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PRODUCTION OF ETHERS OF GLYCEROL FROM CRUDE GLYCEROL - THE BY-PRODUCT OF BIODLESEL PRODUCTION

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Methyl esters of fatty acids (also known as biodiesel), made from the transesterification of vegetable oils and animal fats with methanol, have shown a lot of promise as alternative diesel fuels. Glycerol is the inevitable byproduct of the transesterification process. While there are existing markets for glycerol, a significant increase in availability of glycerol, resulting from the expanded use of vegetable oils and animal fats, would destabilize the glycerol market. Direct addition of glycerol to the fuel is not possible, however, derivatives of glycerol such as ethers have potential for use as additives with biodiesel, diesel or biodiesel-diesel blends. In this study. the etherification of glycerol with isobutylene was investigated. The preparation techniques for this process were optimized. The optimum conditions were determined to be at 80 "C, catalyst loading **>** 5 wt%, 1-2 h of reaction time, and a glycerol to isobutylene molar ratio of approximately 3. Physical properties of ethers of glycerol and different blends of ethers with diesel and biodiesel fuels were measured. Solubility studies determined that these additives are compatible with diesel and biodiesel fuels. A 20% blend of these additives with methyl esters resulted in a 5 "C reduction in cloud point and an 8% reduction in viscosity

Key words: biodiesel. glycerol, additives, glycerol ethers, vegetable oils, transesterification

INTRODUCTION

Since the introduction of biodiesel in South Africa prior to World War 11. work has been done to increase its viability as a fuel substitute. In recent years; efforts in this area have been renewed due to environmental and economic pressures. These pressures began with the oil embargo, continued through the Clean Air Act of 1990 and exist currently in the refinement of processes for biodiesel production. The desired benefits of the improvements are cleaner air, a cheaper product, or better fuel properties [l, 2]. Nonetheless, many problems inherent to biodiesel continue to exist and hamper its widespread commercialization and use. The use of biodiesel can scarcely become widespread unless its poor cold flow properties are improved [3]. The cloud point of neat soy oil methyl esters is 0 "C, as compared to -16 "C for diesel *#2.* Fats and oils with higher concentrations of unsaturated fatty acids, such as tallow, exhibit even higher cloud points than soy oil methyl esters. **A** similar disparity exists when comparing pour points of methyl esters to those of diesel (-2 $^{\circ}$ C vs -27°C). These dissimilarities, as well as those with respect to viscosity, low-temperature flow test and cold-filter plugging point contribute to skepticism regarding the efficacy of replacing diesel fuel with neat methyl esters [4, 51. Some solutions to these problem that have been suggested, such as winterization [6] or biotechnological attempts to alter oil composition to specification [7], may prove promising but are as yet industrially and economically questionable. Other problem with biodiesel have been reported with regard to emissions, most dramatically increased NO, emissions **[g].**
Another pressing problem, which will be created with even modest production of biodiesel, is the overproduction of glycerol. The transesterification of triglycerides results in esters of fatty acids (approximately 90% by weight) and glycerol. The glycerol phase contains a considerable amount of methanol and soluble methyl esters.

The U.S. glycerol market has been stable at about 300 million lbly over the last 30 years. A significant increase in the availability of glycerol will result from the expanded use of triglycerides for fuel purposes. Based on a total U.S. distillate fuel consumption of about 50.000 million gallons for 1990, addition of 20% biodiesel to only 10% of this market would result in about 800 million lb/y of surplus glycerol. An overproduction of this magnitude would destabilize the glycerol market and may considerably reduce the current glycerol market value. Current glycerol uses involve high cost purification steps to produce a product of questionable value which is sold as low-grade glycerol. Low value agricultural use involves mixing crude glycerol with manure for fertilizer or with feed for animals [9]. The potential for bacteriologic transformation of glycerol into products that can be used for plastic production has been demonstrated [7]. The most promising and economically advantageous use that has been demonstrated is the conversion of glycerol into high value products such as(mono- and di-fatty acids)[10 – 11].
One potential solution, which may alleviate sonic of the on biodiesel, is the use of glycerol or its derivatives as fuel additives.

Glycerol cannot be added directly to fuel due toits decomposition ,polymerizationand consequential engine problems at high temparatures.Glycerol must be modified to derivatives &at are compatible with diesel and biodiesel prior to being added to the fuel. The most obvious derivative of glycerol has an analogy in gasoline

reformulation. Oxygenated gasolines are well recognized and the demand for methyl tertiary butyl ethers (MTBEs) has grown to an estimated 473,000 barrels per day worldwide [12]. Glycerol tertiary butyl ether (GTBE) could similarly be used for diesel and biodiesel reformulation. Alkyl ethers of glycerol have been explored in the past and references to mono-tertiary butyl ether can be found dating back to the 1950's. Malinavskii and Vvedenskii made the fist known report of a mono-tertiary butyl ether of glycerol in 1953 [13]. It was prepared by heating glycidol with tertiary butyl alcohol (TBA) inthe presence of 1% H2S0,, yielding exclusively mono-ethers of glycerol. They reported that a 5-fold excess of TBA resulted in the highest yield and that decreasing the quantity of H,SO, lowers the yield. In US Patent No. 5,476,971, glycerol is reacted with isobutylene in the presence of an acid catalyst in a two-phase reaction to produce mono-, `di-,` and tri-tertiary butyl ethers of glycerol [14]. Patents for the use of glycerol ethers also exist. Patents claiming that glycerol ethers (as additives to biodiesel) allow for reductions in methyl ester content have been filed [15], and improved emissions have also been reported [l6].

The goals of this research are to perform a parametric analysis of the reaction conditions necessary for ether production, and to lay the groundwork fir optimization of these conditions. Additionally, mixtures of glycerol ethers are evaluated within biodiesel and biodiesel in selected blends of compatibility an to elucidate physical property effects. Practical aspects regarding the catalyst were also investigated.

The overall objective is to provide coupled production of glycerol ethers and fatty acidmethyl esters (FAME'S). A schematic example of this coupled process is shown in Figure 1. The advantages to this coupled production may prove many-fold. One advantage may be to reduce the production cost of biodiesel by CO-producing valuable products such as monoand di-glycerides. Another advantage is production of an enhanced biodieselproduct. This product would have physical properties more similar to diesel than currently produced biodiesel. Finally, the potential for overproduction of glycerol would be avoided.

EXPERIMENTAL PROCEDURES

Materials:

Pure glycerol (99.9%) was obtained from Sigrna Chemical Company (St. Louis, MO). Pure glycerol was used for the initial baseline reactions. Glycerol from local pilot plant production is referred to here as crude glycerol. Crude glycerol was obtained from the pilot plant in the Biomass Lab at the University of Nebraska (Lincoln, &X). sobutylene used in the reactions was obtained from Linweld (Lincoln, NE) and was 99.8% pure. Amberlyst-15 was obtained from SigmaChemical. Amberlyst-15 is a strong acid, macroporous. highly crosslinked sulphonic ion-exchange resin.

Equipment

The apparatus used for the reactions was a 450 mL bench-top high-pressure reactor with a detachable head (model number 4562; Parr Instrument Company, Moline, IL). The reactor assembly was constructed of type 316 stainless steel. The reactor was equipped with a turbine impeller with a magnetic drive and a 1112 hp variable speed motor, allowing for speeds up to 800 rpm. An electric heating mantel and an internal water-cooling loop maintained the desired temperature throughout each run via a PID controller. A Parr 4843 PID controller was used, which had the ability to ramp to reaction temperature, hold at this temperature, and ramp to the end temperature over user selected time intervals. The reactor was also equipped with a pressure transducer (&l psi) and a thermocouple (& 1 "C) for pressure and temperature input into the controller. A cooling water solenoid valve, actuated by the controller, regulated temperatures in conjunction with the heating mantel. The reactor was fitted with an upper port valve for vapor space venting and a lower port valve for isobutylene and nitrogen addition and purge.

Procedure

Glycerol and catalyst were first charged into the reactor. The reactor was then purged with nitrogen for the removal of air from the vapor space. Isobutylene was then charged into the reactor. The reactor was then pressurized to 250 psig to maintain isobutylene in the liquid state. All reactions were carried out under batchwise constant temperature mode.

Reactions were run at varying conditions for temperature, catalyst loading, molar ratio of glycerol to isobutylene. and reaction time. The reactor contents were agitated continuously with the stirrer operating at 500 rpm.

Analysis

Yields were estimated based on the amount of isobutylene vented after completion of a reaction. When conditions were sufficient to allow for a high conversion of isobutylene (>go%), the samples were run through the GC. A Hewlen-Packard (Wilmington, DE) HP-6890 series GC system equipped with an HP INh'O\5'ax capillary column (30 m x 0.25 mm ID x 0.25 mm), HP Series I1 GC Electronic Pressure Control (EPC), and split-splitless inlet was used for the analysis. The inlet was operated in the split mode with a split ratio of 40:1. Inlet temperature was maintained at 180 "C at a pressure of 24 psi. Helium was used as the camer gas at an average velocity of 49 f i n . This called for a total column flow rate of 108 mL1min with split flow of 103 mL1min. The column was operated in constant pressure mode. The initial oven temperature was 50 "C and held for 2 min. The oven was then ramped to 120 "C at 30 'C per min and held for 1 min. The final ramp was to 250 "C at 10 "C per min. The oven was held at this temperature for 5 min to complete the run. The overall run time for this method was 23.33 min. The GC was equipped with a flame ionization detector. The detector was held at 280 "C with a H, flow of ?g-mL/min, an air flow of 280 mL/min, and a 20 mL/min helium flow.

Figure **1. P**rocess flow diagram for coupled production of glycerol ethers and fatty acid methyl esters.

RESULTS AND DISCUSSION

Reaction optimization

A full factorial optimization approach was performed. The following range of conditions was studied: isobutylene to glycerol molar ratios of 1:1, 2.1, and 3:l; temperatures of 80, 87, and 93 "C; and reaction times of 2, 3. and 4 h. Catalyst loading for these reactions was set at 5 wt%.

Conversion

Conversion is generally a good indicator of reaction progression. In the care of this particular reaction, however, conversion can be somewhat misleading. Conversion in the context of these reactions can be based on either glycerol or isobutylene. Glycerol reacts to form the stepwise ether products. However, since a reacted glycerol may result in a mono-, di-, or hi-ether glycerol, conversion is notagoodindicator of the extent of the reaction. Isobutylene may react to form the C8 dimers (2,4.4 trimethyl l-pentene and 2,4,4 trimethyl 2-pentene) or to form the stepwise ether products. Additionally, if water or methanol is present, it will react to formTBA and MTBE. Hence, a high isobutylene conversion does not necessarily imply a high glycerol conversion. Therefore, it is necessary to base conversion only on the isobutylene consumed to form ethers. All conversions discussed are based on the fraction of total isobutylene added that is consumed to form ethers.

Effect of impurities

Impurities that are likely to be found in crude glycerol streams were added to reaction mixtures in typical quantities and reactions were camed out. These reactions were carried out using pure glycerol under reaction conditions known to produce high yields of ethers, specifically 6.8% catalyst by weight at 97 "C and an isobutylene to glycerol molar ratio of **3** for 4 h. The impurities tested were methyl esters, MeOH, sodium hydroxide, and traces of water. MeOH and water are classified as competitive isobutylene consumer\ becsuie they may react with isobutylene to form MTBE and TBA respectively. They were ruled out as anything other than competitive by reacting enough of the impurity to consume isobutylene to a certain molar ratio. This molar ratio was then reacted without impurities and this reaction produced a similar product composition minus the impurity 's derivative (MTBE/tertiary butanol). The presence of NaOH in crude glycerol is expected to deplete the catalyst and result in lower yields. Thls was experimentally verified and it was concluded that crude glycerol with no pre-treatment may result in inconsistent product compositions and low conversions. To minimize these effects, crude glycerol was neutralized with Amberlyst-15. Amberlyst- 15 effectively removes the sodium ions from crude glycerol without the formation of sodium salts, which are formed if it is neutralized with an acid. Sodium salts are difficult to remove from the solution and aredetrimental to the catalyst (.hberlyst-15) in the etherification reaction. The etherification of the pretreated crude glycerol was identical to that of pure glycerol. This was determined by checking several conditions and noting that the corresponding products were indistinguishable: with theexception of methyl ester content. The presence of methyl esters did not appear to have any unfavorable effect on the etherification reaction.
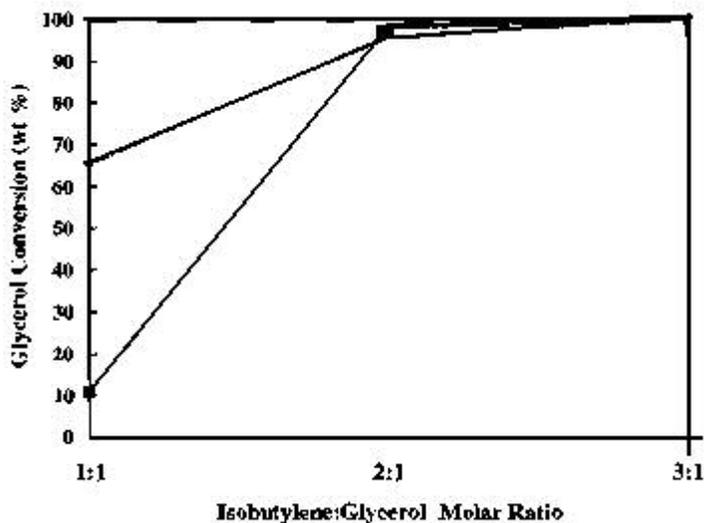
Figure 2. The effect of reactant stoichiometry on thc conversion of glycerol in the etherification reaction. (♦), 93 "C; and (■),80° C.

Effect of reactant stoichiometry

The effect of stoichiometry on the conversion of glycerol at 80 and 93 "C is illustrated in Figure 2. As this figure shows, the amount of glycerol which is consumed increases with the increase in the ratio of the reactants (isobutylene to glycerol). The data also indicate that at the lower temperature of 80 "C. the rate of consumption of glycerol is more swngly dependent on the ratio of the reactants. This behavior may be explained by the reaction stoichiometry. Glycerol contains **3** hydroxyl moieties per molecule; thus requiring 3 isobutylene molecules to form fully substituted ether. In the case of a 1:l molar ratio, hydroxyl moieties are at 200% excess. A molar ratio
of 3:1 provides balanced stoichiometry. Thelitemhue on MTBE seems to stress the importance of a balanced stoichiometry to preserve selectivity and high rate of conversion. This is consistent with our experimental results.
Additional factors may have also contributed to this behavior. First, at a 1:1 molar ratio approximately 1/3 of the reactor was filled with glycerol; very little mixing if any may have taken place. The high viscosity of glycerol may have contributed to this effect. As Figure 2 shows. at the higher temperature of 93 'C, a 1:1 molar ratio of the reactants resulted in significantly higher conversion of glycerol to ethers, although still lower than at the higher ratios. The results at a 1:l isobutylene to glycerol molar ratio are essentially so poor that those conditions warrant no further consideration. Please note that at a 1:l molar ratio, the reaction products consist prima.rily of glycerol monoethers, which are not desirable in the ether additive.

Effect of temperature

It seems appropriate to evaluate temperature effects with respect to the formation of by-products (C8's) and "higher" ethers (di and tri). The effects of temperature on the formation of by-products and higher ethers are summarized in Figures 3-6. It appears that these effects are also dependent upon the molar ratio of the reactants. At a 2:1 molar ratio. C8's increase with temperature andthe formation of higher ethers decreases with temperature (see Figures 3 and 5). At a 3:l molar ratio; C8's decrease with temperature and higher ether formation appears unaffected (see Figures 4 and 6). In the first case (2:l molar ratio) it seems that the available isobutylene is being consumed to form by-products at higherrates at higher temperatures. This results in less isobutylene available to form ethers, approaching the poorer 1:1 molar ratio regime discussed earlier. For the second case (3:1 molar ratio), by-products are produced at higher levels, however, enough isobutylene appears to have remained for the etherification reaction. Further examination of Figures 6 and 8 reveals that the formation of C8's appears to decrease as a function of

temperature: this would suggest that the catalyst favors the formation of by-products over ethers at lower temperatures in ths region. In any event, higher etherproduction is more consistent over a wide range of temperatures at amolarratio of 3:l. Additionally, by-product formation can be reduced by operating at the higher end of this temperature range (93°C).
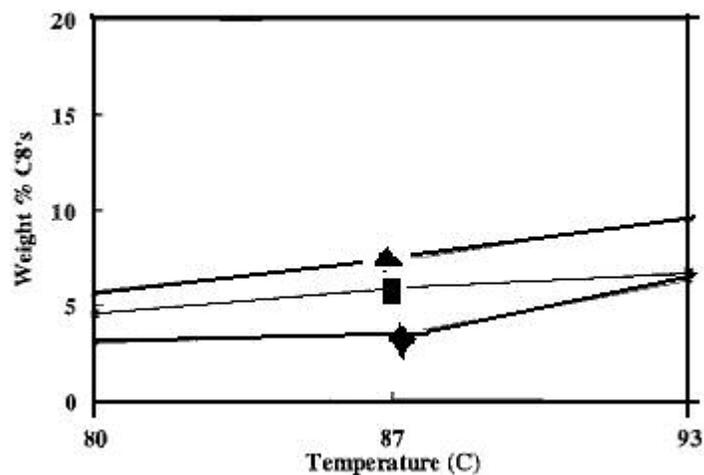

FIG **3.** The effect of temperature on by-products in the etherification of glycerol subject to an isobutylene to glycerol molarratio of 2.1, and 5 wt% catalyst. (♦)2, h; (■),3 h; and (▲),4h.
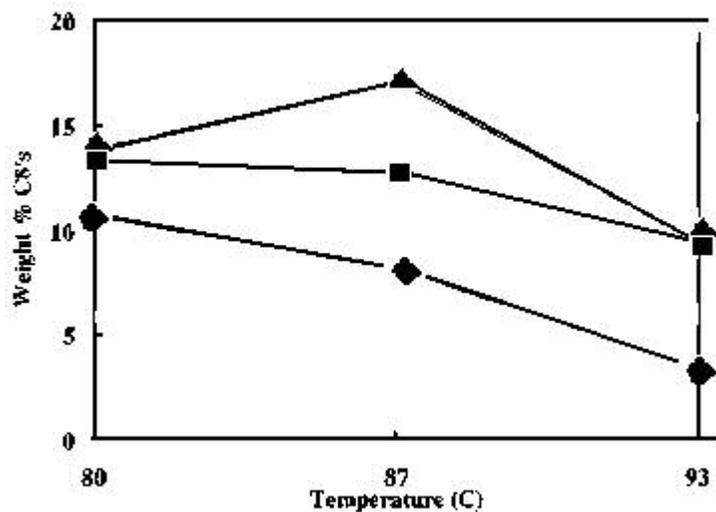
Figure 4. The effect of temperature on by-products in the etherification of glycerol subject to an isobutylene to glycerol molarratio of 3:1, and 5 wt% catalyst. (+), **2** h; (m, *3* h ; and (A), 4 h.
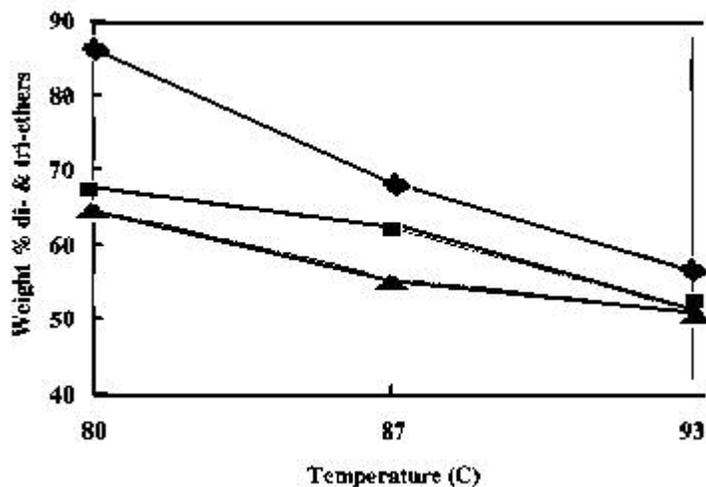
Figure 5. The effect of temperature on higher ethers in the etherification of glycerol subject to an isobutylene to glycerol molarrano of 21, and 5 wt% catalyst. (♦)2, h; (■),3 h; and (▲),4h.
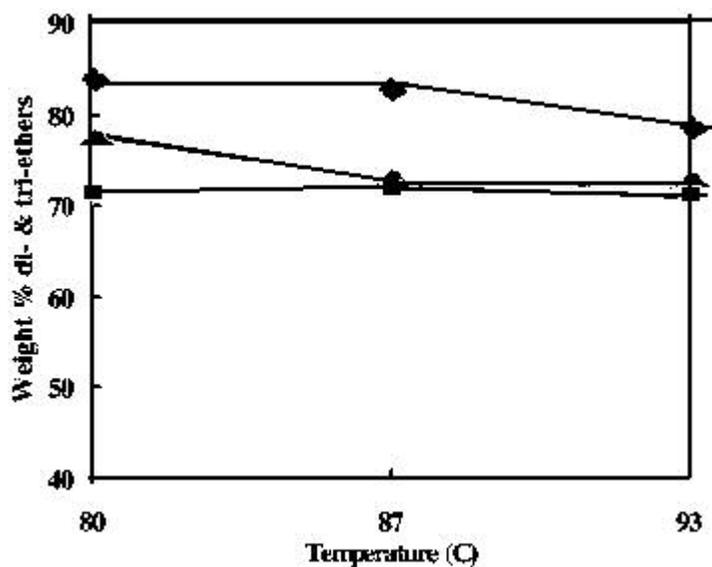

Figure 6. The effect of temperature on higher ethers in the etherification of glycerol subject to an isobutylene to glycerol molarratio of 3:1, and 5 wtGatalyst. (*),2 h; (B), 3 h; and (A), 4 h.

Effect of reaction time

The effect of reaction duration on the product composition for the etherification reactions carried out at 93 "C, a molar ratio of 3: 1 and 5 **wt%** catalyst is illustrated in Figure 7. It seems evident that no additional benefits are awarded for reaction times beyond 2 h. Beyond this point, it appears that an apparent equilibrium is reached and all compositions have practically leveled off. There is a slight decrease in the concentration of higher ethers and a slight increase in the concentration of by-products beyond 1 h. A gradual shift in the apparent equilibrium may be responsible for this behavior. It appears that as equilibrium is reached, the free isobutylene is consumed in the formation of 1- and 2-pentenes, consequently shifting the equilibrium conditions away from higher ethers. This behavior is more apparent when examining a graph of available isobutylene vs. reaction time (Figure 8). As this figure reveals, the formation of 1- and 2 pentene beyond 3 h is at the expense of higher ethers, due to the reversibility of the reaction, and not from free isobutylene. This supports the supposition that reaction times beyond 2 h only serve to consume isobutylene and lower the concentration of higher ethers.
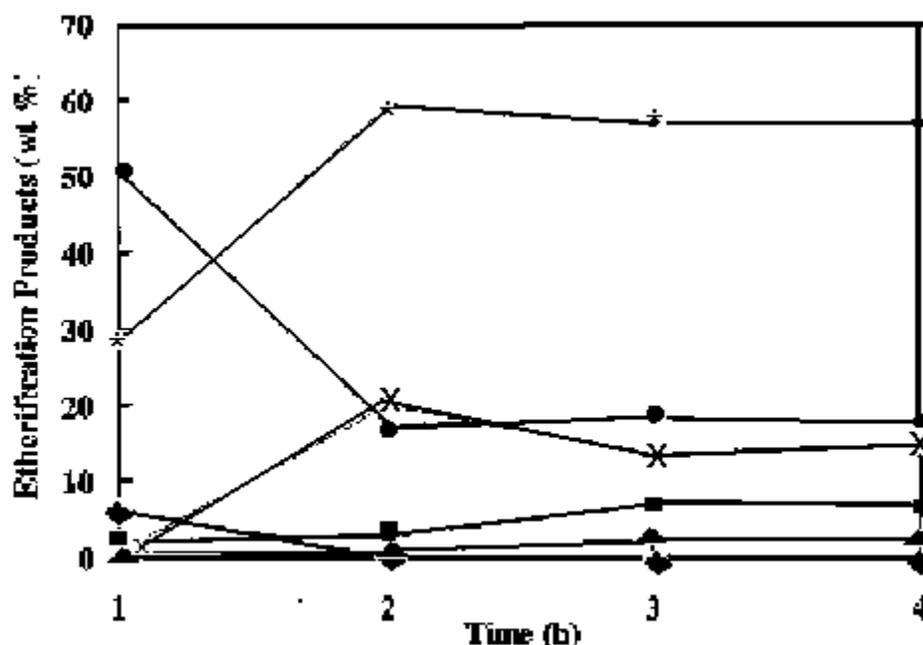

Figure 7. The effect of reaction duration on the product composition during the etherification of glycerol at 93 "C subject to anisobutylene to glycerolmolarratio of 3:1, and5 **wt%** catalyst. (♦), Isobutylene; (■), l-pentene; (▲), 2-pentene; **(X),** triether; **(*)**, di ether; and (●), monoether.

Catalyst characterization

The catalyst was characterized in the etherification reaction with respect to its loading requirements and activity (active life).

Catalyst loading

The effect of catalyst loading on product composition at 93 "C, an isobutylene to glycerol molar ratio of 3:l and 4 h of reaction is illustrated in Fɪ'g ure 9. As this figure shows, ether concentrations begin to level off at around 4 to 5 wt%, and it appears that 5 wt% is sufficient to almost completely convert glycerol to ethers within four hours. However, the by-product concentrations appear to level off toward higher catalyst loadings. It is interesting to note that during packed bed MTBE production, studied by Bahatia and coworkers, no CS's were produced [17]. The high catalyst loading within a packed bed reactor is potentially responsible for this behavior. for 4 h at 93 "C and an isobutylene to glycerol molar ratio of 3:l. These reactions were carried out at the most potentially damaging end of

the temperature range (93 'C) to test the activity of the catalyst. Once each reaction was completed, the products were decanted and another charge of reactants was added, reusing the same catalyst. After 5 consecutive 4-hour runs no significant increase in any of the product compositions was noted, which might be interpreted as no loss in the activity of the catalyst during this period.

Physical Properties

Experiments were performed to characterize certain physical properties of ethers of glycerol. Ether solubility in biodiesel and diesel fuels, vapor pressure. and the effect of ethers on the cloud point (CP), pour point (PP), specific gravity, and viscosity were investigated. The ether composition used in these experiments was as follows: 24 wt% monoethers. 62 wt% diethers and 14 wt% triethers. Characterization experiments were carried out using 100% neat methyl esters, 100% diesel, and various blends of diesel and methyl esters. The formulations included methyl esters obtained as pilot plant product from the Biomass Laboratory at the University of Nebraska, *Catalyst activity* Lincoln. Thepuritybf themethyl esters was verified via HPLC. The diesel fuel #2 was obtained locally.To evaluate the effective life of the catalyst under Table 1 shows the composition of the stock solutions etherification conditions, 5 wt% catalyst was reacted used for the characterization experiments.
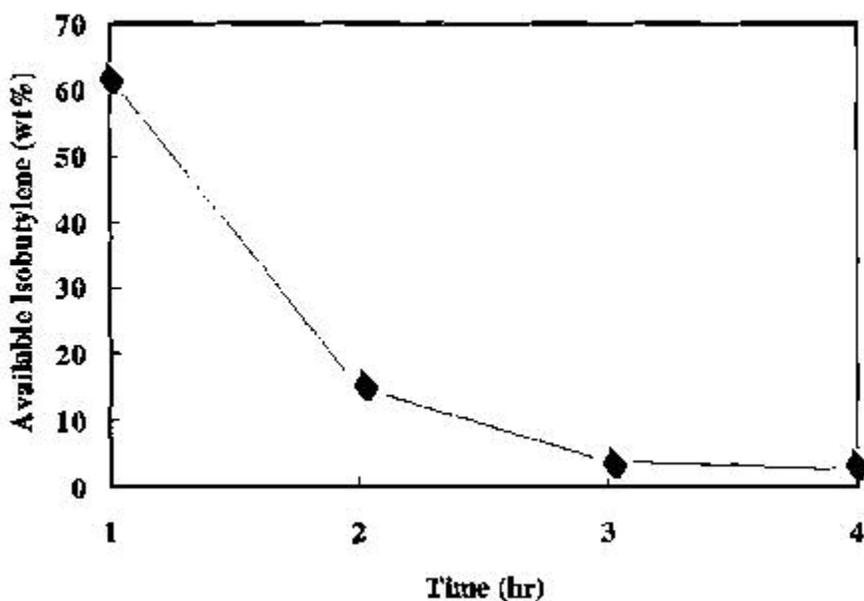

Figure 8. The effect of reaction duration on available isobutylene in the etherification of glycerol at 93 'C subject to an isobutylene to glycerol molar ratio of 3:1, and 5 wt% catalyst.

Solubility

The solubility of glycerol ethers in different blends was determined as a function of temperature. Glycerol ethers showedno solubility limit up to 22 wt% in methyl esters, diesel and all intermediate blends over the full range of temperatures that were investigatedfor the cloud point and pour point experiments. Solubility tests were only doneup to22 wt% because it is highly unlikely that ethers will be added beyond this level.

Vapor pressure

The vapor pressure data were obtained in accordance with ASTM method D5191-96 [l81 using a Grabner Instruments CCA-VP vapor pressure tester. This test involves theuseof automated vapor pressure instruments to determine the total vapor pressure exerted in a vacuum by air-containing volatile liquid petroleum products. Table 2 lists the results from these experiments.

Cloud point

Cloud point (CP) is the temperature at which a suspension of wax crystals begins to form in a liquid. Cloud points were measured in accordance with ASTM method D 2500-91 [19]. Samples were filtered to remove moisture. then sealed in glass jars. The jars were placed in a cooling bath held at -20°C and subjected to cooling. The samples were examined at 1 "C intervals for CP as specified in the method. The results of the tests are summarized in Table 2.Clearly the additive has a significant effect in decreasing the cloud point of neat methyl esters. This effect is of utmost interest and it is likely that the additive's primary role would be as a cloud point depressant.

Table 1. Composition of additive blends used for the characterization. All percentiles are based on weight.

Additive Blend	Composition
Methyl esters	Neat Methyl Esters (ME)
Diesel #2	Diesel #2 (D2)
Biofuel	80% ME + 20%D2 (B20)
Additive	Glycerol Ethers (GE)
ME & additive	80% ME + 20% GE
Diesel #2 & additive	95% D2 + 5% GE
Biofuel & additive	95% B20 + 5% GE

Table 1.

Composition of additive blends used for the characterization. All pecentiles are based on weight.

Pourpoint

Pour point (PP) is the temperature below which a sample fails to pour or show any movement when its container is placed in a horizontal position for 5 s. Usually diesel fuels show operability problems at some temperature between the CP and PP. These tests were conducted in accordance with ASTM method D 97-96a [20]. This procedure essentially calls for gradual lowering of the sample temperature and checking for flow every **3 'C.** The results of these tests are summarized in Table 2.
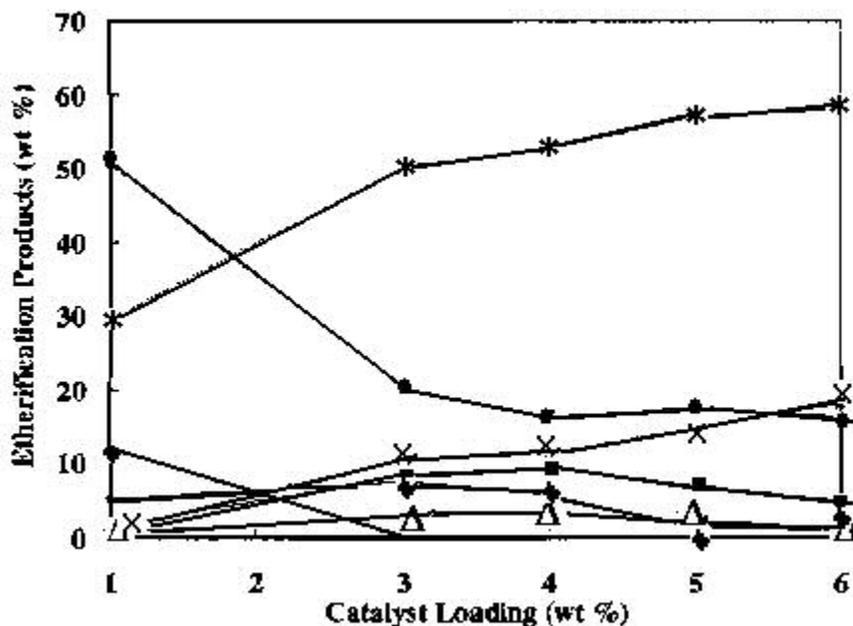

Figure 9. The effect of catalyst loading on the product composition for the etberification of glycerol at 93 "C subject to an isoburyIene to glycerol molar rauo of 3:1 and 4 h of reaction. (♦),Is obutylene; **(■),** l-pentene; (▲), 2-pentene; **(X),** triether: **(∗) ,** dierher; (●), monoether; and (+), glycerol.

Table 2 **Physical properties of additive blends.**

Additive Blend	DVPE (psi)	Cloud point ('C)	Pour point ('C)	Sp. gravity (60/60 'F)
Methyl esters	1.80	0	-3	0.8861
Diesel #2	0.20	-11	-33	0.8501
Biofuel	0.99	-10	-21	0.8502
Additive	6.21	N/A	N/A	0.8689
ME & additive	2.27	-5	-6	0.8825
Diesel #2 & additive	0.52	-11	-33	0.8419
Biofuel & additive	1.10	-10	-21	0.8541

Specific gravity

Specific gravity was determined in accordance with ASTM n~ethodD1 298-85 [21]. This was accomplished by equilibrating the specimen temperature and then measuring the specific gravity by placing a hydrometer in the sample. Standard specific gravities are presented in Table 2. These results show that the ether additives do not have a significant effect on the specific gravity of the blends.

Viscosity

Viscosity data were collected in accordance with ASTM method D 445-96 [22]. Viscometers were operated in accordance with ASTM method D 446- 93 **[23].** Kinematic viscosity was experimentally determined using these procedures, and dynamic viscosity was calculated by multiplying the kinematic viscosity by density. The results are presented in Figure 10. The ether additives tend to decrease the viscosity of methyl esters and biofuel blends by about 8%.
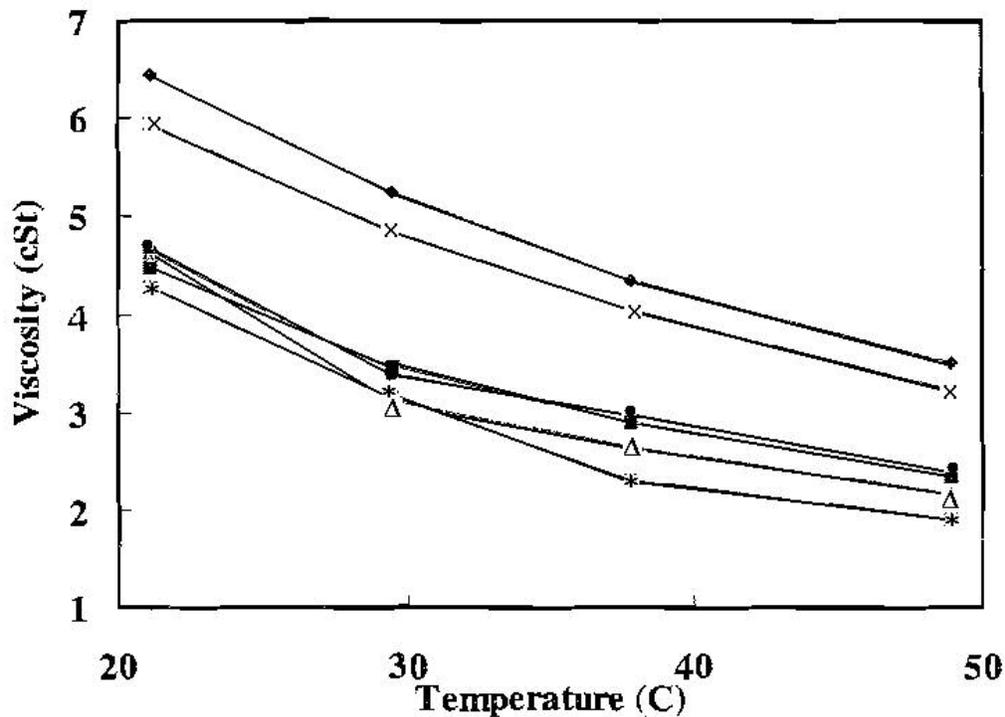
Figure 10. Kinematic viscosity temperature effects for solutions. (♦) methyl esters;(■) diesel #2; (▲),biofuel; **(X),** methyl ester & additive; (*) (diesel#2 &additive: and (●), biofuel & additive.

CONCLUSIONS

Etherification of glycerol with isobutylene can be effectively accomplished using Amberlyst-15 as catalyst under avariety of reaction conditions. Blends of mono-, di-, and tri-tertiary butyl ethers of glycerol are the products and dimers of isobutylene are the by-products. A matrix of experiments was completed in an attempt to optimize the reaction conditions. The best results were obtained for catalyst loading >5 wt%, 1-2 h of reaction time, and a glycerol to isobutylene ratio of approximately 3. Lower temperatures (80 "C) under these conditions resulted in a higher concentration of di- and rri-ethers and lower by-product concentrations. It was determined that the catalyst activity is not affected during the reaction, at least for reaction times up to 30 h. Impurities in the crude glycerol appeared to poison the catalyst, which resulted in poor conversions. To minimize these effects, neutralization and methanol removal from the crude glycerol need to be performed prior to its use. The ethers of glycerol can be effectively added to methyl esters, providing a 5 'C reduction in cloud point and an 8% reduction in viscosity. Further studies, incld ing engine performance and emission tests, need to be completed to determine the suitability of these ethers as fuel additives.

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