# University of Cincinnati

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**I, Jingjing Wang , hereby submit this original work as part of the requirements for the degree of Master of Science in Environmental Science.**

It is entitled:

**Feasibility Study for a Community Scale Conversion of Trap Grease to Biodiesel**

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# Feasibility Study for a Community Scale Conversion of Trap Grease to Biodiesel

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# Abstract

The world is experiencing fossil fuel depletion, global warming and environmental deterioration due to the overuse of fossil fuels. Biodiesel, as an alternative fuel, is considered as part of the solution. Biodiesel has experienced rapid development and commercialization in the past decade, and the technology for biodiesel production has greatly improved in handling multiple feedstocks. But the development of the biodiesel industry is still facing challenges. The major obstacle to the wide use of biodiesel is that biodiesel is not cost-competitive compared with diesel fuels. The industry is constantly searching for low-cost, or even no-cost feedstocks. Therefore, trap grease can potentially serve as a promising biodiesel feedstock to boost the biodiesel industry.

Trap grease is a mixture of oils, food debris and kitchen wastes. It is generated in grease traps in restaurants. In most municipalities in the US, trap grease, after being pumped out from grease traps by grease haulers, is either sent to wastewater treatment plant or directly to landfills. An intensive literature review has been conducted and the following facts have been obtained. In the US, grease is the number one cause of clogging of public sewers, which results in costly sanitary overflow or combined sewer overflows. Various utilization ways of trap grease include composting, land application, anaerobic co-digestion, making biodiesel, combustion, incineration and rendering, etc. If trap grease is utilized as a feedstock for biodiesel production, it is not only beneficial to the biodiesel industry, but also helps solve the trap grease disposal issue. However, the challenge lies in the extraction of the oil fractions from this highly heterogeneous low grade feedstock.

The goal of this study is to evaluate the feasibility of a community scale conversion of trap grease to biodiesel. Trap grease sample used for this study was obtained from the Metropolitan Sewer District of Greater Cincinnati (designated as MSD-TG). The MSD-TG mainly consists of water (58.94%), free fatty acids (FFAs) (20.69%) and unextractable part/solids (18.17%), with the lipid part of the MSD-TG being almost all FFAs.

This study uses waste cooking oil (WCO) to extract the oil faction from the MSD-TG. WCO is also a low-cost biodiesel feedstock oil and using WCO as the solvent removes the solvent recovery step in the pretreatment process. The optimum extraction conditions were studied. It was found that 60℃ is the optimum extraction temperature. And at 60℃, the optimum extraction duration is 90 minutes and the optimum extraction ratio is 4:1 (for every 10g of the MSD-TG 40mL (36g) of WCO is used). The extraction performance of WCO was evaluated by comparing it with three other organic solvents, methanol, hexane and isopropyl alcohol/hexane (2:1, v/v). WCO shows comparable performance among the four solvents. Based on the survey from trap grease haulers, the quantity of the grease trap waste (as semi solids) generated in Cincinnati is estimated to vary from 1.48 to 3.97 million pounds annually.

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## List of Abbreviations

BFPF: Biodiesel Feedstock Production Facility

BMPs: Best Management Practices

CSOs: Combined Sewer Overflows

FFAs: Free Fatty Acids

FOG(s): Fats, Oils and Grease

FAMEs: Fatty Acid Methyl Esters

gpd: Gallons Per Day

LCFAs: Long-chain Fatty Acids

MIU: Moisture, Insolubles, and Unsaponifiables

MSDGC: Metropolitan Sewer District of Greater Cincinnati

MSD-TG: Trap Grease from MSDGC

NREL: National Renewable Energy Laboratory

PTI: Permit-to-Install

POTWs: Publicly Owned Treatment Works

R-TG: Trap Grease from Restaurant

SSOs: Sanitary Sewer Overflows

TG: Trap Grease

WCO: Waste Cooking Oil

WWTA: Water and Wastewater Treatment Authority, Hamilton County

# Chapter 1

# Introduction

## 1.1 Problem Statement and Significance of Using Trap Grease as Biodiesel Feedstock Oil

Fossil fuel depletion and environmental contamination motivate people to try to find a new fuel resource to reduce dependence of our daily life on fossil fuel (Hill *et al*, 2006; Lin, 2009). Biodiesel, a promising renewable biofuel, has drawn much attention in recent years. Compared with petroleum diesel, biodiesel emits less carbon monoxide, particulate matters (PM) and unburned hydrocarbons (Zhang *et al*, 2003). Besides, biodiesel does not contain sulfur (Demirbas, 2007), which means biodiesel itself will not emit sulfur oxides into the atmosphere during the combustion process.

Despite the fact that, in the aspect of environmental protection, biodiesel is superior to traditional diesel fuel and biodiesel production process is mature enough that people can even produce their own biodiesel fuel in their backyard, the development of the biodiesel industry is still facing its own problems. Nowadays, the most commonly-used type of feedstock oil for biodiesel production is plant oil (Cheng *et al*, 2011; Anwar *et al*, 2010). For example, in the EU, the two most widely used feedstock oils for biodiesel production are sunflower oil and rapeseed oil; in America, the amount of soybean oil and animal fats used for biodiesel outnumbers other feedstock oils and in tropical countries palm oil is the first choice (Hass *et al*, 2005). Thus, a debate has recently arisen on the sustainability of biodiesel. The focus of this debate is on the land use and food issue (Cheng *et al*, 2011; Lora *et al*, 2011; Timilsina *et al*, 2011). More biodiesel being produced means more feedstock oils will be consumed. In order to produce more feedstock oils, more arable lands will be used to grow the feedstock-oil plants, which may result in deforestation and less arable lands for food production. Even if deforestation and the influence on arable land for food production could be avoided, the use of edible plant oil as feedstock itself is competing with food supply. In 2007, the biodiesel industry consumed about 7% of edible vegetable oil supplies worldwide (Mitchell, 2008), and this portion of edible oils could have been used to ease hunger in the world. Another disadvantage of biodiesel is that biodiesel is not cost-competitive with petroleum diesel (Zhang *et al*, 2003; Knothe *et al*, 2005) and this is the greatest barrier to its commercialization (Canakci, 2007). While the cost for feedstock oils accounts for more than 50% of the total production cost (Hu *et al*, 2008; Bozbas, 2008; Haas *et al*, 2006); thus low-cost or no-cost feedstock oil will help to make biodiesel profitable. Feedstock diversity has been brought up as a way to lower the high biodiesel production cost (Srivastava *et al*, 2000).

Trap grease as one of the prospective feedstock oils is receiving more and more attention. As a waste material, trap grease has very little or even negative market value (Wiltsee, 1998; Tyson *et al*, 2004). Typically, restaurants need to pay a professional pumping company to get rid of trap grease from grease traps and to haul it away. Restaurants are willing to give their trap grease to someone who can help them get rid of the trap grease for free or with a smaller service fee.

Besides, large amounts of trap grease are estimated to be produced every year. It is estimated by Wiltsee (1998) that the generation of usable trap grease is 13.37 lbs/person/year and it was also found in his survey that the production of trap grease is roughly linear with the population and the number of restaurants. Another data indicating the quantity of grease trap waste generated is from Metropolitan Sewer District of Greater Cincinnati (MSDGC). The MSDGC estimates that there are approximately 10,000,000 gallons of grease trap discharge being dumped into the MSDGC annually.

Taking the MSDGC as an example, though the MSDGC charges the haulers $50 for 1,000 gallons of grease trap waste, the cost of treatment and disposal is much higher than that. Thus, if the waste water treatment plants can utilize trap grease to produce biodiesel, the cost for trap grease treatment and disposal can be lowered and other operating costs can also be reduced by using biodiesel for diesel equipment or diesel fleet.

## 1.2 FOGs Overview

### 1.2.1 Issues with FOGs (Fats, Oils and Grease)

FOG, as the number one contributor to sanitary sewer overflows, has also received more and more attention in recent years. FOG is typically produced from food service establishments during the food preparation and dish washing process. FOG-containing wastewater could cause big problems if it is discharged into sewer systems, because FOGs tend to accumulate onto the walls of sewer pipes (Fig.1.1). Over time, the layer of grease becomes thicker, and the flow of wastewater in the sewer pipes becomes restricted. During heavy rain, sewer overflows can occur and the wastewater in the pipes with plenty of bacteria, pathogens and viruses will result in backup or overflow through manholes into public places, such as streets and parks. These overflows can result in costly clean-up and repairs, severe fines from the regulatory agencies, environmental problems and health hazards. In Connecticut, on average, there are six overflows across the state every month due to FOGs clogging the sewer pipes (McCarthy, 2005). In the city of Los Angeles, more than 2,000 sewer spills happen per year and most of them are caused by FOGs (EPA, 2012).

(a) (b)

**Fig.1.1** (a) A 10' clean sewer pipe (b) Same sewer pipe with grease build-up (*Source: NEIWPCC,2012*)

FOGs are regarded as the most common cause (47%) of sanitary sewer overflows (SSOs) and combined sewer overflows (CSOs) (EPA, 2007) and are also “the greatest threat of obstruction in POTWs” (EPA, 2011). FOGs could cost communities billions of dollars to solve the problems caused by pipes clogged by grease every year (Parjus *et al*, 2011). To be more specific, only in San Francisco, the city spends more than $3.5 million to clean out the grease-clogged pipes each year (San Francisco Water, Power, and Sewer, 2011). A total of more than 19 million gallons of sewer wastewater flowed back up from 1998 to September 2001 in the state of North Carolina (North Carolina, 2002).

**Fig.1.2** Overflowing sewer

### 1.2.2 Regulations on FOGs Discharge

#### 1.2.2.1 EPA’s National Pretreatment Program

Back in 1973, EPA started a National Pretreatment Program to reduce or eliminate the pollutants in the industrial wastewater to be discharged into the sewer systems or water bodies. This program is still in effect today. The industrial dischargers are required to employ treatment techniques and management practices to reduce or eliminate the pollutants in the wastewater stream. In an EPA's report in 2003, the program was considered to be successful in protecting the communities' environment and federal, state and local partnership was considered as the primary contributor to the implementation of the program. The local pretreatment programs are empowered by the National Pretreatment Program to controlling interference with the operation of POTWs under the provisions of Part 403.5(c)(1) & (2). Part 403.5 requires that “Each POTW developing a POTW Pretreatment Program pursuant to 403.8 shall develop and enforce specific limits to implement the prohibitions” and “Each POTW with an approved pretreatment program shall continue to develop these limits as necessary and effectively enforce such limits”. Also under the provision of Part 403.5(b)(3), a user is prohibited to discharge solid or viscous pollutants to a POTW “in amounts which will cause obstruction to the flow in the POTW resulting in interference”.

As part of the pretreatment program within communities, many of them require food service establishments to install oil and grease removal device or adopt Best Management Practices (BMPs). In New York City, the food service establishments are required to install, operate and maintain properly sized and designed grease interceptors and grease interceptors should also be regularly cleaned to ensure that grease trap/interceptor functions properly (NYC DEP

Sewer Use Regulations, 15 RCNY Chapter 19). Inspectors from DEP routinely inspect the grease interceptors in the businesses and the fine for non-compliance with the rules could be as high as $10,000 per day, per violation in 2010 (New York City Department of Environmental Protection, 2010). In Orange County, a FOG Source Control Program and an Ordinance was established to solve the problems caused by FOGs. Food service establishments are required to follow the BMPs and to install grease interceptors to remove FOGs from wastewater. And also, the corresponding measures are taken to ensure the implementation of the program, such as “Administer enforcement measures and costs associated with FOG discharge and blockages”, “Track compliance through inspection of Food Service Establishments, review kitchen Best Management Practices (BMPs) and Grease Interceptor Maintenance Practices, and monitor wastewater discharges” and so on (Orange County, 2004). An ordinance regulating the discharge of FOGs into sewer systems was approved by the Mayor and Board of Aldermen of the City of Cleveland, MS in January 4, 2011, which is referred to as the City of Cleveland Grease Control Program Ordinance. Food service facilities that discharge or may discharge greasy wastewater are required by the ordinance to obtain a permit and a permit fee of $50 need to be paid every year. BMPs are required to be implemented and grease control devices (grease traps/interceptors) are required to be installed and properly maintained.

#### 1.2.2.2 FOG Requirements in the State of Ohio

Ohio EPA's regulations on wastewater discharge could be divided into two groups depending on the type of discharge, direct or indirect. For the direct discharges to waters of the state, dischargers must obtain an NPDES permit from Ohio EPA and usually they are required to remove harmful pollutants, such as grease, oil or chemicals before discharging wastewater. Once any treatment processes need to be performed, a permit-to-install (PTI) may need to be obtained from Ohio EPA for the construction of treatment or storage unit. While for indirect discharges (discharges to a POTW), the food service establishments need to obtain permission directly from the POTW. Pretreatment to eliminate FOGs from wastewater may also be required. Under this circumstance, a PTI for grease trap construction is usually not required to be obtained from Ohio EPA as grease trap is usually built under building codes. It requires that except the greasy wastewater from garbage disposal, all the grease-bearing wastewater should be treated by grease traps. The design standards for the traps are also specified in building codes. But for larger grease interceptors/traps that are not required as part of the building codes, a PTI needs to be obtained from Ohio EPA's Division of Surface Water.

A new FOG Control Program in the City of Columbus was initiated in 2005. This program is mainly composed of three parts. First, Columbus updated Columbus City Code 1145.05 to address sanitary sewer overflows by requiring all new or remodeled food service establishments to install outside interceptors. Columbus City Council approved this city code change in Nov, 2005 and the effective date for this change was Dec 7, 2005. Second, a new director's rule was developed and all licensed food service operations or licensed retail food establishments that discharge or may discharge grease-containing wastewater to the sewer systems are required to develop and implement a Best Management Plan to deal with the grease wastes. By June 1, 2005, the Best Management Plan must be ready for inspection. Third, a new Cost Recovery Director's Rule was established with a minimum charge of $1,500 per sewer blockage caused by improper disposal of grease and became effective in June 1, 2005.

The MSDGC started a FOGs program in 2009. This program consists of four sub-programs including prevention, reaction, rehabilitation and proactive maintenance. The MSDGC makes plans to solve the blockages and helps their new food industry customers make sure appropriate grease traps are installed for their volume load. The MSDGC also helps food service establishments to take proactive action to prevent the future problems.

A Fats, Oils and Grease Management Policy (FOG Program) was authorized by the Hamilton County Water and Wastewater Treatment Authority (WWTA) in May 19, 2010. All the Food Service Establishments and other non-residential food service facilities in the Hamilton County are required to register for this FOG program. Two related programs are included with one being Preventative Maintenance Program and the other being Grease Control Program. It requires the facilities to install grease control equipment and keep it in good condition. WWTA will routinely inspect the practices and compliance of food service establishments with this policy. WWTA will also identify the potential problem areas to prevent blockages caused by grease.

### 1.2.3 FOGs Control Methods

Best Management Practices and grease control devices, such as grease traps/interceptors are the two most commonly used methods nowadays.

Best Management Practice is defined in 40 CFR 403.3(e) as “schedules of activities, prohibitions of practices, maintenance procedures, and other management practices to implement the prohibitions listed in Part 403.5(a)(1) and (b)” and “treatment requirements, operating procedures, and practices to control plant site runoff, spillage or leaks, sludge or waste disposal, or drainage from raw materials storage” are also parts of BMPs. The detailed steps for BMPs may vary in different cities, but the core is the same.

Grease traps work great for eliminating FOGs from wastewater, but proper design, installation and maintenance are also very essential to ensure grease interceptors to function well. One equation is recommended by US EPA to calculate the volume of grease trap that is suitable for the restaurant of any size.

$$\text{Size (gallons)} = D \times GL \times 0.5HR \times LF$$

Where;

D = number of seats in dining room,

GL = 5 gallons of waste per meal,

HR = number of hours restaurant is open,

LF = loading factor: 1.25-interstate highway, 1.0-other freeways and recreational areas, 0.8-main highway, 0.5-other highways.

**Table 1.1** Table for determining the minimum capacity of grease trap (New York City)

| Table I | | Table II | |
|---|---|---|---|
| Aggregate volume in cubic inches of all fixtures listed in this table. | Minimum grease interceptor retaining capacity for: pot sinks, food prep. Sinks, scullery sinks and floor drains which are used for washdown purposes only. | Aggregate volume in cubic inches of all fixtures, vessels and receptacles listed in this table. | Minimum grease interceptor retaining capacity for: scraper sinks, woks, automatic dishwashers and any fixture receiving discharge from soup and stock kettles. |
| up to 2,462 | 8 (lb) | up to 1,231 | 8 (lb) |
| 2,463 to 4,312 | 14 (lb) | 1,232 to 2,156 | 14 (lb) |
| 4,313 to 6,160 | 20 (lb) | 2,157 to 3,080 | 20 (lb) |
| 6,161 to 9,240 | 30 (lb) | 3,081 to 4,620 | 30 (lb) |
| 9,241 to 12,320 | 40 (lb) | 4,621 to 6,160 | 40 (lb) |
| 12,321 to 15,400 | 50 (lb) | 6,161 to 7,700 | 50 (lb) |
| 15,401 to 21,560 | 70 (lb) | 7,701 to 10,780 | 70 (lb) |
| 21,561 to 30,800 | 100 (lb) | 10,781 to 15,400 | 100 (lb) |
| 30,801 to 46,200 | 150 (lb) | 15,401 to 23,100 | 150 (lb) |
| 46,201 to 61,600 | 200 (lb) | 23,101 to 30,800 | 200 (lb) |
| 61,601 to 92,400 | 300 (lb) | 30,801 to 46,200 | 300 (lb) |
| 92,401 to 123,000 | 400 (lb) | 46,201 to 61,600 | 400 (lb) |

The requirements for the proper size of grease traps/interceptors also vary in different places. New York City provides a table (Table 1.1) for food service establishments to determine the minimum capacity of grease trap they should install. In Ohio, the design of grease traps/interceptors should comply with the requirements detailed in OAC. A table (Table 1.2) for the capacity of grease interceptors is also given in the code (OAC 4101:3-10-01).

**Table 1.2** Capacities of Grease Interceptors (Ohio)

| Total Flow Through Rating (gpm) | Grease Retention Capacity (pounds) |
|---|---|
| 4 | 8 |
| 6 | 12 |
| 7 | 14 |
| 9 | 18 |
| 10 | 20 |
| 12 | 24 |
| 14 | 28 |
| 15 | 30 |
| 18 | 36 |
| 20 | 40 |
| 25 | 50 |
| 35 | 70 |
| 50 | 100 |
| 75 | 150 |
| 100 | 200 |

*For total flow-through ratings greater than 100 (gpm), double the flow-through rating to determine the grease retention capacity (pounds)

*For SI: 1 gallon per minute = 3.785 L/m, 1 pound = 0.454 kg

For the maintenance of grease traps/interceptors, Ohio EPA suggests to following the maintenance schedule recommended by the manufactures or following the local requirements. If no useful information could be obtained from the two sources mentioned above, it is recommended by Ohio EPA that grease trap should be cleaned out when the amount of grease and solids in the trap is about 25% of the total liquid volume of the trap. While, it is required in the City of Cleveland Grease Control Program Ordinance that the depth of settled and floating FOGs in the grease traps "shall be less than 25% of the total operating depth of the trap".

### 1.2.4 Methods for FOGs Analysis

EPA Method 413.1 and Standard Method 5520B were used for the analysis of the concentration of oil and grease in the effluent but these two methods have been withdrawn by EPA in the final rules published March 12, 2007; 72 FR 11199, as Freon was used as extraction solvent for these two methods. Now the only approved method is EPA Method 1664A, for which n-hexane is used as the solvent (EPA, 2012). But the Method 1664A is not suitable for on-site analysis due to the complexity and time required for analysis (Rintoul, 2009). An alternative to the EPA method is a rapid ASTM method D7066-04 for FOGs analysis by using infrared analysis and dimer/trimer of chlorotrifluoroethylene (S-316) as extraction solvent (Rintoul, 2007). The instrument used with ASTM Method D7066-04 could be a full spectrum Fourier Transform Infrared (FTIR) spectrometer or could just be a simple, fixed filter infrared analyzer (Rintoul, 2007). A portable FOGs analyzer, infraCal® TOG/TPH analyzer, was developed for on-site measurement of fat, oil and grease concentration in water. It takes 10-15 minutes for measurement (including extraction) and the measurement range is from 2 to 5000+ ppm (Wilks Enterprise Inc, 2010). Fig.1.3 shows the analyzer in use.

**Fig.1.3** InfraCal® TOG/TPH analyzer

### 1.2.5 Definition for Trap Grease

Trap grease is a type of grease obtained from grease traps/interceptors. This definition seems to be accurate, but actually, it results in very different types of trap grease samples. In some papers, trap grease is also referred to as brown grease (Canakci, 2007), while the definition for brown grease is when the FFA content in the feedstock oil exceeds 15%, the feedstock oil can be regarded as brown grease. This type of trap grease is usually oil-like, which is much easier to pre-treat. While in some other papers, trap grease samples are in solid form, containing large amounts of solids and this type of trap grease needs extra effort in pretreatment in order to be purified into a good biodiesel feedstock. The properties of trap grease reported in the published papers differ a lot from each other. But generally speaking, trap grease is mainly a mixture of lipids (FFAs, fats and oils), water, food debris and kitchen waste, among which water content and/or FFA content could be extremely high (Fortenbery, 2005).

## 1.3 Formation Process of Trap Grease and Generation of Free Fatty Acids (FFAs) in Trap Grease

### 1.3.1 In Grease Traps

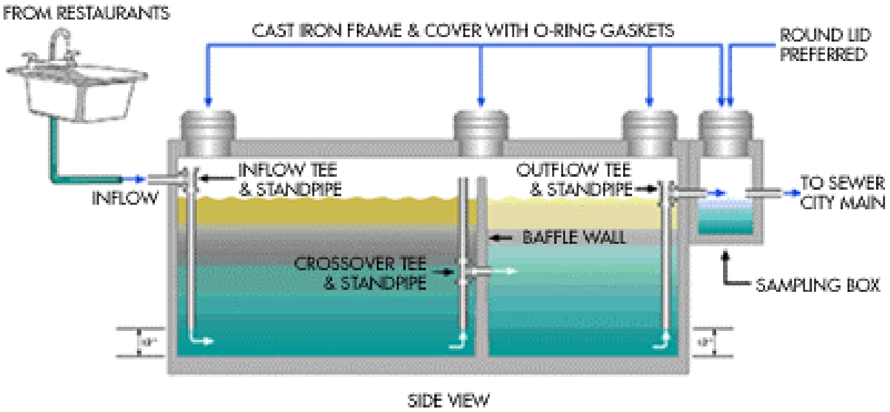


**Fig.1.4** Schematic diagram of grease trap (*Source: Tyson, 2002*)

Trap grease is formed during the process of greasy water flowing down into the sanitary sewer system. Grease traps are located somewhere between the restaurant sink and the sanitary sewer system. The schematic diagram of a grease trap is shown in Fig.1.4. Down from the sink to the grease trap, both the temperature and the flow rate of the greasy water decreases. Grease turns solid at a lower temperature, and the solid grease separates from the less greasy water and floats to the top of the waste water. The less greasy water then goes through the baffle wall and continues to flow into the second chamber of the grease trap (if there is one) and finally flows into the sewer system, while the solid grease layer is blocked and accumulated onto the baffle wall. The trapped grease is pumped out regularly by the pumping companies.

### 1.3.2 In the MSDGC

(a) (b)

**Fig.1.5** (a) Solids floating on the top of waste water is collecting into the pipe (b) Solids collected in the pipe is ready to be removed

Trap grease samples obtained from the MSDGC was formed in the primary settling tank. As a wastewater treatment plant, the MSDGC receives and processes grease trap waste collected by grease haulers. $50 per 1,000 gallons of grease trap waste is charged as the tipping fee. Grease haulers dump the grease trap waste into a specified location and then the grease trap waste is transported into the primary settling tank. In the primary settling tank, it is mixed with the wastewater the MSDGC receives from other sources. Solids floating on the top of the water are skimmed into a half-opened pipe (as shown in Fig.1.5(a)). Solids accumulated in the pipe are removed by water and transported into a separatory tank to roughly remove the water. After that the solids are stored in a holding tank (Fig.1.6) and finally go to landfill.

**Fig.1.6** Holding tank containing trap grease

### 1.3.3 Generation of FFAs in Trap Grease

It is not hard to understand where oils, fats, water, food debris and kitchen waste in trap grease come from, but unlike other components, FFAs are not something that exists from the very beginning of the formation of trap grease. The FFAs existing in trap grease are one of the products of thermolysis, hydrolysis or microbial degradation reactions (Kamali *et al*, 2011). These reactions might take place during the cooking process or during the storage process in the grease traps. During the cooking process, the change of physical and chemical properties of vegetable oils at high temperature favors the reaction between vegetable oil and water existing in the food (Canakci, 2007). And during the period that trap grease stays in the grease trap before being pumped out, the dark wet environment with plenty of nutrients (greases) provides a very good condition for the growth of microorganisms. The activities of microorganisms can also speed up the reaction between oils and water. Fig.1.7 shows the reaction between water and vegetable oil to produce FFAs.

$$\text{Triglycerides} + \text{water} \rightleftharpoons \text{Diglycerides} + \text{Fatty acid}$$

$$\text{Diglycerides} + \text{water} \rightleftharpoons \text{Monoglycerides} + \text{Fatty acid}$$

$$\text{Monoglycerides} + \text{water} \rightleftharpoons \text{Glycerol} + \text{Fatty acid}$$

$$\text{Triglycerides} + 3\ \text{water} \rightleftharpoons \text{Glycerol} + 3\ \text{Fatty acid}$$

**Fig.1.7** Hydrolysis of vegetable oil (source: *Satyarthi et al., 2011*)

## 1.4 Disposal/Potential Utilization Ways of Trap Grease

### 1.4.1 Dumped to Waste Water Treatment Plant

According to the information collected from the inventory, in Cincinnati, most of the grease haulers dump their grease trap waste to the MSDGC. After the grease trap waste is transported to the primary settling tank and processed by primary treatment, the floating part in the tank is skimmed out and collected into a holding tank and finally it is landfilled.

Parjus *et al* (2011) reported that the most common case is for the grease haulers to dump the grease trap waste directly to wastewater treatment plants.

In some cities, grease haulers could also dump the grease trap waste to designated manholes which are connected to a pipe that goes directly to a wastewater treatment plant. Usually the pipe is large enough that blockage by grease is not a concern there.

However, wastewater treatment plants regard grease trap waste as a burden and are reluctant to process it due to its demand for high oxygen concentration, slow biodegradation kinetics and risk of blockage and obstruction caused by grease within the facilities (Brooksbank *et al*, 2007). The cost of processing the trap grease outweighs the charge they impose on the haulers.

### 1.4.2 Landfill

Landfill is a conventional way to dispose grease trap waste. In a Compliance Bulletin published by the Colorado Department of Public Health and Environment (2002), landfill is considered to be the most available option to dispose of grease trap waste. The trap grease generated in the MSDGC is mixed with solids from the pretreatment system and disposed of to landfills. One of the grease haulers that responded to our inventory indicated that the grease trap waste they collected was taken to landfill. Landfill was also the choice for several brown grease treatment companies in Georgia (Kiepper *et al*, 2001). But before landfill, water should be eliminated so that it is dry enough to pass the paint filter test (Method 9095) and the compositions of the trap waste need to be analyzed to make sure that it is non-hazardous before landfilling.

Landfilling grease trap waste, however, is a waste of a potential energy, a nutrient resource and takes up more valuable but limited land resources.

### 1.4.3 Composting and Land Application

Usually, direct spray application of grease trap waste is unfeasible because its FOGs content is always high and the grease could affect the yields or even kill the vegetation by coating the surface of the plants or the soil pores (Zolezzi *et al*, 2010; Coker, 2006). But grease trap waste in liquid with less than 1% total volatile solids could be sprayed onto the soil and the results were acceptable (Kiepper *et al*, 2001). So for grease trap waste with high FOGs content, it could be utilized via being injected or incorporated into the soil to avoid the suffocation of vegetation (Kiepper *et al*, 2001; Coker, 2006). In the Wake County, NC, the sub-surface injection of trap effluent is quite common (Austic, 2010).

Composting is also a way to solve the problem that may be caused by direct application. The bulk part of grease trap waste is compostable (Kiepper *et al*, 2001) and high-energy content enables a rapid increase in composting temperature (Coker, 2006). Grease trap waste could be used in composting either in the form of liquid or in the form of solids after water is removed. If grease trap waste is used in liquid form, it should be co-composted with enough absorptive bulking agents to absorb the water (Coker, 2006). Green waste, dry sawdust and/or yard trimmings can be chosen as the adsorptive bulking agents and along with these materials, grease trap waste could be made into manufactured soil via composting (Belyaeva and Haynes, 2010; Coker, 2006; Parjus *et al*, 2011). However, the odor problem is always a discouraging factor for the utilization of composting; composting grease trap waste is not an exception.

### 1.4.4 Anaerobic Co-Digestion

Grease trap waste/sludge is also considered for anaerobic co-digestion with sewage sludge to produce biogas due to its high organic content and high methane potential (Luostarinen *et al*, 2009; Wan *et al*, 2011; Zhu *et al*, 2011). For anaerobic digestion, using grease trap waste alone as the substrate is not recommended because the long-chain fatty acids (LCFAs) existing in the grease trap waste could inhibit nutrient transport to the cells by adsorbing to microbial surfaces (Pereira *et al*, 2005); thus methanogenesis could be inhibited severely (Luostarinen *et al*, 2009).

Davidsson *et al* (2008) evaluated the anaerobic digestion of grease trap sludge and the anaerobic co-digestion of grease trap sludge with sewage sludge. Batch laboratory tests were performed to determine methane potential of grease trap sludge and it turned out that its methane potential is high (845-928 Nml/g VSin). But the digestion of grease trap sludge failed to maintain stable methane production in the continuous digestion tests. While, for the co-digestion of grease trap sludge with sewage sludge, it achieved success in both tests (batch test and continuous test). Methane yield of the sewage sludge digester increased with the addition of grease trap waste but the sludge production did not change much.

But digestion might not be feasible for a facility that is located in the vicinity of residential areas. For instance, due to restrictions in location and space availability, digestion is not an option at the Mill Creek location. In the past, sludge digesters generated so many complaints from the neighborhood that they were replaced by incineration.

### 1.4.5 Making Biodiesel

Challenges exist since trap grease is more complex than waste cooking oil, as commented by people handling trap grease. As a feedstock, trap grease is a low-cost or no-cost waste material compared with waste cooking oil or virgin oils, and can potentially lower the cost for biodiesel production. But high water content, high FFA content and solids contamination make trap grease a low-quality feedstock oil. Currently, the concern that the value-added utilization of trap grease will raise the market value of trap grease makes the advantage of trap grease, low cost, as biodiesel feedstock uncertain (Hartwig and Moore, 2006).

Converting trap grease into biodiesel has already been practiced in some cities in the US. Some examples of biodiesel production projects are shown in

EPA's website as a demonstration of Water & Energy Efficiency in Water and Wastewater Facilities (EPA, 2012). California seems to be a pioneer in utilizing waste grease to produce biodiesel. San Francisco Public Utility Commission initiated a large-scale brown grease recycling demonstration project in 2009, which is the first in the US. They used the patented technology from BlackGold Biodiesel to convert 250 million gallons of trap grease into 100,000 gallons of biodiesel and used the fuel to power their own diesel equipments. This project is detailed in later section. Eastern Municipal Water District in Perris, CA, which is the 5th largest water district in California obtained a grant from the U.S. Department of Energy with a total amount of $250,000 in January 2010 for their Biodiesel Feedstock Production Facility (BFPF). URS Corporation was selected to provide engineering design services. The BFPF aims at processing about 5 to 10 million gallons of waste every year and recovering about 200,000 – 400,000 gallons of biodiesel feedstock. The project was started in February 2011, for which the cost is estimated to cost $1.5 million but the system is estimated to be able to pay for itself in six years (Zimmerman, 2011). Biodiesel produced can be used not only for the diesel equipment in the facilities but also for the city fleet.

### 1.4.6 Other Disposal Methods

Combustion, incineration and rendering have also been studied or reported in the literature as disposal alternatives for grease trap waste.

Al-Shudeifat and Donaldson (2010) compared the combustion of diesel fuel and dewatered trap grease oil with a gas turbine generator. The viscosity and high heating value of dewatered trap grease oil and diesel fuel were measured. As it is reported in the paper, the dewatered trap grease sample had a lower high heating value but a higher viscosity. Emissions from trap grease oil and diesel were also tested. Less $NO_X$ but higher CO and $CO_2$ emissions at full loads were observed for trap grease combustion compared with diesel combustion. Although trap grease oil was filtered before the injection pump, deposit formation was still observed in the fuel nozzle, in the combustion chamber and on the turbine blades.

Incineration and rendering are also reported in the literatures (Colorado Department of Public Health and Environment, 2002; Davidsson *et al*, 2008; Kiepper *et al*, 2001; Parjus *et al*, 2011; Stoll and Gupta, 1997; Wiltsee, 1998). For incineration, it could be combined with other utilization methods and serves as the last step to deal with the residues. Grease trap waste could be added directly into incinerator, but it is better to eliminate water beforehand. Otherwise, high energy input is needed to achieve the required temperature due to the evaporation of water. A factsheet for restaurant oil and grease rendering prepared by the County Sanitation Districts of Los Angeles County briefly described the rendering process for restaurant oils and grease. According to the factsheet, the first step is contamination test. After that solids are removed from the waste oil and grease in a settling tank and the liquid is heated in a vacuum to eliminate the impurities by volatilization. Then the raw material is sold to companies to be made into soap, animal feeds additives or cosmetic and skin care products. But the cleaning agents contained in trap grease make it more difficult to detect harmful substances (Canakci, 2007). Trap grease is undesirable in the animal feeds market either (Fortenbery, 2005; Hartwig and Moore, 2006) due to its heterogeneity and poorly-defined nature.

### 1.4.7 Combination of the Utilization Methods

San Francisco Water, Power and Sewer (2011) launched a large-scale brown grease recycling demonstration project in 2009. About 300 gpd of brown grease, with less than 2% MIU, were recovered from collected grease trap waste (about 10,000 gpd) by eliminating water and other undesirable impurities. The recovered brown grease was produced into biodiesel in later processes. During the biodiesel production process, a low-grade #6 boiler fuel was also produced. It either was sold as boiler fuel or was added into anaerobic digesters. The remaining 97% high-strength wastewater (white water) with less than 1% FOG went through anaerobic digestion process to produce methane for cogeneration.

## 1.5 Organization of this Thesis

The goal of this study is to analyze the composition and fatty acid profile of trap grease samples obtained from the Metropolitan Sewer District of Greater

Cincinnati (designated as MSD-TG), to find a feasible method to obtain lipids from the MSD-TG and to estimate the quantity of trap grease generated in Cincinnati annually.

Chapter 2 mainly focuses on the properties of trap grease samples obtained for this study. Chapter 3 deals with the method used for obtaining lipids from the MSD-TG and the results and discussions for the study of the optimum experimental conditions. The information sources used for estimating the amount of trap grease generated in Cincinnati and the outcomes are included in chapter 4. Chapter 5 consists of the comparison of extraction performance of WCO with other organic solvents. The literature review for each part of this study is incorporated into each chapter for the purpose of better connection.

# Chapter 2

# Properties of Trap Grease Samples Obtained in this Study

## 2.1 Composition and Fatty Acid Profile of Trap Grease from Former Studies

The feedstock part of trap grease mainly consists of glycerides (triglyceride, diglyceride and monoglyceride) and FFAs. The total amount of triglyceride, diglyceride, monoglyceride and FFAs determines the amount of feedstock oil available per unit trap grease samples. Researchers are also interested in the fatty acid profile for the feedstock part because fatty acid distribution reflects the distribution of the fatty acid chains of glycerides, and thus determines the quality of the biodiesel produced from that feedstock oil. Both the length and the degree of saturation of the carbon chains affect the properties of biodiesel. Fatty acids with a long carbon chain (C14 - C18) are the main sources of energy in the biodiesel produced; that is, the energy production value of trap grease is determined by the heavier fatty acids (Kamali *et al*, 2011). Compared with unsaturated fatty acids, saturated ones are less likely to be oxidized and have a higher cetane number, but crystallization may occur at very high temperatures (Canakci *et al*, 2001). The percentage of the feedstock part in trap grease and the fatty acid profile together determine how good the quality of the trap grease sample is as biodiesel feedstock oil.

Lu *et al* (2010) analyzed the composition of trap grease samples from restaurants in Guangzhou, China. Ngo *et al* (2011) obtained two types of trap grease samples from two different places: one is from San Francisco, CA (SF) and the other from Atlanta, GA (ATL). In the study of Ngo *et al* (2011), water in the trap grease was eliminated beforehand and part of the dry ATL trap grease samples was distilled to remove the contaminations (designated as distilled ATL). The main compositions and the fatty acid profile were analyzed for the three trap grease samples. But the percentage for each lipid composition of their samples (distilled ATL, ATL & SF) was not reported on a basis of the total weight of the trap grease samples. All the lipid percentages were calculated based on the total weight of the lipid part of the samples, which makes it impossible to compare the lipid content of their trap grease samples with others. For the analysis of the fatty acid profile, Ngo *et al* (2011) employed methanolysis to convert the lipid part of trap grease into fatty acid methyl esters (FAMEs) and then FAMEs were analyzed by GC-MS with the column being Supelco (Bellefonte Park, PA, USA) 24022 capillary column (30m × 0.25mm × 0.2μm). The initial oven temperature was 170℃ and lasted for 10 minutes. Then, the oven temperature was ramped at 2℃ per minute to 200℃ and lasted for ten minutes. HPLC equipped with a Chrompack (Raritan, NJ, USA) Spherisorb cyano column (100 × 3.0mm) was used to determine FFAs, FAME, triglycerides and diglycerides.

Park *et al* (2010) and Wang *et al* (2008) were from the same research group, so the composition of their trap grease samples all from Guangzhou, China is similar to each other, but Wang *et al* (2008) also reported the fatty acid distribution of the samples. Canakci and Van Gerpen (2001) listed the fatty acid distribution of brown grease measured by Woodson–Tenent Laboratories, Inc. (Des Moines, IA). Kamali *et al* (2011) also analyzed the fatty acid profile of trap grease samples obtained from Clean Earth Environmental Inc. (Kalamazoo, MI). As no quantitative result was reported in that paper, the GC-MS chromatogram of trap grease analysis is given (Fig.2.1). The quantitative results for the composition of trap grease and the fatty acid profile are summarized and listed in Table 2.1 and Table 2.2 respectively. Table 2.3 is a summary of Table 2.2 by simplifying the categories of the fatty acids.

**Table 2.1** Trap grease compositions from former studies (wt %)

| Composition | | Lu *et al*, 2010 | Ngo *et al*, 2011 | | | Park *et al*, 2010 | Wang *et al*, 2008 |
|---|---|---|---|---|---|---|---|
| | | | Distilled ATL | ATL | SF | | |
| Free Fatty Acids | | 56.60 | 93.70** | 82.90** | 90.30** | 51.45 | 49.60 |
| Glycerides | Mono- | 40.98* | / | / | / | 0.67*** | |
| | Di- | | 0.00 | 6.10** | 3.70** | 9.40*** | |
| | Tri- | | 6.30** | 11.00** | 6.00** | 26.60*** | |
| Glycerol | | / | / | / | / | 4.40*** | |
| Water Contents | | 0.19 | 0.18 | 0.27 | 0.45 | 0.71 | 0.80 |
| Not Measured/Impurity | | 3.00 | / | / | / | 6.77 | 8.86 |

*Concentration for the total glycerides (Mono-,Di- & Tri-)

**Based on the total weight of lipid-class compositions, not the total weight of trap grease samples

***Results from the same research group

The FFA contents of all the trap grease samples shown in Table 2.1 are very high, accounting for around or more than half of the total weight and are much higher than that of glycerides. Though Ngo *et al* (2011) did not report the percentage of FFAs and glycerides based on the total weight of trap grease samples, it can be seen from the results that the useful part in their trap grease samples is mainly composed of FFAs with more than 82%. The water contents for all the samples are very low, all less than 1%.

**Table 2.2** Fatty acid profile from former studies (wt %)

| Fatty acid | Wang *et al*, 2008 | Canakci and Van Gerpen, 2001 | Ngo *et al*, 2011 | | |
|---|---|---|---|---|---|
| | | | Distilled ATL | ATL | SF |
| C10:0 | / | / | 0.41 | 0.41 | 0.34 |
| C12:0 | / | / | 0.3 | 0.74 | 0.75 |
| C14:0 | 1.16 | 1.66 | 1.32 | 2.82 | 2.83 |
| C14:1 | / | / | 0.32 | 0.39 | 0.64 |
| C16:0 | 30.38 | 22.83 | 17.9 | 23.1 | 31.2 |
| C16:1 | 1.42 | 3.13 | 1.46 | 1.84 | 2.14 |
| C18:0 | 6.02 | 12.54 | 11.3 | 10.2 | 12.7 |
| C18:1 | 38.39 | 42.36 | 41.1 | 43.8 | 32.3 |
| C18:2 | 18.83 | 12.09 | 13.4 | 11.3 | 11.5 |
| C18:3 | 1.31 | 0.82 | 1.29 | 0.93 | 1.03 |
| C20:0 | / | / | 0.19 | 0.4 | 1.03 |
| Unknown | 2.49 | 4.57 | 11.1 | 4.07 | 3.54 |
| Saturated | 37.56 | 37.03 | 31.42 | 37.67 | 48.85 |

**Table 2.3** Summary on fatty acid profile from former studies (wt %)

| Fatty acid | Wang *et al*, 2008 | Canakci and Van Gerpen, 2001 | Ngo *et al*, 2011 | | |
|---|---|---|---|---|---|
| | | | Distilled ATL | ATL | SF |
| C10 | / | / | 0.41 | 0.41 | 0.34 |
| C12 | / | / | 0.3 | 0.74 | 0.75 |
| C14 | 1.16 | 1.66 | 1.64 | 3.21 | 3.47 |
| C16 | 31.8 | 25.96 | 19.36 | 24.94 | 33.34 |
| C18 | 64.55 | 67.81 | 67.09 | 66.23 | 57.53 |
| C20 | / | / | 0.19 | 0.4 | 1.03 |
| Unknown | 2.49 | / | 11.1 | 4.07 | 3.54 |
| ≥C14 | 97.51 | 95.43 | 88.28 | 94.78 | 95.37 |

As it can be seen from Table 2.2 and Table 2.3, the fatty acid distributions for the trap grease samples from different sources are similar to each other. The percentage of C18 fatty acids is the highest one among the fatty acids with the minimum being as high as 57.53% and C16 fatty acids the second one. To be more specific, C18:1 fatty acid content and C16:0 fatty acid content are the highest two among all the fatty acids. The saturated fatty acids level varies from 31.42% to 48.85%, while the heavier fatty acids (≥C14) contents of the five trap grease samples are all extremely high, varying from 88.28% to 97.51%.

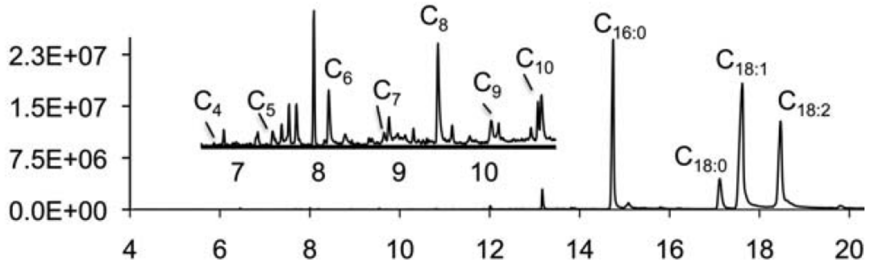
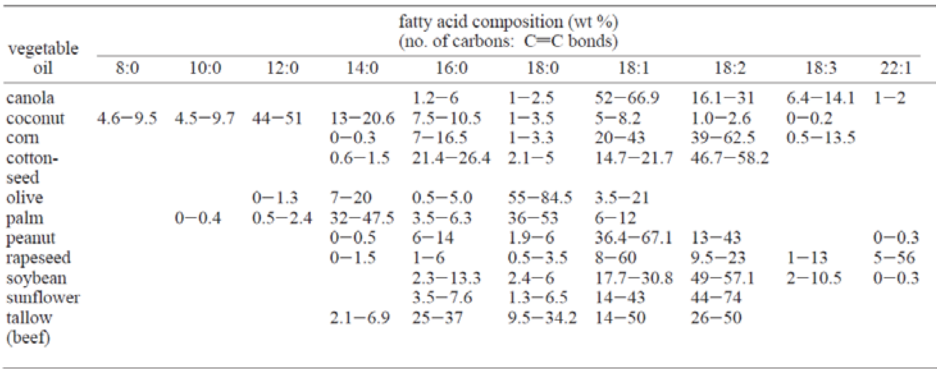


**Fig.2.1** Trap Grease Analysis by GC-MS (*Source: Kamali et al, 2011*)

Though no quantitative results were reported in the paper of Kamali *et al* (2011), this chart (Fig.2.1) gives a lot of information. The dominant peaks shown in this chart stand for fatty acids with long carbon chains, C16:0, C18:1 and C18:2, while other fatty acids with short carbon chains (C4-C10) were also observed.

The fatty acid distribution of the commonly-used vegetable oils may explain why the fatty acids in trap grease samples are mainly C16 and C18 fatty acids. Table 2.4 shows the fatty acid profile for different vegetable oils.

**Table 2.4** Fatty acid profile for different vegetable oils (*Source: Huber et al, 2006*)



| vegetable oil | fatty acid composition (wt %) (no. of carbons: C=C bonds) 8:0 | 10:0 | 12:0 | 14:0 | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 | 22:1 |
|---|---|---|---|---|---|---|---|---|---|---|
| canola | | | | | 1.2−6 | 1−2.5 | 52−66.9 | 16.1−31 | 6.4−14.1 | 1−2 |
| coconut | 4.6−9.5 | 4.5−9.7 | 44−51 | 13−20.6 | 7.5−10.5 | 1−3.5 | 5−8.2 | 1.0−2.6 | 0−0.2 | |
| corn | | | | 0−0.3 | 7−16.5 | 1−3.3 | 20−43 | 39−62.5 | 0.5−13.5 | |
| cotton-seed | | | | 0.6−1.5 | 21.4−26.4 | 2.1−5 | 14.7−21.7 | 46.7−58.2 | | |
| olive | | | 0−1.3 | 7−20 | 0.5−5.0 | 55−84.5 | 3.5−21 | | | |
| palm | | 0−0.4 | 0.5−2.4 | 32−47.5 | 3.5−6.3 | 36−53 | 6−12 | | | |
| peanut | | | | 0−0.5 | 6−14 | 1.9−6 | 36.4−67.1 | 13−43 | | 0−0.3 |
| rapeseed | | | | 0−1.5 | 1−6 | 0.5−3.5 | 8−60 | 9.5−23 | 1−13 | 5−56 |
| soybean | | | | | 2.3−13.3 | 2.4−6 | 17.7−30.8 | 49−57.1 | 2−10.5 | 0−0.3 |
| sunflower | | | | | 3.5−7.6 | 1.3−6.5 | 14−43 | 44−74 | | |
| tallow (beef) | | | | 2.1−6.9 | 25−37 | 9.5−34.2 | 14−50 | 26−50 | | |

## 2.2 Trap Grease Samples for this Study

Two types of trap grease samples (shown in Fig.2.2) were obtained for the study in this chapter: one was from the primary settling tank in the MSDGC (MSD-TG) and the other was from grease trap in a restaurant on the west campus of the University of Cincinnati (R-TG). As the amount of the R-TG was really small, only a few experiments have been done with the R-TG.

**Fig.2.2** (Left) trap grease from Metropolitan Sewer District of Greater Cincinnati; (Right) trap grease from restaurant or residential grease traps

### 2.2.1 Some Physical Properties of Trap Grease Samples

Color, state of matter, and odor of the two trap grease samples are listed in Table 2.5. The color of R-TG is much darker than that of MSD-TG. R-TG is in semi-liquid form, while MSD-TG is composed of solid clumps. Judging from appearance alone, R-TG contains much less impurities as twigs, leaves or even rubber gloves could be found in MSD-TG. Every time, before doing experiments, screening needed to be performed on MSD-TG to eliminate those solid impurities. While for R-TG this step could be ignored.

**Table 2.5** Color, state of matter, and odor of the two trap grease samples

| Type | Color | State of Matter | Odor |
|---|---|---|---|
| MSD-TG | claybank | solid | foul |
| R-TG | black brown | semi-liquid | foul |

Given the formation process of trap grease, trap grease samples may contain large amounts of water. A moisture content test was performed to find out exactly how much water is in the trap grease samples.

The traditional heating method was used. A complete dry beaker was weighed twice by using electronic balance and the average weight was designated as $W_1$. Samples of trap grease were randomly selected from the container and were added into the beaker. The whole part was weighed twice and the average weight was designated as $W_2$. In order to make it easier to eliminate water, the MSD-TG was crushed into small particles, but there was no need to apply this step to the R-TG as it was semi-liquid. After all these steps were done, the beaker was placed onto a hot plate. The temperature was set at 120℃ and the trap grease samples were heated up for about 6 hours. Then the beaker was removed from the hot plate and cooled down to room temperature in a desiccator. After cooling down, the beaker was weighed twice and the average weight was obtained, $W_3$. The beaker was then heated up on the hot plate for another one hour, cooled down in the desiccator and weighed again to obtain its weight, $W_4$. $W_4$ was compared with $W_3$ to see whether the difference was less than 0.05g. If it was not, the steps described above were repeated until the difference was less than 0.05g and the final weight was designated as W. The equation to calculate the moisture content is shown below (Equation 2.1):

$$\text{Moisture Content \%} = \frac{W_2 - W}{W_2 - W_1} \times 100\% \qquad (2.1)$$

- $W_1$ : Weight of the beaker, g
- $W_2$ : Weight of beaker and trap grease sample before heating, g
- W : Final weight of the beaker and trap grease sample after heating, g

A total of 40 samples of the MSD-TG and 9 samples of the R-TG were tested. The results for the two trap grease samples are shown in Table 2.6. A 95%

confidence interval was built for the population mean (μ) based on the data obtained. Sample standard deviation was also calculated. From the results, one can tell that water distributes more evenly in the R-TG than in the MSD-TG and the R-TG contains much more water than the MSD-TG. But water content in the MSD-TG is still very high with more than half of the weight being composed of water.

**Table 2.6** 95% confidence interval and sample standard deviation for the moisture content of the two trap grease samples

| Type | Data Set | 95% Confidence Interval | Sample Standard Deviation |
|---|---|---|---|
| MSD-TG | 40 | $47.64\% \le \mu \le 52.04\%$ | 6.88% |
| R-TG | 9 | $71.85\% \le \mu \le 74.02\%$ | 1.41% |

### 2.2.2 Trap Grease Composition and Fatty Acid Profile

As the two most important properties of trap grease, the composition and fatty acid profile of the MSD-TG were also analyzed. The R-TG was not analyzed in this study because the experiments were mainly conducted with the MSD-TG of large quantity.

A total of six samples for GC-MS analysis were prepared as the following procedures. The weight of the container ($W_1$) and that of the coffee filter ($W_2$) used were measured beforehand. A certain amount of the MSD-TG sample was added into the container and the whole part was weighed ($W_3$). The MSD-TG was heated up for 24 hours to eliminate water. The dry trap grease sample was weighed ($W_4$) and then DCM (methylene chloride) was added into the container at a ratio of 15:1 (mL/g, based on the dry weight of the MSD-TG sample) for sample 1 to 5 and for sample 6 the extraction ratio was 12:1 (mL/g). For example, at the ratio of 15:1, if the dry weight of the MSD-TG is 20g, the volume of the solvent added is 300mL. After 24 hours of extraction at room temperature without stirring, the solids were filtered out by using coffee filters. Vacuum was not employed for the whole filtration process because the bulk of the liquid could easily penetrate the coffee filter. After the bulk of the liquid went through the coffee filter, the rest of the liquid in the funnel was filtered with the aid of vacuum to speed up the filtration process. The volume of the liquids after filtration was measured ($V_1$) and extraction samples were taken from the liquids after filtration. The amount of MSD-TG samples used and the amount of solvent after filtration was listed in Table 2.7.

**Table 2.7** Amount of the MSD-TG used for the GC-MS analysis and amount of solvent after filtration

| Sample | Amount of MSD-TG Used(g) | Amount of Dry MSD-TG(g) | Amount of Solvent After Filtration (mL) |
|---|---|---|---|
| 1 | 23.09 | 9.81 | 114 |
| 2 | 31.91 | 13.13 | 159 |
| 3 | 20.74 | 8.77 | 97 |
| 4 | 29.44 | 12.35 | 151 |
| 5 | 36.56 | 14.43 | 174 |
| 6 | 45.10 | 17.59 | 176 |

After filtration, the weight of the solids was also measured. The solids after filtration consisted of two parts: one was the solids on the coffee filters and the other was the solids left in the containers. As right after filtration, the solids were still containing solvent, the filters and containers were dried out by staying in the hood for 6 hours. Then the containers ($W_5$) and the coffee filters ($W_6$) with solids were weighed and the weight of the solids part can be obtained.

The composition of the MSD-TG samples is listed in Table 2.8. The method of calculating moisture content is described in section 2.2.1. The amount of FFAs was determined by titration and calculated by Equation 3.1. Equation 2.2 was used to calculate the percentage of unextractable part/solids.

$$\text{Unextractable } \% = \frac{(W_5 - W_1) + (W_6 - W_2)}{W_3 - W_1} \times 100\% \qquad (2.2)$$

- $W_1$ — Weight of the container, g
- $W_2$ — Weight of the coffee filter, g
- $W_3$ — Total weight of container and MSD-TG before heating, g
- $W_5$ — Total weight of container and solids after filtration and drying, g
- $W_6$ — Total weight of coffee filter and solids after filtration and drying, g

The MSD-TG mainly consists of water (58.94%), FFAs (20.69%) and unextractable part/solids (18.17%). The lipid part of the MSD-TG, which is usable for biodiesel production, is almost all FFAs and the amount of glycerides (0.212%) in the MSD-TG is very small. The water content in the MSD-TG is much higher than that in other trap grease samples listed in Table 2.1 and compared with those trap grease samples, the MSD-TG is highly contaminated by solids.

**Table 2.8** Composition of the MSD-TG samples

| Sample | Water (%) | Glycerides (%) | | | FFAs (%) | Solid (%) | Unmeasured Part (%) |
|---|---|---|---|---|---|---|---|
| | | Mono- | Di- | Tri- | | | |
| 1 | 57.53 | 0.019 | 0.006 | 0.253 | 21.59 | 18.40 | 2.20 |
| 2 | 58.86 | 0.006 | 0.019 | 0.103 | 20.43 | 19.57 | 1.02 |
| 3 | 57.71 | 0.018 | 0.060 | 0.173 | 20.13 | 18.08 | 3.84 |
| 4 | 58.05 | 0.020 | 0.033 | 0.174 | 22.78 | 18.29 | 0.65 |
| 5 | 60.51 | 0.016 | 0.038 | 0.197 | 19.20 | 17.91 | 2.13 |
| 6 | 61.00 | 0.017 | 0.026 | 0.092 | 20.00 | 16.79 | 2.07 |
| Average | 58.94 | 0.016 | 0.031 | 0.165 | 20.69 | 18.17 | 1.99 |

As after the compositional analysis of the MSD-TG, the fact that FFAs is the overwhelming one among the lipid-class compositions was observed, so the carbon chain distribution for the FFAs was directly analyzed and is used as the fatty acid profile for the MSD-TG. When preparing the samples for GC-MS analysis, to be on the safe side, the extraction samples pipetted out from the liquid after filtration were filtered again by using a disposable syringe filter of 0.45μm in pore size and were diluted ten times with DCM. After that, the samples for FFA profile analysis were ready to be analyzed by GC-MS. GC(HP5890)- MS(HP5970) equipped with Restek Rxi-5ms column (30m × 0.25μl × 1μm) was used for the analysis. The temperature of the injector and the detector was set to be 250℃. The initial temperature of the oven was 40℃, held for 2 minutes. After that the oven temperature was increased to 180℃ at a rate of 10℃/min. Then the increasing rate was changed to 5℃/min until the temperature was increased to 230℃ and then the oven temperature was increased to 380℃ at a rate of 15℃/min, held for 4 minutes. Helium was used and its flow rate was 1mL/min. The results for the FFA/fatty acid profile of the MSD-TG are listed in Table 2.9.

**Table 2.9** Fatty acid profile of the MSD-TG samples

| Fatty Acid | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Average |
|---|---|---|---|---|---|---|---|
| C14:0 | 29.89 | 13.96 | 10.79 | 7.89 | 6.76 | 3.19 | 12.08 |
| C16:2 | 5.49 | 2.72 | 3.56 | 0.00 | 0.00 | 0.63 | 2.07 |
| C16:1 | 4.87 | 2.85 | 3.39 | 0.00 | 0.00 | 1.35 | 2.08 |
| C16:0 | 11.29 | 3.93 | 0.00 | 2.78 | 0.00 | 0.91 | 3.15 |
| C18:3 | 4.75 | 11.68 | 0.00 | 1.83 | 2.94 | 1.38 | 3.77 |
| C18:2 | 4.96 | 0.00 | 0.00 | 0.00 | 5.32 | 0.84 | 1.85 |
| C18:1 | 38.75 | 53.75 | 82.26 | 82.83 | 84.98 | 91.71 | 72.38 |
| C18:0 | 0.00 | 11.10 | 0.00 | 4.67 | 0.00 | 0.00 | 2.63 |

It can be seen from Table 2.9 that the average percentage of C18 fatty acid with one double bond, which is 72.38%, is extremely high compared with other fatty acids. Compared with the fatty acid distribution of the trap grease samples listed in Table 2.2, the average amount of C16:0 fatty acid in the MSD-TG is much lower and the average amount of C14:0 is much higher.

The average molecular weight of the FFAs was calculated by Equation 2.3 according to the fatty acid distribution of the MSD-TG.

$$\text{Average M.W. of FFAs} = \sum P_i * M.W._i \qquad (2.3)$$

- $P_i$— The average percentage of each fatty acid listed in Table 2.9
- $M.W._i$– Molecular weight of the corresponding fatty acid, g/gmole

The average molecular weight of the FFAs in the MSD-TG samples was calculated to be 273.32 g/gmole, which was used in the following experiments to calculate the mass of the FFAs.

### 2.2.3 Ultimate Analysis

**Table 2.10** Ultimate analysis for the MSD-TG (Tested by OKI Analytical, Cincinnati)

| Element | Dry Basis (%) |
|---|---|
| Carbon | 74.36 |
| Hydrogen | 12.47 |
| Nitrogen | 0.20 |
| Ash | 3.92 |
| Sulfur | 0.14 |
| Oxygen | 8.91 |

As it is shown in the table, on a dry basis, the MSD-TG contains a large amount of carbon and a relatively large amount of hydrogen and oxygen. The percentage of nitrogen and sulfur in the MSD-TG is low, less than 1%.

# Chapter 3

# Extraction of the Oil Fraction from Trap Grease

## 3.1 Objective

The purpose of this chapter is to develop a method that is suitable for extracting the oil fraction from the MSD-TG. This is the first and most critical step before biodiesel can be made. As a waste material, trap grease is a low-quality feedstock with varied physical properties, which results in quite different pretreatment methods.

## 3.2 Literature Review

### 3.2.1 Current Methods for Converting Trap Grease into Biodiesel

Based on the literature review, only a few papers have been published on how to convert trap grease into biodiesel. The methods, especially the pretreatment step, reported in the papers are quite different from each other due to the different properties of the trap grease samples.

Lu *et al* (2010) investigated into making biodiesel from trap grease by using a stirring-tank reactor and a plug-flow reactor. The trap grease samples used in their study were from restaurants in Guangzhou, China with a FFA content of about 56.6%. Esterification reaction was employed to lower the FFA content and the reaction took place in the stirring-tank reactor with an ion-exchange resin as the catalyst at 75℃. The water formed was removed every three hours. The paper reports that after 13 hours, the FFA level decreased from

114mg KOH/g to about 2mg KOH/g. After esterification reaction, KOH and methanol were added to the feedstock oil into the plug-flow reactor and the reaction temperature was maintained at 65℃.

Ngo *et al* (2011) reported a one-step method of producing biodiesel from trap grease with five kinds of acid catalysts based on diarylammonium salts. The catalysts turned out to be very effective. It took about one hour to convert trap grease with extremely high FFA concentrations (>90%) into biodiesel at 125℃ with an overall conversion of FFAs and acylglycerols into biodiesel being more than 95%. But the disadvantage of this design is that the experiment temperature (125℃) is higher than that used in the traditional biodiesel production technology, which means not only more energy input is required but also extra effort is needed to prevent the evaporation of methanol as 125℃ exceeds the boiling point of methanol, so the overall production costs may be higher. Park *et al* (2010) employed a two-step process to convert trap grease into biodiesel; esterification followed by alkali transesterification process. They pointed out that the two-step process (esterification & transesterification) is better than the acid only process.

The trap grease samples used in the studies of Lu *et al* (2010), Ngo *et al* (2011) and Park *et al* (2010) were in liquid form and the percentage of lipids in the trap grease samples was very high. The oil fraction did not need to be extracted from the trap grease samples before all the chemical reactions. While the trap grease samples used in the study of Chakrabarti *et al* (2008) and Yuttachana (2006) were contaminated by solids, so an extra pretreatment step was applied to the trap grease samples to extract the oil fraction.

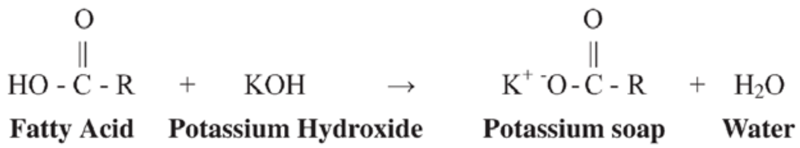
Chakrabarti *et al* (2008) pre-treated trap grease samples obtained from interceptor grease haulers through heating & filtration method. The trap grease samples were heated to about 40℃ and after melting, the mixture was filtered to eliminate solids by using a double-layer screen and then the liquid was allowed to settle overnight. After settling, two layers were formed. The top semi-solid oil layer was separated from the bottom aqueous layer. The semi-solid oil layer was processed into the feedstock oil through several more steps to make sure solids and water no longer exist in the grease. After the pretreatment, acid esterification was employed to lower the FFA level which was more than 50% in their study and it was successful that the FFA content was decreased to about 1% after esterification reaction.

Yuttachana (2006) extracted the feedstock part from trap grease by using a common organic solvent, hexane. Two trap grease samples were collected from a cafeteria in Mahidol University (TG-R) and from a coconut milk industry (TG-CO) respectively. Solids were first removed from the trap grease samples. The rest part was mixed sufficiently to achieve a homogeneous state and was dried. Soxhlet extraction method was used to perform extraction. Two parameters, extraction ratio of trap grease to hexane and extraction duration, were determined. The optimum extraction conditions for the two types of trap grease samples were the same. The optimum extraction ratio of trap grease to hexane was 1:4 and the optimum extraction time was six hours.

McNeff *et al* (2011) obtained a patent for inventing the operation systems and methods of utilizing fatty acid alkyl ester composition (biodiesel) to extract the lipid part (glycerides and FFAs) from low-value/low-cost materials. In their patent, the low-value feedstocks include soap stock, brown grease (also referred to as trap grease in their patent), yellow grease, animal tallow and so on. Advantages of using biodiesel as the extraction agent for lipid extraction from trap grease were summarized by McNeff *et al* (2011). These advantages are also the ones of WCO. First, using biodiesel as the solvent removes the solvent recovery step in the pretreatment process. Second, biodiesel will not end up being an undesirable byproduct or do harm to the production process since biodiesel itself is an end product. They also mentioned an advantage of using extraction as a separation/purification process. Most of the times, the low-quality feedstocks are in solid form at room temperature, using extraction can not only convert the solid feedstocks into liquid but also lower the overall energy costs because no heating or less heating is required to obtain the lipid part from the low-quality materials. Parjus *et al* (2011) also obtained a patent for inventing a method to recover FOGs from grease trap waste by using solvent extraction. Glycerides were reported in the patent as a solvent that can be used in the extraction process.

### 3.2.2 Acid Esterification and Transesterification

Whether or not the feedstock oil can be directly converted into biodiesel via transesterification process depends on the FFA level in the feedstock oil. As it is indicated by Van Gerpen (2005), as long as the FFA level in the feedstock oil is less than 5%, the feedstock oil can be processed directly via transesterification, but extra alkali catalyst, in addition to the amount of the base added as the catalyst, is required to neutralize the FFAs (shown in Fig. 3.1). The soap formed will be removed through water-wash step.

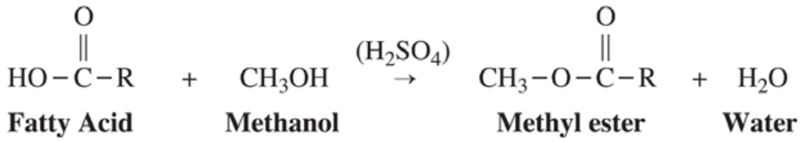


$$HO-\overset{\overset{O}{\|}}{C}-R \quad + \quad KOH \quad \rightarrow \quad K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R \quad + \quad H_2O$$

**Fig.3.1** Formation of soap (*Source: Van Gerpen, 2005*)

If the FFA level is greater than 5%, extra process is necessary before transesterification to lower the FFA level (Van Gerpen, 2005). There are at least four methods (enzymatic methods, glycerolysis, acid catalysis and acid catalysis followed by alkali catalysis) that can be used to lower the high FFA level in the feedstock oils to an acceptable level (Van Gerpen *et al*, 2004). All the four methods have limitations. The enzymatic method needs expensive enzymes and the process can be slow. The glycerolysis process requires a high reaction temperature (around 200℃) but the reaction rate is still slow. The one-step acid catalysis works well to convert FFAs into biodiesel but its efficiency to catalyze the transesterification process is rather undesirable. The problem for the two-step method is that a large amount of energy will be consumed to recover the excess methanol in the distillation process. Otherwise, a large amount of methanol will be wasted. After comparing the four methods, the two-step method acid esterification followed by transesterification, is preferable as it is quicker, more effective, and more economically feasible.

Acid esterification is a process that methanol along with an acid catalyst, typically sulfuric acid, is added into the feedstock oil to convert FFAs into biodiesel (Fig.3.2). As the reaction between FFAs and methanol is reversible, extensively extra amount of methanol is required to enable the reaction to move forward.



$$\underset{\textbf{Fatty Acid}}{HO-\overset{\overset{O}{\|}}{C}-R} + \underset{\textbf{Methanol}}{CH_3OH} \xrightarrow{(H_2SO_4)} \underset{\textbf{Methyl ester}}{CH_3-O-\overset{\overset{O}{\|}}{C}-R} + \underset{\textbf{Water}}{H_2O}$$

**Fig.3.2** Acid esterification (*Source: Van Gerpen, 2005*)

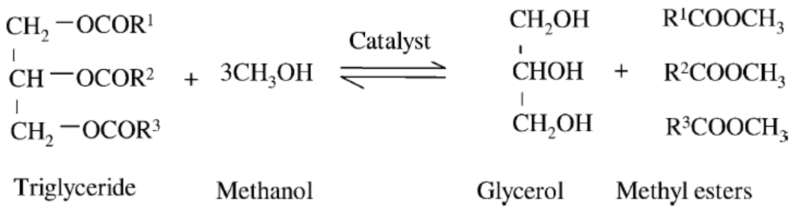


**Fig.3.3** Transesterification reaction (*Source: Meher et al, 2006*)

Transesterification (Fig.3.3) is a reaction between glycerides and methanol to produce biodiesel with glycerol as the by-product. Usually, a base, such as sodium hydroxide or potassium hydroxide, is used as the catalyst.

In summary, not all the methods reported in the published papers can be applied to the MSD-TG samples obtained for this study. The MSD-TG is highly contaminated by solid impurities, so the lipids need to be separated from the solids before all the chemical reactions.

## 3.3 Methodology

There are two methods used in the literatures to separate lipids from grease trap waste, one being the heating & filtration method and the other being the solvent extraction method. The heating & filtration method developed by Chakrabarti *et al* (2008), actually, is not suitable for the MSD-TG either. Oil-like liquid was obtained after heating the MSD-TG samples, but the amount of the oil-like liquid was not large enough to form a separate liquid layer in the beaker, in other words, the oil–like liquid was either at the very bottom of the beaker or on the surface of the solids, so it was very hard to decant it from the beaker. Based on the properties of the MSD-TG samples, solvent extraction is the most applicable approach to this study.

Although extraction with organic solvent is routinely performed in laboratories, this is not a viable option for the actual community scale operations. Biodiesel producers strongly discourage this for two reasons. First is the much higher cost of the solvents and waste disposal and the second is the more stringent requirements on the facilities to handle these solvents, which also adds to operating cost. Therefore, the goal is to find a “solvent” that can extract the oil fraction from the trap grease, while not need the extra requirements of organic solvents. Our unique contribution here is the selection of waste cooking oil for trap grease extraction. If feasible, this will allow the existing biodiesel producers to include trap grease as one of the feedstocks. They can simple mix the trap grease with WCO, and process the mixture via a two-step process. This will open the door for the trap grease to biodiesel process for communities that are plagued by the FOG issues.

The advantages of using WCO as the extraction agent for lipid extraction from trap grease include the following. First, using WCO as the solvent removes the solvent recovery step in the pretreatment process. Second, WCO will not end up being an undesirable byproduct or do harm to the production process. In addition, the WCO can potentially help dilute the FFA concentrations in the trap grease into acceptable levels to avoid the acid process.

### 3.3.1 Titration Method and Calculation

The lipid compositions in trap grease can include glycerides (tri-, di- and mono-) and FFAs. If extraction efficiency is studied, both the amounts of glycerides and FFAs extracted should be analyzed. But as the percentage of glycerides in the MSD-TG is very low (about 0.21%), only the variance of the amount of the FFAs in the WCO during the extraction process was studied.

Titration was used to determine the amount of the FFAs in the WCO. The titration method used in this study is based on the AOCS method Cd 3d-63. But for the AOCS method, the amount of the solvent used is 125mL, which is a very large amount of solvent. In order to reduce the amount of the waste solvent generated in this study, the amount of the solvent used for this study was reduced to 50mL based on the recommendation from an expert (Knothe, 2011).

The extraction samples were titrated with 0.1N of potassium hydroxide (KOH) solution with 50mL of the mixture of isopropyl alcohol and toluene (1:1, volumetric ratio) as the solvent and 0.8mL of 1% phenolphthalein as the indicator. WCO always contains certain amount of FFAs; thus, it was titrated before being mixed with the MSD-TG to obtain the initial amount of the FFAs in the WCO, that is, the blank value. The mass of the FFAs and the FFA content in the MSD-TG were calculated by using Equation 3.1 and 3.2 respectively.

$$\text{Mass of FFAs} = \frac{C_{KOH} * (V_{KOH} - V_b)}{V_S} * V_O * M.W._{FFA} \qquad (3.1)$$

- $C_{KOH}$— Concentration of KOH used for titration, 0.1 mole/L
- $V_{KOH}$ — Amount of KOH used for the titration of 2mL of extraction sample, L

- $V_b$ —Blank value/Amount of KOH used for the titration of 2mL of WCO before extraction, L
- $V_S$ — Amount of the sample, 2mL
- $V_O$ — Amount of the WCO used as the solvent, mL
- $M.W._{FFA}$ — Average molecular weight of the FFAs, 273.32 g/gmole

$$\text{FFA\%} = \frac{\text{Mass of FFAs}}{W_{TG}} \times 100\% \qquad (3.2)$$

- $W_{TG}$ — Total weight of the MSD-TG used, g

### 3.3.2 Test of Hydrolysis

The high (>50%) water content in the MSD-TG can become a concern for the extraction process due to the fact that glycerides, the main component of WCO, can react with water to form FFAs (Fig.1.7). According to Tyagi *et al* (1996), after 70 hours of frying at the temperature of 190℃, the FFA level in fresh soybean oil increased from 0.04% to 1.51%. If during the extraction process, FFAs would be produced in this way, then the amount of FFAs obtained from the titration would be the sum of the FFAs extracted from the MSD-TG plus the FFAs produced via the hydrolysis process, which means the water must be eliminated before the extraction process.

Water and WCO were added into a beaker at a volumetric ratio of 1:1 and the mixture were heated up in water bath. The temperature was maintained at 90℃. Two trials were performed. Stirring was applied to one trial and the other one was performed without stirring. The samples were taken and titrated by KOH solution every 30 minutes.

### 3.3.3 WCO Dosage Estimates

The purpose of the tentative experiments was to find a representative ratio of WCO to the MSD-TG for the study of effect of temperature on extraction duration. These trial experiments were performed at different ratios of WCO (mL) to the MSD-TG sample (g), from1.5:1 to 4.5:1 with an increment of 0.5:1. This ratio system was used with the considerations of the actual plant level operations: the WCO is measured by volume and the trap grease (solids) by the weight. A ratio of 2:1 represents 10g of the MSD-TG sample and 20mL of WCO. As the water in the MSD-TG sample was not eliminated beforehand, the weight of the MSD-TG in the ratio is the total weight. If the unit of the WCO was converted into gram, the ratio of 2:1 (mL/g) would equal to 1.8:1 (g/g).

The WCO was preheated to 90℃. The mixture of the WCO and the MSD-TG was heated up in water bath to maintain the extraction temperature at 85℃. 2mL of sample was taken every 30 minutes until the FFA concentration in the WCO leveled out. The mixture was stirred by hand for about 15 seconds every one hour.

### 3.3.4 Effect of Temperature on Extraction Duration

The role of temperature plays in the extraction process was studied. A total of five temperatures, 85℃, 60℃, 55℃, 50℃ and room temperature were studied.

Preheated (if necessary) WCO was mixed with the MSD-TG samples at a ratio of 3.5:1 (mL/g). For example, for 10g of the MSD-TG sample, 35mL of WCO is added. The mixture was heated in water bath to maintain at the scheduled temperature. Samples were taken every 30 minutes until the FFA concentration in the WCO leveled out. The mixture was stirred by hand for about 15 seconds every 1 hour. Samples were titrated with KOH solution and the results were calculated by using the methods described in section 3.3.1.

### 3.3.5 Effect of Temperature on Extraction Ratio

The optimum extraction ratio may vary at different temperatures. Three temperatures, 85℃, 60℃ and 50℃, were studied. The unit for the extraction ratios is mL/g. mL/g means, for example, at the extraction ratio of 3:1, for 10g of the MSD-TG, 30mL of WCO is added.

Preheated WCO was mixed with the MSD-TG. The mixture of the WCO and the MSD-TG was heated up in water bath and was stirred by hand for about 15 seconds every one hour during the extraction process. Based on the results obtained from the study of the effect of temperature on extraction duration, at 85℃ and 60℃, for each ratio, samples were taken after two hours of extraction. At 50℃, for each ratio, samples were taken after three hours of extraction. The samples were titrated by using KOH solution and the results were calculated by the methods described in section 3.3.1.

### 3.3.6 Filtration and Acid Esterification

After the extraction process, the solids were removed by vacuum with coffee filters. After filtration, the FFA level in the WCO was high, usually varying from 5% to 8%. Acid esterification was employed to lower the FFA level before transesterification.

The exact amount of FFAs in the WCO was determined by titration with KOH solution. The amount of methanol and that of the catalyst, sulfuric acid, were determined based on the amount of FFAs in the WCO, with a molar ratio of methanol to FFAs being 40:1 and a mass ratio of sulfuric acid to FFAs being 12.5:100 (Tu *et al*, 2011). The feedstock oil was preheated before being mixed with the methanol and the sulfuric acid. The temperature was maintained at 60℃ during the reaction. The top of the container was sealed with aluminum foil and Parafilm during the reaction to prevent the loss of methanol due to evaporation. Stirring was applied to this reaction to enable sufficient contact between the methanol and the WCO. The reaction lasted for about one hour.

After the reaction, the mixture was allowed to settle for about five hours in order to separate the methanol from the WCO. The methanol layer was removed and only the WCO layer went through transesterification process.

This is because after the separation, the water formed in the reaction exists in the methanol layer (Van Gerpen, 2005; Park *et al*, 2010) and is harmful to the transesterification process. For this study, the water in the methanol layer may also come from the MSD-TG as the water in the MSD-TG was not eliminated before the extraction process.

### 3.3.7 Transesterification Process

Though the FFA concentration in the feedstock oil after the acid esterification had already been lowered to an acceptable level, titration was still performed to make sure the feedstock oil was still suitable for the transesterification process since acid esterification is a reversible process.

For the transesterification process, sodium hydroxide (NaOH) was employed as the catalyst and methanol as the alcohol. For every 100mL of feedstock oil, 0.35g of NaOH was added as the catalyst. Additional NaOH was also added to neutralize the FFAs determined by the titration. Methanol was added at a volumetric ratio of 1:5 (methanol to WCO). The reaction temperature was maintained at 60℃ and stirring was used. The feedstock oil was preheated before being mixed with the methanol and the sodium hydroxide. The reaction lasted for about 15 minutes and the mixture was allowed to settle overnight to separate glycerol completely from biodiesel. After that, separatory funnel was used to remove glycerol and to wash biodiesel until the PH of the drain-out water became 7. The product, biodiesel, was ready to use as a fuel.

## 3.4 Results and Discussion

### 3.4.1 Test of Hydrolysis

As it can be seen from Fig.3.4, the amount of KOH solution used for titration varies little with time and the difference is only 0.05mL. The slight fluctuation might be caused by sampling and operational errors. This result shows that under the experimental condition of the extraction process for this study, glycerides do not react with water to form FFAs and the amount of the FFAs obtained from the titrations is the amount of the FFAs extracted from the MSD-TG samples.

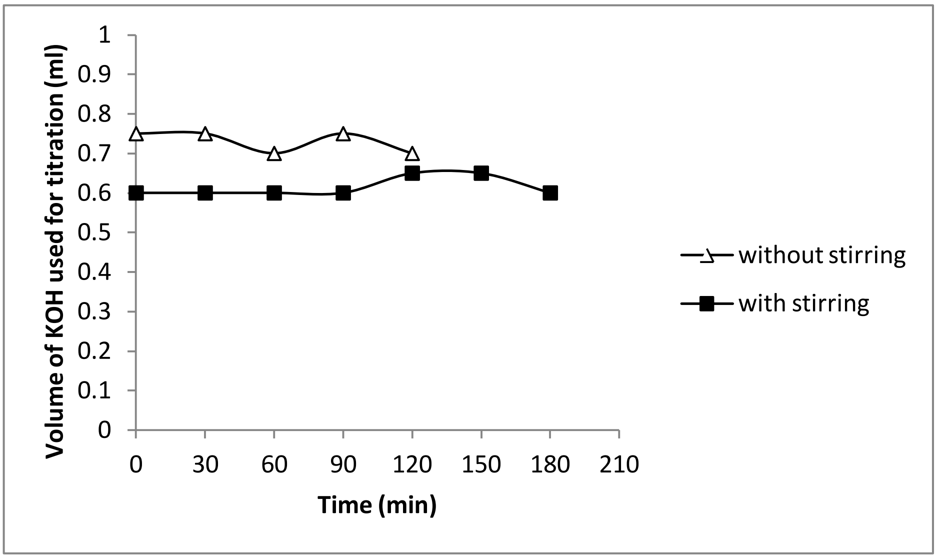
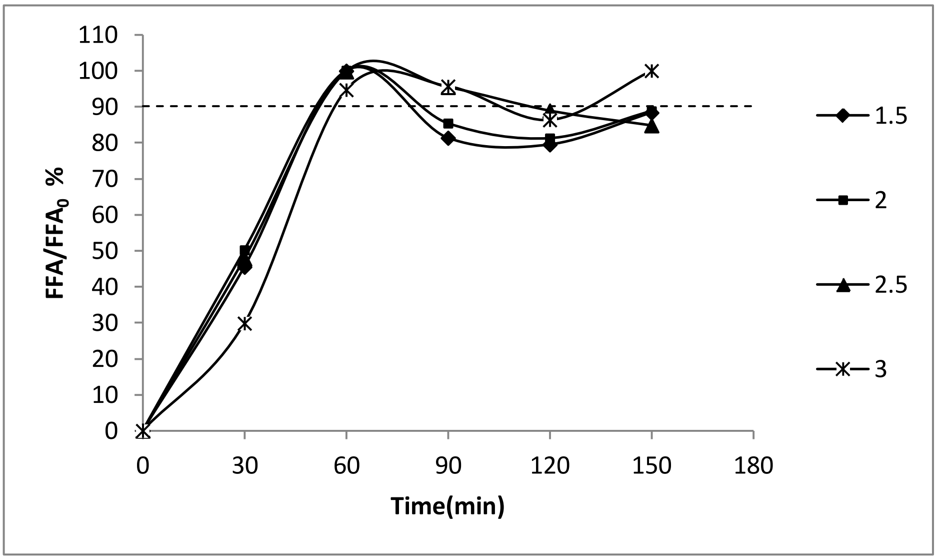
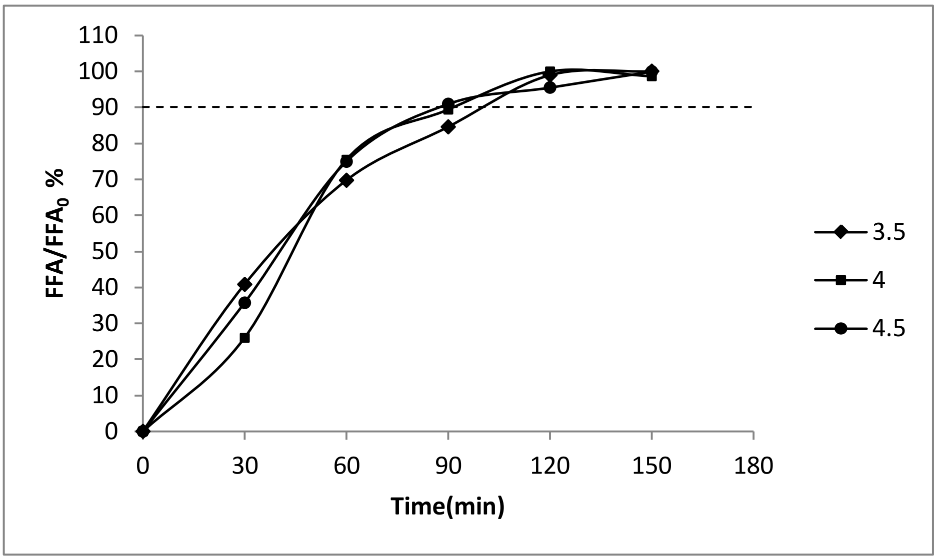


**Fig.3.4** Test of hydrolysis

### 3.4.2 WCO Dosage Estimates



(a)



(b)

**Fig.3.5** Effect of extraction time ((a) from 1.5:1 to 3:1 & (b) from 3.5:1 to 4.5:1) (dashed horizontal line: cutoff line for $FFA/FFA_0 \geq 90\%$)

Fig.3.5 shows the extraction durations for different extraction ratios.

According to the results, the extraction time was divided into two groups. For the extraction ratios, 1.5:1 to 3:1, the amount of the FFAs extracted from the MSD-TG reaches the maximum after one hour (Fig.3.5(a)) and decreases afterwards. This can be partially explained by sampling and operational errors because for the amount of the WCO added to extract lipids from the MSD-TG was so small that most of the WCO was absorbed by the MSD-TG, thus it was very hard to take sample each time.

For the larger ratios, 3.5:1, 4:1 and 4.5:1, the curves tend to level off after two hours of extraction. Compared with the larger ratios, it takes less time for the curves of the lower ratios to level off, which may indicate that the WCO is saturated by the FFAs after one hour of extraction for the lower ratios.

Based on the results and analysis, the ratio of WCO to MSD-TG was chosen to be 3.5:1, which translates to a mass ratio of 3.15:1, for the following studies on the effect of temperature on extraction time. Higher ratios of WCO to trap grease did not shown much better performance than 3.5:1 and also can cost more.

### 3.4.3 Effect of Temperature on Extraction Duration

Room temperature was studied for the reason that if the extraction would work well without heating, a large amount of electricity could be saved. The extraction process first took place at room temperature and lasted for about 26 hours; then the mixture of the WCO and the MSD-TG was heated up to 85℃

in water bath. Fig.3.6 shows the effect of room temperature on the extraction duration. As it is indicated in Fig.3.6, the extraction efficiency at room temperature is really undesirable. After 26 hours of extraction at room temperature, only one third of the extractible FFAs was extracted. Then the mixture of the WCO and the MSD-TG was heated up to 85℃. The concentration of the FFAs in the WCO increased dramatically. Without heating, the extraction process may take several days to complete.

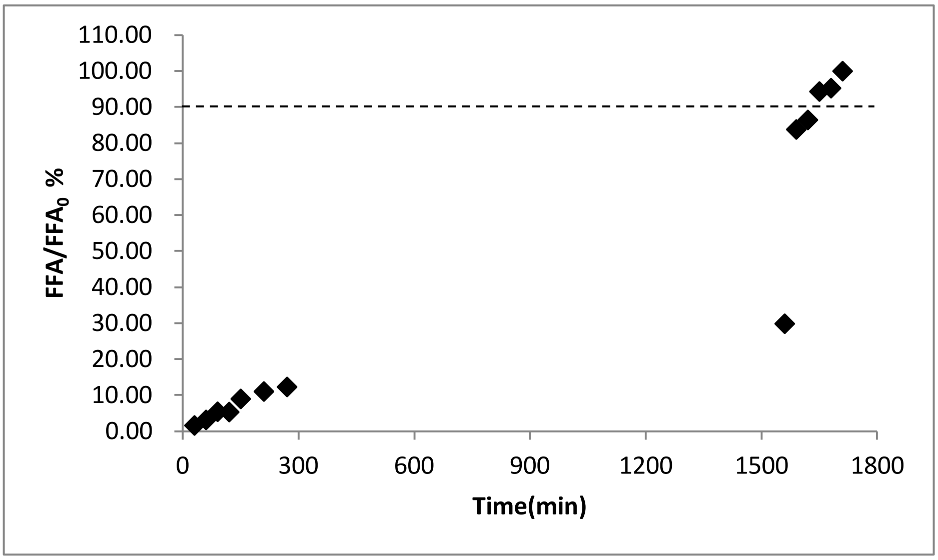


**Fig.3.6** Extraction at room temperature and then at 85℃ (dashed horizontal line: cutoff line for FFA/FFA$_0$≥90%)

Fig.3.7 reflects the effects of temperatures on extraction time. The extraction time (reaching the 90% level) decreases as temperature increases from 50 ℃ to 55℃ and then to 60℃. However, there are no significant differences in the extraction efficiency between 60℃ and 85℃. The two curves tend to level off after one hour and a half and at each sampling point, the percentages of FFAs extracted are close to each other. While for 55℃ and 50℃, the extraction efficiency decreases compared with that of 60℃ and 85℃. The extraction duration for 55℃ is two hours and the curve of 50℃ does not level off until after three hours of extraction. But as a whole, the extraction efficiency increases significantly when heating is applied to the extraction process compared with that when there is no heating.

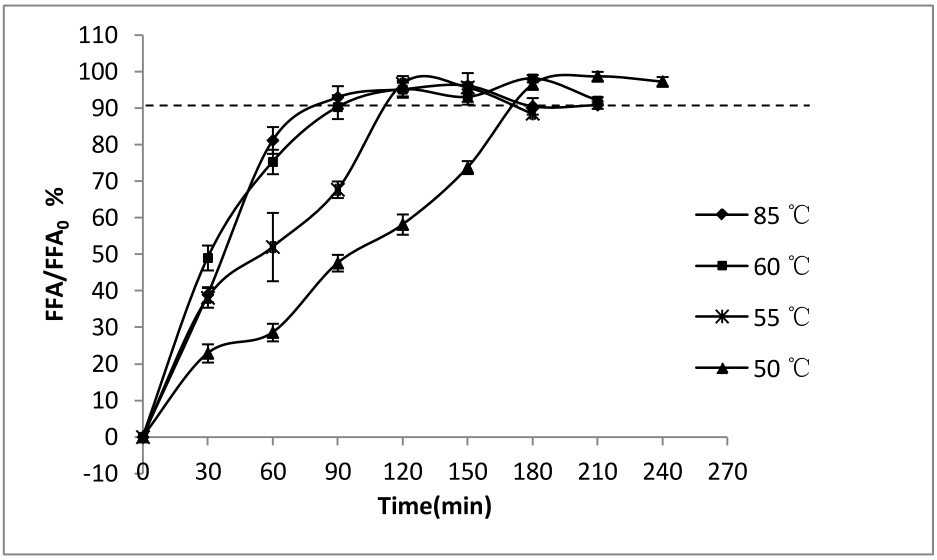


**Fig.3.7** Effects of temperatures (85℃, 60℃, 55℃ and 50℃) on extraction time (dashed horizontal line: cutoff line for $FFA/FFA_0 \geq 90\%$; error bar stands for standard error)

### 3.4.4 Effect of Temperature on Extraction Ratio

As it is seen from Fig.3.8, at 85℃ the extractible FFAs in the MSD-TG samples are almost all extracted at the ratio of 3.5:1. At 60℃, the optimum extraction ratio is 4:1 and for 50℃, the optimum extraction ratio is larger than 5:1. The higher the temperature, the less amount of the WCO is required. For

50℃, though the curve dose not completely level off and appears to have potential to increase after the ratio of 5:1, there is no need to continue the experiment since the difference in extraction efficiency among the three temperatures has been distinguished. For 50℃, not only the extraction time is longer but also the amount of the WCO required is larger and therefore might not be desirable.

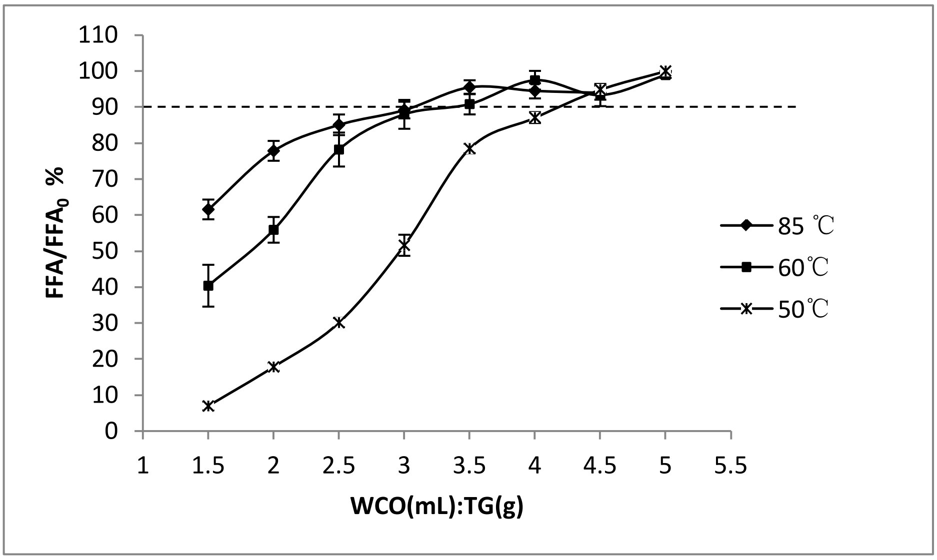


**Fig.3.8** Effects of temperatures (85℃, 60℃, 50℃) on extraction ratio (dashed horizontal line: $FFA/FFA_0 \geq 90\%$; error bar stands for standard error)

## 3.5 Conclusion

For the trap grease oil fraction extraction process, 60℃ is the optimum temperature with respect to the extraction time and WCO dosage. 85℃ is not considered as the optimum temperature because there is almost no difference in extraction efficiency between 60℃ and 85℃ and 60℃ means less heat input.

# Chapter 4

# Quantity of Trap Grease in Cincinnati

## 4.1 Objective

To evaluate the profitability of building a biodiesel production facility to convert trap grease into biodiesel, the first important step is to know the amount of trap grease generated annually, that is an inventory estimate. For the inventory study, literature review was first conducted, followed by data collection from the MSDGC and individual grease haulers.

## 4.2 Existing Studies on Grease Inventory

As trap grease has traditionally been a burden and waste instead of a resource, there has been limited information with regard to its inventory. As we review the three studies found, we also evaluated whether the study approaches reported were suitable for our purposes.

Wiltsee (1998) conducted a survey on the urban waste grease resources in thirty metropolitan areas in America. Most of the reports nowadays use the data from this study as it offers national averages of yellow and brown grease. The estimate of the amount of trap grease generated was 13.37 pounds/person/year and this data only indicates the amount of the grease part in trap grease since the author has already eliminated the amounts of water and other materials possibly existing in trap grease via assumptions. This data is the most widely cited in other literatures though it might be a little bit dated since it was derived in 1998. Survey forms were also created and the information was mainly collected via phone calls. The respondents of the survey include sewage treatment plants, rendering companies, grease collection companies and restaurants. Though a survey had been performed, the author still needed to estimate the amount of trap grease generated as grease collectors did not keep a good record or rendering companies were reluctant to give their data to others.

Hartwig and Moore (2006) investigated the amount of waste restaurant grease collected in South Carolina. The data they used to calculate the estimate was collected from six commercial grease collectors via a survey. The information collected included the quantity of waste grease collected every week, the number of restaurants they served, the disposal/utilization methods they used for the waste grease and so on. Based on the data and information collected from the survey, in South Carolina, 132,857 gallons of waste grease are collected every week. As waste restaurant grease also includes yellow grease and animal fats, in addition to trap grease, the result of this report is not suitable for the estimation of the annual amount of trap grease generated in Cincinnati.

Austic (2010) of Piedmont Biofuels LLC studied the feasibility of building a trap effluent dewatering facility in Raleigh, NC. As part of the study, the quantity of trap effluent generated in and around the Wake County area was estimated by analyzing data collected from three sources. The first estimate for the quantity of trap effluent was calculated based on the data from Wiltsee's report (1998), which is 13.37 lbs/person/year. But the author did not take all of it, since 4/5th of that data was derived from the amount of grease existing in the influent in wastewater treatment facilities, which the author thought was unrecoverable. The data was reformulated and an average amount of 3.79 gallons/person/year of trap effluent was estimated. It is indicated that this data could be out-dated and contain a significant amount of errors. The second estimate was calculated based on the information collected from the pretreatment coordinators of four cities. The collected information includes the quantity of trap locations, the amount of trap effluent produced per trap location per month. The population information was taken from Wikipedia. Based on those data, 16.15 million gallons of trap effluent annually in and around Wake County and 18.65 gallons/person/year of trap effluent were estimated. The third estimate was calculated on the basis of the amount of trap effluent that was disposed of to land application sites and composting operations. That information was obtained from the NC Department of National Resources and the total amount of trap grease disposed of was estimated to be 15,904,810 gallons/year in the Wake County area. It was estimated that only 2% of the total grease trap effluent was usable grease and the density of grease trap effluent was assumed to be 7.3 lbs/gal in Austic's report.

Chesebrough (2008) used two ways to estimate the amount of trap grease generated in South Carolina. One is to use the result derived by Wiltsee (1998) and the other is to use the data obtained from the City of Columbia Metro Septage Receiving Station. The data from receiving station was given weekly for the past six fiscal years, 2002-2008. The average weekly data was calculated and then this average was divided by the population the receiving station serves. An average amount of 0.0545 gallon/week/person of trap grease generated in greater Columbia area was calculated. The population of SC, obtained from the US Census Bureau, was multiplied by 0.0545, which resulted in 12,234,435 gallon/year of trap grease produced in South Carolina. The usable grease part in the total trap grease was estimated to be 5%-10% and the density of trap grease was assumed to be 8 lbs/gal.

### 4.3 Methodology and Results

We estimated the quantity of trap grease generated in Cincinnati in three different ways. One estimate was based on the natioal average from Wiltsee's report; the second was the data obtained from the MSDGC and the third one was based on the data obtained from our survey of the grease haulers serving the Cincinnati area (called the inventory method). The trap grease quantity is reported in different units for different audiences and also for comparison with other studies. The lb/person per year is an average value of the most interests to the general public. And also in Wiltsee's study, the estimate of the amount of usable grease was reported in lb/person/year, so the amount of usable grease in this study was also reported in lb/year.The gallon/year is often used by the MSDGC and grease haulers and refers to the combination of solids and liquids from the grease traps. The number most relevant to the development of a community scale trap grease treatment is the average amount of usable grease.

### 4.3.1 Estimate Based on the Data from Wiltsee (1998)

Many municipalities, such as San Francisco uses the national average estimated by Wiltsee (1998), due to the complexity of data collection, even though the data is dated. The weighted average amount of trap grease (only the amount of usable grease was included in Wiltsee's study) generated annually in 30 metropolitan areas is 13.37 lbs/person. The population of Cincinnati obtained from U.S. Census Bureau was 296,943 in 2010. The total amount of trap grease (the usable grease part) generated in Cincinnati is estimated to be 3,970,127.91 lb/year.

### 4.3.2 Estimate Based on the Data from the MSDGC

The second estimate was calculated based on the amount of grease trap waste MSDGC received annually, which is approximately 10,000,000 gallons/year. A total number of 186 permitted industrial users are registered with MSDGC. MSDGC serves "43 out of 49 Hamilton County, Ohio political subdivisions, as well as parts of the three adjacent counties of Butler, Clermont, and Warren" and "In all, MSD provides wastewater collection and treatment to about 800,000 people" (obtained from MSDGC website). Based on the data from MSDGC, the amount of trap grease produced in Cincinnati is about 12.5 gallon/person/year and the total amount is 3,711,787.5 gallons annually. In order to compare the estimates calculated based on the data from the three sources, the percentage of lipids (usable part) in grease trap waste MSDGC receives was determined to be 5% to 10% as it is the percentage that is indicated in Wiltsee's report. Another assumption also made for the density of usable grease in grease trap waste is that one gallon of usable grease weighs 8 pounds because one gallon of water is about 8.34 pounds (Chesebrough, 2008). Based on these assumptions, the amount of usable grease generated in Cincinnati is about 1,484,715 - 2,969,430 pound/year. Equation 4.1 was used to calculate the estimate.

$$\text{Amount of usable grease} = \frac{V_1}{P_{MSDGC}} \times P_{Cincinnati} \times E \times D$$

- $V_1$ : Amount of grease trap waste MSDGC receives, gallons/year
- $P_{MSDGC}$ : Population MSDGC serves
- $P_{Cincinnati}$ : Population in Cincinnati
- E: Estimated percentage of usable grease in grease trap waste, 5%-10%
- D: Estimated density of the usable grease, 8 lbs/gallon

### 4.3.3 Estimate Based on the Data from Inventory

An inventory was conducted to investigate the amount of trap grease generated annually in Cincinnati and a list of questions was developed for the inventory (Appendix I). The information was collected from grease haulers serving the Cincinnati area. Most of they either send grease trap waste to MSDGC or send the waste to landfill. A list of the grease haulers was obtained from MSDGC. According to the list, a total of 15 companies (Table 4.1) were identified and contacted. The contact information of grease haulers are listed in Appendix II.

**Table 4.1** Fifteen grease haulers contacted (no data was collected from haulers in italic)

| | | |
|---|---|---|
| A.K. Butler Services, LLC | Hack's Septic Service, Inc. | *Rumpke Transportation Company, LLC* |
| Ace Sanitation Service, LLC | Kleenco Maintenance & Construction | Saving's Liquid Waste, Inc. |
| *Allied Plumbing and Sewer Service, Inc.* | Mahoney Liquid Environmental Solutions | *Terminix International Compant Limited Partnership* |
| Griffin Industries, Inc. | Mike Hensley Plumbing, Inc. | Triple A Sanitation |
| Gullet Sanitation Service, Inc. | Roto - Rooter Services Co. | Tri - State Liquid Waste LLC |

The survey was mainly done via telephone and the questions asked did not adhere to the survey strictly. Eleven grease haulers responded to the survey and provided the quantity of grease trap waste they collect every year; one grease hauler responded to the survey but was unable to provide the amount of grease trap waste they collect annually, but based on the responses of other companies indicating the importance of this grease hauler as competitor, the amount of grease trap waste this hauler collects every year was estimated to be 500,000 gallon/year and no data was collected from the rest three grease haulers. As a promise had been made to the haulers that the information collected would not be shared with others, the detailed results are not shown here.

Fig.4.1 is the histogram of the quantity of trap grease collected by grease haulers every year. The quantity of grease trap waste collected by haulers distributes really unevenly with the minimum being 0.005 million gallons and the maximum being 3.3 million gallons. The amount of grease trap waste collected by more than half of the companies is less than 0.5 million gallons.

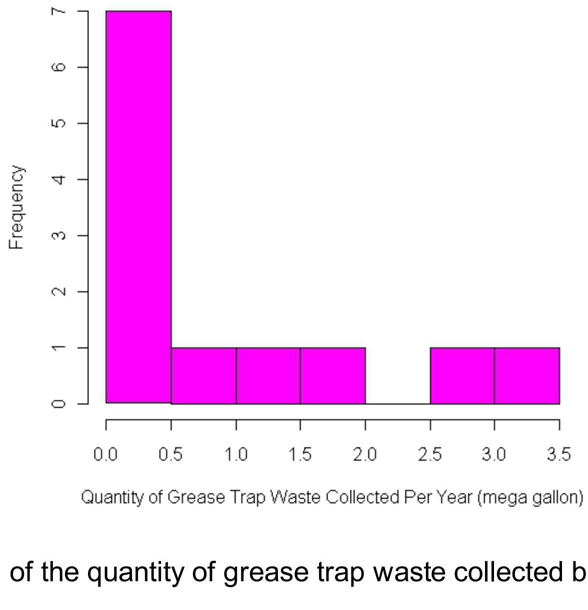


**Fig.4.1** Histogram of the quantity of grease trap waste collected by the grease haulers

The total amount of grease trap waste collected by the twelve grease haulers is 11.16 million gallons per year. This data was divided by the population MSDGC serves, 800,000, resulting in 13.95 gallons/person/year. The total amount of trap grease generated in Cincinnati every year is 4,142,354.85 gallons. The estimation for the percentage of usable grease in grease trap waste is 5% - 10% and the density of the usable grease is 8 lbs/gal. The amount of usable grease, calculated based on the estimations, is 1,656,941.94 – 3,313,883.88 lbs/year.

**Table 4.2** Summary on the estimates for Cincinnati based on the data from the three sources

| Data Source | Grease Trap Waste | | Usable Grease | |
|---|---|---|---|---|
| | Average Amount (gallon/person/year) | Total Amount (million gallon/year) | Average Amount (pound/person/year) | Total Amount (million pound/year) |
| Wiltsee | / | / | 13.37 | 3.97 |
| MSDGC | 12.5 | 3.71 | 5.00-10.00 | 1.48-2.97 |
| Inventory | 13.95 | 4.14 | 5.58-11.16 | 1.66-3.31 |

Table 4.2 listed the estimates for Cincinnati by the three methods. It can be seen from the table that the estimate of the quantity of trap grease calculated based on the data from Wiltsee's study is higher than the estimates based on the data from the other two sources. The quantity of grease trap waste estimated from the inventory is higher than that on the basis of data from MSDGC. This may be due to the fact that the grease trap waste collected by grease haulers was not all dumped to MSDGC. According to the survey, some of the grease haulers, instead of sending the waste grease to the MSDGC, process the waste grease into saleable products such as renewable fuels or raw materials for biodiesel production or send the grease to landfills. Grease

haulers are also making efforts to utilize grease trap waste and to make it more profitable.

**Table 4.3** Summary on the estimates obtained in literature review

| Reference | Average Amount | | Study Area |
|---|---|---|---|
| | Grease Trap Waste (gallon/person/year) | Usable Grease (pound/person/year) | |
| Wiltsee (1998) | / | 13.37 | 30 Metropolitan Areas |
| Austic (2010)* | 18.35-18.65 | 2.68-2.72 | Wake County area |
| Chesebrough (2008)* | 2.83 | 1.13-2.26 | South Carolina |
| This Study for Cincinnati | 12.5-13.95 | 5.00-11.16 | Cincinnati |

*The estimate calculated based on the data from the Wiltsee's report is not included in this table.

Table 4.3 shows the summary on estimates collected from literatures. The purpose of this table is to compare the difference of the results reported in different studies. The estimates in the studies of Austic (2010) and Chesebrough (2008) were reported in gallon but were converted into pound according to the density and the percentage of usable grease in grease trap waste reported in each study. Both Austic (2010) and Chesebrough (2008) calculated the amount of grease trap waste generated in their study area based on the data from Wiltsee's report, but that estimate is not included in this table; otherwise, the differences of the results obtained from different methods/studies could not be compared. The amount of usable trap grease generated in metropolitan areas is much higher than that generated in small cities.

### 4.4 Conclusion

The average trap grease generated in Cincinnati is lower than the National average of 13.37 lb/person/year, but it is very comparable with the 10.33 lbs/person/year reported for Lexington KY, which is also in the Midwest and similar in size. Therefore this number is reasonable. The data collected from grease haulers matched with number provided by MSDGC.

# Chapter 5

# Comparison of Extraction Performance between WCO and Other Organic Solvents

## 5.1 Objective

As shown in Chapter 3, we were able to extract the oil fraction from the MSD-TG samples. The goal of this chapter is to evaluate the efficiency of trap grease extraction with WCO. The extraction performance of WCO is compared with that of organic solvents with the laboratory practice. First a literature review was carried out to select the organic solvents. For this study, methanol, hexane and isopropanol/hexane (2:1, volumetric ratio) were chosen as the solvents. Though chloroform and toluene, as organic solvents, have shown great efficiencies for lipid extraction, these two solvents are much less desirable nowadays for research and industrial production due to their toxicity and non-environmental friendliness. As it is mentioned in Chapter 3, glycerides in the MSD-TG are not the ones that need to be paid attention to when the extraction efficiency of WCO is evaluated because WCO itself is mainly composed of glycerides. So the extraction performances of different solvents were compared via the amount of the FFAs extracted by each solvent and the amount of the FFAs extracted from the MSD-TG was determined by using the titration described in section 3.3.1.

## 5.2 Literature Review on Common Solvents Used in Extraction

Based on the literature review, few papers dealing with lipid extraction from trap grease by using organic solvents have been published. But quite a lot of studies have been conducted on extracting lipids from algae or wastewater sludge with organic solvents. Thus, the organic solvents used for this study were selected from those used for lipid extraction from algae or wastewater sludge.

Siddiquee *et al* (2011) tested methanol and hexane as the solvent to extract lipids from dried municipal primary and secondary sludge. The lipid yield for methanol extraction was higher than that for hexane extraction. Methanol showed a better extraction performance compared with hexane.

Pokoo-Aikins *et al* (2010) evaluated the lipid extraction performances of four organic solvents, methanol, toluene, hexane and ethanol from sewage sludge from the aspect of safety and cost. Ethanol and methanol were characterized as the safest and toluene the least costly. Methanol is recommended in the paper since it is one of the safest among the four evaluated solvents and the one that could be used in the following processes. Reduction of cost is possible if methanol used in the pretreatment step could be recovered and reused in the following biodiesel production process. As far as the yield of lipids is concerned, it seems that there is no big difference among these four solvents. The yield of the FFAs by using toluene, hexane, methanol and ethanol were 24.8%, 24.9%, 25.5% and 25.5% respectively. And a maximum yield of 3.4% for triglyceride stream was reported in the paper.

Taking into consideration of solvent polarity, boiling point, cost and environment, chloroform and toluene was chosen by Boocock *et al* (1992) as the organic solvents for their study. The two solvents showed equal effectiveness for lipid extraction from sewage sludge. But nowadays both chloroform and toluene are definitely not considered to be environmentally-friendly. Other organic solvents, such as methyl ethyl ketone and LPG condensate were also used as the solvents to extract lipids from the waste oily sludge (Zubaidy *et al*, 2010).

For lipid extraction from algae, the most widely used method is the one reported in the paper of Bligh and Dyer (1959) (Wiltshire *et al*, 2000). The organic solvent used was a mixture of chloroform and methanol. Mulbry *et al* (2009) evaluated the extraction performance of three organic solvents, chloroform/methanol (2:1, volumetric ratio), isopropanol/hexane (2:1, volumetric ratio), and hexane. The lipid yield of the extraction with chloroform/methanol is much higher than that of the extraction with the other two organic solvents. Excluding chloroform/methanol, the extraction performance of isopropanol/hexane is much better than that of hexane. The amount of the lipids extracted by isopropanol/hexane is twice as much as that extracted by hexane.

## 5.3 Methodology

**Table 5.1** Amount of the MSD-TG samples (g) and the corresponding amount of the solvent (mL)

| | Sample | Amount of TG (g) | | Amount of Solvent (mL) |
|---|---|---|---|---|
| | | Before Heating | After Heating | |
| Iso&Hexane | 1 | 15.82 | 6.55 | 66 |
| | 2 | 13.54 | 5.90 | 59 |
| | 3 | 11.27 | 5.83 | 58 |
| | 4 | 13.41 | 7.50 | 75 |
| | 5 | 13.55 | 6.52 | 65 |
| | 6 | 13.70 | 6.86 | 69 |
| Methanol | 1 | 13.69 | 6.31 | 63 |
| | 2 | 14.98 | 6.61 | 66 |
| | 3 | 18.13 | 9.02 | 90 |
| | 4 | 14.54 | 7.04 | 70 |
| | 5 | 17.10 | 9.49 | 95 |
| | 6 | 18.07 | 9.72 | 97 |
| WCO | 1 | 22.61 | 12.55 | 126 |
| | 2 | 19.13 | 10.97 | 110 |
| | 3 | 13.54 | 9.4 | 94 |
| | 4 | 16.68 | 6.08 | 61 |
| | 5 | 11.03 | 7.73 | 77 |
| | 6 | 5.93 | 3.16 | 32 |
| Hexane | 1 | 18.11 | 9.34 | 93 |
| | 2 | 16.25 | 9.19 | 92 |
| | 3 | 12.92 | 6.42 | 64 |
| | 4 | 13.48 | 6.93 | 69 |
| | 5 | 15.86 | 8.83 | 88 |
| | 6 | 22.81 | 13.80 | 138 |

As trap grease is highly heterogeneous, in order to compare the extraction performance of the four solvents, about 500 grams of the MSD-TG was measured into a big beaker and was stirred by hand with a glass rod to make it as homogeneous as possible. Then, a certain amount of the MSD-TG in the big beaker was weighed into different smaller, pre-weighed beakers. The

MSD-TG samples in the small beakers were heated up on hot plate to 120℃ for 24 hours to eliminate water. The samples were allowed to cool down. Then, the entirety (the beaker and the dried samples) was weighed. Based on the dry weight of the MSD-TG samples, the amount of the solvent needed was calculated and measured at a ratio of 10:1 (mL/g). For example, for 20g of the dry MSD-TG, 200mL of the solvent was added. The amount of the MSD-TG samples and the corresponding amount of the solvent used are summarized in Table 5.1.

The dry MSD-TG samples were heated up again to melt out the oil-like liquid and then the solvents were added into each beaker to be mixed with the dry MSD-TG. Aluminum foil was used to seal the top of the beaker to reduce the loss of solvent due to evaporation. The extraction process was conducted at room temperature without stirring for 24 hours. Then, 2mL of sample was taken from the supernatant in each beaker and the samples were titrated with KOH solution by the method described in the section 3.3.1.

The method for calculating the amount of the FFAs extracted by the organic solvents is a little bit different from that for calculating the amount of the FFAs extracted by the WCO. For the WCO extraction, Equation 3.1 is just suitable, but for the organic solvents, Equation 5.1 should be used.

$$\text{Mass of FFAs} = \frac{C_{KOH} * (V_{KOH} - V)}{V_S} * V_2 * M.W._{FFA} \qquad (5.1)$$

- $C_{KOH}$— Concentration of KOH used for the titration, 0.1 mole/L
- $V_{KOH}$ — Amount of KOH used for the titration of 2mL of extraction sample, L
- V — Amount of KOH used for the titration of 2mL of organic solvent (blank value), L
- $V_S$ — Amount of the sample, 2mL
- $V_2$ — Final volume of the organic solvent after extraction, mL
- $M.W._{FFA}$ — Average molecular weight of the FFAs, 273.32 g/gmole

Compared with Equation 3.1, two variables in Equation 5.1 were changed, the blank value and the total volume of the solvent after extraction. For the WCO, the blank value is the amount of KOH used for the titration of 2mL of the WCO sample before extraction because WCO itself contains a certain amount of FFAs. For the organic solvents, the pure solvent is free of FFAs but the solvent used for the titration (toluene/isopropyl alcohol, 1:1) consumes a very small amount of KOH during the titration. To prevent errors, 2mL of the pure organic solvent was dissolved into 50mL of toluene/isopropyl alcohol (1:1, V/V) and was titrated with KOH solution. The amount of the KOH consumed in the titration is regarded as the blank value. Though it turned out that the blank values for all the organic solvents were really small, the blank value was still subtracted from the amount of the KOH consumed by each extraction sample.

For the WCO, the amount of the KOH consumed by the titration solvent is included in $V_b$, so there is no need to specify it in the equation.

On the other hand, there must be solvent loss during the organic solvent extraction process as they are easy to evaporate. The final volume ($V_2$) of the organic solvent after extraction is not equal to the original volume ($V_1$). Vacuum filtration could be a way to obtain the final volume of the organic solvent, but vacuum also contributes to solvent loss during filtration, especially for hexane. When vacuum filtration was used to filter out the solids from the hexane, the volume of the liquid recovered was really undesirable and for some hexane samples, even no liquid was recovered. Thus, another method was used and the solvent loss for each solvent was measured in the following way. Empty clean beakers were prepared and heated up to 120℃ on a hot plate. Then the three organic solvents (methanol, hexane and isopropyl alcohol/hexane) were added into each beaker. For each solvent, three trials were performed and for each trial, the volume of solvent used was 30mL, 40mL and 50mL respectively. Aluminum foil was used to seal up the top of the beaker and the solvent stayed at room temperature for 24 hours. After that, the volume of the solvent left was measured by using a cylinder. After the percentage of the loss was determined, the final volume of the organic solvent after extraction was calculated by using Equation 5.2.

$$V_2 = V_1 \times (1 - L) \qquad (5.2)$$

- $V_1$ — Original amount of solvent added into the beaker at the ratio of 10:1, mL
- $V_2$ — Final amount of solvent after extraction process, mL
- L — Average percentage of loss after extraction process

## 5.4 Results and Discussion

The average percentage of loss (L) after the extraction process and after the vacuum filtration for each organic solvent were calculated and summarized in Table 5.2 and the amount of the FFAs extracted by each solvent is shown in Table 5.3.

**Table 5.2** Average percentage of solvent loss after the extraction and vacuum filtration for each organic solvent

| Organic Solvent | Average Percentage of Loss (v%) | |
|---|---|---|
| | After Extraction | After Vacuum Filtration |
| Hexane | 11.11 | 82.89 |
| Isopropyl alcohol & Hexane | 8.67 | 43.85 |
| Methanol | 7.17 | 27.74 |

**Table 5.3** Percentage of the FFAs extracted by each solvent in the dry MSD-TG

| Solvent | FFAs/Dry TG (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Average |
| WCO | 36.21 | 55.35 | 55.35 | 37.58 | 51.93 | 48.51 | 47.49 |
| Iso&Hexane | 38.96 | 26.84 | 44.19 | 51.15 | 48.54 | 76.54 | 47.70 |
| Methanol | 50.63 | 46.88 | 34.17 | 35.33 | 45.70 | 39.26 | 41.99 |
| Hexane | 53.45 | 37.66 | 53.45 | 47.38 | 50.41 | 75.92 | 53.04 |

Based on the dry MSD-TG weight, the amount of the FFAs extracted by using hexane was the highest, with the average percentage of the FFAs in the dry MSD-TG being 53.04%. For the WCO extraction, the average percentage of the FFAs extracted in the dry MSD-TG was 47.49%, which is higher than that extracted by methanol and is only slightly lower than that extracted by isopropyl alcohol & hexane. WCO shows decent extraction performance compared with these three common organic solvents.

# Chapter 6

# Preliminary Results on Other Aspects Related to Trap Grease

The trial experiments presented in this chapter are all related to trap grease, but all not performed in depth due to time limit. The findings and issues are described here, as it is worthwhile to conduct more researches.

## 6.1 A New Solvent for the FFA Titration Method

The traditional titration method to determine the acid value of a WCO sample uses toluene & isopropyl alcohol (1:1, v/v) as solvents. However, toluene is not environmentally friendly (Siddiquee *et al*, 2011), and is part of the BTX (benzene, toluene, xylenes), which is considered a volatile organic pollutant. It also has a strong chemical smell. If another less-toxic solvent could be used to replace toluene in titration, it will be a great improvement to the titration method and a great benefit to health and the environment. Therefore the goal is to test whether the alternative to toluene can archieve the same performance in titration.

In this study, hexane was studied as a potential solvent and some preliminary results were obtained. WCO samples with varied FFA contents for titration were prepared by adding a certain amount of stearic acid into a certain amount of WCO. The mixture was heated up and stirred to enable stearic acid to dissolve into the WCO completely. Before mixing, the WCO was titrated to obtain the initial amount of the FFAs in the oil. Though this number may be small and only has very little effect on the final FFA level, it is still necessary to determine this value beforehand. Equation 6.1 was used to calculate the final amount of the FFAs in the WCO sample and Equation 6.2 was used to calculate the final volume of the WCO sample. An Excel spreadsheet was developed to do the calculation.

$$\text{Final amount of FFAs} = \frac{C_{KOH} * (V_{KOH} - V_{bv})}{V_S} * V_O * M.W._{FFA} + Q_1 \qquad (6.1)$$

- $C_{KOH}$— Concentration of KOH used for titration, 0.1 mole/L
- $V_{KOH}$ — Amount of KOH used for the titration of 2mL of WCO sample, L
- $V_{bv}$ —Blank value of the solvent, L
- $V_S$ — Amount of the sample, 2mL
- $V_O$ — Amount of the WCO used, mL
- $M.W._{FFA}$ — Molecular weight of FFAs, 284 g/gmole
- $Q_1$ — Amount of the stearic acid added into the WCO, g

$$\text{Final volume of the WCO sample} = V_0 + \frac{Q_1}{\rho_1} \qquad (6.2)$$

- $V_0$ — Volume of the WCO used, mL
- $\rho_1$ — Density of stearic acid, 0.847g/mL

- $Q_1$ — Amount of the stearic acid added into the WCO, g

The studied volumetric ratio of isopropyl alcohol to hexane was 2:1. 25mL and 50mL of the solvent were investigated for the titration of the WCO sample, with 0.4mL and 0.8mL of 1% phenolphthalein as indicators, respectively. The titrant was 0.1N of potassium hydroxide solution. As the solvent for the titration can also consume a certain amount of KOH, the base value needs to be obtained. Equation 6.3 was used to calculate the amount of the FFAs obtained by the titration.

$$\text{Mass of FFAs} = \frac{C_{KOH} * (V_{KOH} - V_b)}{V_S} * V_F * M.W._{FFA} \qquad (6.3)$$

- $C_{KOH}$— Concentration of KOH used for the titration, 0.1 mole/L
- $V_{KOH}$ — Amount of KOH used for the titration of 2mL of WCO sample, L
- $V_b$ — Base value of the solvent, mL
- $V_S$ — Amount of the WCO sample, 2 mL
- $V_F$ — Final amount of the WCO sample, mL
- $M.W._{FFA}$ —Molecular weight of stearic acid, 284.47 g/gmole

Table 6.1 shows the two WCO samples prepared for the titrations and Table 6.2 shows the base value for 25mL and 50mL of the solvent. Table 6.3 shows the amount of the FFAs obtained by the titrations and the comparison between the titration results and the theoretical total amounts of the FFAs.

**Table 6.1** WCO samples prepared for the titrations

| WCO sample | Volume of WCO (mL) | Stearic Acid Added (g) | Initial amount of FFAs (g) | Final Volume of WCO Sample (mL) | Total Amount of FFAs in WCO Sample (g) |
|---|---|---|---|---|---|
| 1 | 30 | 1.06 | 0.1 | 31.25 | 1.16 |
| 2 | 30 | 3.04 | 0.1 | 33.58 | 3.14 |

**Table 6.2** Base value for the solvents

| Volume of Solvent (mL) | Base Value (μL) |
|---|---|
| 25 | 50 |
| 50 | 100 |

**Table 6.3** Amount of the FFAs obtained by the titrations and the comparison between the titration results and the theoretical total amount of the FFAs

| WCO Sample | Volume of Solvent (mL) | Trial | Amount of FFAs obtained by titration (g) | Differences from Theoretical Amount of FFAs (%) | Average of Difference (%) |
|---|---|---|---|---|---|
| 1 | 25 | 1 | 1.32 | 14.27 | 19.26 |
|  |  | 2 | 1.41 | 21.76 |  |
|  |  | 3 | 1.41 | 21.76 |  |
|  | 50 | 1 | 1.30 | 12.40 | 10.52 |
|  |  | 2 | 1.26 | 8.65 |  |
| 2 | 25 | 1 | 3.38 | 7.78 | 12.61 |
|  |  | 2 | 3.48 | 10.75 |  |
|  |  | 3 | 3.52 | 12.24 |  |
|  |  | 4 | 3.76 | 19.67 |  |
|  | 50 | 1 | 3.64 | 15.95 | 15.95 |
|  |  | 2 | 3.64 | 15.95 |  |

## 6.2 Glycerolysis

Glycerolysis is a reaction between glycerol and FFAs to form monoglyceride (majority), diglyceride and triglyceride (Fig.6.1). It is another potential way to lower the high concentration of FFAs in feedstock oils as well as to utilize the waste glycerol, the byproduct of the biodiesel production process. Some biodiesel manufacturers have also adopted the glycerolysis process to make biodiesel (Parker, 2009). But one drawback of glycerolysis is that it requires a very high temperature (200℃) during the reaction process to speed up the reaction.

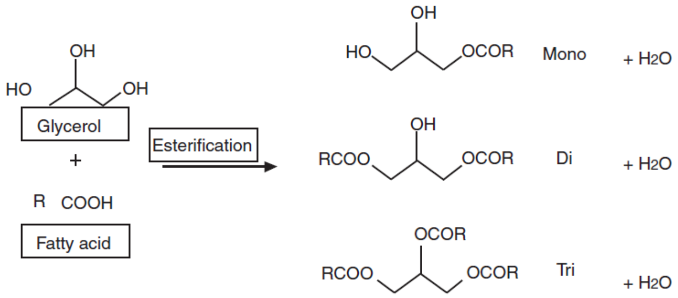


**Fig. 6.1** Reaction between glycerol and free fatty acid (*Source: Felizardo et al, 2011*)

Some experiments have been performed to study the reaction conditions required for glycerolysis. WCO samples with high FFA concentrations were prepared by mixing WCO with stearic acid. The details about how to prepare the WCO samples are described in the section 6.1. Equation 6.1 and Equation 6.2 were used to calculate the final amount of the FFAs in the WCO samples and the final volume of the WCO samples.

Titration was used to determine the variance of the FFA contents with time. 25mL of toluene/isopropyl alcohol was used as the solvent and 0.4mL of phenolphthalein as the indicator. With the increase of the concentration of

FFAs in the WCO samples, the errors of the results obtained from the titration also increases, so it is better to dilute the high-FFA WCO samples before the titration. WCO with low FFA content was used to dilute the high-FFA WCO samples. Table 6.4 shows the final concentrations of the FFAs in the WCO samples (1mL) after being diluted with WCO with an initial FFA content of about 1%.

At the beginning, a WCO sample with 70% of FFAs was prepared and pure glycerol was added at a molar ratio of 2:1 (glycerol to FFAs). The reaction temperature was set to be 150℃ and stirring was used. After 5 hours of reaction, no change was found in the FFA concentrations in the WCO samples, which means it failed. Another WCO sample was prepared also with a FFA content of 70%, and pure glycerol was added at a molar ratio of 2:1. But this time, the reaction temperature was increased to 220℃, and it successfully lowered FFAs to less than 1%. However, the transesterification process performed afterwards did not result in biodiesel.

Glycerolysis of a WCO sample of relatively high FFAs (about 5%) with crude glycerol (biodiesel byproduct) was also investigated at a molar ratio of 1.1:1 (glycerol to FFAs). The result was not good either. After five hours of reaction, The FFA content was only lowered from 6.49% to 4.63% and stopped decreasing after that.

Therefore, the exact reaction conditions, such as temperature and dosage, for glycerolysis should be further investigated.

**Table 6.4** Final concentrations of the FFAs in the WCO samples (1mL) after being diluted with the WCO with an initial FFA content of about 1%

| Initial FFA content in WCO sample with high FFA content (%) | Amount of WCO sample need to be diluted (mL) | Volume of WCO used for dilution (mL) | Initial FFA content in WCO (wt%) | FFA content after dilution (%) |
|---|---|---|---|---|
| 90 | 1 | 6 | 1 | 13.12 |
| | | 7 | | 11.07 |
| | | 8 | | 10.42 |
| | | 9 | | 9.47 |
| | | 10 | | 8.7 |
| | | 12 | | 7.51 |
| | | 16 | | 6.64 |
| | | 18 | | 5.45 |
| | | 20 | | 5.02 |
| 70 | 1 | 5 | 1 | 12.1 |
| | | 6 | | 10.5 |
| | | 7 | | 9.3 |
| | | 8 | | 8.38 |
| | | 9 | | 7.64 |
| | | 10 | | 7.03 |
| | | 12 | | 6.1 |
| | | 14 | | 5.42 |
| | | 18 | | 4.49 |
| 50 | 1 | 5 | 1 | 8.99 |
| | | 6 | | 7.82 |
| | | 7 | | 6.96 |
| | | 8 | | 6.3 |
| | | 9 | | 5.77 |
| | | 10 | | 5.33 |
| | | 12 | | 4.66 |

## 6.3 Solvent Recycle

Each FFA titration can generate 52mL or so waste solvent, so after many titrations needed for the study, the total amount of the waste solvent generated is about 20L. Disposal of the waste organic solvent is expensive ($7 per pound) and also is a waste of materials, as the solvents could be reused. In order to reduce the cost, recycling waste solvent was studied and some preliminary results were obtained.

After titration, the liquid is a mixture of organic solvent, water, WCO, indicator, and soap (product of the reaction between KOH and FFAs), with the organic solvent being the bulk undoubtedly. The amount of water in the final liquid mixture depends on the FFA content in the WCO sample. If the FFA level is high, a large amount of titrant is added and the water content in the final mixture will be relatively high but still low compared with the amount of the organic solvent used.

At atmospheric conditions, the boiling points of isopropyl alcohol and toluene are 82.5℃ and 110.6℃, respectively. At vacuum, the boiling point of the solvent is reduced significantly, which makes it easier to evaporate the organic solvents. For example, at 137mbar, the boiling point of isopropyl alcohol is 40℃. A vacuum evaporator, Rotovap RII, with rotation was used to speed up the recovery process of the organic solvent. When using the vacuum evaporator, the temperature was set at 40℃ and rotation was used. It took about half an hour to recover 30mL of solvent from 50mL of the waste solvent. The recovered solvent was clear, but both the original waste solvent and the leftover of the solvent after recovery were yellow.

One sample of the solvent was analyzed by GC-MS and a sharp peak for toluene was found (Fig.6.2, the huge broad peak is DCM). Isopropyl alcohol was not found as the GC-MS method was only set up for toluene. Further GC-MS analysis is still necessary to analyze the compositions of the recycled solvent.

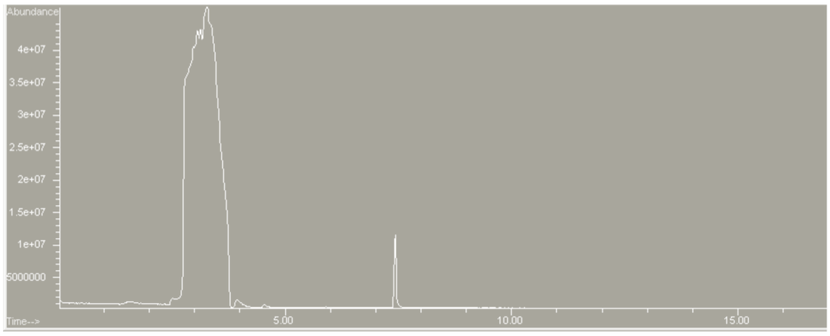


**Fig.6.2** GC-MS spectrum for the waste solvent

### 6.4 Wet Heating Method

The wet heating method has been reported to be used by some small shops in China illegally to process ditch oil (a Chinese equivalence of trap grease) into an oil-like product and the oil-like product is sold as edible oil (Baidubaike, 2012). Due to the highly invisible nature of this practice, details of the process have not been reported.

Only one paper (Wang *et al*, 2005) was found dealing with wet heating treatment for kitchen waste, an oil-containing solid or semi-solid waste produced in kitchens. As it was reported in that paper, water with antioxidants was added into the kitchen waste and the mixture was heated in a completely sealed container to 100℃, 120℃ and 135℃, respectively. The amount of the water they studied was 20 wt%, 38 wt% and 50 wt% of the raw materials. According to the results of that paper, after the wet heating process, three layers were formed in the container with the top being an oil layer, the middle being a water layer and the bottom being a solids layer. However, all the trials we performed on wet heating treatment failed. Solids did not go down to the bottom and they were still floating on the top. One difference between the experiment reported in the paper and the one done in our lab is that the container was not sealed when the procedure was performed. It is suspected that higher pressure may have facilitated the layer separation.

## 6.5 Some Data Obtained for Cost Estimation

The cost analysis for the whole trap grease-to-biodiesel process was not performed due to the complexity of the cost factor and the lack of data. However, some cost information was obtained during this research.

The MSDGC charges grease haulers $50 per 1000 gallons of grease trap waste. And the grease haulers charge the restaurants a service fee ranging from $0.05 to $0.5 per gallon for grease removal. The service fee serves better as the estimated cost of trap grease than MSDGC's charge if one wanted to obtain grease trap waste from restaurants because a grease hauler's service fee must include the cost of labor, the cost of gas consumed by the trucks and the cost of pumping trap grease out.

The cost of the trap grease-to-biodiesel process can be estimated by decision modeling software (Decision Maker for Windows-WinDM) and EXCEL spreadsheets (Crystal Ball).

# Chapter 7

# Conclusions and Future Directions

Trap grease inventory was conducted for MSDGC service area. The grease trap waste produced ranges from 3.71 to 4.14 million gallons per year. The per person trap grease production rate of 10 lb/year is slightly lower than the 13.37 lb/year, a national average based on a 1998 DOE study. According to the information collected from the inventory, most of the grease trap waste generated in Cincinnati (about 70%), after being pumped out by grease haulers, is sent to the MSDGC, mixed with grits from primary treatment and then sent to landfills.

According to the compositional analysis of the MSD-TG samples obtained for this study, the MSD-TG mainly consists of water (58.94%), FFAs (20.69%) and solids (18.17%). The usable part of the MSD-TG, which can be converted into biodiesel, is the FFAs (about 21%). Out of 100g of the MSD-TG, about 22g of biodiesel could be produced.

Based on the properties of the MSD-TG samples obtained for this study, solvent extraction was studied. WCO was used to extract the oil fraction out of the MSD-TG, and the effects of temperature on both extraction time and dosage were studied. For the extraction time, among the five temperatures studied, the extraction duration at 85℃ and 60℃ is the same and is the shortest one. At these two temperatures, it only takes one hour and a half for the two curves to level off. For the study of the effect of temperature on extraction ratio, the higher the extraction temperature, the smaller the amount of the WCO was required. At 85℃, the optimum extraction ratio is 3.5:1 and at 60℃, the optimum extraction ratio is 4:1. Overall, 60℃ is the optimum extraction temperature because it requires less heat input but yet shows almost the same extraction efficiency compared with 85℃. Given these results, it shows that the WCO extraction as the pretreatment process is viable for converting the MSD-TG into biodiesel. Further study indicated that WCO showed equivalent performance in the extraction of the oil fraction of the MSD-TG, compared with three other common organic solvents, hexane, methanol and isopropyl alcohol/hexane (2:1, v/v). Therefore, it is technically feasible to extract the oil fraction from trap grease with a low-cost and low-toxicity “solvent” that is as effective as the standard organic solvents.

As it is indicated in chapter 6, the future directions for this study are glycerolysis, solvent recycle, wet heat method, cost estimation as well as to find a new solvent for the FFA titration method.

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# Appendix I

## Survey Form

| | |
|---|---|
| Hello (introduction). I'm doing a study of trap grease resources for the University of Cincinnati. Do you have a few minutes to answer some quick questions? | |
| 0. Company name:<br>Address:<br>Contact:<br>Phone number: | |
| 1. How many trucks do you have running to collect? About how far must they travel? | |
| 2. What is the quantity of trap grease you collect or process per year (gallons)? | |
| 3. Is the quantity increasing or decreasing? Why? | |
| 4. How much do you charge for the trap grease you collect? | |
| 5. Do you process the trap grease into saleable products? How much does it cost to do so?<br>a. If yes, what products do you make from trap grease and sell? Amounts? Prices?<br>b. If no, where and how do you dispose of the material? Tipping fees? | |
| 6. Who are your biggest competitors? (names, numbers) | |
| 7. Who are your biggest customers? | |
| 8. Do you have any suggestions on how I should estimate the total amount of trap grease generated in the Cincinnati area? | |
| 9. Do you have any suggestions on people I should contact, or approaches I should take? | |

# Appendix II

## Contact Information of Grease Haulers

| Grease Hauler Name | Contact Email | Contact Number | Address |
|---|---|---|---|
| A.K. Butler Services, LLC | | 513.353.9110<br>513.738.3902 | 6316 State Route 128 Cleves, OH 45002 |
| Ace Sanitation Service, LLC | | 513.353.2260 | 4525 State Route 128 Cleves, Ohio 45002 |
| Allied Plumbing and Sewer Service, Inc. | | 513.607.6100 | 3460 Mustafa Dr. Cincinnati OH 45241 |
| Griffin Industries, Inc. | sales@griffinind.com | 859.781.2010 | 4221 Alexandria Pike Cold Spring, KY 41076 USA |
| Gullet Sanitation Service, Inc. | | 513.457.4198 | 118 S Union Street Bethel, OH 45106-1342 |
| Hack's Septic Service, Inc. | | 812.534.3266 | 13994 Works Road Bennington, IN 47011-1679 |
| Kleenco Maintenance & Construction | gtc@kleencousa.com | 765.724.3554 | 8239 St. Rd. 9 North Alexandria, IN 46001 |
| Mahoney Liquid Environmental Solutions | johnm@mahoneyenvironmental.com | 800-892-9392 | 1819 Moen Ave. Joliet, IL 60436 |
| Mike Hensley Plumbing, Inc. | | 513.574.8553 | 2644 Spring Grove Avenue Cincinnati, OH 45214 |
| Roto‐Rooter Services Co. | | 513.853.3926 | 2125 Montana Avenue Cincinnati, OH 45211-2741 |
| Rumpke Transportation Company, LLC | | 513.851.0122 | 10795 Hughes Road Cincinnati, OH 45251-4523 |
| Saving's Liquid Waste, Inc. | ryan@savingsliquidwaste.com | 513.353.1208 | 10415 Campbell Road Harrison, OH 45030-8903 |

(Continued)

| | | | |
|---|---|---|---|
| Terminix International Compant Limited Partnership | | 513.721.6682 | 4785 Emerald Way<br>Cincinnati, OH 45203 |
| Triple A Sanitation | | 937.746.6361 | |
| Tri‐State Liquid Waste LLC | | 513.561.3235 | 4801 State Route 128<br>Cleves, OH<br>45002-9752 |

# Appendix III

## Data for Moisture Content of TG Samples

| MSD-TG (%) | | | | R-TG (%) |
|---|---|---|---|---|
| 53.72 | 48.45 | 29.91 | 48.25 | 73.53 |
| 52.65 | 43.47 | 46.73 | 44.03 | 71.73 |
| 53.34 | 50.34 | 53.87 | 51.91 | 74.25 |
| 47.14 | 48.61 | 55.88 | 49.90 | 74.55 |
| 55.66 | 44.34 | 50.24 | 54.22 | 74.41 |
| 46.76 | 39.49 | 51.59 | 56.51 | 72.53 |
| 49.73 | 44.51 | 44.46 | 53.56 | 71.44 |
| 52.69 | 42.66 | 46.22 | 56.02 | 73.29 |
| 52.72 | 30.58 | 58.56 | 54.43 | 70.69 |
| 49.86 | 63.52 | 56.43 | 60.79 | |

# Appendix IV

## Data for Extraction Duration (MSD-TG)

| Time (min) | Ratio of WCO (mL) to MSD-TG (g) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1:1.5 | 1:2 | 1:2.5 | 1:3 | 1:3.5 | 1:4 | 1:4.5 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 45.49 | 50.21 | 47.81 | 29.83 | 40.82 | 25.98 | 35.72 |
| 60 | 99.94 | 100.08 | 99.76 | 94.68 | 69.73 | 75.44 | 74.93 |
| 90 | 81.33 | 85.41 | 95.43 | 95.70 | 84.57 | 89.36 | 90.93 |
| 120 | 79.49 | 81.26 | 88.89 | 86.32 | 98.94 | 99.95 | 95.50 |
| 150 | 88.34 | 88.81 | 84.79 | 99.99 | 100.02 | 98.62 | 99.95 |

# Appendix V

## Data for Effect of Temperature on Extraction Time (MSD-TG)

### Room Temperature

| Time (min) | $FFA/FFA_0$ |
|---|---|
| 30 | 1.59 |
| 60 | 3.14 |
| 90 | 5.40 |
| 120 | 5.32 |
| 150 | 8.96 |
| 210 | 11.02 |
| 270 | 12.28 |
| 1560 | 29.83 |
| 1590 | 83.77 |
| 1620 | 86.41 |
| 1650 | 94.30 |
| 1680 | 95.23 |
| 1710 | 99.96 |

### 85 ℃

| Time | $FFA/FFA_0$ | | | | | | |
|---|---|---|---|---|---|---|---|
| (min) | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Trial 5 | Trial 6 | Average |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 40.42 | 31.55 | 41.54 | 45.22 | 32.76 | 42.33 | 38.97 |
| 60 | 66.40 | 71.72 | 88.53 | 83.53 | 90.55 | 86.38 | 81.18 |
| 90 | 81.13 | 84.09 | 95.43 | 99.13 | 100.03 | 98.03 | 92.97 |
| 120 | 95.40 | 90.83 | 99.97 | 99.85 | 84.89 | 100.17 | 95.19 |
| 150 | 96.51 | 99.94 | 93.50 | 98.41 | 93.58 | 95.11 | 96.17 |
| 180 | 100.03 | | 89.82 | 84.97 | 88.27 | 89.49 | 90.51 |
| 210 | | | 93.24 | 92.28 | 89.66 | 88.18 | 90.84 |

### 60℃

| Time (min) | $FFA/FFA_0$ | | | | | |
|---|---|---|---|---|---|---|
| | Trial 1 | Trial2 | Trial 3 | Trial 4 | Trial 5 | Average |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 51.72 | 62.55 | 43.84 | 41.02 | 45.96 | 49.02 |
| 60 | 84.74 | 80.31 | 66.29 | 66.69 | 78.44 | 75.29 |
| 90 | 99.93 | 96.53 | 79.23 | 86.66 | 89.19 | 90.31 |
| 120 | 94.13 | 100.08 | 93.45 | 88.63 | 99.29 | 95.12 |
| 150 | 96.92 | 88.81 | 89.01 | 90.38 | 100.09 | 93.04 |
| 180 | | 95.14 | 100.08 | 99.89 | 97.35 | 98.11 |
| 210 | | 94.06 | 93.56 | 89.31 | 91.34 | 92.07 |

55℃

| Time (min) | FFA/FFA$_0$ | | | | |
|---|---|---|---|---|---|
| | Trial 1 | Trial2 | Trial 3 | Trial 4 | Average |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 40.74 | 36.97 | 39.93 | 34.77 | 38.10 |
| 60 | 55.37 | 43.81 | 58.01 | 50.85 | 52.01 |
| 90 | 59.29 | 55.30 | 99.98 | 56.20 | 67.69 |
| 120 | 100.05 | 100.08 | 89.01 | 97.56 | 96.68 |
| 150 | 97.92 | 88.71 | 96.14 | 99.97 | 95.69 |
| 180 | 94.61 | 91.63 | 92.76 | 74.99 | 88.50 |

50℃

| Time (min) | FFA/FFA$_0$ | | | | |
|---|---|---|---|---|---|
| | Trial 1 | Trial2 | Trial 3 | Trial 4 | Average |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 19.74 | 20.75 | 19.58 | 31.51 | 22.90 |
| 60 | 25.50 | 22.94 | 30.52 | 35.47 | 28.61 |
| 90 | 51.82 | 41.55 | 44.82 | 52.19 | 47.59 |
| 120 | 56.05 | 50.79 | 66.04 | 59.75 | 58.16 |
| 150 | 73.69 | 73.41 | 78.99 | 68.94 | 73.76 |
| 180 | 99.93 | 96.67 | 96.88 | 92.44 | 96.48 |
| 210 | 100.51 | 100.02 | 99.89 | 94.45 | 98.72 |
| 240 | 96.64 | 93.65 | 98.86 | 100.08 | 97.31 |

# Appendix VI

## Data for Effect of Temperature on Extraction Ratio (MSD-TG, $FFA/FFA_0$)

85℃

| Trial | Ratio of MSD-TG (g) to WCO (mL) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1:1.5 | 1:2 | 1:2.5 | 1:3 | 1:3.5 | 1:4 | 1:4.5 |
| 1 | / | / | / | 80.00 | / | 100.00 | / |
| 2 | / | / | 74.97 | 75.45 | 100.00 | 91.68 | 87.66 |
| 3 | 70.96 | 91.01 | 89.15 | 100.00 | 89.70 | / | / |
| 4 | 53.46 | 74.67 | 100.00 | 94.40 | 95.43 | / | / |
| 5 | 67.16 | 95.74 | 95.51 | 95.63 | 100.00 | / | / |
| 6 | 57.63 | 69.18 | 66.37 | 80.20 | 100.00 | 90.45 | 91.39 |
| 7 | 53.11 | 72.72 | 82.07 | 86.13 | 100.00 | 97.91 | 95.65 |
| 8 | 54.30 | 79.28 | 74.49 | 80.02 | 100.00 | 85.40 | 95.26 |
| 9 | 49.25 | 62.29 | 89.48 | 100.00 | 77.46 | 79.21 | 80.11 |
| 10 | 83.15 | 73.31 | 88.41 | 85.44 | 92.64 | 100.00 | 96.54 |
| 11 | 60.30 | 69.39 | 73.49 | 82.45 | 93.74 | 100.00 | 95.69 |
| 12 | 68.18 | 84.77 | 97.86 | 99.51 | 99.37 | 100.00 | 97.13 |
| 13 | 61.95 | 80.76 | 90.50 | 95.53 | 96.63 | 96.51 | 100.00 |
| 14 | 58.99 | 80.58 | 83.21 | 93.13 | 96.18 | 98.09 | 100.00 |
| Average | 61.53 | 77.81 | 85.04 | 89.13 | 95.47 | 94.48 | 93.94 |

50℃

| Trial | Ratio of MSD-TG (g) to WCO (mL) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1:1.5 | 1:2 | 1:2.5 | 1:3 | 1:3.5 | 1:4 | 1:4.5 | 1:5 |
| 1 | 4.27 | 12.93 | 25.56 | 56.02 | 75.85 | 80.14 | 90.13 | 100.01 |
| 2 | 4.23 | 15.52 | 31.52 | 62.69 | 74.19 | 84.37 | 95.07 | 100.00 |
| 3 | 5.49 | 16.26 | 25.85 | 58.88 | 79.53 | 88.73 | 99.42 | 99.99 |
| 4 | 2.85 | 17.45 | 27.55 | 58.26 | 76.70 | 94.17 | 92.41 | 99.97 |
| 5 | 9.52 | 19.69 | 29.45 | 41.89 | 79.21 | 85.89 | 98.76 | 99.98 |
| 6 | 11.32 | 19.68 | 34.03 | 41.99 | 76.56 | 85.50 | 92.28 | 100.01 |
| 7 | 6.23 | 18.09 | 35.20 | 47.29 | 79.39 | 86.48 | 98.52 | 100.00 |
| 8 | 11.68 | 22.74 | 31.62 | 45.65 | 86.23 | 91.10 | 92.10 | 99.99 |
| Average | 6.95 | 17.79 | 30.10 | 51.58 | 78.46 | 87.05 | 94.84 | 99.99 |

60℃

| Trial | Ratio of MSD-TG (g) to WCO (mL) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1:1.5 | 1:2 | 1:2.5 | 1:3 | 1:3.5 | 1:4 | 1:4.5 | 1:5 |
| 1 | 56.83 | 51.49 | 81.82 | 87.24 | 91.45 | 100.07 | 94.22 | 96.89 |
| 2 | 37.45 | 50.09 | 79.47 | 94.86 | 94.60 | 99.98 | 97.52 | 100.03 |
| 3 | 29.50 | 56.03 | 64.74 | 76.92 | 82.49 | 89.60 | 84.31 | 100.12 |
| 4 | 37.62 | 65.89 | 86.64 | 92.76 | 94.63 | 99.99 | 97.19 | 98.30 |
| Average | 40.35 | 55.87 | 78.17 | 87.94 | 90.79 | 97.41 | 93.31 | 98.83 |