oxide catalysts.

3. Synthetic diesel fuel production by thermal or catalytic cracking of the vegetable oil triglycerides warrants investigation.

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APPENDIX

Catalyst Parameters

Table 9. Catalyst Parameters.

Catalyst	Measured Acid/Base Strength (pK_a)	Measured Acid/Base Sites (mmol/gm)	Remarks
1. MgO support	$9.3 < pK_a < 15.0$	0.444	Catalyst quantity: 0.496 gmoles
2. Al_2O_3 support	$9.3 < pK_a < 15.0$	0.0115	Catalyst quantity: 0.194 gmoles
3. SiO_2 support	$0.8 < pK_a < 4.8$	0.0214	Catalyst quantity: 0.241 gmoles
4. $CaO \cdot Al_2O_3$ support	$7.2 < pK_a < 9.3$	0.0507	Catalyst quantity: 0.0437 gmoles
5. $CaO \cdot MgO$	$9.3 < pK_a < 15.0$	2.13	Impregnated with $Ca(NO_3)_2 \cdot 4H_2O$ and calcinated at 500°C for 8 hours Catalyst quantity: 0.0479 gmoles
6. $CaO \cdot Al_2O_3$	$15.0 < pK_a < 17.2$	0.533	Impregnated with $Ca(NO_3)_2 \cdot 4H_2O$ and calcinated at 500°C for 8 hours Catalyst quantity: 0.0481 gmoles
7. $CaO \cdot SiO_2$	$9.3 < pK_a < 15.0$	0.560	Impregnated with $Ca(NO_3)_2 \cdot 4H_2O$ and calcinated at 500°C for 8 hours Catalyst quantity: 0.0390 gmoles
8. CaO powder	$9.3 < pK_a < 15.0$	35.7	Catalyst quantity: 0.0320 gmoles
9. $CaO \cdot MgO \cdot Al_2O_3$	$15.0 < pK_a < 17.2$	1.592	Impregnated with $MgCl_2 \cdot 6H_2O$ and calcinated at 800°C for 13 hours; then impregnated with $Ca(NO_3)_2 \cdot 4H_2O$ and calcinated at 600°C for 8 hours Catalyst quantity: CaO: 0.0329 gmoles MgO: 0.0309 gmoles
10. $K_2CO_3 \cdot MgO$	$9.3 < pK_a < 15.0$	6.95	Impregnated directly Catalyst quantity: 0.0321 gmoles

Table 9 (continued)

Catalyst	Measured Acid/Base Strength (pK_a)	Measured Acid/Base Sites (mmol/gm)	Remarks
11. $K_2CO_3 \cdot Al_2O_3$	$9.3 < pK_a < 15.0$	1.63	Impregnated directly Catalyst quantity: 0.0311 gmoles
12. K_2CO_3 powder	$9.3 < pK_a < 15.0$	14.5	Catalyst quantity: 0.0321 gmoles
13. $Na_2CO_3 \cdot MgO$	$9.3 < pK_a < 15.0$	0.946	Impregnated directly Catalyst quantity: 0.00554 gmoles
14. $Na_2CO_3 \cdot Al_2O_3$	$9.3 < pK_a < 15.0$	0.443	Impregnated directly Catalyst quantity: 0.0118 gmoles
15. Na_2CO_3 powder	$9.3 < pK_a < 15.0$	18.87	Catalyst quantity: 0.0320 gmoles
16. Activated Carbon	$pK_a > 9.0$	0.132	Catalyst quantity: 0.817 gmoles
17. Fe_2O_3-on-MgO-support-crush	$7.2 < pK_a < 15.0$	17.45	Catalyst and support in granular form Catalyst quantity: 0.0160 gmoles
18. $CH_3ONa \cdot SiO_2$	$9.3 < pK_a < 15.0$	0.337	Impregnated directly Catalyst quantity: 0.00400-0.00990 gmoles
19. $NaAlO_2 \cdot MgO$	$9.3 < pK_a < 15.0$	0.826	Impregnated directly Catalyst quantity: 0.0176 gmoles
20. $NaAlO_2 \cdot Al_2O_3$	$9.3 < pK_a < 15.0$	0.144	Impregnated directly Catalyst quantity: 0.0149 gmoles
21. Zn metal	––	––	Catalyst quantity: 0.3912 gmoles
22. Cu metal	––	––	Catalyst quantity: 0.459 gmoles
23. Sn metal	––	––	Catalyst quantity: 0.411 gmoles
24. Pb metal	––	––	Catalyst quantity: 0.392 gmoles

Table 9 (continued)

Catalyst	Measured Acid/Base Strength (pK_a)	Measured Acid/Base Sites (mmol/gm)	Remarks
25. $ZnO \cdot MgO$	$0.8 < pK_a < 4.8$	0.0167	Impregnated with $ZnCl_2$ and calcinated at 400°C for 3 hours Catalyst quantity: 0.0502 gmoles
26. $ZnO \cdot Al_2O_3$	$0.8 < pK_a < 4.8$	2.08	Impregnated with $ZnCl_2$ and calcinated at 400°C for 3 hours Catalyst quantity: 0.0757 gmoles
27. $ZnO \cdot SiO_2$	$0.8 < pK_a < 4.8$	0.105	Impregnated with $Zn(NO_3)_2 \cdot 6H_2O$ and calcinated at 425°C for 8 hours Catalyst quantity: 0.0278 gmoles
28. Anion Exchange Resin	$4.8 < pK_a < 7.2$	0.143	Catalyst quantity: 5 gm

DATE	ISSUED TO