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Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils¹

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ABSTRACT

Transesterification reaction variables that affect yield and purity of the product esters from cottonseed, peanut, soybean and sunflower oils include molar ratio of alcohol to vegetable oil, type of catalyst (alkaline vs acidic), temperature and degree of refinement of the vegetable oil. With alkaline catalysts (either sodium hydroxide or methoxide), temperatures of 60 C or higher, molar ratios of at least 6 to 1 and with fully refined oils, conversion to methyl, ethyl and butyl esters was essentially complete in 1 hr. At moderate temperatures (32 C), vegetable oils were 99% transesterified in ca. 4 hr with an alkaline catalyst. Transesterification by acid catalysis was much slower than by alkali catalysis. Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils.

INTRODUCTION

Fatty esters from vegetable oils have shown promise as alternative diesel fuels as a result of improved viscosity and volatility relative to the triglyceride (1-3) and this has stimulated interest in optimization of transesterification reaction conditions (4-7). Transesterification (also called alcoholysis) has been studied intensively by numerous investigators (8-12). Of the more than a dozen US patents on transesterification, the patent of Bradshaw and Meuly (13) is cited frequently.

Our objectives were to develop basic information concerning the transesterification reaction of crude and refined oils to resolve inconsistencies in the literature, such as molar ratios, and to delineate optimum reaction conditions for maximum conversion to fatty esters with both alkali- and acid-catalyzed reactions. The effects of such variables were evaluated quantitatively with an Iatroscan TLC/FID (thin layer chromatography/flame ionization detector) analyzer not available to earlier investigators.

EXPERIMENTAL PROCEDURES

Materials

All refined vegetable oils were edible grade. Refined soybean oil was obtained from Central Soya, Chattanooga,

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Tennessee; sunflower oil from PVO International Inc., Richmond, California; peanut oil from Hain Pure Food Co., Los Angeles, California. Crude vegetable oils were obtained from the following sources: soybean and safflower oil from Arrowhead Mills, Inc., Hereford, Texas; peanut oil from Birdsong Corp., Suffolk, Virginia; cottonseed oil from Texas A&M University; sunflower oil from North Dakota State University.

The crude oils were processed by mechanical pressing, were not further refined and contained sediment but no added preservatives. They were used as received; uniform samples were obtained by thorough mixing of oil and any solids present. The edible-grade oils were degummed, alkali-refined, bleached, filtered and deodorized.

Sodium methoxide, as an anhydrous powder, was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, sodium hydroxide (ACS grade) from J.T. Baker Co., Phillipsburg, New Jersey; concentrated sulfuric acid from Mallinckrodt, Inc., St. Louis, Missouri). Methanol and butanol were MCB Omnisolv (spectrograde) and were stored over molecular sieves 4A. Ethanol was distilled before use and stored over molecular sieves 4A.

Transesterification Reaction Procedures

A 100 mL 3-necked flask equipped with mechanical stirrer, thermometer and condenser (to which a drying tube was attached) was heated to expel moisture. On cooling, 60 g (0.0682 mol, assuming a molecular weight of 879.5 for sunflower oil) edible-grade sunflower oil was added to the flask, followed by 16.572 mL (13.115g, 0.4093 mol) methanol. The mixture was stirred and heated in a silicone oil bath to 60 C, at which point 0.3 g sodium methoxide (0.5%, by weight of oil) was added rapidly. The temperature rose to 63.3 C in 1 min, and the reaction mixture became less turbid. Heating continued for 1 hr at 60-63 C, at which point the reaction was 98% completed as determined by Iatroscan analysis. After the reaction mixture was allowed to cool to room temperature, the ester and glycerol layers were separated in a separatory funnel. Excess methanol in the ester layer was removed on a rotary evaporator at reduced pressure or by distillation at atmospheric pressure. The ester was purified further by dissolving in

petroleum ether (35-60 C), adding water, adding glacial acetic acid or phosphoric acid drop by drop until a pH of ca. 7 was obtained, washing 3 times with water (vigorous shaking causes difficult emulsions), drying the petroleum ether solution over anhydrous magnesium sulfate and filtering and removing solvent on a rotary evaporator or by distillation at atmospheric pressure.

An acid-catalyzed butanolysis of soybean oil was conducted by heating 20 g (0.0253 mol) refined soybean oil, 69.47 mL (56.25 g, 0.759 mol) butanol and 0.2 g concentrated sulfuric acid at 117 C for 4 hr. Samples were withdrawn after 0.1 hr, 0.2 hr, 0.5 hr, 1 hr, 2 hr, 3 hr and 4 hr. On removal of excess butanol on a rotary evaporator at 50 C under reduced pressure and cooling to room temperature, the glycerol and ester separated into 2 phases.

Sample Preparation and Iatroscan TLC/FID Analysis

For alkali-catalyzed studies, 0.5 mL of reaction mixture was withdrawn after 1 min, 2 min, 4 min 30 min and 60 min. For acid-catalyzed studies, samples were taken at longer intervals. Samples were quenched in 0.5 mL water. A drop of the oil layer was weighed on an analytical balance, and chloroform was added to give a concentration of 3.0 mg of oil per mL of solution. A chloroform solution of stearyl alcohol (as an internal standard) of known concentration was added to the solution of reaction mixture so that the weight ratio of oil to stearyl alcohol was 10:1.

Analyses were performed with an Iatroscan TH-10 TLC Analyzer MK. III (Iatron Laboratories, Tokyo, Japan; worldwide distributor, Newman-Howells Assoc., Winchester, Hants, United Kingdom) as previously described (4,14). The FID was operated with hydrogen and air flow rates of 160 and 2000 mL/min. Scan speed (4) was 0.42 cm/sec. The strip chart recorder was a Linear Instrument Corp. (Irvine, California) Model 561 and was used at 1 mV full-scale deflection at a chart speed of 20 cm/min.

Solutions to be analyzed were spotted on Chromarod-S rods with a Hamilton 10 μ L syringe in amounts of 1-2 μ L of solution per rod. Three-to-four replicates were used for each solution. The rods were developed in a glass tank containing petroleum ether (b.p. 35-60 C)/diethyl ether/acetic acid (90:10:1) for 20 min, air-dried for 5 min, oven dried at 110-130 C for 5 min and then placed on the Iatroscan. The signals produced were sent to the recorder and were also integrated by a computer-assisted program. A second computer program printed the percentages of composition of the reaction mixture.

RESULTS AND DISCUSSION

Effect of Moisture and Free Fatty Acid

Wright et al. (15) have noted that the starting materials used for alkali-catalyzed alcoholyses of triglycerides should meet certain specifications. The glyceride should have an acid value less than 1, and all materials should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensated for higher acidity, but the resulting soaps caused an increase in viscosity or formation of gels and interfered with separation of glycerol. As little as 0.3% water in the reaction mixture reduced glycerol yields by consuming catalyst. Other investigators have also stressed the importance of a nearly dry oil substantially free (<0.5%) of fatty acids (13,16,17).

As we show later, when the reaction conditions do not meet the above requirements, ester yields are significantly reduced. Both sodium methoxide and sodium hydroxide should be maintained in an anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon

dioxide. Although transesterifications have been conducted in a nitrogen atmosphere to exclude moisture and carbon dioxide and to prevent oxidation of the oil (17,18), we found this precaution to be unnecessary.

Effect of Molar Ratios

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to vegetable oil employed. The stoichiometry of this reaction requires 3 mol alcohol per mol triglyceride to yield 3 mol fatty ester and 1 mol glycerol. Bradshaw (13,16) stated that a 4.8:1 molar ratio of methanol to vegetable oil led to a 98% conversion, and if the alcohol was added in 3 or 4 portions, this ratio could be reduced from 4.8:1 to 3.3:1. He noted that ratios greater than 5.25:1 interfered with gravity separation of the glycerol and added useless expense to the separation. In contrast, other investigators (17-19) obtained high ester conversions with a 6:1 molar ratio. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerol than did a 3:1 molar ratio (17). These workers also found that glycerol yield increased from 77% to 95% as the sodium hydroxide catalyst increased from 0.2% to 0.8% at the 6:1 molar ratio. Other investigators have used higher molar ratios, up to 45:1, particularly when the triglyceride contained large amounts of free fatty acids (20).

We studied the effect of molar ratio on ester yield, both because of the variation in the molar ratio reported as necessary by various investigators and because no correlation has been found of a systematic variation in molar ratio with ester yield. At the same time, the changes in concentrations of tri-, di- and monoglyceride were also monitored. The results obtained from the methanolysis of sunflower oil, in which the molar ratio was varied from 6:1 to 1:1, are shown in Figure 1. At a 6:1 molar ratio, a 98%

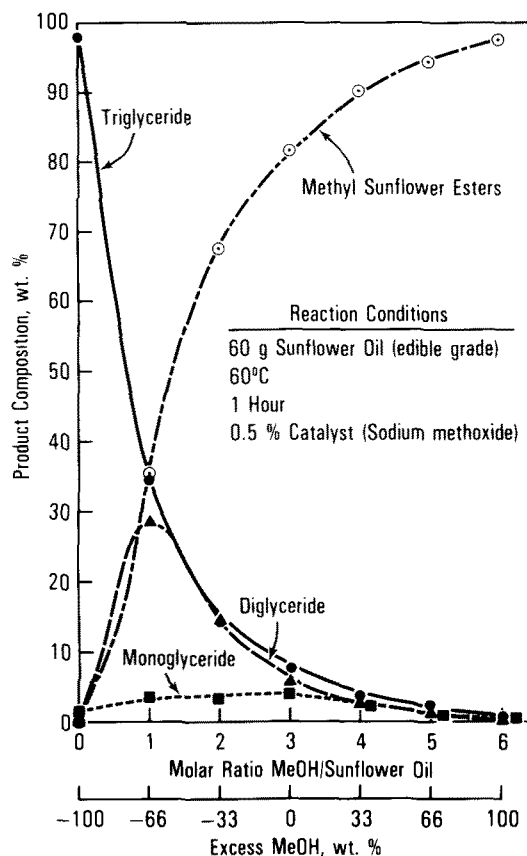


FIG. 1. Product composition in transesterified sunflower oil at various molar ratios.

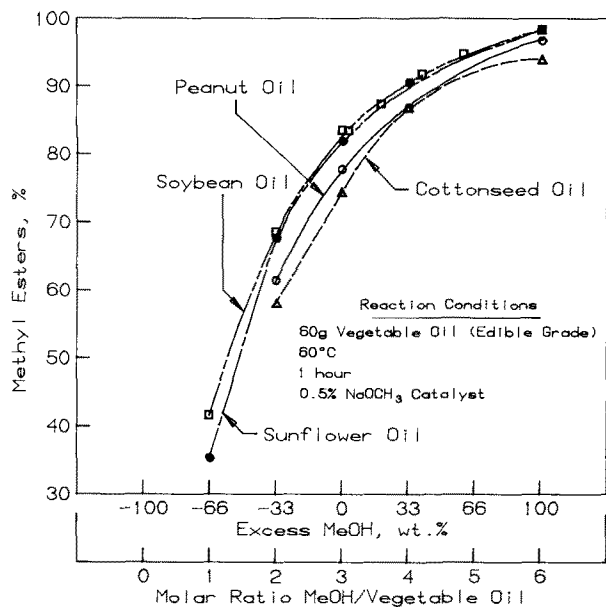


FIG. 2. Ester content in transesterified vegetable oils—effect of reactant ratios.

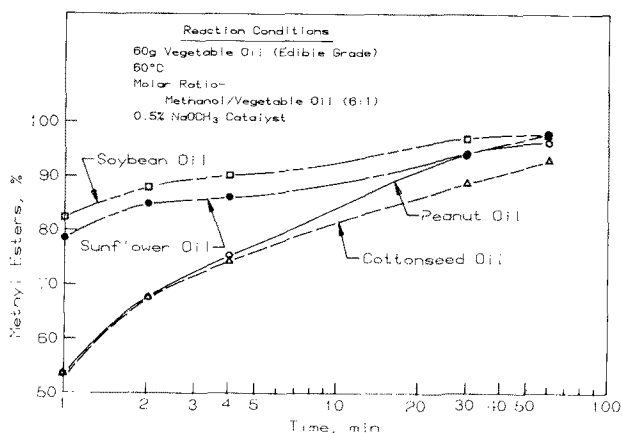


FIG. 3. Effect of time on the alkali-catalyzed transesterification of vegetable oils at molar ratio $\text{CH}_3\text{OH}/\text{oil}$ of 6:1, sodium methoxide catalyst (0.5%).

conversion to the ester was obtained. As the molar ratio decreased to the theoretical ratio of 3:1, the percentage of ester decreased to 82%. Tri-, di- and monoglycerides, which were at low levels at the 6:1 ratio, also increased with decreasing molar ratio, indicating that conversion to the ester was not complete. Our results suggest that for maximum conversion to the ester, a 6:1 ratio should be used. Ratios greater than 6:1 do not increase yields (already at 98-99%), complicate ester and glycerol recovery, and add costs to alcohol recovery. The results of varying the molar ratio of methanol to vegetable oil, when extended to refined soybean, sunflower, peanut and cottonseed oils, showed that these oils behaved similarly, and that highest conversions to esters (93-98%) were observed at the 6:1 molar ratio (Fig. 2).

Effect of Reaction Time on the Alkali-Catalyzed Alcoholysis

Several investigators have followed fatty ester formation with time. In the first 5 min of the ethanolsis of peanut oil, ca. 80% of the ester obtained after 2 hr was formed (17). The alcoholysis of menhaden oil, using a variety of alcohols, has been monitored by thin layer chromatography

(TLC) (18,19). Depending on the alcohol used, reactions at 60-100 C resulted in 80-99% conversions in 2-60 min.

We investigated the methanolysis of the 4 refined vegetable oils, following the conversion to ester with time. Molar ratios of methanol to oil of 6:1 (Fig. 3) and 3:1 were employed. Samples were taken from the reaction mixture after adding catalyst. For soybean and sunflower oils, ca. 80% ester was observed after 1 min, confirming the rapidity of alkali-catalyzed methanolysis. For unknown reasons, ester conversions after 1 min with peanut and cottonseed oils were distinctly lower. After 1 hr, however, the percentage of methyl ester for all 4 oils ranged from 93-98%. Thus, given sufficient time, these 4 oils underwent conversion to about the same extent. As expected for a 3:1 molar ratio, ester conversion for all 4 oils was considerably lower, ranging from 89-74% for soybean oil and cottonseed oil esters, respectively, after 1 hr.

Our study was extended to the alcoholysis of sunflower oil with ethanol and butanol as well as methanol at molar ratios of 6:1 and 3:1. Each reaction was conducted a few degrees below the boiling point of the alcohol and was catalyzed with 0.5% sodium methoxide based on the weight of the oil. At both the 6:1 and 3:1 molar ratios, a higher ester conversion occurred initially with butanol than with ethanol or methanol because of the higher reaction temperature employed (Fig. 4). After 1 hr at the 6:1 ratio, the percentage of ester from all 3 alcohols was nearly identical (96-98%). After 1 hr at the 3:1 ratio, conversion to butyl esters was 88% compared with 81% and 82% for ethyl and methyl esters. These results confirm the importance of using an excess of alcohol compared with the stoichiometric amount for maximum conversion to the ester.

Change in Glyceride Composition During Transesterification

Most investigators have not studied changes in glyceride composition during the alcoholysis of fats and oils. However, Grün et al. (21) reported that the alcoholysis is a step by step process and that mono-, di- and triglycerides are all present in the final product. Feuge and Gros (17) followed glyceride distribution during ethanolsis of peanut oil. The latter investigators used the more complicated classical chemical methods for glyceride analyses in contrast to the more convenient and faster TLC/FID method described here.

We determined differences in glyceride composition between reactions employing a 6:1 vs a 3:1 molar ratio of ethanol to sunflower oil (Fig. 5). As anticipated, total gly-

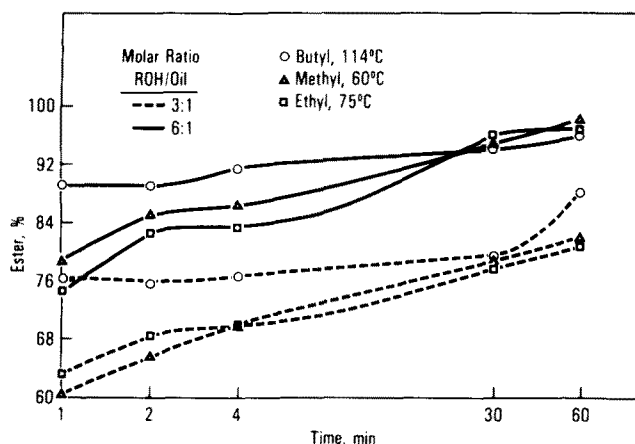


FIG. 4. Transesterification of sunflower oil to methyl, ethyl and butyl esters.

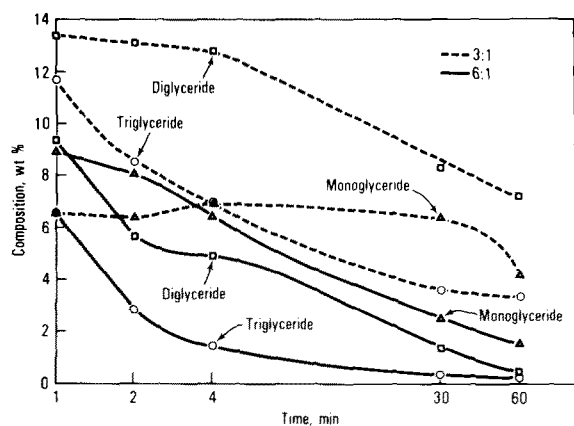


FIG. 5. Glyceride composition during transesterification of sunflower oil to ethyl esters.

cerides during the 6:1 run were generally lower than those during the 3:1 run, indicating that the former reaction was more complete. In both cases triglyceride concentration was lower than di- and monoglyceride concentration after 60 min, showing that the triglyceride had reacted to form intermediates and product. The combination of glycerides and ester accounted for all major components of the reaction mixture; only trace amounts of fatty acids and unknowns were detected. Even under our most suitable conditions for high conversions to the ester, traces of glycerides were still present because of an equilibrium between products and reactants.

Glycerol Recovery

Although the fatty ester is the major product desired, recovery of glycerol, the by-product, is also important. Glycerol has many industrial uses. An estimate has been made that the cost of the transesterification processing could be paid for if suitable markets can be found for the glycerol (A. Aguiar, personal communication). Bradshaw has noted that glycerol produced by alcoholysis of refined fats is anhydrous and can be used directly in many processes without further refining (16).

We have determined the yields of glycerol formed during the transesterification of refined sunflower, peanut and cottonseed oils. Crude glycerol yields were about the same for all 3 oils and depended on the molar ratio of alcohol to oil employed. With sunflower, for example, the molar ratios and resulting yields of crude glycerol were: 6:1,

100%; 5:1, 100%; 4:1, 79%; 3:1, 56%; 2:1, 18%; 1:1, 0%. Thus, for maximum yields of both ester and glycerol, a 6:1 ratio was best.

Methanolysis of Crude and Refined Vegetable Oils

Although a dry, neutral oil is preferred as a starting material, some investigators have reported the use of crude fatty materials for alcoholysis. Bradshaw and Meuly (13,16) stated that their process could accommodate unrefined oils containing small amounts of moisture and free fatty acids. With such oils, reaction required larger quantities of alkali, the soaps formed needed to be acidified before glycerol would separate and glycerol separation was slower. Sprules and Price (20) stated that the use of a large excess of alcohol coupled with alkaline and acid catalysis can also accommodate low quality and unrefined fats and oils.

We compared the transesterification of crude and refined oils. A 6:1 molar ratio of methanol to oil was employed. Free fatty acid and phosphorus contents, the former certainly and the latter possibly leading to catalyst destruction, were determined in the crude oils by standard AOCS methods; both values were higher in the crude than in the refined oils as expected (Table I). The amount of catalyst was adjusted for the acid values of the crude oils. In every case substantial conversion to ester was obtained with the crude oils, but these yields were always noticeably lower than those obtained with refined oils. Part of the reduced yields with the crude oils could be ascribed to the presence of solid, extraneous material present in these oils. For maximum yields the refined oils should be used. However, if the esters are to be used as a diesel fuel, using a crude degummed and filtered oil as starting material for the transesterification may suffice.

Effect of Temperature on Ester Formation

Although alkaline alcoholysis of vegetable oils is normally conducted near the boiling point of the alcohol, researchers have reported that the reaction may be carried out at room temperature (8,15,22). In methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20-35 C at molar ratios of methanol to oil of 6:1 to 12:1 (23). South African scientists have reported a 90% yield of ethyl esters of sunflower oil by conducting a large-scale alkali ethanolysis at room temperature (24).

We studied the methanolysis of refined soybean oil at 60 C, 45 C and 32 C using conditions shown in Figure 6. On adding catalyst to the solution at ambient temperature (28 C), the temperature rose to 32.6 C (because of the

TABLE I

Transesterification of Crude and Refined Vegetable Oils with Methanol

Oil	Type	Acid value ^a	Phosphorus ^b (ppm)	Methyl ester yield (wt. %)
Peanut	Crude	6.66	264	67
	Refined	0.08	5	95
Soybean	Crude	1.67	953	83
	Refined	0.12	1	98
Safflower	Crude	0.44	4	86
	Refined	—	—	—
Cottonseed	Crude	0.28	<1	84
	Refined	0.06	0.5	93
Sunflower	Crude	1.64	85	81
	Refined	0.08	0.7	97

^aAOCS Official Method Cd 3a-63.

^bAOCS Official Method Ca 12-55.

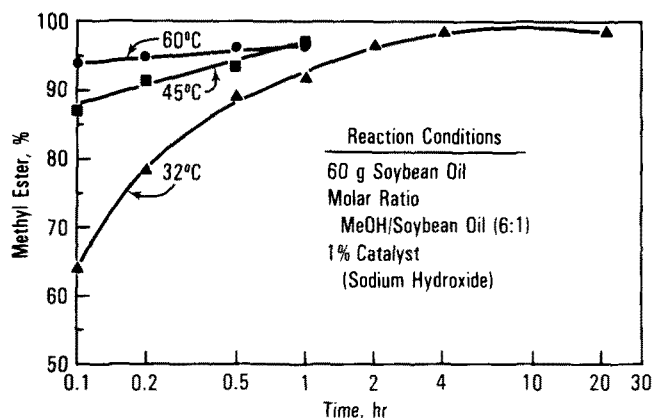


FIG. 6. Effect of temperature and time on methyl ester formation, sodium hydroxide catalyst (1%).

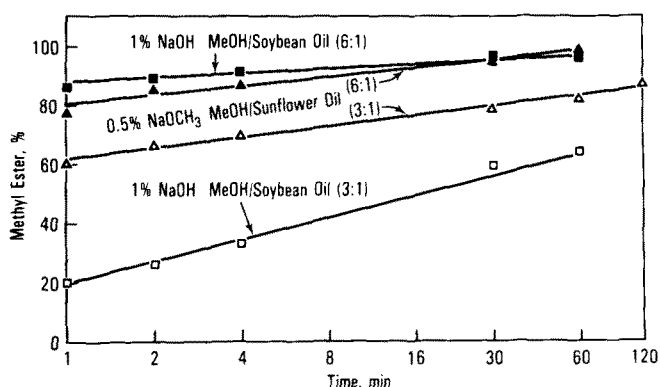


FIG. 7. Comparison of sodium methoxide vs sodium hydroxide catalysts.

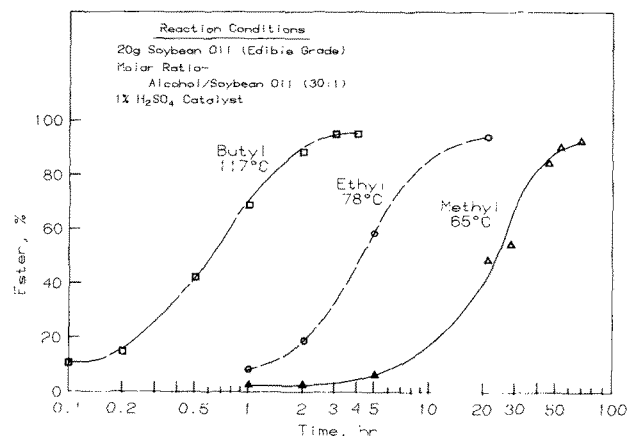


FIG. 8. Transesterification of soybean oil to methyl, ethyl and butyl esters with 1% H_2SO_4 catalyst.

exothermicity of the reaction) and remained at 32 ± 1 C during the run. After 0.1 hr, the esters present in the 60 C, 45 C and 32 C runs were 94%, 87% and 64%, showing the influence of temperature on ester conversion. However, after 1 hr, ester formation was identical for the 60 C and 45 C runs, and only slightly lower for the 32 C run. After 4 hr the ester conversion for the 32 C run slightly exceeded that of the other runs.

Comparison of Sodium Methoxide vs. Sodium Hydroxide Catalysts

Alkali metal alkoxides are the most effective alcoholysis catalysts (8,11,12) and are also effective in interesterification (11,25). The lower cost of sodium hydroxide has

attracted its wide use in large-scale transesterifications. On a laboratory scale, Hartman (26) compared the methanolysis of several triglycerides with various alkali metal catalysts including sodium methoxide and sodium hydroxide. At the 0.5% level for each catalyst, the glycerol set free by the methoxide was ca. 99% compared with ca. 98% with the hydroxide catalyst. Although geometric and positional isomerization might be anticipated as possible side reactions, under the mild conditions employed in alkali-catalyzed alcoholysis such isomerizations are not significant (18).

We compared these 2 catalysts at a 6:1 and 3:1 molar ratio of methanol to vegetable oil (Fig. 7). Ester conversions at the 6:1 ratio for both catalysts were very similar, and after 60 min were essentially identical. Hence at the 6:1 molar ratio, 0.5% sodium methoxide was as effective as 1% sodium hydroxide. At the 3:1 ratio, however, the methoxide catalyst was clearly superior to the hydroxide catalyst during the entire 60-min reaction time.

Acid-Catalyzed Alcoholysis

Alkali catalysis is considerably faster than acid catalysis for the alcoholysis of esters (27-28). Even at ambient temperature, the alkali-catalyzed reaction proceeds rapidly, whereas acid-catalyzed reactions commonly require temperatures above 100 C (8,12). With acid-catalysis, reaction times of 3-48 hr have been reported, except when reactions were conducted under high temperature and pressure (29, 30). Keim (28) has noted that acid-catalyzed alcoholysis can be used when the starting materials are low-grade fats or have a high free fatty acid content; the fatty acids would deactivate an alkaline catalyst.

We compared the transesterification of soybean oil with methanol, ethanol and butanol using 1% concentrated sulfuric acid based on the weight of oil. In preliminary experiments with 6:1 and 20:1 molar ratios at 3 and 18 hr, respectively, conversions to ester were unsatisfactory. A molar ratio of 30:1, however, resulted in a high conversion to the methyl ester. This molar ratio was used during our studies of methanol, ethanol and butanol (Fig. 8). Each alcoholysis was conducted near the boiling point of the alcohol. The number of hours needed to obtain high conversions to the ester were 3, 22 and 69, respectively, for the butyl, ethyl and methyl esters. Reaction temperature rather than the type of alcohol appeared to control the time to completion. To confirm this, alcoholysis was conducted at 65 C for all 3 alcohols. At this temperature, rates of conversion and final conversion to ester after 69 hr were similar for all 3 alcohols.

Recommended Conditions for Ester Formation

To obtain maximum ester formation by transesterification of vegetable oils, refined oils, substantially anhydrous with a free fatty acid content of less than 0.5% (acid value less than 1), should be used. The alcohol should also be moisture free. A molar ratio of alcohol to oil of 6:1 gives optimum conversion to the ester. Either 0.5% sodium methoxide (for laboratory use) or 1% sodium hydroxide (for larger-scale reactions) are effective catalysts. These catalysts should be stored under anhydrous conditions free from air. Ester conversions of 96-98% are obtained by transesterifying refined oils with methanol, ethanol and butanol at 60 C, 75 C and 114 C for 1 hr with 0.5% sodium methoxide.

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