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## Mechanochemical Synthesis of Fuels from Sustainable Sources Utilizing Solid Catalysts

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MECHANOCHEMICAL SYNTHESIS OF FUELS FROM SUSTAINABLE SOURCES  
UTILIZING SOLID CATALYSTS

by

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B.A. Chemistry, Ferris State University, 2008

A dissertation submitted in partial fulfillment of the requirements  
for the Doctor of Philosophy  
in the Department of Chemistry  
in the College of Sciences  
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## ABSTRACT

Mechanochemistry requires less solvents which results in less waste generation. The question becomes can we apply mechanochemistry to current chemical reactions and reduce the generation of waste. This process can be simple or can be very extensive resulting in the generation of large amounts of waste and very little product. A significant advantage of mechanochemistry is the reduced need for solvents that would be common place for reactions. Mechanochemistry transfers energy to reagents via impacts from milling media. Energy can be transferred to the reagents no matter their state-of-matter. Much of the current studies in mechanochemistry today are done using reagents in their solid-state, organic or inorganic compounds. Mechanochemistry is not limited to just solid-state, reactions in liquid-state and even gas-state are possible to utilize for reagents.

The transition to biofuels as a means of curbing the emissions of greenhouse gases has given rise to several questions such as what to use as the feedstock and which process is most cost-efficient. Chapter 2 of this research focused on another question that being the interactions between biofuels and different materials. This research performed a long-term study on the interaction between polymers and biofuels. Similar research has been conducted, but where the difference lies is that the polymer selected was given shape, o-ring, to perform a specific function, stop leaks. What was observed is that after prolonged exposure to biofuels the o-ring decreased in volume, which would result in leaking of fuel. To counter this degradation two different aromatic compounds were tested by dissolving them into the biofuels. With as little as 1% w/w of aromatic

compound the decrease in volume observed in the biofuels without aromatic compounds was not observed.

Propane is commonly used fuel for heating homes, cooking, to fueling vehicles. Currently the primary source of propane is from oil refining. Chapter 3 of this research details the synthesis of propane from biomasses, that would normally be discarded, utilizing mechanochemistry. The methods used reduced the need for solvents and unlike other methods currently employed to make propane, no toxic materials were generated. The starting material was cassava pulp, a biomass high in cellulose. The cellulose was converted to simple sugars, which were then converted to 1,3-dihydroxyacetone, and then finally converted to propane. Each step of this process was performed mechanochemically, reducing the need for solvent, each catalyst was naturally occurring and easily recyclable. The catalyst used for the conversion to propane was itself synthesized mechanochemically with no solvents required.

One aspect of green chemistry is the reduction of waste generation from chemical reactions/process. Another aspect of green chemistry is finding new catalysts that are less environmentally damaging. Mechanochemistry has been proven to reduce the need for solvents, or remove the need all together, and transitioning to solid catalysts can reduce the solvent need to extract the catalyst. Chapter 4 of this research combined mechanochemistry and the use of a solid catalyst for the synthesis of oil of wintergreen, a common esterification reaction. Esterification reactions are common in academia, industry, and pharmacology, and as a result large amounts of solvents are needed for wash and separation steps. Utilizing both mechanochemistry and solid catalysts the amount of solvent can be reduced.

Similar to esterification transesterification is a common chemical reaction that is performed in academia, industry, and pharmacology typically catalyzed with bases i.e. sodium hydroxide. The advantage of catalysts such as these is that the reactions are very quick with high yields. The disadvantage to using catalysts such as sodium hydroxide is that they cannot be recycled. Chapter 5 focused on the synthesis of biodiesel, which is commonly synthesized via transesterification of triglycerides with a short-chain alcohol. Transitioning to solid catalysts would allow for the recycling of the catalyst, which would reduce waste generation. Another focus was the transitioning from methanol to ethanol. Fatty acid *methyl* esters are formed from the transesterification of a triglyceride with methanol and is the more commonly synthesized biodiesel as it requires less energy than longer chain alcohols, thus making it faster as well. However, methanol is toxic to people and the environment, where ethanol is safer. The focus of this research became finding a solid catalyst that would promote transesterification using ethanol as the alcohol via mechanochemistry.

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## LIST OF SYMBOLS

$\lambda$	Wavelength
$\theta$	Angle
$B_N$	Boron substitution for nitrogen
$V_B$	Boron vacancies
$V_N$	Nitrogen vacancies
$E_{XC}$	Exchange-correlation energy
$E_{GGA}^X$	Semi-local exchange function from the revised generalized gradient approximation
$E_{lc}^C$	Local correlation energy
$E_{nlc}^C$	Nonlocal correlation energy
$E_{BE}$	Binding energy
$E_{System}$	Total energy of the molecule on the substrate
$E_{Mol}$	Total energy of the molecule
$E_{BN}$	Total energy of the defective $h$ -BN
$\Delta n(\vec{r})$	Charge density redistribution of the system
$n_{system}(\vec{r})$	Charge density of the system
$n_{Mol}(\vec{r})$	Charge density of $C_2H_2$ molecule
$n_{BN}(\vec{r})$	Charge density of BN sheet with defect

## LIST OF ACRONYMS

AFM	Atomic force microscopy
ATR	Attenuated total reflectance
BPR	Ball-to-powder ratio
CL	Cathodoluminescence
CPCD	Confined-plume chemical deposition
CTAB	Cetyltrimethylammonium bromide
CVD	Chemical vapor deposition
DABCO	1,4-diazabicyclooctane
DEM	Discrete element modeling
DFT	Density functional theory
DMF	Dimethylformamide
DP	Degree of polymerization
EDS	Energy-dispersive X-ray spectroscopy
FFT	Fast Fourier transform
FLP	Frustrated Lewis pairs
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
GC/MS	Gas chromatography / mass spectroscopy
GGA	Generalized-gradient approximation
HAADF	High-angle annular dark-field
HDPE	High-density polyethylene
HMF	5-Hydroxymethylfurfural
ISE	Indentation size effect
PAI	Polyamide-imide
PAW	Projected augmented wave



PIXE	Particle-induced X-ray emission
PTFE	Polytetrafluoroethylene
QCM	Quartz crystal microbalance
REE	Rare-earth elements
RIR	Reference intensity ratio
RPM	Rotations per minute
SA	Surface area
SEM	Scanning electron microscopy
SHS	Self-propagating high temperature synthesis
SIMS	Secondary ion mass spectrometry
SPS	Spark plasma sintering
SSA	Specific surface area
SSM	Self-propagating solid-state metathesis
SSR	Solid-state reaction
STEM	Scanning tunneling electron microscopy
SW	Stone-Wales
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UHPA	Urea hydrogen peroxide adduct
UV	Ultraviolet
VASP	Vienna Ab initio simulation package
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

# CHAPTER 1 : MECHANOCHEMISTRY

## 1.1 Introduction

What is Mechanochemistry? The simplest definition is using mechanical energy to drive a chemical reaction forward. All chemical reactions require energy to go forward, often this energy is referred to as the activation barrier. Some reactions happen spontaneously, others require the input of energy. No matter what the chemical reaction, if the activation barrier is not overcome then the reaction will not proceed.

In traditional, wet chemistry, the energy needed to overcome the activation barrier can be applied by heating or stirring the reaction. Heating a reaction is done through the use of equipment such as heating mantles, hot plates, microwaves, or even hot water bathes. Stirring is as simple as a person using a stirring rod or using a magnetic stir bar with stirring plate. This is as opposed to mechanochemistry where “chemical transformations [are] induced by mechanical means, such as compressions, shear, or friction.”<sup>1</sup> The mortar and pestle will apply these forces and has been used since the stone age.<sup>1</sup> Today a high speed ball mill (HSBM) is capable of applying these forces to chemical reagents at a much faster rate.

In the past few decades mechanochemistry has seen a renewed interest as a viable alternative to making many current reactions more environmentally friendly by reducing their extensive use of solvent. This becomes extremely important for industries such as pharmaceutical companies as standard organic reactions require the use of solvent. Solvent chemistry requires the storage of the solvent before and after reactions are performed. Less solvent results in less storage of the solvent

and waste generated from the multiple washings that many chemical reactions require. With the reduced need for solvent, mechanochemistry provides a more environmentally friendly means of synthesis.

## 1.2 History

As mentioned above the mortar and pestle have been used since the stone-age, but there is no definitive documentation on when the first mechanochemical syntheses were started. There are some processes that have been performed throughout history that one can infer are mechanochemical. The mortar and pestle was utilized for alchemy, the processing of grain, and the making of black powder, each examples of milling and grinding. Today it is understood that these processes are mechanochemical in nature.

Michael Faraday and Matthew Carey Lea are considered to be the founders of modern mechanochemistry, both publishing several papers that describe chemical reactions that occur through mechanical processing. Matthew Carey Lea is best known for his observations while working with silver halides and mercuric chloride. While grinding silver halides and mercuric chloride in a mortar and pestle he observed the materials decomposed. The same reagents either melted or sublimed without any decomposition when heated.<sup>2</sup> From these observations one can reason that mechanochemistry offers chemical pathways not available from heating. Michael Faraday observed that grinding silver chloride with select transition metals (Zn, Sn, Cu, or Fe) reduced silver.<sup>3</sup> Faraday referred to the use of mortar and pestle as the “dry way.”

Mechanochemical activation is not limited to just solids or inorganic compounds, there are several organic reactions that occur via mechanochemistry. Some of the possible reactions include esterification and transesterification, Dieckmann condensation<sup>4</sup>, reduction of aldehydes and ketones<sup>5</sup>, and Grignard reactions. The experiments performed by Lea showed that different pathways occurred during grinding, this has also lead to the discovery of compounds and materials that are only obtained from mechanochemical processing. Fullerenes have a low solubility in common organic solvents, but when mechanical forces such as friction, compression, and shearing the fullerene becomes more reactive. In fact the synthesis of the C120 fullerene is only obtained via mechanochemistry.<sup>6</sup>

### 1.3 Types of Milling Equipment

Equipment utilized for milling varies depending upon the desired synthesis to be performed. Several factors must be taken into account: type of reaction, physical state of the reagents, volume reagents occupy, even the speed of the mill becomes a factor. Each type of mill applies force to the reagents in a different mode. An example of this are the differences between the rolling mill and attrition mill. Both the rolling mill and attrition mill transfer energy to the reagents via bearing impact, but the rolling mill uses gravity to generate kinetic energy and the attrition mill uses a “tree” to stir the bearings at a selected RPM. The advantage the attrition mill has over the rolling mill is the quantity of reagents and amount of force generated. The rolling mill is a scaled down version of the pebble mill and the amount of force generated from each impact is less than the shaker or attrition mills. This example shows just a few of the factors that must be taken into

account when selecting the apparatus for the desired reaction. Insert difference between rolling mill vs attrition mill include where each would be ideal.

**Table 1.**Types of mills, the amount of force each can produce, how the energy is applied, mass each can carry, and advantages of each.

<b>Mill</b>	<b>Application of Force</b>	<b>Kinetic Energy (N)</b>	<b>Mass Range</b>	<b>Advantages</b>
<b>High Speed Ball Mill</b>	Compression, Shear	3053	2-20 g	High Energy, Fast
<b>Planetary</b>	Compressions, Shearing	n/a	250 g	Increased Scale
<b>Attrition</b>	Shearing, Compression, Tumbling	3881	1-100 kg	Large Scale, Temperature and Atmosphere Control
<b>Rolling/Pebble</b>	Tumbling	329	➤ 1000 kg	Industrial Scale

### *1.3.1 High Speed Ball Mill*



**Figure 1. SPEX dual mill. Mills two vials at a time. Vial is fastened into place inside mill. Mill moves vial at 20 Hz.**



Figure 2.SPEX single mill. Similar to dual mill, except only one vial at a time.



**Figure 3. Standard steel vial with lid, bearings, and o-ring. Vial is used in shaker mill and can hold dry or liquid reagents.**

Often referred to as a shaker mill, the high-speed ball mill (HSBM) operates by moving a vial at almost 20 Hz, in a figure eight motion. Inside the vial are bearings that impact the sides of the vial and each other, while moving at speeds up to 5 m/s. Each impact transfers kinetic energy to the chemical reagents, driving the chemical reaction forward. The most commonly used shaker mills are made by SPEX. Figure 1 shows the SPEX 8000D dual mill which allows the user to mill two vials of similar mass at the same time. Figure 2 shows the SPEX 8000M single mill which is for the milling of a single vial without the need of a second vial to balance the milling arm. Figure 3 displays a steel vial, with bearings, lid, and o-ring (used to maintain atmosphere inside vial).



The HSBM is very practical for initial cursory reactions that are smaller in-scale and typically less than 4 grams per vial. These investigative reactions can be either completely new syntheses or an attempt to use mechanochemistry to perform traditional chemical reactions. The amount of energy the HSBM can generate allows the chemist to perform an otherwise long reaction quickly, which provides the data needed to determine if scaling-up is feasible. By utilizing the HSBM the chemist can determine if a reaction will yield the desired product without wasting large amounts of reagents.

### 1.3.2 Planetary Mill



**Figure 4. Planetary mill. Allows for a medium scale-up of reactions. Energy applied to reagents via grinding of bearings against vial wall.**



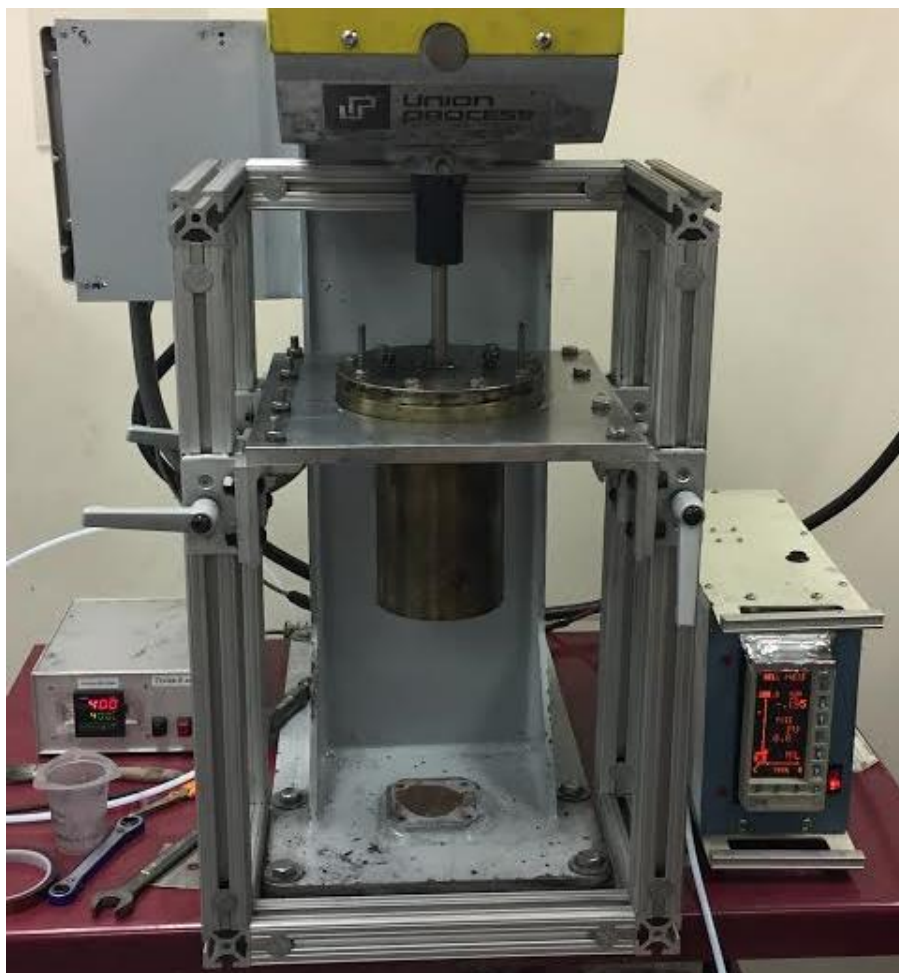
**Figure 5.Vial for Planetary mill**

Planetary mill in Figure 4 is manufactured by Fritsch and allows the chemist to control the speed of rotation. By adjusting the speed of rotation the amount of force generated can be decreased or increased depending upon the needs of the reaction. The vial is secured onto a rotating disk, and as the disk moves in one direction the vial (Figure 5) rotates in the opposing direction. The energy is transferred to the reagents via friction from grinding of the media against the vial. Energy is also transferred via collisions of media with vial.

Planetary mills are often used for processing larger amounts of material into ultrafine powders, but they can also be used for mechanochemical reactions. The advantage of the planetary

mill over the shaker mill is predominantly the amount of material that can be processed. The shaker mills described above (Figures 1 and 2) are limited to less than twenty grams per vial, where the planetary mill can hold up to one hundred grams of material. The energy is transferred to the reagents as the milling media grinds the reagents against the reactor wall. Another advantage of this model planetary mill

### *1.3.3 Attrition Mill*



**Figure 6. Attrition mill. Allows for scaled-up reactions, liquid-liquid, solid-liquid, and even liquid-gas reactions. Applies kinetic energy via rotational motion of bearings.**



**Figure 7. Reactor for Attrition mill. Materials made of 440C stainless steel. Six pounds of media. Tree to rotate media. O-ring liner of reactor maintains pressurized atmosphere.**

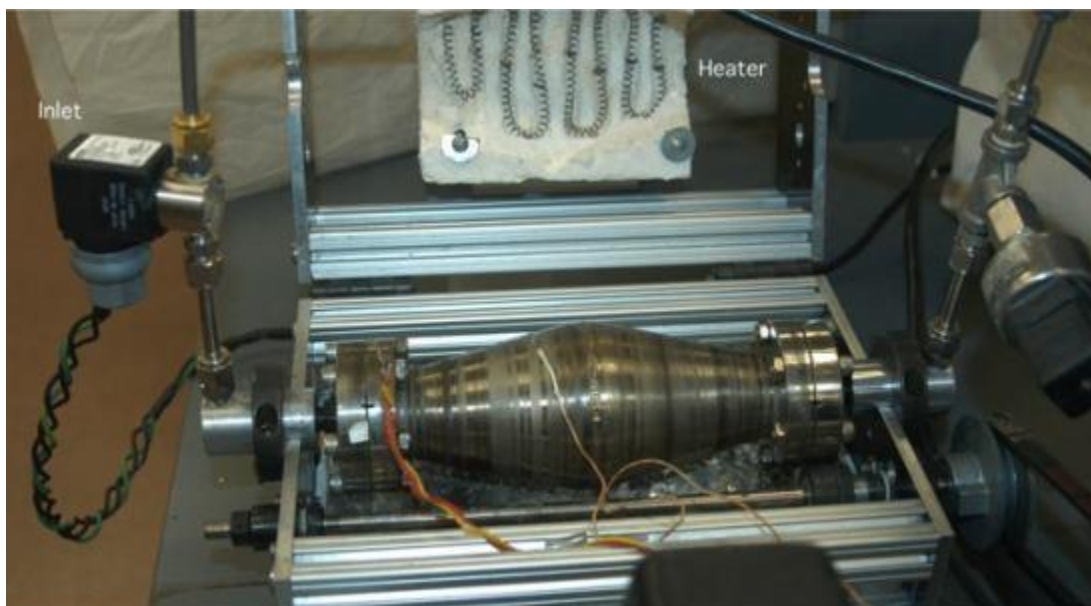
The attrition mill is ideal for laboratory scale-up. Allowing chemists to work on a larger scale, but also allowing work with solids, liquids, and gases. Figure 6 depicts the attrition mill with reactor set up, where Figure 7 shows an empty reactor, steel bearings as the media, the lid (which is designed to allow chemist to control the atmosphere and pressure during reaction), and the tree to stir the media.

The attrition mill is the first real up-scaling of mechanochemistry at the laboratory, academic, level, making it possible to mill kilograms of material. The Union Press mill depicted in Figure 6 has a controller that lets the operator set speeds up to 720 rpm. The motor is connected



to the tree by a coupler which turns the tree. The tree is equipped with steel rods extending out at 90 degree angles, which stirs the steel bearing media. The impacts that drive the reactions forward are generated from bearings colliding with other bearings or the steel rods protruding from the tree. The attrition mill applies the force generated from the bearings to reagents via impact, shearing, and rotation.

#### *1.3.4 Pebble/Rolling Mill*



**Figure 8.**Custom made Rolling mill. Speed and heat can be controlled by operator. Solids, liquids, and gas can be milled.



**Figure 9. Reactor for Rolling/Pebble mill. O-rings maintain atmosphere within reactor. Mixed media to apply kinetic energy.**

The rolling mill is often called a tumbling mill and is utilized in industry to process large quantities of materials, typically hundreds of kilograms. The rolling mill shown in Figures 8 and 9 is scaled-down from industrial size, but it allows the chemist to begin scaling-up the mass of reagents for a chemical reaction in the laboratory setting. This specialized design allows the

chemist to control the speed of rotation. How the energy is transferred to the reagents is influenced by the speed of rotation. At lower speed energy is transferred via grinding. Slightly increasing the speed creates a tumbling effect where the media will transfer energy via both grinding and collisions. This rolling mill has gas inlet and outlet valves and a pressure controller that allows the chemist to control the pressure of gas that is introduced into the system. The gas can be either inert or a reagent, and with the pressure gauges the chemist can determine how much of the reagent gas was used in a reaction.

#### 1.4 Milling Parameters

The type of mill is an important factor in mechanochemical processing, synthesis, and catalysis, but other parameters that need to be considered include:

- Atmosphere
- Free volume
- Temperature
- Grinding material and size
- Milling speed
- Ratio of media to mass of reagents
- Milling time
- Milling Vessel



These variables are not completely independent of each other and must be taken into account when determining the optimal milling parameters to maximize production. Different reactions will depend not only upon the mill type and the factors listed above.

#### *1.4.1 Atmosphere*

There are many traditional solvent-based reactions and solid-state reactions that are very susceptible to the environment, particularly the atmosphere of the reaction. This susceptibility exists with mechanochemistry as well. Reactions that are susceptible to their atmosphere are typically done under inert atmosphere, i.e. argon. Working in an inert atmosphere decreases the exposure to oxygen or water that would result in Those reactions that are not reactive to atmospheric parameters, such as the milling of kaolin, require no additional measures. However, in the case of hydrogenation reactions the reactor can be filled with hydrogen as a reagent.

#### *1.4.2 Free Volume*

The generation of kinetic energy is required for mechanochemistry. This means that the media must be able to move, and to be efficient there must be adequate space for the media to move freely. There is a balance that must be obtained between the amount of material to process and the free space needed for efficient milling. Too little free space and milling is inefficient, too much free space and too little material is being processed. The amount of free volume needed for

efficient processing also depends upon the mill being used, most mills 50% of the vial is the most that can be filled and maintain efficacy, where the attrition mill can be filled up to 80%.

#### *1.4.3 Temperature*

Temperature is a significant factor in wet-chemistry and also in mechanochemical processing and synthesis. Temperature affects diffusion and concentration of defects. From the friction and impacts the outside of a shaker mill vial can reach temperatures near 60°C and the attrition mill can achieve temperatures near 100°C, but the actual temperature within the vials will be higher. Most chemical reactions can benefit from the increase in temperature, there are however reactions that will decompose if the temperature within the vial get too high. One example is the synthesis of gallium nitride (GaN), the reaction will decompose if the temperature gets too high. Possible solutions to high temperatures include a vial that has enough mass to act as a heat sink or using smaller media, but in larger amounts to also act as a heat sink.

#### *1.4.4 Grinding Material and Size*

There are several different materials that make-up the media and vials used for mechanochemistry and that material is another parameter that must be considered. One example is in the activation of boron nitride (BN) for metal-free catalysis. The standard 440C stainless steel vial cannot be used as it may contaminate the BN with iron. The solution is to use a non-

metal vial and grinding media such as zirconia. Examples of other milling media include: tungsten carbide, agate, polycarbonate, acrylic, nylon, copper, and even titanium. Each of these has advantages and disadvantages depending upon the force generated and the mill type, this is one of the reasons why proper selection of material is important. It is also possible that the media can be comprised of the catalyst needed for the reaction being performed. Copper has been used as a catalyst for many coupling chemical reactions, so it is possible that milling media be made of copper such as in Sonogashira reactions.<sup>7</sup>

Given that mechanochemistry requires collisions for the transfer of kinetic energy the size and mass of the media must be considered. Generally smaller diameter media will generate less energy than larger diameter media. In the synthesis of titanium aluminide alloy 5 mm diameter media produced an amorphous material, 15mm diameter media formed alloy, and the 20 mm diameter media did not.<sup>8</sup> Recall that the composition of the media is a factor, as tungsten carbide bearings are twice the mass as 440C stainless steel bearings of equal diameter. The energy generated with each impact is directly related to the mass of the media, too little mass the energy generated may not be sufficient to drive the reaction forward and too great a mass the energy generated may cause different materials to form or no product formation occurs. Less mass or smaller diameter media can be placed in the soft milling category and can create amorphous phases, while the larger diameter or greater mass media are categorized as hard milling and can generate more crystalline products.<sup>9</sup>

#### *1.4.5 Milling Speed*

Milling speed is directly proportional to the amount of energy generated. Kinetic energy is defined as  $KE = \frac{1}{2} m v^2$ , where the velocity is the speed of the mill, in the case of the HSBM the velocity can reach 5 m/s. In general the higher the speed the more kinetic energy generated, the more energy transferred to the reagents, resulting in less time to mill. Higher speeds can result in increased temperature as in the case of the attrition mill when comparing 300 rpm to 700 rpm when the transesterification of canola oil and ethanol to biodiesel. Milling at 700 rpm had temperature measurements closer to 90°C where 300 rpm did not reach the same temperatures.

Increased speed may increase reaction rates, but not all mill types will benefit from increased speeds. The pebble/rolling mill will not benefit from very high speeds, it is possible that if the speed is great enough the media will be pinned against the wall of the reactor and not move at all.

#### *1.4.6 Ratio of Media to Mass of Reagents*

Media mass to reagents ratio is often referred to ball-to-powder ratio (BPR) and is another parameter that must be considered. In general the higher the BPR the less milling time this is because the mean free path of the media is decreased and the result is more collisions in less time. Being inside a vial the most efficient way to increase the BPR is to increase the mass of the media: more media, denser media, or larger media are the simplest methods.<sup>10</sup>

#### *1.4.7 Milling Time*

As in any chemical process the time to complete a reaction is extremely important. The ideal mill time of any reaction is the fastest time in which the most amount of product is formed. However with mechanochemistry long mill times may result in amorphousization of product and even contamination of product from the vessel or media.

#### *1.4.8 Milling Vessel*

With all the impacts and grinding against the vial itself the material the vial is made of becomes another parameter. Each impact cause wear on the vial and in time contamination from the vial can be introduced into the product, in the case of 440C stainless steel vials iron can contaminate the reaction or product. The hardness of the material being milled versus the hardness of the vial must be considered. Any material that is harder than the vial will cause excessive wear on the vial and this is another way contamination can be introduced into the product. SPEX offers several different materials which can vials can be made from: zirconia, tungsten carbide, agate, and hardened steel.<sup>11</sup>

Another factor is the shape of the vial. Altering the shape of the vial will result in a change the amount of energy that each impact will generate. There are several different types of vials for the HSBM, but flat-bottom, round-bottom are the most common. Decreasing the size of the vial will also change the amount of energy produced. More impact will occur if the length of the vial is decreased, but the maximum speed at which the media can achieve would decrease. These

changes may seem minor but they alter the motion of the media and this alters the energy that the media can transfer to the reagents.

#### *1.4.9 Focus of Research*

The following chapters will describe examples of mechanochemical synthesis and catalysis. Some will compare traditional to mechanical synthesis, while also comparing advantages and disadvantages for mechanochemistry. Some chapters will describe the mechanochemical synthesis of catalysts that will be used for other mechanical synthesis. One point that needs to be mentioned is that each chapter will show that mechanochemistry requires little to no solvent or significant increases in temperature or pressure. This is significant when factoring in the costs of scaling-up for the industrial production.

The focus of this research is on utilizing mechanochemistry for the synthesis of catalysts and mechanochemical organic synthesis. There are several organic reactions that require temperatures and pressure that are not practical at the industrial level, unless catalysts are used. This research will show how catalysts and organic synthesis can be completed using shaker mills and attrition mills. That the mechanochemical process can be used to reduce the cost of scale-up to an industrial level.

## **CHAPTER 2 : NATURAL AROMATIC COMPOUNDS ADDED TO BIOFUELS TO PREVENT THE DEGRADATION OF O-RINGS DURING LONG-TERM EXPOSURE**

### **2.1 Introduction**

The world's primary sources for energy are fossil fuels. The three most widely used are natural gas, coal and petroleum, with petroleum by far the most consumed. However, the rate of petroleum consumption is greater than the rate of petroleum replenishment.<sup>12</sup> An alternative to fossil fuels, in particular petroleum, is biologically derived fuels, biofuels.

There are several factors for and against the transition from petroleum-based fuels to biofuels. First, the feedstock must not compete with food stock. Second, coordinating this transition will be costly at the outset, since it requires not only growing a feedstock, that doesn't compete with food supplies, but transporting that feedstock, and converting it to biofuel.<sup>13</sup> Third, as the transition proceeds, further study will be required to quantify the interaction between biofuels and the materials they will come in contact with. Despite these obstacles there are several factors favoring the transition to biofuels. First, biologically derived fuels are sustainable. Second, they can be carbon neutral. Third, this transition allows for a more even distribution of the energy source, than does the current distribution, predominately located in the Middle East.<sup>12</sup>

Unlike petroleum fuel there are several possible sources for renewable biofuels. One is animal fat, which is comprised of a complex mixture of triglycerides that when trans-esterified become a complex mixture of C12-C20 hydrocarbons. Biodiesels derived from animal fats are commonly referred to as tallow.<sup>14-15</sup> Another possibility is vegetable oils such as canola oil, rapeseed oil, and even soybean oil which are all sources of fatty acids that can be converted to

biodiesels.<sup>16-18</sup> Derived from both sources are waste cooking oils (WCO). Another type is extracted from microalgae.<sup>19</sup> Both WCOs and tallow must be filtered and purified to remove any solid particulates which will block fuel lines.<sup>15</sup> Another difference between vegetable oil and tallow, is that vegetable oil can be used directly as biodiesel.<sup>20</sup>

One difference between petroleum and renewable biofuels is the absence of aromatic or sulfur compounds in biofuels.<sup>21</sup> The source and the refining process of crude oil determines the mixture of aliphatic and varying aromatic hydrocarbons in petroleum based fuels.<sup>22</sup> Aromatic compounds vary both in concentration and composition. Examples of aromatics in petroleum based fuels are alkylated benzenes at 1.3 mg/g and 2-methyl naphthalene at 14.9 mg/g.<sup>23</sup>

Although, as previously mentioned, vegetables oils can be used directly as fuels, they do not fully combust, leaving a residue that can block the fuel injection system. A common and simple means for solving this problem is the transesterification of fatty acids into methyl esters.<sup>17-18, 20, 24-25</sup> These methyl esters can be used in diesel engines without any modification to the engine, owing to their very low residue formation and viscosity. Transesterification does result in the formation of side products, typically soaps and glycerin.<sup>26-27</sup> Though valuable these side products result in reduced biodiesel yields. These side reactions can be controlled via the selection of the starting material and catalyst.<sup>18, 28-29</sup>

A problem occurring with prolonged exposure of polymers to biofuels is the degradation of these polymers. This is problematic for polymers used in o-rings and other polymers utilized in various vehicles. The primary purpose of this research is to study polymers used in o-rings after exposure to biodiesels derived from animal fat or to ethanol – both with and without additives --



over a span of one hundred days. Similar studies have been conducted, however over a much shorter-term exposure of fifty days or less;<sup>30</sup> they focused on biodiesel derived from palm or other plant-derived oil, this study used biodiesel from animal fat;<sup>21, 30-32</sup> and they examined the effect of mixing fuels (e.g., A with B or C with D), not with the effects of additives.<sup>33</sup> Finally, though they examined the effects of their chosen fuel mixtures on metal surfaces<sup>31</sup> or various polymers,<sup>32-33</sup> they did not focus on polymers in the form they take in functional applications, such as o-rings. Some studies tested the polymer biofuel interactions after the polymer had been cut into strips or coupons and then exposed to the biofuel.<sup>32-33</sup>

The starting material of this animal-fat biodiesel in this study are triglycerides that consist of long-chain fatty-acid functional groups -- stearic, oleic, palmitic, etc.<sup>34</sup> After transesterification of these triglycerides, the methyl ester of the fatty acid was then hydrocracked in order to remove all oxygen content and produce a JP-8 equivalent fuel. (The mass spectrum of biodiesel indicates it contains no aromatic compounds<sup>35</sup> (Nebraska Bioenergy Facilities, 2015).)

In this study, Nitrile o-rings (N602-70 M29513) were placed in biofuels (the biodiesel just described and, for comparison, ethanol), with and without additives (described below), and changes in mass were recorded weekly. O-rings were selected for this study as they represent a polymer whose primary function is leak prevention, and is dependent on both its composition and size.

Three criteria determined the choice of additives — vanillin and ethyl vanillate — selected for this research. First, they are aromatic compounds — a component absent in biofuels but generally present in petroleum-derived fuels. Secondly, they are not detrimental to the

environment. Thirdly, ethyl vanillate can be produced from vanillin, which in turn can be realized from the depolymerization of lignin, which is both readily available as a cellulosic fuel by-product and economically processed.

Lignin has the most aromatic compounds of any naturally occurring substance.<sup>36</sup> Lignin is typically viewed as a biomass waste of the forestry, pulp, and paper industries,<sup>37-38</sup> and as such burned or allowed to decay over time. Although vanillin has been extracted from lignin in black liquor, only recently has there been a real effort to extract viable chemicals from lignin in an economical and sustainable manner. Chemicals commonly obtained from converting lignin include dimethyl sulfoxide, polymers, active carbon, carbon fibers – and vanillin.<sup>39-40</sup> Several methods have been utilized to process biomass/lignin, these include enzymes, hydrolysis, pyrolysis, high pressure, and even steam.<sup>38, 40-41</sup>

## 2.2 Experimental

### Chemicals and materials

Ethyl vanillate (99.99%) purchased from Indofine Chemical Company Inc.

Vanillin purchased from Fisher Scientific.

Biodiesel and Jet A were provided by United States Air Force Research Laboratory (AFRL).

Nitrile o-rings provided by Parker-Hannifin.

Ethanol purchased from VWR.

### 2.3 Procedure

In the course of this study weekly measurements were conducted on o-rings immersed in 115 mL bottles with various solutions – two with Jet A, two with pure ethanol, two with biodiesel derived from animal fat, three each with 1% w/w and 2% w/w ethyl vanillate by mass in biodiesel and three each with 1% w/w and 2% w/w vanillin by mass in ethanol. (Additives over two percent by mass did not fully dissolve.)

Prior to placing o-rings into solutions their hanging and dry masses were measured. (These measurements are day 1.) In each weekly test (for 15 weeks), the o-rings were removed from the bottles and wiped dried; the dry mass and hanging mass were measured in order to calculate the density and volume. This procedure allowed for measurable comparisons of the volume changes not only of each o-ring from week to week but also between that change and changes of all other o-rings. The following figures show the percent change of volume compared to the initial volume.

## 2.4 Results

### 2.4.1 Test of O-rings in control solutions

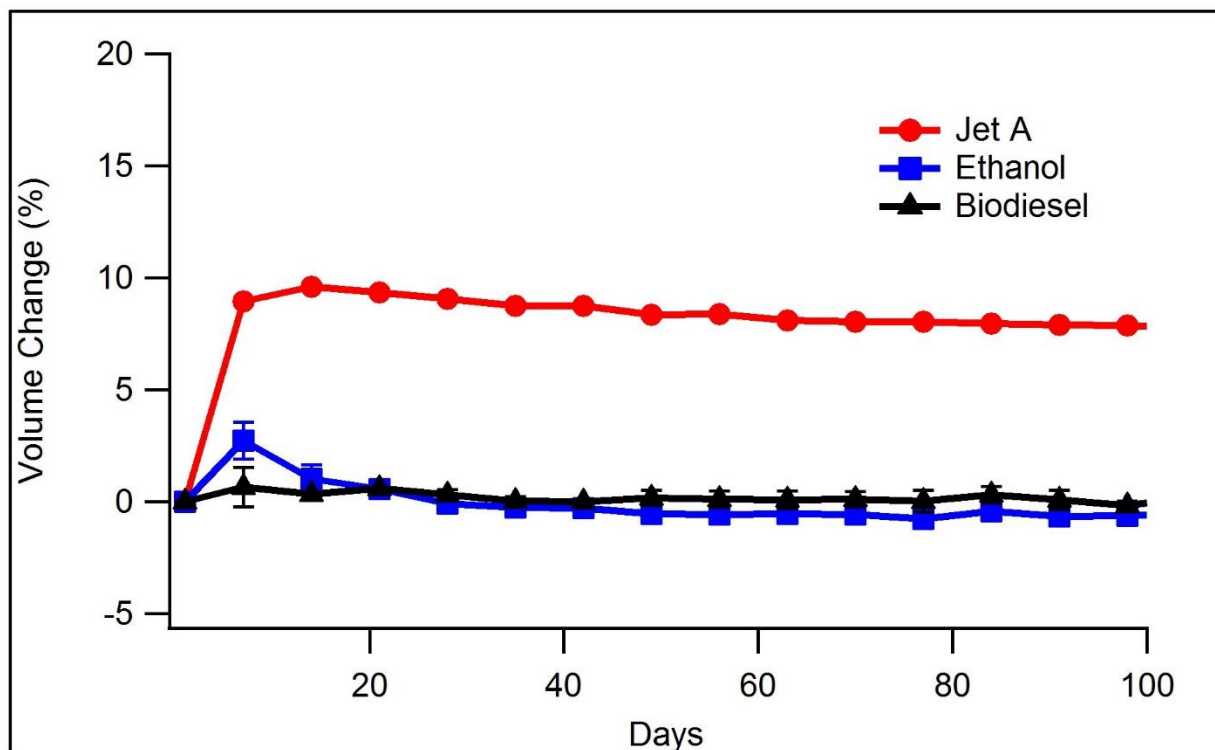


Figure 10. Comparison of volume changes of o-rings in fuels without additives.

Figure 10 shows the average change that occurred in the volumes of the control o-rings over the one-hundred-day trial period. The fuels used were Jet A, provided by US AFRL, biodiesel, and ethanol.

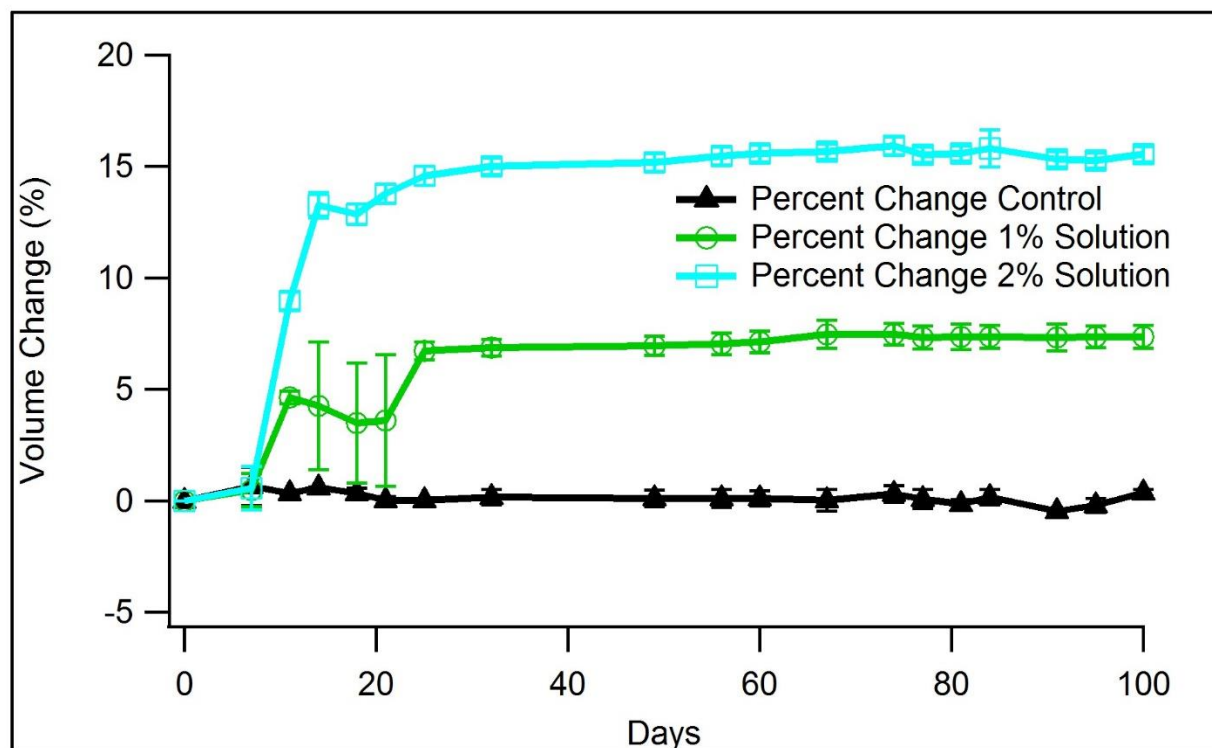
The biodiesel used in this study was derived from animal fat, which was selected as its interactions with polymers resulted in degradation of the polymer.<sup>42</sup> Both vegetable oils and animal fats are comprised of triglycerides consisting of multiple long-chain fatty-acid groups.<sup>34</sup>

This is significant because biodiesels derived from triglycerides retain the profile of the parent fatty-acid functional group<sup>43</sup> and, from observations, absorption and release of these plays a special role in the behavior of o-rings in biofuel environments. Fluctuations in volume were observed over the course of the trial as the various long-chain compounds migrated in and out of the o-ring. Migration of different long-chain compounds leads to multiple cycles of swelling and shrinking that were observed.

As Figure 10 shows, the volume of each o-ring increased as the fuels were absorbed by the o-ring. The volume changes of the o-rings in Jet A never resulted in the volume's being less than the initial volume. In ethanol, the volume swells during the first week, after which it gradually decreased until Day 35, after which it remained below the initial volume.

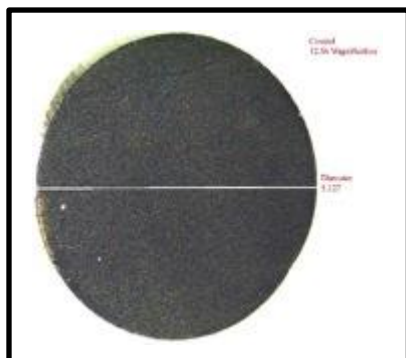
In general, most of the swelling is completed at day 20.

#### 2.4.2 Tests of o-rings in biodiesel with and without additives.

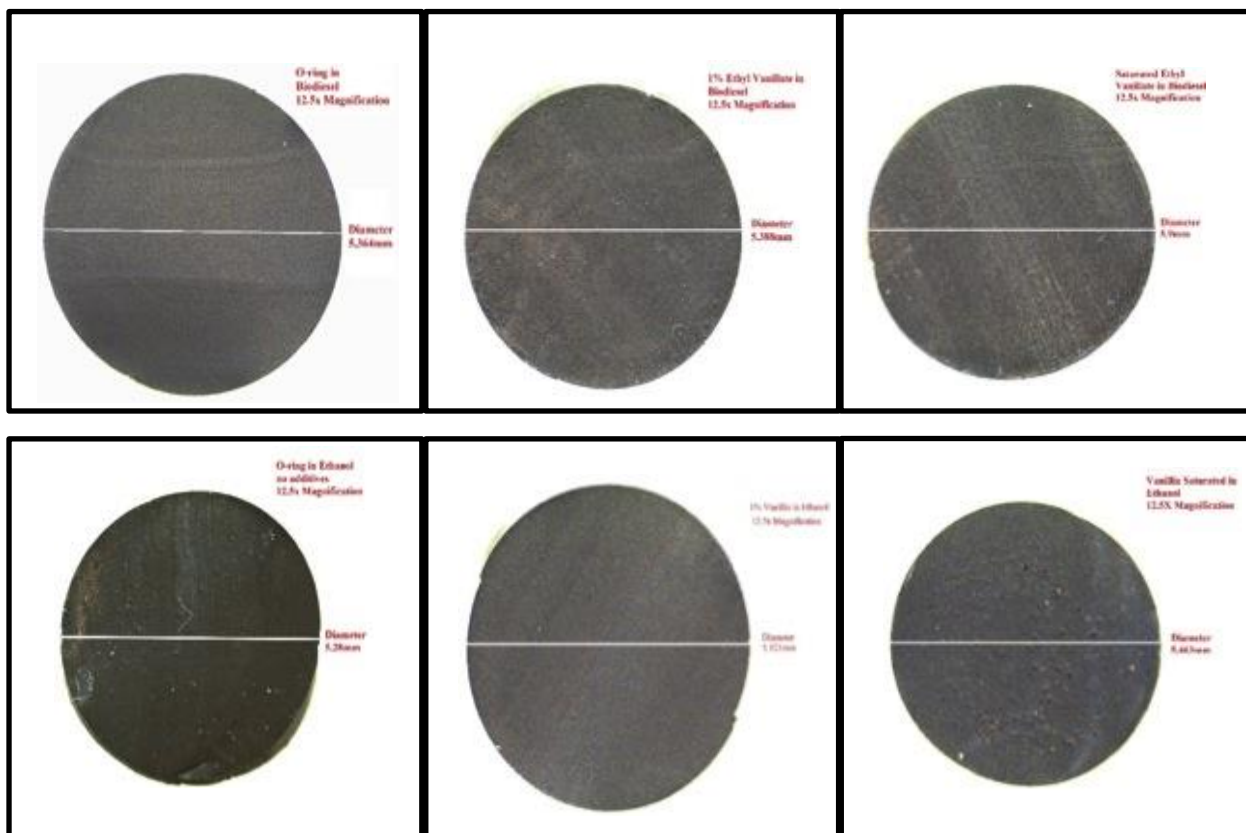


**Figure 11.**Comparison of o-ring volume changes in biodiesel.

Figure 11 compares the average changes in volume of o-rings in biodiesel with and without additive. As in the control, the o-rings in both the 1% w/w and 2% w/w trials had an initial spike in volume as the biodiesel was absorbed, after which slight fluctuations in volume were observed. Unlike the volume in the control the volumes of the o-rings in the 1% w/w and 2% w/w solutions increased after initial swelling.



**Figure 12.**Control o-ring



**Figure 13.** (a) O-ring in biodiesel no additive. (b) O-ring in 1% ethyl vanillate in Biodiesel. (c) O-ring in saturated ethyl vanillate in biodiesel. (d) O-ring in ethanol no additive. (e) O-ring in 1% vanillin in ethanol. (f) O-ring in saturated vanillin in ethanol.

At no point did the o-rings volume in either the 1% w/w or 2% w/w solutions decrease to less than initial; on the contrary, by the end of the experimental trials, the final volume of the o-ring in 1% w/w solution was 7.36% greater than the initial volume, and that in the 2% w/w solution was 15.67%.

#### 2.4.3 Test of o-rings in ethanol with and without additives

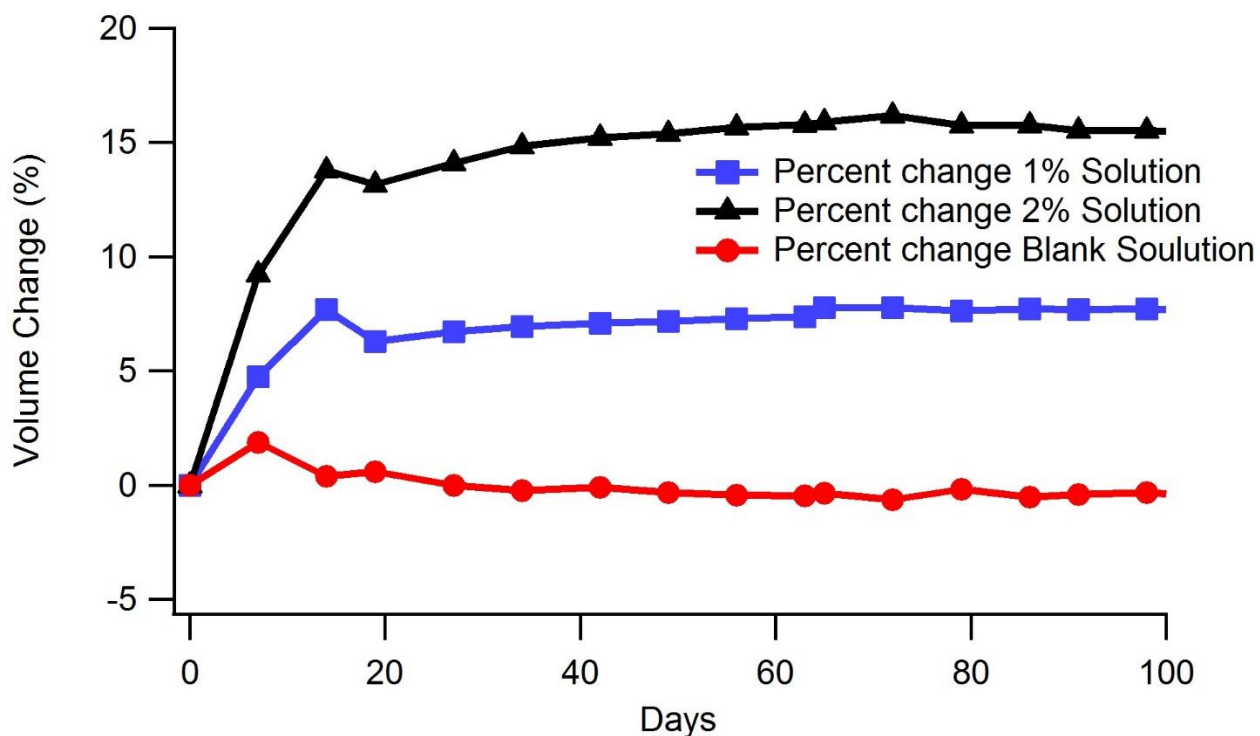


Figure 14. Comparison of o-ring volume changes in ethanol



Figure 14 compares average volume changes of the o-rings in ethanol with and without additive. As in the control and biodiesel trials, there was an initial spike in volume of the o-rings

As with the o-rings in 1% w/w and 2% w/w solutions of biodiesel, those in 1% w/w and 2% w/w solutions of ethanol did not decrease in volume, by the end of the trials, the volumes had greatly increased – this time by 7.67% and 15.45%, respectively, over the initial volumes.

The top row of Figure 13 shows photos of cross sections of o-rings after 100 days in biodiesel solutions: without additives, with 1% w/w and more than 2% w/w additive (Ethyl vanillate). The bottom row show cross-sections of o-rings in ethanol solutions: without additive, with 1% w/w and 2% w/w additive (vanillin). When the pictures in top row are compared each to the other a trend of observable differences emerges. Top row left shows a smooth surface, throughout, whereas both the middle and right pictures exhibit dark spots, at the edges of the o-ring soaked in 1% w/w solution, and throughout the o-ring soaked in 2% w/w solution. These dark spots are a result from the uptake of the aromatic compound not being uniform in the o-ring.

The pattern is similar with comparisons among photos in the bottom row. Similar observations can be made of the o-rings in ethanol trials: no swelling throughout o-ring soaked in pure ethanol; defects at the edges only of o-ring soaked in ethanol with 1% w/w additive; swelling distributed throughout the cross-section of o-ring soaked in ethanol with 2% w/w additive.

These swelling regions are an indication of the intramolecular interactions having been weakened by the absorption of additive. As the biofuel migrates back out of the o-ring, when equilibrium is reached, it carries compounds out of the o-ring. These compounds include plasticizing compounds.

## 2.5 Discussion

As pointed out in the Introduction, studies undertaken up to now of the interactions of polymers and biofuels have not exceeded 50 days.<sup>21, 33, 44</sup> The purpose of the study was to observe the changes that occurred in o-rings from interactions with biofuels for more prolonged periods: up to one hundred days. The study also compared the effects on o-rings of prolonged contact with Jet A fuel, a petroleum-based fuel, which (unlike pure biofuels) contains aromatic compounds. As in the previous studies (using, as described, other fuels, and unformed polymers), there was an observed initial increase of the volume, as the fuel was absorbed into the o-ring.

The absorption of the biofuel by the o-ring stems from the principle of favorable polymer plasticizer interactions.<sup>32</sup> The extended time of this study, however, allowed observations that the volume decreases from this early peak over time, the amount of shrinkage depending upon which biofuel: in pure ethanol, the volume dips below initial volume by 0.24% around Day 35, and maintains an average of 0.38% less than initial volume; in pure biodiesel, it does not fall below initial volume until Day 81, after which it expands beyond initial volume and, after 2 weeks, fell to beneath initial volume; in either ethanol or biodiesel with additives, it never falls below the initial volume. This may be due to a lower solubility of the plasticizer in the o-ring elastomer in the longer chain aliphatic compounds present in bio-derived jet fuel.

The decrease in volume, however, presupposes the initial absorption of biofuels. The swelling causes the polymer chains, in the o-ring, to relax.<sup>21, 44-45</sup> Biofuel also functions as a

solvent,<sup>45</sup> and when it migrates back out of the o-ring, it carries along compounds that have dissolved in it<sup>21, 32, 45</sup> because the latter have a greater affinity for the biofuels than for the polymers that constitute the o-ring. These compounds include plasticizers,<sup>21, 30</sup> which are able to easily migrate out of the polymer once as the polymer bonds have been relaxed. This process results in a three-fold degradation: permeation by defects, weakened bonds, and shrinkage that hinders the o-ring from performing its primary function: preventing leaks.

Tests of o-rings in solutions of biofuels with additives also showed initial swelling followed by cycles of smaller shrinking and swelling, they exhibited significant differences from those of o-rings soaked in pure biofuels: at no point did the volume of the o-rings in additive tests ever decrease to less than the initial volume, as they did in those with fuels without additive.

Cross-section images of o-rings show ‘defects’ in the material. These ‘defects’ are indication that even though the o-rings did not shrink when placed in biofuel with additive, they are indication that a weakening of the material did occur. The data shows that, even at low concentrations, the addition of an aromatic compound will inhibit the degradation observed in o-rings exposed to pure biofuels. The aromatic additives replace components removed by the biofuel.

## 2.6 Conclusion

This study compared the interactions between biofuels and polymers, but with three distinct differences from previous studies: extended time, use of additives, and the shape of polymer, o-rings instead of strips or coupons.

Volumes of o-rings decreased in pure biofuels, this is indicative of a loss of plasticizer. Volumes of o-rings increased in biofuels with additives. The most probable cause of this increase is the o-ring absorbing aromatic compounds added to biofuel. As little as 1% additive prevents shrinking.

## CHAPTER 3 : MECHANOCHEMICAL CONVERSION OF BIOMASS TO PROPANE

### 3.1 Introduction

Every nation requires energy to create and maintain infrastructure. The most widely used sources of energy are fossil fuels. Dependence upon fossil fuels has had a negative impact upon the environment<sup>46-47</sup> and human health.<sup>48</sup>

Looking forward, it becomes necessary to find an alternative source to meet our current fuel demands. Whatever its source, the fuel itself needs to have a minimal negative impact upon the environment. One such fuel already in use today is propane.

The combustion of propane, a three-carbon chain alkane, results in less CO<sub>2</sub> and CO emissions, than that of longer-chain hydrocarbons common in gasoline or diesel. Propane is a widely versatile fuel, finding uses ranging from cooking and heating, to powering automobiles and generating electricity. Because it is easily transported, many rural environments (cut off from natural-gas grids) rely on it as an alternative to expensive electricity to heat homes and provide energy for some farm equipment.<sup>49</sup>

The primary source of propane today is from the refinement of either natural gas or petroleum. Natural gas is mostly comprised of propane and butane, and is the primary source of these gases<sup>49</sup>. Distilling crude oil will permit the extraction of propane, yet propane from crude oil needs to be further treated to remove sulfur.

The continuous extraction of natural gas as the source of propane is similar to the extraction of fossil fuels, for the purpose of gasoline or diesel, in that it is not a feasible long-term option.

What is needed is an alternative source of propane, just as the transesterification of triglycerides is an alternative to fossil fuels for diesel.<sup>50</sup>

One alternative source that has attracted a great deal of research is biomass. Biomass can be derived from grass, trees, plants, crops, etc..<sup>51</sup> The benefits of using biomass are that it is economically advantageous, easily obtained, and classified as a renewable energy source.<sup>52</sup> The significance of a renewable fuel is the time in which the fuel can be replenished. Both fossil fuels and biofuels contain carbon, and release CO<sub>2</sub> upon combustion, the difference is in the time it takes for the carbon in the released CO<sub>2</sub> to become that fuel again. Fossil fuels (oil) takes millions of years to replenish, where the source of the biofuel can be replaced over a couple of years.<sup>53</sup>

There are various current methods for the production of propane, such as conversion of syngas to propane, using a hybrid catalyst (for example, X), or conversion of cellulose to propane, using bacteria.<sup>54-55</sup> What makes these processes ideal is that they both can use biomass as their starting material.

Converting syngas into propane is a common method. Syngas itself is derived mainly from natural gas, coal, or biomass.<sup>56-57</sup> There are three processes for conversion: direct,<sup>57-59</sup> indirect,<sup>60</sup> and semi-direct.<sup>60</sup> The most common of these uses a hybrid catalyst consisting of a methanol synthesis catalyst (such as Cu-Zn, Cr-Zn<sup>57</sup>, or a palladium-supported catalyst<sup>58</sup>) together with a zeolite (such as a Y-type,<sup>61</sup> Y-type modified with palladium,<sup>59</sup> or  $\beta$ -type<sup>57</sup>).

Converting biomass to syngas requires the gasification of biomass.<sup>57-58</sup> Gasification converts all the carbon in an organic material (whether biomass or a fossil fuel) into CO, CO<sub>2</sub>, or H<sub>2</sub>. But neither CO nor CO<sub>2</sub> are environmentally friendly. Moreover, this process requires high

temperatures (350-500°C) and a low-oxygen atmosphere (as excess oxygen results in the combustion of the biomass).<sup>52, 62-63</sup>

An alternative to the gasification of biomass is to convert the biomass to sugar and then use bacteria convert the sugar to the desired fuel. This process, however, involves expensive complications. The bacteria need to be extensively modified to enable them to produce the desired alkane chain.<sup>54-55</sup> Moreover, the conditions required to sustain the bacteria are problematic. (Additionally, the fact that the most commonly used bacterium is *E. coli* requires the reliable employment of special safety measures.)

The question thus arises: could there be an economical process that uses biomass without gasification and converts sugar to fuel without bacteria? The answer is yes.

The process described in this research converts biomass to sugar using a naturally occurring catalyst, kaolin, via mechanochemistry (a high-speed ball mill [HSBM]) to convert various kinds of biomass normally today discarded or burned into sugar.

The sugar, in turn, is converted to 1,3-dihydroxyacetone. The catalysts examined for this conversion were kaolin, boron nitride, erbium oxide, and using various mixtures of these catalysts. Thin-layer chromatography was used to determine which catalyst converted sugar to 1,3-dihydroxyacetone.

The final step converts the 1,3-dihydroxyacetone to propane using a hydrodeoxygenation (HDO) catalyst under hydrogen. For this step, instead of an HSBM an attrition mill was used.

This final stage of conversion utilized an HDO. HDOs are commonly used with bio-oils. Bio-oils are another alternative to fossil fuels that are formed from the pyrolysis of biomass. Because bio-oils have very high oxygen content, HDOs are needed to remove the oxygen.<sup>64-65</sup>

The formation of the HDO used in this research was also performed using mechanochemistry. Typically, HDOs are formed using incipient wetness impregnation, which requires metal salt precursors,<sup>66</sup> long drying times, and calcination.<sup>67</sup> The process for the synthesis of molybdenum cobalt sulfur introduced in this research began with the elements in their natural state, and not salts.

The benefits of this process are that no toxic gasses were formed, no increase in temperature was required, and no specific conditions were needed to maintain bacteria. The generation of the 1,3-dihydroxyacetone also has a second (though niche) economic advantage as it serves as a self-tanning agent.

One of several advantages to this process at each stage of this process the products formed are stable and all are products with diverse purposes. The most significant advantage of this process is in the actual conversion of 1,3-dihydroxyacetone to propane. This final stage yielded product within an hour.



## 3.2 Experimental

### 3.2.1 *Materials*

Boron Nitride from Saint-Gobain Ceramics.

Cobalt (99.998%) from Alfa Aesar.

Dicyandiamide from Alfa Aesar.

Molybdenum disulfide from Asbury Graphite Mills.

Molybdenum from Alfa Aesar.

Fructose from Fischer.

Dextrose from Fischer.

Xylose from Fischer.

### 3.2.2 *Preparation of catalyst supports*

Carbon nitride was synthesized by heating dicyandiamide at 500°C for 1 hour.

Both boron nitride (BN) and carbon nitride (C<sub>3</sub>N<sub>4</sub>) supports were prepared by heating to 180°C for 18 hours under vacuum, then transferred to an inert atmosphere. Each was then milled in a zirconia vial with four ½-inch zirconia bearings for two hours.

### 3.2.3 *Preparation of catalyst*

The HDO catalyst studied here was synthesized under inert atmosphere by milling 1.195 grams of molybdenum, 0.209 grams of cobalt, and 0.004 grams of sulfur within a tungsten carbide (WC) vial using four ½-inch WC bearings, using an 8000D SPEX mill.

Milling proceeded in ½-hour increments for a total time of four hours, after which ten grams of support were added to the WC vial and the mixture milled an additional 6 hours at ½-hour increments.

Cobalt on C<sub>3</sub>N<sub>4</sub> support was likewise synthesized under inert atmosphere. Two grams of activated carbon nitride and 0.10 grams of cobalt were put into a WC vial with four ½ inch WC bearings and milled for six hours at ½ hour increments.

### 3.2.4 *Conversion of biomass to sugar.*

Using a 440C steel vial with 3 ½ inch steel bearings, 1.0 gram of biomass and 1.0 gram of kaolin were milled. Mill times ranged from ½ hour to 3 hours, at ½-hour increments. Products from each increment of reaction were gravimetrically analyzed.

### 3.2.5 *Conversion of sugar to 1,3-dihydroxyacetone.*

Fructose, dextrose, and xylose were selected as starting materials. Catalysts selected were kaolin, boron nitride, erbium oxide, and various mixtures of these catalysts. Mill times ranged from ½ hour to 2 hours, at ½-hour increments.

### *3.2.6 Conversion of 1,3-dihydroxyacetone to propane.*

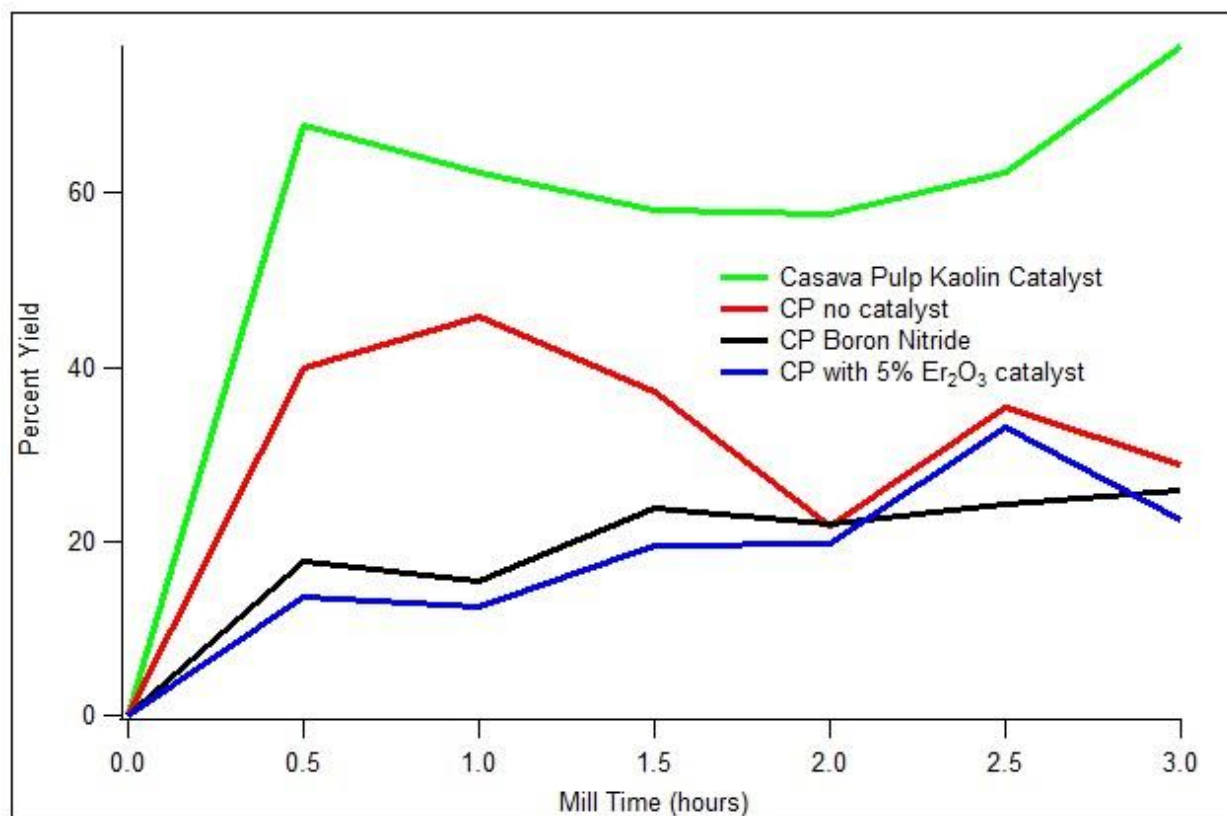
Catalysts selected for the synthesis of propane included boron nitride, carbon nitride, molybdenum disulfide, molybdenum cobalt sulfide (supported by either boron nitride or carbon nitride), and cobalt supported on carbon nitride.

Reaction was performed using a Union Press Attrition mill HD-01 series. Ten grams of 1,3-dihydroxyacetone and 5% reagent mass of catalyst were sealed in a 440C stainless steel container with six pounds of ¼-inch steel bearings. The system was purged repeatedly with hydrogen gas to remove air. Milling was done at 700 rpms at one-hour intervals for a total of four hours.

### *3.2.7 Preparation of samples for GCMS*

Vials for sample collection were sealed inside of an argon glovebox. A syringe was used to transfer gas from reactor into vial. Samples were collected at hourly intervals and analyzed using a GCMS Agilent 6850.

### 3.3 Data



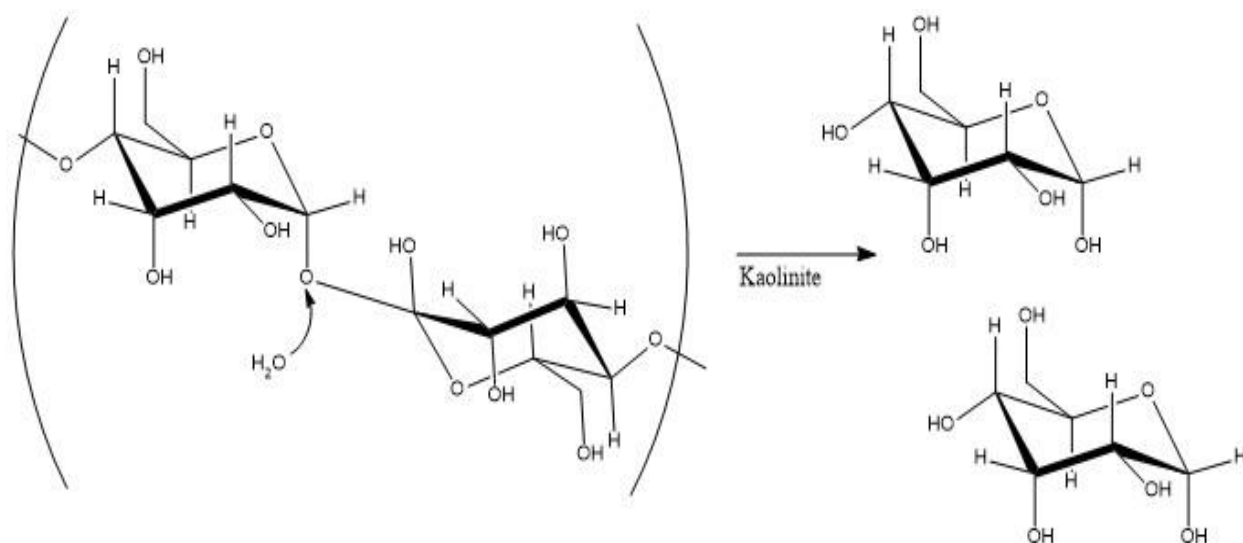
**Figure 15.** Comparison of percent yields of converting cassava pulp to sugar with various catalysts.

#### 3.3.1 *Biomass to sugar*

Three biomasses were selected for study: palm leaves, de-inked paper, and cassava pulp. Catalysts utilized in this research included kaolin, boron nitride, and erbium oxide., singly and in various combinations

Biomasses were tested with each catalyst and results compared to determine which biomass and catalyst yielded the highest conversion. The biomass that had the highest conversion was

cassava pulp. The catalyst that best promoted this conversion was kaolin. Figure 15 shows all data collected for cassava pulp with each catalyst tested.



**Figure 16. Cellulose to simple sugar with kaolinite.**

### 3.3.2 Sugar to 1,3-dihydroxyacetone

This is a retro-aldol reaction typically catalyzed with a base. Thin layer chromatography was utilized to determine conversion of sugar to 1,3-dihydroxyacetone. Standards were made of fructose, dextrose, xylose, and 1,3-dihydroxyacetone. Each glucose and catalyst combination were compared to the standards to determine which produced 1,3-dihydroxyacetone. Fructose and dextrose both converted in the presence of a catalyst mixture of 5% erbium oxide with 95% BN. Erbium oxide is a base and BN is basic because the edge nitrogens act as amines.

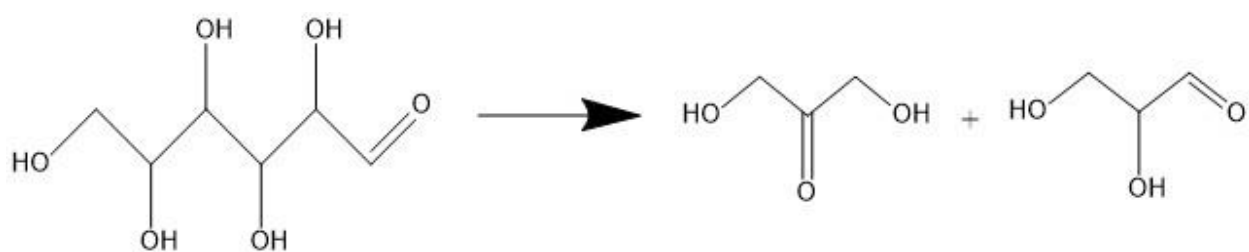


Figure 17. Simple sugar converted to 1,3-dihydroxyacetone and glyceraldehyde. Base catalyzed.

### 3.3.3 1,3-dihydroxyacetone to propane

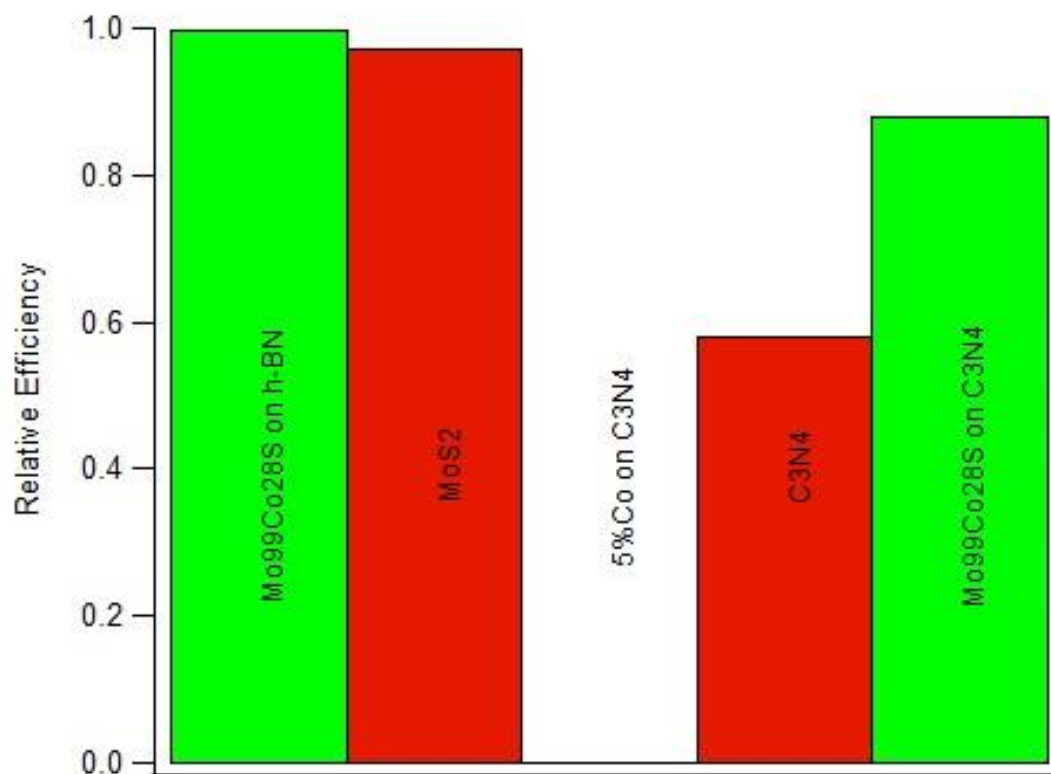
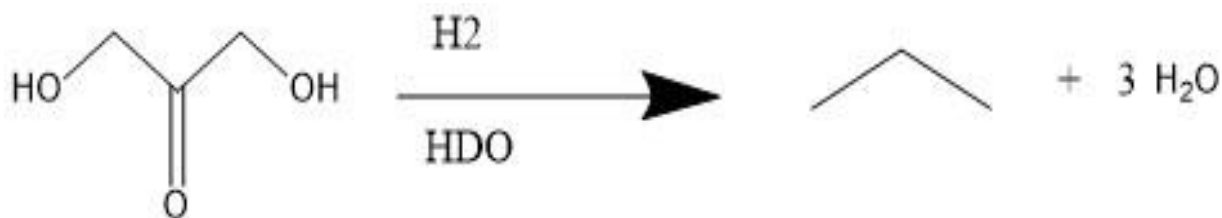


Figure 18. Relative efficiency of catalysts investigated



**Figure 19. 1,3-dihydroxyacetone converted to propane using HDO catalyst while under hydrogen atmosphere.**

Figure 18 shows the comparison of the efficacies of the tested catalysts to convert 1,3-dihydroxyacetone to propane. Molybdenum cobalt sulfide (MoCoS) supported on BN had the greatest efficiency for the conversion of 1,3-dihydroxyacetone to propane. Molybdenum disulfide (MoS<sub>2</sub>) was 97% as efficient as MoCoS on BN. Cobalt supported on C<sub>3</sub>N<sub>4</sub> yielded no measurable product of propane. Carbon nitride was nearly 60% as efficient as MoCoS on BN. Molybdenum cobalt sulfide supported on C<sub>3</sub>N<sub>4</sub> was approximately 90% as efficient as MoCoS on BN.

### 3.4 Discussion

No matter what the process or catalyst, the biomass source must be comprised of cellulose. Several processes have been developed for the conversion of cellulose-rich biomass to fuels, but important disadvantages attach to the ones so far in use.

The formation of syngas from biomass generates gases that are damaging to the environment and toxic to people. By converting biomass to sugars far less in the way of environmentally-damaging materials are produced.

The conversion of biomass to sugar has been well researched via acid hydrolysis or bacteria. A common acid used for the acid hydrolysis is sulfuric acid. Prior to WWII several plants attempted to utilize it, but failed owing to low production.<sup>68</sup> The most prevalent acid process today uses dilute sulfuric acid, but advances in this industry require an economically favorable process, that also easily recovers the acid catalyst.

The alternative standard method for converting biomass to sugar utilizes bacteria. This method began to attract research effort in the 1970s. Several pilot plants have been built worldwide, but no large-scale facilities so far.<sup>68</sup>

The process explored in the current study mechanochemically converted biomass to glucose using kaolin as a solid acid catalyst,<sup>69</sup> which only required water to extract glucose from biomass.

The second stage requires the conversion of glucose to 1,3-dihydroxyacetone (Figure 17). This conversion occurs via a base-catalyzed isomerization followed by a retro-aldol reaction. The advantage of this process is that there are no strict environmental conditions that must be maintained to keep bacteria alive. Another advantage is the independent commercial value of 1,3-dihydroxyacetone. It is stable and can be used in self-tanning products.

The final stage of this process easily converts 1,3-dihydroxyacetone to propane (Figure 18). Molybdenum disulfide ( $\text{MoS}_2$ ) is widely used as an HDO catalyst. Typical synthesis of  $\text{MoS}_2$  involves mixed metal oxides,<sup>70</sup> extensive time,<sup>70</sup> high temperatures,<sup>71</sup> radiation,<sup>72</sup> high pressure,<sup>73</sup> chemical vapor deposition,<sup>74</sup> and use of solvents. The catalytic activity occurs at the edges of the sulfur terminating layers, either by the vacancy of a sulfur atom or by two sulfurs forming an S-S



bond.<sup>75</sup> The addition of cobalt increases the stability of defects at the edges of the sulfur-terminating layers, thus intensifying catalytic activity.

The synthesis described in this research starts with the elements in their naturally-occurring state, milled them at stoichiometric ratios for four hours, and then milled with the support for another six hours. No high temperatures, pressures, or solvents are required.

During the course of this research it was also found that  $C_3N_4$  exhibits properties characteristic of HDO catalysts. It is true that compared to  $MoS_2$ , (a commonly used HDO catalyst)  $C_3N_4$  is only 60% as efficient. But when  $C_3N_4$  is used as a support for  $MoCoS$ , the efficiency increases by 150% of  $C_3N_4$  alone, or to about 90% of that of  $MoCoS$  on BN.

When one compares  $MoS_2$  to  $MoCoS$  (supported on BN) there is one factor that indicates the advantage of  $MoCoS$ : only 0.500 grams of catalyst needed added for each reaction. This means is that 100% of the 0.500 grams of  $MoS_2$  is  $MoS_2$  and of the  $MoCoS$  supported on BN, only 12.3% of that 0.500 grams is  $MoCoS$  (just 0.0615 grams). In other words,  $MoCoS$  produces more propane per unit catalyst than  $MoS_2$ .

### 3.5 Conclusion

This process studied here takes a biomass (high in cellulose), which would normally have been discarded, and converted it to sugar. This step was performed using a naturally occurring catalyst, kaolin. The subsequent conversion of sugar to 1,3-dihydroxyacetone was performed without any extravagant modification to the catalyst.

The final stage of this process utilized an HDO catalyst synthesized from its naturally occurring elements via mechanochemistry. The formation of the HDO catalyst used for this research required no metal salt precursors, no solvents, and no addition of heat (drying or calcination) -only the required elements in their natural.

This research shows that mechanochemistry is a viable process for synthesizing a desirable fuel from a renewable source without the need to form syngas or to use caustic acids or hard-to-maintain bacteria. Future research can now focus on synthesizing longer-chain fuels that can be used in gasoline engines.

## CHAPTER 4 : MECHANOCHEMICAL ESTERIFICATION OF THE OIL OF WINTERGREEN

### 4.1 Introduction

Esterification is a common synthesis utilized in both laboratories and industry all over the world. Esters themselves have a large variety of uses including as solvents, plasticizers, and even in the pharmaceutical industry.<sup>76-77</sup> Most notably esters serve to provide pleasant aromas for perfumes and as flavoring agents.<sup>78</sup>

Currently the general process for the formation of an ester is a reaction between a carboxylic acid and an alcohol in the presence of an acid catalyst, most commonly a mineral liquids acid, for example sulfuric acid.<sup>76, 79</sup> Since first described in 1895 by Emil Fischer,<sup>80</sup> this process has been extensively studied and gradually modified to maximize the product yield.

Over the past several years the production of fuels from biological sources has increased in response to demand for renewable sources and for lower build-up of atmospheric carbon dioxide. Production of such fuels requires esterification and/or transesterification. Continued use of liquid mineral acids as the catalysts in these processes is undesirable however in at least three respects. For one, it is today recognized that these mineral acid catalysts are highly corrosive (requiring regular maintenance of equipment) and environmentally hazardous, (aluminum chloride and zinc chloride, commonly used in industry, result in heavy-metal wastes)<sup>77</sup> – an unfortunate counterbalance to the otherwise green aspects of biofuels. For another, the water and free fatty acids generated by such catalysts both react with them in unwelcome ways -- reversing the

process or (in the case of fatty acids) forming side products (e.g., soap) that lower the overall yield of biofuel.<sup>26-27</sup> A third problem with such catalysts is that they can be difficult to separate from product.<sup>79</sup> Currently the only real advantage of continuing the use of traditional catalysts is that the yield of biofuels is both high percent and fast, whereas heterogeneous catalysts produce lower yields and may be slower.<sup>81</sup>

Nevertheless there are several advantages to transitioning to solid catalysts. Solid catalysts are significantly less corrosive to equipment. They themselves and their products are far less damaging to the environment.<sup>76</sup> Their more selective chemistry which results in fewer side reactions than currently-used catalysts.<sup>82-83</sup> Most importantly perhaps, with a solid catalyst the reaction is heterogeneous, thus facilitating the extraction of product from catalyst.<sup>79, 84</sup> As a result, solid catalysts can be more easily recycled multiple times, so that less waste is produced in academic or industrial settings.<sup>76</sup>

While there is a little information on solid-state esterification, what is currently being studied typically uses anhydrides as starting reagents,<sup>85</sup> potassium halide salts as catalysts,<sup>86</sup> or involves elevated temperatures (greater than 100° C) and extensive drying times.<sup>87</sup> Examples of solid catalysts that are in use today include zeolites,<sup>84</sup> ion-exchange resins,<sup>76, 82</sup> and superacids.<sup>79</sup> A very common method for making solid acid catalysts is the adsorption of a mineral acid onto the surface of a solid material and then using that complex as the catalyst. As part of their activation zeolites are at some point exposed to sulfuric acid,<sup>77</sup> as are coal fly ash<sup>88</sup> and zirconia.<sup>89</sup> Peat, for activation, is similarly exposed to sodium hydroxide.<sup>90</sup> Though these solid catalysts are less damaging to the environment, than traditional catalysts, what is even more desirable is a

catalyst that has sufficient acidic or basic properties to eliminate the need for adsorption. One possibility is clay.

The use of a clay catalyst has been studied by Bougeurra et al.<sup>27</sup> Their research has focused specifically on four distinct forms of Montmorillonite. However, as other researchers have done with non-clay solid catalysts, Bougeurra performed his reactions using reflux and distillation.<sup>27, 79, 82, 91</sup>

The process of esterification studied in the research reported here was accomplished via mechanochemistry -- through simply inputting, by mechanical means, the energy needed for the reaction to go forward for example, by grinding (as with mortar and pestle), sonochemistry (application of soundwaves), or ball milling.<sup>92-93</sup> This research utilized in particular high-speed ball milling to input energy. What makes mechanochemistry so ideal for green chemistry is that it reduces the need for solvents.<sup>93</sup> With the reduction of solvents less waste is produced for storage and treatment.

The aim of this research was to synthesize an ester utilizing a naturally occurring acidic catalyst via mechanochemistry. The clay used for this research was Kaolin, which is composed of layers of aluminum, oxygen, silicon, and hydrogen. Since kaolin is naturally acidic (unlike the solid catalysts mentioned above), no adsorption of a mineral acid is needed. Because kaolin is a solid, it is easily separated from the products. And as a naturally occurring material, it is not hazardous to the environment.

## 4.2 Experimental

### 4.2.1 *Materials*

Kaolin purchased from Old Time Pottery of Oviedo, FL.

Methanol purchased from Mallinckrodt Chemicals.

Decane 99%+ purchased from Acros.

Hydrochloric Acid purchased from Fischer Scientific.

Acetylsalicylic acid purchased from EM Science.

### 4.2.2 *Preparation of Acidified of Kaolin*

Ten grams of kaolin were weighed and placed in 1000ml glass beaker with 120ml of distilled water. Water was heated to boiling and 80ml of concentrated hydrochloric acid added to beaker. The solution was heated for two hours and then vacuum filtered. The resulting acidified kaolin was placed in oven at 100°C overnight.

### 4.2.3 *Preparation of Delaminated Kaolin*

Three grams of kaolin were placed in a tungsten carbide vial with four half-inch tungsten carbide bearings and milled at half hour intervals for a total of two hours. This process was repeated for four- and ten-hour kaolin samples.

#### 4.2.4 *Milling*

Reactants and catalyst were placed in a 440C stainless steel vial with three half-inch 440C steel bearings. Milling was performed using an 8000D SPEX mill at half hour intervals for a total of eight hours for each sample.

#### 4.2.5 *Sample preparation*

Starting materials for each reaction was comprised of 2.000g acetylsalicylic acid and 9.000mL of methanol, placed in each of twenty 65mL vials, four for each of the five catalysts under study (untreated, acidified, two-hour delaminated, and ten-hour delaminated kaolin), each catalyst being apportioned among its 4 vials at 0.250g, 0.500g, 0.750g, and 1.000g. To each vial, 40.000μL decane was added, as internal standard.

#### 4.2.6 *GCMS sample preparation*

After every half hour milling, 50μL of reaction was removed from vial and added to 5mL of dichloromethane. Each such sample was stirred and then subjected to centrifugation to separate the solid catalyst from liquid (starting materials, reaction product, and decane). After centrifugation, the liquid portion of the sample was transferred to a GCMS vial for analysis.

### 4.3 Data

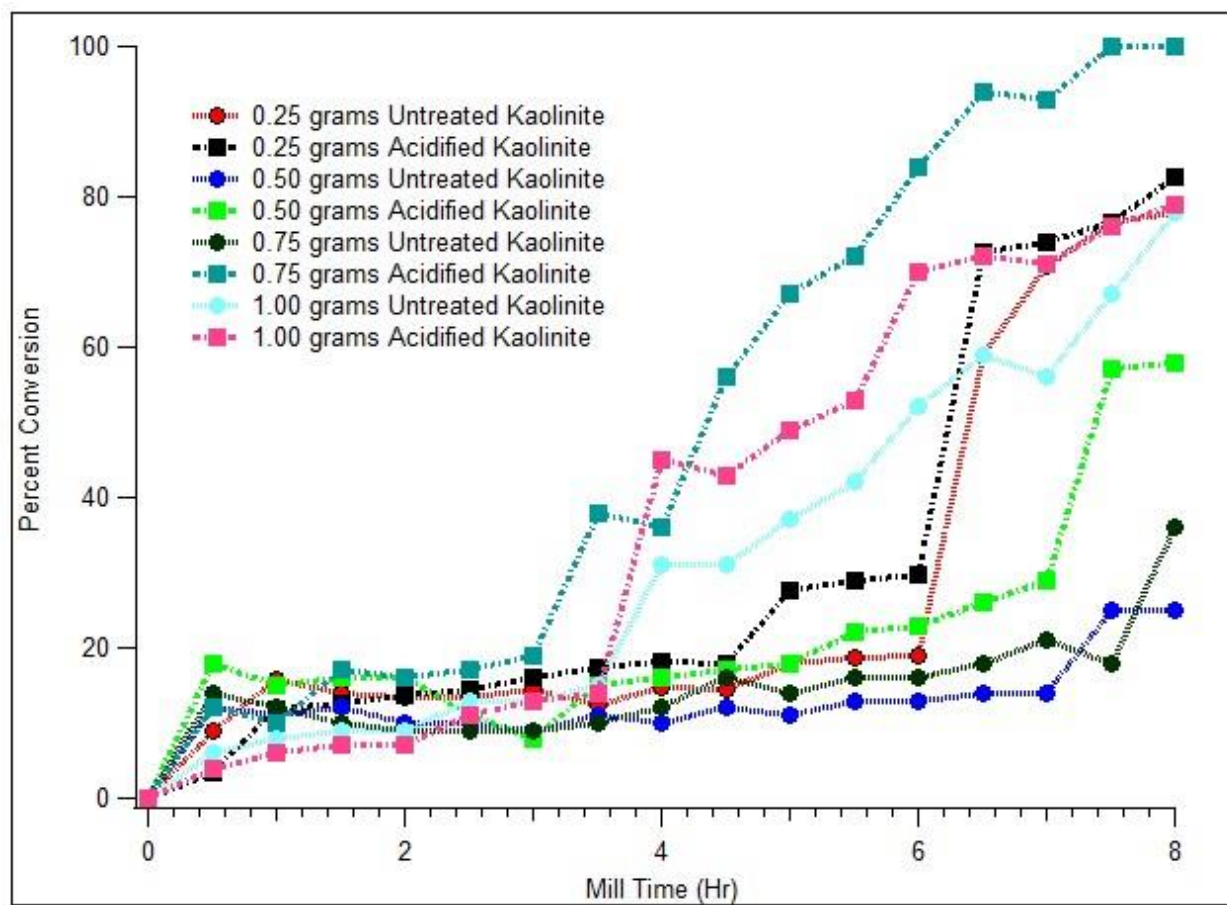


Figure 20. Comparison of acidified kaolinite to untreated kaolinite for the synthesis of oil of wintergreen.



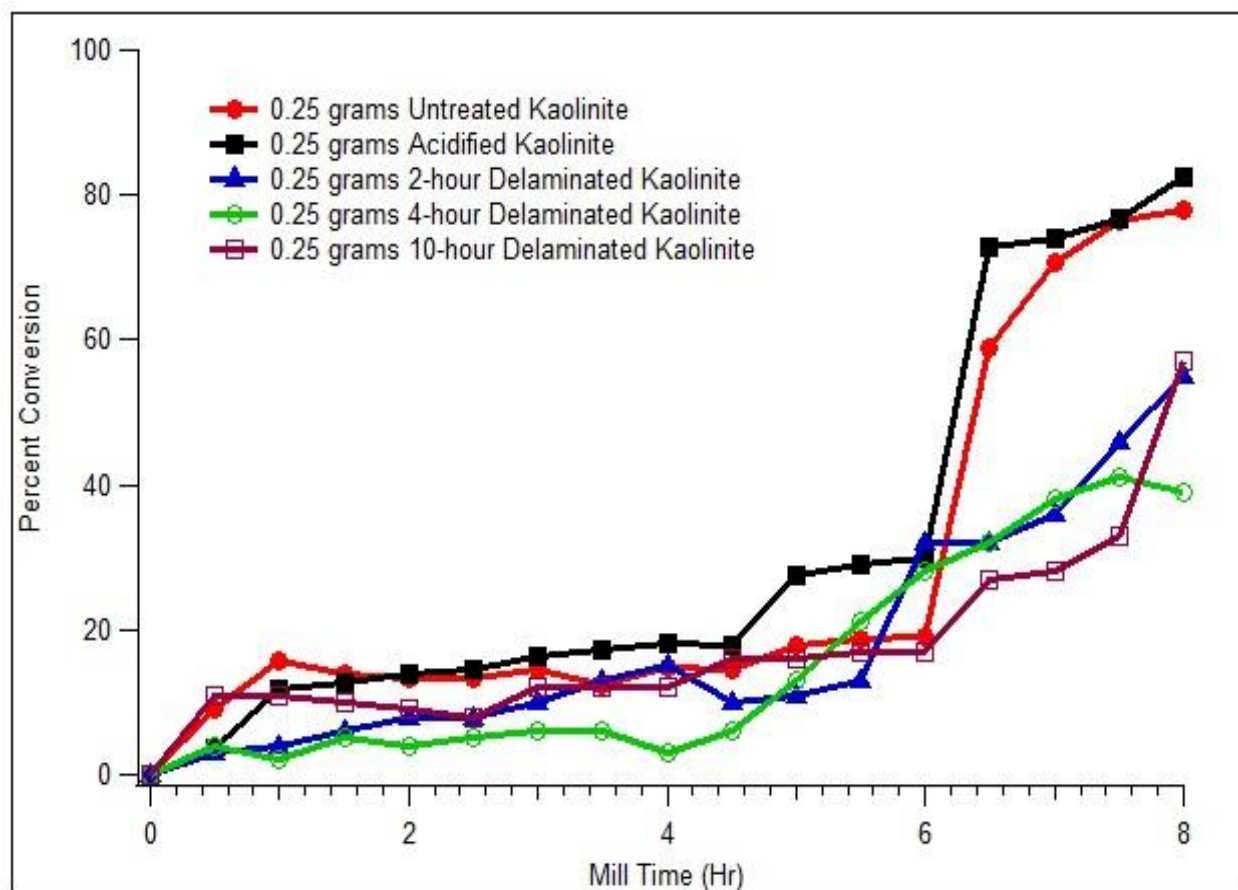


Figure 21. Percent conversion to oil of wintergreen using 0.25 grams catalyst

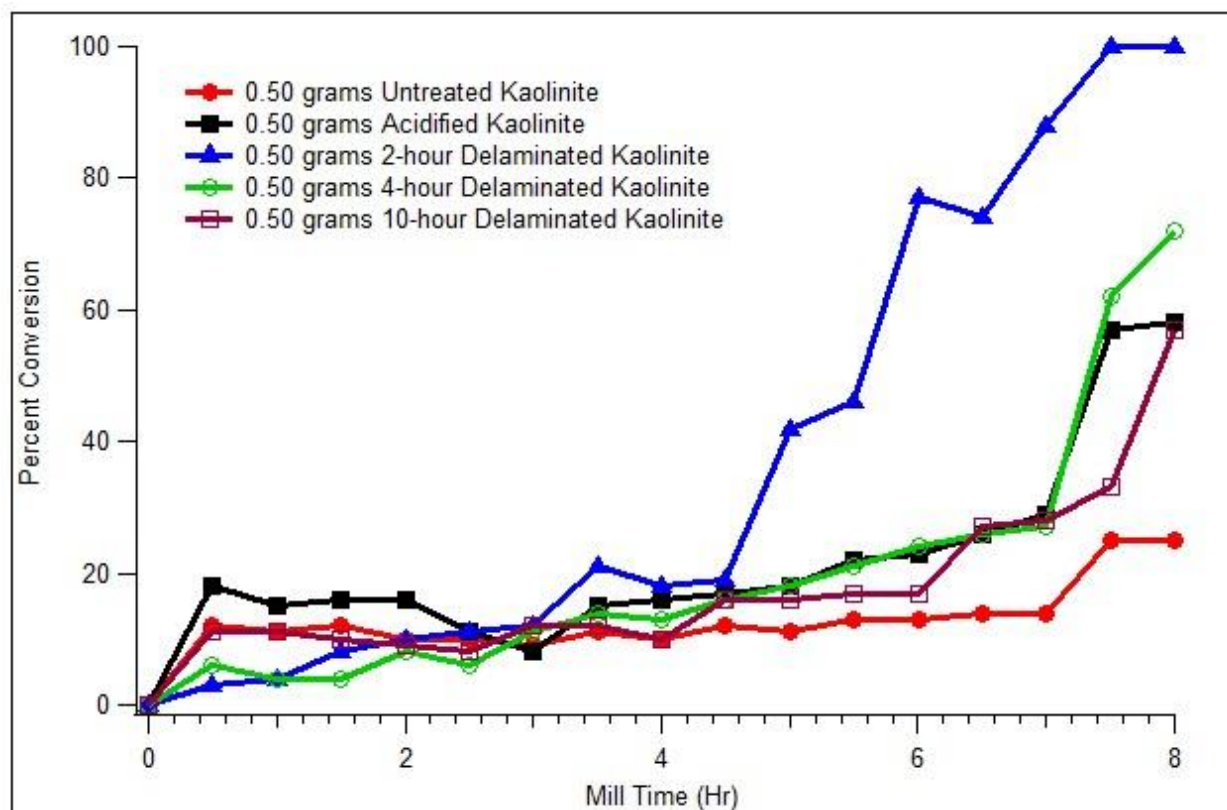


Figure 22. Percent conversion to oil of wintergreen using 0.50 grams catalyst

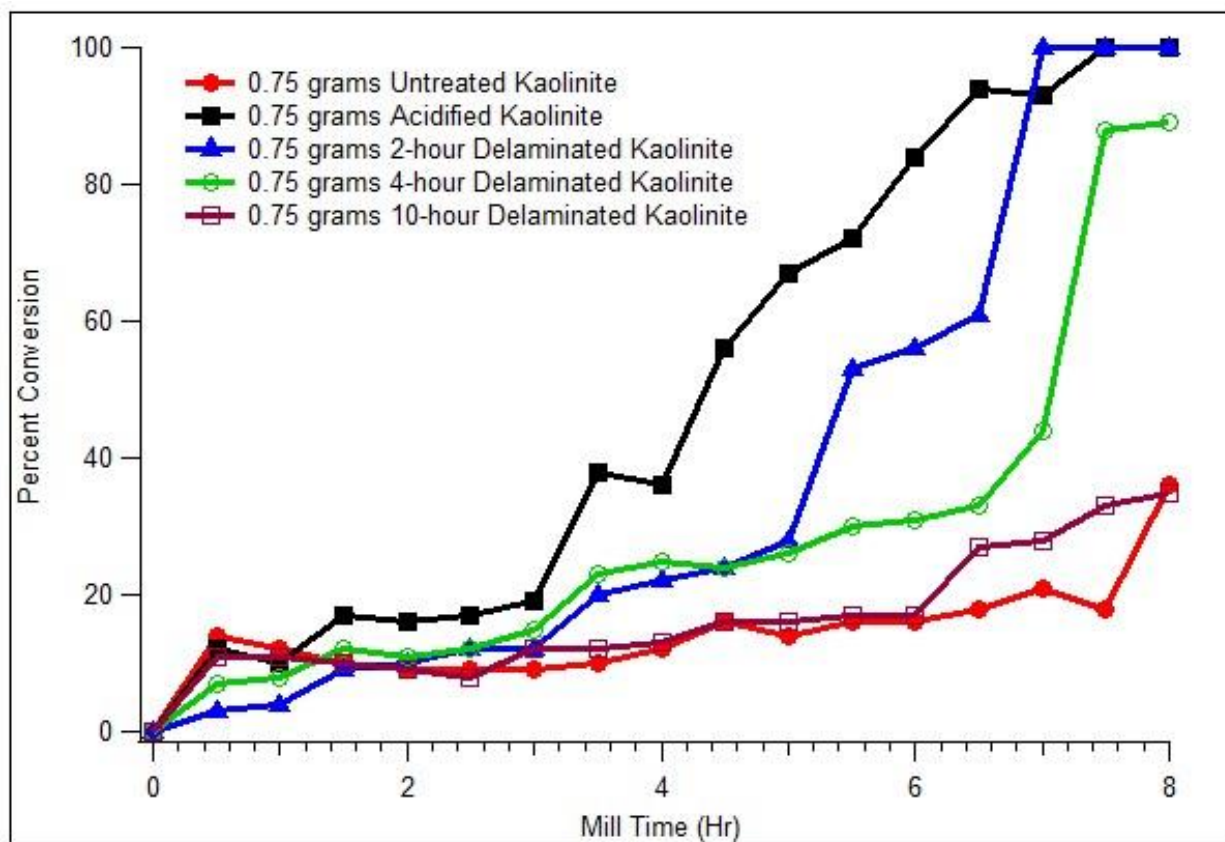
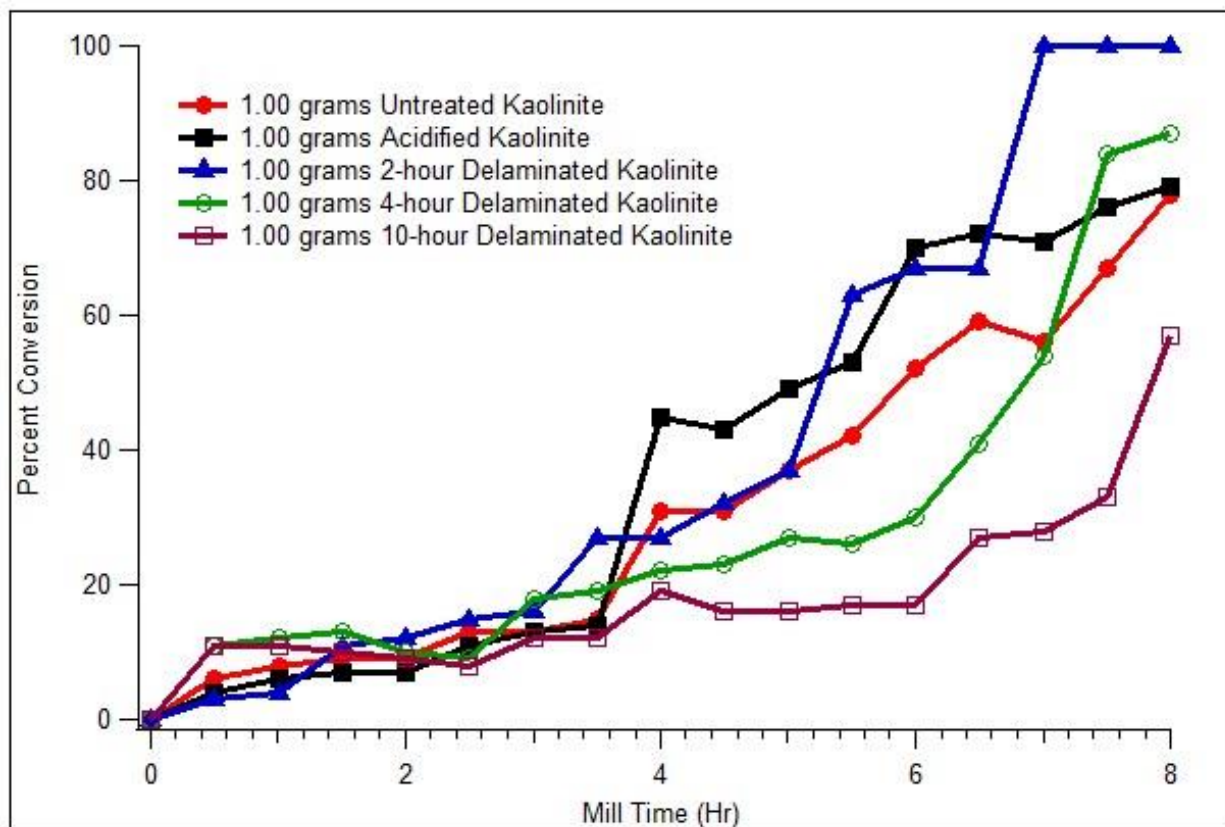
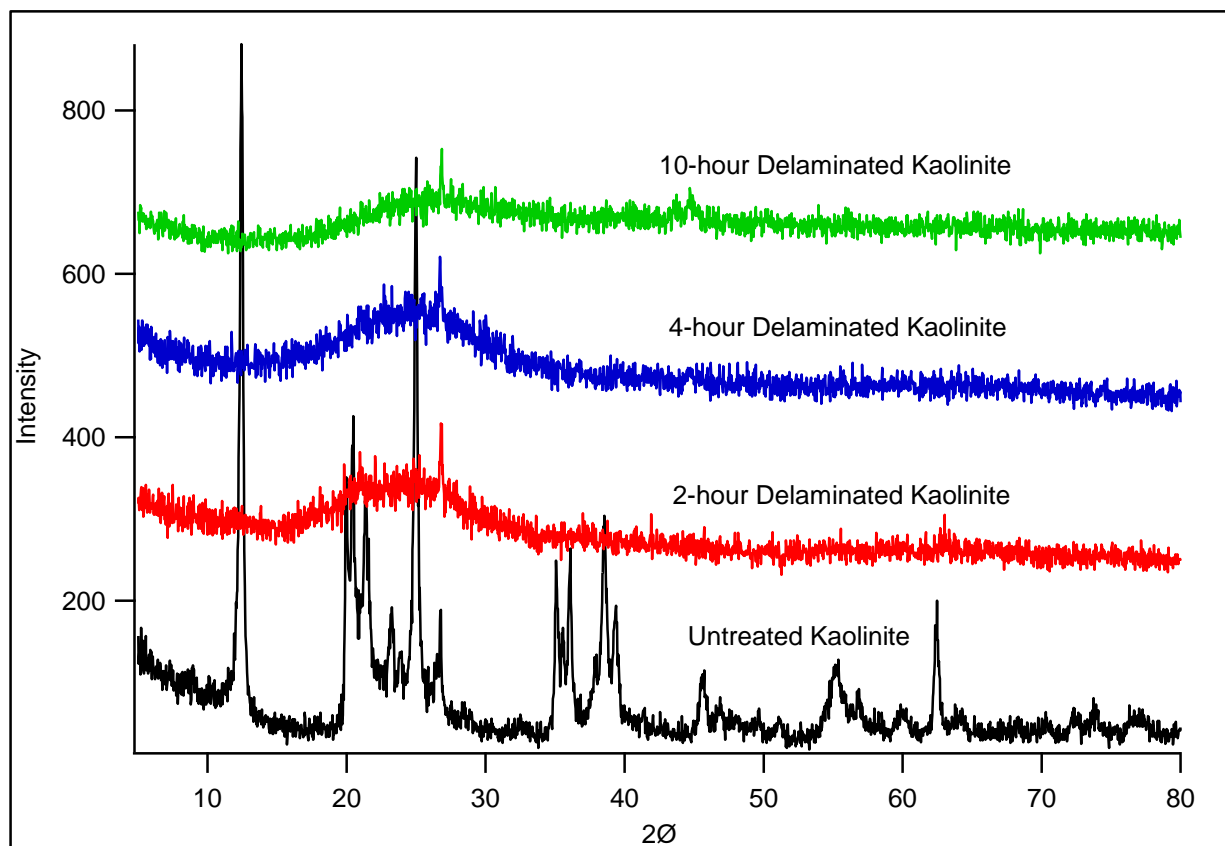


Figure 23. Percent conversion to oil of wintergreen using 0.75 grams catalyst



**Figure 24. Percent conversion to oil of wintergreen 1.00 grams catalyst.**

Each of the above figures shows the amount of catalyst used, the different treatments to the kaolin, the time of milling, and the percentage product yield for each form of treated kaolin.



**Figure 25.** X-ray diffraction (XRD) showed that after milling kaolin became amorphous.

#### 4.4 Discussion

The purpose of this research was to form an ester via mechanochemistry with a naturally occurring material as the catalyst. Kaolin exceeded this requirement. Being clay, kaolin is obviously not detrimental to the environment. Being a solid, it is easier to separate from the products and remaining starting materials. The varying treatments that were performed on the kaolin were undertaken in order to determine whether and how the catalytic properties of kaolin might be improved.

Figure 20 shows the comparison between acidified and untreated kaolinite. The acidified kaolinite did catalyze one reaction to a 100 percent yield, but did not have consistent conversion yields. Overall there was no significant advantage of acidifying kaolinite. An observation of this data shows that there was a period of induction, three hours, before any significant amount of product was formed.

Figure 21 compares the percent yield based upon the different treatments to the kaolin and using an 8:1 ratio of aspirin to catalyst. Figure 22 shows the percent product yields using a 4:1 ratio of aspirin to catalyst. Figure 23 shows the percent yields using a 2.6:1 ratio of aspirin to catalyst. Figure 44 shows the percent yields using a 2:1 ratio of aspirin to catalyst.

Delamination is performed to expose more acidic sites. Yet during the process of delamination the kaolin becomes amorphous., Figure 25. Extended milling continues to break the delaminated sheets even further. This decreases the acidic properties of the kaolin.

Untreated kaolin did promote the esterification process, but as the data indicates there was never more than an 80% conversion. Comparing the treated forms of kaolin one can see how it is possible to increase yield with minimal effort.

Although acidification of kaolin does increase the product yield, the amount of time involved in the acidification process takes more than 24 hours. The use of mineral acid was somewhat beneficial, but compared to just a simple 2-hour mill time to delaminate the kaolin, acidification is not the ideal route. Figure 21 shows that acidified kaolin has no significant advantage over untreated kaolin. In fact, untreated kaolin is a better catalyst than 2-hour, 4-hour, and 10-hour delaminated versions.

From Figures 22, 23, and 24, one can determine that the 2-hour delaminated kaolin yields a significant increase in product percentage, and decreases the total mill time needed for full conversion of aspirin to product. Acidified kaolinite also had one reaction with a 100 percent yield, but failed to have consistent yields. The 2-hour delaminated kaolinite was consistent in product formation.

The 4-hour delaminated kaolin does improve the esterification process, but when compared to the 2-hour delaminated kaolin, it is inferior. The product percentage did increase as the amount of catalyst increased, but even at 1.00 gram of catalyst the product percentage never reached 100 percent, while the 2-hour delaminated reached 100 product percentage in less time and with less catalyst.

The 10-hour delaminated kaolin never yields more than 60 percent. These results allow one to conclude that milling for this length of time to delaminate is not necessary, because compared to the 2-hour and 4-hour millings, the 10-hour milling not prove beneficial.

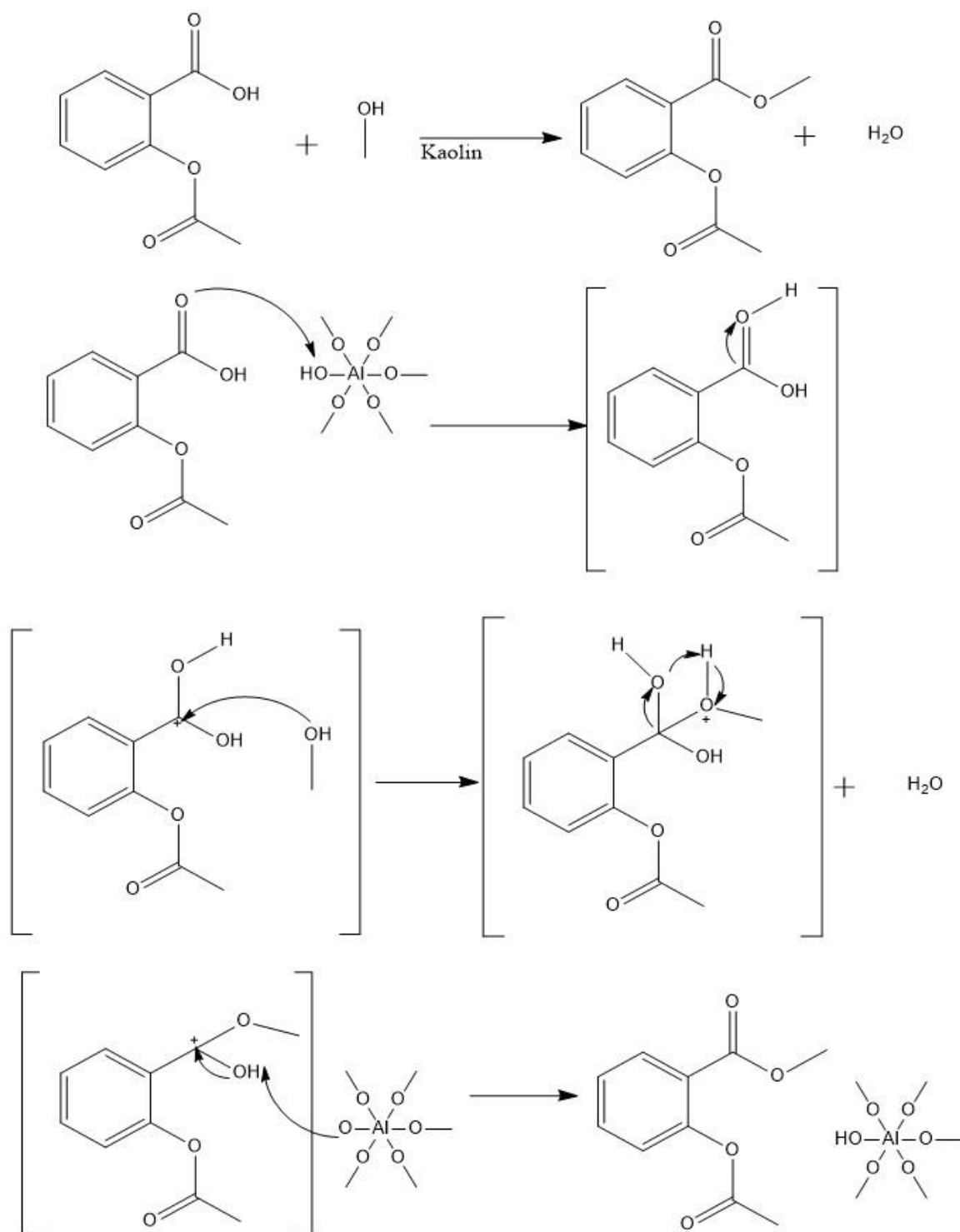
The acidification process involves the use of a mineral acid, washing, and drying. The entire process requires a great deal of time. Acidified kaolin does have advantages over untreated kaolin, but from the data here one can see that these advantages do not result in a significant increase of product yield or decrease in milling time. Overall, acidification has no significant benefit.

Among the different delaminated kaolin treatments, the obvious choice is the 2-hour delaminated. When one compares the product percentages and times to maximum yield the 2-

hour has significant advantages in both product yield and total mill time over the 4-hour and 10-hour delaminated.

Comparing the untreated, acidified, and delaminated kaolinites one can conclude that the 2-hour delaminated has significant advantages over all the other versions of kaolin.





**Figure 26. Proposed Mechanism of Oil of Wintergreen using Kaolinite as catalyst.**

#### 4.5 Conclusion

The aim of this research was to utilize a naturally occurring solid acid catalyst for esterification. The findings presented here indicate that the 2-hour HSBM pretreatment of kaolin is an ideal substitute for mineral acids.

This finding suggests that a fruitful avenue for future research is to investigate how this catalyst functions with longer-chain alcohols and different carboxylic acids, for applications in academic, industrial, and pharmaceutical contexts.

## **CHAPTER 5 : MECHANOCHEMICAL TRANSESTERIFICATION OF FATTY ACID ETHYL ESTERS USING RECYCLABLE BASE**

### **5.1 Introduction**

The world is dependent upon fossil fuels as its primary energy source. The combustion of fossil fuels such as coal or oil has a negative effect on the environment<sup>46-47</sup> and its emissions are harmful to human health.<sup>48</sup> Moreover, they are not practically renewable.

Since fossil fuels in the long term are thus not a sustainable source of energy, an alternative must be found. Requirements for alternative energy sources include: renewability, and minimal environmental impact. Whatever the source, it needs to fit within the current distribution infrastructure. Some examples of alternatives being explored include: solar, wind, geothermal, and biofuels.<sup>12</sup> Each has excellent merits, however with our current infrastructure biofuels are the most viable option.

There are several advantages to transition from fossil fuels to biofuels. One advantage of biofuels is reduction in CO<sub>2</sub> emissions.<sup>94</sup> Another is the time to regenerate the feedstock of the biofuels. Fossil fuels can take millions of years to regenerate, where the biomass used for biofuels can be regenerated in as little as one year.

Biofuels are any fuels that derived from biomass.<sup>12</sup> The first-generation biofuels were primarily made from food crops (grain, sugars, or vegetable oils),<sup>94-96</sup> a downside to these feedstocks is that they directly subtract from food-stock available to people.<sup>95, 97</sup> And though

vegetable oil can be used as fuel in diesel engines, it is a poor fuel: its high viscosity hinders the atomization needed to maximize combustion in a diesel engine.<sup>98</sup>

The second-generation biofuels are from various plant stocks comprised of cellulose or lignocellulose (forestry residues, switchgrass, even tree bark).<sup>94, 97</sup> One major advantage of these sources is that they do not compete with food stock: large areas of land are required for the growing of crops, resulting in less land for growing crops for food. A second advantage is that cellulose and lignocellulose are both found in all parts of the biomass, where first-generation sources require a high sugar content.

Third generation biofuels are generated from an aquatic source, generally algae. They bring several advantages, two being that algae does not reduce food sources and that the land requirement for growing it is far lower than that required for first- and second-generation feedstocks. However, a significant disadvantage of algae is the high capital start-up cost needed to maintain required environmental parameters.<sup>99-101</sup>

The question arises: if biofuels are better overall, then why has the transition from fossil fuels to biofuels not already occurred? The most significant obstacle to the transitioning to biofuels has been the scale-up that is required to off-set the current demand for energy from fossil fuels. In the case of the first- and second-generation biofuels, it is the amount of land needed to grow enough feed-stock to satisfy the current energy demand.<sup>102</sup> As for the primary obstacle to shifting to third-generation biofuels, it is the size and the cost of the facilities needed to meet current energy requirements.<sup>100</sup>

Currently the most common synthesis of biodiesel is the transesterification of triglycerides with short-chain alcohols using a base catalyst. Acid catalysts have been shown to transesterify triglycerides, but the process is slower and requires more energy.<sup>24</sup> The most common bases used in transesterification reactions are sodium hydroxide or potassium hydroxide. There are several drawbacks to the use of these catalysts. They are highly caustic to people and the environment (requiring expensive cleanup if a spill occurs). That these catalysts are also liquid makes the overall synthesis homogeneous, so that the separation of the catalyst requires additional steps. Even the water used for extraction of the catalyst is highly toxic and environmentally damaging.<sup>103</sup> Additionally, synthesis of biodiesel using the liquid catalysts mentioned can result in saponification.<sup>104</sup>

The two most common forms of biodiesel synthesized are fatty-acid methyl ester (FAME) and fatty-acid ethyl ester (FAEE). Both FAME and FAEE can be made from vegetable oils or animal fats via transesterification with an alcohol. FAME is the more commonly synthesized because it is easier to make. The overall process for converting methanol to a methoxide anion is cheaper, faster, and requires less energy than is that required to convert ethanol to an ethoxide anion.<sup>105</sup> A serious problem in using methanol is that its primary source is petroleum, which renounces the green advantage attaching to the transition to biofuels in the first place. Another is that methanol is highly toxic to humans: exposure to it may lead to nausea, blindness, and even cancer. Lastly since all the products from FAME synthesis are contaminated with methanol, additional steps are required to remove the methanol before the products are safe for people. Although FAEEs require more time and energy to produce than FAMEs, they are far more friendly

to the environment; as ethanol is derived from renewable agricultural sources, is not detrimental to the environment or toxic to people.<sup>106</sup>

In order to avoid the use of caustic-liquid catalysts, many researchers have studied the synthesis of FAME with solid acid or base catalysts. The transition to solid catalysts will have an initial high starting cost, but the benefits will easily outweigh this initial cost. Solid catalysts have several advantages over traditional liquid catalysts. First, they are easier to separate from both reagents and products, by a single step – centrifugation.<sup>107</sup> Second, solid catalysts are recyclable, whereas liquid catalysts can be used only once.<sup>108</sup> One solid catalyst, calcium oxide, was observed to catalyze the transesterification of soybean oil to biodiesel up to eight times before needing to be reactivated.<sup>107-109</sup> Third, solid catalysts are environmentally safer. Calcium oxide has even been used in agricultural fields to adjust the pH of soil.<sup>110</sup>

Some solid base catalysts that have been researched include Mg/Zr,<sup>111</sup> NaX loaded with KOH,<sup>112</sup> and KI supported on silica.<sup>113</sup> Solid acid catalysts researched include sulfonated zirconia,<sup>114</sup> zeolites,<sup>115-116</sup> and carbon-based acids.<sup>117</sup> Similar to liquid acid catalysts, solid acids had lower yields compared to solid bases.<sup>118</sup> The significant disadvantage of these catalysts is in their synthesis. Several require the use of caustic reagents, which defeats the purpose of green chemistry. In the case of NaX loaded with KOH, KOH itself is environmentally damaging. The standard precipitation synthesis of sulfonated zirconia uses both ammonia hydroxide and sulfuric acid.

The chief criterion for catalyst selection for the present research adherence to the goals of green chemistry. Catalysts chosen had to be environmentally benign or significantly less

environmentally destructive than traditional catalysts. They had to be recyclable and either naturally occurring or their synthesis should, if possible, not be environmentally destructive. A secondary criterion is a catalyst's accessibility.

Moving to recyclable solid catalysts is only one step in the transition to biodiesels; the next step is improving the synthesis process. Currently, refluxing with solid catalysts to synthesize biodiesels requires prolonged reaction times. Scaling-up this process would also require large reactors and substantial energy inputs for heating. The combination of these factors make the cost of scale-up very high. However, utilizing mechanochemical processing makes the large-scale production of biodiesel a real possibility.<sup>119-121</sup>

Mechanochemistry is inducing a chemical reaction through compression, friction, and shearing forces<sup>1</sup>. Since the heating needed for transesterification is provided by the friction of bearings striking each other, no external heating is required. The compressive and shearing forces are capable of breaking existing chemical bonds. Because mechanochemistry reduces the need for solvents, there is less storage of solvent or waste at the industrial level. Each impact generates enough energy that, when combined with the catalyst, overcomes the energy barrier that would otherwise inhibit the synthesis of biofuel from canola oil and ethanol.

The focus of this research was the synthesis of biodiesel from canola oil and ethanol e utilizing naturally occurring non-toxic catalysts via mechanochemistry.

## 5.2 Experimental

### 5.2.1 *Materials*

Canola oil from supermarket.

Ethanol from Chemistry Department University of Central Florida.

Seashells collected from Gulf of Mexico were used as source of limestone.

Boron Nitride from Saint-Gobain Ceramics

Talc from IMERYS.

Magnesium Oxide from J.T. Baker.

Strontium Oxide from Alfa Aesar.

### 5.2.2 *Synthesis of Calcium Oxide*

Limestone was calcined at 1000°C for two hours.

### 5.2.3 *Synthesis of Calcium Hydroxide*

Calcium hydroxide was prepared by placing 50g of calcium oxide into 1000mL glass beaker and then adding 500mL of deionized water. Stirred overnight at 100 rpm. Vacuum filtration performed to remove excess water and material then dried in oven at 100°C overnight.



#### *5.2.4 Delamination of Talc*

Milling was done using SPEX 8000D mill at ½ hour intervals for total mill times of 2, 10, and 20 hours, using 440C steel vials with three ½ inch 440C steel bearings.

#### *5.2.5 Calcination of Talc*

Calcination of un-milled talc was done at 550°C for two hours.

#### *5.2.6 Activation of Boron Nitride*

Boron nitride was milled for two hours in a 440C stainless steel vial with three ½ inch 440C stainless steel bearings. Milling done using SPEX 8000D mill.

#### *5.2.7 Synthesis biodiesel via reflux with calcium oxide*

Into 50 mL round bottom flask 25 mL of canola oil and 16 mL of ethanol were poured into. Temperature was set to 85°C, magnetic stirring set to 100 rpm, then 1.00 gram of calcium oxide was added.

### 5.2.8 *Synthesis biodiesel via attrition mill with calcium oxide or strontium oxide*

Into attrition mill poured 300 milliliters of vegetable oil, 160 milliliters of ethanol, and 11.6 grams of calcium oxide or strontium oxide then added. Milled for one to four hours at 700 rpm and repeated at 300 rpm. Milling done using Union Press attrition mill.

### 5.2.9 *Synthesis via attrition mill with magnesium oxide or any talc variation*

Into attrition mill 300 milliliters of vegetable oil, 160 milliliters of ethanol, and either 11.6 or 25 grams of catalyst were then added. Milled for four, eight, or twelve hours at 700 rpms. Milling done using Union Press attrition mill.

**Table 2. List of the catalysts studied, their turnover frequency, the time to maximum product yield and percent converted.**

<b>Identifier</b>	<b>Mass Catalyst</b>	<b>Turnover Frequency (s<sup>-1</sup>)</b>	<b>Time (hrs)</b>	<b>Percent Converted</b>
Strontium Oxide	11.6	0.00231205	1	99.3
Calcium Oxide	11.6	0.000274391	4	87.1
Calcium Hydroxide	11.6	0.000252634	4	60.7
Magnesium Oxide	11.6	8.26309E-6	8	7.3
Magnesium Oxide	25	4.62189E-6	8	4.4
Untreated Talc	11.6	0.000137776	12	19.4
10-Hour Delaminated Talc	25	5.30537E-5	12	16.1
2-Hour Delaminated Talc	11.6	0.000164053	8	15.4
20-Hour Delaminated Talc	11.6	0.000294017	4	13.8
20-Hour Delaminated Talc	25	6.77176E-5	8	13.7
10-Hour Delaminated Talc	11.6	7.59898E-5	12	10.7
Untreated Talc	25	3.31174E-5	8	6.7
2-Hour Delaminated Talc	25	1.54877E-5	4	4.7
Calcined Talc 500°C	25	1.97716E-6	25	0.6

### 5.3 Data

Table 2 provides the results of the catalysts tested in the transesterification of canola oil and ethanol to FAEE. The data provided is the highest percent converted in the least amount of time.

### 5.4 Discussion

#### *5.4.1 Mechanochemistry vs. Reflux*

Part of the transition to “green” chemistry is not only replacing hazardous reagents with safer reagents, but also utilizing recyclable catalysts. Today, even though many researchers are transitioning to solid catalysts, they are still performing transesterification via reflux. The range of times to complete a reaction varied from two hours<sup>122</sup> to ten hours,<sup>123</sup> which is a significant disadvantage for industrial scale-up. One means of decreasing the time of transesterification was the pretreatment of the catalyst. Pretreatment typically involves placing a given amount of catalyst in methanol and refluxing for an hour to 1.5 hours. Kawashima et al. compared pretreated to untreated calcium oxide and found that the reaction times decreased and yields of FAME increased.<sup>123</sup>

Another disadvantage the industrial scale-up of reflux would have is the use of methanol. The most distinct advantage ethanol has over methanol is that ethanol is less toxic. Ethanol is safe for human consumption (in moderation), methanol is toxic and unsafe for human consumption.<sup>105</sup>

The primary source of methanol today is from petroleum. This means that using methanol for biodiesel production would still require fossil fuels.<sup>106</sup> Ethanol does require more energy and time for the formation of biodiesel, but the primary source is agricultural and is far safer than methanol.

During the course of this research, FAEE was synthesized by recreating the most common conditions utilized for the synthesis of FAME via reflux. Reaction temperature was set to 85°C and the stirring rod was set to 100 rpm. No pretreatment was applied to the calcium oxide. Reaction was stopped at 40 hours with only a 91% conversion.

The amount of time to make FAEE via reflux overshadows any advantages ethanol and solid catalysts have. What is needed is a process that will overcome the time disadvantage of using ethanol.

The synthesis of FAEE via mechanochemistry converted 87% of the canola oil in only four hours, using calcium oxide as the catalyst. When compared to the reflux, the mechanochemical process took 1/10th the amount of time and had only 4% less conversion of canola oil. Mechanochemistry significantly reduced the time needed for synthesis. Another advantage would be no external heat is required, as the friction from the bearings generates heat.

#### 5.4.2 *Metal Oxides*

Table 2 shows the percent of canola oil converted to biodiesel in the presence of multiple catalysts. Strontium oxide (SrO) had the best catalytic activity with 99.3% conversion in an hour. Calcium oxide (CaO) had an 87.1% conversion at 4 hours and magnesium oxide (MgO) converted

less than 10%, regardless of mill time or amount of catalyst. This reinforces the trend of catalytic activity of alkaline-earth metals; strontium is greater than calcium and calcium vastly greater than magnesium<sup>124-125</sup>.

Wang, L. and Yang, J. were able to utilize nano-MgO and obtained a 99% conversion of soybean oil.<sup>126</sup> They obtained this conversion at 523°C and 24 MPa; these parameters, however, are not realistic for industrial scale-up.

#### 5.4.3 *Talc*

Talc was selected, as it is a naturally occurring base that is non-toxic to people and safe for the environment. The composition of talc consists of layers of magnesium oxide, magnesium hydroxide, and silicon oxide. Although normal magnesium oxide is basic, it is face-centered cubic (fcc), meaning that not all of the basic sites are exposed. By milling talc, the layers are delaminated, exposing the magnesium oxide and hydroxide basic sites. The silicon oxide layer acts as a support to the now dispersed magnesium oxide and hydroxide sites.

Table 2 shows that when the 11.6-gram catalyst load transesterifications are compared, the percent of product formed decreased as the pretreatment time increased. When the 25-gram catalyst load transesterifications are compared, there was only an increase in product formation with the 10-hour delaminated talc, followed by a decrease of product formation with the 20-hour delaminated talc.

The pretreatment process was performed with a shaker mill; this process delaminated the talc, which exposed additional basic sites. However, the layers of talc remain subjected to the high-energy impacts of the media in the shaker mill. The impacts on the separated layers continue to break the material down and this increases the amorphous state of the catalyst. The result is a decrease in basicity of the catalytic sites.

When comparing the product yields of each form of talc the untreated had the highest percentage of product. This is attributed to the attrition mill performing two operations at once: delamination of catalyst and transesterification. As the talc is delaminated each layer is pulled away by the oil and ethanol in the reactor. Being liquids they hinder the fracturing of the talc layers, which allows for the basic catalytic sites to promote transesterification.

When comparing the 11.6 gram to 25 gram catalyst loadings one can observe that the untreated talc worked best at the lower catalyst loading while the 10-hour delaminated work better at the higher loading. This is attributed to the amount of catalyst that was processed. The increase in mass inhibited the untreated and 2-hour delaminated talcs from catalyzing the transesterification process. The increase in mass did provide enough basic catalytic sites that the 10-hour delaminated talc was able to catalyze the transesterification process. The 20-hour delaminated talc took twice the time to achieve almost the exact same percent conversion.

#### 5.4.4 *Recyclability*

As explained in the introduction liquid catalysts are not recyclable, where solid catalysts can be recycled multiple times. Magnesium oxide and talc had no significant yields, as a result neither were selected for recycling.

The amount of strontium oxide recovered after milling was 2.04 grams, which is 17.5% of the 11.60 gram starting amount. This significant loss of catalyst negates any benefits gained from utilizing strontium oxide, as it would require the addition of new catalyst with each run.

Calcium oxide was the only catalyst selected for recycling as it had both high percent conversion and retained mass of catalyst. After catalyst was separated from product and reactants it was immediately used in another reaction, this was repeated for three more conversions. Each four-hour milling resulted in an average of ten percent decrease in product conversion. Reduction in product conversion was also observed by Granados et al. when they observed a ten percent reduction between first and second reactions.<sup>108</sup> This decrease is easily overcome by extending the mill time. Other studies have proven the recyclability of calcium oxide with methanol. Though an increase in viscosity was observed

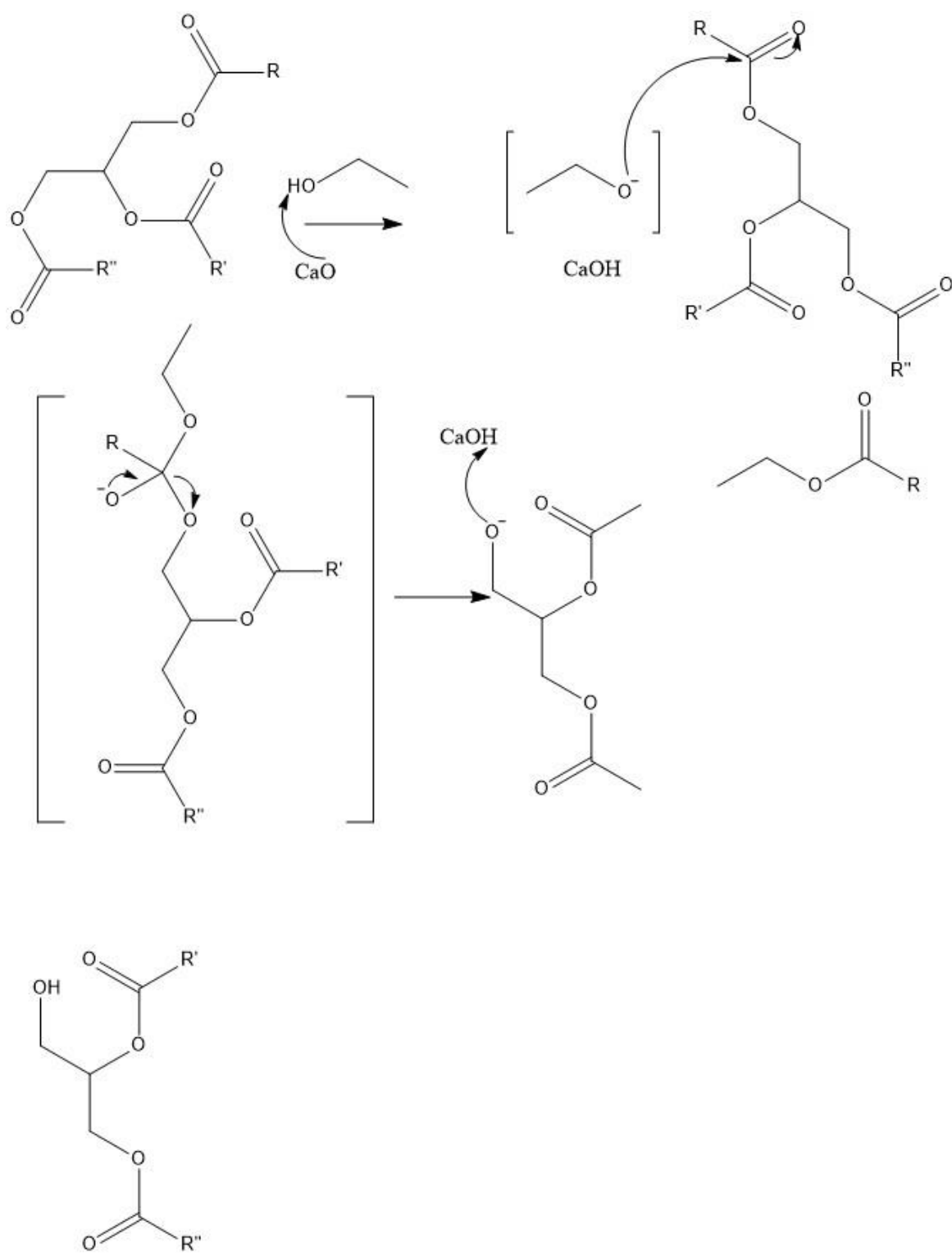


Figure 27. Step one proposed Mechanism synthesis of FAEE with calcium oxide catalyst.



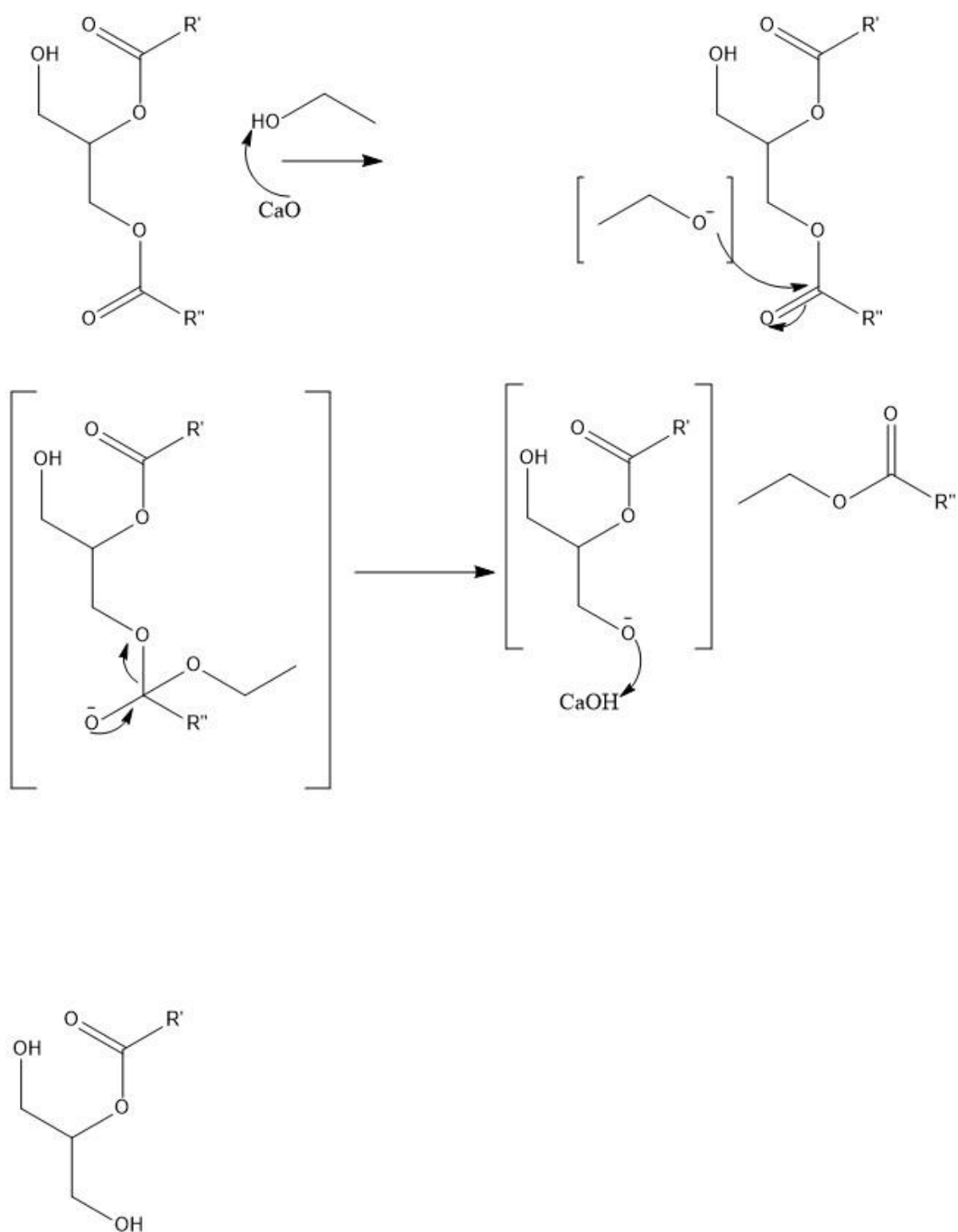


Figure 28. Step two proposed Mechanism synthesis FAEE with calcium oxide catalyst.

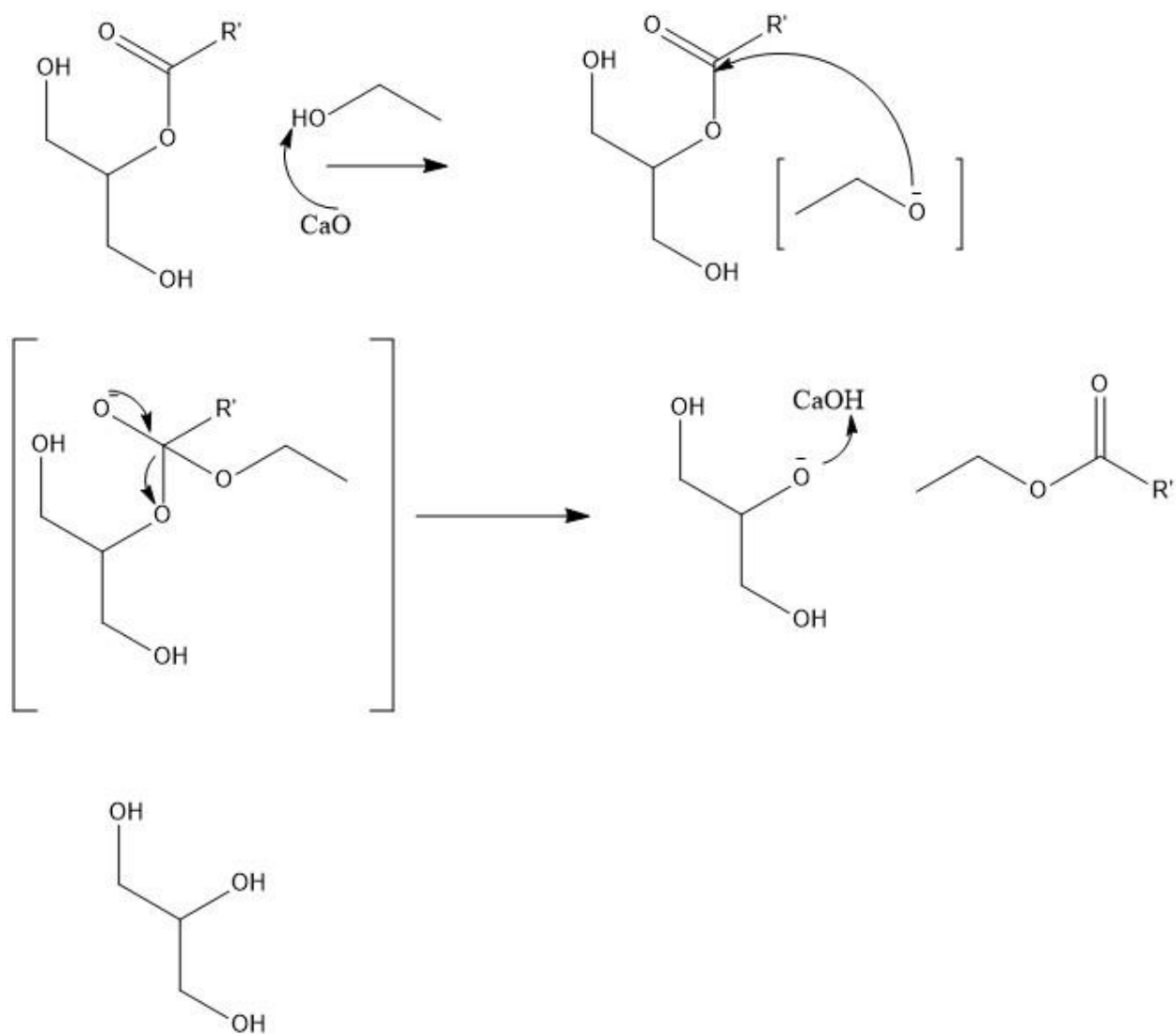


Figure 29. Step two proposed Mechanism synthesis FAEE with calcium oxide catalyst.

## 5.5 Conclusion

Magnesium oxide had no significant catalytic effect on the transesterification of canola oil with ethanol. Talc, which has a layer of magnesium oxide, was more effective than magnesium oxide alone, but only had a maximum yield of 19.4%.

Both strontium and calcium oxide readily catalyze the synthesis of biodiesel. Strontium oxide had the highest percent conversion in the least time, but require adding more catalyst for every reaction. Calcium oxide does lose catalytic activity with each subsequent milling. This can be rectified by calcining the catalyst to reactivate sites.

Mechanochemistry provides advantages for the synthesis of biodiesel. First it provides the energy needed to synthesize FAEEs, allowing for the transition from FAMEs. Second, mechanochemistry reduced the synthesis time from days to hours. Third, mechanochemistry can be readily scaled up compared to traditional reflux.

## CHAPTER 6 : CONCLUSION

Research into biofuels has seen significant focus on the sources and actual synthesis of biofuels. Another area that is seeing attention is material interactions with biofuels. This leads to the long-term study of polymer interactions with biofuels. Observing the interactions between biofuels and polymers demonstrated the need to change either the composition of polymers, that interact with biofuels or change the biofuels so that they are not destructive to polymers. Currently biofuels are not a significant source of fuel thereby making it easier to change biofuels than to change the entire polymer industry. The addition of a simple aromatic compound (which can be derived from biomass waste) is enough to prevent the degradation of polymer. Lignin can be used as a source of these compounds and kaolinite can be used to extract these compounds via mechanochemistry. By using lignin one can recycle a material that would otherwise be discarded as waste to be burned for fuel or buried. Then the question became could one of the aromatic compounds be bonded to the fuel? Ethanol being a short-chain alcohol could be easily bonded to an aromatic compound with an acid functional group, a simple esterification reaction.

Then the question becomes is it possible to perform an esterification reaction via mechanochemistry? Esterification is a reaction that is widely used in industry, pharmacy, and academia, but large amounts of waste are being generated as this reaction commonly uses caustic acids that cannot be recycled as catalysts. The transition to solid catalysts will reduce waste produced because they can be recycled. Solid catalyst used today are most often made from the adsorption of an acid onto the solid, yet when adsorption was performed here one can observe inconsistent results. The data lead to the idea to mechanical grind kaolinite to peel back the layers

that make up kaolinite exposing more catalytic sites. This simple process reduced the overall time needed to prepare the catalyst, didn't require the use of caustic acids, and had consistent yields higher than the acidified kaolinite. In the end, it was proven that esterification can be done both with a solid catalyst and mechanochemically. This led to the idea of applying this transition to mechanochemistry with a solid catalyst into another area similar to esterification, transesterification.

The transesterification reaction conducted in this research focused on the synthesis of biodiesel. The synthesis of biodiesel was not just a transition to solid catalysts, but also the use of mechanochemical synthesis instead of reflux/distillation, and the transition to ethanol from the more common (toxic) methanol. Transesterification, like esterification, is commonly performed in industry, academia, and pharmacy by using liquid catalysts that cannot be recycled, which results in generating large amounts of waste. The transition to a solid catalyst allows for the recycling of that catalyst, reducing overall waste generated. Mechanochemistry processing has distinct advantages over refluxing the first being the amount of energy generated easily allows for the transition from methanol to ethanol. This transition reduces the toxicity that is inherent using methanol. A second advantage is the time to synthesize, using ethanol, is significantly reduced compared to reflux. Refluxing using calcium oxide required days, where the transition to mechanochemistry will reduce that time to hours. A third advantage is in the overall scale-up using mechanochemistry. Both the transition to ethanol and the reduced time to synthesize make mechanochemistry ideal for the industrial production of FAEE.

The next stage in research focused on synthesizing another widely used fuel from biological sources using mechanochemistry with solid catalysts. Both esterification and

transesterification were one-pot reactions, the synthesis of propane from biomass required three distinct steps, with each step requiring a different catalyst. The first step of this process starts with a biomass containing cellulose and converting to sugar using mechanochemistry catalyzed by kaolinite. This is a hydrolysis reaction and typically catalyzed with a liquid acid. Kaolinite was used instead as it is acidic and being solid recyclable. The second step required the conversion of sugar to 1,3-dihydroxyacetone. This step is a base catalyzed retro-aldol reaction, and similar to the first step the commonly used liquid catalyst is replaced by a solid base, specifically a mix of 5% erbium oxide and 95% boron nitride, which can be recycled. The final step converted the reagents, 1,3-dihydroxyacetone and  $\text{H}_2(\text{g})$ , into propane using an attrition mill and a hydrodeoxygenation (HDO) catalyst. The HDO catalyst was synthesized mechanochemically by milling stoichiometric ratios of sulfur, cobalt, and molybdenum. Overall each stage of this conversion to propane was done via mechanochemistry resulting in reduction of waste.

Over the course of this research there were several points where mechanochemistry demonstrated that it was better suited than traditional synthesis. In the case of propane synthesis not all reactions needed to be in solution; this reduced the need for solvents, which decreased the overall waste produced. The energy produced from impacts is more than sufficient to allow the transition to safer reagents, i.e. ethanol, that require more energy. When compared to traditional synthesis (reflux/distillation), mechanochemistry reduced the time needed for synthesis to a practical timeframe, hours instead of days. Mechanochemistry allows for a practical and ready scale-up to an industrial level without the cumbersome equipment requirements common with mass-scale traditional synthesis.

There are several fields of study and synthesis that require large amounts of solvents and generate large amounts of waste to achieve products. With the cost of purchasing solvent and storing waste, which must be treated so not to be harmful to people or the environment, there are some synthesis that are not cost efficient and thus either not made or studied. One area where mechanochemistry can be of benefit is pharmacy. By reducing the need for solvents and waste generate these reactions become more cost efficient. Allowing the synthesis and study of products that would typically not be done given the cost of production. Another area for the application of mechanochemistry is the synthesis of biodiesel, which is ideal for both future study of biodiesel synthesis and for the scale-up to industrial levels. With the significant reduction in production time and transition to ethanol, the synthesis of biodiesel with less toxic reagents and by-products is now practical and feasible.

This research has proven that viable fuels (propane and biodiesel) can be synthesized from biological sources (vegetable oil and/or cassava pulp) via mechanochemical processing using a solid catalyst. What this research has also shown is that mechanochemical processes using solid catalysts has the potential to reduce, even negate, the need for solvents.

Where this reduction would have the greatest benefit is in all areas that utilize chemistry, industry (all aspects), academia, and pharmacy. Reducing the overall need for solvent will reduce the overall waste generated from chemical processes. Reducing the need for solvent also means less storage space required for the solvents and the waste generated.

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