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# Separation And Use Of Oxygenated Byproducts From Non-Catalytically Cracked Triglycerides And Their Methyl Esters

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# SEPARATION AND USE OF OXYGENATED BYPRODUCTS FROM NON-CATALYTICALLY CRACKED TRIGLYCERIDES AND THEIR METHYL ESTERS

by

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Bachelor of Science, University of North Dakota, 2011

A Thesis

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of the

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Master of Science

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This thesis, submitted by Benjamin Jones in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Committee Member

This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the Graduate School at the University of North Dakota, and is hereby approved.

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Benjamin Jones

Friday, November 30, 2012

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# ABSTRACT

The world is dependent on petroleum as its main source of fuels and chemicals. Supply limitations and global warming have generated a great deal of interest in research to reduce this dependence through renewal fuels and chemicals.

Non-catalytic cracking and subsequent distillation of triacylglyceride (TAG) oils and methyl esters derived from these oils (TMEs) produces an organic liquid product (OLP) that is rich in potential fuels and chemicals. A major fraction of the OLP is made up of oxygenated compounds, either short chain fatty acids (SCFAs) if TAG oil is cracked, or short chain methyl esters (SCMEs) if TMEs are cracked. These oxygenated byproducts are substandard fuel components compared to hydrocarbons. However, the SCFAs and SCMEs are valuable as byproducts in a bio-refining scheme. It is therefore desirable to separate and recover these compounds as usable byproducts.

Separation of the SCMEs from TME-derived OLP was explored using batch liquid –liquid extraction experiments with polar solvents. Additionally, continuous multistage extraction was modeled. The partial mutual miscibility of the hydrocarbon and polar phases complicated the results and created inaccuracies in modeling. Despite this, it was determined that acetic acid was the most successful solvent, reducing the SCME concentration by 23% in a single stage extraction while allowing only 10% of the hydrocarbons to overlap into the polar phase. An 88% SCME reduction was calculated as a rough estimate for a 20 stage extraction using a solvent to OLP flow ratio of 3:1. It

is unclear how the phase overlap will effect multistage extraction, so future multistage LLE experiments are recommended to determine if this method is commercially viable.

Acetic acid, an SCFA, is one of the most abundant oxygenated products in cracked TAG oil. Its recovery and use as a byproduct were studied at the bench scale. The acetic acid was successfully separated from cracked TAG oil distillates using liquid-liquid extraction with water and then purified via azeotropic distillation. About 1.6 L of approximately 99 wt% pure acetic acid was produced from 250 L of soybean oil using this process.

The acetic acid was reacted with ethylene over a palladium (Pd) catalyst to produce renewable vinyl acetate monomer (VAM). The VAM was purified using batch distillation to about 99 wt%. This work successfully demonstrated that a renewable product generated from TAG oil cracking is chemically identical to its petroleum derived analog. This product is projected to be interchangeable with the current standard.

# CHAPTER I

# OVERVIEW

## 1. Present Situation

At present, the world's chemical and transportation fuel industries are almost exclusively dependent on petroleum. There are three major issues involved with continuing to use petroleum as the main source of fuels and chemicals.

1. Worldwide supplies of petroleum are limited and will eventually run out.
2. As a major source of anthropogenic carbon dioxide, petroleum and petroleum products likely have an influence on global climate change.
3. In most parts of the world a large fraction of petroleum products are imported from abroad making it very difficult to know for certain that future energy needs can be met at consistent prices.

Over the past several decades, increased awareness of these problems with fossil fuel based products has generated a growing interest in fuels and chemicals from renewable resources.

Presently, ethanol and biodiesel are the most widely utilized biofuels. Ethanol is produced through fermentation of sugars and starches and is currently used as a fuel in varying fractions with gasoline (*1*). Biodiesel is produced primarily by the transesterification of triacylglycerols (fats and oils) with methanol and an acid or base catalyst and is used as a fuel in varying fractions with petroleum diesel (*2*). Both of these fuels are chemically different and inferior to the petroleum products that they substitute. Liquid transportation fuels need to have high energy densities in order to provide a sufficient power/weight ratio. This is especially important for jet fuel to avoid substantial decreases in aircraft operating range. Specifically it is vital for transoceanic commercial flights and high performance military jets. This need makes the production of high grade renewable fuels very challenging.

The main problem with these fuels lies in the fact that they are made up of oxygenated compounds; ethanol is an alcohol and biodiesel is made up of methyl esters. Oxygenated compounds typically generate less energy when combusted than hydrocarbons of similar molecular weights because they are already partially oxidized. Additionally, the presence of carbon-oxygen bonds in these compounds makes them much more polar than the petroleum fuels that they are meant to substitute. For this reason, the vapor pressure of ethanol is too low to function in low temperatures (*3*) and biodiesel can have flow problems at low temperatures (*2*). Because of these limitations, ethanol and biodiesel use is limited in areas with cold climates.

## 2. Thermal Cracking of TAG/TME

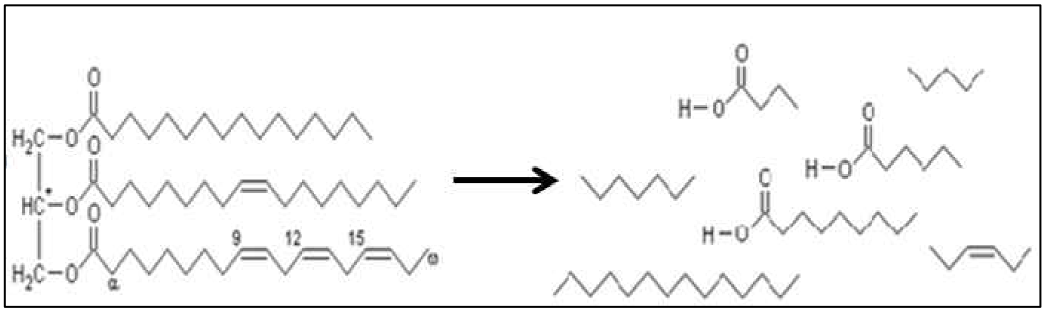
Triacylglycerols (TAGs) are naturally occurring compounds commonly referred to as fats and oils. They are produced by a wide variety of plants and animals, and even some microorganisms (*4*). TAGs consist of 3 fatty acid chains attached to a glycerol backbone by ester bonds. TAG molecules can be converted into TAG methyl esters

(TMEs) by transesterification with methanol and a basic catalyst. TMEs are commonly referred to as biodiesel.

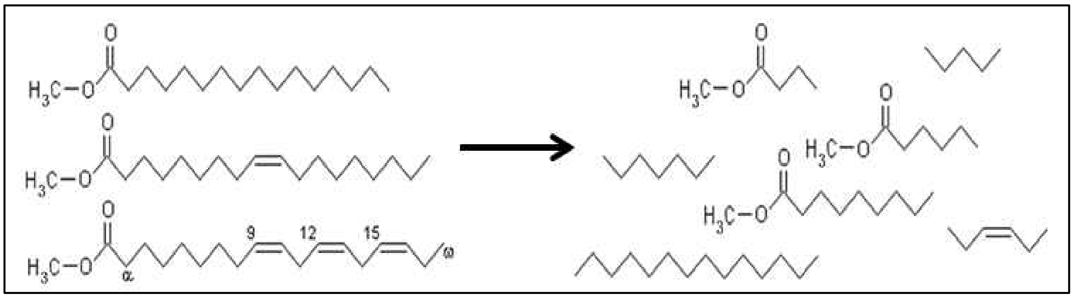
Researchers throughout the world are exploring methods of converting vegetable oils into high energy fuels – diesel and jet fuel – using a wide variety of chemical processes. These processes include hydro-treating, catalytic cracking, Fischer-Tropsch synthesis, pyrolysis, and many others (*5*, *6*). The goal being to create a product that meets current fuel specifications so it can interface with existing infrastructure. A research group at the University of North Dakota has explored thermal cracking as a method to produces renewable fuels. Thermal cracking occurs when TAG oils or TMEs are heated to temperatures around 400 to 470 °C in the absence of oxygen. Thermal cracking has been performed on soybean and canola oils (TAGs) as well as soybean and canola methyl esters (TMEs) to generate renewable fuels and fuel intermediates (*7*–*9*).

Thermal cracking yields an organic liquid product (OLP) that has improved fuel characteristics. The OLP contains a variety of hydrocarbons and either short chain fatty acids (SCFAs) or short chain methyl esters (SCMEs) depending on the feedstock, TAG or TME, respectively. In addition to the liquid product, some non-condensable gases and solids (coke/tar) are formed. These gaseous and solid effluents can be processed into byproducts such as propylene, hydrogen, and high grade carbon (*10*). The OLP can be processed into a variety of valuable fuels and chemicals.

Thermal cracking reactions for TAGs and TMEs are shown in Reaction (1) and Reaction (2) respectively. The reactants and products shown are vastly simplified, and the reactions are only meant to show how the different feedstocks (TAG and TME) yield different oxygenated products (SCFAs and SCMEs). The actual product mixtures contain hundreds of different compounds including but not limited to linear, branched, and/or cyclic alkanes, alkenes, and either SCFAs or SCMEs, as well as aromatic compounds. However, linear saturated alkanes and linear SCFAs or SCMEs make up the majority of the OLP.



**(1)**



**(2)**

The product of thermal cracking (crackate) can be condensed at room temperature except for the light gases (e.g. $CO_2$, propylene) which are separated from the liquid product and tars in a knockout drum. The OLP then is typically separated from the tars/coke by atmospheric or vacuum distillation. Additionally, distillation can be used to separate desired cuts of liquid products for specific fuels such as diesel, heavy fuel oil, and jet fuel. The goal of the process is to yield products that are chemically similar to petroleum fuels and meet all of their specifications. A few selected specifications for military and commercial jet fuels are listed in Table 1. The specifications shown are particularly difficult to achieve with TAG and TME feedstocks using thermal cracking alone.

**Table 1.** Selected Jet Fuel Specifications (*11*, *12*).

| Fuel | Freeze Point | Net Heat of Combustion | Acidity |
|---|---|---|---|
| | (°C) | (MJ/kg) | (mgKOH/g) |
| Jet A | -40 | 42.8 | 0.1 |
| JP-8 | -47 | 42.8 | 0.015 |

ASTM standards for diesel fuel are much less specific; the cloud point (point where crystals begin to form) must, "be no more than 6 °C higher than the 10th percentile minimum ambient temperature for the month the fuel will be used (*13*)." This ranges from -25 to -35 °C in the northern United States during winter months. Net heat of combustion needs only to be reported, and there is no acidity specification. However, the fuel must pass an elevated temperature copper strip corrosion test.

These specifications can be difficult to meet in OLP due to the presence of SFCAs and SCMEs. Both SCFAs and SCMEs are oxygenated compounds, and thus have lower heating values than simple hydrocarbons. Also, the polarity of these molecules leads to poor cold flow properties. Additionally, SCFAs are corrosive and give the TAG OLP a high acidity. In thermal cracking research at the University of North Dakota, Luo concluded that these compounds, "need to be extracted or converted to alkanes in order to provide a viable fuel (*9*)."

## 3. SCMEs and SCFAs

The physical properties of SCFAs and SCMEs make them inferior fuel components to alkanes and other non-oxygenated hydrocarbons. For example the freezing points and heats of combustion of the linear saturated C10 alkane, carboxylic acid, and methyl ester are shown in Table 2. The heats of combustion are much lower for the oxygenated compounds than for the alkane.

**Table 2.** Properties of C10 Alkane, Methyl Ester, and Carboxylic Acid (*14*).

| Compound | Freeze Point (°C) | Heat of Combustion (MJ/kg) |
|---|---|---|
| Decane | -29 | 48 |
| Methyl Nonanoate | -35 | 36 |
| Decanoic Acid | 30.8 | 36 |

Also the freeze point of the SCFA is drastically higher than the alkane or methyl ester. In addition, the SCFAs in the TAG OLP give it a very high acid number, typically well in excess of 80 mg of KOH per gram. Therefore, to produce transportation fuels it is absolutely essential that the SCFAs be removed from TAG OLP or converted, and it is highly beneficial to remove or convert the SCMEs from TME OLP.

In addition to the improvement of fuel properties, removing the SCFAs and SCMEs provides another significant benefit: SCFAs and SCMEs can be sold as valuable byproducts in a renewable fuel/chemical process. In fact, if a renewable fuel process is to be developed, byproducts will likely be necessary to make prices competitive with petroleum based products. Many of these compounds are high value specialty compounds used in fragrances, flavorings, and polymers. The prices for purified SCFAs and SCMEs are much higher on a weight basis than the prices for transportation fuels. Thus, if these oxygenated components can be separated and purified for minimal added costs, the profitability of a thermal cracking fuel production scheme can be increased. Prices for C2-C9 SCFAs and SCMEs are shown in Table 3.

**Table 3.** 2009 Bulk Prices of Short-Chain Oxygenated Products in \$/lb (*15*).

| | SCFA | SCME* |
|---|---|---|
| Acetic (C2) | 0.58 | 0.475 |
| Propionic (C3) | 0.91 | 0.81-0.94 |
| Butyric (C4) | 1.13 | 0.91-1.08 |
| Valeric (C5) | 1.16 | 0.98-1.21 |
| Caproic (C6) | 2.25 | 2.0-3.0 |
| Enanthic (C7) | 1.85 | 2.0-3.0 |
| Caprylic (C8) | 2.13 | 2.0-3.0 |
| Pelargonic (C9) | 2.1 | No Data |

*Prices listed for esters (not specified methyl esters)

The 2009 price of bulk price of diesel fuel was about \$0.28 per pound (\$1.95/gallon) (*16*). The oxygenated products shown in Table 3 have prices 2 to 8 times higher; therefore, converting these compounds to additional fuel would greatly reduce the total product value.

## 4. Removal/Conversion of Oxygenated Compounds

The oxygenated compounds in OLP can be dealt with by either converting them to produce more suitable transportation fuel compounds or separation from the other hydrocarbons. Possible reaction methods to deoxygenate these compounds include reduction, decarboxylation, and decarbonylation. Also, due to the fact that the SCMEs are more effective as fuel components than SCFAs, esterification could be a viable conversion for TAG oil OLP. This would improve the cold flow properties and acidity of TAG oil OLP, but the energy density would remain low.

Because the boiling points of SCFAs and SCMEs in OLP have a great deal of overlap with hydrocarbon boiling points, it is not practical to separate the oxygenated compounds using distillation. The property that the SCFAs and SCMEs have in common that differs from the hydrocarbons is their polarity. To take advantage of this property difference, liquid-liquid extraction with polar solvents can theoretically be used to separate these polar compounds out of the OLP.

### *4.1 SCFAs*

Conversion of fatty acids to alkanes by catalytic decarboxylation has been studied by a number of research groups (*17–19*). These studies were carried out at temperatures in excess of 300 °C and with hydrogen added to the reaction mixture. In most cases, unsaturated fatty acids led to saturated alkane products. Jet fuel that nearly reached JP-8 acid number specification was generated from TAG oil OLP by decarboxylation of SCFAs with a palladium catalyst and hydrogen (*17*). The OLP was reduced to an acid number of 0.1mgKOH/g with a single stage batch reaction and as low as 0.03 using two stages.

Extraction of SCFAs from TAG oil OLP using water was explored by a research group at the University of North Dakota (*20*). Full recovery of C2 and C3 SCFAs was demonstrated, and varying degrees of recovery for C4 to C6 SCFAs were achieved extracting with cold water, hot water, and dilute aqueous NaOH.

Liquid-liquid extraction (LLE) of SCFAs from TAG oil OLP using aqueous amines was studied in depth by Braegelmann and coworkers (*21*) and Vosgerau and coworkers (*22*) at the University of North Dakota. The separation was successful in a single stage mixed extractor with trimethylamine and dimethyl ethanolamine. The formation of ion pairs between SCFAs and the amine resulted in single stage extraction efficiencies in excess of 95%.

### *4.2 SCMEs*

Although the ester group is significantly less reactive than the carboxyl group, SCMEs can be catalytically deoxygenated by decarboxylation. This process has been demonstrated using large amounts of excess hydrogen feed (*19*, *23*), and thus may not be cost effective.

SCMEs are significantly less polar than SCFAs and cannot form ion pairs with aqueous amines. Many of them are more miscible with non-polar hydrocarbons than they are with polar solvents; this problem increases with increasing carbon number. Separation of SCMEs from OLP using LLE is much more difficult than with SCFAs. However, their properties are more conducive to meeting transportation fuel specifications, so near-100% removal is not necessary. Chapter II of this thesis will explore LLE of SCMEs from TME OLP using polar solvents.

## 5. Byproducts

In order for a renewable fuel production refinery to be economically competitive to a fossil fuel process, additional products need to be generated. Both commodity and specialty chemicals will be useful revenue generators. Many of the medium-chain C4-

C12 acids and esters are specialty chemicals having uses in fragrances, flavorings, polymers, and lubricants (*15*).

Acetic acid is one of the most plentiful SCFAs in TAG oil OLP. It is also a widely used commodity chemical with a global demand of 10.0 million metric tons in 2008 (*15*). The main use for acetic acid is the manufacture of vinyl acetate, which is the basis of glue, latex paint, polymers in safety glass, film products, and adhesives (*24*). Chapter III of this thesis describes the recovery and purification of acetic acid from TAG oil OLP and the production of renewable vinyl acetate monomer (VAM) by the addition of renewable acetic acid to renewable ethylene over a Pd-Au catalyst.

# CHAPTER II

# LIQUID-LIQUID EXTRACTION OF SHORT CHAIN METHYL ESTERS FROM CRACKED TRIGLYCERIDE METHYL ESTERS

## 1. Introduction

Non-catalytic cracking of triglyceride methyl esters (TMEs) and subsequent distillation of the liquid crackate produces an organic liquid product (OLP) that consists of various hydrocarbons and short chain methyl esters (SCMEs). SCMEs have lower heats of combustion than hydrocarbons, making them undesirable components in transportation fuels. Separation of these esters would improve the OLP's properties as a transportation fuel and provide valuable byproducts to the renewable fuel production process. The SCMEs present in OLP vary greatly in their boiling points which overlap with those of the hydrocarbons present in OLP, making it impractical to separate these compounds by distillation.

The purpose of this work was to determine if a polar solvent could efficiently separate the SCMEs from OLP by liquid-liquid extraction (LLE). Liquid-liquid extraction takes advantage of a property common among the various SCMEs, their polarity, which is due to the carbon-oxygen bonds in the ester functional group. This functional group is absent from hydrocarbons. Because of the polarity of the ester group, polar solvents have higher miscibility with SCMEs than with hydrocarbons.

Liquid-liquid extraction involves contacting an SCME-lean solvent with an immiscible fluid that contains the SCMEs, in this case OLP. The SCMEs are then absorbed into the solvent liquid from the OLP because of a concentration gradient. Choosing a solvent with a high solubility of SCMEs will help them to preferentially leave the OLP and enter the solvent.

The degree of improvement in cold flow properties and heat of combustion that occur when the SCMEs concentration is reduced was also studied.

## 2. Background.

### 2.1 *Justification*

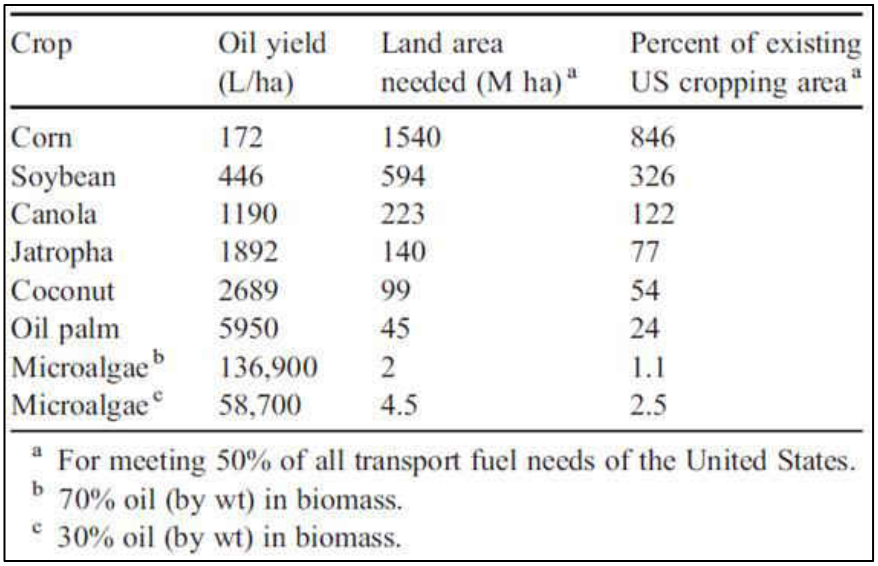
Non-catalytic cracking of TAG oil and TMEs produce similar liquid products, the main difference being whether SCFAs or SCMEs are produced as the oxygenated product. Separation of the full range (C2-C16) of fatty acids from TAG oil OLP has been successfully demonstrated using LLE with aqueous TMA (*21*, *22*). This process can be used for refining high grade fuels from TAG oil.

The alternative method involves first transesterifying TAG oil to TMEs, then cracking to obtain an OLP that can be further processed into fuels and chemicals. This alternative has not been developed to the point of refining high grade fuels. This process adds an extra step (transesterification) in the process of converting TAG oil into renewable fuels and chemicals. Despite the added step, there are reasons that production of fuels via the cracking of TMEs should be studied.

SCMEs have fewer drawbacks as renewable fuel components than SCFAs. The main drawback they both share is their low heats of combustion compared to hydrocarbons. However, the other drawbacks associated with SCFAs (high freeze point and acid number), are not present in SCMEs (See Table 2). Therefore, OLP derived from thermally cracked TMEs is more acceptable in transportation fuels without any deoxygenation. This OLP may even meet the specifications for diesel fuels without further modification.

The other major reason to study fuel production from thermally cracked TMEs is related to a cutting edge method for algal oil processing. Algae is potentially the most important future feedstock for biofuels due to its high, per acre, yield of oil and its ability to grow in areas that are unable to support traditional oil crops like palm, canola, and soybeans. Table 4 from Chisti (*25*) shows the oil yields for various crops. Microalgae can produce oil yields that are orders of magnitude higher than traditional crops.

**Table 4.** Comparison of Sources of TAG oil (*25*).



| Crop | Oil yield (L/ha) | Land area needed (M ha)[a] | Percent of existing US cropping area[a] |
|---|---|---|---|
| Corn | 172 | 1540 | 846 |
| Soybean | 446 | 594 | 326 |
| Canola | 1190 | 223 | 122 |
| Jatropha | 1892 | 140 | 77 |
| Coconut | 2689 | 99 | 54 |
| Oil palm | 5950 | 45 | 24 |
| Microalgae[b] | 136,900 | 2 | 1.1 |
| Microalgae[c] | 58,700 | 4.5 | 2.5 |

[a] For meeting 50% of all transport fuel needs of the United States.
[b] 70% oil (by wt) in biomass.
[c] 30% oil (by wt) in biomass.

The main challenge with algal oil is the difficulty associated with separating the oil from the algae cells and the water in which they are grown. Direct esterification of algae has been proposed as a more efficient way to obtain algal oils from algae biomass compared to traditional pressing and chemical extraction of TAGs. Several studies have described improved methods for the processing algae into fuel. These methods would increase economic feasibility, but they resulted in esterified products (*26–28*). These studies involved using processes that transesterified and extracted the algal oils in a single step. With this method the TAG oil has already been converted to TMEs upon recovery. Thus, TMEs would need to be processed if a more advanced biofuel was desired.

## *2.2 Literature Review*

Fortunately, if TMEs can be recovered, they can be cracked to upgrade their fuel properties. Further, if the SCMEs are removed, fuel properties improve more and the SCMEs have value as chemical products. The uses and production methods for SCMEs with C2 to C9 alkyl groups present in TME generated OLP are described in Table 5. Methyl acetate (C2) and methyl propionate (C3) can be produced chemically from reactions involving methanol and carbon monoxide and are used as solvents or to generate other chemicals such as acetic anhydride and methyl methacrylate. Methyl propionate can also be produced by Fischer esterification of the corresponding short chain fatty acid (propionic acid). Fischer esterification occurs when an alcohol is added to a carboxylic acid in the presence of an acid catalyst (*29*). The alkyl group from the alcohol replaces the carboxyl hydrogen, giving water as a byproduct.

**Table 5.** Short Chain Methyl Ester (SCME) Origins and Uses (*15*, *30*, *31*)

| **Methyl Ester (alkyl carbon chain)** | **Origin** | **Use** |
|---|---|---|
| Acetate (C2) | Carbonylation of Methanol Byproduct | Solvent, Acetic Anhydride Production |
| Propionate (C3) | Fischer Esterification or Carbonylation Combining Ethylene, Methanol, and Carbon Monoxide | Methyl Methacrylate Production, Fast Drying Solvent |
| Butyrate (C4) | Fischer Esterification, Distillation from Essential Oils of Certain Fruits | Fragrance/Flavoring: Apple or Pineapple |
| Valerate (C5) | Fischer Esterification | Medication, Softening Agent in Plastic, Insecticide, and Fragrance/Flavoring: Fruity and Nutty |
| Caproate (C6) | Fischer Esterification | Fragrance/Flavoring: Pineapple and Apricot |
| Enanthate (C7) | Fischer Esterification | Fragrance/Flavoring: Berries |
| Caprylate (C8) | Fischer Esterification | Fragrance/Flavoring: Herbal and Citrus |
| Pelargonate (C8) | Fischer Esterification | Fragrance/Flavoring: Not Specified |

The C4-C9 esters are produced almost exclusively by Fischer esterification. The C4 to C9 methyl esters are used mostly in fragrances and flavorings (*31*). Formic acid (C1) methyl ester is not present in crackate. Any C10+ methyl esters would be less likely to be extracted by a polar solvent and are less detrimental to heating value due to their higher carbon to oxygen ratio. These medium to long chain methyl esters would not likely be a byproduct of a TME bio-refining process.

Commercially produced SCMEs are typically found in aqueous/methanol media, so their purification is straightforward and provides no basis for this research. Recovery can be accomplished via distillation of methanol and phase separation from water. These and other similar esters are also present in low concentrations in living organisms, especially fruits. Separation of esters in these matrices have been studied for analytical purposes using methods such as reactive and micro-extraction (*32*), liquid and gas chromatography (*33*), and specialized extractions targeting specific esters(*34*). However, these methods were carried out on a very small scale and are not practical for industrial scale applications.

Research on long chain C16 – C22 methyl esters (aka TMEs) present in biodiesel is also available, but any literature focused on ester separation is either selective to certain unsaturated esters (*35*) or is for biodiesel related analysis (*36*).

Some literature on binary mixtures of SCMEs and hydrocarbons is available (*37–39*), but its focus is simply evaluating the physical properties (e.g. viscosity, density, excess volumes) of such mixtures. Some information is available on the miscibility of SCMEs with water and polar solvents, and a few studies even generated 2-phase composition data on tertiary mixtures of methyl acetate, methanol, and various individual alkanes (*40–42*). Mixtures containing a wide range of SCMEs and hydrocarbons are not mentioned in literature, and it is unlikely that one would encounter such a mixture other than by the cracking of TMEs. For this reason, research concerning this application of LLE is very limited.

The separation of a somewhat similar mixture by LLE has been studied in depth. SCFAs were separated from TAG oil OLP using liquid-liquid extraction with water(*20*) and various aqueous amines(*21*). The major difference between the SCMEs and this analog is the presence of a methyl group in place of hydrogen on the solute compounds. This difference significantly reduces the polarity of the solute compounds and eliminates the ability of the solute to form ion pairs with amines via weak-acid/weak-base reactions. Therefore, methods for SCME recovery must rely only on solvation as a driving force into polar solvents.

## *2.3 Liquid-Liquid Extraction*

Liquid-liquid extraction involves contacting a solvent with an immiscible fluid that has a high concentration of a solute. This solute is absorbed into the solvent because of a concentration gradient. Liquid-liquid extraction (LLE) it is one of the lowest cost means of separation and it was successfully demonstrated in the SCFA analog to this study. So it is a logical method to explore for SCME removal. In this case the solutes are the SCMEs, the immiscible fluid is OLP, and the solvent is a yet to be determined polar compound or solution.

The first step in determining a solvent for LLE is finding extraction solvents that have a high miscibility with SCMEs, but not with hydrocarbons. The SCMEs have very limited miscibility with water. Methyl acetate (C2) and methyl propionate (C3) are miscible with water up to about 27 wt% (*43*) and 6 wt % (*44*), respectively, at 20 °C. Solubility of methyl esters in 20 °C water decreases with increasing molecular weight, reaching less than 0.5 wt% for methyl valerate (C5) (*44*).

Some limited data on methyl ester solubility is available for a number of polar and nonpolar solvents (*45*). This research describes the solubility of methyl esters with C8, C12, C13, C14, C16, and C18 alkyl chains in a number of solvents at varying temperatures. As with C2-C5 methyl esters in water, trends in the data suggest that lower molecular weight esters are more soluble in polar solvents. This is in general agreement with the alchemist's "like-dissolves-like" principal. Lower molecular weight methyl esters have smaller non-polar chains to negate their polar end, making them more "like" the polar solvents. Full miscibility of methyl caprylate with a number of solvents is reported at 20 °C (e.g. methanol, acetonitrile, chloroform, ethyl acetate, and acetone). This suggests that lower molecular weight methyl esters would be soluble in these compounds as well. This full miscibility makes these compounds good candidates for testing as extraction solvents.

The distribution coefficient ($k_D$) is defined as the ratio of concentrations in the different phases of a 2-phase system. A $K_D$ value of 1.0 indicates an equal partitioning of a solute between phases. For the purposes of this research the extracting phase concentration (polar) was divided by the originating (hydrocarbon) phase concentration.

Multiphase equilibrium data is available on mixtures of methyl acetate, methanol, and various individual n-alkanes (C6-C12) (*40–42*). $K_D$ values calculated from data in the literature ranged from about 1 to 1.5 in samples with total methyl acetate concentrations near the total ester concentrations found in TME OLP. This indicates that methyl acetate (the most polar SCME in OLP) could be mostly separated from a hydrocarbon in just a few stages of separation.

This literature (*40–42*) also revealed two interesting trends. First, as the concentration of methyl acetate was increased, the polar solvent (methanol) and hydrocarbon became increasingly miscible. This suggests that problems with phase overlap may occur when contacting methanol (or other solvents) with OLP. Second, as the temperature is increased the two phases become increasingly miscible. Thus, high temperatures could increase issues with phase overlap.

The ability of a solvent to extract a solute is a complex phenomenon that is affected by the interactions of the individual molecules of each phase. For this reason the orientation/geometry of polar groups on an extraction solvent could make a significant difference in its solvating ability toward SCMEs. However, such a phenomenon would be difficult to predict accurately. Studying a wide variety of polar solvents with different polar functional groups will increase the likelihood of discovering an efficient solvent for SCME extraction.

## *2.4 Fuel Properties*

Diesel fuel specifications require only that heat of combustion be reported, not that a certain minimum value be achieved. However, aviation fuels have specific heat of combustion requirements.  TME OLP in the distillate range used for this work only has a heat of combustion of about 40 MJ/kg.  It is unlikely that TME OLP could be used as jet fuel due to the large fraction of short chain methyl esters (SCMEs) present.  Figure 1 shows the heat of combustion plotted against carbon number for methyl esters and normal alkanes in the C4-C19 range.  These values were all determined using a bond energy-based heat of combustion calculation, as explained in Clymer (*46*).

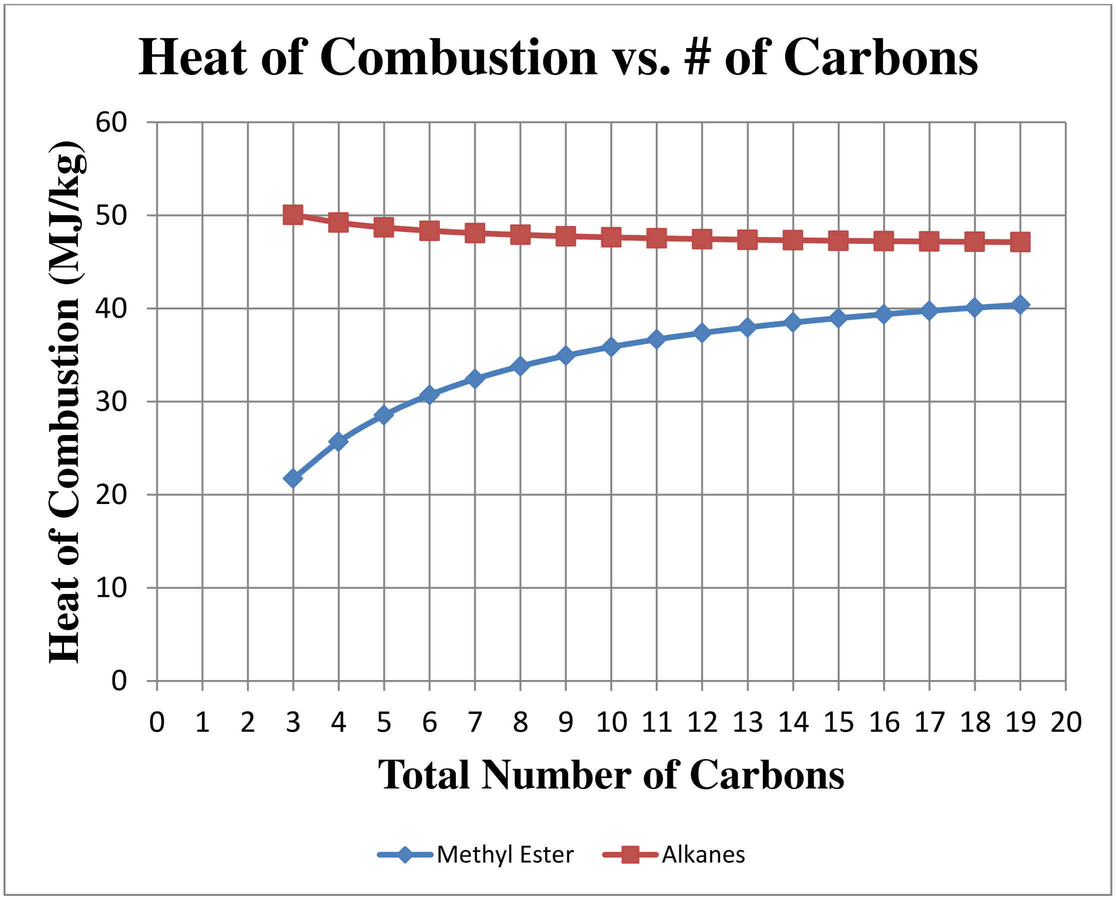


**Figure 1.** Heat of Combustion vs. Carbon Number for Methyl Esters and Alkanes

Every ester in this range has a heat of combustion below the aviation jet fuel requirement, but every n-alkane has a heat of combustion in excess of the required value (42.8 MJ/kg).  Thus, to produce a renewable fuel that meets the same specifications as petroleum jet fuels, some of the SCMEs need to be removed or deoxygenated. This illustrates the potential benefits of a SCME LLE technology. This figure also indicates that low molecular weight esters have a more pronounced impact on the heat of combustion of a jet fuel product.

## 3. Materials and Methods

### *3.1 Materials*

Canola Methyl Esters (CMEs) were donated by an Archer Daniels Midland (ADM) plant in Velva, ND. Extraction solvents (methanol, ethylene glycol, sulfolane, acetic acid, dimethyl sulfoxide, acetonitrile, citric acid, acetone, tetrahydrofuran, and chloroform) were purchased from Sigma-Aldrich Co., St. Louis, MO and VWR International, Radnor, PA. All solvents were 98% pure or greater.

### *3.2 Experimental Systems*

Non-catalytic cracking was carried out in a 4584 Series Floor Stand 5.5 L (1.5 gal) Reactor from PARR Instrument Company (Moline, IL). The stainless steel reactor was equipped with a magnetic stirrer, a removable ceramic electric heater, and a loop of tubing for cooling water. The reactor conditions (temperature and pressure) were controlled and monitored using a PARR 4848 Reactor Controller. The reactor is shown in Figure 2.

Distillation was carried out in a lab-scale distillation apparatus (fabricated in house) with a 5 L round bottom pot flask and a 30.5 cm (12 in) tall, 2.5 cm (1 in) diameter glass column packed with 0.64 cm (1/4 in) ceramic rings. The distillate was condensed using a water-cooled glass condenser, and the product fraction was collected manually in an Erlenmeyer flask.  This distillation apparatus is shown in Figure 3.

**Figure 2.** PARR 4584 series 5.5 L (1.5 gal) Floor Stand Reactor.

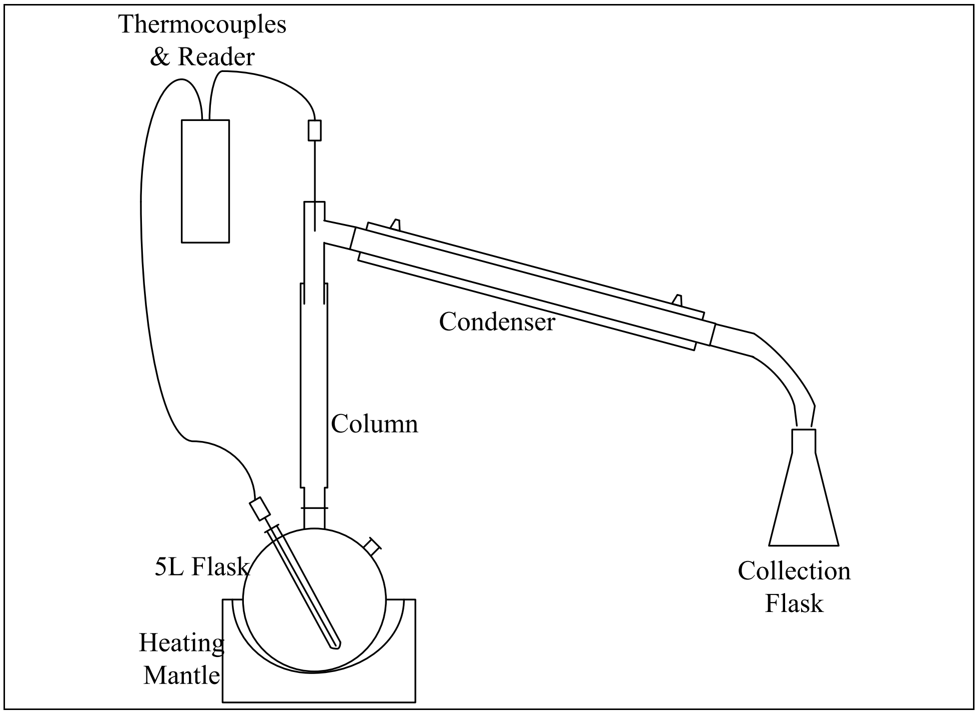


**Figure 3.** Distillation Apparatus for TME Crackate.

Liquid-liquid extractions were carried out in batch in 20 mL vials with caps. Elevated temperature trials were warmed and shaken in a Max Q 4000 auto-shaker by Thermo Scientific (Waltham, MA). Ambient temperature trials were shaken by hand, because a previous experiment had shown no difference between shaking methods. Sonication was avoided, because preliminary testing had revealed that it resulted in emulsions.

## *3.3 Procedure*

### *3.3.1 Generation of TME OLP*

CMEs were non-catalytically cracked in 2 L batches. The CMEs were placed under nitrogen atmosphere at ambient pressure, heated to 435 °C, and held between 420 and 440 °C for 1.5 hours. Temperature could not be maintained at an exact value due to the endothermic nature of the cracking reactions. The products were cooled to ambient temperature and gaseous components were vented. The cracked product was collected and distilled in batch. The fraction with a distillate temperature of 120 to 290°C was kept as OLP for SCME removal testing.

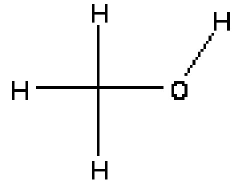
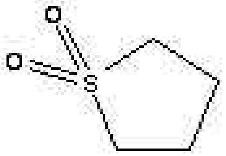
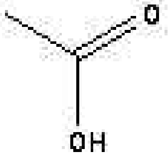
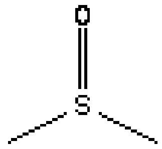
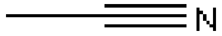
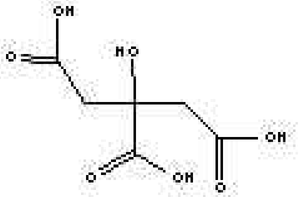
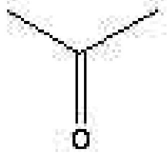
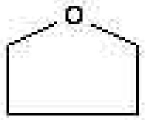
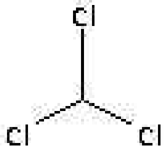
The OLP was analyzed using a 7890N GC in conjunction with a HP-5975C MS having an Agilent 7683B series auto sampler and a flame ionization detector. The separations occurred in a 0.25 mm ID by100 m long DB-Petro capillary column with a 0.5µm film thickness. The carrier gas was helium flowing at a rate of 1.5ml/min. The analysis procedure was developed in the UND Chemistry Department and is described in detail in Sťávová (*47*). TME OLP was found to be 38 wt% SCMEs by GC analysis.

### *3.3.2 Solvent Miscibility Tests*

Ten polar compounds were selected for testing as LLE solvents for the removal of SCMEs from OLP. The solvents selected have a wide variety of polar groups. Different polar groups were selected to account for the fact that a specific group's geometry may enhance or hinder its ability to interact with, and thus solvate, the methyl ester polar group. The 10 selected solvents are shown in Table 6.

Two mL of each of the ten solvents were added to test tubes containing two mL of TME OLP to check for phase separation. For solvents that did not phase separate from the OLP, small amounts of water were added drop-wise. For many of the solvents a small fraction (less than 10% by volume) of water was needed to force phase separation from the hydrocarbon-rich OLP. Three solvents (acetone, tetrahydrofuran, and chloroform) would not phase separate from the OLP, but rather stayed in the hydrocarbon phase leaving any added water as a separate phase at the bottom of the test tubes. These solvents would be unusable in SCME LLE and were eliminated from further testing.

**Table 6.** Solvents selected for OLP miscibility screening tests. Images from NIST Chemistry WebBook (*48*).

| | |
|---|---|
| Methanol |  |
| Ethylene Glycol |  |
| Sulfolane |  |
| Acetic Acid |  |
| Dimethyl Sulfoxide (DMSO) |  |
| Acetonitrile |  |
| Citric Acid (aq. Solution) |  |
| Acetone |  |
| Tetrahydrofuran (THF) |  |
| Chloroform |  |

### *3.3.3 Qualitative Solvent Screening*

Qualitative solvent screening consisted of performing batch extractions in vials. Each solvent was mixed with water in 3 different volumetric ratios. The volume fractions for each solvent (with water) are listed in Table 7. Five mL of each water/solvent mixture were added to 5 mL of OLP and the immiscible fluids were shaken thoroughly.

**Table 7.** Aqueous Polar Solutions Selected for Qualitative Solvent Screening.

| Solvents | Volume Fraction (balance is water) | | |
|---|---|---|---|
| Methanol | 0.65 | 0.8 | 0.9 |
| Ethylene Glycol | 0.4 | 0.75 | 1 |
| Sulfolane | 0.4 | 0.75 | 0.9 |
| Acetic Acid | 0.4 | 0.75 | 0.9 |
| DMSO | 0.4 | 0.75 | 1 |
| Acetonitrile | 0.4 | 0.75 | 0.9 |
| *Citric Acid | 25% saturated | 50% saturated | saturated |

*Citric acid (powder) solutions were mixed by percent of saturation rather than volume fraction.

Maximum solvent volume fractions were based on approximate phase separation limitations from the miscibility test (Section 3.3.2). Minimum volume fractions were selected to provide wide experimental intervals. The volume fractions for methanol vary from the other solvents because they are based on previous experiments to separate SCMEs from OLP. These previous experiments are presented in Appendix A. For each of the solvent/water mixtures in Table 7, experiments were performed at ambient temperature and at 45°C. In addition trials were performed using pure water as a control. The raffinates from each sample were analyzed using Fourier Transform Infrared (FT-IR) spectroscopy and compared to virgin OLP.

### *3.3.4 Quantitative Solvent Screening*

Based on results from the qualitative solvent screening, selected experiments were performed in triplicate using the same methods. However in these experiments, phase separation was quantified. The weights of polar and hydrocarbon phases were measured separately before and after the experiments. Additionally, raffinate samples from all experiments were washed with water to remove any residual polar solvents that might affect the analysis. The water-wash mass was recorded before and after rinsing in order to quantify the amount of polar solvent removed. Both raffinate and extract phases were analyzed by FT-IR. By quantifying the phase separations and determining final SCME concentrations, phase overlap could be calculated. Phase overlap is the amount of solvent transferred into the OLP hydrocarbon phase and the amount of OLP hydrocarbons transferred into the polar solvent phase.

### *3.3.5 Final Extraction Experiments - Distribution Coefficient*

Based on the screening experiments, the solvents with the best results were selected for final extraction experiments to determine their distribution coefficients. New volume fractions were selected for each solvent based on the preliminary results. Phase separation was quantified in a manner similar to the quantitative screening experiments. SCME concentration in the raffinate solutions were determined using FT-IR spectroscopy, and SCME concentrations in the extract solutions were determined using GC analysis. The distribution coefficients were calculated by taking the quotient of the polar phase SCME concentration with respect to the organic phase SCME concentration.

Using the distribution coefficients, LLE charts, and LLE mass balance equations, simple counter-current extraction systems were modeled. The fraction of SCMEs that could be recovered from OLP using a 20 stage counter-current extraction was estimated.

## *3.4 Chemical Analysis*

### *3.4.1 Fourier Transform Infrared Spectroscopy*

The carbon – oxygen double bond (C=O) in esters has a stretching vibration that occurs at approximately 1750 $cm^{-1}$ in FT-IR analysis. The absorbance at this frequency is directly proportional to the molar concentration of esters in the samples, according to Beer-Lambert Law (*49*). All samples were analyzed in the linear range of the detector.

The height of this peak for each raffinate sample in the qualitative screening experiments was compared to the peak height for the virgin OLP. The ratio of the two peak heights was used to calculate the relative reduction in SCME concentration.

The C=O in acetic acid has a stretching vibration near the ester C=O, and the peaks can overlap causing errors in the analysis. Raffinate samples in the qualitative screening experiments containing acetic acid were washed with water to remove any residual acetic acid that would interfere with the analysis.

For quantitative screening experiments, five point calibration curves were produced to calculate the absolute SCME concentration based on C=O peak height. Calibration standards were produced using C4, C8, and C12 alkyl chain methyl esters. The linear calibration curve fit the data well having an $R^2$ value of 0.995. This calibration was used to determine SCME concentrations in raffinate solutions for each replicated experiment. This analysis method was also used to quantify SCME concentration in the raffinate samples from the distribution coefficient experiments.

Additional calibrations were used to analyze the polar phase solutions from the quantitative screening experiments. Separate four point calibrations were prepared with DMSO and ACN solvents. Both calibrations used methyl butyrate (C4) as the SCME standard. The linear calibration curves fit the data well, having $R^2$ values of 0.992 and 0.994 for DMSO and ACN, respectively. Methanol interfered with the C=O peak height, so polar phase samples containing methanol were not analyzed for SCME concentration.

### *3.4.2 Polar Phase Gas Chromatography*

Polar phase extracts from the final $K_D$ experiments were analyzed using a gas chromatograph (GC). Analysis was performed on a Perkin Elmer Clarus 480 GC equipped with a split/splitless injector and a flame ionization detector (FID). Helium was used as a carrier gas under constant inlet pressure control at 203 kPa (15.0 $psi_g$). Using a 10 μL syringe, 0.6 μL volumes of each sample were manually injected. The injector temperature was maintained at 300 °C and used split mode with a split ratio of 30:1. Separations occurred on a Restek Stailwax-DA 30m long, 0.25 mm ID column with a film thickness of 0.25 μm. The column oven temperature was held initially at 50 °C for 3 min, and then increased at 3.5 °C/min to 140 °C. Next the column oven was ramped to 225 °C at 30.0 °C/min where it was held for 8 minutes. Analytes were detected using an FID operated with a hydrogen flow of 45 mL/min and an air flow of 450 mL/min.

Polar samples and standards were prepared by dilution in methanol, with the addition of butanol as an internal standard. Five point calibrations were used for each analyte: C2-C10, C12 SCMEs. The calibration curves each had a high degree of fit with $R^2$ values greater than 0.992 except for C9 which was 0.980. Analytes were quantified by calculating the quotient of their peak area relative to the peak area of the internal standard. Data from the calibrations are available in Appendix A.

# 4. Results

## *4.1 TME OLP Analysis*

The TME OLP was analyzed using GC. Only the methyl esters and n-alkanes were quantified. Summarized results from the TME OLP characterization are shown in Table 8. The full set of quantified compounds is available in Appendix A. Methyl acetate was too volatile to be quantified using this GC method. However, considering the OLP was distilled from 120-290 °C, and the fact that methyl acetate boils at 57 °C, the amount of methyl acetate in the OLP was probably negligible. The majority of the esters are in the C4 to C11 range with C7 and C8 esters having the highest concentrations. The 7.1 wt percent of other methyl esters includes small concentrations of branched, cyclic, unsaturated, and di methyl esters.

### *4.1.1 Qualitative Screening Experiments*

The results from qualitative screening experiments to select solvents for further testing are shown in Table 9. The best solvents were methanol, DMSO, and acetonitrile. Trials using these solvents showed reductions in SCME concentration by 30% or more. Some of the trials using acetic acid reduced the SCME concentration by 20-25%. A single trial with sulfolane showed a SCME concentration reduction of 21.2%. All other solvents tested removed 10% of the SCMEs or less. Water, the control, removed only 0.6% and 0.3% of the SCMEs at 24 and 45 °C, respectively.

**Table 8.** Summarized Analysis of TME OLP.

| Compound(s) | Wt% |
|---|---|
| Methyl Acetate | ND |
| Methyl Propionate | 0.48 |
| Methyl Butanoate | 1.36 |
| Methyl Valerate | 2.71 |
| Methyl Caproate | 4.24 |
| Methyl Enanthate | 5.85 |
| Methyl Octanoate | 5.54 |
| Methyl Nonanoate | 3.49 |
| Methyl Decanoate | 3.14 |
| Methyl Undecanoate | 1.36 |
| Methyl Laurate | 0.79 |
| Methyl Tridecanoate | 0.53 |
| Methyl Myristate | 0.42 |
| Methyl Pentadecanoate | 0.19 |
| Methyl Palmitate | 0.79 |
| Methyl Heptadecanoate | 0.04 |
| Methyl Stearate | 0.32 |
| Methyl Eicosanoate | 0.02 |
| Other Methyl Esters | 7.10 |
| Total Methyl Esters | 38.36 |
| Total n-Alkanes | 21.77 |

In general, higher solvent-to-water ratios resulted in greater extraction of SCMEs. Because most of the SCMEs are not very soluble in water, the addition of large amounts of water decreased the driving force toward dissolution in the polar phase. Methanol, DMSO, and Acetonitrile were selected for quantitative screening extraction experiments.

**Table 9.** Results from Qualitative Screening Experiments.

| Label | Solvent | Volume Fraction of Solvent Feed (balance $H_2O$) | Temperature (°C) | Percent Reduction in SCME Concentration |
|---|---|---|---|---|
| E3R1 | Methanol | 0.65 | 24 | 14.7 |
| E3R2 | Methanol | 0.65 | 45 | 17.9 |
| E3R3 | Methanol | 0.8 | 24 | 24.5 |
| E3R4 | Methanol | 0.8 | 45 | miscible |
| **E3R5** | **Methanol** | **0.9** | **24** | **32.6** |
| **E3R6** | **Methanol** | **0.9** | **45** | **45.9** |
| E3R7 | Ethylene Glycol | 0.4 | 24 | 0.3 |
| E3R8 | Ethylene Glycol | 0.4 | 45 | 2.4 |
| E3R9 | Ethylene Glycol | 0.75 | 24 | 1.6 |
| E3R10 | Ethylene Glycol | 0.75 | 45 | 4.2 |
| E3R11 | Ethylene Glycol | 1 | 24 | 3.9 |
| E3R12 | Ethylene Glycol | 1 | 45 | 7.1 |
| E3R13 | Sulfolane | 0.4 | 24 | 4.0 |
| E3R14 | Sulfolane | 0.4 | 45 | 7.4 |
| E3R15 | Sulfolane | 0.75 | 24 | 8.9 |
| E3R16 | Sulfolane | 0.75 | 45 | 12.0 |
| E3R17 | Sulfolane | 0.9 | 24 | 12.1 |
| E3R18 | Sulfolane | 0.9 | 45 | 21.2 |
| E3R19 | Acetic Acid | 0.4 | 24 | 4.7 |
| E3R20 | Acetic Acid | 0.4 | 45 | 5.8 |
| E3R21 | Acetic Acid | 0.75 | 24 | 11.2 |
| E3R22 | Acetic Acid | 0.75 | 45 | 11.8 |
| E3R23 | Acetic Acid | 0.9 | 24 | 25.0 |
| E3R24 | Acetic Acid | 0.9 | 24 | 21.7 |
| E3R25 | Acetic Acid | 0.9 | 24 | 23.0 |
| E3R26 | Acetic Acid | 0.9 | 45 | 20.7 |
| E3R27 | DMSO | 0.4 | 24 | 1.6 |
| E3R28 | DMSO | 0.4 | 45 | 3.8 |
| E3R29 | DMSO | 0.75 | 24 | 8.1 |
| E3R30 | DMSO | 0.75 | 45 | 16.9 |
| **E3R31** | **DMSO** | **1** | **24** | **51.4** |
| **E3R32** | **DMSO** | **1** | **45** | **65.5** |
| E3R33 | Acetonitrile | 0.4 | 24 | 28.9 |
| E3R34 | Acetonitrile | 0.4 | 45 | 29.8 |
| **E3R35** | **Acetonitrile** | **0.75** | **24** | **39.0** |
| **E3R36** | **Acetonitrile** | **0.75** | **45** | **49.5** |
| **E3R37** | **Acetonitrile** | **0.9** | **24** | **37.2** |
| **E3R38** | **Acetonitrile** | **0.9** | **45** | **42.7** |
| E3R39 | Citric Acid | ¼ saturated | 24 | 0.9 |
| E3R40 | Citric Acid | ¼ saturated | 45 | 1.9 |

**Table 9** (Continued)

| Label | Solvent | Volume Fraction of Solvent Feed (balance $H_2O$) | Temperature (°C) | Percent Reduction in SCME Concentration |
|---|---|---|---|---|
| E3R41 | Citric Acid | ½ saturated | 24 | 0.1 |
| E3R42 | Citric Acid | ½ saturated | 45 | 1.1 |
| E3R43 | Citric Acid | saturated | 24 | 0.9 |
| E3R44 | Citric Acid | saturated | 45 | 1.4 |
| E3R45 | Water | 100% $H_2O$ | 24 | 0.6 |
| E3R46 | Water | 100% $H_2O$ | 45 | 0.3 |

### *4.2 Quantitative Screening Experiments*

Trials using methanol, DMSO, and acetonitrile were repeated in triplicate in quantitative screening experiments. The results from the quantitative triplicate experiments are shown in Table 10. The percent reduction of SCME concentration in the OLP is shown for analyses both before and after washing the polar phase solvents out of the raffinate OLP.

**Table 10.** Results from Batch LLE replicated experiments. Each set of conditions was tested in triplicate.

| Solvent | Volume Fraction Solvent (Balance H2O) | Temperature (°C) | Average SCME Reduction Before Wash (Stdev) | Average SCME Reduction After Wash (Stdev) |
|---|---|---|---|---|
| Methanol | 0.9 | 24 | 34% (3.1) | 15% (0.9) |
| Methanol | 0.9 | 45 | 35% (1.8) | 15% (0.02) |
| DMSO | 1 | 24 | 60% (3.3) | 17% (0.3) |
| DMSO | 1 | 45 | 58% (4.9) | 17% (2.0) |
| Acetonitrile | 0.9 | 24 | 40% (0.5) | 24% (0.9) |
| Acetonitrile | 0.9 | 45 | 38% (1.4) | 23% (0.3) |

Based on the large SCME concentration discrepancy, it is apparent that the polar solvents which transferred to the OLP during mixing affected the analysis. The solvents altered the C=O peak height. Therefore, without the water wash step, the analytical results are subject to systematic error by interaction of the SCMEs with the polar solvent contaminants. It is likely that some of the C=O groups were "tied up" in polar complexes and did not absorb IR energy at the 1750 $cm^{-1}$ frequency. Solvent interactions affecting the frequency and intensity of C=O stretching vibrations is consistent with literature (*50*, *51*).

During the qualitative screening experiments, raffinates from trials using acetic acid were the only trials which used a water wash. The results in Table 9 show that acetic acid reduced the SCME concentration by nearly as much as DMSO, acetonitrile, and methanol. Therefore, it is likely that a corrected analysis would show acetic acid was actually on par with these other solvents. The final extraction experiments included acetic acid for this reason.

Quantification of separate phase masses during the quantitative screening experiments made it possible to calculate the amount of phase overlap. The amount of hydrocarbon mass transferred from the OLP into the polar extract phase was calculated. Also, the fraction of polar phase material transferred from the extraction solvent into the OLP raffinate was calculated. Both phase overlap values are shown for the quantitative screening experiments in Table 11. These results show significant coexistence of polar and non-polar compounds in each phase. The data show a trend toward more phase overlap at higher temperatures. For this reason, higher temperatures were not used in the final solvent experimentation.

**Table 11.** Phase Overlap Percentages for the Quantitative Screening Experiments. Each set of conditions was tested in triplicate.

| Solvent | Volume Fraction Solvent (Balance H2O) | Temperature (°C) | Average Hydrocarbon Mass into Extract (Stdev) | Average Solvent Mass into Raffinate (Stdev) |
|---|---|---|---|---|
| Methanol | 0.9 | 24 | 18% (3.8) | 13% (3.9) |
| Methanol | 0.9 | 45 | 25% (3.7) | 17% (3.3) |
| DMSO | 1 | 24 | 24% (2.1) | 11% (1.3) |
| DMSO | 1 | 45 | 27% (1.7) | 10% (1.6) |
| Acetonitrile | 0.9 | 24 | 29% (3.3) | 14% (2.2) |
| Acetonitrile | 0.9 | 45 | 34% (1.0) | 16% (0.7) |

### *4.3 Distribution Coefficient Testing*

Table 12 shows the distribution coefficients for the different solvents at various volume fractions. Acetic acid and acetonitrile had the highest $K_D$'s. $K_D$ generally increased with volume fraction of solvent. These $K_D$ values are low for extraction solvents.

**Table 12.** Distribution Coefficients

| Solvent | Volume Fraction (Balance is $H_2O$) | Distribution Coefficient ($k_D$) |
|---|---|---|
| Methanol | 0.85 | 0.10 |
| Methanol | 0.9 | 0.14 |
| Methanol | 0.95 | 0.21 |
| DMSO | 0.9 | 0.04 |
| DMSO | 0.95 | 0.08 |
| DMSO | 1 | 0.15 |
| Acetonitrile | 0.87 | 0.23 |
| Acetonitrile | 0.91 | 0.25 |
| Acetonitrile | 0.95 | 0.30 |
| Acetic acid | 0.85 | 0.25 |
| Acetic acid | 0.9 | 0.20 |
| Acetic acid | 0.95 | 0.33 |

These data were used to model a counter-current extraction system. Using the $K_D$ values and a chart from Shuler (*52*) shown in Figure 4, the amount of solute removed using a specific number of stages can be estimated. The computation requires that the extraction factor (E) is calculated. E is simply $K_D$ times the ratio of solvent flow rate to OLP flow rate. As a simplification, flow ratios of 1.0 and 3.0 are used so that E equals 1.0 and 3.0 times $K_D$, respectively. Figure 4 was used to estimate what degree of separation a 20 ideal stage extraction would provide. Table 13 shows the results of this calculation for all $K_D$ values in Table 12. Estimated SCME removal varied greatly, ranging from 10-88 wt % depending on solvent, volume fraction, and flow ratio. This model assumes that $K_D$ is constant and that the two fluids are totally immiscible. The inaccuracy of these assumptions will be discussed in the discussion section.

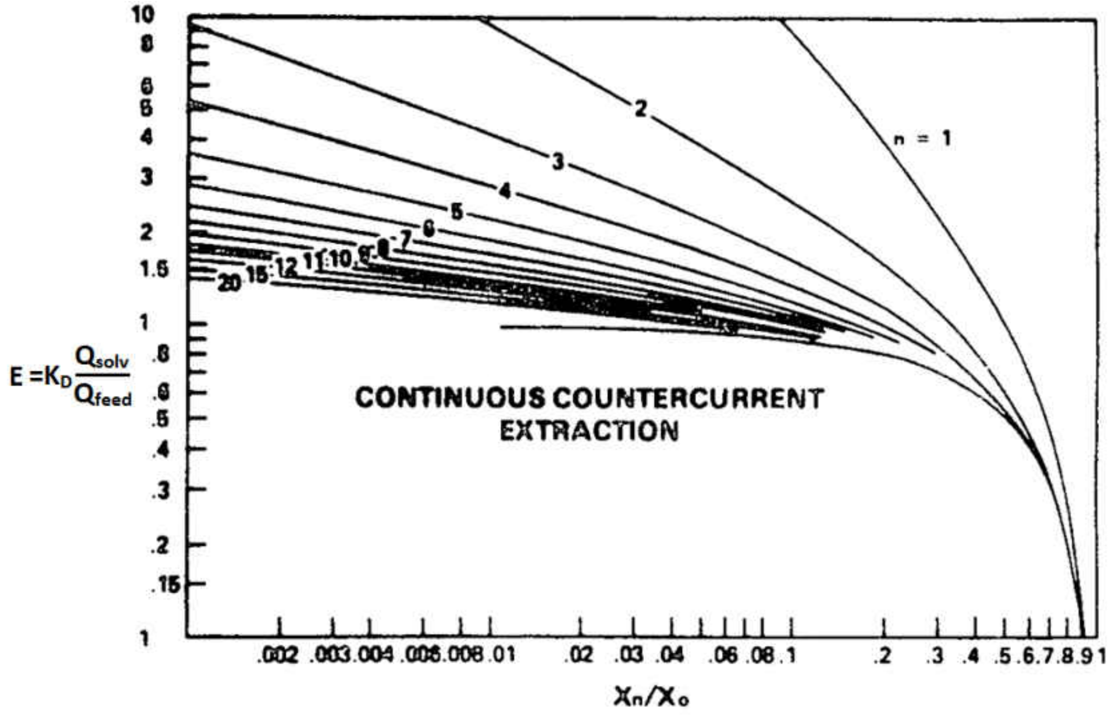


**Figure 4.** Relationship Between Unextracted Solute, Extraction Factor, and Number of Stages in Continuous Counter-Current Extraction. (Taken directly from (*52*))

**Table 13.** Estimated SCME Removal Using Various Extraction Solvents.

| Solvent | Volume Fraction (balance is H2O) | Percent SCME Removal for 20 Stage Separation | |
|---|---|---|---|
| | | $E = 1.0K_D$ | $E = 3.0K_D$ |
| MeOH | 0.85 | 15% | 29% |
| MeOH | 0.9 | 17% | 42% |
| MeOH | 0.95 | 21% | 61% |
| DMSO | 0.9 | 10% | 16% |
| DMSO | 0.95 | 12% | 22% |
| DMSO | 1 | 18% | 44% |
| ACN | 0.87 | 22% | 68% |
| ACN | 0.91 | 26% | 70% |
| ACN | 0.95 | 29% | 80% |
| Acetic acid | 0.85 | 26% | 71% |
| Acetic acid | 0.9 | 29% | 56% |
| Acetic acid | 0.95 | 32% | 88% |

Because of the relatively high SCME removal numbers using acetic acid, a set of experiments to determine its phase overlap were performed. Similar to the quantitative screening experiments the trial was performed in triplicate. However, only ambient temperature trials were performed, and analysis was only done after the raffinate had been washed with water to remove the acetic acid. The results from these trials are shown in Table 14 as the average and standard deviation of the three replicates.

**Table 14.** Quantitative Experiment Results with Acetic Acid at Ambient Temperature.

| Volume Fraction Acetic Acid (Balance H2O) | Average Hydrocarbon Mass into Extract (Stdev) | Average Solvent Mass into Raffinate (Stdev) | Average SCME Reduction (Stdev) |
|---|---|---|---|
| 0.9 | 12.3% (1.8) | 21.4% (2.6) | 23% (0.36) |

Compared to the other solvents tested in the quantitative screening experiments (Table 10, Table 11) acetic acid removed about as many SCMEs as the best previous solvent (acetonitrile) and had less overlap of hydrocarbons into the polar extract. However, the raffinate absorbed more of the polar acetic acid than with the other solvents.

### *4.4 Property Testing*

Table 15 shows the freeze points and heating values for a fully deoxygenated jet fuel fraction from TAG oil OLP, unprocessed TME OLP, and a 50/50 volumetric blend of the two. The 50/50 blend provides an estimate of the properties to be expected in a TME OLP sample which has had about half of the SCMEs extracted. Freeze points test were performed with 4 replicates, the averages and standard deviations are shown.

The deoxygenated OLP meets both freeze point and heat of combustion specifications. The unprocessed TME OLP nearly meets the freeze point for Jet A (-40 °C) fuel, but not for JP-8 (-47 °C). It also has a heat of combustion slightly below the specification for both aviation fuels (42.8 MJ/kg). However, the 50/50 blend meets both of these specifications for the aviation fuels.

It may seem unusual that the freeze point of the blend is so much closer to the freeze point of the deoxygenated fuel than it is to the TME OLP. This can be explained by dissolution of the high molecular weight esters in the hydrocarbons, which are a large percentage of the total composition in the blend.

**Table 15.** Fuel and Intermediate Properties.

| Sample | Heat of Combustion (MJ/kg) | Freeze Point (°C) Average (Stdev) |
|---|---|---|
| Deoxygenated TAG oil OLP | 47.04 | -48.5 (0.08) |
| TME OLP | 40.38 | -39.8 (0.75) |
| 50/50 Blend | 43.12 | -48.5 (0.29) |

# 5. Discussion

## *5.1 Solvent Miscibility Tests*

Miscibility tests revealed that seven of the ten polar solvents were miscible with OLP. Adding small amounts of water caused 4 of them to phase separate from the OLP. Some of the compounds (methanol, acetonitrile, acetic acid) are only slightly miscible in saturated hydrocarbons, but fully miscible OLP when no water is present (*53*, *54*). This is likely due to the SCMEs in OLP acting as a "bridge" between the polar solvents and non-polar hydrocarbons. This would theoretically occur in the same manner that soaps and other surfactants allow the mutual solubility between polar and non-polar compounds. Figure 5 shows the similarity of methyl ester to a soap molecule because of the non-polar tail and polar head.

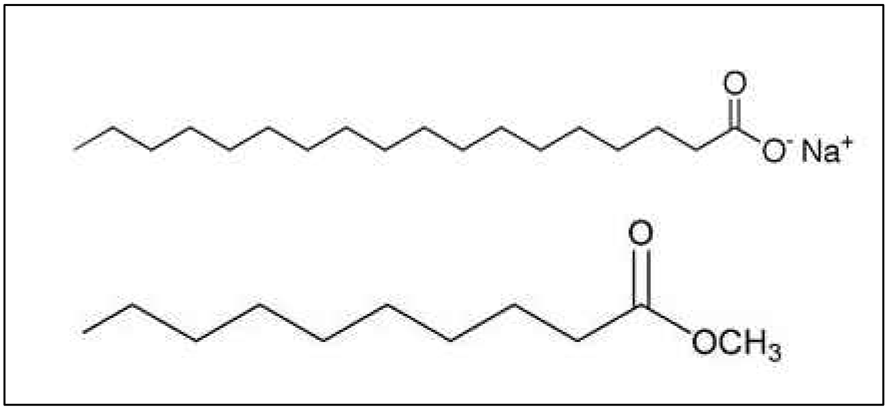


**Figure 5.** The Polar Head and Non-Polar Tail of Sodium Stearate (a soap) and Methyl Caprate.

The methyl group on the head of the ester is significantly less polar than the sodium ion of the soap molecule. For this reason the methyl ester will not “bridge” between polar and non-polar molecules nearly as well as soap does, but it must to some degree because there is mutual miscibility of these solvents with n-alkanes.

### 5.2 *Qualitative Solvent Screening Experiments*

Some of the results from the quantitative screening experiments confirmed that analytical methods in the qualitative screening experiments generated systematic error. The results in Table 9 are a reflection of not only the reduction in SCME concentration in the OLP, but also the degree to which the polar solvent interacts with the SCMEs in the hydrocarbon phase.

Although the absolute reductions in SCME concentration are erroneous, relative results can still be used to ascertain some information about the LLE. For instance, with every solvent SCME extraction decreased when more water was added to the polar solvents. This implies that water is only useful up to the point that it ensures phase separation from the OLP. Any water added beyond this point just reduces the solubility of the esters in the polar solvents. This trend was considered when choosing solvent/water ratios in the final extraction experiments.

These tests were conclusive enough to eliminate ethylene glycol, sulfolane, and citric acid solutions from subsequent extraction experiments. With thousands of polar solvents available, a much larger number may need to be screened to determine which solvent is best. However, the general flaws that occurred with the extraction will likely be present when any solvent is used in a similar manner.

### *5.3 Quantitative Solvent Screening Experiments*

The quantitative solvent experiments indicated that significant phase overlap was occurring during the extraction experiments. As much as 35% of the hydrocarbons in OLP were lost to the polar solvents during mixing, and as much as 20% of the solvents were transferred into the TME OLP. The polar solvent can be washed out of the OLP with water, essentially adding a unit operation to a SCME solvent extraction process. Such a process may recover additional SCMEs in the water wash. Removal of the hydrocarbons from the polar solvents would be more complex. Any attempt to phase separate the solvent-hydrocarbon-SCME mixture would likely divide the SCMEs among the 2 phases, further decreasing the amount of SCMEs recovered. Distillation would be difficult due to the overlapping hydrocarbon and SCME boiling points also present in the OLP. No matter how the hydrocarbons are removed it would add at least one, but likely several, additional operations to a SCME extraction process.

SCME removal was relatively unaffected by temperature, however, phase overlap was more prominent at the higher temperature (45°C). It might be possible to reduce phase overlap further by operating the extraction at sub-ambient temperatures. Also, the solubility of methyl esters in water increases slightly with decreasing temperature (*44*), so SCME removal may improve as well.

### *5.4 Final Extraction Experiments*

The final extraction experiments focused on determining distribution coefficients for the SCMEs between the polar solvents and TME OLP. The use of gas chromatography for the polar phase analysis ensures the validity of the $K_D$ values calculated from these experiments.

Overall, the $K_D$ values were low, implying that extraction may require a large number of stages and be a difficult separation method. The values were much lower than those found in previous studies (*40–42*) with methyl acetate and various individual hydrocarbons. The better $K_D$'s with methyl acetate are expected because it is the most polar SCME in TME OLP.

Acetic acid and acetonitrile had significantly higher $K_D$ values than methanol and DMSO, leading to greater predicted extraction values in the 20 ideal stage model. Phase overlap showed some interesting results when additional experiments were added for acetic acid. Acetic acid had a greater overlap of solvent into raffinate, but much lower overlap of hydrocarbons into the extract. This is preferred because the polar solvent can easily be recovered with a water wash, but the recovering the hydrocarbons without losing SCMEs will be a challenge. These results indicate that acetic acid is the best option of the solvents considered for SCME extraction.

### *5.5 Multistage Extraction*

Modeling showed that 20 ideal stages of separation would recover significant amounts of SCMEs, 10-88% depending on solvent and flow ratios. However, assumptions behind these models were inaccurate. The model made two assumptions that point out flaws in separating SCMEs from OLP via LLE. First, the model assumed that the two fluids were totally immiscible. This assumption is certainly not accurate; Table 11 shows the amount of phase overlap that occurred when polar solvents are contacted with TME OLP. Second, the model assumed that $K_D$ was constant. The nature of the TME OLP makes it unlikely that this assumption is accurate. The SCMEs are not a single compound, but a range of compounds with varying physical properties. The more polar, low molecular weight SCMEs would be removed at first, but once they were mostly extracted from the OLP, only the less polar SCMEs would remain, reducing the $K_D$ significantly.

It is difficult to say at this point how the inaccuracy of these assumptions would affect how much real world results would differ from the model. The phase overlap generally makes both phases more hospitable for the SCMEs. Because of the phase overlap, both phases contain more of a combination of both polar and non-polar groups. This makes them better solvents for the SCMEs. It's hard to predict which phase's absorption of the SCMEs will be increased more by the phase overlap.

It is still unknown if multiple stages will increase the amount of phases overlap in the final extract and raffinate solutions. Perhaps more SCME transfer means more hydrocarbon transfer due to the "bridge" effect mentioned earlier.

Up to this point samples have been shaken by hand, but in a continuous extractor agitation will likely be necessary. Mixing is a factor that will need to be thoroughly evaluated in a multistage extraction scheme.

The uncertainties from modeling multistage extraction suggest that experimental work using multistage extraction will be necessary to accurately determine if LLE is a viable method to remove and recover large amounts of SCMEs from the TME OLP.

### *5.6 Eliminating Phase Overlap*

The assumptions for the model are important factors to successfully performing a separation by LLE, especially in a case where full recovery of the solute is desired. Due to phase overlap, several unit operations would be necessary to extract the SCMEs, recover the solvents and hydrocarbons in phase overlap, and finally recover the SCMEs themselves. A large methyl ester byproduct stream may not be worth the cost of a complex recovery process. However, to meet the specifications for aviation fuels, it is likely that only a small fraction of the SCMEs will need to be removed.

The property testing results in Table 15 show how close TME OLP is to meeting the specifications for Jet A aviation fuel. The heating value only needs to be increased by about 3 MJ/kg. Meeting this property would require only a small portion of the SCMEs be recovered and a preferential extraction toward the lowest molecular weight esters would be beneficial. The much lower heating values of these esters are shown in Figure 1.

An extraction strategy focused on separating the lowest molecular weight esters (methyl propionate, methyl butyrate, and methyl valerate) may be more successful. Compounds with stronger polarity and the use of more water could be considered for

LLE in order to reduce the significance of phase overlap. If phase overlap could be avoided, fewer recovery steps would be needed, making the process more practical and cost effective. However, the low molecular weight esters are not high value specialty products like the C6-C10 methyl esters and carboxylic acids. Bulk prices are shown for comparison in Table 3.

Large fractions of TME OLP meet the specifications of diesel fuels without modification. These fractions could be separated via distillation and used with little or no further processing. Further, fractionation of the TME OLP prior to extraction may improve separation efficiency in the aviation fuel fractions by segregating the longer chain methyl esters that are more prone to "bridge" between the polar and non-polar compounds. Such a strategy would also decrease the volume of OLP that would flow through the extraction process.

If advanced fuel processing from TME OLP is necessary, a focus on recovering the shortest methyl esters may be a better course of action than dealing with phase overlap to obtain higher yields of SCMEs.

### *5.7 SCME Recovery*

Any extracted SCMEs will need to be recovered from the solvent and separated into pure compounds to be sold as chemical products. Individual SCMEs will likely be separated by distillation. However, recovery of the solvent might use a different method; this is a factor that should be considered when determining which solvent is best.

Selection of extraction solvents with boiling points distant from the recovered SCMEs would ease the recovery process. For a process focused on extracting the shortest methyl esters, selection of non-volatile extraction solvents would be best. The SCMEs could be driven out of the solvent using distillation.

If a full range of SCMEs is recovered, both distillation and other alternatives should be considered, especially since hydrocarbons from phase overlap may be mixed in with the product. The boiling point of acetic acid is between boiling points for methyl butyrate (101.85 °C) and methyl pentanoate (136.85 °C). Because its boiling point is >15 °C from either ester it should be possible to separate by distillation. Additionally, it has a fairly low latent heat (402 kj/kg), so energy consumption can be kept fairly low. Reactive separation of acetic acid may also be possible. As a carboxylic acid it can react to form salts that could potentially be precipitated from the mixture as insoluble carboxylate salts and subsequently regenerated using a strong acid.

## 6. Conclusions

LLE with polar solvents to remove all or most of the SCMES from OLP is complicated due to the overlap of the polar and hydrocarbon phases. The driving force for the SCMEs into the studied polar solvents is low with $K_D$'s under 0.5. Acetic acid stood out as the best solvent for extracting the SCMEs from TME OLP, but modeling of LLE using multistage extractions was inconclusive due to the inaccurate assumptions that had to be made. Further experimental work with continuous counter-current extraction is necessary to determine if LLE of a large range of SCMEs would be a cost effective process. Additional extraction tests at sub-ambient temperatures are also recommended.

Due to the differences between SCMEs and SCFAs, unmodified TME OLP is much closer to meeting fuel specifications for aviation and diesel fuels than unmodified

TAG oil OLP. Fuels that have some chemical differences from petroleum counterparts but meet required standards can potentially be produced via TME cracking and distillation.

A less invasive LLE approach should be considered. The OLP could be fractionated prior to extraction, and the focus could then be on removing only the low molecular weight SCMEs from the jet fuel fraction. The goal would be to ensure the fraction meets the heating value specification for jet fuel. Focusing on removal of these solutes with highly polar solvents may lead to extractions without phase overlap. These changes may lead to a more practical process to separate some of the SCMEs from TME OLP.

Catalytic deoxygenation by decarboxylation is another option to reduce the quantity of the SCMEs in the TME OLP. This method is efficient with SCFAs in TAG oil OLP and should be explored as an option for the TME based process as well.

Previous work with TAG oil has shown that the recovery of SCFAs as a byproduct stream in a TAG oil cracking scheme is practical and efficient. The direct cracking of TAG oil for bio-refining fuels and chemicals seems to be the more economically viable option at this point.

# CHAPTER III

# VINYL ACETATE MONOMER (VAM) PRODUCTION WITH RENEWABLE RESOURCES

## 1. Introduction

Bio-based jet and diesel fuels can be produced through the non-catalytic cracking of triacylglycerol (TAG) oil followed by de-oxygenation. However, side products will be beneficial to supplement revenues in a bio-refining scenario. Acetic acid is present in usable quantities in crackate intermediates. Depending on reaction conditions, liquid crackate contains approximately 0.5 to 2.0 wt% acetic acid. De-oxygenation of acetic acid in OLP would result in low value hydrocarbon gases so it makes sense to recover it as a side product prior to any de-oxygenation step.

Acetic acid is a major commodity chemical with a global demand of 10.0 million metric tons (2008)(*15*). About 75% of acetic acid is produced by the carbonylation of petroleum-derived methanol (*55*). However, the FDA requires that vinegar – dilute acetic acid for human consumption – must be produced via acetous fermentation (*56*). Thermal cracking of TAG oil will provide another renewable method to produce acetic acid.

The largest user of acetic acid is the vinyl acetate monomer (VAM) manufacturing industry. VAM is the basis of white glue, laminating wallboard, and latex paint. Polymers derived from VAM are used in safety glass, film products, and hot-melt adhesives (*24*). Worldwide VAM production in 2007 was about 6.1 million tons (*57*).

Renewable polymer production is an emerging market. For example, Frito-Lay recently came out with a renewable polylactic acid bag made from corn (*58*, *59*), and Coke has plans for a 100% renewable PET plastic bottle (*60*). Generating renewable VAM from TAG oil derived acetic acid offers a segue into the renewable polymer market.

Most VAM is produced by the addition of acetic acid to ethylene over palladium (Pd) based catalysts. Both gas and liquid phase reactions are used, but the gas phase is much more common. The reaction is performed industrially using either a packed bed reactor (PBR) or a fluidized bed reactor (*61*).

Renewable ethylene can be produced from ethanol by dehydration over a catalyst at high temperatures (*62*) or by a proprietary process involving a butylene intermediate developed by Braskem (*63*, *64*). Usable amounts of ethylene and ethane (which can be dehydrogenated to ethylene) are also present in the gas phase effluent of non-catalytic cracking.

The goals of this work are:

1. Develop a lab/bench scale process for producing and recovering renewable acetic acid from TAG oil via thermal cracking.
2. Determine if VAM can be produced using renewable acetic acid from TAG oil, and renewable ethylene from ethanol

3. Explore a range of conditions to efficiently produce kg amounts of VAM using renewable reactants.

When thermally cracked TAG oil is distilled to 140 °C a polar aqueous layer is present in the distillates. Through decanting of the polar layer, and LLE of the organic phase distillates with additional water, aqueous acetic acid can be separated from the mixture. Purification of the acetic acid can be carried out using azeotropic distillation to remove water.

A purified renewable acetic acid product was added to renewable ethylene over a Pd-Au catalyst in a PBR to produce VAM via a gas phase reaction. This renewable VAM was separated from unused reactants and byproducts by distillation.

## 2. Background

### *2.1 Acetic Acid Production*

#### *2.1.1 Traditional Processes*

Acetic acid is a building block commodity chemical used mainly for the production of VAM, terephthalic acid, acetate esters, and acetic anhydride (*65*). Most acetic acid is currently produced by the rhodium catalyzed carbonylation of methanol, a process developed by Monsanto in the 1960s (*66*). Acetic acid yields are high: 99% based on methanol and 85% based on CO. Other methods for acetic acid production include methyl formate isomerization, synthesis gas to acetic acid, oxidation of ethylene, and the fermentation of ethanol (*65*, *67*).

Vinegar is a dilute form of acetic acid meant for human consumption. It is used mostly in condiments and as a food preservative and is produced by the fermentation of ethanol using Acetobacter bacteria (*67*). This form of acetic acid is renewable; however, it is dilute (typically around 10 percent by volume) (*68*). The inefficiency of batch processing along with the need to concentrate from a dilute aqueous solution make fermentation a less desirable bulk production method than continuous methanol carbonylation.

### *2.1.2 Acetic Acid From TAG Oil*

Acetic Acid can be produced as a byproduct of a non-catalytic TAG oil cracking scheme. This renewable method for producing acetic acid involves four major steps: non-catalytic cracking, crackate distillation/decanting, aqueous extraction, and water removal distillation. During these steps, several other products, intermediates, and waste streams are produced. Their uses and further processing are beyond the scope of this project. The block flow diagram in Figure 6 shows the four major steps as well as their inputs and outputs.

#### *2.1.2.1 Non-Catalytic Cracking*

Non-catalytic cracking of TAG oil has been explored at length at the University of North Dakota (*7–10*). The reaction occurs when the oil is heated to temperatures ranging from 400-470 °C in the absence of oxygen. Various reactor configurations have been used, including batch, semi-batch, and continuous apparatuses. The main products when the TAG molecules break apart are hydrocarbons and carboxylic acids of various chain lengths. The range of products depends on the temperature, pressure, and residence time of the reaction.

Industrially, thermal cracking would occur in a multiple-pass tube bundle heated by either a direct fired furnace, or a heat exchange fluid such as molten salt. For this project thermal cracking was carried out continuously in a bench-scale Turbulent Tubular Reactor (TTR). The only major difference from an industrial cracking unit was the heating method. The bench-scale reactor was heated using electric heating elements in an insulated ceramic enclosure.

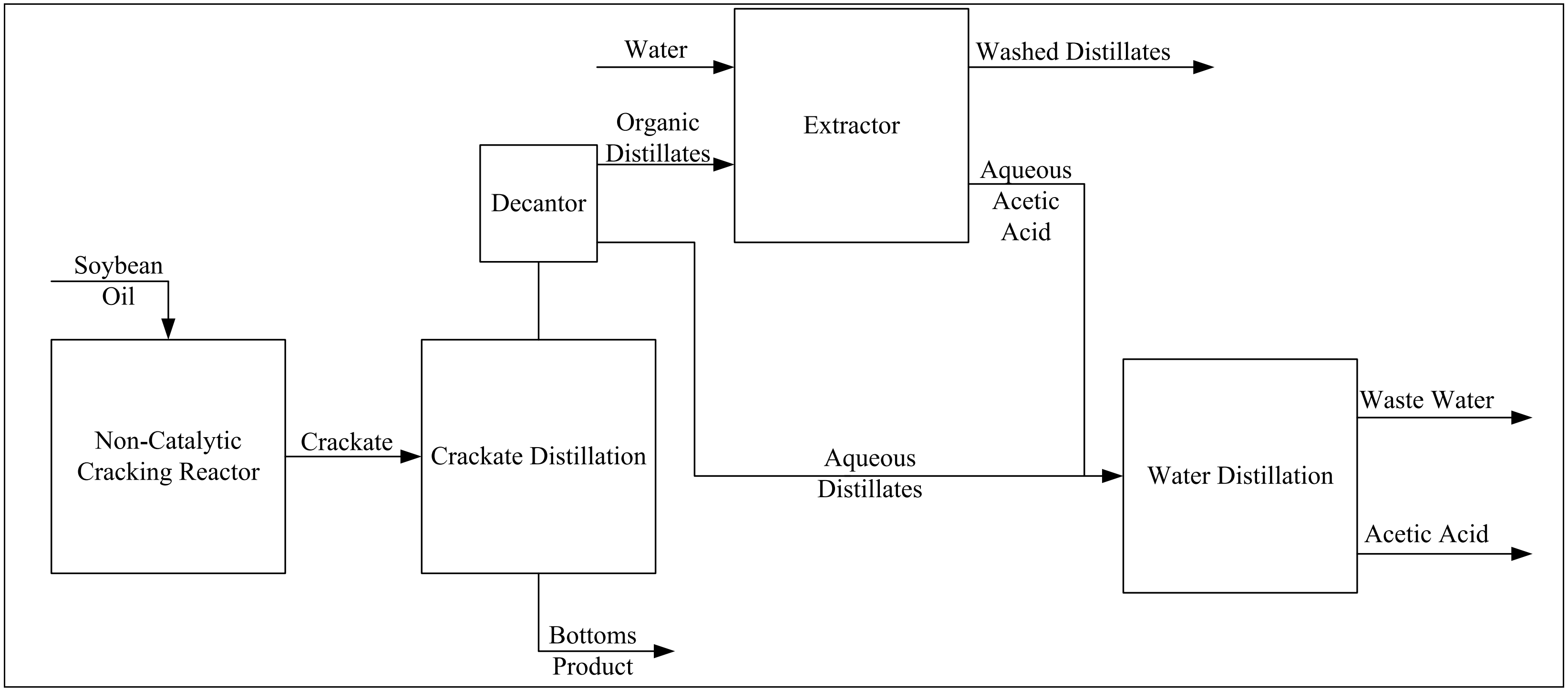


**Figure 6.** Block Flow Diagram for Soybean Oil to Acetic Acid Process

### *2.1.2.2 Crackate Distillation*

Crackate consists of hundreds of different compounds with a wide range of properties; the first step in separating these components to produce various fuels and chemicals is distillation. In an industrial process crackate distillation would be carried out in two major steps. First the volatile compounds would be distilled atmospherically. Depending on what products are desired, this first distillation can be as simple as a flash separation or as complex as a vacuum distillation system. This step may recover compounds with boiling points up to as high as 250 °C or as low as 100 °C. The next step would involve distillation of all compounds that can be removed from the tars without reaching cracking temperatures. This step will likely use vacuum pressures to increase the yield of product in the overhead stream.

To optimize the recovery of acetic acid, overhead temperature in the first distillation column should be well in excess of the boiling point for acetic acid (118 °C). Keeping the total volume of overhead product low will result in a higher concentration of acetic acid in the distillate. This in turn will increase the efficiency of the subsequent steps needed to recover the acetic acid. Therefore, it is important not to choose a control temperature so high that unnecessary amounts of product are recovered in the distillate. The compromise of these two factors typically results in an distillate temperature around 140 °C.

### *2.1.2.3 Aqueous Extraction*

A small amount of aqueous phase that contains a high concentration of acetic acid is present in the overhead product from the first crackate distillation. Industrially (and in the lab) this phase will be decanted for acetic acid recovery or neutralization. Some acetic acid will remain in the organic phase distillates. In an industrial process this acetic acid will be removed by continuous counter-current extraction with water.

For lab-scale processing the aqueous phase distillates are drawn off and the remaining acetic acid is removed from the organic distillates by a series of washes with water. Previous work concluded that all C2 and C3 SCFAs could be recovered using a single stage extraction with ambient water (*20*). However, this research reported equal volumes of water and OLP, which resulted in a very dilute aqueous acetic acid solution (< 10 wt%).

In the final acetic acid recovery step, the vapor-liquid-equilibrium (VLE) of acetic acid and water creates a very challenging scenario. The VLE diagram in Figure 7 shows a pinch point around 95% water, 5% acetic acid. When concentrating the acetic acid it is difficult to distill off water that does not contain about 5% acetic acid. Therefore, beginning with a more concentrated aqueous acetic acid solution will result is less product lost in the overhead waste water stream. To obtain a more concentrated acetic acid solution, multiple extractions with very small volumes of water are used, rather than a single-stage equal-volume extraction.

#### *2.1.2.4 Water Distillation*

The final step in acetic acid recovery is distillation to remove the water, and thus concentrate/purify the acetic acid. In order to overcome the pinch point shown in Figure 7 isobutyl acetate is added to the water/acetic acid solution. Isobutyl acetate (IBA) is used as an entrainer to reduce the boiling temperature of water, and thus the concentration of acetic acid in the overhead stream of the distillation. Water and IBA form a low boiling heterogeneous azeotrope. The IBA entrainer results in a much smaller loss of acetic acid in the distillate stream (*69*).

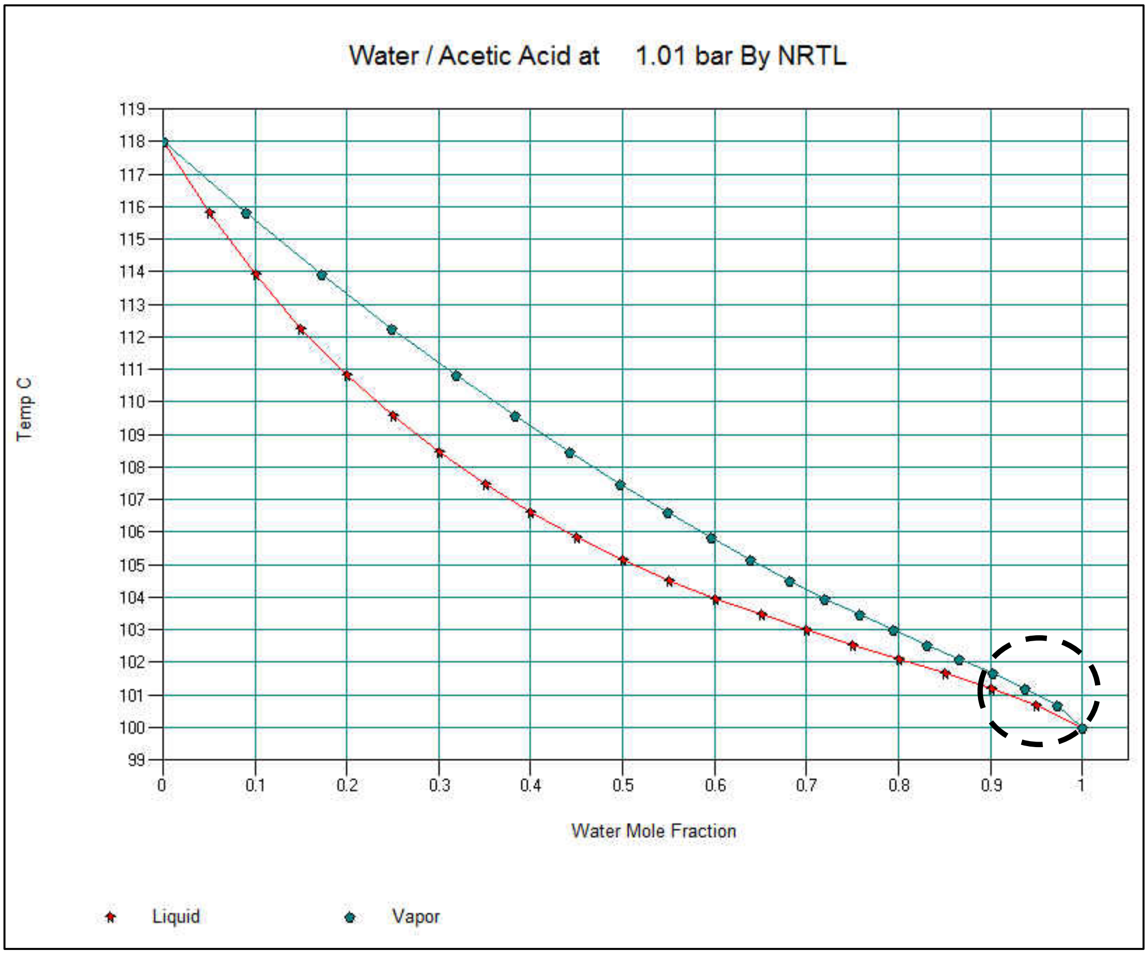


**Figure 7.** Vapor-Liquid-Equilibrium of Water and Acetic Acid.

An industrial-scale continuous distillation system can remove almost all of the water using this method without sacrificing any acetic acid (*70*, *71*). However, the use of batch distillations in the lab creates a more challenging scenario. Rather than dealing with a constant feed composition at steady-state, the “feed” in the flask at the bottom of the column varies as the distillation progresses. As water is driven off, the acetic acid is concentrated making it more difficult to separate the water without removing some of the acetic acid as well. For this reason, two distillation steps must be used in the lab. First, the majority of the water is driven off with an entrainer to concentrate the acetic acid solution. The best way to perform this step is by recycling the IBA recovered in the distillate back into the boiling pot.

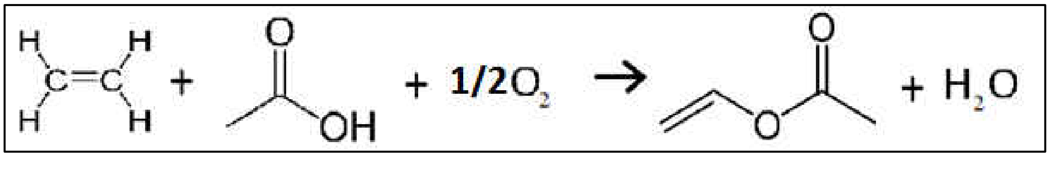
When carrying out batch distillations with an IBA entrainer, it is important to note that in the absence of water, acetic acid and IBA form an azeotrope and would be more difficult to separate than an acetic acid and water solution. Therefore, it is important not to remove *all* of the water while still leaving IBA in the acetic acid solution.

Second, a high reflux batch distillation is used to purify the acetic acid and to separate it from the heavier (C3-C5) acids. Some acetic acid does leave with the water, but because the solution is sufficiently concentrated in the first step, losses of acetic acid in the distillate stream will be minimal.

## *2.2 Vinyl Acetate Monomer Production*

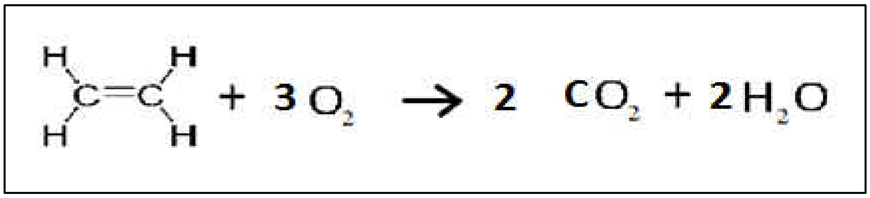
### *2.2.1 VAM Reaction*

Vinyl acetate is produced by the oxidative addition of acetic acid to ethylene; this is shown in Reaction (3). This is an exothermic reaction with a standard heat of -176.2 kJ/mol(*72*). Therefore, it is necessary to remove heat during the reaction to maintain isothermal conditions which is typically achieved using a water-cooled jacket around the reactor.



**(3)**

Due to the presence of oxygen in the reactor, oxidation of ethylene can occur as an undesirable side reaction. This oxidation reaction is shown in Reaction (4). It has a high heat of reaction, -1322.8 kJ/mol, so it can complicate heat removal (*72*). Also, it consumes the oxygen and ethylene that are meant for VAM production. For these reasons, this side reaction must be kept to a minimum.



$$H_2C{=}CH_2 + 3O_2 \rightarrow 2\ CO_2 + 2H_2O$$

**(4)**

Reaction (4) has a much higher activation energy than Reaction (3): 30.5 kJ/mol for (3), the VAM reaction, and 84.1 kJ/mol for (4) the oxidation reaction (*73*). Thus, keeping the reactor temperature sufficiently low will reduce the rate of Reaction (4) relative to the rate of the Reaction (3). Also, since oxygen is a 3rd order reactant in Reaction (4) and only a ½ order reactant in Reaction (3), keeping the $O_2$ concentration low will help reduce the rate of ethylene oxidation. An $O_2$ concentration of less than 8% will also to prevent an explosive mixture of ethylene and oxygen (*74*). The need for such a low concentration of oxygen leads to low conversions of ethylene and acetic acid.

### *2.2.2 VAM Production Process*

A simplified version of the process used to produce VAM from acetic acid and ethylene is shown as a block flow diagram in Figure 8.

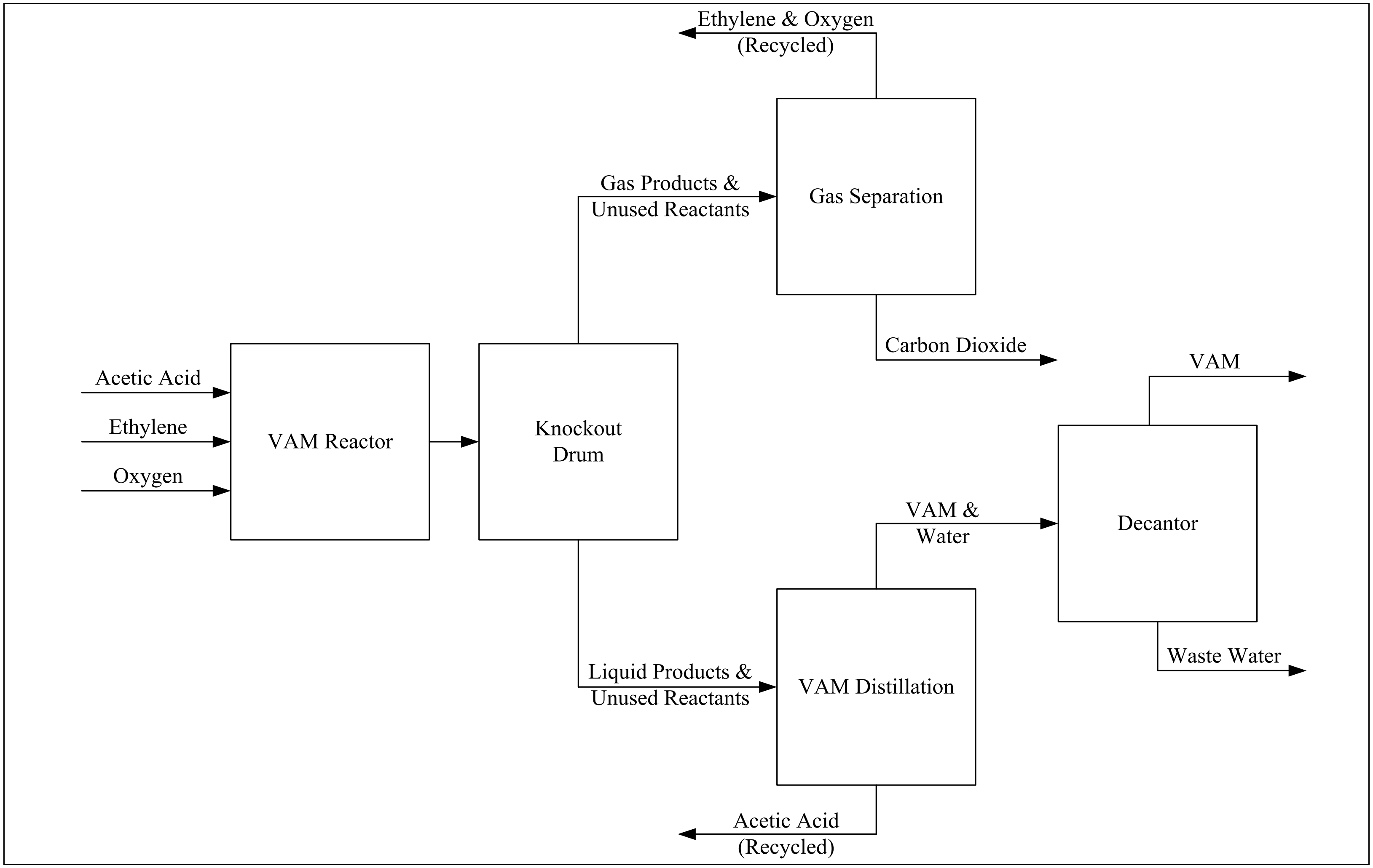


**Figure 8.** Block Flow Diagram of the VAM Production Process

#### *2.2.2.1 Industrial Process*

VAM is typically produced by the oxidative addition of acetic acid to ethylene in a packed or fluidized bed reactor containing a palladium-gold (Pd-Au) catalyst. Industrially, the reaction is embedded within a large recycle loop (*73*). Typically the reactor feed contains about 2-3 times the stoichiometric requirements for ethylene, but only about ¼ the oxygen needed to convert the acetic acid to VAM. Therefore, oxygen is the limiting reactant. Single pass conversions for acetic acid and ethylene do not typically exceed 20% and 10%, respectively (*61*). After the reactor effluent is cooled the product gases and liquids are separated using a knockout drum. Each stream is then processed further to recover unreacted feedstocks.

The gas stream contains ethylene, oxygen, $CO_2$, ethane (if it is in the ethylene source), nitrogen (if air is the oxygen source), and trace amounts of the desired product VAM. This stream is first compressed and then sent on to a series of unit operations to recover the products and unconverted reactants. The VAM is recovered using an acetic acid scrubber and added to the liquid product stream (this step is not shown in Figure 8). The gas product stream then enters a $CO_2$ removal system, which could be any standard removal process (e.g. Rectisol, amine scrubbing, etc.) (*73*). After a purge of the inert gases, the $CO_2$ free gas stream is recycled back to the front of the process so that the ethylene and oxygen can be reused.

The liquid product stream contains VAM, water, and acetic acid. VAM and water form a low-boiling azeotrope at 92.7 wt% VAM and 7.3 wt% water (*75*). The VAM and water are separated from the acetic acid using an azeotropic distillation. The acetic acid in the bottoms is recycled back to the beginning to the reaction loop. VAM and water are mostly immiscible, so they are easily separated in a decanter drum. The VAM will contain about 1% water, and the water will contain about 2 wt% VAM. If necessary, additional water can be removed using a desiccant. Overall conversion using such a reaction loop can be as high as 94% for ethylene and 99% for acetic acid (*72*).

#### *2.2.2.2 Lab-Scale Conversion of TAG oil Derived Acetic Acid to VAM*

In the lab, VAM was produced by reacting acetic acid with ethylene and oxygen in a continuous packed bed reactor containing Pd-Au catalyst supported on silica and promoted by potassium acetate (*76*). Carrying out this reaction on a lab scale without the vapor-phase recycle system that is present in industrial VAM plants presents a major challenge. Single pass conversions of acetic acid and ethylene are low, and any unreacted gasses will be vented, so large amounts of excess ethylene are needed.

In a lab setting, the unreacted acetic acid has to be recovered by batch distillation to be reused in additional VAM reactor runs. Thus, in order to reduce the number of cycles needed to convert a given amount of acetic acid to VAM, maximum single pass conversion of acetic acid is desired. However, it is still safest to keep the gas phase reactants below the limits of an explosive mixture, meaning that the oxygen mole fraction should remain around 0.08 or lower on an acetic acid free basis (*74*). Therefore, as with the industrial process oxygen will be the limiting reactant. The goal is to convert all of the oxygen via Reaction (3) to achieve maximum conversion of acetic acid. It may be beneficial to increase the amount of oxygen fed relative to the amount of acetic acid. There are two ways to accomplish this without exceeding the explosive limit. The amount of ethylene and oxygen can be increased together, further increasing the excess ethylene that will be vented, or an inert gas can be added to the gas reactants diluting the oxygen.

The liquid product stream of the packed bed reactor contains VAM, acetic acid, and water. VAM and water form a low boiling azeotrope and can be recovered from acetic acid using a batch distillation. Because the amount of water generated in the VAM reaction is small, this distillation is much less challenging than the acetic acid purification distillation with IBA. The target purity for lab produced VAM is 99%.

## 3. Materials and Methods

### *3.1 Materials*

### *3.1.1 Experimental Materials*

Food grade soybean oil for thermal cracking was purchased from Columbus Oil (Chicago, IL). Isobutyl acetate for the azeotropic distillation was purchased from Sigma-Aldrich Co. (St. Louis, MO) and was 98% pure. Acetic Acid for VAM production experiments was at least 99.7% pure and was purchased from VWR International (Radnor, PA). Oxygen and non-renewable ethylene were both 99.9 % pure and were purchased from Praxair Inc. (Danbury, CT). Renewable ethylene was provided by Braskem. The ethylene was 99.9% pure and was produced from ethanol by Braskem's plant in Triunfo, Rio Grande do Sul, Brazil. Palladium-gold catalyst was provided by Evonik Industries (Parsippany, NJ).

### *3.1.2 Analytical Materials*

Analytical standards and solvents (methanol, butanol, acetic acid, propionic acid, butanoic acid, and pentanoic acid) were purchased from Sigma Aldrich and were all 98.5% pure or greater. Vinyl acetate standard was purchased from VWR international and was 99% pure. Chromatography gases – helium, hydrogen, argon, and air – were all obtained from Praxair and were 99.999% pure unless otherwise specified.

## *3.2 Experimental Procedure*

### *3.2.1 Non-catalytic Cracking*

Non-catalytic cracking was carried out in a bench-scale two liter continuous tubular reactor held in an insulated ceramic enclosure containing electric heating elements with a total heat output of about 6000W. Soybean oil was fed to the tubular turbulent reactor (TTR) at an inlet flow rate of 1 L/hr using a Neptune model 515-A-N3 proportioning pump. The tubular reactor consisted of 16 sections of 1.5 m (5 ft) long 3/8" Inconel 625 tubing. The tubes were connected by manifolds on both ends so that the oil would flow through 24.4 consecutive meters (80 ft) of tubing while being cracked. The reaction system is shown in Figure 9.

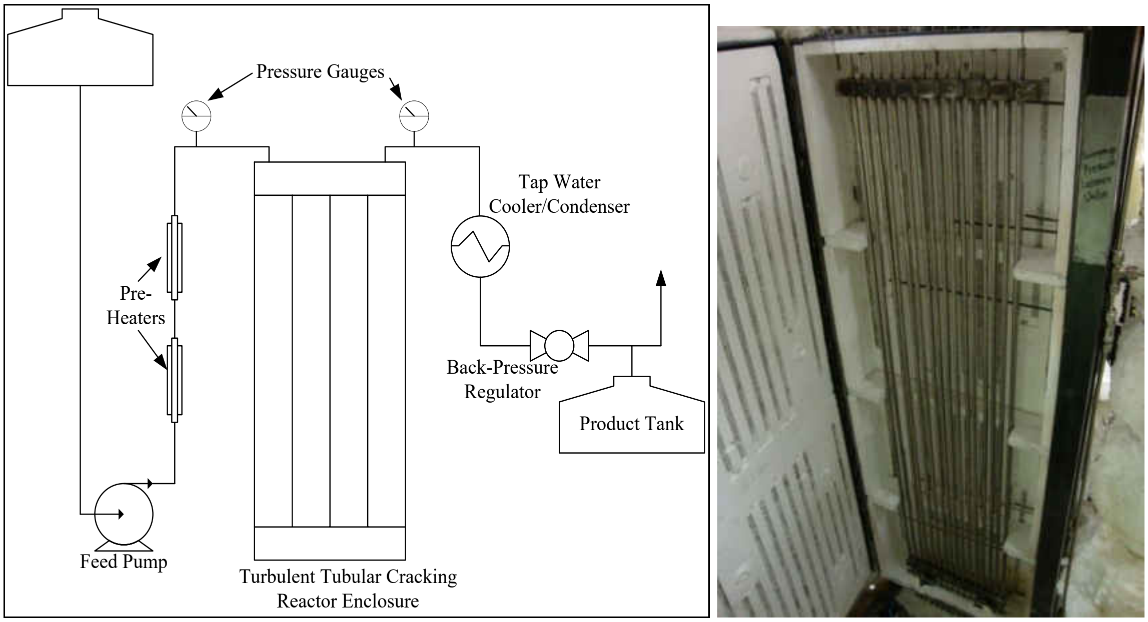


**Figure 9.** Diagram (left) and Picture (right) of the UND Bench-Scale Turbulent Tubular Non-Catalytic Cracking Reactor

Two tubular electric pre-heaters were used to take the soybean oil to a temperature of 385 °C before the oil entered the reaction vessel. The reactor was maintained at an average thermal cracking temperature of approximately 430 °C. The temperature was monitored using eight thermocouples in the enclosure and three thermocouples in the fluid. Temperature was controlled via National Instruments (Austin, TX) LabVIEW by regulating the current supplied to the heating elements. The reactor pressure was monitored using PX309-1KG5V pressure transducers from Omega Engineering Inc. (Stamford, CT). Reactor pressure was maintained manually at 1723 kPa (250 $psi_g$) using a Swagelok (Solon,OH) back-pressure regulator and products were condensed and cooled using a shell and tube heat exchanger with a high flow rate of cold water. These conditions were determined during previous work, and were selected because they resulted in the highest flow-rate at near optimum cracking conditions.

### *3.2.2 Crackate Distillation*

Crackate was distilled continuously in an insulated 1.83m (6 ft) tall, 10.2 cm (4 in) diameter distillation column packed with 1.27 cm (½ in) ceramic rings. The cracked oil was fed at an average rate of 40 g/min. The column's feed was approximately 0.91 m (3 ft) from the bottom of the column. An electric heat source was wrapped around the bottom 15 cm (6 in) of the column. A schematic of the crackate distillation column is shown in Figure 10.

The light key in this distillation was acetic acid, and full recovery was necessary. The liquid crackate was distilled to an overhead vapor temperature of approximately 140°C. Overhead temperature was monitored using a thermocouple in the vapor phase distillate stream, and controlled by varying the heat supplied in the bottom of the column. Distillates were condensed in a water cooled heat exchanger and recovered in a reflux drum. Zero reflux was used for this distillation. The bottom of the column was operated in a semi-batch manner. A valve was opened to allow the bottoms product to flow out when the level in the column reached 0.3 m (1 ft), which was indicated by a side draw. The aqueous phase from the distillate stream was decanted off of the organic phase using a separatory funnel.

### *3.2.3 Aqueous Extraction*

Organic phase distillates from the crackate distillation were washed four times with distilled deionized water. The first wash was performed using a 50:1 ratio of distillates to water. The following washes used 75:1, 100:1, and 100:1 distillate to water ratios. The relative amount of water was reduced in each wash to maintain concentrated extract while removing acetic acid from a more and more dilute source.

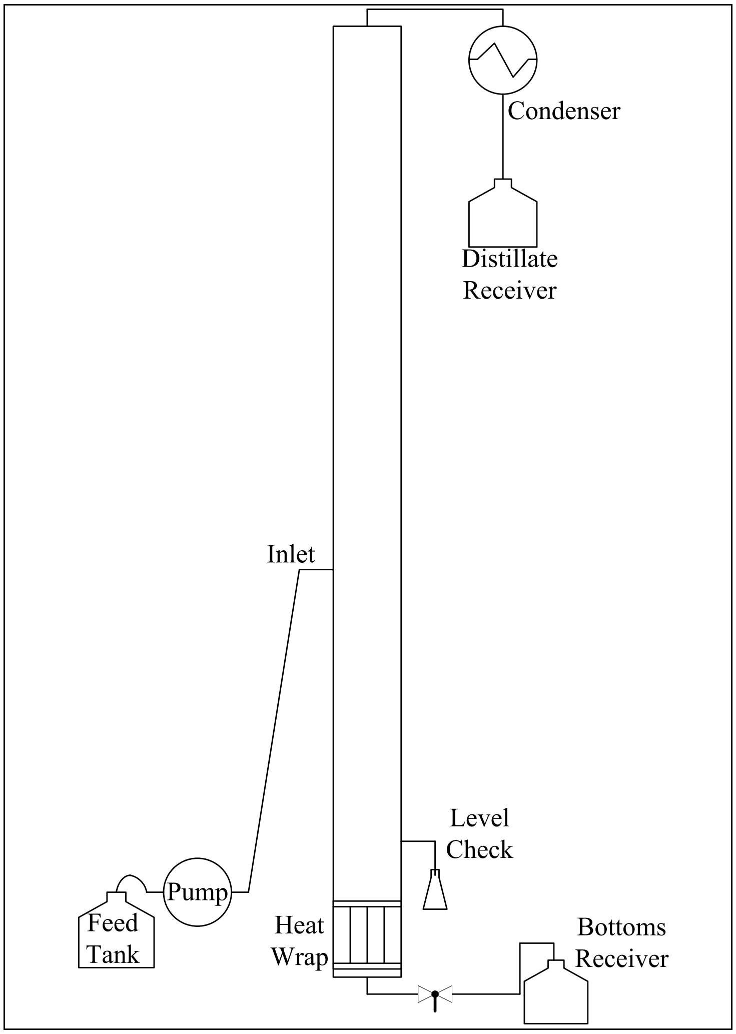


**Figure 10.** Schematic of the UND Bench-Scale Continuous Crackate Distillation Column

### *3.2.4 Azeotropic Distillation of Aqueous Acetic Acid*

Aqueous acetic acid was concentrated through the removal of water by azeotropic distillation using IBA as an entraining agent for water. This distillation was carried out in a lab-scale distillation apparatus with a 5 L round bottom pot flask and a 30.5 cm (12 in) tall, 2.5cm (1 in) diameter glass column packed with 0.64cm (1/4 in) ceramic rings. The aqueous acetic acid solution was concentrated in 2 L batches with 200 mL of IBA added to each batch. The distillate was condensed using a water-cooled glass condenser, and then entered a separatory funnel where water was removed while IBA was periodically refluxed into the distillation column using a peristaltic pump. This apparatus is shown in Figure 11. Waste water from the separatory funnel was disposed. Each batch was distilled until 1 L of water had been removed. At this point, the IBA recycle was stopped and the remaining IBA was distilled out of the more concentrated acetic acid solution.

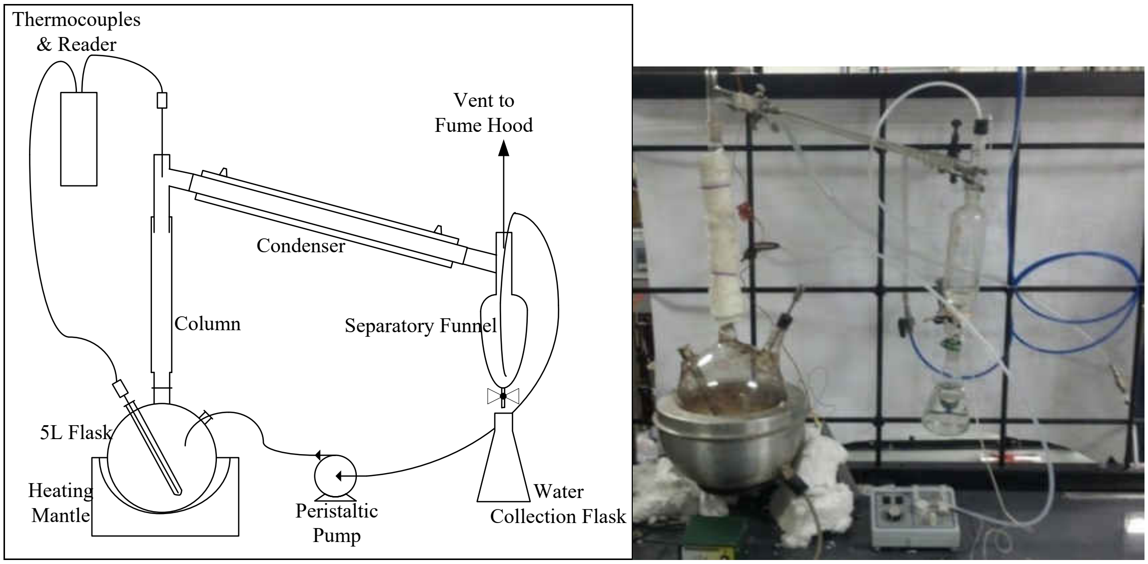


**Figure 11.** Diagram (left) and Picture (right) of the IBA Recycle Distillation Apparatus

### *3.2.5 Purification of Acetic Acid by Multistage Distillation*

Further purification was performed using a B/R Instrument 18-100 High Efficiency Distillation System. This instrument is shown in Figure 12. The distillation column was equipped with a Teflon spinning band capable of producing up to 200 factory reported stages of separation. An 8 receiver fractionating carousel was used to automatically collect fractions based on overhead temperature.

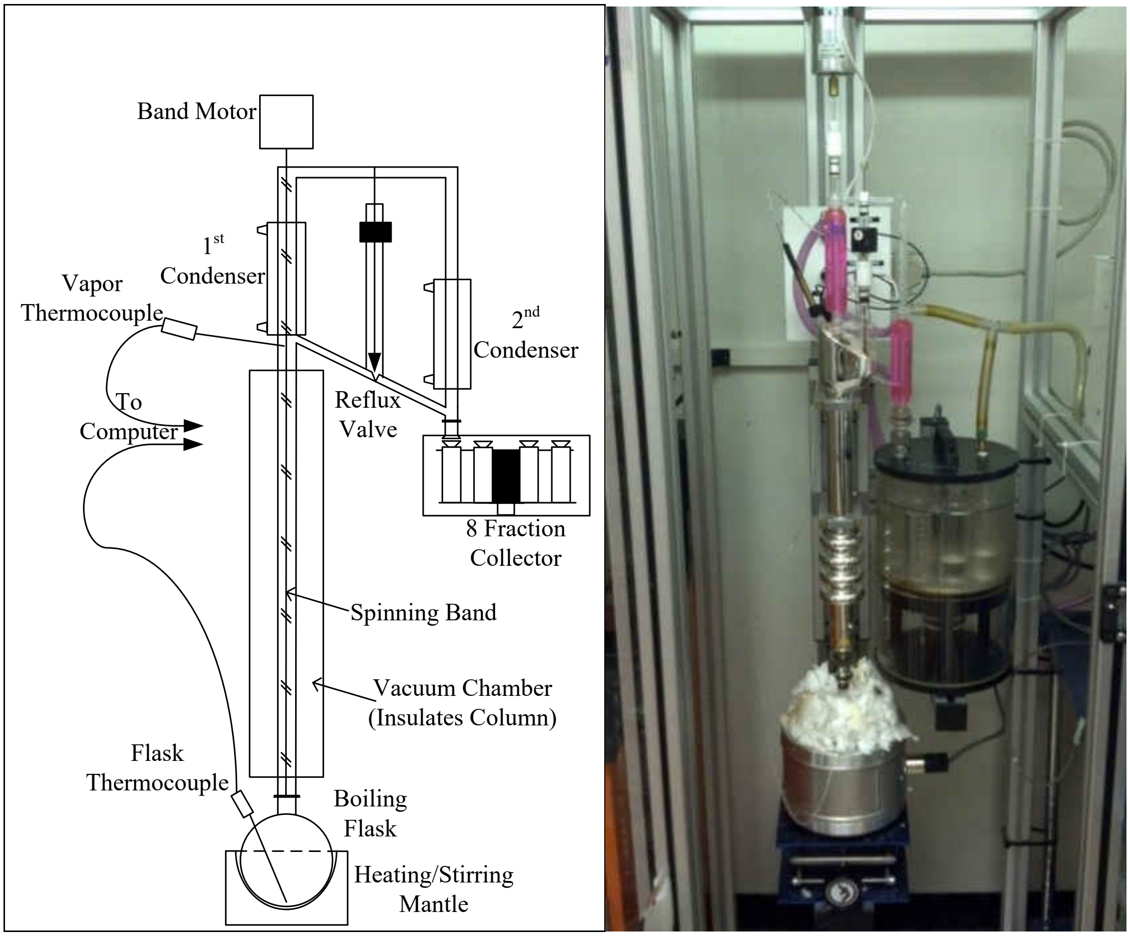


**Figure 12.** Diagram (left) and Picture (right) of the Automated Spinning Band Distillation Column

During fractionation water was distilled off primarily in the first fraction. As the water remaining in the acetic acid solution was removed overhead, the acetic acid and heavier compounds were concentrated in the pot. As the distillate temperature increased, fractions of gradually increasing acetic acid concentration (and less water) were recovered until 118 °C, the boiling point of acetic acid. After this point, the percentage of acetic acid in the distillate product fractions decreased as the percentage of propionic acid increased. The fraction collected for the range from 115-121 °C contained a high concentration of acetic acid, in excess of 85 wt%. However, the semi-purified fractions containing 20-85 wt% acetic acid (and either water or propionic acid as the balance) accounted for a larger volume of product. The semi-purified fractions were then further purified in subsequent distillations, which resulted in additional semi-purified fractions. Full purification of the renewable acetic acid required an iterative procedure using many batch distillations.

### *3.2.6 Catalytic Reactor Testing and Production of Renewable VAM*

VAM is produced by the oxidative addition of acetic acid to ethylene over a Pd-Au catalyst Reaction (3). This reaction was studied first using non-renewable feeds before the renewable reactants were used to produce renewable VAM.

The VAM reaction vessel consisted of a 2.5 cm (1 in) diameter, 35.5 cm (14 in) long tubular packed bed reactor jacketed with a 5 cm (2 in) diameter shell for water cooling. The water jacket was fed by a 177 mL/min maximum variable speed diaphragm pump. The acetic acid was fed using a 10.0 mL/min maximum high pressure positive displacement pump. Gas phase reactants and inerts were fed through thermal mass flow controllers and all reactant streams were mixed together before entering the reactor. Both utility water and process streams were pre-heated in 0.64 cm (¼ in) steel tubing coils inside insulated ceramic enclosures containing electric heating elements. Both utility and process streams were also cooled after the reactor using water-cooled heat exchangers.

The double-pipe reactor and the VAM reactor/heater system are shown in Figure 13 and Figure 14, respectively.

**Figure 13.** Double-Pipe VAM Reactor Bed

Pressure was controlled manually at the outlet for both utility and process fluids via Swagelok back-pressure regulators. However, the VAM reactor effluent was first routed through a pressurized knockout drum to collect product liquids at the reaction pressure. The depressurized reactor effluent gas from this drum was routed through a desiccant bed and into a cryogenic condenser at -45 °C to collect additional entrained product liquids. Finally, the dry gas effluent was vented into a fume hood. Product gas composition was monitored periodically by GC analysis.

Temperatures in the process and utility streams were monitored before and after the reactor using k-type thermocouples. Reactor temperature was measured using a thermocouple inserted directly into the bed, and controlled by the back-pressure of the water/steam jacket. Utility water was heated to near saturation before entering the jacket, at which point the heat of reaction would vaporize some of it to steam. This method takes advantage of the much larger sum of energy needed to vaporize water than is needed to heat it to saturation.

Uniform temperature was readily maintained throughout the reactor bed by operating the water jacket at a pressure with a saturated water temperature just below the desired reaction temperature. This set-up allowed the bed to be warmed to reaction temperature quickly. Saturated steam tables were used to set the utility water pressure for a desired temperature. The flow-rate of water was kept sufficiently high that the reaction could not generate enough heat to vaporize it all to steam.

The inlet flow-rate of acetic acid was controlled by setting the volumetric rate on the pump, measuring the mass flow rate with the feed flask on a scale, and adjusting accordingly.

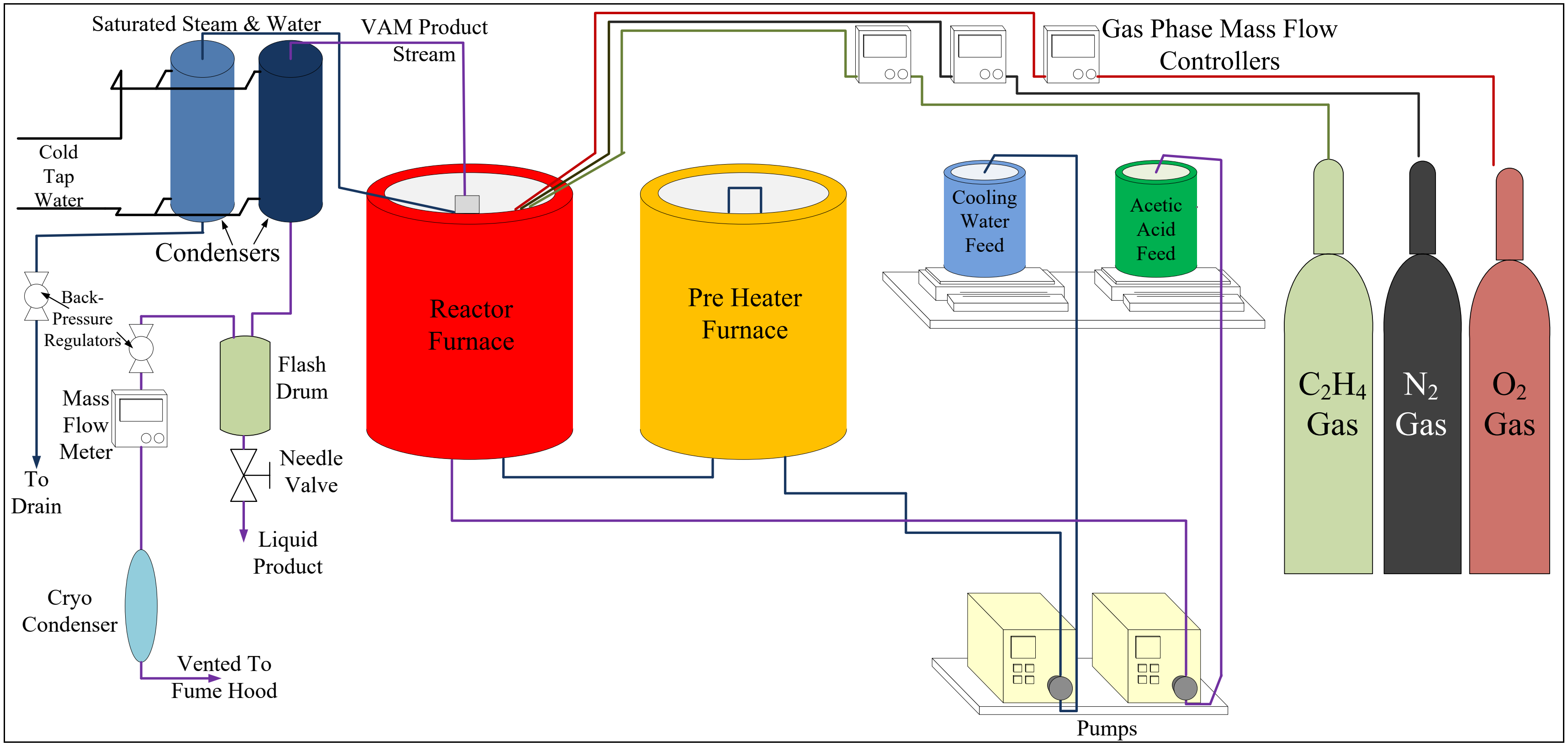


**Figure 14.** Diagram of VAM Reactor/Heater System

The VAM reaction was studied by varying temperature, pressure, and reactant feed rate (i.e. residence time). Studies were performed using non-renewable acetic acid and ethylene. The knockout drum was emptied for each experimental trial and as needed when bulk-generating VAM.

A ¼ fraction factorial set of experiments was used to determine the best range of pressures, temperatures, and reactant flow rates for renewable VAM production. Ethylene flow was based on a molar ratio to acetic acid. For this study, the ethylene to acetic acid molar ratio was maintained at 2.5 based on common practices in industry(*72*, *73*). Oxygen and nitrogen flow-rates were determined using gas phase mole fractions (calculated on an acetic acid free basis). The factors and values studied for the VAM reaction are indicated in Table 16.

**Table 16.** Fractional Factorial Experimental Settings For VAM Reaction Optimization

| **Factors** | **Settings** | | |
|---|---|---|---|
| | **Low** | **Mid** | **High** |
| **Temperature (°C)** | 135 | 155 | 175 |
| **Pressure kPa (psi$_g$)** | 415(60) | 760(110) | 1100(160) |
| **Acetic Acid Flowrate (mL/min)** | 0.6 | 1.8 | 2.5 |
| ***Gas Phase $O_2$ Mole Fraction** | 0.06 | 0.08 | 0.10 |
| ***Gas Phase $N_2$ Mole Fraction** | 0 | 0.1 | 0.2 |

* Gas phase balance is ethylene. Based on an Ethylene/Acetic acid molar ratio of 2.5

Based on the results of the initial factorial experiments, a few additional trials were performed to find a feasible and efficient set of conditions for the bulk renewable VAM processing. The goal of these trials was a compromise of three desired results:

1. High conversion of acetic acid to decrease the number of reactant recovery cycles

2. High enough flow-rates to efficiently produce kg amounts of VAM in limited time
3. High enough conversion of ethylene to reduce the amount vented to the fume hood

Renewable acetic acid and ethylene were then reacted at the chosen conditions to produce two kg of renewable vinyl acetate monomer (VAM).

### *3.2.7 Product Purification*

VAM and water were distilled out of the unreacted acetic acid using the B/R 18-100 distillation column shown in Figure 12. The two immiscible fluids were then separated using a separatory funnel. The acetic acid remaining in the bottoms flask of the batch distillation was purified in an additional batch distillation and reused in the VAM reactor. This cycle of react and recover had to be repeated several times before the full amount of the acetic acid was converted to VAM.

## *3.3 Chemical Analysis*

### *3.3.1 Liquid Phase GC Analysis*

Analysis was performed on a Perkin Elmer Clarus 480 Gas Chromatograph equipped with a split/splitless injector and a flame ionization detector (FID). Helium was used as a carrier gas under constant inlet pressure control at 101.3 kPa (15.0 $psi_g$). Using a 10 µL syringe, 0.6 µL volumes of each sample were manually injected at 300 °C using split mode with a split ratio of 30:1. Separations occurred on a Restek Stailwax-DA 30m long 0.25 mm ID column with a film thickness of 0.25 µm. The column temperature was held initially at 40 °C for 2 min, and then increased at a rate of 15.0 °C/min to 135 °C. Next the column oven was ramped to 225 °C at a rate of 40.0 °C/min where it was held for 3 minutes. The FID was operated using a hydrogen flow of 45 mL/min and an air flow of 450 mL/min.

Aqueous samples and standards were prepared by dilution in isopropyl alcohol, with the addition of butanol as an internal standard. Five point calibrations were used for each analyte: C2-C4 SCFAs, isobutyl acetate, and vinyl acetate. The linear calibration curves each had a high degree of fit with $R^2$ values greater than 0.996. Analytes were quantified based on their peak areas relative to the peak area of the internal standard. More details and data from the calibrations are available in Appendix B.

### *3.3.2 Gas Phase GC Analysis*

Gas phase products of the thermal cracking and VAM reactions were analyzed using an SRI 9610C gas chromatograph. The splitless chromatograph injector was maintained at a temperature of 192 °C. 100 µL injections were made manually using a 1mL syringe. Separations were performed using an 8’ Hayasep D packed column with Ar carrier gas maintained at a constant pressure of 83 kPa (12 $psi_g$). Analytes were detected using an FID with a methanizer maintained at a temperature of 375 °C. The column oven was held at a temperature of 40 °C for 2 minutes, then ramped at 20 °C/min to 250 °C, and held for 15 minutes.

The sample compositions were normalized to 100% neglecting the water vapor, $O_2$ and $N_2$ in each sample. Response factors for each compound were determined using a manually prepared calibration gas standard consisting of a mixture of $H_2$, CO, $CO_2$, and $C_2H_4$ diluted in Ar.

# 4. Results

## *4.1 Acetic Acid Production/Purification*

### *4.1.1 Non-Catalytic Cracking of Soybean Oil*

Non-catalytically cracked soybean oil from the cracking reactor had a liquid mass yield of 89 percent. The remaining mass was accounted for in non-condensable gases. The crackate was distilled in a single stage D-86 style distillation for analysis. After this distillation, 30 wt% residue was left in the flask. This was considered evidence that the sample was sufficiently cracked based on previous cracking runs. The overhead product from this analytical distillation had both organic and aqueous phases.

### *4.1.2 Crackate Distillation and Aqueous Extraction*

About 26 wt% of the crackate distilled was recovered in the overhead stream of the crackate distillation column. Aqueous distillates accounted for 1.5 wt% of the feed, and organic distillates accounted for 24.5wt % of the feed. The remaining 74% was bottoms product, which is typically converted to various other fuels and is out of the scope of this work. The aqueous distillates contained 28 wt% acetic acid.

The organic phase distillates were washed several times with deionized water to extract acetic acid. Both aqueous distillates and washes were analyzed for SCFAs using liquid phase GC analysis. The aqueous phase distillates and all of the aqueous washes contained water, C2 to C5 linear saturated carboxylic acids, and trace amounts of dissolved hydrocarbons. The amounts of acetic acid extracted during each of the aqueous washes on a typical batch of organic distillates are shown in Table 17.

**Table 17.** Aqueous Extracts of Acetic Acid From the Organic Phase of the Overhead Product From Cracked Soybean Oil Distillation

| Aqueous Washes | Distillates to Water Ratio | Weight Percent Acetic Acid |
|---|---|---|
| Wash 1 | 50:1 | 25.7 |
| Wash 2 | 75:1 | 22.8 |
| Wash 3 | 100:1 | 18.6 |
| Wash 4 | 100:1 | 18.5 |

A fifth wash was performed on the organic distillates for analytical purposes. This wash used a larger amount of water (10:1 distillate to water ratio) to remove any trace amounts of acetic acid remaining in the organic phase. The final wash contained about 3.4 wt% acetic acid.

Based on the quantities extracted, the organic phase distillates contained approximately 1.9 wt% acetic acid. The quantity of acetic acid in the distillates was used to calculate the concentration of acetic acid in the crackate. Assuming no acetic acid was left in the bottoms, the crackate contained 0.89 wt% acetic acid. Table 18 shows a typical set of inputs and outputs from the crackate distillation.

**Table 18.** Analysis of Acetic Acid in Distillates and Crackate

| Inputs/Outputs | Mass (kg) | Acetic Acid Wt% |
|---|---|---|
| Crackate Feed | 30.9 | 0.89 |
| Organic Distillates | 7.58 | 1.9 |
| Aqueous Distillates | 0.48 | 28 |
| Bottoms Product | 22.8 | *0 |

*It was assumed no acetic acid made it into the bottoms product.

### *4.1.3 Acetic Acid Purification*

Azeotropic distillation with IBA was used to concentrate the aqueous acetic acid solutions to approximately 40 wt%. Aqueous distillates and washes were blended prior to the concentration step to obtain 2 L batches. Thus, acetic acid concentrations varied slightly in aqueous solutions both before and after the azeotropic distillation. In each case the concentrated product was further processed via batch distillation to purify the acetic acid.

The B/R 18-100 distillation system is meant for high purity, low throughput batch distillations. Because several liters of aqueous acetic acid had to be processed, a trade-off was made between purity and processing time. Purification carried out via 0.5L batch distillations resulted in several fractions containing varying concentrations of acetic acid. A typical breakdown of these fractions from an initial purification distillation is shown in Table 19.

**Table 19.** Typical Breakdown of Fractions Recovered in Purification Distillations

| | Mass (g) | Acetic Acid Concentration (wt%) | Propionic Acid Concentration (wt%) |
|---|---|---|---|
| Feed | 500 | 40% | Not Analyzed |
| Fractions | | | |
| <100 °C | 75 | 12% | 0% |
| 100-105 °C | 250 | 22% | 1% |
| 105-115 °C | 60 | 70% | 4% |
| 115-121 °C | 70 | 89% | 7% |
| 121-130°C | 45 | 72% | 22% |

Because many of the fractions contained less than 80% acetic acid, an iterative process of recovering and analyzing semi-purified fractions, then fully purifying those fractions with more distillations, was utilized. A more thorough description of the iterative batch distillation products and procedures is available in Appendix B. The final product of these iterative distillations was 98 wt% pure acetic acid that contained about 2 wt% propionic acid and only unquantifiable trace amounts of water. Such a process was necessary only for lab-scale purification of acetic acid and was used to achieve nearly full recovery of the acetic acid in a limited time.

Industrial scale purification of aqueous acetic acid can be achieved using a single continuous azeotropic distillation step. This process was modeled using ChemCAD simulation software. The model used the NRTL equation of state and latent heat model for enthalpy. A stream of 150 kg/hr of IBA, 75 kg/hr of water, and 25 kg/hr of acetic acid was fed to a 20 ideal stage column. The stream was successfully separated into a 24.9 kg/hr, 99.4 wt% pure acetic acid product and a 75.1 kg/h,r 99.7 wt% pure water product using a reflux ratio of 6.5. The water product purity is after decanting from IBA. Table 20 shows the liquid tray compositions in the model column. The 1st stage shows the product from the total condenser that is fed to the reflux drum, and the 20th stage shows the bottoms product from the partial reboiler. This table demonstrates that acetic acid and water can be separated with a well-controlled continuous distillation column.

**Table 20.** Tray Compositions in the Model IBA Azeotropic Distillation

| Stage | Water kg/hr) | Acetic Acid (kg/hr) | Isobutyl Acetate (kg/hr) | Total (kg/hr) |
|---|---|---|---|---|
| 1 | 490.5 | 1.6 | 982.9 | 1475.1 |
| 2 | 646.6 | 4.9 | 3.4 | 654.8 |
| 3 | 653.9 | 9.9 | 0.4 | 664.2 |
| 4 | 652.0 | 19.2 | 0.4 | 671.6 |
| 5 | 649.0 | 35.4 | 0.5 | 684.9 |
| 6 | 644.3 | 61.9 | 0.6 | 706.8 |
| 7 | 636.6 | 102.0 | 0.9 | 739.5 |
| 8 | 626.2 | 159.0 | 1.4 | 786.6 |
| 9 | 611.7 | 236.5 | 2.4 | 850.6 |
| 10 | 592.3 | 341.1 | 4.5 | 937.9 |
| 11 | 670.1 | 575.3 | 10.6 | 1256.0 |
| 12 | 622.5 | 848.2 | 1.5 | 1472.2 |
| 13 | 549.8 | 1251.3 | 0.5 | 1801.6 |
| 14 | 449.5 | 1797.7 | 0.3 | 2247.5 |
| 15 | 335.5 | 2441.9 | 0.2 | 2777.6 |
| 16 | 226.9 | 3059.0 | 0.3 | 3286.2 |
| 17 | 141.6 | 3556.4 | 0.4 | 3698.4 |
| 18 | 83.3 | 3909.0 | 0.6 | 3992.9 |
| 19 | 47.1 | 4133.8 | 0.9 | 4181.7 |
| 20 | 0.2 | 24.7 | 0.0 | 24.9 |

## *4.2 VAM Production and Recovery*

### *4.2.1 VAM Production*

VAM production was studied using a ¼ fraction factorial set of experiments with non-renewable reactants. The results of these experiments are shown in Table 21. Trial 8 had to be eliminated because the cooling jacket could not maintain reactor temperature due to the heat of reaction. Nitrogen mole fraction was adjusted from 0.2 to 0.15 in trial 9 due to limits of the mass flow controller.

**Table 21.** Fractional Factorial Set of Experiments for VAM Production from Acetic Acid and Ethylene

| Trial | Temperature (°C) | Pressure kPa(psig) | Liquid Flow Rate (mL/min) | Oxygen Concentration (mol%) | Nitrogen Concentration (mol%) | Acetic Acid Conversion (%) |
|---|---|---|---|---|---|---|
| 1 | 155 | 760(110) | 1.8 | 8 | 10 | 13.1 |
| 2 | 135 | 1100(160) | 0.6 | 6 | 20 | **28.6** |
| 3 | 135 | 1100(160) | 2.5 | 6 | 0 | 1.6 |
| 4 | 135 | 415(60) | 2.5 | 10 | 0 | 2.3 |
| 5 | 135 | 415(60) | 0.6 | 10 | 20 | 9.1 |
| 6 | 175 | 1100(160) | 0.6 | 10 | 0 | 4.8 |
| 7 | 175 | 415(60) | 0.6 | 6 | 0 | 4.5 |
| 9 | 175 | 415(60) | 2.5 | 6 | 15 | 4.7 |
| 10 | 155 | 760(110) | 1.8 | 8 | 10 | 5.1 |

Trial 2 stood out, having an acetic acid conversion of 28.6%. Increasing pressure and nitrogen mole fraction had a positive effect on acetic acid conversion, but increasing temperature, flow rate, and oxygen mole fraction had negative effects on conversion. In general, keeping driving forces for oxidation low, while increasing residence time, gave the best results. Also, the center point performed for the last trial had significantly lower conversions than the 1st trial. This difference is likely evidence that partial catalyst deactivation occurred during the experiments, possibly due to the temperature of 175 °C

Figure 15 shows the half-normal plot for this set of experiments generated using Minitab Solution statistical software. All effects were insignificant at a 95% confidence level. Because the number of trials was small for the number of factors, effects were statistically lost among noise in the data. However, useful information was still taken from the experimental trends mentioned above.

An additional trial was performed at conditions similar to Trial 2 in the factorial set of experiments. The flow rate was adjusted up to 0.7 mL/min in order to decrease the processing time for a desired amount of product. Also, the oxygen concentration was increased to 6.5% to increase the potential conversion of acetic acid. This trial was performed with a mass balance on acetic acid over twelve hours to ensure no product was lost and conversion could be maintained. Conversion was high for the first few hours, ranging from 20-35%. However, after approximately 5 hours the conversion began to decline. It eventually dropped to 3-4% and remained in that range until shutdown, indicating that catalyst deactivation had occurred. Throughout the 12 hour trial the acetic acid mass balance closure was 97.3%.

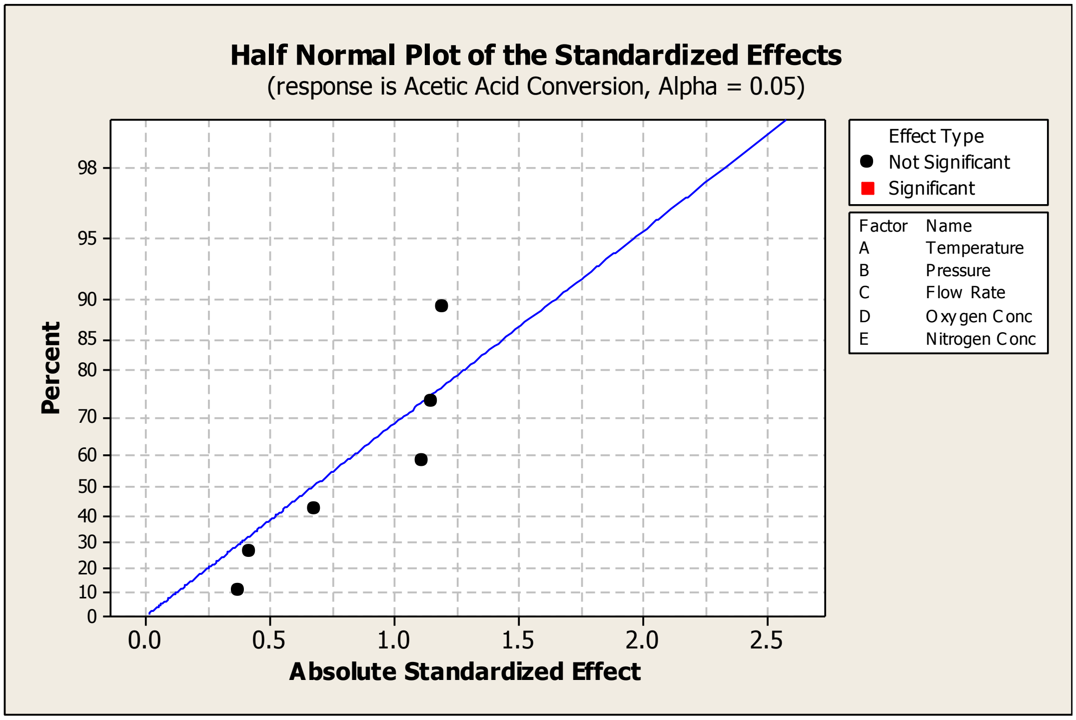


**Figure 15.** Half Normal Plot of VAM Reaction Effects

A possible mechanism for the catalyst deactivation is migration of palladium acetate within the catalyst due to contact with liquid-phase acetic acid (*77*, *78*). At the temperature and pressure used in the 12 hour trial, it is likely that there was some liquid acetic acid in the reactor bed, especially near the inlet before the reactants were fully warmed. As an attempt to solve this problem another trial was performed with the operating pressure lowered to 80 psi and the $N_2$ mole fraction increased to 30%. Other parameters remained the same. More gas flow and a lower pressure increased the driving force to vaporize the acetic acid. Also, a minor modification was made to the reactor system to ensure vaporization of acetic acid; electric heating tape was added to the inlet tubing for the reactant streams.

The low pressure trial maintained acetic acid conversion at about 39% for a 24 hour period. The same conditions were used for renewable VAM production. Conversion using these operating conditions is slightly higher than in commercial processes. This gain was achieved by having a much longer residence time (about 40 seconds) than typical commercial processes (about 10 seconds). The VAM reactor effluent from the renewable feedstocks contained 30 wt % VAM, meaning acetic acid conversion was about 38% on average.

### *4.2.2 VAM Purification*

VAM purification was run on the B/R 18-100 distillation system, Figure 12. The first fraction containing VAM and water was taken from 45-95 °C. Water was then separated from the VAM product using a separatory funnel. An additional fraction from 95-102.5 °C was taken to remove any additional water from the acetic acid so that it could be reused in the VAM reactor. The VAM product from this distillation was recovered over a very wide interval to ensure that all VAM was recovered. An additional distillation was used to further purify the VAM, removing small amounts of water, acetic acid, and other impurities. Final VAM product was approximately 99 wt% pure.

As with the IBA distillation, the VAM purification could be performed industrially using a single continuous distillation system. This was demonstrated using a model in ChemCAD simulation software. The model used the NRTL equation of state and latent heat model for enthalpy. A stream of 15 mol/hr (0.27 kg/hr) of VAM, 70 mol/hr (1.29 kg/hr) of water, and 15 mol/hr (4.2 kg/hr) of acetic acid was fed to a 20 ideal stage column. The stream was successfully separated into a 16.3 mol/hr (1.3 kg/hr) 97 wt%

pure VAM product and a 69.6 mol/hr (4.2 kg/hr) 99.9 wt% pure acetic acid product using a reflux ratio of 4.8. The stated VAM product purity is after decanting the water.

Table 22 shows the liquid tray compositions in the model column. The 1st stage shows the product from the total condenser that is fed to the reflux drum, and the 20th stage shows the bottoms product from the partial reboiler.

The feed stage for this column was stage 11. The VAM still contained about 1.3 wt% water. Industrially, the VAM would be dried by passing it through a bed of 3 angstrom molecular sieves to achieve a moisture content of less than 400 ppm (*72*).

**Table 22.** Liquid Tray Compositions for the VAM Purification Model Distillation

| Stage | Water (kg/h) | Acetic Acid (kg/hr) | Vinyl Acetate (kg/hr) | Total (kg/h) |
|---|---|---|---|---|
| 1 | 1.27 | 0.20 | 6.19 | 7.66 |
| 2 | 2.26 | 0.64 | 0.06 | 2.96 |
| 3 | 2.27 | 1.02 | 0.01 | 3.31 |
| 4 | 2.19 | 1.49 | 0.02 | 3.70 |
| 5 | 2.07 | 2.12 | 0.02 | 4.21 |
| 6 | 1.91 | 2.98 | 0.04 | 4.93 |
| 7 | 1.69 | 4.15 | 0.06 | 5.91 |
| 8 | 1.42 | 5.60 | 0.10 | 7.12 |
| 9 | 1.13 | 7.16 | 0.15 | 8.44 |
| 10 | 0.87 | 8.61 | 0.19 | 9.67 |
| 11 | 1.10 | 16.37 | 0.39 | 17.87 |
| 12 | 0.87 | 18.26 | 0.09 | 19.23 |
| 13 | 0.64 | 19.72 | 0.02 | 20.38 |
| 14 | 0.46 | 20.89 | 0.01 | 21.36 |
| 15 | 0.31 | 21.75 | 0.00 | 22.07 |
| 16 | 0.21 | 22.41 | 0.00 | 22.62 |
| 17 | 0.13 | 22.88 | 0.00 | 23.02 |
| 18 | 0.09 | 23.17 | 0.00 | 23.26 |
| 19 | 0.05 | 23.36 | 0.00 | 23.41 |
| 20 | 0.01 | 4.16 | 0.00 | 4.17 |

## 5. Discussion

### *5.1 Acetic Acid Production from TAG oil*

The processing of TAG oil into renewable acetic acid was successfully achieved. The lab-scale batch separation processes made purification a time intensive process and resulted in a product that was only moderately pure (98 wt%). Simulation has demonstrated that these lab-scale inefficiencies and challenges can be overcome by well controlled continuous industrial separation equipment.

The non-catalytic cracking of TAG oils was carried out efficiently at conditions based on earlier research. The product of these reactions had a composition typical of previous TAG oil crackate at the chosen conditions. About 250 L of soybean oil were cracked to produce about l.6 kg of acetic acid. Further discussion on the non-catalytic cracking of TAG oils and theory on the reaction mechanisms are available elsewhere (*7–10*, *79*).

Cracked product from an earlier design using a continuous stirred tank reactor (CSTR) contained a greater concentration of acetic acid, 1-2 wt%. Prior to this study the CSTR was taken out of commission in favor of a tubular design to reduce problems with coking. Cracking reactor design was out of the scope of work for this project, but exploration of this and other reactor designs could lead to a higher yield of acetic acid in the crackate.

Crackate distillation had been developed prior to this study. Conditions were chosen to optimize the recovery of acetic acid, and product compositions were comparable to estimates based on results from similar previous runs. For this study distillate temperature was kept at 140 °C to ensure all acetic acid was recovered. Optimization with a more precisely controlled distillation column would likely yield distillates with a higher concentration of acetic acid. This is a unit operation that could be improved in an industrial scale setting by precisely controlling heat rates and reflux ratios. The complexity of the crackate composition makes distillation very difficult to model accurately so some trial and error would likely be needed when moving to a steady state process.

Aqueous extraction of organic distillates was carried out in batches in a separatory funnel. The concentration in the extract solutions was successfully kept high by using small amounts of water in a series of several extractions. The success of multiple stages suggests a continuous counter-current extraction scheme would be an efficient design to recover the acetic acid.

Although distillation of water from the extract is more efficient on an industrial scale, it would still be beneficial to keep acetic acid concentration in the extract high. This would reduce the amount of energy need to distill water out of the acetic acid solution. Therefore, an industrial-scale process would also benefit from a high distillates-to-water ratio in the extraction step.

Due to the small amount of water relative to distillates in the extraction, careful design work would be needed to ensure thorough contacting of the two fluids in a continuous design. Using such a design on an industrial scale would be more efficient and less laborious than methods used in the lab.

The most time intensive step in recovering acetic acid from cracked TAG oil is the separation of acetic acid from the aqueous solvent solution. This was accomplished through two separate distillations. The first distillation used IBA as an entrainer for water to concentrate the acetic acid solution while preventing the loss of acetic acid in the distillate. This method was successful in achieving its goal of concentrating the extract solution to about 40 wt% acetic acid.

The second series of batch distillations used to purify the acetic acid was more challenging. Purity in distillation products is generally improved by increasing the number of stages or the reflux ratio. Because the number of stages in the lab-scale distillation apparatus was fixed, increasing reflux was the only way to improve purity. This presented a trade-off between processing time and product purity. To overcome this challenge concentrated acetic acid solutions were first distilled using low reflux ratios. This resulted in a small fraction of sufficiently purified acetic acid and several larger semi-purified fractions. The semi-purified fractions were then further purified in subsequent distillations using high reflux ratios. This process resulted in distilling times which were shorter than a single distillation at high reflux. However, this step still took hundreds of hours to purify only 1.6 L of acetic acid to greater than 95 wt% purity.

Continuous distillations using a low boiling azeotrope entrainer to reach purity efficiently are common in industry, so it is likely that a continuous industrial-scale distillation could easily purify acetic acid to greater than 99 wt%. This process is commonly used to recovery acetic acid from aqueous solution in the terephthalic acid industry (*80*). Simulation has shown that such a design can efficiently recover a purified acetic acid product.

### *5.2 Renewable VAM Production*

The results of the factorial set of experiments showed that flow rate must be kept low to generate high single pass conversion. This is due to the higher residence times at low flow rates. Because the reaction occurs in the gas phase, higher pressures also result in longer residence times by reducing the volumes of the gas-phase reactants.

Adding an inert gas (nitrogen) to the reaction mixture allowed the *oxygen flow rate* to increase relative to the acetic acid flow rate without increasing the gas phase *oxygen concentration*. The result is that at a given conversion of oxygen, conversion of acetic acid will be higher, and explosive concentrations of oxygen will not be reached. However, adding an inert gas also reduces the concentrations of the other reactants, and thus, the driving force for the desired reaction. Trends in the factorial experiments suggest that a 20-30 mol% feed of nitrogen is beneficial in this lab-scale set up.

As for the other two factors, oxygen concentration and temperature, operating at the high end of studied intervals reduced acetic acid conversion. This trend suggests that a temperature of 175 °C and an oxygen concentration of 10 mol% will increase the amount of reactants consumed by Reaction (4), the oxidation of ethylene. These high end values of oxygen concentration and temperature should be avoided

Reaction temperatures, pressures, and feed compositions in the lab-scale reactor gave the best results at values similar to industrial conditions (*73*). However, to get the higher single pass conversions desired in the lab, a much higher residence time was required. Thus, trials having low feed rates gave the best results. Because of the number of runs used in the ¼ fraction factorial set of experiments, interaction terms were not individually analyzed. Also, due to the high noise to effect ratio, no factors were found to be significant at a 95% confidence level. To gain more use out of this experimental design, a much greater number of trials would need to be performed. The goal of this work was to find a set of conditions that were sufficient for procuring kg amounts of renewable VAM. This goal was achieved in a small set of experiments, so lab-scale reaction conditions were not fully optimized.

Based on experiments for this study, moving toward a lower flow rate with higher pressures would likely further optimize acetic acid conversion. However, pressure must be increased carefully to ensure acetic acid remains in the gas-phase throughout the reactor bed. Lowering the flow rate would reduce the total amount of product generated. A strategy optimizing total outlet mass flow rate of VAM (instead of conversion) may be more beneficial in future lab-scale work.

In an industrial setting the acetic acid would be more fully purified, and the reaction would be embedded in a recycle loop as is typical in VAM production. Challenges encountered in this lab-scale research, such as the need for higher single-pass yield, would be of less consequence in an industrial renewable VAM production plant. Industrial VAM production conditions have been optimized over decades and those same conditions would be appropriate for renewable VAM production. The only differences in the renewable reactants would be what impurities are present in trace amounts. Correcting for these differences would be quite similar to the quality control issue of adjusting for differences in reactants from different suppliers. Such issues are typically monitored and dealt with by industrial process plants on a regular basis.

## 6. Conclusions

A lab/bench-scale process to generate acetic acid from TAG oil has been demonstrated. This process involves four major steps: non-catalytic cracking, crackate distillation, aqueous extraction, and acetic acid purification via distillation. Many of the challenges present in the lab-scale process will be easy to overcome in a large scale industrial process. In the lab, 1.6 L of 98 wt% pure renewable acetic acid was produced from about 250 L of soybean oil. The main contaminants were propionic acid and water; the effects at their observed concentrations would be minimal.

VAM was successfully produced from the TAG oil-derived renewable acetic acid and ethanol derived renewable ethylene. Lab-scale reaction conditions were studied and efficient conditions were determined. VAM with approximately 99 wt% purity was produced in kg amounts.

# CHAPTER IV

# CONCLUSIONS

In order to reduce dependence on petroleum it is important to push forward with research on processes that can replicate the many products we derive from it. Transportation fuels are particularly challenging to replicate using natural sources due to their high heating values. Non-catalytic cracking of TAG oils and their methyl esters is one of the most promising methods in biofuel development being researched today. It creates a mixture with a wide array of potential fuels and chemicals that can be fractionated and refined in a manner analogous to petroleum processing. The greatest challenge to fuel production via non-catalytic cracking is dealing with the large fraction of oxygenated compounds in the product. The choice of feedstock affects the oxygenated product. Cracking of TAG oil yields SCFAs, and cracking of TMEs yields SCMEs. Removal or conversion of these compounds is a complex problem with a diverse array of possible solutions. Successful recovery of oxygenated components can yield valuable byproducts.

Removal of SCMEs from TME OLP was attempted using LLE with a variety of polar solvents. Moderate amounts of the SCMEs (15-25 wt%) were separated from the OLP using batch extractions, but significant amounts of the polar solvent phase and OLP hydrocarbon phase overlapped into one another (10-25 wt%). Acetic acid was the best solvent for LLE based on SCME removal and phase overlap. Phase overlap complicates the extraction process scheme; a number of unit operations would be required for recovery of the solvent, hydrocarbons, and SCMEs. Modeling of continuous multistage extraction using results from batch experiment was inconclusive, and multistage experimental work will be necessary to determine if SCME removal by LLE is economically viable.

The physical properties of TME OLP are close to meeting desired specifications for many transportation fuels. An alternative method of LLE that recovers only a small amount of the low molecular weight SCMEs using a more polar solvent should be considered as well. Such a process may eliminate phase overlap and simplify the recovery process greatly. Another method that should be considered for reducing the quantity of esters in TME OLP is decarboxylation. This method has proven effective at deoxygenation of TAG oil OLP.

Methods to remove SCFAs in TAG oil OLP via LLE with aqueous amines and to convert SFCAs in TAG oil OLP via decarboxylation have both been studied previously and proven successful. If SCFA conversion is utilized acetic acid should be recovered prior to any deoxygenation step due to its corrosive nature and low value after deoxygenation (as methane). Bench-scale recovery of acetic acid via water extraction and azeotropic distillation was studied. Kilogram amounts of 98 wt% renewable acetic acid were successfully produced as a byproduct of TAG oil cracking.

Vinyl acetate monomer (VAM) production uses more acetic acid than any other industrial process. TAG oil derived acetic acid and ethanol derived ethylene were combined with oxygen over a Pd-Au catalyst to produce renewable VAM. The bench-scale process demonstrated that a byproduct of non-catalytic cracking can be used to produce a commodity chemical that is the interchangeable with the petroleum counter-part.

Many combinations of products can be manufactured by cracking and further processing of TAG oils or their methyl esters. These experiments provide insight to some of the possible alternatives that are available. Optimization of a non-catalytic cracking based bio-refining process will be an ongoing process as the technology continues to develop.

# APPENDICES

# APPENDIX A

## LIQUID-LIQUID EXTRACTION OF SHORT CHAIN METHYL ESTERS FROM CRACKED TRIGLYCERIDE METHYL ESTERS

Appendix A is the appendix for Chapter IV covering LLE of SCMEs from cracked TMEs. This appendix includes the following information.

- Complete TME OLP Analysis
- Previous Extraction Experiments with Methanol
- Intermediate Data and Results
- Analytical Calibration Data

**Table 23.** Full Analysis of TME OLP. N-alkane and n-ester retention times were confirmed with standards. Analytes listed as C# ester are branched, cyclic, unsaturated, and/or di esters which were identified using mass spectrometry.

| Compound | **wt%** |
|---|---|
| Pentane | 0.06 |
| Hexane | 0.41 |
| Methyl Propionate | 0.48 |
| C4 Methyl Ester | ND |
| Heptate | 4.01 |
| Methyl Butyrate | 1.36 |
| C5 Methyl Ester | 0.03 |
| C5 Methyl Ester | 0.06 |
| Octane | 4.53 |
| Methyl Valerate | 2.71 |
| C6 Methyl Ester | 0.04 |
| C6 Methyl Ester | 0.09 |
| C6 Methyl Ester | 0.05 |
| Nonane | 3.73 |
| Methyl Caproate | 4.24 |
| C7 Methyl Ester | 0.16 |
| C7 Methyl Ester | 0.10 |
| C7 Methyl Ester | 0.12 |
| Decane | 2.32 |
| Methyl Enanthate | 5.85 |
| C7 Methyl Ester | 0.50 |
| C7 Methyl Ester | 0.30 |
| C8 Methyl Ester | 0.20 |
| C8 Methyl Ester | 0.29 |
| Undecane | 1.86 |
| Methyl Caprylate | 5.54 |
| C7 Methyl Ester | 0.07 |
| C8 Methyl Ester | 0.07 |
| C9 Methyl Ester | 0.06 |
| C7 Methyl Ester | 0.23 |
| Dodecane | 1.16 |
| Methyl Nonanoate | 3.49 |
| C10 Methyl Ester | 0.11 |
| C10 Methyl Ester | 0.35 |
| C8 Methyl Ester | 0.13 |
| Tridecane | 1.23 |
| Methyl Caprate | 3.14 |
| C12 Methyl Ester | 0.16 |
| C12 Methyl Ester | 0.22 |
| C11 Methyl Ester | 0.17 |

**Table 23** Continued

| **Compound** | **wt%** |
|---|---|
| C12 Methyl Ester | 0.31 |
| Tetradecane | 0.64 |
| Methyl Undecanoate | 1.36 |
| C8 Dimethyl Ester | 0.22 |
| C13 Methyl Ester | 0.21 |
| C12 Methyl Ester | 0.10 |
| Pentadecanoate | 0.90 |
| Methyl Myristate | 0.79 |
| C9 Dimethyl Ester | 0.28 |
| C13 Methyl Ester | 0.10 |
| Hexadecane | 0.41 |
| Methyl Tridecanoate | 0.53 |
| C10 Dimethyl Ester | 1.03 |
| C10 Methyl Ester | 0.07 |
| C14 Methyl Ester | 0.10 |
| Heptadecane | 0.32 |
| Methyl Tetradecanoate | 0.42 |
| C11 Dimethyl Ester | 0.21 |
| C13 Methyl Ester | 0.14 |
| C15 Methyl Ester | 0.12 |
| Octadecane | 0.11 |
| Methyl Pentadecanoate | 0.19 |
| C12 Dimethyl Ester | 0.10 |
| C15 Methyl Ester | 0.03 |
| C15 Methyl Ester | 0.04 |
| Nonadecane | 0.06 |
| Methyl Palmitate | 0.79 |
| C13 Dimethyl Ester | 0.03 |
| C19 Methyl Ester | 0.02 |
| Eicosane | 0.02 |
| Methyl Heptadecanoate | 0.04 |
| C18 Methyl Ester | 0.01 |
| C18 Methyl Ester | 0.18 |
| C18 Methyl Ester | 0.05 |
| C17 Methyl Ester | 0.05 |
| C18 Methyl Ester | 0.11 |
| C17 Methyl Ester | 0.03 |
| Methyl Stearate | 0.32 |
| C18 Methyl Ester | 0.03 |
| C19 Methyl Ester | 0.00 |
| Methyl Eicosanoate | 0.02 |
| C22 Methyl Ester | ND |
| Methyl Behenate | ND |

**Table 24.** Results from Previous Experiments Using Methanol.

| Run # | Volume Methanol(mL) | Volume Water (mL) | Volume TME OLP (mL) | %Reduction in SCMES |
|---|---|---|---|---|
| 1 | 0 | 20 | 20 | 0.01 |
| 2 | 5 | 15 | 20 | 0.02 |
| 3 | 10 | 10 | 20 | 0.08 |
| 4 | 15 | 5 | 20 | 0.17 |
| 5 | 19 | 1 | 20 | 0.03 |

**Table 25.** Complete Results from Quantitative Solvent Screening Experiments (SCME Reduction).

| Solvent | Volume Fraction Solvent (Balance H2O) | Temperature (°C) | Percent SCME Reduction Before Wash | Percent SCME Reduction After Wash |
|---|---|---|---|---|
| Methanol | 0.9 | 24 | 33% | 14% |
| Methanol | 0.9 | 24 | 38% | 16% |
| Methanol | 0.9 | 24 | 32% | 16% |
| Methanol | 0.9 | 45 | 33% | 15% |
| Methanol | 0.9 | 45 | 36% | 15% |
| Methanol | 0.9 | 45 | 35% | 15% |
| DMSO | 1 | 24 | 63% | 16% |
| DMSO | 1 | 24 | 61% | 17% |
| DMSO | 1 | 24 | 56% | 17% |
| DMSO | 1 | 45 | 60% | 18% |
| DMSO | 1 | 45 | 52% | 15% |
| DMSO | 1 | 45 | 61% | 18% |
| Acetonitrile | 0.9 | 24 | 39% | 25% |
| Acetonitrile | 0.9 | 24 | 40% | 23% |
| Acetonitrile | 0.9 | 24 | 40% | 23% |
| Acetonitrile | 0.9 | 45 | 40% | 23% |
| Acetonitrile | 0.9 | 45 | 37% | 23% |
| Acetonitrile | 0.9 | 45 | 39% | 23% |

**Table 26.** Complete Results from Quantitative Solvent Screening Experiments (Phase Overlap).

| Solvent | Volume Fraction Solvent (Balance H2O) | Temperature (°C) | Percent of Hydrocarbon Mass into Polar Extract | Percent of Polar Solvent Mass into OLP Raffinate |
|---|---|---|---|---|
| Methanol | 0.9 | 24 | 16.7% | 13.8% |
| Methanol | 0.9 | 24 | 15.9% | 8.4% |
| Methanol | 0.9 | 24 | 22.8% | 16.1% |
| Methanol | 0.9 | 45 | 26.0% | 18.1% |
| Methanol | 0.9 | 45 | 28.9% | 20.4% |
| Methanol | 0.9 | 45 | 21.6% | 14.0% |
| DMSO | 1 | 24 | 23.5% | 9.9% |
| DMSO | 1 | 24 | 23.0% | 9.8% |
| DMSO | 1 | 24 | 26.8% | 12.1% |
| DMSO | 1 | 45 | 27.8% | 11.5% |
| DMSO | 1 | 45 | 27.2% | 11.3% |
| DMSO | 1 | 45 | 24.6% | 8.6% |
| Acetonitrile | 0.9 | 24 | 25.3% | 12.5% |
| Acetonitrile | 0.9 | 24 | 29.3% | 16.4% |
| Acetonitrile | 0.9 | 24 | 31.9% | 12.7% |
| Acetonitrile | 0.9 | 45 | 34.8% | 15.1% |
| Acetonitrile | 0.9 | 45 | 33.2% | 15.6% |
| Acetonitrile | 0.9 | 45 | 32.9% | 16.5% |

**Table 27.** Complete Results from Quantitative Acetic Acid Phase Overlap Experiments.

| Volume Fraction Acetic Acid (Balance H2O) | Percent of Hydrocarbon Mass into Polar Extract | Percent of Polar Solvent Mass into OLP Raffinate | Percent SCME Reduction |
|---|---|---|---|
| 0.9 | 16.6% | 24.4% | 23% |
| 0.9 | 13.4% | 20.2% | 23% |
| 0.9 | 13.9% | 19.7% | 23% |

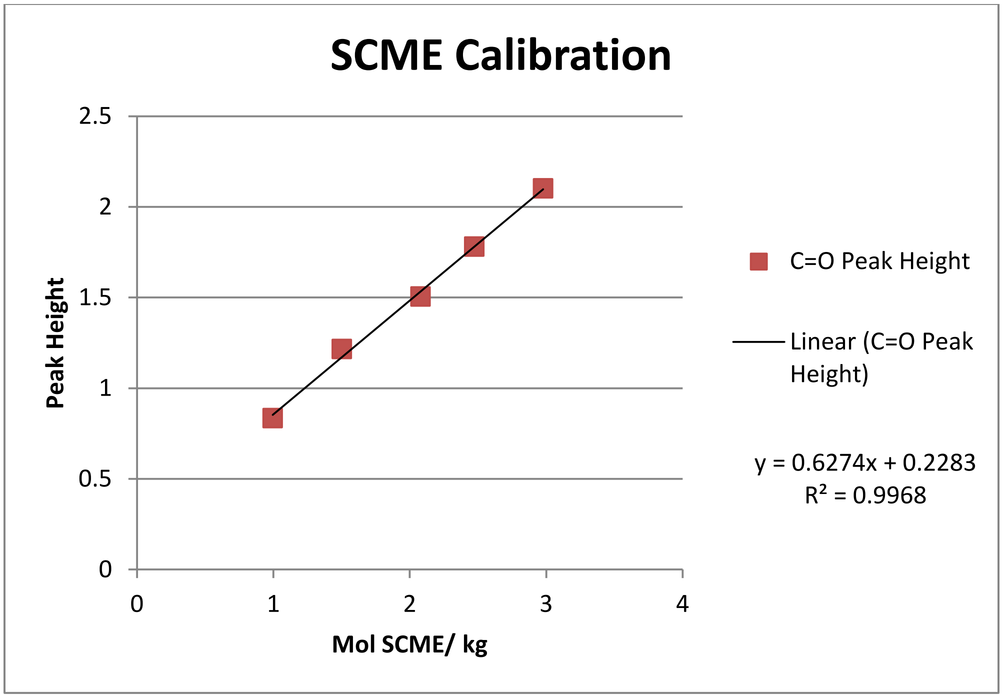


**Figure 16.** SCME Calibration from FTIR analysis.

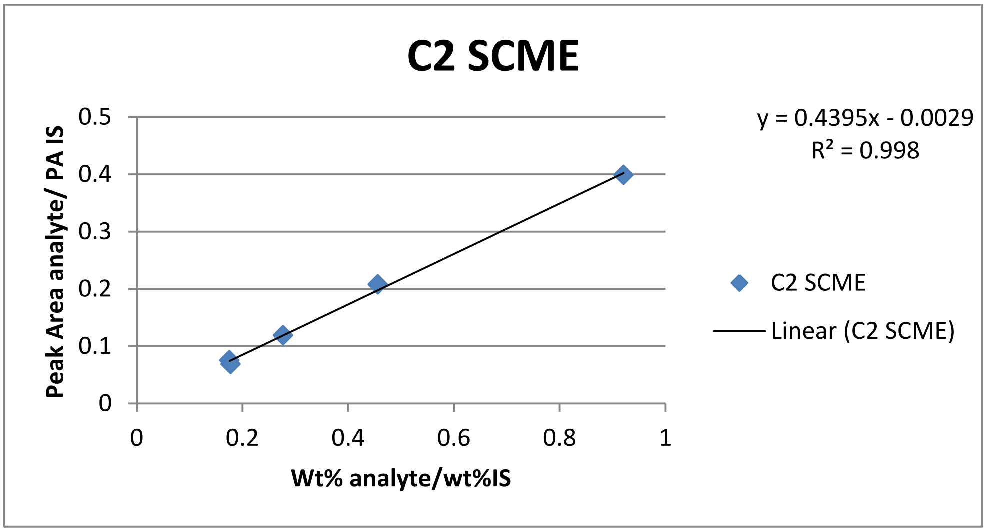


**Figure 17.** C2 SCME Calibration from GC analysis.

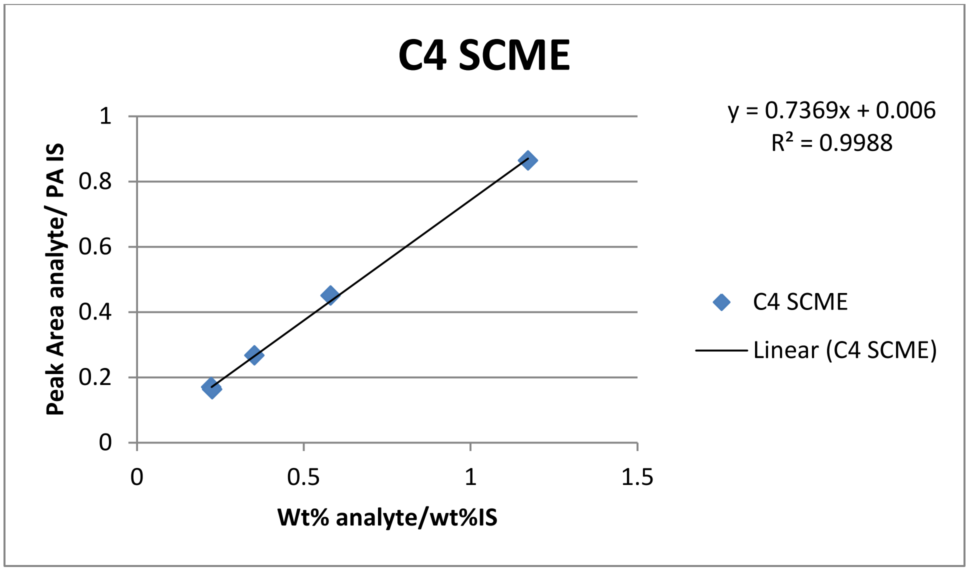


**Figure 18.** C4 SCME Calibration from GC analysis.

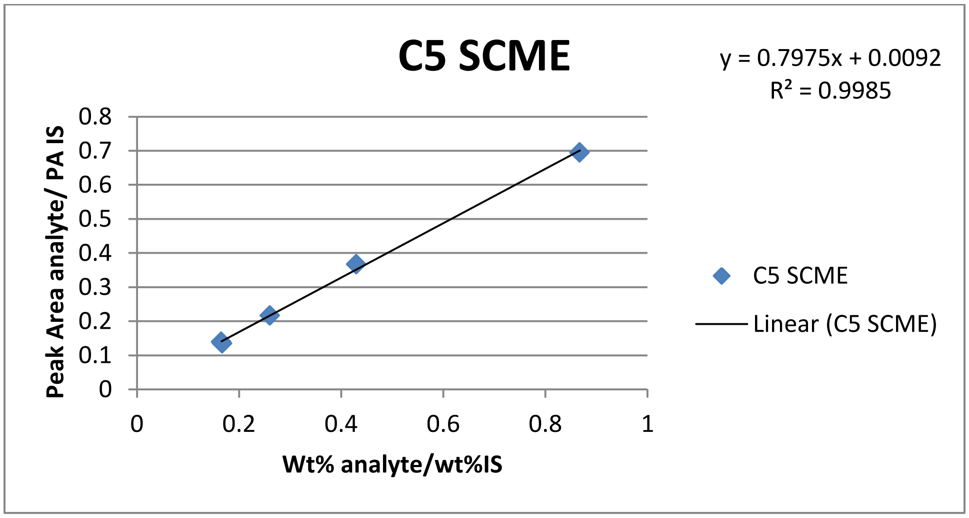


**Figure 19.** C5 SCME Calibration from GC analysis.

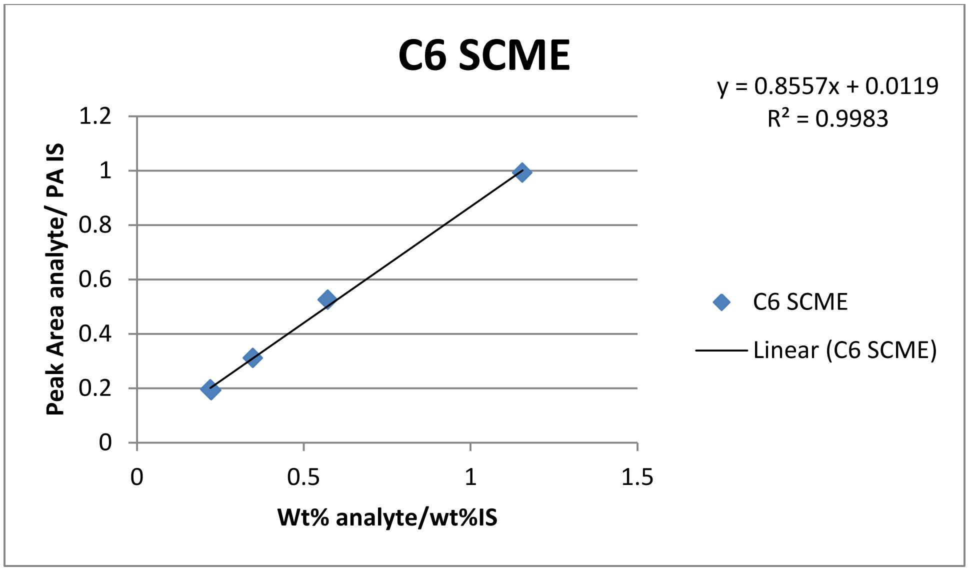


**Figure 20.** C6 SCME Calibration from GC analysis.

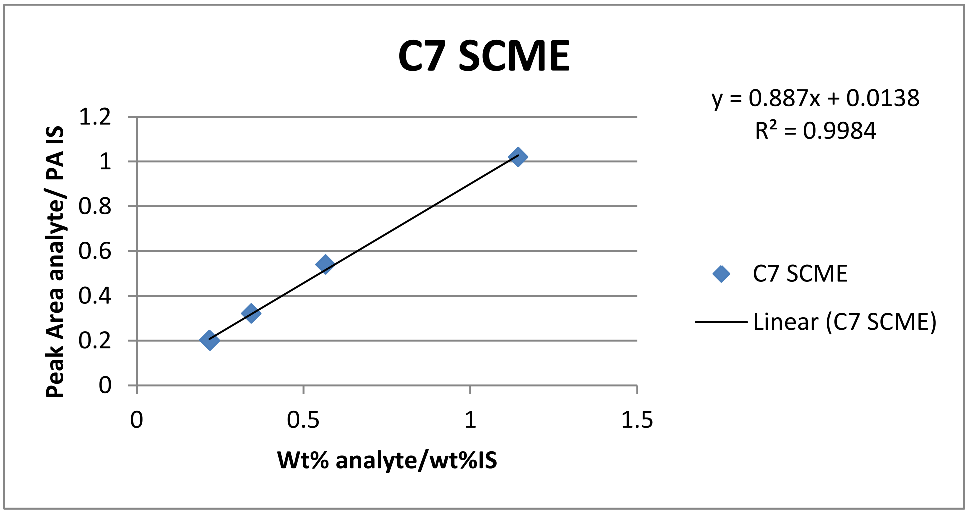


**Figure 21.** C7 SCME Calibration from GC analysis.

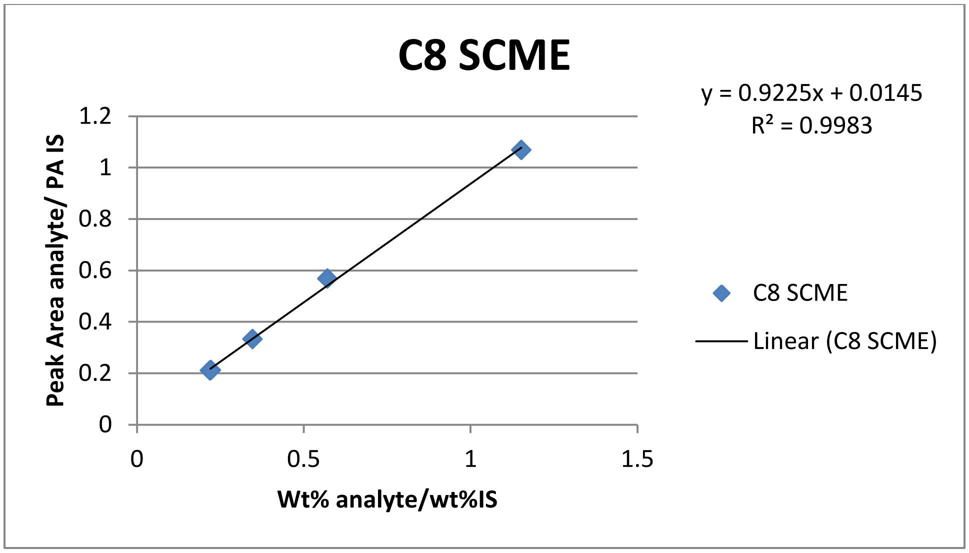


**Figure 22.** C8 SCME Calibration from GC analysis.

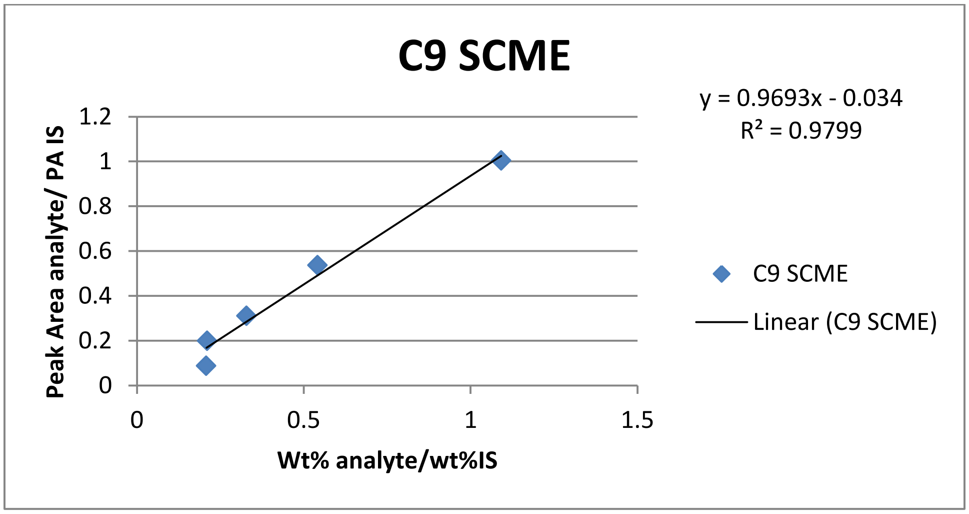


**Figure 23.** C9 SCME Calibration from GC analysis.

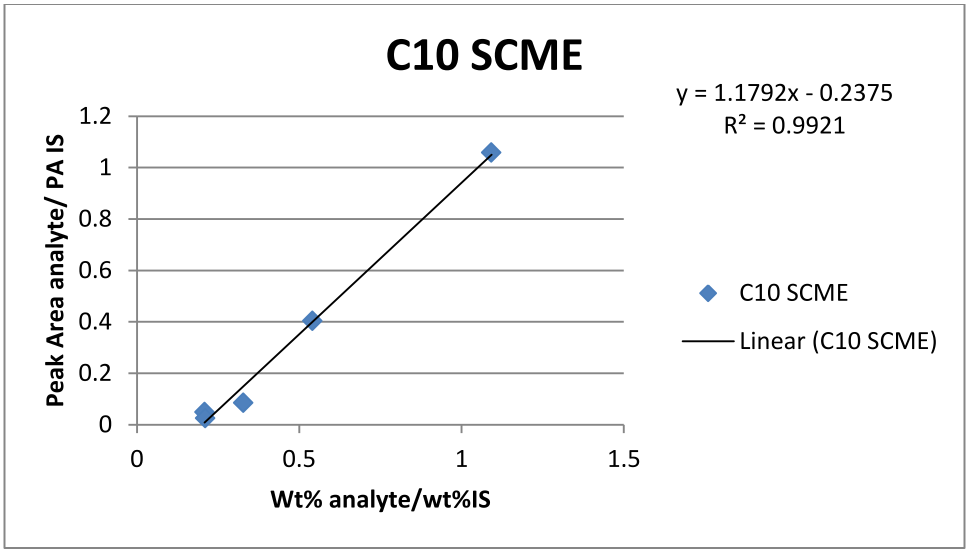


**Figure 24.** C10 SCME Calibration from GC analysis.

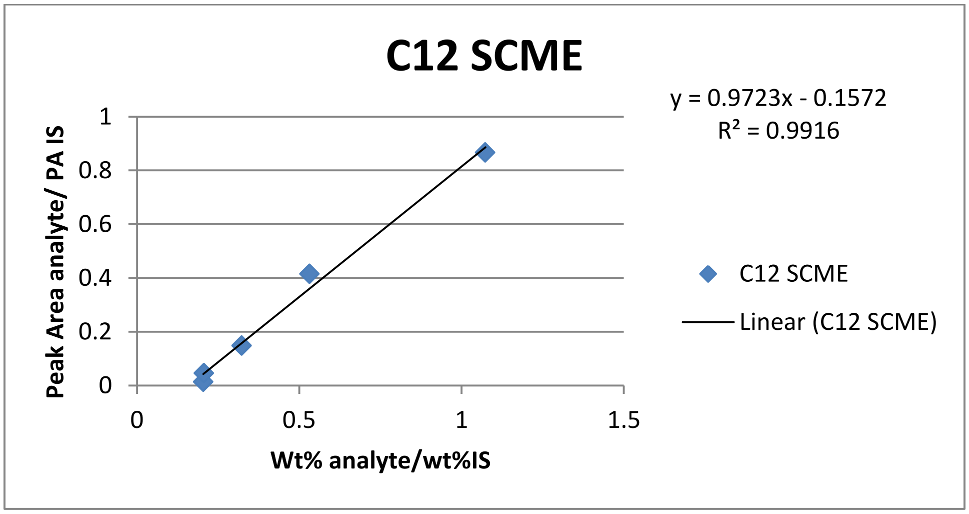


**Figure 25.** C12 SCME Calibration from GC analysis.

Standards were not available for the C3 and C11 SCMEs. Slope and intercept values for the C3 and C11 SCME calibrations were estimated by averaging the calibration values for the SCME above and below.

## APPENDIX B

# VINYL ACETATE MONOMER (VAM) PRODUCTION WITH RENEWABLE RESOURCES

Appendix B is the appendix for Chapter IV covering renewable acetic acid production and its conversion to VAM. This appendix includes the following information.

- Iterative Distillation Strategy
- Intermediate Data and Results
- Analytical Calibration Data

In order to obtain high yields of purified acetic acid an iterative system of batch distillations was used. Figure 26 shows how the semi purified fractions were used in subsequent distillations. An initial distillation was performed at low reflux (2-6) to quickly obtain several fractions at varying boiling points. The 50-100 °C fraction was waste water, and the bottoms containing higher molecular weight SCFAs was removed and stored. The 100-105 °C fraction went to another distillation to remove more water, and the 105-115 °C fraction went to the high reflux purification distillation. The 115-121 °C fraction was pure enough to be product, and the 121-130 °C fraction went to a distillation where more acetic acid was recovered from the heavier acids.

The water removal distillation and heavy fraction distillation were run at medium reflux (about 10), and the purification distillation was run at high reflux (about 20). Reflux ratio could be varied by fraction and was generally high for fraction containing acetic acid. The three additional distillations all had multiple fractions; there uses are shown in Figure 26. The main goal of this procedure was to obtain purified acetic acid in a reasonable amount of time. This was accomplished by only operating distillations with high concentrations of acetic acid at high reflux.

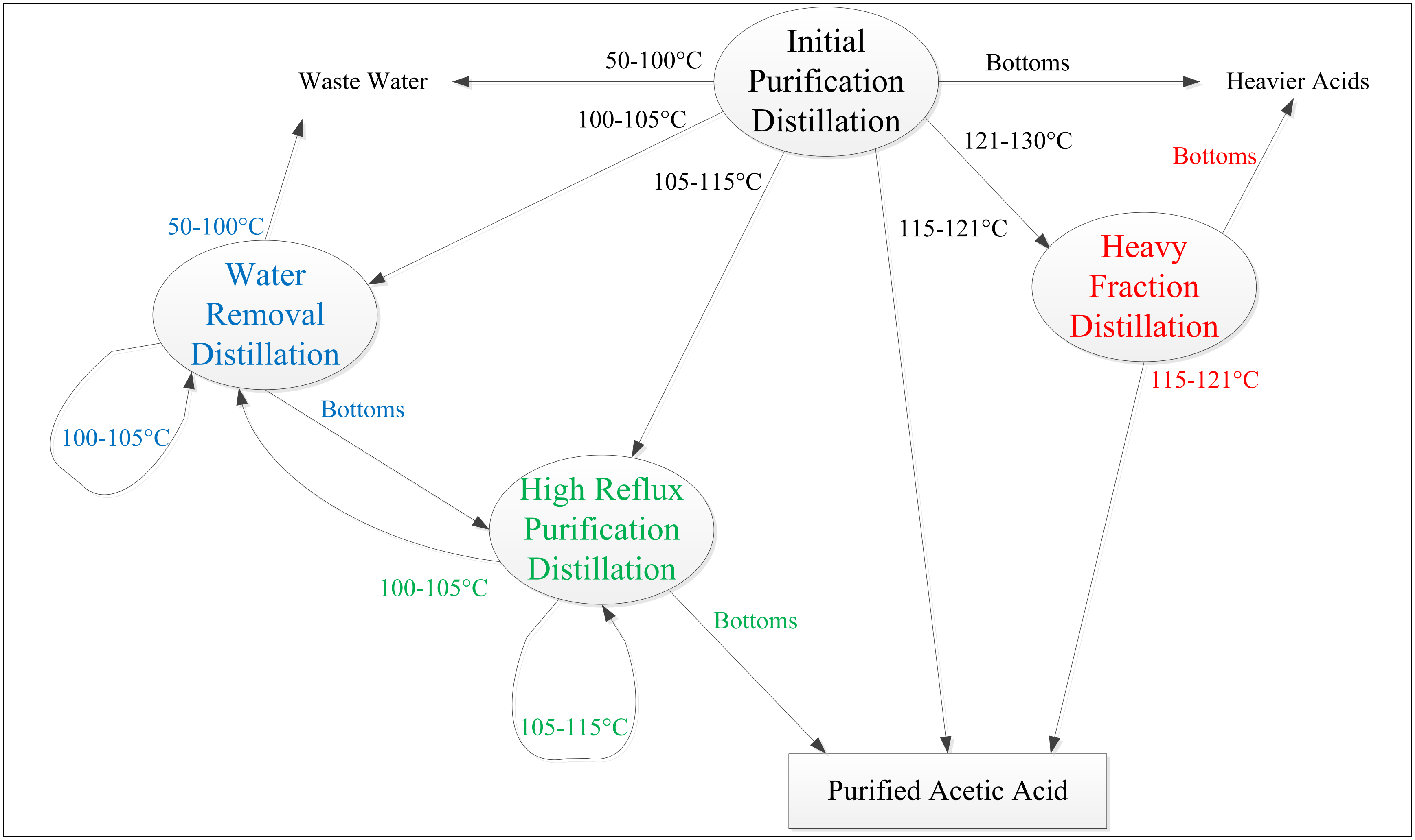


**Figure 26.** Flowchart of Iterative Distillation Procedure.

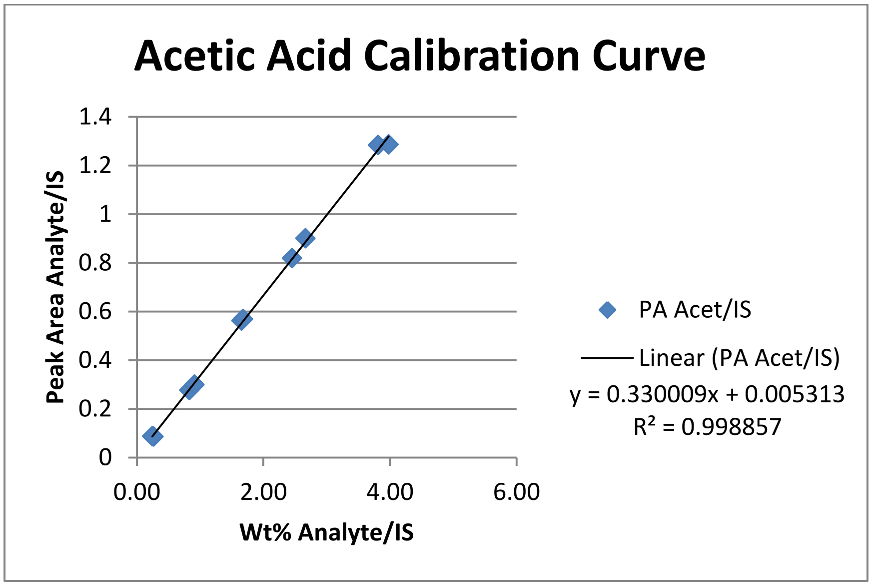


**Figure 27.** GC Calibration for Acetic Acid Analysis

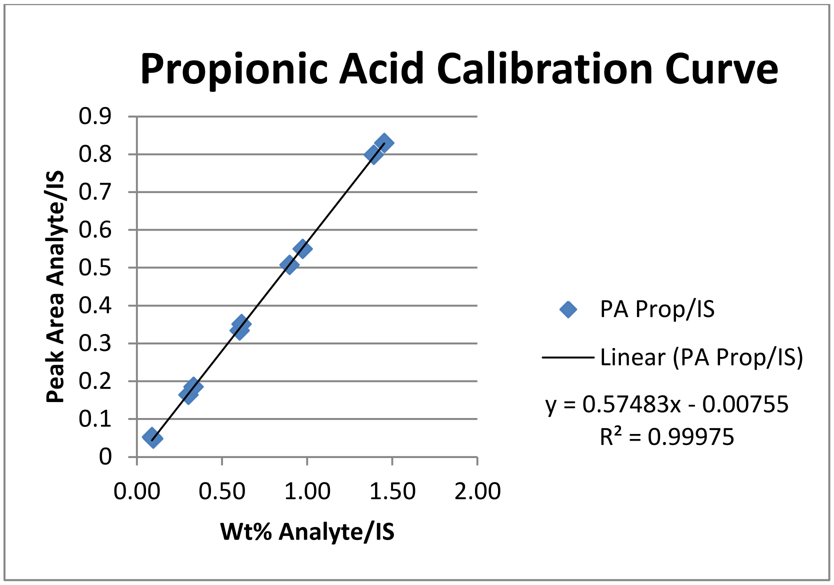


**Figure 28.** GC Calibration for Propionic Acid Analysis

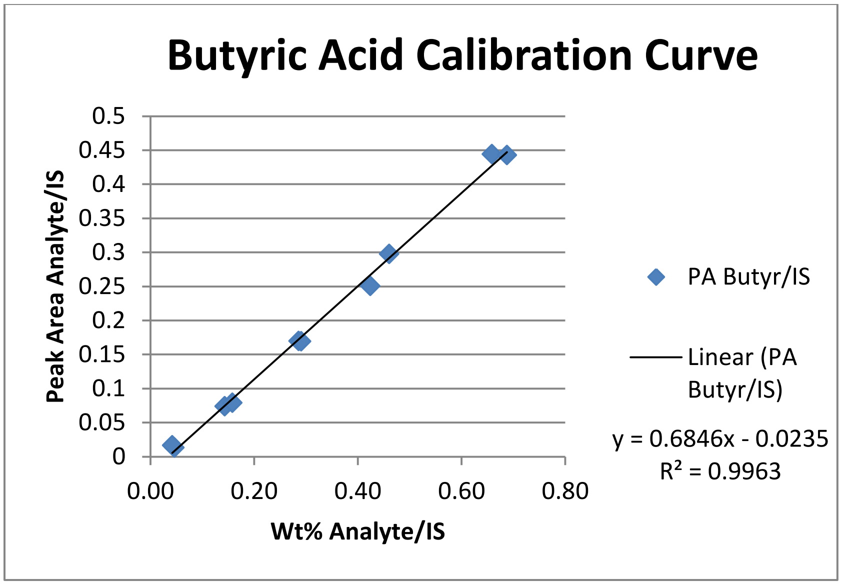


**Figure 29.** GC Calibration for Butyric Acid Analysis.

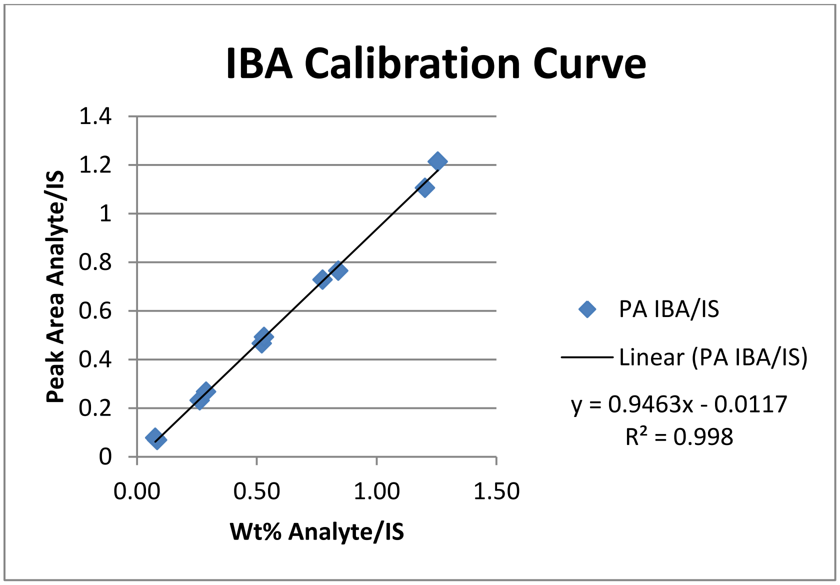


**Figure 30.** GC Calibration for Isobutyl Acetate Analysis.

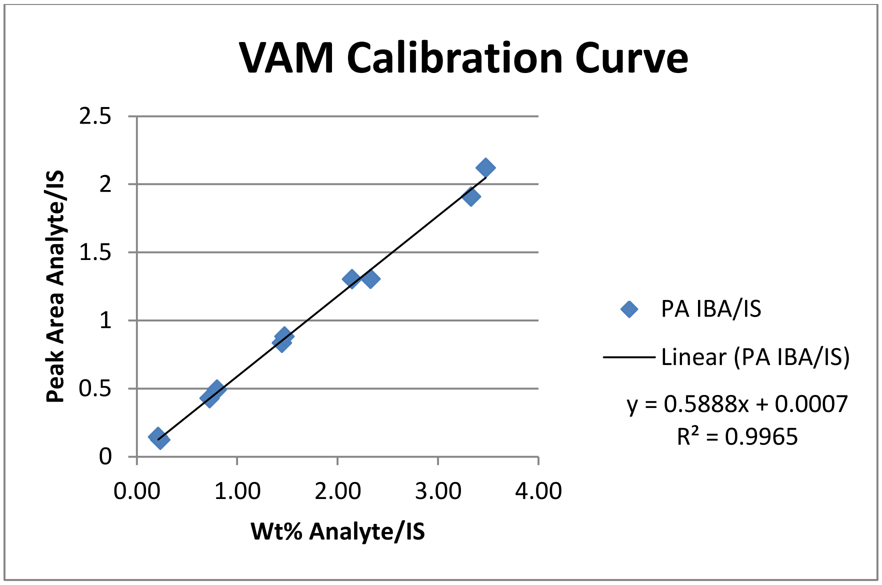


**Figure 31.** GC Calibration for Vinyl Acetate Monomer Analysis.

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