PROGRESS REPORT
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BIODIESEL SYNTHESIS FROM ANIMAL FATS USING SOLID CATALYSTS: HIGH TEMPERATURE REACTION

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1.0 Summary:

As part of ongoing efforts to explore the potential use of animal lipid feedstocks for biodiesel synthesis, we are studying a novel methodology for processing a variety of lipid compounds such as animal fats and greases to biodiesel using solid acid catalysts at elevated temperatures. Use of these feedstocks to produce transportation fuels, e.g. biodiesel, advances national energy security and provides an environmentally friendly outlet for recycling the abundant animal fats and inedible vegetable oils into valuable commodities.

In conventional biodiesel production, typically refined vegetable oils (primarily consisting of triglyceride (TG) molecules) are treated with a low molecular weight alcohol (i.e., methanol, ethanol) using an alkali homogeneous catalyst (CH_3ONa, NaOH and KOH) in a one phase batch reactor. The price of these feedstocks can be 60-75% of the per gallon cost of biodiesel [Lotero et al., 2005]. To reduce the cost of these raw materials and to make biodiesel cost competitive with petroleum diesel fuel without tax subsidies, expensive food-grade vegetable oils must be replaced with cheaper waste grease feedstocks, and costly production processes must be simplified. However, processing low-cost waste grease feedstocks using standard biodiesel productions poses a challenge due to undesired reactions associated with the presence of free fatty acids (FFA) and water in these feedstocks. Compared to alkali liquid catalysts, strong liquid acids do not show any sensitivity to the presence of free fatty acids (FFAs), permitting the efficient conversion of waste grease to biodiesel, although at a much slower rate. Use of solid catalysts, however, as opposed to liquid catalysts would eliminate corrosion and environmental problems associated with homogeneous catalyst usage. In addition, the use of heterogeneous (solid) catalysts in general industrial processing is attractive since such catalysts can reduce the number of downstream separation steps, improving overall process economics.

The study presented in this report focused on the applicability of solid acid catalysts for the transesterification and hydrolysis of oils and fats as a means to ultimately lower the capital and operating costs for biodiesel synthesis by conducting the reaction at moderate reaction conditions (110-150°C and atmospheric pressure). Since the esterification of FFAs is faster than transesterification of triglycerides on acid catalysts, there may be a possibility to construct a more efficient biodiesel synthesis process around the use of simultaneous hydrolysis-esterification on solid acids rather than what is now done with a 4-step process [pre-esterification (homogeneous acid catalyzed) – separation (removal of acid and water) – transesterification (homogeneous base catalyzed) – separation (removal of the base catalyst)]. This would permit the use of low cost feedstocks containing > 5-15% FFAs and high concentrations of water.

2.0 Objectives:

- To propose and study efficient heterogeneous catalytic reaction systems that can produce a biodiesel cost competitive to petroleum-based diesel.

- To investigate catalyst performance for biodiesel synthesis at high reaction temperatures (>100°C) and atmospheric pressure in a multiphase process.
- To explore the conversion of cheaper feedstocks to biodiesel.

3.0 Project Overview:

Global warming and energy security have placed additional importance upon establishing viable alternatives to traditional petrochemical-based transport fuels. Biomass is considered to be green source for transportation fuels, e.g. biodiesel in the case of animal fats and vegetable oils. Biodiesel can replace directly petroleum-derived diesel without engine modifications and provides environmental and technological advantages including its being from a renewable source, completely biodegradable, cleaner burning than petroleum-based diesel, low in sulfur, and resulting in CO_2 recycle.

Biodiesel can be produced from highly refined vegetable oils, animal oil/fats, tallow and waste greases via the chemical process called transesterification of triglycerides (TGs) and esterification of free fatty acids (FFAs) [Lotero et al., 2005]. In conventional biodiesel production, the transesterification reaction (also known as alcoholysis) of refined vegetable oils is achieved by using homogeneous alkali catalysts (CH_3ONa, NaOH and KOH). To make biodiesel more cost-competitive with petroleum diesel, refined oils, whose cost has been estimated to potentially account for 88% of the total estimated production cost of biodiesel [Hass et al., 2006], can be replaced with lower cost feedstocks, such as waste greases (e.g., yellow grease, which contain over 5 wt% FFAs). However, the synthesis of biodiesel from low quality oils is challenging due to undesirable side reactions as a result of the presence of FFAs and water. On one hand, the presence of water favors the formation of FFAs by hydrolysis of TGs (the primary component of vegetable oils and waste greases) rather than ester products (biodiesel). Formation of FFAs in the presence of base homogeneous catalysts gives rise to soap formation, creating serious problems for product separation and ultimately hindering catalytic activity. For the above reasons, cheaper waste grease and animal fat feedstocks cannot be directly processed with conventional biodiesel synthesis technology using just homogeneous base catalysts, and an acid catalyzed pre-esterification step with subsequent water separation steps are necessary to reduce the FFA and the water concentrations below an optimum threshold limit, i.e., FFAs < 1 wt% and water < 0.5 wt% [Issariyakul et al., 2007]. Contrary to alkali liquid catalysts, acid catalysts can carry out both esterification of FFAs and TG transesterification [Suwannakarn et al., 2008; Mittelbach et al., 1995; Furuta et al., 2006]. This offers the possibility to carry out simultaneously both reactions in a single reactor [Zheng et al., 2006; Zhang et al., 2003].

The utilization of environmentally friendly heterogeneous (solid) catalysts in large scale biodiesel production is more preferable in order to eliminate the drawbacks associated with homogeneous catalysts (i.e., corrosiveness, production of waste, excess use of water in washing steps, and energy intensive separation operations). Moreover, solid catalysts permit the application of continuous reaction systems that improve overall process economics.

Since catalysis by solid acids or bases is restricted by limited surface site concentrations per mass of catalyst, use of higher reaction temperatures to increase significantly catalyst activity has been tried [Liu et al., 2007; Di Serio et al., 2006]. However, most investigations at these higher temperatures have used higher pressures in order to keep all reactants in the liquid phase. On the other hand, the use of reaction temperatures higher than the boiling point of water in a continuous three phase reaction system for FFA-TG mixtures using a solid acid catalyst and operating at atmospheric pressure should lead to the simultaneous co-distillation of impurity/byproduct water and any unreacted alcohol. This would also minimize the poisoning effect of water on the acid catalyst [Liu et al., 2006b] and should drive esterification to completion. In addition, the use of low concentrations of the alcohol favors the esterification reaction, as it has been shown that at high temperatures the alcohol can have a negative reaction order for esterification catalyzed by solid acids [Suwannakarn et al., 2007a]. Therefore, the use of solid acid catalysts coupled with more efficient reactor systems, such as a continuous multiphase reaction system, and reaction at elevated temperatures should significantly reduce biodiesel production cost by permitting efficient use of a variety of inexpensive feedstocks including waste greases as well as a remarkable reduction in downstream separation steps. Despite the potential benefits of continuous multiphase reaction for biodiesel synthesis, only a handful of studies are found in the literature for this application [Joelianingsih et al., 2007; Santacesaria et al., 2007; Kiss et al., 2006].

Our initial investigations showed that the use of tungstated zirconia (WZ) for the methanolysis of simulated mixtures of yellow grease using a continuous multiphase reaction system resulted in a high biodiesel yield within acceptable reaction times. By using the solid acid catalyst, water generated during FFA esterification enhanced the overall rate of TG transformation to methyl esters via TG hydrolysis followed by FFA esterification. Since acid catalyzed esterification is an order of magnitude faster than transesterification of TGs, this can result in a more rapid conversion of TGs to biodiesel.

This research explored the feasibility of using solid acid catalyzed hydrolysis of oils and fats for the synthesis of FFAs, a platform reaction of the oleochemical industry and a possible reaction in a novel 2-step (hydrolysis-esterification) biodiesel synthesis process using low cost feedstocks containing > 5-15% FFAs. The commercial production of free fatty acids (FFAs) in the oleochemical industry is typically carried out through the non-catalytic hydrolysis of triglycerides (TGs) using great amounts of superheated steam in large reactors made of expensive corrosion-resistant materials, making the process energy intensive and costly.

In the present study, TCp was used as a model compound for larger TGs and for mixtures (as are typical in fats and oils) in order to facilitate the kinetic study. The catalysts chosen for this study were SAC-13 and tungstated zirconia (WZ). SAC-13 is a Nafion®/silica nanocomposite catalyst, containing only Brønsted acid sites with an acid strength similar to concentrated H_2SO_4, as estimated by Hammett H_0 values ($-H_0 \sim 12$) [Harmer, 1996]. As a result, SAC-13 should catalyze TG hydrolysis - on a site basis - as effectively as H_2SO_4 [Liu, 2006a; Zimmermann, 2002]. The other catalyst chosen for this study, WZ, is a strong inorganic solid acid catalyst, which has been used successfully for a wide range of acid catalyzed reactions, such as dehydration, esterification, hydrocarbon isomerization and cracking [Hua, 2002; Lopez, 2005; Lopez, 2007b; Yori, 1997]. A three-phase reaction system configuration operating at atmospheric pressure was used in the first part of this study, with water being continuously pumped at a low flow rate into a slurry of the TG and solid catalyst at > 100°C. This three-phase configuration limited the amount of water in the reactor at any time, desirable since it is known that water has a deleterious poisoning effect on Brønsted acid catalysts [Liu, 2006a, 2006b]. A well-stirred semi-batch reactor was used to measure initial reaction kinetics and longer term conversion data since use of a fixed bed reactor for three-phase reaction studies would have been more problematic for measuring accurate kinetics. The well-stirred semi-batch reactor functions more-or-less like a CSTR during the initial conversion (<10%) measurements for the reaction. Catalyst reusability and regeneration studies for WZ and SAC-13 were also carried out to establish the applicability of these catalysts.

Based on the results to date, the characteristics of a catalyst play an important role in reaction selectivity, apparent activation energy, and deactivation. TCp conversion and TOF (turnover frequency or rate per site) values calculated for WZ and SAC-13 indicate that both catalysts have the capacity to successfully catalyze the TG hydrolysis reaction with 100% selectivity of the carboxylic acid side chains on the triglyceride to HCp (see Fig. 1). The WZ catalyst exhibited a 2-fold higher initial rate of TCp conversion than SAC-13 but with similar HCp yields at higher conversions. The surface characteristics of the catalysts were found to play an important role in catalyst selectivity and deactivation behavior (see Fig. 2). Catalyst recycling experiments showed continuous activity loss for both catalysts. Characterization of the used catalysts indicated that deactivation is likely caused by the strong adsorption of bulky reaction intermediates on the catalytic acid sites, blocking reactant accessibility. For WZ, recalcination in air was an effective regeneration method resulting in the recovery of 100% of its original activity. Regeneration by calcination was not possible for SAC-13 due to its temperature sensitivity. Methanol washing of used WZ and SAC-13 catalysts only partially regenerated catalyst activity.

Figure 1. Effect of temperature on the catalytic activity in the hydrolysis of TCp at a water flow rate of 5 μL/min using: (a) WZ and (b) SAC-13.

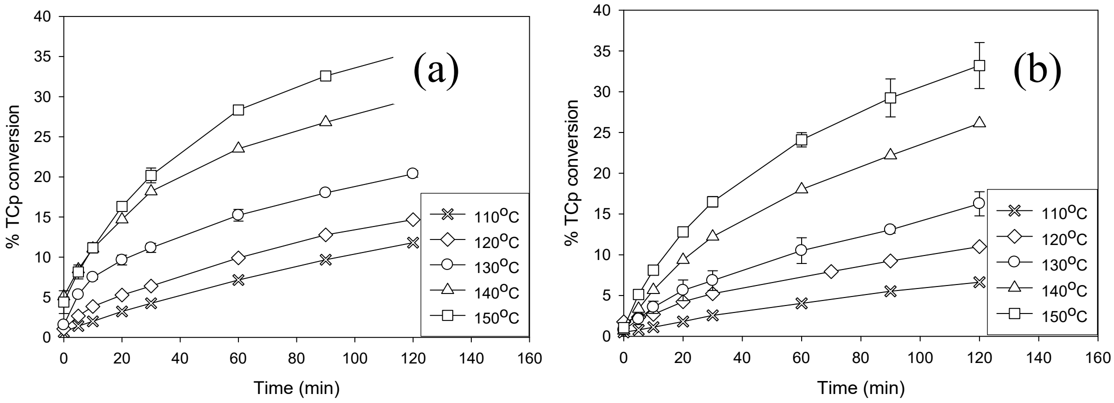
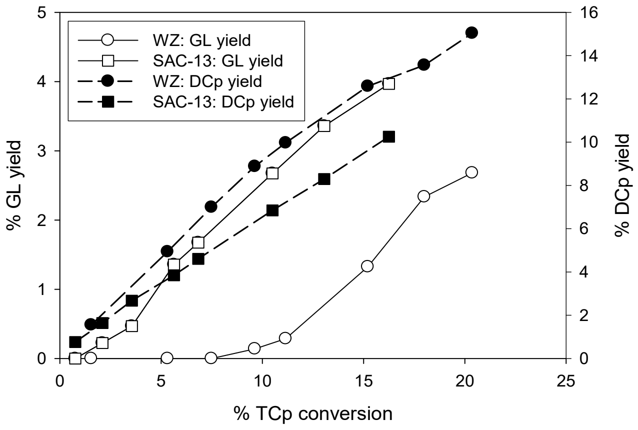


Figure 2. Effect of Surface Polarity on initial selectivity: GL and DCp yields in WZ and SAC-13 catalyzed TCp hydrolysis as a function of TCp conversion.



Since hydrolysis and transesterification offer a potential novel pathway to the synthesis of biodiesel from low quality feedstocks with high concentrations of FFAs and water, investigations of the mechanistic pathways in hydrolysis and in transesterification were carried out at a relatively high temperature (100–130°C) and at moderate pressures (120–180 psi) with tricaprylin and water for hydrolysis or tricaprylin and methanol for transesterification using a tungstated zirconia catalyst in a batch reactor. For similar reaction conditions [hydrolysis of TCp (H_2O:TCp = 1:1) and transesterification of TCp with methanol (MeOH:TCp = 1:1)], WZ exhibited similar rates of reaction for hydrolysis and transesterification. It was found that upon increasing the concentration of TCp, the reaction rates for both hydrolysis and transesterification increased at all conditions (see Table 1).

Table 1. Orders of reaction for WZ catalyzed hydrolysis of TCp and transesterification of TCp with methanol at 130°C for various reactant molar ratios.

Apparent order	α [c]			β [g]		
Water or MeOH:TCp ratio	0.3–0.8[d]	0.8–1.2[e]	1.2–1.7[f]	0.6–0.8[h]	0.8–1.2[i]	1.2–7.0[j]
Hydrolysis [a] $r_{initail} = C_{TCp}^{\alpha} C_{W}^{\beta}$	–	1.34	–	–	–1.15	–
Transesterification [b] $r_{initail} = C_{TCp}^{\alpha} C_{M}^{\beta}$	1.13	0.98	0.85	0.66	0.17	–0.72

In contrast, water inhibited the reaction rate of hydrolysis by poisoning the active sites. For transesterification, the apparent reaction order of methanol evolved from positive to negative as the concentration of methanol relative to TCp increased. Using a reaction model discrimination procedure, it was found that hydrolysis on WZ could be successfully described by an Eley-Rideal single site mechanism with adsorbed TCp reacting with bulk phase water. The mechanistic pathway for transesterification also seems to follow a similar mechanism, identical to the one previously proposed for transesterification on a solid acid catalyst (SiO_2-supported Nafion-SAC-13) at lower temperature (60°C).

4.0 Impact and Significance:

Typical methodologies for the current biodiesel production involve using homogeneous catalysts in batchwise single phase reactors, yielding products that require extensive downstream washing, a source of waste harmful to the environment. In addition, the glycerin byproduct obtained by the current technology can be contaminated by the catalyst residues, methanol, and other reaction byproduct, limiting its use to cheap heating fuel that sells for as low as 1-2 cents a pound (comparing with a market price of 98 cents/pound for a cleaner glycerin). Utilization of heterogeneous (solid) catalysts would eliminate environmental problems associated with liquid catalysts and could significantly reduce the number of reaction and downstream separation steps, allowing for more economical processing. As importantly, a cleaner glycerin byproduct would have a wider range of applications and could be sold for a better price. Use of lower quality feedstocks containing high levels of FFAs and water would improve the economics of biodiesel synthesis.

In the past 5 years, we and others have clearly shown the applicability of solid catalysts for the commercial synthesis of biodiesel, including economic advantages. The results of this study show that biodiesel synthesis can be carried out directly on animal fats and vegetable oils containing FFAs and water using solid acid catalysts. Triglycerides are converted in the presence of water impurities via 2 pathways to biodiesel: (1) hydrolysis followed by esterification of the resulting FFAs with MeOH (methanol) and (2) direct transesterification with MeOH. The original FFAs are directly converted to biodiesel via esterification with MeOH. While the presence of water is necessary to drive the hydrolysis reaction, it also acts as a poison on the solid acid causing the reaction rates of hydrolysis, transesterification, and esterification to decrease with higher concentrations of water. Based on the results of this investigation, biodiesel can be carried out in a one step process using a solid acid catalyst using lower grade feedstocks containing water and FFAs. The economics of doing this will be determined by the savings of not having to remove the water and FFAs from the feedstock and the decrease in the number of separation steps.

5.0 Publications (funded or partly funded by this project):

* "Transesterification of Poultry Fat with Methanol Using Mg-Al Hydrotalcite Derived Catalysts," ***Applied Catalysis A:General*** 331 (2007) 138-148 (Yijun Liu, Edgar Lotero, James G. Goodwin, Jr., and Xunhua Mo).
* "Activation and Deactivation Characteristics of Sulfonated Carbon Catalysts," ***Journal of Catalysis*** 254 (2008) 332-338 (Xunhua Mo, Dora E. López, Kaewta Suwannakarn, Yijun Liu, Edgar Lotero, **James G. Goodwin, Jr.**, Changqing Lu).

* “Esterification and Transesterification using Modified-Zirconia Catalysts,” ***Applied Catalysis A:General*** 339 (2008) 76-83 (Dora E. López, James G. Goodwin, Jr., David A. Bruce, Satoshi Furuta).

* “Stability of Sulfated Zirconia and the Nature of the Catalytically Active Species in the Transesterification of Triglycerides,” ***Journal of Catalysis*** 255 (2008) 279-286 (Kaewta Suwannakarn, Edgar Lotero, James G. Goodwin Jr., and Changqing Lu).

*“Simultaneous Free Fatty Acid Esterification and Triglyceride Transesterification Using a Solid Acid Catalyst with *In-Situ* Removal of Water and Unreacted Methanol,” ***Industrial & Engineering Chemistry Research*** 48 (2009) 2810-2818 (Kaewta Suwannakarn, Edgar Lotero, Kanokwan Ngaosuwan, and James G. Goodwin, Jr.).

*“Hydrolysis of Triglycerides using Solid Acid Catalysts,” ***Industrial & Engineering Chemistry Research*** 48 (2009) 4757-4767 (Kanokwan Ngaosuwan, Edgar Lotero, Kaewta Suwannakarn, James G. Goodwin, Jr., and Piyasan Praserthdam).

*“Reaction kinetics and mechanisms for hydrolysis and transesterification of triglycerides on tungstated zirconia,” ***Topics in Catalysis***, in press (2009) (Kanokwan Ngaosuwan, Xunhua Mo, James G. Goodwin Jr., and Piyasan Praserthdam).

6.0 Outside funding:

Project Title	**Funding Agency**	**Amount of Res. $**	**Dates**
FUNDED			
"Heterogeneous Catalyst Development for Biodiesel Synthesis" – **PI** (with D. Bruce, RTI, Süd-Chemie, Biodiesel Industries)	USDA	$894,203	10/1/03-9/30/07
"Biodiesel Synthesis from Animal Derived Fats using Heterogeneous Catalysis" **– PI**	FPRF thru ACREC	$16,995	5/1/04-4/30/05
"Biodiesel Synthesis from Poultry Derived Fats Using Solid Acid Catalysis" YEAR 1 **- PI**	PP&FC of USPEA	$68,862	6/15/04-6/30/06
“The Use of Three Phase Reaction for Biodiesel Production from Simulated Animal Fat Feedstocks” - **PI**	ACREC	$15,000	3/22/06-3/21/07
“Biodiesel Synthesis from Animal Fats using Solid Catalysts: High Temperature Reaction I”- **PI**	ACREC	$25,487	7/1/07-6/30/08
“Biodiesel Synthesis from Animal Fats using Solid Catalysts: High Temperature Reaction II”- **PI**	ACREC	$34,854	7/1/08-6/30/09
PROPOSED			
“Ozone-Enhanced Chemical-Microbiological Synthesis of Fuels from Waste and Non-Food Biomass” – **PI** (with A. Greene, D. Bruce, and C. Kitchens)	NSF: EFRI-HyBi	$1,999,527	9/1/09-8/31/13

7.0 Future work:

This project wraps up the investigation of the kinetics and mechanistic pathways in solid acid catalyzed (using WZ) hydrolysis and transesterification in the temperature range of 100-130°C.

8.0 Acknowledgments:

ACREC, FPRF, Dr. Edgar Lotero, and Dr. Kaewta Suwannakarn.

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