

**FINAL REPORT**  
**Sept, 2005**

**Biodiesel Synthesis from Animal Derived Fats Using Heterogeneous Catalysis**

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**Duration of Project:** 12 months

## **Objective (s)**

- To investigate the use of strong solid acids (heterogeneous catalysts) for transesterification of triglycerides, compounds that constitute the main components of animal fats.
- To obtain preliminary data that will permit us to pursue more extensive research in the development of active solid catalysts for biodiesel synthesis.

## **Project Overview**

The synthesis of diesel fuel from biomass (biodiesel) provides an effective way for utilizing more effectively renewable resources, a means to recycle carbon dioxide, a way to convert vegetable oils and animal fats to a useful product, and produces a fuel that is biodegradable, non-toxic and has a low emission profile. Fats and oils are primarily made up of triglycerides, esters of glycerol (mono- and diglycerides) and free fatty acids (FFA) (carboxylic acids). Vegetable oils, and even more so animal fats, effectively cannot be used directly as diesel fuels due to their high viscosity, polymerization as a result of the reactivity of C-C double bonds that may be present, incomplete combustion, and coking. Animal fats have a more diverse composition than vegetable oils and are therefore more complex.

Alkali (either NaOH or KOH) can be used to catalyze the reaction of triglycerides with a simple alcohol (i.e., MeOH or EtOH) to form esters and glycerol. However, this reaction does not tolerate the presence of water or fatty acids. Fatty acids can be acid-catalyzed to esters by reaction with a simple alcohol in the presence of a strong acid such as sulfuric, phosphoric, or hydrochloric acid. However, use of such liquid acids pose environmental and corrosion problems. Little research has been done to develop solid acid catalysts for carrying out the esterification of fatty acids, especially with the goal to produce biodiesel. Acid catalysts are also active for transesterification of triglycerides. Some acid catalysts can etherify glycerol to a useful diesel component. Use of solid acid catalysts would eliminate the corrosion problem in process equipment and possibly could reduce the number of reaction steps required, would reduce separations required, would permit continuous processing, and would allow long-term use of the catalyst.

Research was conducted to investigate solid catalysts for use in the transesterification of triglycerides (TGs), compounds that constitute the main components of lipid feedstocks like animal fats. The research involved catalyst synthesis/modification/activation and reaction studies. Reaction studies focused on a model compound for TGs, triacetin, which is the smallest member of the triglyceride family, in order to measure precise reaction kinetics. Solid catalysts studied included acid catalysts such as a resin catalyst (Amberlyst-15), and tungstated zirconia (WZ), as well as base catalysts such as ETS-10 and MgO in order to compare solid acid vs. solid base catalyst performances. Here, the activation and deactivation profiles of these solid catalysts are shown and some discussion has been given to probable deactivation causes.

## **Impact and Significance**

To be economically viable and to compete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve as few reaction steps as possible and to minimize separation steps. This could be easily accomplished with the use of heterogeneous (solid)

catalysts. However, the use of heterogeneous catalysts for the commercial production of biodiesel has been overlooked because of a lack of research and understanding of the main variables affecting solid catalysts activity for biodiesel forming reaction such as transesterification and esterification. The aim of this research has been to fill in part the knowledge gap that exists in the area of heterogeneous for biodiesel synthesis.

## **Project Activities**

- **Methodology**

- **Materials**

All experiments were carried out using commercially available catalysts. The microporous materials ETS-10 (Na, K) (6.14 wt% Na and 5.22 wt% K) was obtained from Engelhard (Iselin, NJ). Magnesium Electron Inc. (MEI, Manchester, UK) provided the tungstated zirconia (13.4 wt% W). Amberlyst-15 (with an acid site concentration of 4.9 meq/g) and pure MgO were purchased from Sigma-Aldrich. Sodium hydroxide (98.9 wt %) and liquid sulfuric acid (98 wt %) were purchased from Fisher Scientific.

A mixture of reactant/products (4 wt% glycerol, 26 wt% monoacetin, 45 %wt diacetin, and 25 wt% triacetin), glycerol (99 wt%), methyl acetate (99 wt%), triacetin (99 wt%) and anhydrous methanol (99 wt%) were purchased from Fisher Scientific for GC/MS calibration and reaction experiments. Toluene and 2-isopropanol were purchased from Fisher Scientific and used as an internal standard and a solvent (for GC analysis), respectively. Reactants and standards were high purity (anhydrous) chemicals and used as received.

- **Solid Catalyst Pretreatment**

Solid catalysts were pretreated for 3 h in flowing UHP air using the conditions summarized in Table 1 except for Amberlyst-15, which was dried under vacuum. After pretreatment, the catalysts were crushed and sieved ( $\geq 40$  mesh) to minimize internal diffusion resistance.

- **Catalyst Characterization**

BET surface area ( $S_{\text{BET}}$ ) analyses were conducted for every solid catalyst after its respective calcination or dehydration. Prior to surface area analysis, the catalyst samples were degassed at  $10^{-3}$  mm Hg for 3 h with the exception of Amberlyst-15 (degassed overnight). These adsorption measurements were carried out using UHP  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  in a Micromeritics ASAP 2010.

Information about catalyst composition was either obtained from the catalyst supplier or determined by elemental analysis using ICP or AA techniques (Galbraith Laboratory, Knoxville, TN).

$\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD spectra were recorded using an Altamira AMI-1 to characterize the site adsorption distribution for acid and base catalysts, respectively. A 0.3 g sample of catalyst was

heated to 315°C in 30 ml/min of helium for 1 h to remove adsorbed impurities. Next, the sample was cooled to room temperature and saturated for 2 h using 100 ml/min of either 10% NH<sub>3</sub>/He or 10% CO<sub>2</sub>/He. The system was flushed for 2 h with helium (30 ml/min) at room temperature and then the temperature was increased to 60 °C at a rate of 2 °C/min where it was held for 4 h to eliminate physisorbed NH<sub>3</sub> or CO<sub>2</sub>. For TPD of the probe molecules, the temperature was increased to 600 °C at a rate of 10 °C/min. A TCD detector was used to measure the NH<sub>3</sub> or CO<sub>2</sub> desorption profile. A blank study of the TPD ramp was obtained in order to account for the background.

Monochromatic powder X-ray diffractograms were recorded in the 5° to 90° 2 $\theta$  range for WZ, ETS-10 (Na, K), and MgO using a XDS 2000 (Scintag Inc.) instrument. The diffractometer used Cu K $\alpha$  radiation with a wavelength of  $\lambda = 1.54 \text{ \AA}$ .

Table 1: Catalyst pretreatment conditions

Catalyst	Pretreatment Temperature (°C) and Time (h)
Amberlyst-15	90 <sup>a</sup> (3h)
WZ	700 (1h)
ETS-10 (Na, K)	500 (2h)
MgO	600 (2h)

<sup>a</sup> In a partial vacuum of 17 mmHg

### ○ Reaction Studies

#### ▪ Reaction Systems

All reaction experiments used a mixture consisting of anhydrous methanol and triacetin in a 6:1 (methanol: triacetin) initial molar ratio (2 x stoichiometry for complete conversion). Prior to reaction, a sample of the reactant mixture was analyzed in order to obtain initial concentrations. Catalyst loading (wt cat/wt reaction mixture) was 2 wt%, 0.5 wt%, and 0.025 wt% for solid catalysts, H<sub>2</sub>SO<sub>4</sub>, and NaOH, respectively. Reactions were carried out in 50 ml flasks in a Innova Reactor Shaker System (model 4080) with constant temperature bath.

#### ▪ Catalyst Comparison and Deactivation Studies

Catalyst activity studies were carried out in the Innova Reactor Shaker System set at 150 rpm and 60 °C. The catalyst was quickly added to approximately 2 ml of the triacetin/methanol reaction mixture contained in a stoppered 50 ml Erlenmeyer flask. NaOH was previously dissolved in approximately 10 wt% of the required methanol and then added to the appropriate reactant mixture. Sibling sample flasks were prepared for each catalyst and the reaction quenched at different times in order to follow the progress of the reaction. The reaction mixture samples were centrifuged prior to analysis, to separate the solid catalyst from the reactant mixture and to stop the reaction. Because

of the small amount of reactant used in the flask, the reacting mixture was well mixed. The reaction experiments were all repeated in order to estimate the standard deviation, which was approximately  $\pm 2\%$  triacetin conversion.

For the catalyst deactivation studies, reaction was started as previously described, except that 10 ml of the triacetin/methanol reaction mixture was used. After 2 h of reaction, the reaction mixture was centrifuged, the catalyst recovered, and the reaction mixture analyzed. A new reaction solution was mixed with the recovered catalyst, and a new reaction cycle was started. This process was repeated several times, and decreases in catalytic activity with each cycle were recorded.

#### ▪ **Method of Analysis**

Concentrations for reaction samples were determined using an HP 6890 gas chromatograph equipped with an HP 5973 mass selective detector. The collection and analysis of data was carried out using HP chemstation software. An Alltech Econo-Cap EC-WAX fused silica capillary column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ) was used for analyte separation. UHP helium was used as the carrier gas. Reaction samples were diluted with 2-propanol using 1:2.2 v/v (reaction mixture/2-propanol) and a toluene internal standard using 1:16 v/v (toluene/2-propanol). One microliter of this mixture was injected into the column using the splitless mode option. The injector and detector temperatures were set to 255°C and 280°C, respectively. The oven temperature program was held at 50 °C for 3 min, then ramped up at a rate of 90°C/min to 210°C and held there for 9 min.

#### • **Experimental Results**

##### ○ **Catalyst Characterization**

XRD experiment results showed a tetragonal structure for the zirconium oxide present in WZ calcined at 700°C. No XRD structures were observed involving  $\text{WO}_x$  crystal formation. Diffraction patterns for ETS-10 (Na, K) and MgO were in accordance to published literature data.

Table 2 provides a summary of physical properties for the catalysts evaluated in this study, determined by BET, elemental analysis, and TPD.

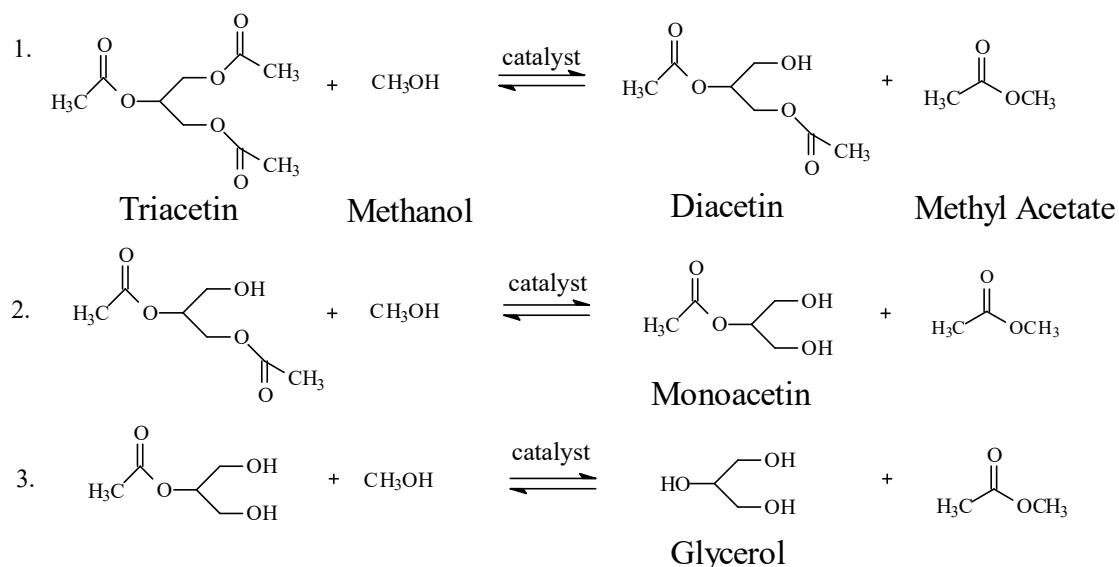
Table 2: Physical properties of catalysts studied

Catalyst	Description	Parameter		
		S <sub>BET</sub> (m <sup>2</sup> /g)	Elemental analysis (wt %)	Site concentration (μmol/g)
<b>ACIDS</b>				
Amberlyst-15	Sulfonated polystyrene-based ion-exchanged resin Dry average pore diameter: 250 Å <sup>a</sup> Dry Porosity: 0.3 cc/g <sup>a</sup>	37.8 ± 2.6	13.5% (S)	4210 <sup>b</sup>
WZ	Tungsta modified zirconia Strong acid catalyst	89.2 ± 1.4	13.42% (W)	54 <sup>c</sup>
H <sub>2</sub> SO <sub>4</sub>	Concentrated strong acid Density: 1.84 <sup>a</sup>	NA	98% (H <sub>2</sub> SO <sub>4</sub> ) <sup>a</sup>	NA
<b>BASES</b>				
ETS-10 (Na, K)	Titanosilicate with Na and K cations	226.6 ± 8.6	6.14% (Na), 5.22% (K)	-
MgO	Magnesium oxide	0.45 ± 0.07	99.9% MgO <sup>a</sup>	50 <sup>c</sup>
NaOH	Pellets Strong base catalyst	NA	99% NaOH <sup>a</sup>	NA

### ○ Reaction Chemistry

Transesterification of TGs with alcohols proceeds via 3 consecutive and reversible reactions where the FFA moieties combine with the alcohol to produce a fatty acid alkyl ester, di- and monoglyceride intermediates, and finally a glycerol by-product. Figure 1 shows the reactions for the transesterification of triacetin with methanol. The stoichiometric reaction requires one mole of triacetin and 3 moles of methanol to produce 3 moles of methyl acetate and 1 mole of glycerol. Figure 2 shows the evolution of the reaction with time for ETS-10 (Na, K).

### Stepwise reactions:



### Overall reaction:

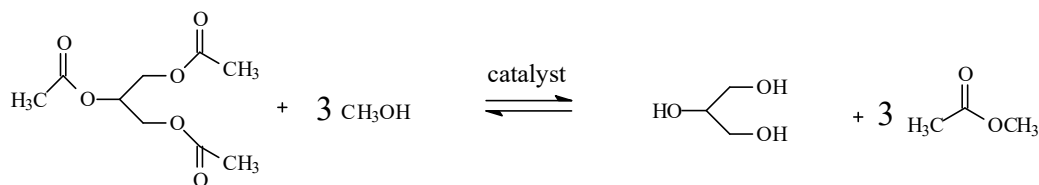


Figure 1: Transesterification reactions of triacetin with methanol.

#### ○ Relative Catalyst Activity

All catalysts were studied during the transesterification of triacetin and methanol at 60°C over an arbitrary time period of 8 h. For all reactions, the initial molar ratio of reagents was 6:1 (methanol: triacetin), which is the suggested proportion for based-catalyzed transesterification (Freedman et al., 1984). Previous results have shown that higher molar ratios are needed in acid-catalyzed transesterification (Mittelbach et al., 1996; Siler-Marinkovic and Tomasev, 1998) on account of slower reaction rates. However, in this study, the same reagent molar ratio was maintained for all catalysts for comparison reasons. A blank reaction study showed the absence of autocatalysis at this temperature (60°C).

Figure 2 summarizes base catalyst activity results. The homogenous catalyst, NaOH, exhibited the highest activity. For instance, transesterification of triacetin with methanol using NaOH was so fast under our experimental conditions that, on the time scale used, the first data point was near equilibrium conversion. The highest activity (by weight) among solid catalysts was observed for the basic form of ETS-10, achieving approximately 99% triacetin conversion in 8h.

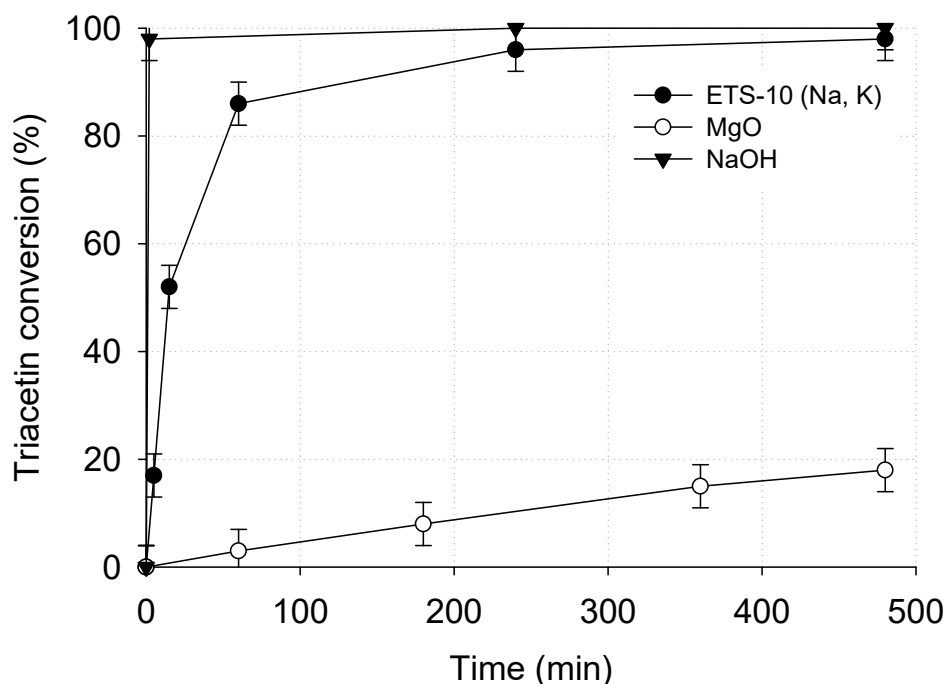


Figure 2: Relative activities of base catalysts for transesterification of triacetin with methanol using a 6:1 (methanol: triacetin) initial molar ratio and  $60 \pm 1^\circ\text{C}$  (NaOH = 0.025 wt%, solid bases = 2 wt%).

Unexpectedly, the catalytic activity of MgO was very low compared to ETS-10. Most probably, the low surface area of the MgO utilized in this study ( $\sim 0.45 \text{ m}^2/\text{g}$ ) and the low temperature employed ( $60^\circ\text{C}$ ) for reaction experiments were the reasons for this result.

On the other hand, the catalytic activity observed for acid catalysts was lower than for both NaOH and ETS-10 base catalysts (Figure 3). This result is in agreement with earlier reports showing how reaction rates for soybean transesterification with methanol using sulfuric acid were 4000 times slower than those observed for the same reaction using NaOH (Freedman et al., 1986; Mittelbach et al., 1996). Among acid catalysts the order of reactivity was:  $\text{H}_2\text{SO}_4 > \text{Amberlyst-15} > \text{WZ}$  on a weight basis.

#### o Deactivation Studies

Unlike homogenous catalyst, heterogeneous catalysts have the potential to be recovered, regenerated and reused. Thus, besides measuring catalyst activity, studies involving the measurement of catalyst activity loss and reusability have to be conducted in order to determine the full potential that solid catalysts have to carry out biodiesel forming reactions such as transesterification of triglycerides. Figure 4, 5 and 6 shows results for five successive 2 h reaction cycles for ETS-10 and the two solid acid catalysts used in this study. After all reaction cycles were



completed, catalysts were washed with methanol, dried overnight at 70 °C, and active species loadings re-analyzed.

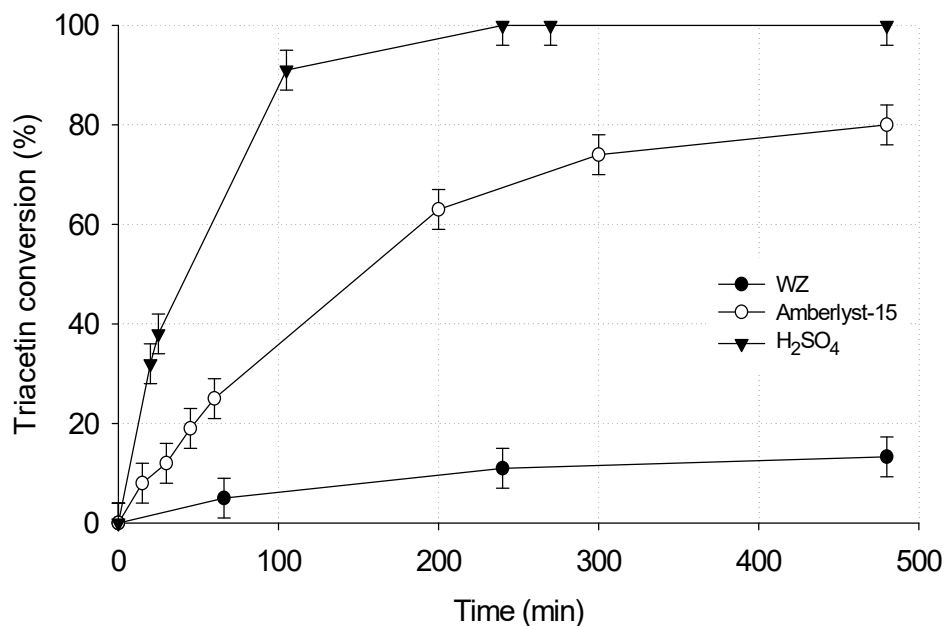


Figure 3: Relative activities of acid catalysts for transesterification of triacetin with methanol using a 6:1 (methanol: triacetin) initial molar ratio and  $60 \pm 1^\circ\text{C}$  ( $\text{H}_2\text{SO}_4 = 0.25 \text{ wt}\%$ , solid acids = 2 wt%).

According to Figure 4, ETS-10 (Na, K) exhibited a significant drop in activity from 90% triacetin conversion (at 2 h) in the first cycle to 28% triacetin conversion (at 2h) in the fifth cycle. In addition, a new composition of 3.45 wt% Na and 2.71 wt% K was found for the spent ETS-10 material, corresponding to only 56 wt% and 55 wt% of the original alkali content, respectively. When the reaction with ETS-10 (Na, K) was allowed to proceed uninterrupted for 24 h, it was found that the sodium content of the reaction liquid was 172 ppm (14 wt% of the Na originally present on the catalyst). These observations support the hypothesis that a homogeneous-like mechanism is actually responsible for the catalytic activity observed for reactions using this material. For instance, in a homogeneous-like mechanism alkali methoxide species leached out (Figure 7) from the porous framework of the titanosilicate to the bulk solution to carry out homogenous catalyzed reactions (Lotero, 2005). This result also means that in order to maintain the high activity observed with ETS-10 during the first cycle, a catalyst regeneration cycle has to be applied to this material; otherwise, catalytic activity will seriously decreased with catalyst use.

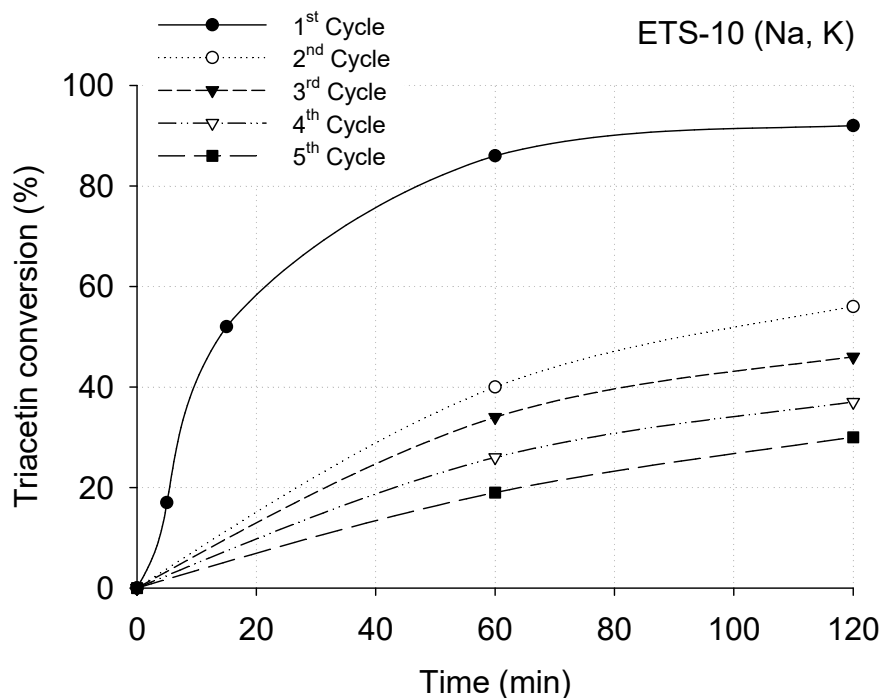


Figure 4: Catalyst deactivation for ETS-10 during multiple reaction cycles for the transesterification of triacetin and methanol using a 6:1 (methanol: triacetin) initial molar ratio:  $T = 60 \pm 1^\circ\text{C}$  and 2 wt% catalyst.

Amberlyst-15 and WZ exhibited decreases in rate of triacetin conversion of 40% and 44%, respectively, after 5 reaction cycles of 2 h each (Figure 5 and 6). New compositions of 12.42% S for Amberlyst-15 and 12.71% W for WZ were found for spent catalysts, representing 92% and 95% of the original values, respectively. Since the concentration of the species related to the active sites did not change significantly (considering the experimental error), it is probable that the observed catalyst deactivation was the result of site blockage by adsorbed intermediates or product species that were considerably more polar than the original reagents. Coking at this low temperature ( $60^\circ\text{C}$ ) is unlikely to be a major reason for deactivation. Therefore, a simple catalyst calcination to remove irreversible adsorbed species in WZ and a more efficient methanol washing of polar species on Amberlyst-15 should in principle help the regeneration of surface active sites in these catalysts, making possible their reuse for multiple catalytic runs.

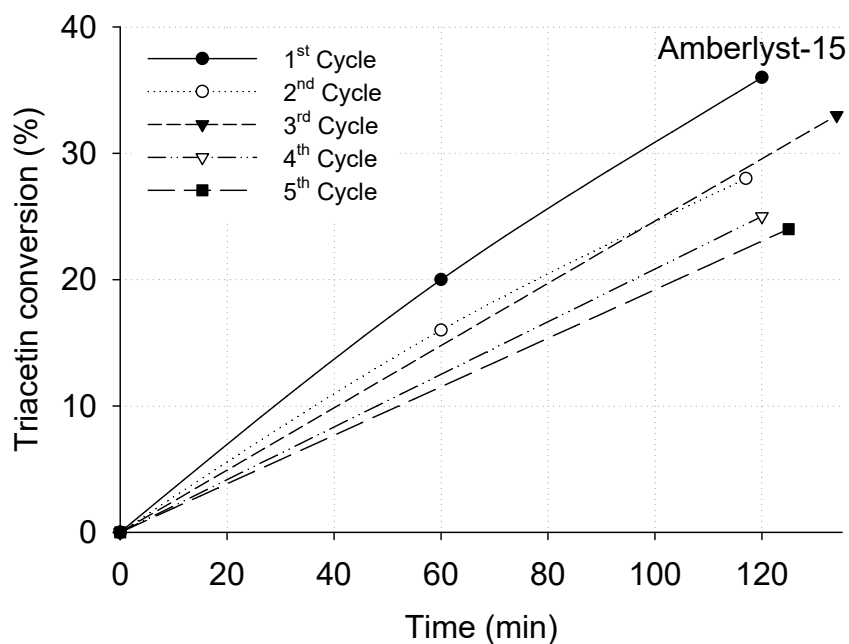


Figure 5: Catalyst deactivation for Amberlyst-15 during multiple reaction cycles for the transesterification of triacetin and methanol using a 6:1 (methanol: triacetin) initial molar ratio:  $T = 60 \pm 1^\circ\text{C}$  and 2 wt% catalyst.

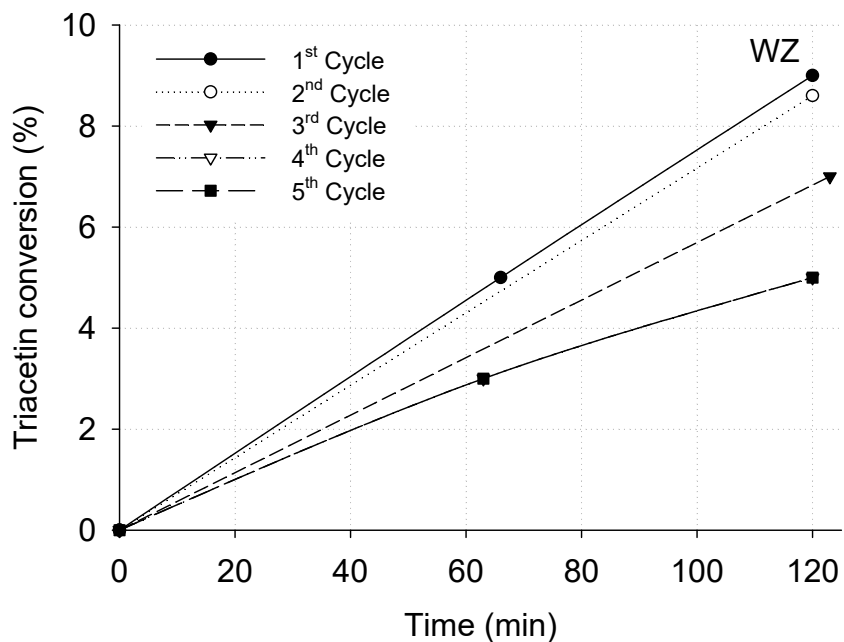


Figure 6: Catalyst deactivation for WZ during multiple reaction cycles for the transesterification of triacetin and methanol using a 6:1 (methanol: triacetin) initial molar ratio:  $T = 60 \pm 1^\circ\text{C}$  and 2 wt% catalyst.

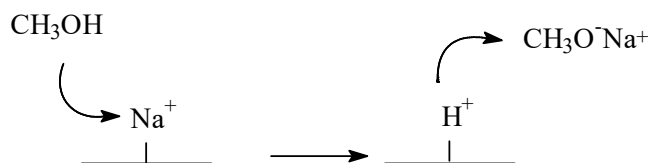


Figure 7: Hypothesized formation of methoxide active species with a ETS-10 (Na, K) catalyst given rise to a homogeneous-like mechanism for the transesterification of triacetin with methanol.

## Summary of Results

The following conclusions can be drawn from this study: (1) homogeneous catalysts were more active than heterogeneous ones on a weight basis because of the greater number of active sites, (2) ETS-10 exhibited probable homogeneous catalysis as the cations were leached out, (3) the solid acids studied underwent less deactivation than ETS-10 (Na, K) under these experimental conditions, (4) Amberlyst-15 and WZ showed reasonably good activities at this moderate temperature, suggesting that they could constitute alternatives to homogeneous catalysts without the drawbacks of corrosion, difficulty in handling, and once through use provided more mass of catalyst is used. In addition, use of these solid catalysts would permit the application of higher temperatures (to greatly increase reaction rate) without the need for high pressures since such catalysts can easily function in 3-phase situations.

## Publications

Dora E. Lopez, James G. Goodwin Jr., David A. Bruce, and Edgar Lotero, "Transesterification of Triacetin with Methanol on Solid Acid and Base Catalysts." Submitted to *Applied Catalysis A: General*, March/2005. [Supported in part by this funding].

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