Biodiesel from Low Quality Feedstocks Using Solid Super Acids

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Abbreviations

FFA = free fatty acid (a carboxylic acid)
FTIR = Fourier transform infrared spectroscopy
GC = gas chromatography
LD_{50} = lethal dose (g of compound/kg subject) at which 50% of the test subjects die
NMR = nuclear magnetic resonance spectroscopy
OMC = ordered mesoporous carbon
PTFE = polytetrafluoroethylene
TG = triglyceride

Responsiveness to Regional and National Priorities

The proposed research effort touches on several priorities. First, it encompasses aspects associated with *agriculturally-related manufacturing technology*. Southwestern Virginia is an economically disadvantaged region of the U.S. with a per capita income of \$ 20,000.[1] 14 % of the residents of this portion of Virginia live below the poverty line.[1] The region itself is predominantly rural with Roanoke being the largest metropolitan area. Funding of the proposed research effort will not only translate into immediate jobs but will set the stage for future job growth in the area during the Phase II and III stages of this project. The end result is the development of a specialized manufacturing base that will be unique to the region and the country as a whole. This novel approach will also allow biodiesel to be prepared regionally from locally derived feedstocks. This will lower fuel costs and benefit those who reside in rural settings, particularly those in agriculture who depend on diesel fuel to power equipment. Second, the research effort is based on a new methodology for the production of biodiesel; a viable *alternative and renewable form of energy*. As a result of daily activities millions of tons of low quality grade oils/greases are produced in the U.S. every year.[2] These materials represent a valuable fuel resource but typically go unutilized due to difficulties encountered in their conversion to biodiesel. The technology that will result from this research effort will transform these waste products into useful fuel. This will have a positive impact on the environment by eliminating an entire waste stream (*i.e.* yellow/brown greases) and because biodiesel is non-toxic and produces lower quantities of harmful gases. The increase in biodiesel production that will result will reduce the country's overall dependence on fossil fuels.

Identification and Significance of the Problem or Opportunity

Biodiesel is an ecologically friendly fuel made from renewable plant and animal derived feedstocks. Biodiesel is safer to handle than petrodiesel and is less polluting in terms of emissions. Biodiesel has many beneficial characteristics.

1. It is non-toxic by oral ingestion (LD_{50} > 17.4 g/kg).[3] NaCl (LD_{50} = 3.75 g/kg)[4] is four times more toxic!
2. It is four times more biodegradable (~ 85 % degraded in 28 days) than petroleum diesel.[3]
3. Its flash point (> 260 °F)[3] is more than twice that of regular diesel (125 °F).[3]
4. Emissions from biodiesel are reduced (CO {50 % less}, hydrocarbons {95 % less}, particulates {30 % less}, cancer causing aromatic hydrocarbons {75 % less to eliminated}, sulfur oxides/sulfates {eliminated}).[5,6]
5. It has high lubricity and prolongs engine life whereas petroleum diesel requires lubricating additives.[5,6a,7]
6. It is the only transportation fuel to pass EPA Tier I & II health effects as set under the Clean Air Act.[6a,e]
7. Biodiesel has the highest energy balance of any transportation fuel (3.2).[6a,6c,8]
8. It is fully compatible with today's diesel engines and commercial/domestic boilers.[5,6c]

The only area that biodiesel can not outperform petrodiesel in is cost. The high cost of biodiesel (up to 75 %) can be traced to high purity plant oils required by traditional methods of manufacture.[9] The chemical constituents of biodiesel (alkyl esters) can in theory be derived from both high and low purity feedstocks. At the present moment most commercial processes rely on homogeneous base catalyzed transesterification of pure triglyceride (TG) feedstocks as this method produces biodiesel at acceptable rates under mild conditions without the need for equipment of specialized construction.[10] This approach has a detrimental impact on the environment as it generates large quantities of highly basic wastewater.[11]

Yellow and brown greases are waste products that result from daily activities such as cooking. These materials contain high levels (< 15 wt % for yellow and > 15 wt % for brown) of free fatty acid (FFA) contaminates.[12] These greases are abundant in large quantities (*e.g.* millions of tons) and have no utility as they cannot even be used as feed for livestock.[13] They do represent a potential and valuable fuel source. A new methodology that allows for the production of biodiesel from these cheap feedstocks in an environmentally conscious manner is needed.

Background and Rationale

In the synthesis of biodiesel, base catalysts are incompatible with FFAs and water; materials that are present in low grade feedstocks.[14] In order to allow the use of cheap starting materials the catalyst must be tolerant of these impurities. Acid catalysts can operate in the presence of such impurities. Homogeneous acid catalysts are corrosive and require specialized handling. They also typically exhibit low activities in the preparation of biodiesel.[15]

Homogenous catalysts (both acid and base) have severe limitations from an environmental standpoint.[16] Typically isolation of the product is complicated and requires destructive quenching of the catalyst. This generates large volumes of highly acidic or basic waste streams and is wasteful as the catalyst cannot be reused. Heterogeneous catalysts are environmentally friendly and have a high atom economy because they are readily separated from the reaction mixture by techniques such as filtration and are reusable. These materials are less corrosive and non-volatile reducing equipment and safety demands. With these characteristics and because they are readily adapted for use in continuous processes solid catalysts are industrially desirable.

A number of heterogeneous acid and base catalysts have been developed for use in biodiesel manufacture. Solid base catalysts are still incompatible with low grade starting materials but do eliminate wastewater (*vide infra*). Solid acid catalysts are ideal as they can convert the cheapest feedstocks into biodiesel without generating a waste stream. The main barrier to implementation of solid acid catalysts is that many possess low activities or cannot withstand the reaction conditions and lose their efficacy over time (*vide infra*). In order to circumvent this problem, a solid acid with both high acidity and stability is needed.

This research will focus on Brönsted acids supported on inorganic oxides. The inorganic supports used in this research will serve two main functions. First, the support will impart insolubility or heterogeneous characteristics to a normally soluble or homogenous acid. The parent acid will be chemically attached to the support for added stability to the process conditions. Second, the support itself will intensify the acidity of the acid functionality through electronic effects (*i.e.* electron withdrawing). This will impart super acid characteristics to the catalyst and increase the activity of the parent acid group in both transesterification and esterification thereby lowering the process conditions required to effect these reactions. In its ultimate configuration the resulting solid super Brönsted acid will be able to convert wastes of low purity (*e.g.* yellow or brown grease) into biodiesel under ambient conditions in a continuous, safe, and green manner. The end result will be a competitive advantage for biodiesel compared to petroleum derived fuels.

Relationship with Research or Research and Development

The Phase I effort is vital in laying the groundwork for the Phase II R&D effort. In the Phase I effort a matter of composition (*i.e.* supported super Brönsted acid catalyst) is developed and evaluated on a gram scale. The data obtained from this initial stage will be essential for its proper implementation on a larger, commercial scale. The cost of conducting this introductory research will be minimal (tens of thousands) in comparison to its returns (hundred of millions). The developed technology will lower the cost of fuel to the consumer and will reduce the country's overall dependence on foreign fuel sources. It will also generate jobs in the immediate area and job growth will spread as the technology is implemented throughout the U.S. This will increase the standard of living and enhance the Nation's security. The target catalysts also have broad reaching implications in a number of other industrial processes that currently rely on environmentally objectionable homogeneous acids. This will in turn lead to further cost savings for the chemical industry and be of great benefit to the environment.

Technical Objectives

The first technical objective is the synthesis of a supported super Brönsted acid. Various inorganic supports covering key portions of the periodic table will be investigated with special emphasis on those known to form stable solids while simultaneously increasing acidity. Ease of catalyst preparation and cost will key factors that will also be examined. The second objective will be to test these catalysts in both model transesterification and esterification reactions that mimic those that will be encountered in the conversion of brown/yellow greases into biodiesel. This will give a good indication as to the ability of these materials to operate with low quality feedstocks. The final technical objective will be to employ the top two catalysts in the preparation of biodiesel from yellow grease obtained from local sources. This will provide a real measure of the ability of each catalyst to aid in the synthesis of biodiesel from waste greases.

Work Plan

The tasks to be carried out in this research effort are as follows.

1. Preparation of supported super Brönsted acids.
2. Testing for catalytic activity in the transesterification of triacetin with methanol.
3. Testing for catalytic activity in the esterification of acetic acid with methanol.
4. Preparation of biodiesel from yellow grease.

Preparation of Supported Super Brönsted Acids

As the chemical compositions of the catalysts to be used in these studies are highly proprietary in nature a generalized procedure for their preparation is provided. Synthesis of each supported super Brönsted acid is conducted using Schlenk techniques in an effort to maximize attachment of the precursor acid to the support. The end product itself will be an air stable solid.

To a 250 mL Schlenk flask fitted with a high vacuum PTFE stopcock is added 9.00 g of an inorganic support and a magnetic stir bar. The flask is fitted with a septum, connected to a Schlenk line and placed under dynamic vacuum. The inorganic support is then dried at 200 °C for 4 hours under dynamic vacuum. The flask and its contents are allowed to equilibrate to room temperature and then placed under nitrogen. 100 mL of dichloromethane (previously dried by vacuum transfer from trioctylaluminum) is cannulated into the Schlenk flask. Next, 1.00 g (1.00×10^{-2} mol) of a precursor acid with a tether bearing a functional group of mutual reactivity to the support is added slowly with stirring. The septum is removed and a reflux condenser fitted with an air inlet adapter is then attached to the Schlenk flask under a purge of nitrogen from each vessel. The reaction mixture is allowed to reflux for a period of 6 hours after which the condenser is replaced with a Schlenk frit affixed to a round bottom flask under a purge of nitrogen. The reaction mixture is filtered and washed with additional dry dichloromethane. The collection flask is replaced with a hollow cap and all volatiles are removed under reduced pressure. The resultant solid acid containing 1.00×10^{-3} mol acid sites/g catalyst (theoretical) is stored in a glove box under nitrogen until use.

Characterization of Supported Super Brönsted Acids

Prior to application in transesterification or esterification reactions the solid acids will be tested for traces of unsupported precursor acid and the concentration of acidic groups (mol acid per gram of catalyst) will also be determined.

Detection of Unsupported Precursor Acid

It is vital that the supported acids are free of unsupported precursor acid in order to get a true measure of the activity of the former in the production of biodiesel. The following is a generalized procedure for detecting the presence of unsupported acids.

1.00 g of a supported super Brönsted acid is added to a funnel bearing a fine glass frit affixed an Erlenmeyer flask with tubulation. The flask is attached to a water aspirator and the solid acid is washed with 20 mL of deionized water. The filtrate is collected and its pH is measured using a digital pH meter. Filtrate that shows no change in pH is indicative of the absence of unsupported precursor acid. If the pH of the filtrate tests acidic then a 10 mL aliquot is taken for titration. A few drops of bromothymol blue indicator solution are added and the aliquot is titrated with fresh NaOH(aq) of known concentration to determine the amount of unsupported acid present per gram of solid acid. If desired the titration can be followed using a digital pH meter. Solid acids that test positive for unsupported precursor acid will be washed with dry dichloromethane until the free acid level is below 1.00×10^{-5} mol unsupported acid/g catalyst.

Determination of Acid Group Concentration

In order to get an accurate measure of catalytic activity all reactions need to be conducted in the presence of identical quantities of acid sites. To do this it is important to know the concentration of acid groups is per unit weight of a given solid catalyst. An example of how this might be done is summarized below.

1.00 g of supported super Brönsted acid, a magnetic stir bar, 20 mL of deionized water, and several drops of bromothymol blue indicator solution are added to a 125 mL Erlenmeyer flask. The mixture is stirred rapidly and titrated with freshly prepared NaOH(aq) of known concentration. A value of 1.00×10^{-3} mol acid sites/g catalyst is an indication of complete tethering of the precursor acid to the substrate.

Transesterification of Triacetin with Methanol

Triacetin (glyceryl triacetate) is a triglyceride formed by the esterification of glycerin with acetic acid. Due to its small size and simple chemical structure it is readily characterized by techniques such as gas chromatography (GC) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy as are its products from transesterification with methanol (e.g. methyl acetate). Triacetin of high purity is also available commercially at low cost. Given these characteristics triacetin is a good model compound for more complex triglycerides typically used in biodiesel production. The transesterification of triacetin with methanol will be a convenient method for gauging the activity of each solid acid in the production of biodiesel from triglyceride containing feedstocks. Transesterification might be conducted in the following manner.

To a 100 mL 2 neck round bottom flask is added 0.500 g supported super Bronsted acid, 32.0 g (40.5 mL {1.00 mol}) dry methanol, and a magnetic stir bar. A reflux condenser fitted with a drying tube packed with Drierite® is affixed to the central neck of the flask and the side neck is fitted with a septum inlet/stopcock assembly. The mixture is heated with stirring to reflux (65 °C) at which 109 g (31.4mL {5.00×10^{-1} mol}) triacetin is injected via a syringe through the septum inlet. A stopwatch is started and 1.00 mL aliquots are withdrawn every 10 minutes using a syringe and stored in labeled PTFE capped vials. 1.00 g of each aliquot is dissolved in 10.0 mL methanol containing 7.73×10^{-1} g (8.77×10^{-3} mol) 1,4-dioxane (standard). 0.5 μL of this solution is injected into a GC fitted with a flame ionization detector under a standard set of conditions (*i.e.* inlet temp. = 250°C; detector temp. = 250°C; 70psi Helium; flow rate 25mL/min). Conversion can be determined by comparison of the integrated values for the peaks corresponding to triacetin and standard. For ^{1}H NMR analysis use of 1,4-dichlorobenzene as a standard is preferred. After the reaction has been concluded the catalyst is isolated by filtration through a funnel with a fine glass frit. The catalyst is then washed 3 times with 10 mL portions of methanol and is dried under dynamic vacuum prior to reuse.

Esterification of Acetic Acid with Methanol

Acetic acid is a simple carboxylic acid that is commercially available in high purity at low cost. Acetic acid and its product from esterification with methanol (i.e. methyl acetate) are easily characterized using methods such as GC and ^{1}H NMR. Acetic acid will serve as good model compound for fatty acids typically encountered in low grade oil/greases. The esterification of acetic acid with methanol is a good measure of the *catalytic activity of each solid acid for the production of biodiesel from feedstocks containing fatty acid. This might be conducted as follows.*

To a 100 mL 2 neck round bottom flask is added 0.500 g supported super Bronsted acid, 32.0 g (40.5 mL {1.00 mol}) dry methanol, and a magnetic stir bar. A reflux condenser fitted with a drying tube packed with Drierite® is affixed to the central neck of the flask and the side neck is fitted with a septum inlet/stopcock assembly. The mixture is heated with stirring to reflux (65 °C) at which 30 g (28.6 mL {5.00×10^{-1} mol}) acetic acid is injected via a syringe through the septum inlet. A stopwatch is started and 1.00 mL aliquots are withdrawn every 10 minutes using a syringe and stored in labeled PTFE capped vials. 1.00 g of each aliquot is dissolved in 10.0 mL methanol containing 4.84×10^{-1} g (5.49×10^{-3} mol) 1,4-dioxane (standard). 0.5 µL of this solution is injected into a GC. Conversion can be determined by comparison of the integrated values for the peaks corresponding to acetic acid and standard. For ^{1}H NMR analysis use of 1,4-dichlorobenzene as a standard is preferred. After the reaction has been concluded the catalyst is isolated by filtration through a funnel with a fine glass frit. The catalyst is then washed 3 times with 10 mL portions of methanol and is dried under dynamic vacuum prior to reuse.

Production of Biodiesel from Yellow Grease

Upon completion of the model transesterification and esterification studies each catalyst will be ranked by product yield, reaction rate, and retention of catalytic activity on reuse. The two most active catalysts will then be screened in the production of biodiesel from yellow grease. The goal is to single out one catalyst that can be used in a fixed bed arrangement that will enable production of biodiesel in a continuous manner from yellow grease at ambient pressure and temperature. An example procedure follows.

A 1 L sample of yellow grease is obtained from a local restaurant. The grease is filtered to remove any particulates and allowed to stand in a 1 L separatory funnel to allow water to separate. The water is drawn off and a 1.00 g aliquot of grease is taken for titration to determine the FFA content. The grease is also analyzed with GC prior to reaction. To a 200 mL 2 neck round bottom flask is added 1.00 g supported super Bronsted acid, 90.0 g (114 mL {2.81 mol}) dry methanol, and a magnetic stir bar. A reflux condenser fitted with a drying tube packed with Drierite® is affixed to the central neck of the flask and the side neck is fitted with a septum inlet/stopcock assembly. The mixture is heated with stirring to reflux (65 °C) at which 9.00 g yellow grease is injected via a syringe through the septum inlet. A stopwatch is started and 1.00 mL aliquots are withdrawn every 10 minutes using a syringe and stored in labeled PTFE capped vials. 1.00 g of each aliquot is dissolved in 10.0 mL methanol containing a predetermined amount of 1,4-dioxane (standard). Conversion can be determined by comparison of the integrated values for the peaks associated with the product alkyl esters to that for the standard. Once the reaction has been finished the catalyst will be recovered by filtration, washed with methanol, dried and reused. Follow up experiments will be conducted at ambient temperature under otherwise identical conditions. The most active catalyst will be synthesized on a kilogram scale for further investigation in the Phase II effort in a fixed bed arrangement under ambient reaction conditions.

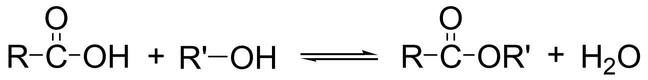
Related Research and Development

This section covers the basic concepts of the chemistry involved in the synthesis of biodiesel and provides an overall review of approaches developed for biodiesel production. Due to the scope of these topics this discussion is not meant to be comprehensive.

Basic Chemistry

The chemical constituents of biodiesel are alkyl esters derived from fats and oils of plant or animal origin. Esters (**1**) are formed in a process called esterification (Scheme 1) involving the condensation of a carboxylic acid (**2**) with an alcohol (**3**) that also produces water.[17] Since water is a reactant in the reverse of esterification (*i.e.* hydrolysis) the use of dry reagents and catalysts aid in the production of ester. Esterification is an equilibrium process and the position can be shifted towards products by several ways.

1. Using an excess of either reactant (carboxylic acid or alcohol).
2. Continual removal of one of the products as it is generated (*i.e.* H_2O).
3. Combination of both strategies.



$$\underset{\mathbf{2}}{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{\mathbf{3}}{R'{-}OH} \rightleftharpoons \underset{\mathbf{1}}{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + H_2O$$

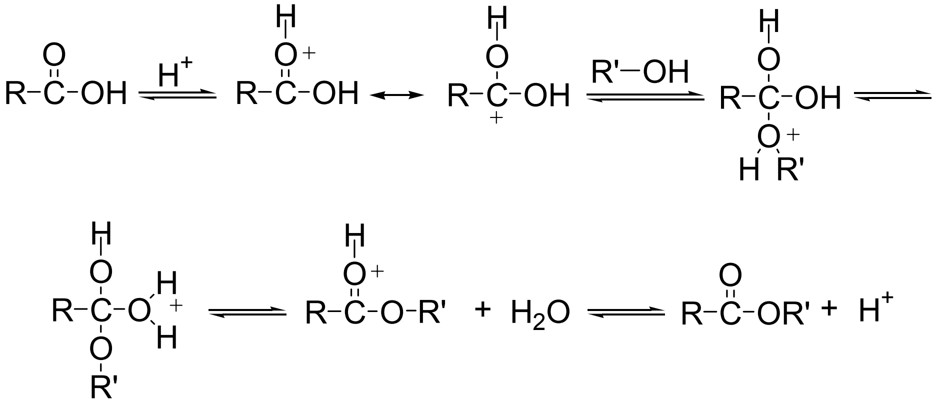
2 **3** **1**

R = organic substituent and R' = 1° or 2° alkyl

Scheme 1

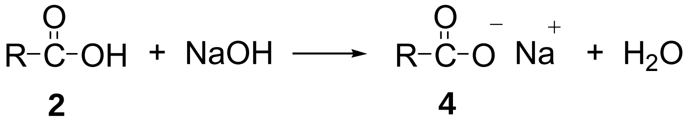
Even in the case of a favorable equilibrium the kinetics of esterification may not be feasible commercially. The use of heat and/or catalysts is typically required to produce the target ester on a useful timescale.

Esterification is acid catalyzed (Scheme 2) because a base will react directly with the carboxylic acid in an irreversible manner (Scheme 3) to form a salt of the acid (*i.e.* soap, **4**).[17] The acid catalyst withdraws electrons from the carbonyl group of the acid making the carbonyl carbon atom more electrophilic and susceptible to nucleophilic attack by alcohol.



Counterions excluded for clarity.

Scheme 2

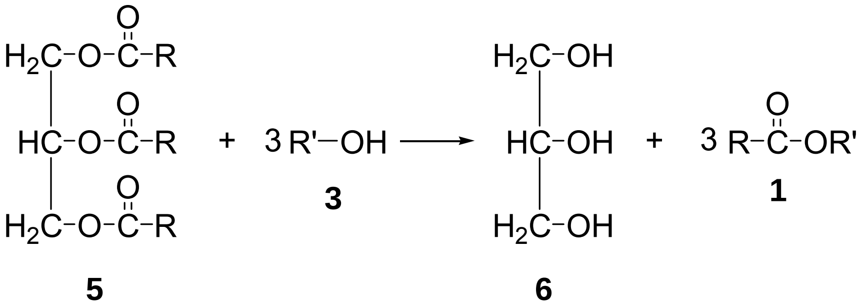


$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + \mathrm{NaOH} \longrightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O^{-}\,Na^{+}} + \mathrm{H_2O}$$

2 **4**

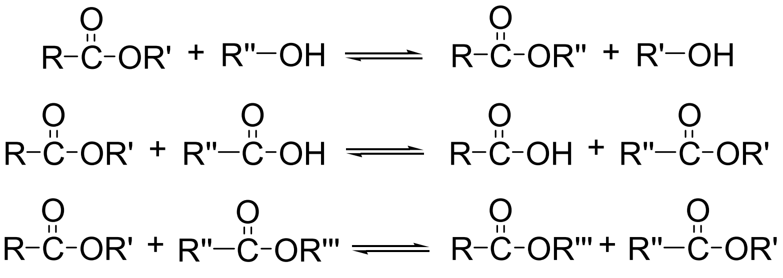
Scheme 3

Biodiesel is traditionally manufactured by transesterification of triglycerides (*i.e.* triacylglycerols) contained in plant oils and animal fats with alcohols (Scheme 4).[10] TGs are natural esters (**5**) of glycerol (**6**) and long chain carboxylic acids called fatty acids (FAs). Transesterification involves the conversion of a starting ester into a new ester via reaction with an alcohol, carboxylic acid, or ester (Scheme 5).[17] This also produces a new alcohol, carboxylic acid, or ester respectively. Transesterification with an alcohol is referred to as *alcoholysis*.



5 **3** **6** **1**

Scheme 4



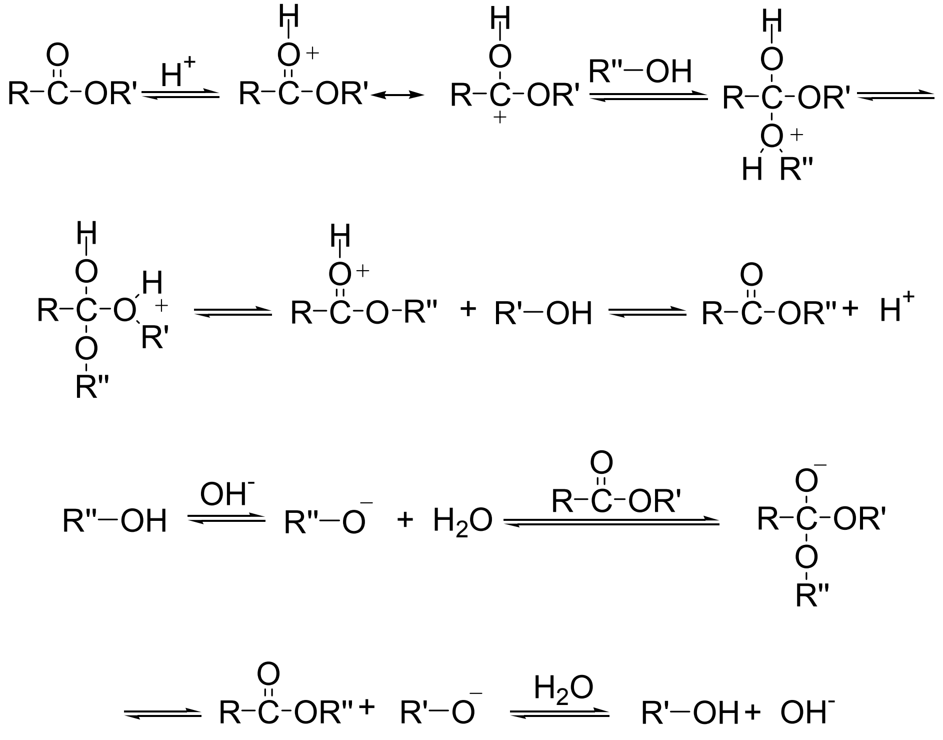
$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \mathrm{R''{-}OH} \rightleftharpoons \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR''} + \mathrm{R'{-}OH}$$

$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \mathrm{R''{-}\overset{O}{\overset{\|}{C}}{-}OH} \rightleftharpoons \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + \mathrm{R''{-}\overset{O}{\overset{\|}{C}}{-}OR'}$$

$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \mathrm{R''{-}\overset{O}{\overset{\|}{C}}{-}OR'''} \rightleftharpoons \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR'''} + \mathrm{R''{-}\overset{O}{\overset{\|}{C}}{-}OR'}$$

Scheme 5

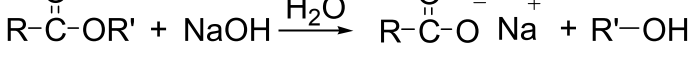
Alcoholysis is catalyzed by both acids and bases (Scheme 6).[17] Acids promote the reaction by withdrawing electrons from the carbonyl group of the ester making the carbonyl carbon atom more electrophilic and susceptible to nucleophilic attack by alcohol. Bases catalyze the reaction by converting the alcohol into an alkoxide, the latter being a much stronger nucleophile.



Counterions excluded for clarity.

Scheme 6

Base catalysts are used almost exclusively as reaction rates are about 4,000 times higher under mild conditions.[18] Bases are also less corrosive than acids and lend themselves to industrial settings as equipment of specialized construction is not required. Base catalysts do have a number of drawbacks. Bases react with FFAs irreversibly to form soaps (Scheme 3). This consumes catalyst and can emulsify the biodiesel making isolation difficult. Basic catalysts are also problematic as they aid in the hydrolysis of esters to form soaps in an irreversible reaction (Scheme 7).[17] This process is termed *saponification* and consumes catalyst, TG, and biodiesel alkyl esters. Quenching of the basic reaction mixture can led to saponification of biodiesel if precautions are not taken.[11a] Under acidic conditions hydrolysis is the reverse of esterification and its negative effects can be counteracted by simply removing water as it is formed. It has been found that for biodiesel manufacture to be viable under basic conditions the feedstock must not possess more than 0.5 wt % FFAs or 0.1-0.3 wt % water.[14] The requisite use of high purity TGs and anhydrous alcohol increases production costs.[9]



$$\underset{\mathbf{1}}{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + NaOH \xrightarrow{H_2O} \underset{\mathbf{4}}{R{-}\overset{O}{\overset{\|}{C}}{-}O^{-}\,Na^{+}} + \underset{\mathbf{3}}{R'{-}OH}$$

1 **4** **3**

Scheme 7

Biodiesel Production Using Homogeneous Catalysts

All of the practical methods for manufacture of biodiesel developed to date have relied on the use of homogeneous catalysts. Most plants make use of bases as they produce biodiesel at acceptable rates under mild conditions. Their reactivity (vide supra) places restrictions on what feedstocks can be used; a number of approaches have been devised to allow the use of starting materials containing significant amounts of FFAs. All of these methodologies possess drawbacks that limit their practicality.

The combined use of acid and base catalysts, termed the *integrated process*, is one of the earliest strategies devised to convert TG feedstocks high in FFAs into alkyl esters.[19] In one version (Chart 1) the first stage involves acid catalyzed (*e.g.* H_2SO_4) esterification of the FFAs. During this stage alcoholysis and hydrolysis of TGs can also occur. Once all FFAs are consumed the reaction mixture is cooled, neutralized, and if desired glycerol is removed. Un-reacted TGs are then subjected to base (*e.g.* KOH) catalyzed alcoholysis. After completion excess alcohol is removed and recycled. The remaining alkyl ester/glycerol mixture is neutralized and the glycerol is removed to yield the target alkyl esters.

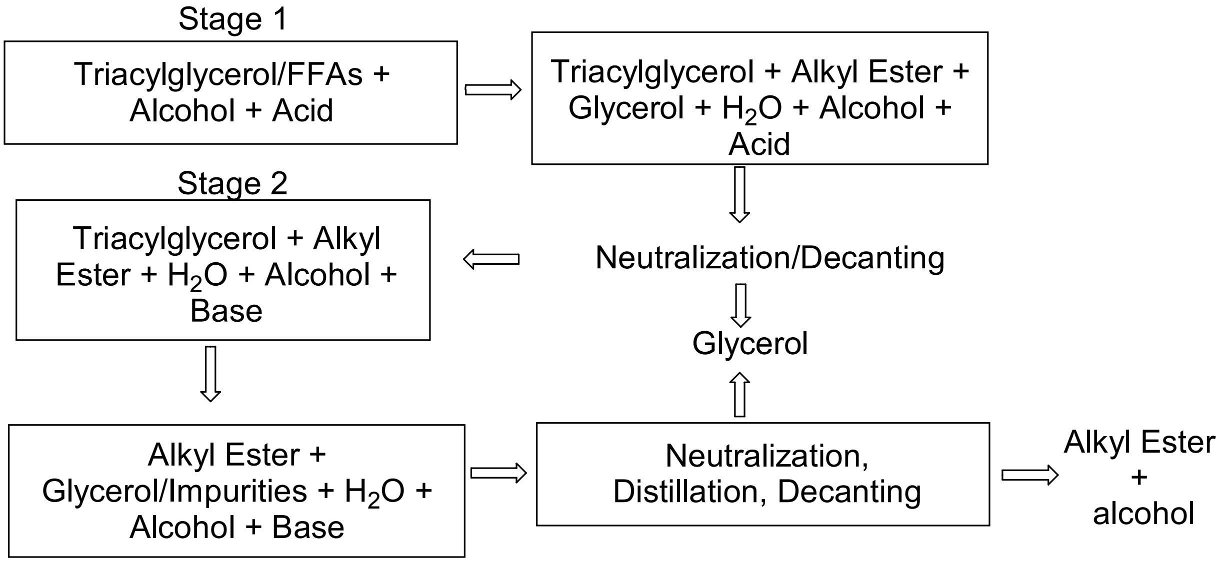


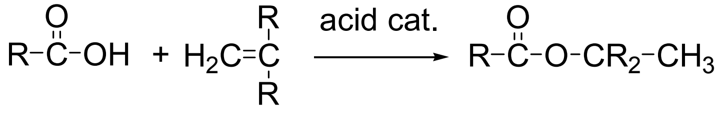
Chart 1

Another variation of the integrated process involves initial reaction under basic conditions.[20] During this stage TGs undergo alcoholysis to form alkyl esters and FFAs that are converted into soaps. Basic hydrolysis of TGs can also occur as water is liberated during soap formation. After the conclusion of the reaction all soaps are removed and acidified to produce FFAs that are then subjected to acid catalyzed esterification to afford additional alkyl ester. The main disadvantage to the integrated process is it generates large quantities of wastewater compared to a single catalyst approach. Methods have been developed that reduce wastewater but involve elaborate setups.[21] Production times are also longer compared to single catalyst processes due the large number of steps.

Numerous single catalyst technologies have been invented to overcome the negative aspects of the integrated process. One method involves the use of base catalysts in two stages.[22] In the first stage enough base is added to convert all FFAs into soaps that are then removed. In the second stage alcohol and additional base are added to a feedstock now devoid of FFAs and alcoholysis is conducted. Since the feedstock at this point is primarily TGs only very small amounts of base are required to catalyze biodiesel production. This approach suffers in that fuel production and catalyst use are inversely and directly proportional to FFA content of the starting material, respectively.

The majority of single component catalyst systems rely on the use of homogeneous acids. One method makes use of stannic (IV) halides as Lewis acid catalysts for the transesterification of a starting ester with a carboxylic acid (*i.e.* transesterification with an ester, Scheme 5).[23] Reaction is conducted in an autoclave at high temperatures (≥ 100 °C) and pressures (30 ATM) and gives rise to high yields. This approach is tolerant of FFAs but not useful for fuel production as no net gain of ester is obtained, the catalysts are highly reactive/toxic, and specialized equipment is needed.

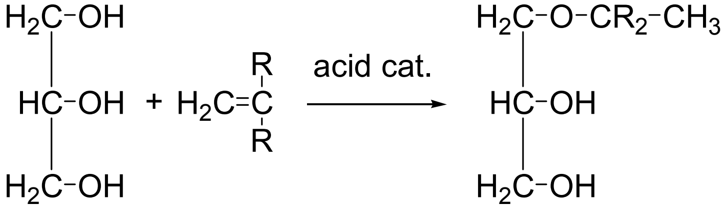
Another procedure for producing biodiesel from FFA containing feedstocks involves reaction with olefins in the presence of a strong Brönsted (*e.g.* H_2SO_4) or Lewis (*e.g.* $AlCl_3$) acid catalyst (Scheme 8).[24] The starting materials are cracked at high temperatures (up to 260 °C) in the presence of the acid catalyst to produce carboxylic acids. These carboxylic acids can then be esterified with alcohols or alkylated with olefins to produce biodiesel. The latter approach does not form any byproduct and can also led to etherification of glycerol (Scheme 9) to give a mixture of products (*i.e.* mono, di, trifunctional ethers).[17] These glycerol ethers have added fuel value and eliminate the glycerol waste stream. The negative aspects of this chemistry are that specialized equipment is needed to deliver olefins, withstand the high reaction temperatures, and handle the highly corrosive/toxic catalysts.



$$R-\overset{O}{\overset{\|}{C}}-OH + H_2C=\underset{R}{\overset{R}{C}} \xrightarrow{\text{acid cat.}} R-\overset{O}{\overset{\|}{C}}-O-CR_2-CH_3$$

R = H, alkyl, etc.

Scheme 8



$$\begin{array}{l}H_2C-OH\\ \quad|\\ \;HC-OH\\ \quad|\\ H_2C-OH\end{array} + H_2C=\underset{R}{\overset{R}{C}} \xrightarrow{\text{acid cat.}} \begin{array}{l}H_2C-O-CR_2-CH_3\\ \quad|\\ \;HC-OH\\ \quad|\\ H_2C-OH\end{array}$$

Scheme 9

One of the more novel systems developed makes use of barium and calcium acetate as weak Lewis acid catalysts.[25] These materials are not corrosive and are easily handled. Their low activity requires reaction be conducted at high temperatures (≥ 200 °C) and pressures (≥ 400 psi) necessitating the use of bomb-type autoclaves and limiting the utility of this approach to biodiesel production.

Biodiesel Production Using Heterogeneous Catalysts

In an effort to reduce waste streams both solid acid and base catalysts have been researched for the manufacture of biodiesel. This section summarizes key work preformed using both solid acid and base catalysts.

Heterogeneous Acid Catalysts

Solid acids are ideal catalysts for biodiesel production as they are compatible with low cost feedstocks rich in FFAs, do not contaminate the product, and can be reused. Despite these desirable qualities all of the solid acid catalysts developed to date possess inadequacies that prevent their use industrially. The following summarizes some of the key work performed in this area.

Sulfonated Carbonaceous Materials

Carbonaceous supports bearing sulfonic acid groups are some of the most effective solid acids developed to date for biodiesel production. The basic strategy used to prepare these materials involves incomplete carbonization of an organic material followed by sulfonation. Hara and co-workers were one of the first groups of researchers to report the use of these materials in the preparation of biodiesel.[26] They prepared a solid acid by sulfonating incompletely pryolyzed D-glucose. The resultant acid consisted of amorphous sheets of carbon bearing hydroxyl, carboxyl, and sulfonic acid groups and was insoluble in both polar (*e.g.* water, methanol) and non-polar (*e.g.* benzene, hexanes) media. The activity of this material for the synthesis of biodiesel from oleic and stearic acids was slightly greater than half that exhibited by sulfuric acid but unlike the latter the solid acid was easily recovered and reused without loss of activity. The low activity of this catalyst makes it less than desirable for use in commercial biodiesel production as long reaction times are required.

Smith and co-workers also explored this catalyst along with a number of other solid acids in the manufacture of biodiesel.[27] The following order of esterification activities was determined, D-glucose based catalyst > sulfated zirconia > amberlyst > niobic acid. The sugar derived catalyst also maintained 93% of its original catalytic activity after 50 cycles of successive reuse. Although this catalyst is very promising, reaction times of 5 hours at 80 °C were required to reach high conversions making this system less than optimal for biodiesel production.

Feng et. al explored sulfonated ordered mesoporous carbon (OMC) as a catalyst for synthesis of biodiesel.[28] It was reasoned that an ordered mesoporous support would give rise to a more uniform distribution of sulfonic acid groups with good accessibility leading to improved activity. These researchers first synthesized an OMC by polymerizing furfuryl alcohol around a silica template (Al-SBA-15). The resultant OMC was then pyrolyzed at 850 °C under vacuum and then the silica template was removed using HF. The resultant OMC was then functionalized with 4-benzene-diazoniumsulfonate in the presence of hydrophosporus acid to impart benzene sulfonic acid functionalities. The OMC based acid was tested in the esterification of acetic acid with ethanol and was shown to have moderate activity (80 % yield after 6 hours at 70 °C) and could be reused multiple times without loss of activity. The low activity of this material precludes its use commercially.

Heteropolyacids

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has been explored by Su and co-workers as a strong solid acid for biodiesel production from *Eruca sativa* Gars oil.[29] The material was calcined at 300-400 °C prior use and gave rise to 96 % yield of biodiesel within one hour at 60 °C. A co-solvent (tetrahydrofuran) was required and catalytic activity dropped on reuse. Small amounts of water (0.5 wt % or 1 wt %) led to drastic reductions in yield (to 80 % and 4 %, respectively). The need for solvent and the intolerance to water limit the utility of this catalyst.

Modified Metal Oxides

A number of metal oxide derivatives have been explored as solid acid catalysts for the preparation of alkyl esters. Three general approaches have been used to modify the precursor metal oxide; sulfation and doping with other metal species or heteropolyacids.

Sulfated Metal Oxides

Mittlebach et al. reported on the use of layered aluminosilicates modified with sulfuric acid as catalysts for the transesterification of rapeseed oil.[30] Sulfated montmorillonite KSF was the most active; 100 % conversion was obtained within 4 hours at 220 °C and 52 bar. This catalyst was not reusable due to leaching of sulfate species into the reaction mixture. As a result of leaching the activity of this catalyst cannot be described as being completely heterogeneous in nature. This catalyst is not practical given the harsh reaction conditions and its instability with respect to sulfate leaching.

Sulfated zirconia is a promising solid acid for a number of organic transformations. This material has been explored for the esterification of dodecanoic acid with a number of alcohols at high temperatures (> 100 °C).[31] It has been shown to catalyze biodiesel forming reactions as effectively as sulfuric acid on a site activity basis but suffers deactivation when used in liquid-phase reactions due to sulfate leaching, which occurs even at mild temperatures (*e.g.* 60 °C).[32] As a result, a number of other approaches have been used to boost the acidity of this support material. Furuta and co-workers adopted a technique where zirconia was doped with various metals.[33] Zirconia catalysts doped with titanium, aluminum, and potassium were prepared and calcined at 400 °C. These catalysts along with tungstated zirconia-alumina were tested in the transesterification of soybean oil with methanol at 250 °C. Despite the high reaction temperature none of the catalysts gave rise to biodiesel yields exceeding 80 %. Dalai et al. impregnated zirconia, silica, alumina, and activated carbon with 12-tungstophosphoric acid.[34] Each catalyst was screened in the transesterification of canola oil containing 20 wt % FFAs with methanol under 600 psi at a reaction temperature of 200 °C for 10 hours. All catalysts could be reused with negligible loss in activity and under optimized conditions the zirconia based catalyst gave the highest yields (90 %). The demanding conditions and long reaction times limit the utility of these catalysts.

Heterogeneous Base Catalysts

Compared to acids, base catalysts typically allow for transesterification to be conducted on an industrially useful time scale. In contrast to acids, they cannot be used with low quality feedstocks containing FFAs. A number of studies have focused on the use of solid bases to catalyze biodiesel production in an effort to reduce wastewater while maintaining favorable kinetics. An overview of this work follows.

The largest class of solid bases that have been explored are metal oxides. Calcium oxide (CaO) in particular has received a great deal of attention due to its moderate cost, poor solubility, low toxicity, and ready availability.[35] Studies have shown that CaO can convert a variety of feedstocks ranging from pure soybean oil to waste cooking oil containing 5 wt % FFAs into the corresponding methyl esters within 2 hours under reflux.[35a] The CaO can be recovered and reused with some loss of activity. In order to have appreciable activity CaO must be activated under an inert gas (*e.g.* He) at high temperatures (*i.e.* 700 °C).[35b] It must be protected against moisture and CO_2 as these materials poison CaO to produce inactive $Ca(OH)_2$ and $CaCO_3$ respectively. CaO also undergoes reaction with FFAs to form soaps and catalyst recovery is inversely proportional to FFA content of the feedstock.

Wilson and co-workers found that Li doping greatly increases the base strength of CaO.[35c] These researchers impregnated CaO with an aqueous solution of $LiNO_3$ followed by drying at 100 °C to yield a solid catalyst containing 1.23 wt % Li. This catalyst was very effective for the transesterification of glycerol tributyrate with methanol resulting in 100 % conversion within 30 minutes at 60 °C. On reuse the catalyst showed 10 % loss in activity possibly due to the leaching of $LiNO_3$. The increased activity was ascribed to the formation of surface Li^+ species. CaO based catalysts are viable alternatives to homogenous base catalysts provided that high purity feedstocks are used and the stringent activation and handling requirements are met. If these conditions are met CaO based catalysts have the potential to reduce pollution resulting from biodiesel manufacture but will not give biodiesel a competitive advantage over petrodiesel.

A number of solid base catalysts have been prepared by incorporating salts and or metals into metal oxides other than CaO followed by calcination to generate super basic sites. One such material was prepared by calcinating a mixture of Na/NaOH/γ-Al_2O_3 at 320 °C under nitrogen.[36] Sodium aluminate was purported to be the main basic species (Scheme 10). At a molar ratio of methanol:oil of 9:1 in the presence of hexane this catalyst gave rise to a 90 % yield of biodiesel from pure soybean oil within 1 hour at 60 °C. It was not reported if the catalyst could be reused. The requisite use of hexane detracts from the potential environmental benefits that this system could offer.

Another solid base catalyst with alumina as a support was prepared by solution intercalation of potassium nitrate followed by calcination at 500 °C.[37] The basic sites of this catalyst were claimed to be K_2O. This catalyst gave 87% conversion of pure soybean oil to biodiesel within 7 hours at reflux using a molar ratio of methanol:oil of 15:1. It was not stated if the catalyst could be recycled. This catalyst is not attractive due to the long reaction time and need for high amounts of methanol. Three solid bases were made from KF, KOH, and K_2CO_3 supported on ZnO and were investigated by Xie and Huang.[38] All materials were calcinated at 600 °C. It was believed that the basic sites were F^- ions for the KF/ZnO catalyst and O_2^- ions for both the KOH/ZnO and K_2CO_3/ZnO catalysts. All three ZnO supported catalysts had low catalytic activity for the transesterification of soybean oil with methanol. Reaction required 9 hours at reflux with a molar ratio of 15:1 methanol:oil with a highest yield of 87 %.

$$Al_2O_3 + 2\ NaOH \longrightarrow 2\ NaAlO_2 + H_2O$$

Scheme 10

Alternative Systems for Biodiesel Production

A number of alternative systems have been developed that do not rely on the use of chemical catalysts for the production of biodiesel. A brief summary of some of the main alternative strategies follows.

Catalyst-Free Systems

Noncatalytic chemical transformations are attractive as problems stemming from the use and removal of catalyst are eliminated. Supercritical methanol is an emerging catalyst-free technology for biodiesel production.[39] This involves conducting reaction in the supercritical state for methanol (*i.e.* 350 °C and 45 MPa). The polarity of methanol drops in the supercritical state due to a decrease in the degree of hydrogen bonding making it a better solvent for hydrophobic TGs and FAs.[39a,b] This in turn promotes both alcoholysis and esterification. Under these conditions the ionic product of methanol (*i.e.* self ionization) is increased such that it acts as an acid catalyst that accelerates reaction. Saka and Kusdiana have determined that a molar ratio of TG to methanol of 1:42 is optimum for transesterification which is complete within 4 minutes under supercritical conditions.[39d] Esterification of FAs was found to be even more facile.[39a,b] This technology is also highly tolerant of water. Reaction of waste palm oil containing > 20 wt % FFAs and > 61 wt % water resulted in a 96% yield of biodiesel.[39b] From a commercial standpoint the need for specialized pressure reaction equipment is not desirable. Another drawback is the large excess of methanol required, which must ultimately be removed from the biodiesel.

Enzyme Catalyzed Production of Biodiesel

Enzymatic production of biodiesel is a potential alternative to chemical catalyst methodologies.[40] Studies have shown that immobilized enzymes perform better than free enzymes as the former are not as easily deactivated.[40a] *P. cepacia* lipase immobilized within a phyllosilicate sol-gel matrix has been shown to be effective for the conversion of restaurant grease into biodiesel with various primary and secondary alcohols when used in conjunction with molecular sieves. Long reaction times (*e.g.* 18

hours) were necessary to reach high conversion. In many cases free enzymes are sensitive to the reaction conditions (*e.g.* FFA content) and may require the use of added solvents (*e.g.* hexane) and/or dry feedstocks making their use less than ideal.[40b] The main disadvantages to the using enzymes are that reaction conditions must be carefully controlled and reaction times can be on the order of days. A comprehensive discussion of this topic is beyond the scope of this research proposal.

Satisfying the Public Interest

The proposed research effort will lower the cost of biodiesel fuel well below that of petrodiesel. This will in turn aid agriculture producers by providing them with a cheap fuel that they can use in farm equipment. Economic opportunities in rural areas (*e.g.* Southwest Virginia) will increase due to job creation resulting from this effort. This will spur a new and highly specialized manufacturing base unique to the area that will further improve the living standards of residents of Southwest VA. The quality of life will increase elsewhere due to lower fuel costs and reduced pollution. By displacing a segment of fossil fuels this research will enhance the Nation's resource base making it less dependent on foreign derived energy sources. The reduced emissions from biodiesel and consumption of waste grease will benefit the environment as a whole.

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