Waste Cooking Oil-to-Biodiesel Conversion for Space Heating Applications

Daniel J. Bruton

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Waste Cooking Oil-to-Biodiesel Conversion for Space Heating Applications

by

Daniel J. Bruton

A THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Sustainable Systems

Department of Sustainability

Golisano Institute for Sustainability
Rochester Institute of Technology

May 2014

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Daniel J. Bruton
Waste Cooking Oil-to-Biodiesel Conversion for Space Heating Applications

By

Daniel J. Bruton

Submitted by Daniel J. Bruton in partial fulfillment of the requirements for the degree of Master of Science in Sustainable Systems and accepted on behalf of the Rochester Institute of Technology by the thesis committee.

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(Committee Chair and Thesis Advisor)

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Dr. Eric Hittinger: ____________________________ Date

Sustainable Systems Program
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May 2014
Abstract

Golisano Institute for Sustainability
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Degree: Master of Science  Program: Sustainable Systems
Name of Candidate: Daniel J. Bruton  Title: Waste Cooking Oil to Biodiesel for Space Heating Applications

Transesterification is a process that converts triglycerides, like vegetable oil, into fatty acid methyl esters, commonly known as biodiesel. This conversion reaction requires the triglyceride feedstock, an alcohol, and an alkali-catalyst to produce the biodiesel. Biodiesel is a versatile biofuel that is renewable, biodegradable, and environmentally beneficial in the sense that combustion adds only biogenic carbon to the atmosphere. The main limitation of commercialization of biodiesel is cost. However, developing closed-loop systems that have an available triglyceride supply, such as waste cooking oil, as well as demand for diesel based fuels, can achieve substantial emissions reductions and energy avoidance, while simultaneously solving a waste disposal issue. Thus, an analysis of the development of a closed-loop waste cooking to biodiesel fuel production process is warranted.

A waste-to-energy (WtE) system like this offers great potential to institutions. Thus, this analysis includes the development of a waste cooking oil to biodiesel fuel program utilizing the available waste cooking oil of a university, the production of the fuel, the internal use of the fuel, and subsequent analysis of the fuel characteristics, emissions, and the life cycle environmental and energy impacts of the production process and ultimate use.
The results show that the waste cooking oil derived biodiesel meets the required American Society for Testing and Materials (ASTM) standard specifically for biodiesel, ASTM D6751. The produced biodiesel was blended with commercially available fuel oil, which met the ASTM specification D396-13b. Therefore, a blend of these two ASTM compliant fuels also met the required ASTM standards. The ASTM standards require high quality fuel characteristics and ensure proper utilization and combustion.

Biodiesel blended heating fuels were utilized in two distinct heating facilities, both showing comparable emissions to conventional fuel oil. Small (500 mL) and large (1L) volume biodiesel blends were utilized in a conventional residential furnace. Emissions data were obtained through the exhaust ducting with a combustion gas analyzer. The same fuel blends were utilized in a lab-scale burner apparatus without a heat exchanger, which enabled near-flame interrogation and visualization of the combustion process. The emissions of both heating facilities were comparable to the incumbent fuel oil.

The life cycle assessment results demonstrate the benefits of increasing the approved blends of biodiesel heating fuels. Currently, most oil burners are only approved up to a B5 blend (5% biodiesel, 95% fuel oil). The results show higher blends achieve substantial life cycle reduction in global warming potential and cumulative energy demand, as well as an energy return on investment of above 4, indicating more energy is obtained from the fuel than required to produce it.
Acknowledgments

I would first like to express my gratitude to my advisor, Dr. Thomas A. Trabold, for his unwavering support and encouragement throughout the process of this thesis and advisement during my academic career at the Golisano Institute for Sustainability. Dr. Trabold always had positive and encouraging feedback and inspired me to research waste to renewable energy systems.

I would also like to acknowledge Dr. Callie Babbitt for her life cycle assessment expertise and consistent support over the course of the life cycle assessment portion of this thesis.

Additionally, I would like to specifically acknowledge David Fister (Senior Staff Engineer at NYS Pollution Prevention Institute at RIT) for his irreplaceable consultation throughout this process and willingness to go above and beyond in providing assistance in furnace burner data collection.

Lastly, I would also like to extend my gratitude and appreciation to Domenic Maiola (Structures/Material Mechanical Technician at RIT Center for Integrated Manufacturing Studies) for his rigorous work on the experimental design and fabrication portions of this project.

The United States Environmental Protection Agency provided funding for the development of a closed loop biodiesel production process and the subsequent analysis of potential greenhouse gas emission reduction and energy return on investment. The views, results and conclusions reflect those of Daniel J. Bruton and do not reflect the views of the United States Environmental Protection Agency.
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### Nomenclature

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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CED</td>
<td>cumulative energy demand</td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand</td>
</tr>
<tr>
<td>CWCO</td>
<td>crude waste cooking oil</td>
</tr>
<tr>
<td>EIA</td>
<td>Energy Information Administration</td>
</tr>
<tr>
<td>EROI</td>
<td>energy return on investment</td>
</tr>
<tr>
<td>EHS</td>
<td>environmental health and safety</td>
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<tr>
<td>FGA</td>
<td>flexible gas analyzer</td>
</tr>
<tr>
<td>FFA</td>
<td>free fatty acids</td>
</tr>
<tr>
<td>FMS</td>
<td>facilities and management services</td>
</tr>
<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>GWP</td>
<td>global warming potential</td>
</tr>
<tr>
<td>HC</td>
<td>(unburned) hydrocarbons</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>LCA</td>
<td>life cycle assessment</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value</td>
</tr>
<tr>
<td>MC</td>
<td>Monroe County</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory (United States)</td>
</tr>
<tr>
<td>NWW</td>
<td>non-water washed</td>
</tr>
<tr>
<td>OT</td>
<td>oil-to-transesterification</td>
</tr>
<tr>
<td>PWBD</td>
<td>prewashed biodiesel</td>
</tr>
<tr>
<td>RFS</td>
<td>renewable fuel standard</td>
</tr>
<tr>
<td>RIT</td>
<td>Rochester Institute of Technology</td>
</tr>
<tr>
<td>SHO</td>
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</tr>
<tr>
<td>TAN</td>
<td>total acid number</td>
</tr>
<tr>
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<tr>
<td>WtE</td>
<td>waste-to-energy</td>
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Chapter 1: Introduction

Background

The unprecedented levels of industrial production that began in the late 18th century marked the beginning of fossil fuel use on a global scale. In 1827, Joseph Fourier first formulated the term “greenhouse effect” after observing that the Earth’s atmosphere behaves similarly to a greenhouse [1]. By the mid-19th century, John Tyndal determined water vapor and carbon dioxide were the dominating heat trapping gases in the atmosphere, despite their relatively low concentrations [2]. Despite these findings, it was not until the end of the 19th century before Svante Arrhenius theorized that burning fossil fuels could add enough heat trapping gases to the atmosphere to create widespread warming [3]. Currently, the scientific community widely agrees the combustion of fossil fuels is a main driver of climate change, which is a rapidly growing concern for current and future generations. In order to undertake the challenges of climate change, another paradigm shift must occur to move our industrial society toward a more sustainable one.

Developing closed-loop energy systems utilizing available waste products as feedstocks could have substantial environmental and economic benefits. Greenhouse gas emission and cumulative energy demand reductions on a life cycle basis can be achieved by waste-to-energy systems, such as a closed-loop waste cooking oil to biodiesel production process. Biodiesel is a diverse fuel that can be utilized in several ways, including diesel-based space heating applications, which are heavily utilized in the northeastern United States. An institutional sized closed-loop biodiesel production process can provide a consistent supply of alternative heating fuel reducing greenhouse gas emissions and energy demand. One of the most advantageous aspects of combusting
this fuel is that it releases purely biogenic carbon, as it is derived from plant matter. When these plants uptake carbon from the atmosphere it is stored until they are burned as a biofuel. Thus, the combustion of this biofuel only returns the carbon the plants took out of the atmosphere initially. Conversely, burning the incumbent fossil fuels releases carbon into the atmosphere that was previously sequestered within the Earth and not part of the carbon balance on a natural timescale.

Although biofuels have largely been developed to date as alternative transportation fuels, there is also significant potential to utilize these renewable materials in other energy-intensive processes, such as a space heating and distributed power generation. During the Phase 1 portion of an Environmental Protection Agency (EPA) Climate Showcase Communities Grant with New York’s Monroe County, waste cooking oil biodiesel was only utilized in vehicular applications. The research documented in this thesis specifically addresses biodiesel utilization in space heating applications from the Phase 2a portion of the EPA funded program. The total demand for diesel-based heating oil (commonly referred to as No. 2 oil, No.2 fuel oil, heating oil, or fuel oil) is much smaller than that for diesel transport fuel (4.17 and 36.3 billion gallons/year, respectively) [4]. However, the heating application has quite different performance, approved biodiesel blends, and emissions metrics. Currently, the largest constraint in converting waste cooking oil to biodiesel for heating fuel is not an oil supply issue or a technological gap, but a maximum blend constraint of B5 (5% biodiesel, 95% diesel heating fuel by volume). Until this relatively low blend maximum is increased, the demand for biodiesel as a substitute heating fuel will remain low. However, there is substantial potential to reduce greenhouse gas emissions and energy demand with higher volume biodiesel
blends in diesel-based heating applications. Thus, a comprehensive study of higher volume biodiesel heating fuels as a potential sustainable alternative is warranted and timely.

**Research Objectives**

There were six principal research objectives of this thesis relating to the closed-loop utilization of waste cooking oil as a feedstock for biodiesel production and utilization in space heating applications. The research objectives were to:

- Develop a widely adaptable waste cooking oil-to-fuel process at the Rochester Institute of Technology. The development of this process included collaboration with the university’s Dining Services, Auxiliary Services, Facilities and Management Services, Parking and Transportation Department, Environmental Health and Safety Department, and the Senior Sustainability Advisor.

- Characterize the chemical and physical properties of the waste cooking oil biodiesel. Samples of the produced biodiesel were sent to an external lab for American Society for Testing and Materials (ASTM) analysis to ensure the fuel met the necessary quality standards.

- Measure and analyze combustion emissions of various heating fuel blends with a commercially available residential scale oil burner mounted in a conventional residential furnace, and compare to the incumbent fuel oil baseline emissions.

- Measure and analyze emissions from the same fuel blends in a lab-scale apparatus that enables near-flame interrogation and visualization of the combustion process.
• Conduct a life cycle assessment (LCA) of a community scale waste cooking oil-to-fuel process to analyze the global warming potential and obtain cumulative energy demand (CED), specifically for space heating applications.
• Calculate the energy return on investment (EROI) of waste cooking oil-fuel process for biodiesel space heating applications, using the CED.

Chapter 2: Literature Review

Process Overview

As defined by the U.S. Environmental Protection Agency, biofuels are derived from renewable biomass, such as ethanol from corn kernels, corn stover, perennial grasses, and woody biomass or biodiesel from soybeans and algae [5]. Biofuels offer an alternative to conventional fossil fuels for various energy purposes. However, there has been much criticism of agricultural crop-based biofuels [6-11]. Biodiesel is a biofuel that can be produced by dedicated agricultural crops, mainly soybean in the United States, or by converting vegetable oil, such as waste or used cooking oil via transesterification [12].

Because of the widespread concern over use of food crops for fuel production, waste-to-energy (WtE) systems utilizing waste vegetable oil and cooking oil are very attractive, as the fuel feedstock already exists. Typical crop-based biofuels require large amounts of energy and water for planting, cultivating, irrigation, and harvesting. Furthermore, fuel is required for agricultural equipment and transportation of the crop feedstock to the biofuel production facility. Starting with a waste or used product effectively reduces or eliminates most of these upfront energy requirements, as well as the energy requirements, greenhouse gas emissions and issues of proper disposal.
Waste derived biofuels offer great potential in achieving emissions reductions of greenhouse gases and other air pollutants, as well as requiring less energy to produce because the fuel feedstock already exists. This effectively leads to a greater energy return on investment (EROI) value for several waste derived biofuels like biodiesel originating from waste cooking oil. The process of converting waste cooking oil into biodiesel can be broken down into five primary sequential steps (Figure 1):

![Figure 1. Generalized waste cooking oil-to-biodiesel fuel process flow diagram.](image)

1. The first step is the **waste oil collection**. While each collection technique can be different, it requires coordination between the collectors and the oil producing facility (restaurant, community, cafeteria, municipality, etc.).

2. The second step is a **pre-treatment process**, which is broken into two sub-steps. The oil is most likely to contain residual water, as well as solid food particles. Therefore, the first pre-treatment step is to separate out the water and solids. This is crucial to ensure full conversion of oil to biodiesel, described further below. Once separated, the oil is then titrated to determine the concentration of free fatty acids (FFA). This determines the necessary amount of catalyst for the transesterification reaction.

3. Following the pre-treatment process, the waste cooking oil feedstock is ready for the **transesterification reaction**. The oil, a triglyceride, reacts with an alcohol,
typically methanol, in the presence of a catalyst to produce fatty acid esters (Figure 2) [13]. The oil is composed of three fatty acid chains with a glycerin “back bone.” The alcohol breaks off the three fatty acid chains from the glycerin and then attaches to each of the three free fatty acid chains making a fatty acid ester, or commonly known as biodiesel. The broken off glycerin is the by-product of this production process.

4. Once the transesterification reaction is complete, the biodiesel and glycerin will separate with time, due to their different densities. When the products separate, there will be two distinct layers with visible color and viscosity differences. The glycerin will be the bottom layer because it is denser than biodiesel. The glycerin separation step is simply draining off the bottom layer of glycerin.

5. Once separated, the biodiesel and glycerin by-product can be utilized in appropriate applications. Biodiesel can be used as a substitute for petroleum diesel fuels (fuel oil for heating applications), while glycerin has numerous uses as a food additive, soaps production, etc.

\[
\begin{align*}
\text{CH}_2\text{-OOC-R}_1 & \quad \text{CH}_2\text{-OOC-R}_2 \quad \text{CH}_2\text{-OOC-R}_3 \\
\text{CH-OOC-R}_2 & + \quad 3\text{R'}\text{OH} \quad \text{Catalyst} \quad \text{R}_1\text{-COO-R'} & \quad \text{R}_2\text{-COO-R'} \quad \text{R}_3\text{-COO-R'} \\
\text{CH}_2\text{-OH} & \quad \text{CH}_2\text{-OH} \\
\text{Triglyceride} & \quad \text{Alcohol} \quad \text{Fatty acid esters} & \quad \text{Glycerol}
\end{align*}
\]

**Figure 2.** General equation for transesterification of a triglyceride with an alcohol [13].
The production ratio, on a volume basis, of biodiesel to glycerin is roughly 4:1. According to the U.S. Department of Energy, unrefined glycerin can be sold for up to $0.10/lb in 2010 [14]. However, the biodiesel industry is producing glycerin quantities that surpass current demand on the commodity market. Growth within the biodiesel industry will only exacerbate this glycerin surplus and possibly drive glycerin prices down to unprofitable levels for large glycerin refiners [15]. Therefore, several alternative applications for glycerin are becoming more attractive.

An alternative pathway is through on-site refinement, mainly methanol removal, and purification at the biodiesel producing facility. The refined glycerin can then either be sold for up to $0.50/lb (as of 2013) or kept on-site for internal applications [15]. Glycerin can be used for soap, as a degreaser, and several other commercial applications (Figure 3). In addition, glycerin can also be used as a feedstock for renewable hydrogen production. Through steam reformation, unrefined glycerin can produce hydrogen, but only produces 70% of the yield compared to pure (refined) glycerin [17]. This avenue is a viable option for glycerin and in the future may prove to be a better option than refinement and purification for on site applications.

Consequently, biodiesel producers have several options to utilize the glycerin. An institution with an available oil supply and diesel fuel demand can achieve considerable environmental and economic benefits by developing a closed-loop system. This concept and the required process development will be discussed in greater detail in Chapter 3.
Benefits of Waste Cooking Oil Biodiesel

Like most biofuels, biodiesel has several advantages compared to the incumbent petroleum diesel fuels. Arguably the most beneficial attribute of biodiesel is its similar properties to diesel fuel (Table 1) [12]. This allows biodiesel to be used directly in any diesel engine without significant modifications to the engine or fuel infrastructure. With some engine modifications, biodiesel can be burned at a 100% ratio (i.e., with no diesel blending). Typical biodiesel applications involve blending with conventional petroleum-based diesel fuels. Biodiesel and diesel blends have been well documented to decrease pollutant emissions such as CO, SO\textsubscript{2}, VOC and particulate matter in vehicle applications [18-21]. Table 2 outlines general technical properties of biodiesel.

In addition to the emissions reductions and blending capabilities, biodiesel can be produced from various vegetable oil feedstocks, including waste cooking oils. The properties of biodiesel vary depending on which vegetable oil feedstock is used (Table 3).
The ability to produce biodiesel from a wide array of feedstocks makes this a versatile and widely applicable alternative fuel. Locations with any type of the suitable vegetable oils outlined in Table 3 have a potential fuel source.

**Table 1.** Properties of diesel fuel oil and soybean-based biodiesel.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Diesel Fuel Oil&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Biodiesel&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>MJ/kg</td>
<td>45.1</td>
<td>39.8 - 41.3</td>
</tr>
<tr>
<td>LHV</td>
<td>MJ/kg</td>
<td>42.9</td>
<td>37</td>
</tr>
<tr>
<td>Viscosity (40°C)</td>
<td>mm&lt;sup&gt;2&lt;/sup&gt;/s</td>
<td>2.7</td>
<td>4 – 5.2</td>
</tr>
<tr>
<td>Density (15°C)</td>
<td>kg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>855</td>
<td>865-880</td>
</tr>
<tr>
<td>Flash Point</td>
<td>°C</td>
<td>64</td>
<td>168 - 185</td>
</tr>
<tr>
<td>Cetane number</td>
<td>-</td>
<td>52</td>
<td>45-60.9</td>
</tr>
</tbody>
</table>

**References:**<sup>1</sup>[12], <sup>2</sup>[13, 22-26]

Facilities utilizing cooking oil such as restaurants, school districts, hospitals, or universities, produce a viable fuel feedstock, because waste oils are far less expensive than food-grade oils [31]. Currently, most waste cooking oils are being sold to rendering companies for animal feed production, however, there is concern with these waste oils being used for this purpose [32]. During frying, many harmful compounds are formed between the oil and water within the food [33]. Feeding the oil to animals could result in the introduction of these harmful compounds into the food supply chain, which could ultimately present human health risks. In addition, improper disposal of these waste oils may contaminate freshwater sources [32]. As a result, several developed countries have
assessed fines for the disposal of waste oil through the public water drainage systems [34].

Table 2. Technical properties of biodiesel [12,27].

<table>
<thead>
<tr>
<th>Common name</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common chemical name</td>
<td>Fatty acid (m)ethyl ester</td>
</tr>
<tr>
<td>Chemical formula range</td>
<td>C14-C24 methylesters or C15-25H28-48O2</td>
</tr>
<tr>
<td>Kinematic viscosity (40°C)</td>
<td>3.5-5.2 mm²/s</td>
</tr>
<tr>
<td>Density (15°C)</td>
<td>860-894 kg/m³</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>insoluble</td>
</tr>
<tr>
<td>Reactivity</td>
<td>Stable but avoid strong oxidizing agents</td>
</tr>
</tbody>
</table>

Institutions with a waste cooking oil supply have a few options. The waste oil can be sold for animal feed production for a small revenue with the risk of introducing harmful compounds into the food supply chain. Another option is to properly dispose the oil. However, complying with disposal regulations can be costly and cumbersome. The final option is to retain possession of the oil and produce a fuel for internal applications. With some capital investment and planning, a waste cooking oil-to-fuel program can rapidly become financially self-sustaining. Institutions with climate action plans, including RIT, have a lot to benefit from supplementing diesel usage with biodiesel. Waste cooking oil-derived biodiesel will likely not displace all diesel fuel, but can provide a substantial volume of fuel to offset emissions from petroleum-based fuel, as well as provide educational opportunities for students and an opportunity to engage
various institutional groups. However, this may also be a social barrier in terms of coordinating and aligning multiple stakeholders (e.g. dining services, maintenance, EH&S). The development of a waste cooking oil-to-biodiesel depends heavily on the multiple stakeholders agreeing to take on the additional effort.

As discussed above, the conversion of waste cooking oil to biodiesel produces substantial amounts of glycerin, which has several potential economical utilization pathways. Each biodiesel producing institution thus has the added opportunity to develop an individualized glycerin utilization strategy. This diversity of glycerin options adds to the versatility and wide applicability of producing biodiesel from waste cooking oil.

**Table 3.** Biodiesel properties depending on the vegetable oil feedstock.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>MJ/kg</td>
<td>40.5</td>
<td>39.8-41.3</td>
<td>41.1</td>
<td>39.8-40.8</td>
<td>47.05</td>
</tr>
<tr>
<td>LHV</td>
<td>MJ/kg</td>
<td>37.2</td>
<td>38.95</td>
<td>-</td>
<td>-</td>
<td>43.98</td>
</tr>
<tr>
<td>Viscosity (40°C)</td>
<td>mm²/s</td>
<td>4.2-6.7</td>
<td>4.6</td>
<td>3.6-4.2</td>
<td>4.4-5.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Density (15°C)</td>
<td>kg/m³</td>
<td>857-882</td>
<td>860-884</td>
<td>873-884</td>
<td>867</td>
<td>800</td>
</tr>
<tr>
<td>Flash Point</td>
<td>°C</td>
<td>180-192</td>
<td>157-183</td>
<td>139-154</td>
<td>147.5</td>
<td>99.5</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>51-59.7</td>
<td>46.6-60.9</td>
<td>60.9</td>
<td>59.2</td>
<td>52</td>
</tr>
</tbody>
</table>

References: ¹[12, 22, 24], ²[12, 23, 24, 25], ³[12, 24] ⁴[28,29], ⁵[30] (FT fuel = Fischer Tropsch fuels)
Overview of Biodiesel Utilization Applications

Biodiesel is a versatile fuel that can be produced from several readily available virgin or waste vegetable oils. Regardless of the type of vegetable oil feedstock, biodiesel can be utilized in the following ways:

1. Heating applications
2. Vehicular applications
3. Electrical generation applications via diesel generators

Statewide tax credits, government mandates, climate commitment plans and process economics largely dictate the optimal biodiesel pathway. In 2010, the Energy Information Administration (EIA) reported the U.S. transportation sector to be the country’s sole consumer of biodiesel, with a demand of 0.034 quadrillion Btu (3.56x10^{10} MJ), or only 0.4% of the total renewable energy consumed [35]. However, with the Renewable Fuel Standard (RFS) increasing the required consumption of all renewable fuels, including biomass-based diesel, this percentage is expected to increase [36]. The transportation sector will likely continue to be the largest consumer of biodiesel because the infrastructure for vehicle biodiesel is well developed. However, biodiesel consumption in space heating is also likely to increase for several reasons. First, low volume biodiesel blends do not require any modifications to current fuel oil heating systems [12]. Secondly, New York State Assembly and Senate passed legislation in June 2013 mandating all heating oil sold statewide must contain at least 2% biodiesel by volume by 2015 [37]. Moreover, in rural regions without access to natural gas, biodiesel
may provide an economical and convenient alternative to conventional heating fuels, such as No. 2 fuel oil (diesel) and propane.

The following sections discuss in greater detail biodiesel utilization for heating applications including the advantages, constraints, and potential for further development.

*Heating Applications*

Biodiesel can be substituted for fuel in oil-based heating applications. Biodiesel is well suited as a substitute heating fuel because it can be readily added to conventional fuel oil and blended heating fuel can be stored similarly to pure diesel fuel oil. Biodiesel heating fuel blends have been documented to yield decreases in CO, SO₂, VOC and particulate matter emissions [18-21]. Currently, oil burner manufacturers only warranty heating fuel blends up to 5% biodiesel. Therefore, 95% of the fuel mix is still petroleum-based fuel oil. This is the main constraint for biodiesel in heating applications, but as in the case of vehicle applications, biodiesel fraction will likely increase over time as capacity of specific components (e.g., elastomer seals) is validated. Fatty acid methyl esters (biodiesel) cause some of the elastomer seals within diesel oil burners to soften and swell or harden and crack, as well as contributing to the corrosion of aluminum and zinc components [82].

Further development of oil burners that can burn higher percentages of biodiesel will promote growth of biodiesel utilization in heating applications. However, there are a few oil burner manufacturers selling furnaces and boilers that can burn pure biodiesel, pure waste cooking oil, and blends of these fuels [83]. As emissions reduction goals
become more stringent, an increase in burner manufacturers selling these types of heating systems will undoubtedly occur.

The focus of this thesis is utilizing biodiesel as a substitute fuel in residential scale oil burners. The research objectives were to understand emissions reductions, life cycle environmental impact, and the energy return on investment of the complete waste cooking oil-to-biodiesel-space heating process. Previous studies on the heating application of biodiesel fuel are summarized in Table 4.

**Evaluation of WCO Biodiesel Heating Application Potential**

One of the few reports quantifying yellow grease (waste cooking oil) in the U.S. reported there is an average of about 23 pounds (10.3 kg) of yellow grease produced annually per person [38]. Thus, there is a considerable amount of available waste feedstock for biodiesel production. However, nationwide or regional commodity companies are collecting the majority of this waste cooking oil for animal feed production. Institutions may need to first negotiate new contracts before considering waste cooking oil biodiesel production.

According to a 2011 EIA report, out of 7.3 million housing units in the U.S using fuel oil for space heating, 2.2 million housing units were in New York State [39]. In other words, roughly 30% of the homes utilizing fuel oil for heating in the entire country are in New York. Thus, there is great potential in our local region for biodiesel as a substitute heating fuel.

New York’s residential sector consumes 29.6% of the state’s total energy and is second only to the commercial sector, which consumes 32.7% of the state’s total energy.
This highlights the considerable potential for biodiesel as a home heating fuel, as well as the potential environmental and economic benefits from using a domestic, clean, and renewable fuel source. New York’s most common home heating fuel is natural gas with 55.8% of homes, but fuel oil is second at 27.5% [39].

Overall, New York’s current home heating oil usage data demonstrates it is an ideal area for biodiesel heating applications. Despite cheap natural gas, a substantial number of homes, specifically in rural areas use home heating oil (diesel fuel oil). In addition, New York’s recent and on-going policy initiatives are positioning the State as a prime candidate for biodiesel heating applications.

**Key Policy Drivers for Biodiesel Heating Fuel in New York State**

Former New York State Governor David Paterson signed State of New York Executive Order No. 24 in 2009, which established a goal to reduce greenhouse gas emissions by 80% by 2050 [40]. This further committed New York’s pursuit of renewable and clean fuels, and more specifically, there have since been several key mandates at the city and state level promoting growth of biodiesel as a heating fuel.

First, New York City’s Administrative Code § 24-168.1 (clean heating oil) mandated all heating oil of grade numbers 2, 4, and 6 must contain at least 2% biodiesel by volume [41]. As a result of New York City’s action, state legislation was passed in June 2013 extending this 2% biodiesel by volume minimum throughout the entire state by 2015 [37]. In compliance with these mandates, the Renewable Fuel Standard (RFS) requires U.S. consumption of all renewable fuels to increase to 36 billion ethanol-
equivalent gallons by 2022 (1 gallon of biodiesel is counted as 1.5 ethanol-equivalent gallons) [36].

The transesterification of waste cooking oil into biodiesel almost has 1:1 oil to biodiesel conversion efficiency. Thus, biodiesel from readily available waste oil sources can provide a considerable amount of this increase in renewable fuel. Furthermore, New York’s Refundable Clean Heating Fuel Tax Credit has been extended to 2016 despite several previous expirations [42]. This personal income tax credit applied to biodiesel purchases for residential space heating and water heating uses. The tax credit is $0.01/gallon for each percent of biodiesel blended with conventional heating oil, with a maximum of $0.20/gallon. For example, a purchaser of a mixture of 5% biodiesel and 95% conventional heating oil is entitled to a tax credit of $0.05/gallon. The extension of this tax credit encourages homeowners to purchase higher biodiesel blends of heating oil.

The combination of government mandates, climate commitment plans, and tax credits sets the stage for exceptional growth of biodiesel within the New York State. The most constraining aspect of biodiesel utilization in heating systems is the 5% warranty on oil burning furnaces and boilers. Further development on appliances that can utilize a higher percent biodiesel blend will greatly increase biodiesel utilization in heating applications.
Table 4. Summary of prior studies of biodiesel in heating applications (all included physical and chemical characteristics of fuels).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Biodiesel feedstocks and blends studied</th>
<th>Heating Apparatus</th>
<th>Key measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alonso et al. 2012 [43]</td>
<td>Glycerin, used vegetable oil, raw soybean oil, refined soybean oil, rapeseed oil, raw sunflower oil, refined sunflower oil, animal by-products not intended for human consumption</td>
<td>Open-air heating circuit equipped with AR-CO Bruciatori BR5 model (low pressure auxiliary air fluid pulverization burner)</td>
<td>Combustion efficiency, emissions of polluting gases (CO, NO\textsubscript{X}, PM), greenhouse gas effect (CO\textsubscript{2})</td>
</tr>
<tr>
<td>Barnes et al. 2010 [44]</td>
<td>Waste vegetable oil biodiesel (feedstock not specified) and kerosene</td>
<td>Twin-hob, twin oven Aga cooker equipped with sleeve-type vaporizing burner</td>
<td>Burner performance</td>
</tr>
<tr>
<td>Bazooyar et al. 2011 [45]</td>
<td>Biodiesels of grape seed, corn oil, sunflower oil, soybean oil, olive oil, rice bran oil</td>
<td>Semi industrial boiler equipped with Sterling 90UK Spec pressure jet type oil burner</td>
<td>Combustion gas emissions (CO, CO\textsubscript{2}, NO\textsubscript{X}, SO\textsubscript{2}), optimum combustion pressure, A/F influence on emissions and performance, combustion efficiency</td>
</tr>
<tr>
<td>Gan et al. 2010 [46]</td>
<td>Palm oil biodiesel</td>
<td>Residential hot water boiler equipped with Lamborghini Calor Eco 8/00870012 oil burner</td>
<td>Impacts of antioxidants (BHA, BHT, TBHQ) on gas NO and CO emissions</td>
</tr>
<tr>
<td>Ghorbani et al. 2011 [20]</td>
<td>Soybean and sunflower biodiesel</td>
<td>150 kW hot water boiler equipped with pressure jet type oil burner</td>
<td>Combustion efficiency, air flow impact on flue gas emissions (CO, CO\textsubscript{2}, NO\textsubscript{X}, SO\textsubscript{2}), coolant/out water and exhaust temperatures, fuel flow rates</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td><strong>Oil Type</strong> and <strong>Biodiesel Blend</strong></td>
<td><strong>Boiler Type and Burner</strong></td>
<td><strong>Emissions and Characteristics</strong></td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------------------</td>
<td>---------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Jiru 2010 et al. [47]</td>
<td>Degummed soybean heating oil (SHO)</td>
<td>Thermo Pride forced air boiler (CHB68-112B) equipped with a Beckett AFG model oil burner</td>
<td>Seal compatibility, long-term storage, laboratory and field combustion</td>
</tr>
<tr>
<td>San José et al. 2011 [48]</td>
<td>Sunflower oil biodiesel B10, B20, B30, B100</td>
<td>26.7 kW cast iron AR/25 GT (ROCA) boiler equipped with KADET-TRONIC (ROCA) pressure pulverizing oil burner</td>
<td>Combustion efficiency, greenhouse effect of process (CO$_2$), pollution of process (CO, unburnt solids, NO$_x$, SO$_2$)</td>
</tr>
<tr>
<td>Krishna, C.R. 2003 [26]</td>
<td>Soybean biodiesel not meeting ASTM requirement D6751, B0, B10, B20, B50 with No. 2 fuel oil and No. 6 oil (residual oil)</td>
<td>Residential and commercial boilers equipped with high efficiency oil burners</td>
<td>Comparison to ASTM biodiesel blends, steady state combustion emissions in both boilers (CO, CO$_2$, smoke, and NO$_x$), ignition performance (CO, smoke),</td>
</tr>
<tr>
<td>Lee et al. 2004 [19]</td>
<td>Soybean biodiesel B20 with No. 2 fuel oil</td>
<td>30 kW cast iron residential hot water boiler equipped with high efficiency pressure jet type oil burner</td>
<td>Combustion emissions (O$_2$, CO$_2$, CO, NO$_x$, SO$_2$, PM), inlet/outlet water temperatures</td>
</tr>
<tr>
<td>Macor and Pavanello 2009 [21]</td>
<td>Biodiesel feedstock not specified B100 and home heating oil (No. 2 fuel oil)</td>
<td>400 kW fire –tube hot water boiler equipped with RIELLO RL38 two-stage oil burner</td>
<td>Regulated (CO, SO$_2$, NO$_x$, PM) and unregulated (PAH, VOC, and aldehydes) emissions</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Fuel Type</td>
<td>Combustion Chamber Details</td>
<td>Experimental Details</td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------------------</td>
<td>-------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ng and Gan 2010 [49]</td>
<td>Palm oil biodiesel</td>
<td>Non-pressurized, water-cooled combustion chamber equipped with Lamborghini Calor Eco 8/00870012 oil burner</td>
<td>Pump pressure impacts on emissions (O₂, CO₂, CO, NO, soot), water flow rate</td>
</tr>
<tr>
<td></td>
<td>No. 2 fuel oil control B10, B20, B40, B60, B80, B100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sequera et al. 2008 [50]</td>
<td>Soybean biodiesel (SOME), emulsified bio-oil (SOEE)</td>
<td>Atmospheric pressure burner with air-atomized injector</td>
<td>Visual flame images, emissions (NOₓ, CO)</td>
</tr>
<tr>
<td></td>
<td>SOME20, SOME100, SOEE20</td>
<td></td>
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</tr>
</tbody>
</table>
Chapter 3: Closed Loop Waste Cooking Oil Biodiesel Production

Process Development

EPA Region 2 Climate Showcase Communities Grant

The U.S. EPA Climate Showcase Communities Program aids local governments to fund innovative, cost effective and replicable community-based projects that reduce greenhouse gas emissions. In 2012, New York’s Monroe County was awarded a grant from this program, and partnered with researchers at Rochester Institute of Technology (RIT) to convert community residential waste cooking oil to biodiesel fuel. The various aspects of the EPA-funded program are presented in Figure 4.

**Figure 4.** Full EPA-funded waste cooking oil-to-biodiesel program.
Phase 1 - Monroe County

Community residents are able to drop off used cooking oil at Monroe County’s centrally located EcoPark [51]. The RIT researchers collected the used cooking oil from the EcoPark and transported it to the university to undergo conversion into biodiesel. RIT researchers found the residential used cooking oil varied widely in quality and type (soybean, canola, olive, etc.). These inconsistencies led to several incomplete conversion reactions, ultimately attributed to excess water. As a result, two steps were added to the conversion process methodology.

First, a 24-hour gravity separation step in a conical settling tank was added, to allow water dispersed within the oil to settle to the bottom, because water is denser than oil. Additionally, any solid food particles in the oil settled to the bottom as well. This allowed the water and food particles to be drained off the bottom of the settling tank, leaving pure cooking oil feedstock for subsequent processing.

Secondly, the oil feedstock was subjected to an additional “dry cycle” within the BioPro190, which was the oil-processing machine utilized for this conversion process. During the dry cycle, the BioPro190 ran a 15-hour heat cycle to evaporate any residual water in the oil. The addition of these two steps solved the excess water issue and the RIT researchers ultimately achieved complete oil to biodiesel conversions. Furthermore, this biodiesel met ASTM standards necessary for biodiesel to be used in vehicle applications.

Upon successful conversion of oil to biodiesel, the fuel was first utilized in Monroe County lawn mowers at several town parks. Lawn mowers were chosen for a few reasons. First, blends of biodiesel above B20 (20% biodiesel, 80% diesel) invalidate
the warranty of many diesel engines. However, these lawn mowers were well beyond the warranty period. Therefore, higher blends of biodiesel were possible. Secondly, off-road vehicles, like lawn mowers, do not have exhaust treatment and have less strict emissions regulations. Thus, off-road vehicles have large emission reduction potential from biodiesel utilization. A process flow diagram for the Monroe County program is outlined in Figure 4.

This community-based biofuel program reduced lifecycle greenhouse gas emissions of biodiesel production, while solving a waste disposal problem and associated costs. However, there were still some weak points of this program. First, despite the centralized oil drop-off location at the EcoPark, not as many residents participated as expected. This caused oil collection from the EcoPark to be a sporadic and somewhat unreliable fuel supply. Additionally, the oil that was dropped off varied in vegetable oil type and quality. These inconsistencies made the conversion process difficult. Despite the RIT researchers’ ultimate success, such an inconsistent fuel feedstock is a cause for concern for the conversion process. A much more consistent fuel feedstock is preferable for this process. Furthermore, the transportation required for oil collection and distribution, while relatively small, reduces the overall benefit. Minimizing or eliminating transportation required for oil collection and final fuel distribution benefits the lifecycle greenhouse gas emissions and energy return on investment for the entire biofuel program.

Figure 5. Simple process flow diagram of Monroe County residential cooking oil to biodiesel program.
Upon completion of the first phase of the Climate Showcase Communities Grant the EPA shifted focus of the remainder of the project to RIT (Phase 2). The oil processing equipment was already located at RIT and preliminary data indicated RIT consumes about 5,400 gallons of soybean cooking oil a year. Oil availability and consistency made RIT a productive follow up to Monroe County’s first phase of this program. Additionally, the transportation distances for oil collection were minimal compared to the Monroe County Phase 1 activity and developing a fueling station at the production site essentially eliminated the need for distribution transportation. A constrained system, like a university campus, allows for close monitoring of supply and demand, which was one of the weaknesses of the initial larger-scale process. However, the first phase with Monroe County EcoPark laid the groundwork for a similar process to be developed at RIT.

**Phase 2 – RIT**

*Background*

The research results documented in this thesis were part of the RIT-focused Phase 2b of the EPA-funded project (Figure 4). The RIT biodiesel team organized a university-wide stakeholders meeting in March 2013. Personnel from Finance and Administration, Auxiliary Services, Dining Services, Environmental Health and Safety (EHS), Facilities and Management Services (FMS), and RIT’s Senior Sustainability Advisor were present.

With the help of Auxiliary Services and Dining Services, a single dining cafeteria was identified to be the sole supplier of waste cooking oil. The research team was
determined to partner with a single cafeteria for several reasons. First, it streamlined communication between the cafeteria’s employees and the researchers. Second, it was important to establish a consistent oil feedstock source because each university cafeteria uses cooking oil at different rates. Each cafeteria changes the cooking oil when necessary (approximately weekly), so oil availability for collection and oil quality vary among the cafeterias. Lastly, another important consideration was that the cafeteria chosen was one of the closest to the biodiesel-producing lab in the Golisano Institute for Sustainability. This was a conscious decision by the researchers to minimize transportation in the oil collection stage.

RIT EHS provided the following information:

1. Volume limits for waste cooking oil transport (intra-campus)
2. Volume limits for waste oil, biodiesel, and methanol storage
3. Volume limit for interior heating oil storage

According to EHS, whether or not NYS regulations apply to waste cooking oil depends on its flash point. The flashpoint of a liquid is the lowest temperature at which it can vaporize and form a flammable mixture with air. EHS reported, as long as the flashpoint is above 200°F (93.3 °C), it is not regulated as a hazardous material, meaning no shipping papers, shipping placards or volume limits are required [52]. According to several publications, the flashpoint of soybean vegetable oil is well above 200°F (93.3°C) [12, 22, 53-55]. Thus, there were no concerns with the transportation of the waste cooking oil. Since the biodiesel-producing lab was also acting as the vehicle fueling station, biodiesel transportation was not a consideration.
Methanol is a required substance for the transesterification of vegetable oil into biodiesel and is also a Class IB flammable liquid, according to EHS. The volume limit for storing methanol indoors is 120 gallons. Thus, the methanol was obtained in small amounts and never exceeded a total volume of 55 gallons. Both waste oil and biodiesel are Class IIIB combustible liquids and EHS reported the maximum storage limits as 13,200 gallons per control area (within a 1 hour fire barrier separation of all flammable and combustible liquids that are IIIB). This was also a non-issue, as researchers were never dealing with volumes of waste cooking oil or biodiesel greater than 55 gallons at a time. Lastly, EHS reported the volume limit for interior heating oil storage to be 660 gallons and consequently, interior heating oil storage never exceeded 10 gallons.

RIT’s Senior Sustainability Advisor also provided guidance on which stakeholders to involve and played a vital role in setting the serious and committed tone in the stakeholder meeting. Involving the President’s Sustainability Advisor allowed for a direct line of communication between the researchers and important stakeholders at the university.

The following sections outline the several stages of the RIT Closed Loop Biodiesel Production Process.

**Waste Cooking Oil Collection Stage**

Once all necessary safety regulations were understood and all stakeholders were committed to the program, the waste cooking oil-to-fuel process development was initiated by partnering with RIT’s Crossroads dining cafeteria. Crossroads is one of the
closest dining cafeterias to the biodiesel production lab housed within the Golisano Institute for Sustainability. Currently, the university has an annual contract with Baker Commodities to collect all of the university’s waste cooking oil. According to data provided by RIT Dining Services, RIT purchased 1,269 cases containing 4.55 gallons of soybean oil at $21.26/case from July 2012 to June 2013 [56]. Thus, a total of 5,774 gallons of cooking oil were obtained. Dining Services also reported a 10% loss during frying. Therefore, only 5,197 gallons of the original 5,774 remain after use. Baker Commodities purchases the waste cooking oil for $0.50/gallon and collects it from oil collection vessels they provide for each cafeteria. For this pilot scale project, Baker Commodities agreed to donate 110 gallons of waste cooking oil to the RIT research effort for educational purposes.

The cooking oil in Crossroads cafeteria is changed at least every 2 weeks, depending on the time of year. The oil turnover rate during the school year is much more rapid than the summer months simply because more students are on campus. Crossroads employees change the cooking oil in the fryers by pumping the oil through a filter and into the oil collection vessel provided by Baker Commodities. The filter traps large food particles, which prevents the pump from clogging, but even more importantly ensures good quality oil for the biodiesel conversion process.

During the duration of the EPA-funded project, Crossroads employees notified the RIT researchers once the waste oil collection vessel contained at least 50 gallons of waste cooking oil. The RIT researchers then collected up to 55 gallons of oil by transferring it from the collection vessel into plastic containers with an electric pump. RIT’s Facilities and Maintenance Service (FMS) organization provided a vehicle for the
transport of the oil from Crossroads cafeteria to the Golisano Institute for Sustainability, which totaled just over 1 mile one-way (Figure 6). Once the waste oil was transported to the Golisano Institute for Sustainability, it was transferred into a conical settling tank to begin the pre-treatment stage.

![Figure 6](image.png)

**Figure 6.** Map of the oil collection transportation from Crossroads cafeteria to the Golisano Institute for Sustainability.

*Pre-Treatment Stage*

The first step in the pre-treatment stage is a simple 24-hour gravity separation in a conical settling tank (Figure 7). This separation allows water and solid particles to settle to the bottom, as they are denser than the oil. Once the oil has been allowed to settle for 24 hours, the water and solids can then be drained off the bottom, leaving only the high quality oil feedstock behind. This separation technique requires no energy to perform and is highly effective.
There were minimal amounts of water and almost no solids in the oil obtained from Crossroads cafeteria. Researchers believe the reason for the high quality of oil was a result of the rapid oil turnover rate and the oil filtering during the oil turnover process. Because of this, RIT researchers did not incorporate any additional water or solids removal steps. However, other oil sources may not have as high of quality oil and contain a substantial amount of water. If this is the case, an additional drying step can be implemented by transferring the oil into the automated BioPro190 and applying the heat cycle for a period of 15 minutes. This will heat the oil up to 135°F (57.2°C) and evaporate the residual water out of the waste cooking oil.

The second and final step in the pre-treatment stage is a titration of the waste cooking oil. Cooking oil is a triglyceride, which is composed of a chain of three fatty acid molecules and one glyceride molecule. During use, the fatty acid molecules can break off from the glyceride molecule to form free fatty acids (FFAs) and leave behind diglycerides (two fatty acid molecules and one glyceride molecule) or monoglycerides (one fatty acid molecule and one glyceride molecule). The FFA molecules float within the oil and react quickly with any base to produce soap and not the desired methyl ester product (biodiesel).

This poses a problem for converting waste cooking into biodiesel because a catalyst base is utilized during the transesterification reaction to convert oil into biodiesel. Therefore, the FFAs must be neutralized before transesterification. This can be achieved by utilizing excess base catalyst to first neutralize the FFAs and then complete the transesterification reaction. The amount of excess base catalyst required to neutralize the FFAs depends on the oil’s initial FFA concentration. A titration of the waste cooking oil
feedstock provides the FFA concentration and thus allows one to determine the amount of base catalyst required.

Figure 7. The conical settling tank for gravity separation of oil, water and solids in the pre-treatment stage.
This titration step requires the chemical indicator phenolphthalein, distilled water, isopropyl alcohol, the biodiesel oil feedstock, and the catalyst to be used in the transesterification reaction. A simple titration procedure for biodiesel production from waste cooking oils is presented below [57, 58]:

1. The first step is to make the titration solution, consisting of 1g of the base catalyst dissolved in 1L of distilled water. It is necessary to use the same catalyst base in the titration solution as the transesterification reaction. Otherwise, the titration will provide an inconsistent FFA concentration. Potassium hydroxide (KOH) was utilized as the base catalyst for both the titration solution and transesterification reaction.

2. After the titration solution is made, the titration sample must be made by combining 10 mL of isopropyl alcohol, 1 mL of waste cooking oil, and 2-3 drops of phenolphthalein.

3. A syringe is filled with 10 mL of the titration solution. The titration begins by slowly emptying the syringe into the titration sample. The endpoint of the titration is marked by the titration sample turning and remaining pink for at least 10 seconds. Record the required mL of titration solution emptied into the titration sample. Repeat the same procedure 2 additional times and record each required mL of titration solution. Finally, the average of the three titration values provides the amount of excess catalyst mass (in grams) per liter of oil required to neutralize the FFAs.

4. Converting virgin oil (i.e., no excess FFA) into biodiesel requires 7.0 grams of KOH catalyst per liter of oil. However, this assumes a catalyst purity of 100%.
To adjust this to the appropriate value, divide the 7.0 by the catalyst purity. Equation 1 calculates the adjusted amount of catalyst for 90% purity.

\[
\frac{7.0 \text{ g KOH catalyst/L oil}}{0.90 \text{ KOH purity}} = 7.8 \text{ g KOH catalyst/L oil} \tag{1}
\]

5. Still assuming 90% purity, WCO requires the original 7.8 grams of catalyst per liter of oil plus the excess amount calculated from the titration. For example, if the averaged titration value equaled 1.0 g/L, the amount of catalyst required equals 8.8g/L of oil. Assuming a batch size of 50 gallons of oil, the total amount of catalyst can be determined. However, the batch size must be converted into liters to use the calculated 8.8g of catalyst/ L of oil value. With the batch size in appropriate units, the total amount of catalyst for the batch can be calculated. This value assumes the catalyst is 100% pure, which is most likely not the case. This value needs to be adjusted for the typical 90% catalyst purity (Equations 2 and 3).

\[
50 \text{ gallons oil} \times \left(\frac{3.7851 \text{ L}}{1 \text{ gallon}}\right) = 189.25 \text{ L oil} \tag{2}
\]

\[
189.25 \text{ L} \times \left(\frac{8.8 \text{ g}}{1 \text{ L}}\right) = 1,665.4 \text{ g KOH catalyst} \tag{3}
\]

**Transesterification Stage**

As outlined in the Process Overview section (Chapter 2), transesterification reacts a triglyceride (cooking oil) with an alcohol (methanol), in the presence of a catalyst
(potassium hydroxide). The oil is composed of three fatty acids molecules and one glycerin molecule. The methanol breaks the fatty acid molecules off the glycerin molecule to form a fatty acid ester, known as biodiesel. The excess catalyst neutralizes the FFAs and the glycerin molecules become free-floating molecules.

An electric oil pump was utilized to transfer 50 gallons of the pre-treated waste cooking oil from the conical settling tank into the BioPro 190 (Figure 8). The electric oil pump was utilized in both the oil collection stage and the transfer of oil from the conical settling tank to the BioPro 190 because it was essentially transporting the same oil in both functions.

Figure 8. The pre-treated waste cooking oil is transferred from conical settling tank (right) to the BioPro 190 (center) with an electric oil pump.
With 50 gallons of waste cooking oil in the BioPro 190, 10 gallons of methanol were added, using a hand pump from a 55-gallon drum to direct the methanol into the appropriate ports of the BioPro 190 (Figures 9 and 10). Next, the potassium hydroxide catalyst was added to the larger (left) methanol port.

The final step was to add 190 mL of sulfuric acid, which enables the FFAs to react with the methanol and form biodiesel, rather than reacting with the catalyst to form soap. Generally, the addition of small amounts of sulfuric acid increases the biodiesel yield.

Figure 9. Methanol ports (black) and sight glasses (vertical glass) of the BioPro 190.
Figure 10. 55-gallon methanol drum with hand pump and hose in larger methanol port.
Biodiesel and Glycerin Separation Stage

Upon completion of the transesterification process, the biodiesel and glycerin by-product settled and separated at the bottom of the BioPro 190, with visible color and viscosity distinctions observed between the biodiesel and glycerin layers. The biodiesel layer remained on top because it is less dense than glycerin. The distinction between the biodiesel and glycerin was observed by locating where the Bio Pro 190 metal stir bar was no longer visible (Figure 11).

The viscosity difference between these liquids is important in the separation stage. The valve on the bottom of the BioPro 190 was opened to separate and drain the glycerin layer into 5-gallon containers until a noticeable viscosity and color change was observed. Glycerin is more viscous than biodiesel, and thus the point at which the liquid drained changed from a thick substance to a more water like liquid indicated all the glycerin had been drained and only biodiesel remained in the BioPro 190.

The observed biodiesel yield from 50 gallons of waste cooking oil (WCO) averaged about 48 gallons. In addition, the volumetric production ratio of biodiesel to glycerin averaged 4:1. Consequently, each batch conversion produced roughly 48 gallons of biodiesel and 12 of gallons glycerin from inputs of 50 gallons WCO and 10 gallons methanol.

Before proceeding to the water wash stage, the biodiesel underwent a simple “27-3” test to ensure full oil-to-biodiesel conversion. The “27-3” test procedure is outlined below:

1. Add 27 mL methanol to a small plastic container with lid.
2. Add 3 mL of biodiesel to methanol and close the lid.
3. Shake the container.

4. The biodiesel passes the “27-3” test if the mixture clears up immediately after being shaken and there is no visible fallout of oil or biodiesel.

5. The biodiesel fails the “27-3” test if the mixture remains cloudy after being shaken, or if any oil or biodiesel is visible in the mixture.

If the biodiesel passed the “27-3” test, then it proceeded to the water wash stage. If the biodiesel failed the “27-3” test,” reasons for incomplete reaction and a re-processing strategy were determined. The most typical reason for an incomplete reaction is insufficient excess catalyst to neutralize the FFAs and additional catalyst must be added to drive the reaction to completion [58].

Figure 11. Separation line between biodiesel (top) and glycerin (bottom) layers indicated where metal stir bar is no longer visible above the 10-gallon mark.
Water Wash Stage

The water wash stage follows the transesterification process and removes residual components within the biodiesel fuel, mainly methanol. Two 55-gallon drums are required for the water wash cycle. The first is filled with 55-gallons of water to provide clean in-flow for the wash cycle. The second is initially kept empty because it serves as the container for the outlet wastewater. With the clean water drum filled, both water drums were positioned next to the BioPro 190 with the inlet and outlet hoses placed in the respective drums (Figure 12). Both water wash hoses were labeled on the back of the BioPro 190 (Figures 13 and 14). The “Water Wash” option on the BioPro 190 was selected, which initiated the 24-hour cycle. All port covers (methanol, oil, and acid) on the BioPro 190 were removed and remained open during the water wash cycle to allow water vapor to escape.

The final step of the water wash stage was the wastewater disposal. The wastewater chemical oxygen demand (COD) was within acceptable levels in relatively small quantities relative to the total wastewater volume for the RIT campus. Thus, it was hand pumped down the drain with sufficient dilution water.
Figure 12. In-flow water drum (left) and outlet wastewater drum (right) for water wash cycle.
**Figure 13.** Inlet port on BioPro 190 for clean water for the water wash stage.

**Figure 14.** Outlet port on BioPro 190 for wastewater to exit during the water wash stage.
Utilization Stage

Once the water wash stage was complete, the finished biodiesel was sent out for external analysis and testing to ensure it met the ASTM quality standards before utilization. By meeting ASTM standards, the biodiesel fuel is suitable for the wide array of applications outlined previously (heating applications, vehicular applications, or electrical generation applications). This thesis focuses on the utilization of biodiesel in heating applications and the subsequent chapters further discuss fuel characterization, emissions tests, lifecycle global warming potential and energy return on investment of this biodiesel, specific to utilization as a heating fuel. The vehicular application of the biodiesel on RIT campus is presented separately [59]. The full waste cooking oil process diagram is outlined in Figure 15.
Figure 15. Full waste cooking oil-to-biodiesel process diagram with collection, transportation, pre-treatment, transesterification, water wash, final fuel, and utilization in residential furnace (left) and lab-scale heating apparatus (right).
Chapter 4: Biodiesel Fuel Property Characterization, Production Cost, and Payback Period

Background

Two successful batches of waste cooking oil biodiesel were produced from the closed loop production process developed as part of the EPA Climate Showcase Communities Grant. Both batches utilized waste cooking oil collected from the Rochester Institute of Technology cafeterias. Overall, the two batches produced consistent quality biodiesel, however, differences arose during the individual production processes, which led to marginal fuel characteristic differences.

Results

Batch 1

Once the oil was collected and pre-treated, a local consultant performed an initial off-site oil titration and calculated the FFA concentration of the waste cooking oil to be 4.42%. About 2 gallons of “water and solids” were drained off from the waste cooking oil in the conical separation tank (Figure 7), but nearly all 2 gallons were later determined to be usable oil. It is believed that the lack of water and solids in the raw WCO was due to the filtering step the university cafeterias employ when changing the cooking oil. Due to the high FFA concentration of the oil, 2,350 g of potassium hydroxide catalyst was used for the transesterification process. The standard 10 gallons of methanol and 190 mL sulfuric acid were also added.

After the transesterification reaction was complete, about 12 gallons of glycerin was separated and drained from the biodiesel. The biodiesel was then subjected to the
“27-3” test and failed. The batch then proceeded to the water wash stage to remove residual methanol and any solids in the biodiesel fuel to attempt to pass the “27-3” test. However, the biodiesel failed the “27-3” test a second time after the water wash stage (Figure 16). To drive the partially reacted oil to complete conversion, an additional 200 g of potassium hydroxide catalyst and 2.5 gallons of methanol were added. The catalyst and methanol were mixed with the incomplete biodiesel using the BioPro 190’s stir option. “Reaction 1” was skipped (only a heat and stir phase) to proceed straight to the transesterification “Reaction 2.” After being re-processed, the biodiesel passed the “27-3” test and a fully converted batch was achieved (Figure 17).

![Image of failed test result](image)

**Figure 16.** The failed 27-3 test from Batch 1 with visible oil accumulation at the bottom.
Figure 17. The failed (left) 27-3 test from the initial reaction and the passed (right) 27-3 test from the re-processed fuel after being shaken.

Once a fully converted batch of biodiesel was produced, samples were sent out for external analysis. Section 4.3.1 and 4.3.2 of American Society for Testing and Materials (ASTM) designation D396-13b state:

4.3.1 - “If biodiesel is a component of any fuel oil, the biodiesel shall meet the requirements of Specification D6751.”

4.3.2 - “Fuel oil containing up to 5 vol% biodiesel shall meet the requirements for the appropriate grade No. 1 or No. 2 fuel as listed in Table 1.”

Thus, a sample of the biodiesel was sent to Bently Tribology Services (Sparks, Nevada) for ASTM Specification D6751 testing to ensure the biodiesel met the required
standards before usage in RIT campus heating or vehicular applications. The key ASTM test results for Batch 1 are displayed in Table 5. The full ASTM D6751 results and the requirements for fuel oil containing up to 5% biodiesel by volume are presented in Appendix A.

Initially, the biodiesel passed all required tests except the carbon residue test due to a testing error. A second sample was provided to Bently Tribology Services for a rerun of the carbon residue test, which resulted in a passing value of 0.05 (wt %). At this point, the RIT biodiesel team had produced biodiesel meeting ASTM standards. Since the biodiesel met the ASTM standards and commercially available fuel oil has to pass ASTM standards before being sold on the market, it was assumed a blend of these fuels would still meet the ASTM requirements. Therefore, the ASTM tests outlined for fuel oils containing up to 5% biodiesel by volume were not specifically conducted with the waste cooking oil derived biodiesel. However, the pour point of a 5% biodiesel heating fuel along with three other blends was obtained because no pour point measurements were completed in the ASTM D6751. Pour point is the temperature at which fuel becomes thick enough it can no longer be poured or pumped. This is an important measurement to understand for heating applications because of the cold conditions where heating systems are located.
Table 5. Key ASTM results for Batch 1.

<table>
<thead>
<tr>
<th>Test Name</th>
<th>ASTM Test Method</th>
<th>Limit</th>
<th>Results</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Glycerin (mass %)</td>
<td>D6584</td>
<td>MAX 0.020</td>
<td>0.000</td>
<td>PASS</td>
</tr>
<tr>
<td>Monoglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.078</td>
<td>N/A</td>
</tr>
<tr>
<td>Diglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.013</td>
<td>N/A</td>
</tr>
<tr>
<td>Triglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.007</td>
<td>N/A</td>
</tr>
<tr>
<td>Total Glycerin (mass %)</td>
<td>D6584</td>
<td>MAX 0.240</td>
<td>0.098</td>
<td>PASS</td>
</tr>
<tr>
<td>Flash Point, Closed Cup (°C)</td>
<td>D93</td>
<td>MIN 93</td>
<td>150</td>
<td>PASS</td>
</tr>
<tr>
<td>TAN (mg KOH/g)</td>
<td>D664</td>
<td>MAX 0.50</td>
<td>0.47</td>
<td>PASS</td>
</tr>
<tr>
<td>Viscosity @ 40°C (cSt)</td>
<td>D445</td>
<td>1.9-6.0</td>
<td>5.00</td>
<td>PASS</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>D2500</td>
<td>N/A</td>
<td>1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

A second sample of biodiesel was sent to Paradigm Environmental Services in Rochester, NY to obtain the lower heating value of the fuel. Lower heating value (LHV) is the amount of the energy released when a fuel is combusted. This measurement allows one to calculate the functional equivalence between the produced biodiesel and traditional diesel fuel to ensure the same function is provided by a blended fuel. The LHV of biodiesel is lower than that of diesel-based heating oil. Thus, more biodiesel is required to provide the equivalent amount of energy output. The LHV of Batch 1 biodiesel measured 16,800 btu/lb or 39.1 MJ/kg. This value falls within the range of the published lower heating value data for biodiesel [12, 13, 22-26]. As expected, the biodiesel lower heating value was lower than the accepted lower heating value for diesel heating oil of 42.9 MJ/kg [12]. Using these lower heating values and measured densities of the fuels, the functional equivalence was calculated using the equations below (Equations 4 – 6).
\[ X_{FO} = LHV_{FO} \times P_{FO} \]  \hspace{1cm} (4)

\( X_{FO} \) = energy content of fuel oil (MJ/gal)

\( LHV_{FO} \) = lower heating value of fuel oil (MJ/kg)

\( P_{FO} \) = density of fuel oil (kg/gal)

\[ X_{BD} = LHV_{BD} \times P_{BD} \]  \hspace{1cm} (5)

\( X_{BD} \) = energy content of biodiesel (MJ/gal)

\( LHV_{BD} \) = lower heating value of biodiesel (MJ/kg)

\( P_{BD} \) = density of biodiesel (kg/gal)

\[ V_{FO} \times X_{FO} = V_{BD} \times X_{BD} \]  \hspace{1cm} (6)

\( V_{FO} \) = volume of fuel oil (gal)

\( V_{BD} \) = volume of biodiesel (gal)

Like traditional diesel heating oil, biodiesel has restricted flow properties in cold conditions. By nature, potential heating applications of biodiesel are located in geographically cold conditions. Thus, it is important to understand the cold flow properties of various biodiesel heating fuels. Two of the most important cold condition measurements are cloud point and pour point. Both of these measurements were obtained at RIT through the use of a cold chamber (Figure 18). Cloud point is the temperature at which the fuel forms cloudy wax crystals and begins to gel. Pour point is the lowest temperature at which the liquid will flow. Cloud point and pour point are less of a concern for heating applications since heating fuel is regularly stored inside, typically in a
basement. In vehicular applications, cloud point and gelling are cause for great concern because the fuel is subjected to outside temperatures.

Figure 18. RIT cold chamber used for cloud point and pour point tests of the biodiesel heating fuels.
Table 6. Cloud point data of biodiesel blends from RIT cafeteria waste cooking oil Batch 1 and Monroe County residential oil Batch 1.

<table>
<thead>
<tr>
<th>Percentage Biodiesel</th>
<th>RIT (°C)</th>
<th>MC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-6</td>
<td>-2</td>
</tr>
<tr>
<td>20</td>
<td>-15</td>
<td>-13</td>
</tr>
<tr>
<td>10</td>
<td>-18</td>
<td>-17</td>
</tr>
<tr>
<td>5</td>
<td>-22</td>
<td>-22</td>
</tr>
</tbody>
</table>

Four 50 mL samples of biodiesel heating fuel were prepared and placed in the cold chamber (Figure 19). The four fuel blends tested were B5, B10, B20, and B50. The number following the B” represents the percentage of the fuel blend composed of biodiesel (e.g. B5 is a 5% biodiesel and 95% heating fuel blend). The temperature of the cold chamber was lowered at a rate of 2°C every 2 minutes using the temperature control. The samples were visually inspected for cloudiness after 1 minute at each new temperature. From the ASTM results in Table 5, the 100% biodiesel had a cloud point of 1°C. Diesel heating fuel has a lower cloud point of -9°C [60]. Thus, it was expected to see increasing cloud points with increasing biodiesel percentages. This trend was observed for the four biodiesel heating fuel samples tested (Figure 20). The cloud point data obtained from the RIT waste cooking oil biodiesel followed the trend in cloud point data from the Monroe County residential waste cooking oil biodiesel in Phase 1 of the EPA Climate Showcase Communities Grant (Table 6). However, the RIT biodiesel displayed improved (i.e., lower) cloud point at a B50 blend.
Figure 19. The biodiesel heating fuel blend samples in the cold chamber used to obtain the cloud point and pour point of the fuels.
Figure 20. Cloud points of Batch 1 blended into B5, B10, B20 and B50 biodiesel heating fuels.

The same procedure was employed to obtain the pour point measurements. However, the fuels were visually inspected for loss of flow rather than cloudiness. Similar to cloud point, higher biodiesel percentages were expected to have higher pour points, and this trend was indeed observed for the four samples tested (Figure 21). Overall, the pour point data obtained closely matched the data from the U.S. National Renewable Energy Laboratory (NREL) (Table 7) [61].
**Figure 21.** Pour points of Batch 1 blended into B5, B10, B20, and B50 biodiesel heating fuels.

**Table 7.** Pour point data obtained from Batch 1 RIT biodiesel and NREL pour point data [61].

<table>
<thead>
<tr>
<th>Percentage Biodiesel</th>
<th>RIT Pour Point (°C)</th>
<th>NREL Pour Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-12</td>
<td>-10</td>
</tr>
<tr>
<td>20</td>
<td>-18</td>
<td>-17</td>
</tr>
<tr>
<td>10</td>
<td>-20</td>
<td>-18</td>
</tr>
<tr>
<td>5</td>
<td>-23</td>
<td>-21</td>
</tr>
</tbody>
</table>
Batch 2

A second batch of biodiesel was produced from RIT’s cafeteria waste cooking oil. Unfortunately, Crossroads, the original partner cafeteria for the EPA project, did not have a full 50-gallon quantity of waste cooking oil available. Only 10 gallons were obtained from Crossroads and just over 40 gallons were taken from three other university cafeterias. Once the oil was collected, it was transported back to the Golisano Institute for Sustainability for the gravity pre-treatment and titration.

An oil titration was independently performed and it was determined that the FFA concentration of the oil was 3.30%. Analogous to Batch 1, 2 gallons of “water and solids” were drained off from the waste cooking oil, but nearly all 2 gallons were usable oil. Again, the relatively low water and solids content was attributed to the filtration during the oil turnover process. The remaining 50 gallons of processable oil were transferred to the BioPro 190 to begin the transesterification stage. However, based on the initially incomplete reaction during Batch 1, two alterations were made to the process. First, an additional 1 hour heat and stir step was completed. This step was added to evaporate dissolved water in the oil and ensure a full conversion to biodiesel. Secondly, based on the relatively high FFA concentration and the unsuccessful first conversion attempt in Batch 1, 200 additional grams of potassium hydroxide were added to reach a total of 2,550 g of catalyst. The standard 10 gallons of methanol and 190mL of sulfuric acid were also added to begin the transesterification process.

After the transesterification stage, 12 gallons of glycerin were separated and drained from the biodiesel. Following the glycerin separation, a “27-3” test was performed on the biodiesel. Like Batch 1, the biodiesel failed this test, which meant the
oil was not fully converted to biodiesel. It was hypothesized that water was still present, despite the addition of a 1-hour heat and stir step. Therefore, before any additional catalyst or methanol were added, a 2-hour heat and stir cycle was performed. After 2-hours time, 200 g of potassium hydroxide (now totaling 2750 g) and 2 gallons of methanol were added. The transesterification reaction was run again by skipping to the BioPro 190’s “Reaction 2.”

Upon completion of “Reaction 2”, about 1 gallon of additional glycerin was drained and the re-processed biodiesel underwent the “27-3” test a second time and passed. At this point, 2 gallons of unwashed biodiesel were drained off for the lab scale heating tests because the effect on the combustion emissions of unwashed biodiesel compared to the energy offset by eliminating the water wash cycle was an important research question to answer (described further below).

The remaining biodiesel proceeded to the water wash stage. However, due to operator error, the BioPro 190 port covers were not removed. This procedural error did not allow water vapor to escape during the water wash stage and led to water accumulation within the fuel. Therefore, the biodiesel was subjected to an 8-hour heat and stir cycle to evaporate the substantial amount of water in the fuel. After the extended heat and stir cycle, the biodiesel was again subjected to the “27-3” test and passed. The Batch 2 biodiesel color varied slightly from Batch 1 (Figure 22). An additional water was cycle was performed to remove the cloudy appearance of the fuel. The port covers on the BioPro 190 were opened properly and removed during this water wash cycle.
After the second water wash cycle, samples of the biodiesel were sent out for external analysis identical to Batch 1. A sample was sent to Bently Tribology Services for ASTM specification D6751 testing to ensure this biodiesel also met the required standards before utilizing the fuel in campus applications. The key ASTM results for Batch 2 are presented in Table 8. The full ASTM D6751 results are presented in Appendix A.

The Batch 2 biodiesel initially failed the carbon residue test due to the identical testing error in Batch 1. A carbon residue test rerun was completed and Tribology Services notified RIT the most common cause of excess carbon residues leading to a
failed carbon residue is a high amount of total glycerin [62, 63]. Given the fact that the total glycerin in the Batch 2 biodiesel was substantially below the maximum, there is no reason for a carbon residue test failure.

In addition, Batch 2 failed the total acid number (TAN) test. TAN is an indicator of acidity and is measured in terms of the mass of potassium hydroxide required to neutralize the acids in 1 g of oil. In attempt to lower the TAN value, a third and final water wash cycle was completed. Even with this third wash, the TAN value did not change and therefore, still exceeded the 0.50 mg KOH/g limit. Despite failing the TAN test a second time, work proceeded to move forward with Batch 2 utilization. It was later determined that there was an error in the Tribology Services measurement, and the TAN test was indeed passed for Batch 2.

### Table 8. The key ASTM D6751 results for Batch 2.

<table>
<thead>
<tr>
<th>Test Name</th>
<th>ASTM Test Method</th>
<th>Limit</th>
<th>Results</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Glycerin (mass %)</td>
<td>D6584</td>
<td>MAX 0.020</td>
<td>0.002</td>
<td>PASS</td>
</tr>
<tr>
<td>Monoglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.061</td>
<td>N/A</td>
</tr>
<tr>
<td>Diglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.011</td>
<td>N/A</td>
</tr>
<tr>
<td>Triglycerides (mass %)</td>
<td>D6584</td>
<td>N/A</td>
<td>0.000</td>
<td>N/A</td>
</tr>
<tr>
<td>Total Glycerin (mass %)</td>
<td>D6584</td>
<td>MAX 0.240</td>
<td>0.074</td>
<td>PASS</td>
</tr>
<tr>
<td>Flash Point, Closed Cup (°C)</td>
<td>D93</td>
<td>MIN 93</td>
<td>136.5</td>
<td>PASS</td>
</tr>
<tr>
<td>TAN (mg KOH/g)</td>
<td>D664</td>
<td>MAX 0.50</td>
<td>0.65</td>
<td>FAIL</td>
</tr>
<tr>
<td>Viscosity @ 40°C (cSt)</td>
<td>D445</td>
<td>1.9-6.0</td>
<td>5.90</td>
<td>PASS</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>D2500</td>
<td>N/A</td>
<td>1</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Another sample of biodiesel from Batch 2 was sent to Paradigm Environmental Services in Rochester, NY to obtain the lower heating value of the fuel. The lower heating value of this batch of biodiesel was 15,900 Btu/lb or 37.0 MJ/kg. This was slightly lower than the lower heating value of the first batch, which was 39.1 MJ/kg. These two lower heating values were averaged to 38.05 MJ/kg and then used to update the functional equivalence calculation using Equations 4-6. According to the calculation, the energy content of 1 gallon of biodiesel is equal to that of 0.941 gallons of diesel heating oil. The full calculation is provided in Appendix A.

Identical to Batch 1, cloud point and pour point measurements of the four biodiesel heating fuel blends were obtained through the use of a cold chamber. The same procedure used for the Batch 1 tests was employed for batch 2. The temperature of the cold chamber was lowered at a rate of 2°C every 2 minutes using the unit’s automatic temperature control. In the cloud point tests, the samples were visually inspected for cloudiness after 1 minute at each new temperature. The Batch 2 cloud point data were nearly identical to Batch 1 and the Monroe County residential oil biodiesel cloud point data (Table 9). As expected, the cloud point of biodiesel fuel blends increased with higher biodiesel percentages (Figure 23). At a B50 blend, there some evidence that the Monroe County biodiesel samples had poorer cloud point performance.
Table 9. Cloud point data obtained from RIT Batches 1 and 2 and Monroe County (MC) Batches 1 and 2.

<table>
<thead>
<tr>
<th>Percentage Biodiesel</th>
<th>RIT 1 (°C)</th>
<th>RIT 2 (°C)</th>
<th>MC 1 (°C)</th>
<th>MC 2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-6</td>
<td>-6</td>
<td>-2</td>
<td>-4</td>
</tr>
<tr>
<td>20</td>
<td>-15</td>
<td>-14</td>
<td>-13</td>
<td>-15</td>
</tr>
<tr>
<td>10</td>
<td>-18</td>
<td>-17</td>
<td>-17</td>
<td>-19</td>
</tr>
<tr>
<td>5</td>
<td>-22</td>
<td>-22</td>
<td>-22</td>
<td>-22</td>
</tr>
</tbody>
</table>

Table 10. Pour point data obtained from RIT Batches 1 and 2 and NREL published pour point data [61].

<table>
<thead>
<tr>
<th>Percentage Biodiesel</th>
<th>RIT 1 (°C)</th>
<th>RIT 2 (°C)</th>
<th>NREL (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-12</td>
<td>-10</td>
<td>-10</td>
</tr>
<tr>
<td>20</td>
<td>-18</td>
<td>-17</td>
<td>-17</td>
</tr>
<tr>
<td>10</td>
<td>-20</td>
<td>-22</td>
<td>-18</td>
</tr>
<tr>
<td>5</td>
<td>-23</td>
<td>-24</td>
<td>-21</td>
</tr>
</tbody>
</table>

Analogous to Batch 1, the same procedure was employed for the pour point measurements. However, the fuels were visually inspected for loss of flow rather than cloudiness. Similar to cloud point and Batch 1 trends, higher biodiesel percentages were expected to have higher pour points, and this trend was again observed for Batch 2 (Figure 24). Overall, the Batch 2 pour point data closely mirrored Batch 1 and NREL pour point data (Table 10) [61].
Figure 23. Cloud point data obtained from RIT Batches 1 and 2 and Monroe County (MC) Batches 1 and 2.

Figure 24. Pour point data obtained from RIT Batches 1 and 2 with published pour point data from NREL [61].
Waste Cooking Oil Biodiesel Production Cost per gallon

The cost per gallon of the produced biodiesel was calculated based upon the individual costs of the methanol, KOH, sulfuric acid, electricity inputs and assumed wages. At the small volumes needed to produce Batches 1 and 2, methanol was purchased for $4.09/gallon, KOH for $0.005/g and sulfuric acid for $0.0684/mL. Given each batch requires 10 gallons of methanol, 2550 g of KOH and 190 mL of sulfuric acid the cost per batch for each input equaled $40.91 for methanol, $13.02 for KOH, and $13.00 for sulfuric acid. An electric rate of $0.09/kWh was assumed based on the delivered cost of electricity paid by RIT. The total electricity required per batch totaled 34.2 kWh, which equated to a cost of $3.08/batch. Lastly, an undergraduate co-op wage rate of $12.50/hour and 6 man-hours of total work were assumed, resulting in a labor cost of $75/batch. Each cost per batch value was divided by the assumed per batch biodiesel yield of 48 gallons to obtain a cost per gallon for each input. These values were summed to obtain an overall cost per gallon of biodiesel to equal $3.02 (Table 11). As of March 2014, the U.S. residential heating oil price was $4.12/gallon and as of January 2014 the U.S. average prices for B20 and B100 were $3.97 and $4.28, respectively [64, 65]. Thus, the biodiesel produced is economically competitive with current fuels.

However, the assumption of 6 labor hours may be a best-case scenario, and if this input is increased to 8 hours, the production cost increases to $3.54/gallon. Additionally, these production costs assume no cost to obtain the waste cooking oil, as Baker Commodities donated it. Including the $0.50/gallon price RIT sells the waste cooking oil for as lost revenue increases the production cost to $3.52 (6 hours of labor) or $4.04 (8 hours of labor).
Table 11. Costs of biodiesel production inputs and cost per gallon.

<table>
<thead>
<tr>
<th>Input</th>
<th>Cost</th>
<th>Amount/batch</th>
<th>Cost/batch</th>
<th>Cost/gallon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>$4.09/gallon</td>
<td>10 gallons</td>
<td>$40.90</td>
<td>$0.85</td>
</tr>
<tr>
<td>KOH</td>
<td>$0.005/grams</td>
<td>2550 grams</td>
<td>$13.02</td>
<td>$0.27</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>$0.0684/mL</td>
<td>190 mL</td>
<td>$13.00</td>
<td>$0.27</td>
</tr>
<tr>
<td>Electricity</td>
<td>$0.09/kWh</td>
<td>34.2 kWh</td>
<td>$3.08</td>
<td>$0.06</td>
</tr>
<tr>
<td>Labor</td>
<td>$12.50/hour</td>
<td>6 hours</td>
<td>$75.00</td>
<td>$1.56</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$145.00</strong></td>
<td></td>
<td><strong>$3.02</strong></td>
<td></td>
</tr>
</tbody>
</table>

Payback period

The payback period for the WCO-to-biodiesel production process is presented graphically in Figure 25 and outlined in detail in Table 12. The payback period calculations are presented in Equations 7-11. An assumed WCO volume per week was converted to annual biodiesel production volume assuming a 96% conversion rate, 50 annual working weeks, and the functional unit of 0.941 for comparison to diesel fuel oil offsets (Equation 7). The annual biodiesel production volume was multiplied by $4.12/gal price of diesel fuel oil to obtain the fuel oil costs avoided (Equation 8). The annual biodiesel production cost was calculated with the previously calculated production costs of $3.02/gallon and $3.54/gallon (Equation 9). The annual heating fuel savings were determined by subtracting the annual biodiesel production costs from the fuel oil costs (Equation 10). Finally, the payback period in years was calculated by dividing the assumed capital costs of the BioPro 190 and other equipment reported by previous work (Equation 11) [51]. The payback period was calculated to be 4.6 years for 50 gallons of WCO per week (2,258 gallons biodiesel annually). The same method was applied to 100,
150, 200, and 250 gallons of WCO per week and payback periods of 2.3, 1.2, and 0.9 years were calculated, respectively.

\[
\frac{50 \text{ gals WCO}}{\text{week}} \times \frac{0.96 \text{ gals biodiesel}}{1 \text{ gal WCO}} \times \frac{50 \text{ weeks}}{\text{year}} \times 0.941 = 2,258 \text{ gals biodiesel/year} \quad (7)
\]

\[
2,258 \frac{\text{gals}}{\text{year}} \times \frac{$4.12}{\text{gal}} = $9,304.61 \text{ fuel oil savings/year} \quad (8)
\]

\[
\frac{2,258 \text{ gals biodiesel}}{\text{year}} \times \frac{$3.02}{\text{gal}} = $6,820.37/\text{year} \quad (9)
\]

\[
$9,304.61 - $6,820.37 = $2,484.24/\text{year} \quad (10)
\]

\[
\frac{$11,443.00}{$2,484.24} = 4.6 \text{ years} \quad (11)
\]

Table 12. Payback period of WCO-to-biodiesel production process.

<table>
<thead>
<tr>
<th>WCO (gals/wk)</th>
<th>Biodiesel (gals/yr)</th>
<th>Fuel costs ($/yr)</th>
<th>Production cost ($/yr)</th>
<th>Fuel savings ($/yr)</th>
<th>Payback Period (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2,400</td>
<td>$9,304.61</td>
<td>$7,248.00</td>
<td>$2,056.61</td>
<td>5.6</td>
</tr>
<tr>
<td>100</td>
<td>4,800</td>
<td>$18,609.22</td>
<td>$14,496.00</td>
<td>$4,113.22</td>
<td>2.8</td>
</tr>
<tr>
<td>150</td>
<td>9,600</td>
<td>$37,218.43</td>
<td>$28,992.00</td>
<td>$8,226.43</td>
<td>1.4</td>
</tr>
<tr>
<td>200</td>
<td>12,000</td>
<td>$46,523.04</td>
<td>$36,240.00</td>
<td>$10,283.04</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Figure 25. Payback period of WCO-to-biodiesel production as a function of annual WCO biodiesel production.

Overall, the payback periods of WCO-to-biodiesel production are not encouraging. Biodiesel production volumes over 10,000 gallons/year require an additional BioPro unit, which would increase the initial capital cost. Thus, WCO-to-biodiesel programs will not likely be pursued solely for economic benefits, but for a balance of environmental, economic, and social impacts, through greenhouse gas emissions reductions, energy avoidance, and educational opportunities for students.
Chapter 5: Biodiesel Heating Application Emissions Testing

Background

New York State’s residential sector directly contributes to greenhouse gas emissions. As mentioned previously, fuel oil is the second most common heating fuel in New York State and is the main heating fuel in 27.5% of homes [66]. Thus, there is substantial potential to utilize domestically produced biodiesel as a heating fuel substitute to reduce greenhouse gas emissions.

The following sections describe residential furnace and lab-scale testing of the biodiesel produced from RIT waste cooking oil and the associated emission impacts.

Methods

Experimental Fuels

Several biodiesel heating fuel blends were tested utilizing the biodiesel produced from RIT cafeteria waste cooking oil. The tested fuels included commercially available fuel oil (No. 2 diesel) as a control, and heating fuel blends ranging from B5 to B50 for both water washed and non-water washed biodiesel. The non-water washed biodiesel was tested to examine if a trade-off exists between emissions and the avoided water wash energy requirement. The number following the “B” in the fuel blends represents the percentage by volume of biodiesel the fuel blend contains (e.g. B5 is 5% biodiesel and 95% diesel fuel oil). Two separate rounds of testing with two distinct procedures were executed in an attempt to fully understand the emissions results. A third round of testing was conducted on an experimental apparatus designed and fabricated in-house with no
heat exchanger, in an attempt to exaggerate emissions differences with varying biodiesel content.

**Round 1 Description**

Two sets of nine 500 mL fuel samples were prepared for Round 1 testing. The fuels were tested in the same order for both sets of Round 1 experiments, as outlined in Table 13. Both water washed and non-water washed biodiesel samples were tested. The samples were prepared on a volume basis. For example, the B5 fuel samples consisted of 25 mL biodiesel and 475 mL fuel oil. Both sets of the nine prepared fuel samples are illustrated in Figure 26.

![Figure 26. The prepared biodiesel heating fuel samples before Round 1 emissions tests.](image)
Table 13. Round 1 emissions testing order of biodiesel heating fuel blends (500 mL samples).

<table>
<thead>
<tr>
<th>Set</th>
<th>Test Order of Fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fuel oil, B10 WW, B5 WW, B20 WW, B50 WW, B10 NWW, B5 NWW, B20 NWW, B50 NWW</td>
</tr>
<tr>
<td>2</td>
<td>Fuel oil, B10 WW, B5 WW, B20 WW, B50 WW, B10 NWW, B5 NWW, B20 NWW, B50 NWW</td>
</tr>
</tbody>
</table>

WW = water washed biodiesel; NWW = non-water washed biodiesel

Round 2 Description

The second round of testing utilized larger volume fuel samples as a result of initial fuel mixing concerns in the fuel line with Round 1. It was assumed longer volume fuel samples would provide enough time for the prior fuel blend to completely burn off, and the emissions would represent the desired fuel blend. One set of nine 1L fuel samples were prepared for this second round of testing. The B10 fuel blend was omitted from this round because the goal was to examine the impacts of larger variations in biodiesel volumes. The testing order for Round 2 is outlined in Table 14.

Table 14. Round 2 emissions testing order of biodiesel heating fuel blends (1L samples).

<table>
<thead>
<tr>
<th>Set</th>
<th>Test Order of Fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B20 WW, B5 WW, B50 WW, B20 NWW, B5 NWW, B50 NWW</td>
</tr>
</tbody>
</table>

WW = water washed biodiesel; NWW = non-water washed biodiesel
**Furnace and Burner Unit**

A Thermo Pride furnace (OL5-85, Thermo Pride Products, North Judson, IN) was employed for Round 1 and Round 2 combustion tests (Figure 27). The furnace was equipped with a Thermo Pride Model “AF” series oil burner (Figure 28). The nozzle in this burner is 0.60x80H, where the first figure is the fuel flow rate in gallons per hour, and the second value designates the nozzle spray angle (80°) and pattern. The “H” denotes the nozzle atomizes and sprays the fuel in a hollow cone pattern. This nozzle is smaller than the Thermo Pride standard 0.75x80H nozzle, but achieves the same firing rate because the burner pump pressure is pre-set to a higher value of 145 psi (1,000 kPa). The burner had an excess air control with an arbitrary number scale ranging from 0-10. Lower numbers on the control minimize excess air, which increases overall efficiency. The excess air setting remained at “3” throughout the testing.

![Figure 27. Thermo Pride OL5-85 furnace used for Round 1 and 2 emissions tests.](image-url)
Figure 28. Thermo Pride AF series oil burner used for Round 1 and 2 emissions tests.
**Fuel Delivery System**

A fuel delivery system was designed specifically for the experimental sequences. The fuel tank was designed to mimic an intravenous (IV) drip to ensure enough head pressure for fuel flow and enable direct visual determination of the fuel flow rate. An inverted 1L polyethylene bottle acted as the fuel tank. A threaded fuel line adapter was fabricated and attached to the bottom of the bottle and connected to a ball valve to control fuel flow (Figure 29). The main fuel line to the burner was disconnected at the burner pump and the specially-designed fuel tank was connected to the burner with a clear polyethylene hose serving as the fuel line (Figure 30). It was determined prior to testing that this hose material is capable with biodiesel fuel blends.

![Figure 29](image_url). Fuel tank designed specifically small volume tests with 100mL markings and fuel line adapter connecting to a ball valve.
Figure 30. Designed fuel tank with clear polyethylene fuel line connected with hose clamps to the Thermo Pride burner.

Round 3 Description

In an attempt to exaggerate any emissions variations among the biodiesel blends, a third round of emission testing was conducted outdoors in an experimental set up with no heat exchanger, unlike the normal configuration in a residential furnace system. A Beckett NX oil burner was utilized for these tests and mounted vertically upward into the
bottom of an in-house fabricated Inconel combustion chamber (Figure 31). A horizontal analyzer port allowed for exhaust sampling for emissions measurements. Black exhaust piping was used to block all natural light from reaching the cad cell (control made from cadmium sulfide that changes resistance in response to light) in the burner air tube, which does not allow ignition when detecting light.

**Combustion gas analyzer**

A Snap-on Flexible Gas Analyzer (FGA) was used to measure the flue gas composition of the Thermo Pride furnace exhaust in Rounds 1 and 2 and the Beckett NX oil burner in Round 3 (Figure 32). In Rounds 1 and 2, the FGA emissions probe was placed in a small hole that was drilled in the Thermo Pride furnace exhaust ducting and secured onto the furnace body (Figure 33). In Round 3, the FGA emissions probe was connected to a stainless steel sample tube, and was fed through the horizontal sample port in the side of the Inconel combustion chamber (Figure 31). The sample tube extended down into the combustion so that the upstream end was approximately 10 cm from the top of the flame during burner operation. The FGA performance ranges, accuracy and resolution for each gas constituent are outlined in Table 15.

**Table 15.** Flexible Gas Analyzer (FGA) performance ranges, accuracy and resolution.

<table>
<thead>
<tr>
<th>Gas Constituent</th>
<th>Performance Range</th>
<th>Accuracy</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0-30,000 ppm</td>
<td>+/-3%</td>
<td>1 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>0-15%</td>
<td>+/-3%</td>
<td>0.01%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0-20%</td>
<td>+/-3%</td>
<td>0.01%</td>
</tr>
<tr>
<td>O₂</td>
<td>0-25%</td>
<td>+/-5%</td>
<td>0.01%</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0-5,000 ppm</td>
<td>+/-4%</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>
Figure 31. Round 3 experimental set up with specially-designed fuel tank, Inconel combustion chamber, horizontal analyzer port, and black exhaust piping.
Figure 32. Snap-on Flexible Gas Analyzer (FGA) used in emissions tests.
Figure 33. The FGA emissions probe (black wand) in the Thermo Pride furnace exhaust system.

Round 1 Testing Procedure

Water washed and non-water washed biodiesel samples were blended with No. 2 fuel oil prior to testing to prepare 500 mL fuel blends of B5, B10, B20, and B50. The B50 was selected to be the upper limit because published studies reported flame ignition difficulty with blends above 50% biodiesel [19, 47]. In addition, oil burners are currently warranted to a maximum blend of B5 and it was believed that exceeding B50 posed an unknown and unacceptable risk to burner durability.
In both sets of tests in Round 1, the No. 2 fuel oil control was tested first and followed by the various biodiesel heating fuel blends. The test order was identical for both sets of fuel samples and the testing was a continuous process (Table 13), i.e., the furnace was not turned off between samples. Once poured into the fuel tank, each fuel blend was combusted for 3 minutes before a 1-minute emissions sample was recorded. After the emissions data were saved, the FGA emissions probe was removed from the exhaust system and a zero calibration was performed. Once zeroed, the FGA emissions probe was returned to the drilled hole in the exhaust system. This ensured the emissions readings were accurate throughout each test, and eliminated the risk of an instrument-initiated zeroing sequence during a measurement. Once the current fuel blend was consumed, the next fuel blend was poured into the fuel tank and again a 1-minute emissions sample was taken after 3 minutes had passed.

**Round 2 Testing Procedure**

Round 2 was also conducted as a continuous testing process. Two 500 mL fuel samples were prepared for each fuel blend tested. The first 500 mL was added and allowed to burn completely. Once the first 500 mL was consumed, the next 500 mL was added and combusted for 3 minutes before taking two separate 1-minute emissions readings. Once the total 1L of fuel was consumed, the next 500 mL fuel blend was added and allowed to burn completely before adding the additional 500 mL. The FGA was zero calibrated after each fuel blend to ensure accurate emissions readings. The first 500 mL of each fuel blend was allowed to burn completely to ensure no mixing between fuel
blends still remained when emissions data were recorded. The testing order is presented in Table 14.

Round 3 Testing Procedure

The test order for Round 3 is outlined in Table 16. Similar to Round 1 and Round 2 testing, 500 mL fuel samples were prepared prior to testing. The same specifically-designed fuel tank design with bottle was utilized in this round. However, instead of a polyethylene hose as a fuel line, a copper fuel line was connected to the ball valve attached to the bottle. This copper fuel line connected to a flexible fuel line and ultimately a quick disconnect at the burner pump (Figure 34). The burner was turned on by initiating a call for heat by turning on a switch on the burner. Once a flame was established, the burner was allowed to run for a 5-minute period to achieve flame stability. After the 5-minute stabilization period, a 1-minute emissions sample was taken and saved. The FGA was zeroed after each emissions test and before the next emissions sampling.
**Figure 34.** Copper fuel from the specifically-designed fuel tank connecting to flexible fuel line with quick disconnect to the Beckett NX oil burner.

**Table 16.** Round 3 emissions testing order of biodiesel heating fuel blends.

<table>
<thead>
<tr>
<th>Set</th>
<th>Test Order of Fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fuel oil, B5 WW, B5 NWW, B10 WW, B10 NWW, B20 WW, B20 NWW, B50 WW, B50 NWW</td>
</tr>
</tbody>
</table>

*WW = water washed biodiesel; NWW = non-water washed biodiesel*
Results

The extensive experimental results from the furnace burner experiments are presented in this section in a number of different ways. For Rounds 1, 2 and 3, both temporally-varying and time-averaged emissions data are presented for the various heating fuel blends, derived from both water washed and non-water washed biodiesel. The tabulated time-averaged data is provided in Appendix B.

Round 1

The CO₂ emissions data for Round 1 Set 2 are relatively constant over time (Figure 35). The water washed B5 and non-water washed B50 samples displayed the most variation over the 1-minute emissions sample, with both increasing about 0.2% from initial CO₂ levels. The overall trend of the Round 1 Set 2 CO₂ data appears to be decreasing CO₂ with increasing biodiesel percentages. The two B5 CO₂ data were the highest and the non-water washed B50 data was the lowest. The remainder of the fuel samples, including water washed B50, all were within a narrow band.
Figure 35. Round 1 Set 2 temporally-varying CO₂ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

The overall Round 1 (Set 1 and Set 2) time-averaged CO₂ emissions do not show a trend as a function of biodiesel content (Figure 36). As the water washed biodiesel fraction increases, CO₂ appears to decrease at first, but then increases at B50. However, the emissions of the water washed blends are comparable to the diesel heating fuel baseline (Figure 37), and the water washed CO₂ data are all within the 3% accuracy band of the FGA unit. As the non-water washed biodiesel fraction increases, CO₂ increases slightly, but decreases at B50. The non-water washed fuel samples are comparable to the diesel heating fuel baseline, except B50 (Figure 37). However, despite being the lowest overall CO₂ level, the non-water washed B50 data are within the 3% accuracy band of the
FGA unit. Because of the overlapping uncertainty bands, these results generally show little if any effect of biodiesel content on CO₂ emission level.

Figure 36. Round 1 time-averaged CO₂ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 3% FGA CO₂ accuracy).

Figure 37. Round 1 average CO₂ data as a function of biodiesel fraction (% volume) (error bars = 3% FGA CO₂ accuracy).
Figure 38. Round 1 Set 2 temporally-varying O₂ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

Similar to CO₂, the Round 1 Set 2 O₂ emissions data are relatively constant over time and the non-water washed B50 fuel samples fluctuated the most during the 1-minute emissions sample (Figure 38). Both B5 fuels emitted the least O₂ and the non-water washed B50 fuel emitted the highest. The water washed B50 fuel sample falls on the upper end of the narrow band of data. This O₂ increase with increasing biodiesel volume is expected because the molecular formula of biodiesel contains some oxygen, while that of conventional petroleum diesel fuel does not (Equations 12-13) [12, 67].

\begin{align*}
\text{Biodiesel molecular formula range: } & C_{15}H_{28}O_2 - C_{25}H_{48}O_2 & (12) \\
\text{No.2 diesel fuel oil: } & C_8H_{18} - C_{25}H_{52} & (13)
\end{align*}
The overall average O$_2$ emissions data show no distinct trend in relation to biodiesel volume (Figure 39). The water washed biodiesel fuel samples show an O$_2$ increase from B5 to B10, but blends higher than B10 show a decrease in O$_2$ emissions. The non-water washed biodiesel fuel samples show a decrease in O$_2$ until B50. Both water washed and non-water washed biodiesel fuel samples show O$_2$ emission results comparable to the diesel fuel oil baseline, with the exception of the non-water washed B50 (Figure 40). All of the O$_2$ emissions data are within the 5% accuracy band of the FGA unit.

**Figure 39.** Round 1 time-averaged O$_2$ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 5% FGA O$_2$ accuracy).
Figure 40. Round 1 average O\textsubscript{2} data as a function of biodiesel fraction (% volume) (error bars = 5\% FGA O\textsubscript{2} accuracy).

The Set 2 NO\textsubscript{X} emissions appear to be the most variable over time within Round 1 (Figure 41). Note that the seemingly binary response is a result of the 1-ppm instrument resolution. The water washed B5 and B50 fuel samples emitted the highest NO\textsubscript{X} levels, while the non-water washed B50 emitted the lowest levels. The water washed B5 was initially in the middle of the reoccurring tight band of data, but increased over the course of the 1-minute emissions reading.

The time-averaged emissions display a general increase in NO\textsubscript{X} with increasing biodiesel volume (Figure 42). The water washed biodiesel fuels generally increase, with the exception of B10. The non-water washed biodiesel fuel increase until B50. Most of the NO\textsubscript{X} data are within the 4\% accuracy band of the FGA unit, except for the water washed B50 fuel sample. Despite these relatively small inconsistencies, there is a general trend of increasing NO\textsubscript{X} levels with increasing biodiesel volumes. Both water washed
and non-water washed fuels show an increase in NO\textsubscript{X} compared to the diesel fuel oil baseline (Figure 43).

**Figure 41.** Round 1 Set 2 temporally-varying NO\textsubscript{X} emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.
**Figure 42.** Round 1 time-averaged NO\textsubscript{X} data for water washed and non-water washed biodiesel heating fuel blends (error bars = 4% FGA NO\textsubscript{X} accuracy).

**Figure 43.** Round 1 average NO\textsubscript{X} emissions data as a function of biodiesel fraction (%) volume (error bars = 4% FGA NO\textsubscript{X} accuracy).

**Round 2**

Round 2 displayed consistent CO\textsubscript{2} emissions over time (Figure 44). The non-water washed B50 fuel sample had the most variability, but was still within the range of
the other data. The water washed B5 data were the highest and water washed B20 was the lowest. Compared to Round 1 (500 mL fuel samples) data, Round 2 (1L fuel samples) data shows a wider range of CO₂. However, a distinct overall trend is again not visible (Figure 45). For the water washed fuels, CO₂ decreased from B5 to B20, but increased from B20 to B50. The water washed B5 and B20 CO₂ results fall outside of the manufacturer’s specified +/-3% accuracy band as a result of a testing procedure deviation. During the B5 fuel test, a “low flow” error occurred due to condensation and water accumulation within the FGA emissions analyzer. This accumulation of water led to the low flow of emission gas and is believed to be reason for this result. Despite the initial experimental difficulties of Round 2, the associated B50 CO₂ emissions fall within the range of Round 1 results.

![Figure 44. Round 2 temporally-varying CO₂ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.](image-url)
Figure 45. Round 2 time-averaged CO$_2$ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 3% FGA CO$_2$ accuracy).

Figure 46. Round 2 average CO$_2$ emissions data as a function of biodiesel fraction (% volume) (error bars = 3% FGA CO$_2$ accuracy).

The Round 2 CO$_2$ emissions data are comparable to the diesel fuel oil baseline, excluding the water washed B5 and B20 as a result of experimental difficulties (Figure 46). The non-water washed fuel samples remain relatively constant with increasing
biodiesel volumes. It has been reported that similar CO$_2$ and O$_2$ emissions levels indicate good control of burner excess air conditions and consistent combustion [19].

![Figure 47](image.png)

**Figure 47.** Round 2 temporally-varying O$_2$ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

Round O$_2$ emissions data remained relatively consistent over the 1-minute emissions sampling, again with the exception of non-water washed B50 (Figure 47). Similar to Round 1, the water washed B5 fuel sample was the lowest. However, Round 2 results show water washed B20 be the highest. Again, the experimental difficulties are believed to have contributed error in both of these measurements. Excluding the data for water washed B5 and B20, the Round 2 O$_2$ data appears to be relatively consistent over time, with the non-water washed B50 fuel averaging the highest O$_2$ emissions.
The Round 2 time-averaged O$_2$ data again show no distinct trend as a function of biodiesel content, and support the consistent O$_2$ emissions found in Round 1 (Figure 48). The non-water washed fuel O$_2$ data all fall within the 5% accuracy band of the FGA unit. The water washed B50 fuel is also within the range of Round 1 B50 data and the 5% accuracy band of the Round 2 non-water washed fuel samples.

**Figure 48.** Round 2 time-averaged O$_2$ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 5% FGA O$_2$ accuracy).

**Figure 49.** Round 2 average O$_2$ emissions data as a function of biodiesel fraction (% volume) (error bars = 5% FGA O$_2$ accuracy).
Similar to CO$_2$, the O$_2$ data is comparable to the diesel fuel oil baseline and does not widely varying (Figure 49). As discussed in the CO$_2$ results, similar O$_2$ emissions between diesel fuel oil and biodiesel blends indicates good control of burner excess air conditions and consistent combustion.

**Figure 50.** Round 2 temporally-varying NO$_X$ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

Analogous to Round 1, Round 2 NO$_X$ are the most variable over time (Figure 50). Disregarding the water washed B20 fuel sample due to experimental difficulties, the NO$_X$ data all fall within about a 15 ppm band. The water washed B50 fuel sample was the highest and the non-water washed B5 fuel sample the lowest. The non-water washed B50 fuel fluctuated substantially, which may indicate inconsistent combustion, but the fluctuations remain within the range of the other data.
Unlike Round 1, the time-averaged Round 2 NOₓ data does not show a slight upward trend (Figure 51). The non-water washed fuel samples and water washed B50 show NOₓ emissions to be relatively consistent with increasing biodiesel volumes. In comparison to the diesel fuel oil baseline, the averaged Round 2 NOx data does display a slight increase increasing biodiesel content (Figure 52).

**Figure 51.** Round 2 time-averaged NOₓ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 4% FGA NOₓ accuracy).

**Figure 52.** Round 2 average NOₓ emissions data as a function of biodiesel fraction (% volume) (error bars = 4% FGA NOₓ accuracy).
Round 3

There were no detectable hydrocarbon (HC) emissions in Round 1 or 2, therefore, no HC emission results were reported. This may be due to the presence of a heat exchanger (which facilitates the space heating function of the furnace), which likely causes HC condensation, deposition, and the familiar “soot” build-up over time. However, Round 3 tests were conducted without a heat exchanger, and the results show substantial emissions of HC, but with no monotonic trends (Figure 53). The water washed data appear to decrease from B5 to B10, and then increase to over 150 ppm for a B50 blend. The non-water washed data show a maximum of about 100 ppm at B10, but then decrease to approximately 70 ppm at B20 and B50.

![Figure 53](image-url)

**Figure 53.** Round 3 temporally-varying HC emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.
The non-water washed biodiesel contains residual methanol, which the water wash cycle removed from the water washed biodiesel. It has been reported that methanol blended diesel fuels show decreased HC and increased NO$_x$ emissions compared to diesel in vehicle applications, due to higher cylinder temperatures allowing the fuel to react easier with oxygen and the additional oxygen content of the alcohol enhances NO$_x$ formation [68, 69]. Compared to diesel fuel oil, there was an average decrease in HC emissions of approximately 45%, 35%, 57%, and 55% for B5, B10, B20 and B50 respectively, for non-water washed biodiesel. Although there is not a monotonic trend, the expected HC decrease with a methanol-containing fuel was observed (Figures 54 and 55).

**Figure 54.** Round 3 time-averaged HC data for water washed and non-water washed biodiesel heating fuel blends (error bars = 3% FGA HC accuracy).
**Figure 55.** Round 3 average HC emissions data as a function of biodiesel fraction (% volume) (error bars = 3% FGA HC accuracy).

**Figure 56.** Round 3 temporally-varying CO$_2$ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.
The Round 3 CO₂ emissions data show water washed B5 and non-water washed B50 to have the highest and lowest CO₂ emissions, respectively (Figure 56). The water washed data decrease from B5 to B10, and then increase to about 3.9% for a B50 blend (Figure 57). The non-water washed data show an overall decrease with a maximum of 3.86% at B5 and 3.64% at B50. Compared to diesel fuel oil, both water washed and non-water washed data show a CO₂ decrease with increasing biodiesel volumes (Figure 58). The water washed data show an averaged decrease of 7.9%, 5.3%, and 2.5% for B10, B20, and B50, respectively. B5 showed a 1.2% increase in CO₂ emissions. The non-water data had a more distinct decreasing trend with averaged decreases of 3.9%, 8.0%, 7.0%, and 9.5% for B5, B10, B20, and B50, respectively.

![Figure 57](image)

**Figure 57.** Round 3 time-averaged CO₂ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 3% FGA CO₂ accuracy).
Figure 58. Round 3 average CO\textsubscript{2} emissions data as a function of biodiesel fraction (% volume) (error bars = 3% FGA CO\textsubscript{2} accuracy).

The Round 3 O\textsubscript{2} data show non-water washed B50 and water washed B5 to be highest and lowest O\textsubscript{2} data, respectively (Figure 59). The non-water wash B20 sample increases to the non-water washed B50 data. This may be a result of the methanol content in the non-water washed biodiesel, especially since these two fuel samples have the largest volume of non-water washed biodiesel.

The water washed data show a slight increase in O\textsubscript{2} with increasing biodiesel volumes, which can be attributed to the increasing oxygen content with increasing biodiesel volumes. The non-water washed data show a clear upward trend from 15.7\% for B5 up to 16.4\% for B50. The oxygen content of the methanol in the non-water washed biodiesel may be the cause for the larger O\textsubscript{2} increase compared to the water washed data. Even though the data are all within the 5\% O\textsubscript{2} accuracy of the FGA unit, there is an upward trend (Figure 60).
**Figure 59.** Round 3 temporally-varying O₂ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

**Figure 60.** Round 3 time-averaged O₂ data for water washed and non-water washed biodiesel heating fuel blends (error bars = 5% FGA O₂ accuracy).
Both water washed and non-water washed data show an O$_2$ decrease from the baseline diesel fuel oil to B5. However, the non-water washed data show small O$_2$ increases compared to diesel fuel oil with averaged increases of 0.27% and 1.1% for B20 and B50, respectively (Figure 61). Despite the increasing oxygen content, the water washed data show averaged decreases of 4.1%, 1.7%, 2.0%, and 2.7% for B5, B10, B20, and B50, respectively. These decreases may be a result of the open-air apparatus design, which has the potential for entrained air to enter the heating apparatus and influence the emissions measurements obtain near the top of the open burner flame.

**Figure 61.** Round 3 O$_2$ emissions data as a function of biodiesel fraction (% volume) (error bars = 5% FGA O$_2$ accuracy).
Figure 62. Round 3 temporally-varying NO$_x$ emissions of water washed (WW) and non-water washed (NWW) biodiesel heating fuel blends.

Round 3 NO$_x$ data show non-water washed B50 to have the largest NO$_x$ emissions (Figure 62). The remainder of the data appear to be within 10 ppm of each other. The water washed data increase from 10 ppm at B5 to above 30 ppm for B50. The non-water washed data increase from about 10 ppm at B5 to about 15 ppm for B10, but then decrease to about 13 ppm for B20 and B50.

There is an obvious upward trend in NO$_x$ emissions with increasing biodiesel volumes for the water washed data (Figure 63). Each fuel tested is outside the 4% accuracy band for FGA unit. The non-water washed data show less of a trend, and most data fall within the 4% accuracy band.
**Figure 63.** Round 3 time-averaged NO\textsubscript{X} data for water washed and non-water washed biodiesel heating fuel blends (error bars = 4% FGA NO\textsubscript{X} accuracy).

**Figure 64.** Round 3 NO\textsubscript{X} emissions data as a function of biodiesel fraction (% volume) (error bars = 4% FGA NO\textsubscript{X} accuracy).
Compared to diesel fuel oil, the non-water washed data show averaged NO\(_X\) increases of 39%, 2%, and 13% for B10, B20, B50, respectively (Figure 64). As mentioned previously, NO\(_X\) increase for non-water washed biodiesel can be attributed to the additional oxygen content from the methanol (CH\(_3\)OH) present in the biodiesel, as well as possibly higher reaction temperatures allowing the fuel to react more readily with oxygen and form NO\(_X\). The water washed data show a distinct increase in NO\(_X\) emissions compared to diesel fuel oil with averaged increases of 20%, 65%, and 168% for B10, B20, and B50, respectively. The NO\(_X\) increase with increasing biodiesel volume for the water washed data may be a result of the increasing oxygen content of the fuel. However, one would assume the non-water washed data would show higher NO\(_X\) levels compared to water washed data, due to the additional oxygen content from the methanol in the fuel. More detailed assessment of the non-water washed biodiesel fuel is warranted, to understand the effects of specific constituents on resulting exhaust emissions. It is interesting that these results suggest the presence of small amounts of residual methanol may actually yield lower emissions than emissions that can be achieved with water washed fuel that meets ASM standards.

**Conclusions**

Overall, the CO\(_2\) emissions data for all three Rounds show minimal changes compared to diesel fuel oil. The water washed CO\(_2\) data for Rounds 1-3 fluctuate above and below the diesel baseline for all biodiesel fuel blends. All of the averaged B50 data for Rounds 1-3 were within 2% of diesel baseline value of 8.79% CO\(_2\). Round 1 averaged 2% above, Round 2 averaged almost exactly equal to the baseline data, and
Round 3 was 2% below the baseline data. The non-water washed CO₂ data show larger variability, but no monotonic trend exists. Round 1 and 3 B50 averaged data were 5.9% and 9.5% below the baseline data, respectively. While Round 2 B50 averaged data were 2.0% above baseline data.

B20 blends of biodiesel heating fuel have been reported to show a decrease in CO₂ emissions ranging from 0-4% [19, 20, 48]. The B20 water washed data presented here show an average CO₂ decrease of 3%, compared to diesel fuel oil. Additionally, CO₂ decreases of 1%, 2.25%, and 6% have been reported for blends of B5, B10, and B50, respectively [20]. The water washed data presented here show an average increase of 0.7% for B5, but average decreases of 4.5% and <1% for water washed B10 and B50, respectively. The non-water washed data presented here shows average decreases of 0.7%, 3.8%, 3.3%, and 4.4% for B5, B10, B20, and B50, respectively. The CO₂ data presented here are generally within the ranges of previous studies.

The O₂ data also show minimal changes and no absolute trend across the various biodiesel heating fuel blends tested in all three rounds. The averaged water washed O₂ data do not differentiate from the diesel baseline data by more than 4.5% for any fuel blend. The Round 2 water washed data varying substantially going from a 15% O₂ decrease at B5 to a 15% increase at B20. However, the “low flow” error occurred during these tests, which explains the variability. The Round 2 water washed B50 data shows a 2.4% O₂ increase compared to diesel fuel oil, which is within the range of the B50 data of Round 1 and 3. The non-water washed data are similar to the water washed data in the sense there is no monotonic trend. Both Rounds 1 and 3 remain within a 4% band of the diesel fuel oil data, until B50 where Round 1 increases to above an 8% increase. The B5
and B20 non-water washed Round 2 data are slightly skewed to the experimental error, but the B50 data show a 1.3% O₂ decrease compared to diesel fuel oil. The overall expected trend of increased O₂ emissions with increasing biodiesel volume was not observed. The three round average data for water washed and non-water washed B5 show about a 2% decrease in O₂ emissions, while the three round average data for water washed and non-water washed B50 show a 0.8% decrease and 2.9% increase, respectively.

The minimal changes in CO₂ and O₂ emissions with increasing biodiesel volume have also been reported previously and may indicate good burner control of excess air and stable combustion [19]. A destabilization of the burner would result in varying levels of CO₂ and O₂ levels, as well as detectable CO if combustion became poor enough.

The averaged NOₓ data of all three rounds of testing show a distinct upward trend for the water washed data and no monotonic trend for the non-water washed data. However, the non-water washed data show an overall NOₓ increase with the utilization of biodiesel in diesel fuel oil. This overall increase in NOₓ emissions was also reported previously [20]. Despite the hypothesis of methanol contributing additional oxygen and a more favorable temperature for NOₓ formation, the non-water washed data show a smaller increase in NOₓ emissions. It is interesting that these results show comparable CO₂ and O₂ emissions between the water wash (ASTM standard meeting fuel) and the non-water washed fuel, but fewer NOₓ emissions. In terms of emissions, there does not appear to be a direct benefit to completing the water wash cycle. However, this question will be further explored using the life cycle global warming potential and cumulative energy demand in the life cycle chapter of this thesis.
The Round 3 experimental set up presented differences in all emissions and substantial amounts of HCs. The relatively high O$_2$ levels and low CO$_2$ levels are believed to be a result of the open design without a heat exchanger, which may have enabled substantial entrainment of ambient air. This also may have played a role in the formation of NO$_X$ and the detection of unburned hydrocarbons, which would be expected to condense and deposit on the heat exchanger in a conventional furnace.
Chapter 6: Life Cycle Assessment and Energy Return on Investment of Waste Cooking Oil Biodiesel Heating Fuel

Background

It is widely accepted that biodiesel utilization in vehicular applications reduces several important emissions criteria at the point of use [70-72]. However, there has been much criticism of dedicated biofuel crops and their true benefit in reducing greenhouse gas emissions, as well as the energy required to produce the biofuel [5-10]. On the surface, waste derived biofuels would appear to require substantially less input energy than a dedicated crop-based biofuel. Therefore, it is necessary to evaluate the environmental impacts and energy requirements of waste derived biofuels on a life cycle basis. Life cycle assessment (LCA) is an analysis technique that examines environmental impacts, such as global warming potential or cumulative energy demand, for processes and production systems from raw material acquisition to product end-of-life. This analysis is commonly referred to as a “cradle-to-grave” approach.

Various publications have found the utilization of WCO biodiesel as a transportation fuel provides a net life cycle greenhouse gas emissions benefit [73, 74]. However, there is no published literature on the life cycle assessment of WCO biodiesel for heating applications. Moreover, few researchers have considered the case of relatively small, distributed WCO-to-biodiesel processes operating in constrained environments where both the oil supply and fuel demand are controlled. Therefore, LCA of WCO biodiesel for heating fuel applications was considered to be an important gap that should be addressed in the current research program.
Methods

Goal and Scope

The goal of an LCA outlines the intended application, objective, and targeted audience of the analysis. The goal of this analysis is to complete a LCA on a community level, closed-loop WCO-to-biodiesel production process for heating fuel. The objective of this analysis is to inform community level decision makers, institution (e.g. universities, school districts, hospitals, or municipalities) stakeholders, and biofuel researchers the global warming potential (GWP) and the cumulative energy demand (CED) of the WCO to biodiesel heating fuel process. The CED is used to calculate the energy return on investment (EROI) of the waste-derived biofuel, which is an important metric to compare different fuels. The targeted audience includes community level decision makers, institution stakeholders, and biofuel and renewable energy researchers.

The scope of an LCA assists the practitioners in reaching the outlined goal and includes the functional unit, the reference flows, and system boundary. The different aspects of the scope of this LCA are outlined below.

- Functional Unit

The functional unit is 1,600 MJ of energy output from a B5 blended heating fuel (5% by volume biodiesel, 95% by volume fuel oil). This was selected as the functional unit because it is the amount of energy required to heat the 2010 average new single-family home (2,613 sq ft) for one day (assuming 12 hours of heating), using the heating industry energy required per square foot rule of thumb (50 BTU/hr/sq ft) [75]. The calculation to obtain the functional unit is presented below in Equations 14 and 15.
The reference flow is the number of batches of WCO biodiesel required to produce enough biodiesel for a B5 blend to provide 1,600 MJ and is equal to 0.0153 batches of WCO biodiesel. This assumes 48 gallons of biodiesel are produced per batch and make up the 5% biodiesel volume of the final B5 fuel. The lower heating value of biodiesel was obtained through external analysis and a lower heating value for diesel fuel oil was assumed based on published data [12].

The life cycle stages included in this LCA are WCO collection, transportation, and pre-treatment, transesterification, water wash, blending, and combustion. The upstream boundary for this assessment is established as the existing waste cooking oil because it is a product that already exists regardless of biodiesel production, and would otherwise be discarded. Figure 65 displays the system for this LCA.
Figure 65. The WCO-to-biodiesel system with the life cycle process blocks utilized in this LCA for B5 blended heating fuel.

System definition

The studied system is defined by the four main stages: collection, pre-treatment, transesterification, and water wash. Each stage has various inputs and outputs including fuel, electricity, chemicals, emissions, energy, glycerin and biodiesel. The RIT WCO-to-biodiesel production process provided data on a per-batch basis. The RIT process was a relatively constrained system, which allowed for streamlined quantification of inputs and outputs for the LCA inventory. The densities used throughout the LCA are presented in Appendix C.

Methodology

SimaPro 7.3.3 software was employed to complete the life cycle assessment of the WCO to biodiesel process (PRé Consultants, the Netherlands). SimaPro inputs and outputs with ecoinvent databases were selected when available and applicable because these are the most complete databases and produce the most representative model.
Life Cycle Inventory

The life cycle inventory stage of the LCA involves the collection and organization of all inputs and outputs for the defined system. The inputs for this system include raw materials, energy, and fuel (e.g. waste cooking oil, electricity, diesel, etc.). The outputs include glycerin, wastewater, biodiesel, energy in the form of heat, and GHG emissions. The model of this system is illustrated in Figure 66. All data were obtained from the RIT WCO biodiesel production process, a batch process producing 48 gallons of biodiesel from 50 gallons of WCO. Therefore, the reference flow was adjusted to be the number of batches required to produce the required amount of biodiesel for the specified fuel blend to provide the functional unit of 1,600 MJ. A B5 fuel blend required 0.0153 batches of WCO biodiesel to provide enough biodiesel for a B5 fuel to provide 1,600 MJ.

Process blocks were created in SimaPro to reflect the four production stages and two use stages defined by the system. The titles of the SimaPro process blocks correspond to the output of that individual process block. For example, the WCO collection stage in Figure 65 was named “Crude Waste Cooking Oil” because the output of the collection stage is crude WCO. The output of the pre-treatment stage is processable oil. Therefore, the pre-treatment process block was named “Oil to Transesterification.”

It is important to note the “Diesel Heating Oil” block in Figure 66 is a dashed line, which denotes this input value and the avoided volume of diesel heating oil will vary depending on the biodiesel heating fuel blend. The avoided diesel heating oil input block has an associated credit for displacing diesel based heating fuel. The larger volume of biodiesel blended in heating fuel, the larger this credit becomes.
Figure 66. System model for WCO-to-biodiesel production process and heating application utilization.
Table 17. Crude Waste Cooking Oil SimaPro Process Block (parameter values in per 1 WCO biodiesel batch basis).

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<th>Unit</th>
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<td>Electricity</td>
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<td>Transport</td>
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<td>52 gallons of Crude WCO feedstock prior to pre-treatment</td>
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**Crude Waste Cooking Oil Process Block**

The “Crude WCO” process block includes the collection and transportation of the WCO, as well as the electricity demand to transfer the WCO from the restaurant collection vessels via an electric oil pump (Figure 66). The selected database inputs and assumptions are presented in detail in Table 17.

**Oil to Transesterification Process Block**

The “Oil to Transesterification” process block incorporates the gravity pre-treatment on the 185.4 kg of crude WCO collected in the “Crude WCO” process block, the electricity demand to transfer the WCO into the automated transesterification
Table 18. Oil to Transesterification SimaPro Process Block (parameter values in per 1 WCO biodiesel batch basis).

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The selected database inputs and assumptions are presented in detail in Table 18.

**Prewashed Biodiesel Process Block**

The “Prewashed Biodiesel” process block includes the oil to biodiesel conversion reaction and therefore includes the several transesterification inputs (WCO, methanol, potassium hydroxide, and sulfuric acid) and produces an assumed 161.7 kg (48 gallons) of prewashed biodiesel and 41.8 kg (12 gallons) of glycerin (Figure 66). The “Prewashed Biodiesel” process block is presented in detail in Table 19.

The glycerin is drained from the bottom of the BioPro 190 and has several applications. As a result of this by-product’s value and the potential of glycerin for soap production, an economic allocation of the biodiesel and glycerin by-product was applied.
As of July 2013, the U.S. nationwide average price of B100 (100% biodiesel) was $4.19/gallon [76]. Thus, the total economic value of biodiesel per batch equals $201.12, assuming 48 gallons of biodiesel are produced per batch. The U.S. DOE also reported refined glycerin can be sold up to $0.50/lb [13,14]. Therefore, the total economic value of refined glycerin per batch equals $45.97, with a density of 3.48 kg/gal and assuming 12 gallons of glycerin are produced per batch and no significant volume loss during glycerin refinement. Using the total economic values per batch, the economic allocation was determined to be 81% biodiesel and 19% glycerin.

**Water Washed Biodiesel Process Block**

The “Water Washed Biodiesel” Process Block models the electricity demand and 208 kg (55-gallons) of water required for the water wash cycle, as well the treatment of the wastewater. It is important to note there is no loss of biodiesel during the water wash cycle. Therefore, all 161.7 kg of prewashed biodiesel are converted to 161.7 kg of water washed biodiesel. The selected database inputs, descriptions, and assumptions are presented in detail in Table 20.
Table 19. Prewashed Biodiesel SimaPro Process Block (parameter values in per 1 WCO biodiesel batch basis).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Selected Process</th>
<th>Description and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil to Trans-</td>
<td>178.3</td>
<td>kg</td>
<td>Oil Transesterification</td>
<td>WCO feedstock input</td>
</tr>
<tr>
<td>esterification</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>10.65</td>
<td>kWh</td>
<td>Electricity, low voltage, at grid/US U</td>
<td>Electricity to run BioPro 190 and complete oil to biodiesel conversion reaction</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.9</td>
<td>kg</td>
<td>Methanol, at regional storage</td>
<td>10 gallons of methanol required per batch WCO biodiesel</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>0.35</td>
<td>kg</td>
<td>Sulfuric Acid, at plant/kg/RNA</td>
<td>190 mL Sulfuric acid required per batch WCO biodiesel</td>
</tr>
<tr>
<td>KOH</td>
<td>2.55</td>
<td>kg</td>
<td>Potassium hydroxide, at regional storage</td>
<td>2,550 kg of KOH required per batch WCO biodiesel</td>
</tr>
<tr>
<td>Transport</td>
<td>2.63</td>
<td>tkm</td>
<td>Transport, lorry &gt; 16t, fleet average/RER U</td>
<td>Transport of chemicals to biodiesel production facility, summed mass of chemicals, assumed distance of 80km</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prewashed Biodiesel</td>
<td>161.7</td>
<td>kg</td>
<td>Prewashed Biodiesel</td>
<td>Biodiesel before water washing</td>
</tr>
<tr>
<td>Glycerin</td>
<td>41.8</td>
<td>kg</td>
<td>Glycerin</td>
<td>12 gallons of glycerin are produced from WCO biodiesel production, on average</td>
</tr>
</tbody>
</table>
Table 20. Water Washed Biodiesel SimaPro Process Block (parameter values in per 1 WCO biodiesel batch basis).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Selected Process</th>
<th>Description and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prewashed Biodiesel</td>
<td>161.7</td>
<td>kg</td>
<td>Prewashed Biodiesel</td>
<td>Prewashed biodiesel before water wash cycle</td>
</tr>
<tr>
<td>Electricity</td>
<td>22.69</td>
<td>kWh</td>
<td>Electricity, low voltage,</td>
<td>Measured electricity to run BioPro 190 Water Wash cycle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>at grid/US U</td>
<td></td>
</tr>
<tr>
<td>Wash Water</td>
<td>208</td>
<td>kg</td>
<td>Water, cooling, drinking</td>
<td>55 gallons of water required for water wash cycle</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Washed</td>
<td>161.7</td>
<td>kg</td>
<td>Water Washed Biodiesel</td>
<td>Biodiesel final product</td>
</tr>
<tr>
<td>Biodiesel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Water</td>
<td>208.2</td>
<td>L</td>
<td>Treatment, fibre board</td>
<td>Water used during water wash cycle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>production effluent, to</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>wastewater treatment,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>class 3/CH U</td>
<td></td>
</tr>
</tbody>
</table>

**B5 Fuel for Space Heating Process Block**

The “B5 Fuel For Space Heating” process block blends one batch worth of WCO biodiesel with fuel oil to produce a B5 blended heating fuel. Since blended fuels are on a volume basis, 48 gallons (161.7 kg) of water washed biodiesel were assumed to make up the 5% biodiesel portion. Therefore, the final fuel volume was determined to equal 960 gallons (3,065 kg), with 912 gallons (2,903 kg) making up the 95% diesel heating oil portion (Figure 66). The “B5 Fuel For Space Heating” process block also includes the electricity to pump the biodiesel out of the BioPro 190 (0.0393 kWh) and the amount of diesel heating oil avoided by utilizing 5% biodiesel (143.8 kg of diesel heating oil) using...
the functional equivalence formula calculated in Chapter 4 (1 gallon of biodiesel = 0.941 gallons of diesel heating oil). Table 21 presents the “B5 Fuel For Space Heating Process Block” in detail with assumptions.

### Table 21. B5 Fuel For Space Heating SimaPro Process Block (parameter values in per 1 WCO biodiesel batch basis).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Selected Process</th>
<th>Description and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>161.7</td>
<td>kg</td>
<td>Water Washed Biodiesel</td>
<td>Utilizing 1 batch worth of biodiesel (48 gallons) as the 5% of a B5 blended heating fuel (5% biodiesel, 95% fuel oil)</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.0393</td>
<td>kWh</td>
<td>Electricity, low voltage, at grid/US U</td>
<td>Measured electricity to pump biodiesel out of BioPro 190, assumed 0.25 hour operation</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>2903</td>
<td>kg</td>
<td>Light fuel oil, at regional storage/RER U</td>
<td>95% portion of B5 blended heating fuel (912 gallons)</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5 Fuel for Space Heating</td>
<td>3,065</td>
<td>kg</td>
<td>B5 Fuel for Space Heating</td>
<td>Production of B5 fuel with the utilization of 1 batch of biodiesel (48 gallons) making up the 5% of the final fuel mix</td>
</tr>
<tr>
<td><strong>Avoided products</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>143.8</td>
<td>kg</td>
<td>Light fuel oil, at regional storage/RER U</td>
<td>Avoided amount of fuel oil by calculating the functional equivalent of 161.7 kg biodiesel based on lower heating values</td>
</tr>
</tbody>
</table>
The “B5 Combustion in Space Heating” process block is modeled in terms of per 1 MJ output from a B5 fuel, and then later related to the functional unit of 1,600 MJ output in the product stage of SimaPro. The amount of B5 fuel required to provide 1 MJ of energy was calculated by determining the lower heating value of a B5 heating fuel with the measured lower heating value, published lower heating value for diesel heating fuel and the respective percentages of biodiesel and diesel heating oil (Equations 16 and 17). A burner efficiency of 80% was assumed, which is roughly the annual fuel utilization efficiency (AFUE) reported by Thermo Pride [77]. According to the calculations, 0.0293 kg of B5 fuel is required to provide 1 MJ of energy output with the assumed 80% efficiency.

\[
B5 \, LHV = (0.05 \times LHV_{BD} + 0.95 \times LHV_{DHO}) \tag{16}
\]

\[
B5 \, LHV = 42.66 \, MJ/kg
\]

\[
1 \, MJ \times \left( \frac{1 \, kg \, B5}{42.66 \, MJ} \right) / 0.8 = 0.0293 \, kg \, B5 \tag{17}
\]

In addition, the relative energy contributions of biodiesel and diesel heating oil to the required 1 MJ output were calculated using the fuel percentages and assumed efficiency (Equations 18 and 19).

\[
MJ_{DHO} = 0.95/0.8 \tag{18}
\]

\[
MJ_{DHO} = 1.1875 \, MJ
\]
\[ M_{BD} = 0.05/0.8 \]

\[ M_{BD} = 0.0625 \, MJ \]

Inputs from the technosphere were created for the energy contributions. A light fuel oil energy process was copied to create the biodiesel energy contribution input. However, the carbon in the light fuel oil energy process was removed because burning biodiesel releases only biogenic carbon, which was carbon originally in plant matter and part of the natural carbon cycle. Furthermore, all the upstream inputs were removed from this energy process because the upstream impacts of producing the biodiesel are captured in previous process blocks. This input is solely the burning of the biodiesel fuel. The Switzerland average light fuel oil burned in boiler 10kW, non-modulating with the upstream impacts removed was selected for the fuel oil energy input. Analogous to the biodiesel energy process, the impacts of the production of the fuel oil were captured in previous process blocks. The “B5 Combustion in Space Heating” process block is presented in detail in Table 22.

The “B5 Combustion in Space Heating” process block was the sole input for the SimaPro product stage titled “B5 Heating” (Table 23). This product stage marked the use stage with output energy intended for heating purposes and was in terms of the 1,600 MJ functional unit.
Table 22. B5 Combustion in Space Heating SimaPro Process Block (parameter values in per 1 MJ basis for B5).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Selected Process</th>
<th>Description and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5 Fuel</td>
<td>0.0293</td>
<td>kg</td>
<td>B5 Fuel For Space Heating</td>
<td>Amount of B5 fuel required to provide 1 MJ using calculated B5 lower heating value</td>
</tr>
<tr>
<td>For Space Heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>1.1875</td>
<td>MJ</td>
<td>Light fuel oil, burned in</td>
<td>Energy contribution from 95% portion of fuel oil with an assumed 80% burner efficiency [77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>boiler 10 kW, non-modulating/CH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>U no upstream</td>
<td></td>
</tr>
<tr>
<td>B100</td>
<td>0.0625</td>
<td>MJ</td>
<td>B100, burned in boiler 10 kW,</td>
<td>Energy contribution from 5% portion of biodiesel with an assumed 80% burner efficiency [77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>non-modulating</td>
<td></td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5 Combustion</td>
<td>1</td>
<td>MJ</td>
<td>B5 Combustion in Space Heating</td>
<td>The combustion of B5 blended heating fuel providing 1 MJ energy output</td>
</tr>
<tr>
<td>in Space Heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 23. B5 Heating SimaPro product stage for the functional unit (1,600 MJ).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Selected Process</th>
<th>Description and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5 Combustion in Space Heating</td>
<td>1,600</td>
<td>MJ</td>
<td>B5 Heating for</td>
<td>Product stage of B5 Heating system providing 1,600 MJ of energy output with assumed 80% burner efficiency [77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>functional unit</td>
<td></td>
</tr>
</tbody>
</table>

Life Cycle Impact Assessment

Impact Assessment Categories

The two impact assessment categories studied in this LCA were GWP and CED. GWP was selected because GHG emissions and climate change are a high concern and interest for current and future energy sources. The CED was selected to calculate the energy return on investment (EROI) to compare this waste-derived biofuel to other biofuels, as well as the incumbent fossil fuel, No. 2 fuel oil. SimaPro Methods TRACI 2 Version 4 and Cumulative Energy Demand V1.08 were used to quantify GWP and CED.

Results

The LCA results show a life cycle GWP of 165 kg CO₂ eq and 2,340 MJ per the functional unit of 1,600 MJ and are displayed graphically by process block in Figures 67 and 68. The combustion process block contributes the most to GWP with 143 kg CO₂ eq (87%) and the B5 fuel process block requires the largest amount of energy with 2,300 MJ (98%). Intuitively, these results make sense as the combustion of fuel releases the largest amount of GHG and the B5 fuel process block includes the production and transportation of the diesel fuel oil.
The use stages account for 99.5% and 99% of the total GWP and CED, respectively. The production process only accounts for the remainder 0.5% GWP and 1.0% CED totals. Thus, increasing the percentage of biodiesel utilized will substantially decrease total GWP and CED as a result of the relatively non-energy intensive production process and the avoidance of the production and utilization of fuel oil.

Within the four WCO production process stages, the “Prewashed Biodiesel” process block contributes the most to GWP and also requires the most amount of energy. This is a direct result of the 24-hour transesterification reaction during this process block and the chemicals required for the reaction, specifically methanol production, which requires 14.2 of the total 17.3 MJ, or 82% of all the “Prewashed Biodiesel” process block energy demand.

**Figure 67.** GWP of WCO-to-biodiesel production by process block.
Sensitivity analysis was performed on three separate modeling parameters. First, sensitivity on the selected data for methanol within SimaPro was conducted as the methanol input displayed the largest contribution to GWP and CED to the “Prewashed Biodiesel” process block. This sensitivity analysis was completed by changing the selected SimaPro input from “Methanol at Regional Storage /CH Ecoinvent database” to “Methanol at plant/RNA USLCI database.”

The sensitivity analysis on methanol resulted in a change of GWP from 0.47 kg CO$_2$ e/1,600 MJ output to 0.38 kg CO$_2$ e/1,600 MJ output, a 19% decrease. The CED decreased from 17.3 MJ/1,600 MJ output to 16.2 MJ/1,600 MJ output, a 6.4% decrease.
These decreases are not truly observed through fewer greenhouse gas emissions or the process requiring less energy, but display the change as a result of changing modeling parameters and the process block selected. The USLCI data is typically less complete than ecoinvent data (original input process block selected). Additionally, the “Prewashed Biodiesel” process block accounts for only 0.29% and 0.74% of the total GWP and CED, respectively. Therefore, while the methanol input is a substantial portion of the “Prewashed Biodiesel” process block because of the transesterification reaction, it is not a substantial contributor toward the life cycle GWP and CED for a B5 blended heating fuel.

Sensitivity analysis was also conducted on the percent biodiesel content present in the heating fuels. Separate process blocks were made for biodiesel heating fuel blends of B20, B50, B85, and B100. The same methods employed to create the B5 process blocks were used to create the higher volume biodiesel heating fuel process blocks.

Additionally, non-water washed biodiesel heating fuel blends were created by copying the water washed process blocks and replacing the “Water Washed Biodiesel” input with the “Prewashed Biodiesel” input. The water wash cycle was the most energy intensive process during production and also requires 55-gallons of freshwater that is sent to wastewater treatment. By utilizing non-water washed biodiesel heating fuel, these energy and water inputs and waste output are avoided, effectively reducing life cycle GWP and CED. The lower heating value of non-water washed biodiesel was assumed to equal water washed biodiesel, as a lower heating value of non-water washed biodiesel was not available. This is an area for further exploration to examine if there is a trade-off between avoiding the water wash cycle and energy content of the biodiesel fuel. Non-
water washed biodiesel heating fuel process blocks were created for B5, B20, B50, B85, and B100. Minimal changes in GWP and CED were observed at low biodiesel blends. However, the differences between water washed and non-water washed biodiesel heating fuels increases with higher blends of biodiesel because the relative impacts of the production of the biodiesel fuel increase with decreasing diesel-based heating fuel content.

Increasing the blend of heating fuel from B5 to B20 results in a decrease of GWP from 165 kg CO$_2$ e/1,600 MJ output to 138 kg CO$_2$ e/1,600 MJ output, respectively, about a 16.0% reduction. The CED decreased from 2,340 MJ/1,600 MJ output to 1,690 MJ/1600 MJ output, respectively, a 28% reduction. Increasing the biodiesel blend further to a B50 blend results in a life cycle GWP and CED of 84.6 kg CO$_2$ e and 339 MJ, respectively. This is a 49% reduction in GWP and 85% reduction in CED compared to the B5 fuel base case. The B85 heating fuel blend displayed 86% and 154% decreases in GWP and CED, respectively. The CED for a B85 heating fuel displays a negative CED value, as a result of the credit associated with avoiding the production and use of diesel based fuel oil. A B100 heating fuel shows negative values for both GWP and CED of -4.46 kg CO$_2$ e and -1980 MJ, respectively. These values show a 103% and 185% reduction in GWP and CED, respectively. Analogous to B85, the negative GWP and CED values are a result of the credit associated with avoiding the production and use of diesel-based heating fuel. The life cycle GWP and CED for the various biodiesel heating fuel blends are illustrated in Figures 69 and 70. Linear trend lines ($r^2 = 0.99$; not shown in Figures 69 and 70) were applied to both the water washed and non-water washed biodiesel heating blends to determine the critical biodiesel content that displays “net
“net zero” GWP (Equations 20 and 21). Blends of B98 and B94 for water washed and non-water washed biodiesel, respectively, were determined to be the critical biodiesel contents for “net zero” GWP. The critical biodiesel blends for “net zero” CED were determined to be B57 and B55 for water washed and non-water washed biodiesel, respectively.

Net Zero GWP Water Washed Biodiesel: $y = -1.7817x + 173.86$  \hspace{1cm} (20)

$0 = -1.7817x + 173.86$

$x = 98$

Net Zero GWP Non-Water Washed Biodiesel: $y = -1.8515x + 173.72$  \hspace{1cm} (21)

$0 = -1.8515x + 173.72$

$x = 94$

Figures 71 and 72 display the relative GWP and CED contributions of the production phase and use phase process blocks for various biodiesel heating fuel blends. The blend at which the upstream process blocks become comparable and exceed the use phase is observed where the data intersect. For GWP, the production phase process blocks become comparable to the use (combustion) phase at a blend of about B75. The CED of the production process blocks equal the use phase at about a B40 blend. These two points are important as they mark the blend at which the production process becomes critical to GWP and CED. Blends above these two points will show an increasing importance of the production phase until B100 (i.e. 100% biodiesel) is met.
Figure 69. Life cycle GWP as a function of percentage biodiesel heating fuel.

Figure 70. Life cycle CED as a function of percentage biodiesel heating fuel.
**Figure 71.** GWP contribution of production and use phase process blocks for various biodiesel heating fuel blends.

**Figure 72.** CED contribution of production and use phase process blocks for various biodiesel heating fuel blends.
Energy Return on Investment

The energy return on investment (EROI) for 1 kg of biodiesel was calculated using the CED (MJ/kg) to produce the fuel. A range of EROI values are presented for both water washed and non-water washed biodiesel to include variability in production inputs and biodiesel energy content. The formula used to calculate EROI is simply energy out divided by energy in (Equation 22). For these calculations, the obtained lower heating values (37.0 and 39.1 MJ/kg) of the biodiesel fuel were used as the “energy out” value and the CED (MJ/kg) to produce 1 kg of the respective fuel was used for the “energy in” value. An EROI value greater than 1 denotes more energy is produced than required to produce the fuel.

The EROI of 1 kg of water washed biodiesel ranged from 2.6 - 4.2 (Equations 23-24). The lower bound EROI value includes a higher CED as a result of additional production steps due to operator error. However, without the additional production steps, the EROI value is significant as it is within the reported range of EROI for both large-scale soybean oil based and WCO biodiesel. It has been reported that large-scale soybean oil biodiesel EROI ranges from 3.7-4.6 and WCO EROI ranges from 3.2-5.8 [78-81]. As of the late 2000s, the EROI for the production of conventional oil and gas in the U.S. is reported to be around 11, which has decreased exponentially over the past century from an estimated EROI of 1200 in the early 20th century [84]. Despite the calculated EROI values for WCO biodiesel being less than those of conventional fossil fuels, it is important to keep in mind the EROI of fossil fuels will continue to decrease, assuming no significant advance in technology, as they are a finite resource.
The EROI for 1 kg of non-water washed biodiesel ranged from 5.2-5.5 (Equations 25 and 26). The CED for the non-water washed biodiesel was adjusted to exclude the energy intensive water wash cycle, effectively reducing the required amount of energy to produce 1 kg of biodiesel from 9.41 MJ to 7.07 MJ. It is important to note that the lower heating value for the non-water washed biodiesel was assumed to be equal to that of water washed biodiesel as a lower heating value for non-water washed biodiesel was not obtained. This is an area for future work to explore the potential of a trade-off between avoiding energy by avoiding the water wash cycle, but producing a fuel with a lower energy content.

\[
EROI = \frac{E_{OUT}}{E_{IN}} \quad (22)
\]

\[
Water Washed Lower Bound = \frac{37.0 \text{ MJ/kg}}{14.1 \text{ MJ/kg}} \quad (23)
\]

\[
EROI = 2.6
\]

\[
Water Washed Upper Bound = \frac{39.1 \text{ MJ}}{9.41 \text{ MJ}} \quad (24)
\]

\[
EROI = 4.2
\]

\[
Non - Water Washed Lower Bound = \frac{37.0 \text{ MJ/kg}}{7.07 \text{ MJ/kg}} \quad (25)
\]

\[
EROI = 5.2
\]

\[
Non - Water Washed Upper Bound = \frac{39.1 \text{ MJ/kg}}{7.07 \text{ MJ/kg}} \quad (26)
\]

\[
EROI = 5.5
\]
Additionally, the EROI values for the production and use of B5, B20, and B50 both water washed and non-water washed were calculated with the respective CEDs and energy output equaling the functional unit of 1,600 MJ for all. The life cycle EROI results are summarized in Table 24. Despite the water wash requiring the most amount of electricity of the production process blocks, the overall contribution to the life cycle CED and EROI is minimal until a blend of B50. The EROI values for both B50 heating fuels are greater than the B100 EROI because of the avoided impact credit SimaPro applies to not producing or utilization the diesel fuel oil. This avoided impact also assumes that the diesel fuel oil is not consumed elsewhere. In reality, the EROI of blended biodiesel heating fuels cannot exceed the upper B100 EROI values of 4.2 and 5.2, but this result highlights the benefit of higher biodiesel blended heating fuels and avoiding diesel fuel oil.

**Table 24.** The EROI for the production and use of various biodiesel blended heating fuels.

<table>
<thead>
<tr>
<th>Heating Fuel Type</th>
<th>CED (MJ) ($E_{\text{in}}$)</th>
<th>Energy output (MJ) ($E_{\text{out}}$)</th>
<th>EROI</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5 Water Washed</td>
<td>2,340</td>
<td>1,600</td>
<td>0.68</td>
</tr>
<tr>
<td>B5 Non-Water Washed</td>
<td>2,340</td>
<td>1,600</td>
<td>0.68</td>
</tr>
<tr>
<td>B20 Water Washed</td>
<td>1,680</td>
<td>1,600</td>
<td>0.95</td>
</tr>
<tr>
<td>B20 Non-Water Washed</td>
<td>1,660</td>
<td>1,600</td>
<td>0.96</td>
</tr>
<tr>
<td>B50 Water Washed</td>
<td>339</td>
<td>1,600</td>
<td>4.7</td>
</tr>
<tr>
<td>B50 Non-Water Washed</td>
<td>280</td>
<td>1,600</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Conclusions

The results clearly show increasing the percentage of biodiesel in the heating fuel decreases the GWP and CED on a life cycle basis. The functional equivalent of heat can be provided from a higher biodiesel blended heating fuel, while contributing less to GWP and requiring less energy. This suggests further development of heating systems suitable for burning higher percentages of biodiesel. The current B5 maximum blend in heating fuel is the largest constraint of achieving substantial reductions in GWP and CED. The environmental and energetic impacts do not justify the use of biodiesel heating fuel blends below B20, especially because of the marginal economic impacts.

Furthermore, the additional energy required to produce the water washed biodiesel is minimal at heating fuel blends of B20 or less. Non-water washed biodiesel has potential for free glycerin and or methanol, which may cause corrosion of components, filter clogging, or nozzle coking. Thus, water washed biodiesel is the better option when using heating fuel blends at B20 or less to prevent burner malfunction. The B50 heating fuel blend with non-water washed biodiesel saw a 59 MJ, or 17%, reduction in CED, which is relatively low in terms of the overall CED.

Within the production process blocks, the “Prewashed Biodiesel” was the largest contributor to both GWP and CED because of the methanol required for the transesterification reaction. Thus, alternative alcohols like ethanol, or alternative methods of methanol production, should be explored to reduce the energy required for the production of the biodiesel. However, at a B5 blended heating fuel, the “Prewashed biodiesel” process block only contributes 0.29% and 0.74% of the life cycle GWP and CED, respectively. This contribution is less than 1% and can be considered negligible.
However, the higher the biodiesel blend, the more important the production phase becomes. The critical blends where GWP and CED of the production phase become greater than the use phase are B75 and B45. The utilization of blends above these levels must focus all efforts on minimizing the impact of the production phase. This suggests the need for future work in the area of methanol production or alternative alcohol options suitable for the transesterification reaction, as well as the utilization of renewable energy sources for energy demand of the production process.
Chapter 7: Conclusions and Future Work

The development of a closed-loop waste cooking oil-to-biodiesel production process at RIT demonstrates the ability to develop a waste-to-energy system at the community scale. Closed loop systems such as this highly depend on the increasing pressure of emissions reductions from climate action plans, the willingness to fund pilot scaled projects, and an overall commitment to renewable energy.

The biodiesel produced from the RIT closed-loop production process met ASTM standards after adjusting the alkaline catalyst content to account for the elevated free fatty acid concentration in the raw WCO feedstock. This provided a solid empirical foundation for the project, and highlights the applicability of the development of a closed-loop biodiesel production system at other institutions like universities, hospitals, school districts, or even municipalities. However, if all of the waste cooking oil (10.3 kg/person) in New York State (19.65 million people) was converted to biodiesel with a 96% conversion efficiency as observed at RIT, only 1.2% of the 2012 U.S. diesel heating oil demand would be offset [4,38, 85]. This effectively means there is not enough waste cooking oil available in New York State to satisfy the 2% biodiesel blend mandate.

The emissions data obtained from the experimental portion of this research demonstrated that waste cooking oil biodiesel can be utilized in space heating applications and provides a functionally equivalent amount of heat as diesel heating fuel. The averaged CO$_2$ and O$_2$ emissions data do not show substantial impacts across three separate rounds of experimental testing. These minimal overall changes compared to diesel fuel oil may be the result of good burner control of excess air conditions and consistent combustion. However, within each round, the data show CO$_2$ generally
decreases and O\textsubscript{2} increases with increasing biodiesel percentage. Round 3 data show detectable levels of HC as a result of no heat exchanger and decreasing HC emissions with increasing non-water washed biodiesel percentage. The Round 3 NO\textsubscript{X} data show an increase with increasing biodiesel volume for both water washed and non-water washed biodiesel, but the water washed data present a larger increase.

The life cycle portion of this thesis highlights the importance of the biodiesel blend. The current B5 maximum blend in heating fuel makes minimal contributions to greenhouse gas emissions and energy reductions. Thus, future work includes the development of heating systems suitable for substantially higher biodiesel heating fuel blends. The environmental and energetic impacts of blends below B20 do not justify the use of WCO biodiesel blended heating fuel, especially because the current economic impacts are neutral. Biodiesel heating fuel blends of B75 and B45 mark the critical point at which the production phase impacts toward GWP and CED, respectively, outweigh the impacts from the use phase. Thus, the benefits of blends above these thresholds are directly related to the impact of the production process.

In addition, the energy return on investment of 1 kg of waste cooking oil biodiesel was determined to range from 2.6-4.2 for water washed and 5.2-5.5 for non-water washed biodiesel. These are substantial findings, as these EROI values are comparable to large-scale WCO and soybean oil biodiesel production. This supports the need for future waste-to-energy systems, as this thesis demonstrates the minimal energy required to produce useable energy. With that being said, a large portion of the waste cooking oil biodiesel production process energy is attributed methanol, which is a necessary input for
the transesterification conversion reaction. Therefore, future work on alternative alcohols for the reaction or alternative methanol production methods is recommended.

An additional area for future exploration is the potential to directly combust waste cooking oil without first converting to biodiesel, as this would substantially reduce the CED by essentially eliminating the energy required to produce the fuel. However, the waste cooking oil would have to transport from the dining location to the heating system location. Thus, there would still be a required amount of energy, as well as associated emissions of collection and transport, but minimal compared to converting to biodiesel. Additionally, the potential trade-off between of the avoided conversion energy and energy content of the fuel would have to be explored.

The glycerin by-product of the waste cooking oil biodiesel production process can be viewed as a significant issue, due to the amount of commercially available glycerin, or as an opportunity to utilize another ”waste” as a feedstock for a production process. The refinement of the process for purification of the by-product glycerin is a highly attractive option that should be further explored to enhance the economic and environmental viability of the WCO-to-biodiesel process.

Lastly, institutions would benefit from the development of a multi-criteria analysis to identify the optimal utilization pathway for biodiesel, or whether to convert the waste cooking oil to biodiesel at all. Such a model could be optimized seasonally to match varying fuel demands throughout the year.
Appendix A – Biodiesel Fuel Property Characterization supporting information

Figure A-1. Batch 1 full ASTM D6751 results from Bently Tribology Services.
Table A-1. Requirements for Fuel Oil containing up to 5% biodiesel by volume from Table 1 in ASTM designation D396-13b.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Test Method</th>
<th>No. 2 S500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point, °C, min</td>
<td>D93</td>
<td>38</td>
</tr>
<tr>
<td>Water and sediment, % vol, max</td>
<td>D2709</td>
<td>0.05</td>
</tr>
<tr>
<td>Distillation Temperature °C</td>
<td>D86</td>
<td></td>
</tr>
<tr>
<td>90% volume recovered, min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90% volume recovered, max</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C, mm²/s min</td>
<td>D445</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Copper strip corrosion rating, max, No. 3</td>
<td>D130</td>
<td></td>
</tr>
<tr>
<td>3 h at a minimum control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature of 50°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ramsbottom carbon residue on 10% distillation residue % mass, max</td>
<td>D524</td>
<td>0.35</td>
</tr>
<tr>
<td>Density at 15°C, kg/m³ max</td>
<td>D1298</td>
<td>876</td>
</tr>
<tr>
<td>Pour Point °C, max</td>
<td>D97</td>
<td>-6</td>
</tr>
</tbody>
</table>
Figure A-2. Batch 2 full ASTM D6751 results from Bently Tribology Services.
Figure A-3. Calculation of functional equivalence using averaged lower heating value of biodiesel Batches 1 and 2.
Appendix B: Biodiesel Heating Application Emissions Testing
supporting information

Table B-1. Tabulated time-averaged emissions data.

<table>
<thead>
<tr>
<th>Round</th>
<th>Fuel Blend</th>
<th>CO2 (%)</th>
<th>HC (ppm)</th>
<th>O2 (%)</th>
<th>NOx (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Baseline</td>
<td>8.79</td>
<td>0</td>
<td>8.56</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>B5 WW</td>
<td>8.81</td>
<td>0</td>
<td>8.54</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>B10 WW</td>
<td>8.70</td>
<td>0</td>
<td>8.74</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>B20 WW</td>
<td>8.73</td>
<td>0</td>
<td>8.65</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>B50 WW</td>
<td>8.99</td>
<td>0</td>
<td>8.39</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>B5 NWW</td>
<td>8.71</td>
<td>0</td>
<td>8.66</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>B10 NWW</td>
<td>8.82</td>
<td>0</td>
<td>8.61</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>B20 NWW</td>
<td>8.83</td>
<td>0</td>
<td>8.50</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>B50 NWW</td>
<td>8.27</td>
<td>0</td>
<td>9.32</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>B5 WW</td>
<td>9.91</td>
<td>0</td>
<td>7.33</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>B20 WW</td>
<td>7.57</td>
<td>0</td>
<td>9.92</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>B50 WW</td>
<td>8.77</td>
<td>0</td>
<td>8.77</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>B5 NWW</td>
<td>9.04</td>
<td>0</td>
<td>8.15</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>B20 NWW</td>
<td>9.25</td>
<td>0</td>
<td>7.83</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>B50 NWW</td>
<td>8.98</td>
<td>0</td>
<td>8.45</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>Baseline</td>
<td>4.02</td>
<td>158</td>
<td>16.2</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>B5 WW</td>
<td>4.07</td>
<td>117</td>
<td>15.6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>B10 WW</td>
<td>3.70</td>
<td>82</td>
<td>16.0</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>B20 WW</td>
<td>3.81</td>
<td>116</td>
<td>15.9</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>B50 WW</td>
<td>3.92</td>
<td>155</td>
<td>15.8</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>B5 NWW</td>
<td>3.86</td>
<td>87</td>
<td>15.7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>B10 NWW</td>
<td>3.70</td>
<td>102</td>
<td>16.0</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>B20 NWW</td>
<td>3.74</td>
<td>67</td>
<td>16.3</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>B50 NWW</td>
<td>3.64</td>
<td>71</td>
<td>16.4</td>
<td>13</td>
</tr>
</tbody>
</table>
Appendix C: Life Cycle Assessment and Energy Return on Investment of Waste Cooking Oil Biodiesel Heating Fuel supporting information

Table C-1. Measured densities of various substances used throughout LCA inventory.

<table>
<thead>
<tr>
<th>Substance</th>
<th>g/mL</th>
<th>kg/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100</td>
<td>0.89</td>
<td>3.37</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>0.83</td>
<td>3.13</td>
</tr>
<tr>
<td>B5 Heating Fuel</td>
<td>0.84</td>
<td>3.19</td>
</tr>
<tr>
<td>B20 Heating Fuel</td>
<td>0.85</td>
<td>3.22</td>
</tr>
<tr>
<td>B50 Heating Fuel</td>
<td>0.87</td>
<td>3.28</td>
</tr>
<tr>
<td>Glycerin</td>
<td>0.92</td>
<td>3.48</td>
</tr>
<tr>
<td>Waste Cooking Oil</td>
<td>0.94</td>
<td>3.57</td>
</tr>
<tr>
<td>Solids and Water</td>
<td>0.92</td>
<td>3.48</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.79</td>
<td>2.99</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>0.0018</td>
<td>0.007</td>
</tr>
</tbody>
</table>
References


[41] New York City Administrative Code § 24-168.1 (Clean heating oil). Effective October 1, 2012. Accessed September 2013. Available at: http://public.leginfo.state.ny.us/LAWSSEAF.cgi?QUERYTYPE=LAWS+&QUERYDATA=$SADC24-168.1$@TXADC024-


[52] Personal communications from Dave Armanini (RIT Environmental Health and Safety), March 2013


[56] Personal communications from Dean Engdahl (RIT Dining Services), December 2013


[82] Personal Communication from Kurt Beiswenger (R.W. Beckett Corporation), January 2014

[83] Personal Communication from Dean Brubacher (Clean Burn Furnaces and Boilers), December 2013
