New technologies for the complete rendering and economic conversion of waste oils to biofuels

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Abstract

A novel process was developed for the biorefining of floatable wastewater scum and other waste oils from water treatment facilities into biodiesel and other value-added bio-products. To test the scalability and commercial potential of the technology, a 7,000 liter/year pilot-scale system was designed and built. Scum from a waste water treatment facility, located in St. Paul, Mn, was collected and converted into methyl esters (biodiesel) according to the process chemistry. All the incoming and outgoing process streams were sampled, tested, weighed and recorded to calculate both the process efficiency and product quality. Data from the pilot-scale systems operation was compared to laboratory results and the theoretically expected values for each individual unit operation. The product quality was tested using a third-party laboratory and confirmed the biodiesel produced during a single batch process met all of EPA's test requirements for commercial-grade biodiesel.

As a substrate for biodiesel, scum derived oil requires more pretreatment consideration than standard waste oils like used vegetable oil or brown grease. Combining acid hydrolysis and solvent extraction, a free fatty acid and acyl-glycerol rich product was produced from a highly impure source. Free fatty acids (FFA) present were converted to acyl-glycols via a high temperature (238°C) glycerin esterification process known as glycerolysis. The inorganic catalysts zinc aluminum oxide and sodium sulfate was tested during glycerolysis to compare the reaction kinetics of converting FFA to acyl-glycerols. It was concluded that the zinc-based catalyst increased the reaction rate significantly, from a "k" value of 2.57 (uncatalyzed) to 5.63, completing the reaction in

60 minutes, half the time it took the uncatalyzed reaction (120 min). Sodium sulfate's presence however slowed the reaction, resulting in a "k" value of 1.45, completing the reaction in 180 minutes. Use of the external catalyst $Zn-Al_2O_3$ showed the greatest catalytic potential, but also assumes additional costs.

In the U.S., the total amount of municipal solid waste is continuously rising each year. Millions of tons of solid waste and scum are produced annually that require safe and environmentally sound disposal. The availability of a zero-cost energy source like municipal waste scum is ideal for several types of renewable energy technologies. However, the way the energy is produced, distributed and valued also contributes to the overall process sustainability. An economic screening method was developed to compare the potential energy and economic value of three waste-to-energy technologies; incineration, anaerobic digestion, and biodiesel. A St. Paul, MN wastewater treatment facility producing 3,175 "wet" kilograms of scum per day was used as a basis of the comparison. After applying all theoretically available subsidies, scum to biodiesel was shown to have the greatest economic potential, valued between \$491,949-\$610,624/year. The incineration of scum yielded the greatest reclaimed energy potential at 29 billion kilojoules/year.

The use of vacuum distillation for biodiesel production has become a reliable post-treatment method for removing multiple impurities, to consistently produce commercial-grade biodiesel. The waste produced from biodiesel distillation, vacuum distillation bottoms (VDB), is a mixture of higher molecular weight methyl esters (84%) and derivatives. Microwave-assisted pyrolysis (MAP) has been researched as a methyl ester recovery process for VDBs leaving vacuum distillation. Two types of MAP

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processing, dMAP and fMAP, were developed and tested to determine the optimal reaction conditions for producing a biodiesel analogue. The results indicate that after dMAP, 85.9% wt/wt of the VDBs were recovered as a transparent bio-oil then blended back into B100 biodiesel and certified for sale using ASTM D6751. Blending dMAP bio-oil (10% wt/wt) with B100 biodiesel met all certification requirements and demonstrated that MAP processing could be a significant yield improvement technology for any commercial biodiesel producer utilizing vacuum distillation.

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Chapter 1 Introduction into waste to biodiesel technology

1.1 Background

Scum is a waste material skimmed from the surface of primary and secondary settling tanks at wastewater treatment plants. It is made of a variety of sources including animal fats, waste cooking oil, food wastes, plastic material, soaps, and other trace impurities discharged from restaurants, households, and industry. Environmental concerns have risen over the immediate and long-term effects of landfilling scum, including, costs, sustainability, the leaching of metals and non-metals into freshwater systems and eventually the ocean. Since scum contains mostly fats and oils, a process was developed to make full use of all scum generated by converting the usable portions to biodiesel and incinerating any residual biosolids. R&D efforts funded in part by grants from LCCMR, MCES, UMN MNDrives and Center for Biorefining have resulted in a novel process for converting scum to biodiesel. Biodiesel is one of the most widely used biofuels in the U.S. and backed by state and federal subsidies. At present, the largest is economic barrier faced by biodiesel producers is the relative high cost of fats and oils needed. Therefore, reducing biodiesel production costs is of urgent need. Currently, for biodiesel producing from vegetable oil, the feedstock cost accounts for 70-80% of the total production cost (Cooperation, 2010). Replacing vegetable oil with low-value spent oil or waste oil, such as waste cooking oil, and wastes from animal or vegetable oil plants, for biodiesel production has been confirmed to lower the total production cost (Hama et al., 2013). When comparing different pathways that recover the energy in scum, converting scum to biodiesel is the best option in terms of reducing fossil fuel depletion. In addition, the

biodiesel produced has much better life cycle impacts than biodiesel from soybeans as it has no alternative use, or unit value-added. Although the total amount of scum in wastewater treatment plants is not enough to replace vegetable as a feedstock, it provides an environmental friendly source for renewable fuels in the U.S.

Scum innately contains unique impurities and oil-like contaminants that require removal or modification before processing. By combining previously separate reaction conditions, acid hydrolysis and solvent extraction, a free fatty acid and acyl-glycerol rich product can be produced. Catalyzed glycerolysis of free fatty acids and post-transesterification free glycerin removal are two unique process components currently being studied. Different inorganic catalysts were tested during high temperature glycerolysis (460°F) to study the reaction kinetics when converting free fatty acids (FFA) to mono and di acyl-glycerols. The glycerin introduced during glycerolysis must be removed in subsequent processes. A combination of reactive distillation, mid-condenser phase separation, and adsorbent filtration are being researched in order to remove residual unbound glycerin. Removing unbound glycerin passively during the distillation stage makes water washing and vacuum drying the final product no longer necessary. Successfully eliminating this final stage greatly reduces batch cycle time, resulting in higher production volumes and lower utility costs. The process serves the dual purpose of converting scum to a higher value product (biodiesel), while at the same time reducing environmental pollutants in both landfills and water resources. As a result, 70% of the dried and filtered scum oil can be converted to biodiesel which is equivalent to about 140,000 gallons of biodiesel and $400~500K profit per year. An estimated 6.2 million tons of scum are generated in the United States of America each year (Kargbo, 2010). A

scum to biodiesel conversion process for the treatment and complete utilization of scum has the potential to be both more economical and environmentally sound than current practices. Process modeling was based on an extensive review of current literature, technology reports, databases, and interviews with researchers who develop biodiesel technology, both commercially and at the University research level.

1.2 Impacts and significance

1.2.1 Environmental benefits of improved waste management technology

Scum is an oily waste stream of the wastewater treatment process. Currently scum is treated either by anaerobic digestion to produce biogas which has low energy density or landfilled which causes many environmental problems. One major concern of landfilling biosolids or the direct land application of biosolids onto farm land is the risk to human, animal, and plant health. Despite its long history, the simple reuse of organic waste generated by plants and animals as a source of agricultural nutrients is not without issue. There are many potential problems with directly applying wastewater, biosolids, or effluent from anaerobic digesters. Trace elements and heavy metal compounds innate to biosolids and sludge from wastewater treatment facilities can have inhibitory effects on the soils uptake abilities. Not only can this affect agriculture from a plant health and nutrition perspective, but also in the sense of human health consumption. Additionally, the fates of certain organic compounds found in biosolids that are toxic to humans are not completely understood. Many potential harmful organics can be broken down

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intentionally using certain biodegradation methods like volatization, photodecomposition, and degradation (Epstein, 2003). However, these mechanisms are effective only to a certain point, making them suitable for passive methods of bioremediation. They do not, however, justify or excuse the intentional contamination of plants or animals destined for human or animal consumption.

The release of certain metals and non-metals into neighboring water systems or rivers is a large concern, as it represents local pollution as well as a continued contamination. Long-term studies of two large rivers in the Midwest have traced nitrate levels and have concluded that a large increase in nitrates occurred between 1960 and 1980, while small or negligible increases have occurred between 1980 and 2004 (Kelly, 2015). The nitrates presence was primarily contributed two different sources; surface runoff from fertilizers used in agriculture and point-source contamination from facilities like wastewater treatment plants or confined livestock feeding lots. Regardless of the source, the effects of these contaminates, nitrates specifically, can be disastrous and expansive. Recent research has suggested that nitrates in rivers are a potential contributing factor to hypoxia zones in the ocean. Although it is well published that there can be positive relationships between nitrogen and phosphorus levels in waste systems, there is a concentration threshold and subsequent limit to the positive effects. If the load of nutrients to freshwater or marine systems exceeds the capacity for assimilation, then the water quality will start to degrade. Impacts can include noxious and toxic algal blooms, increased turbidity with a subsequent loss of submerged aquatic vegetation, oxygen deficiency, disruption of ecosystem functioning, loss of habitat, loss of biodiversity, shifts in food webs, and loss of harvestable fisheries (Rabalais, 2002).

In the case of anaerobic digestion, the scum breaks down to generate biogas, mainly methane (CH_4). Biogas is then burned and electricity is generated. It has been shown that despite the relatively high cost of erecting above ground tanks for the digesters, off-setting land, and expending energy associated with the operation, it is possible to achieve a net-positive energy scheme. Certain processes even claim to clean the effluent to comparable levels as conventional processes (Remy, 2014). What this means is that after you strip away the energy gained from the anaerobic digestion of municipal wastes, you still have an effluent stream that contains a very high chemical oxygen demand (COD), biological oxygen demand (BOD), and active acteogenic and methanogenic bacteria. These contaminants will still require remediation before they can be discharged, which is becoming more costly, especially in dryer regions with low rain fall. Despite a net-gain in terms of energy, it is still not economical to build and maintain these facilities, primarily due to the current low cost of energy on the market. Hydraulic fracturing or "fracking" has made electricity cheap, making it difficult for alternative energy sources to compete. Government and state subsidies have made it easier for municipal water treatment facilities to profit from anaerobic digestion, but not to the point where a privately held company could make a sizable return on its investment.

By rendering scum oil from scum, which can contain up to 62% usable oil, a third option for the disposal of waste organics is possible. Even though the oil fraction of scum is not the most environmentally detrimental component, our patented process by which it is rendered also passively concentrated and dewaters most of the organic residues. By combining a solids filtration stage along an acid hydrolysis, biosolids, metals, and non-metals can be extracted and concentrated passively during the biodiesel conversion

process. These biosolids account for roughly 20% of the total scum weight, with another 22-32% attributed to water that saturated the scum. Assuming the extracted waste water is sent back to the water treatment facility and the oil converted to biodiesel, the process will in theory reduce environmental landfill volumes by 80%. The process represents a significant advance to current waste water treatment efficiencies as well as a step towards a more sustainable waste management system.

1.2.2 Economics benefits of a scum to biodiesel process

The economic modeling of a scum to biodiesel process must make several assumptions to predict potential outcomes. The first major assumption was estimating the potential volume of available material. The MCES Metro Wastewater Treatment facility produces roughly 3.5 tons or 7,000 lbs of wet scum each day. The solids portion of the scum accounts for roughly 20% or less of the scum material, while the moisture content can vary anywhere from 22% to 32%. Assuming a constant supply of scum material over 365-day period, a yield of between 189,000-216,500 gallons of dry "oil" could be produced annually. At the conservatively estimated process efficiency of 69%, the oil could yield between 130,000 and 149,500 gallons of biodiesel each year.

The second major consideration for modeling the process was the price of the starting material. The single largest advantage of a scum to biodiesel process is that the initial oil is completely free. The purchasing and procurement of the initial substrate can account for almost 70-90% of the operating costs of running a biodiesel plant. This is usually the lynch pin in determining whether commercial operations will be successful in

the long-term. Scum oil is not only free, but by converting roughly 65% of the scum into biodiesel, and another 20% removed as distillation bottoms, the process saves roughly 85% of the liquid organic scum from landfill or 68% reduction overall. This can result in the immediate savings of $68,000 per year in costs associated with land filling scum at the Metro Plant facility in addition to the revenue generated.

The third assumption that has significant weight in the economics model is the value we assign the finished biodiesel. How we value the biodiesel directly effects investor concerns like "return on investment" and loan payback periods. Assuming the finished biodiesel is used directly by the Metro plant personnel in their vehicles, it can be valued at the exact same price as the petroleum diesel. Since each gallon produced will off-set the purchase of one gallon of petroleum diesel, the model is simplified. A gallon of diesel costs roughly $3.00/gallon at retail, so even off-setting the purchase of the conservative estimation of 130,000 gallons of biodiesel would saves the Met Council $390,000 in fuel costs. Fortunately, this isn't the only source of potential income the plant would offer. Biodiesel production is tracked in the U.S. using Renewable Identification Numbers (RINs) by the EPA (1.5 RINs/gallon of biodiesel produced). These RINs have market value because they can be purchased by industrial companies as credits in order to meet EPA guidelines (Irwin, 2014). As of 3/1/15, one RIN is worth 0.80 cents. The total RIN potential for the biodiesel produced would be approx. $168,000 annually. The last income stream comes in the form of the $1.00 biodiesel tax subsidy. This is a one-dollar tax credit for every gallon of biodiesel produced, potentially equaling $140,000/year.

The last key assumption that needed to be made was the conversion cost per gallon and labor costs. By using nationally sourced, chemical whole sale information, a cost benefit analysis was created using a mass balance to reveal a conversion cost of approximately $1.32/gallon of biodiesel. The labor cost was capped at $120,000 for two employees to be working during all operation hours. Applying this conversion cost to the projected annual production yields an annual cost of production of $185,000. Subtracting the costs from the total revenue from all sources yields a net potential profit of over $500,000/year.

Using a free oil source combined with the lack of transportation and handling costs makes a scum to biodiesel process very attractive financially. Recycling waste heat from the solids management building would further improve the economic model. Based on the previous assumptions and an estimated capital cost of 1.2 million, a payback period of 2.36 years is expected.

Chapter 2 Development and operation of innovative scum to biodiesel pilot-system for the treatment of floatable wastewater scum

2.1 Scum derived oil to biodiesel history and patent development

As a renewable fuel, biodiesel has become an attractive alternative to petroleum diesel as both a fuel additive or fuel substitute. Although vegetable oil is still the major source for global biodiesel production (Krawczyk, 1996; Cvengroš & Cvengrošová, 1994), waste oil to biodiesel technologies has gained popularity as commercial producers seek cheaper

and more abundant sources. In 2016 vegetable oil was the largest biodiesel feedstock in the U.S with 8,532 million lbs processed into biodiesel (76.7% of all feedstock types). The second largest source was from animal derived oil with 1200 million lbs (10.8%), while the remaining 1,389 million lbs (12.5%) of oil came from recycled or waste sources like yellow and brown grease (U.S. Department of Energy, 2017). Historically, pristine sources like vegetable and animal derived oils have kept the total production costs of biodiesel in the U.S. to high to compete with petroleum diesel. Among the production cost, the feedstock alone can account for between 70-80% (Knothe et al, 15) of the total. Recent commercial efforts have focused on using recycled or waste oils, such as used cooking oil, brown grease, wastes from animal or vegetable oil processing, and waste generated from water treatment centers to reduce production costs (Haas et al, 2006; Canakci & Sanli, 2008). The expanded use of recycled and waste oils has brought about an expansion in the development of new pretreatment and purification technologies. Researchers at the University of Minnesota have taken the floatable waste water scum skimmed from the surface of primary and secondary settling tanks in wastewater treatment plants and converted the oil component to ASTM grade biodiesel (Bi et al, 2014).

Scum is a combination of animal fat, vegetable oil, food wastes, plastic material, soaps, waxes and many other impurities discharged from restaurants, households and other facilities. Based on a US EPA's Office of Solid Waste report, approximate 1 to 3 billion gallons of waste fats, oil, and grease (FOG) are produced every year in the 30 metropolitan areas in the United States (Wiltsee, 1998). Approximately 40% of the FOG comes from single-use oil, collected from restaurants and slaughter houses and converted

to biodiesel. These oils are relatively clean with filtration and free fatty acid remediation being the only pretreatment needed for biodiesel conversion, however, around 60% enters the sewer systems and end up in wastewater treatment plants. Due to its lower density relative to water, the waste oil floats on the surface of treatment facilities and is emulsified with other organics to form scum, making it a rich source of potential energy for recovery. The oil content of scum averages between 60-65% wt/wt, of which approx. 82% is in the form of free fatty acids and the rest as acyl-glycerides (Anderson et al, 2016; ASTM D1980-87, 1998). The traditional approach to scum energy recovery is to co-process it with sludge during anaerobic digestion, producing biogas that can be used to generate electricity (Outwater & Tansel, 1994). However, scum's high oil content can cause it to float and foam on the top of digesters, forming a thick layer that can impede the digesters performance. As a result, many wastewater treatment plants choose to directly incinerate the scum or dispose of it in a landfill. Scum disposal not only increases the cost of treatment for the facilities, but can cause additional environmental problem if the impurities leach into our water systems, a potential source for underground water pollution.

In previous publications, an alternative process/technology was developed and patented by our research team to recover energy from scum while reducing the environmental impacts of landfilling organic waste (Bi et al, 2014). Energy was recovered from the waste scum by extracting all of the usable oil and converting it to commercial-grade biodiesel. Currently in the biodiesel industry, the most common process for biodiesel conversion is through base-catalyzed transesterification where acyl-glycerides react with methanol to form Fatty Acid Methyl Esters (FAME). Potassium

Hydroxide (KOH) or Sodium Methoxide ($NaOCH_3$) is the most common catalyst. However, feedstock's must be free of water and free fatty acid (FFA) prior to the reaction, otherwise soap formation and catalyst neutralization will hinder the reaction progress (Knothe et al, 15). Low grade feedstock such as yellow grease or brown grease can have FFA concentrations as high as 30-50%. Conventional FFA treatments like acid-esterification are limited to FFA concentrations below 30% and produce "wet" methanol as a by-product, the drying of which is very energy intensive. Alternatively, "glycerolysis" or glycerin esterification can reduce any FFA concentration to an acid value below 2 mg KOH per g of oil, releasing water as a by-product. At temperatures above 230°C, the water of reaction is driven out of the oil, leaving a dry oil substrate ideal for any biodiesel conversion process. The effects and application of glycerolysis as an FFA remediation technology have been studied and patented in previous works by the authors research team (Anderson et al, 2015). Once complete, the glycerized oil was analogous to any low FFA waste oil and ready for standard biodiesel processing.

A pilot-scale conversion process was designed and built to test the performance and scalability of the proposed scum to biodiesel process. The goal of the study was to confirm the conversion efficiency and product quality obtained in the laboratory setting, proving the FOG content in the scum could be successfully extracted and converted to ASTM-grade biodiesel economically. The end product was a liquid transportation fuel with a greater economic value than the equivalent electricity generated through a potential anaerobic digestion process. In addition, the byproduct glycerol and biosolids can be used as a heating source, decreasing the energy input and reducing the operational

cost of the process. In a word, the current developed process has obvious economic and environmental advantages over other conventional treatments and disposal processes.

2.2 Materials and methods

The design basis of the mobile scum to biodiesel system was based on a combination of theoretical mass balance and experimental rate and efficiency yields generated during multiple batch-wise laboratory experiments. A process flow diagram, including all reagent, product, and wastes streams is illustrated in Appendix B. Approx. 1000-gram batches were performed to isolate variables and optimize both the conversion efficiency as well as product yield. Data from the laboratory results was analyzed and extrapolated to determine the design scale and individual component specification for the pilot-scale scum to biodiesel process. The laboratory process, reaction times, and reagent ratio were also used as the basis for the scaled-up operating procedure.

2.2.1 Equipment and reagents

A 7.5'x16' mobile trailer unit was purchased as the platform on which the scum to biodiesel system was built. The stainless-steel reactors were designed by the research team members and fabricated by local metal works. The distillation reactor and peripheral equipment were obtained from B/R Instruments, Maryland. Piping and electrical purchased from Menards and installed by the research team members. Scum samples were collected from Metropolitan Wastewater Treatment Plant at St. Paul, MN.

Sulfuric acid (98%, AR) was obtained from Mallinckrodt Baker, Inc. Paris, Kentucky.

Butanetriol (1000mg/ml), tricaprin (8000mg/ml), and N-methyl-N-(trimethylsilyl)

trifluotoacetamide (MSTFA) were obtained from Sigma-Aldrich, Inc. Sodium methoxide

(30% in methanol), methanol (anhydrous, 99.8%), n-heptane (HPLC grade), potassium

hydroxide concentrate (0.1 N), and glycerol (99.9%) were obtained from Thermo Fisher

Scientific, Inc. Distilled water was obtained from Premium Waters, Inc. MN, USA.

2.2.2 Scum to biodiesel - Process and Instrumentation Drawings (P&IDs)
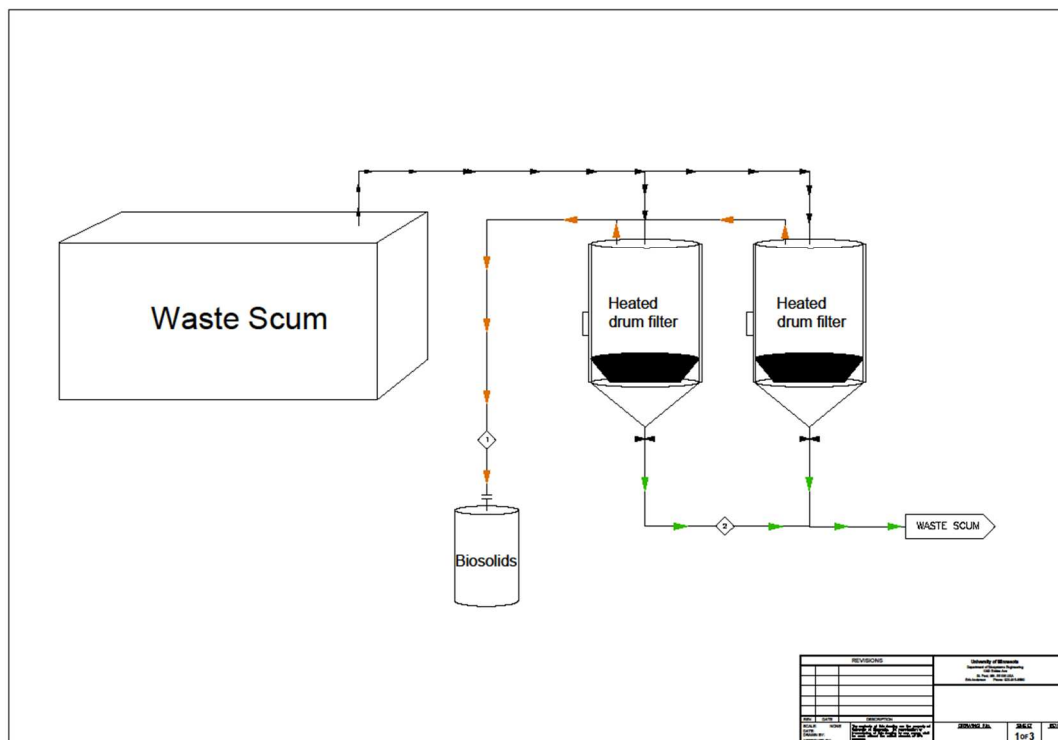
Figure 1: Process and instrumentation drawing for the initial scum loading, heating, and liquid extraction process. Biosolids greater than 1.0 mm in diameter were physically separated from the liquid phase prior to entering the chemical extraction stage.

The scum to biodiesel process and subsequent patent is illustrated in the combine process flow and instrumentation diagrams, shown in Figures 1-3. All reagent tanks were made from stainless steel, fixed with pressure relief valves and secured to the trailer system. Mass transfer between tanks was performed by centrifugal pumps, while reagents were fed using a combination of level-controlled volume displacement and metering pumps. Temperature and pressure control systems are in place where they are needed along with all peripheral instrumentation i.e. pH meters, vacuum pumps, manometers. Chilled water circulators were assigned to condense and cool reaction liquids. The figure above, Figure 1, shows the initial loading and physical separation of the scum into its liquid and solid fractions. In the current scum disposal process, dilute scum is pumped into large holding tanks, fitted with mesh screens to allow water to filter through, concentrating the solid scum. The concentrated scum is then moved into the two fixed, 208-liter barrels shown in Figure 1. The barrels were fitted with two layers of filter mesh at the bottom used to screen the biosolids from the liquid FOG/water phase. Scum was heated to temperatures above 82°C using insulated electric barrel heaters. The FOG and water fraction of scum liquefied then drained passively through the filter system and was collected in drum basins below. From the drum basins, centrifugal pump #1 forced the liquid scum through an additional in-line screen filter, further removing the biosolids from the liquid. The liquid fraction was pumped to reactor #1 (drawing 2 of 3), while the biosolids were collected and stored for further study.

Figure 2 (below) shows the first reaction vessel (reactor #1) in the conversion process, which represents the chemical extraction and glycerolysis/transesterification stage.
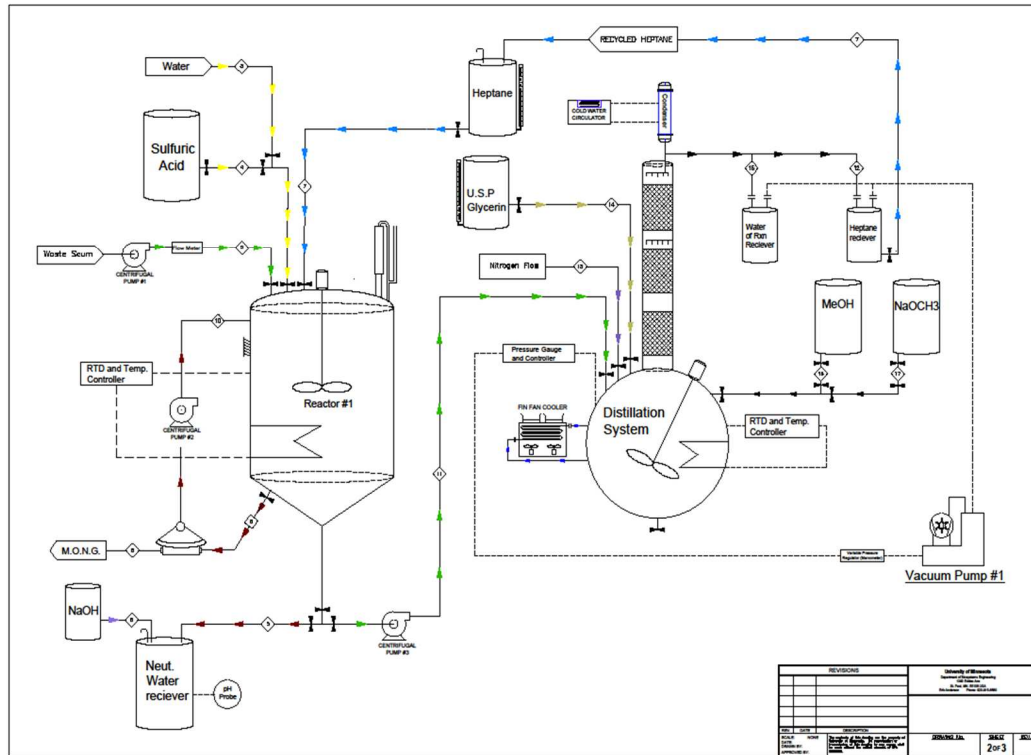
Figure 2: Process and instrumentation drawing for the novel chemical extraction and free fatty acid remediation stages of the waste oil rendering process.

Reagent streams were charged to the reactor from above, while waste streams were removed from the reactors cone bottom using control valves. An explosion-proof (XP) rated electric agitator was used to mix the oil and reagents while a reflux condenser was mounted to the top of reactor #1 to condense any solvent vapors during the chemical extraction stage back into the reactor. A liquid solid centrifuge was mounted to the trailer floor, next to reactor #1, in order to continuously remove solid precipitate throughout the extraction process. Centrifugal pump #2 was used to circulate the purified liquid stream

back into reactor #1. A waste holding tank was used to passively collect and neutralize the acidic waste water generated during the extraction. Once all of the operations of the extraction stage are performed, centrifugal pump #3 transported the liquid the second reactor (distillation reactor). The first operation performed is the low vacuum stripping of the residual solvent suspending the oil phase. Vaporized solvent was sent up the reactor column and out of the system to be condensed and collected for reuse later. Glycerolysis or glycerin esterification followed solvent stripping and required the calculated addition of free glycerin at high temperatures, followed by the continuous removal of water generated from the reaction. The last reaction represented in Figure 2 is the base-catalyzed transesterification reaction, where the acyl-glyceride component is converted to methyl esters. The reagents required for the reaction were pumped into the reactor using a chemically resistant transfer pumps. The distillation column was used as a reflux condenser by closing the distillate receiver line, sending 100% reflux back into the reactor.

The drawing below, Figure 3, depicts the distillation reactor and its peripheral equipment
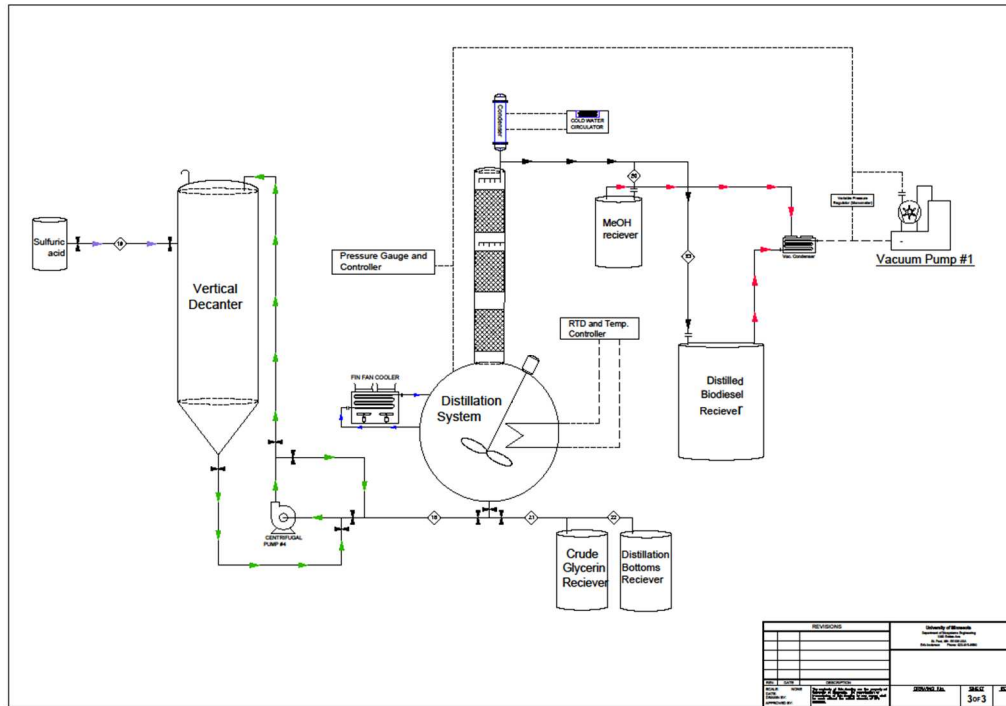
Figure 3: Process and instrumentation drawing for the following stages;
transesterification, catalyst neutralization, methanol vacuum stripping, biodiesel/glycerin
separation, and biodiesel distillation.

immediately following transesterification. After the reaction, the two by-product phase's
gravity separate, allowing the lower glycerin layer to be separated out of the bottom of
the reactor and pumped into the vertical decanter using centrifugal pump #4. Once
separate, the glycerin layer, containing virtually all of the residual polar methanol and
base-catalyst, can be neutralized with acid. After neutralization of the base-catalyst, the
glycerin phase is recombined with the methyl ester phase in the distillation reactor and
vacuum stripped of the co-solvent methanol. The methanol is collected and stored for
recycling into the next batch. After vacuum stripping is completed, the glycerin

component will gravity separate again before being removed from the system entirely and stored until it can be recycled into the next batches glycerolysis operation. The remaining methyl ester phase is now ready for the final binary distillation. The distillation system itself was designed and built to operate at full vacuum. Pressure and temperature controls were placed throughout the system while a secondary condenser trap was placed prior to entering the vacuum pump. Methyl esters are purified as they move up the column and removed through a collection duct at the top of the column connected to the vacuum line. Purified methyl esters and residual bottoms material are collected after distillation for analytical analysis.

2.2.3 Pilot-scale scum to biodiesel system; design and fabrication of the mobile trailer unit

In November of 2016, the trailer mounted scum to biodiesel pilot plant was completed. The trailer module required a 240-volt, 50-amp power source and access to a water source and drain. Biodiesel produced from the system was stored in, and distributed from a rear holding tank, while waste products required physical removal. The mobile trailer was operated by the University of Minnesota biodiesel research group members. For better resource allocation, the trailer was operated in parallel with the facilities current scum disposal technology. For simplicity, all pretreatment, conversion, polishing stages were contained within the mobile system, along with final product storage. External storage and waste holding tanks were considered for improved ease of operations and overall economics.

The size and specification of each reactor, pump, condenser, and heating element was assigned using a theoretical mass balance created by extrapolating the experimental laboratory mass balance to the predetermined pilot-scale. The metals and materials used to fabricate the reactors, pumps, and transfer tubing was cross-referenced with the chemicals each component was exposed to throughout the process. Chemical and heat resistant materials were used during all processes that required them. Cold chilling circulators were used to condense the vapor streams as well as cool process equipment.

2.2.4 Utility requirements and power monitoring

The total potential electrical load (watts and amps) required by the scum to biodiesel trailer was calculated by totaling the theoretical individual component loads throughout a single batch. The power outputs were taken from the factory specification sheets of each purchased component that required electricity to operate during a batch. The wiring and powering of each piece of equipment was performed by a certified electrician on-site at the University of Minnesota, under the instruction of the project P.I. A 100-amp circuit breaker was installed to act as a "relay switch" or on/off control for each individual electric motor. The circuit breaker itself was wired to a 240-volt, 50-amp male outlet plug. According to the systems operating procedure, there is little to no overlap in process operation, so no two operations were run at the same time. This meant that at no time throughout the batch process was there be a load on the system greater than 30 amps. Individual components ranged from 115-240 volts, all wired appropriately to the circuit breaker. All components were wired for 1-phase power, except for the 3-phase liquid-

solid centrifuge. A static frequency converter was purchased to convert the incoming

single-phase power to 3-phases for that single utility only.

2.2.5 Drainage and waste requirements

According to the theoretical mass balance, producing a single batch of biodiesel (63 kgs)

would generate the following waste streams;

-24.3 kgs of filtered biosolids (moisture level < 30%)

-50.5 kgs of waste water (contains neutralized Na_2SO_4)

-11.5 kgs of organic waste (MONG)

-43.4 kgs of heptane (recycled to next batch)

-8.1 kgs of methanol (recycled to next batch)

-4.5 kgs of water of reaction (glycerolysis)

-19.5 kgs of crude glycerin (recycled to next batch)

-15.5 kgs of distillation "bottoms"

In theory, all the organic waste streams (biosolids, MONG, organic emulsifications, and

distillation bottoms) can be combined with sludge wastes currently fed to the facilities

incinerators for the cogeneration of power. Each waste water stream has a small

concentration of COD and BOD, but should be suitable to enter the water treatment

process directly. All solvent streams can be recycled as reagent grade chemicals during

the next subsequent batch. Analytical testing has confirmed that repeat use of the heptane

and methanol does not have negative effects on the process quality or outcome. All waste and product streams have their own designated plastic holding tanks, capable of retaining several batch productions worth of material. The finished product biodiesel tank has a fixed fuel pump attached for easy loading of the product into fleet vehicles.

2.2.6 Safety and storage requirements

Due to the unknown site of operation, the scum to biodiesel mobile trailer was designed to be operated outside, open to atmosphere. There are no positive pressures throughout the process that would require additional safety precautions. The following is a list of specific design implementations that were chosen to address all potentially harmful scenarios.

1) Water-proof electrical conduit was used throughout the entire trailer to protect against accidental leakage, chemical or reagent spills/leaks, or rainfall.
2) A water-proof circuit breaker box was purchased to house the systems relay switches.
3) A metal box was purchased to house the ABB drive (digital phase converter) in order to protect it from the elements.
4) An explosion-proof (xp-rated) agitator was purchased for the heptane and oil mixing stage.
5) An explosion-proof transfer pump was purchased to move the heptane/oil mixture from reactor #1 to the vacuum stripping vessel.
6) A dephlagmator (reflux-condenser) was purchased to condense ALL heptane vapors and return them to the reaction vessel as a liquid.
7) Additional equipment involved in the heptane/oil extraction was designed so that they do not come into direct contact with the liquid or vapor phase.
8) The electrical components of the distillation reactor were not innately water-proof and were covered when not in use, if stored outside.
9) Charging of the reagents sulfuric acid, heptane, methanol, and sodium methoxide was performed using metering pumps, as to eliminate the potential for human contact. All chemicals were stored in appropriately specified plastic holding tanks and mounted to structural storage racks.

Due to the nature of scum and its inherent odor, the optimal location for the scum to biodiesel trailer would be outside, next to the solids management building (SMB) located within the St. Paul waste water treatment facility. A water source (hose) was available for process water and as an emergency source of dowsing water in case of fire. Alternatively, the trailer could be operated inside of the solids management building, next to the scum collection tanks. This would allow for better access to the initial scum to the system, as well as easier disposal of all waste streams, possibly eliminating the need for additional waste holding tanks.

2.3 Results and discussion

2.3.1 Scum to biodiesel – system inspection and start-up

After the complete installation and mounting of the scum to biodiesel process equipment onto the trailer, the system was tested to confirm the controls, heating, cooling, and pumps worked properly. A full vacuum was applied to the system while simultaneously heating water inside the reactor. Once it was confirmed the instrumentation working correctly, the pressure was relieved and the test water drained from the system. Finally, the system was visually inspected one last time before start-up. The chemical reagents necessary for the process were ordered and delivered safely to the test facility and stored on a spill containment pallet. According to the process mass balance, enough chemical reagents were acquired to perform two full batches of scum to biodiesel at max system

capacity. In addition to the chemical requirements, nitrogen and propane was sent to the research facility and secured to the wall. Pressure regulators were mounted to the tanks and gas rotameters used to measure the flow-rate to the reactors. To safely power the trailer, an electrician was hired to install an outlet equipped with 3-phase power at 50-amps and 240-volts. Copper grounding rods were also purchased and attached at several locations throughout the mobile system.

2.3.2 Experimental process results

2.3.2.1 Scum collection

Scum was collected from the St. Paul Waste Water Treatment Facility in January of 2017. According to the facilities standard practices, scum had been collecting for approx. 14 days in a large semi-trailer sized filter bed made from mesh plastic. Dilute scum water was pumped into the large filter bed after being skimmed off the top of larger holding ponds. During a 1-2-week period, the filter bed was continuously fed from the top with the dilute scum water. At the same time, filtered water left through a port in the bottom of the semi-trailer. Slowly over the 1-2-week period, solid scum accumulated until it reached the top of the filter bed. Using (3) 208 L plastic garbage bins lined with plastic, approximately 272 kgs of scum was transferred into the bins using spade shovels before being trucked to pilot-system.

2.3.2.2 Scum filtration

The newly sampled scum was loaded into the heated drum barrels using a spade shovel; the weight of scum (177.0 kgs) was measured using a 20 L pale and a commercial scale before entering the drums. The lids were sealed using a bull-ring while the bung holes were left open to avoid any pressure build-up inside the drum filters. Once the barrels were sealed, the drums were heated to 120°C and maintained for 24 hrs to ensure complete liquefaction of the liquid phase. The fat/oil/grease and water mixture drained through two stainless steel filters (1 and 5 mm^2 respectively) and collected below into heated conical bottoms. The liquid phase was intermittently pumped into reactor #1 as it was collected. After the filtering was complete, 113.5 kgs of oil/water mixture was transferred to reactor #1. According to previous research conduct by our research team, approx. 62.5% of the scum material by weight is a fat/oil derivative. Most of the scum takes the form of high energy fats, oils, and greases, while the second largest fraction is water (Anderson et al, 2016). Due to the uncontrolled evaporation of the water during the extended heating, approx. 16.8 kgs of scum material was unrecovered at this stage. Most of the unaccounted-for material was in the form of evaporated water, while some of it could be light carboxylic acids or volatile organics. Once all the oil/water mixture was removed, the drums were emptied of all residual material (filtered bio-solids) and weighed. Samples of the filtered biosolids were taken for heat of combustion analysis using bomb calorimetry.

2.3.2.3 Acid hydrolysis

After 113.5 kgs of scum entered reactor #1 from the filtration system, electric heating was applied. The mass and volume of the material transferred was determined independently using a scale (batch-wise measurements for mass) and an in-line digital flow-meter (volume). Two side-mounted 6 kW immersion heaters were used to heat the mixture to 68°C while a 0.5 horsepower agitator with explosion proof electric motor was used to homogenize the oil and water. Any independent water phase "fall-out" resulting from higher temperatures was weighed and recorded, then removed through a valve on the bottom of the tank and released to holding tank #1. In a separate container, 98% concentrated sulfuric acid (5.7 kgs) and water (34.0 kgs) was premixed before being pumped into reactor #1 using reagent pump #1. The oil/water/acid mixture was agitated for 30 minutes while maintaining 68°C. A reflux condenser or dephlegmator circulating an ethylene glycol and water mixture at 10°C ran continuously on the top of the reactor to condense water and solvent vapors back into the reactor. After the complete reaction time, the agitation was removed and the mixture let settle for 45 minutes. The denser acidic aqueous phase separated to the bottom of the reactor while the hydrolyzed oil phase remained as an upper layer. The lower acidic aqueous phase was drained into holding tank #1 and neutralized to a pH of 7 using incremental additions of 1N sodium hydroxide and a pH meter. The upper oil layer was left in the reactor, continuously mixed while maintaining a temperature of 68°C in preparation of the solvent extraction stage. In its present form, the primary component in the scum derived oil was free fatty acids, some innate to the oil while others a result of hydrolyzing soaps. The second largest

fraction was acyl-glycerides (mono-, di-, and tri-glycerides), the chemical precursors of the commercial biodiesel production process. The rest of the oil was comprised of a complex mixture of polar-organics, possibly a combination of protein breakdown, carbohydrate derivatives, humic acids, or pharmaceutical by-products entering the waste water system. The waste stream collectively is known as MONG (matter organic, non glycerol) and can hinder the biodiesel conversion process if not removed.

2.3.2.4 Chemical extraction

During the chemical extraction stage, the high solubility of free fatty acids and acyl-glycerides in hydrocarbon solvents was exploited to purify the oil stream before entering the biodiesel conversion process. Heptane (27.4 kgs) and water (19.0 kgs) was charged to reactor #1 using reagent pump #1. The mixture was heated and agitated at 76°C for 20 minutes with the reflux condenser set at 10°C to condense any solvent vapors back into the system. After the reaction was complete, the agitation was removed and the mixture allowed to settle for 30 minutes. During this time, the lighter oil and solvent phase rose to the top of the reactor, leaving an aqueous mixture of water and polar-organics in the lower phase. The polar organic phase or MONG was decanted along with the aqueous phase into holding tank #1. To remove any residual MONG from the oil phase, the heptane/oil mixture was circulated through the liquid-solid centrifuge, and then back into reactor #1 using pump #2. The mixture was continuously circulated for 2-3 hrs, shutting down only to remove solids build-up. Once the residual MONG was physically removed, the oil and solvent mixture (100.7 kgs) was transferred to the distillation reactor using

pump #3. The distillation reactor was used throughout the rest of the procedure as the primary reactor, controlled using a PLC (programmable logic controller) with pre-set heating and vacuum profiles. Once the oil and heptane was completely charged, the system was sealed and all safety checks performed. The agitation and chilled circulator were started approx. 1 hour before the start of the reaction, to reach their desired set-points prior to charging any chemical reagents. A heptane receiver (75 L) was attached and the vacuum system integrity was checked. To start the solvent removal process, program #1 (HEPTANE EXTRACTION) was run on the distillation system software. The parameters for program #1 ramp the temperature from room temperature to 120°C, under a vacuum of 8 kPa. Once these parameters were reached, the reaction conditions were maintained for 20 minutes. The heptane solvent vaporized and moved upward through the packed distillation column before exiting through the distillate line. After the reaction was completed (all of the solvent was removed), the vacuum was broken with nitrogen and the pressure returned to atmospheric (101.3 kPa). However, the heat was not reduced because the next unit operation required temperatures higher than 120°C. Instead, program #1 was halted and the system prepared for the next operation.

2.3.2.5 Glycerin esterification of free fatty acids

Free fatty acids present in the oil must be remediated prior to a base catalyzed transesterification reaction. Glycerin esterification was previously researched by our team members as a method to combine the free, unbound glycerin reagent with the free fatty acids (86% wt/wt) to form mono- and di-glycerides and water (Anderson et al, 2015). To

ensure an inert atmosphere during glycerolysis, nitrogen was used to purge the reactor

prior to the reaction. This was critical to glycerolysis as any oxygen present in the system

could oxidize the scum oil, creating unwanted derivatives. A 19 L distillation receiver

was inserted into the collection stream and the vacuum pressure was tested. Program #2

(GLCEROLYSIS) was run on the PLC while the vacuum pressure was reduced to 80 kPa

to assist in the removal of water generated during the reaction from the system. With an

initial temperature of 120°C, the oil was heated to 240°C under an inert nitrogen blanket.

Once the reaction temperature was reached and maintained for 5 minutes, 14.8 kgs of

U.S.P. glycerin was charged to the reactor using reagent pump #2. Once the mixture

reached a steady state, the temperature was maintained for 3.5 hrs. Water generated

throughout the reaction by the dehydration synthesis was immediately vaporized at

240°C and removed from the system through the distillation column. The water, along

with low-weight carboxylic acids, was condensed using a cold trap maintained at 10°C.

The heat supply was removed after 3.5 hrs and the free fatty acid content tested to

confirm it was < 1% FFA. An air-compressor was used through a quench coil to reduce

the temperature below 100°C faster than by radiant cooling alone. The system was

purged with nitrogen during cooling to avoid unintentional oxidation of the oil.

2.3.2.6 Transesterification using a liquid base-catalyst

The reaction product of glycerolysis was a mixture of mono- and di-glycerides. To

convert these molecular precursors to biodiesel, methanol and the base catalyst sodium

methoxide was needed to trans-esterify the acyl-glycerides into methyl esters and

glycerin. Program #3 (TRANSESTERIFICATION) was run on the PLC while the agitator and reflux condenser were started simultaneously. According to the run parameters, the oil was heated to 76°C before charging a 30% wt/wt $NaOCH_3$ in methanol solution (3.0 kgs) and excess MeOH (25.0 kgs) to the distillation system using reagent pump #2. Once the reaction mixture reached a steady-state, the temperature was maintained for 60 minutes while agitating. After the reaction was complete, the heat was removed and the agitation stopped. In order to separate the product biodiesel from the product glycerin, gravity decanting was employed. The mixture (118.0 kgs) was allowed to settle for 1.5 hrs with no agitation or heat at atmospheric pressure. The two products phases separated based on their respective densities, biodiesel (0.88 g/ml) and glycerin (1.26 g/ml), both mixed in the co-solvent methanol (0.79 g/ml). During most commercial biodiesel processes, these two-product streams would be processed separately from here on out. One unique nuance to the process described in this manuscript is the combined processing of the byproducts biodiesel and glycerin. By adding 98% sulfuric acid (1.8 kgs) directly to the lower glycerin phase, the polar $NaOCH_3$ present in the glycerin phase was neutralized without affecting the upper biodiesel phase. It was important to agitate the separated mixture very gently during acid neutralization into order to mix the acid within the glycerin layer, without disturbing or emulsifying the two phases. A pH meter was used to determine the end-point of neutralization (ph=8.5) in conjunction with a theoretical limit (3.3 kgs) based on the stoichiometric equivalence of sulfuric acid to $NaOCH_3$. Once neutralized, the biodiesel/glycerin/methanol mixture (119.8 kgs) was ready for the simultaneous removal of the co-solvent methanol.

2.3.2.7 Methanol stripping and glycerin separation

To prepare the distillation system for solvent vacuum stripping, a methanol distillation receiver (40 L) was installed and the reactor purged with nitrogen. On the PLC, program #4 (METHANOL STRIPPING) was run while agitation and heat was applied. According to the run parameters, the pot and column temperatures were set to 120°C and maintained for 20 minutes. The methanol vapor was condensed at 15°C and removed from the system. The majority of methanol was removed under these conditions, prior to any vacuum being applied. After atmospheric stripping was complete, vacuum was applied to the system until a pressure of 8 kPa was maintained at steady-state conditions for 20 minutes. Once the vacuum removal of the co-solvent was complete, the pressure was returned to atmospheric and the temperature returned to 20°C (room temp). Agitation was halted at the end of the reaction and the biodiesel/glycerin mixture was allowed to settle for 2 hrs. Unlike the gravity decant following transesterification, the two components lacked the co-solvent that previously lowered the density differential between them. In theory, the higher density differential allowed the glycerin to separate more efficiently from the methyl ester phase, resulting in a smaller emulsion layer between the two phases, lowering product loss. No additional heat was introduced during the gravity decant, but the insulation surrounding the reactor allowed for the separation to occur between 100-110°C. After the gravity decant, crude glycerin was removed from the bottom of the reactor until only biodiesel remained. Any impurities introduced into the transesterification process manifested themselves at this point as a "rag layer", emulsifying the plane of separation between the oil and glycerin layers. The rag layer was

removed along with the glycerin phase to ensure a higher quality biodiesel move onto the next operation. An air compressor and quench coil was used to reduce the temperature faster than through radiant heating alone.

2.3.2.8 Biodiesel distillation

To consistently produce biodiesel that meets ASTM certification, reflux distillation was employed to purify the methyl ester stream. A Mccabe Thiele diagram was created using Microsoft Excel to calculate the theoretical vapor velocity and subsequent distillation column size, shown in Appendix A. Based on the mass balance, a 75 L distillation receiver was installed for biodiesel collection and the system purged with nitrogen. Distillation was initiated by the running of program #5 (BD DISTILLATION) on the PLC. While the system was beginning to heat under vacuum, the agitation was started using a mechanically sealed, flange-mounted agitator. Program #5 heated the system to its maximum temperature of 260°C under the negative pressure of 0.25 kPa with continuous mixing. The initial distillate first appeared (condensed) at approx. 180°C, and the final distillate was collected at 270°C. As the biodiesel vapors traveled up the reflux column they were condensed using "bulb condensers", collected using an internal trough, then removed from the column via a condensate line that perforated the column wall and connected with the collection trough inside the column. The distillate collection was broken into 3 separate "cuts" or collections. The cuts were broken into 3 groups; the beginning, middle, and end. The primary difference between the cuts was the average temperature at which each one was distilled. Smaller chain methyl esters vaporize at

lower temperatures because of their lower molecular weight relative to longer chain methyl esters, which inversely distill at higher temperatures.

When distillation was complete, as indicated by the lack of distillate stream at temperatures above 270°C, the heat source was turned off and the system pressure was returned to atmospheric by slowly introducing nitrogen into the reactor before cooling. The product distillate from each cut was collected for the final polishing stage and the residual distillation bottoms were drained from the bottom of the reactor.

2.3.2.9 Water washing and vacuum drying

The final stage of the biodiesel production process is the removal of residual free glycerin carried through during methyl ester distillation. Water washing biodiesel will solubilize the polar glycerin molecule completely and allows it to be physically removed via gravity decanted phase separation. Water washing was crucial to ensuring no free glycerin remained in the fuel that could cause it to fail the ASTM D6751 specification of 0.02%. To water wash the biodiesel, de-ionized water (8.6 kgs) was added to the distilled product (20% wt/wt) at 60°C and mixed rapidly to guarantee adequate mass transfer. After 15 minutes of mixing at the desired reaction temperature, the mixture was allowed to settle in a separator flask for 60 minutes. The heavier aqueous phase fell to the bottom of the flask and was removed after the 60 minutes gravity decant, with little or no loss of product due to emulsion. The upper biodiesel layer was then placed into a vacuum dryer and heated to 120°C under a vacuum of 8 kPa. The vacuum drying conditions were maintained for 10 minutes until the mixture no longer generated steam bubbles. The

biodiesel was cooled and collected for complete analytical analysis using the EPA

certified ASTM D6751 test protocol.

2.3.3 Experimental mass balance analysis

One of the objectives of designing and building the pilot-scale scum to biodiesel system

was to test the laboratory extraction and conversion yields of scum derived oil. Proving

the process technology can be utilized at any scale would give greater confidence to

municipalities considering the waste-to-energy process. Shown below on Table 1, a

Table 1: Pilot-scale experimental mass balance results set against the theoretically

expected values. Analysis of the resulting differences identified specific unit operations

the over or under performed.

Individual Unit Operation	Laboratory Mass Balance (kg)	Theoretical *expected* (kg)	Experimental *actual* (kg)	Theo. vs. Exp. Error (%)
Heating and Filtration				
Scum "In"	177.0	177.0	177.0	n/a
Biosolids "Out"	24.3	24.3	46.8	n/a
Liquid Organics and Water Phase "Out"	152.7	152.7	130.2	-14.7%
Acid Hydrolysis and Solvent Extraction				
Liquid Organics and Water phase "In"	152.7	130.2	130.2	n/a
Oil "Out"	76.2	65.0	80.9	24.5%
Glycerolysis (FFA pretreatment)				
82% FFA Oil "In"	76.2	80.9	80.9	n/a
1% FFA Oil "Out"	89.7	95.0	91.9	-3.3%
Transesterification and MeOH Stripping				
Dry Acyl-glyceride oil "In"	89.7	91.9	91.9	n/a
Biodiesel and Glycerin "Out"	99.1	101.5	100.2	-1.3%
Biodiesel/Glycerin Phase Separation				
Biodiesel/Glycerin "In"	99.1	100.2	100.2	n/a
Crude Glycerin "Out"	19.5	19.0	19.5	n/a
Crude Biodiesel "Out"	79.6	81.2	80.7	-0.6%
Biodiesel Distillation				
Crude Biodiesel "In"	79.6	80.7	80.7	n/a
Distilled Biodiesel "Out"	63.7	64.6	42.0	-34.9%
Water Washing Free Glycerin				
Distilled Biodiesel "In"	63.7	42.0	42.0	n/a
ASTM-certified B100 Biodiesel "Out"	63.0	41.6	41.6	0.0%

comparison of several mass balances for the entire scum to biodiesel process can be seen. The first column, "laboratory mass balance", represents the laboratory conversions efficiencies and yields throughout each stage of the process, as applied to the experimental starting mass of scum (177 kg). These values represent the expected weights of the incoming and out coming streams, assuming the same initial mass of scum, equivalent equipment capabilities, and zero loss from transfer or human error. The second column, "theoretical *expected*", are the expected values for each unit operation, assuming the starting mass is equal to that of the previous stages experimental mass outcome. In this way, the results are a function of the theoretical mass balance, as it's applied to the experimental results of each unit operation. The third column, "experimental *actual*", listed the experimental results of each unit operation, not taking into account loss due to transfer. The second and third column results were used as the basis of comparison in the fourth column, "theoretical versus experimental error". The percent error was calculated using the formula, % error = {(experimental-theoretical)/theoretical}. Four of the 7-unit operations had percent errors below 3.5%, but 3 of the results deviated from the theoretical outcomes more significantly. The first unit operation, heating and filtration, yielded -14.7% less liquid phase than expected. The suggested reason for this was the uncontrolled evaporation of water during the extended heating period. As water removal was a function of the second unit operation, acid hydrolysis and solvent extraction, the mass balance corrected itself by accounting for the loss of all water. The organic fraction was concentrated as the water evaporated during the first unit operation, so the yield after the second operation, which included water

removal, was much higher than the mass balance prediction. The percent error for the second unit operation was +24.5%, while the overall yield after two unit operations was +9.8% above the expected value. The last discrepancy between actual versus expected was seen during biodiesel distillation. Due to several system failures during methyl ester distillation, the distillation timeline was over 4 times the expected value. In addition, valve failure inhibited the vacuum system for a significant amount of time at high temperatures, possibly allowing for unintended side reactions or oxidation of the product methyl ester. Due to these unforeseen operation errors, the distillation yield was significantly lower than expected, -34.9%. Distillation yields at the laboratory scale were consistently higher (85%) and the reason for the depressed outcome was thought to be mechanical in nature. Further system improvements and testing should improve distillation yields.

2.3.4 Analytical and certification results

To test and certify the product biodiesel was fit for use in diesel engines, the full range of the ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels was employed. In total, 6 liters of scum derived biodiesel was sent to a private third-party testing facility, Gorge Analytical, LLC, located in Hood River, OR. Gorge Analytical is a certified biodiesel testing facility, able to supply certificates of analysis that meet biodiesel quality assurance specifications for the EPA's requirements for sale and tax credit valuation. The laboratory also participates in the BQ-

9000 biodiesel quality assurance program, ensuring their testing methods meet the

highest standard available.

The list of analytical tests, their respective methods, and the results can be seen below in

Table 2. The results and the reporting criteria with units are listed next to one another

with a "pass" or "fail" indicating the analytical test was within the range of certification.

As the tests indicate, the fuel passed the full range of ASTM D6751 tests required for

biodiesel certification. Results for several different temperature collection ranges or

"cuts" are shown to determine any early or late stage compounds that may come over as

an

Table 2: Complete test profile results for the Standard Specification for Biodiesel Fuel

Blend Stock (B100) for Middle Distillate Fuels, ASTM D6751. Results from the initial,

Analytical Test	Analytical Method	Pass Criteria	Cut #1	Cut #2	Cut #3	Avg. Results	Pass/Fail
Distillation Temp	ASTM D1160	360°C max	343	351	350	348	Pass
Copper Strip Corrosion	ASTM D130	No. 3 max	1a	1a	1a	1a	Pass
Cloud Point	ASTM D2500	n/a (°C)	16	11	8	12	n/a
Water and Sediment	ASTM D2709	0.05 % max	0	0	0	0	Pass
Visual Instepction-Part 1	ASTM D4176-P1	Haze rating	1	1	1	1	n/a
Visual Instepction-Part 2	ASTM D4176-P2	No particulate	No debris	No debris	No debris	No debris	Pass
Kinematic Viscosity @ 40°C	ASTM D445-40	1.9-6.0 mm^2/s	4.193	4.607	4.484	4.428	Pass
Micro-carbon Residue	ASTM D4530	0.05 % max	< 0.001	< 0.001	< 0.001	< 0.001	Pass
Phosphorus by ICP-OES	ASTM D4951	0.001 % max	< 0.0001	< 0.0001	< 0.0001	< 0.0001	Pass
Sulfur by UVF -S500, 1B criteria	ASTM D5453	500 ppm	17	77.2	12.4	35.5	Pass
Free & Total Glycerin	ASTM D6584-total	0.240 % max	0.007	0.008	0.008	0.008	Pass
Free Gycerin	ASTM D6584-free	0.020 % max	0.004	0.005	0.004	0.004	Pass
Total Mono-glycerides	ASTM D6584-1	n/a	0.008	0.006	0.002	0.005	n/a
Total Di-glycerides	ASTM D6584-2	n/a	< 0.013	< 0.013	< 0.013	< 0.013	n/a
Total Tri-glycerides	ASTM D6585-3	n/a	0.019	0.022	0.031	0.024	n/a
Total Acid Number	ASTM D664	0.50 mg KOH/g	0.26	0.78	0.37	0.47	Pass
Derived Cetane Number	ASTM 6890	47 min	74.1	65.8	68.5	69.5	Pass
Cold Soak Filtration Test	ASTM D7501	360 seconds	89	100	91	93	Pass
Sulfated Ash	ASTM D874	0.020 % max	< 0.005	< 0.005	< 0.005	< 0.005	Pass
Flash Point, Pensky Martens	ASTM D93	93°C	159.5	177.5	175.5	170.8	Pass
Ca, Mg by ICP-OES	EN 14538:2006-Ca, Mg	5 ppm	< 2.0	< 2.0	< 2.0	< 2.0	Pass
Na, K by ICP-OES	EN 14538:2006-Na, K	5 ppm	< 2.0	< 2.0	< 2.0	< 2.0	Pass
Oxidative Stability at 110°C	EN15751:2009	3 hrs	7.3	6.7	5.1	6.4	Pass

middle, and final distillate cuts were reported along with the batch average.

azeotropic mixture with methyl esters. Cut #1 was collected between the temperature ranges of 182-209°C, Cut #2 collected between 209-238°C, and Cut #3 collected between 238°C and the final temperature of 270°C. The reporting column, "averaged results" reports the overall test result by averaging the 3 temperature range results, as if they had been collected into a single vessel. One result of the fuel property testing was that the cetane number of the scum derived biodiesel was unexpectedly high. The derived cetane number is a function of the oils free fatty acid characteristics and can be broad in range (Ramos et al, 2009). Biodiesel from vegetable oil typically falls between 46-52, while biodiesel from animal sources generally have higher cetane numbers between 56-60 (Knothe, 2014; Suryanarayanan, 2007). Scum derived biodiesel returned an average cetane number of 69.5. As the inverse function of a fuels ignition delay, a higher cetane number equates to a shorter ignition delay period in diesel engines compared to fuels with a lower cetane number.

2.3.5 Impact and significance of on-site waste to energy generation

According to the St. Paul waste water treatment facility, they produce approx. 3,175 kgs of wet scum each day. Applying the conversion efficiencies obtained during pilot-scale testing, a potential 530,000 liters of certified biodiesel could be produced each year from this one facility. Based on the facilities internal estimations, this would off-set the purchase of over 20% of the facilities annual diesel usage, while at the same time

removing the material from landfill. Combining the experimental results with previously

published cost and energy data regarding the process indicates a conversion cost of

$0.36/liter of biodiesel. Extrapolating this figure to a full-scale production yields an

annual cost of $190,400/yr. The assumed costs were calculated using current market data

for all chemicals, electricity, heat, and labor required throughout the process (Anderson et

al, 2016). The value of the biodiesel can be determined by its off-set savings of petroleum

diesel. With an average price at the pump between $3.0-3.5/gallon, using fuel produced

on-site could save the facility between $420,000 and $490,000 each year. In addition, the

EPA's $1.00/gallon tax credit and Renewable Identification Number (RIN) biodiesel

production credit could also be applied for additional revenue streams of $140,000 and

$168,000, respectively (OPIS ethanol and Biodiesel, 2017).

2.4 Conclusion

A pilot-scale system was designed, fabricated, and operated based on a recent patented

scum to biodiesel process. The objective was to confirm the patents product quality and

process efficiency was not a function of process scale. According to third party analytical

analysis, biodiesel generated from scum meets all the same federal and state testing

guidelines imposed upon the commercial biodiesel industry. Based on previous models, a

full-scale system could produce approx. 530,000 L of biodiesel each year at the St. Paul

water treatment plant. Indirectly, this would be removing approx. 87% of the scum

material from the landfill each day.

2.4.1 Research and funding acknowledgments

Chapter 3 Glycerin esterification of scum derived free fatty acids for biodiesel production

3.1 Waste oil impurities and remediation background

Scum is an oily waste by-product of the wastewater treatment process. Currently, scum is treated either by anaerobic digestion to produce low energy density biogas or by landfilling, the latter of which raises great environmental concern. Research efforts have resulted in a novel process for extracting and converting the oil generated from scum to biodiesel. Scum-sourced oil is a broad mixture of several hydrophobic organic compounds, the most prevalent being acyl-glycerols, glycerides, and free fatty acids. Additionally, the extracted oil contains many impurities that require removal or modification before processing, such as herbicides, insecticides, and other organic macromolecules (Bi et al, 2015). Elemental analysis showed soluble metal and non-metal compounds present in the filtered scum oil. Traditionally, acid washing with water has been the most prominent method for removing such impurities for biodiesel production from alternative fuel sources (Knothe & Van Gerpen, 2010). Based on previous findings,

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sulfuric acid was chosen over phosphoric and hydrochloric acid for the acid hydrolysis of scum oil (Bi et al, 2015). By combining previously separate purification stages, acid hydrolysis and solvent extraction, a free fatty acid and acyl glycerol rich product can be produced. The resulting oil has an Acid Value (AV) of approx. 170-174, which correlates to a free fatty acid (FFA) concentration of approx. 86%.

Before the oil can be converted to methyl esters (biodiesel), the FFA needs to be converted to an acyl-glycerol. Without a pretreatment, the FFA will react preferentially with the base-catalyst to form alkali soap. Traditionally, the most prevalent pretreatment method has been the acid-esterification, since it can be done at relatively low process temperatures. Acid esterification is the direct conversion of FFA's into methyl esters using sulfuric acid as a catalyst, with an excess of methanol (Knothe & Van Gerpen, 2010). During acid esterification, each mole of fatty acid converted to methyl esters produces one mole of water. The resulting wet methanol must then be decanted, neutralized, and dried via fractional distillation with high reflux rates before the methanol can be re-used. Methanol drying columns can cost millions of dollars and consume the largest percent of processing plants' energy. By not having to dry wet methanol after acid esterification, biodiesel plants can cut their thermal energy consumption in half (Anderson, 2014).

Alternatively, glycerin esterification or "glycerolysis" can reduce FFA in low-grade oils without the use of acid, methanol or vacuum stripping (Jackam et al, 2014). When glycerin is combined with the scum-derived oil at a temperature of approximately 238°C, the free fatty acids will react with glycerin to form an acyl glycerol or glyceride and water. The resulting glycerides formed during glycerolysis can then be converted

directly to biodiesel via base-catalyzed trans-esterification. Since glycerolysis is done at such high temperatures, any water formed is driven out immediately via a nitrogen purge. The continuous removal of water throughout the process via a nitrogen purge is important for multiple reasons. Drying the feed oil to moisture levels below 0.5% avoids the formation of excess soaps during base-catalyzed transesterification and the decanting problems that can occur (Leung et al, 2010). Purging the water from the system will also shift the reaction equilibrium toward the product side, allowing the free fatty acid concentration to fall below 0.2%. This is the result of Le Chatelier's principle, or "the equilibrium law", which states that when a system at equilibrium is subjected to change (i.e. removal of water at low concentrations), the system will readjust itself to counteract the effect of the change, establishing a new equilibrium. This principle has been used to manipulate the outcomes of reversible reactions, often to increase the yield of a specific product (Atkins, 1993). Along with water, volatile organic compounds and light carboxylic acids are removed during the purge. These compounds are the result of organic oxidation and can be very odorous. Blanketing the system with nitrogen avoids any further oxidation of the oil components at high temperature.

The only reagent needed for successful glycerolysis is glycerin, a co-product of the trans-esterification of acyl glycerols. In plants using glycerolysis, the glycerin produced during trans-esterification can be recycled back into the process, and the excess glycerin can be refined for sale as a valuable byproduct (Kome et al, 2013). Catalysts present in the glycerin phase after trans-esterification must be neutralized using an acid then removed via filtration. Sulfuric acid is a cheap and available mineral acid that will form sodium sulfate when used to neutralize the base catalyst sodium methoxide. As

shown later, the presence of sodium sulfate in glycerin bound for glycerolysis can have benefits extending beyond reaction rate and acyl glycerol formation.

The rate of the glycerolysis reaction is determined by two variables: initial concentration of FFA and temperature. In batch systems using refined free glycerin, FFA concentrations over 90% have been reduced to below 0.3% in only 3 hrs of reaction time. The optimum temperature range for non-catalyzed glycerolysis is between 221-238°C (Jackam et al, 2014). The presence of an inorganic catalyst can also have a large effect on reaction rate and may serve to lower reaction temperatures. Many biodiesel plants run their processes at operating temperatures of 176°C or below. Although glycerolysis can be run at lower temperatures, reaction rates are vastly improved when run at temperatures around 232°C (Anderson, 2014). Operating temperatures approaching 260°C are not recommended due to possible glycerin decomposition (Albin, 1962).

Catalyzed free fatty acid reduction via glycerolysis is one approach being studied to address production limitations. Different inorganic catalysts were tested during high temperature glycerolysis (238°C) to study the reaction kinetics of converting free fatty acids (FFA) to mono-, di-, and tri-acyl-glycerol. The glycerin introduced during glycerolysis must be removed in subsequent processes. A combination reflux distillation, mid-condenser phase separation, and adsorbent filtration are being researched to remove residual unbound glycerin. By modeling of all reactions present, reaction conditions and residence times can be optimized to produce biodiesel as energy efficiently as possible. The process serves the dual purposes of converting scum to a higher value product (biodiesel) and reducing environmental pollutants in both landfills and water resources. As a result, 70% of the dried and filtered scum oil can be converted to biodiesel, the

equivalent of approximately 140,000 gallons of biodiesel and $400~500K profit per year (Haas et al, 2006). A scum-to-biodiesel conversion process for the treatment and complete utilization of scum has the potential to be both more economical and environmentally sound than current practices.

The objective of the research performed was to compare two different inorganic catalysts during high temperature glycerolysis (238°C) against a third uncatalyzed reaction. By analyzing the concentrations of all the reaction components, the catalytic potential of each scenario could be assessed, assuming a first-order reaction. Factoring in the catalytic potential along with projected catalyst costs, the economic potential of each scenario could also be determined. Additionally, different acyl-glycerol formation reactions were studied to understand the effects of metallic catalysts on glyceride formation. Understanding the final concentrations of various acyl-glycerols could allow for improved modeling data for changes in bulk density and volume throughout glycerolysis. The sulfur reduction potential of the catalyst was determined by removing the catalyst after glycerolysis. Any reduction in sulfur levels was attributed to the binding or complexing of the metal catalyst with sulfur.

3.2. Materials and Methods

3.2.1 Material and reagent

The scum samples were collected from Metropolitan Wastewater Treatment Plant at St. Paul, MN. Sulfuric acid (98%, AR) and Hydrochloric acid (36.5-38.0%, AR) were

obtained from Mallinckrodt Baker, Inc. Paris, Kentucky. Phosphoric acid (85.0%, GR) was obtained from EM Industries, Inc. Butanetriol (1000mg/ml), tricaprin (8000mg/ml), and N-methyl-N-(trimethylsilyl) trifluotoacetamide (MSTFA) were obtained from Sigma-Aldrich, Inc. Sodium methoxide (30% in methanol), methanol (anhydrous, 99.8%), n-heptane (HPLC grade), potassium hydroxide concentrates (0.1 N), ~50 micron filter paper, and glycerol (99.9%) were obtained from Thermo Fisher Scientific, Inc. Distilled water was obtained from Premium Waters, Inc. MN, USA.

3.2.2 Oil rendering process and experimental design

The general process for the preparation of scum derived oil can be summarized according to the following six steps:

Heat Scum→Filter→Acid hydrolysis→Solvent Extraction→ Solvent distillation→ Glycerolysis

The detailed experiment procedures are described in sections 3.2.2.1-3.2.2.4.

3.2.2.1 Scum filtration and analysis

4500.0 grams of raw scum was heated to 82°C in a 4L beaker. The removal of plastics, cellulosic biomass and other non-oils from the scum oil is the first stage in the rendering process. The heated scum is combined with a waste acid water stream before being sent through a paper filter (~1000 micron), removing solids and some water-soluble salts from

the oil. The scum was separated as a liquid oil and water mixture and initially allowed to

separate via gravity separation. Water that fell out of solution was removed in a

separatory funnel before the oil was transferred to a drying apparatus. After being dried at

121°C and 100mmHg (13.3kPa) for 5 minutes, the oil fraction yielded 2430.0 grams. The

oil contains many metals and non-metals that require removal via acid hydrolysis.

Sulfuric acid (98%) was used for its ability to solubilize metal and non-metal

components, primarily, Ca, Fe, Al, Mg, Zn, N, and P.

3.2.2.2 Acid hydrolysis and solvent extraction

Starting with 2430.0 grams of dry filtered scum oil, a combination of 121.5 grams (5.0%

wt/wt) of 98% sulfuric acid and 1215.0 grams D.I. water (2:1 oil to water) was charged to

the oil at 66°C. The temperature was maintained while being mixed thoroughly with an

agitator. After 30 minutes the mixing was slowed significantly and the mixture could

settle for an additional 30 minutes. Once settled and two distinct solution phases were

present, the acidic water and white precipitate were decanted from the bottom of the

reaction vessel. A second water wash using 50% wt/wt D.I. water and 50% wt/wt heptane

was then added to the oil at 49°C and mixed for 15 minutes. Any residual mineral acid in

the oil dissolves in the water then decanted after 30 minutes of settling with slight

agitation. The heptane and oil phase floats to the top while the bottom acidic water phase

and middle slightly polar hydrophobic regions are decanted as waste. The oil extraction

method combines two independent processes commonly used in separate industries into 1

single stage acidulation and solvent extraction. By repeating the process after the acidic

water decant in a batch system, the oil volume builds until the heptane solution is completely saturated. After the last decant, the oil/heptane mixture was removed from the decanter and placed in a 5 liter, 3-necked round bottom flask, affixed with agitator, thermometer and nitrogen spurge tube. The oil and heptane solution was heated to 238°C to remove the heptane solvent from the oil. The high temperature will vaporize any heptane and water still present and the nitrogen flow will carry the vapor into a separate condensing vessel. The resulting 2235.6 grams of suspended oil is a mixture of acyl-glyceride, free fatty acids. The solvent distillation process allows for an easy and efficient method for recycling of the heptane.

3.2.2.3 Glycerolysis catalyst comparison: acyl glycerol formation

Before the scum extracted oil could be used to compare glycerolysis catalysts, the co-solvent heptane needed to be removed. The oil was heated to 204°C, under a slight vacuum (100mmHg or 13.3kPa) and the heptane vapor was condensed and collected in a separate collection vessel. The solvent extracted oil was separated in order to compare three different reaction conditions; catalyzed with $Zn-Al_2O_3$, catalyzed with Na_2SO_4, and uncatalyzed. Each separate reaction condition or "batch" contained 600.0 grams of "dry" oil before glycerolysis. The oil was heated to 238°C while being agitated inside an inert nitrogen environment, and then 18% wt/wt U.S.P. glycerin was charge to the reaction chamber, with or without a catalyst present. When the reaction was complete, any catalyst present was filtered out of the reaction mixture using ~50-micron filter paper. Any potential ability to recycle and reuse the catalyst is unknown now. The glycerin

however can be recycled with great efficiency. After glycerolysis, the oil will undergo a base-catalyzed transesterification, effectively releasing free glycerin and allowing it to physically separate from the methyl esters. Depending upon the catalyst used, it will need to be filtered from the system before the base-catalyzed transesterification and subsequent recycling of the resulting glycerin. Nitrogen was introduced subsurface and aided in the removal of water through side ports of the reaction vessel, above the liquid level. During the heating process water, residual heptane, and volatile organic compounds were vaporized and carried out of the reaction vessel before being recaptured using a chilled water condenser. Small amounts of FFA could also be carried over during the purging of nitrogen, but at 238°C and atmospheric pressure, the theoretical molar fraction of FFA in the water vapor is less than 2%.

3.2.2.3.1 Catalyst #1 – 1.8% Zn-Al$_2$O$_3$

Once the scum derived oil reached 238°C, 18.2% wt/wt (109.3g) U.S.P. glycerin and 1.8% wt/wt Zn-Al$_2$O$_3$ (10.6g) was charged to the oil (600.0g) while under a nitrogen blanket. The catalyst is Zn (20 wt %)/Al$_2$O$_3$ (acid), approx. 20% wt/wt Zn loaded onto Al$_2$O$_3$. The catalyst is prepared using the impregnation method. To get 100 grams of catalyst, 91 grams Zn (NO$_3$)2·6H$_2$O was dissolved in 60ml distilled water then added to 80 grams acid Al$_2$O$_3$ powder and mixed. The mixture is aged for 10 hrs and then dried at 105°C for 24 hrs and finally calcined at 500°C for 5 hrs to get the catalyst. The reaction mixture was stirred vigorously for 1 hr while maintaining a temperature of 238°C. Nitrogen was metered into the reaction vessel at 380 ml/min to purge the system of water

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and prevent thermal oxidation. 2.0-2.5-gram samples were taken at 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, and 60.0 minutes, using a 10ml glass pipette. Heat was removed after 1 hr and nitrogen was removed once the oil temperature fell below 150°C.

3.2.2.3.2 Catalyst #2 – 1.0% Na_2SO_4

When the scum derived oil reached 238°C, 18% wt/wt (108.0g) recycled glycerin containing 1.0% wt/wt Na_2SO_4 (6.08g) was charged to the oil (600.0g) while under a nitrogen blanket. The 1.0% Na_2SO_4 was the result of neutralizing the base-active glycerin co-product of trans-esterified scum oil with 98% sulfuric acid. Therefore, the 1.0% Na_2SO_4 present was limited by the amount of sodium methoxide present during trans-esterification. The reaction mixture was stirred vigorously for 3 hrs while maintaining a temperature of 238°C. Nitrogen was metered into the reaction vessel at 380 ml/min to purge the system of water and prevent thermal oxidation. 2.0-2.5-gram samples were taken at 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 90.0, 120.0, 150.0 and 180.0 minutes, using a 10ml glass pipette. Heat was removed after 3 hrs and nitrogen was removed once the oil temperature fell below 150°C.

3.2.2.3.3 Non- catalyzed #3 – U.S.P. glycerin

After the scum derived oil reached 238°C, 18% wt/wt (108.2g) U.S.P. glycerin was charged to the oil while under a nitrogen blanket. The reaction mixture was stirred vigorously for 2.5 hrs while maintaining a temperature of 238°C. Nitrogen was metered

into the reaction vessel at 380 ml/min in order to purge the system of water and prevent

thermal oxidation. 2.0-2.5-gram samples were taken at 5.0, 10.0, 20.0, 30.0, 40.0, 50.0,

60.0, 90.0, and 120.0 minutes, using a 10ml glass pipette. Heat was removed after 2.0 hrs

and nitrogen was removed once the oil temperature fell below 150°C.

3.2.2.4 Sulfur reduction potential of metal catalysts

The sulfur levels were monitored before and after glycerolysis to determine if any of the

metal catalysts tested could serve as a sulfur binding agent. Since each reaction was

performed using the same bulk starting material, only one test was required for the initial

sulfur concentration before glycerolysis. After glycerolysis, the catalyst was removed via

a centrifuge to determine residual sulfur concentrations. Immediately after glycerolysis,

the oil from each reaction was cooled below 94°C and centrifuged at 4000 rpm for 5.0

minutes in order to remove any insoluble heterogeneous catalysts.

3.2.3 Analytical methods

3.2.3.1 Acid value (AV) determination

Acid value (mg KOH/g oil) is an indicator of the free fatty acid content in the scum oil.

Standard Test Method for Acid Value of Fatty Acids and Polymerized Fatty Acids

ASTM D1980-87 (1998) was used to determine the acid value. Variations in acid value

results were minor with a standard deviation of less than 1%. Changes in acid value throughout the glycerolysis reaction were monitored and the rate constant "k" was determined for each of the three different reaction parameters.

3.2.3.2 Free and total glycerin (F&TG) analysis

To obtain mono-, di-, and tri-acyl-glycerol and free glycerin concentrations throughout glycerolysis, the ASTM D6584-13e1 method was employed. Samples were taken via a glass transfer pipette at time intervals 0, 5, 10, 20, 30, 40, 50, 60 90, 120, 150, 180 minutes. Immediately after sampling and transferring to a closed vial, cold water was used to cool the oil and halt the reaction. Once cooled below 94°C, 11.0 mg of sample was transferred to a 20ml sealed screw-top vial for GC-FID testing. Samples were used for GC-FID analysis of the reaction components and for the titration of free fatty acids. Results from GC analysis were reported on a mass percentage basis for a total composition analysis. Four point GC calibrations curves were generated prior to the study for all components with an average R^2 value of 0.993. Further study is required to determine the actual variance of the data points themselves.

3.2.3.3 Sulfur analysis

Oil samples taken before and after glycerolysis were submitted to Gorge Analytical, LLC in Oregon (Hood River, OR) to perform elemental sulfur analysis. The ASTM method D5453-12, Standard Test Method for Determinations of Total Sulfur in Light

Hydrocarbons, Spark Ignition Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence was used to determine sulfur concentrations. Post glycerolysis oil samples were filtered before testing to remove the catalyst and any potential catalyst bound sulfur.

3.3 Results and discussion

3.3.1 Scum filtration

The 4500.0 grams of original scum oil contained a significant amount of water, bio solids, soluble metals and non-metals compounds, and other organic macromolecules like herbicides and insecticides. The filtration process reduced the scum to a 3555.0-gram liquid fraction, approx. 79% of the original scum weight. The filtered bio solids were roughly 50% by weight oil and may have potential as a high energy substrate for gasification or pyrolysis (Harris et al, 2010). A vacuum bag filtration system was used for the sake of the cost, but due to "filter blinding", was slow and inefficient. Screw presses filtering or a solid/liquid centrifuge would be recommended for any scale-up of the technology.

3.3.2 Acid Hydrolysis

Previous research on metal and non-metal removal from scum was conducted by Bi et al, 2015. It concluded that most sediment was formed when H_2SO_4 was used as a proton

donor, while less sediment was seen using H_3PO_4 or HCL. It was hypothesized that the

SO_4^{2-} and PO_4^{3-} were more likely to form insoluble salts with the metallic elements, such

as $CaSO_4$, $Fe_2(SO_4)_3$, etc (Bi et al, 2015). Once the metals precipitate out of solution and

removed through filtration, the acidic water can be used to pretreat incoming scum.

The nitrogen content of the scum can be considered an indicator of surfactant present, as

it may form various hydrophilic groups such as $-NH_3$, $-NH_2^+$, etc (Goddard &

Ananthapadmanabhan, 1993; Hayashita et al., 1994).

3.3.3 Heptane Extraction

At this stage, a sample of the liquid mixture was dried at 121°C and 65mmHg (8.6 kPa).

This resulted in a 25% loss in weight, which would theoretically drive off approx. 1125.0

grams of moisture from the entire batch. The dry, solids free oil represents 54% of the

initial scum weight, but still contained organic impurities. After the heptane wash and

subsequent extraction process were completed, the overall process yielded 2235.6 grams

of free fatty acid rich oil (86% FFA), with the total extraction yield at approx. 49.7%. The

purpose of the heptane washing is to force slightly polar, non-oil impurities out of the

solvent phase. Without the solvent extraction, impurities would be carried through the

process, causing unwanted side reaction and emulsions. Once the scum, heptane, and

water mixture was settled, a distinct grey middle layer formed between the top solvent

and oil layer and the bottom water layer. The grey matter was an assorted combination of

unknown organic impurities, not polar enough to be water soluble, but also not soluble in

a hydrocarbon solvent like heptane.

The pretreatment process alone represents the largest reduction in volume throughout the entire process. Since one of the goals of the process is to reduce landfill volumes at waste water treatment facilities, the entire pretreatment process boasts a 46% reduction in land volume. The reduced volume is attributed to combined solids and suspended organics removal, as well as the separation of water from the oil. Since water separation is an innate part of the process, the weight attributed to water in the scum can be considered savings from landfill because landfills charge on a per weight basis (Trueblood, 2015).

3.3.4 Glycerolysis Catalyst Comparisons

By varying the presence of different metal-based catalysts, different reaction parameters were measured and FFA reduction rates determined. The catalysts chosen for the experiment represented 3 distinct groups of catalyst sources; salt already present in recycled glycerin (Na_2SO_4) from a biodiesel process, an externally purchased metallic catalyst ($Zn-Al_2O_3$), and no catalyst at all. Once the FFA concentrations were plotted against time, the resulting curves seem to follow an exponential decline model. However, the acyl-glycerol formation reactions were distinctly different between all reaction conditions, both in rate and final concentration. Details of the formation reactions and the effects of a catalytic presence are described below.

3.3.4.1 Acyl-glycerol formation

Looking at the graphs in Figures 1-3, several different reactions can be seen proceeding as various rates. All possible acyl-glycerol formation reactions shown in the figures are summarized below in equations 1-4. When research first began it was assumed that the primary reaction responsible for the reduction in free fatty acids was Eq. 1, FFA reacting with unbound glycerin in a dehydration reaction to create mono-acyl-glycerols and water. However, the results suggest that there is little stearic hindrance to cause FFAs to distinguish between an unbound glycerin and a mono-acyl-glycerol. In almost all cases, the initial rate of formation of mono-acyl-glycerols was only slightly greater or equal to the rate of di-acyl-glycerol formation (Eq. 2). Additionally, a second trend of acyl-glycerol reordering occurred when the concentrations of unbound glycerin and mono-acyl-glycerols were relatively equal. At this stage, the continued trend in acyl-glycerol formation is dependent upon the presence and type of metallic catalyst in solution.

Free Fatty Acid + Glycerol → Mono-acyl-glycerol + Water   Eq. 1

Free Fatty Acid + Mono-acyl-glycerol → Di-acyl-glycerol + Water   Eq. 2

Free Fatty Acid + Di-acyl-glycerol → Tri-acyl-glycerol + Water   Eq. 3

Tri-acyl-glycerol + Glycerol → Mono-acyl-glycerol + Di-acyl-glycerol   Eq. 4
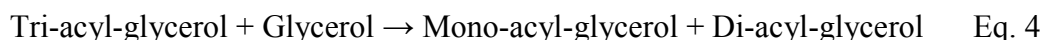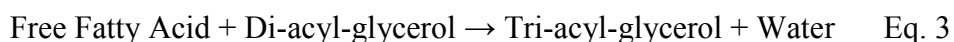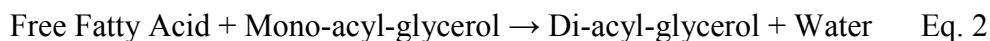
The amount of glycerin charged to the oil was determined through trial and error. It was discovered that slightly more glycerin than was stoichiometrically required to convert all of the FFAs present resulted in the fastest reaction rates. Adding more glycerin beyond 18% wt/wt only diluted the FFA's without increasing reaction speed or lowering the final FFA concentration. Since mono- and di-acyl-glycerols will also react significantly with FFAs, the reason for the need for an excess of glycerin is unknown. One theory suggests that excess glycerin allows for a faster conversion of higher amounts of low-order acyl-

glycerols. Additional research involving a glycerin starved environment may result in greater levels of high-order acyl-glycerols.

3.3.4.2 Acyl-glycerol formation during 1.8% Zn-Al$_2$O$_3$ catalyzed glycerolysis

The first reaction condition studied was the use of the heterogeneous metallic catalyst zinc aluminum oxide. The catalyst was chosen for its ability to increase the ionization potential of the solution while staying stable at the high temperatures glycerolysis requires (Ozgur et al, 2005). The 1.8% wt/wt used was determined as a hypothetical maximum, with any higher concentration being unrealistic in a commercial setting. In a perfect world, a full study would be conducted to determine the actual cost to benefit ratio of various concentrations of each catalyst. However, 1.8% wt/wt was chosen as it represented a reasonable maximum for filterable material before product loss due to saturation became an issue. Using any heterogeneous catalyst at all may prove to be uneconomical because of the additional cost of processing required i.e. filtration and catalyst recovery.

The use of a Zn-Al$_2$O$_3$ catalyst resulted in the fastest reduction of FFAs across all three experiments. FFA levels were reduced below 0.72 mg KOH/ mg of oil (0.36% FFA) within 60.0 minutes of the reaction. Figure 1 showed the initial formation of mono and di-acyl-glycerols occurred at almost identical rates, indicating that in the presence of the inorganic catalyst, Eq. 1 and Eq. 2 are equal in reaction rate. A change in formation rates occurred once the concentrations of FFA equaled that of mono and di-acyl-glycerols, approx. 30% wt/wt each. After the three components reached equilibrium, the formation

of mono-acyl-glycerols leveled off before slowly falling to a final concentration of

26.5%. The formation of di-acyl-glycerols continued to increase until concentrations

reached a final of 59.5%. Tri-acyl-glycerol formation remained steady throughout the

entire reaction, starting at 1.3% with a final concentration of 11.7%. As one of the

primary reactants, free glycerin slowly decreased as a function of time, with a final

concentration of 1.9%.
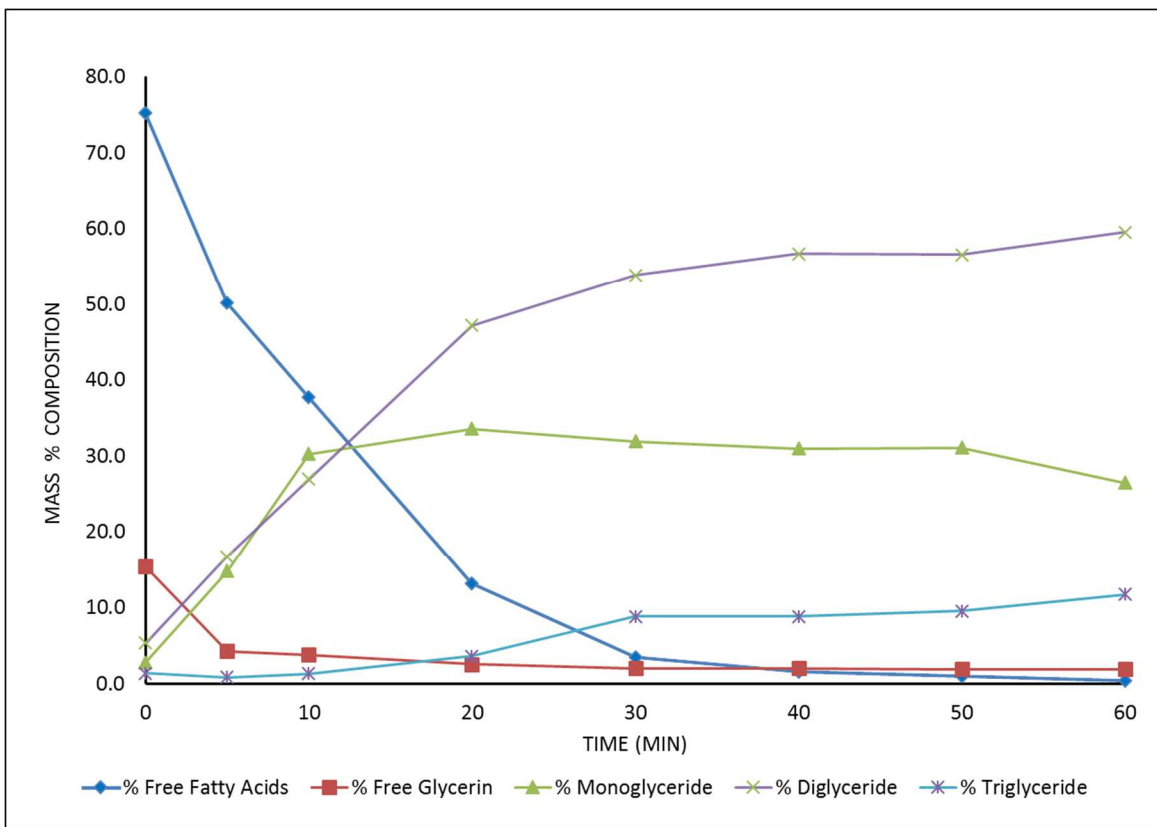
Figure 1. Free fatty acid reduction and acyl-glycerol formation during glycerolysis using

a 1.8% wt/wt Zn-Al$_2$O$_3$ catalyst.

3.3.4.3 Acyl-glycerol formation during 1% Na$_2$SO$_4$ catalyzed glycerolysis

The second reaction condition studied was the use of recycled Na_2SO_4 salt produced

during the biodiesel conversion process. It was hypothesized that the salts innate ability

to lower the ionization energy of the reaction mixture would increase the FFA reduction

rate. As the sodium salt is a potential by-product of the biodiesel process, it would not

require additional purchasing or handling, unlike the $Zn-Al_2O_3$. This has potential

advantages to commercial operations seeking to increase yields without increasing

conversion costs.

The Na_2SO_4 catalyst yielded the lowest reaction rate of all three experiments, primarily

due to the time it took FFA concentrations to fall to the desired 0.5%.
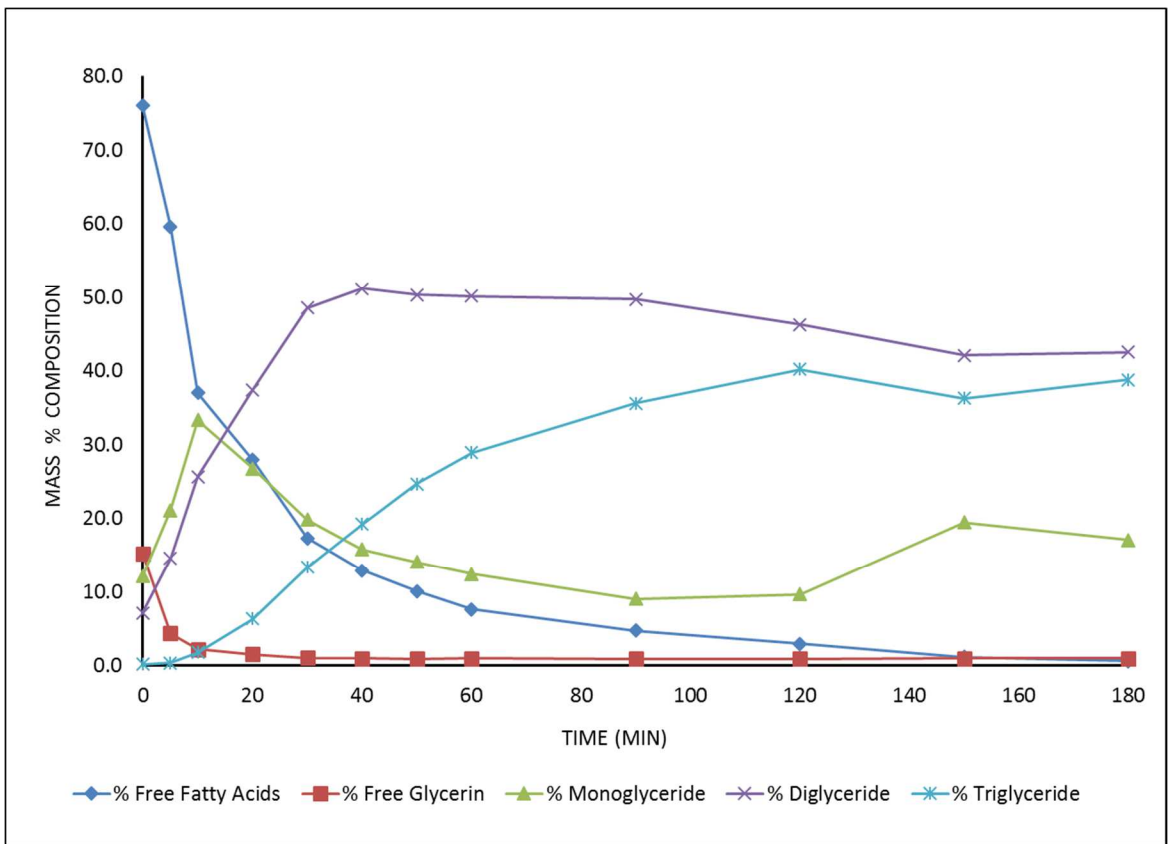
Figure 2. Free fatty acid reduction and acyl-glycerol formation reactions using a 1.0%

wt/wt Na_2SO_4 catalyst.

It took 180.0 minutes for the FFA concentration to reach 1.2 mg KOH/ mg of oil (0.63% FFA). Figure 2 shows that like the zinc catalyzed reaction, the mono- and di-acyl-glycerol rate of formation was almost identical until matching the concentration of free glycerin. After 15 minutes of reaction time, the free glycerin was in equal concentration with the mono- and di-acyl-glycerols at approx. 32.0% each. However, unlike the Zn catalyzed reaction, once the components reached equilibrium the mono-acyl-glycerols started to decrease immediately while the tri-acyl-glycerols began to increase in formation rate. The di-acyl-glycerols rate remained steady until maxing out at 50.0% wt/wt, then slowly declining throughout the reaction. Looking at Figure 2, the slow depletion of di-acyl-glycerols after 40.0 minutes and the continued formation of tri-acyl-glycerols suggest Eq. 3 is the dominant formation reaction throughout the majority of the process. Interestingly, at 120.0 minutes a change in formation was seen as the tri-acyl-glycerol concentration dropped along with di-acyl-glycerol, finally reaching 38.8% and 42.5% respectively. Alternatively, the mono-acyl-glycerol concentration increased during the last 60.0 minutes, ending at 17.0%. One theory is that at 120.0 minutes, the FFA levels had dropped to insignificant levels, eliminating the Eq. 1 reaction and forcing different acyl-glycerol rearrangements. After the reaction was completed, the free glycerin still present accounted for only 1.0% of the total solution.

3.3.4.4 Acyl-glycerol formation during uncatalyzed glycerolysis

An uncatalyzed glycerolysis reaction was performed as a reference point in order to compare the catalytic benefits of the two compounds in question. U.S.P. certified

glycerin, without any additional salts or emulsifying agents was used as the only reactant

charged to the oil. The U.S.P. glycerin does not represent the co-product glycerin

produced during trans-esterification, but a higher purity glycerin that requires additional

purchasing. Free Fatty Acid reduction during uncatalyzed glycerolysis claimed the

second fastest rate of reaction of all three of the reaction conditions.
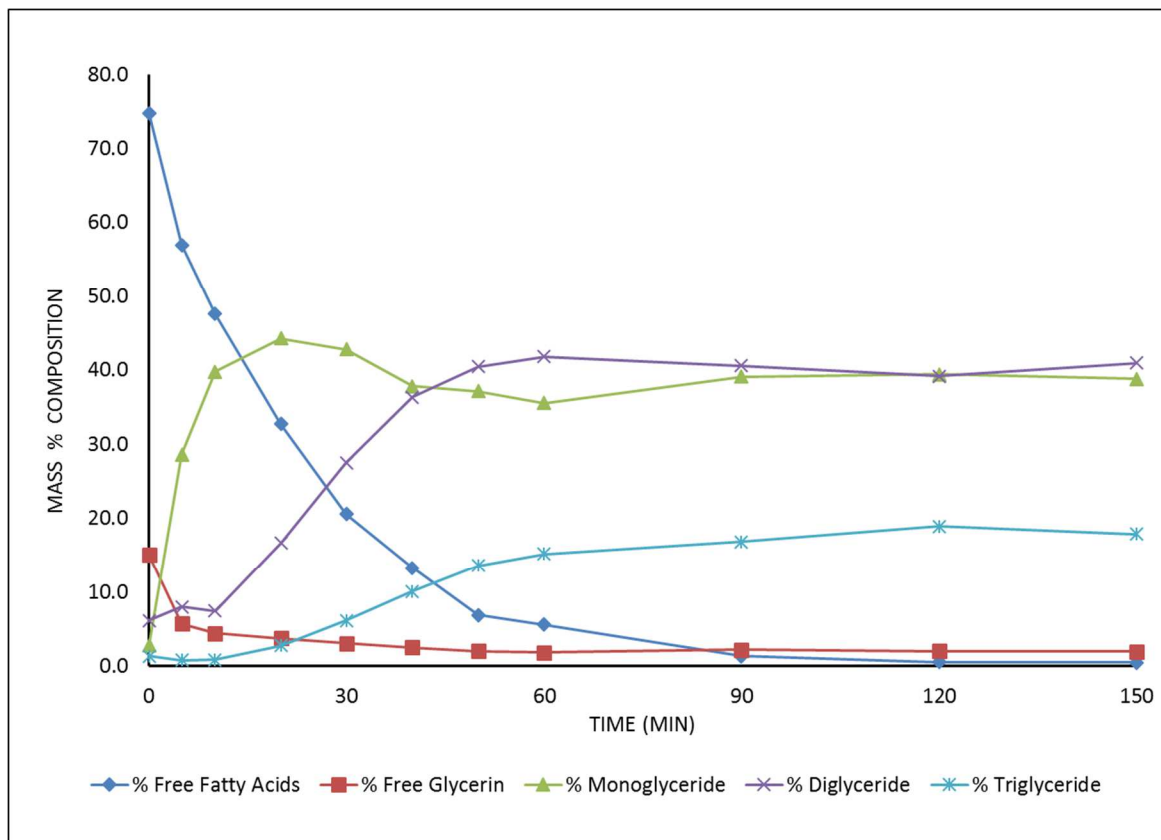
Figure 3. Uncatalyzed free fatty acid reduction and acyl-glycerol formation during

glycerolysis.

FFA concentration of 0.96 mg KOH/ mg of oil (0.48% FFA) were achieved in only 120.0

minutes, faster than the Na_2SO_4 catalyzed glycerolysis. Figure 3 shows the formation of

mono-acyl-glycerol (Eq. 1) as the dominant reaction. Di-acyl-glycerol appeared to have

roughly half the rate of formation of mono-acyl-glycerol, but roughly twice that of tri-

acyl-glycerols. The steady increase in concentration of all three at various rates indicates a hierarchy to the reaction formation, with Eq. 1 > Eq. 2 > Eq. 3. Despite occurring at very different rates of formation, mono- and di-acyl-glycerol concentrations both reached comparable equilibrium at 38.8% and 40.9% respectively. The tri-acyl-glycerol formation increased almost continuously until stopping at 17.9% after 120.0 minutes. The 1.93% free glycerin remaining at the end of the reaction is the highest among all three trials.

3.3.4.5 Free fatty acid reduction kinetics

Studying acyl-glycerol formation during glycerolysis benefits our understanding of the process, but it is the reduction of FFA that is essential for the production of biodiesel. Understanding the rate of FFA depletion and final concentration equilibrium are vital to the scale-up and use of glycerolysis in an industrial setting. By monitoring the acid value (AV) and concentrations of mono-, di- and tri-acyl-glycerols throughout the reactions, rate related metrics were established. The first was the rate of reaction or "k" value of the first-order reaction seen in Eq. 1. A first-order reaction model was used because reaction speed was dependent upon the concentration of only one reactant (FFA). The presence of multiple reactions schemes during the reduction of FFA is of no consequence as the rate at which FFA is reduced is the only reaction of interest. The first-order model equation is $C=C_0*e^{-kt}$, where C is the percent concentration of free fatty acid (FFA), C_0 the initial concentration at time 0, and t is time in hrs (Conners, 1990; Berrios et al, 2007). Using the relationship AV = 1.99% FFA, the free fatty acid concentrations at each sampling

time interval were determined (Gerpen, 2004). Once the FFA concentrations were calculated for all reactions, "k" values were determined for each of the reaction conditions using actual data. By plotting the natural log (ln) of C/Co against time in hours, the slope of the linear line "k" was calculated for each reaction (Figure 4). The resultant "k" values for the $Zn-Al_2O_3$, Na_2SO_4, and uncatalyzed reactions were 5.63, 1.45, and 2.57 respectively. The results assume that glycerolysis follows a strict first-order reaction model. However, as discussed below, mono- and di-acyl-glycerols formed during glycerolysis can also act as binding sites for unbound glycerin. It was hypothesized that these additional reactions could affect the speed of FFA reduction, without affecting the final concentration equilibrium. Therefore, further analysis was required to consider potential reaction rate increases.
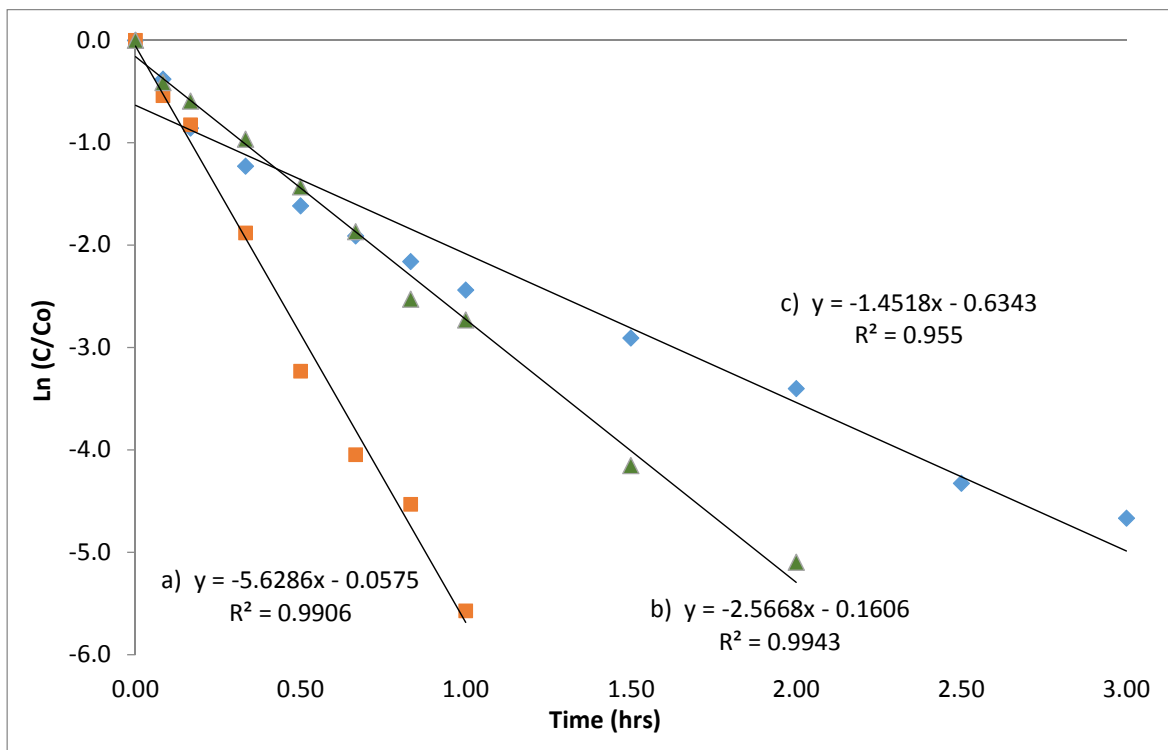
Figure 4. Linear regression model showing the slope of the curve or "k" and R^2 values for a) $Zn-Al_2O_3$ catalyzed b) uncatalyzed and c) Na_2SO_4 catalyzed glycerolysis.

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Looking at Figure 4, the line R^2 values for each reaction are shown below their respective line equations. The closer the R^2 value is to 1, the closer the given reaction followed a strict first-order reaction. Both the $Zn-Al_2O_3$ and the uncatalyzed reactions obtained relatively high R^2 values of 0.9906 and 0.9943 respectively. Glycerolysis using Na_2SO_4 however had a lower R^2 value of 0.955, indicating that other reactions beyond Eq. 1 were present and contributed to the FFA rate of reduction. For both the $Zn-Al_2SO_4$ and uncatalyzed reactions, progress increased initially, and then slowed to match the predicted outcome of the first-order reaction. In the case of Na_2SO_4 however, the initial FFA reduction proceeded much faster than was predicted, then slowed to a rate lower than expected during the second half of the reaction. The change in expected rate for Na_2SO_4 can be seen in Figure 4 - line c, with data points below the trend line during the first half of the reaction and above the trend line during the final half. The assumed reason for the deviation in experimental data was the presence of mono- and di-acyl-glycerols formed during the reaction with the Na_2SO_4 salt. Figure 2 illustrates how the formation of mono-acyl-glycerols stops and reverses minutes into the reaction. Meaning the primary reactant during Na_2SO_4 catalyzed glycerolysis was not free glycerin alone, but a combination of mono- and di-acyl-glycerols (Eq. 2 and Eq. 3). The results were unique from the other two experiments, in which Eq. 1 was by far the most prevalent. It is not known why the presence of Na_2SO_4 yielded higher-order glycerides as it was an unintended consequence of the reaction. As discussed later, the reaction of mono- and di-acyl-glycerols with FFA is a significant alternate reaction during glycerolysis. Although the peripheral reactions reduced FFA concentration faster than the first-order reaction

equation predicted, the rate eventually slowed until the FFA concentrations matched final predicted outcomes. This meant that although the reaction progressed much faster during the first 2 hours of FFA reduction, it also slowed significantly during the final hour, resulting in the lowest "k" value among the three experiments (k=1.45).

The second metric studied was the time it took for each reaction to reduce its acid value (AV) to below 1.0 mg KOH/g of oil. An acid value this low correlates to a free fatty acid concentration below 0.5%, ideal when moving into a base-catalyzed transesterification reaction. Less free fatty acids present during transesterification means that less base-catalyst is unintentionally neutralized by the organic acids. The $Zn-Al_2O_3$ catalyzed reaction was the fastest reaction and achieved an acid value below 1.0 mg KOH/g of oil within 60 minutes. The Na_2SO_4 catalyzed reaction reached the desired acid value after 180 minutes, 3 times longer than the other catalyst tested. Interestingly, the uncatalyzed reaction using only U.S.P. glycerin was able to achieve the same low acid value after only 120 minutes, faster than the reaction using Na_2SO_4.

3.3.4.6 Sulfur Reduction

Sulfur levels were monitored before and after glycerolysis to determine if any of the metal catalysts tested could serve as a sulfur binding agent. Filtration of the oil glycerized with the $Zn-Al_2O_3$ catalyst resulted in 473.0 ppm sulfur. The Na_2SO_4 catalyzed and filtered oil yielded 573.4 ppm sulfur and when no catalyst was used the sulfur levels were 621.3 ppm. The actual form sulfur takes in the oil is not known, but previous testing has indicated that several functional groups are present, including thiol

esters, disulfide bonds, and hydrogen sulfide. There is no proposed mechanism for the sulfur removal. It was hypothesized that the sulfur engages in a redox reaction and ligates itself to the metal catalysts. Alternatively, the mere polarity of the catalyst could act as a binding agent to sulfur through electrostatic interaction, removing it in subsequent filtering. Regardless of the mechanism, showing that a metallic catalyst can affect sulfur levels during glycerolysis improves that catalysts economic viability as a process reagent. It also alleviates the responsibility of sulfur removal in subsequent processing stages like glycerin decanting and reflux distillation. Most of the sulfur is assumed to be bonded to high molecular weight compounds like FFA's or glycerides, due to the fact the biggest reduction of sulfur is seen during a multiple stage reflux distillation. Whatever form sulfur takes, its concentration is reduced to below 10 ppm after the final polishing stage of the finished biodiesel.

3.3.4.7 Future work

Any residual free glycerin still present after glycerolysis and subsequent trans-esterification must be removed in subsequent processes. The most common method for free glycerin removal is simple water washing of the biodiesel. This requires the biodiesel to be vacuum dried after washing to remove trace amounts of water, a costly and time-consuming process. A combination of reflux distillation, mid-condenser phase separation, and adsorbent filtration is being researched to remove residual unbound glycerin. Removing unbound glycerin passively during the distillation stage makes water washing and vacuum drying the final product no longer necessary. Successfully

eliminating this final stage greatly reduces batch cycle time, resulting in higher

production volumes and lower utility costs.

3.4 Conclusions

By studying the effects of metallic catalysts against a control group, the economic

viability of each scenario was assessed. Results indicated that the Zn-Al_2O_3 alone

yielded a measurable catalytic effect ("k" = 5.63) above the uncatalyzed reaction, which

yielded a "k" value of only 2.57. In contrast, Na_2SO_4 catalyst yielded the lowest rate of

reaction with a "k" value of 1.45. Na_2SO_4's presence appeared to prolong the reaction

time when compared to an uncatalyzed reaction; however, the reaction did yield a higher

concentration of di- and tri-acyl-glycerols than compared to the other two reaction

conditions.

3.4.1 Acknowledgments

Chapter 4 Economic Screening of Renewable Energy Technologies: Incineration, Anaerobic Digestion, and Biodiesel as Applied to Waste Water Scum

4.1 Current state of renewable energy from waste water by-products

The treatment and management of waste water from residential and industrial run-off is critical to the sustainability of our water systems. Therefore, it is crucial for treatment technologies to be as energy efficient and as economically viable as possible if they are to compete with cheaper, less environmentally acceptable alternatives. As a consequence of the increasing global population, the total amount of municipal solid waste is continuing to rise. An annual rise of 2-3% in solid waste was estimated by Salhofer et al, in 2007. Historically, reclaiming energy from organic wastes concentrated during water treatment, also called bio-energy, has financially been limited to a combination of incineration or combustion, anaerobic digestion, and landfill. If the technology is available, properly designed, constructed, and managed, landfills can be used to generate energy by recovering its methane production (Nayono, 2010).

Incineration of municipal waste for energy recovery is one of several waste-to-energy systems commonly used today. It is the direct combustion or incineration of the scum at high temperatures (>1100°C), without any filtration or extraction of any kind (Caputo et al, 2004). The process is capable of reducing the solid mass of waste by 80–85% and the volume by 95–96%, depending on composition and degree of recovery of certain materials like metals from the ash for recycling (RenoSam, 2006).

The utilization of anaerobic digestion at waste water treatment facilities is particularly suited for the treatment of waste water activated sludge (S.K.K. et al, 2015). Anaerobic digestion of waste scum could help reduce the number of organics sent to landfill, while producing an energy source (methane) for heat or electricity generation. The reduced burden of transportation to and from landfilling sites would also reduce carbon emissions from the life cycle of scum. If localized anaerobic digestion facilities were embedded within an electrical distribution network, they would help reduce the electrical losses associated with transporting electricity over a national grid (Renewable Energy Framework).

New research focused on the extraction of oils and fats from waste water scum has expanded the technology platform for bio-energy production. Of the two primary by-products created during the waste water treatment process; sludge and scum, the improved economic remediation of scum was the focus of the following study. Although scum represents less than 2% of the total organics through the system, its high fat and oil content make it attractive as an alternative energy source (Bi et al, 2015). Scum is composed of the floatable portion of organic waste and the only assumed source of energy considered in the following economic comparison. By focusing on the purification and separation of different scum components, usable oils can be extracted and converted to methyl esters (biodiesel) (Bi et al, 2015). Biodiesel produced from a municipal water treatment facility can be used directly to run utility equipment, or sold to a retailer in order to collect state and federal subsidies.

In addition to the fats and oils present in scum, there is significant amount of organic biosolids made of an eclectic mixture of woody biomass, hydrophobic impurities,

metals and non-metals. For two of the three technologies compared, incineration and anaerobic digestion, biosolids represent an additional source of energy either as a carbon source or energy source. For comparison, energy derived from the scum oil and biosolids was described in several ways for each technology. Using a combination of cited literature and experimental data; the total amount of energy theoretically produced for each technology was established. For modeling purposes, scum from St. Paul, Minnesota's Metro water treatment facility was used as a base for the comparison. The facility currently disposes the bulk of their biosolids (sludge) using incinerators equipped with a 4.7 MW turbine generator to produce enough electricity to meet 20% of the facilities energy needs (Metropolitan Council Environmental Services, 2011). In addition to sludge, the plant also generates approximately 3,175 kilograms of floatable scum each day. According to facility personnel, the scum is collected, dewatered, and then sent to landfill at the cost of approximately $100,000/year. In the past, attempts to feed the floatable scum to the incinerators were hindered by material handling and residual building-up issues. It was concluded by plant engineers that additional equipment, process consideration, and capital ($) would be required if scum incineration was to be employed (Metropolitan Council Environmental Services, 2011). Anaerobic digestion is not currently used at this specific location. In order to compare the anaerobic digestion of scum, it was assumed that the scum would be fed directly to a "theoretical" digester, on-site. For economic purposes, the theoretical digester would be designed to handle all sludge and scum generated at the facility, making scum a small percentage (1.04%) of the overall material loading (Metropolitan Council Environmental Services, 2011). As a

consequence, it was assumed that the additional energy associated with the anaerobic digestion of scum was negligible.

One major consideration for the economic modeling of all three processes was determining the cost per unit of the initial substrate. In the case of biodiesel, purchasing and procurement of the oil can account for 70-90% the systems operating costs (Knothe et al, 2010). Floatable scum is not only free, but represents a waste material that requires additional costs to dispose of via landfilling. The second major consideration for economic modeling was the assumed price of the bioenergy produced. Using market values of natural gas ($/kJ), electricity ($/kWh), and petroleum diesel ($/gal), averaged throughout the U.S. for 2015, extrapolations of economic values were determined for three potential bio-energy products; combustion heat, electricity generated from steam, and biodiesel. After experimental determination of scum's composition and energy content, a method to screen the economic viability of each waste to energy technologies was developed. Operational and labor costs were considered when relevant and established federal subsidies were applied when available for a more accurate comparison.

4.2 Materials and Methods

4.2.1 Foundation for theoretical comparison

Each of the three technologies was modeled using functions and iterative calculations developed with Microsoft Excel software. Theoretical energy outputs were economically

standardized for comparison using averaged market prices for respective electrical, thermal, and economic costs. To compare three different renewable energy routes, a common variable was established to determine the size and energy requirements of each technology. The variable chosen for the fundamental basis of this study was the volume of floatable organic scum generated from the St. Paul waste water treatment facility in one year. According to the facilities operations director, the facility produces approximately 3,175 kilograms of "wet" scum per day and operates 365 days a year. Waste water coming into the treatment facility is first screened for large debris before entering large sedimentation tanks. The tanks are used to allow the heavier sludge component to settle to the bottom, while grease, fats, and oils rise to the surface and mechanically skimmed off (Hammer, 1996). At this stage, the scum is collected and its pathway through a hypothetical energy reclaiming process would begin. As reported before (Bi et al, 2015), the amount of moisture, extractable oil, and residual biosolids were determined experimentally for raw scum. Residual biosolids were removed during filtration and solvent extraction then analyzed using ASTMs D3172-13, Standard Practice for Proximate Analysis of Coal and Coke. The results of the proximate analysis can be seen combined with the oil and water compositions in Figure 1. Results showed that 62.5% of the incoming 3,175 kilograms of scum could be extracted as oil suitable for biodiesel conversion. This represents the primary energy source theoretically available to all three of the proposed conversion technologies compared in this study. The second largest source of potential energy comes from the biosolids, which accounted for 13.7% of the total scum mass. The rest of the material present in the mixture was considered "water", which was averaged at 29.9% (wt/wt). As discussed later, residual organics and

biosolids extracted from the oil could also be used as an energy source during anaerobic digestion and incineration. The additional energy source was accounted for in the mass and energy balance for all applicable cases.
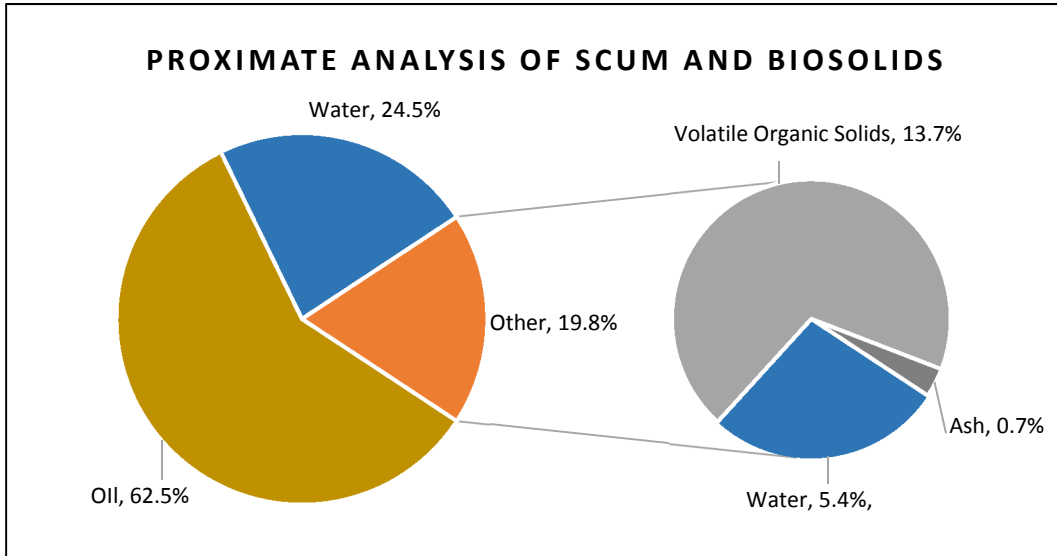
Figure 1: The composition of water, biosolids, and extractable oil from raw scum (left) based on filtering, drying, and solvent extraction. After extraction, residual biosolids and were dried, then combusted to determine a proximate analysis (right).

To apply literature cited heating values to the oil and biosolids, the scum was broken down into its respective components, shown in Figure 1. To accurately determine the composition of the scum, a method for separating the moisture, biosolids, and oil was employed. During the first stage scum was acid washed using 5% (wt/wt) sulfuric acid in 40% (wt/wt) D.I. water at 65°C while being agitated thoroughly. After 20 minutes of agitation, the mixture could settle without agitation at 50°C for 1 hr. for phase separation of oil and water. The bottom aqueous phase was removed through the bottom of a separatory funnel before subjecting the remaining organic phase to additional

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purification. Oil was extracted from the top organic phase using 40% (wt/wt) heptane.

After separating the organic conglomerate that settled to the bottom of the heptane

solution, a final vacuum stripping stage recovered the heptane. A final yield of 62.5% dry

oil was extracted from the "wet" scum, leaving behind 13.7% dried biosolids.

4.2.2 Renewable energy route #1 - direct incineration

The direct incineration of scum for electricity generation via steam turbines was the first

energy route modeled. The first stage in scum processing from St. Paul's waste water

treatment plants is a dewatering process, where the scum is concentrated in large holding

tanks fit with a mesh screen. The screen allows for water carried over from the holding

tanks to be passively drained from the bottom of the tanks, leaving behind the

conglomerated "wet" scum. Based on an approximate analysis, the scum contains on

average 24.5% moisture. However, this value was dependent on drain time and moisture

content was shown to fluctuate more than any other component. Assuming the moisture

is removed from oil and biosolids, the combined amount of organic material available for

incineration represent 76.2% of the original "wet" scum. The high heating value (HHV)

of the raw biosolids was analytically determined to be 25,118 kJ/kg, using ASTM method

D5865. In contrast, oil derived from scum oil has an assumed heat value of 37,216 kJ/kg,

as it contains mostly free fatty acids and mono-, di-, tri-glycerides (Hing, 1998).

However, raw scum containing trace moisture and elemental impurities like sulfur,

phosphorous, and metals first needs to be rendered and dried before being considered for

the higher heating value.

Based on analytical analysis of dried scum using ASTM D5865 Standard Test Method for Gross Calorific Value of Coal and Coke, the energy value was determined to be 37,740 kJ/kg. This estimate was very close to the literature cited value of 38,844 kJ/kg from scum (Hing, 1998). Therefore, the experimentally generated value was used to extrapolate energy potentials from the "organic portions" of scum. Factoring in water's heating capacity of 4.184 $kJ/kg^{-1}K^{-1}$, the amount of thermal energy (sensible and latent heat) required to dry the oil and sludge mixture was calculated and subtracted from the overall thermal output of combusting the oil and sludge (Edgar, 2008). Applying the newly generated energy value for the incineration of raw scum to the facility parameters at the St. Paul treatment plant, electrical generation potentials were calculated and compared to anaerobic digestion and biodiesel.

4.2.3 Renewable energy route #2 - anaerobic digestion

Modeling the theoretical electrical and economic potential of an anaerobic digestion system using waste water scum required several assumptions be made. The first was that there was no antibacterial component present in the scum that could have a negative impact on the bacterial culture population or metabolic rate related to methane production. The second assumption was that 90% of the weight of biosolids present in the scum represented some form of carbohydrates i.e. cellulose from woody biomass, while the remaining 10% represented a mixture of proteins and hydrophobic impurity. Proportions were based on experimental fraction ratios of biosolids filtrate, acid hydrolyzed organics released during phase separation and solvent extraction. The

methane produced per unit mass of biosolids is dependent upon this ratio as proteins have a much higher Chemical Oxygen Demand (COD) per unit mass than carbohydrates. The protein component of the scum, more specifically the nitrogen containing portion, was considered negligible as the amount of protein confirmed in the scum was less than 1.5%. Moreover, any nitrogen present in protein would not oxidize due to the low process temperatures and leave the system as either ammonia or elemental nitrogen, neither of which affects COD.

Two methods of calculation were employed to estimate the system's methane potential. The first (method #1) was to establish a relationship between the COD of each component in the reaction and the amount of methane hypothetically produced. COD is commonly used to indirectly measure the number of organic compounds in water by calculating the amount of oxygen required to fully oxidize all organics to their fullest potential (De Mes et al, 2003). Creating a balanced equation of the complete oxidation of each species with O_2 yielded a theoretical COD per gram of each species. A designated "model" compound was chosen to represent each component to standardize and extrapolate empirical data. The fat and oil portion was assumed to be oleic acid, the carbohydrate was assumed to be a single glucose molecule $C_6H_{12}O_6$. As proteins can be very large, an average molecular weight was calculated by multiplying the number of amino acid units (20) by their average molecular weight (MW=136 grams/mole), then to account for the loss of water due to polysaccharide bonds, 18 times the number of amino acids, minus 1, was subtracted for a final molecular weight of 2394 grams/mole. After the model compounds were established, the amount of COD per grams of oil, carbohydrate, and protein was calculated and extrapolated to estimate the overall methane potential.

The second method (method #2) for calculating methane potential was to use a balanced hydrolysis equation, in which each species is reacted with water to form methane and CO_2. The resulting moles of methane produced from 1 mole of theoretical substrate (protein, oil, etc.) was divided by the molar mass of that substrate then multiplied by the total amount of available material and assumed conversion efficiency (80%) (De Mes et al, 2003). This was repeated to calculate each species respective methane potential, then totaled for the entire system's potential. The results of each approach were compared to evaluate the effectiveness of the two methods, and to test the claim that methane potential can be measured as a function of the chemical oxygen demand of the system.

4.2.3.1 Methane potential as a function of Chemical Oxygen Demand (Method #1)

To model the oxidation and subsequent hydrolysis of all of the organic components of scum, it was necessary to establish some generic equations pertaining to all possible scenarios. Equations 1 and 2 below show the balanced pathways for the oxidation and hydrolysis of an unknown organic species with formula $C(x)$: $H(y)$: $O(z)$, where x, y, and z are the number of atomic units associated with each elemental species.

(Eq. 1) <u>Oxidation</u> $(x)C : (y)H : (z)O + (d)O_2 \rightarrow (x)CO_2 + (y/2)H_2O$

(Eq. 2) <u>Hydrolysis</u> $(x)C : (y)H : (z)O + (w)H_2O \rightarrow (A)CH_4 + (B)CO_2$
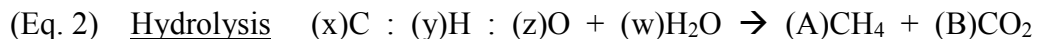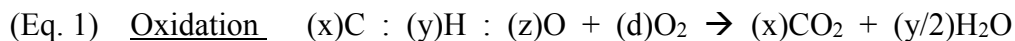
Depending on the values for x, y, and z - the organic material could be carbohydrate, hydrocarbon, or lipid. The following equations were developed based on the

stoichiometric relationships above, to determine how many moles of methane (A) will be

generated relative to how many moles of oxygen (d) is required to fully oxidize the

organic material. Balancing the oxygen required in the oxidation equation (Eq. 1) yielded

the following equation;

$$2*x + y/2 = 2*d + z$$

which can be rearranged to solve for "d", the amount of oxygen required to fully oxidize

the organic portion of scum (Eq. 3).

(Eq. 3) $d = x - z/2 + y/4$

Next, relationship equations amongst the hydrolysis equation (Eq. 2) were determined by

balancing the moles of carbon, hydrogen, and oxygen between the products and reactants.

Rearranging the equations yielded Eq. 4, where A is the amount of potential methane

formed by the hydrolysis of carbon by anaerobic bacteria.

(Eq. 4) $A = (x - z/2 + y/4) * 1/2$

Looking at Eq. 3 and Eq. 4, the relationship $A/d = (1/2)$ can be inferred, or for every mole

of oxygen consumed (d), exactly 1/2 moles of methane (A) will be produced. On a purely

weight basis, one mole of diatomic oxygen or COD is equal to 32 grams, while 1/2 mole

of methane (CH_4) weighs 8 grams. This relationship states that for every gram of oxygen

consumed, 0.25 grams of CH_4 will be produced. Factoring in methane's density of 0.714

grams/liter at STP (14.7 psi and 20°C), the final product metric becomes 350 mls/gram of

COD. This relationship should hold true for any combination of lipid, carbohydrate, or

hydrocarbon.

4.2.4 Renewable energy route #3 - biodiesel from scum derived oil

The last renewable energy route model was the conversion of scum derived oil to

biodiesel. Previous research performed by the authors showed that oil derived from

floatable scum collected at St. Paul's waste water treatment facility could be rendered and

converted to biodiesel (Bi et al, 2015). The published and patent pending method for

converting scum to biodiesel was used as the model process for the economic

comparison. According to the research, oil was extracted from the scum waste using a

combination of heated filtration, acid hydrolysis, and solvent extraction. Next, glycerin

esterification was performed to lower the relatively high Free Fatty Acid (FFA) value to

below 0.5% (wt/wt). Glycerin esterification bonds FFA with free glycerin to form

monoglycerides and water, eliminating the need for acid-esterification. Once the FFA

was remediated, the oil was converted to biodiesel using a traditional base-catalyzed

transesterification reaction, followed by gravity separation of the biodiesel and glycerin.

Vacuum separation and distillation of the methanol and biodiesel respectively were

employed to guarantee the product met all ASTM D6751 standards for B100 (Anderson

et al, patent pending). A conversion efficiency of 68% was calculated using experimental

data generated from multiple batch-wise conversions performed in laboratory glass-ware.

Applying this process efficiency to the previously stated annual volumes of available fat and oil yielded a theoretical production of over 137,000 gallons (518,600 liters) of biodiesel a year. It is important to state that during a scum to biodiesel conversion process; only the fat and oil portion of the scum could be utilized while the biosolids and metals must be discarded. In theory, any biosolids removed and concentrated during processing could be fed directly to an on-site incinerator, but this scenario was not applied for this comparison.

For this study biodiesel was valued in two ways, as both a source of energy for electrical generation and as a transportation fuel, competitive with petroleum diesel. In the case of electrical generation, the final product (methyl esters) would be fed directly to an incinerator to generate steam, which in turn will be run through a gas turbine for electricity generation. The average methyl ester has an assumed heat capacity of 37,216 kJ/kg, the same assumed value as the initial scum derived oil (Hing, 1998). Since the heat capacity for methyl esters and scum derived oil were considered equal, it implied the total amount of electrical generation possible from methyl esters is a mere fraction of that possible from dried scum, making it unsuitable for any practical application. As a transportation fuel however, the value of biodiesel can be inflated relative to its energy value due to outside factors. There are several government and state incentive programs currently in place to promote the production of biodiesel. A $1.00/gallon federal tax credit along with state subsidies can be applied immediately or retroactively to a biodiesel production facility to improve said facilities economic portfolio (Rincón et al, 2014). If the biodiesel is sold as a transportation fuel, it can qualify for additional income in the form of Renewable Identification Numbers (RINs). These act as credits attached to

each gallon of biodiesel created in the U.S. RIN credits can be bought, sold, or traded throughout the fuel industry in order for companies to meet annual production and blending quotas, set forth by the Environmental Protection Agency (EPA) (Kesan et al, n.d.).

The last key assumption was the conversion cost and labor costs associated with a scum to biodiesel process. Using nationally sourced, chemical whole sale information, a total annual cost analysis was created for the chemical reagents (methanol, catalysts, acids, etc) needed using the processes mass balance. In addition, a complete energy balance of the process was developed based on the systems design parameters. Establishing the necessary heating loads, pump sizes, and mixing requirements during all stages of the process allowed for the calculation of the total energy and subsequent cost of producing biodiesel from scum. Scaling the reaction conditions to the full amount of scum available to the St. Paul facility yielded the assumed thermal and electrical costs to operate the biodiesel process. Totaling all of the associated costs and dividing by the estimated biodiesel production revealed a conversion cost of approximately $1.29/gallon. This figure represents the total operational cost of producing 1 gallon of biodiesel, including required energy, reagents, and labor. The labor cost was made as a conservative assumption, $120,000 for two employees working all operating hours.

4.2.5 Energy production and economic value determination

Energy outputs were estimated in the same way for all three systems. The annual available volumes of each of the three high energy by-products; biodiesel, methane, and

scum were multiplied by their innate energy contents, measured in kJ/kg. Applying

production volumes generated from experimental data to theoretical mass balances, the

total amount of available renewable energy was calculated for each technology route.

Whereas incineration is the direct combustion of a substance, both anaerobic digestion

and biodiesel conversion pathways yield higher value molecules that can be sold at a

premium in specific energy markets. In the case of anaerobic digestion, the product

methane can be combusted and used to generate electricity via a gas turbine (Beer, 2007).

However, in order to properly compare biodiesel to the other two technologies, both

energy content and liquid fuel value were considered. This allowed for a two-fold

comparison of the available energy, as well as the economic potential of a biodiesel

process coupled to a waste water treatment facility of comparable size. The energy

content of the two conversion technology by-products was taken from literature and are

as follows; 37,216 kJ/kg of biodiesel, 49,853 kJ/kg methane (Gunaseelan, 1997). The

energy content of scum however was derived from a combination of literature and

experimental data. The oil (a mixture of monoglycerides and free fatty acids) was

assumed to contain 37,216 kJ/kg, while raw biosolids were experimentally found to

contain 25,118 kJ/kg (Edgar, 2008). Experimental data was generated throughout several

batch extractions to determine the percent mass of biosolids and oil used to extrapolate

energy predictions. Scum was heated to 82°C then filtering through a plastic filter with a

1.0 mm diameter pore size. The filtered biosolids were weighed and the resulting liquid

phase was subjected to an acid hydrolysis (5% sulfuric acid + 20% D.I. H_2O) then solvent

extraction (30% heptane + 20% D.I. H_2O). The resulting oil weights were averaged and

used as the standard for the percent of oils within scum.

The economic value of energy derived from scum incineration was considered several ways. For direct incineration, energy contained within scum was assumed to generate electricity via a steam turbine. Before incineration however, the amount of energy required to completely dry the system was calculated using the sensible and latent heat equations shown below. In the context of drying water, $Q_{sensible}$ represents the energy required to raise the water temperature to boiling, while Q_{latent} is the energy required to completely effect a phase change during vaporization. In both equations, (m) is equal to the mass of water being heated in kilograms, (c) is the specific heat capacity of water (4.184 kJ/kg^{-1}K^{-1}), (L) is the heat of vaporization of water (2,256 kJ/kg), and ΔT is the change in temperature (K) (Coulson and Richardson, 1977; Edgar, T., 2008).

Sensible heat equation: $Q_{sensible} = mc\Delta T$

Latent heat equation: $Q_{latent} = mL$

Incinerating all organics within the scum at temperatures above 900°C, which account for 81.6% of the scum composition, will release all available energy (Mckendry, P. 2001). Converting a portion of the energy to steam and sending it through a turbine can generate electricity at a conversion efficiency of approximately 10,551 kJ/kWh, according to data from coal power plants (Wang et al, 2008).

Anaerobic digestion of scum produces the high energy molecule CH_4, or methane. Assuming an 80% conversion of all organic material, the resulting biogas can range anywhere from 60-75% methane (Jones and Ogden, 1986). Biogas is a mixture of methane, CO_2, nitrogen, oxygen and trace amounts of H_2S and NH_3. Assuming the biogas

is filtered through scrubbers and compressed to a state similar to compress natural gas, it can be fed to a methane turbine with a conversion efficiency of 38%, or 9,360 kJ/kWh (EPA's Landfill Methane Outreach Program, 1995).

In the case of biodiesel, two distinct economic pathways were considered. The first was to assume that the biodiesel contained 37,216 kJ/kg, and would be incinerated and converted to electricity in a pathway similar to scum incineration, but without the aforementioned material handling issues. The second pathway considered was the selling or direct use of biodiesel as a transportation fuel, off-setting the purchase of petroleum diesel. According to U.S. Energy and Information Administration (E.I.A., 2016), the average price of petroleum diesel from 2010 to 2015 was $3.54/gallon, with 2015 average price at $2.70/gallon. It should be stated that biodiesel volumes are expressed here in U.S. gallons because U.S. subsidies are awarded and reported on a per gallon basis.

4.3. Results and discussion

4.3.1 Energy and economic outcomes for the incineration of scum

The composition of scum was determined experimentally and can be seen in Figure 1. Overall composition varied from batch to batch because of differences in the allowed scum dewatering time. During the treatment of waste water, scum collected from the tops of holding ponds is pumped into holding tanks fitted with an internal mesh. The semi-permeable mesh filter allows free water to pass through, leaving conglomerated organics

behind. Variations in time spent within the separation tanks lead to some variance in determining the percent composition.

Table 1.

In-coming scum	kg/day	Wt %	kg/year	Liters/year
Protein (biosolids)	41	1.28%	14,871	17,722
Carbohydrates (biosolids)	367	11.54%	133,835	159,496
Water (biosolids)	161	5.06%	58,614	58,591
Fats & Oils	1,859	58.52%	678,403	754,578
Water	729	22.94%	265,934	265,830
Ash/Inerts	21	0.66%	7,598	7,043
Total	3,176	100.00%	1,159,256	1,263,261

Several batches of scum separation and proximate analysis were performed and the results were standardized in Table 1. Of the components studied, only two represent available energy sources, biosolids and oils. The remaining portion is a combination of water and inorganic metals and non-metals. Although the biosolids were separated into their respective protein and carbohydrate fractions, the overall energy content of the combined and dried biosolids was experimentally determined to be 25,118 kJ/kg. According to Table 1, there is a combined 826,875 kg/year of biosolids, fats, and oils available for energy generation via incineration. The remaining portion is composed of water (324,456 kg/year) and inert inorganic metals (7,595 kg/year). Although the metals and ash content can be fed to the incinerator and removed without issue, moisture levels must be lowered for more complete combustion.

According to the St. Paul waste water treatment facility, approximately 8.5 million kWh/year are required to operate their 3 on-sight incinerators, boiler, and turbine. Adding the kg/day of protein, carbohydrates, and oils shown in Table 1 shows a total of 2,268 kg/day of dry volatile organics are available for incineration, sourced completely

from floatable scum. According to facility engineers, this represents approximately

1.04% of the total available material for incineration or 217,724 dry kg/day. Assuming

the mixture of protein, carbohydrate, and oil is mixed homogeneously into the other

organics meant for incineration; the potential electrical load was deduced. Scum's

additional electrical load to the incinerator was estimated to be 243 kWh/day or 88,651

kWh/year, shown in Table 4.

Table 4.	Biodiesel	Anaerobic Digestion	Direct Incineration
Electrical energy required (kWh/year)	5,720	n/a	88,651
Thermal energy required (kJ/year)	483,148,699	n/a	861,854,795
Conversion energy costs ($/year)	$2,090	n/a	$9,203
Energy production (kJ/year)	17,049,212,154	21,208,232,081	29,038,413,793
Potential electrical generation (kWh/year)	1,615,947	2,265,718	2,759,145
Value of electricity generated ($)	$113,116	$158,600	$193,140
Value of energy relative to natural gas ($)	$59,621	$74,186	$101,547
Savings to landfill ($)	$87,000	$80,000	$93,000

According to the U.S. Energy Information Administration (E.I.A., 2016), the average

price of industrial electricity in Minnesota for 2015 was $0.07/kWh. Using $0.07/kWh as

a modeling value for electricity, the annual electrical costs were projected to be

$6,189/year. The total thermal load applied on the incinerator by scum was

conservatively estimated by calculating the number of kilojoules required to completely

dry the system. Table 1 shows a total of 324,456 kg/year of both free water and water

suspended in solid material (biosolids). The sensible and latent heats were calculated and

totaled at 858,686,240 kJ/year. As natural gas is the primary energy fuel source for

incineration heat, the value associated with energy was $3.49/million kJ, as this was the average price for natural gas supplied to industry in the U.S. in 2015 (E.I.A., 2016). For modeling purposes, $3.49/million kJ was applied with a standard boiler efficiency of 80% to estimate an annual expense of $3,014 for thermal energy (Caputo et al, 2004). Although it should be noted that facilities like waste water treatment plants often have available waste heat that could be utilized to offset any energy requirements.

The energy produced from the complete combustion of scum is derived from the biosolids and oils. Multiplying the available annual weight by the respective energy content yielded the annual potential energy from scum, shown in Table 4. Applying the previously stated conversion efficiency to the available energy yielded a possible 0.31 Megawatts of electrical power generation every hour. At $0.07/kWr, the annual energy production was calculated and shown in Table 4. Once the assumed costs of operating the incinerator (latent and sensible heat required to dry the material) were accounted for, the total economic potential became $183,937/year.

If the heat generated from scum combustion is not used to generate electricity then the economic value of the energy was considered differently. When the annual kilojoules output was priced relative to natural gas at $3.49/million kJ, the economic savings to the water treatment facility can be seen in Table 4 (E.I.A., 2016). It was clear that the value of the heat evolved from the incineration was significantly lower than the value of the potential electricity. However, this study does not consider the additional cost of capital required to purchase a steam powered electric generator compared to the cost of utilizing the waste heat directly.

The last economic factor considered was the potential savings to annual landfilling costs. According to the Metropolitan Council, the St. Paul waste water treatment facility spends approximately $100,000/year in associated landfill disposal fees. This annual cost was used to estimate the potential financial savings each technology offered. In the case of scum incineration, almost all of the scum can be redirected from the landfill. The oil and biosolids are fed to the incinerator, while the water is removed through a combination of passive decanting and thermal drying. The only portions remaining for disposal are the inorganic ash component which accounts for 0.66% of the floatable scum. Applying this reduction to the annual cost resulted in the potential savings shown in Table 4. Note, incomplete combustion of organics was not considered as a contributor to landfill wastes.

4.3.2 Modeling outcomes for the anaerobic digestion of scum

For the modeling of the anaerobic digestion of floatable scum, the same composition analysis used for incineration was applied. Since methane represented the product compound of interest, two methods were established to predict methane potential. Method #1 utilizes equations developed in section 2.3.1, yielding a relationship of 350.3 mls of methane per gram of COD. Table 2 shows the various components, their weight percentages, and their respective Chemical Oxygen Demand (COD) per unit mass.

Table 2.

In-coming scum	kg/day	Wt %	COD/lb	COD/day
Protein (biosolids)	41	1.28%	1.79	172
Carbohydrates (biosolids)	367	11.54%	1.07	921
Water (biosolids)	161	5.06%	0.00	0
Fats & Oils	1,859	58.52%	2.89	12660

Water	729	22.94%	0.00	0
Ash/Inerts	21	0.66%	0.00	0
Total	3,176	100.00%	5.75	13752

In order to establish a COD per unit mass for each component, model compounds were chosen to represent the different fractions of scum; oils, carbohydrates, and proteins. For the oil phase, oleic acid was used, with a molecular formula of C-18: H-34: O-2 and molecular weight (MW) of 282 grams/mole. Fully oxidizing 1 mole of oleic acid to CO_2 and H_2O requires exactly 25.5 moles of oxygen (O_2). This oxygen represents the COD of oleic acid and can be represented as 2.894 grams of COD/gram of oleic acid. Applying Eq. 4 (section 2.3.1) to the daily amount of available oil yielded a hypothetical 1,148 kgs of methane. The model compound used for a generic carbohydrate was glucose, C-6: H-12: O-6. A balanced oxidation equation shows that 6 moles of oxygen are required or 1.067 grams of COD/gram of glucose. Applying this relationship to the amount of carbohydrates available each day results in approximately 83 kgs of methane. The last component to model was the protein. As described in section 2.3, a theoretical protein with a MW of 2,394 grams per mole was established, resulting in 134 moles of oxygen required to fully oxidize 1 mole of protein or 1.791 grams of COD/gram of protein. Applying this final relationship to the available protein yielded approximately 15 kgs of methane each day from proteins. Totaling the methane from each source (1,148 kgs/day oil, 83 kgs/day carbohydrate, and 15 kgs/day protein) resulted in a potential generation of 1,251 kgs of methane a day or 455,360 kgs annually.

The second model used to estimate the methane potential (method #2) from scum was to create a balanced chemical equation for each scum component during the anaerobic digestion process. Using the theoretical molecular formulas of each model species plus an

excess of water, the CH_4 and CO_2 potentials were determined. As the nature of anaerobic

digestion relies on a lack of oxygen present, the source of oxygen for the oxidation is

H_2O. In the case of proteins, additional by-products such as ammonia and hydrogen

sulfide were also quantified based on the balanced chemical reaction equation. Applying

the moles of methane generated from each species to the daily volume of scum

components yielded a potential kgs per day of methane. For this study, a conversion

efficiency of 80% was applied to the total methane potential. The conversion efficiency is

a function of bacterial activity limits and cannot be overcome (De Mes et al, 2003). The

results of the model yielded the following methane potentials from each scum species;

1,075 kgs/day from oil, 78 kgs/day from carbohydrates, and 12 kgs/day from protein. The

total methane potential for a scum to methane anaerobic digestion system running at an

assumed 80% conversion efficiency became 1,166 kgs/day or 425,492 kgs of methane

annually, slightly lower than method #1.

4.3.2.1 Energy and economic outcomes for the anaerobic digestion of scum

The determination of an economic metric associated with the by-product of anaerobic

digestion (methane) required two critical assumptions. The first regarded the methane

potential models while the second pertained to the assumed cost to operate an anaerobic

digester. Of the two methods used to estimate the potential methane generated during

anaerobic digestion, method #2 was chosen as a basis for an economic comparison,

acting as a more conservative estimate for extrapolation.

The cost to operate the anaerobic digester was deemed negligible and not included in the total economic prediction. Because the driving force of organic breakdown and conversion is biological, the only energy input to consider is in the form of temperature regulation and mixing. Since it has been stated by facility personal that waste heat in the form of low-pressure steam is readily available, temperature control was not considered. The amount of energy required for pumping liquid, agitating the mixture, and compressing the methane for combustion was deemed negligible and not included.

The daily methane output calculated using method #2 was multiplied by the EPA cited lower heating value (LHV) of 49,853 kJ/kg to establish an energy production of 2,421,022 kJ/hr (Engineering Toolbox). Applying that figure to a continuously operating anaerobic digestion system yielded an annual potential energy, shown in Table 4. Assuming the methane is fed directly to a gas turbine for electrical generation, an efficiency of 40.4% (LHV) or 9,360 kJ/kWh was expected (Beer, 2007). At this efficiency, a total of 0.26 megawatts of possible electricity could be generated. At an assumed value of $0.07/kWh, the price of the offset purchase of electricity can be seen in Table 4.

As with incineration, if the heat generated from the combustion of methane is not used to generate electricity then the economic value of the energy was considered differently. By pricing the annual energy output relative to natural gas, modeled at $3.49/ million kilojoules, the annual potential savings were calculated and shown in Table 4 (E.I.A., 2016). Like incineration, the value of the heat evolved from the methane by-product is significantly lower than the value of the potential electricity generated.

Considering the potential savings to annual landfilling costs, anaerobic digestion was assumed to reduce the scum waste stream by 80%. This was the volatile organic conversion efficiency used to estimate the performance of the anaerobic digesters. It states that 80% of the organics entering the digester will be converted to a gas product after digestion is complete. According to the Metropolitan Council, the St. Paul waste water treatment facility spends approximately $100,000/year in associated landfill disposal fees. Applying the annual cost to the percent material reduced resulted in the potential savings shown in Table 4.

4.3.3 Energy and economic outcomes for the conversion of scum derived oil to biodiesel

The economic modeling of scum to biodiesel relies heavily on two variables; the amount of available material and the efficiency of the conversion technology. As stated, there is approximately 1,263,400 liters of scum available to the Metro plant each year which contains an estimated 789,637 liters (62.5%) of usable oil. Applying the previously mentioned conversion efficiency of 68% yields 519,434 liters (137,220 gallons) of ASTM D6751 certified biodiesel produced annually.

Using the energy balance created from the model process, the thermal and electrical requirements for a year's worth of production totaled 483,146,800 kJs and 5,720 kWh, respectively. Table 4 shows the associated costs of the annual energy requirements to convert scum to biodiesel.

Of the two separate economic pathways considered, the incineration of biodiesel for energy yielded a considerably lower economic outcome when compared to biodiesel as a transportation fuel. According to Table 4, the potential energy derived from the incineration of biodiesel is only a fraction of the energy potential innate to scum. Also shown in Table 4 is the potential electricity generated from the energy, economic value of the electricity, and value of the energy relative to natural gas. Biodiesel as an energy source was shown to be impractical since it was assumed to have the exact same energy content as the oils contained in scum. Since scum contains other high energy components removed during biodiesel conversion, it innately has higher value as a heating fuel. The second pathway considered was the sale and use of biodiesel as a transportation fuel. Assuming the finished biodiesel was used directly by the Metro plant personnel in their utility vehicles, it could be valued at the same price as petroleum diesel. Since each gallon produced would off-set the purchase of one gallon of petroleum diesel, the model is simplified. According to the U.S. Energy Information Administration (E.I.A., 2016), the average price for 1 gallon of petroleum diesel in 2015 was $2.70/gallon at retail. For additional analysis, the average price of diesel in the U.S. between 2010-2015 ($3.54/gallon) was also considered. The results of off-setting the purchase of 137,220 gallons of biodiesel are shown in Table 4, based on the average fuel price for 2015 and the 5-year average fuel price. Fortunately, this isn't the only source of potential income biodiesel has as a transportation fuel source. Table 3 identifies several sources of potential revenue and their qualifying amounts relative to the capacity of the St. Paul facility.

Table 3.	2015	2010-2015
Value as a transportation fuel ($)	$370,494	$486,101
Value of $1.00 Tax credit ($)	$137,220	$137,220
Potential RINs value ($)	$164,664	$164,664
Estimated annual operational costs ($)	$177,361	$177,361
Net Profit ($)	$495,017	$610,624

The first comes in the form of the $1.00 biodiesel tax subsidy (Rincón et al, 2014). This is a one-dollar tax credit for every gallon of biodiesel produced. Biodiesel production is also tracked in the U.S. using Renewable Identification Numbers (RINs). These are serial numbers assigned to each gallon of biodiesel produced for the purpose of tracking its production, use, and trading. The EPA credits 1.5 RINs for every gallon of biodiesel produced. These RINs have market value because they can be purchased by industrial companies as credits in order to meet EPA guidelines (Kesan et al, n.d.). As of 3/1/16, one RIN was worth $0.80 (OPIS, 2016).

Considering the potential environmental benefits, a scum to biodiesel process could reduce the material to landfill by an estimated 87%. This represents the total amount of biodiesel produced plus the concentrated biosolids and dewatered organic wastes. Any water removed during processing that would otherwise be landfilled with the scum was also attributed to the landfill reduction volume. According to the Metropolitan Council, the St. Paul waste water treatment facility spends approximately $100,000/year in associated landfill disposal fees. Applying this to the annual cost resulted in the potential savings shown in Table 4.

4.3.4 Future work

The results of the economic modeling presented in this paper are based on a combination of literature review, process modeling, and current market prices for heat and electricity. However, additional research surrounding the total project costs and the amount of capital required to successfully launch each technology would be of great use to any municipality or waste water treatment operation. By actively accounting for previous unknowns in the model (capital costs, Net Present Value (NPV), depreciation value) any variance in the results can be minimized while improving investor confidence.

4.4 Conclusions

Considering current market values and federal subsidies, renewable energy route #3 was shown to have the greatest economic potential of all three conversion pathways studied. When used as a transportation fuel, the off-set use of petroleum diesel raises the value/cost ratio of scum derived biodiesel. Alternatively, renewable energy route # 1 was shown to yield the most potential bio-energy from scum in the form of heat. These observations can help determine the best technology for future water treatment facilities. Refining waste scum is an opportunity to reduce the burden on landfills and rivers, while creating renewable energy locally.

4.4.1 Acknowledgments

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Chapter 5 Valorization of biodiesel vacuum distillation bottoms using flash and distillation microwave-assisted pyrolysis to improve fuel properties and process yield

5.1 Background and trends: biodiesel purification using vacuum distillation

As the consumption of petroleum based fossil fuels throughout the world is outpaced by its abiogenic production, there is a finite supply of liquid transportation fuel remaining in the earth (Sorrell, 2009). Utilizing alternative biogenic sources of carbon for liquid transportation fuels has been a growing science for several decades, producing ethanol, biodiesel, renewable diesel, renewable natural gas, and hydrogen from pristine or waste organic material. As the commercialization of liquid biomass to fuel expanded, economic questions were raised over what material should be utilized. The most predominant substrate for biodiesel production within the U.S. is vegetable oil (Knothe et al, 2010), however, vegetable oils are also used in the food processing industry for foods meant for human and animal consumption. To avoid competition with other markets, increase potential procurement sources, and generate greater economic potential, waste fats, oils, and greases (FOG) have started to be incorporated into the substrate spectrum, mostly as a blend substrate with more pristine sources (Kleinová et al, 2013).

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The addition of low-grade oils can increase the range and concentration of impurity types within the oil. Accounting for the higher presences of impurities; free fatty acids, sulfur, oligomers of acyl-glycerides, and matter organic non-glycerol (MONG) has made it difficult for producers to routinely produce ASTM grade biodiesel using traditional conversion systems. Aside from obvious challenges converting low-quality feedstock to crude ester, purification methods must be robust and adaptable to handle feedstock variability. Vacuum distillation has been shown to be effective in purifying methyl esters (biodiesel) from impurities such as heavier analogs, metals, and sulfur containing species. Biodiesel distillation has grown from being relatively rare to a process that is now installed in more than 350 MMgy of U.S. plant capacities (Smith, 2017). The purified transparent methyl ester yield can range depending on the feedstock quality, but can be as high as 95% wt/wt the original material and routinely meets EPA quality testing. The waste produced during biodiesel distillation, vacuum distillation bottoms (VDB), are dark in color with a higher viscosity, relative to biodiesel. They can range in component type, but are primarily a mixture of C18 saturated and unsaturated methyl esters, dimerized methyl esters, inorganic impurities, and unreacted acyl-glycerides left over from transesterification (Kotrba, 2013). The formation of heavier dimerized and branched derivatives can cause yield loss during fractional distillation, as heavier compounds are not vaporized and leave as a "bottoms cut". Non-saturated methyl esters can react with each other to form heavier derivative compounds. To avoid further derivatization of the product methyl ester, faster heating rates are required to reduce the hydraulic residence time of the methyl esters during vaporization. Microwave-assisted pyrolysis (MAP) was researched as a methyl ester recovery process for VDBs, because it can achieve rapid

heating in short-time. As MAP is performed at almost atmospheric pressure under inert conditions, thermal decomposition was controlled by the exposure conditions of the liquid VDBs on the fixed-bed catalyst, silicon carbide (SiC). Traditional thermal oil systems used during biodiesel distillation cannot reach MAP temperatures (550ºC) without decomposing themselves. Using microwave radiation on the susceptor SiC solves the problem of forming additional derivatives through rapid heating of the VDBs.

The energy content contained within the VDBs is significant, with a calculated high heating value (HHV) of 43.1 Mj/kg, relative to biodiesels 41.3 MJ/kg (Sheng, C., Azevedo, J., 2005). Despite the high energy content, VDBs do not currently have high economic value beyond a no. 6 heating fuel (Kotrba, 2013; Edgar, 2008). The high energy content, lack of market value, low oxygen content, and liquid state of the VDBs make it an ideal substrate for MAP. Historically, pyrolysis using cellulosic biomass has material loading limitations and produces a low-quality bio-oil that contains many oxygenated derivatives (Dunn, 2005). Oxygen contained within low-density solid biomass has a greater potential for partial oxidation, creating a lower grade bio-oil (Chen et al, 2014). As a low-oxygen containing liquid oil, VDBs can be pumped with ease and preheated before entering the reactor, avoiding unwanted oxidation.

VDBs do not have the dielectric properties required to absorb microwave radiation directly. The susceptor silicon carbide (SiC) was chosen as an irradiation absorption catalyst, to absorb radiant heat generated by a microwave and transfer it to the VDBs through convection heating. Traditional thermal oil heating systems are limited to a few hundred degrees centigrade, while microwave heating can achieve > 1000°C (Fernandez

et al, 2011). In addition to its susceptor abilities, SiC was chosen to test whether there were any positive catalytic effects on the bio-oil component selectivity (Wan et al, 2009).

The primary objective of the following research was to produce a bio-oil from MAP using VDBs that could qualify as B100 or a biodiesel blend. The resulting bio-oil would be tested by ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels and ASTM 7467 Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20). The second objective was to determine if there are any positive effects of the susceptor SiC, regarding bio-oil product selectivity. Two reaction scenarios were designed and carried out: 1) distillation microwave-assisted pyrolysis (dMAP) and 2) flash microwave-assisted pyrolysis (fMAP). The first scenario, dMAP, mimicked traditional methyl ester distillation by maintaining a continuous liquid-level above the SiC catalyst and flashing the volatile oil from the liquid surface. The second scenario, fMAP, did not allow for any liquid to collect inside the reactor, but instead flashed from the surface of the SiC. Analyzing the product bio-oil from each scenario could identify potential surface catalytic effects of the fixed-bed catalyst. The weights of each product type; bio-oil, residual solids, and off-gas were also studied to determine the optimal method for bio-oil production, as the bio-oil has the greatest economic potential if it can be tested and certified as a biodiesel analogue.

5.2 Material and methods

The preparation of VDBs was done so conscientiously to represent a commercial grade methyl ester distillation by-product. Approx. 55 gallons of non-distilled B100 biodiesel

was obtained from the New Leaf Biofuels in San Diego, CA and sent to Artisan Industries, Inc in Stoughton, MA. As a leader in separation technology, Artisan Industries could perform pilot-scale, continuous flash-distillation on the non-distilled methyl esters (biodiesel) using 1 ft^2 stainless steel horizontal thin film evaporator. Approx. 90-92% of the biodiesel was evaporated and condensed as a "light-ends" stream composed of a purified methyl ester stream, the rest leaving as VDBs. The reactor was heated with a thermal oil utility system that could operate as high as 290°C. The wiper blades in the Rototherm ran at 20 linear feet per second with a 1 kW variable speed drive. Rectified methyl ester vapors were condensed in a vertical, stainless steel condenser, cooled with water at 32°C. The non-rectified material was removed from the reactor through a bottoms port and collected in a nitrogen purged collection tank. Non-rectifiable methyl esters, or VDBs, were the substrate of interest in the following experiment, aimed at further purifying the distillation bottoms for improved biofuel production yield.

5.2.1.1 Experimental design for the microwave assisted pyrolysis of VDBs in a continuous system.

The equipment used to model the two distinct continuous pyrolysis systems was a modified CEM Corporation MARS 6 Microwave Digestion System. The microwave is equipped with a 1000-Watt primary magnetron and an 800-Watt secondary magnetron, totaling 1.8 kW of available input energy. The equipment was modified to allow for two glass adapters to enter and exit the top of the microwave. These modifications allowed the continuous feeding and removal of organic material during operation. Figure 1 below

shows a diagram depicting the components of the experimental set-up, including

1: Mars 6 microwave (1,800 Watts)
2: Distillation "bottoms" feeder flask
3: Pyrolysis reactor (quartz)
4: Silicon carbide (SiC)
5: Temperature thermocouple
6: Bio-oil collection flask
7: Chilled condenser (15°C)
8: Manometer (pressure control)
9: Vacuum pump
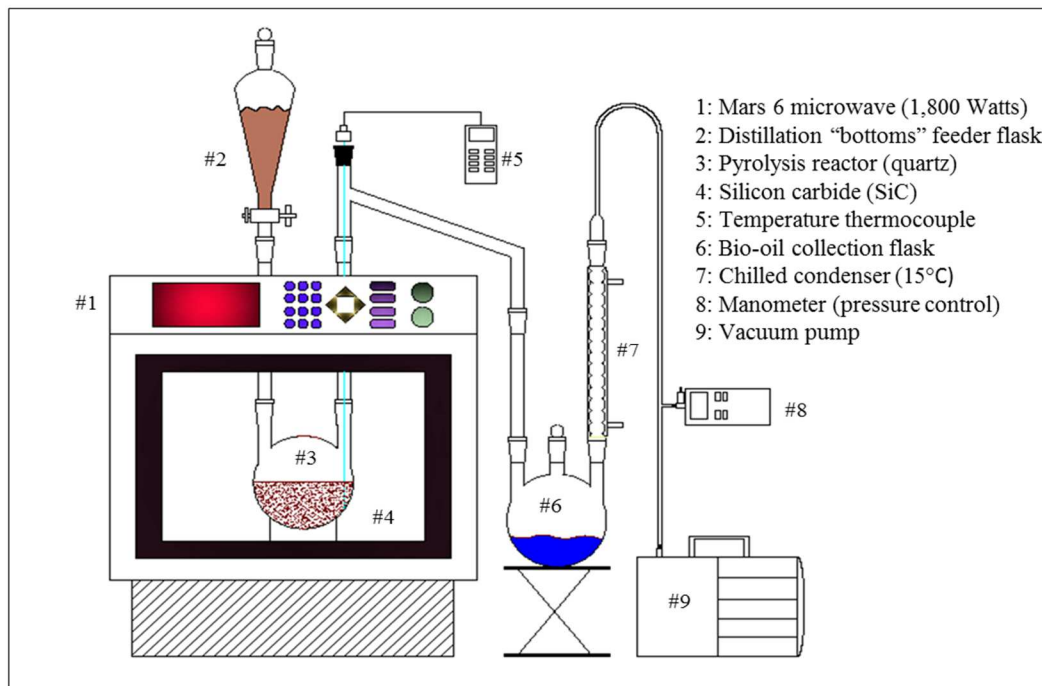
Figure 1: Experimental set-up and key for the continuous microwave pyrolysis
(distillation and flash) of liquid VDBs. Temperature and pressure inside the reactor was
maintained at 550°C and 80 kPa.

Temperature, pressure, and flow-rate control. During distillation and slow-pyrolysis, the
liquid VDBs were heated to 120°C and mixed in a feeder flask (#2), then drawn into the
quartz pyrolysis reactor (#3) through a needle valve by a slight vacuum of 80 kPa,
maintained inside the reactor by a manometer (#8) and vacuum pump (#9). The flow-rate
was held constant by the control of a needle valve and recorded during each experiment.
The 500-ml quartz reactor was filled with 500 grams of silicon carbide (SiC) beads (#4),
with an average particle diameter of 1.8 cm. The amount of silicon carbide was held
constant at 500 grams throughout all reactions to standardize the absorption potential,

indirectly maintaining a constant heating rate during the microwave irradiation of the susceptor, silicon carbide. Off-gases and volatile organics generated from the pyrolysis of VDBs were sent out of the reactor through a glass adapter into a liquid cooled ringed condenser (#7), maintained at 18°C. The off-gas temperature was measured using a thermocouple with digital display (#5), prior to the gas entering the condenser. The volatile organics were condensed and collected below the condenser in the bio-oil collection flask (#6). The off-gases, composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and non-condensable gases, passed through the condenser and out of the system via the vacuum pump.

5.2.1.2 Determination of pressure and temperature conditions for the microwave-assisted pyrolysis (MAP) of liquid VDBs

Unlike other pyrolysis systems, which allow the innate vapor velocity of the newly formed syn-gas to move through the system, dMAP and fMAP were operated at negative pressure. The pressure inside the pyrolysis system was under slight vacuum for two reasons: 1) to avoid any positive pressure inside the reactor during liquid vaporization and 2) to reduce the vaporization temperature of the methyl esters. As the vaporization temperature of the methyl esters depends on the system pressure, a standard operating pressure needed to be established first (Ramasamy, 2009). Based on testing using the bench top reactor, a pressure of 80 kPa (600 mmHg) was chosen as an ideal vacuum pressure, with low risk of leaking air into the system. At this pressure, the volatiles were

still easily condensable at 32°C while maintaining a vapor velocity equal to the evolution of volatiles from the liquid biomass.

To determine the optimal pyrolysis temperature for both systems (at 80 kPa), a fixed amount of VDBs (50 grams) was heated in the presence of SiC to establish a temperature profile of the volatile components present. By plotting the temperature vs. time, the volatility range of VDBs was determined experimentally. This temperature was used to standardize both the distillation and flash pyrolysis experimental conditions.

5.2.2 Continuous feeding of VDBs during distillation pyrolysis (dMAP)

Using the system set-up described in section 2.1, microwave-assisted pyrolysis was created in a laboratory setting while continuously maintaining a liquid-level of VDBs just above the SiC catalyst present inside the quartz reactor. This required fine control of the needle valve inlet separating the feeding flask from the reaction chamber. Since the reactor is sealed and no visual assessment could be made during the reaction, the rate of the bio-oil collection was used to control the VDBs feed rate. Theoretically, to achieve the steady-state feed rate required to maintain a constant liquid-level, the rate of bio-oil collection must be equal to the initial rate of feeding, multiplied by the percent of bio-oil that is potentially condensable in the VDBs. Experimental mass balance trials were conducted using a fixed amount of VDBs. The VDBs were heated, vaporized, and then condensed outside of the reactor in order to establish the average weights of products; bio-oil, residual solids, and off-gas (measured by difference). The amount of bio-oil expected from the VDBs was approx. 85.9% (wt/wt), resulting in a ratio of 1.16:1, VDBs

fed to bio-oil collected. This figure was used to determine both the expected bio-oil collection rate, and by extension, the required rate of VDBs fed to the reactor to maintain a steady-state.

As measuring the rate of collection by mass was not an option due to the fixed-nature of the system, collection by volume was accomplished by graduating the receiver/collection flask. By timing the reaction with a stop-watch, the rate of collection was calculated in real-time and the feed rate was adjusted accordingly in order to maintain a continuous liquid level during distillation-pyrolysis.

After establishing the correct rate ratio, it was necessary to select an experimental feed rate. The feed rate is limited as a function of both the overall power to biomass input as well as the exposed surface area of VDBs, above the SiC. A relatively slow flow-rate of 4.0 g/min was chosen as the amount of energy required to vaporize the flow was determined small relative to the energy used to maintain the system at 550°C, guaranteeing vaporization was not limited as a function of residence time.

Without any liquid removal stream, the experimental reaction time was limited as a function of inert, non-volatile build-up. Distillation-pyrolysis was run for 30-40 minutes, depending on the sample size. Bio-oil was collected throughout the reaction into a single flask, without fractionalization or "cuts". The bio-oil was tested and analyzed for its properties as a transportation fuel.

5.2.3 Continuous feeding of VDBs during flash-pyrolysis (fMAP)

Using the same experimental set-up as distillation pyrolysis, flash-pyrolysis was created in a laboratory setting by heating the SiC catalyst present inside the quartz reactor to 550°C first. After the fixed-bed SiC was heated and maintained an average temperature of 550°C, the flow of VDBs started to mimic a true "flash" pyrolysis. This required fine control of the needle valve inlet to avoid any build-up or pooling of VDBs. To standardize the exposure time or hydraulic retention time of the VDBs in the reactor the desired flow rate was based on the results of the distillation-pyrolysis rate determination experiments, 4.0 g/min. As the figure was calculated to maintain a continuous liquid level, in theory there should be no build-up of material during flash pyrolysis. As the VDBs entered the reactor at 4.0 g/min, the volatile components of the material (85.9% wt/wt) were vaporized and sent out of the reactor to be condensed, while the inert residual solids remained in the reactor. One assumption made during flash-pyrolysis was that the build-up of the non-vaporized material did not affect the microwave absorption efficiency or catalytic potential of the SiC. Unlike distillation-pyrolysis, where SiC is strictly a susceptor for heat generation, flash-pyrolysis involves significant catalytic activity due to the much higher catalyst to VDBs ratio. Significant build-up of inert, non-volatile material on the catalyst bed could potentially cause a drop in catalytic activity due to lowered surface area. However, at the average weight concentration of less than 5%, the build-up of residual solids was determined negligible to absorption efficiency and catalytic activity.

As with distillation-pyrolysis, flash-pyrolysis testing was limited to 30-40 minutes due to potential solids build-up. During pilot or commercial scale operations the residual solids could theoretically be continuously removed from the system. For dMAP, a

continuous solids filtration system could circulate from the maintained liquid-level of VDBs inside the reactor, back to the incoming VDB stream entering the reactor. For fMAP, the SiC catalyst can be continuously mixed, allowing the residual solids to filter through the ceramic medium, collecting at the bottom.

Bio-oil was collected throughout the reaction into a single flask, without fractionalization or "cuts". The resulting bio-oil was collected and prepped for testing. Two testing scenarios were considered for each type of pyrolysis oil; blending the total bio-oil collected during pyrolysis back into the theoretical amount of distilled biodiesel removed during the initial distillation and blending the bio-oil directly with petroleum diesel as a potential biodiesel substitute. Each of the test scenarios were analyzed for their properties as a transportation fuel currently being certified and used throughout developed countries.

5.2.4 Data Analysis and Fuel Testing

The VDBs and product bio-oil was tested for a series of compound types to establish a complete profile of the major components. A GC-Mass spec 6890 was used for the characterization of methyl ester, hydrocarbons, cyclic and oxy-cyclic-hydrocarbons, according to ASTM E2997–16 Standard Test Method for Analysis of Biodiesel Products by Gas Chromatography-Mass Spectrometry. A Hewlett-Packard GC-FID 6890 was used to quantify the acyl-glycerides and methyl esters according to ASTM D6584-13e1 standard test method for determination of total monoglycerides, total diglycerides, total triglycerides, and free and total glycerin in B-100 biodiesel methyl esters by gas

chromatography. An Elemental Analyzer: Model 440 CHN/O/S was used to establish

theoretical empirical formulas for mass balance estimation modeling. The "wet"

chemistry method ASTM D664 - 11a(2017) Standard Test Method for Acid Number of

Petroleum Products by Potentiometric Titration was used to estimate the free fatty acid

concentration in the initial VDBs substrate. A third-party testing laboratory, Gorge

Analytical Inc., was employed to test the blended biodiesel end-product for all the 18

criteria included in ASTM D6751 Standard Specification for Biodiesel Fuel (B 100)

Blend Stock for Distillate Fuels. ASTM D7467 - 17 Standard Specification for Diesel

Fuel Oil, Biodiesel Blend (B6 to B20) was also employed to test the bio-oils potential as

an unblended, biodiesel alternative. Sulfur was measured before and after pyrolysis to

track and characterize the form and molecular weight of the sulfur functional group.

Sulfur by ultraviolet fluorescence (UVF), ASTM 5453 was used as the sulfur detection

method for the VDBs and resulting bio-oil. A four-decimal mass balance by Intelligent

Weighing Technology was used to measure the reagents and products before and after

each experiment to establish an experimental mass balance.

5.3 Results and discussion

5.3.1 Vacuum distillation bottoms (VDB) characterization

The individual components and combined properties of the VDBs were determined using

several different analytical methods. Initial GC-FID analysis of the biodiesel distillation

by-product yielded an initial acyl-glyceride concentration of $10.11 \pm 0.83\%$ wt/wt (5.4%

mono-, 4.2% di-, and 0.51% tri-acyl-glyceride) and free glycerin concentration of 0.03% wt/wt. The free fatty acid concentration was $5.81 \pm 0.33\%$ wt/wt, assuming an average molecular weight of 282, as determined by the titrated acid number of the VDBs.

As the purpose of biodiesel distillation is to separate methyl esters from unreacted acyl-glycerides, free fatty acids, soaps, etc., the high amount of impurities was to be expected. The rest of the material accounted for $84.05 \pm 2.10\%$ wt/wt of the VDBs and was a mixture of C16, and C18 methyl esters and methyl ester derivatives, shown in Table 1. The derivate species were likely a mixture two separate sources, 1) organic impurities or MONG (matter organic non-glyceride) carried into the process with the initial oil and 2) a by-product of unwanted oxidation reactions during biodiesel distillation (~250°C at 0.26 kPa). Any oxygen introduced during distillation through a pin-hole leak could partially oxidize the methyl ester into biodiesel-like derivatives (Ramasamy, 2009). Characterization of this component mixture was difficult as the quality of the NES-LAB library matching was low. Analytical results indicated most of the mixture was C16 and C18 methyl esters, while the rest was a combination of trace derivatives, ranging in various forms of cyclic and non-cyclic, oxygenated hydrocarbons.

To make several predictions about the average VDBs compound, an elemental analysis was performed to establish a base empirical formula. The results showed the VDBs were composed of 70.40% carbon, 11.38% hydrogen, 0.94% nitrogen, 0.008% sulfur, and 17.27% oxygen. By making certain assumptions about the molecular weights of the components already identified, the elemental analysis could be improved to better represent the methyl ester component. Model compounds were used to extrapolate the molecular weights (MW) of the free fatty acids, mono-, di-, and tri-acyl-glycerides based

on their respective concentrations and then accounted for in the elemental analysis. Once all the know components were accounted for and removed from the molar balance, the empirical formula represented the methyl ester and derivative fraction only at; 70.0% carbon, 11.36% hydrogen, 0.94% nitrogen, 0.008% sulfur, and 17.16% oxygen. Using the modified elemental analysis, an averaged compound was created, assuming both the methyl ester and its derivatives share the resulting carbon/oxygen ratio of 5.44 ± 0.10. With two moles of oxygens per mole of methyl ester, the theoretical average methyl ester had an estimated chain-length of 10.88 ± 0.21 carbons. The resulting averaged chain-length was of great interest because it differed from what was expected (C20+) in the VDBs. A review of what was already known about the VDBs was researched to resolve the discrepancy. After biodiesel distillation, the residual material not vaporized (vacuum distillation bottoms) was caused by a lack of expressed vapor pressure at a given set of conditions. Essentially, liquids can be separated as a function of boiling temperatures, which in turn correlates with a rise in the molecular weight (MW) of compounds being distilled. Other factors can contribute to the expressed vapor pressure of a substance, like intermolecular adhesion, but MW is the most significant contributor to differences in the relative volatility of two substances. Therefore, the VDBs must have a MW as high as or higher than the distilled biodiesel. As the highest heaviest compound in biodiesel distillate is a C18 methyl esters with trace amounts of C20, it is unlikely a methyl ester blend of C10 and C12 (average chain-length = 10.88) would be left behind in the bottoms without flashing out of the system with the distillate product. It was concluded that the methyl esters must have reacted with themselves, possibly through a dimerization reaction on unsaturated pi-bonds of the fatty acid, to form heavier C20-C22 derivative

compounds. The combined MW of two C10s or C12s (potential dimerized product) falls

immediately outside the upper distillate range of biodiesel and would be collected in the

distillate bottoms.

5.3.2 Vacuum distillation bottoms (VDB) heat rate and vaporization limits

As explained in section 2.1.2., the heating rate of the VDBs and SiC catalyst was

calculated experimentally to establish upper and lower vaporization temperatures. A

measure of the hold temperature was also performed on the SiC catalyst without any

substrate added. This was used to access the average deviation in temperature control

during steady-state heating. Figure 2 below shows the temperature versus time for both
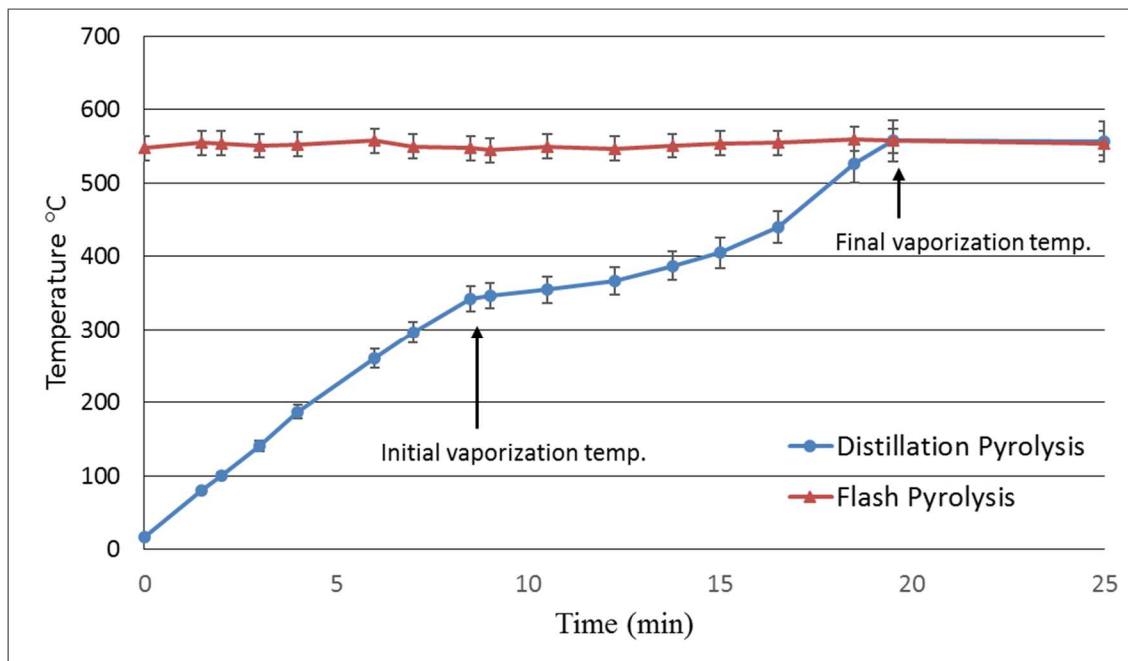
Figure 2: Microwave heating rate analysis for continuous liquid-level (Distillation) pyrolysis of VDBs using a silicon carbide heating catalyst. The experimental vaporization parameters deduced from batch heating were used to determine the experimental continuous "Flash" pyrolysis operating temperature of 550°C (also shown).

pyrolysis reaction scenarios illustrated the heating rate and fluctuation of the reactor temperature during microwave heating. Distillation pyrolysis heating, with the VDBs pre-loaded onto the SiC fixed-bed as explained in section 2.1.2, yielded a heat rate of 38ºC/min, from 21ºC to 350ºC. As the VDBs reached 350ºC, they vaporized and migrated up the column. As the transfer from simple to latent heating continued, less of heat input remained contained within the reactor, lowering the perceived heating rate of the reactor mixture. The vaporization transition can be seen in Figure 2 as the temperature increase slowed down and became non-linear. As the organic fraction was removed from the system, the heating rate slowly increased, until a final temperature of 550°C was reached. This was considered the endpoint for any vaporization potential as it represented the linearly predicted temperature outcome of the initial heating rate of 38ºC/min, at that time (min). Therefore, the vaporization range of the VDBs was between 350°C and 550°C. To guarantee complete vaporization while maintaining energy efficiency, the upper boundary temperature of 550°C was chosen as the fixed reaction temperature for both sets of reaction conditions; distillation and flash pyrolysis. To determine the temperature control of the system, the reactor was heated to the desired temperature and maintained for 25 minutes. The results were plotted in Figure 2 and yielded an average temperature of 552 ± 4°C.

5.3.3 Pyrolysis mass balance and product yields

One of the primary objectives of the following research was to determine the most optimal conditions for the continuous pyrolysis of biodiesel VDBs. To compare process efficiencies, the final weight of each product stream was measured and recorded. To accurately measure the weight of the bio-oil produced during pyrolysis, each of the glass reactor components were weighed to account for all condensed bio-oil. After each reaction, the reactor containing the SiC catalyst was removed and weighed, then compared to the initial weights of each to account for any non-pyrolyzed, residual solids. To complete the mass balance, any weight not reported as bio-oil or residual solids was considered off-gas. Although syn-gas is often the product of interest for biomass pyrolysis, the purpose of this study was to reclaim methyl esters from the VDBs, so off-gas analysis was not performed. Figure 3 illustrates the average mass balance of the

product streams; bio-oil, residual
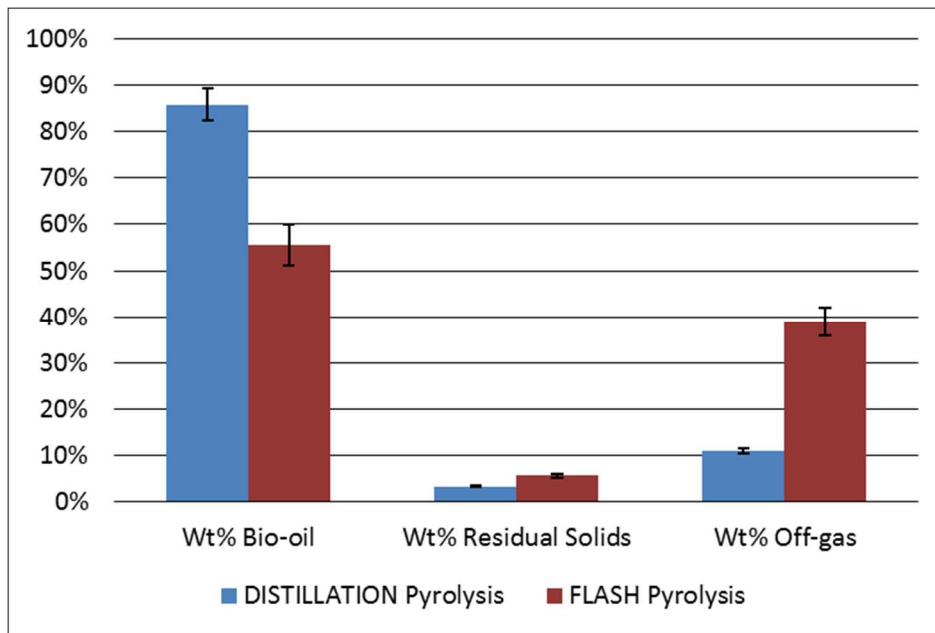
Figure 3: Mass composition of microwave pyrolysis by-products; bio-oil, residual solid, and off-gas for distillation and flash pyrolysis.

solids, and off-gas, for distillation and flash pyrolysis. As previously stated, bio-oil was the desired byproduct and maximizing its yield potential could have the most economic impact on whether reclaiming methyl esters using microwave pyrolysis is a viable process.

According to the results, dMAP performed the best, reclaiming $85.9 \pm 2.3\%$ of the initial 47.5 ± 8.7 grams of VDBs as a transparent bio-oil. Alternatively, fMAP only recovered $55.6 \pm 4.8\%$ of the initial 53.8 ± 5.7 grams of VDBs as bio-oil. The residual solids for dMAP and fMAP were relatively similar, at $3.2 \pm 0.07\%$ and $5.6 \pm 0.05\%$ respectively. As the initial substrate for each reaction scenario was the same, the inert

content should be constant. A plausible explanation for the minor rise in residual material during fMAP is the formation of tars and other stable oxygenated oil derivatives caused during the flashing of the material against the catalyst surface. The removal of residual solids from the reactor was not considered during the experiment; however, the rate at which residual solids were created is vital for the eventual development of a continuous process. Averaging the final residual solids over the total reaction time yielded a solids rate formation of 0.036 ± 0.004 g/min for distillation pyrolysis and 0.075 ± 0.011 g/min for flash pyrolysis. The amount of off-gas produced during fMAP was the highest at $38.9 \pm 1.72\%$, while dMAP only produced $10.9 \pm 2.5\%$ wt/wt off-gases during the reaction time.

5.3.4 Bio-oil product analysis from dMAP and fMAP using GC-MS and GC-FID

Using GC-Mass spectroscopy, the bio-oil products from dMAP and fMAP were analyzed and compared to initial VDBs profile. Figure 4 shows the GC-Mass chromatograms for a)

the initial VDBs, b) dMAP derived bio-oil, and c) fMAP derived bio-oil. The
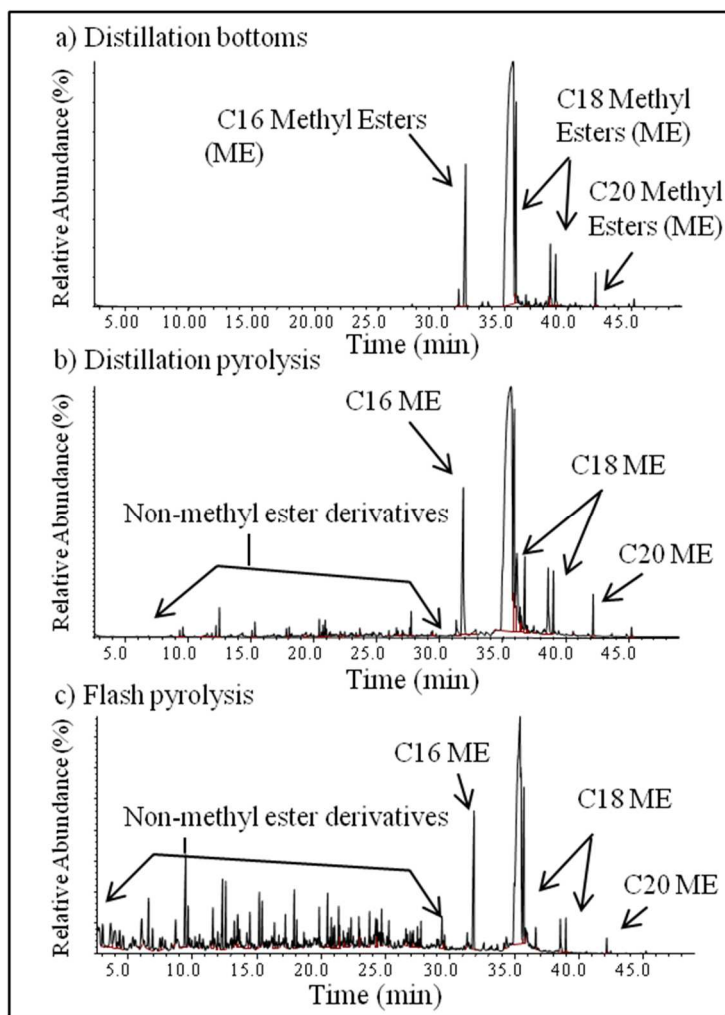
Figure 4: GC-mass spectroscopy results for relative abundance (%) of a) non-pyrolyzed VDBs, b) distillation pyrolysis at 550°C, and c) flash pyrolysis at 550°C.

chromatogram on top represents the VDBs, showing the majority of the detected

compounds were methyl esters, with only trace amounts of other detectable compounds.

The middle chromatogram represents bio-oil derived from dMAP processing, and shows

the appearance of smaller molecular weight, non-methyl ester derivative compounds. The

bottom chromatogram shows the fMAP derived bio-oil. There is a clear increase in the

relative abundance of non-methyl ester derivatives in the fMAP chromatogram, as compared to dMAP and the original VDBs. As a result of derivative species formation, the relative abundance of methyl esters in the fMAP bio-oil decreased, lowering the overall methyl ester content of the bio-oil.

The newly formed compounds were a mixture of hydrocarbons, oxygen containing derivatives, and branched and dimerized methyl esters. Shown in Table 1, the derivatives species were categorized into several groups, based on the compound type; methyl ester, dimerized methyl ester, branched methyl ester, aldehyde, free fatty acid, hydrocarbon,

Table 1: Relative frequency and component characteristics of the initial pyrolysis substrate and resulting bio-oils. GC-Mass Spec. test results averaged from 3 separate samples each.

Substrate and Bio-Oil Component Profiles	Relative Freq (%)	Carbon/Mole Ratio	Average M.W.
Distillation Bottoms			
Methyl Ester =	84.05%	18.0	296
Monoglyceride =	5.40%	18.0	350
Diglyceride =	4.20%	39.0	610
Triglyceride =	0.51%	57.0	860
Free Fatty Acid =	5.81%	18.0	271
Free Glycerin =	0.03%	3.0	32
Bio-Oil – Distillation Pyrolysis			
Methyl Esters =	90.34 ± 4.02%	17.4 ± 0.4	287 ± 6
Dimerized Methyl Esters =	1.19 ± 0.76%	10.1 ± 0.3	220 ± 5
Branched Methyl Esters =	3.94 ± 4.35%	15 ± 8.7	256 ± 149
Aldehydes =	0.88 ± 1.52%	6 ± 10.4	264 ± 153
Free Fatty Acids =	1.53 ± 0.91%	14.8 ± 8.6	239 ± 139
Hydrocarbons =	3.31 ± 2.02%	14.2 ± 0.3	199 ± 3
Cyclic-Hydrocarbons =	0.31 ± 0.18%	8.8 ± 5.1	155 ± 95
Oxy-Cyclic-Hydrocarbons =	0.64 ± 0.47%	13 ± 8.5	193 ± 111
Bio-Oil – Flash Pyrolysis			
Methyl Esters =	73.97 ± 1.37%	15.3 ± 0.3	257 ± 3
Dimerized Methyl Esters =	0.51 ± 0.36%	10.0 ± 7.1	136 ± 96
Branched Methyl Esters=	0.00%	0.0	0
Aldehydes =	0.00%	0.0	0
Free Fatty Acids =	0.00%	0.0	0
Hydrocarbons =	20.09 ± 5.27%	10.9 ± 0.3	157 ± 5
Cyclic-Hydrocarbons =	3.79 ± 3.93%	11.2 ± 1.7	149 ± 15
Oxy-Cyclic-Hydrocarbons =	1.89 ± 0.33%	10.5 ± 0.3	154 ± 6

* Distillation bottoms were averaged from 3 separate tests of the same substrate. The bio-oil products were average from 3 separate samples, generated from identical reaction conditions.

oxygenated hydrocarbon (ether), and cyclic oxygenated hydrocarbon. The relative frequencies of the different derivative compounds in each bio-oil are also listed in Table 1, along with the relative frequencies of the compounds in the initial VDBs. In addition, the average carbon per mole, and the molecular weight was reported as a method to gauge average chain length of the derivative.

As the formation of these derivatives compounds is not reported during commercial biodiesel production, they were thought to be a result of a several altered reaction conditions i.e. flashing evaporating in the presence of a catalyst, increased temperature, and increased pressure. Based on the results of GC-MS, the presence of surface flashing from the catalytic surface was the major contributor in the formation of

derivatives species. This was illustrated in Figure 4, where the there is significantly less

derivative species formation during dMAP processing. As the mechanism for

vaporization of the VDBs i.e. catalyst surface flashing vs. liquid-surface distillation, was

the only independent variable, it was the assumed cause for the increase in derivative

species. However, as the chemical mechanism of the derivatization was not the focus of

the study, not all the possible contributing factors are discussed in this report. As

traditional biodiesel distillation is performed at lower temperatures and pressures

(~200°C and 0.26 kPa), MAP vaporization occurs at a significantly higher temperature

and pressure (550°C and 101 kPa). The extreme conditions of MAP vaporization, relative

to traditional biodiesel distillation, could contribute to the greater thermal decomposition

seen during MAP processing.

Table 1 shows that bio-oil from dMAP contained 16.4% wt/wt more methyl

esters than fMAP. Alternatively, fMAP bio-oil contained 16.8% wt/wt more hydrocarbon

content than dMAP, as a result of the methyl ester reformation. In addition to increased

hydrocarbon content after fMAP processing, there was also an increase in oxygenated-

hydrocarbons and cyclic, oxygenated-hydrocarbons. Alternatively, dMAP processing

showed an increase in methyl ester derivatives, dimerized and branched, relative to

fMAP. These dimerized and branched methyl esters can have improved characteristics,

such as greater lubricity and depressed cloud points, relative to their analogous straight-

chain methyl esters (Knothe, 2005; Lee et al, 1995).

Analysis of the average carbon content per mole of each species was performed on the

bio-oils, and reported in Table 1. As expected, the initial oil substrate contained the

highest average carbon content per mole, with methyl esters at C:18. The resulting bio-

oils averaged lower carbon per mole ratios, with their methyl esters averaging C:17.0 ±

0.4 for dMAP and C:15.3 ± 0.3 for fMAP. As the carbon content per mole was reduced,

the average molecular weight of each species dropped, as shown in Table 1.

5.3.5 Analytical analysis of the blended bio-oils with biodiesel and petroleum diesel

The purpose of using VDBs from a commercial biodiesel facility as a substrate for MAP

processing was to test the technologies' potential as a secondary methyl ester rectification

process, either inserted immediately following the initial biodiesel distillation or as a

separate process. Both the dMAP and fMAP systems were designed to mimic two

different continuous processes, each producing a distinct bio-oil with varying

concentrations of methyl esters and unique derivatives. As a methyl ester reclamation

technology, the desired product of each system would be a liquid fuel that closely

resembled B100 biodiesel. Therefore, the bio-oil was prepared in two ways; as a B20

blend in petroleum diesel and as a B100 blend with previously distilled biodiesel. As a

B20 petroleum blend, the MAP bio-oil represents a B100 replacement, in which a MAP

system could operate independently of a biodiesel production facility. By blending the

pyrolysis oil with B100, the MAP system could operate in series with a commercial

biodiesel facility, blending the resulting bio-oil back into the initially distilled B100.

Critical tests from ASTM D7467-Standard Specification for Diesel Fuel Oil,

Biodiesel Blend and ASTM D6751 Standard Specification for Biodiesel Fuel Blend

Stock (B100) for Middle Distillate Fuels were chosen to test the product quality and

repeatability of the process. Table 2 shows the tests and methods performed, reporting

criteria, and

Table 2: Analysis of bio-oil from distillation and flash pyrolysis, blended with a)

petroleum diesel and b) distilled biodiesel (methyl esters) to represent potential end-use

forms.

A) 20% wt/wt Bio-Oil in Petroleum Diesel				
Analytical Test	**ASTM Method**	**Report Criteria**	**Dist. Pyrolysis**	**Flash Pyrolysis**
Ash Content	D482	0.01% max	< 0.005	< 0.005
Biodiesel Content	D7371	% (v/v)	21.72 ± 2.48	22.47 ± 0.77
Cloud Point	D2500	n/a	< -15°C	< -15°C
Copper Strip Corrosion	D130	No. 3 max	1a	1a
Oxidation Stability	EN 15751	6 min	13.6 ± 1.20	12.90 ± 2.70
Micro-Carbon Residue	D4530	0.35% max	0.04 ± 0.01	0.02 ± 0.02
Sulfur by UVF	D5453	500 ppm (wt/wt)	96.80 ± 4.50	97.35 ± 2.15
Kinematic Viscosity	D445	1.9-4.1 mm^2/s	2.95 ± 0.08	2.56 ± 0.12
Acid Number	D664	0.3 mg KOH/g	2.58 ± 0.80	3.34 ± 0.27
Water Content (KF)	D6304-16e1	0.05% vol.	< 0.0015	< 0.0015
B) 10% wt/wt Bio-Oil in Distilled B100 Biodiesel				
Analytical Test	**ASTM Method**	**Report Criteria**	**Dist. Pyrolysis**	**Flash Pyrolysis**
Ash Content	D482	0.01% max	< 0.005	< 0.005
Cloud Point	D2500	n/a	12.9 ± 0.8°C	12.1 ± 0.6°C
Copper Strip Corrosion	D130	No. 3 max	1a	1a
Oxidation Stability	EN 15751	6 min	7.93 ± 0.76	7.86 ± 0.59
Micro-Carbon Residue	D4530	0.35% max	0.004 ± 0.001	0.002 ± 0.001
Sulfur by UVF	D5453	500 ppm (wt/wt)	23.18 ± 1.83	23.23 ± 1.54
Kinematic Viscosity	D445-40	1.9-6.0 mm^2/s	4.07 ± 0.11	4.03 ± 0.09
Acid Number	D664	0.5 mg KOH/g	0.49 ± 0.16	0.57 ± 0.19
Water Content (KF)	D6304-16e1	0.05% vol.	< 0.0015	< 0.0015

*Analytical results in section A) were performed and reported according to ASTM D7467, while results for section B) were reported according to ASTM D6751.

average results for dMAP and fMAP. Based on the results of the B20 blend with

petroleum diesel (Table 2, section A), the blended fuels from both systems passed all test

criteria, except for the Acid Number (AN). For dMAP and fMAP, the AN was 8.6x and

11.1x times the ASTM reporting criteria of 0.3 mg KOH/g. The high acid value of the

bio-oil indicates further processing is required before the bio-oil from process, fMAP or dMAP, can be used as a direct replacement for B100 in a B20 petroleum blend. Table 2, section B shows the results of MAP bio-oil blended into distilled B100 biodiesel. Assuming an initial distillation efficiency of 90% wt/wt, leaves 10% wt/wt in the form of VDBs. According to lab results, a bio-oil recovery efficiency of 85% wt/wt, relative to the weight of the initial VDBs, was used to calculate the blend ratios of the B100 and bio-oil. Once blended, the mixture was sent to a third-party laboratory for B100 certification. According to the results, the dMAP derived bio-oil and B100 blend passed all the ASTM D6751 test criteria, while the fMAP derived bio-oil blend was marginally over the AN upper reporting limit of 0.5 mg KPH/g, at 0.57 mg KPH/g. Depending on unknown performance characteristics of the fMAP bio-oil, further processing could reduce the AN to below reporting criteria. However, further study would be required to prove the improved characteristics over the dMAP generated bio-oil, to justify any additional processing.

5.4 Conclusions

Two continuous microwave-assisted pyrolysis systems were designed to reclaim methyl esters from biodiesel VDBs. The dMAP system yielded the most recovered liquid bio-oil (85.9% wt/wt) with the highest concentration of methyl ester, 90.3%. The fMAP system reclaimed less bio-oil (55.6% wt/wt) and less of the recovered material remained as a methyl ester, 74%. Both the dMAP and fMAP bio-oils failed the Acid Number as a B20 petroleum blend, while dMAP derived bio-oil passed all test criteria as a blend with B100

biodiesel, concluding that dMAP is a suitable technology for the recovery of methyl esters from VDBs.

5.4.1 Funding and support acknowledgments

BIOGRAPHICAL SKETCH

Over the past decade, my interest in renewable energy has transformed from an academic curiosity into a lifelong pursuit. After receiving my bachelor's degree in Chemistry from Gustavus Adolphus College in 2008, I began my career as a research chemist for Superior Process Technologies, Inc. The company's focus is the engineering of commercial scale renewable energy systems and the consulting of existing plants. For two years I worked on the process development of several renewable energy technologies, including biodiesel, the anaerobic digestion of food waste, and the gasification of meat and bone meal. In 2011, I was promoted to laboratory manager and over saw all lab research efforts.

In 2014 I was nominated and elected to the National Biodiesel Accreditation Committee for a three-year term. I serve with 11 other commissioners and vote on issues of accreditation and quality assurance for the BQ-9000 program. The position requires monthly quorums with industry professionals from around the country and annual conferences at the NBAC headquarters to revise program guidelines.

Soon after starting my career in renewable energy I decided to get my Masters in Biological Science at the University of Minnesota. My project of interest seeks to biorefine waste scum by extracting metals and non-metals, converting the oil to biodiesel, and using the glycerin byproduct to feed algae growth. Since starting the project, I have been involved in the publishing of several manuscripts and am named co-inventor on a patent application regarding the conversion technology of scum to biodiesel.

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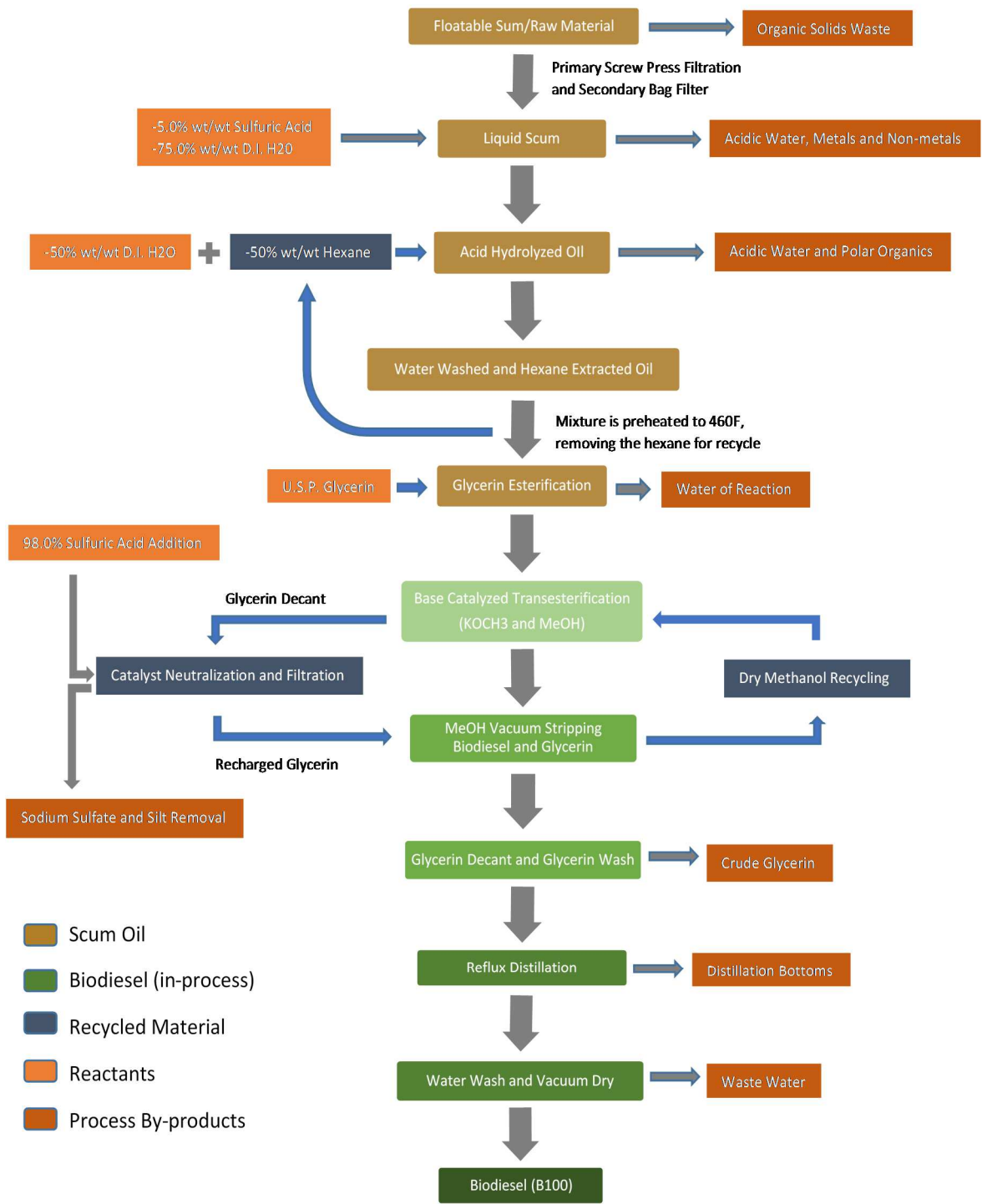
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Mass balance
Column design

	(g/hr)	%		
ME's	1224	0.998	$Y_1 = 0.996$	

>>>vapor load 1226   1

	(g/hr)	%
ME's	918.2	0.998
Mono's	1.84	0.002
Total Distillate	920	1

<<< Reflux (g/hr)= 306   >

(92% yield)

Y_1

1st stage

1st stage $X_1=Y_1/(Rv(1-Y_1)+Y_1)$

$X_1 =$ 0.98422

X_1 * reflux   301.1715976   g/hr (liquid down)

X_1 Y_2

$Y_2 = \dfrac{301.17 + 920}{1226} = 0.9961$

2nd stage

2nd stage $X_2=Y_2/(Rv(1-Y_2)+Y_2)$

$X_2 =$ 0.969338581

X_2 * reflux   291.9372492   g/hr (liquid down)

X_2 Y_2

$Y_3 = \dfrac{291.94 + 920}{1226} = 0.9885$

	(g/hr)	%
ME's (g/hr)	990	99.0%
Mono's (g/hr)	10	1.00%
Total Feed	1000	>>>>>

Heating Coil

	(g/hr)	wt %
ME's	71.84	89.8%
Mono's	8.16	10.2%
Total Bottoms	80	100.0%

>>>>>

Appendix A: Distillation column design for the separation of methyl esters from mono-glycerides.

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Appendix B: Scum to biodiesel process flow diagram.