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Illinois Sustainable Technology Center

Low-Temperature Diesel Additives from Extracted Oil
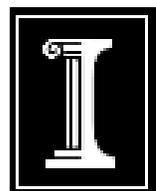
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Low-Temperature Diesel Additives from Extracted Oil

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ABSTRACT

Under funding from the Waste Management Research Center, now called the Illinois Sustainable Technology Center (ISTC), and the U.S. Department of Energy, the Energy & Environmental Research Center conceived of, verified, and optimized a two-step ozonolysis process on the bench scale for production of high-value chemicals derived from glycerol and cold-weather biodiesel additive derived from biodiesel. The first step of the process, which oxidizes glycerol into high-value chemicals, shows high conversion selectivity to valuable glyoxal in aqueous solution, based on limited tests. A by-product of this step consists of short-chain oxygenated carboxylic acids present as glyceryl esters. These acid by-products include glycolic acid, which is valuable in the cosmetics industry and as a raw material for production of biodegradable polymers. The glyceryl esters could be transesterified for recovery of the acids as methyl esters and the glycerol portion of the ester recycled for further conversion. The second step of the process yields a product with improved cold-weather properties relative to biodiesel. However, when the product is blended with biodiesel at ratios less than approximately 1:2, minimal effect on cloud point or pour point is observed. A brief economic assessment of the process suggests that the as-designed process would not be economical on a large scale. The process was designed inefficiently and could possibly be made economical with a better plant design. However, the expected selling price for the additive product from the second step would prohibit its use as a cold-weather biodiesel, and the process can only be made economical if the biodiesel ozonolysis step is removed.

[Editorial note: This project was funded on a limited basis by ISTC as a seed project. The results and conclusions should be considered preliminary, and more detailed analyses could be performed to clarify some of the test results on the production of high-value chemicals.]

LOW-TEMPERATURE DIESEL ADDITIVES FROM EXTRACTED OIL

EXECUTIVE SUMMARY

Under work funded by the U.S. Department of Energy through the Energy & Environmental Research Center's (EERC's) Center for Biomass Utilization® and the Illinois Department of Natural Resources through the Waste Management and Research Center (now called the Illinois Sustainable Technology Center with the University of Illinois at Urbana-Champaign), the EERC developed and optimized a method for batchwise catalytic glycerol ozonolysis on the bench scale. Ozone was bubbled through a solution of glycerol and 5-molar sulfuric acid in an electrically heated flask. Vapor exiting the flask was condensed, and both the distillate and the material remaining in the flask were analyzed. The distilled product in some tests was a high-purity solution of glyoxal. The refluxed product appeared to consist of unreacted glycerol and the glyceryl esters of carboxylic acid products. If recovered, the expected acid products could be sold as precursors for biodegradable polymers at a higher expected market price than that of glycerol.

The ozonolysis reaction used to convert glycerol to aldehydes and carboxylic acids requires excess ozone that can be passed to a second ozonolysis reactor to react with biodiesel. Since ozonolysis of biodiesel produces shorter-chain methyl esters than those found in unreacted biodiesel, it was thought that the ozonolysis product might be useful as a cold-weather additive and oxidative stabilizer for biodiesel. However, when short-chain methyl esters were produced by ozonolysis in the laboratory and blended with biodiesel, the observed effect on pour point and cloud point was minimal. Other researchers have reported similar behavior, suggesting that ozonolysis products are not well suited for use as cold-weather biodiesel additives.[1,2,3]

An economic assessment revealed that the process has a negative gross profit when both the glycerol and biodiesel ozonolysis processes are utilized. When only glycerol ozonolysis is carried out, the gross profit is positive, but the process designed in this work is still not economically favorable. The economics could be improved by more efficient plant design and by better sizing the unit operations to match the intended flow rates and heat duties.

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[1] Soriano, N.U.; Migo, V.P.; Matsumura, M. Ozonized Vegetable Oil as Pour Point Depressant for Neat Biodiesel. *Fuel* **2006**, *85*, 25–31.

[2] Lee, I.; Pfalzgraf, L.; Poppe, G.; Powers, E.; Haines, T. The Role of Sterol Glucosides on Filter Plugging. *Biodiesel Magazine* **2007**, *April*.

[3] Archer-Daniels Midland Company. *Processes of Producing Biodiesel and Biodiesel Produced There from*. International Patent WO 2007/076163 A2. July 5, 2007.

LOW-TEMPERATURE DIESEL ADDITIVES FROM EXTRACTED OIL

INTRODUCTION

Technical work on this project was completed on June 30, 2007, and large amounts of the data were collected in 2006. Prior to discussing the results of this work, it must be noted that the price of glycerol has risen significantly since the project was completed (1). Much of the work described in this report was based on glycerol being a cheap feedstock that would be available in large quantities at biodiesel facilities. It is now clear that this will not be true anytime in the near future, so the limited technical success of this project has become largely irrelevant against new economic constraints.

As the biodiesel industry expanded in scope during the early part of this decade, the market for the glycerol by-product of traditional fatty acid methyl esterification (FAME) was rapidly becoming saturated. To allow for further increases in the scale of the biodiesel industry, it was apparent that either new markets must be found for glycerol or a new process must be found to eliminate the glycerol by-product.

One option for eliminating the glycerol by-product of the FAME process is conversion of glycerol into chemical feedstocks. This can be achieved by a number of routes. The Belgian company Solvay recently began producing epichlorohydrin, an epoxy precursor, from glycerol around 2006 (2). Cargill and other companies pursued conversion of glycerol to propylene glycol, a nontoxic antifreeze agent (3). Melero and others studied esterification with acetic acid to produce glyceryl acetate, which shows promise as a fuel additive for both gasoline and biodiesel (4).

Glycerol can be also converted into chemical feedstocks by oxidation to aldehydes and carboxylic acids. One such method is to cleave the glycerol oxidatively and selectively use periodic acid (5). Although this method is efficient, the high cost of periodic acid would likely make this process economically unfavorable on a commercial scale. Another possible option for glycerol oxidation is reaction with ozone. Reaction of glycerol with ozone is thermodynamically favorable; however, the kinetic rate of reaction is effectively zero for direct ozonolysis by traditional methods. As such, a catalytic method is required to make the rate of glycerol ozonolysis favorable.

It was recognized early in the project that, to be successful in the near term, any approach to glycerol transformation must utilize the existing biodiesel infrastructure. The simplest solution to dealing with glycerol is not replacement of FAME facilities with new biodiesel plants but add-on modification of existing facilities. Ideally, such a process should utilize only those resources already available to a biodiesel plant, eliminating the need to coordinate new chemical transportation or to expand an existing tank farm.

While the Energy & Environmental Research Center (EERC) project funded by the U.S. Department of Energy (DOE) and the Waste Management and Research Center (WMRC), now called the Illinois Sustainable Technology Center, during the 2006 fiscal year was initially

envisioned as a process to produce low-temperature biodiesel additive, the project instead found a process for converting glycerol into high-value chemical feedstocks. The process could function as a slipstream parallel reaction in a traditional FAME facility and could be installed without modification of the existing facility. Moreover, a potential by-product of the process is a biodiesel additive that could improve low-temperature properties of purified traditional FAME biodiesel, thus fulfilling the original intent of the DOE- and WMRC-funded project.

The process tested by the EERC under the 2006 funding involves simultaneous glycerol dehydration and ozonolysis in a single reactor. During acid-catalyzed dehydration, glycerol briefly transforms into one of two unstable intermediate enol tautomers, as shown in Equations 1 and 2 (6):

[Eq. 1]

[Eq. 2]
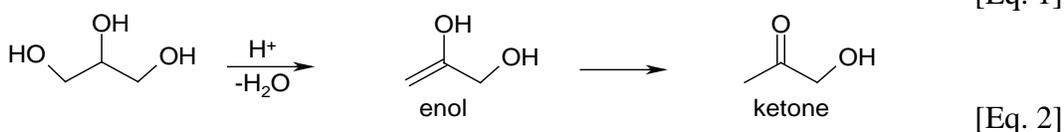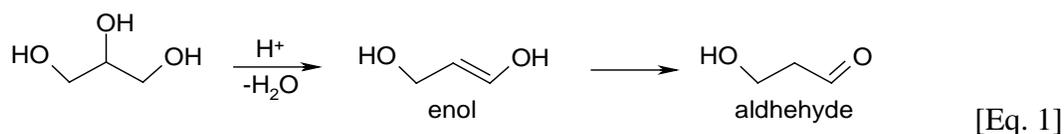
The enol tautomers are susceptible to ozonolysis (Equation 3). Ozonides are unstable and tend to undergo rearrangement to malozonides, as seen in Equation 4. Laboratory and commercial ozonolysis processes allow for this rearrangement and are designed to transform the malozonide product into two carboxylic acids or two aldehydes, as shown in Equations 5 and 6, respectively.

[Eq. 3]

[Eq. 4]

[Eq. 5]

[Eq. 6]
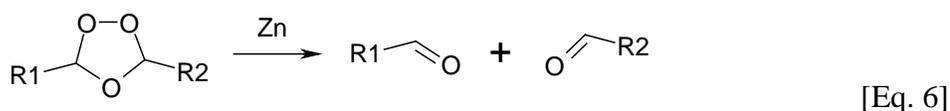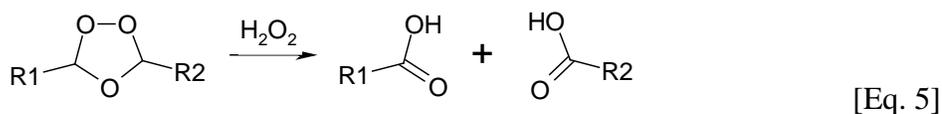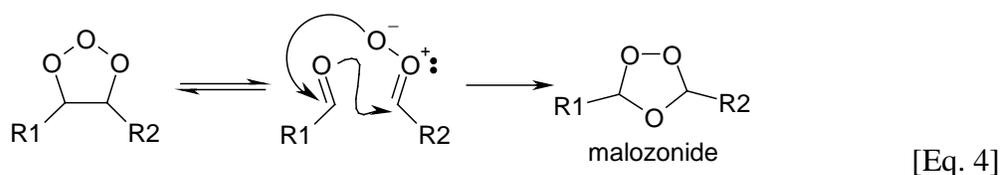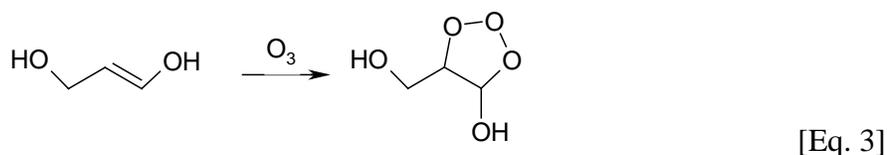
However, in the presence of an alcohol, malozonide formation can be disrupted, and instead, an aldehyde and a hydroperoxyhemiacetal are formed. At elevated temperatures, the hydroperoxyhemiacetal is not stable and may undergo a number of decomposition reactions,

several of which result in formation of a water molecule and an ester. Glycerol, containing three hydroxyl (OH) groups, may function as the alcohol in this reaction, giving a glyceryl ester:

[Eq. 7]
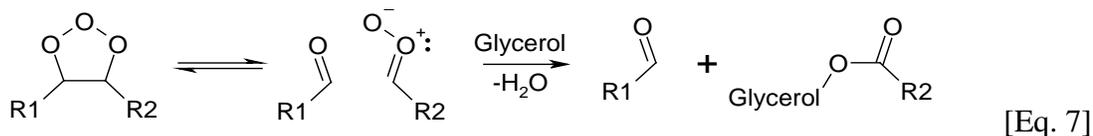
The glyceryl ester may then be transesterified with methanol to give methyl ester and glycerol, or it may be hydrolyzed with water to give carboxylic acid and glycerol. The exact carboxylic acid(s) produced by this process depends on the process conditions but may include glycolic acid, glyoxylic acid, or formic acid. The aldehydes may include formaldehyde, glycolaldehyde (also known as hydroxyacetaldehyde), or glyoxal. The structures of these compounds are presented in Figure 1, and Table 1 lists their common uses.

The acid catalyst used to affect glycerol dehydration may be sulfuric acid, which is typically used in FAME facilities to neutralize basic product after transesterification. Methanol, which can be used to recover carboxylic acid products, is one of the primary reagents of FAME biodiesel and is in abundant supply at any biodiesel facility. Thus all of the chemicals required to produce the products listed in Table 1 should be readily available at any commercial FAME biodiesel facility.

Since the enol tautomers in Equations 1 and 2 are not stable, excess ozone must be used to ensure that the ozonolysis reaction takes place with high selectivity. The excess ozone from this process can be bubbled through biodiesel to recover short-chain fatty acids (FAs) and/or aldehydes using several well-established processes (7–13). The products from these processes have a wide variety of uses, including pharmaceutical and cosmetic application (14, 15), resin production (11), production of nylon and other polymers (16, 17), and biodiesel improvement (18–21).

The method used to react glycerol with ozone could also be used on olefins, the typical feedstocks for ozonolysis. In this case, alcohol would be mixed with the olefin to provide a replacement for the glycerol in Equation 7. Each double bond would be cleaved, with one carbon forming an aldehyde and the other forming an ester. Vegetable oil and biodiesel both contain olefins and could be used as a feedstock. To maximize product slate from a FAME facility, ozonolysis could be performed in a heated solution of methanol and triglyceride, yielding the variety of compounds listed in Table 2. However, separation may be an issue for recovering each of the individual components, and the technical barriers to commercializing ozonolysis in a heated methanol solution were not examined in great detail during this study.

A simple process flow diagram of the glycerol ozonolysis process is illustrated in Figure 2. As shown in the drawing, the reactor system can be installed on the back end of an existing biodiesel facility to increase product slate and to improve the cold-weather properties of the FAME biodiesel product. This avoids the locating, permitting, and shakedown issues associated with greenfield construction of new chemical plants.

3
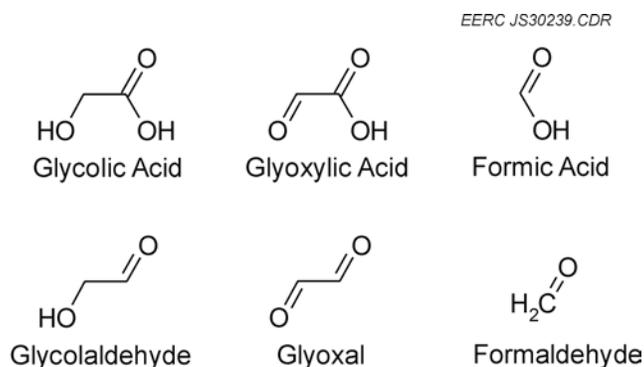
Figure 1. Compounds produced by glycerol ozonolysis.

Table 1. Marketability Data for Various Glycerol Ozonolysis Products

Compound	Market Application
Formic Acid	Solvent, disinfectant, textile processing (dyeing fabrics and tanning leather), electroplating, latex rubber preparation, grain preservation, intermediate for numerous chemicals and pharmaceuticals.
Formaldehyde	Wood products (including pressed wood, paper, and wood adhesives), cosmetics, disinfectants, textiles, paints.
Glycolic Acid	Cosmetics, biodegradable polymers, cleaning agent, textile processing, flavoring agent and preservative, paints.
Glyoxylic Acid	Chemical platform for materials used in various industries, including agrochemicals, pharmaceuticals, polymers, and aroma compounds.
Glyoxal	Browning agents (food industry).
Glycolaldehyde	Browning agents, cosmetics.

GOALS AND OBJECTIVES

The original goals of the proposal were to develop an ozonolysis-derived additive for biodiesel and to test the pour point (PP) and cloud point (CP) suppression of the product. Production of chemicals from glycerol was to be a minor component of the project. However, early in the literature review, it became apparent that low blend levels of ozonolysis products into biodiesel would not achieve significant suppression of PP and CP (18, 22, 23). Research has since shown that many cold-weather issues can be resolved by removing select components from biodiesel (24, 25). Although additives used in conjunction with biodiesel purification might have an appreciable effect on the cold-weather properties of biodiesel, the high capital and operating costs of large-scale ozonolysis suggest that purification alone is the most economical route to improving biodiesel cold-weather properties.

Table 2. Theoretical List of Compounds Produced by Ozonolysis of Soybean Oil in Methanol (saturated FAs are assumed to transesterify with methanol to form methyl esters)

Name	Formula	Boiling Point, °C	Hypothetical Yield, wt%[1]
1-Propanal	$OCHCH_2CH_3$	49[2]	0.5%
Methyl Propionate	$CH_3\text{-}O\text{-}COCH_2CH_3$	80[2]	0.8%
Malondialdehyde	$OCHCH_2CHO$	N/A[3]	3.2%
Methyl 3-Oxopropanoate	$CH_3\text{-}O\text{-}COCH_2CHO$	N/A	9.0%
Dimethyl Malonate	$CH_3\text{-}O\text{-}COCH_2CO\text{-}O\text{-}CH_3$	183	5.8%
1-Hexanal	$OCH[CH_2]_4CH_3$	129	7.0%
Methyl Caproate	$CH_3\text{-}O\text{-}CO[CH_2]_4CH_3$	150	9.1%
1-Nonanal	$OCH[CH_2]_7CH_3$	191	4.4%
Methyl 1-Nonanoate	$CH_3\text{-}O\text{-}CO[CH_2]_7CH_3$	214	5.3%
Methyl 9-Oxononanoate	$CH_3\text{-}O\text{-}CO[CH_2]_7CHO$	N/A	20.4%
Dimethyl Azelate	$CH_3\text{-}O\text{-}CO[CH_2]_7CO\text{-}O\text{-} CH_3$	156	23.7%
Methyl Palmitate	$CH_3\text{-}O\text{-}CO[CH_2]_{14}CH_3$	>185[2]	7.7%
Methyl Stearate	$CH_3\text{-}O\text{-}CO[CH_2]_{16}CH_3$	>215[2]	3.1%

[1] Hypothetical yield on a dry, glycerol-free basis. The yield calculations were based on the following assumptions: 1) atoms connected by an unsaturated bond have equal probabilities of becoming methyl esters or aldehydes, 2) all unsaturated bonds are broken, 3) ozonolysis products do not undergo further reactions, and 4) all triglycerides are transesterified to give methyl esters.

[2] Pure compound requires cool or cold storage, indicating high volatility or reactivity.

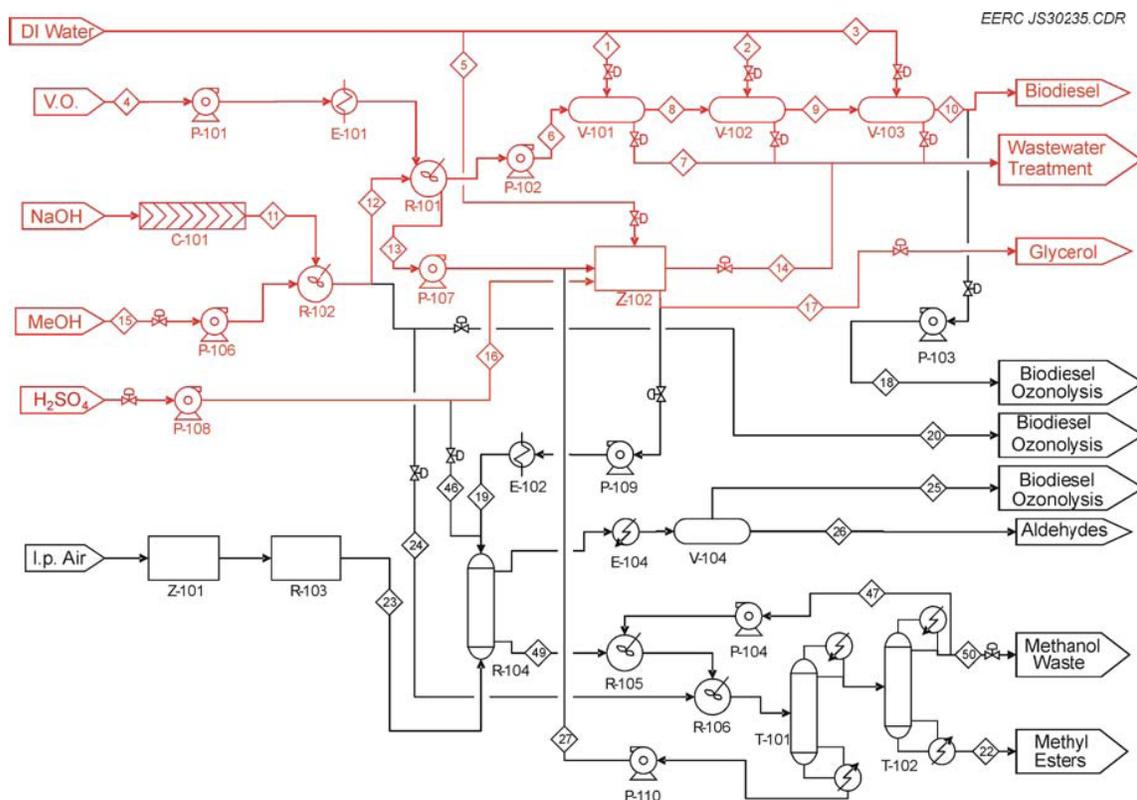[3] Not available because product is either rare or unstable.

Figure 2. Process flow diagram of a slipstream glycerol reactor system installed at a preexisting biodiesel facility. The biodiesel facility is drawn in red, while the new construction is in black.

Because ozonolysis for biodiesel additives did not appear promising, the primary goal of the project shifted to chemical production from glycerol. The original goal was maintained by considering potential by-products of the glycerol ozonolysis process as biodiesel additives.

Two of the objectives in producing chemicals from glycerol via ozonolysis were to identify a pathway with low capital and operating costs relative to traditional ozonolysis and to identify the likely products of this pathway. A third objective was to test and then optimize the proposed pathway on the bench scale. A further objective was to estimate the economic favorability of the proposed pathway. The final objective was to determine whether a similar process could yield products with some ability as PP or CP suppressants and, if not, whether a traditional ozonolysis route would be economically favorable as a back-end process to the proposed glycerol ozonolysis process.

EXPERIMENTAL

Glycerol Ozonolysis

Prior to testing, an extensive review of literature on known ozonolysis mechanisms was conducted to predict the likely products of glycerol ozonolysis. Reaction pathways were ranked in terms of favorability at various conditions. Once a preliminary reactor scheme was envisioned, the most likely products at reaction conditions were identified.

The glycerol ozonolysis portion of the process depicted in Figure 2 was optimized in the laboratory by conducting a matrix of tests. The experimental design of this test matrix was a Box-Behnken design, as shown in Table 3. As can be seen from Table 3, the parameters tested included temperature, time, and amount of catalyst (in this case, 5-molar H_2SO_4). The parameter ranges were selected after extensive initial testing using a variety of reactor setups. This initial testing revealed that temperatures higher than 180°C tended toward runaway dehydration with minimal ozonolysis, while temperatures lower than 150°C generally gave unacceptably slow reaction rates. Similar effects were observed and used to define the upper and lower limits for time and amount of sulfuric acid used.

The test order in Table 3 was randomized and run in the order shown in the second column. After several tests using the Box-Behnken design, it became clear that the combination of test conditions was too extreme. For instance, screening tests showed that using 3 mL of sulfuric acid would allow for successful ozonolysis, as would temperatures of 180°C or reaction times of up to 3 hours. When two or more of the conditions were combined (as in Test Number 8 in Table 3), the glycerol underwent rapid exothermic dehydration, forming a blackened char that became hot enough to autoignite. Because of the potential for damage to labware and injury to workers, the test matrix was revised from a standard Box-Behnken design to the test matrix shown in Table 4. The changes were made in such a way as to minimize the number of tests that would need to be repeated while keeping the run order shown in Table 3.

Table 3. Planned Box-Behnken Test Design

Test Number	Run Order	Temperature, °C	Test Time, hours	Sulfuric Acid, mL
1	12	150	1	2
2	7	180	1	2
3	6	150	3	2
4	15	180	3	2
5	13	150	2	1
6	11	180	2	1
7	3	150	2	3
8	4	180	2	3
9	9	165	1	1
10	10	165	3	1
11	2	165	1	3
12	5	165	3	3
13	8	165	2	2
14	1	165	2	2
15	14	165	2	2

Table 4. Modified Test Design

Test Number	Temperature, °C	Test Time, hours	Sulfuric Acid, mL
1	150	1	2
2	135	1	2
3	150	1.5	2
4	135	1.5	2
5	150	2	1
6	135	2	1
7	150	2	3
8	135	2	3
9	165	1	1
10	165	1.5	1
11	165	1	3
12	165	1.5	3
13	165	2	2
14	165	2	2
15	165	2	2

The reactor setup used to perform the test matrix is shown in Figure 3. Ozone is generated from bottled oxygen in the Orec Model 03B1-0 Ozonator reactor shown in Figure 4. This generator is a water-cooled unit capable of delivering up to 12 liters per minute of gas at pressures of up to 30 psig. Output voltage is alternating current (AC) and can be varied between zero and 100 volts, giving rms amperages of up to 5 amps. Flow can be delivered to a reaction vessel or to a small sample port that can be used for online calibration. In the event of a fuse failure or a loss in power, gas flow is automatically stopped at the inlet to prevent ozone leakage. Removable access panels are located on the front and both sides of the reactor for maintenance and internal leak checking, and a spring-loaded safety kill switch is opened when the access
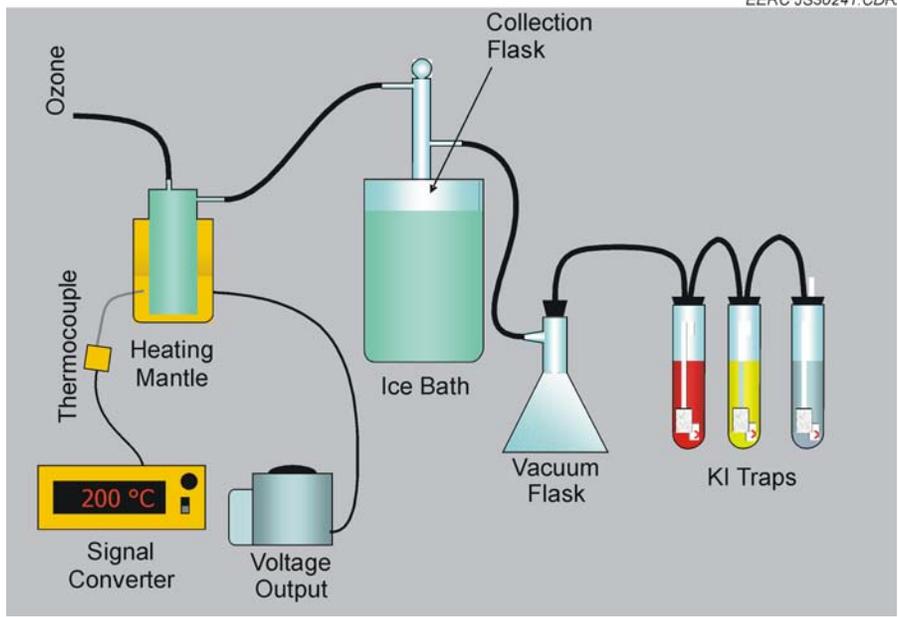
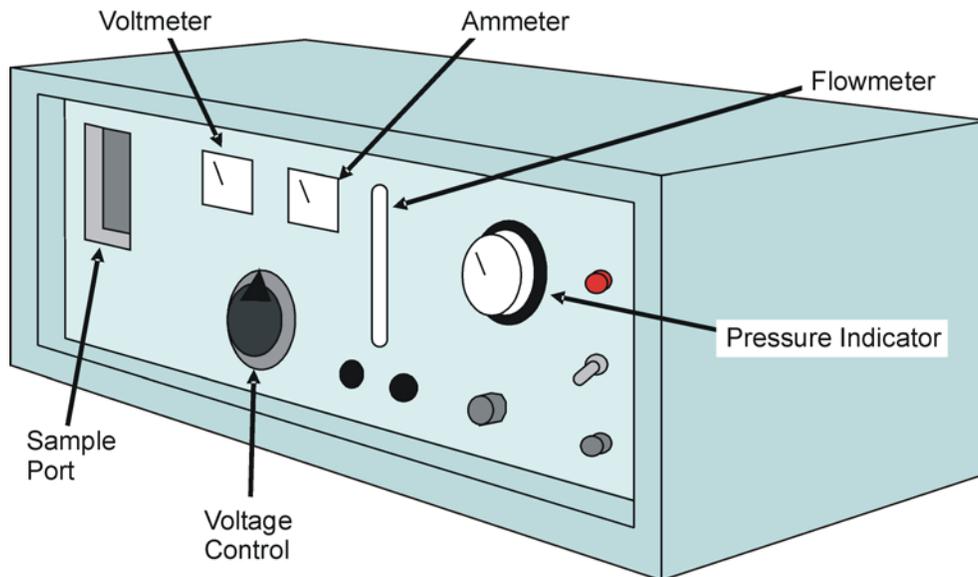Figure 3. Laboratory reactor system used to optimize ozonolysis process.

Figure 4. Ozone generator.

panel nearest the power source is removed. At full power and flow, the generator is capable of delivering well over 200 mg of ozone per minute. Under the conditions used during the Box-Behnken testing, ozone delivery was approximately 70 mg/min.

The reactor in Figure 3 consists of a 50-mL glass vial that is externally heated by a heating mantle. The heating mantle contains a thermocouple near the hot surface that is used for temperature control. Ozone is preheated through a Teflon line wrapped in heating tape and is introduced to the reactor through a fitting that is submerged beneath the liquid reagent (a solution of glycerol and acid catalyst).

Gas exits the reactor through a short horizontal crossover (approximately 1½") and enters a condenser cooled by ice water. Volatile material condenses and runs down into a 25-mL round bottom flask, where it is collected after the test. Uncondensed gas exits the round-bottom flask and passes through a water trap before being bubbled through a series of potassium iodide (KI) traps. The water trap is an empty glass container intended to prevent KI solution from being pulled back into the condenser in the event of a pressure drop. The KI traps convert ozone to harmless oxygen, which is then vented into a fume hood. As the traps become saturated, iodide ions are oxidized to iodine, and the solutions change color from clear to deep red. The color change is used as an indicator that solutions need to be replaced to prevent ozone leakage. During each of the tests, the ozone inlet line was heated to 65°C; 15 g of glycerol were used in each test. The ozone generator was consistently set to 1.0 lpm of flow with an output current of 4.0 amps (AC, rms). These conditions were kept to ensure that the only changes between tests were those listed in Table 4.

After each test, the distillate (the product in the collection flask) was recovered and diluted to 1% on a weight basis in distilled, deionized (DI) water. The undistilled reflux product (the material remaining in the reactor) was also diluted to a 1% solution in DI water. The diluted distillate and reflux product of each test were analyzed by high-performance liquid chromatography (HPLC) to determine product yield and composition.

The HPLC used for analysis uses a dual analyzer to detect products. A Waters 2487 ultraviolet (UV) detector operating with sensitivity to 210 nm light is used to detect carbonyl compounds including carboxylic acids, aldehydes, and ketones. In addition, a 2414 refractive index (RI) detector is used to detect all product components with a RI different than water. While the RI detector will detect virtually any species present in solution, its sensitivity is low, and it is susceptible to baseline drift when solutions are analyzed with pH different than the pH of the carrier/purge solution. As such, UV results are preferred. Using the results of the HPLC analyses, theoretical optimum process conditions were calculated using regression analysis.

After the optimum process conditions for product yield were calculated, a test was performed at these conditions to ensure that the regression model was accurate. A sample of the best-available product was then submitted to WMRC for HPLC–mass spectroscopy (MS) analysis. A proposed separation technique was attempted on this product to determine technical feasibility. The separation process involves methyl esterification by refluxing the product from the reactor in methanol for 1 hour. As short-chain methyl esters are formed, they are volatilized and may be condensed downstream. This permits the separation of compounds that would

otherwise polymerize in their pure states. Moreover, the separation process uses only methanol and heat, both of which are readily available at any commercial FAME biodiesel facility.

Vegetable Oil Ozonolysis

Prior to conducting ozonolyis of vegetable oil, a literature review was conducted of known ozonolysis pathways and of the PP and CP suppression effects of ozonolysis products. A possible pathway toward novel cold-weather additives was proposed and tested in the laboratory.

Vegetable oil ozonolysis was carried out by pouring 12.4 mL soybean oil and 19.0 mL methanol into an electrically heated glass reactor connected by a short crossover to an ice-cooled condenser. This is the same reactor system used for glycerol ozonolysis (Figure 3). Mixing of the liquid layers was achieved by the action of bubbling gas. The immiscible liquids were heated mildly to 40°C while oxygen bubbled through the reactor. Once the reactor reached temperature, the ozone generator was turned on to convert some of the bubbling oxygen into ozone.

Preheating served three purposes. First, higher temperatures encouraged methyl esterification of free FAs produced by ozonolysis. Second, higher temperatures encouraged destruction of unstable hydroperoxyhemiacetals into methyl esters or other products. Third, higher temperatures prevented buildup of ozonides or malozonides, both of which are stable at lower temperatures but can explode if allowed to build up to high concentrations.

Following ozonolysis, the product was rinsed with DI water and allowed to separate into two layers. The aqueous layer was removed, and the product was rinsed again in DI water. After the final rinse, the product was dried over mild heat until clear and colorless. The dried product was then mixed with biodiesel at blends of 1%, 5%, and 10% at volumes of 10 mL apiece. Because only 5.8 mL of additive was available, preparation of separate blends higher than 10% was not feasible. Instead, 1.25 mL of the ozonolysis product was added to the 10% blend to give 11.25 mL of a 20% blend, after which an additional 2.95 mL of product was added to give 14.2 mL of a 37% blend. The CP of each blend was tested using a Phase Technology CPA-T30 analyzer. The CP of a 10-mL sample of unblended biodiesel was also measured to use as a baseline.

To test PP, a sample size of approximately 50 mL was required. All of the solutions from the CP testing (0%, 1%, 5%, and 37%) were combined to give 44.2 mL of a blend of 13% ozonolysis product in biodiesel. The PP of this blend was determined using a CPP-5Gs analyzer. The PP of pure biodiesel was also measured for comparison.

RESULTS AND DISCUSSION

Glycerol Ozonolysis

HPLC UV analysis of the distillate products revealed a single strong aldehyde peak for almost all tests. In most cases, RI analysis of the distillate samples also revealed no other peaks. HPLC UV analysis of the reflux products revealed smaller aldehyde peaks. RI analysis revealed

peaks corresponding to unreacted glycerol as well as to what appeared to be glyceryl esters. Ion spectrometry further suggested that the secondary peaks were glyceryl esters. Ion spectrometry results are shown in Figure 5 for a preliminary reflux sample that was produced prior to the test matrix in Table 4 and, as such, had lower concentrations of products and higher concentrations of unreacted glycerol than most samples.

Attempts to correlate UV peak area and height to concentration of aldehydes in distillate products yielded physically impossible results. For example, some product solutions showed concentrations twice as high as concentrations found in pure crystalline structures. RI peak areas could not be used to estimate concentration because of low sensitivity and baseline drift.

The reason for nonsensically high concentrations predicted from the UV-based calibration equation is uncertain. The error may have been due to contamination in or damage to the HPLC. It is also possible that unexpected carbonyl compounds may have formed during ozonolysis and been confused with known standards. However, HPLC-MS results (discussed later) suggest that the products were those expected and not unknown compounds.

Table 5 lists the results of testing according to the modified test matrix. It should be noted that the table reports free glycerol remaining in the reflux product rather than glycerol conversion. This is because the acidic ozonolysis products were esterified with some of the glycerol that had not undergone ozonolysis, so the amount of free glycerol remaining in solution
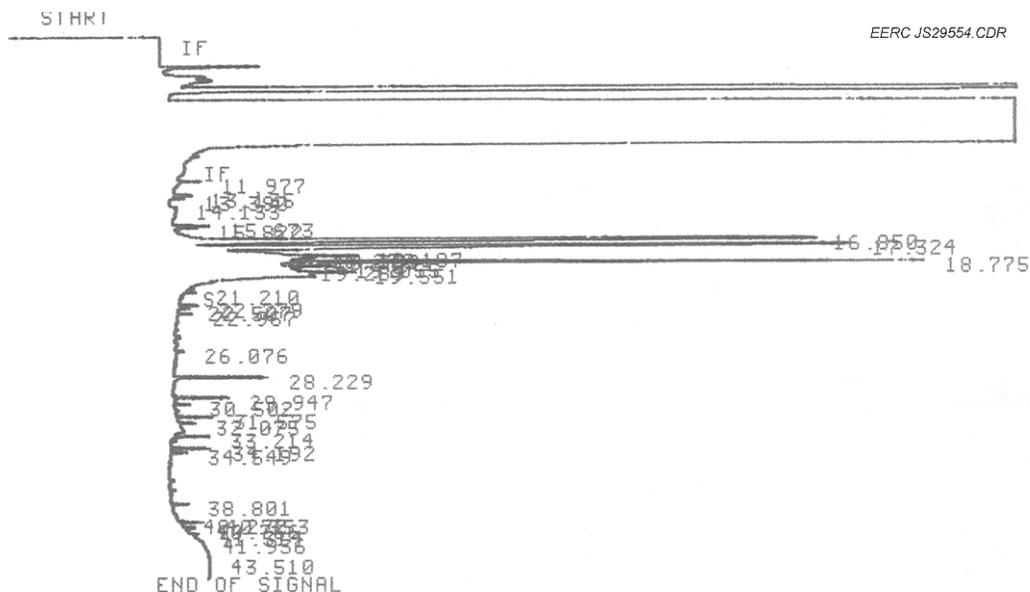

Figure 5. Ion chromatograph of an early glycerol ozonolysis product. The large peak at top is glycerol; the peaks between 14 and 22 minutes are monoesters; the peaks between 28 and 34 minutes are diesters; and the peaks at 38 minutes and above are triesters.

Table 5. Glycerol Ozonolysis Test Results

Test Number	Distillate Yield, g	Aldehyde Peak Area (AU·s) in Distillate Product[1]	Refluxed Product, g	Free Glycerol Remaining[2]
1	0.3542	36,008	13.5623	86%
2	0.5248	54,657	12.0162	73%
3	0.9471	74,270	13.3675	81%
4	0.7423	78,734	11.3200	62%
5	0.7617	358,322	10.1471	36%
6	0.4514	90,543	11.7019	77%
7	2.2154	61,747	10.6463	40%
8	1.0677	22,660	10.8131	57%
9	0.1280	14,522	9.6765	65%
10	1.7079	216,209	9.6032	21%
11	1.1854	51,872	13.8756	87%
12	0.3327	17,483	13.5178	54%
13	1.6399	97,263	8.9436	29%
14	2.1821	113,247	9.5832	24%
15	1.1969	88,227	10.0868	37%

[1] Results from HPLC using UV detector.
[2] Based on total mass of glycerol detected in products divided by 15 g (starting glycerol). Glycerol detection is by RI only, as glycerol does not have a UV peak at 210 nm.

does not directly translate to glycerol conversion efficiency. It should also be noted that HPLC UV peak area rather than product concentration is reported for the distillate product. This is because the UV-based calibration equation gave nonsensical product concentrations, as discussed above.

From Table 5, it is apparent that both yield and conversion were low for every test in the matrix; 15 g of glycerol was used as the starting material in each test. Test 10, which had the lowest amount of free glycerol remaining, yielded only 11.3 g of total product, giving 74% yield by mass. The reason for the low yields is likely that an undesirably large amount of glycerol was oxidized to uncondensed products such formaldehyde, CO, or CO_2. The situation is worse when one considers that the desired product is the distillate. The maximum yield of distillate was observed in Test 7, and the yield was only 15% by mass.

The test with the lowest free glycerol remaining (Test 10) had at least 21% of the initial glycerol remaining unconverted, meaning that the maximum conversion was 79%. Given that some glycerol was tied up as glycerol esters formed from reaction with acidic products, the actual conversion was probably even poorer.

The distillate sample from Test 10 was shipped to WMRC for HPLC–MS analysis. Recall that all distillate samples showed the same single peak. Assuming that the HPLC–MS results from WMRC on the distillate sample from Test 10 apply to all distillate samples, the distillate samples are a solution of glyoxal and formic acid.

The reason that two compounds were found by MS while only a single peak was seen in the UV results is not clear. It is possible that the HPLC UV equipment was malfunctioning, which would explain why the known calibration curve did not produce meaningful data when

applied to distillate samples. It is also possible that glyoxal and formic acid undergo polymerization or some other reaction in strong solution, causing the product UV peaks to either overlap or become nondetectable by UV at 210 nm.

Although at least one sample of the distillate product was identified by HPLC–MS, the reflux products were not successfully separated or purified for further identification. Because of budget constraints, only the best reflux product was to be separated and analyzed. Carboxylic acid separation from this reflux product was attempted but abandoned after the reflux product was inadvertently destroyed. Part of the separation test involved taking a small portion of the best-available sample and refluxing in a dilute methanol solution. Poor communication between project management and a laboratory assistant resulted in the entire best-available sample being heated to boiling without methanol present. This caused volatile product to boil off while free glycerol in the sample underwent dehydration and polymerization, giving a thick brown liquid rich in acrolein. The time and cost required to attempt a second separation test was beyond the project budget.

Because the reflux product was a complex solution that would require significant separation to recover salable products, the distillate product was considered the most promising reaction product. The results from the modified test matrix in Tables 4 and 5 were used to generate a regression equation predicting optimum operating conditions for generating large yields of high-purity distillate. As stated previously, calibration equations could not be used to determine distillate product concentration based on UV detection. HPLC peak areas rather than concentrations were used to construct the equation for predicting optimum yield.

The resulting equation proved inaccurate when tests were performed at the predicted optimum conditions. The equation predicted a maximum distillate product yield of 51% by weight at 165°C over 1 hour with 1 mL 5-molar H_2SO_4, while the actual distillate product yield was 2.7% at these conditions. Similarly, the equation predicted that the reflux product obtained at these conditions would contain essentially no free glycerol, while the actual product (which was not analyzed) was similar in color, clarity, and viscosity to pure glycerol. It is because optimum conditions could not be predicted that the best-available sample (Test 10) was sent to WMRC for HPLC–MS analysis instead of the optimized product.

The inability of the regression equation to accurately predict optimum test conditions was due to the change in experimental design. One of the key features of a Box-Behnken design is its mathematical symmetry. When the Box-Behnken design was altered in this work, its design symmetry was lost. This caused an unequal weighting toward higher temperatures and longer residence times. More importantly, fewer tests were performed at average temperatures or residence times, meaning that an abundance of data were available for extreme conditions but very little data were available at average conditions. Not surprisingly, the resulting equation shows high curvature at extreme conditions but relatively flat behavior at average conditions.

Although the equation was not useful in predicting optimum test conditions, limited conclusions were drawn from the best-case tests. One advantage of the process developed in the project is that cost and safety may not be as severe as they are for traditional ozonolysis. One of the reasons for the historically high cost of ozonolysis has been the safety concerns associated

with ozonolysis. These safety concerns arise because ozonides and malozonides can accumulate during reaction and build up to explosive concentrations. The glycerol ozonolysis process destroys ozonides and malozonides as they are formed and is, therefore, much less prone to explosion.

An analogy may be taken from the flare at a chemical plant producing flammable gases. Although flammable gases would form a dangerous and explosive cloud if simply vented, they are quickly combusted at high flare temperatures and can be vented safely. Similarly, traditional ozonolysis occurs at subzero temperatures and allows high concentrations of explosive compounds to form, while glycerol ozonolysis occurs at high temperatures. Ozonides are unstable at these conditions and rapidly decompose into more stable products (Equation 7).

A clear demonstration that explosive solutions do not form in glycerol ozonolysis was observed in one of the early tests, when a temperature excursion led to rapid exothermic dehydration. Although ozonolysis had been ongoing for approximately 1 hour with no ozone detected in the gas outlet stream (demonstrating that all available ozone was reacting with the liquid), the product autoignited without exploding. Had ozonides been forming over the hour of ozonolysis, they would have been present at a high enough concentration to cause a major explosion. The fact that the reaction solution instead caught fire and was safely extinguished strongly suggests that ozonides were not present at appreciable concentrations.

Vegetable Oil Ozonolysis

Figure 6 provides results on the CP testing of the ozonolysis product of vegetable oil in methanol. Only at the highest blend ratio (37%) was an appreciable drop in CP observed. The PP test showed a net increase in PP from −8.0° to −6.0°C when the ozonolysis product was added to biodiesel.

The CP of pure biodiesel decreased as ozonolysis product was added to biodiesel, while the PP increased slightly. This is in contrast with the results of Soriano et al., who reported that blending ozonolysis product into biodiesel caused a decrease in PP but not in CP relative to pure biodiesel (18). This difference may be due to differences in the degree of unsaturation of oil feedstocks, in the amount of steryl glucoside present in the blend, or in the ozonolysis method used to produce the fuel additive. The time and budget constraints of this project did not allow for further substantiation or delineation of these factors.

Given the high blend ratio required to cause a measurable effect on cold-temperature properties and the small effect observed even at this high blend ratio, direct use of the ozonolysis product generated in this work does not appear to be a viable solution to improving the cold-weather properties of biodiesel. Distillation or other separation techniques may yield a product that is better able to suppress cold-weather properties, but this will add further processing costs to the ozonolysis product. Alternatively, low-temperature oxidative ozonolysis could be performed on biodiesel to preferentially yield methyl esters that could have a greater impact on the cold-weather properties of biodiesel (19).
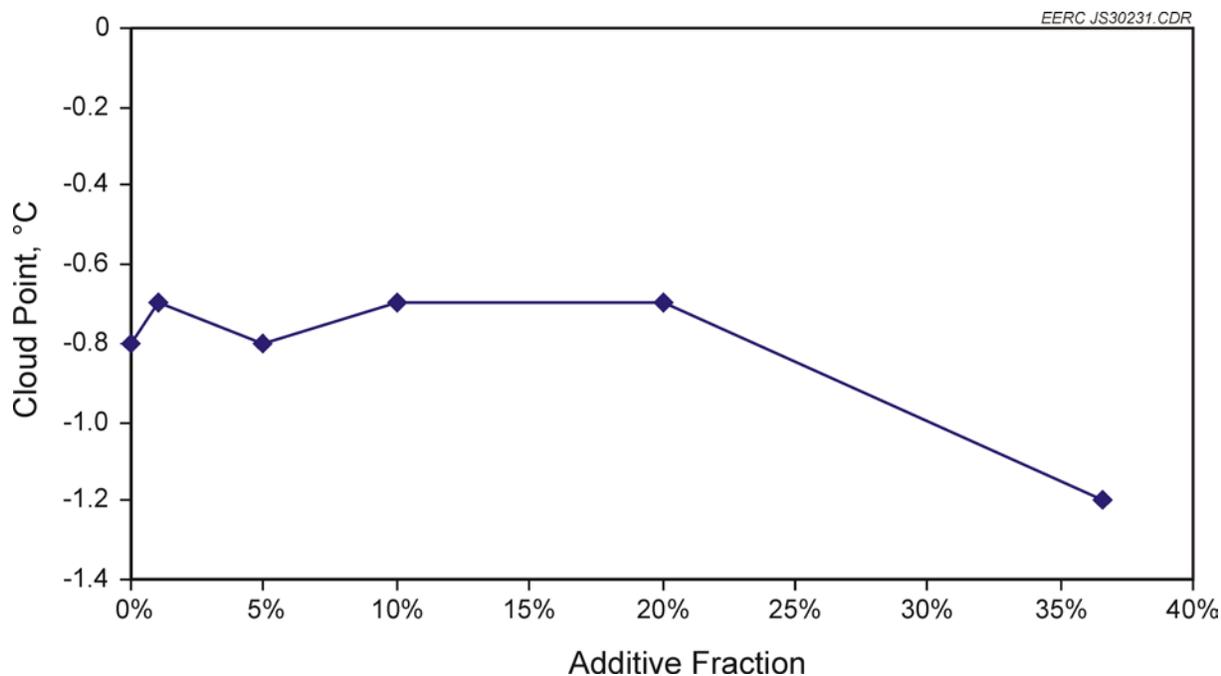
Figure 6. Effect of additive blending on biodiesel CP.

After this project was proposed, various studies began to show that the poor cold-weather properties of soy-based biodiesel are due in large part to steryl glucosides present in the fuel (22– 25). This being the case, no additive will fully correct the cold-weather properties of soy biodiesel, because steryl glucosides can condense at relatively high temperatures regardless of the bulk composition or average freeze point of the methyl ester portion of the fuel. The best solution to preventing clouding and freezing of biodiesel at cold temperatures is not through use of additives but rather by removal of steryl glucosides from the biodiesel product (23). With the removal of steryl glucosides, existing additives may have more success at suppressing PP and CP. At this point, it does not appear favorable to pursue further research into novel biodiesel PP suppressants.

ECONOMIC ANALYSIS

Prior to discussing process economics, it should be stressed again that the economic climate for glycerol ozonolysis has seen substantial changes since this work was completed. The assessment provided here is no longer accurate.

Limited chemical commodity cost data are available for the chemicals used and produced by the process described in this report. For many chemicals, no data are readily available. Traditionally, the trade journal *Chemical Market Reporter (CMR)* has provided commodity data. However, this practice was ended March 21, 2005.

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Figure 7 provides cost data for glycerol, formaldehyde, methanol, oleic acid, and propionic acid for the period September 25, 2004, to March 24, 2005, as taken from *CMR*. Although data for other products were not listed, analogous products are used where applicable. For glycolic acid, lactic acid is used to estimate cost, as both products have similar application, have similar (traditional) production methods, and are used together to manufacture biodegradable polylactic glycolic acid (PLGA) polymer. For glycolaldehyde, acetaldehyde is substituted. Not shown in Figure 7 but taken from *CMR* are the costs for sodium hydroxide, sodium sulfate, sulfuric acid, and dichloromethane (methylene chloride in *CMR*). Also taken from *CMR* were the costs for maleic anhydride and low-grade oleic acid, which were used to estimate the costs of malonic acid and capric acid, respectively.

Part of the separation in the envisioned process required the use of petroleum ether. The cost of petroleum ether is unknown from *CMR*, and so the cost of snow white petrolatum was used as an estimate. This value was not used because snow white petrolatum is chemically similar to ether; in fact, petrolatum, more commonly known as petroleum jelly, is a solid at room temperature and is used primarily in the cosmetics industry. Rather, the cost for snow white petrolatum was used because it was the highest-priced petroleum product reported in the final issue of *CMR* to include chemical commodity prices and so was considered a worst-case estimate.

As can be seen, the cost of glycerol (glycerine in *CMR*) dropped by nearly half over the period of reporting. Looking further back, glycerol costs had risen between 1998 and 2003 from $0.53 per pound to $0.66 per pound as glycerol found increased application in cosmetics. The expansion of the biodiesel industry then produced a large excess of glycerol that temporarily
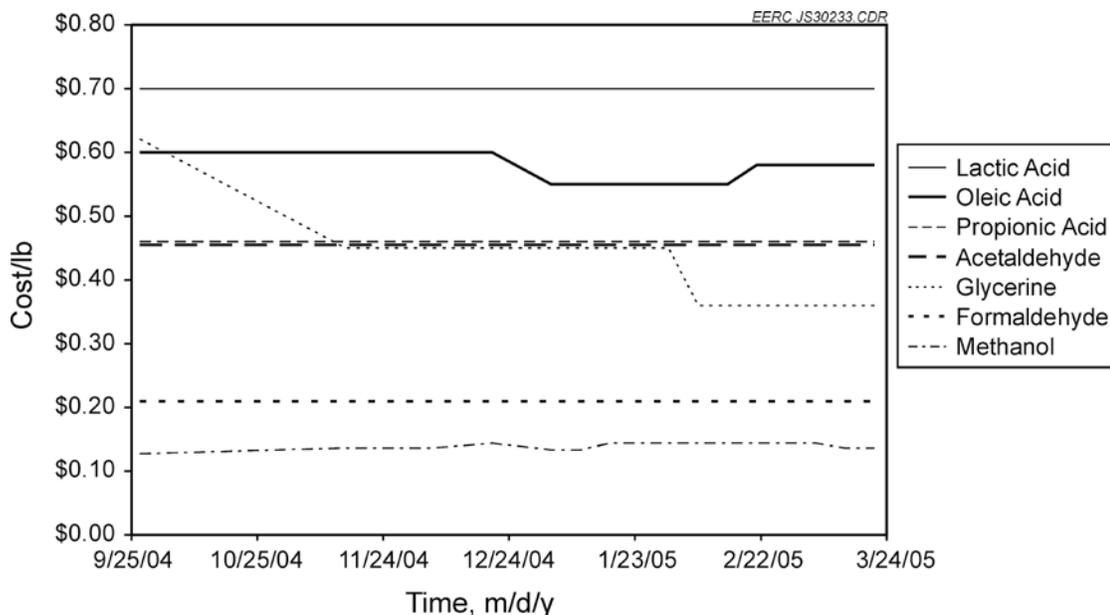

Figure 7. Bulk chemical costs as reported by CMR during the period September 25, 2004, to March 24, 2005.

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drove the price down. Thus the cost of $0.36/lb in March 2005 represented its lowest value in at least 7 years. There were reports that crude glycerin was selling for less than $0.05/lb for a short time (26). However, glycerol has since found increased use in food and personal care products. As of March 2, 2008, spot prices were reported above $1.00/lb (1). This has negatively impacted the economics of chemical production using glycerol as starting material. At the time that this study was conducted, the economics looked favorable, and many of the original conclusions have since been falsified.

Over the period of reporting shown in Figure 7, the cost of lactic acid remained steady at $0.70/lb without fluctuation. Assuming that the cost of lactic acid is similar to the cost of glycolic acid and that the market behavior is similar, this suggested that glycolic acid would continue to be both a more valuable product than glycerol and also a more stable investment. As stated above, this assumption has since proved false as glycerol prices have risen dramatically.

As mentioned in the Introduction, heated vegetable oil ozonolysis in methanol solution may yield a maximum number of total products, but the economics of this process were not considered. The number of separations required to recover each product to appreciable purity would likely increase the capital and operating costs too greatly to justify such a process. Instead, a more conventional process involving low-temperature oxidative ozonolysis was assumed for converting biodiesel. The products of biodiesel ozonolysis are a mix of carboxylic acids and dicarboxylic acids, including propionic acid. Figure 7 shows both propionic and oleic acid prices as being fairly stable over a 6-month period. Other sources (27) have shown average propionic prices as increasing from $0.46 in 2000 to $0.62/lb in 2005, without downward fluctuations. Recovery of propionic acid represents a significant value increase as compared to simple vegetable oil esterification, as biodiesel typically sold in bulk for around $0.30/lb during the same period. In addition, the total volume and mass of salable fuel would increase, as ozonolysis of 100 g of soybean-derived vegetable oil is capable of producing up to 148 g of methyl ester product.

For conducting a preliminary economic analysis, the results of the optimization study can be used to estimate product yields. Using Test 10 from Table 5 as a model, 37% of the glycerol (based off a detailed kinetic mass balance) can be expected to undergo ozonolysis in a single pass. For every pound of glycerol fed both as fresh feed and as recycle, 0.13 lb of the reaction product will be distilled by heat of reaction and condensed downstream as an aqueous solution of formic acid and glycolaldehyde, which is the preferred aldehyde product owing to its price and range of applications (28); 0.51 lb of the product will be glycolic acids present as glyceryl glycolate esters that can be transesterified to 0.30 lb methyl esters, distilled, and recovered in high purity; 0.02 lb of the undistilled reaction product will be aldehydes that are unrecovered; and 90% of the unreacted glycerol (including that recovered from transesterification of the glyceryl glycolate) can be recovered and recycled back into the ozonolysis reactor, which will be fed a gas stream containing 20% excess ozone.

The excess ozone could be passed to a fatty acid reactor to produce short-chain methyl esters from biodiesel. 100% of the ozone can be expected to react. This will convert 6.1% of the total biodiesel produced by the FAME plant into products. 0.2% of the biodiesel will be converted to methyl propionate; 1.7% of the biodiesel will be converted to dimethyl malonate

that can be distilled to high purity for recovery; 1.4% of the biodiesel will be converted to methyl caproate that can be distilled and recovered; and the remaining biodiesel will either remain unreacted or will be present as nine-carbon methyl esters. These longer-chain products can be left in the biodiesel to act as a cold-flow additive and to dilute unsaturated methyl esters. This will give a premium biodiesel product that can be sold for an estimated $0.10 per gallon more than standard biodiesel. The prices per pound for the methyl esters are taken to be the same as the costs per pound for the respective carboxylic acids. This is approximately correct if the cost of the methanol portion of the methyl esters is added to the cost of the acid portion of the esters.

The plant capacity is assumed to be 5 million gallons per year (MMGY) biodiesel, which was the approximate median plant size as of 2007 (29). The assumptions given above are listed in Table 6, along with the results of a brief economic analysis based on the process flow diagram from Figure 2 and a process flow diagram for a low-temperature biodiesel ozonolysis process as shown in Figure 8. As can be seen from Table 6, the proposed ozonolysis process has a negative net present value (NPV) when collocated with a 5-MMGY biodiesel plant.

The reason for the negative NPV is that the costs of the raw materials are greater than the selling prices of the products, even using 2005 values. Analysis of the overall process reveals that the losses are almost entirely due to the biodiesel ozonolysis process. Olefin ozonolysis has been practiced commercially since at least the 1950s for production of cosmetics (15). However, in traditional olefin ozonolysis, the products are high-purity specialty carboxylic acids or aldehydes that can be sold for a high price. While such products are likewise produced in this scenario, a significant fraction of the ozonolysis products are left undistilled in the biodiesel to act as a fuel additive. The estimated selling price for the resulting premium biodiesel blend is

Table 6. Results of Economic Analysis and Assumptions Used to Construct Economic Analysis

Assumptions, glycerol reactor (single-pass values)	
Glycerol Conversion, single-pass	37%
Aqueous Aldehyde Yield, per pound glycerol basis	13%
Methyl Ester Yield, per pound glycerol basis	30%
Glycerol Recycle Efficiency	90%
Excess Ozone	20%
Assumptions, biodiesel ozonolysis reactor	
Biodiesel Conversion (mole percent)	6.10%
Methyl Propionate Yield, per mole biodiesel basis	0.18%
Dimethyl Malonate Yield	1.74%
Methyl Caproate Yield	1.38%
C9 Concentration in Premium Biodiesel Product	2.72%
Results[1]	
Capital Cost (5 MMGY biodiesel capacity)	$12,900,000
20-year Net Present Value vs. FAME Process	-$38,000,000
Discounted Rate of Return	N/A
Discounted Paypack Period	N/A

[1] All results are calculated assuming a 10-year modified accelerated cost reduction system (MACRS) depreciation and a 20-year plant life.
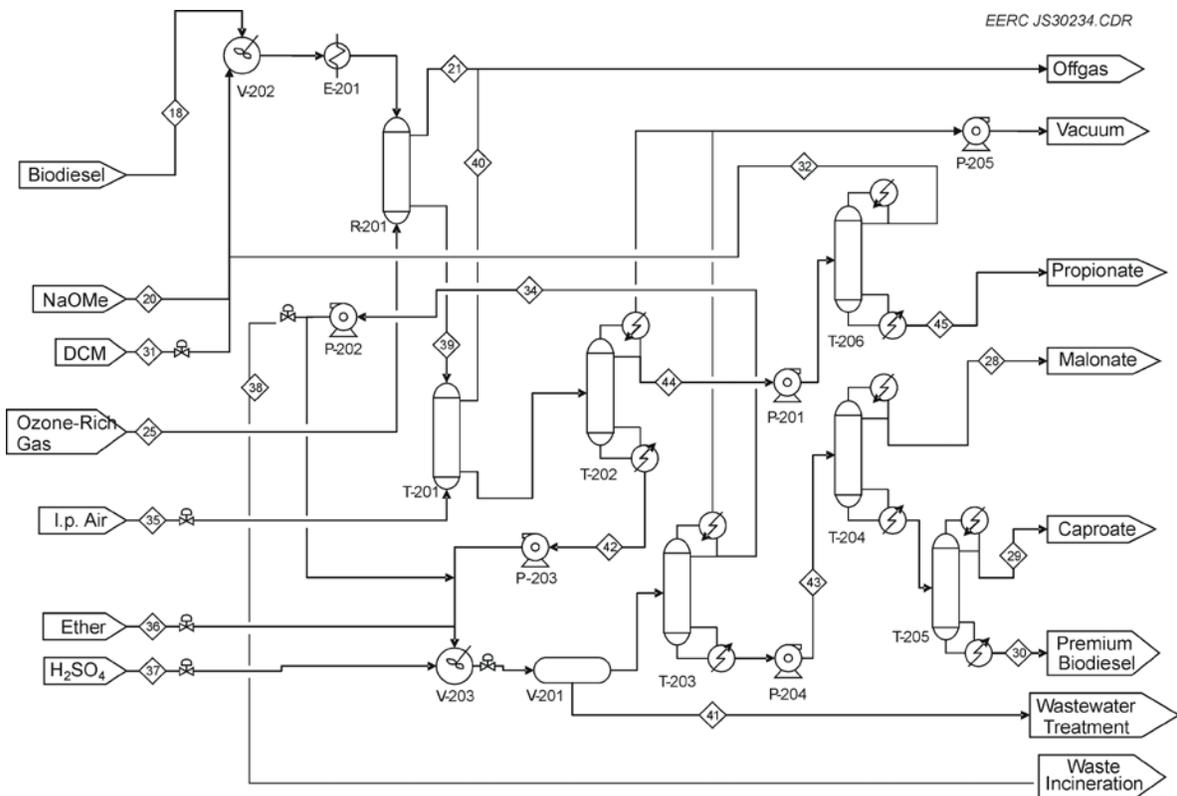
Figure 8. Biodiesel ozonolysis plant with fractionation to recover separate products.

only $0.10/gallon higher than the selling price for base biodiesel, which presents a negative gross profit in terms of revenue minus cost of raw materials.

In addition to producing chemical streams with a combined revenue lower than the cost of raw materials, the biodiesel ozonolysis process requires equipment that must be explosion-rated and must operate at extremely low temperatures. As such, the gross profit must be high to achieve a relatively short payback period. Thus, in general, biodiesel ozonolysis to produce fuel is unlikely to be economically viable on the commercial scale even with a positive gross profit.

The process economics can be improved if the biodiesel ozonolysis section of the plant is removed and the excess ozone from glycerol ozonolysis is instead sent to a collocated water treatment facility. Under this scenario, there is no revenue gained from the excess ozone, but there is also no cost of raw materials beyond what is required for glycerol ozonolysis. This would result in a positive gross profit on a basis of revenue minus cost of raw materials using the costs from 2005 presented in Figure 7. However, the process remains uneconomical in this simulation because of the costs of utilities, operating labor, taxes, and depreciation. Moreover, the price of glycerol has since risen substantially, making the process even less economically favorable.

A sensitivity analysis was performed on the example of a glycerol ozonolysis facility without a biodiesel ozonolysis facility, as this was the example with a positive gross profit.

Economic sensitivity was determined by varying equipment costs, chemical market prices, utility costs, and number of new operators. Each of these variables is listed with the sensitivity range in Table 7. Fixed capital investment is varied between −50% and +100% because of the uncertainty in actual costs of equipment. Utility costs are varied more drastically, between −80% and +100%, because much of the equipment was probably oversized and because of uncertainty in the actual electrical, steam, and water demands for each unit operation. The baseline case assumes four new operators for 25 new unit operations added onto an existing 5-MMGY biodiesel facility, with auxiliary units such as pumps and heat exchangers for distillation counted as individual unit operations. This number was calculated by taking the number of operators needed for the plant shown in Figure 2 and subtracting the number of operators needed for the biodiesel portion of the plant (30, 31). This method may not be appropriate because the FAME biodiesel process is sufficiently simple that it likely requires fewer operators than expected, while a 220-lb/h ozone generator is so complicated that it likely requires more operators than expected. As such, it is unlikely that fewer than four new operators will be needed, but it is probable that more than four operators will be required. The sensitivity analysis was performed by allowing up to 14 new operators without allowing for fewer than four operators. The value of 14 was chosen as an upper limit because this is the number of operators required for the 25 stand-alone unit operations of the ozonolysis facility.

Table 7. Sensitivity Analysis Parameters

Variable	Baseline	Range Min	Range Max
Fixed Capital Investment	$6.6 MM[1]	$3.3 MM	$13.2 MM
Chemical Market Prices (cost/year)			
Raw Materials	$1.4 MM	$720 M[2]	$2.9 MM
Products	$2.0 MM	$1.0 MM	$4.0 MM
Utility Costs	$664 M	$130 M	$1.3 MM
Number of New Operators	4	4	14

[1] MM = million.
[2] M = thousand.

The uncertainty in each area—capital costs, utility costs, chemical market prices, and number of operators—was used to conduct a Monte Carlo simulation of process economics. The results of the sensitivity analysis are displayed in Figure 9. As can be seen, there were no scenarios encountered under which the glycerol ozonolysis process would have a positive NPV.

CONCLUSIONS

Vegetable oil ozonolysis in methanol to produce biodiesel cold-weather additives does not appear to be a technically feasible goal. Literature data show that removal of biodiesel contaminants such as steryl glucosides has a significant effect on filter plugging from soy biodiesel. The combined effect of cold-weather additives and biodiesel purification on CP and
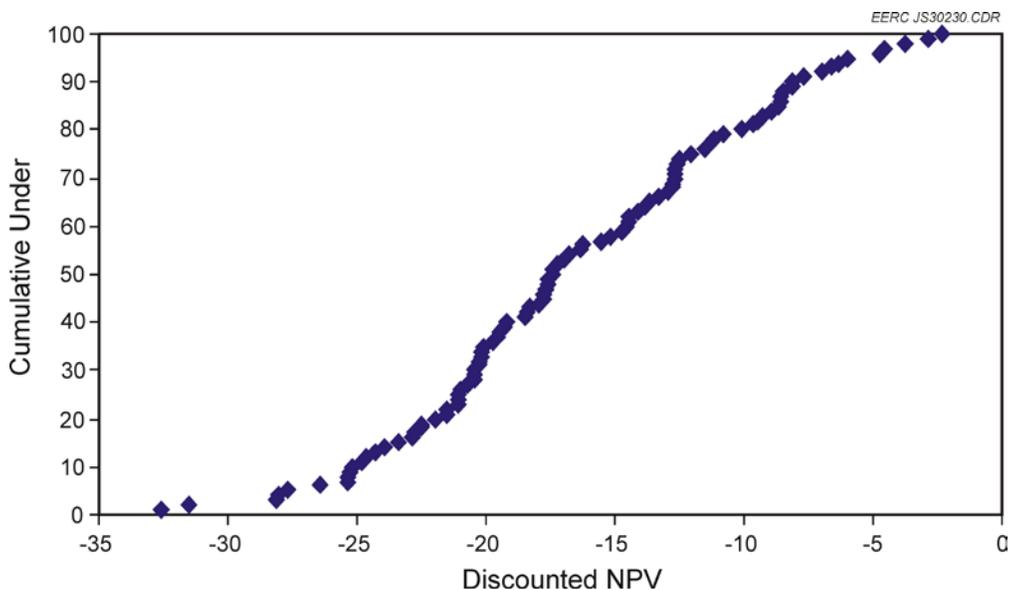
Figure 9. Results of 100-case Monte Carlo sensitivity analysis using parameters in Table 7.

PP could be more pronounced than the effect of either variable alone, but this concept was not investigated in this study. Moreover, it is possible that existing cold-weather additives will be sufficiently effective when combined with purification that expensive and hazardous ozonolysis processes will not be justifiable for producing novel additives.

Glycerol ozonolysis is technically feasible and appears to be safer than traditional ozonolysis. However, the conversion efficiency and yield observed in this testing were low. Both properties could be potentially improved through process optimization. If optimization is attempted in future work, continuous reaction in a countercurrent columnar reactor with glycerol entering from the top and ozone entering from the bottom would be preferable to further study in a batch reactor, as reaction temperature and glycerol-to-ozone stoichiometry would both be more easily controlled. Moreover, a continuous countercurrent reactor would better represent the type of ozonolysis reactor likely to be used on a larger scale.

The feasibility of product separation remains uncertain. Glyoxal and formic acid are easily recovered during reaction, as they are significantly more volatile than glycerol or glyceryl esters and thus can be distilled during reaction and condensed downstream. However, heavier acid products form esters with available glycerol during ozonolysis and remain in the liquid state. If these esters can be easily transesterified with methanol to more volatile methyl esters, they can be distilled off of unreacted glycerol, which could then be recycled. Barring this, some more expensive method of separation may be necessary, or glycerol recycle may be limited.

The process economics for the collocation of a glycerol ozonolysis plant with a 5-MMGY biodiesel plant are unfavorable. Given the high price of glycerol today, the process is unlikely to be economically favorable at any time in the foreseeable future.

If glycerol prices do drop at some point in time, or the cost of short-chain aldehydes and acids rises above the cost of glycerol, the proposed process could be improved through more efficient plant design. For instance, in the design used to conduct the economic assessment, all pumps and mixing drives are assumed to be electrically driven and to have one identical backup. If the motors could instead be powered by auxiliary streams, utility costs could be decreased. Mixers or pumps that are sized identically could have shared backup units, decreasing the plant's capital cost. This would indirectly improve yearly economics by reducing the depreciation costs. Similarly, there is no effort made to recover process heat, although in some cases one stream entering a reactor is preheated with steam while a second stream exiting the same reactor is cooled with water. If the two utility-driven heat exchangers were replaced by a single countercurrent heat exchanger, the utility, operator, and capital costs would be further decreased. Such changes could be sufficient to make the process economically favorable if glycerol prices drop to very low values or short-chain aldehydes and acids see dramatically increased cost and demand. However, at this point in time, the technical and economic obstacles to commercialization are too large to recommend any further work in the area of glycerol ozonolysis.

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