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It is entitled:
Fats, Oils and Greases to Biodiesel: Technology Development and Sustainability Assessment

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Fats, Oils and Greases to Biodiesel: Technology Development and Sustainability Assessment

A dissertation submitted to

Department of Biomedical, Chemical and Environmental Engineering

Division of Graduate Studies

University of Cincinnati

In partial fulfillment of the requirement for the degree of

DOCTORATE OF PHILOSOPHY

2015

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Abstract

Fats, oils and greases (FOG) in the wastewater stream have long been a nuisance to the environment because they clog sewer pipes, causing overflows and damages. FOG can be classified as trap grease if obtained directly from food services, or sewer grease if mixed with FOG in the sewer system. This dissertation evaluated the technical feasibility and several sustainability parameters of converting trap/sewer grease into biodiesel. This waste-to-energy practice can provide the dual benefit of waste reduction and biofuel production.

Monte Carlo simulations were conducted to model the energy consumption and GHG emissions from trap grease-to-biodiesel production life cycle at a wastewater treatment plant. Results were highly dependent on both the trap grease properties (e.g., FOG concentration, free fatty acid (FFA) concentration, etc.) and the utilization of non-lipid fraction of the FOG. Trap grease can provide lower energy consumption and lower GHG emissions for biodiesel production when compared to other feedstocks. This is particularly true for the trap grease with high FOG concentrations, low FFA concentrations, and a high performance anaerobic digestor (AD). As compared to other feedstocks, the probabilities that energy consumption of trap-grease biodiesel production life cycle would be lower were 46% (vs oil crops), 65% (vs waste cooking oil and animal fats) and 88% (vs algae). The probabilities were 89%, 67%, and 93%, respectively, when GHG emissions were compared. Of all the cases that energy consumption of trap-grease biodiesel was lower, the average reductions were 24% (vs oil crops), 36% (vs waste cooking oil and animal fats) and 73% (vs algae). When GHG emissions were compared, the average reductions were 76%, 54%, and 84%, respectively.
Both sewer and trap grease have FFA levels higher than the acceptable level (15-20%) of the current biodiesel industry. Due to emulsion, the lipid fraction of the sewer grease cannot be directly obtained by heating. Two innovative technologies, glycerolysis and in-situ transesterification, were tested to make biodiesel from these FOGs. The goal is to short circuit the solvent extraction process, which is impractical for the biodiesel industry. For trap grease, the results of glycerolysis showed that crude glycerin was effective in reducing the FFA% to < 1 wt% with an optimum condition of 230 °C for 150 min and 1:1 molar ratio between glycerin and FFA. The study on the time series of the mono-, di-, tri-glycerides (MAG, DAG, TAG), FFA and glycerin was conducted to better understand the reaction mechanisms, and the FFA reduction kinetics were estimated (as it fits the first order approximation). The advantages and disadvantages of this process were compared against the two-step process, an industry standard among biodiesel producers. For sewer grease, a direct transesterification process (in-situ conversion) was developed to extract the lipid and make biodiesel in one step. The optimum condition was determined as 20% (of dry sewer grease) H₂SO₄, 65 °C and 7hr, under which a 85.43% extraction rate (biodiesel+unreacted FOG vs. total FOG) and a 76% FOG-to-biodiesel conversion rate (biodiesel vs. total FOG) were achieved.
Acknowledgement

Sincere gratitude is extended to my adviser, Dr. Mingming Lu, for her guidance throughout my entire period of graduate study. Thanks are given to the other committee members, Dr. Tim Keener, Dr. Ting Lu, Dr. Drew C. McAvoy, and Dr. Raymond Smith, for their advice and suggestions for this dissertation.

Special thanks are given to Dr. Ming Chai (Greenleaf Biofuels) and Dr. Gerhard Knothe (Bio-oils unit, USDA-ARS) for their suggestions and help with the analytical work. I would also like to say thank you to my colleagues, Yang Liu, Tongyan Li, Thiansathit Worrarat, and Junsong Zhang for their help during my graduate study.

Many thanks also go to the US EPA People, Prosperity and the Planet (P3) Phase I (SU836038) and Phase II grant (SU835291) for providing financial support for part of the study.

Last but not least, I would like to thank my wife, Lijuan Sang, my parents, and the rest of my family for their love and support in helping me to accomplish the degree.
Disclaimer

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the research described herein. It has been subjected to the Agency administrative review and has been approved for external publication. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.
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Chapter 1. Overview of the Dissertation

1.1 Introduction

Fats, oils and greases (FOGs) in the sewer system come from the discharge of FOG-containing wastewater from sinks, drains or grease traps. The FOGs attach to the inner surface of the sewer pipelines after cooling and solidifying in the sewer system (Williams et al., 2012). The presence of FOGs in the sewer system is the major cause of pipeline blockage, leading to severe overflow problems in the US (He et al., 2011). In addition, the FOGs in the sewer system can also cause erosion of the sewer pipeline. The biological activities of anaerobic bacteria that are fed on FOGs lead to the formation of \( \text{H}_2\text{S} \) gas. The \( \text{H}_2\text{S} \) gas, once dissolved in water, forms \( \text{H}_2\text{SO}_4 \) which causes the erosion of the metal pipes (US EPA, 1992). Restaurants and food processing facilities are the major generators of FOGs and are required by law to have their grease trap pumped by grease haulers on a regular basis in order to prevent clogging of the sewer system. The FOG-containing waste pumped out of the grease trap is therefore referred to as “trap grease”. After collection, the haulers send the trap grease to a wastewater treatment plant (WWTP) for dewatering after which the FOGs and remaining solid are sent to a landfill. Although grease trap maintenance is regulated, some of the FOG-containing water still escapes the grease trap, flows into the sewer system and eventually converges into the WWTPs. The floating substances containing FOGs are collected from the skimmer of the primary clarification tank, dried and usually sent to landfill. To be distinguished from trap grease, this type of FOG-containing waste is defined as “sewer grease” in this dissertation. As compared with trap grease, sewer grease is contaminated with a significant amount of solids and scum, making it difficult to separate FOG by using the conventional “heating & filtration” process. Handling trap grease and sewer grease
causes issues (e.g. waste storage, odor) and increases the operation cost for the WWTPs. Therefore, efforts have been taken to utilize these FOG-containing wastes for beneficial purposes, and biodiesel production has been one of the major applications (Ragauskas et al., 2013).

Biodiesel is a renewable fuel that can be a direct replacement of diesel fuel in both on-road and non-road diesel engines. The US biodiesel industry is in a mature status and every year several hundred million gallons of biodiesel are produced. This significant amount of biodiesel production relies heavily on soybean oil as the feedstock. However, there have been several concerns about using soybean oil for biodiesel production. Firstly the high price of soybean oil raises the production cost of biodiesel, making it less competitive in the fuel market. Next, the growth of soybean requires a large quantity of resource input, such as irrigation water, fertilizers, land use, etc. All these resource uses bring about the concern of the sustainability of biodiesel as a renewable fuel. As a result, biodiesel producers are seeking cheap and sustainable feedstocks, including waste cooking oil, animal fat and trap grease.

1.2 Goal Statement

As a newly emerging idea, research is needed to ensure diverting FOGs from trap/sewer grease for biodiesel production is technically proven and environmentally sound. Accordingly, this dissertation covers two general topics: (1) assessing existing FOG-to-biodiesel technologies and operations from a life cycle perspective, and (2) technology development to improve the FOG extraction and biodiesel conversion efficiency specific to trap/sewer grease as a feedstock.
The first research topic aims to evaluate the life cycle energy consumption and greenhouse gas (GHG) emission from the trap grease-to-biodiesel production at a wastewater treatment plant (Chapter 2). The goal of this topic is to benchmark the energy consumption and GHG emissions of the trap grease-to-biodiesel production life cycle with currently available data sources and to compare the results with those of biodiesel made from other feedstocks. The life cycle model is constructed in Python, and Monte Carlo simulation is applied to investigate the uncertainty of the data sources and to evaluate its impact on the results of the study. The study is based on the most commonly used technologies and practices in the industry. The scope of the study is “cradle-to-gate” and the system boundary includes raw trap grease acquisition, FOG extraction and pretreatment, biodiesel production, and waste disposal. The potential energy saving opportunities at the WWTP, such as energy co-generation by an anaerobic digester (AD), exhaust heat utilization, etc., are incorporated as alternative scenarios.

The second research topic involves developing technologies to accommodate both trap grease and sewer grease for biodiesel production. Chapter 3 presents the study on applying a glycerolysis process as a pretreatment technology to reduce the FFA concentration in the FOG derived from trap grease. A three-phase research approach is taken with the focus on: 1) characterization of trap grease and determining the factors of interest for improving the glycerolysis process; 2) determination of the effectiveness of catalyst for improving the glycerolysis process; and 3) parametric study to find the desired combination of experimental parameters for the glycerolysis process. An extended topic (Chapter 3.6) stemmed from this research subject is to create conceptual models for comparing the sustainability (e.g. energy consumption, hazardous waste disposal, economics) between the glycerolysis process and the 2-
step acid-catalyzed esterification process (most widely used FFA pretreatment technology in current biodiesel industry). Chapter 4 presents the study on applying the *in-situ* conversion process to directly convert FOG in the sewer grease into biodiesel. The *in-situ* conversion avoids the FOG extraction step for the sewer grease, which is crucial to improving the feasibility of utilizing sewer grease as a biodiesel feedstock. Chapter 5 serves as an overall summary of the findings from this dissertation and provides recommendations for future work in the field of FOG-to-biodiesel research.
1.3 References


Chapter 2. Evaluation of Life Cycle Energy Consumption and Greenhouse Gas (GHG) Emissions for Biodiesel Production from Trap Grease

2.1 Introduction

In recent years, efforts have been focused on the reuse of trap grease in order to reduce the burden on landfills. One way is to separate the FOG from the trap grease and use it as the industrial lubricant or “bio-crude” to prime and clean boilers (Ward, 2012). Another option is to feed the trap grease to an anaerobic digester (AD) for co-digestion with other organic wastes. The FOG in the trap grease are digested by the microorganisms, generating biogas which can then be used to produce electricity and heat. However, it is found that the FFA concentration of the FOG in the trap grease can inhibit the microbial process in the AD. Therefore, the addition of trap grease needs to be carefully controlled (Luostarinen et al., 2009; Pereira et al, 2005; Wang et al., 2013). Also, it is reported that biogas generation is a less efficient way of utilizing the energy content of the FOG when compared with biodiesel production (Chakrabarti et al., 2008; Turner et al., 2011). Another option is to use trap grease as a feedstock for biodiesel production. Biodiesel is a mixture of fatty acid methyl esters (FAME) made from oil sources, such as soybean oil, canola oil and waste cooking oil (Chai et al., 2014). Compared with using petroleum-based diesel, the air pollutant emissions (e.g. CO, PM, SO\textsubscript{2}) from the combustion of biodiesel are significantly lower (EIA, 2004). Currently, the primary biodiesel feedstock in the US is soybean oil which can account for up to 80% of the total production cost (Haas, 2010). As it is considered a waste, the cost of obtaining trap grease is expected to be much lower than that of soybean oil, which makes trap grease a lower cost option for biodiesel producers. Wiltsee (1998) estimated that over 400 million gallons of biodiesel could be produced from trap grease every year in the US. Also, using trap grease instead of dedicated oil crops avoids resource
consumption (e.g. irrigation, land use) that otherwise would have occurred during feedstock growth. In addition, separating FOG from trap grease for biodiesel production instead of sending the entire mixture to an AD may help maintain a stable AD performance (López et al., 2014).

Characterization of life cycle energy consumption and GHG emission has been performed for biodiesel production from a variety of feedstocks (Table 2.1&2.2), including soybean oil (Luque et al., 2010; Pradhan et al., 2011; Sheehan et al., 1998), palm oil (Cho et al., 2013; Luque et al., 2010), waste cooking oil and animal fats (Dufour and Iribarren, 2012; López et al., 2010; Talens Peiró et al., 2010) and algae (Azadi et al., 2014; Frank et al., 2012; Sander and Murphy, 2010; Shirvani et al., 2011; Sills et al. 2012; Stephenson et al., 2010). These studies provide insights for understanding and comparing the life cycle energy use and GHG emissions of biodiesel production from different feedstocks. However, such a study has not yet been conducted for a trap grease-to-biodiesel process. There are multiple occasions where the energy and material consumption of the trap grease-to-biodiesel process may be significantly different from that of biodiesel made from other feedstocks. For example, a three-phase separation process is typically applied to separate FOG, water and solids in trap grease (Turner et al., 2011). In this process, energy consumption for pumping and heating is involved. In addition, the FFA concentration is usually very high (e.g. over 90% by weight) in the FOG derived from trap grease (Chakarabarti et al., 2008; Ngo et al., 2011). FFA is detrimental to the biodiesel production process because it reacts with the alkaline catalyst in the process, generating soap and reducing the yield of the biodiesel. The esterification reaction catalyzed by \( \text{H}_2\text{SO}_4 \) is typically used to convert FFA into esters in order to reduce the FFA concentration in the feedstock oil (Chai et al., 2014). Therefore, in the case of the FOG derived from trap grease, a rigorous esterification step which involves
energy-intensive processes such as methanol recovery is needed before it can be used for biodiesel production. Accordingly, the life cycle GHG emissions associated with energy and material consumption are also expected to be different from that of other feedstock-to-biodiesel processes in the existing studies. Therefore, understanding the energy consumption and GHG emissions involved in the trap grease biodiesel production life cycle is an indispensable step toward evaluating the cost-effectiveness and sustainability of this practice.

In addition, existing life cycle studies typically report the life cycle analysis result in a single value. However, it is rational to expect that uncertainties exist in the assumptions, data sources, and unit processes for the studies, which may render a single value not sufficiently representative of all possible circumstances. The influence of these uncertainties on the results should be addressed. Therefore, it has been recommended that the result from life cycle studies be reported as a range of values instead of a single value when variations and uncertainties are involved (Sills et al., 2012).

2.2 Goal and Scope Definition

The goal of the current study is to analyze the life cycle energy consumption and GHG emissions for biodiesel production from trap grease on a “cradle-to-gate” scope and to present the results in ranges by using Monte Carlo simulation. The concept of life cycle energy was applied to account for both the direct energy consumption (e.g. the embedded energies of electricity and natural gas) and indirect energy consumption (e.g. the energy consumption associated with the production of materials). The current study also evaluated the impact on life cycle energy consumption and GHG emissions from utilizing solids separated from the raw trap grease for energy co-generation.
via anaerobic digestion. The system boundary of the study is shown in Figure 2.1. The biodiesel production facility was assumed to be co-located within a wastewater treatment plant (WWTP), as suggested by most existing feasibility studies (Chakrabarti et al., 2008; Turner et al., 2011).

It is noteworthy that although raw trap grease is included in the system boundary, its impact on energy consumption and GHG emission is not included in the calculation, because the trap grease is not considered to be “intentionally generated for fuel production”. The same assumption has been applied in existing life cycle studies of waste-derived biodiesels (Dufour and Iribarren, 2012; López et al., 2010; Talens Peiró et al., 2010). So, there are five common stages in the life cycle: (1) raw trap grease transportation, (2) FOG separation, (3) FOG pretreatment (acid esterification), (4) biodiesel production (alkaline transesterification) and (5) transportation of waste solids to a landfill. One additional stage was included in the life cycle if the solids were utilized for anaerobic digestion. In this study, biodiesel production life cycle starts with raw trap grease acquisition, where grease haulers collect raw trap grease from restaurants and transport it to the WWTP (raw trap grease transportation stage). Upon arrival at the WWTP, raw trap grease undergoes a process to separate FOG, solids and water through a three-phase separation technology (FOG separation stage). The FOG portion is sent to a treatment process for further refining (FOG pretreatment stage), while the solids are sent to an anaerobic digester for biogas generation (AD stage) or directly to a landfill in the alternative scenario (transportation of waste solids stage). The separated water portion is discharged for wastewater treatment and solid waste from the anaerobic digester is sent to a landfill. After refining, the FOG is converted into biodiesel in the biodiesel production process (biodiesel production stage). This life cycle model was constructed using Python 2.7 programming
language (www.python.org), and a Monte Carlo simulation was performed to account for the uncertainties within the variables used in the current study (e.g. the variation of FOG concentration in raw trap grease) and to report the life cycle energy consumption and GHG emissions with a range of values. A sensitivity analysis was also conducted to identify the most important variables that contribute to life cycle energy consumption and GHG emissions in biodiesel production from trap grease.

2.3 Functional Unit and Assumptions

The functional unit for this study is one gallon of biodiesel from trap grease (1gal). Accordingly, the results of life cycle energy consumption and GHG emissions were normalized to the functional unit, as “MJ/gal” or “g CO2 eq/gal”. It was assumed that differences in the energy content of biodiesel made from different feedstocks (e.g. trap grease, soy oil) were negligible. The energy consumption and GHG emissions associated with capital investments, such as the construction and manufacturing of facilities, instruments and vehicles, were excluded from the scope of this study.

2.4 Methodology

2.4.1 Data sources

The data sources for each stage of the trap grease-to biodiesel life cycle are summarized as follows: transportation distances and fuel consumption for transferring raw trap grease from restaurants to the wastewater treatment plant were estimated based on information collected from the grease haulers registered with the Metropolitan Sewer District of Greater Cincinnati (MSDGC). The distance between the wastewater treatment plant and the landfill site was estimated based on the literature search (Sills et al., 2012). For the FOG separation stage, a
comprehensive data collection was performed in order to characterize the composition of raw trap grease, i.e., the percentages of FOG, water and solids. A survey was conducted among professionals in wastewater treatment, biodiesel production, trap grease hauling, fundamental research, federal regulation, and non-governmental organizations (NGOs). In addition to the survey, a comprehensive literature review of existing peer-reviewed journal articles, technical reports, presentations and online resources was performed to enrich the data pool of the raw trap grease composition (Table S2.12 in the supporting information). Likewise, the data of initial FFA concentration in the FOG and the dose of chemicals for FOG treatment (acid esterification) were obtained from a literature review as well as personal communications with industrial experts (Table S2.13 & S2.14 in the supporting information). For the biodiesel production (alkaline transesterification) and anaerobic digestion stages, process input data, i.e., material and energy inputs, was retrieved from the peer-reviewed journal articles.

2.4.2 Unit processes

Transportation

Transportation of materials between individual stages of the biodiesel life cycle is sometimes excluded from the study due to uncertainties involved in the data (King and Weber 2008). For the studies that account for transportation, two methods are typically applied to estimate the distance traveled between stages. One is to estimate the average distance from several case studies. For example, Sheehan et al. (1998) estimated the transportation of soybean oil from crushing facility to a biodiesel production plant by averaging the distances traveled between the two facilities from the data of 14 urban areas. The other way is to apply a ballpark estimation value, the selection of which is usually based on the economic concerns. For instance, a 50 mile
radius for feedstock acquisition was selected for a small biodiesel plant in the feasibility report for biodiesel production in Mississippi (Dagher et al., 2004). In this study, the transportation of collected raw trap grease from restaurants to hauler’s facilities, transferring raw trap grease from hauler’s facilities to the waste water treatment plant and sending solid waste from primary setting to a landfill are the three major transportation activities of concern. For the transportation activity between a restaurant and a grease hauler’s holding facility, the average travel distance of 75 miles was estimated based on the survey results from haulers registered with MSDGC. The distance traveled from the hauler’s holding facility to the wastewater treatment was estimated by averaging the distance between the holding facility of the individual grease hauling company and the MSDGC. Accordingly, the average distance between grease haulers and the MSDGC was estimate to be 23.7 miles and hence for one truck load of raw trap grease that travels from a hauler’s facility to MSDGC, the round trip distance was 47.4 miles. The distance between the wastewater treatment plant and the landfill where solid waste is sent was estimated to be 50 miles for this study. The trucks used by haulers and the MSDGC to transport raw trap grease and solid waste were assumed to be the same: a diesel truck of 3,600 gallons/load and an average mpg of 6.5 miles per gallon.

*Trap Grease Pretreatment (FOG Separation)*

A common method to separate FOG from raw trap grease is to apply moderate heating and gravity settling (Chakrabarti et al., 2008; Turner et al., 2011). A flow chart of the FOG separation process used in this study is provided in Figure 2.2. This process is a replica of a commercial process designed for Eastern Municipal Water District to convert the trap grease into biodiesel (van Keppel, 2011). The process does not involve energy-intensive equipment, such as centrifuge and distillation. Additionally, this process is assumed to be applicable to the entire
data pool of the crude trap grease compositions. The crude trap grease is dumped in the receiving tank where part of the solids is settled and removed (Flow #11) to the solids disposal tank. Next, the bulk part of the trap grease is pumped (Flow #1) to the screening tank where the majority of the remaining solids are removed and transferred (Flow #10) to the solids disposal tank. The trap grease continues to flow into (Flow #2) the serial gravity settling tank (Tank #1-3), in which the remaining solids, water and FOG are separated. The solids part is transferred to the solids disposal tank (Flow #9) and bulk “white water” (water with minimal amount of FOG and solids) is pumped into the White Water Disposal Tank #1 (Flow #4). The “FOG-concentrate” flow (Flow #3) is then heated to raise the temperature of the flow from room temperature (68 °F) to a temperature near the boiling point of water (210 °F). The heated flow continues to be transferred to Tank #4 for further separation (1st heating step). After this separation, the flow contains mostly FOG with little residual water. This flow is then pumped (Flow #6) to the flash evaporator (Evaporator) for final removal of water and the resulting FOG flow (Flow #8) is transferred to the Grease Storage Tank (2nd heating step). In the evaporator, the flow is completely dewatered by heating it to the boiling point of water (212 °F). The evaporated water is condensed and transferred to the White Water Disposal Tank #2 (Flow #7). Water removal is of key importance to the separation of FOG from the trap grease mixture and hence, energy input applied for water removal in this unit process is expected to be the predominant source of energy consumption.

*FOG Treatment (Acid Esterification)*

FOG is collected and sent to the esterification unit for further treatment after the separation process. The function of esterification is to convert FFA in the FOG into esters. A demonstration
of the esterification process adopted in this study is shown in Figure 2.3. The purpose of converting FFA into esters is to avoid the reaction between FFA and alkaline catalyst in the transesterification process, which may lead to the formation of soap and a reduction in the yield of biodiesel. The concentration of FFA in FOG varies among FOG samples, as indicated from the collected data. The high FFA concentrations could be a result of hydrolysis of FOG in the aqueous environment (e.g. grease trap). During the esterification reaction, FFA reacts with methanol with H2SO4 as the catalyst at atmospheric pressure and a temperature close to 65 °C. The dosage of methanol and catalyst are related to the concentration of FFA in the FOG and therefore they vary from case to case. After the reaction is complete, NaOH is added to neutralize the catalyst before the treated FOG is sent to the next stage. Depending on the quality of the FOG, the esterification process may be conducted twice to ensure that FFA is reduced to an acceptable level (Canakci and Van Gerpen, 2001). After the esterification stage, a 100% conversion of FFA into esters is assumed for this study.

Biodiesel Production (Alkaline Transesterification)

After the esterification process, the mixture of esters and FOG is sent to transesterification unit for the final production of biodiesel. The unit proposed in this study is composed of two sequential transesterification reactors, each having a conversion efficiency of 90%. The proposed transesterification process for this study is shown in Figure 2.4. During the transesterification process, the FOG is converted into esters by being reacted with methanol under the catalysis of NaOCH3. It is assumed that after esterification process, the resulting FOG can be treated by the same operational conditions as those for soybean oil from the literature. The composition of the ester and FOG mixture is determined from the preceeding esterification process. Similar to
esterification stage, excessive methanol is used and needs to be recovered to reduce the cost of
the process. Also included in the transesterification stage is the purification of crude biodiesel
and glycerin. After separation, the crude biodiesel and glycerin are separated and weakly acidic
water is added to remove the impurities from crude biodiesel in the washing tank.

*Anaerobic Digestion*

The solids separated from the raw trap grease pretreatment step can be feed to an anaerobic
digester for biogas generation, which can be captured and utilized for electricity and heat. The
performance of a digester is measured based on the destruction of the volatile solids (VS) in the
feed. The operational conditions of the anaerobic digester proposed in this study are cited from
Sills et al. (2012): a completely mixed reactor operated at 35 °C with a hydraulic retention time
(HRT) of 15 days. After the digestion process, biogas is sent to a scrubbing unit to remove H₂S
before combustion in a combined heat and power generation unit (CHP). The destruction rate of
VS for a 15-day digestion time was assumed to be 56% (Tchobanoglous et al., 2003). The
remaining solids from the digester is collected and sent to landfill.

2.4.3 Randomization and Monte Carlo simulation

Monte Carlo simulation is an approach to evaluate the influence that arises from the uncertainty
within a specific variable/set of variables on the outcome of the model. The core of a Monte
Carlo simulation is to create a mechanism to conduct random sampling (randomization) for the
variables of interest repetitively for a given number of times. An illustration of randomization
and Monte Carlo simulation is shown in Figure 2.5. The prerequisite for creating a
randomization algorithm is to define the cumulative density function (cdf) for the variable of
interest. The cdf of a variable (\(V\)) describes the probability for it to have a value equal to or less
than a specific value $x$. An example of the cdf of a variable is shown in Figure S2.9 in the supporting information this chapter (SAS, 2010). The variable of interest in the example is the “breaking strength (psi)” at which the “cord” will break. The x-axis is the range of possible values for the variable, and the y-axis shows the corresponding possibilities (%). It is indicated from Figure S2.9 that there is a possibility of approximately 48% that the “breaking strength” will be 7 psi or less. Once the cdf is defined for the variables, the next step in a randomization process is to generate a random number between 0 and 1 from a uniform distribution. The generated value is used as the y-axis value (possibility) for the cdf, and then the corresponding x-axis value (the value for the variable) can be determined by solving the equation of the specific cdf. A Monte Carlo simulation simply executes the randomization process for a specified number of times. During the Monte Carlo simulation, the outcome of each model run is stored and a range of the outcomes from the model are used instead of a single value. For this study, the variables of interest for Monte Carlo simulation and their cdfs are summarized in Table S2.15 in the supporting information of this chapter.

2.5 Results

2.5.1 Baseline case (sample calculation)

A sample calculation (or nominal case) was performed to demonstrate the procedure of quantifying the life cycle energy consumption and GHG emission for producing biodiesel from trap grease. The mass of the raw trap grease was assumed to be 100,000 lbs. The data for raw trap grease composition and FFA concentration in the FOG was cited from an industry professional (van Keppel, 2011) and the operational conditions of the AD were cited from Sills et al. (2012). The parameter values are summarized in Table 2.3. When more than one product
was generated at the end of a stage, allocation of energy consumption and GHG emissions were performed based on the mass portion of the co-products obtained at the end of the stage, as indicated from many existing LCA studies (Dufour and Iribarren, 2012; López et al., 2010; Pradhan et al., 2011; Talens Peiró et al., 2010). The detailed procedure for the sample calculation can be found in Appendix S1 to S6 in the supporting information.

2.5.1.1 Life cycle energy consumption

The esterification stage consumed 36.18 MJ of energy per gallon biodiesel produced, which was mainly due to natural gas consumption for recovery of excessive methanol during the two consecutive esterification steps. Transesterification, on the other hand, accounted for 4.62 MJ/gal, which was approximately 13% of the consumption by esterification. Also, transportation consumed a large amount of energy because of the low fuel economy of the truck (6.5 mpg) and long travel distances. Energy input for the transportation stage differed based on whether AD was included in the calculation. Energy consumption was 33.25 MJ/gal for the scenario w/AD and 33.79 MJ/gal for the scenario w/o AD, which was due to the difference in the amount of solids landfilled at the end of the life cycle. Energy consumption involved in the FOG separation stage was 12.70 MJ/gal, since no energy-intensive equipment was used in the stage. It is noteworthy that although the energy input for operating the AD was high (46.31 MJ/gal), the energy output was considerable (67.80 MJ/gal, 22.37 MJ in the form of electricity and 45.43 MJ in the form of heating by natural gas). It is noteworthy that the avoided life cycle energy consumption associated with using the energy output from AD was 101.68 MJ/gal, instead of the “apparent” energy output of 67.80 MJ/gal. This is due to the fact that to quantify the effect of displacing electricity and natural gas inputs, the life cycle energy, not the embedded energy, of
these utilities should be used in the calculation. As a result, the life cycle energy consumption for the sample calculation was 31.39 MJ/gal for AD-included (w/ AD) and 87.29 MJ/gal for AD-excluded (w/o AD) scenarios. It is evident that incorporating an AD into the biodiesel production process has the potential to significantly reduce the energy consumption for biodiesel production from trap grease. Figure S2.5 in the supporting information shows energy inputs (consumption) and outputs of the sample calculation. Figure S2.6 in the supporting information categorizes the life cycle energy consumption by utility and materials uses. It is obvious that by using the energy generated from AD, the consumption of electricity could be completely avoided and the use of natural gas could be reduced by 51.82%. This again indicates the necessity to integrate an AD into the trap grease biodiesel production system. Energy consumption associated with the use of chemicals was the same for both scenarios and the fuel consumption was slightly lower in the scenario w/AD because fewer solids were sent to the landfill.

2.5.1.2 Life cycle GHG emission

Similar to the life cycle energy consumption analysis, esterification (2,179.03 g CO$_2$ eq/gal) and transportation (2,410.11 g CO$_2$ eq/gal when AD is included in the system) were the two major contributors to the total GHG emission, followed by FOG separation (873.35 g CO$_2$ eq/gal) and transesterification (234.06 g CO$_2$ eq/gal). It is shown that utilizing solids for anaerobic digestion can significantly reduce GHG emissions, which eventually rendered the life cycle GHG emission negative (-55.49 g CO$_2$ eq/gal). This is due to the fact that the excess electricity from the biodiesel production life cycle was assumed to replace the electricity generated from Ohio grid, which is primarily powered by coal (Tu et al., 2015). In comparison, when solids were treated as waste and sent to a landfill, the GHG emissions were 5,735.22 g CO$_2$ eq/gal.
2.5.2 Monte Carlo simulation

2.5.2.1 Life cycle energy consumption

The input variables with distributions for the Monte Carlo simulation were: FOG concentration in raw trap grease (wt%), FFA concentration in separated FOG (wt%), VS concentration in solids (wt%), electricity for mixing in AD (kWh/kg VS), heating energy consumption for AD (MJ/kg VS), CH₄ generation rate (L/g VS), and CHP electric efficiency (%). The distributions of each variable are summarized in Table S2.15 in the supporting information. The Monte Carlo simulation were performed with 100,000 runs, and the results are shown in Figure 3&4. It is shown that the potential biodiesel production ranged from approximately 14 to 4,400 gallons. As is expected, the distribution of the volumes of biodiesel was consistent with the distribution of FOG concentration in raw trap grease. The extremely low volume (e.g. 14 gallons) represents the situation where the concentration of FOG in the raw trap grease was extremely low (e.g. lower than 1%). The empirical cumulative density of the life cycle energy consumption when AD was included in calculation is provided in Figure 2.6(a). The range was approximately between 20 and 760 MJ/gal. The high values (e.g. 760 MJ/gal) occur when the volume of biodiesel produced was close to the lower end of the range (e.g. 14 gallons). This result indicates that the probability that the life cycle energy consumption would be less or equal to 100 MJ/gal was around 80%. Figure 2.6(b) shows the result when AD was excluded. The range was approximately between 40 and 1,700 MJ/gal and the probability that the life cycle energy consumption would be equal or less than 100 MJ/gal was approximately 60%. In addition, the results were compared in pair for each of the 100,000 runs to see if there would be a situation where life cycle energy consumption would be lower when solids were treated as waste instead being utilized for anaerobic digestion.
It was observed that the energy consumption for making one gallon of biodiesel from trap grease was almost always lower when AD was included in the production life cycle (>99.9% of the simulation results). However, it is interesting that there would be some outliers when the avoided life cycle energy consumption associated with the energy output from AD was less than the energy consumption to operate the AD (<0.01% of the simulation results). This represents the situation where the AD is poorly operated (e.g. the CH$_4$ generation rate is low).

2.5.2.2 Life cycle GHG emission

The empirical cumulative density of the life cycle GHG emission for the trap grease-to-biodiesel process is provided in Figure 2.7. When AD was included in the system (Figure 2.7a), the result ranged approximately from -2,700 to 25,000 g CO$_2$ eq/gal. The negative values of the GHG emission indicate that in certain circumstances the GHG reduction from the energy credit generated through the AD could outweigh the GHG emission associated with energy and materials consumption. In comparison, when AD was excluded from the system boundary, the range was from approximately 2,400 to 121,000 g CO$_2$ eq/gal. Similar to the life cycle energy consumption analysis, the extremely high values of GHG emission were due to the very low volume of biodiesel produced. Also, the life cycle GHG emission was almost always lower when AD was included in the system boundary (>99.9% of the simulation results). As indicated from Figure 2.13(a), the probability was over 90% that the life cycle GHG emission for the trap grease biodiesel production would be less than or equal to 10,000 g CO$_2$ eq/gal. On the other hand, the probability decreased to about 70% when AD was excluded from the system boundary (Figure 2.7b). This again indicates the necessity to utilize the solids for AD.
2.5.3 Sensitivity analysis

2.5.3.1 Life cycle energy consumption

A sensitivity analysis was performed to evaluate the impact on life cycle energy consumption caused by the uncertainty within individual variables. To conduct the sensitivity analysis, 100,000 runs of Monte Carlo simulation were executed for a single variable (e.g. FOG concentration in raw trap grease) while holding the other variables constant. The results of the sensitivity analysis are presented in the form of box-whisker plots. The lower and upper “whiskers” indicate the data points at the 5th and 95th percentiles of the entire data set, respectively. Similarly, the lower, middle, and the upper lines of the “box” indicate the 25th, 50th and 75th percentiles of the entire data set, respectively. The result of the sensitivity analysis for life cycle energy consumption is shown in Figure 2.8. For the scenario w/ AD (Figure 2.8a), the uncertainty within the FOG concentration had a higher impact than any other variable, because it directly affects the volume of biodiesel that could be generated. This indicates the importance of the quality of the raw trap grease. The CH\textsubscript{4} generation rate had the second largest influence on the life cycle energy consumption due to the fact that it had the most impact on the energy generation from the AD. FFA concentration (%) had the third largest impact on the life cycle energy consumption because it directly affected the methanol input and accordingly the energy consumption for recovering the methanol during the esterification stage. On the other hand, VS concentration, electricity consumption for mixing in the AD, heating energy for AD and electricity generation efficiency of the CHP had minimal influence on the life cycle energy consumption. For the scenario w/o AD, FOG and FFA concentrations were the only two variables that would affect the life cycle energy consumption (Figure 2.8b). Likewise, the
uncertainty caused by the variation in FOG concentration was more than one order of magnitude higher than that of FFA concentration.

### 2.5.3.2 Life cycle GHG emission

The results of the sensitivity analysis for life cycle GHG emission are provided in Figure 2.9. When the AD was included in the system boundary (Figure 2.9a), it was found that the FOG concentration was no longer the most dominant variable that impacts the sensitivity of the result. Instead, CH₄ generation rate had the highest impact. This indicates the importance of maintaining high AD performance. The impact of the FFA concentration ranked second, mainly due to the large range of variation in energy and material consumption associated with the change in FFA concentration. Changes in the life cycle GHG emission caused by the variation in FOG concentration and electricity generation efficiency of the CHP were close to each other, followed by the variation in VS concentration. The two operational variables, electricity consumption for mixing and heating energy for the AD had the lowest impact on the sensitivity of GHG emissions. This result was similar to the sensitivity analysis for life cycle energy consumption when AD was excluded from the system boundary of the study (Figure 2.9b). Also, no negative value of GHG emission was observed when solids were treated as waste.

### 2.6 Discussion

#### 2.6.1 Comparison with existing studies

#### 2.6.1.1 Life cycle energy consumption

Studies on the life cycle assessment (LCA) of biodiesel production have been conducted for a variety of other feedstocks. The values for energy consumption from the literature are summarized in Table 2.1. The values are shown in their original units and also converted into the
normalized units of the current study for comparison. Details for the conversion can be found in Appendix S-8 in the supporting information of this chapter.

Overall, the system boundaries vary among existing studies, which makes it difficult to compare each study directly. Generally, the system boundary of the existing studies starts with the feedstock collection for the biodiesel production from waste-derived feedstock, i.e. waste cooking oil, animal fats and sewage sludge. Rendering as a feedstock pretreatment stage is included in the system boundary by some authors (Dufour and Iribarren 2012; López et al., 2010). On the other hand, biodiesel production from oil crops and algae include crop growth and algae cultivation before the collection/harvesting stage. Oil extraction is typically a necessary stage before transesterification though it is usually not included as part of the system boundary when waste-derived feedstock is used. The last step included in the system boundary for the existing studies is either biodiesel production stage (tranesterification) or biodiesel use stage (combustion in diesel engine). In addition, allocation methods are not consistent among the existing studies. While most of the studies applied mass-based allocation (Dufour and Iribarren, 2012; López et al., 2010; Pradhan et al., 2011; Talens Peiró et al., 2010), system expansion and displacement (Sander and Murphy, 2010; Shirvani et al., 2011) or a hybrid method was also used (Frank et al., 2012; Stephenson et al., 2010). In order to compare results of the current study with those reported in the literature, the system boundary of the existing studies were altered whenever possible and the values of energy consumption were adjusted and converted into the normalized unit of current study. As is shown in Table 2.1, the values vary significantly from case to case due to the differences in model scopes, allocation methods, data sources, and assumptions. Similar to the findings from this study, the existing studies indicate that utilizing co-products for energy generation significantly reduces the life cycle energy consumption and
the process can even be “self-sustaining” (negative value of energy consumption) under certain circumstances (Sander and Murphy, 2010). This, again, proves the importance of having energy generation facility on site to utilize the co-products. By grouping the feedstocks into oil crop (soybean, rapeseed, palm and sunflower), waste (waste cooking oil, animal fat and sewage sludge) and algae (open pond), the grouped results from the existing studies range from 13.87 to 46.24, 6.17 to 64.17, and -832.71 to 225.96 MJ/gal, respectively. Results from Monte Carlo simulation were compared with the higher end of the ranges reported in the existing studies. By comparison with other waste feedstocks, the probability that the life cycle energy consumption of the trap grease-to-biodiesel life cycle was less than 64.17 MJ/gal was approximately 65 % when AD was included in the system boundary and was about 39% otherwise. Compared to oil crops, the probability that the life cycle energy consumption of the trap grease-to-biodiesel life cycle was less than 46.24 MJ/gal was approximately 46 % when AD was included in the system boundary and was about 13% otherwise. Compared to algae (with open pond system), the probability that the life cycle energy consumption of the trap grease-to-biodiesel life cycle was less than 225.96 MJ/gal was approximately 88 % when AD was included in the system boundary and was about 79% otherwise. Compared to petroleum diesel, the probability that the life cycle energy consumption of the trap grease-to-biodiesel life cycle was less than 162.08 MJ/gal was approximately 85% when AD was included in the system boundary and was about 74% otherwise. As compared with the biodiesels produced from waste oil and grease, oil crops and algae, the average reductions in life cycle energy consumption (w/ AD) for trap grease biodiesel are 36%, 24%, and 73%, respectively.
2.6.1.2 Life cycle GHG emission

The results of the life cycle GHG emissions from the existing literature were converted into “g CO\textsubscript{2} eq/gal” and are summarized in Table 2.2. Similar data grouping was performed for the GHG emissions and the ranges were 5812.11 to 8,734.96, 890.78 to 2,786.66, and -2663.47 to 16,589.37 g CO\textsubscript{2} eq/gal for oil crop (soybean, rapeseed, palm and sunflower), waste (waste cooking oil, animal fat and sewage sludge) and algae (open pond), respectively. Likewise, a comparison between the results of the current study and the higher end of the ranges reported by the existing literature was conducted. Compared to other waste feedstocks, the probability that the life cycle GHG emission of the trap grease-to-biodiesel life cycle was less than 2,786.66 g CO\textsubscript{2} eq/gal was approximately 67% when AD was included in the system boundary and was about 11% when AD was not included. Compared to oil crops, the probability that the life cycle GHG emission of the trap grease-to-biodiesel life cycle was less than 8,734.96 g CO\textsubscript{2} eq/gal was approximately 89% when AD was included in the system boundary and was about 68% otherwise. Compared to algae (with open pond system), the probability that the life cycle GHG emission of the trap grease-to-biodiesel life cycle was less than 16,589.37 g CO\textsubscript{2} eq/gal was approximately 93% when AD was included in the system boundary and was about 80% when AD was not included. Finally, compared to petroleum diesel, the probability that the life cycle GHG emission of the trap grease-to-biodiesel life cycle was less than 11,643.86 g CO\textsubscript{2} eq/gal was approximately 91% when AD was included in the system boundary and was about 74% when AD was not included. As compared with the biodiesels produced from waste oil and grease, oil crops and algae, the average reductions in life cycle GHG emission (w/ AD) for trap grease biodiesel are 54%, 76%, and 84%, respectively.
2.6.2 Limitation of the study

The life cycle model developed in this chapter can be further strengthened by expanding the system boundary to include the decomposition of solids in the landfill. The inclusion of this additional stage will enable the exploration of more alternative scenarios for the treatment of solids. The volatile portion of the solids, once decomposed in the landfill, will also form methanol and CO$_2$. The methanol may be treated in different ways (e.g. uncaptured, flared or recovered as biogas), leading to significantly different GHG emission. However, to construct such an additional stage with multiple technical options requires a robust effort for data collection and analysis, and hence is proposed as future work for improving the life cycle model.

2.7 Summary of the chapter

Results from this study indicate that trap grease could provide lower energy consumption and lower GHG emissions for biodiesel production when compared to oil crop and algae feedstocks. This is particularly true for high FOG concentration, low FFA concentration, and high AD performance. This result is an encouraging finding for promoting trap grease-to-biodiesel production. This analysis illustrated both a positive impact and ideal solution for both waste management and biodiesel production. The life cycle model presented in this study could be used by WWTPs to evaluate the prospects of utilizing trap grease for biodiesel production by using site-specific data. This model may also be used to evaluate the trap grease-to-biodiesel fuel pathway against certain GHG-related programs (e.g. Renewable Fuel Standard).
Figure 2.1. System boundary of current study
Figure 2.2. Flowchart for the FOG separation stage (EMWD case study)
Figure 2.3. Flow chart for esterification stage
Figure 2.4. Flowchart for the transesterification stage
Figure 2.5. Randomization and Monte Carlo simulation
Figure 2.6. Empirical cumulative density plot of life cycle energy consumption (a: w/AD; b: w/o AD)
Figure 2.7. Empirical cumulative density plot of life cycle GHG emission (a: w/AD; b: w/o AD)
Figure 2.8. Sensitivity analysis for life cycle energy consumption (a: w/ AD; b: w/o AD)
1-FOG concentration; 2-FFA concentration; 3-VS concentration; 4-electricity consumption for mixing in the AD; 5-heating energy consumption for the AD; 6-CH4 generation rate; 7-electricity generation efficiency of the CHP
Figure 2.9. Sensitivity analysis for life cycle GHG emission (a: w/AD; b: w/o AD)
1-FOG concentration; 2-FFA concentration; 3-VS concentration; 4-electricity consumption for mixing in the AD; 5-heating energy consumption for the AD; 6-CH4 generation rate; 7-electricity generation efficiency of the CHP.
Table 2.1. Values of life cycle energy consumption for biodiesel production from different feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Life cycle energy consumption</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original value</td>
<td>Original unit</td>
</tr>
<tr>
<td>Sunflower</td>
<td>3.2</td>
<td>MJ BioD/MJ non-renewable energy</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Palm fatty acid distillate</td>
<td>3.23</td>
<td>Net energy ratio (NER)</td>
</tr>
<tr>
<td>Soybean</td>
<td>5.60</td>
<td>MJ/L BioD</td>
</tr>
<tr>
<td>WCO</td>
<td>1054.62</td>
<td>MJ/tonne BioD</td>
</tr>
<tr>
<td>WCO</td>
<td>13.80</td>
<td>MJ/kg BioD</td>
</tr>
<tr>
<td>Tallow</td>
<td>16.80</td>
<td></td>
</tr>
<tr>
<td>Poultry fat</td>
<td>19.10</td>
<td></td>
</tr>
<tr>
<td>WCO</td>
<td>4325.56</td>
<td>MJ/tonne BioD</td>
</tr>
<tr>
<td>Tallow</td>
<td>2718.86</td>
<td></td>
</tr>
<tr>
<td>Poultry fat</td>
<td>3171.88</td>
<td></td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>2343.07</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>1.70</td>
<td>Energy balance ratio (EBR)</td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>HG: 0.50</td>
<td>Energy balance ratio (EBR)</td>
</tr>
<tr>
<td></td>
<td>AD: 0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-CHP: 1.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-FT: 1.81</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>-6670.34</td>
<td>MJ/kMJ BioD</td>
</tr>
<tr>
<td></td>
<td>-3768.34</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>548,329</td>
<td>Btu/ MMBtu of BioD</td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>6.50</td>
<td>GJ/ton BioD</td>
</tr>
<tr>
<td>Algae (PBR)</td>
<td>199.50</td>
<td></td>
</tr>
<tr>
<td>Petroleum diesel</td>
<td>1.19</td>
<td>MJ/MJ Diesel</td>
</tr>
</tbody>
</table>

Results were based on mass-based partition between biodiesel (88.5%) and glycerin (11.5%) (López et al., 2010), unless specified in the literature; OP: open pond; PBR: photobioreactor

*Sander and Murthy, 2010: algae biomass was assumed to replace corn for ethanol production, generating significant amount of energy credit by avoiding corn growth; lower energy consumption (-6670.34 MJ/kMJ BioD) by using filter pressing for dewatering

**EBR: the ratio of non-renewable energy consumed to energy from biodiesel; HG=hydrothermal gasification; AD=anaerobic digestion; G-CHP= gasification-power generation; G-FT=gasification-Fischer-Tropsch

***EBR: the ratio of non-renewable energy consumed to energy from biodiesel; HG=hydrothermal gasification; AD=anaerobic digestion; G-CHP= gasification-power generation; G-FT=gasification-Fischer-Tropsch

****NER: ratio between total energy outputs and total energy inputs
Table 2.2. Values of life cycle GHG emission for biodiesel production from different feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Original value</th>
<th>Original unit</th>
<th>g CO₂ eq/gal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>2.6</td>
<td>tonne CO₂ eq/tonne BioD</td>
<td>8,734.96</td>
<td>Luque et al., 2010</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>1.79</td>
<td></td>
<td>6,013.68</td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td>1.73</td>
<td></td>
<td>5,812.11</td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>0.27</td>
<td></td>
<td>907.09</td>
<td></td>
</tr>
<tr>
<td>Palm fatty acid distillate</td>
<td>53.12</td>
<td>g CO₂ eq/MJ BioD</td>
<td>6,631.39</td>
<td>Cho et al., 2013</td>
</tr>
<tr>
<td>WCO</td>
<td>299.60</td>
<td>kg CO₂ eq/tonne BioD</td>
<td>890.78</td>
<td>Talens Peiró et al., 2010</td>
</tr>
<tr>
<td>Tallow</td>
<td>576.02</td>
<td>kg CO₂ eq/tonne BioD</td>
<td>1,734.60</td>
<td>Dufour and Iribarren, 2012</td>
</tr>
<tr>
<td>Poultry fat</td>
<td>829.46</td>
<td></td>
<td>2,786.66</td>
<td></td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>725.07</td>
<td></td>
<td>2,435.95</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>26</td>
<td>g CO₂ eq/MJ BioD</td>
<td>3,245.79</td>
<td>Shirvani et al., 2011</td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>HG: 10</td>
<td></td>
<td>1,248.38</td>
<td>Azadi et al., 2014</td>
</tr>
<tr>
<td></td>
<td>AD: 55</td>
<td></td>
<td>6,866.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-CHP: 78</td>
<td></td>
<td>9,737.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-FT: 93</td>
<td></td>
<td>11,609.93</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>-21.56</td>
<td>kg CO₂ eq/kMJ BioD</td>
<td>-2,691.51</td>
<td>Sander and Murthy, 2010</td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>135.05</td>
<td></td>
<td>16,589.37</td>
<td></td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>-25,441</td>
<td>g CO₂ eq/MBtu of BioD</td>
<td>-2,663.47</td>
<td>Frank et al., 2012</td>
</tr>
<tr>
<td>Algae (OP)</td>
<td>713</td>
<td>kg CO₂ eq/tonne BioD</td>
<td>2,395.39</td>
<td>Stephenson et al., 2010</td>
</tr>
<tr>
<td>Algae (PBR)</td>
<td>11,919</td>
<td></td>
<td>40,043.07</td>
<td></td>
</tr>
<tr>
<td>Petroleum diesel</td>
<td>638.35</td>
<td>g CO₂ eq/bhp-h</td>
<td>11,643.86</td>
<td>Sheehan et al., 1998</td>
</tr>
</tbody>
</table>

*Results were based on mass-based partition between biodiesel (88.5%) and glycerin (11.5%) (López et al., 2010), unless specified in the literature; OP: open pond; PBR: photobioreactor; fuel use stage was excluded during the conversion of the data for all cases.

**Sander and Murthy, 2010: algae biomass was assumed to replace corn for ethanol production, generating significant amount of energy credit by avoiding corn growth; negative GHG emission (-21.56 kg CO₂/kMJ BioD) by using filter pressing for dewatering

***Sheehan et al., 1998: including the tailpipe CO₂ emission

****EBR: the ratio of non-renewable energy consumed to energy from biodiesel; HG=hydrothermal gasification; AD=anaerobic digestion; G-CHP= gasification-power generation; G-FT=gasification-Fischer-Tropsch
Table 2.3. Summary of key parameters for the sample calculation (100,000 lbs raw trap grease)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOG concentration in raw trap grease</td>
<td>4.23 wt%</td>
<td>van Keppel, 2011</td>
</tr>
<tr>
<td>Water concentration in raw trap grease</td>
<td>86.35 wt%</td>
<td></td>
</tr>
<tr>
<td>Solids concentration in raw trap grease</td>
<td>9.42 wt%</td>
<td></td>
</tr>
<tr>
<td>Volatile solid (VC) concentration in solids</td>
<td>94%</td>
<td>Wang et al., 2013</td>
</tr>
<tr>
<td>CH$_4$ generation rate</td>
<td>0.3 L/g VS</td>
<td></td>
</tr>
<tr>
<td>CHP electricity generation efficiency</td>
<td>33%</td>
<td>Sills et al., 2012</td>
</tr>
<tr>
<td>CHP heat generation efficiency</td>
<td>43%</td>
<td></td>
</tr>
</tbody>
</table>
2.8 References


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2.9 Supporting Information for Chapter 2

Appendix S-1: Sample calculation: trap grease pretreatment (FOG separation)

Appendix S-2: Sample calculation: FOG pretreatment stage (acid esterification)

Appendix S-3: Sample calculation: biodiesel production (alkaline transesterification)

Appendix S-4: Sample calculation: anaerobic digestion

Appendix S-5: Sample calculation: transportation

Appendix S-6: Sample calculation: allocation

Appendix S-7: Monte Carlo simulation

Appendix S-8: Unit conversion of energy consumption and GHG emission values for existing studies

Appendix S-9: Explanation of the “TG LC ENER+GHG model”

References
Appendix S-1: Sample calculation: trap grease pretreatment (FOG separation)

The sample calculation below demonstrates how the material consumption, energy consumption and GHG emission were calculated for the trap grease-to-biodiesel life cycle. The total mass of the raw trap grease in this sample calculation was 100,000 lbs. The composition of the raw trap grease was cited from the reference\textsuperscript{51} as 4.23 wt% FOG, 86.35 wt% water and 9.42 wt% of solids. Table S2.1 summarizes the life cycle energy consumption and GHG emission factors for materials and utilities used in this calculation. The capacity of the trap grease-to-biodiesel facility was assumed to be 5 million gallons per year (MGPY) of raw trap grease.

<table>
<thead>
<tr>
<th>Material/utility</th>
<th>Life cycle energy consumption</th>
<th>Reference</th>
<th>Life cycle GHG emission (g CO\textsubscript{2} eq/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>32.95 MJ/kg</td>
<td>[S6,S7]</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>-2.44 MJ/kg</td>
<td>[S8]</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>1.5 MJ/kg</td>
<td></td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>1.7 MJ/kg</td>
<td></td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>42.5 MJ/L</td>
<td>[S6]</td>
<td>3.62</td>
<td>[S3]</td>
</tr>
<tr>
<td>NaOCH\textsubscript{3}</td>
<td>31.7 MJ/kg</td>
<td></td>
<td>2.21</td>
<td>[S4]</td>
</tr>
<tr>
<td>Electricity</td>
<td>7.4 MJ/kWh</td>
<td>[S6,S7]</td>
<td>881.59 g CO\textsubscript{2}-eq/kWh</td>
<td>[S5]</td>
</tr>
<tr>
<td>NG</td>
<td>49.09 MJ/kg</td>
<td></td>
<td>3.37</td>
<td></td>
</tr>
</tbody>
</table>

It is noteworthy that the life cycle energy of H\textsubscript{2}SO\textsubscript{4} is negative. This is due to the fact that sulfuric acid manufacturing is overall an exothermic process.\textsuperscript{59}

As shown in Figure 2.2, the raw trap grease was dumped in the receiving tank where part of the solids was settled and removed (Flow #11) to the solids disposal tank. Next, the bulk part of the trap grease was pumped (Flow #1) to the screening tank where the majority of the remaining solids were removed and transferred (Flow #10) to the solids disposal tank. The trap grease continued to flow into (Flow #2) the serial gravity settling tanks (Tank #1-3), in which the remaining solids, water and FOG were separated. The solids part was transferred to the solids disposal tank (Flow #9) and bulk “white water” (water with minimal amount of FOG and solids)
was pumped into the White Water Disposal Tank #1 (Flow #4). The “FOG-concentrate” flow (Flow #3) was then heated to raise the temperature of the flow from room temperature (68 °F) to a temperature near the boiling point of water (210 °F). The heated flow continued to be transferred to Tank #4 for further separation (1st heating step). After this separation, the flow contained mostly FOG with a little residual water. This flow was then pumped (Flow #6) to the flash evaporator (Evaporator) for final removal of water and the resulting FOG flow (Flow #8) was transferred to the Grease Storage Tank (2nd heating step). In the evaporator, the flow was completely dewatered by heating it to the boiling point of water (212 °F). The evaporated water was condensed and transferred to the White Water Disposal Tank #2 (Flow #7).

The energy consumption in this stage was divided into two categories: thermal energy and electricity energy. The thermal energy was used for the processes such as heating and evaporation of water while electricity energy supported the operation of pumps and electric chiller. The sample calculation was performed as an illustration to reveal the energy consumption of the major consumption equipment: heater, evaporator, air-cooled chiller and pumps. Total Energy Input ($E_T$) was the sum of the energy consumed by the above equipment. The sample calculation was based on the Eastern Municipal Water District (EMWD) case. The composition of the raw trap grease was calculated based on the flow data of the process summarized in Table S2.2 (Flow #1+Flow#11). The change in the mass of the individual component, i.e., FOG, water and solids, after the processing steps (e.g. heating, dewatering) was calculated based on the flow data in Table S2.2 as well.
**Table S2.2.** Flow balance for sample calculation (Flow #s are from Figure 2.2)

<table>
<thead>
<tr>
<th>Flow</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOG</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>0.5</td>
<td>0.5</td>
<td>2.1</td>
<td>0.0</td>
<td>2.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Water</td>
<td>46.8</td>
<td>46.8</td>
<td>9.4</td>
<td>46.3</td>
<td>8.9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Solids</td>
<td>2.6</td>
<td>2.4</td>
<td>0.5</td>
<td>1.8</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.6</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Total</td>
<td>52</td>
<td>51.8</td>
<td>12.5</td>
<td>48.6</td>
<td>9.9</td>
<td>2.6</td>
<td>2.1</td>
<td>0.6</td>
<td>2.1</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* The flows are in gallon
** The density of FOG was estimated to be 7.4 lb/gal; water: 8.34 lb/gal; and solids 13.4 lb/gal<sup>3,10</sup>
*** The standard heat capacity of water: 4.1813 J/(g·K); FOG: 1.67 J/(g·K); latent heat of boiling water under 1 atm: 2,260 J/g

1. Total heat input

Total heat input \( E_H \) summarized the thermal energy consumption for both heating and evaporation. Due to proprietary reason, details about the type or brand of the equipment used were not disclosed so the total heat input was estimated by calculating the theoretical heat input needed for the process and was related to the real-life situation by applying an empirical heat loss factor (150%). The calculation of the \( E_H \) was based on the assumptions below:

(i) Evaporation of water was negligible in Tank #4 due to short contact time in the Heater
(ii) The heat loss along pipes was accounted for by multiplying the result by a factor of 150%
(iii) The evaporation of FOG in the Flash Evaporator was negligible

Heat input in the 1<sup>st</sup> heating step

All the heat input was calculated based on the standard heat capacity (C) of FOG and water.

After gravity separation, the trap grease was heated to 210 °F through the heater and was further separated in the Tank #4. The heat input during this process could be calculated by the following equations:

\[
Q_{H2O} = C_{H2O} \times \Delta T \times m_{H2O} \times conversion \ factor \quad \text{Eq. S1}
\]

Where:

\[
Q_{H2O} = \text{heat input (MJ)}
\]

\[
C_{H2O} = \text{standard heat capacity of water (J/(g·K))}
\]
\[ \Delta T = \text{temperature difference (K)} \]

\[ m_{H2O} = \text{mass of water (lb)} \]

*Conversion Factors* = conversion factors for mass, volume, energy, power, etc.

By using the ratio between Flow#3 and Flow #1 (Table S2.2), the mass of the remaining water was estimated to be around 17,220 lbs after dewatering through Tank#1-3. By plugging in the mass of the remaining water into Eq. S1, the heat input for raising the temperature of water \( Q_{H2O} \) was approximately 2,582.41 MJ. Similarly, applying Eq. S1 to the FOG portion, the heat input \( Q_{FOG} \) was estimated to be about 256.78 MJ. To compensate for the heat loss during trap grease transfer in the pipelines, a factor of 150\% was applied to the result. Therefore, the final value (combined) was 4,258.79 MJ. Hereafter, the results were all presented in the form of “final value”; *i.e.*, results had all been converted by applying the heat loss factor of 150\%.

**Heat input in the 2\textsuperscript{nd} heating step**

Following the same procedure as described above, the heat input due to the temperature increase (210 °F to 212 °F) was calculated for both water and FOG, resulting 2.61 and 3.94 MJ, respectively. In addition, since in the flash evaporator the remaining water was removed by evaporation, the latent heat of boiling water should be considered. The heat input for supplying the latent heat was calculated by Eq. S2 below:

\[ Q_{H2O}^L = L_{H2O} \times m_{H2O} \times Conversion\ Factors \]

Where:

\[ Q_{H2O}^L = \text{heat input for water evaporation (MJ)}; \]

\[ L_{H2O} = \text{latent heat of water under 1 atm at 212 °F (J/g)}; \]

\[ m_{H2O} = \text{mass of water (lb)}; \]

*Conversion Factors* = conversion factors for mass, volume, energy, power, etc.
As the remaining water entering the 2nd heating step was decreased to approximately 916 lbs after Tank#4, \( Q_{H2O} \) was estimated to be 1,409.71 MJ and therefore the total heat input for 2nd heating step was 1,416.25 MJ.

In summary, the total heat input \( E_H \) during the trap grease pretreatment stage was the sum of the aforementioned results and in this case would be 5,675.05 MJ for 100,000 lbs of raw trap grease. During the actual production process, the heat input is commonly supplied by burning natural gas. The embedded energy of natural gas is 36.6 MJ/m\(^3\) (45.75 MJ/kg),\(^{66}\) therefore, for 5,675.05 MJ heat input, the amount of natural gas supply was 124.04 kg. As there are also energy consumptions associated with the production of natural gas, it is reasonable to include them in the quantification of total energy inputs for the FOG separation stage. Accordingly, the life cycle energy of natural gas used in the current study was 49.09 MJ/kg.\(^{66,67}\) Therefore, the life cycle energy consumption of heating in this stage was approximately 6,089.36 MJ.

**Air-Cooled Chiller**

As indicated from the reference\(^{51}\), the capacity of the FOG treatment facility is usually small. So the processing capacity of raw trap grease was assumed to be 5 million gallons per year (MMgpy) for the current study. Accordingly, an air-cooled chiller was selected for this small processing capacity. The Energy Efficiency and Renewable Energy (EERE) program of US Department of Energy (US DOE) has a Federal Energy Management Program that provides an “energy cost calculator for air-cooled electric chillers”.\(^{58}\) By using the default setting of the calculator, the energy consumption of 1.23 kWh/tonne was estimated. The flow of water to be condensed varied from case to case and depended on the initial composition of the crude trap grease. The energy consumption was calculated by the following equation:
\[ E_C = 1.23 \times m_{H2O, ini} \times (1 - 79.91\%) \times (1 - 94.86\%) \times Conversion \ Factors \]  

**Eq. S3**

Where:

- \( E_C \) = electricity input for air-cooled chiller (MJ);
- \( m_{H2O, ini} \) = initial water content (lb);
- 79.91\%, 94.86\% = water removal efficiency of room temperature (68 F) and heated (210 F) gravity settlings (Tank#1-4)

\( Conversion \ Factors \) = conversion factors for mass, volume, energy, power, etc.

For the sample calculation, the electricity consumption for cooling was 0.52 kWh.

**Pumps**

As the biodiesel production facility was assumed to be located within a wastewater treatment plant, the energy consumption of pumps was calculated by using an estimation of the average electricity consumption for pump operation in the US wastewater plants.\(^5^{11}\) From the reference, the electricity consumption was approximately 1,200 kWh per million gallons of wastewater treated and the share of wastewater pumping was around 12 \%. By applying this rate, the corresponding \( E_p \) was 1.67 kWh for the sample calculation (100,000lbs/11,628 gallons).

Similar to heating supply, the energy consumptions related to the production of electricity are also accounted for in this stage and therefore the life cycle energy of electricity was 7.4 MJ/kWh.\(^5^6\)

The sample calculation in the above section illustrated how the utility consumption was calculated in each step of the FOG separation stage. The total life cycle energy consumption for the trap grease pretreatment stage then was obtained by summing up all the calculated results, as shown in Eq.S4:
Therefore the $E_T$ for this sample calculation was 6,105.56 MJ and by applying the GHG emission factors in Table S2.1, the life cycle GHG emission from this stage (before allocation) is summarized in Table S2.3.

**Table S2.3.** Life cycle energy consumption and GHG emission from FOG separation stage (before allocation)

<table>
<thead>
<tr>
<th>Material/utility</th>
<th>Consumption</th>
<th>Life cycle energy consumption (MJ)</th>
<th>Life cycle GHG emission (g CO$_2$ eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>2.19 kWh</td>
<td>16.20</td>
<td>1,930.37</td>
</tr>
<tr>
<td>Natural gas</td>
<td>124.04 kg</td>
<td>6,089.36</td>
<td>418,030.78</td>
</tr>
<tr>
<td><strong>Total energy/GHG</strong></td>
<td><strong>6,105.56 MJ</strong></td>
<td></td>
<td><strong>419,996.15</strong></td>
</tr>
</tbody>
</table>
Appendix S-2: Sample calculation: FOG pretreatment stage (acid esterification)

A comprehensive literature review (Table S2.14) showed that there was a good linear relationship ($R^2:0.8754$) between the “MeOH-to-FOG mass ratio” and the initial FFA concentration in FOG (Figure S2.1), with the regression equation of Eq. S5.

$$R_{MO} = 0.0214FFA_{100}$$  \hspace{1cm} \text{Eq. S5}

Where:

$R_{MO}$: mass ratio between methanol and FOG;

$FFA_{100}$: value of initial FFA concentration in FOG (e.g. 60 for 60% FFA concentration);

![Figure S2.1. Linear regression “MeOH-to-FOG mass ratio” and the initial FFA concentration in FOG ($n=20$)](image)

On the other hand, there was no definitive correlation observed for the dose of $H_2SO_4$. The authors tried to correlate the $H_2SO_4$ dose with FOG and/or initial FFA concentration by mass or molar basis. It was indicated that there might be an explicit correlation between “$H_2SO_4$-to-FOG
wt% (dose of H$_2$SO$_4$ as % of FOG mass, Table S2.14)” and initial FFA concentration by applying data grouping. Data grouping was performed to group the initial FFA concentrations into 4 data bins: 5-10 wt%, 11-30 wt%, 30-40 wt%, and >90 wt%. The corresponding “H$_2$SO$_4$-to-FOG wt%” values were averaged and a regression was performed between the averaged “H$_2$SO$_4$-to-FOG wt%” values and the mean values of data bins (e.g. 7.5, 20.5, 35, 95 wt%). The results after data grouping showed a good logarithmic fit ($R^2$: 0.8278) in Figure S2.2.

$$R_{HO} = 0.9656 \ln(FFA_{100}) - 1.0827$$ \hspace{1cm} \textbf{Eq. S6}

Where:

$R_{HO}$: mass percentage between H$_2$SO$_4$ and FOG, %;

FFA$_{100}$: value of FFA concentration in FOG (e.g. 60 for 60% FFA concentration);

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s2.png}
\caption{Correlation between “H$_2$SO$_4$-to-FOG wt%” and the initial FFA concentration ($n=21$; grouped into 4 bins)}
\end{figure}
Hence, the material inputs of methanol and H$_2$SO$_4$ were calculated based on the initial FFA concentration in FOG through the relationships developed above. Another material input for the esterification process was the addition of NaOH to neutralize the acid catalyst after the reaction. The amount of NaOH added was calculated based on the stoichiometric ratio between NaOH and H$_2$SO$_4$ for neutralization. The process energy input for the esterification stage mainly consisted of electricity and heat (natural gas) consumptions. As excessive methanol is required to propel the esterification reaction towards the end, methanol recovery is an indispensable step. Methanol recovery is commonly performed by distillation, which requires heat input by burning natural gas. Therefore, the mass ratio between the natural gas input and excessive methanol used in current study was derived from Canakci and Van Gerpen$^{12}$ as following:

$$m_{NM} = 0.04m_M$$ \hspace{1cm} \text{Eq. S7}

Where:

$m_{NM}$: mass of natural gas input for recovery of excessive methanol, kg;

$m_M$: mass of excessive methanol, kg;

Other than energy input for methanol recovery, other process-related energy inputs were also derived from Canakci and Van Gerpen$^{12}$ as following:

$$m_{Nh} = 0.00464m_{FOG}$$ \hspace{1cm} \text{Eq. 8}

Where:

$m_{Nh}$: mass of natural gas input for heating purpose, kg;

$m_{FOG}$: mass of FOG, kg;
\[ I_e = 0.028 \left( \frac{kWh}{kg} \right) m_{FOG} \]  

Eq. S9

Where:

- \( I_e \): electricity input for pumping, kWh;
- \( m_{FOG} \): mass of FOG, kg;

**Calculation procedure**

As is calculated from the previous FOG separation step, the FOG input for esterification was approximately 3,416.54 lbs. The corresponding FFA concentration was 66.33 % and according to Eq. S5&S6, the inputs of MeOH (both consumptive and excessive) and H\(_2\)SO\(_4\) were 4,849.65 lbs and 101.39 lbs, respectively. Since the stoichiometric ratio between FFA and methanol was 1:1 for the esterification reaction, the theoretical consumption of methanol was approximately 261.18 lbs. Therefore the excessive methanol that needed to be recovered was 4588.47 lbs. From Eq. S7& S8, the total amount of natural gas consumption for recovering the excessive methanol and for heating purpose was 199.39 lbs. Also, the electricity consumption was determined as 43.43 kWh. The dosage for NaOH addition was determined through the stoichiometric ratio between NaOH and H\(_2\)SO\(_4\) in the neutralization reaction (2:1). Hence the amount of NaOH added in this sample calculation was about 82.77 lbs. Since the initial FFA concentration was higher than 15%, a second esterification step was necessary to bring the FFA level down to acceptable value.\(^{13}\) Therefore the dosage for chemicals and utility consumption were doubled. The corresponding life cycle energy consumption and GHG emission are summarized in Table S2.4. The amount of biodiesel generated in this step was approximately 2,380.32 lbs.
### Table S2.4. Life cycle energy consumption and GHG emission of FOG pretreatment (esterification) stage (before allocation)

<table>
<thead>
<tr>
<th>Material/utility</th>
<th>Amount</th>
<th>Life cycle energy input (MJ)</th>
<th>Life cycle GHG emission (g CO₂ eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>237.15 kg (actual consumption)</td>
<td>7,814.21</td>
<td>296,442.10</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>92.06 kg</td>
<td>-224.63</td>
<td>19,333.20</td>
</tr>
<tr>
<td>NaOH</td>
<td>75.16 kg</td>
<td>112.73</td>
<td>35,322.07</td>
</tr>
<tr>
<td>Electricity</td>
<td>86.86 kWh</td>
<td>642.78</td>
<td>76,576.74</td>
</tr>
<tr>
<td>Natural gas</td>
<td>181.02 kg</td>
<td>8,887.61</td>
<td>610,129.40</td>
</tr>
<tr>
<td><strong>Total energy/GHG</strong></td>
<td></td>
<td><strong>17,232.70</strong></td>
<td><strong>1,037,803.51</strong></td>
</tr>
</tbody>
</table>
Appendix S-3: Sample calculation: biodiesel production (alkaline transesterification)

The dosage of material and energy for this stage was cited from an Argonne National Laboratory report authored by Huo et al.\textsuperscript{514} Table S2.5 shows the material and energy inputs from the two LCA studies cited in the report.

| Table S2.5. Material and energy consumption for the transesterification of one lb soybean oil |
|---------------------------------|-----------------|-----------------|-----------------|
| Input                          | Haas et al. (2006) | Sheehan et al. (1998) | Average         |
| Methanol (lb)                  | 0.100            | 0.086            | 0.093           |
| NaOCH$_3$ (lb)                 | 0.012            | 0.023            | 0.018           |
| HCl (lb)                       | 0.007            | 0.007            | 0.007           |
| Natural gas (Btu)              | 887.113          | 751.429          | 819.271         |
| Electricity (Btu)              | 45.954           | 42.857           | 44.406          |

Hence, by applying the average values in Table S2.5 and assuming a linear relationship between the consumption and the mass the FOG, the material and energy consumption for the transesterification process in this study could be quantified. As 66.33% of the FOG (as FFA) was converted into biodiesel in the preceeding esterification step, remaining FOG was 1,150.35 lbs which were converted into 1,144.07 lbs of biodiesel at the end of the transesterification step. Therefore, total biodiesel production from both esterification and transesterification stages of the sample calculation was approximately 3,524.39 lbs, equal to 476.27 gallons. Accordingly, the life cycle energy consumption and GHG emissions from the transesterification stage are summarized in Table S2.6.

| Table S2.6. Life cycle energy consumption and GHG emission of biodiesel production (alkaline transesterification) stage (before allocation) |
|---------------------------------|-----------------|-----------------|-----------------|
| Material/utility               | Amount          | Life cycle energy input (MJ) | Life cycle GHG emission (g CO$_2$ eq) |
| Methanol                        | 49.59 kg        | 1,634.02 MJ     | 61,988.79       |
| NaOCH$_3$                       | 9.63 kg         | 305.15 MJ       | 21,254.79       |
| HCl                             | 3.86 kg         | 6.56 MJ         | 2,895.79        |
| Electricity                     | 6.96 kWh        | 51.48 MJ        | 6,133.41        |
| Natural gas                     | 10.09 kg        | 495.26 MJ       | 33,999.19       |
| Total energy input              | 2,492.48        |                 | 126,271.97      |
Appendix S-4: Sample calculation: anaerobic digestion

As mentioned in the section 2.4.2, the operation conditions of the AD were cited from Sills et al.\textsuperscript{S15} and details are summarized in Table S2.7.

Table S2.7. Parameters for the anaerobic digester\textsuperscript{S15}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing</td>
<td>kWh/kg VS</td>
<td>0.3</td>
</tr>
<tr>
<td>H$_2$S removal</td>
<td>kWh/kg VS</td>
<td>0.25</td>
</tr>
<tr>
<td>Heat input</td>
<td>MJ/kg VS</td>
<td>2.7</td>
</tr>
<tr>
<td>CH$_4$ generation rate</td>
<td>L/g VS</td>
<td>0.1</td>
</tr>
<tr>
<td>CHP electric efficiency</td>
<td>%</td>
<td>33</td>
</tr>
<tr>
<td>CHP heat efficiency</td>
<td>%</td>
<td>43</td>
</tr>
</tbody>
</table>

In this sample calculation, the amount of solids from the FOG separation process was 9,420 lbs. By assuming a 94 wt% for VS in the solids,\textsuperscript{S16} the amount of VS available for anaerobic digestion was 4,020,079.2 g. By applying the factors in Table S2.7, the electricity and heat consumption was 1,407.03 kWh and 237.25 kg NG, respectively. The corresponding life cycle energy consumption and GHG emission were 22,057.72 MJ and 2,039,956.08 g CO$_2$ eq (Table S2.8). On the other hand, the generation of methane was calculated as 795.98 kg. With an energy content of methane of 53.38 MJ/kg\textsuperscript{S17} and by applying the overall CHP efficiency of 76%, the total energy generated from 9,420 lbs of solids were 32,291.78 MJ, among which 14,021.43 MJ was in the form of electricity. By assuming that the mass of non-volatile solids remained unchanged during the digestion and that the VS destruction rate was 56%, the mass of the remaining solids was 4,461.3 lbs, which was transferred to a landfill by truck after the process.

Table S2.8. Life cycle energy consumption and GHG emission from anaerobic digestion stage (before allocation)

<table>
<thead>
<tr>
<th>Material/utility</th>
<th>Consumption</th>
<th>Life cycle energy consumption (MJ)</th>
<th>Life cycle GHG emission (g CO$_2$ eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>1,407.03 kWh</td>
<td>10,412.01</td>
<td>1,240,421.57</td>
</tr>
<tr>
<td>Natural gas</td>
<td>237.25 kg</td>
<td>11,645.71</td>
<td>799,534.44</td>
</tr>
<tr>
<td>Total energy/GHG</td>
<td>22,057.72</td>
<td></td>
<td>2,039,956.01</td>
</tr>
</tbody>
</table>
Appendix S-5: Sample calculation: transportation

For the transportation activity between restaurant and grease hauler’s holding facility, the average travel distance of 75 miles was estimated based on the survey results from haulers registered with MSDGC. Similarly, the distance traveled from the hauler’s holding facility to the WWTP was estimated by averaging the distance between the holding facility of the individual grease hauling company and the MSDGC. Accordingly, the average distance between grease haulers and the MSDGC was estimated to be 23.7 miles and hence for one truck load of raw trap grease travel from hauler’s facility to MSDGC, the total distance was 47.4 miles. The distance between the WWTP and the landfill where waste solids was sent was estimated to be 50 miles for current study.\(^{515}\) The trucks used by haulers and the MSDGC to transport raw trap grease and waste solids were assumed to be the same: a diesel truck with a capacity of 3,600 gallons/load and an average fuel economy of 6.5 miles per gallon. The transportation distances for this sample calculation are summarized in Table S2.9.

### Table S2.9. Summary of transportation distances (round trip)

<table>
<thead>
<tr>
<th>Transportation</th>
<th>Distance (miles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Restaurant-to-hauler’s facility</td>
<td>150</td>
</tr>
<tr>
<td>Hauler’s facility-to-WWTP</td>
<td>47.4</td>
</tr>
<tr>
<td>WWTP-to-landfill</td>
<td>100</td>
</tr>
</tbody>
</table>

Accordingly, the diesel fuel consumption for transporting the raw trap grease from a restaurant to MSDGC was approximately 98.1 gallons. The embedded and life cycle energy of diesel are 35.9 MJ/L and 42.5 MJ/L, respectively.\(^{56}\) So, the corresponding life cycle energy consumption and GHG emission were 15,759.02 MJ and 1,142,208.30 g CO\(_2\) eq.

On the other hand, the fuel consumption for disposing solid wastes was dependent on the management of the solids after the FOG pretreatment stage. One scenario (w/AD) proposed in the study was to use the solids from the FOG separate process as the feed to an anaerobic
digester. Under this circumstance, the amount of the solid wastes was significantly reduced after the digestion process. On the other hand, if the solid wastes was sent to a landfill without any further application (w/o AD), the amount was assumed to remain unchanged (from the end of the FOG pretreatment stage). As was shown in the Appendix S-4 section, the remaining solids from the digestion process was 4,461.3 lbs. Hence the fuel consumption for this amount of solid waste was 1.42 gallon and the corresponding life cycle energy consumption and GHG emission were 228.57 MJ and 16,566.81 g CO$_2$ eq. If the solid waste did not go through the anaerobic digestion process, the amount of solids that needed to be transported to a landfill would be 9,420 lbs, and the corresponding fuel consumption and total energy input were 3.00 gallon and 482.63 MJ, respectively. The life cycle GHG emission was 34,980.59 g CO$_2$ eq.
Appendix S-6: Sample calculation: allocation

For the sample calculation, the total incoming flow of raw trap grease consisted of 4,230 lbs of FOG, 86,345 lbs of water and 9,420 lbs of solids. The mass balance showed that the final product of biodiesel was 3,524.39 lbs and the mass of the remaining solids was 4,461.3 lbs or 9,420 lbs for the AD and non-AD scenarios, respectively. The life cycle energy input (consumption) and output (generation) and GHG emission for sample calculation of trap grease biodiesel production are summarized in Table S2.10.

Table S2.10. Life cycle energy input/output and GHG emission for trap grease production in the sample calculation (before allocation)

<table>
<thead>
<tr>
<th>Life cycle stage</th>
<th>Energy input (MJ)</th>
<th>Energy output (MJ)</th>
<th>GHG emission (g CO₂ eq)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation of raw trap grease</td>
<td>15,759.02</td>
<td>NA</td>
<td>1,142,208.30</td>
<td></td>
</tr>
<tr>
<td>FOG pretreatment</td>
<td>6,105.56</td>
<td>NA</td>
<td>419,96.15</td>
<td></td>
</tr>
<tr>
<td>Esterification</td>
<td>17,232.70</td>
<td>40,156.00</td>
<td>1,037,803.50</td>
<td>Energy output = embedded energy of 2,380.32 lbs biodiesel</td>
</tr>
<tr>
<td>Transesterification</td>
<td>2,492.48</td>
<td>19,300.46</td>
<td>126,271.97</td>
<td>Energy output = embedded energy of 1,144.07 lbs biodiesel</td>
</tr>
<tr>
<td>Anaerobic digestion (AD)</td>
<td>22,057.72</td>
<td>32,291.78</td>
<td>2,039,956.01</td>
<td>Energy generated from CH₄</td>
</tr>
<tr>
<td>Transportation of waste solids</td>
<td>228.57</td>
<td>NA</td>
<td>16,566.81</td>
<td>With AD</td>
</tr>
<tr>
<td></td>
<td>482.63</td>
<td>NA</td>
<td>34,980.59</td>
<td>Without AD</td>
</tr>
</tbody>
</table>

Mass allocation was applied at the end of each stage of the life cycle and the allocation factors for each stage are listed in Table S2.11.

Transportation of raw trap grease
For the stage of transporting raw trap grease to the WWTP, the energy consumption and GHG emissions were allocated among: (1) potential biodiesel made from the FOG, (2) the amount of solids, (3) potential glycerin made from the FOG and (4) the potential loss of FOG during the subsequent FOG separation stage. No energy consumption or GHG emission was allocated to water because it was not “intentionally” treated in this stage and was not used as input for any of the following stages in the life cycle. The allocation factors for this stage were calculated by Eq.S10-S13.

\[
F_{\text{raw trans BioD}} = R_{\text{raw}} \times \text{RecFOG} \times R_{\text{est}} + R_{\text{raw}} \times \text{RecFOG} \times (1 - R_{\text{est}}) \times F_{\text{trans}} \quad \text{Eq. S10}
\]

Where:

- \( F_{\text{raw trans BioD}} \): allocation factor for the potential biodiesel made from the FOG
- \( R_{\text{raw}} \): wt% of FOG in the FOG-solids mixture \( \left( \frac{m_{\text{FOG}}}{m_{\text{FOG}} + m_{\text{solids}}} \times 100\% \right) \) at the end of the raw trap grease transportation stage
- \( \text{RecFOG} \): recovery of FOG (2.1/2.6) at the end of the FOG separation stage
- \( R_{\text{est}} \): mass ratio between biodiesel (esters) and oil at the end of the esterification stage
- \( F_{\text{trans}} \): allocation factor between biodiesel and glycerin at the end of the transesterification stage

\[
F_{\text{raw trans solids}} = 1 - R_{\text{raw}} \quad \text{Eq. S11}
\]

Where:

- \( F_{\text{separation solids}} \): allocation factor for the solids in the FOG-solids mixture

\[
F_{\text{raw trans glycerin}} = R_{\text{raw}} \times \text{RecFOG} \times (1 - R_{\text{est}}) \times (1 - F_{\text{trans}}) \quad \text{Eq. S12}
\]

Where:
\( F_{\text{raw} \text{trans} \text{- glycerin}}: \text{allocation factor for the potential glycerin made from the FOG} \)

\[
F_{\text{raw} \text{trans} \text{- lostFOG}} = R_{\text{raw}} \times (1 - \text{RecFOG}) \quad \text{Eq. S13}
\]

Where:

\( F_{\text{raw} \text{trans} \text{- lostFOG}}: \text{allocation factor for the part of FOG that would be lost to Flow#4 in the subsequent FOG separation stage} \)

Because the solids part will either be sent to the AD stage or directly to a landfill, its share of life cycle energy consumption and GHG emission should be solely attributed to biodiesel production. Similar principle was applied to the lost FOG during separation.

*Trap grease pretreatment (FOG separation)*

The allocation factors were derived by using the flow data shown in Table S2.2. The recovery rate of FOG during the FOG pretreatment stage was 2.1 (Flow #6) out of 2.6 gallons (Flow #1). The remaining FOG was drained with bulk water through Flow #4. On the other hand, solids were collected in solids disposal tank from Flow #11, 10, 9 as well as with white water from Flow #4. The total amount of solids was 3.2 gallons.

There are four contributors sharing the life cycle energy consumption and GHG emission from this stage: (1) potential biodiesel made from the FOG, (2) the amount of solids, (3) potential glycerin made from the FOG, and (4) the mass of lost FOG during the FOG separation stage. Therefore, the allocation factors for the FOG separation stage were calculated from Eq.S14-17.

\[
F_{\text{separation} \text{- BioD}} = R_{\text{fs}} \times R_{\text{est}} + R_{\text{fs}} \times (1 - R_{\text{est}}) \times F_{\text{trans}} \quad \text{Eq.S14}
\]

Where:
\( F_{\text{separation-BioD}} \): allocation factor for the potential biodiesel made from the FOG

\( R_{fs} \): wt\% of recovered FOG in the FOG-solids mixture \( \left( \frac{m_{\text{FOG}\_rec}}{m_{\text{FOG}\_rec} + m_{\text{solids}} + m_{\text{FOG}\_loss}} \times 100\% \right) \) at the end of the separation step

\( R_{\text{est}} \): wt\% of biodiesel (esters) in the ester-oil mixture \( \left( \frac{m_{\text{BioD}}}{m_{\text{BioD}} + m_{\text{oil}}} \times 100\% \right) \) at the end of the esterification step

\( F_{\text{trans}} \): allocation factor for biodiesel at the end of the transesterification step

\[ F_{\text{separation\_lostFOG}} = R_{\text{lossFOG}} \] \hspace{1cm} \text{Eq. S15}

Where:

\( F_{\text{separation\_lostFOG}} \): allocation factor for the part of FOG lost to Flow#4 at the end of the FOG separation stage

\( R_{\text{lossFOG}} \): wt\% of lost FOG in the FOG-solids mixture \( \left( \frac{m_{\text{FOG}\_loss}}{m_{\text{FOG}\_rec} + m_{\text{solids}} + m_{\text{FOG}\_loss}} \times 100\% \right) \) at the end of the separation step

\[ F_{\text{separation\_solids}} = 1 - R_{fs} - R_{\text{lossFOG}} \] \hspace{1cm} \text{Eq. S16}

Where:

\( F_{\text{separation\_solids}} \): allocation factor for the solids in the FOG-solids mixture

\[ F_{\text{separation\_glycerin}} = R_{fs} \times (1 - R_{\text{est}}) \times (1 - F_{\text{trans}}) \] \hspace{1cm} \text{Eq. S17}

Where:
$F_{\text{separation-glycerin}}$: allocation factor for the potential glycerin made from the FOG

**FOG pretreatment (acid esterification)**

The life cycle energy consumption and GHG emissions from esterification process was assigned only to the biodiesel since there was no by-product generated in this stage. In the transesterification stage, the amount of biodiesel generated after the two-step transesterification process (99% overall efficiency) was 1,144.07 lbs and accordingly the formation of glycerin was 121.49 lbs. It was assumed that the glycerin after the proposed purification process had a mass concentration of 80%, hence the total mass of glycerin mixture became 151.86 lbs. The calculated mass allocation factors for the biodiesel and glycerin were 0.88 and 0.12.

**Anaerobic digestion**

Similar to esterification stage, the life cycle energy consumption and GHG emissions from the anaerobic digestion stage were solely attributed to the solids and hence the allocation factor was 1.

**Transportation of waste solids**

When the remaining solid waste was disposed of in a landfill, the life cycle energy consumption and GHG emissions for the transportation of this waste to a landfill were allocated solely to the biodiesel regardless of whether an anaerobic digester was applied or not.
<table>
<thead>
<tr>
<th>Life cycle stage</th>
<th>Allocation factor</th>
<th>Life cycle energy consumption allocated to Biodiesel (MJ)</th>
<th>Life cycle GHG emission allocated to Biodiesel (g CO₂ eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw trap grease transportation</td>
<td>0.24 (biodiesel)</td>
<td>15,601.43</td>
<td>1,131,293.21</td>
</tr>
<tr>
<td></td>
<td>0.69 (solids)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01 (glycerin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06 (lost FOG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOG pretreatment</td>
<td>0.24 (biodiesel)</td>
<td>6,044.50</td>
<td>415,947.94</td>
</tr>
<tr>
<td></td>
<td>0.69 (solids)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01 (glycerin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06 (lost FOG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esterification</td>
<td>0.88 (biodiesel)</td>
<td>17,232.70</td>
<td>1,037,803.5</td>
</tr>
<tr>
<td></td>
<td>0.12 (glycerin)</td>
<td>2,193.38</td>
<td>111,475.37</td>
</tr>
<tr>
<td>Anaerobic digestion (AD)</td>
<td>1</td>
<td>22,057.72</td>
<td>2,039,956.01</td>
</tr>
<tr>
<td>Energy output from AD</td>
<td>1</td>
<td>-32,291.78*/-48,426.01**</td>
<td>-4,779,469.28**</td>
</tr>
<tr>
<td>Transportation of waste solids to</td>
<td>1</td>
<td>228.57 (w/ AD)</td>
<td>16,566.81</td>
</tr>
<tr>
<td>a landfill</td>
<td></td>
<td>482.63 (w/o AD)</td>
<td>34,980.59</td>
</tr>
<tr>
<td>**Total life cycle energy</td>
<td></td>
<td>14,932.29**</td>
<td>-26,426.44**</td>
</tr>
<tr>
<td>consumption/GHG emission (w/ AD)</td>
<td></td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>**Total life cycle energy</td>
<td></td>
<td>41,554.64</td>
<td>2,731,500.61</td>
</tr>
<tr>
<td>consumption/GHG emission (w/o AD)</td>
<td></td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>**Normalized to one gal BioD (w/</td>
<td></td>
<td>31.39 MJ/gal**</td>
<td>-55.49 g CO₂ eq/gal**</td>
</tr>
<tr>
<td>AD)</td>
<td></td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>**Normalized to one gal BioD (w/</td>
<td></td>
<td>87.29 MJ/gal</td>
<td>5,735.22 g CO₂ eq/gal</td>
</tr>
<tr>
<td>AD)</td>
<td></td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

* The “apparent” energy output from AD
** The total energy output/GHG savings considering the life cycle energy consumption/GHG emission of the electricity and natural gas consumption avoided by utilizing the “apparent” energy from AD
It should be noted there were two results for the energy output from the AD. The “apparent” energy output was the exact amount of energy generated from CH\textsubscript{4} in the AD. However, it is necessary to take into consideration of the avoided life cycle energy consumption from using the “apparent” energy output generated from the AD to displace the use of electricity and natural gas. So in this case, the “apparent” energy output from the AD was 32,291.78 MJ. However, the avoided life cycle energy consumption was 48,426.01 MJ. Accordingly, the GHG reduction was calculated based on the avoided life cycle energy consumption.
Appendix S-7: Monte Carlo simulation

Data for Monte Carlo simulation

The concentrations of water, solids and FOG in the raw trap grease vary from case to case. The composition of the raw trap grease is largely affected by the frequency of the grease cleaning. The more frequently maintained grease trap will have less FOG in the raw trap grease. A comprehensive search was conducted for the current study to gather data of the raw trap grease composition. Twenty-nine data points were collected from peer-reviewed papers, reports, and personal communication with professionals in the industry. The summary of the data can be found in Table S2.12. The Goodness of Fit test was performed in MiniTab® 17 to find a best-fit distribution to represent the data and to be used for Monte Carlo simulation. The results showed that the Weibull distribution possessed the highest p-value and hence it was selected as the best distribution to represent the FOG concentration in the raw trap grease. As the concentration of water was derived based on concentration of FOG from the regression model (Eq. S18), algorithm was developed to limit the random values generated from the Weibull distribution within a certain range such that the values of the concentrations for FOG, water and solids were all within the physically meaningful range (0% ≤ FFA concentration ≤ 100%). Likewise, the Goodness of Fit test was performed for FFA concentration in separated FOG based on 16 data points (Table S2.13) collected from literature and personal communications. Based on p-values, Logistic distribution was selected as the distribution for FFA concentration in separated FOG for the Monte Carlos simulation. Similar to the FOG concentration, truncation was needed to limit the random values generated by this distribution within the physically meaningful range. In addition, the VS concentration in solids was assumed to follow a uniform distribution from
88% to 99%. Triangular distribution was used to generate the values of operational parameters for the AD, as indicated by Sills et al. Table S2.15 summarizes the distributions used by the current study.

A total of 29 data sets were retrieved from literature review and survey for the composition of raw trap grease (Table S2.12). The FOG concentration ranged from 0.04% to 62.5% with most of the data points resided at the lower end of the range. A good linear relationship was found between the concentrations of water and FOG, as shown in Figure S2.3.

![Figure S2.3. Linear regression between water (wt%) and FOG (wt%) in raw trap grease](image)

As a result, the concentration of water can be determined through Eq. S18 below:

\[
C_{H2O} = -1.3575C_{FOG} + 94.56 \quad \text{Eq. S18}
\]

Where:

\(C_{H2O}\): value of the water concentration (e.g. 60 for 60%);

\(C_{FOG}\): value of the FOG concentration (e.g. 10 for 10%);

Finally the concentration of solids was determined by 100% -\(C_{H2O}\) - \(C_{FOG}\).

Model for Monte Carlo simulation
The model for the Monte Carlo simulation (Figure S2.4) was constructed in Python 2.7. The mass of the raw trap grease was given a fixed value of 100,000 lbs at the beginning of each simulation run. The simulation started with the generation of a random value for FOG concentration, from which the composition of the raw trap grease was determined. The life cycle energy consumption and GHG emissions were calculated and the corresponding allocation factor was applied for each stage of the model. Certain values (e.g. mass of FOG, mass of solids) were passed down from one stage to the next when necessary. A random value was generated for FFA concentration when the calculation proceeded to esterification stage. Accordingly the mass of FFA was calculated based on the FFA concentration and the value of FOG mass passed down from the FOG separation stage. The mass of biodiesel generation, utility and chemical consumptions were calculated based on the mass of FFA by following the procedure in the sample calculation. Likewise, randomization was carried out based on the distributions for the selected parameters in the AD stage. Finally, the allocated total energy consumption and GHG emission at each stage were summed and the result was divided by the volume of biodiesel produced from the 100,000 lbs of raw trap grease during this simulation run (MJ/gal or g CO₂ eq/gal). A total of 100,000 runs were performed for the Monte Carlo simulation in the current study.
Figure S2.4. Model structure for Monte Carlo simulation
Appendix S-8: Unit conversion of energy consumption and GHG emission values for existing studies

* “Current study” hereafter refers to the study conducted in Chapter 2.

- **Life cycle energy consumption**

  **Cho et al. (2013)**

  The authors calculated the net energy ratio (NER), which was the ratio between total energy out and total energy input, for the biodiesel produced from palm fatty acid distillation. The NER was 3.23 (MJBioD/MJ). By assuming a density of 7.4 lb/gal and an energy content of 118,296 Btu/gal (16.87 MJ/lb) for biodiesel, the result was converted into “MJ/gal biodiesel” by:

  \[
  \frac{MJ}{gal \ BioD} = \left( \frac{MJ_{BioD}}{MJ_{NR}} \right)^{-1} / (Biodiesel \ energy \ content)^{-1} / Biodiesel \ density
  \]

  **Azadi et al. (2014)**

  Azadi et al. (2014) investigated both wet and dry oil extraction technologies and proposed four utilization approaches for the residual algal biomass after oil extraction: anaerobic digestion (after wet oil extraction), hydrothermal gasification (after wet oil extraction), gasification-power generation (after dry oil extraction) and gasification-Fischer-Tropsch (F-T) process (after dry oil extraction). The life cycle non-renewable energy consumption was defined as the energy balance ratio (EBR), which was the ratio of non-renewable energy consumed to energy from biodiesel (MJ/MIb). Accordingly, the EBR for the four technical routes were: 0.5, 0.96, 1.48, and 1.81 for hydrothermal gasification, anaerobic digestion, gasification-power generation and gasification-Fischer-Tropsch, respectively. By assuming a density of 7.4 lb/gal and an energy content of 118,296 Btu/gal (16.87 MJ/lb) for biodiesel, the following equation was used to convert the result from EBR to “MJ/gal biodiesel”:

  \[
  \frac{MJ}{gal \ BioD} = \left( \frac{MJ_{BioD}}{MJ_{NR}} \right)^{-1} / (Biodiesel \ energy \ content)^{-1} / Biodiesel \ density
  \]
\[ \frac{MJ}{gal \ BioD} = \frac{MJ_f}{MJ_b} \times \text{Biodiesel energy content} \times \text{Biodiesel density} \]

**Shirvani et al. (2011)**

The EBR of algae-to-biodiesel life cycle was 1.70 when the algal oil cake was utilized for energy generation in a CHP. Similar to Azadi et al. (2014), the following equation was used to convert the result from EBR to “MJ/gal biodiesel”:

\[ \frac{MJ}{gal \ BioD} = \frac{MJ_f}{MJ_b} \times \text{Biodiesel energy content} \times \text{Biodiesel density} \]

**Luque et al., (2010)**

Table 2 in Luque et al. (2010) summarizes energy return for biodiesel produced from four types of feedstocks. The results were 3.2, 2.7, 3, 9 MJ of BioD/MJ of non-renewable energy (MJ\text{BioD}/MJ\text{NR}) consumed for soybean, rapeseed, palm and wood. By assuming a density of 7.4 lb/gal and an energy content of 118,296 Btu/gal (16.87 MJ/lb) for biodiesel, the life cycle energy consumption can be converted in the unit of “MJ/gal biodiesel” by using the following equation:

\[ \frac{MJ}{gal \ BioD} = (\frac{MJ_{\text{BioD}}}{MJ_{\text{NR}}})^{-1}/(\text{Biodiesel energy content}^{-1}/\text{Biodiesel density}) \]

**Pradhan et al. (2011)**

As shown in Table 4 in Pradhan et al. (2011), the allocated total energy consumption for soybean biodiesel was 5.9 MJ/L biodiesel. In order to match the scope of current study, the 0.3 MJ/L energy consumption associated with the transportation of biodiesel was subtracted, leading to the adjusted value of 5.6 MJ/L biodiesel.

**Talens Peiró et al. (2010)**

Table 1 in Talens Peiró et al. (2010) lists the usage of diesel, electricity and steam for producing 1 ton of biodiesel. As the authors did not indicate the use of life cycle energy when calculating the electricity and steam consumptions, the energy content of diesel was assumed to be 35.9
MJ/L (embedded the energy from Pradhan et al.\textsuperscript{56}). The density of diesel is approximately 0.84 g/ml.\textsuperscript{562} The mass-based allocation factor is calculated between the amounts of biodiesel (1 ton) and glycerin (0.0981 ton): 0.91066 vs. 0.008934. Therefore for 1 ton of biodiesel, the allocated energy consumption is:

\[
\left( 516.08 \text{ MJ} + 642 \text{ MJ} + 0.0201 \text{ ton diesel} \times \frac{1000,000 \text{ g}}{\text{ton}} \times \frac{1 \text{ ml diesel}}{0.84 \text{ g diesel}} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{35.9 \text{ MJ}}{1 \text{ L diesel}} \right) \times 0.91066 = 1836.91 \text{ MJ}
\]

The volume of 1 ton of biodiesel is:

\[
1 \text{ ton BioD} \times \frac{1000,100 \text{ g}}{1 \text{ ton}} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{1 \text{ gal BioD}}{7.4 \text{ lb BioD}} = 297.654 \text{ gal}
\]

Therefore, the normalized energy consumption is 6.17 MJ/gal

\textit{López et al. (2010)}

Scenario II of the López et al. (2010) includes animal by-products or grease collection, rendering, biodiesel production and transportation between stages. In order to make the system boundary comparable to the current study, the energy consumption associated with biodiesel distribution was excluded for the unit conversion. So, according to Table 9, the allocated energy consumptions are 16.9, 19.2, and 13.9 MJ/kg biodiesel for biodiesels derived from tallow, poultry fat and waste (soybean) cooking oil, respectively. By subtracting the transportation related to biodiesel distribution (0.1 MJ/kg), the energy consumptions were converted in the functional unit as following (tallow biodiesel as an example):

\[
Tallow BioD: (16.9 - 0.1) \frac{\text{MJ}}{\text{kg BioD}} \times \frac{\text{kg}}{1000 \text{ g}} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{7.4 \text{ lb BioD}}{1 \text{ gal BioD}} = 56.44 \text{ MJ/gal}
\]

\textit{Dufour and Iribarren (2012)}

Table 1 in Dufour and Iribarren (2012) summarizes the electricity and thermal energy consumptions for the rendering, esterification and tranesterification stages. Table 1 also shows
the transportation of products between stages, but since there is no information about the fuel
economy of the lorry used in their study, the energy consumption associated with transportation
is calculated by using the data from López et al.⁵⁷:

1. By-products to rendering plant: tallow (0.6 MJ/kg BioD), poultry fat (1.1 MJ/kg BioD),
waste cooking oil (0.3 MJ/kg BioD)

2. Rendered lipids to biodiesel plant: 0.3 MJ/kg BioD for all feedstocks

Thus, the energy consumption for tallow biodiesel before allocation, as an example, is:

\[
\begin{align*}
T_{\text{allow BioD}}: & \quad \frac{(175.94 + 1743.88) MJ}{\text{ton BioD}} + \frac{(28.93 + 30.36) kWh}{\text{ton BioD}} \times \frac{3.6 MJ}{1 kWh} + \frac{(0.6 + 0.3) MJ}{\text{kg BioD}} \\
& \times \frac{1000 kg}{\text{ton}} = 3033.26 MJ/\text{ton}
\end{align*}
\]

The allocation method was similar to what is used for converting the result of energy
consumption into “MJ/gal” from Talens Peiró et al. (2010). The mass-based allocation factor was
calculated between the amounts of biodiesel (1 ton) and glycerin (0.11564 ton): 0.89634 vs.
0.10365. Therefore for 1 gallon of biodiesel produced from tallow, the allocated energy
consumption was:

\[
3033.26 \frac{MJ}{\text{ton BioD}} \times \frac{1 \text{ ton BioD}}{297.654 \text{ gal BioD}} \times 0.89634 = 9.13 \frac{MJ}{\text{gal}}
\]

**Sander and Murphy (2010)**

Sander and Murphy (2010) used system expansion to allocate the energy consumptions. The co-
product credit was significant by using algae biomass to replace corn as ethanol feedstock and
animal feeds. As a result, the total energy consumption for making 1000 MJ biodiesel was -6,680
and -3,778 MJ for filter press and centrifuge dewatering processes, respectively. By subtracting
the energy consumption associated with biodiesel distribution (9.66 MJ/kMJ BioD), the total
energy consumption was -6670.34 and -3768.34 MJ/kMJ BioD, respectively. By assuming the

79
energy content of neat biodiesel being 118,296 Btu/gal BioD (16.87 MJ/lb BioD), the converted values are:

\[
\text{Filter press: } - 6670.34 \frac{MJ}{kMJ BioD} \times \frac{1 \text{kMJ}}{1000 \text{MJ}} \times 16.87 \frac{MJ}{lb BioD} \times \frac{7.4 \text{ lb BioD}}{1 \text{ gal BioD}} = -832.71 \text{ MJ/gal}
\]

\[
\text{Centrifuge: } - 3768.34 \frac{MJ}{kMJ BioD} \times \frac{1 \text{kMJ}}{1000 \text{MJ}} \times 16.87 \frac{MJ}{lb BioD} \times \frac{7.4 \text{ lb BioD}}{1 \text{ gal BioD}} = -470.43 \text{ MJ/gal}
\]

Frank et al. (2012)

Figure 4 in Frank et al. (2012) summarizes the “well-to-pump” fossil energy consumption of algae biodiesel production (548,329 Btu/ MMBtu of biodiesel). By assuming a mass-based allocation factor of 0.885 (López et al.\textsuperscript{57}) and an energy content of 118,296 Btu/gal for biodiesel, the energy consumption was converted as following:

\[
548,329 \frac{Btu}{\text{1 MMBtu} - \text{BioD}} \times 118,296 \times 10^{-6} \frac{\text{MMBtu}}{\text{1 gal BioD}} \times 0.001055056 \frac{MJ}{1 \text{ Btu}} \times 0.885 = 60.57 \text{ MJ/gal}
\]

Stephenson et al. (2010)

Stephenson et al. (2010) conducted LCA for both open pond and PBR systems. The allocated values were 6.5 and 199.5 GJ/ton biodiesel, as reported in Table 4 and 5. The unit conversion was performed as following:

\[
\text{OP: } 6.5 \frac{\text{GJ}}{\text{ton BioD}} \times \frac{1000 \text{ MJ}}{1 \text{ GJ}} \times \frac{1 \text{ ton}}{1000,000 \text{ g}} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{7.4 \text{ lb BioD}}{1 \text{ gal BioD}} = 21.84 \text{ MJ/gal}
\]

\[
\text{PBR: } 199.5 \frac{\text{GJ}}{\text{ton BioD}} \times \frac{1000 \text{ MJ}}{1 \text{ GJ}} \times \frac{1 \text{ ton}}{1000,000 \text{ g}} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{7.4 \text{ lb BioD}}{1 \text{ gal BioD}} = 670.24 \text{ MJ/gal}
\]

Sheehan et al., 1998
Table 122 in Sheehan et al. (1998) shows the life cycle energy consumption for producing and using 1 MJ of petroleum diesel. To match the system boundary of current study, the energy consumption associated with diesel fuel transportation was subtracted and the resulting value became 1.19 MJ/MJ diesel. By assuming the energy content of diesel being 35.9 MJ/L, the converted life cycle energy consumption for petroleum diesel was 162.08 MJ/gal.

- **Life cycle GHG emission**

  Azadi et al., (2014)

  The GHG emission for four technical routes in Azadi et al. (2014) were 86 g CO\textsubscript{2}-eq/MJ biodiesel for anaerobic digestion, 41 g CO\textsubscript{2}-eq/MJ biodiesel for hydrothermal gasification, 109 g CO\textsubscript{2}-eq/MJ biodiesel for gasification-power generation and 124 g CO\textsubscript{2}-eq/MJ biodiesel for gasification-F-T process. As the authors included the indirect GHG emission from plant construction, in order to be consistent with scope of current study, this part of the GHG emission was subtracted during the calculation here. It was indicated by the authors that the construction-related GHG emission accounted for 27-35 g CO\textsubscript{2}-eq/MJ biodiesel, therefore an average value of 31 g CO\textsubscript{2}-eq/MJ biodiesel was subtracted from the results of each technical routes. Similar to converting EBR to “MJ/gal”, the following equation was used to convert the GHG emission result into “g CO\textsubscript{2}-eq/gal”:

  \[
  \frac{g \text{ CO}_2 \text{ eq}}{M_J} \times \text{Biodiesel energy content} \times \text{Biodiesel density}
  \]

  Shirvani et al. (2011)

  According to Figure 4 of Shirvani et al. (2011), the life cycle GHG emission of algae biodiesel was approximately 100 g CO\textsubscript{2}-eq/MJ biodiesel. Since the authors include the combustion stage of the biodiesel, the corresponding GHG emission was subtracted during this calculation in order
to be consistent with the scope of the current study. A value of 73 g CO\textsubscript{2}-eq/MJ biodiesel (equal to the CO\textsubscript{2} emission from complete combustion of petroleum diesel) was subtracted and the resulting life cycle GHG emission for algae biodiesel was then 26 g CO\textsubscript{2}-eq/MJ biodiesel.

Similar to Azadi et al. (2014), the following equation was used to convert the value into “g CO\textsubscript{2} eq/gal BioD”

\[
\frac{g \text{ CO}_2 \text{ eq}}{MJ_b} \times \text{Biodiesel energy content} \times \text{Biodiesel density}
\]

*Cho et al. (2013)*

The GHG emission in original unit was 53.12 g CO\textsubscript{2} eq/MJ BioD. Similar to Azadi et al. (2014), the following equation was used to convert the value into “g CO\textsubscript{2} eq/gal BioD”

\[
\frac{g \text{ CO}_2 \text{ eq}}{MJ_b} \times \text{Biodiesel energy content} \times \text{Biodiesel density}
\]

*Luque et al., (2010)*

Table 2 in Luque et al. (2010) summarizes life cycle GHG emission for biodiesel produced from four types of feedstocks. The results were 2.6, 1.79, 1.73, 0.27 tonne CO\textsubscript{2} eq/tonne biodiesel for soybean, rapeseed, palm and wood. By assuming a 7.4 lb/gal density for biodiesel, 1 tonne of biodiesel was approximately 297.65 gallons in volume. Therefore, the converted values of GHG emission were 8,734.96, 6,013.68, 5,812.11, and 907.09 g CO\textsubscript{2} eq/gal for soybean, rapeseed, palm and wood, respectively.

*Talens Peiró et al. (2010)*

According to Table 7 of the paper, the life cycle GHG emission was 299.60 kg CO\textsubscript{2} eq/ton biodiesel. By assuming the density of biodiesel being 7.4 lb/gal, the converted value was approximately g CO\textsubscript{2} eq/gal biodiesel:
Table 2 in Dufour and Iribarren (2012) summarizes the GHG emission for the rendering, esterification and tranesterification stages, material transportation and methanol production. It is noted that the transportation of biodiesel production to distribution terminals was excluded from the calculation here, in order to be consistent with the system boundary proposed in current study. The life cycle GHG emission is therefore calculated by the following equation:

\[ \text{GHG}_{T,i} = \text{GHG}_{\text{rendering},i} + \text{GHG}_{\text{ester},i} + \text{GHG}_{\text{trans},i} + \text{GHG}_{\text{transport},i} + \text{GHG}_{\text{MeOH},i} \]

Where:

\( \text{GHG}_{T,i} \): life cycle GHG emission from a certain feedstock-to-biodiesel process “i”. “i” could be waste cooking oil, tallow, poultry fat or sewage sludge; (kg CO\_2 eq/tonne biodiesel)

\( \text{GHG}_{\text{rendering},i} \): GHG emission from rendering stage for a certain feedstock-to-biodiesel process “i”; (kg CO\_2 eq/tonne biodiesel)

\( \text{GHG}_{\text{ester},i} \): GHG emission from esterification stage for a certain feedstock-to-biodiesel process “i”; (kg CO\_2 eq/tonne biodiesel)

\( \text{GHG}_{\text{trans},i} \): GHG emission from transesterification stage for a certain feedstock-to-biodiesel process “i”; (kg CO\_2 eq/tonne biodiesel)
\( \text{GHG}_{\text{transport},i} \): GHG emission from transporting materials (e.g. rendered fat) for a certain feedstock-to-biodiesel process “i”; (kg CO\(_2\) eq/tonne biodiesel)

\( \text{GHG}_{\text{MeOH},i} \): GHG emission from production of methanol; (kg CO\(_2\) eq/tonne biodiesel)

Accordingly, the life cycle GHG emission for the four feedstocks, i.e., waste vegetable oil, tallow, poultry fat and sewage sludge, were 576.02, 820.41, 829.46, and 725.07 kg CO\(_2\) eq/ton biodiesel, respectively.

The allocation method was similar to what was used for converting the GHG emission into “g CO\(_2\) eq/gal” from Talens Peiró et al. (2010). The mass-based allocation factor was calculated between the amounts of biodiesel (1 ton) and glycerin (0.11564 ton): 0.89634 vs. 0.10365.

Therefore for example, for 1 gallon of biodiesel produced from tallow, the allocated GHG emission was:

\[
\frac{820.41 \text{ kg CO}_2 \text{ eq}}{\text{ton BioD}} \times \frac{1 \text{ ton BioD}}{297.654 \text{ gal BioD}} \times \frac{1000g}{1kg} \times 0.89634 = 2470.54 \text{ g CO}_2 \text{ eq/gal}
\]

\( \text{Sander and Murphy (2010)} \)

According to Table 4 in Sander and Murphy (2010), the CO\(_2\) emission was -20.90 and 135.71 kg CO\(_2\)/1,000 MJ algae biodiesel for filter press and centrifuge options. After subtracting the CO\(_2\) emission associated with biodiesel distribution (0.66 kg CO\(_2\)/1,000 MJ algae biodiesel), the total CO\(_2\) emission was -21.56 and 135.05 kg CO\(_2\)/1,000 MJ algae biodiesel, respectively. By assuming the energy content of neat biodiesel being 118,296 Btu/gal BioD (16.87 MJ/lb BioD), the converted values are:
**Filter press:**  
\[
\text{Filter press: } -21.56 \frac{\text{kg} \ CO_2}{\text{kMJ BioD}} \times \frac{1 \ \text{kMJ}}{1000 \ \text{MJ}} \times 16.87 \frac{\text{MJ}}{\text{lb BioD}} \times \frac{7.4 \ \text{lb BioD}}{1 \ \text{gal BioD}}
\]

\[
= -2,691.51 \ \text{g} \ CO_2 \ \text{eq/gal}
\]

**Centrifuge:**  
\[
\text{Centrifuge: } 135.05 \frac{\text{kg} \ CO_2}{\text{kMJ BioD}} \times \frac{1 \ \text{kMJ}}{1000 \ \text{MJ}} \times 16.87 \frac{\text{MJ}}{\text{lb BioD}} \times \frac{7.4 \ \text{lb BioD}}{1 \ \text{gal BioD}}
\]

\[
= 16,859.37 \ \text{g} \ CO_2 \ \text{eq/gal}
\]

*Frank et al. (2012)*

Figure 5 in Frank et al. (2012) summarizes the “well-to-pump” GHG emission for algae biodiesel production (-25,441 g CO$_2$ eq/MMBtu of biodiesel). By assuming a mass-based allocation factor of 0.885 and an energy content of 118,296 Btu/gal for biodiesel, the energy consumption is converted as following:

\[
-25,441 \ \frac{\text{g} \ CO_2 \ \text{eq}}{\text{1 MMBtu - BioD}} \times \frac{118,296 \times 10^{-6} \ \text{MMBtu}}{1 \ \text{gal BioD}} \times 0.885 = -2,663.47 \ \text{g} \ CO_2 \ \text{eq/gal}
\]

*Stephenson et al. (2010)*

Table 4 and 5 in Stephenson et al. (2010) summarize the GHG emission for algae biodiesel production with open pond (713 kg CO$_2$ eq/ton BioD) and PBR systems (11,919 kg CO$_2$ eq/ton BioD). The unit conversion was performed as following:

\[
\text{OP: } 713 \ \frac{\text{kg} \ CO_2 \ \text{eq}}{\text{ton BioD}} \times \frac{1 \ \text{ton}}{1,000,000 \ \text{g}} \times \frac{454 \ \text{g}}{1 \ \text{lb}} \times \frac{7.4 \ \text{lb BioD}}{1 \ \text{gal BioD}} \times \frac{1,000 \ \text{g}}{1 \ \text{kg}} = 2,395.39 \ \text{g} \ CO_2 \ \text{eq/gal}
\]

\[
\text{PBR: } 11,919 \ \frac{\text{kg} \ CO_2 \ \text{eq}}{\text{ton BioD}} \times \frac{1 \ \text{ton}}{1,000,000 \ \text{g}} \times \frac{454 \ \text{g}}{1 \ \text{lb}} \times \frac{7.4 \ \text{lb BioD}}{1 \ \text{gal BioD}} \times \frac{1,000 \ \text{g}}{1 \ \text{kg}}
\]

\[
= 40,043.07 \ \text{g} \ CO_2 \ \text{eq/gal}
\]
Sheehan et al., 1998

Figure 96 and 114 in Sheehan et al. (1998) show the life cycle CO₂ and CH₄ emission for petroleum diesel. It is noteworthy that although the life cycle GHG emission of petroleum diesel was high (638.35 g CO₂ eq/bhp-h), most of it was from the consumption stage (CO₂ release from tailpipe). If the CO₂ release from tailpipe was excluded, the GHG emission of petroleum diesel production was 90.33 g CO₂ eq/bhp-h. As the amount of petroleum diesel needed to produce 1 bhp-h was approximately 0.172 kg (pp. 213 of Sheehan et al., 1998), the GHG emission after unit conversion was approximately 1,647.59 g CO₂ eq/gal (11,643.86 g CO₂ eq/gal, if the combustion stage was included).
Figure S2.5. Energy inputs and outputs (MJ/gal) from baseline (sample) calculation.
Figure S2.6. Life cycle energy consumption by utility and material consumption (sample calculation)
Table S2.12. Data of raw trap grease composition from references

<table>
<thead>
<tr>
<th>FOG (%)</th>
<th>Water (%)</th>
<th>Solids (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>95.00</td>
<td>2.00</td>
<td>S18</td>
</tr>
<tr>
<td>3.00</td>
<td>90.00</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>99.20</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>5.60</td>
<td>87.70</td>
<td>6.60</td>
<td>S19</td>
</tr>
<tr>
<td>9.20</td>
<td>74.20</td>
<td>16.60</td>
<td></td>
</tr>
<tr>
<td>19.60</td>
<td>67.60</td>
<td>13.60</td>
<td></td>
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<tr>
<td>57.50</td>
<td>12.50</td>
<td>30.00</td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>90.00</td>
<td>7.00</td>
<td>S20</td>
</tr>
<tr>
<td>4.00</td>
<td>86.00</td>
<td>10.00</td>
<td>S21</td>
</tr>
<tr>
<td>12.20</td>
<td>81.50</td>
<td>6.34</td>
<td>S22</td>
</tr>
<tr>
<td>49.30</td>
<td>40.50</td>
<td>10.20</td>
<td></td>
</tr>
<tr>
<td>62.50</td>
<td>15.54</td>
<td>21.96</td>
<td>S23</td>
</tr>
<tr>
<td>20.00</td>
<td>46.00</td>
<td>34.00</td>
<td>S24</td>
</tr>
<tr>
<td>19.00</td>
<td>49.00</td>
<td>31.00</td>
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</tr>
<tr>
<td>5.00</td>
<td>90.00</td>
<td>5.00</td>
<td>S25</td>
</tr>
<tr>
<td>12.41</td>
<td>81.70</td>
<td>5.89</td>
<td></td>
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<tr>
<td>4.00</td>
<td>84.00</td>
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</tr>
<tr>
<td>10.00</td>
<td>75.00</td>
<td>15.00</td>
<td>S27</td>
</tr>
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<td>5.00</td>
<td>90.00</td>
<td>5.00</td>
<td>S1</td>
</tr>
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<td>3.96</td>
<td>95.05</td>
<td>0.99</td>
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<td>95.00</td>
<td>0.00</td>
<td>S29</td>
</tr>
<tr>
<td>3.00</td>
<td>95.00</td>
<td>2.00</td>
<td>S30</td>
</tr>
<tr>
<td>0.26</td>
<td>97.63</td>
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<td></td>
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<tr>
<td>0.50</td>
<td>92.17</td>
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<tr>
<td>0.40</td>
<td>92.02</td>
<td>7.58</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>99.56</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>97.13</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>95.00</td>
<td>3.00</td>
<td>S32</td>
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<tr>
<td>3.10</td>
<td>89.40</td>
<td>7.50</td>
<td>S33</td>
</tr>
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</table>

\(n=29\)

*Personal communication*

Table S2.13. Data of FFA concentration from references

<table>
<thead>
<tr>
<th>FFA</th>
<th>Oil</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.02%</td>
<td>25.98%</td>
<td>S18</td>
</tr>
<tr>
<td>58.39%</td>
<td>41.61%</td>
<td>S34</td>
</tr>
<tr>
<td>97.67%</td>
<td>2.33%</td>
<td>S19</td>
</tr>
<tr>
<td>56.84%</td>
<td>43.16%</td>
<td></td>
</tr>
<tr>
<td>3.63%</td>
<td>96.37%</td>
<td></td>
</tr>
<tr>
<td>50.40%</td>
<td>49.60%</td>
<td>S35</td>
</tr>
<tr>
<td>Ini. FFA (wt%)</td>
<td>MeOH-to-FOG Mass Ratio</td>
<td>H2SO4-to-FOG (wt%)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>2.99</td>
<td>0.207</td>
<td>0.150&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5.00</td>
<td>0.288</td>
<td>0.625</td>
</tr>
<tr>
<td>8.13</td>
<td>0.347</td>
<td>1.000</td>
</tr>
<tr>
<td>8.50</td>
<td>0.235</td>
<td>2.500</td>
</tr>
<tr>
<td>8.80</td>
<td>0.345</td>
<td>0.037</td>
</tr>
<tr>
<td>10.00</td>
<td>0.115</td>
<td>1.000</td>
</tr>
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<td>11.90</td>
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<td>0.500</td>
</tr>
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<td>14.00</td>
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<td>14.90</td>
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<td>0.998</td>
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<td>0.253</td>
<td>1.013</td>
</tr>
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<td>0.350</td>
<td>2.044</td>
</tr>
<tr>
<td>20.00</td>
<td>0.254</td>
<td>1.000</td>
</tr>
<tr>
<td>22.33</td>
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<td>0.728</td>
</tr>
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<td>23.20</td>
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<td>0.749</td>
</tr>
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<td>33.30</td>
<td>0.522</td>
<td>0.999</td>
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<td>35.00</td>
<td>0.726</td>
<td>1.999</td>
</tr>
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<td>37.96</td>
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<td>4.001</td>
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<td>39.60</td>
<td>0.987</td>
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</tr>
<tr>
<td>96.20</td>
<td>0.200&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.762</td>
</tr>
<tr>
<td>98.00</td>
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<td>0.588</td>
</tr>
<tr>
<td>100.00</td>
<td>2.250</td>
<td>5.000</td>
</tr>
</tbody>
</table>

<sup>a</sup>: these data points were obvious outliers and thus were not included in regression for the MeOH-to-Oil mass ratio
<sup>b</sup>: these data points were obvious outliers and thus were not included in regression for the H2SO4-to-Oil (wt%)
<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Distribution</th>
<th>Unit</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOG concentration in raw trap grease</td>
<td>Weibull</td>
<td>%</td>
<td>Shape: 0.6917</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scale: 8.585</td>
</tr>
<tr>
<td>FFA concentration in separated FOG</td>
<td>Logistic</td>
<td>%</td>
<td>Location: 0.6208</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scale: 0.1576</td>
</tr>
<tr>
<td>VS concentration in solids</td>
<td>Uniform</td>
<td>%</td>
<td>Min: 88%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Max: 99%</td>
</tr>
<tr>
<td>Electricity for mixing in AD</td>
<td>Triangular</td>
<td>kWh/kg VS</td>
<td>Min: 0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Max: 0.122</td>
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<td></td>
<td></td>
<td></td>
<td>Mode: 0.1</td>
</tr>
<tr>
<td>Heating for AD</td>
<td>Triangular</td>
<td>MJ/kg VS</td>
<td>Min: 2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Max: 3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mode: 2.7</td>
</tr>
<tr>
<td>CH$_4$ generation rate</td>
<td>Triangular</td>
<td>L/g VS</td>
<td>Min: 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Max: 0.4</td>
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<td></td>
<td></td>
<td></td>
<td>Mode: 0.3</td>
</tr>
<tr>
<td>CHP electric efficiency</td>
<td>Triangular</td>
<td>%</td>
<td>Min: 28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Max: 38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mode: 33</td>
</tr>
</tbody>
</table>
Appendix S-9: Explanation of the “TG LC ENER+GHG model”

Nomenclature:

Complete Monte Carlo Simulation: simultaneously generate random value from the cumulative density function of each key variable (e.g. FOG concentration in raw trap grease) and perform the calculation of life cycle energy consumption and GHG emission.

Sensitivity Analysis: Generate random value from the cumulative density function of one key variable while hold the value of other key variables constant and perform the calculation of life cycle energy consumption and GHG emission.

Nominal case: the calculation is performed based on constant values for the key variables, such as FOG concentration in raw trap grease, FFA concentration in FOG, CH₄ generation rate in the anaerobic digester, etc.

Scope and system boundary of the model

The scope of the study is “cradle-to-gate” and the system boundary includes (1) raw trap grease acquisition, (2) FOG extraction and (3) pre-treatment, (4) biodiesel production, and (5) waste disposal. The potential energy saving opportunities at the WWTP, such as energy co-generation by an anaerobic digester (AD), exhaust heat utilization, etc., are incorporated as alternative scenarios.

The function of the model: estimate the life cycle energy consumption (MJ/gal) and GHG emission (g CO₂ eq/gal) for the trap grease-to-biodiesel process.

Structure of the model:
Frontend User Module

Frontend User Module contains the class “Sensi_MC_and_complete_MC” which calls the Main Code Module by its initialization method “__init__”. This class contains methods for the users to run the Monte Carlo simulation (“exe_complete_MC”) and sensitivity analysis (“exe_sensi”) for the life cycle energy consumption and GHG emission. The user can plot and save the figures of the result by using the method “plot_results_sensi” and “plot_results_completeMC”. The user can also calculate the life cycle energy consumption and GHG emission for the nominal case with constant values for the key variables (method “nominalcheck”). The details of the nominal case are shown in the later section.

Main Code Module

The Main Code Module contains the class “TG_LC” which calls five modules: Constants Module, Distribution Module, Regression Module, Allocation Module and Update Module. This class contains the method for determining the initial composition of the raw trap grease (“rawTG_composition”), the method for each stage of the trap grease-to-
biodiesel life cycle, the method for allocation (“allocation”), and the method to normalize
the result to desired units (“wrapup”).

- Constants Module

  The Constants Module contains the value of the constants (e.g. density, energy content,
  GHG emission factors) used for the calculation

- Distribution Module

  The Distribution Module contains the class “Distribution” which contains the methods
  for generating random numbers from a given distribution (e.g. Weibull distribution for
  FOG concentration in the raw trap grease) for the key variables.

- Regression Module

  The Regression Module contains the class “Regression” which contains the methods for
  calculating the value for certain dependent variables based on a given regression, such as
  the regression equation for determining water concentration in the raw trap grease based
  on its relationship with the FOG concentration.

- Allocation Module

  The Allocation Module contains the class “Allocation” which contains the allocation
  method for each stage of the trap grease-to-biodiesel life cycle.

- Update Module

  The Update Module contains the class “Update” which contains the method to update the
  values of material consumption, energy consumption and GHG emission for each stage
  of the trap grease-to-biodiesel life cycle. This class also contains the method to update the
  value of a certain component (e.g. FOG mass) for each stage of the trap grease-to-
  biodiesel life cycle.
How to use the model

Step 1:
Create an object by instantiate from the class “Sensi_MC_and_complete_MC” in the Frontend User Module. The class requires the input of argument for four parameters, i.e. mass of raw trap grease, number of variables for sensitivity analysis, number of runs for Monte Carlo simulation, on/off switch for Monte Carlo simulation, on/off switch for anaerobic digestion. See example below:

```python
test1=Sensi_MC_and_complete_MC(100000,7,10000,True,True)
```

Where:
- Test1: the name of the object created from the class “Sensi_MC_and_complete_MC”
- Input arguments (from left to right in the parenthesis of the class): mass of raw trap grease=100,000 lbs; number of variables for sensitivity analysis=7; number of runs for Monte Carlo simulation=10000; Monte Carlo simulation=True; Anaerobic digestion included in the simulation=True

Step 2:

To perform a complete Monte Carlo simulation, see example below:

```python
test1.exe_complete_MC()
```

To perform a sensitivity analysis, see example below:

```python
test1.exe_sensi()
```

To perform a nominal case calculation, see example below:
test1.nominalcheck()

* Note: when execute the “nominalcheck” method, the parameter of “on/off switch for Monte Carlo simulation” will be automatically given an argument of “False”, that is, no Monte Carlo simulation will be performed for the nominal case calculation.

Step 3:

To plot the figures for the results, such as the empirical cumulative density function plots or boxplots, see example below:

For the results of the complete Monte Carlo simulation:

    test1.plot_results_completeMC()

For the results of the sensitivity analysis:

    test1.plot_results_sensi()

**Table S2.16.** Details of the key variables used for nominal case and Monte Carlo/sensitivity analysis calculations

<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Unit</th>
<th>Nominal case</th>
<th>Monte Carlo simulation or Sensitivity analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Distribution</td>
</tr>
<tr>
<td>FOG concentration in raw trap grease</td>
<td>%</td>
<td>4.23</td>
<td>Weibull</td>
</tr>
<tr>
<td>FFA concentration in separated FOG</td>
<td>%</td>
<td>66.33</td>
<td>Logistic</td>
</tr>
<tr>
<td>VS concentration in solids</td>
<td>%</td>
<td>94</td>
<td>Uniform</td>
</tr>
<tr>
<td>Electricity for mixing in AD</td>
<td>kWh/kg VS</td>
<td>0.1</td>
<td>Triangular</td>
</tr>
<tr>
<td>Heating for AD</td>
<td>MJ/kg VS</td>
<td>2.7</td>
<td>Triangular</td>
</tr>
</tbody>
</table>
The concentrations of water, solids and FOG in the raw trap grease vary from case to case. The composition of the raw trap grease is largely affected by the frequency of the grease cleaning. The more frequently maintained grease trap will have less FOG in the raw trap grease. A comprehensive search was conducted for this study to gather data of the raw trap grease composition. Twenty-nine data points were collected from peer-reviewed papers, reports, and personal communication with professionals in the industry. The Goodness of Fit test was performed in MiniTab® 17 to find a best-fit distribution to represent the data and to be used for Monte Carlo simulation. The results showed that Weibull distribution possessed the highest $p$-value (0.22) and hence it was selected as the best distribution to represent the FOG concentration in the raw trap grease. Figure S2.7 shows empirical cumulative density function (ECDF) fitting of the 29 data points by using Weibull distribution. As the concentration of water is derived based on concentration of FOG from the regression model, algorithm was developed to limit the random values generated from Weibull distribution within in a certain range such that the values of the concentrations for FOG, water and solids were all within the physically meaningful range (0%≤FFA concentration≤100%). Likewise, the Goodness of Fit test was performed for FFA concentration in separated FOG based on 16 data points collected from literature and personal communication. According to the $p$-values, Logistic distribution (>0.25) was selected as the distribution for FFA concentration in separated FOG for the Monte Carlos simulation. Figure
S2.8 shows the ECDF of Logistic distribution for 16 FFA concentration data points. It is noteworthy that the fitting curve extrapolated beyond the two limits, i.e., 0% and 100%, which required truncation to limit the random values generated by this distribution within the physically meaningful range. In addition, the VS concentration in solids was assumed to follow a uniform distribution. Triangular distribution was used to generate the values of operational parameters for the AD, as indicated by Sills et al., 2012.

**Figure S2.7.** ECDF of FOG concentration in raw trap grease
**Figure S2.8.** ECDF of FFA concentration in separated FOG
Figure S2.9. An example of cumulative density function plot (SAS, 2010)
References

S1. C. van Keppel, personal communication.


S23. Whole-cell biocatalysts for producing biodiesel from waste greases, 


S25. Evaluating the profitability of a trap effluent dewatering facility in the Raleigh area, 


S27. K. Ruhmer, personal communication.

S28. V. Karri, personal communication.

S29. R. Robin, personal communication.


2.10 Code of the “TG LC ENER+GHG model” and the associated modules

Constants module (“constants.py”)

This module contains all the constants that may be used in different stages of the life cycle model.

class Constants():
    def __init__(self):
        # Density Constants
        self.den_FOG = 7.5 #lb/gal
        self.den_water = 8.34 #lb/gal
        self.den_solids = 13.4 #lb/gal
        self.den_CH4 = 0.66 #g/L
        self.den_FAME = 7.4 #lb/gal

        # Energy Constants
        self.embeddedenergy_NG = 45.75 #MJ/kg
        self.embeddedenergy_elect = 3.6 #MJ/kWh
        self.embeddedenergy_CH4 = 53.38 #MJ/kg
        self.LCenergy_NG = 49.09 #MJ/kg
        self.LCenergy_elect = 7.4 #MJ/kWh
        self.LCenergy_MeOH = 32.95 #MJ/kg
        self.LCenergy_H2SO4 = -2.44 #MJ/kg
        self.LCenergy_NaOH = 1.5 #MJ/kg
        self.energycontent_FAME = 16.87 #MJ/lb
        self.LCenergy_NaOCH3 = 31.7 #MJ/kg
        self.LCenergy_HCl = 1.7 #MJ/kg
        self.LCenergy_diesel = 160.65 #MJ/gal
        self.FOGRecoveryFactor = 2.1/2.6
        self.glycerinpurity = 0.8

        # Molecular Weight
        self.MW_FFA = 278 #g/mol
        self.MW_oil = 872 #g/mol
        self.MW_FAME = 292 #g/mol
        self.MW_MeOH = 32.04 #g/mol
        self.MW_H2SO4 = 98 #g/mol
        self.MW_NaOH = 40 #g/mol
        self.MW_gly = 92.09 #g/mol

        # Other Constants
        self.water_specific_heat = 4.1813 #J/(g.k)
self.FOG_specific_heat=1.67 #J/(g.k)
self.water_latent_heat=2260 #J/g

# Conversion constants
self.Joule2Btu=0.00094781712 #Btu/J
self.Btu2MJ=0.0010551 # MJ/Btu
self.lb2gram = 454 #g/lb
self.tonne2lb = 2204.62 #lb/metric ton (2000 lb/short ton)
s self.kWh2MJ=3.6 #MJ/kWh

# GHG Constants
self.GHG_MeOH=1.25 #g CO2-eq/g; ISCC 2011 (Euro data)
self.GHG_NaOH=0.47 #g CO2-eq/g; ISCC 2011 (Euro data)
self.GHG_H2SO4=0.21 #g CO2-eq/g; ISCC 2011 (Euro data)
self.GHG_HCl=0.75 #g CO2-eq/g; ISCC 2011
self.GHG_diesel=3.6239832421 #g CO2-eq/g (including combustion); sheehan et al., 1998
self.GHG_NaOCH3=2.208 #g CO2-eq/g; Edwards et al., 2012 (Euro data)
self.GHG_elect=881.59 #g CO2-eq/kWh; UC GHG paper (Ohio grid)
self.GHG_NG=3.37 #g CO2-eq/g; UC GHG paper
**Distribution module (MCdistributions.py)**

This module contains all the cdf distributions and corresponding equations for Monte Carlo simulation.

```
import random, numpy

class Distribution():

    def D_Weibull(self, scale, shape):
        self.W_scale = scale  
        self.shape = shape
        #this is supposed to generate the value of FOG %, e.g. 5 for 5%
        self.Weibull_output = random.weibullvariate(self.W_scale, self.shape)

    def D_Logistic(self, scale, location):
        self.L_scale = scale
        self.location = location
        #this is supposed to generate the FFA %, e.g. 0.05 for 5%
        self.Logistic_output = numpy.random.logistic(self.location, self.L_scale)

    def D_Triangular(self, minimum, maximum, mode):
        self.minimum = minimum
        self.maximum = maximum
        self.mode = mode
        self.Trianguler_output = random.triangular(self.minimum, self.maximum, self.mode)

    def D_Uniform(self, minimum, maximum):
        self.U_min = minimum
        self.U_max = maximum
        self.Uniform_output = random.uniform(self.U_min, self.U_max)
```
Regression module ("regression.py")

This module contains regression equations for material dosage and utility use

from math import log, exp

class Regression():
    each method represents one regression equation
    
    def __init__(self):
        Initiate the constants (e.g. slope and intercept) for regression equations
        
        self.water_conc_slope=-1.3575
        self.water_conc_intecept=94.56
        self.MeOH_FOG_massratio_slope=0.0214
        self.H2SO4_FOG_massratio_slope=0.9656
        self.H2SO4_FOG_massratio_intecept=-1.0827

    def raw_TG_comp (self, FOG_conc):
        #_conc means input absolute number of the percentage, e.g. 4 for 4%
        self.FOG_conc=FOG_conc
        self.water_conc=self.FOG_conc*self.water_conc_slope+self.water_conc_intecept
        self.solids_conc=100-self.FOG_conc-self.water_conc

    def MeOH_FOG_massratio (self, FFA_conc): #for esterification stage
        #_conc means input absolute number of the percentage, e.g. 4 for 4%
        self.FFA_conc=FFA_conc
        self.MeOH_r=self.FFA_conc*MeOH_FOG_massratio_slope #MeOH-to-FOG mass ratio

    def H2SO4_FOG_massratio (self, FFA_conc): #for esterification stage
        #_conc means input absolute number of the percentage, e.g. 4 for 4%
        self.FFA_conc=FFA_conc
        self.H2SO4_r=(log(self.FFA_conc)*H2SO4_FOG_massratio_slope \ 
                      +self.H2SO4_FOG_massratio_intecept)/100 #H2SO4-to-FOG mass ratio, converted to decimal
Allocation module ("allocation_factors.py")

This module contains methods for calculating the allocation factor for each stage

```python
class Allocation():
    def __init__(self, FOG_rawTG, FOG_recovered, solids_rawTG,FAME_esteri,oil_esteri, FAME_trans, glycerin, FOG_rec=2.1/2.6):
        self.FOG_rawTG=FOG_rawTG #mass of FOG in the raw TG
        self.solids_rawTG=solids_rawTG #mass of solids in the raw TG
        self.R_raw=self.FOG_rawTG/(self.FOG_rawTG+self.solids_rawTG)#wt% of FOG in the raw FOG-solids mixture
        self.FAME_esteri=FAME_esteri #mass of FAME generated at the end of esterification stage
        self.oil_esteri=oil_esteri #mass of oil at the end of esterification stage
        self.R_esteri=self.FAME_esteri/(self.FAME_esteri+self.oil_esteri) #wt% of biodiesel (esters) in the ester-oil mixture
        self.R_FOG_rec=FOG_rec #FOG recovery factor
        self.FAME_trans=FAME_trans
        self.glycerin_trans=glycerin
        self.F_trans=self.FAME_trans/(self.FAME_trans+self.glycerin_trans)#allocation factor between biodiesel and glycerin at the end of the transesterification stage
        self.FOG_recovered=FOG_recovered #mass of FOG recovered at the end of separation stage
        self.FOG_loss=self.FOG_rawTG
        self.R_recovered=self.FOG_recovered/(self.FOG_recovered+self.solids_rawTG)#wt% of FOG in the recovered FOG-solids mixture (including lost FOG for mass balance)
        self.F_waste_transport=1
        self.F_AD=1
        self.F_esteri=1
        self.R_lossFOG=self.FOG_loss/(self.FOG_loss+self.FOG_recovered+self.solids_rawTG) #wt% of lost FOG in the FOG-solids mixture (including lost FOG for mass balance)

def allocation_raw_transport (self):
    #allocation factor with respect to FAME for the transportation of raw TG stage
    #allocation factor with respect to solids
    self.f_raw_transport_solids=1-self.R_raw
    #allocation factor with respect to glycerin (gonna happen in transesterification stage)
    #allocation factor with respect to lost FOG (gonna happen in FOG separation stage)
    self.f_raw_transport_lostFOG=self.R_raw*(1-self.R_FOG_rec)
    #all four allocation factors should add up exactly to 1

def allocation_FOG_separation(self):
    #allocation factor with respect to FAME for the FOG separation stage
    self.f_separation_FAME=self.R_recovered*self.R_esteri+ \
```

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# allocation factor with respect to solids
# allocation factor with respect to glycerin (gonna happen in transesterification stage)
# allocation factor with respect to lost FOG
self.F_separation_lostFOG=self.R_lossFOG # allocation factor for lost FOG
# all three allocation factors should add up exactly to 1
Update module ("update.py")

This module updates the following key variables for each stage of the life cycle:

key variables:
- usage of each type of energy
- LC energy consumption from use of energies
- LC energy consumption from use of chemicals
- LC GHG emission from use of energies
- LC GHG emission from use of chemicals

import constants

class Update():

def __init__(self):
    self.Up_constants=constants.Constants()
    # initialize quantity related variables
    self.Q_diesel=[None]*6
    self.Q_NG=[None]*6
    self.Q_elect=[None]*6
    # initialize LC energy consumption related variables
    self.LCenergy_con_diesel=[None]*6
    self.LCenergy_con_NG=[None]*6
    self.LCenergy_con_elect=[None]*6
    self.LCenergy_con_chemicals=[None]*6
    # initialize LC GHG emission related variables
    self.LCGHG_diesel=[None]*6
    self.LCGHG_NG=[None]*6
    self.LCGHG_elect=[None]*6
    self.LCGHG_chemicals=[None]*6
    # initialize components
    self.m_FOG=[None]*6
    self.m_water=[None]*6
    self.m_solids=[None]*6
    self.m_FFA=[None]*6
    self.m_oil=[None]*6
    self.m_FAME=[None]*6
    self.vol_FOG=[None]*6
    self.vol_water=[None]*6
    self.vol_solids=[None]*6
    self.vol_FFA=[None]*6
    self.vol_oil=[None]*6
    self.vol_FAME=[None]*6
def update_key(self, stage_num, diesel_con, NG_con, elect_con, LCEnergy_chemicals, \
    LCGHG_chemicals):
    """
    this method takes in the consumption of:
    -diesel, gal
    -NG, kg
    -electricity, kWh
    -LCEnergy consumtion associated with chemical use, MJ
    -LC GHG emission associated with chemical use, g CO2-eq
    and updates the relevant variables
    
    Note: algorithm is different for AD stage (Stage_num=5)
    """
    self.Q_diesel[stage_num-1]=diesel_con
    self.Q_elect[stage_num-1]=elect_con
    self.Q_NG[stage_num-1]=NG_con
    self.LCenergy_con_diesel[stage_num-1]=diesel_con*self.Up_constant.LCenergy_diesel
    self.LCenergy_con_elect[stage_num-1]=elect_con*self.Up_constant.LCenergy_elect
    self.LCenergy_con_NG[stage_num-1]=NG_con*self.Up_constant.LCenergy_NG
    self.LCenergy_con_chemicals[stage_num-1]=LCEnergy_chemicals
    self.LCGHG_elect[stage_num-1]=elect_con*self.Up_constant.GHG_elect
    self.LCGHG_NG[stage_num-1]=NG_con*1000*self.Up_constant.GHG_NG
    self.LCGHG_chemicals[stage_num-1]=LCGHG_chemicals

def update_components (self,stage_num, m_FOG, m_water, m_solids, m_FFA, m_oil, m_FAME):
    """
    this method updates the mass (lb) and vol (gal) of FOG, water, solids, FFA and oil
    in each stage
    
    the method takes in the mass of each component and calculate the corresponding
    volumes
    
    Note:
    1) to avoid confusion, "oil" refers to the part of the FOG that is not FFA
    2) for components, "na" means this specific component is either no longer used in following
    stages or its value is not known at this stage (e.g. m_FFA in the stages before esterification)
    for example, m_FOG becomes "na" after separation stage (m_oil starts to become numerical instead)
    """
    self.m_FOG[stage_num-1]=m_FOG
    self.m_water[stage_num-1]=m_water
    self.m_solids[stage_num-1]=m_solids
self.m_FFA[stage_num-1]=m_FFA
self.m_oil[stage_num-1]=m_oil
self.m_FAME[stage_num-1]=m_FAME

#calculate correspondin vol (vol of FFA and oil is not needed)
if self.m_FOG[stage_num-1]=="na":
    self.vol_FOG[stage_num-1]=self.m_FOG[stage_num-1]
else:
    self.vol_FOG[stage_num-1]=self.m_FOG[stage_num-1]/self.Up_constants.den_FOG

if self.m_water[stage_num-1]=="na":
    self.vol_water[stage_num-1]=self.m_water[stage_num-1]
else:
    self.vol_water[stage_num-1]=self.m_water[stage_num-1]/self.Up_constants.den_water

if self.m_solids[stage_num-1]=="na":
    self.vol_solids[stage_num-1]=self.m_solids[stage_num-1]
else:
    self.vol_solids[stage_num-1]=self.m_solids[stage_num-1]/self.Up_constants.den_solids

if self.m_FAME[stage_num-1]=="na":
    self.vol_FAME[stage_num-1]=self.m_FAME[stage_num-1]
else:
    self.vol_FAME[stage_num-1]=self.m_FAME[stage_num-1]/self.Up_constants.den_FAME
Main module ("TG_LC_EnergyandGHG_main_code.py")
# This is the main body of the model

This model is used to quantify the life cycle energy consumption and GHG emission from the trap grease-to-biodiesel life cycle.

import random, constants, allocation_factors, MCdistributions, regression, \update, numpy, scipy

class TG_LC():
    def __init__(self, ini_raw_TG_mass): # asks for input of raw TG mass

        # initialize the modules
        self.constants=constants.Constants()
        self.MCdistributions=MCdistributions.Distribution()
        self.regression=regression.Regression()
        self.update=update.Update()

        # take in raw TG mass and initialize raw TG vol
        self.raw_TG_mass=ini_raw_TG_mass
        self.raw_TG_vol=None

        # initialize MC_flag
        self.MC_flag=False

        # initialize raw TG composition
        self.FOG_percent=None
        self.solids_percent=None
        self.water_percent=None
        self.FFA_percent=None
        self.oil_percent=None

        self.FFAmass=None
        self.oilmass=None
        self.FAMEmass=None
        self.FOGmass=None
        self.watermass=None
        self.solidsmass=None
        self.FOGvol=None
        self.watervol=None
        self.solidsvol=None

        # initialize transporation-related variables
        self.truckvol=None
        self.diesel_use_per_gal_load=None
        self.distance_raw_TG=None
        self.distance_wastesolids=None
        self.mpg=None
        self.diesel_use_raw_TG=None
# initialize process energy output
self.P_energy_output=[None]*6

def rawTG_composition(self, MC_flag):
    self.MC_flag=MC_flag
    if not self.MC_flag:
        self.FOG_percent=0.0423 #4.23 wt%
        self.solids_percent=0.0942 #9.42 wt%
        self.water_percent=0.8635 #86.35 wt%
    else:
        self.check_converge_comp=None
        while self.check_converge_comp!=1 or self.FOG_percent<0 or self.water_percent<0 or
            self.solids_percent<0:
            #keep loop until the sum of % of three components equal to 1 and no negative value is generated
            self.MCdistributions.D_Weibull(8.5855,0.69173)
            # the D_Weibull method generates absolute value of FOG%
            self.FOG_percent=self.MCdistributions.Weibull_output/100
            self.regression.raw_TG_comp(self.FOG_percent*100)
            # the regression accepts and outputs absolute values
            self.water_percent=self.regression.water_conc/100
            self.solids_percent=self.regression.solids_conc/100
            self.check_converge_comp=self.FOG_percent+self.water_percent+self.solids_percent
            self.FOGmass=self.FOG_percent*self.raw_TG_mass #lb
            self.watermass=self.water_percent*self.raw_TG_mass #lb
            self.solidsmass=self.solids_percent*self.raw_TG_mass #lb
            self.FOGvol=self.FOGmass/self.constants.den_FOG #gal
            self.watervol=self.watermass/self.constants.den_water #gal
            self.solidsvol=self.solidsmass/self.constants.den_solids #gal
            self.raw_TG_vol=self.FOGvol+self.watervol+self.solidsvol #gal

    # 1st stage: raw TG transportation, no MC option for now
    def rawTG_transport(self, stage_num=1, distance=197.4, MPG = 6.5, truckvol = 3600):
        truck for transporting the raw TG: volume=3600 gal/load, mpg=6.5
        average distance=restaurant<->hauler's holding facility<->WWTP

diesel_use_per_gal_load=distance/MPG/truckvol #gal
    # total diesel consumption for transporting the raw trap grease
    self.diesel_use_raw_TG=stage_num*100
            #update the key variables
            self.update.update_key(1,self.diesel_use_raw_TG,0,0,0,0)
# update the components
self.update.update_components(1, self.FOGmass, self.watermass, \
    self.solidsmass, "na", "na", "na")

# update process energy output
self.P_energy_output[stage_num-1]=0

# 2nd stage: FOG separation (multiple steps involved), no MC option for now; update of key variables and components is performed in the "elect" step

def FOG_separation_dewater1 (self, temp_diff=79, water_decant_factor1=9.4/46.8, empirical_heatloss_factor=1.5):
    
    the first step in the FOG separation stage: remove majority of water by gravity settling (decanting) and 1st heating (to raise the temperature of the remaining mixture close to water boiling pt)

    # decanting and heating water
    self.vol_water_left_after_decant1=water_decant_factor1*self.watervol
    self.mass_water_left_after_decant1=self.vol_water_left_after_decant1*self.constants.den_water*self.constants.lb2gram # g of water
    self.heat_water_dewater1=self.mass_water_left_after_decant1*temp_diff*self.constants.water_specific_heat/1000000*empirical_heatloss_factor #MJ

    # heating FOG (assume no FOG loss during this step)
    self.heat_FOG_dewater1=self.FOGmass*self.constants.lb2gram*temp_diff*self.constants.FOG_specific_heat/1000000*empirical_heatloss_factor #MJ

    self.heat_total_dewater1=self.heat_water_dewater1+self.heat_FOG_dewater1 #MJ by heating
    self.heat_total_dewater1_inNG=self.heat_total_dewater1/self.constants.embeddedenergy_NG #kg NG

def FOG_separation_dewater2 (self, temp_diff=1, water_decant_factor2=0.5/46.8, empirical_heatloss_factor=1.5):
    
    # heating water to evaporate
    self.vol_water_left_after_decant2=water_decant_factor2*self.watervol
    self.mass_water_left_after_decant2=self.vol_water_left_after_decant2*self.constants.den_water*self.constants.lb2gram # g of water
    self.heat_water_dewater2_1=self.mass_water_left_after_decant2*temp_diff*self.constants.water_specific_heat/1000000*empirical_heatloss_factor #MJ
# evaporate water (latent heat)

```python
self.heat_water_dewater2_2 = self.mass_water_left_after_decant2 * self.constants.water_latent_heat / 1000000 * empirical_heatloss_factor  # MJ
```

# heating FOG (assume FOG recovery factor=2.1/2.6)

```python
self.mass_FOG_left_after_recovery = self.FOGmass * self.constants.lb2gram * self.constants.FOGRecoveryFactor  # g
```

```python
self.heat_FOG_dewater2 = self.mass_FOG_left_after_recovery * temp_diff * self.constants.FOG_specific_heat / 10000 * empirical_heatloss_factor  # MJ
```

```python
self.heat_total_dewater2 = self.heat_water_dewater2_1 + self.heat_water_dewater2_2 + self.heat_FOG_dewater2  # MJ by heating
```

```python
self.heat_total_dewater2_inNG = self.heat_total_dewater2 / self.constants.embeddedenergy_NG  # kg NG
```

```python
def FOG_separation_elect(self, stage_num=2, elect_use_cond_factor=1.23, elect_use_pump_factor=1200 / 1000000 * 0.12):
    # elect_use_cond_factor=1.23 kWh/tonne for water condensation; elect_use_pump_factor=total elect use for WWTP (1200 kWh/1 millio gal of wastewater treated)*12% for pumping wastewater
    # this step involves electricity consumption for: (1) the condensation of evaporated water by electric air-chiller;
    # and (2) pumping the components
    stage_num = 2
    # electricity consumption for condensation
    self.elect_cond_water = self.mass_water_left_after_decant2 / 1000000 * elect_use_cond_factor  # kWh
    self.elect_cond_water_inMJ = self.elect_cond_water * self.constants.kWh2MJ  # MJ

    # electricity consumption for pumping
    self.elect_pump_TG = self.raw_TG_vol / 1000000 * elect_use_pump_factor  # kWh
    self.elect_pump_TG_inMJ = self.elect_pump_TG * self.constants.kWh2MJ  # MJ

    self.elect_separate_total = self.elect_cond_water_inMJ + self.elect_pump_TG_inMJ  # MJ
```

# update the key variables

```python
self.update.update_key(2, 0, self.heat_total_dewater1_inNG + self.heat_total_dewater2_inNG, self.elect_cond_water + self.elect_pump_TG, 0, 0)
```

# update the components

```python
self.update.update_components(2, self.mass_FOG_left_after_recovery / self.constants.lb2gram, "na", self.solidsmass, "na", "na", "na")
```
# update process energy output
self.P_energy_output[stage_num-1]=0

# 3rd stage: esterification
def Esterification (self, MC_flag):
    self.MC_flag=MC_flag
    stage_num=3
    if not MC_flag:
        self.FFA_percent=0.6633 #66.33%
        self.oil_percent=1-self.FFA_percent
    else:
        self.check_converge_Esteri=None
        while self.check_converge_Esteri!=1 or self.FFA_percent<0 or self.oil_percent<0:
            # keep loop until the sum of FFA% and oil% equal to 1 and no negative value is generated
            self.MCdistributions.D_Logistic(0.1576,0.6208)
            # the D_Logistic method generates the FFA % (decimal), e.g. 0.05 for 5%
            self.FFA_percent=self.MCdistributions.Logistic_output # decimal
            self.oil_percent=1-self.FFA_percent
            self.check_converge_Esteri=self.FFA_percent+self.oil_percent

    # beginning composition
    self.FFAmass=self.FFA_percent*self.mass_FOG_left_after_recovery #g
    self.oilmass=self.oil_percent*self.mass_FOG_left_after_recovery #g
    self.FFAmole=self.FFAmass/self.constants.MW_FFA #mole
    self.oilmole=self.oilmass/self.constants.MW_oil #mole

    # after-esterification composition
    self.FAMEmass=self.FFAmole #mole
    self.FAMEmass=self.FAMEmole*self.constants.MW_FAME #g
    self.oilmass_after_esteri=self.oilmass/self.constants.lb2gram #lb

    # chemical consumption
    self.regression.MeOH_FOG_massratio(self.FFA_percent*100)# use the method to generate the attribute for MeOH-FOG mass ratio factor
    # the MeOH_FOG_massratio method takes in absolute value of the FFA%
    self.MeOH_input_esteri=self.regression.MeOH_r*self.mass_FOG_left_after_recovery/1000 #kg MeOH input
    (excessive)
    self.MeOH_con_esteri=self.FFAmole*self.constants.MW_MeOH/1000 #kg MeOH consumed
    self.MeOH_recovered_esteri=self.MeOH_input_esteri-self.MeOH_con_esteri #kg MeOH recovered
    self.regression.H2SO4_FOG_massratio(self.FFA_percent*100) # use the method to generate the attribute for H2SO4-FOG mass ratio (return in decimal)
    # the H2SO4_FOG_massratio method takes in absolute value of the FFA%
    self.H2SO4_con_esteri=self.regression.H2SO4_r*self.mass_FOG_left_after_recovery/1000 #kg H2SO4 consumed
self.NaOH_con_esteri = self.H2SO4_con_esteri * 1000 / self.constants.MW_H2SO4 * 2 * self.constants.MW_NaOH / 1000
# kg NaOH consumed

# energy consumption
self.NG_MeOHrecover_usageratio = 0.04 # kg NG/kg recovered MeOH
self.NG_heatingFOG_usageratio = 0.00464 # kg NG/kg FOG
self.elect_pumpingFOG_usageratio = 0.028 # kWh/kg FOG

self.elect_esteri = self.elect_pumpingFOG_usageratio * self.mass_FOG_left_after_recovery / 1000 # kWh
self.elect_esteri = self.elect_pumpingFOG_usageratio * self.mass_FOG_left_after_recovery / 1000 # kWh
self.elect_esteri = self.elect_pumpingFOG_usageratio * self.mass_FOG_left_after_recovery / 1000 # kWh
self.elect_esteri = self.elect_pumpingFOG_usageratio * self.mass_FOG_left_after_recovery / 1000 # kWh

self.NG_esteri_MeOHrecover = self.NG_MeOHrecover_usageratio * self.MeOH_recovered_esteri # kg NG
self.NG_esteri_heatingFOG = self.NG_heatingFOG_usageratio * self.MeOH_recovered_esteri # kg NG

# convert chemical consumption into corresponding LC energy consumption
self.LCenergy_con_MeOH_esteri = self.MeOH_con_esteri * self.constants.LCenergy_MeOH # MJ
self.LCenergy_con_H2SO4_esteri = self.H2SO4_con_esteri * self.constants.LCenergy_H2SO4 # MJ
self.LCenergy_con_NaOH_esteri = self.NaOH_con_esteri * self.constants.LCenergy_NaOH # MJ

# calculate LC GHG from chemical consumption
self.GHG_con_MeOH_esteri = self.MeOH_con_esteri * 1000 * self.constants.GHG_MeOH # g CO2-eq/
self.GHG_con_H2SO4_esteri = self.H2SO4_con_esteri * 1000 * self.constants.GHG_H2SO4 # g CO2-eq/
self.GHG_con_NaOH_esteri = self.NaOH_con_esteri * 1000 * self.constants.GHG_NaOH # g CO2-eq/

# update the key variables (make judgement if chemical LC energy and GHG emission need to be x2)
if self.FFA_percent > 0.15: # if initial FFA% is larger than 15%, double the material, energy and GHG emission
    self.update.update_key(3, 0, (self.NG_esteri_MeOHrecover + self.NG_esteri_heatingFOG) * 2, self.elect_esteri * 2, 
    (self.LCenergy_con_MeOH_esteri + self.LCenergy_con_H2SO4_esteri + self.LCenergy_con_NaOH_esteri) * 2, 
    (self.GHG_con_MeOH_esteri + self.GHG_con_H2SO4_esteri + self.GHG_con_NaOH_esteri) * 2)
else:
    self.update.update_key(3, 0, (self.NG_esteri_MeOHrecover + self.NG_esteri_heatingFOG) * 1, self.elect_esteri * 1, 
    (self.LCenergy_con_MeOH_esteri + self.LCenergy_con_H2SO4_esteri + self.LCenergy_con_NaOH_esteri) * 1, 
    (self.GHG_con_MeOH_esteri + self.GHG_con_H2SO4_esteri + self.GHG_con_NaOH_esteri) * 1)

# update the components
self.update.update_components(3, "na", "na", 
    self.solidsmass, 0, self.oilmass_after_esteri, self.FAMEmass / self.constants.lb2gram)

# update process energy output
self.P_energy_output[stage_num - 1] = self.FAMEmass * self.constants.energycontent_FAME # MJ
# 4th stage: transesterification, no MC option for this stage for now

def transesterification(self, stage_num=4, elect_usageratio_ref=0.013, NG_usageratio_ref=0.019,
MeOH_usageratio_ref=0.095, NaOCH3_usageratio_ref=0.018,
                      HCl_usageratio_ref=0.007): # all factors are converted into unit/kg FOG already

    this stage uses the dose of material and energy consumption from the average of Sheehan and Haas:
    - elect_usageratio_ref and NG_usageratio_ref are in Btu/lb soybean oil
    - chemical useageratio is in lb/lb soybean oil

    the issue of excessive MeOH and recovery is not explicitly handled because it is assume to be accounted
    for by the dose factors in the references

    stage_num=4
    # beginning composition
    self.oilmass_trans=self.oilmass_after_esteri # lb
    self.oilmole_trans=self.oilmass_trans*self.constants.lb2gram/self.constants.MW_oil # mole

    # after composition
    self.oilmass_after_trans=self.oilmass_trans*0.01 # lb, assume 1% unreacted
    self.FAMEmole_trans=self.oilmole_trans*3 # mole
    self.FAMEmass_trans=self.FAMEmole_trans*self.constants.MW_FAME # g
    self.FAMEmass_trans_99_percent=self.FAMEmass_trans*0.99, assume 99% production efficiency
    self.glycerinmole_trans=self.oilmole_trans # mole
    self.glycerinmass_trans=self.glycerinmole_trans*self.constants.MW_gly # g
    self.glycerinmass_trans_80_percent=self.glycerinmass_trans/0.80, assume 80% purifity

    # energy and chemical consumption factors
    self.elect_trans_usageratio=elect_usageratio_ref # kWh/kg FOG
    self.NG_trans_usageratio=NG_usageratio_ref # kg NG/kg FOG
    self.MeOH_trans_usageratio=MeOH_usageratio_ref # kg MeOH/kg FOG
    self.NaOCH3_trans_usageratio=NaOCH3_usageratio_ref # kg NaOCH3/kg FOG
    self.HCl_trans_usageratio=HCl_usageratio_ref # kg HCl/kg FOG

    # energy consumption
    self.elect_con_trans=self.elect_trans_usageratio*self.oilmass_trans*self.constants.lb2gram/1000 # kWh
    self.NG_con_trans=self.NG_trans_usageratio*self.oilmass_trans*self.constants.lb2gram/1000 # kg NG

    # chemical consumption
    self.MeOH_con_trans=self.MeOH_trans_usageratio*self.oilmass_trans*self.constants.lb2gram/1000 # kg MeOH
    self.NaOCH3_con_trans=self.NaOCH3_trans_usageratio*self.oilmass_trans*self.constants.lb2gram/1000 # kg NaOCH3
    self.HCl_con_trans=self.HCl_trans_usageratio*self.oilmass_trans*self.constants.lb2gram/1000 # kg HCl

    # convert chemical consumption into LC energy consumption
    self.LCenergy_con_MeOH_trans=self.MeOH_con_trans*self.constants.LCenergy_MeOH # MJ
self.LCenergy_con_NaOCH3_trans=self.NaOCH3_con_trans*self.constants.LCenergy_NaOCH3 #MJ
self.LCenergy_con_HCl_trans=self.HCl_con_trans*self.constants.LCenergy_HCl #MJ

# calculate LC GHG from chemical consumption
self.GHG_con_MeOH_trans=self.MeOH_con_trans*1000*self.constants.GHG_MeOH #g CO2-eq/
self.GHG_con_NaOCH3_trans=self.NaOCH3_con_trans*1000*self.constants.GHG_NaOCH3 #g CO2-eq/
self.GHG_con_HCl_trans=self.HCl_con_trans*1000*self.constants.GHG_HCl #g CO2-eq/

#update the key variables
self.update.update_key(4,0,self.NG_con_trans,self.elect_con_trans,
self.LCenergy_con_MeOH_trans+self.LCenergy_con_NaOCH3_trans+self.LCenergy_con_HCl_trans,
self.GHG_con_MeOH_trans+self.GHG_con_NaOCH3_trans+self.GHG_con_HCl_trans)

#update the components
self.update.update_components(4, "na", "na",
self.solidsmass, 0, self.oilmass_after_trans,
self.FAMEmass_trans_99_percent/self.constants.lb2gram)

#update process energy output
self.P_energy_output[stage_num-1]=self.FAMEmass*self.constants.energycontent_FAME #MJ

# 5th stage: anaerobic digestion
def AD (self, AD_flag, MC_flag, MC_VS_conc_flag, MC_elect_mixing_flag,
MC_heat_flag, MC_CH4_gen_flag, MC_elect_gen_eff_flag):
    stage_num=5
    self.elect_usageratio_H2Sremoval_AD=0.25 #kWh/kg VS, constant value
    self.CHP_overallefficiency_AD=0.76 #%, constant value
    self.VS_destoryrate=0.56 # %of VS destoryed after AD, constant value
    if not AD_flag:
        # in this case, the AD is not included in the life cycle
        #update the key variables
        self.update.update_key(5,0,0,0,0,0)
        #update the components
        self.update.update_components(5, "na", "na",
self.solidsmass, "na", "na", "na")
        #update process energy output, tricky here: this energy output is the apparent energy output from AD
        self.P_energy_output[stage_num-1]=0 #MJ
    elif not MC_flag:
        self.VS_percent=0.94 #%
        self.elect_usageratio_mixing_AD=0.1 #kWh/kg VS
        self.heating_usageratio_AD=2.7 #MJ/kg VS
123
self.CH4_gen_rate_AD=0.3 #L/g VS

self.CHP_elect_gen_rate_AD=0.33 #%
self.CHP_heat_gen_rate_AD=self.CHP_overallefficiency_AD-self.CHP_elect_gen_rate_AD #%

else:
    if MC_VS_conc_flag:
        self.MCdistributions.D_Uniform(0.88,0.99)
        self.VS_percent=self.MCdistributions.Uniform_output #%
    else:
        self.VS_percent=0.94 #%
if MC_elect_mixing_flag:
    self.MCdistributions.D_Triangular(0.08,0.122,0.1)
    self.elect_usageratio_mixing_AD=self.MCdistributions.Trianguler_output #kWh/kg VS
else:
    self.elect_usageratio_mixing_AD=0.1 #kWh/kg VS
if MC_heat_flag:
    self.MCdistributions.D_Triangular(2.4,3.0,2.7)
    self.heating_usageratio_AD=self.MCdistributions.Trianguler_output #MJ/kg VS
else:
    self.heating_usageratio_AD=2.7 #MJ/kg VS
if MC_CH4_gen_flag:
    self.MCdistributions.D_Triangular(0.1,0.4,0.3)
    self.CH4_gen_rate_AD=self.MCdistributions.Trianguler_output #L/g VS
else:
    self.CH4_gen_rate_AD=0.3 #L/g VS
if MC_elect_gen_eff_flag:
    self.MCdistributions.D_Triangular(0.28,0.38,0.33)
    self.CHP_elect_gen_rate_AD=self.MCdistributions.Trianguler_output #%
else:
    self.CHP_elect_gen_rate_AD=0.33 #%
self.CHP_heat_gen_rate_AD=self.CHP_overallefficiency_AD-self.CHP_elect_gen_rate_AD #%

if AD_flag:
    # beginning of the AD stage
    self.solidsmass_AD=self.solidsmass*self.constants.lb2gram/1000 #kg
    self.VSmass=self.VS_percent*self.solidsmass_AD #kg
    # after AD stage
    self.VSmass_after_AD=self.VSmass*(1-self.VS_destoryrate) #kg, leftover VS
    self.solidsmass_after_AD=(self.solidsmass_AD-self.VSmass)+self.VSmass_after_AD #kg, non-VS
(unchanged)+leftover VS
    
    # energy consumption
    self.elect_con_AD=self.VSmass*(self.elect_usageratio_mixing_AD+self.elect_usageratio_H2Sremoval_AD) #kWh
self.heating_con_AD = self.VSmass * self.heating_usageratio_AD # MJ
self.NG_con_AD = self.heating_con_AD / self.constants.embeddedenergy_NG # kg NG

# CH4 generation and energy output from AD
self.CH4_gen_AD_vol = self.CH4_gen_rate_AD * self.VSmass * 1000 # L
self.CH4_gen_AD_mass = self.CH4_gen_AD_vol * self.constants.den_CH4 # g

self.CH4_energyout_overall_AD = self.CH4_gen_AD_mass / 1000 * self.CHP_overall_efficiency_AD * self.constants.embeddedenergy_CH4 # MJ

self.CH4_electout_AD_inMJ = self.CH4_energyout_overall_AD * (self.CHP_elect_gen_rate_AD / self.CHP_overall_efficiency_AD) # MJ

self.CH4_heatout_AD = self.CH4_energyout_overall_AD - self.CH4_electout_AD_inMJ # MJ

self.CH4_electout_AD_inkWh = self.CH4_electout_AD_inkWh # avoided kWh
self.CH4_heatout_AD_inNG = self.CH4_heatout_AD / self.constants.embeddedenergy_NG # kg NG

# *tricky part: calculate net elect and NG consumption (should be negative in most cases)

this section calculates the net elect and NG consumption which is the difference between consumed energy and energy output from the AD

self.avoided_CH4_electout_AD_inkWh = self.CH4_electout_AD_inkWh # avoided kWh
self.avoided_CH4_heatout_AD_inNG = self.CH4_heatout_AD_inNG # avoided kg NG
self.net_elect_con_AD = self.elect_con_AD - self.avoided_CH4_electout_AD_inkWh # net elect consumption, kWh
self.net_NG_con_AD = self.NG_con_AD - self.avoided_CH4_heatout_AD_inNG # net NG consumption, kg

# update the key variables
self.update.update_key(5, 0, self.net_NG_con_AD, self.net_elect_con_AD, 0, 0)

# update the components
self.update.update_components(5, "na", "na", self.solidsmass_after_AD * 1000 / self.constants.lb2gram, "na", "na", "na")

# update process energy output, tricky here: this energy output is the apparent energy output from AD
self.P_energy_output[stage_num-1] = self.CH4_energyout_overall_AD # MJ

# 6th stage: transportation of leftover solids, no MC option for now
def leftover_solids_transport(self, AD_flag, Stage_num=6, distance=100, MPG=6.5, truckvol=3600):

    truck for transporting the leftover solids: volume=3600 gal/load, mpg=6.5
    average distance=WWTP<>landfill

    assume leftover solids has a density of 13.4 lb/gal

    """
stage_num=6
# diesel consumption for transporting 1 gal of solids from WWTP to landfill (round trip)
self.diesel_use_per_gal_load=distance/MPG/truckvol #gal

if AD_flag:
    # total diesel consumption for transporting the leftover solids from AD stage
    self.diesel_use_leftover_solids=self.solidsmass_after_AD*1000/self.constants.lb2gram/self.constants.den_solids*self.diesel_use_per_gal_load #gal
else:
    # total diesel consumption for transporting the leftover solids without AD stage (leftover solids=solids in raw TG)
    self.diesel_use_leftover_solids=self.solidsmass/self.constants.den_solids*self.diesel_use_per_gal_load #gal

#update the key variables
self.update.update_key(6,self.diesel_use_leftover_solids,0,0,0,0)

#update the components
self.update.update_components(6, "na", "na", 0, "na", "na","na")

#update process energy output
self.P_energy_output[stage_num-1]=0

# Allocation
def allocation(self):
    """
    this stage calculates the allocation factors for the relevant stages
    """
    # initialize the allocation module
    self.allocation_factors=allocation_factors.Allocation(self.FOGmass,self.mass_FOG_left_after_recovery/self.constants.lb2gram, 
                                                        self.solidsmass,self.FAMEmass/self.constants.lb2gram,self.oilmass_after_esteri, 
                                                        self.FAMEmass_trans_99_percent/self.constants.lb2gram,self.glycerinmass_trans_80_percent/self.constants.lb2gram) #input required arguments for the parameters here
    # initialize sum-up variables (before allocation) foreach stage (LC energy)
    self.LCenergy_beforealloc_bystage=[None]*6 # use index to refer to specific stage
    # initialize sum-up variables (before allocation) foreach stage (GHG)
    self.GHG_beforealloc_bystage=[None]*6 # use index to refer to specific stage
    # initialize allocated variables for each stage (LC energy)
    self.LCenergy_alloc_rawTG_transport_FAME=None # allotted to FAME
    self.LCenergy_alloc_rawTG_transport_solids=None # allotted to solids (passed on to AD or directly to landfill)
self.LCenergy_alloc_rawTG_transport_glycerin=None  # assume to be neglected in this study, just for record here
self.LCenergy_alloc_rawTG_transport_lostFOG=None  # used in this study
self.LCenergy_alloc_FOGseparate_FAME=None  # allotted to FAME
self.LCenergy_alloc_FOGseparate_solids=None  # allotted to solids (passed on to AD or directly to landfill)
self.LCenergy_alloc_FOGseparate_glycerin=None  # assume to be neglected in this study, just for record here
self.LCenergy_alloc_FOGseparate_lostFOG=None  # used in this study
self.LCenergy_alloc_esteri=None
self.LCenergy_alloc_trans_FAME=None
self.LCenergy_alloc_trans_glycerin=None  # assume to be neglected in this study, just for record here
self.LCenergy_alloc_AD=None
self.LCenergy_alloc_leftover_solids_transport=None
# initialize allocated variables for each stage (GHG emission)
self.GHG_alloc_rawTG_transport_FAME=None  # allotted to FAME
self.GHG_alloc_rawTG_transport_solids=None  # allotted to solids (passed on to AD or directly to landfill)
self.GHG_alloc_rawTG_transport_glycerin=None  # assume to be neglected in this study, just for record here
self.GHG_alloc_rawTG_transport_lostFOG=None  # used in this study
self.GHG_alloc_FOGseparate_FAME=None  # allotted to FAME
self.GHG_alloc_FOGseparate_solids=None  # allotted to solids (passed on to AD or directly to landfill)
self.GHG_alloc_FOGseparate_glycerin=None  # assume to be neglected in this study, just for record here
self.GHG_alloc_FOGseparate_lostFOG=None  # used in this study
self.GHG_alloc_esteri=None
self.GHG_alloc_trans_FAME=None
self.GHG_alloc_trans_glycerin=None  # assume to be neglected in this study, just for record here
self.GHG_alloc_AD=None
self.GHG_alloc_leftover_solids_transport=None
# initialize subtotal allocated LC energy consumption by stage
self.LCenergy_alloc_rawTG_transport_subtotal=None
self.LCenergy_alloc_FOGseparate_subtotal=None
self.LCenergy_alloc_esteri_subtotal=None
self.LCenergy_alloc_trans_subtotal=None
self.LCenergy_alloc_AD_subtotal=None
self.LCenergy_alloc_leftover_solids_transport_subtotal=None
# initialize subtotal allocated GHG emission by stage
self.GHG_alloc_rawTG_transport_subtotal=None
self.GHG_alloc_FOGseparate_subtotal=None
self.GHG_alloc_esteri_subtotal=None
self.GHG_alloc_trans_subtotal=None
self.GHG_alloc_AD_subtotal=None
self.GHG_alloc_leftover_solids_transport_subtotal=None

# sum up LC energy consumption and GHG by stage, tricky part: no discriminate against w/AD or not (should have been accounted for in previous stages)
self.alloc_stage_num=6  # in w/o AD, the LC energy consumption and GHG emission should be zero for [4] for i in range (self.alloc_stage_num):
self.LCenergy_beforealloc_bystage[i]=self.update.LCenergy_con_diesel[i]+self.update.LCenergy_con_elect[i] \
+self.update.LCenergy_con_NG[i]+self.update.LCenergy_con_chemicals[i]

self.GH_beforealloc_bystage[i]=self.update.LCGHG_diesel[i]+self.update.LCGHG_elect[i] \
+self.update.LCGHG_NG[i]+self.update.LCGHG_chemicals[i]

# start allocation of LC energy consumption and GHG emission by stage
# stage 1: raw TG transportation
self.allocation_factors.allocation_raw_transport() # run the method to generate allocation factor

self.LCenergy_alloc_rawTG_transport_FAME=self.LCenergy_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport_FAME #MJ

self.LCenergy_alloc_rawTG_transport_solids=self.LCenergy_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport_solids #MJ

self.LCenergy_alloc_rawTG_transport_glycerin=self.LCenergy_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport_glycerin #MJ, just for record, not used in the study

self.LCenergy_alloc_rawTG_transport_lostFOG=self.LCenergy_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport_lostFOG #MJ, used in the study

self.LCenergy_alloc_rawTG_transport_subtotal=self.LCenergy_alloc_rawTG_transport_FAME+self.LCenergy_alloc_rawTG_transport_lostFOG

self.GHG_alloc_rawTG_transport_FAME=self.GHG_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport
FAME #g CO2 eq

self.GHG_alloc_rawTG_transport_solids=self.GHG_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport
solids #g CO2 eq

self.GHG_alloc_rawTG_transport_glycerin=self.GHG_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport
glycerin #g CO2 eq, just for record, not used in the study

self.GHG_alloc_rawTG_transport_lostFOG=self.GHG_beforealloc_bystage[0]*self.allocation_factors.F_raw_transport
lostFOG #g CO2 eq, used in the study

self.GHG_alloc_rawTG_transport_subtotal=self.GHG_alloc_rawTG_transport_FAME+self.GHG_alloc_rawTG_transport
lostFOG

# stage 2: FOG separation
self.allocation_factors.allocation_FOG_separation() # run the method to generate allocation factor
self.LCenergy_alloc_FOGseparate_FAME=self.LCenergy_beforealloc_bystage[1]*self.allocation_factors.F_separation_FAME #MJ

self.LCenergy_alloc_FOGseparate_solids=self.LCenergy_beforealloc_bystage[1]*self.allocation_factors.F_separation_solids #MJ

self.LCenergy_alloc_FOGseparate_glycerin=self.LCenergy_beforealloc_bystage[1]*self.allocation_factors.F_separation_glycerin #MJ, just for record, not used in the study

self.LCenergy_alloc_FOGseparate_lostFOG=self.LCenergy_beforealloc_bystage[1]*self.allocation_factors.F_separation_lostFOG #MJ, used in this study

self.LCenergy_alloc_FOGseparate_subtotal=self.LCenergy_alloc_FOGseparate_FAME+self.LCenergy_alloc_FOGseparate_lostFOG

self.GHG_alloc_FOGseparate_FAME=self.GHG_beforealloc_bystage[1]*self.allocation_factors.F_separation_FAME #g CO2 eq

self.GHG_alloc_FOGseparate_solids=self.GHG_beforealloc_bystage[1]*self.allocation_factors.F_separation_solids #g CO2 eq

self.GHG_alloc_FOGseparate_glycerin=self.GHG_beforealloc_bystage[1]*self.allocation_factors.F_separation_glycerin #g CO2 eq, just for record, not used in the study

self.GHG_alloc_FOGseparate_lostFOG=self.GHG_beforealloc_bystage[1]*self.allocation_factors.F_separation_lostFOG #g CO2 eq, used in this study

self.GHG_alloc_FOGseparate_subtotal=self.GHG_alloc_FOGseparate_FAME+self.GHG_alloc_FOGseparate_lostFOG

# stage 3: esterification
self.LCenergy_alloc_esteri=self.LCenergy_beforealloc_bystage[2]*self.allocation_factors.F_esteri #MJ,
allocation factor for esterification is 1
self.LCenergy_alloc_esteri_subtotal=self.LCenergy_alloc_esteri

self.GHG_alloc_esteri=self.GHG_beforealloc_bystage[2]*self.allocation_factors.F_esteri #g CO2 eq, allocation factor for esterification is 1
self.GHG_alloc_esteri_subtotal=self.GHG_alloc_esteri

# stage 4: transesterification
self.LCenergy_alloc_trans_FAME=self.LCenergy_beforealloc_bystage[3]*self.allocation_factors.F_trans #MJ
self.LCenergy_alloc_trans_glycerin=self.LCenergy_beforealloc_bystage[3]*(1-self.allocation_factors.F_trans) #MJ, just for record, not used in the study
self.LCenergy_alloc_trans_subtotal=self.LCenergy_alloc_trans_FAME
self.GHG_alloc_trans_FAME=self.GHG_beforealloc_bystage[3]*self.allocation_factors.F_trans #g CO2 eq
self.GHG_alloc_trans_glycerin=self.GHG_beforealloc_bystage[3]*(1-self.allocation_factors.F_trans) #g CO2 eq,
just for record, not used in the study
self.GHG_alloc_trans_subtotal=self.GHG_alloc_trans_FAME

# stage 5: AD (if w/o AD, the allocated LC energy consumption and GHG from rawTG transport and FOG
separation still passed on to this stage)
self.LCenergy_alloc_AD=self.LCenergy_beforealloc_bystage[4]*self.allocation_factors.F_AD #MJ, allocation
factor for AD is 1
self.LCenergy_alloc_AD_subtotal=self.LCenergy_alloc_AD+self.LCenergy_alloc_rawTG_transport_solids+self.LCenergy_alloc_FOGseparate_solids #passed on from rawTG transport and FOG separateion
self.GHG_alloc_AD=self.GHG_beforealloc_bystage[4]*self.allocation_factors.F_AD #g CO2 eq, allocation factor
for AD is 1
self.GHG_alloc_AD_subtotal=self.GHG_alloc_AD+self.GHG_alloc_rawTG_transport_solids+self.GHG_alloc_FOGseparate_solids #passed on from rawTG transport and FOG separateion

# stage 6: transportation of leftover solids
self.LCenergy Alloc leftover solids transport=self.LCenergy_beforealloc_bystage[5]*self.allocation_factors.F_waste_transport #MJ, allocation factor for waste solids transport is 1
self.LCenergy Alloc leftover solids transport subtotal=self.LCenergy Alloc leftover solids transport
self.GHG Alloc leftover solids transport=self.GHG_beforealloc_bystage[5]*self.allocation_factors.F_waste_transport #g CO2 eq, allocation factor for waste solids transport is 1
self.GHG Alloc leftover solids transport subtotal=self.GHG Alloc leftover solids transport

# Wrap up after allocation

def wrapup(self):
    """
    this step sums up the allocated LC energy consumption and GHG emission of the TG biodiesel life cycle
    """
    self.wrapup_stage_num=6
    # initialize total LC energy consumption and GHG emission
    self.wrapup_LCenergy Alloc total=0
    self.wrapup_LCGHG Alloc total=0
    # initialize total energy consumption (material can not be counted because of no common ground)
    self.wrapup_con_diesel total=0
    self.wrapup_con_elect total=0
    self.wrapup_con_NG total=0
    # sum up allocation LC energy consumption and GHG emssion from all stages
self.wrapup_LCenergy_alloc_total = self.LCenergy_alloc_rawTG_transport subtotal + self.LCenergy_alloc_FOGseparate subtotal + self.LCenergy_alloc_esteri subtotal + self.LCenergy_alloc_trans subtotal + self.LCenergy_alloc_AD subtotal + self.LCenergy_alloc_leftover_solids_transport subtotal

self.wrapup_LCGHG_alloc_total = self.GHG_alloc_rawTG_transport subtotal + self.GHG_alloc_FOGseparate subtotal + self.GHG_alloc_esteri subtotal + self.GHG_alloc_trans subtotal + self.GHG_alloc_AD subtotal + self.GHG_alloc_leftover_solids_transport subtotal

# normalized to 1 gal of biodiesel produced


for i in range(self.wrapup_stage_num):
    # sum up energy consumption by category
    self.wrapup_con_diesel_total += self.update.Q_diesel[i] # gal
    self.wrapup_con_elect_total += self.update.Q_elect[i] # kWh
    self.wrapup_con_NG_total += self.update.Q_NG[i] # kg

# normalized to 1 gal of biodiesel produced

self.wrapup_con_diesel_total_N = self.wrapup_con_diesel_total / (self.update.vol_FAME[2] + self.update.vol_FAME[3]) # gal/gal

self.wrapup_con_elect_total_N = self.wrapup_con_elect_total / (self.update.vol_FAME[2] + self.update.vol_FAME[3]) # kWh/gal

self.wrapup_con_NG_total_N = self.wrapup_con_NG_total / (self.update.vol_FAME[2] + self.update.vol_FAME[3]) # kg/gal
Frontend user module ("sensitivity_analysis_and_complete_MC.py")

This module calls the "TG LC Energy+GHG_main_code" module and performs sensitivity analysis

indexlist for sensitivity analysis
[0]: FOG concentration
[1]: FFA concentration
[2]: VS concentration
[3]: Electricity use for mixing in AD
[4]: Heating for AD
[5]: CH4 generation rate
[6]: CHP electricity generation efficiency

import TG_LC_EnergyandGHG_main_code
import numpy as nprom scipy import stats
import matplotlib as mpl
import matplotlib.pyplot as plt
from matplotlib.ticker import MaxNLocator
mpl.use (‘agg’)

class Sensi_MC_and_complete_MC():
    def __init__(self, rawTGmass_in_lb, sensi_num, MC_run_time, AD_flag, AD_MC_flag): #initilize how many sensitivity categories; how many times the MC runs
        self.use_code=TG_LC_EnergyandGHG_main_code.TG_LC(rawTGmass_in_lb) #load the module
        self.MC_run_time=MC_run_time
        #initialize the list for storing final (normalized & allocated) LCGHG result for each sensitivity category
        self.sensi_FOG_store_LCGHG=[None]*self.MC_run_time
        self.sensi_FFA_store_LCGHG=[None]*self.MC_run_time
        self.sensi_VS_store_LCGHG=[None]*self.MC_run_time
        self.sensi_Elect4mix_store_LCGHG=[None]*self.MC_run_time
        self.sensi_Heat4AD_store_LCGHG=[None]*self.MC_run_time
        self.sensi_CH4_gen_store_LCGHG=[None]*self.MC_run_time
        self.sensi_Elect_eff_store_LCGHG=[None]*self.MC_run_time
        self.sensi_LCGHG_overallstore=[self.sensi_FOG_store_LCGHG,self.sensi_FFA_store_LCGHG,self.sensi_VS_store_LCGHG,
                                      self.sensi_Elect4mix_store_LCGHG,self.sensi_Heat4AD_store_LCGHG,self.sensi_CH4_gen_store_LCGHG,
                                      self.sensi_Elect_eff_store_LCGHG] # use a overall list to store the list of LC GHG result of sensi category
        #initialize the list for storing final (normalized & allocated) LCenergy consumption result for each sensitivity category
        self.sensi_FOG_store_LCenergy=[None]*self.MC_run_time
        self.sensi_FFA_store_LCenergy=[None]*self.MC_run_time

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self.sensi_VS_store_LCenergy=[None]*self.MC_run_time
self.sensi_Elect4mix_store_LCenergy=[None]*self.MC_run_time
self.sensi_Heat4AD_store_LCenergy=[None]*self.MC_run_time
self.sensi_CH4_gen_store_LCenergy=[None]*self.MC_run_time
self.sensi_Elect_eff_store_LCenergy=[None]*self.MC_run_time

self.sensi_LCenergy_overallstore=[self.sensi_FOG_store_LCenergy,self.sensi_FFA_store_LCenergy,self.sensi_VS_store_LCenergy, 
    self.sensi_Elect4mix_store_LCenergy,self.sensi_Heat4AD_store_LCenergy,self.sensi_CH4_gen_store_LCenergy, 
    self.sensi_Elect_eff_store_LCenergy] # use a overall list to store the list of LCenergy result of sensi category

#initialize the list for storing biodiesel vol result for each sensitiviy category
self.sensi_FOG_store_BioDvol=[None]*self.MC_run_time
self.sensi_FFA_store_BioDvol=[None]*self.MC_run_time
self.sensi_VS_store_BioDvol=[None]*self.MC_run_time
self.sensi_Elect4mix_store_BioDvol=[None]*self.MC_run_time
self.sensi_Heat4AD_store_BioDvol=[None]*self.MC_run_time
self.sensi_CH4_gen_store_BioDvol=[None]*self.MC_run_time
self.sensi_Elect_eff_store_BioDvol=[None]*self.MC_run_time

self.sensi_BioDvol_overallstore=[self.sensi_FOG_store_BioDvol,self.sensi_FFA_store_BioDvol,self.sensi_VS_store_BioDvol, 
    self.sensi_Elect4mix_store_BioDvol,self.sensi_Heat4AD_store_BioDvol,self.sensi_CH4_gen_store_BioDvol, 
    self.sensi_Elect_eff_store_BioDvol] # use a overall list to store the list of BioD vol result of sensi category

self.sensi_indexlist=[[True,False,False,False,False,False,False], 
    [False,True,False,False,False,False,False], 
    [False,False,True,False,False,False,False], 
    [False,False,False,True,False,False,False], 
    [False,False,False,False,True,False,False], 
    [False,False,False,False,False,True,False], 
    [False,False,False,False,False,False,True]] # create a list to store "True or False" conditions from all sensitivity categories

self.sensi_by_category=[[None]*sensi_num #create a list to receive the "True or False" condition for a specific sensitivity category when it's its turn
    self.AD_flag=AD_flag #initialize to see if AD is on
    self.AD_MC_flag=AD_MC_flag
    self.complete_MC=[True,True,True,True,True,True,True]
    self.nominal_check=[False,False,False,False,False] #check the nominal/baseline case
    self.completeMC_LCGHG_overallstore=[None]*self.MC_run_time
    self.completeMC_LCenergy_overallstore=[None]*self.MC_run_time
    self.sorted_completeMC_LCGHG_overallstore=[None]*self.MC_run_time
    self.sorted_completeMC_LCenergy_overallstore=[None]*self.MC_run_time
    self.sorted_sensi_LCGHG_overallstore=[None]*self.MC_run_time
    self.sorted_sensi_LCenergy_overallstore=[None]*self.MC_run_time

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self.BioD_gen_store_completeMC=[None]*self.MC_run_time #store result of the biodiesel volume generated for complete MC
self.sorted_BioD_gen_store_completeMC=[None]*self.MC_run_time
self.FOG_check_percent=[None]*self.MC_run_time #check the generation of FOG% at the beginning of the run
self.Weibull_gen_check=[None]*self.MC_run_time #should be the absolute value of weibull distribution output
self.FFA_check_percent=[None]*self.MC_run_time #check the generation of FFA% at the beginning of the run
self.Logistic_gen_check=[None]*self.MC_run_time #should be the absolute value of Logistiv distribution output

# cut range
self.select_lowlim=int(0.05*self.MC_run_time)-1 #5th percentile data pt
self.select_highlim=int(0.95*self.MC_run_time)-1 #5th percentile data pt
self.yvals_common_select=np.linspace(0,1,(self.MC_run_time-(self.select_lowlim+1)*2)) #y axis for both complete MC and sensi's ecdf

# Method for sensitivity analysis by doing MC for each sensi category at once
def exe_sensi(self):
    for i in range (len(self.sensi_indexlist)):
        self.sensi_by_category=self.sensi_indexlist[i]
        for j in range (self.MC_run_time):
            self.use_code.rawTG_composition(self.sensi_by_category[0])
            self.use_code.rawTG_transport()
            self.use_code.FOG_separation_dewater1()
            self.use_code.FOG_separation_dewater2()
            self.use_code.FOG_separation_elect()
            self.use_code.Esterification(self.sensi_by_category[1])
            self.use_code.transesterification()
            self.use_code.AD(self.AD_flag,self.AD_MC_flag,self.sensi_by_category[2],self.sensi_by_category[3],self.sensi_by_category[4],
                                self.sensi_by_category[5],self.sensi_by_category[6])
            self.use_code.leftover_solids_transport(self.AD_flag)
            self.use_code.allocation()
            self.use_code.wrapup()

    self.sensi_LCGHG_overallstore[i][j]=self.use_code.wrapup_LCGHG_alloc_total_N #store the invidual LCGHG result by sensi category(i) and location(j)
    self.sensi_LCenergy_overallstore[i][j]=self.use_code.wrapup_LCenergy_alloc_total_N #store the invidual LCenergy result by sensi category(i) and location(j)
    self.sorted_sensi_LCGHG_overallstore[i]=np.sort(self.sensi_LCGHG_overallstore[i]) #sort the LCGHG results of each sensi category
    self.sorted_sensi_LCenergy_overallstore[i]=np.sort(self.sensi_LCenergy_overallstore[i]) #sort the LCenergy results of each sensi category

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self.yvals_sensi=np.linspace(0,1,len(self.sorted_sensi_LCGHG_overallstore[0])) #y axis value from 0-1, w/same bins for LCGHG and LCenergy for each sensi category

# Complete MC by doing MC for all categories at once
def exe_complete_MC(self, targetLCenergy, targetLCGHG): # target: the LC energy or GHG to compare with
    self.targetLCenergy=targetLCenergy
    self.targetLCGHG=targetLCGHG
    self.BetterPool_LCenergy=[] # a list to store the difference between models results that are better (smaller)
    and the target values
    self.BetterPool_LCGHG=[] # a list to store the difference between models results that are better (smaller)
    and the target values
    for i in range(self.MC_run_time):
        self.use_code.rawTG_composition(self.complete_MC[0])
        self.use_code.rawTG_transport()
        self.use_code.FOG_separation_dewater1()
        self.use_code.FOG_separation_dewater2()
        self.use_code.FOG_separation_elect()
        self.use_code.Esterification(self.complete_MC[1])
        self.use_code.transesterification()
        self.use_code.AD(self.AD_flag,self.AD_MC_flag,self.complete_MC[2],self.complete_MC[3],self.complete_MC[4],
        self.complete_MC[5],self.complete_MC[6])
        self.use_code.leftover_solids_transport(self.AD_flag)
        self.use_code.allocation()
        self.use_code.wrapup()
        self.completeMC_LCGHG_overallstore[i]=self.use_code.wrapup_LCGHG_alloc_total_N #store the invidudal LCGHG result for each complete MC run
        self.completeMC_LCenergy_overallstore[i]=self.use_code.wrapup_LCenergy_alloc_total_N #store the invidudal LCenergy result for each complete MC run
        self.FOG_check_percent[i]=self.use_code.FOG_percent*100 #check the distribution of FOG% generated
        self.Weibull_gen_check[i]=self.use_code.MCdistributions.Weibull_output #check the value of Weibull output
        self.FFA_check_percent[i]=self.use_code.FFA_percent*100 #check the distribution of FFA% generated
        self.Logistic_gen_check[i]=self.use_code.MCdistributions.Logistic_output #check the value of Logistic output
        self.sorted_FOG_check_percent=np.sort(self.FOG_check_percent)
        self.sorted_BioD_gen_store_completeMC=np.sort(self.BioD_gen_store_completeMC)
        self.sorted_completeMC_LCGHG_overallstore=np.sort(self.completeMC_LCGHG_overallstore) #sort results for ecdf plot
        self.sorted_completeMC_LCenergy_overallstore=np.sort(self.completeMC_LCenergy_overallstore) #sort results for ecdf plot
        self.yvals_completeMC=np.linspace(0,1,len(self.sorted_completeMC_LCGHG_overallstore)) #y axis value from 0-1, w/same bins for LCGHG and LC energy

        # first, truncate the complete MC results list by taking out the first (5th percentile) and last 5 percentile (95th percentile) of the data (outliers)
self.truncate_range = int(self.MC_run_time * 0.9)
self.truncate_locator = int((self.MC_run_time * 0.1 / 2) - 1)
self.truncated_completeMC_LCGHG_overallstore = []
self.truncated_completeMC_LCenergy_overallstore = []

for n in range(self.truncate_range):
    self.truncated_completeMC_LCGHG_overallstore.append(self.sorted_completeMC_LCGHG_overallstore[n + self.truncate_locator])
    self.truncated_completeMC_LCenergy_overallstore.append(self.sorted_completeMC_LCenergy_overallstore[n + self.truncate_locator])

# compare model results with target values (LCGHG)
for k in range(len(self.truncated_completeMC_LCGHG_overallstore)):
    if self.truncated_completeMC_LCGHG_overallstore[k] < self.targetLCGHG:
        self.BetterPool_LCGHG.append(self.targetLCGHG - self.truncated_completeMC_LCGHG_overallstore[k])
        continue
self.AveImprov_LCGHG = np.average(self.BetterPool_LCGHG)

# compare model results with target values (LCenergy)
for m in range(len(self.truncated_completeMC_LCenergy_overallstore)):
    if self.truncated_completeMC_LCenergy_overallstore[m] < self.targetLCenergy:
        self.BetterPool_LCenergy.append(self.targetLCenergy - self.truncated_completeMC_LCenergy_overallstore[m])
        continue
self.AveImprov_LCenergy = np.average(self.BetterPool_LCenergy)

# Nominal check method
def nominalcheck(self):
    self.use_code.rawTG_composition(self.nominal_check[0])
    self.use_code.rawTG_transport()
    self.use_code.FOG_separation_dewater1()
    self.use_code.FOG_separation_dewater2()
    self.use_code.FOG_separation_elect()
    self.use_code.Esterification(self.nominal_check[1])
    self.use_code.transesterification()
    self.use_code.AD(self.AD_flag, self.AD_MC_flag, self.nominal_check[2], self.nominal_check[3], self.nominal_check[4],
                     self.nominal_check[5], self.nominal_check[6])
    self.use_code.leftover_solids_transport(self.AD_flag)
    self.use_code.allocation()
    self.use_code.wrapup()

# Plot method (plots are saved to the C:\users\username folder)

def plot_results_sensi(self):
    # start plotting results for sensi
    self.fig_num = 0
self.ecdfplot_indexlist_sensi=[0,1,2,3,4,5,6]
self.sensi_ecdf_LCGHG=[None]*len(self.ecdfplot_indexlist_sensi)
self.sensi_ecdf_LCenergy=[None]*len(self.ecdfplot_indexlist_sensi)

[0]: ecdf plot for FOG concentration
[1]: ecdf plot for FFA concentration
[2]: ecdf plot for VS concentration
[3]: ecdf plot for Electricity use for mixing in AD
[4]: ecdf plot for Heating for AD
[5]: ecdf plot for CH4 generation rate
[6]: ecdf plot for CHP electricity generation efficiency

# start plot ecdf plot of LCGHG and LCenergy for each sensi category
# while self.fig_num in self.ecdfplot_indexlist_sensi:
# plt.figure(1,figsize=(9,6))
# plt.plot(self.sorted_sensi_LCGHG_overallstore[self.fig_num][self.select_lowlim:self.select_highlim],self.yvals_common_select)
# plt.xlabel('Life cycle GHG emission (g CO2-eq/gal)')
# plt.ylabel('Empirical cumulative density function')
# plt.savefig('LCGHG_ecdf_sensi'+str(self.fig_num)+'.png')
# plt.close()

# plt.figure(1,figsize=(9,6))
# plt.plot(self.sorted_sensi_LCenergy_overallstore[self.fig_num][self.select_lowlim:self.select_highlim],self.yvals_common_select)
# plt.xlabel('Life cycle energy consumption (MJ/gal)')
# plt.ylabel('Empirical cumulative density function')
# plt.savefig('LCenergy_ecdf_sensi'+str(self.fig_num)+'.png')
# self.fig_num+=1
# plt.close()

# boxplot (w/o broken axis) for sensi in total (LCGHG)
# self.LCGHG_bp_sensi=plt.figure(1,figsize=(9,6))
# self.ax_sensi_LCGHG=self.LCGHG_bp_sensi.add_subplot(111)
# self.ax_sensi_LCGHG.set_xlabel('Life cycle GHG emission')
# self.ax_sensi_LCGHG.set_ylabel('g CO2-eq/gal BioD')
# self.bp_sensi_LCGHG=self.ax_sensi_LCGHG.boxplot(self.sensi_LCGHG_overallstore,whis=[5,95],sym='') # do
# not plot "outliers" that are beyond plus or minus 1.5 IQR
# self.LCGHG_bp_sensi.savefig('LCGHG_bp_sensi',bbox_inches='tight')
# plt.close()

# broken axis boxplot for sensi in total (LCGHG); ONLY for w/o AD (w/AD use the code ABOVE)
# use the top (ax) for the extremely high values, and the bottom (ax2) for the majority of the results
fig=plt.figure()
ax0=fig.add_subplot(1,1,1) # add a big subplot to place common x,y labels as background
ax1=fig.add_subplot(5,1,1)
ax2=fig.add_subplot(5,1,(2,5),sharex=ax1) # 5 row by 1 column layout, the bottom fig takes up 2~5 rows
ax1.boxplot(self.sensi_LCGHG_overallstore,whis=[5,95],sym='')
ax2.boxplot(self.sensi_LCGHG_overallstore,whis=[5,95],sym='')
# zoom-in / limit the view to different portions of the data
ax1.set_ylim(120000,130000)  # extremely high values only
ax1_ytick_frequency=np.arange(ax1.get_ylim()[0], ax1.get_ylim()[1]*1.002, 5000) # multiplied by 1.002 to make sure the top tick is visible
ax1.set_yticks(ax1_ytick_frequency)
ax2.set_ylim(0, 15000)  # most of the results
# hide the spines between ax and ax2
ax1.spines['bottom'].set_visible(False)
ax2.spines['top'].set_visible(False)
ax1.xaxis.tick_top() # place ticks on top of the plot
ax1.tick_params(labeltop='off')  # don't put tick labels at the top
ax2.xaxis.tick_bottom() # place ticks at bottom of the plot
# start to add diagonal lines
d = .0075  # how big to make the diagonal lines in axes coordinates
kwargs = dict(transform=ax1.transAxes, color='k', clip_on=False)
ax1.plot((-d, +d), (-d, +d), **kwargs)        # top-left diagonal
ax1.plot((1 - d, 1 + d), (-d, +d), **kwargs)  # top-right diagonal
ax1.plot((1 - d, 1 + d), (1 - d, 1 + d), **kwargs)  # bottom-right diagonal
ax2.plot((1 - d, 1 + d), (1 - d, 1 + d), **kwargs)  # bottom-right diagonal
# change the distance between the label and the axis
ax0.set_xlabel('Life cycle GHG emission')
ax0.set_ylabel('g CO2-eq/gal BioD')
ax0.set_ylabel('g CO2-eq/gal BioD')
# boxplot (w/o broken axis) for sensi in total (LCenergy)
self.LCenergy_bp_sensi=plt.figure(1,figsize=(9,6))
self.ax_sensi_LCenergy=self.LCenergy_bp_sensi.add_subplot(111)
self.ax_sensi_LCenergy.set_xlabel('Life cycle energy consumption')
self.ax_sensi_LCenergy.set_ylabel('MJ/gal BioD')
# self.LCenergy_bp_sensi.savefig('LCenergy_bp_sensi',bbox_inches='tight')
# plt.close()

# broken axis boxplot for sensi in total (LCenergy)
# use the top (ax) for the extremely high values, and the bottom (ax2) for the majority of the results
fig = plt.figure()
ax0 = fig.add_subplot(1, 1, 1)  # add a big subplot to place common x,y labels as background
ax1 = fig.add_subplot(5, 1, 1)
ax2 = fig.add_subplot(5, 1, (2, 5), sharex=ax1)
ax1.boxplot(self.sensi_LCenergy_overallstore, whis=[5, 95], sym='')
ax2.boxplot(self.sensi_LCenergy_overallstore, whis=[5, 95], sym='')
# zoom in / limit the view to different portions of the data
ax1.set_ylim(1300, 1900)  # extremely high values only; (1300, 1900) for w/o AD; (200, 600) for w/AD
ax1_xtick_frequency = np.arange(ax1.get_ylim()[0], ax1.get_ylim()[1] * 1.002, 300)  # multiplied by 1.002 to make sure the top tick is visible
ax1.set_yticks(ax1_xtick_frequency)
ax2.set_ylim(0, 200)  # most of the results; (0, 200) for w/o AD; (0, 100) for w/AD
# hide the spines between ax and ax2
ax1.spines['bottom'].set_visible(False)
ax2.spines['top'].set_visible(False)
ax1.xaxis.tick_top()  # place ticks on top of the plot
ax1.tick_params(labeltop='off')  # don't put tick labels at the top
ax2.xaxis.tick_bottom()  # place ticks at bottom of the plot
# start to add diagonal lines
d = .0075  # how big to make the diagonal lines in axes coordinates
kwargs = dict(transform=ax1.transAxes, color='k', clip_on=False)
ax1.plot((-d, +d), (-d, +d), **kwargs)  # top-left diagonal
ax1.plot((1 - d, 1 + d), (-d, +d), **kwargs)  # bottom-left diagonal
kwargs.update(transform=ax2.transAxes)  # switch to the bottom axes
ax2.plot((-d, +d), (1 - d, 1 + d), **kwargs)  # top-right diagonal
ax2.plot((1 - d, 1 + d), (1 - d, 1 + d), **kwargs)  # bottom-right diagonal
# Turn off axis lines and ticks of the background subplot
ax0.spines['top'].set_color('none')
ax0.spines['bottom'].set_color('none')
ax0.spines['left'].set_color('none')
ax0.spines['right'].set_color('none')
ax0.tick_params(labelcolor='w', top='off', bottom='off', left='off', right='off')
ax0.set_ylabel('Life cycle energy consumption')
ax0.set_xlabel('MJ/gal BioD')
# change the distance between the label and the axis
ax0.tick_params(axis='y', which='major', pad=20)
ax0.tick_params(axis='x', which='major', pad=6)
plt.savefig('LCenergy_bp_sensi', bbox_inches='tight')
plt.close()
# boxplot for sensi BioD vol
#self.BioDvol_bp_sensi=plt.figure(1,figsize=(9,6))
#self.ax_sensi_BioDvol=self.BioDvol_bp_sensi.add_subplot(111)
#self.ax_sensi_BioDvol.set_xlabel('Biodiesel production')
#self.ax_sensi_BioDvol.set_ylabel('Gal')
#self.bp_sensi_BioDvol=self.ax_sensi_BioDvol.boxplot(self.sensi_BioDvol_overallstore,whis=[5,95],sym='')
#self.BioDvol_bp_sensi.savefig('Biodiesle production_bp_sensi',bbox_inches='tight')
#plt.close()

def plot_results_completeMC(self):
    # all plots are from data range (5th to 95th percentile) except FOG% and FFA% check
    # boxplot for complete MC (LCGHG)
    self.LCGHG_bp_completeMC=plt.figure(1,figsize=(9,6))
    self.ax_completeMC_LCGHG=self.LCGHG_bp_completeMC.add_subplot(111)
    self.ax_completeMC_LCGHG.set_xlabel('Life cycle GHG emission')
    self.ax_completeMC_LCGHG.set_ylabel('g CO2- eq/gal BioD')
    self.bp_completeMC_LCGHG=self.ax_completeMC_LCGHG.boxplot(self.completeMC_LCGHG_overallstore,whis=[5,95],sym='')
    self.LCGHG_bp_completeMC.savefig('LCGHG_bp_completeMC',bbox_inches='tight')
    plt.close()
    
    # boxplot for complete MC (LCenergy)
    #self.LCenergy_bp_completeMC=plt.figure(1,figsize=(9,6))
    #self.ax_completeMC_LCenergy=self.LCenergy_bp_completeMC.add_subplot(111)
    #self.ax_completeMC_LCenergy.set_xlabel('Life cycle energy consumption')
    #self.ax_completeMC_LCenergy.set_ylabel('MJ/gal BioD')
    #self.bp_completeMC_LCenergy=self.ax_completeMC_LCenergy.boxplot(self.completeMC_LCenergy_overallstore,whis=[5,95],sym='')
    #self.LCenergy_bp_completeMC.savefig('LCenergy_bp_completeMC',bbox_inches='tight')
    #plt.close()
    
    # ecdf for complete MC (LCGHG and LCenergy)
    plt.figure(1,figsize=(9,6))
    plt.plot(self.sorted_completeMC_LCGHG_overallstore[self.select_lowlim:self.select_highlim],self.yvals_common_select)
    plt.xlabel('Life cycle GHG emission (g CO2-eq/gal)')
    plt.ylabel('Empirical cumulative density function')
    plt.savefig('LCGHG_ecdf_completeMC')
    plt.close()
    plt.figure(1,figsize=(9,6))
    plt.plot(self.sorted_completeMC_LCenergy_overallstore[self.select_lowlim:self.select_highlim],self.yvals_common_select)
    plt.close()
plt.xlabel('Life cycle energy consumption (MJ/gal)')
plt.ylabel('Empirical cumulative density function')
plt.savefig('LCenergy_ecdf_completeMC')
plt.close()

# ecdf for biodiesel generation
plt.figure(1,figsize=(9,6))
plt.plot(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim],self.yvals_common_select)
plt.xlabel('Biodiesel production (gal)')
plt.ylabel('Empirical cumulative density function')
plt.savefig('Biodiesel production_completeMC')
plt.close()

# pdf for biodiesel generation
self.density_BioD = stats.gaussian_kde(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim])
self.density_BioD.covariance_factor=lambda:.01
self.density_BioD._compute_covariance()
self.xaxis_BioD=np.linspace(min(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim]),
                           max(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim]),
                           len(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim]))
# x axis
plt.plot(self.xaxis_BioD, self.density_BioD(self.xaxis_BioD))
plt.savefig('pdf_Biodiesel production')
plt.close()

# ecdf for FOG% in raw TG
plt.figure(1,figsize=(9,6))
plt.plot(self.sorted_FOG_check_percent,self.yvals_completeMC)
plt.xlabel('FOG in raw TG (%)')
plt.ylabel('Empirical cumulative density function')
plt.savefig('FOG in raw TG percent check_completeMC')
plt.close()

# histogram for FOG% in raw TG
plt.hist(self.FOG_check_percent,bins=100)
plt.xlabel('FOG in raw TG (%)')
plt.ylabel('Frequency')
plt.savefig('Hist_FOG in raw TG percent check_completeMC')
plt.close()

# histogram for FFA% in FOG
plt.hist(self.FFA_check_percent,bins=100)
plt.xlabel('FFA in FOG (%)')
plt.ylabel('Frequency')
plt.savefig('Hist_FFA in FOG percent_check_completeMC')
plt.close()

# histogram for biodiesel generation
plt.hist(self.sorted_BioD_gen_store_completeMC[self.select_lowlim:self.select_highlim],bins=100)
plt.xlabel('Biodiesel production (gal)')
plt.ylabel('Frequency')
plt.savefig('Hist_Biodiesel Production_completeMC')
plt.close()

# main code (w/AD):100,000 run may take a very long time, if pdf plot is on (50,000 may be a proper #)
test1=Sensi_MC_and_complete_MC(10000,7,10000,False,False)
#test1.nominalcheck()
#print test1.use_code.wrapup_LCGHG_alloc_total_N, test1.use_code.wrapup_LCenergy_alloc_total_N

#test1.exe_complete_MC()
#find 5th and 95th percentile of the data
#print "5th/95th percentile of BioD vol:",np.percentile
(test1.sorted_BioD_gen_store_completeMC,5),np.percentile (test1.sorted_BioD_gen_store_completeMC,95)
#print "5th/95th percentile of LC GHG:",np.percentile
(test1.sorted_completeMC_LCGHG_overallstore,5),np.percentile
(test1.sorted_completeMC_LCGHG_overallstore,95)
#print "5th/95th percentile of LC energy:",np.percentile
(test1.sorted_completeMC_LCenergy_overallstore,5),np.percentile
(test1.sorted_completeMC_LCenergy_overallstore,95)

#test1.plot_results_completeMC()
test1.exe_sensi()
test1.plot_results_sensi()
#print test1.FFA_check_percent
#print test1.Logistic_gen_check
Chapter 3. Glycerolysis of High FFA Oil from Trap Grease

3.1 Introduction

The transesterification process yields two products: biodiesel and glycerin. As a by-product of biodiesel production process, sales of glycerin have long been an important revenue flow for biodiesel producers. The sales price of glycerin depends on its purity. The common categories for the purity of glycerin are USP grade (≥99.5% purity), technical grade (95%–99.5%) and crude grade (approximately 80% by weight after methanol recovery). The major impurities in the crude glycerin include salts, catalyst, residual methanol, and water. The salts and water are formed during the neutralization of FFA in the parent oil. Distillation is a common way for purification of glycerin however the process is energy-intensive and the capital cost can be prohibitive for the small biodiesel producers (Lancrenon and Fedders, 2008). Glycerin is a widely used ingredient in cosmetic and pharmaceutical industries. Additional market for glycerin is to be used as a platform chemical for producing value-added chemicals, such as propane diols, acetol, acrylic acid, etc. (Kenar, 2007; Yang et al., 2012; Werpy et al., 2012), however these applications are mostly still in the R&D stage. With the rapid growth of the biodiesel industry, the glycerin market starts to saturate. Therefore, to diversify the market for glycerol becomes an important task for the biodiesel companies to secure their revenue.

Using glycerol for FFA treatment through the glycerolysis process may offer an opportunity to create a market for the surplus glycerin and at the same time improve the capability of the biodiesel producers to make use of low cost, high FFA feedstocks. As mentioned in the previous
chapter, the most commonly used FFA treatment technology in the biodiesel industry is acid-catalyzed esterification. However, for a feedstock with significantly high FFA concentration (>20%), such as FOG from trap grease, a large amount of methanol (e.g. 40:1 molar ratio between MeOH and FFA) has to be used in order to improve the efficiency of the reaction. Another drawback of the acid-catalyzed esterification is the formation of water during the reaction, which not only comprises the efficiency (through reverse reaction) but also increases difficulty in recovering high purity methanol (e.g. 99.9% purity) after the process. So, when feedstock with significantly high FFA concentration (e.g. >15%) is treated, a multi-stage esterification process has to be applied, which requires the intermittent shutdown of the reactor to drain the water (Canakci and Van Gerpen, 2001; Chai et al., 2014). On the other hand, glycerolysis of FFA is the reaction between glycerin and FFA to form mono-glyceride/Monoacylglycerols (MAG) (Eq. 3.1). In addition to FFA, glycerol may also react with MAG, diacylglycerols (DAG) and triacylglycerols (TAG) when both FFA and oil are present. Therefore, there may be 5 reversible reactions occurring simultaneous during the glycerolysis of FFA-containing oil (Eq.3.1-3.5; Moquin et al., 2006). As compared with the conventional acid-catalyzed esterification process, glycerolysis avoids the usage of sulfuric acid and methanol (Szulczyk and McCarl, 2010). Also, the reverse reactions can be eliminated by evaporating the water that is generated during the process (due to high reaction temperature). In addition, the potential of utilizing crude glycerol (with minimal purification) for the process may save the purification cost for the biodiesel producers. Therefore, using glycerin for FFA treatment may be a solution for two major issues facing the biodiesel industry: losing margin in the glycerol market and difficulty in utilizing feedstock oils containing high FFA concentration.

\[ \text{Gly} + \text{FFA} \leftrightarrow \text{MAG} + \text{H}_2\text{O} \]  
\text{Eq.3.1}
3.2 Literature review

Table 3.1 summarizes the existing studies on glycerolysis with different FFAs, FAMEs and oils. Guner et al. (1996) performed glycerolysis for oleic acid under different concentrations of sulfated iron oxide as the catalyst. An equivalent amount of glycerol was used and the temperature ranged from 180°C to 240°C. The authors found that the difference in the concentration of the catalyst did not show significant impact on reaction rate until the temperature was raised to 220°C. Sanchez et al. (1997) used a slightly basic Y-zeolite as the catalyst for the glycerolysis of oleic acid. A positive correlation was observed between MAG formation and the operational parameters, i.e., catalyst concentration, temperature and glycerol to acid molar ratio. Based on the findings from this study, Sanchez et al. (1997) performed a parametric optimization through factorial design. The result of the response surface method showed that the optimized yield of MAG (84%) was achieved at 180°C and 5wt% catalyst concentration. Szelag and Sadecka (2009) studied the glycerolysis between lauric acid (LA) and propylene glycerol (PG) with the presence of sodium dodecyl sulfate (SDS) as the catalyst. The authors indicated that a maximum concentration of MAG in the product was achieved when the molar ratio between PG, LA and SDG were 1:1.25:0.01. Pouilloux et al. (1999) used ion-
exchange resins as the catalyst for glycerolysis of oleic acid. It was indicated that increasing the molar ratio between glycerol and FFA favored the formation of MAG but reaction rate was lowered due to the difficulty for the diffusion of FFA in the resin. It is noteworthy that as compared with other studies, using ion exchange resin required relatively lower reaction temperature but much longer reaction time due to the swelling and induction period of the resin. Pouilloux et al. (2000) also studied the efficacy of some acid and basic catalysts as well as the influence of solvents. It was observed that Na₂CO₃ led to the formation of soap while paratoluene sulfonic acid (PTSA) resulted in a low MAG selectivity. The comparison between MgO and ZnO showed that MgO was more active than ZnO due to the higher basicity while ZnO displayed a higher selectivity towards MAG. Four solvents were investigated in their study: toluene, dimethylsulfoxide (DMSO), N,N-dimethyl-formamide (DMF) and bis(2-methoxyethy)ether (diglyme). It was reported that addition of solvent without the presence of catalyst inhibited the glycerolysis process. When ZnO was present, it was shown that toluene increased the reduction of stearic acid due to the fact that it increased the miscibility of MAG in stearic acid, leading to the formation of DAG. On the other hand, the use of diglyme showed an increase in both activity and selectivity of the glycerolysis process. A further optimization of the dosage indicated that 50 wt% with respect to reactants was the best concentration for diglyme to avoid the dilution effect. The authors also discovered that excessive glycerol did not have an impact on either the stearic acid reduction or the selectivity, which did not agree with observations reported in other studies.

On the other hand, many studies have also been done on the glycerolysis of oil or FAME. Kaufman and Garti (1982) found that the presence of both catalyst (NaOH) and soap (sodium stearate) had the best effect for glycerolysis of FAME into MAG and DAG. The authors also
observed that excessive glycerol improved the consumption of FAME. The presence of soap also increased the contact between MAG and glycerol and thus further converted MAG into DAG. Similarly, increasing temperature led to an increase in consumption of FAME, which also resulted in the conversion of MAG into DAG. Noureddini and Medikonduru (1997) studied production of MAG and DAG from crude glycerin from biodiesel production. Both soybean oil and FAME were used as reagents and only methanol removal was applied to the crude glycerol. No significant difference in product components was observed between using crude and pure glycerols for the one-step glycerolysis with FAME. Noureddinid et al. (2004) investigated a continuous process for the glycerolysis of soybean oil. The optimum condition was determined as 230°C, 0.18wt% catalyst concentration, 2.5:1 glycerol-to-oil molar ratio, 40 ml/min total flow and 25 min reaction time. Under the optimum condition the concentrations of MAG and DAG were 56% and 36% when crude glycerol was used and 58% and 33% when pure glycerol was used. Fregolente et al. (2006) conducted a 2³ factorial design to investigate the effect of glycerol-to-oil molar ratio, temperature and catalyst concentration on MAG formation from soybean oil. The results showed that all three variables have positive impacts and glycerol-to-oil molar ratio had significantly higher impact than the other two. The optimum yield of MAG was approximately 50 wt% in 90 min. The author also noted that no temperature higher than 210°C was tested in order to avoid considerable polymerization of the unsaturated fatty acids. Echeverri et al. (2011) used crude glycerin from biodiesel production to produce MAG from soybean oil. The crude glycerin underwent methanol recovery and residual catalyst and soap were not removed. It was observed that the reaction rate was positively correlated with the concentration of residual catalyst. The authors indicated that converting residual catalyst into soap would lower the reaction rate since soap is a weaker base than the alkaline catalysts. Being an emulsifier, soap
was also found to increase the miscibility between MAG and oil, leading to the conversion of
MAG into DAG. Echeverri et al. (2013a) also studied the glycerolysis of castor oil and its methyl
esters by crude glycerin from biodiesel production. The optimum condition for MAG from castor
oil glycerolysis was 180°C and 30 min (50.4% MAG and 34% DAG). For methyl esters, the
tradeoff between temperature and reaction time indicated that two sets of optimum conditions
could be adopted: (1) 180°C and 20 min; (2) 200°C and 5 min. Another study conducted by
Echeverri et al. (2013b) focused on influence of temperature and glycerol-to-FAME molar ratio.
The increase in temperature boosted the reaction rate and yielded a higher total concentration of
MAG and DAG in the product. The optimum condition for highest yield of MAG in their study
was 200°C, 1.5:1 glycerol-to-FAME ratio, and 10 min. Rukprasoot et al. (2005) conducted
glycerolysis of palm stearin with crude glycerol and the optimum condition was 200°C, 2.5:1
glycerol-to-oil molar ratio and 20 min reaction time. Schulz et al. (2011) studied producing
MAG from linseed oil methyl esters. Three catalysts were compared and the optimum condition
was determined as 130°C, 5% NaOH, 5:1 glycerol-to-FAME molar ratio, and 10 hours reaction
time, under which the conversion of biodiesel was 85% and the concentration of MAG in the
product mixture was 72%. Zhong et al. (2013) studied producing MAG from soybean oil under
low temperature range. Out of eight basic catalysts, only NaOH and KOH were found to be
effective at the temperature range from 35°C -55°C. The authors also indicated that NaOH had
the highest catalytic performance and the optimum dosage was 0.45 wt% of oil. Felizardo et al.
(2011) performed a research on glycerolysis of acidulated soap stocks. The result of the study
resonated with that of Pouilouix et al. (2000) that reaction kinetics were positively correlated with
temperature and excessive glycerol did not improve the reaction activity. Anderson et al. (2016)
studied the kinetics of FFA reduction in the glycerolysis of high FFA scum oil. The authors
assumed 1st order reaction for FFA reduction and calculated the values for the reaction constant under both catalyzed and un-catalyzed glycerolysis conditions. The results showed that reaction constant was 2.57 min\(^{-1}\) when no catalyst was used. The reaction constant increased to 5.63 min\(^{-1}\) when Zn-Al\(_2\)O\(_3\) was used but decreased to 1.45 min\(^{-1}\) with N\(_2\)SO\(_4\) as the catalyst.

In most cases, the temperature for glycerolysis was in the range of 160°C -240°C. Most studies indicated a stoichiometric molar ratio was sufficient to completely consume the FFA, oil or FAME. The glycerolysis process was found to be facilitated by the presence of surfactants and catalysts. Surfactants, such as sodium/potassium soaps, were able to increase the miscibility between glycerol and the other reagent by reducing the surface tension (Echeverri et al., 2011). Another way to improve the miscibility was to add co-solvents. In addition to miscibility, catalysts were used in most of the studies to increase the reaction rate. For FFA, the catalyst were often metallic oxides and solid catalysts while for oil/FAME, basic catalysts (e.g. NaOH and KOH) were preferred.
Table 3.1. Summary of the experimental conditions from various literatures for glycerolysis (with FFA, FAME)

### Pure Fatty Acids (FFA)

<table>
<thead>
<tr>
<th>References</th>
<th>Acid</th>
<th>Surfactant/Catalyst</th>
<th>FFA-to-glycerol molar ratio</th>
<th>Surfactant/Catalyst concentration</th>
<th>Temperature (°C)</th>
<th>Duration (hr/min)</th>
<th>Grade of glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartman (1966)</td>
<td>C8:0;C10:0; C12:0;C14:0; C16:0;C18:0; C18:1;C18:2</td>
<td>None</td>
<td>1:1 (equivalent &amp; equimolar)</td>
<td>N/A</td>
<td>180</td>
<td>0.5-10</td>
<td>Analytical grade</td>
</tr>
<tr>
<td>Guner et al. (1996)</td>
<td>C18:1</td>
<td>Sulfated iron oxide</td>
<td>1:1 (equivalent)</td>
<td>2.44, 3.47, 5.10, 7.62 wt%</td>
<td>180, 200, 220, 240</td>
<td>200 min</td>
<td>Analytical grade</td>
</tr>
<tr>
<td>Sanchez et al. (1997)</td>
<td>C18:1</td>
<td>Y-zeolite</td>
<td>0.33:1, 1:1, 3:1</td>
<td>0.3, 1, 3, 5 wt%</td>
<td>160, 170, 180</td>
<td>5</td>
<td>Pure</td>
</tr>
<tr>
<td>Sanchez et al. (1997)</td>
<td>C18:1</td>
<td>Y-zeolite</td>
<td>1:1</td>
<td>5 wt%</td>
<td>180</td>
<td>3</td>
<td>Pure</td>
</tr>
<tr>
<td>Szelag and Zwierzykowski (1998)</td>
<td>C12:0;C14:0; C16:0;C18:0 and mixture (C18:0, 57%; C16:0, 30.8%; C18:1, 7.2%)</td>
<td>Sodium/Potassium Soaps</td>
<td>1:1</td>
<td>1:0.7; 1:0.11; 1:0.15 (max/min=2.14) (Molar ratio; Glycerol:Cat.)</td>
<td>140, 150, 160±1</td>
<td>6</td>
<td>Analytical grade</td>
</tr>
<tr>
<td>Macierzanka and Szelag (2004)</td>
<td>C12:0;C14:0; C16:0;C18:0</td>
<td>ZnC</td>
<td>1:1</td>
<td>1:0.00625; 1:0.0125; 1:0.025; 1:0.05 (max/min=5) (Molar ratio; Glycerol:Cat.)</td>
<td>130, 140, 150, 160±1</td>
<td>6</td>
<td>Analytical grade</td>
</tr>
<tr>
<td>Szelag and Sadecka (2009)</td>
<td>C12:0</td>
<td>NaC₂H₃SO₄ (SDS)</td>
<td>1:1.25</td>
<td>0.001, 0.005, 0.01, 0.025, and 0.05 mol (max/min=50)</td>
<td>150±1</td>
<td>6</td>
<td>Propylene glycol (C₃H₈O₂)</td>
</tr>
<tr>
<td>Pouilloux et al. (1999)</td>
<td>C18:1</td>
<td>ion-exchange resin</td>
<td>1:6</td>
<td>NA</td>
<td>90</td>
<td>up to 50</td>
<td>Pure</td>
</tr>
<tr>
<td>Pouilloux et al. (2000)</td>
<td>C18:0</td>
<td>Na₂CO₃, MgO, ZnO, PTSA</td>
<td>1:1</td>
<td>3 wt%</td>
<td>110</td>
<td>24</td>
<td>NA</td>
</tr>
</tbody>
</table>

### Oil/Methyl Esters (ME)

<table>
<thead>
<tr>
<th>References</th>
<th>Oil/Methyl Esters</th>
<th>Surfactant/Catalyst</th>
<th>Glycerol to Oil/ME molar ratio</th>
<th>Surfactant/Catalyst concentration</th>
<th>Temperature (°C)</th>
<th>Duration (hr/min)</th>
<th>Grade of glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaufman and Garti (1982)</td>
<td>Methyl Stearate</td>
<td>NaOH</td>
<td>0.25:1-3:1</td>
<td>0.15%</td>
<td>95-150</td>
<td>8</td>
<td>Pure</td>
</tr>
<tr>
<td>Noureddini and Medikonduru (1997)</td>
<td>Soybean oil ME</td>
<td>NaOH</td>
<td>ME: 1:0.25-1:1 (pure)</td>
<td>ME: 0.1 wt% (pure)</td>
<td>230-240 (pure)</td>
<td>30 min</td>
<td>1) Pure</td>
</tr>
</tbody>
</table>

1) Pure
2) Crude (purified from
<table>
<thead>
<tr>
<th>Authors</th>
<th>Oil (or FAME)</th>
<th>NaOH or KOH</th>
<th>Oil Ratio</th>
<th>NaOH or KOH</th>
<th>Temp.</th>
<th>Purity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noureddini et al. (2004)</td>
<td>Soybean oil</td>
<td>NaOH</td>
<td>2:1, 2.5:1, 3:1</td>
<td>0.18 wt%</td>
<td>200-240</td>
<td>20 min</td>
<td>(purified from biodiesel production) 1) Pure 2) Crude</td>
</tr>
<tr>
<td>Fregolente et al. (2006)</td>
<td>soybean oil</td>
<td>NaOH</td>
<td>0.18, 0.24, 0.3:1</td>
<td>0.14, 0.2, 0.26 wt%</td>
<td>190-210</td>
<td>90 min</td>
<td>Pure</td>
</tr>
<tr>
<td>Echeverri et al. (2011)</td>
<td>Soybean oil</td>
<td>NaOH/NaOCH₃</td>
<td>2.5:1</td>
<td>dependent on the transesterification</td>
<td>160,180,200,220</td>
<td>60 min</td>
<td>1) Pure 2) Crude (only MeOH removal)</td>
</tr>
<tr>
<td>Echeverri et al. (2013)</td>
<td>Caster oil ME</td>
<td>NaOH/Soap</td>
<td>2.5:1</td>
<td>NaOH (1.7% of glycerin) Soap (7.4% of glycerin)</td>
<td>180 (oil) 180/200 (FAME)</td>
<td>30 min (oil) 20/5 min (FAME)</td>
<td>88.1% purity glycerin</td>
</tr>
<tr>
<td>Echeverri et al. (2013)</td>
<td>Soybean FAME</td>
<td>NaOH/Soap</td>
<td>1.5-3:1</td>
<td>NaOH (1.73% of glycerin) Soap (7.41% of glycerin)</td>
<td>160-200</td>
<td>up to 60 min</td>
<td>1) Pure 2) 88.07% purity glycerin</td>
</tr>
<tr>
<td>Rukprasoot et al. (2005)</td>
<td>Palm stearin (98.7% with TAG, 1.3 DAG)</td>
<td>NaOH (only for pure glycerol)</td>
<td>2:1, 2.5:1, 3:1</td>
<td>2.8 wt%</td>
<td>180, 200, 230, 250</td>
<td>15,20,30,60,90 min</td>
<td>1) Commercial grade (≥95%); 2) Crude (70% with 3.7% MAG, 2.8% Na₂O)</td>
</tr>
<tr>
<td>Schulz et al. (2011)</td>
<td>FAME of linseed oil</td>
<td>H₂SO₄, CaO, NaOH</td>
<td>3:1, 4:1, 5:1, 6:1</td>
<td>0.5, 1.5</td>
<td>130</td>
<td>0.5-15</td>
<td>Pure</td>
</tr>
<tr>
<td>Zhong et al. (2013)</td>
<td>soybean oil</td>
<td>NaOH KOH tert-butanol (TB) or tert-pentanol (TP) as solvent</td>
<td>4:1~6.5:1</td>
<td>0.23-0.68 wt%</td>
<td>35-55</td>
<td>1</td>
<td>Pure</td>
</tr>
<tr>
<td>Felizardo et al. (2011)</td>
<td>20-50% FFA in acidulated soap-stocks</td>
<td>Zn, AcZn</td>
<td>1:1.04~1:1.65</td>
<td>0.1, 0.2, 0.3 wt% (mass of Zn)</td>
<td>180,210,220,230</td>
<td>90,180 min</td>
<td>Crude and neutralized by H₂SO₄</td>
</tr>
<tr>
<td>Gole and Gogate (2014)</td>
<td>Nagchampa oil</td>
<td>Zinc acetate</td>
<td>2:1</td>
<td>0.1% of oil</td>
<td>200, 105 (microwave)</td>
<td>240 min 25 min (microwave)</td>
<td>Pure</td>
</tr>
<tr>
<td>Costa et al. (2015)</td>
<td>Sludge from WWTP</td>
<td>NA</td>
<td>1:2 (by mass)</td>
<td>NA</td>
<td>200</td>
<td>120 min</td>
<td>Pure</td>
</tr>
<tr>
<td>---------------------</td>
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<td>------</td>
</tr>
<tr>
<td>Anderson et al. (2016)</td>
<td>Scum form WWTP</td>
<td>1) Zn-Al₂CO₃</td>
<td>1) 18.2 wt% (of oil)</td>
<td>1) 1.8 wt% of oil</td>
<td>238</td>
<td>1) 60</td>
<td>Pure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2) Na₂SO₄</td>
<td>2) 18 wt% (of oil)</td>
<td>2) 1 wt% of oil</td>
<td>2) 180</td>
<td>2) 120 (w/o catalyst)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3) 120 (w/o catalyst)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C12:0 = Lauric acid; C14:0 = Myristic acid; C16:0 = Palmitic acid; C18:0 = Stearic acid; C18:1 = Oleic acid; C18:2 = Linoleic acid; C18:3 = Linolenic acid
Equivalent = equivalent amount of reactants
Equimolar = equivalent moles of reactants
“1:1” refers to Equimolar unless specified
The existing studies provide guidance for the application of glycerolysis in biodiesel feedstock pretreatment while still leaving some important knowledge gaps to be filled. Understanding these unknown aspects of glycerolysis is the key to its successful application in biodiesel industry. As most of the existing studies focused solely on one type of substance, i.e. FFA, oil, or FAME, several questions should be answered in order to obtain the optimum condition for the glycerolysis of FFA/oil mixture: 1) Is equal molar ratio between glycerol and FFA sufficient to reduce FFA to the acceptable level (1%) when both FFA and oil are present? 2) Is crude glycerin (after methanol removal) suitable for the process? 3) If crude glycerin is used for the process, is additional catalyst necessary, since crude glycerol from biodiesel production process already contains a certain amount of soap and basic catalyst (from transesterification process)?

The goal of this study is to fill the knowledge gaps mentioned above. The outcome of this study is expected to strengthen the scientific basis for application of glycerolysis in the biodiesel industry.

3.3 Methodology

3.3.1 Materials

Waste cooking oil was collected from dining facility on-campus. Oleic acid, pure glycerol (ACS grade) and zinc stearate were purchased from Fisher USA (www.fishersci.com). The glyceride standards (triolein, diolein, monoolein) and two internal standard materials (tricaprin and (S)-(−)-1,2,4-Butanetriol) were purchased from Nu-Chek-Prep, Inc. (www.nu-chekprep.com). MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide) was purchased from Restek (http://www.restek.com/). Other chemicals such as toluene (HPLC grade, 99.7%), isopropanol
(HPLC grade, 99.7%), HCl (ACS grade, 37%), methanol (ACS grade, 99.8%), pyridine (ACS grade, 99.0%), n-heptane (HPLC grade, 99.7%), NaOH (ACS grade, 97%) and Bromophenol Blue (ACS grade, 99.9%) were all purchased from the chemical stockroom in University of Cincinnati. Trap grease samples were obtained from JTM Food Group (OH, USA). Crude glycerol was obtained from biodiesel production in the lab.

3.3.2 Experimental setup

(1) Preparation of high FFA oil/FOG
Two types of oil/FOG were prepared for this study. The synthetic high FFA oils were prepared by mixing the waste cooking oil (FFA% close to 5%) with oleic acid at designated ratios. The trap grease FOGs were prepared by heating & filtration method: raw trap grease was heated at 105°C to remove water. After the evaporation of water, the FOGs were separated from the solids through filtration.

(2) Preparation of crude glycerol. Biodiesel production was conducted in a 1L flask by mixing waste cooking oil with methanol and NaOH under heating condition. Crude glycerol was separated from mixture after reaction and methanol was removed through a rotary evaporator. The dose of chemicals used for the transesterification reaction was determined from Agnew et al. (2009).

(3) Glycerolysis was performed in a 250 ml flask on a hotplate with a magnetic stirrer. The high-FFA oil and glycerol were heated separately to the desired temperature before mixing. After the reaction, an aliquot of the sample was taken for FFA titration.
3.3.3 Experimental design

This study was conducted in three phases. Phase I was focused on characterization of trap grease and determining the important factors that might affect the performance (FFA reduction) of the glycerolysis process. This task was fulfilled by applying a 2-level full factorial experimental design (of the operational parameters) to the glycerolysis of the synthetic high oil. In addition to these operational parameters, the initial FFA concentration was also of interest and therefore the experiments were performed on two different FFA concentrations. The findings from the glycerolysis of synthetic oil was verified on the FOG derived from trap grease. Because zinc-containing catalysts were reported to be able improve the glycerolysis of pure FFA by several existing studies (Pouilloux et al., 2000; Macierzanka and Szelag, 2004; Felizardo et al., 2011), Phase II of the study was hence focused on determining if the zinc stearate catalyst was effective in improving the glycerolysis process without negative influence on the following transesterification process. The selection of zinc stearate (zinc carboxylate) as the catalyst of interest was based on the consideration that once proven effective, similar zinc carboxylate catalyst could be produced from residual FFA in the solids of trap grease. Phase III was focused on parametric optimization of the glycerolysis process based on the findings from Phase I and II of the study. Another task of the Phase III was to study the concentration change of other components (glycerin, mono-, di-, tri-glycerides) during the glycerolysis process.
3.3.4 Analytical methods

**Acid value**

The FFA level of the oil can be expressed in the form of acid value (mg KOH/g oil). The conversion ratio between acid value and mass percentage of FFA was 2:1, based on the average molecular weight of FFAs (Chai et al., 2014). AOCS method Cd 3d 63 (AOCS, 2007) was applied to determine the acid value of the sample. The solvent for titration was a mixture of toluene and isopropyl alcohol at the blend ratio of 1:1 (v/v). A 0.1 N KOH solution was used as the titrant and 1% (w/v) phenolphthalein solution (in isopropyl alcohol) was the indicator. The acid value was calculated by the following equation:

\[
\text{Acid Value} = (A - B) \times N \times \frac{56.1}{W}
\]

Eq. 3.7

Where:

- **Acid Value**: mg KOH/g of sample
- **A**: volume, ml of KOH solution used in the titration
- **B**: volume, ml of KOH solution used in the neutralization of solvent
- **N**: normality of KOH solution
- **W**: mass, grams of the sample

**Soap and catalyst concentrations**

The concentrations of soap and catalyst were determined by a modified method based on AOCS Cc 17-79 (Van Gerpen et al., 2004). The method is a two-step sequential titration process. The 1st titration reports the amount of alkaline catalyst in the crude glycerol and the 2nd titration shows how much soap is present. The detailed procedure is shown below:
1\textsuperscript{st} titration

1) Prepare an acetone solution containing 2% distilled water; prepare 0.1 N HCl solution; prepare a 1% phenolphthalein solution (in isopropanol); prepare a bromophenol blue indicator solution (0.4% in water)

2) Prepare 5 g of crude glycerol sample

3) Dissolve the sample in 100 ml acetone solution

4) Add 2 ml of 1% phenolphthalein indicator solution

5) Titrate with 0.1 N HCl solution until the phenolphthalein end point (color changes from pink to clear)

2\textsuperscript{nd} titration

6) Add 1 ml of bromophenol blue indicator solution

7) Titrate with 0.1 N HCl solution until the bromophenol end point (color changes from blue to yellow)

The calculation of catalyst and soap concentrations from titration results is performed by the following two equations:

\textbf{1\textsuperscript{st} titration}

\textit{Catalyst}\% = \frac{A \times 0.1 \times MW_c}{1000 \times W} \quad \textit{Eq.3.8}

Where:

\textit{Catalyst}\% = \text{catalyst concentration, g/g sample}

\textit{A} = \text{amount of 0.1 N HCl, ml}
\[ W = \text{amount of sample, g} \]
\[ MW_c = \text{molecular weight of the catalyst, g/mole} \]

2\textsuperscript{nd} titration

\[ \text{Soap}\% = \frac{B \times 0.1 \times MW_s}{1000 \times W} \quad \text{Eq.3.9} \]

Where:

\( \text{Soap}\% \) = soap concentration, g/g sample

\( B \) = amount of 0.1 N HCl, ml

\( W \) = amount of sample, g

\( MW_s \) = molecular weight of the soap, g/mole

**Measurement of glycerol and glycerides**

The concentrations of glycerol and glycerides (mono-/di-/tri-glycerides) were measured in accordance to the ASTM D6584 method (ASTM, 2013). A Hewlett-Packard gas chromatograph (model 5890) with a flame ionization detector and an auto sampler (model 7673) was used for analysis. The GC-FID system was equipped with a Restek Rtx-Biodiesel TG column (10 m * 0.32 mm * 0.1 um; with a 2 m * 0.53 mm guard column). The column temperature was programmed as follows: the initial temperature was set at 50 °C and was held for 1 min. Then the temperature was first increased to 180 °C with a rate of 15 °C /min. Next, the temperature was further increased to 230 °C with a rate of 7 °C /min. Finally, the temperature was increased to 380 °C with a rate of 30 °C/min and was held for 10 min. The detector temperature was set at 380 °C and the carrier gas was H₂ with a flow rate of 3 mL/min.
The method requires a calibration function for each compound in order to convert its area into corresponding mass percentage. The calibration function was derived from the analysis of 5 standard solutions prepared from Table 3 of the ASTM D6584 method. Each standard solution contained 5 standard materials: triolein, diolein, monoolein, (S)-(−)-1,2,4-Butanetriol (internal standard 1) and tricaprin (internal standard 2). The calibration function was derived by Eq.3.10.

\[ \frac{W_x}{W_{IS}} = a_x \times \left( \frac{A_x}{A_{IS}} \right) + b_x \]  \hspace{1cm} \text{Eq.3.10}

Where:

- \( W_x \) = mass of the reference substance (e.g. glycerin), mg
- \( W_{IS} \) = mass of the internal standard (IS 1 for glycerin; IS 2 for glycerides), mg
- \( A_x \) = peak area of the reference substance
- \( A_{IS} \) = peak area of the internal standard
- \( a_x \) = slope of the calibration function for the reference substance
- \( b_x \) = intercept of the calibration function for the reference substance

The actual concentration of glycerin and glycerides were determined through Eq.3.11-3.12:

**Glycerin:**

\[ G = \left( a_g \times \frac{A_g}{A_{IS1}} + b_g \right) \times \frac{W_{IS1} \times 100}{W} \]  \hspace{1cm} \text{Eq.3.11}

Where:

- \( G \) = mass percent of glycerin in sample, %
\[ A_g = \text{peak area of glycerin} \]

\[ A_{IS1} = \text{peak area of the internal standard 1} \]

\[ W_{IS1} = \text{mass of internal standard 1, mg} \]

\[ W = \text{mass of the sample, mg} \]

\[ a_g = \text{slope of the calibration function for glycerin} \]

\[ b_g = \text{intercept of the calibration function for glycerin} \]

**Individual glycerides:**

\[ G_{li} = \left( a_i \times \frac{A_i}{A_{IS2}} + b_i \right) \times W_{IS2} \times 100/W \] \hspace{1cm} \text{Eq.3.12}

Where:

\[ G_{li} = \text{mass percent of the individual glycerides (e.g. triglycerides) in sample, \%} \]

\[ A_i = \text{peak area of the individual glycerides} \]

\[ A_{IS2} = \text{peak area of the internal standard 2} \]

\[ W_{IS2} = \text{mass of internal standard 2, mg} \]

\[ W = \text{mass of the sample, mg} \]

\[ a_i = \text{slope of the calibration function for the individual glycerides} \]

\[ b_i = \text{intercept of the calibration function for the individual glycerides} \]

**Measurement of fatty acid profile**
The fatty acid profile of the FOG was determined by analyzing its fatty acid methyl ester (biodiesel). The FOG was converted into biodiesel through a two-step process. The first step was to reduce FFA % by an acid catalytic esterification. The esterification was conducted by following the procedure in Chai et al. (2014). The second step was to convert the treated FOG into biodiesel through an alkaline transesterification. This step was conducted by following the procedure described in Agnew et al. (2009). The fatty acid profile of the resulting biodiesel was measured by Bio-oils Research Unit at the United States Department of Agriculture-Agricultural Research Service (USDA-ARS; Peoria, IL, USA). The analytical method used was developed by Knothe et al. (2015) and described as following: for gas chromatograph (GC) analysis, a Perkin-Elmer (Norwalk, CT, USA) Clarus 580 gas chromatograph equipped with a flame ionization detector was used. The column used was DB-88 column (30 m × 0.25 mm ID × 0.20 lm film thickness). The initial oven temperature was held at 150 °C for 15 min and then was increased to 210 °C at a rate of 2 °C/min. Next, the temperature was increased at a rate of 50 °C/min to 220 °C and was held for 5 min. Helium (He) was the carrier gas and flow rate was 9.6 mL/min. The injector and detector temperatures were set at 240 and 280 °C, respectively. For mass spectrometric (MS) analysis, the same type of column and temperature program were used in an Agilent (Santa Clara, CA, USA) 6890 GC equipped with an Agilent 5973 mass selective detector.
3.4 Results and Discussion

3.4.1 Phase I results

3.4.1.1 Characterization of trap grease

Trap grease samples were collected from three different sampling positions in a grease trap and their compositions (wt%) and FFA% in FOG are shown in Table 3.2. The highest FOG concentration was observed in the samples taken from the manhole that was closest to the inlet of the grease trap (manhole#1) and the concentration (and corresponding variation) decreased along the length of the grease trap towards the outlet. On the other hand, the FFA% in FOG increased from manhole#1 to #3.

<table>
<thead>
<tr>
<th>Source</th>
<th>Bulk water %</th>
<th>Solids %</th>
<th>FOG %</th>
<th>FFA% in FOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manhole#1</td>
<td>44.55±6.49</td>
<td>19.82±4.08</td>
<td>35.64±10.15</td>
<td>35.17±4.82*</td>
</tr>
<tr>
<td>Manhole#2</td>
<td>64.82±3.62</td>
<td>25.38±3.16</td>
<td>9.79±4.5</td>
<td>54.93±3.80*</td>
</tr>
<tr>
<td>Manhole#3</td>
<td>79.71±1.24</td>
<td>17.76±0.76</td>
<td>2.53±0.58</td>
<td>66.12±4.32*</td>
</tr>
</tbody>
</table>

*Collected in the same batch

Figure 3.1 (a-d) show the pictures of raw trap grease in the manhole and the heating process of obtaining FOG from the trap grease. After FOG separation, the samples of the trap grease solids and FOG were sent to the Center for Applied Energy Research at University of Kentucky for ultimate analysis and the results are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>% ash</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% S</th>
<th>% O</th>
<th>HHV (Btu/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOG</td>
<td>0.01</td>
<td>76.71</td>
<td>11.90</td>
<td>&lt;0.01</td>
<td>0.22</td>
<td>11.13</td>
<td>16,842</td>
</tr>
<tr>
<td>Solids</td>
<td>1.32</td>
<td>54.46</td>
<td>10.21</td>
<td>3.81</td>
<td>0.48</td>
<td>29.72</td>
<td>11,280</td>
</tr>
</tbody>
</table>
Table 3.4 summarizes the fatty acid profile of several oil feedstocks. The fatty acid profile of FOG from trap grease was mainly characterized by palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1), which is close to that of brown grease and yellow grease reported by Canakci and Van Gerpen (2001). The brown and yellow grease in their study were both from a rendering plant (differed in FFA%). On the other hand, the fatty acid profile of soybean oil is dominated by linoleic acid (C 18:2) and oleic acid.

Table 3.4. Fatty acid profile of the FOG from trap grease

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>FOG from trap grease</th>
<th>Brown grease*</th>
<th>Yellow grease*</th>
<th>Soybean oil*</th>
<th>Palm oil*</th>
<th>Tallow&amp;</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td>3.1</td>
<td>1.66</td>
<td>2.43</td>
<td>0.5-2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>16:0</td>
<td>26.8</td>
<td>22.83</td>
<td>23.24</td>
<td>10.18</td>
<td>32-45</td>
<td>27</td>
</tr>
<tr>
<td>16:1</td>
<td>2.7</td>
<td>3.13</td>
<td>3.79</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:0</td>
<td>16.6</td>
<td>12.54</td>
<td>12.96</td>
<td>4.76</td>
<td>2-7</td>
<td>7</td>
</tr>
<tr>
<td>18:1</td>
<td>45.2</td>
<td>42.36</td>
<td>44.32</td>
<td>22.52</td>
<td>38-52</td>
<td>48</td>
</tr>
<tr>
<td>18:2</td>
<td>5.5</td>
<td>12.09</td>
<td>6.97</td>
<td>52.34</td>
<td>5-11</td>
<td>2</td>
</tr>
<tr>
<td>18:3</td>
<td>0.82</td>
<td>0.67</td>
<td>8.19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Canakci and Van Gerpen (2001)
http://www.chempro.in/fattyacid.htm
http://web.pdx.edu/~wamsenc/C336S12/fat.pdf
3.4.1.2 Study on the important parameters

A $2^4$ full factorial design was conducted for the synthetic high FFA oils. The 4 parameters of interest were glycerol-to-FFA molar ratio, soap & catalyst concentration, reaction temperature and reaction time, and the two levels of each parameter are shown in Table 3.5. The selection of these values was based on the information provided in the existing literature (Table 3.1). Two initial FFA concentrations were prepared: 17.81±0.11% and 55.24±0.20%. The Parte charts (Figure 3.2 and 3.3) show the terms that have significant impact on the FFA reduction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol-to-FFA molar ratio</td>
<td>1:1</td>
<td>2:1</td>
</tr>
<tr>
<td>Soap &amp; catalyst concentration (%)</td>
<td>0</td>
<td>3.64</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>Time (hr)</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

Overall, temperature and time were the most influential parameters. For the 17.81±0.1% FFA oil, the FFA reduction ranged from 22.22% to 98.36% and all four parameters as well as the interaction between “soap & catalyst concentration” and “glycerol-to-FFA molar ratio” had significant impacts on the result. This indicated that excessive glycerol might be necessary to favor the glycerolysis of FFA. It was also indicated that the presence of soap and catalyst in the crude glycerol facilitated the contact between glycerol and FFA (Szelag and Zwierzykowski, 1998). But it was also observed that increasing glycerol-to-FFA molar ratio and using crude glycerol at the same time did not necessarily double the effect. On the other hand, the range of FFA reduction was from 50% to 99.49% for the 55.24±0.2% FFA oil. As is shown in Figure 3.4, temperature and time had much more significant impact on FFA reduction than other parameters.
A 2-level full factorial analysis for key parameters was also performed for the FOG derived from trap grease. The experimental conditions applied are summarized in Table 3.6. The result of the
analysis (Figure 3.5) confirmed the assumption that temperature and time were the parameters that had dominant effect on the FFA reduction.

**Table 3.6.** Values of the parameters for the 2-level full factorial design (29.48±4.4% initial FFA)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol-to-FFA molar ratio</td>
<td>1:1</td>
<td>2:1</td>
</tr>
<tr>
<td>Soap &amp; catalyst concentration (%)</td>
<td>0</td>
<td>3.78</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>200</td>
<td>230</td>
</tr>
<tr>
<td>Time (min)</td>
<td>120</td>
<td>240</td>
</tr>
</tbody>
</table>

**Figure 3.4.** Pareto chart of effects (29.48±4.4% FFA)

### 3.4.2 Phase II results

The FFA reduction was compared between using zinc stearate catalyst and the w/o catalyst situations at three combinations of temperature and time: 200 °C & 240 min, 215 °C & 240 min, and 230 °C & 180 min. For each combination, two levels of catalyst dose were investigated. The selection of the doses was based on the range reported in the literature, where the lower level
(1:0.025) was the lowest effective value reported while the higher level (1:0.1) was doubled the highest value reported by Macierzanka and Szelag (2004).

Table 3.7 shows the ANOVA single factor test results of the comparison. It is indicated that there was no significant difference in the final FFA reduction between using and absence of catalyst (all $p$-values were greater than 0.05). In addition, the separation of the catalyst after the glycerolysis reaction, e.g. through filtration or centrifuge, was not successful. Therefore, the use of zinc stearate catalyst was considered unnecessary.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catalyst dose*</th>
<th>Reaction time (min)</th>
<th>Average final FFA reduction (%)</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>w/o catalyst</td>
<td>w/catalyst</td>
</tr>
<tr>
<td>200</td>
<td>1: 0.025</td>
<td>240</td>
<td>90.55±3.16</td>
<td>90.26±2.40</td>
</tr>
<tr>
<td></td>
<td>1: 0.1</td>
<td></td>
<td>89.44±3.03</td>
<td>0.64</td>
</tr>
<tr>
<td>215</td>
<td>1: 0.025</td>
<td>240</td>
<td>92.41±3.37</td>
<td>91.32±2.67</td>
</tr>
<tr>
<td></td>
<td>1: 0.1</td>
<td></td>
<td>90.57±3.18</td>
<td>0.48</td>
</tr>
<tr>
<td>230</td>
<td>1: 0.025</td>
<td>180</td>
<td>98.22±1.22</td>
<td>98.48±1.45</td>
</tr>
<tr>
<td></td>
<td>1: 0.1</td>
<td></td>
<td>98.39±1.45</td>
<td>0.92</td>
</tr>
</tbody>
</table>

*Catalyst dose = FFA: catalyst molar ratio

3.4.3 Phase III results

3.4.3.1 Parameter optimization

According to the results from Phase I and II of the study, parameter optimization was focused on reaction temperature and time. The average initial FFA concentration of the FOG used for the optimization was 29.11±3.7% FFA. Therefore, an average FFA reduction of 97% was necessary in order for the treated oil to meet the common FFA threshold of 1% for the alkaline transesterification process. Figure 3.5 shows the influence of temperature and time on the FFA reduction. Overall, a temperature of 230 °C was necessary for lowering the FFA % in the treated oil to 1% or less. As compared to 200 °C, the FFA reduction was faster under 215 °C until 210
min, however, there was no significant difference in the final reduction of FFA between the two
temperatures at 240 minutes (p-value: 0.39). So, 230 °C and 150 min was chosen as the preferred
combination of temperature and time for the glycerolysis process.

Figure 3.5. The impact of temperature and time on FFA reduction
(Average initial FFA concentration: 29.11±3.7%; crude glycerol-to-FFA molar ratio: 1:1; w/o catalyst)

3.4.3.2 Analysis of FOG composition change during glycerolysis process

Calibration and standardization for ASTM D6584

Five standard solutions were prepared by following the procedure in ASTM D6584 method.

Table 3.8 shows the mass of each component in the standard solutions. The corresponding areas
of the standards solutions are summarized in Table 3.9. Accordingly, the calibration functions
for glycerin, mono-, di- and tri-glycerides were calculated. The slope (a*) and intercept (b*) of
the calibration function were derived from Figure 3.6-3.9 for the components of interest.
Table 3.8 Mass of each component in the standard solutions

<table>
<thead>
<tr>
<th>Component (ug)</th>
<th>Std 1</th>
<th>Std 2</th>
<th>Std 3</th>
<th>Std 4</th>
<th>Std 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-diolein</td>
<td>51.6</td>
<td>103.2</td>
<td>206.4</td>
<td>361.2</td>
<td>516</td>
</tr>
<tr>
<td>Glycerol</td>
<td>5.28</td>
<td>15.84</td>
<td>26.4</td>
<td>36.96</td>
<td>52.8</td>
</tr>
<tr>
<td>Monoolein</td>
<td>102.6</td>
<td>256.5</td>
<td>513</td>
<td>769.5</td>
<td>1026</td>
</tr>
<tr>
<td>Triolein</td>
<td>51.7</td>
<td>103.4</td>
<td>206.8</td>
<td>361.9</td>
<td>517</td>
</tr>
<tr>
<td>Internal Std 1 ((S)-(−)-1,2,4-Butanetriol)</td>
<td>104</td>
<td>104</td>
<td>104</td>
<td>104</td>
<td>104</td>
</tr>
<tr>
<td>Internal Std 2 (Tricaprin)</td>
<td>808</td>
<td>808</td>
<td>808</td>
<td>808</td>
<td>808</td>
</tr>
</tbody>
</table>

Table 3.9 Area of components

<table>
<thead>
<tr>
<th>Component</th>
<th>RT (min)</th>
<th>Std 1</th>
<th>Std 2</th>
<th>Std 3</th>
<th>Std 4</th>
<th>Std 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerin</td>
<td>~5.9</td>
<td>3257.3</td>
<td>5900.2</td>
<td>9611.8</td>
<td>17594.5</td>
<td>22054.5</td>
</tr>
<tr>
<td>IS1</td>
<td>~6.5</td>
<td>56181.8</td>
<td>34225.6</td>
<td>34178</td>
<td>45828.2</td>
<td>40245.5</td>
</tr>
<tr>
<td>Monoolein</td>
<td>~16.1, 17.5, 17.6</td>
<td>30583.9</td>
<td>46695.6</td>
<td>97407.5</td>
<td>142929.1</td>
<td>200881.1</td>
</tr>
<tr>
<td>IS2</td>
<td>~19.8</td>
<td>182761.4</td>
<td>111131.1</td>
<td>113109.6</td>
<td>109640.7</td>
<td>111107.2</td>
</tr>
<tr>
<td>1,3-diolein</td>
<td>~20.9-21.4</td>
<td>13670.6</td>
<td>15664.4</td>
<td>29200.6</td>
<td>51584.7</td>
<td>79058.8</td>
</tr>
<tr>
<td>Triolein</td>
<td>~24.1, 25</td>
<td>10551.5</td>
<td>12186.6</td>
<td>17505.4</td>
<td>29288.7</td>
<td>43580</td>
</tr>
</tbody>
</table>

Figure 3.6. Calibration function for glycerin

\[ y = 1.0666x + 0.0071 \]
\[ R^2 = 0.999 \]
Figure 3.7. Calibration function for monoglycerides

Figure 3.8. Calibration function for diglycerides
Analysis of samples

3 temperature levels (200 °C, 215 °C and 230 °C) and 8 time intervals (30-240 min) were tested. Therefore a total of 48 samples (with replicates) were analyzed. A typical GC profile (retention times and peaks) of the components are shown in Figures 3.10-3.12. Figures 3.13-3.15 show the actual concentration of each component in the FOG over the time under different temperatures.

The composition of the FOG before the start of the reaction was: 24.30% FFA, 5.22% of glycerin (added for the reaction), 67.5% TAG, 2.76% DAG and 0.22% MAG. Some common phenomena were observed for all temperature levels. Firstly, for all the three temperatures, the final concentrations of the di- and triglycerides all increased over time, the FFA level decreased, the MAG level increased rapidly during the first 30 minutes and then decreased. For example, the average increase of triglycerides concentration was 11.31%, 11.68% and 13.28% under 200 °C, 215 °C and 230 °C, respectively. Secondly, the change of the concentration of each component over time followed a similar pattern. For instance, an evident decrease of the
triglycerides concentration was observed after 30 min of the reaction under all temperatures, after which the concentration of triglycerides started to increase and the final concentration was approximately 80%. On the other hand, the changes in the concentrations of di- and monoglycerides were different. For example, the concentration of diglycerides peaked in a short time then started to level out throughout the reaction. For monoglycerides, the concentration increased in the first 30 min and then started to decrease. Similar pattern was reported by Szelag and Zwierzykowski (1998) and Anderson (2014) as well. The results also indicated that the reactions involved in the glycerolysis process might occur in a two-stage manner: during the first stage, i.e. the first 30 minutes, glycerin was quickly consumed by FFA and TAG to form MAG and DAG respectively, and resulted in a rapid increase of MAG and DAG as well as a decrease in TAG (Eq.3.1 and 3.4). Glycerin was also consumed by DAG (Eq.3.5) to form MAG. During the second stage, i.e. after 30 minutes, the MAG reacted with FFA to form DAG (Eq.3.3), which quickly consumed the MAG formed during the first stage. Meanwhile, DAG reacted with FFA to form TAG (Eq.3.2) which is attributed to the increase of TAG concentration after first 30 minutes of the process.

A 1st order model for the reduction of FFA during the glycerolysis process was assumed, according to Anderson et al. (2016). The integrated form of 1st order reaction is shown in Eq. 3.13.

\[ kt = \ln\left(\frac{C_{FFA,t}}{C_{FFA,0}}\right) \]

Where:
\[ k = \text{reaction constant, hr}^{-1} \]

\[ C_{FFA,0} = \text{initial FFA concentration in the FOG, \%} \]

\[ C_{FFA,t} = \text{FFA concentration in the FOG at a specific time, \%} \]

\[ t = \text{reaction time, min} \]

Therefore, the reaction constant \( k \) can be determined by solving for the slope of the graph of “\( \ln(C_{FFA_t}/C_{FFA0}) vs t \)”. Figure S4.1-4.3 show the “\( \ln(C_{FFA_t}/C_{FFA0}) vs t \)” plots for 200, 215 and 230 °C and the corresponding values for reaction constant \( k \) are -0.4957, -0.6063, and -1.4245 hr\(^{-1}\).

As compared with the values reported by Anderson et al. (2016), the reaction constant at 230 °C of this study is very close to the value under the catalysis of Na\(_2\)SO\(_4\) (-1.4518 hr\(^{-1}\)). This is possibly due to the catalytic effect from the residual Na catalyst and soap in the crude glycerin.

The activation energy \( (E_a) \) of the FFA reduction in this study was calculated by Arrhenius equation and result was 69.14 kJ/mole.
Figure 3.10. Overall retention times and peaks of components (FOG before reaction)
Figure 3.11. Retention times and peaks for diglycerides (FOG before reaction)
Figure 3.12. Retention times and peaks for triglycerides (FOG before reaction)
Figure 3.13 (a). Composition of each component over time (200 °C)

Figure 3.13 (b). Composition of MAG and glycerin over time (200 °C)
Figure 3.14 (a). Composition of each component over time (215 °C)

Figure 3.14 (b). Composition of MAG and glycerin over time (215 °C)
Figure 3.15 (a). Composition of each component over time (230 °C)

Figure 3.15 (b). Composition of MAG and glycerin over time (230 °C)
3.4.4 Converting (glycerolysis) treated oil into biodiesel

The treated oil after glycerolysis process was dark and highly viscous (Figure 3.16), which agrees with the findings reported by another study (Felizardo et al., 2011). The treated oil was converted into biodiesel by the same approach mentioned in section 3.3.2. The color and viscosity of the resulting biodiesel were close to the treated oil before transesterification. As there was no observable layers of crude biodiesel and glycerin, the glycerin could not be separated by draining. Instead, water washing was directly applied in absence of the draining step (Figure 3.17). Multiple batches of water washing were performed to dissolve and remove the glycerin. Due to the significant emulsion occurred during the water washing step, the recovery of purified biodiesel was less than 50% of original amount of FOG used for biodiesel production. An alternative separation method to water wash is “glycerol wash” where extra glycerol is added to the biodiesel-glycerol mixture to facilitate the two components (Bi et al., 2015). The effectiveness and optimum condition of glycerol wash will be studied in the future.

The water washed biodiesel gelled up at a temperature close to 40 °C while the biodiesel after distillation stayed in liquid form at room temperature (Figure 3.18 a and b). The fuel composition of the water washed biodiesel were measured by Eurofins QTA (West Chester, OH) and the results are summarized in Table 3.10. It is indicated that the conversion is not complete even after an extended reaction time (4 hrs). The issue of incomplete conversion was also observed by Costa et al. (2015). Improving the biodiesel conversion rate will be part of the future work.
Figure 3.16. Treated oil after glycerolysis process

Figure 3.17. (a) Crude biodiesel and glycerin mixture after 1st batch of water washing; (b) Purified biodiesel (top layer) and water (bottom layer)
Figure 3.18. (a) water washed biodiesel at 40°C; (b) distilled biodiesel at 20°C

Table 3.10 QTA analysis results for biodiesels produced from the FOG pretreated by different technologies (www.eurofins.com)

<table>
<thead>
<tr>
<th>Characteristics (%)</th>
<th>BioD from two-step esterification treated FOG</th>
<th>BioD from glycerolysis-treated FOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.99</td>
<td>1.10</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>0.35</td>
<td>3.64</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>0.07</td>
<td>7.45</td>
</tr>
<tr>
<td>FFA#</td>
<td>0.76</td>
<td>0.68</td>
</tr>
<tr>
<td>FAME*</td>
<td>97.83</td>
<td>87.04</td>
</tr>
</tbody>
</table>

#Titrated value  
*FAME=100%-monoglycerides%-diglycerides%-triglycerides%-FFA%  
^Average of results for IM-1 and IM-2

3.4.5 Comparison between glycerolysis and acid-catalyzed esterification

Table 3.11 provides a summary of material use, reaction time and temperature for pretreating 200 ml FOG derived from trap grease using acid-catalyzed esterification and glycerolysis. The two technology pathways are shown in Figure 3.19. The initial FFA of the FOG was 35.69±0.74% and in both cases the final FFA concentration was reduced to < 1%. Considering
the high initial FFA concentration, a 2-step acid esterification process was used. The MeOH and H\textsubscript{2}SO\textsubscript{4} inputs for each step were calculated by Eq.3.14 and 3.15 (Chai et al., 2014).

\[
V_{MeOH} = 139.72 \times (FFA\% \times 100)^{-0.689} \times V_{FOG} \times \rho_{FOG} \times FFA\%/MW_{FFA} \times MW_{MeOH}/\rho_{MeOH} \\
\text{Eq. 3.14}
\]

Where:

\[
V_{MeOH} = \text{volume of MeOH used for esterification, ml}
\]

\[
FFA\% = \text{FFA concentration in FOG, wt%}
\]

\[
V_{FOG} = \text{volume of FOG, ml}
\]

\[
\rho_{FOG} = \text{density of FOG, 0.9 g/ml}
\]

\[
MW_{FFA} = \text{average molecular weight of FFA, 278 g/mole}
\]

\[
MW_{MeOH} = \text{molecular weight of methanol, 32 g/mole}
\]

\[
\rho_{MeOH} = \text{density of methanol, 0.79 g/ml}
\]

\[
V_{H2SO4} = 30.455 \times (FFA\% \times 100)^{-0.64}/100 \times V_{FOG} \times \rho_{FOG} \times FFA\%/\rho_{H2SO4} \\
\text{Eq.3.15}
\]

Where:

\[
V_{H2SO4} = \text{volume of H}_2\text{SO}_4 \text{ used for esterification, ml}
\]

\[
FFA\% = \text{FFA concentration in FOG, wt%}
\]

\[
V_{FOG} = \text{volume of FOG, ml}
\]
\[ \rho_{\text{FOG}} = \text{density of FOG, } 0.9 \text{ g/ml} \]

\[ \rho_{\text{H}_2\text{SO}_4} = \text{density of H}_2\text{SO}_4, 1.84 \text{ g/ml} \]

Accordingly, the MeOH and H\textsubscript{2}SO\textsubscript{4} used for the first step of the two-step acid catalyzed esterification were 111 and 1.07 ml, respectively. This corresponded to a MeOH-to-FFA molar ratio of 11.86:1 and a H\textsubscript{2}SO\textsubscript{4} to FFA wt% of 3.06%. After the 2-hr reaction at 65 °C, the FFA % in the resulting oil was 1.82%. According to the stoichiometry of esterification reaction, the formation of water is equal molar to the reduction of FFA. Therefore, by calculating the moles of FFA diminished during the first step, the amount of water formed was approximately 4.38 g.

Although no water layer was observed after the first step of esterification, the oil-methanol mixture was allowed to settle for 30 min before the methanol layer was separated from the oil in the separation funnel. This separation of wet methanol from the oil is recommended by Canacki and Van Gerpen (2001) to minimize the negative impact of water in the second step of esterification. By using the same equations, the dose of MeOH and H\textsubscript{2}SO\textsubscript{4} for the second step was calculated as 22 and 0.18 ml, respectively. This corresponded a MeOH-to-FFA molar ratio of 46.09:1 and a H\textsubscript{2}SO\textsubscript{4} to FFA wt% of 10.11%. The same reaction time and temperature were applied to the second esterification step and the final FFA% in the resulting oil was 0.28%. On the other hand, the input of crude glycerin was 16.80 ml (1:1 glycerin-to-FFA molar ratio) for 200 ml FOG and the reaction time and temperature were 150 min and 230 °C, respectively. The total processing time (reaction + settling) of a 2-step acid-catalyzed esterification was nearly twice as much as the reaction time of glycerolysis, while the reaction temperature of glycerolysis was more than 3 times as much as that of the esterification process. As mentioned earlier, one
disadvantage of esterification process is that energy consumption may be significant for purifying the wet methanol (separating methanol from water), as indicated by Anderson (2014). In order to compare the overall energy consumption of the two processes, data needs to be collected from pilot-scale operations or process simulations.

After pretreatment (glycerolysis and esterification), both of the resulting oils were converted into biodiesel by the same transesterification process (2hr, 65 °C, 3.5 g NaOH/L FOG and 6:1 molar ratio between FOG and MeOH). The QTA analysis results (Table 3.10) showed that the biodiesel produced from FOG treated by two-step acid catalyzed esterification had a fatty acid methyl ester (FAME) content of 97.83% while the biodiesel produced from FOG treated by glycerolysis had a FAME content of 87.04%.

Table 3.11. Summary of material use, reaction time and temperature for pretreating 200 ml FOG derived from trap grease

<table>
<thead>
<tr>
<th>Pretreatment process</th>
<th>Material use</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-catalyzed esterification</td>
<td>123 ml MeOH, 1.25 ml H$_2$SO$_4$</td>
<td>65 °C</td>
<td>240 min reaction time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 min settling time (for removing wet MeOH) after 1$^{st}$ step</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15 min for MeOH recovery in a rotoray evaporator</td>
</tr>
<tr>
<td>Glycerolysis</td>
<td>16.89 ml glycerin</td>
<td>230 °C</td>
<td>150 min</td>
</tr>
</tbody>
</table>
Figure 3.19. Technology pathways for FFA pretreatment: acid-catalyzed esterification vs glycerolysis
3.5 Summary of the chapter

A lab-scale experimental study was performed to evaluate glycerolysis as a high FFA oil pretreatment technology. As compared to the 2-step acid-catalyzed esterification process, the glycerolysis process possesses the following advantages and disadvantages:

Advantages

- As H₂SO₄ is not used in the glycerolysis process, the neutralization and separation of H₂SO₄ from the treated oil can be avoided, which leads to reduced hazardous chemical use and waste disposal.
- As methanol is not used in the glycerolysis process, the high energy consumption needed to recover the excess methanol was avoided, which leads to a potential reduction in energy consumption for the high FFA oil pretreatment step.
- As glycerolysis process can reduce the FFA concentration to the desired level (< 1%) in one step, the overall reaction time can be reduced (150 min in total) as compared to the 2-step acid-catalyzed esterification process (285 min in total)

Disadvantages

- The reaction temperature of glycerolysis process (230 °C) is higher than that of the 2-step acidic esterification process (65 °C)
- The treated oil after glycerolysis process has a much darker color and higher viscosity, which may increase the difficulty in separation of crude biodiesel from glycerin after the transesterification process.
The outcome of this study also provides the answer to the three research questions proposed in section 3.2 of this chapter:

- An equal molar ratio between glycerol and FFA is sufficient to reduce the FFA % in the treated oil down to 1% or less within a short time period (150 min).
- The crude glycerin obtained from biodiesel production, after methanol removal, is as effective as the pure glycerin. This indicates the possibility of using crude glycerin for glycerolysis without extensive purification procedure, and hence reduces the potential environmental impact and cost of the glycerolysis process.
- The zinc carboxylate catalyst is the most commonly used catalyst for glycerolysis in the literature; however, the result of this study indicates that the positive effect on the glycerolysis process brought by using zinc carboxylate (zinc stearate) catalyst, either by reducing reaction temperature or shortening reaction time, is insignificant. Therefore, it is concluded that the use of zinc catalyst for glycerolysis process is not necessary. This avoids the separation and waste disposal of the zinc catalyst, and hence reduces the potential environmental impact and cost of the glycerolysis process.
3.6 Design of conceptual models for comparing sustainability between the two FFA pretreatment technologies

3.6.1 Overview of the design

The purpose of this section is to design conceptual process models for acid-catalyzed esterification and glycerolysis processes in ChemCAD (www.chemstations.com). ChemCAD is a chemical engineering process simulation software that has been used by several studies for the design and evaluation of biodiesel production process (Chiu et al., 2005; Hernandez et al., 2005; Ruiz-Mercado et al., 2013; Chilev and Simeonov, 2014). The process models created in this section can be used to estimate the infrastructure (e.g. number of reactors, size of the distillation column), material and energy needed for upgrading the technologies (acid-catalyzed esterification and glycerolysis) to commercial-scale production. Additionally, the data obtained from the simulation can be used as an input to sustainability assessment tools, such as GREENSCOPE (“Gauging Reaction Effectiveness for Environmental Sustainability of Chemistries with a multi-Objective Process Evaluator”; Ruiz-Mercado et al., 2013), to evaluate and compare the sustainability of the two high FFA oil pretreatment processes.

A general procedure of designing a simulation process model in ChemCAD includes: choosing the chemical compounds of interest from the component database, selecting a proper thermodynamic model for simulation, deciding the process capacity (e.g. incoming feedstock flowrate), and “mapping out” the process model by selecting proper “unit operations (e.g. reactors, separators)”. The chemical compounds used in these two process models are listed in Table 3.12. As is show, for some chemicals (e.g. methanol), there are exact counterparts in the
built-in component database (from ChemCAD). For others, such as TAG, proxy is used (e.g. triolein) in order to reduce complexity, as indicated by existing studies (Zhang et al., 2003; Ruiz-Mercado et al., 2013; Chilev and Simeonov, 2014). As both process models involve highly polar compounds, such as methanol and glycerin, non-random two liquid (NRTL) model was selected by thermodynamic calculations. The feedstock flowrate of the two conceptual process models are both assumed to be 10 million gallons of high FFA oil (33 wt%) per year, or 6,037 kg/hr, according to Haas et al. (2003). The details of the design are summarized in the following subsections.

Table 3.12. Summary of chemical compounds used in the two process models

<table>
<thead>
<tr>
<th>Chemical compound of interest</th>
<th>Chemical compound used in ChemCAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Methanol</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>Water</td>
<td>Water</td>
</tr>
<tr>
<td>FFA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>Triglycerides (TAG)</td>
<td>Triolein</td>
</tr>
<tr>
<td>Diglycerides (DAG)</td>
<td>Diolein</td>
</tr>
<tr>
<td>Monoglycerides (MAG)</td>
<td>Monoolein</td>
</tr>
<tr>
<td>Methyl ester from FFA</td>
<td>Methyl oleate</td>
</tr>
</tbody>
</table>

3.6.2 Description of the models

3.6.2.1 Design for the 2-step acid-catalyzed esterification process

As mentioned in the previous chapter, acid-catalyzed esterification is the reaction between FFA and methanol with H₂SO₄ as the catalyst. Due to the high FFA concentration (33%), it is reported that a 2-step acid-catalyzed esterification process is required in order to pretreat the oil to the desired (1% FFA) quality (Canakci and Van Gerpen, 2001). Therefore, a 2-step acid-catalyzed esterification process model is created. The operational conditions applied in the process model for the two esterification reactions are summarized in Table 3.13 and the fractional conversion
(for FFA) is assumed to be 90% for each reactor (Canakci and Van Gerpen, 2001). Figure 3.20 shows the process model created in ChemCAD and major parts of the model are described individually as following:

**Mixing of feedstock and chemicals**

Three input streams on the left are: high FFA oil (stream 101), H$_2$SO$_4$ (stream 102), and makeup methanol (stream 103). As the excess methanol is used in both of the two esterification reactors, only a small portion of makeup methanol is needed for a new series of reactions each time. The high FFA oil is heated to 60 °C before being mixed with other chemicals. The recycled (excess) methanol stream is mixed with makeup methanol stream by a mixer (M101) and then mixed with H$_2$SO$_4$ stream via another mixer (M102). The mixed stream (steam 107) has a temperature close to 60 °C due to the temperature (60 °C) of the recycled (excess) methanol (stream 206), therefore no heating is applied to steam 107. The heated high FFA oil and the MeOH-H$_2$SO$_4$ mixture are mixed and sent to the 1$^{st}$ reactor (R101).

**Acid-catalyzed esterification reactions**

The oil and chemicals go through the acid-catalyzed esterification in the 1$^{st}$ reactor (stoichiometric reactor). After the reaction, the mixture (steam 101) go through a flash (F201) where the majority of methanol (with water) are evaporated (stream 201). The flash process is controlled such that sufficient amount of methanol are left in the bottom flow from the Flash (F201) for the second reaction. The bottom flow is then sent to the 2$^{nd}$ reactor (R102). Similar to the procedure for the first reaction, the resulting mixture flow (stream 112) go through another
flash (F202) to remove and recycle most of the remaining methanol (stream 202) from the bottom flow (stream 113).

**Catalyst neutralization**

The bottom flow (stream 113) is sent to a neutralization reactor (R301) where the $\text{H}_2\text{SO}_4$ in the flow is neutralized by sodium hydroxide (stream 301). The resulting mixture is then separated (S301) into waste stream (stream 307) and treated oil (stream 305) that can be used for the alkaline transesterification.

**Methanol recovery**

The top flows from the flashes (F201 & 202) are mixed (M201) and sent to a distillation tower (T201) to separate methanol from water. The top stream (steam 204) from the distillation tower contained recycled methanol with high purity ($>99.9\%$) and goes through a heat changer before being mixed with the makeup methanol flow.

**Table 3.13. Operational conditions of the two esterification reactions**

<table>
<thead>
<tr>
<th>Operational condition</th>
<th>1\textsuperscript{st} reaction</th>
<th>2\textsuperscript{nd} reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor temperature</td>
<td>60 °C</td>
<td>60 °C</td>
</tr>
<tr>
<td>Methanol-to-FFA molar ratio</td>
<td>20:1</td>
<td>40:1</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ dose (wt% of FFA mass)</td>
<td>10%</td>
<td>10%</td>
</tr>
</tbody>
</table>

**3.6.2.2 Design for the glycerolysis process**

Figure 3.21 shows the process model for glycerolysis. The operational condition for the reaction is determined from section 3.4.3, as: 1:1 molar ratio between glycerin and FFA and 230 °C. The two input streams are both heated to the desired temperature (230 °C) before mixing (M101) and the resulting flow (stream 105) is sent to the reactor (R101). After the reaction, the resulting
mixture (stream 107) is sent to a flash where the water formed during the glycerolysis reaction is removed (stream 202) and the treated oil (stream 203) can be used for the alkaline transesterification.

As compared with the 2-step acid-catalyzed esterification process, the glycerolysis model is significantly simplified. Firstly, there are two input flows instead of three and no complicated recovery steps is involved because glycerol is almost completely consumed during the reaction, as indicated from the lab-scale experiments in Chapter 3. However, since the glycerolysis reaction is to be performed under much higher temperature, the overall economic and environmental impacts will need to be evaluated before conclusion could be drawn on which process is more sustainable.

3.6.3 Preliminary results

A preliminary test was conducted for the 2-step acid-catalyzed esterification model by using the information summarized in Table 3.1. The fractional conversion \( F_c \) for FFA in the two reactors were estimated by Eq. 3.16.

\[
F_c = \frac{(m_{oil,i} \times FFA\%_i - m_{oil,e} \times FFA\%_e)}{m_{oil,i} \times FFA\%_i} \times 100\% \quad \text{Eq. 3.16}
\]

Where:

\( F_c \) = fractional conversion \( F_c \) for FFA, %

\( m_{oil,i} \) = mass flow rate of oil before reaction (using triolein as surrogate), kg/hr

\( m_{oil,e} \) = mass flow rate of oil after reaction (using triolein as surrogate), kg/hr

\( FFA\%_i \) = mass % of FFA in the oil before reaction (using oleic acid as surrogate)
\[ \text{FFA}_{e}^{\%} = \text{mass} \% \text{ of FFA in the oil after reaction (using oleic acid as surrogate)} \]

Also, the amount of excess methanol to be recycled after 1\textsuperscript{st} reaction was calculated Eq. 3.17.

\[ m_{\text{MeOH},r} = m_{\text{MeOH},i} - m_{\text{oil},e} \times \frac{\text{FFA}_{e}^{\%}}{M_{\text{FFA}}} \times R_{2nd} \times M_{\text{MeOH}} \quad \text{Eq. 3.17} \]

Where:

\[ m_{\text{MeOH},r} = \text{mass flow rate of methanol to be recycled after 1\textsuperscript{st} reaction, kg/hr} \]

\[ m_{\text{MeOH},i} = \text{mass flow rate of methanol input for 1\textsuperscript{st} reaction, kg/hr} \]

\[ M_{\text{FFA}} = \text{molecular weight of FFA (oleic acid as surrogate), kg mole/kg} \]

\[ M_{\text{MeOH}} = \text{molecular weight of methanol, kg mole/kg} \]

\[ R_{2nd} = \text{molar ratio between methanol and FFA (oleic acid as surrogate)} \]

Accordingly, the operational conditions for the reactors (R101, R102, R301), separators (F101, F102, T201) and other equipment were configured to meet the specified fractional conversion \( F_c \) and excess methanol recycle rate. Table 3.15 and 3.16 summarize the stream composition and operation condition of the equipment. As is shown in Table 3.15 (b), stream 305, the final FFA\% in oil is 0.49\% which agrees with the experimental results reported by Canakci and Van Gerpen (<1\%). Also, it is indicated the purity of the recycled methanol, stream 206, is over 99.9\% and the makeup methanol for each series of reactions is 243.36 kg/hr (stream 103). On the other hand, it is observed that a significantly higher energy input is needed for recycling and purifying
(separating water from methanol) the excess methanol than for operating the three reactors (2 esterification reactors and 1 neutralization reactor). As mentioned in section 3.6.1., the data of energy input, material use and waste generation from this model can be used as inputs to the GREENSCOPE tool that may be used to evaluate the sustainability of the 2-step acid-catalyzed esterification process based on the built-in methodology and indicators.

3.6.4 Future work

As the glycerolysis process involves multiple reactions occurring simultaneously, the process could not be model by using stoichiometric reactor. Instead, the kinetics reactor should be used. The activation energy ($E_a$) and pre-exponential factor ($A$) of each reaction are required for the simulation with kinetics reactor. Therefore, in order to determine the activation energy ($E_a$), the reaction constant ($k$) of each reaction at different temperatures need to be solved for. As water was continuously evaporated under the current experimental setup (Chapter 3), the reverse reactions involved in Eq.3.1-3.3 could be neglected. This reduces the number of unknown reaction constant ($k$) from 10 to 7. As is shown in the section 3.4, the concentration of monoglycerides (MAG) was always very low throughout the entire glycerolysis process; therefore, it may be plausible to neglect the reverse reaction of Eq.3.4 and 3.5. After all the assumptions are applied, the Eq.3.1-3.5 can be re-written as following:

\[
\begin{align*}
Gly + FFA & \rightarrow^{k_1} MAG + H_2O \quad \text{Eq.3.18} \\
DAG + FFA & \rightarrow^{k_2} TAG + H_2O \quad \text{Eq.3.19} \\
MAG + FFA & \rightarrow^{k_3} DAG + H_2O \quad \text{Eq.3.20} \\
TAG + Gly & \rightarrow^{k_4} DAG + MAG \quad \text{Eq.3.21}
\end{align*}
\]
Accordingly, the ordinary differential equation (ode) for each component can be expressed as following:

\[
\frac{d[FFA]}{dt} = -k_1[FFA][Gly] - k_2[FFA][DAG] - k_3[FFA][MAG] \quad \text{Eq.3.23}
\]

\[
\frac{d[MAG]}{dt} = k_1[FFA][Gly] - k_3[FFA][MAG] + k_4[TAG][Gly] + k_5[DAG][Gly] \quad \text{Eq.3.24}
\]

\[
\frac{d[DAG]}{dt} = -k_2[FFA][DAG] + k_3[FFA][MAG] + k_4[TAG][Gly] - k_5[DAG][Gly] \quad \text{Eq.3.25}
\]

\[
\frac{d[TAG]}{dt} = k_2[FFA][DAG] - k_4[TAG][Gly] \quad \text{Eq.3.26}
\]

\[
\frac{d[Gly]}{dt} = -k_1[FFA][Gly] - k_4[TAG][Gly] - k_5[DAG][Gly] \quad \text{Eq.3.27}
\]

One common way to solve for such a group of odes is to fit the experimental data (observed data) for each component of interest through an ode solver and use least square method to estimate the value of the reaction constant \((k)\) for each reaction. This will be the future work for this part of the research.
Figure 3.20. Process model of the 2-step acid-catalyzed esterification process

Figure 3.21. Process model of the glycerolysis process
Table 3.14.

<table>
<thead>
<tr>
<th></th>
<th>Reaction temperature (°C)</th>
<th>FFA% before reaction</th>
<th>MeOH-to-FFA molar ratio</th>
<th>H$_2$SO$_4$ wt% (of FFA mass)*</th>
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<tr>
<td>1$^{\text{st}}$ step</td>
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<td>2$^{\text{nd}}$ step</td>
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*The H$_2$SO$_4$ after 1$^{\text{st}}$ reaction was assumed to remain in the output stream from 1$^{\text{st}}$ reactor
Table 3.1(a). Summary of stream composition for 2-step acid-catalyzed esterification process

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Table 3.15 (b). Summary of stream composition for 2-step acid-catalyzed esterification process (continued)

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Table 3.16. Summary of equipment for 2-step acid-catalyzed esterification process

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3.7 References


Anderson, E (2014) “Glycerolysis for lowing free fatty acid levels”,
https://d10k7k7mywg42z.cloudfront.net/assets/5435820ed4c961629a00f540/Glycerolysis.pdf, accessed Oct. 2015.


Figure S3.1 “ln(C\text{FFA}/C\text{FFA}_0) vs t” plot for glycerolysis conducted under 200 °C, 1:1 glycerin-to-FFA molar ratio

$y = -0.4957x - 0.0148$

$R^2 = 0.9437$
Figure S3.2 “$\ln(C_{FFA}/C_{FFA0})$ vs $t$” plot for glycerolysis conducted under 215 °C, 1:1 glycerin-to-FFA molar ratio

$y = -0.6063x - 0.1824$

$R^2 = 0.9828$
Figure S3.3 “ln(C_{FFA}/C_{FFA0}) vs t” plot for glycerolysis conducted under 230 °C, 1:1 glycerin-to-FFA molar ratio (240 min data point was not included as the reaction reached equilibrium after 210 min)
### Table S3.1 Analytical results of FOG composition by ASTM D6584 method (200 °C)

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<td>ave</td>
<td>max</td>
<td>min</td>
<td>ave</td>
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</tr>
<tr>
<td>180</td>
<td>1.87</td>
<td>7.48</td>
<td>2.34</td>
<td>0.00</td>
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</tr>
<tr>
<td>210</td>
<td>2.57</td>
<td>4.67</td>
<td>1.64</td>
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</tr>
<tr>
<td>240</td>
<td>0.47</td>
<td>2.57</td>
<td>0.24</td>
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</tr>
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</table>

### Table S3.2 Analytical results of FOG composition by ASTM D6584 method (215 °C)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>FFA</th>
<th>Glycerin</th>
<th>MAG</th>
<th>DAG</th>
<th>TAG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>ave</td>
<td>max</td>
<td>min</td>
<td>ave</td>
</tr>
<tr>
<td>0</td>
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<td>25.96</td>
<td>1.35</td>
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<tr>
<td>30</td>
<td>1.83</td>
<td>15.84</td>
<td>1.30</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>60</td>
<td>2.96</td>
<td>11.38</td>
<td>1.87</td>
<td>0.00</td>
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<tr>
<td>90</td>
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<td>1.74</td>
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</tr>
<tr>
<td>120</td>
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<td>5.82</td>
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<tr>
<td>150</td>
<td>2.49</td>
<td>4.59</td>
<td>1.64</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>180</td>
<td>1.30</td>
<td>3.25</td>
<td>1.43</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>210</td>
<td>0.68</td>
<td>3.02</td>
<td>0.88</td>
<td>0.00</td>
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</tr>
<tr>
<td>240</td>
<td>0.63</td>
<td>2.03</td>
<td>1.09</td>
<td>0.00</td>
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</tr>
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</table>

211
<table>
<thead>
<tr>
<th>230 °C</th>
<th>FFA</th>
<th>Glycerin</th>
<th>MAG</th>
<th>DAG</th>
<th>TAG</th>
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<tbody>
<tr>
<td></td>
<td>min</td>
<td>ave</td>
<td>max</td>
<td>min</td>
<td>ave</td>
</tr>
<tr>
<td>0</td>
<td>25.96</td>
<td>1.35</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
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<td>8.05</td>
<td>4.42</td>
<td>0.01</td>
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<td>60</td>
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<td>0.68</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>90</td>
<td>1.15</td>
<td>2.55</td>
<td>2.13</td>
<td>0.01</td>
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</tr>
<tr>
<td>120</td>
<td>1.56</td>
<td>1.56</td>
<td>2.34</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>150</td>
<td>0.52</td>
<td>0.52</td>
<td>1.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>180</td>
<td>0.26</td>
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</tr>
<tr>
<td>210</td>
<td>0.17</td>
<td>0.17</td>
<td>0.35</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
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</tbody>
</table>
Chapter 4. *In-situ* Conversion of FOG in Sewer Grease into Biodiesel

4.1 Introduction

Producing biodiesel from sewer grease have the potential to significantly reduce the cost for the biodiesel producers and more importantly, improve the sustainability of biodiesel production by switching from oil crops (e.g. soybean oil) to waste materials and hence minimizing water and land footprints. However, due to its highly heterogeneous nature, one issue related to the utilization of sewer grease is the difficulty in applying the conventional two-step processing technology, i.e., extraction-transesterification, which is commonly used when other feedstocks are processed into biodiesel. Therefore, direct transesterification, or *in-situ* conversion, is investigated in this study as an alternative to address this problem. *In-situ* conversion refers to the process where the reagent and catalyst directly contact the FOG content in the feedstock substrate without extraction (Velasquez-Orta et al, 2012). The elimination of the extraction step can benefit the biodiesel production by lowering cost and energy consumption, as well as the reduction in facility footprint (Haas et al., 2004). Several studies have been performed to explore the feasibility of applying *in-situ* conversion for different feedstock, including algae (Haas et al., 2011; Velasquez-Orta et al, 2012), Jatropha (Shuit et al., 2010; Hailegioris et al., 2011; 2013), rice bran (Özgül-Yücel and Türkay 2002; Yustianingsih et al. 2009) and activated sludge (Revellame et al. 2010). Although there are a few studies that investigated the feasibility of making biodiesel from sewer grease (primary sludge) (Mondala et al. 2009; Choi et al., 2014), the reported operation conditions vary from case to case and no optimization study was performed. Since sewer grease differs significantly in physical and chemical properties from
other feedstocks (Tu et al., 2012), it is necessary to understand the influence of operational parameters and optimize the yield of biodiesel made from this specific feedstock.

4.2 Literature review

A summary of existing literature on in-situ conversion of feedstocks into biodiesel is presented in Table 4.1. Haas et al. (2004) studied the alkaline in-situ tranesterification in soybean. The influence of temperature, methanol use, catalyst concentration, and FFA level were examined. Through parametric optimization it was reported that the best condition was a methanol input of 2.5 ml/g sample, 1.75% NaOH (to sample), 60°C and 8 hours for an overall transesterification yield close to 80% of total saponifiable materials (soybean oil and FFA). Haas and Scott (2007) studied the impact of moisture on the efficiency of alkaline in-situ tranesterification in soybean. The negative impact of the presence of moisture was identified and the drying of soybean flake resulted in a 60% reduction in the methanol input and 56% decrease in NaOH use. Under the optimum condition, the tranesterification yield was close to 100% (of saponification materials) in dried soybean flake and was 97.3% when 0.8% moisture was present. Haas and Wagner (2011) looked into four different physical soybean grain pretreatment procedures and their influences on the methanol requirement for in-situ conversion. It was found that the combination of flaking, extrusion and drying led to a minimal threefold reduction in methanol input as compared to flaking and drying alone. The optimum condition after the combined pretreatment of flaking, extrusion and drying was 0.3 ml MeOH/g sample, 0.324% NaOCH₃, 23 °C and 4 hours. Haas and Wagner (2011) also studied acidic in-situ conversion of algal oil into biodiesel by using H₂SO₄ as the catalyst. Different temperatures, methanol ratios and catalyst concentrations were examined and the results showed the optimum condition for achieving an 83% yield (of
saponification materials) in 2 hours was 4 ml MeOH/g sample, 78.4% H₂SO₄ and 65°C. Wahlen et al. (2011) conducted research on *in-situ* conversion of different algae, cyanobacteria and mixed cultures. The optimum condition was found to be 20 ml MeOH/g sample, 66.24% H₂SO₄, 80°C and 20 min with the assistance of microwave. Velasquez-Orta and Harley (2012) studied both acidic and alkaline *in-situ* processes for algae and concluded that alkaline catalysis possessed the advantage of reduced reaction time and less catalyst usage. The optimum condition for alkaline *in-situ* process was 7.5 ml MeOH/g sample, 0.19% NaOH, 60 °C, and 75 min. Mondala et al. (2009) studied biodiesel production from primary and secondary sludge via *in-situ* transesterification. The highest yield (mass of biodiesel/mass of sludge) for primary and secondary sludge was 14.5% and 2.5%, respectively. The optimum conditions were 15.2 ml MeOH/g sample, 140% H₂SO₄, 75 °C, and 24 hours (primary)/8 hours (secondly). Similarly, Revellame et al. (2010) conducted an acidic *in-situ* conversion for activated sludge. The optimum condition was 23.4 ml MeOH/g sample, 172% H₂SO₄, 55 °C and 24 hours for a yield (mass of biodiesel/mass of sludge) of 4.79%. Özgül-Yücel and Türkay (2002) performed an acidic *in-situ* conversion of rice bran oil into biodiesel. The optimum condition was determined to be 4 ml MeOH/g sample, 18.4% H₂SO₄, 65°C and 1 hour for an ester concentration around 85% (of saponifiable materials) in the final product mixture. Yustianingsih et al. (2009) also studied *in-situ* conversion of rice bran oil via the aid of ultrasound. It was found that the application of ultrasound greatly increased the yield of the reaction and the optimum condition was 10 ml MeOH/g sample, 27.6% H₂SO₄, 60 °C and 1 hour. Widayat et al. (2012) used rubber seed as the feedstock for *in-situ* production. Both alkaline and acidic catalysis were tested and the optimum conditions were 3 ml MeOH/g sample, 1.38% H₂SO₄/0.3% KOH, 65 °C and 2/1.5 hours, respectively. Kaul et al. (2010) performed *in-situ* conversion for Jatropha seeds. It was
reported the highest conversion rate of 98% (of saponifiable materials) was obtained with the condition of 9.87 ml MeOH/g sample, 3.95% NaOH, 65°C and 1 hour. Surya Abadi Ginting et al. (2012) studied *in-situ* process for *Jatropha curcas*. A maximum yield of 99.98% (of saponifiable materials) was achieved under a condition of 2% NaOCH$_3$, 30 ℃ and 2 hours. Shi et al. (2013) produced biodiesel from high oil corn by using 6 ml MeOH/g sample, 11.04% H$_2$SO$_4$, 65 ℃ and 12 hours for the *in-situ* process. Chapagain et al. (2009) tried to desert date as an oil crop for *in-situ* biodiesel production. The average yield was approximately 90% (of saponifiable materials) with the condition of 2 ml EtOH/g sample, 2% KOH and 6 hours. Georgogianni et al. (2008) produced biodiesel from sunflower seed by using ultrasound to accelerate the reaction. The results showed that a 95% yield (of saponifiable materials) could be obtained when the operational condition was 10 ml MeOH/g sample, 2% NaOH, 60°C, and 20 min. On the other hand, when ethanol was used (98% yield), the optimum condition was 13.3 ml EtOH/g sample, 2% NaOH, 80°C, and 40 min.

In this chapter, a preliminary study (Phase I) was conducted to investigate the influence of experimental parameters, i.e., methanol to sewer grease ratio (v/m), catalyst concentration (wt%), temperature, and reaction time, on the yield of biodiesel. Based on the results from the preliminary study, another set of experiments (Phase II) were conducted to improve the yield of biodiesel and narrow down the range of values for the experimental parameters.
Table 4.1. Summary of existing studies on *in-situ* conversion for biodiesel

<table>
<thead>
<tr>
<th>Reference</th>
<th>Feedstock</th>
<th>Sample (g)</th>
<th>Methanol (ml/g)</th>
<th>H$_2$SO$_4$ (wt%)</th>
<th>Alkaline (wt%)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson and Wen 2009</td>
<td>algae</td>
<td>1</td>
<td>3.4</td>
<td>110.4</td>
<td>NA</td>
<td>40min (90°C)</td>
</tr>
<tr>
<td>Ehimen et al. 2010</td>
<td>algae</td>
<td>15</td>
<td>4</td>
<td>27.6</td>
<td>NA</td>
<td>4 (60°C)</td>
</tr>
<tr>
<td>Carvalho Junior et al. 2011</td>
<td>algae</td>
<td>2</td>
<td>85</td>
<td>HCl 1266</td>
<td>NA</td>
<td>2 (80°C)</td>
</tr>
<tr>
<td>Haas and Wagner 2011$^b$</td>
<td>algae</td>
<td>2.5</td>
<td>3.2-8</td>
<td>58.8-125.44</td>
<td>NA</td>
<td>2 (23-65°C)</td>
</tr>
<tr>
<td>Li et al. 2011</td>
<td>algae</td>
<td>1</td>
<td>4</td>
<td>19.6</td>
<td>NA</td>
<td>2 (90°C)</td>
</tr>
<tr>
<td>Xu and Mi, 2011</td>
<td>algae</td>
<td>0.5</td>
<td>3.33</td>
<td>NA</td>
<td>KOH (9.7%)</td>
<td>1 (RT)</td>
</tr>
<tr>
<td>Wahlen et al. 2011</td>
<td>algae</td>
<td>0.1</td>
<td>20</td>
<td>66.24</td>
<td>NA</td>
<td>20min (Microwave,80°C)</td>
</tr>
<tr>
<td>Sanchez et al. 2012</td>
<td>algae</td>
<td>1000</td>
<td>14.1</td>
<td>NA</td>
<td>NaOH 1</td>
<td>11 (60°C)</td>
</tr>
<tr>
<td>Tsigie et al. 2012</td>
<td>wet algae</td>
<td>5 (1g dry algae+4 g water)</td>
<td>4</td>
<td>NA</td>
<td>NA</td>
<td>4 (175°C)</td>
</tr>
<tr>
<td>Velasquez-Orta and Harley 2012</td>
<td>algae</td>
<td>7</td>
<td>7.5</td>
<td>1.06</td>
<td>NaOH 0.19</td>
<td>75 min (60°C)</td>
</tr>
<tr>
<td>Mondala et al. 2009</td>
<td>primary/secondary sludge</td>
<td>5</td>
<td>15.2</td>
<td>139.75</td>
<td>NA</td>
<td>24/8 (75°C)</td>
</tr>
<tr>
<td>Revellam et al. 2010</td>
<td>activated sludge</td>
<td>1</td>
<td>23.4</td>
<td>172.22</td>
<td>NA</td>
<td>24 (55°C)</td>
</tr>
<tr>
<td>Choi et al. 2014</td>
<td>primary/secondary sludge</td>
<td>Wet: 150</td>
<td>Wet: 2, 10</td>
<td>Wet: 19.8</td>
<td>NA</td>
<td>Wet:1,2,8 (55,105°C)</td>
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<td></td>
<td></td>
<td>Dry: 22.5</td>
<td>Dry: 2,5,10</td>
<td>Dry:0.88, 2, 2, 4.4</td>
<td></td>
<td>Dry:8 (55°C)</td>
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<td>Haas et al. 2004</td>
<td>soybean</td>
<td>5</td>
<td>2.5</td>
<td>NA</td>
<td>NaOH: 1.75</td>
<td>8 (60°C)</td>
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<td>Haas and Scott, 2007</td>
<td>soybean</td>
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<td>1. dry:2.4 2. wet:3.6</td>
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<td>NaOH 1.096 2.144</td>
<td>1.10 2.16</td>
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<tr>
<td>Wyatt and Haas 2009</td>
<td>soybean</td>
<td>22.5</td>
<td>2.4</td>
<td>14.72</td>
<td>NaOCH$_3$ (did not work)</td>
<td>10 (121°C)</td>
</tr>
<tr>
<td>Haas and Wagner et al. 2011$^a$</td>
<td>soybean</td>
<td>5</td>
<td>0.3</td>
<td>NA</td>
<td>NaOCH$_3$: 0.324</td>
<td>4 (23°C)</td>
</tr>
<tr>
<td>Haagenson et al. 2010</td>
<td>canola</td>
<td>40</td>
<td>6.06</td>
<td>NA</td>
<td>KOH:3.20</td>
<td>6(60°C)</td>
</tr>
<tr>
<td>Georgogianni et al. 2008</td>
<td>sunflower</td>
<td>20</td>
<td>MeOH:10 EtOH:13.3</td>
<td>NA</td>
<td>NaOH 2</td>
<td>ultrasonic MeOH: 20 min (60°C) EtOH: 40 min (80°C)</td>
</tr>
<tr>
<td>Authors</td>
<td>Species</td>
<td>Concentration</td>
<td>Yield (%)</td>
<td>pH</td>
<td>Alkali</td>
<td>Temperature</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------</td>
<td>---------------</td>
<td>-----------</td>
<td>-----</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>Shi et al. 2013</td>
<td>corn</td>
<td>5</td>
<td>6</td>
<td>11.04</td>
<td>NA</td>
<td>12 (65°C)</td>
</tr>
<tr>
<td>Ozgül-Yücel and Türkay 2002</td>
<td>rice bran</td>
<td>50</td>
<td>4</td>
<td>18.4</td>
<td>NA</td>
<td>1 (65°C)</td>
</tr>
<tr>
<td>Yustianingsih et al. 2009</td>
<td>rice bran</td>
<td>10</td>
<td>10</td>
<td>27.6</td>
<td>NA</td>
<td>1,2,4,6 (Ultrasound assisted, 60°C)</td>
</tr>
<tr>
<td>Widayat et al. 2012</td>
<td>rubber seed</td>
<td>100</td>
<td>3</td>
<td>1.38</td>
<td>KOH (0.3)</td>
<td>2/1.5 (60°C)</td>
</tr>
<tr>
<td>Boey et al. 2011</td>
<td>palm oil (in spent bleaching clay)</td>
<td>2</td>
<td>2</td>
<td>NA</td>
<td>KOH 5.4</td>
<td>2 (ultrasound assisted, 60°C)</td>
</tr>
<tr>
<td>Mat et al. 2011</td>
<td>palm oil (in spent bleaching earth)</td>
<td>50</td>
<td>4</td>
<td>2</td>
<td>NaOH (2)</td>
<td>5 (65°C)</td>
</tr>
<tr>
<td>Kaul et al. 2010</td>
<td>jatropha</td>
<td>14</td>
<td>9.87</td>
<td>NA</td>
<td>NaOH 3.948</td>
<td>1 (65°C)</td>
</tr>
<tr>
<td>Shuit et al. 2010</td>
<td>jatropha</td>
<td>20</td>
<td>7.5</td>
<td>15</td>
<td>Na</td>
<td>24 (60°C)</td>
</tr>
<tr>
<td>Hailegiorgis et al. 2011</td>
<td>jatropha</td>
<td>20</td>
<td>EtOH 7.5</td>
<td>NA</td>
<td>NaOH 0.675</td>
<td>150 min(30°C)</td>
</tr>
<tr>
<td>Prabaningrum et al. 2011</td>
<td>jatropha</td>
<td>20</td>
<td>4.93</td>
<td>NA</td>
<td>NaOCH3 1.58</td>
<td>2 (60°C)</td>
</tr>
<tr>
<td>Surya Abadi Ginting et al. 2012</td>
<td>jatropha</td>
<td>NA</td>
<td>EtOH (total volume 140 ml)</td>
<td>NA</td>
<td>NaOCH3: 2</td>
<td>2 (30°C)</td>
</tr>
<tr>
<td>Hailegiorgis et al. 2013</td>
<td>jatropha</td>
<td>20</td>
<td>1) MeOH: 7.5 2) EtOH: 8.23</td>
<td>NA</td>
<td>NaOH 1) 1.52 2) 1.38</td>
<td>1)1.72 (37.63°C) 2) 1.54 (34.9°C)</td>
</tr>
</tbody>
</table>
4.3 Methodology

4.3.1 Materials

Sewer grease samples were obtained from the Metropolitan Sewer District of Greater Cincinnati (MSDGC). Methanol (HPLC grade, Fisher Chemical®), sulfuric acid (99.8%, Fisher Chemical®), hexane (98.5%, Fisher Chemical®) and dichloromethane (HPLC grade, Fisher Chemical®) were purchased from chemical stockroom in University of Cincinnati. Before use for experiments, sewer grease was dried on a hotplate at 80 °C for 48 hrs to remove the moisture.

The FOG of the sewer grease was extracted by the hexane/isopropanol (1:1 vol/vol) solution in a soxhlet system (the details of the system are explained section 4.3.2.2 below). The FFA wt% in the extracted FOG was determined by using AOCS Cd 3d 63 method (shown in Chapter 3).

4.3.2 In-situ experiment procedure

4.3.2.1 Flask setup (Phase I)

A flask reaction system was used for the preliminary study. Approximately 10 g of dried sewer grease samples were added in a 250 ml three-necked flask. The flask was immersed in a water bath through which the reaction temperature was maintained at desired level. The water bath was heated by a hotplate with magnetic stirring function. A condensation column was placed on top of the flask to prevent the loss of methanol. A thermometer was inserted into the flask to monitor the temperature of the reaction. The designated amounts of methanol-H₂SO₄ mixture were preheated to desired temperature before being added into the flask. The content in the flask was mixed by a stirring bar at approximately 600 rpm. After in-situ conversion, the solid-liquid
mixture was left to settle and the solid substrate was separated by filtration. The liquid phase was transferred to a rotary evaporator to recover the methanol. After evaporation, the remaining liquid was transferred to a container and dried under air flow for 24 hrs, after which 25 ml hexane was added to the liquid and the mixture was stirred for 10 minutes. After stirring, the mixture was allowed to stand for 10 minutes and the hexane layer was transferred to another container and stored in the freezer before analysis. The solid substrate was dried under in the hood and kept in a dessicator for further analysis.

4.3.2.2 Soxhlet setup (Phase II)

A soxhlet system was used for conducting the Phase II experiments after the preliminary study. Approximately 40 g of dried sewer grease were held in the cellulose thimble which was placed in the extraction tube of the soxhlet system. The extraction tube was wrapped by a heating tape to keep its temperature at approximately 65 °C. A condensation column was placed on top of the extraction tube to prevent the escaping of the methanol vapor. The extraction tube and condensation column were mounted upon a 500 ml round-bottom flask which contained 250 ml methanol (w/ or w/o H$_2$SO$_4$, depending on the experimental condition). A heating mantle was used to heat the round-bottom flask and temperature was controlled such that the loss of methanol due to evaporation was under control (within 5%). After the in-situ process, the liquid (methanol, reaction products, and H$_2$SO$_4$) was put in a rotary evaporator where methanol was separated and recovered. The resulting liquid was washed by hot water (approximately 80 °C) for multiple times until the PH of the washing water effluent was the same as that of the input water. The washing process is expected to remove the residual H$_2$SO$_4$, methanol and the glycerin that is formed during the in-situ conversion process. After washing, the resulting liquid sample was transferred to a 50 ml centrifuge tube and was centrifuged at 5000 rpm for 30 min. After
centrifuge, the supernatant liquid layer was separated from the trace amount of heterogeneous materials by decanting. Finally, the decanted liquid was heated on a hotplate at 80 °C for 24 hrs to remove the residual water (from the washing step).

4.3.2.3 Impregnation of dried sewer grease

Impregnation is the process where chemicals (e.g. H$_2$SO$_4$) of interest are mixed with the substrate (e.g. dried sewer grease) before the subsequent reaction. Impregnation is commonly used in the preparation of activated carbons to obtain the properties of interest (e.g. surface function groups) (Reffas et al., 2010; Akasaka et al. 2011; Ching et al., 2011). In this study, impregnation of dried sewer grease was conducted before in-situ conversion due to the concern that otherwise the catalyst (H$_2$SO$_4$) would not be effectively involved in the reaction in a soxhlet system (the boiling point of H$_2$SO$_4$ is 337 °C at atmospheric pressure). The designated amount of H$_2$SO$_4$ (20 wt% of dried sewer grease) was dissolved in water to form a 10% H$_2$SO$_4$ solution. The solution was mixed with dried sewer grease on a hotplate with a magnetic stirrer at 80 °C for 3 hours as suggested by Tu (2012). After impregnation, the mixture was placed in the oven at 105 °C for 24 hours to remove the water. The resulting impregnated sewer grease were ground into fine particles and stored in a desiccator before in-situ conversion. As a control group, experiments were also conducted in flask system (same setup as Phrase I study) where H$_2$SO$_4$, methanol and dried sewer grease were mixed without impregnation in advance.

4.3.2.4 Experimental matrix

Phrase I (preliminary study) experiments

A $2^4$ full factorial experiment design is applied for the 4 operational parameters of concern: temperature, MeOH-to-sewer grease ratio (v/wt), H$_2$SO$_4$ concentration, and reaction time. Table
4.2 shows the details of the experiment matrix design. The values of the two levels are selected based on the ranges of the value of the corresponding parameters in the literature.

**Table 4.2.** $2^4$ full factorial experiment design

<table>
<thead>
<tr>
<th>Parameter</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>MeOH-to-TG ratio (v/wt)</td>
<td>5:1</td>
<td>10:1</td>
</tr>
<tr>
<td>H$_2$SO$_4$ % (wt% of titrated FFA)*</td>
<td>25%</td>
<td>50%</td>
</tr>
<tr>
<td>Time (hr)</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

* Titrate FFA: the mass of FFA calculated based on the FFA% (via titration) of the extracted FOG

**Phrase II experiments**

Based on the findings from Phase I study, the experimental condition for Phrase II was selected as following:

- H$_2$SO$_4$ concentration: 20/40 wt% of dried sewer grease
- Reaction temperature: 65 °C
- Reaction time: 5, 7 and 12 hrs
- Reaction system: soxhlet (w/ impregnation), soxhlet (w/o impregnation), and flask

**4.3.2.5 Yield of the in-situ conversion**

The “gross yield” of the in-situ conversion is defined as the mass ratio between the liquid (after washing, centrifuge and final moisture removal) and the dried sewer grease used for the reaction. The overall biodiesel yield is defined as the ratio between total amount of biodiesel in the recovered liquid (mass of gross yield liquid) and total mass of dried SG used for the in-situ conversion (Eq.4.1).

$$Y_{BioD,overall} = \frac{C_{BioD,Sample} \times m_{rec,Sample}}{m_{SG}}$$  \hspace{1cm} \text{Eq.4.1}
Where:

\[ Y_{BioD,overall} = \text{overall yield of biodiesel, wt\%} \]

\[ C_{BioD,sample} = \text{concentration of biodiesel in recovered liquid sample, wt\%} \]

\[ m_{rec,sample} = \text{mass of total recovered liquid, g} \]

\[ m_{SG} = \text{mass of the SG samples used for the in-situ conversion, g} \]

4.3.3 Analytical methods

The characterization of fatty acid methyl ester (FAME) was performed by a GC/MS equipped with a Restek Rxi®-5ms (Bellefonte, PA) column (30 m, 0.25 mm i.d., and 0.25 μm df). The operational condition for GC was programed as following: injection temperature: 250 °C; initial temperature: 40 °C, hold 2 min; increase the temperature to 230 min with a rate of 10 °C/min, hold 5 min; increase the temperature to 330 °C with a rate of 15 °C/min, hold 4 min. Helium is used as the carrier gas at 1 mL/min flow rate. The measurement of FFA is performed in accordance to the AOCS Cd 3d 63 method. The determination of glycerides was performed by following ASTM D6584 method and the details about the analytical method are reported in the Analytical Methodology section of Chapter 3.

4.4 Results and Discussion

4.4.1 Results of preliminary study (Phase I)

Table 4.3 summarizes several properties of the sewer grease used in this study. The mass concentration of moisture, FOG in the dried sewer grease, and the FFA % in the FOG ranged from 35.39% to 55.08%, 20.86% to 32.28%, and 49.81% to 61.71%, respectively.
Table 4.3. Properties of the sewer grease used in this study

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt%)</td>
<td>42.65±6.92</td>
</tr>
<tr>
<td>FOG (wt%)</td>
<td>26.02±4.72</td>
</tr>
<tr>
<td>FFA (wt%) in FOG</td>
<td>56.71±5.43</td>
</tr>
</tbody>
</table>

Elemental analysis of the sewer grease samples was performed on dried sewer grease by a third-party laboratory (OKI Analytical, Cincinnati, OH) and the results are summarized in Table 1. The heating value of sewer grease (dry basis) was approximately 34,890 kJ/kg (15,000 Btu/lb) which is higher than that of coal (23,534 kJ/kg or 10,118 Btu/lb for US average; EIA 2012). This indicated that sewer grease can be a potential fuel source. The elemental composition of sewer grease in this study is close to other studies of trap grease based FOGs (Czernik et al., 2013; Ikura et al., 2007). This is expected since the sewer grease from MSDGC contains a significant amount of trap grease. The result of Thermo-gravimetric analysis (TGA) for raw sewer grease is shown in Figure S.4.1. Three peaks were observed in the derivative curve, representing the weight loss of moisture (79.94 °C), FFA (309.56) and FOG (466.23). The results of current study agree with those reported by other authors (Ikura et al., 2007).

Seven experiment runs were conducted for the preliminary test and the experimental conditions are summarized in Table 4.4.

Table 4.4. Experimental conditions for the preliminary study

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>MeOH-TG ratio (v/wt)</th>
<th>H₂SO₄ %</th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (ITG3)</td>
<td>10:1</td>
<td>25</td>
<td>65</td>
<td>4</td>
</tr>
<tr>
<td>2 (ITG4)</td>
<td>10:1</td>
<td>50</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>3 (ITG5)</td>
<td>10:1</td>
<td>50</td>
<td>65</td>
<td>2</td>
</tr>
<tr>
<td>4 (ITG8)</td>
<td>10:1</td>
<td>50</td>
<td>65</td>
<td>4</td>
</tr>
<tr>
<td>5 (ITG9)</td>
<td>5:1</td>
<td>50</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>6 (ITG12)</td>
<td>10:1</td>
<td>25</td>
<td>55</td>
<td>4</td>
</tr>
<tr>
<td>7 (ITG15)</td>
<td>5:1</td>
<td>50</td>
<td>65</td>
<td>2</td>
</tr>
</tbody>
</table>
The average yield of biodiesel was 8.27% and the results for the preliminary study is summarized in Figure 4.1. The majority of the results were below 8% and the two higher conversion results were achieved from the high dose of methanol and H$_2$SO$_4$, which is expected. In addition to biodiesel, a certain amount of oil also dissolved into methanol and was extracted from the sewer grease. The amount of oil extracted (as % of dry SG) varied from case to case and the average value was 11.88% (Figure 4.2). As compared with biodiesel yield, the yield of oil extraction was more stable under different experimental conditions. The combined yield of oil and biodiesel for each experimental run are summarized in Figure 4.3; and the corresponding values of the ratio between oil and biodiesel in the final product (after in-situ conversion) are summarized in Figure 4.4.

![Figure 4.1. Preliminary results on the FAME yield](image-url)
Figure 4.2. Preliminary results on the yield of oil

Figure 4.3. Preliminary results on the yield of oil+biodiesel
4.4.2 Phrase II results

4.4.2.1 Gross yield

The results of Phrase II study are summarized in Table 4.5. “IS” denotes the in-situ reaction in the soxhlet system where impregnation was not applied, while “IM” denotes the ones with impregnation. “NS” denotes the reaction performed in the flask system. “1” denotes the first batch of a specific experiment and “2” denotes the repeat of the same experimental condition. “20” denotes a 20% H_2SO_4 concentration and “40” denotes 40%. It is shown that impregnation improved gross yield of the in-situ process in soxhlet system. For example, the average gross yield after the 7-hr reaction was 16.93% for “IS” experiments was 21.76% for “IM” experiments. Similar findings can be observed for the 12-hr reactions. On the other hand, the difference in gross yield between soxhlet (impregnated) system and flask system was minimal. For example, the average gross yield after the 7-hr reaction was 21.60%. This may be explained by the fact that H_2SO_4 was well mixed with the sewer grease and methanol in the flask system and

Figure 4.4. Ratio between oil and FAME in the final product
therefore, availability of H$_2$SO$_4$ (as the catalyst) for the reaction was no longer a limiting factor (as was in the case of non-impregnated soxhlet system). In practice, this may greatly simplify the *in-situ* process by eliminating impregnation and drying steps. In addition, by comparing the gross yield between 7-hr and 12-hr reactions, it is indicated that extended reaction time (beyond 7 hrs) did not lead to a significant improvement of the yield (*p*-value =0.25). The FFA % was higher in the final products from the non-impregnated soxhlet system, indicating that the conversion of FFA into biodiesel was not as complete as those in the other conditions (“IM”s and “NS”s). This may also be attributed to the inefficient *in-situ* process due to the limitation of H$_2$SO$_4$ availability. In order to determine if the reaction time could be further reduced, 5-hr reactions were performed and the resulting gross yield was considerably lower as compared to 7-hr reactions (*p*-value =2E-06). Another effort was taken to determine if increasing the H$_2$SO$_4$ concentration would result in a lower final FFA in the recovered liquid. The H$_2$SO$_4$ concentration was doubled for reactions with different time spans, none of which showed a significant different final FFA as compared to the counterpart with 20% H$_2$SO$_4$ (*p*-value =0.88). The relatively high final FFA concentration in the biodiesel produced from SG was also observed by Bi et al. (2015). As indicated by the authors, a neutralization step (alkaline water wash) will be sufficient to reduce the FFA concentration to the acceptable level.

**Table 4.5.** The gross yield and FFA % of the resulting product from *in-situ* process (constant experimental parameters: MeOH: 250 ml, H$_2$SO$_4$: 20/40 wt%, temperature: 65 °C)

<table>
<thead>
<tr>
<th>ID</th>
<th>Time (hr)</th>
<th>Dried sewer grease (g)</th>
<th>Gross yield (%)</th>
<th>Titrated FFA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS_1_7</td>
<td>7</td>
<td>39.28</td>
<td>16.62%</td>
<td>2.81</td>
</tr>
<tr>
<td>IS_1_12</td>
<td>12</td>
<td>43.63</td>
<td>16.46%</td>
<td>2.64</td>
</tr>
<tr>
<td>IS_2_7</td>
<td>7</td>
<td>41.47</td>
<td>17.24%</td>
<td>3.25</td>
</tr>
<tr>
<td>IS_2_12</td>
<td>12</td>
<td>43.53</td>
<td>17.32%</td>
<td>2.81</td>
</tr>
<tr>
<td>IM_1_7</td>
<td>7</td>
<td>45.46</td>
<td>21.60%</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>IM_1_12</td>
<td>12</td>
<td>44.86</td>
<td>22.00%</td>
<td>1.12</td>
</tr>
<tr>
<td>IM_2_7</td>
<td>7</td>
<td>43.32</td>
<td>21.91%</td>
<td>1.40</td>
</tr>
<tr>
<td>IM_2_12</td>
<td>12</td>
<td>45.55</td>
<td>21.84%</td>
<td>1.12</td>
</tr>
<tr>
<td>NS_1_7</td>
<td>7</td>
<td>42.85</td>
<td>22.08%</td>
<td>1.23</td>
</tr>
<tr>
<td>NS_1_12</td>
<td>12</td>
<td>45.84</td>
<td>22.12%</td>
<td>1.12</td>
</tr>
<tr>
<td>NS_2_7</td>
<td>7</td>
<td>42.85</td>
<td>21.12%</td>
<td>0.84</td>
</tr>
<tr>
<td>NS_2_12</td>
<td>12</td>
<td>45.08</td>
<td>21.85%</td>
<td>1.12</td>
</tr>
<tr>
<td>NS_2_12_40</td>
<td>12</td>
<td>45.36</td>
<td>21.21%</td>
<td>1.12</td>
</tr>
<tr>
<td>NS_2_12_40</td>
<td>12</td>
<td>41.23</td>
<td>22.24%</td>
<td>1.01</td>
</tr>
<tr>
<td>NS_1_5_40</td>
<td>5</td>
<td>40.77</td>
<td>15.62%</td>
<td>1.29</td>
</tr>
<tr>
<td>NS_2_5_40</td>
<td>5</td>
<td>40.76</td>
<td>16.00%</td>
<td>1.51</td>
</tr>
<tr>
<td>NS_1_5_20</td>
<td>5</td>
<td>41.83</td>
<td>16.23%</td>
<td>1.40</td>
</tr>
<tr>
<td>NS_2_5_20</td>
<td>5</td>
<td>40.54</td>
<td>15.07%</td>
<td>1.51</td>
</tr>
<tr>
<td>NS_1_7_40</td>
<td>7</td>
<td>41.33</td>
<td>22.33%</td>
<td>1.29</td>
</tr>
<tr>
<td>NS_2_7_40</td>
<td>7</td>
<td>40.73</td>
<td>21.92%</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Figure 4.5.** (from left to right): dried sewer grease, sewer grease after *in-situ* process in flask system, and sewer grease after *in-situ* process in soxhlet (non-impregnated)
Figure 4.6. (a) Impregnated sewer grease before and (b) after *in-situ* process in soxhlet system

Figure 4.7. Crude product from *in-situ* process in soxhlet system (non-impregnated; after methanol removal)
4.4.2.2 Biodiesel yield

The composition of selected samples are summarized in Table 4.6. Overall, the concentration of biodiesel in the sample is approximately 90% for all cases, except IS-2-7 (7 hr reaction in soxhlet setup w/o impregnation). Similar to gross yield, the concentration of biodiesel in the sample are close between the IM and NS setups and the there is no significant difference between 7 hr and 12 hr reactions. On the other hand, the biodiesel % in the sample from IS setup is lower than those from IM and NS setups for the 7 hr reactions but no significant difference is found when the reaction time is 12 hr. It is shown that the overall biodiesel yield is similar between IM and NS setups and is higher than the IS setup, which is primarily due to the lower gross yield of the liquid from the IS setup. As the FOG concentration in the dry SG was approximately 25.47%, the average FOG-to-biodiesel conversion rate was about 76.31% under the optimum experiment condition of 7 hr, 65°C and 20% H2SO4 (IM-1-7 and IM-2-7). Likewise, the “extraction rate” (gross yield/FOG concentration) was 85.43%. Table 4.7 summarizes the optimum experimental conditions from this chapter and those reported in the literature. It is shown that both reaction
time and H₂SO₄ use are significantly reduced as compared to the values reported by other studies (Mondala et al., 2009; Choi et al., 2014). However, since the two references in Table 4.7 did not report the maximum available FOG in the dried SG, the FOG-to-biodiesel conversion rate could not be calculated for these two studies; hence no comparison could be made between current study and these existing studies on the overall biodiesel yield.

Table 4.8 provides a summary of material use, reaction time and temperature for making biodiesel from 100 g raw SG (26% FOG concentration, 43% moisture) using two production pathways (Figure 4.9). The operational condition of the in-situ process is estimated based on the data in Table 4.7. The operational conditions of the “waste grease extraction” (WGE) process are estimated from Tu et al. (2015). WGE process first mixes waste cooking oil (WCO) with raw SG (3.15:1, wt/wt) under 70 °C for 240 min, during which the FOG in the sewer grease transfers to the liquid (WCO) phase. The extraction rate was close to 100%. After this extraction step, the solid and liquid phases are separated and typically the FFA concentration in the resulting WCO increases (e.g. from 2.68 wt% to 8.48 wt% in this case). The WCO is then treated with acid-catalyzed esterification before being made into biodiesel. The dose of chemicals was calculated by Eq.3.14 and 3.15. It is should be noted that the values in Table 4.8 only reflect the amount of chemicals (i.e. methanol, NaOH and H₂SO₄) used for converting the FOG that was extracted by WGE method (26 g out of 100 g raw SG) into biodiesel. The reaction time was 2 hr and temperature was 65 °C. The reaction time and temperature for transesterification process were 2 hr and 65 °C. The chemical doses were 3.5 g NaOH/L WCO and 6:1 molar ratio between WCO and MeOH. It is shown that the in-situ process contains fewer steps than the WGE process while the overall reaction time are similar between the two production pathways. The methanol and H₂SO₄ inputs are significantly higher in the in-situ process, although most of the methanol is
recovered after the conversion. As the dose of WCO was based on the mass of raw SG, which typically contains a large amount of water (e.g. 43% in this case), a considerable amount of WCO is needed for the WGE method. The benefit of WGE process is the avoidance of drying step for the raw SG. The moisture of the WCO after WGE process was fairly low (1.3-2.8% in this case), and can be easily removed by applying a mild heating (e.g. 80 °C for 1 hr). In addition, WGE process showed a higher extraction rate and a more complete conversion (Table S4.2).

Therefore, the future work will be improving both the extraction rate and completeness of the in-situ process. One potential improvement to investigation is “acid wash (hydrolysis)”. Acid wash was found to be effective in breaking down the emulsion in the SG, converting soap into FFA and hence maximizing the biodiesel yield from SG (Bi et al., 2015). Acid wash was claimed to be able to remove various metal and other impurities in the SG and thus improve the efficiency of the acid catalyzed esterification process (Bi et al., 2015). In addition, it is presumed that the in-situ yield was primarily contributed by the esterification of FFAs, not the transesterification of triglycerides. One fact supporting this presumption is that the activation energy ($E_a$) of the esterification reaction (20.7 kJ/mol, Chai et al, 2014) is much lower than that of alkaline tranesterification (33.5 kJ/mol, Noureddini and Zhu, 1996), let alone the acidic transesterification (Lotero et al., 2005). A lower $E_a$ is correlated with a higher reaction rate and therefore, the formation of methyl esters during the given reaction time may be primarily the result of esterification between FFA and methanol. This presumption leads to the need to test the hypothesis that converting triglycerides into FFA (by acid wash/hydrolysis) before in-situ conversion will improve the yield and/or reduce the reaction time of the process. With more FFA present in the sewer grease, the in-situ process is expected to be more dominated by the
esterification reaction which will lead to the formation of increased amount of FAME during the same period of time.

**Table 4.6.** Summary of composition and overall biodiesel yield for selected samples

<table>
<thead>
<tr>
<th>ID</th>
<th>TAG</th>
<th>DAG</th>
<th>MAG</th>
<th>FFA</th>
<th>BioD wt% in sample</th>
<th>Overall BioD yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS-2-7</td>
<td>4.80%</td>
<td>7.22%</td>
<td>0.24%</td>
<td>3.25%</td>
<td>84.49%</td>
<td>14.57%</td>
</tr>
<tr>
<td>IS-2-12</td>
<td>2.96%</td>
<td>4.75%</td>
<td>0.44%</td>
<td>2.81%</td>
<td>89.04%</td>
<td>15.42%</td>
</tr>
<tr>
<td>IM-1-7</td>
<td>4.60%</td>
<td>5.99%</td>
<td>0.36%</td>
<td>0.95%</td>
<td>88.10%</td>
<td>19.03%</td>
</tr>
<tr>
<td>IM-2-7</td>
<td>2.16%</td>
<td>5.47%</td>
<td>0.39%</td>
<td>1.40%</td>
<td>90.58%</td>
<td>19.84%</td>
</tr>
<tr>
<td>NS-1-12</td>
<td>1.64%</td>
<td>8.48%</td>
<td>0.46%</td>
<td>1.12%</td>
<td>88.31%</td>
<td>19.53%</td>
</tr>
<tr>
<td>NS-2-7</td>
<td>4.77%</td>
<td>7.22%</td>
<td>0.24%</td>
<td>0.84%</td>
<td>86.93%</td>
<td>18.36%</td>
</tr>
</tbody>
</table>

IS: soxhlet setup (w/o impregnation)  
IM: soxhlet setup (w/ impregnation)  
NS: flask setup

**Table 4.7.** Summary of optimum experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>MeOH (ml/g)</th>
<th>H₂SO₄ (wt% of SG)</th>
<th>Biodiesel yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>65</td>
<td>7</td>
<td>6.25</td>
<td>20%</td>
<td>19.2%</td>
</tr>
<tr>
<td>Mondala et al., 2009</td>
<td>75</td>
<td>24</td>
<td>15.19</td>
<td>140%</td>
<td>14.5%</td>
</tr>
<tr>
<td>Choi et al., 2014</td>
<td>55</td>
<td>8</td>
<td>10</td>
<td>92%</td>
<td>8.04%</td>
</tr>
</tbody>
</table>

**Table 4.8.** Summary of material use, reaction time and temperature for making 100 g biodiesel from SG

<table>
<thead>
<tr>
<th></th>
<th>Material use</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ conversion</td>
<td>356 mL MeOH 6.33 mL H₂SO₄</td>
<td>65 °C</td>
<td>420 min reaction</td>
</tr>
</tbody>
</table>
| WGE + acid-catalyzed esterification + transesterification | - WGE: 350 ml WCO  
- Esterification: 10.30 ml MeOH, 0.11 ml H₂SO₄  
- Transesterification: 5.85 ml MeOH, 0.08 g NaOH | - WGE: 70 °C  
- Esterification: 65 °C  
- Transesterification: 65 °C | - WGE: 240 min  
- Esterification: 120 min  
- Transesterification: 120 min |
The fatty acid profile of the biodiesel produced from SG shows a high degree of saturation. The dominant components are methyl palmitate (61.33±2.67%) and methyl stearate (19.40±2.57%), followed by methyl oleate (10.33±1.45%) and methyl myristate (3.25±0.38%). Similar results were reported by Mondala et al. (2009) and Choi et al. (2014), nonetheless the relative dominance of these components are different. This can be attributed to the heterogeneous nature of the sewer grease.
4.5 Summary of the chapter

Different experimental setups were evaluated to convert the FOG in the SG into biodiesel via *in-situ* process. The results showed that there was no significant difference in either the gross yield or the overall biodiesel yield between soxhlet setup and flask setup, as long as impregnation was performed prior to the experiment under soxhlet setup. It was also found that a high gross yield (21.68%) and FOG-to-biodiesel conversion rate (76.31%) could be achieved under the experiment condition of: 7 hr, 65°C and 20% H₂SO₄. The biodiesel produced from SG was found to be primarily composed of methyl palmitate (61.33±2.67%), methyl stearate (19.40±2.57%), methyl oleate (10.33±1.45%) and methyl myristate (3.25±0.38%).
4.6 References


Chai, M., Tu, Q., Lu, M., Yang, Y.J. 2014. Experimental and parametric study of free fatty acid esterification in waste cooking oil as a biodiesel pretreatment process. Fuel Processing Technology, 125, 106-113.


Shi, Aimin, Zhenyi Du, Xiaochen Ma, Yanling Cheng, Min Min, Shaobo Deng, Paul Chen, Dong Li, and Roger Ruan. "Production and evaluation of biodiesel and bioethanol from high oil corn using three processing routes." Bioresource technology 128 (2013): 100-106.


### Table S4.1. Elemental analysis of sewer grease (this study) and trap grease samples (from literature)

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Czernik et al., 2013</th>
<th>Ikura et al., 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
<td>74.6</td>
<td>75.5</td>
<td>74.44</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>12.47</td>
<td>11.8</td>
<td>11.37</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.2</td>
<td>0</td>
<td>0.42</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>8.91</td>
<td>12.7</td>
<td>13.72</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>0.14</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>3.92</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HHV (Btu/lb)</td>
<td>15,083</td>
<td>NA</td>
<td>15,000</td>
</tr>
</tbody>
</table>

### Table S4.2. QTA analysis results for biodiesels produced from *in-situ* conversion and WGE process

<table>
<thead>
<tr>
<th>Characteristics (%)</th>
<th><em>In-situ</em> conversion</th>
<th>WGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.38</td>
<td>1.20</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>5.73</td>
<td>0.38</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>3.38</td>
<td>0.11</td>
</tr>
<tr>
<td>FFA</td>
<td>1.26</td>
<td>0.84</td>
</tr>
<tr>
<td>FAME*</td>
<td>89.34</td>
<td>97.47</td>
</tr>
</tbody>
</table>

*Titrated value

$^*$FAME=100%-monoglycerides%-diglycerides%-triglycerides%-FFA%

$^\sim$Average of results for IM-1 and IM-2
Figure S4.1. TGA result for raw sewer grease
Chapter 5. Conclusions and Future Directions

5.1 Conclusions

A life cycle model was constructed for the trap grease-to-biodiesel production to characterize its energy consumption and GHG emission. Results showed that the AD process would need to be an integral part of the system to achieve a reduction in both energy consumption and GHG emissions. Results from the Monte Carlo simulation and sensitivity analysis showed that the range of life cycle energy consumption and GHG emissions varied significantly. The life cycle energy consumption and GHG emissions were highly correlated to FOG concentration in the raw trap grease, FFA concentration in the FOG, and CH₄ generation rate of the AD. In order to minimize the energy consumption and GHG emissions, a high conversion rate of the solids (from trap grease) into CH₄ is needed in the AD. When compared to the results for biodiesel production from other feedstocks reported in the existing literature, the use of trap grease could be an energy efficient (low energy consumption) and environmentally-friendly (low GHG emission) feedstock for biodiesel production under certain conditions (e.g. high FOG concentration, low FFA concentration, high AD performance).

Lab-scale research were performed to improve the new technologies for producing biodiesel from trap grease and sewer grease. As an alternative to the conventional two-step esterification process, glycerolysis has the potential advantages of avoiding the use of hazardous chemicals (e.g. H₂SO₄ and methanol), byproduct reuse (crude glycerin) and simplifying the operational condition (one-step reaction). Experimental results showed that the crude glycerin obtained from
biodiesel production, could be used as an effective replacement for pure glycerin after methanol removal. This indicates the possibility of using crude glycerin for glycerolysis without extensive purification procedure, and hence reduces “the glycerin glut” and cost of biodiesel production. The optimum condition for reducing the FFA to less than 1 wt% is found at 230 °C for 150 min, with 1:1 molar ratio of glycerol and FFA. The disadvantages of glycerolysis that need to be improved in future study include the loss of biodiesel during the separation step and an incomplete FOG-to-biodiesel conversion. The decision on which FFA pretreatment technology to use for the trap grease FOG will be dependent on a combination of factors, such as the initial FFA concentration, the constraint on hazardous chemical disposal, and thermal system configuration. For example, if the initial FFA concentration in the FOG is below 15% (e.g. yellow grease), it is likely the acid-catalyzed esterification will be a preferred choice since the FFA concentration can be reduced to < 1% with a single step. On the other hand, if the initial FFA concentration is much higher (e.g. 30%), glycerolysis may become a better choice, considering the simplicity of the process and the avoidance of using a large amount of hazardous chemicals.

For sewer grease (SG), two new technologies have been tested. In-situ conversion of sewer grease to biodiesel combines oil extraction and conversion (to biodiesel) into one step, which eliminates the solvent extraction step and the associated cost. The optimum operation condition of the in-situ process for the sewer grease was 20% H₂SO₄, 65 °C and 7 hr, under which 85.43% of the FOG in the sewer grease was extracted and mostly converted into biodiesel. The FOG-to-biodiesel conversion rate overall was approximately 76%. Another alternative technology for utilizing sewer grease is an oil extraction process with waste cooking oil (WGE) that has been researched in a separate study. Compared with the in-situ process, WGE avoids the drying of raw
sewer grease that is necessary for the \textit{in-situ} process. Also, the market for WGE process is more flexible due to the minimum viable intermediate product. The WGE process results in an intermediate with less than 15\%, which can be sold as yellow grease to biodiesel producers, instead of being converted to biodiesel ourselves at a small scale. On the other hand, the \textit{in-situ} conversion process contains less steps and does not require a supply of used cooking oil; and hence may reduce the complexity and capital investment of the production system. Due to mass transfer limit, a significant amount of excess methanol is needed for the \textit{in-situ} conversion process (6.25 ml/g), which requires a process to recover excess methanol after the conversion.

5.2 Future work

The life cycle model developed in this dissertation can be used by the WWTPs, such as MSD, to evaluate the potential of producing biodiesel from trap grease. In order to customize the model for site-specific use, the following data are needed:

1) The probability density functions (pdf) of existing variable for Monte Carlos simulation, i.e., FOG concentration, FFA concentration, volatile solids concentration, methane generation rate, AD electricity and heat uses, and electricity generation rate of the CHP, need to be updated. For example, once adequate amount of the samples are collected and analyzed, the pdf of FOG concentration in the trap grease can be obtained by conducting a “goodness-of-fit” test of the sampling data via a statistics software, such as Minitab (www.minitab.com).

2) The users can further calibrate the model by updating regression equations (e.g. the equations for calculating the material and energy inputs for the FOG separation,
pretreatment and biodiesel conversion stages). These regression equations can be updated by using data collected from pilot operations of the production system.

The current life cycle model can be further enhanced by incorporating more variables into the Monte Carlo simulation and sensitivity analysis. For example, the variation transportation distances for raw trap grease and waste disposal may significantly impact the life cycle energy consumption and GHG emission and hence needs be evaluated when sufficient data are available (e.g. from grease haulers and contractors of waste disposal). As mentioned in Chapter 2, a module to model the decomposition of solids in the landfill may be added to expand the system boundary of the life cycle and explore more scenarios. Another potential scenario that can be added is the combustion of trap grease which may enable the users to compare, e.g. GHG emission between trap grease-to-biodiesel and trap grease-to-combustion pathways. In addition to GHG emission, the evaluation of other environmental impacts of the trap grease-to-biodiesel life cycle may be included in a future study to upgrade the model into a full life cycle assessment tool. A cost module could be integrated into the current model to enable the estimation of the production cost of trap grease biodiesel.

In order to integrate the glyceorlysis process to the full-scale biodiesel production, future work is needed on improving two aspects of the process. Firstly, a better separation (e.g. glycerin wash) of crude biodiesel from glycerin is needed to reduce the loss of biodiesel. Distillation is an effective but energy intensive option. Therefore, optimization of the operational condition of distillation process (e.g. temperature, vacuum pressure, time) will be a key factor affecting the cost of the biodiesel production. As mentioned in Chapter 3, glycerol washing may be another feasible separation approach and likewise, the optimum addition of glycerin (and its quality)
needs to be determined in order to main the operation cost of biodiesel production at a competitive level. Secondly, as shown in Table 3.10, the glycerides concentration in the biodiesel was 12.2%, indicating that the conversion was not complete even after an extended reaction time. Therefore, another focus will be improving the conversion rate of glycerolysis-treated oil. One potential approach is to apply multi-step transesterification. After each step, glycerin formed during transesterification will be remove by distillation or glycerin wash, and thus enhance the forward reaction (towards forming biodiesel) in the next step.

Although the research work in this dissertation has resulted in an improved operational condition for the in-situ conversion of sewer grease, future work is needed to improve the extraction rate and FOG-to-biodiesel conversion rate of the process so that this technology can be applied in industrial-scale biodiesel production. As mentioned in Chapter 4, both rates may be augmented by breaking down the surfactants and glycerides in the sewer grease into FFA, through an acid wash or pressurized hydrolysis prior to the in-situ conversion. Therefore, future work will be focused on evaluating a range of factors that may contribute to an optimum condition of the hydrolysis “pretreatment” of the sewer grease, including water-to-sewer grease ratio, pressure, temperature, and reaction time.

The choice of the technologies studied in this dissertation is likely to be dependent on overall production costs, which should be evaluated at a pilot-scale production system. The use of byproducts from each technology has not been discussed in this dissertation. The better use of byproducts should be explored to increase the value of the above new technologies for making biodiesel from trap/sewer grease.