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FINAL PROJECT REPORT

Cost-Effective Waste to Biodiesel Production at a Wastewater Treatment Plant

Prepared for: California Energy Commission
Prepared by: East Bay Municipal Utility District

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PREFACE

Assembly Bill 118 (Núñez, Chapter 750, Statutes of 2007) created the Clean Transportation Program, formerly known as the Alternative and Renewable Fuel and Vehicle Technology Program. The statute authorizes the California Energy Commission (CEC) to develop and deploy alternative and renewable fuels and advanced transportation technologies to help attain the state’s climate change policies. Assembly Bill 8 (Perea, Chapter 401, Statutes of 2013) reauthorizes the Clean Transportation Program through January 1, 2024, and specifies that the CEC allocate up to $20 million per year (or up to 20 percent of each fiscal year’s funds) in funding for hydrogen station development until at least 100 stations are operational.

The Clean Transportation Program has an annual budget of about $100 million and provides financial support for projects that:

- Reduce California’s use and dependence on petroleum transportation fuels and increase the use of alternative and renewable fuels and advanced vehicle technologies.
- Produce sustainable alternative and renewable low-carbon fuels in California.
- Expand alternative fueling infrastructure and fueling stations.
- Improve the efficiency, performance and market viability of alternative light-, medium-, and heavy-duty vehicle technologies.
- Retrofit medium- and heavy-duty on-road and nonroad vehicle fleets to alternative technologies or fuel use.
- Expand the alternative fueling infrastructure available to existing fleets, public transit, and transportation corridors.
- Establish workforce-training programs and conduct public outreach on the benefits of alternative transportation fuels and vehicle technologies.

To be eligible for funding under the Clean Transportation Program, a project must be consistent with the Energy Commission’s annual Clean Transportation Program Investment Plan Update. The Energy Commission issued PON-09-604. In response to PON-09-604, the recipient submitted an application which was proposed for funding in the Energy Commission’s notice of proposed awards August 12, 2010, and the agreement was executed as ARV-10-022 on July 13, 2011.

ABSTRACT

This report presents the results for the Cost Effective Waste to Biodiesel Production at a Wastewater Treatment Plant, a project conducted by the East Bay Municipal Utility District located in Oakland, California. The project will provide valuable input into the logistics of full-scale integration of fat, oil and grease waste receiving facilities and technical feasibility of biodiesel processes that fit into existing wastewater treatment plants.

The construction of a dedicated 60,000-gallon fat, oil and grease receiving facility at East Bay Municipal Utility District has demonstrated successful integration of a waste resource into the wastewater treatment process for renewable energy generation through anaerobic digestion and possibly future biodiesel production once the technology is ready for implementation.

In parallel, a bench-scale study was conducted to optimize the waste fats, oil and grease-to-biodiesel conversion processes and investigate sulfur removal methods for biodiesel made from brown grease. Bench testing demonstrated that a combination of silica gel adsorption and hydrogen peroxide oxidation desulfurization processes significantly reduced biodiesel sulfur by more than 90 percent at mild reaction conditions (ambient pressure and close to ambient temperature). The treated biodiesel met the American Society for Testing and Materials 6751 ultra-low sulfur standard of 15 ppm for several trials conducted, however not consistently. With the exception of not meeting the total sulfur limit, the brown grease biodiesel made by East Bay Municipal Utility District met all other Standard 6751 requirements. Further research is necessary to identify sulfur contaminant sources in the fats, oil and grease waste stream and to advance the biodiesel processing technology.

In addition, feasibility of converting alternate waste material, commonly found in wastewater treatment plant sewage streams, into biodiesel feedstock was investigated. Laboratory-scale tests were performed to harvest wax-like mycolic acids from *Nocardia* (a nuisance bacterium commonly found in the wastewater treatment process), and culture *Corynebacterium glutamicum* in wastewater for mycolic acid production to process as feedstock for biodiesel.

Keywords: Biodiesel, brown grease, sulfur standard, desulfurization, renewable energy, biofuel

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EXECUTIVE SUMMARY

Fat, oil, and grease waste (FOG) discharged into wastewater collection systems can cause sewer backups and overflows. Recently, wastewater treatment plants (WWTPs) have begun accepting trucked FOG as a supplement to their anaerobic digesters to increase biogas production and renewable energy generation. Alternatively, brown grease harvested from FOG, can be processed into biodiesel, which is a biodegradable, viable green fuel alternative to petroleum diesel. Interest in this alternative increases when fuel prices rise, greenhouse gas emissions are a concern, and diesel emissions negatively impact local air quality.

This project, partially funded by a California Energy Commission (Energy Commission) grant, investigated options to provide a FOG-to-biodiesel process that could economically fit into existing wastewater treatment plants and encourage widespread acceptance of FOG at treatment plants. EBMUD seeks to efficiently utilize this waste stream to its full renewable energy potential through anaerobic digestion and future biodiesel production once the technology is ready for implementation.

The specific objectives were to:

- Construct a 60,000-gallon FOG receiving facility at the EBMUD's Main Wastewater Treatment Plant (MWWTP), and
- Conduct a Wastes to Biodiesel study to:
    - Identify and test potential low-cost methods for converting FOG into biodiesel;
    - Demonstrate removal of sulfur and other impurities from FOG-derived biodiesel to comply with the ultra-low sulfur ASTM 6751-S15 standards (i.e., maximum of 15 ppm total sulfur) for B100 biodiesel; and
    - Investigate feasibility of converting other waste materials, commonly found in WWTP sewage streams, into biodiesel feedstock that may further improve the economic viability of the process at WWTPs.

FOG Receiving Facility Construction at EBMUD MWWTP

Most of the CEC grant funding for this project supported the construction of a facility to receive FOG waste from tanker trucks 24 hours a day, seven days per week. The FOG receiving facility includes**:**

- Five separate truck unloading bays
- Two 30,000-gallon, below-grade, concrete tanks to receive FOG
- Rock interceptor and bar screen to remove large solids
- Three FOG grinders to macerate material
- Three FOG pumps to deliver FOG to blend tanks
- Two FOG heat exchangers and recirculation pumps
- An odor treatment system (biofilter)
- A waiting station with a bathroom for truck drivers

FOG-to-Biodiesel Study

Technology Review

A comprehensive literature review was conducted to identify the best methods for extracting brown grease from FOG, converting brown grease into biodiesel, and removing sulfur to meet the ASTM 6751 ultra-low 15 ppm sulfur standard. Brown grease contains high free fatty acids (70–90 percent), high sulfur compounds (300–500 ppm), metals, and other impurities including odorous compounds. Processing brown grease into biodiesel requires a complex two-step process, prohibiting the acceptance of brown grease as a sole or co-feedstock for biodiesel production. Further, there is limited research being conducted on FOG (brown grease)-to- biodiesel conversion and sulfur removal processes to meet the ASTM 6751 ultra-low 15 ppm sulfur standard in FOG-derived biodiesel. In addition, the sources and forms of sulfur compounds in FOG are unknown. In contrast, extensive research has been conducted in the past decade on low-cost petroleum diesel desulfurization. Therefore, the literature review conducted in this study was expanded to cover these diesel sulfur removal technologies. Promising desulfurization technologies requiring mild reaction conditions were trialed under this study.

Bench-scale Tests

Potential low-cost alternatives for extracting brown grease from FOG and converting brown grease into biodiesel were tested. Over a hundred tests were completed to identify methods for removing sulfur and other impurities from biodiesel to comply with the ultra-low sulfur ASTM 6751 standards for B100 biodiesel.

Brown Grease Extraction from FOG

- Heating FOG directly on a hot plate or by addition of hot water, followed by centrifugation was identified to be the most efficient brown grease extraction method of the many tested.

Brown Grease-to-Biodiesel Conversion Process Investigations

- The typical two-step esterification and transesterification method was found to be the best compared to other brown grease-to-biodiesel conversion methods tested under this study. Additional tests on reaction conditions and reagents dose were conducted to further optimize the two-step process, and Figure 4.20 presents the optimized reaction conditions.
- Explored other potential process improvements such as:
    - Utilization of a solid catalyst in the esterification step, in lieu of sulfuric acid, for converting brown grease free fatty acids (FFAs) into biodiesel, though a longer reaction time was found to be necessary
    - Application of a low-cost lipase catalyst, in lieu of acid catalysts used in the esterification process. This method was successful; however, a minimum of 6 hours or longer reaction time was required

Sulfur Removal to Comply with the Ultra-Low Sulfur ASTM 6751 (S-15) Standards for B100 Biodiesel

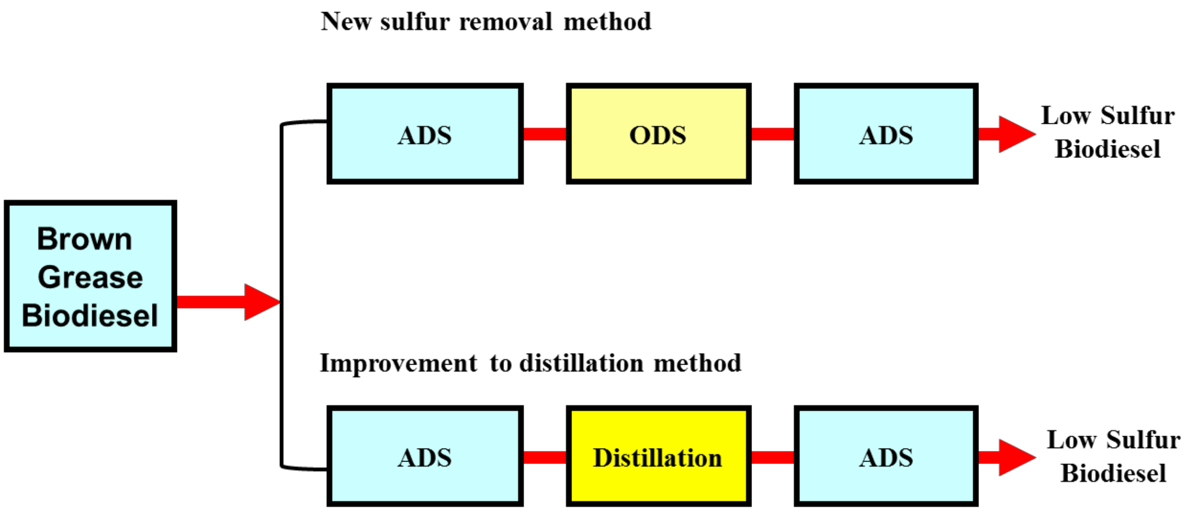
- Bench sulfur removal tests were conducted with both brown grease (containing ~400-500 ppm total sulfur) and biodiesel product (containing ~300 ppm total sulfur). The following process variations were investigated
    - *Brown grease:* adsorptive desulfurization (ADS) using various adsorbents mostly by batch treatment, hydrogen peroxide oxidative desulfurization (ODS) with and without ultrasonic assistance, ADS and ODS in various combinations, ion exchange with polymer resins, acid wash, precipitation, and biological sulfur removal
    - *Biodiesel:* ADS using various adsorbents by both batch treatment and fixed- column filtration, ODS with different oxidants and catalysts—with or without ultrasonic assistance, ADS and ODS in various combinations, ion exchange with polymer resins, chemical extraction, precipitation, base wash, and vacuum distillation in combination with ADS
- Bench biodiesel desulfurization tests showed that:
    - Silica gel proved to be the most efficient sulfur removal adsorbent for brown grease (45 percent) and biodiesel (70 percent) of the many adsorbents tested under ADS treatment. It also removes the color in brown grease and biodiesel;
    - ODS treatment in combination with ADS significantly removed biodiesel total sulfur by more than 90 percent;
    - Sulfur removal was maximized by combining ADS and ODS sequentially as follows: ADS-ODS-ADS, at times resulting in biodiesel sulfur below 15 ppm (Figure ES.1). The final total sulfur content, however, was usually in the 20–50 ppm range, above the ASTM limit of 15 ppm for B100 biodiesel. This method has the potential to be a low cost sulfur treatment option compared to the more common vacuum distillation method, due to its near ambient reaction conditions.
- Although specific sulfur compounds were not identified, results from this study showed that the unknown sulfur compounds had the following characteristics:
    - Concentrated in the bottom distillate fraction after vacuum distillation per ASTM D1160 method (10 mmHg vacuum and 360 0C max);
    - Removed by silica gel ADS and ODS;
    - Unaffected by many treatment methods tried (i.e., removal efficiency of 0–30 percent) for removing sulfur from brown grease or brown grease biodiesel (Refer to Chapter 4).
- Also found in this study:
    - Sulfuric acid used in the two-step biodiesel production process is not a significant contributor to the total sulfur present in brown grease biodiesel;
    - A mixture of kitchen and laundry detergents purchased from a supermarket contained total sulfur as high as 44,000 ppm. It is unclear whether this could be a significant source accounting for the high sulfur found in FOG and brown grease.
    - The sulfur treatment methods developed under this study (Figure ES-1 below) can be used alone or in combination with the distillation method for brown grease biodiesel sulfur removal.

Investigation of Alternative Biodiesel Feedstocks and Process Enhancements

Investigations were conducted to evaluate the feasibility of converting other waste materials, commonly found in WWTP sewage streams, into biodiesel feedstock which might be used to increase the amount of wastewater materials that are available as a biodiesel feedstock, to further improve the economic viability of the biodiesel process at WWTPs.

- Investigated the feasibility of harvesting nuisance bacteria (Nocardia) prevalent in wastewater treatment processes to convert this unsuitable material into material suitable as a biodiesel feedstock.
- Cultured bacteria (Corynebacterium) that can be grown in wastewater treatment processes to produce hexane extractable materials from non-hexane-extractable organic carbon compounds found in sewage.
- Conducted a literature review which identified the most reliable method of processing sewage sludge, an organic waste generated during wastewater treatment, into biodiesel feedstock was through sludge drying followed by FFA extraction. However, the drying and FFA extraction processes are expected to increase the production cost of biodiesel significantly compared to biodiesel produced from FOG.

Figure ES.1: Brown Grease Biodiesel Sulfur Removal Methods



Oxidative desulfurization (ODS) with or without ultrasound assistance

- H_2O_2+ phosphotungstic acid + Tetraoctylammonium bromide, or
- H_2O_2+ acetic acid + activated carbon catalyst

Adsorptive desulfurization (ADS)

- Silica gel, or silica gel mixed with alumina

Source: EBMUD

Conceptual Design of a Biodiesel Production Facility

This section presents a conceptual design of a full-scale FOG-to-biodiesel production facility, using processes developed or identified in this study. Potential environmental benefits including reduced air pollutants, GHG emissions and sewer blockages are projected. An estimation of green jobs creation with full-scale implementation is also provided.

Conclusions and Recommendations

This project has made significant progress towards developing a potentially low-cost method in making biodiesel from FOG and removing sulfur in brown grease-derived biodiesel. However, the FOG-to-biodiesel technology has not demonstrated cost effectiveness or sufficient robustness in meeting the ASTM 6751 ultra-low sulfur standard (S-15) yet. Further work is necessary to identify sulfur contaminant sources in FOG waste and to advance processing technology.

CHAPTER 1: Introduction

Fat, oil and grease waste (FOG) is responsible for 50–75 percent of sewer overflows nationwide[1] and results in millions of dollars of sewer cleaning and maintenance every year. The detrimental effect of waste grease on collection systems has led the industry to increase focus on eliminating FOG from the sewers. More recently, some wastewater treatment plants (WWTPs) have started accepting trucked FOG as a supplement to their anaerobic digesters to produce more energy. Expanding interest in energy yield from FOG and other wastes at WWTPs has given rise to new innovations aimed to harvest brown grease from FOG and utilize it more directly as a renewable feedstock for producing biodiesel. With rising fuel prices, concerns of greenhouse gas (GHG) emissions, and negative impacts of diesel emissions on local air quality, refining brown grease, extracted from FOG, to biodiesel has become an appealing option.

Based on estimates for the total supply of waste grease in the U.S., as much as 2 billion liters per year of biodiesel could be produced.[2] For most commercial biodiesel producers, however, brown grease is not an appealing feedstock as it presents more process challenges compared to alternative feedstocks such as virgin oil, waste cooking oil, and yellow grease.

Brown grease contains high amounts of: free fatty acids (FFAs), requiring additional pretreatment to produce biodiesel rather than soap; metal impurities; and sulfur (200–500 ppm), presenting a substantial challenge to meeting the ultra-low 15 ppm sulfur standard cost effectively. Further, brown grease makes up only 3–7 percent of FOG by weight[3] leaving 93–97 percent wastewater that requires treatment.

WWTPs are uniquely positioned to take advantage of this waste resource while reducing the negative impacts of FOG on the sewer systems. WWTPs are likely to have anaerobic digesters for harvesting additional energy from these process wastewaters while also providing treatment, be located close to FOG generating population centers, and can use the biodiesel produced to fuel fleet trucks.

Limited research has been done on FOG-to-biodiesel and subsequent sulfur removal to meet the ASTM 6751 ultra-low sulfur standard (15 ppm) for biodiesel used in vehicles made after 2007.

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[1] Southerland, R. Sewer Fitness: "Cutting the Fat." *American City and Country* 2002, 117(15), 4.

[2] Wiltsee, G. *Urban Waste Grease Resource Assessment;* NREL/SR-570-26141; USDE/ACG-7-17090-01; Appel Consultants, Inc.; National Renewable Energy Laboratory: Golden, Colorado,1998.

[3] Jolis, D.; Martis, M. *Brown Grease Recovery and Biofuel Demonstration: Oceanside Water Pollution Control Plant Baseline Summary;* Final Report to the California Energy Commission Contract Number PIR-06-001; CEC-500-2013-038; San Francisco Public Utilities Commission and URS Corporation; California Energy Commission: CA, 2013

This project worked to develop a FOG-to-biodiesel process that could economically fit into existing WWTPs and construct a FOG receiving facility at the East Bay Municipal Utility District (EBMUD). This report summarizes EBMUD's research which investigated economical processes for brown grease recovery from FOG, conversion of brown grease to biodiesel, and removal of sulfur from the biodiesel product to comply with current ASTM standards. In addition, EBMUD investigated additional novel processes such as recovering oil from wastewater that may be processed into biodiesel feedstock to further improve the economic viability of converting FOG to biodiesel at municipal WWTPs.

Project Objectives

The specific project objectives were to:

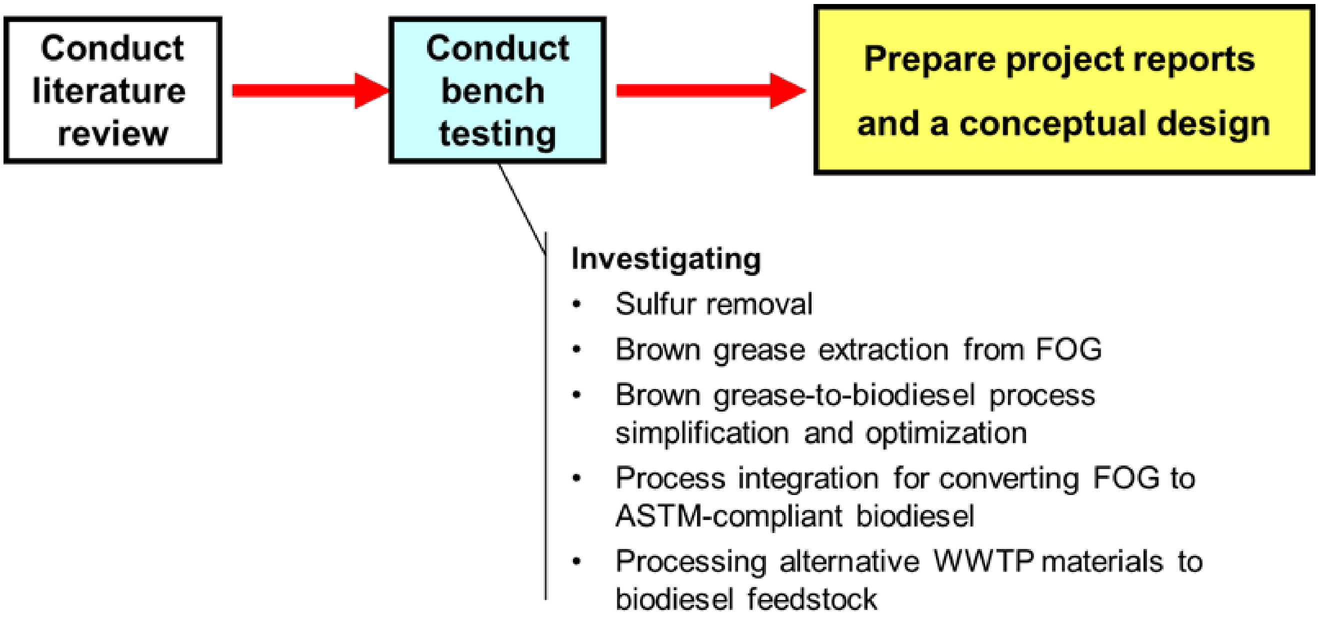
- Construct a 60,000-gallon FOG receiving facility at the EBMUD's Main WWTP; and
    - ✓ Conduct a Wastes to Biodiesel study to:
        - ○ Identify and test potential low-cost alternatives for converting brown grease into biodiesel;
        - ○ Demonstrate sulfur removal from FOG-derived biodiesel to comply with the ultra-low sulfur ASTM 6751-S15 standards for B100 biodiesel;
        - ○ Investigate feasibility of converting alternative waste material, commonly found in WWTP sewage streams, into biodiesel feedstock.

This project was possible with funding support from the California Energy Commission and significant in-kind contributions from the EBMUD.

Project Approach

A parallel approach was employed for this project, i.e., the FOG receiving facility construction and the Wastes to Biodiesel study were conducted at the same time. Figure 1 depicts the general approach adopted for the Wastes to Biodiesel study portion.

Figure 1: Schematic of Wastes to Biodiesel Study Approach



Source: EBMUD

Report Organization

This report documents and discusses the execution and findings of the study and is organized as follows:

Chapter 1. Introduces the project objectives and approach conducted under the California Energy Commission Alternative and Renewable Fuel and Vehicle Technology Program Grant.

Chapter 2. Describes the FOG Receiving Facility construction at EBMUD's Main Wastewater Treatment Plant (MWWTP) by showing the facility location, its role in the treatment processes, design details and phases of construction and commissioning.

Chapter 3. Provides the results of an extensive literature review on waste feedstocks, brown grease and biodiesel production processes, as well as polishing methods for sulfur contaminants. Based on this review, potentially viable technologies for brown grease extraction, biodiesel production and desulfurization were selected for testing.

Chapter 4. Describes bench-scale tests conducted to develop and optimize FOG-to-biodiesel processes based on literature review findings from Chapter 3 including: (1) FOG- to-brown grease process optimization, (2) brown grease-to-biodiesel process simplification and optimization, (3) sulfur compounds speciation efforts, and (4) desulfurization process development and optimization.

Chapter 5. Describes literature review findings and EBMUD's bench testing to investigate alternative biodiesel feedstocks, including oils from sludge, conversion of wastewater materials not suitable as biodiesel feedstocks into materials that could be processed into biodiesel using *Nocardia* (a nuisance bacterium in WWTPs) and a bacterium cultured in wastewater. Methane-to-methanol technology review is also included.

Chapter 6. Presents a conceptual design of a biodiesel production facility, showing process flow diagrams and descriptions, projected environmental benefits of reduced air pollutants and GHG emissions, reduced sewer blockages, and estimation of green jobs creation with full-scale implementation at a WWTP.

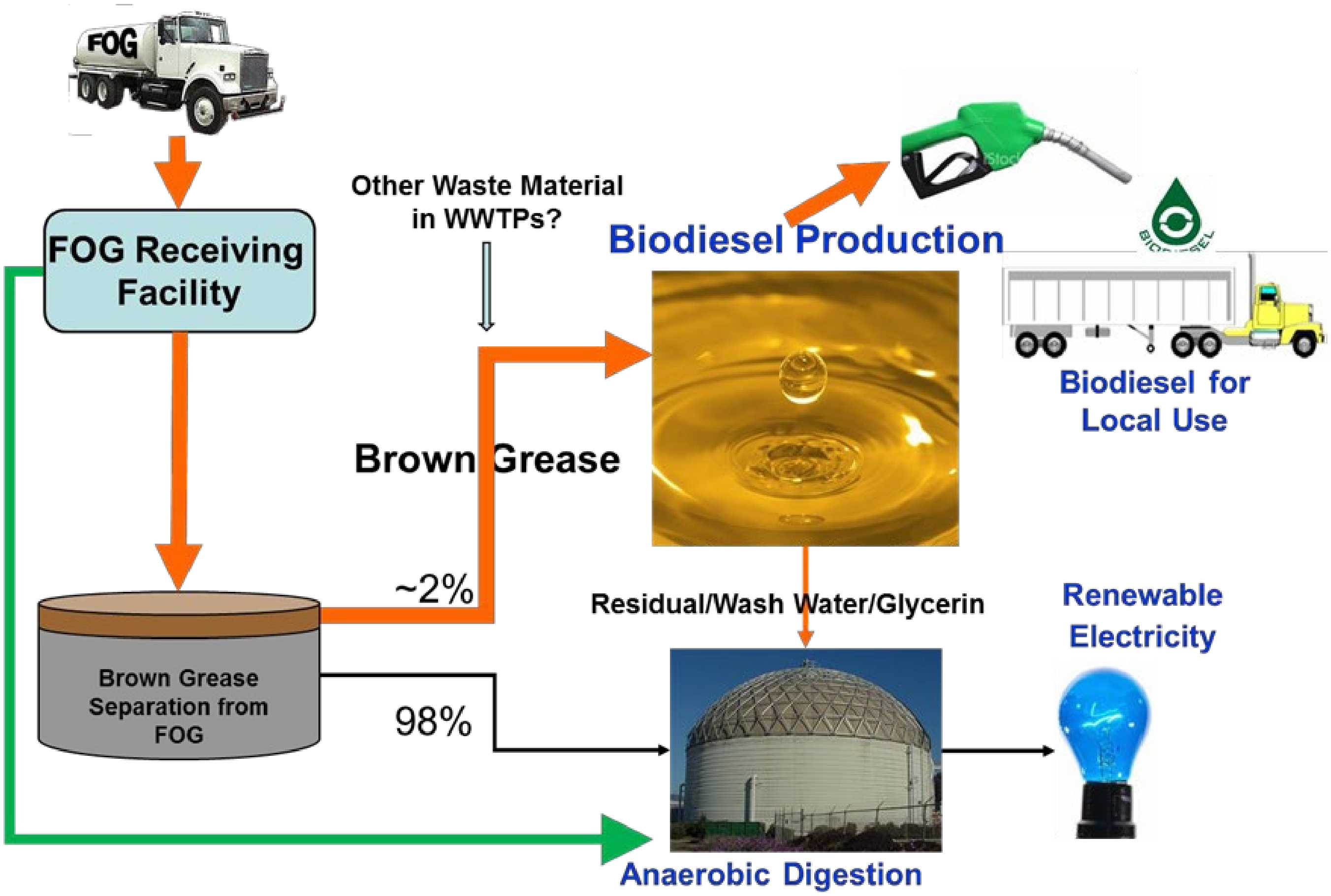
CHAPTER 2:
Construction of the FOG Receiving Facility

This section presents the construction of EBMUD's new FOG Receiving Facility. This new facility allows waste receiving from tanker trucks 24 hours a day, seven days per week, and the facility also has a waiting station for truck drivers to use. Over 60 percent of the Energy Commission grant funded part of the construction of this FOG Receiving Facility.

Background

FOG receiving as seen in Figure 2 is the first step for converting FOG waste into biodiesel and/or renewable energy in the form of biogas or electricity at WWTPs.

Figure 2: FOG Receiving - First Step in Converting FOG Waste into Renewable Energy and Biofuel at WWTPs

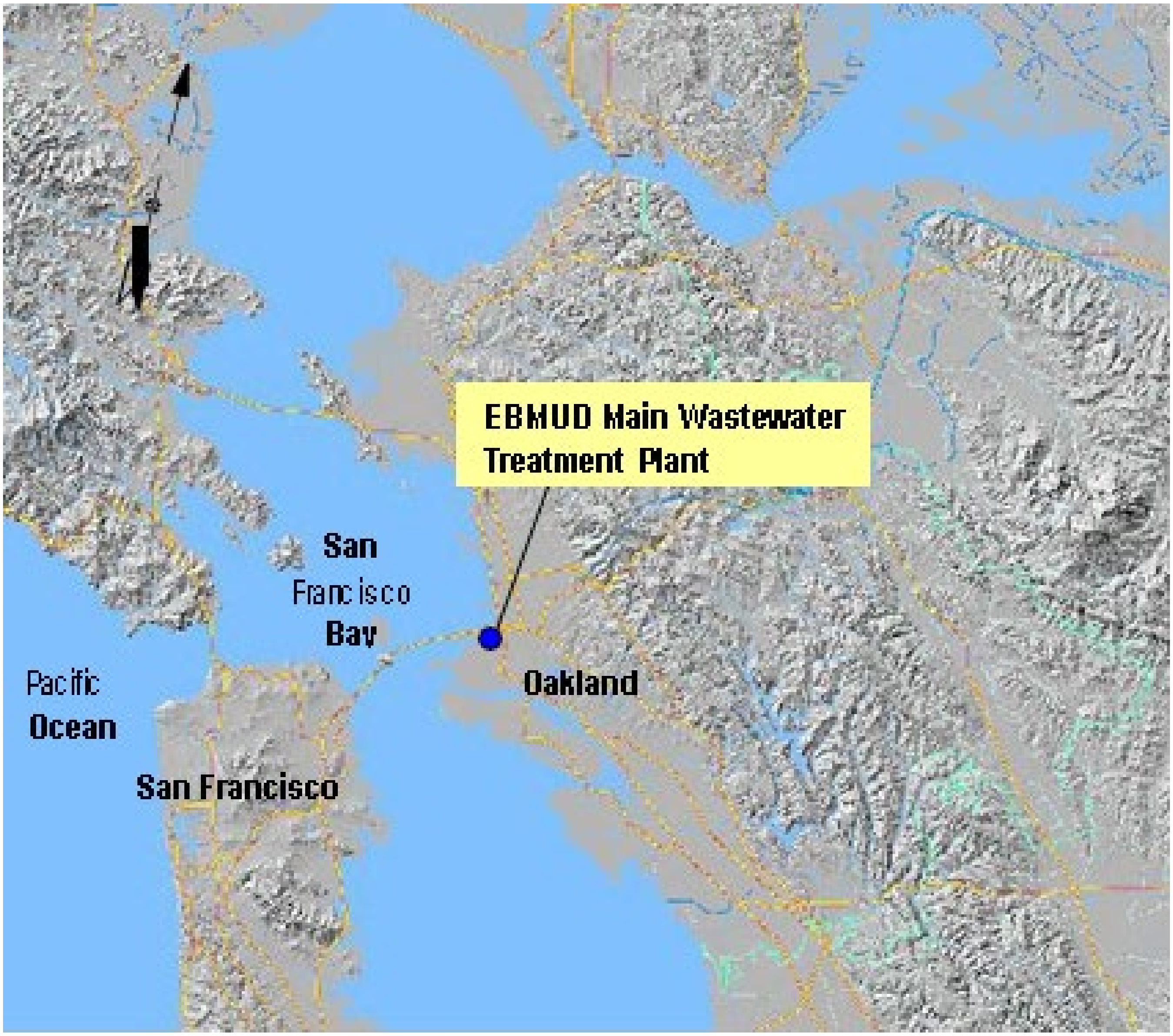


Source: EBMUD

FOG Receiving Facility Location

The FOG Receiving Facility is located at EBMUD's MWWTP as shown in Figures 3 and 4.

Figure 3: Location of EBMUD MWWTP in Oakland, CA (Project Site)



Source: EBMUD

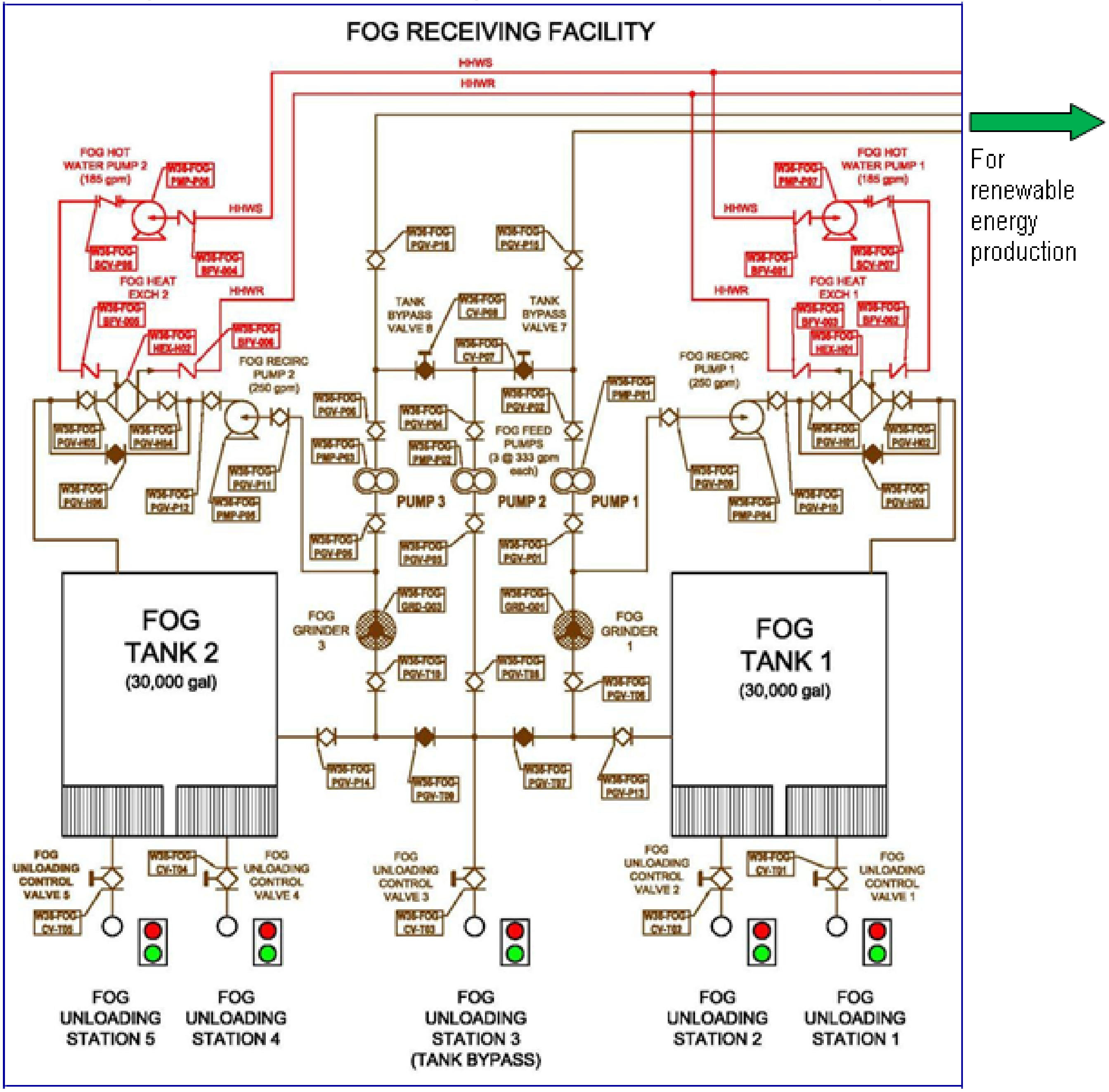
Figure 4: Location of FOG Receiving Facility at EBMUD MWWTP

Source: EBMUD

Process Flow Diagram and Design

The process flow diagram for the FOG Receiving Facility is shown in Figure 5.

Figure 5: Process Flow Diagram for EBMUD FOG Receiving Facility



Source: EMBUD

The FOG Receiving Facility includes:

- Five separate truck unloading bays
- Two 30,000-gallon, below-grade, concrete tanks to receive FOG
- A rock interceptor and bar screen to remove large solids
- Three FOG grinders to macerate material
- Three FOG pumps to deliver FOG to blend tanks

- Two FOG heat exchangers and recirculation pumps
- An odor treatment system (biofilter)
- A truck driver waiting station with a bathroom

Construction

Construction photos of the FOG Receiving Facility over time are shown in Figure 6 through 15.

Figure 6: FOG Receiving Facility Construction Over Time

Source: EBMUD

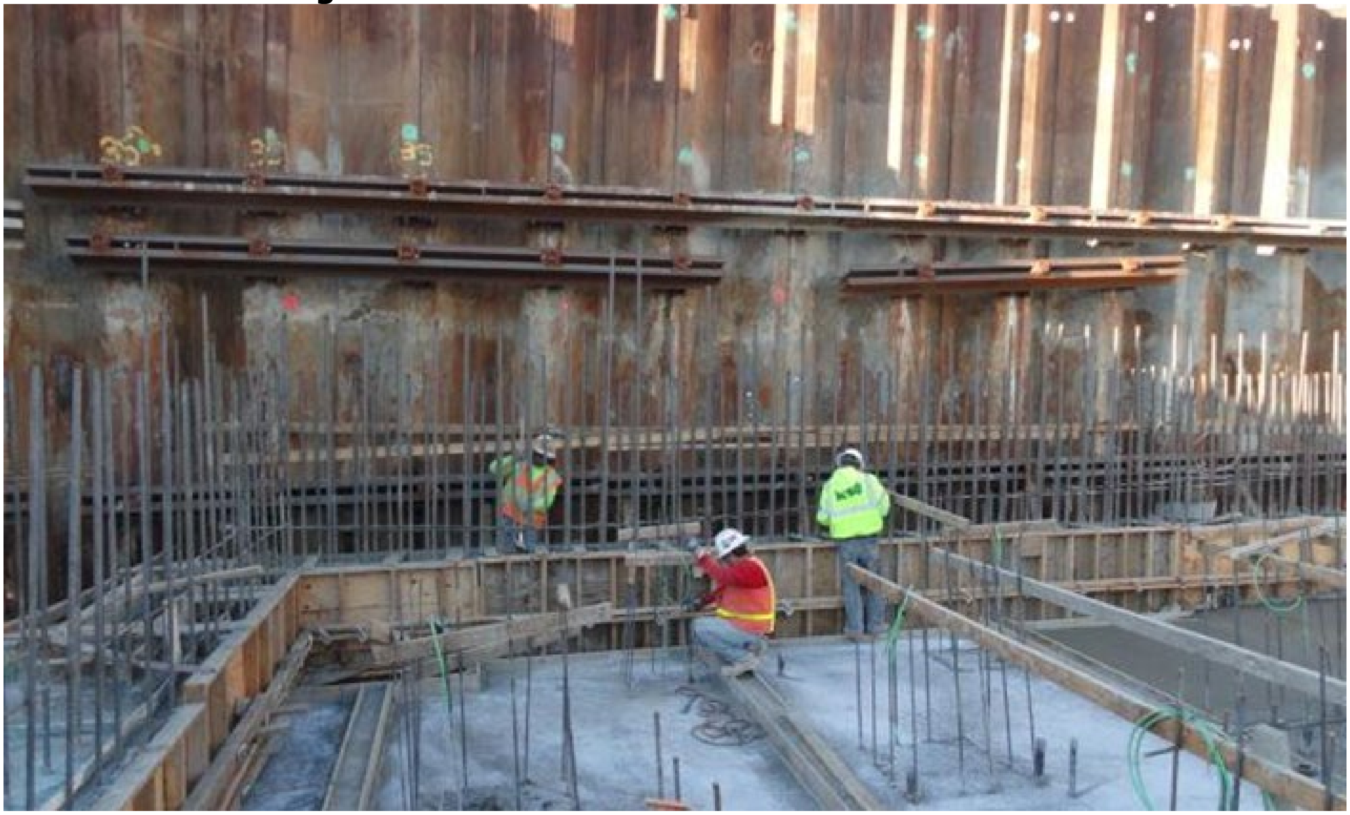
Figure 7: FOG Tank Base Excavation and Pour

Source:EBMUD

Figure 8 : FOG Tank Base Foundation Poured

Source: EBMUD

Figure 8: FOG Tank Wall Framework Installation



Source: EMBUD

Figure 9: FOG Tank Top

Source: EMBUD

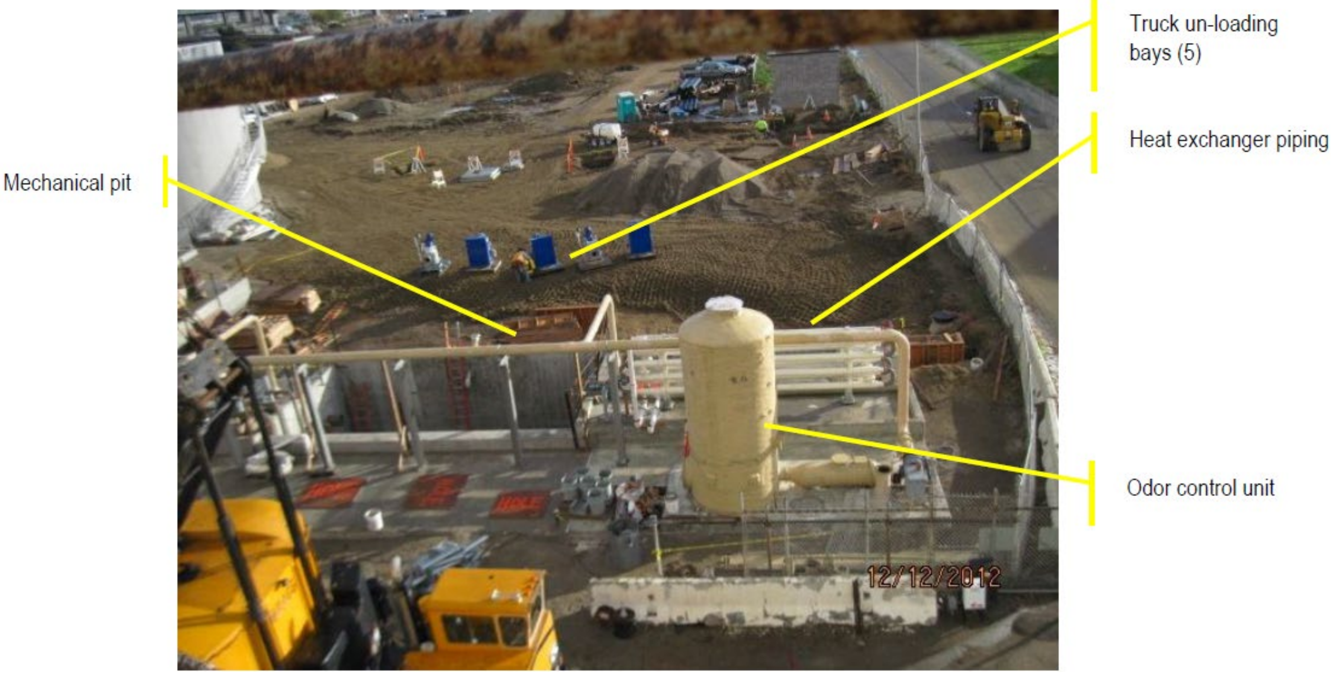
Figure 10: FOG Tank Top (June 2012)

Source: EBMUD

Figure 11: Heat Exchange and Mechanical Piping Installation (June 2012)

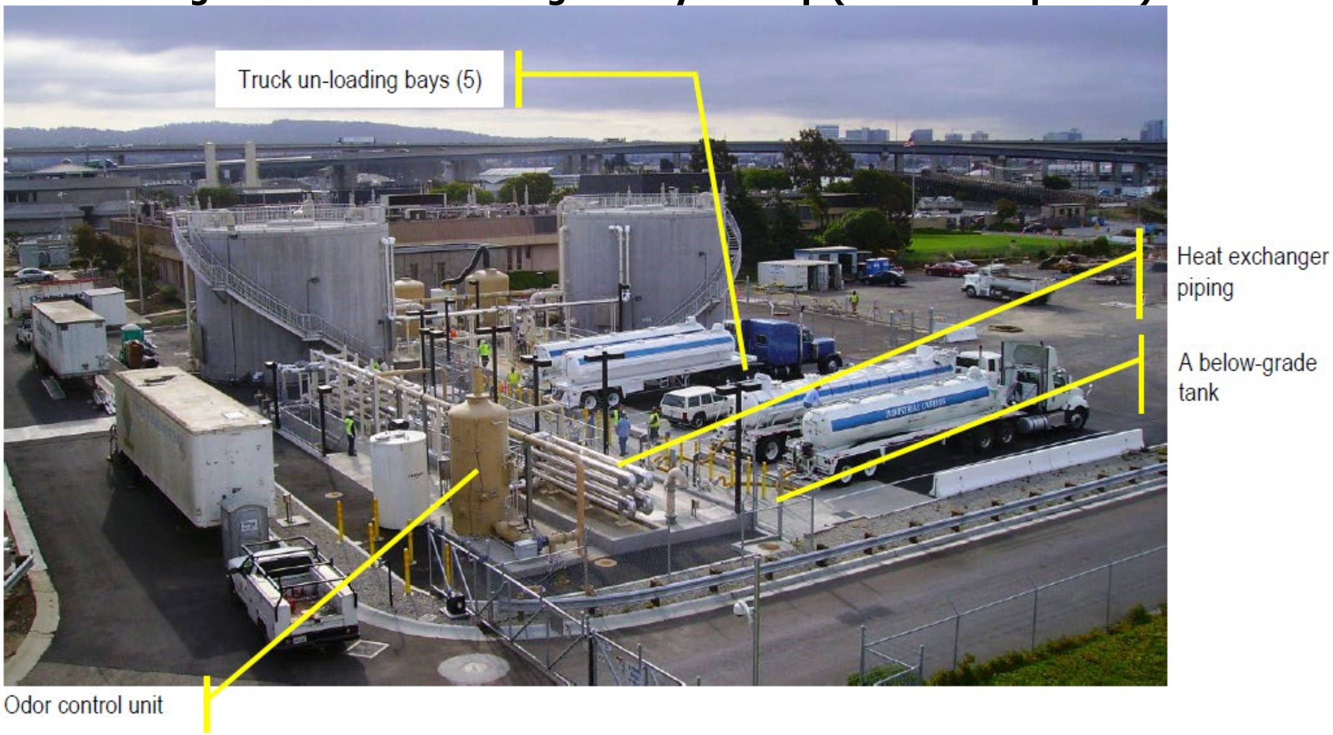
Source: EBMUD

Figure 12: Construction of FOG Facility



Source: EBMUD

Figure 13: FOG Receiving Facility Startup (Waste Acceptance)



Source: EBMUD

Figure 14: FOG Receiving Facility Truck Driver Waiting Room

Source: EMBUD

CHAPTER 3:
Biodiesel Technology Review and Selection for Testing

This section summarizes the literature review conducted for this study of cost effective biodiesel production and desulfurization technologies. In addition, criteria used for selecting technologies for testing are discussed.

Approach

A comprehensive literature review of available brown grease to biodiesel and sulfur removal technologies was conducted prior to process testing. Because of the limited work previously done with brown grease, the literature review was expanded to include process development of converting other feedstocks such as yellow grease to biodiesel. In addition, desulfurization of petroleum diesel which has been greatly advanced over the past decade, due to the ultra-low sulfur federal and state regulations placed on vehicle fuels, is also included in the review.

Over a hundred papers and patents were included in the review as well as information found from internet searches. Specifically, the literature review comprises:

- Methods to cost effectively harvest brown grease from FOG
- Current technologies on biodiesel production from brown grease and other feedstocks
- Potential sulfur sources in brown grease biodiesel
- Sulfur removal methods for brown grease and biodiesel treatment to meet the ultra-low sulfur transportation fuel standard
- Current desulfurization technologies to cost effectively remove sulfur from petrodiesel

The literature review effort continued over the course of the study to incorporate new developments that might benefit this project.

FOG to Biodiesel

FOG

FOG is the waste stream trapped in grease interceptors installed at drain lines of commercial food processing establishments. It is a complex and variable mixture of oil, grease, water, residual food and other solids. Accumulated FOG must be periodically removed from the grease interceptors to avoid causing sewer system overflows due to FOG blockage.

FOG is hydrophobic and normally exists in solid form at room temperature. If excessive soaps are present in the wastewater, an emulsion of FOG and water may form. FOG trucked to the EBMUD consisted of different types of free fatty acids (FFAs) ranging from C_{10} to C_{20} (Table 1) that have different physical and chemical properties.[4]

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[4] Suto, P.; Gray, D.M.; Larsen, E.; Hake, J. Innovative anaerobic digestion investigation of fats, oils, and grease. In *Bridging to the Future,* Proceedings of the Residuals and Management Biosolids Conference

Table 1: FFA Composition of FOG Received by EBMUD (Suto et al., 2006)

Fatty Acid	C:D[1]	Wt% (range)
Capric Acid	10:0	1.3 (0.1–8.6)
Lauric Acid	12:0	3.0 (0.3–15.5)
Myristic Acid	14:0	8.4 (1.8–23)
Palmitic Acid	16:0	23.1 (14.6–36.7)
Palmitoleic Acid	16:1	NM[2]
Stearic Acid	18:0	9.8 (0–16.3)
Oleic Acid	18:1	36.1 (5.5–70.7)
Linoleic Acid	18:2	15.3 (0–25.7)
Linolenic Acid	18:3	NM[2]
Arachidic Acid	20:0	2.1 (0.1–16.5%)
Total Fatty Acids (wt%)		**99.1%**

1. C:D: Carbon atoms:double bonds; 2. NM: Not Measured

Source: Suto et al, 2006.

Brown Grease Extraction from FOG

Brown grease is about 3–7 percent of FOG by weight[5] and needs to be extracted from FOG before it can be used as a feedstock to produce biodiesel.

Heating and/or Extraction

Since FOG tends to partially solidify at room temperature, it is often heated to allow easy separation of brown grease from the water and other constitutes. In bench tests conducted by EBMUD in 2007, FOG was heated to 40 °C, filtered through a double layer screen mesh, and then settled overnight. After settling, the semi-solid oil upper layer was separated from the translucent liquid lower layer and heated again to allow a lighter portion to rise to the top. The upper oily layer was scooped off, heated again and filtered using a 5-µm cloth filter.[6] Heating FOG for separation is also employed by the Pacific Biodiesel Technologies (see Table 2).

2006*,* Greater Cincinnati, OH, March 12-15, 2006; Water Environmental Federation: Alexandria, VA, 2006.

[5] Jolis, D.; Martis, M. *Brown Grease Recovery and Biofuel Demonstration: Oceanside Water Pollution Control Plant Baseline Summary;*Final Report to the California Energy Commission Contract Number PIR-06-001; CEC-500-2013-038; San Francisco Public Utilities Commission and URS Corporation; California Energy Commission: CA, 2013.

[6] Chakrabarti, A.R.; Hake, J.M.; Zarchi, I.; Gray, D.M. Waste Grease Biodiesel Production at a Wastewater Treatment Plant. *Proceedings of the 81st Annual Water Environment Federation Technical Exhibition and Conference,* Chicago, IL, October 18-22, 200 8; Water Environmental Federation: Alexandria, VA, 2008.

Non-polar solvents such as alkanes and substituted alkanes may be added to FOG while heating.[7] Jiang reported that mixing grease trap waste (10 g) with hexanes (50 mL) at 50 degrees Celsius extracted brown grease contained more than 95 percent FFAs. The researcher was also successful in extracting brown grease by mixing equal weight of soybean oil with grease trap waste (10 g each) at 25 degrees Celsius.

The addition of inorganic salt such as aluminum sulfate and cationic polymer can neutralize the electrical charges and split oil emulsions.[8] Addition of acid or bases to adjust the pH of grease trap waste during heating can minimize emulsion and assist extraction.[9]

Separation

Since brown grease is less dense than the solids and water present in FOG, settling tanks or centrifuges can be used for oil-water-solid phase separation. Table 2 is a summary of companies providing equipment or technology for brown grease separation from FOG.

Table 2: Summary of Brown Grease Separation Technology from FOG

Company	Equipment Type	Temperature (°F)	Separation Technology	Capacity
Pacific Biodiesel Technologies	Tanks	Hot water supply at 180–200[1]	Heating + gravity separation	6,000–45,000 gpd[2]
Burt Waste Incorporated (BWI)	GTW separator, SV-2	NA[3]	Filtration + settling	200 gpm
FogBusters, Inc	Goslyn™	110	Heating + gravity-driven hydraulic separation	25–400 gpm
Abanaki Corporation	Grease Grabber belt oil skimmer	NA[3]	Skimmer belt	Up to 160 gph
Dolphin Marine and Industrial Centrifuges	MAPX 309 MAPX 313 WHPX 513	NA[3]	Centrifuge	2 to 100 gpm

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[7] Jiang, R. Brown Grease Treatment Processes. U.S. Patent 20110197497 A1, August 18, 2011.

[8] Alther, G. Cleaning wastewater: Removing oil from water with organoclays. *Filtration & Separation* **2008,** *45*(3), 22-24.

[9] Jiang et al. 2011.

Company	Equipment Type	Temperature (°F)	Separation Technology	Capacity
Separ Filter	Separ 2000 series	NA[3]	Centrifuge + filtration	1–48 gpm
PA Biodiesel Supply	Wvo centrifuge	160–420	Centrifuge	65–400 gph
PA Biodiesel Supply	Oil centrifuge filtration unit	150–170	Centrifuge + filtration	108 gph
Hydrasep Inc.	Model # RCT DNAPL (Mix with water<50%)	NA[3]	"Bubble Spin" principle	30 gpm
Midwest Energy Group Inc.	Proprietary heating method via a metal pipeline	203	Heating + centrifugation	NA[3] (Bench scale described in a patent[4])

1. Jolis and Martis, 2013; 2. Williams, 2009; 3. NA = not available; 4. Jiang, 2011

Source: EBMUD

Pacific Biodiesel Technologies

This process was demonstrated at the San Francisco Public Utilities Commission (SFPUC) with a design capacity of 10,000 gallons grease trap waste per day. The process included three steps: (1) unloading and screening of the grease waste trucked to wastewater treatment plant; (2) heating and gravity separation of the trap waste; and (3) optional polishing to reduce solids through filtration and/or moisture using vacuum treatment.[10]

Burt Waste Incorporated

This process involves separation of trash, sand and foreign objects by first screening grease trap waste delivered by trucks. Then, a two-stage gravity fractionation system with heat input is employed to separate out brown grease (top layer) from the remaining FOG. Typical yield was reported to be about 2 percent.

FogBusters, Inc

In this process, the solids in FOG are first removed by up to 90 percent before FOG enters a heated primary tank. Next, the FOG (in the liquid form due to heating) is delivered to a separation tank. The separator hydraulically removes the oil (“oil spurs out the top”) by means

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[10] Jolis and Martis. 2013.

of a “pressurized flotation technology”. The extracted oil is highly pure with low moisture content. Should the oil content be greater than 50 percent in the incoming FOG, then dilution of FOG is required for the separation process to work successfully.

Abanaki Corporation

The Grease Grabber® utilizes the differences in specific gravity and surface tension between oil and water. These physical characteristics allow the skimmer belt to attract grease, oil, and other hydrocarbon liquids as the belt passes across the surface of the water.

In addition to the above, available separation process and technology employed in food engineering which could be useful in brown grease/FOG separation is also reviewed and a summary is provided in Table 3.

Table 3: Summary of Separation Technology in Food Engineering

Rank	Method	Equipment/ Material/ Condition	Advantage and Disadvantage[1]	References
1	Centrifugation based on density differences	Centrifuge	✓ Commonly used for solids/liquid or liquid/liquid separations	Example: Seperation equipment sales inc. (http://centrifugesys.com/index.html)
2	Foam separation	Chemicals Mixer	✓ Used for protein concentration and separation	(Zhang et al., 2011)
3	Sonication	Sonicator	✓ No heating needed × May not work on FOG-water separation	(Patist and Bates, 2008)
4	Membrane processes (2–14 bar)	Membrane High pressure or high temperature	× High temperature or high pressure	(Ciacchi et al., 2002; Hafez et al., 2007)
5	Supercritical fluids (e.g., CO2)	High pressure High temperature	✓ Can separate oil-water ✓ Processing cost is competitive to other processes	(Brunner, 2009)
6	Adsorption	Hierarchical mesoporous silica materials	✓ Easy steps × Low efficiency × Expensive media	(Brady et al., 2008)
7	Screening based on size differences		✓ May not be suitable for FOG/water separation	(Huffman and Harper, 1999)

1. ✓ indicates advantage and × indicates disadvantage

Source: EBMUD

Challenges of Using Brown Grease as Biodiesel Feedstock

Brown grease extracted from FOG typically consists of waste vegetable oil, animal fat and grease. It is a low or no cost feedstock for biodiesel production, but it is an inconsistent, complex and challenging feedstock.[11] When brown grease is used as the biodiesel feedstock, the following problems are anticipated.[12], [13]

- **Melting point:** Brown grease usually solidifies at room temperature; brown grease storage tanks need to be heated to keep brown grease in a liquid state. Furthermore, biodiesel made from brown grease can solidify at colder ambient temperatures.
- **Free fatty acid content:** Brown grease contains over 50 percent free fatty acids and as such requires an extra pretreatment step to produce biodiesel.[14] This extra step can increase the overall production cost due to an increased amount of methanol (reactant) required for the pretreatment. Acid catalyzed esterification is often used for brown grease pretreatment.
- **Sulfur content:** Brown grease contains high amounts of sulfur, making it extremely challenging to meet the ultra-low sulfur regulatory standard. Removing sulfur from brown grease or brown grease derived biodiesel can significantly increase overall processing costs.

In addition, brown grease also contains impurities such as water, detergents, trace metals, pesticides, polycyclic aromatic hydrocarbon, chlorinated compounds, and sterols.[15] All these challenges have limited brown grease's use as a sole or co-feedstock for biodiesel production. So far, the authors are not aware of any full-scale commercial plant in operation for converting brown grease into ASTM-quality biodiesel in the United States. Nonetheless, brown grease is still an appealing feedstock due to its negative to low cost, which is critical because the cost of feedstock can account for about 70–80 percent of the total biodiesel production cost.[16]

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[11] Berry, W.W.; Ratigan, B.J. Process of Making Alkyl Esters of Free Fatty Acids. U.S. Patent 7,767,839 B2, August 3, 2010.

[12] Anderson, D.; Masterson, D.; McDonald, B.; Sullivan, L. *Industrial Biodiesel Plant Design and Engineering: Practical Experience,* Proceedings of the International Palm Oil Conference (PIPOC), Putrajaya Marriot Hotel, Putrajaya, Malaysia, August 24-28, 2003; Crown Iron Works Company. P.O. Box 1364. Minneapolis, Minnesota 55440, USA, 2003

[13] Jiang et al. 2011.

[14] Lam, M.K.; Lee, K.T.; Mohamed, A.R. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol. Adv.* **2010,** *28*(4), 500-518.

[15] Tyson, K.S. Brown Grease Feedstocks for Biodiesel. *National Renewable Energy Laboratory*, Jun 19, 2002.

[16] Siddiquee, M. N.; Rohani, S. Lipid extraction and biodiesel production from municipal sewage sludges: A review. *Renewable and Sustainable Energy Rev.* **2011,** *15* (2), 1067-1072.

Biodiesel Production from Brown Grease

This section presents an overview of technological advancements in biodiesel production processes.

Biodiesel

Biodiesel is a biodegradable diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters that can be used in modern diesel engines. It can be made from vegetable oils such as soybean oils and the oils from peanut, sunflower, corn, cottonseed, canola, mustard seeds. It can also be made from animal oil/fats, tallow and waste oils.

Biodiesel is considered the better fuel than petroleum diesel, because:

- It is less toxic: it biodegrades 10 times faster than petroleum diesel.[17]
- It provides an overall 86 percent reduction of greenhouse gases when produced from waste grease.[18]
- It is a potential lubricant: addition of 1 percent biodiesel into petroleum diesel can increase the lubricity of diesel fuel by up to 65 percent.[19]
- It has excellent solvent properties, resulting in less deposits in the engine.[20]

Review of Biodiesel Production Processes

A number of review articles have summarized the processes of converting waste cooking oil into biodiesel[21], [22], [23], [24] which are categorized as:

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[17] Williamson, A.-M.; Badr, O. Assessing the Viability of Using Rape Methyl Ester (RME) as an Alternative to Mineral Diesel Fuel for Powering Road Vehicles in the UK. *Appl. Energy* **1998,** *59*(2–3), 187-214. DOI: (http://dx.doi.org/10.1016/S0306-2619(98)00002-6)

[18] Schnepf, R.; Yacobucci, B.D. *Renewable Fuel Standard (RFS): Overview and Issues;* Congressional Research Service Report for Congress: Washington, DC, July 2010.

[19] Knothe, G.; Steidley, K.R. Lubricity of Components of Biodiesel and Petrodiesel. The Origin of Biodiesel Lubricity. *Energy Fuels* **2005,** *19*(3), 1192-1200.

[20] Demirbas, A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Prog. Energy Combust. Sci.* **2005,** *31*(5– 6), 466-487. DOI: (http://dx.doi.org/10.1016/j.pecs.2005.09.001)

[21] Chakrabarti, A.R.; Hake, J.M.; Zarchi, I.; Gray, D.M. Waste Grease Biodiesel Production at a Wastewater Treatment Plant. *Proceedings of the 81st Annual Water Environment Federation Technical Exhibitation and Conference,* Chicago, IL, October 18-22, 2008; Water Environmental Federation: Alexandria, VA, 2008.

[22] Helwani, Z.; Othman, M.R.; Aziz, N.; Fernando, W.J.N.; Kim, J. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Process. Technol.* **2009,** *90*(12), 1502-1514.

[23] Lam, M.K.; Lee, K.T.; Mohamed, A.R. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol. Adv.* **2010,** *28*(4), 500-518.

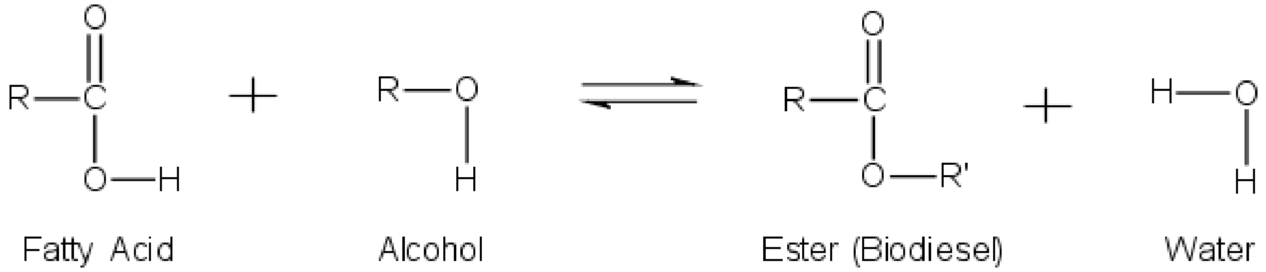
[24] Leung, D.Y.C.; Guo, Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process. Technol.* **2006,** *87*(10), 883-890.

- Homogenous acid-catalyzed process
- Homogenous base-catalyzed process
- Acid and base-catalyzed two-step process
- Hydrolysis of triglycerides followed by acid-catalyzed process
- Heterogeneous (solid) acid or base-catalyzed process
- Supercritical alcohol process
- Enzyme-catalyzed process

Homogenous Acid-catalyzed Process

In this process, the FFAs in feedstock react with alcohol to form alkyl esters using a homogeneous acid-catalyzed esterification reaction shown below in Figure 16 and Table 4:

Figure 15: Homogeneous Acid-Catalyzed Esterification Reaction



Source: EBMUD

As the reaction is reversible, an excess of alcohol is typically added in order to drive the reaction towards product formation. Sulfuric acid is commonly used to catalyze this reaction because it is a cheap but effective catalyst. Heterogeneous (solid) acid or base-catalyzed process.

Table 4: Homogeneous Acid-Catalyzed Esterification of Yellow/Brown Grease

Feedstock	Catalyst/ Dose	Methanol:Oil Ratio	Temp (^{o}C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
Waste Cooking Oil	H_2SO_4 4 wt%	20:1 (molar ratio)	95	20	>90%	(Wang et al., 2006)	✓ High yield × Sensitive to FFA and water × Separation problem
Vegetable Oil	H_2SO_4 1 wt%	30:1 (molar ratio)	65	69	~90%[2]	(Freedman et al., 1984)	
High FFA Feedstock (animal fats, used cooking oils, trap grease)	H_2SO_4 6.25 g[3]	1:2	115	1	>88%	(Berry and Ratigan, 2010)	✓ High reaction rate ✓ Less sensitive to FFA and water × High pressure (80–90 psi) × High temperature × Acid esterification (2 times) × Distillation separation (can be costly)

1 √ indicates advantage and × indicates disadvantage

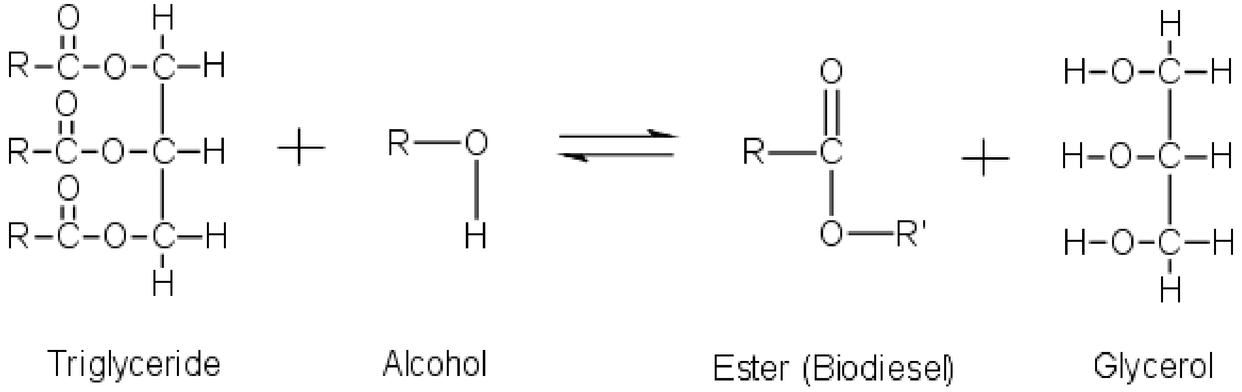
2 Yield was estimated from Figure 8, transesterification of soybean oil to methyl esters with 1% H_2SO_4 catalyst

3 6.25 g H_2SO_4 to 1 L methanol and then to 2 L restaurant trap grease as described in Example 1

Source: EBMUD

Homogeneous Base-catalyzed Process
The most commonly used method of making biodiesel is via base-catalyzed transesterification. The transesterification reaction converts triglycerides to esters as shown in the following reaction:

Figure 16: Transesterification Reaction Converting Triglycerides to Esters



Source: EBMUD

Sodium hydroxide and potassium hydroxide are usually selected as base catalysts because they are relatively inexpensive and readily available.

Table 5: Homogeneous Base-catalyzed Transesterification of Brown Grease/Yellow Grease

Catalyst	Catalyst Loading (wt%)	Methanol/ Oil	Temp (°C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
KOH	6	9:1	87	2	86-88[2]	(Demirbas, 2009)	✓ Very fast reaction rate[3] ✓ Cheap Catalyst × Separation problem × Soap formation × Sensitive to FFA and water
NaOH	1.1	7:1	60	0.33	88.8[4]	(Leung and Guo, 2006)	

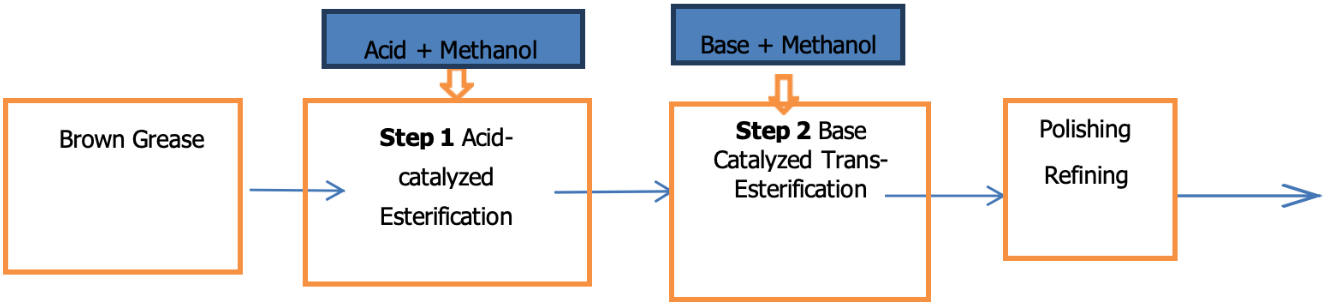
1. ✓ indicates advantage and × indicates disadvantage
2. Values were estimated from Figures 1, 2, and 3. Values were for waste cooking oil
3. Reaction rate of base-catalyzed is 4000 times faster than that of the acid-catalyzed transesterification reaction (Fukuda et al., 2001). Most of the transesterification reaction takes place in the first few minutes at 50 °C
4. Values were for used frying oil (UFO) from Chinese restaurants

Source: EBMUD

Acid- and Base-catalyzed Two-step Process

A two-step process is used to produce biodiesel from feedstock with FFA concentrations above 50 percent.[25] A block diagram of the two-step process is shown in Figure 16.

Figure 17: Block Diagram of Acid-base Two-step Biodiesel Process



Source: EBMUD

The first step esterification reaction converts FFAs to biodiesel and produces water as a waste product. A separation process (typically gravity) is necessary following the reaction to remove water, sulfuric acid and alcohol from the oil. The oil phase is expected to have a low FFA concentration. If the FFA concentration is high, acid esterification step is repeated until FFA content is less than 1 wt percent.[26] Otherwise, high FFA can react with the base catalyst used in the second step (transesterification reaction) to form fatty acid salts, which are commonly used as soaps. These soaps can cause significant product loss, especially if water washing is employed in post separation. Typically, less than 2 percent FFA is recommended for achieving an acceptable biodiesel yield.[27]

Table 6 shows some example biodiesel production methods from brown grease and yellow grease using the acid-base two-step process.

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Table 6: Two-step Acid Esterification Base Transesterification of Brown / Yellow Grease

Catalyst	Step	Catalyst Loading (wt%)	Methanol/Oil Molar Ratio[1]	Temp (°C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[2]
H_2SO_4 Followed by CH_3ONa	Acid	2–5	13:1–19:1 40:1[3]	80	6	97	(Chakrabarti et al., 2008)	✓ Cheap Catalyst ✓ No soap formation × Long reaction time × Separation problem × Sensitive to FFA
	Base	3–5[4]	0:1	~30	4			
$Fe_2(SO_4)_3$ Followed by KOH	Acid	2	10:1	95	4	97	(Wang et al., 2006)	✓ Environmentally friendly compared to sulfuric acid ✓ Easy to separate ✓ More efficient than sulfuric acid ✓ Reusable ✓ Less corrosion
	Base	1	6:1	65	1			
H_2SO_4 Followed by KOH	Acid	0.68	6:1	51	1	90.6	(Charoenchaitrakool and Theinmethangkoon, 2011)	
	Base	1	9.1:1	55	1			
$Fe_2(SO_4)_3$ Followed by CaO	Acid	0.4 g[5]	7:1	60	3	81	(Wan Omar et al., 2009)	✓ Same as above
	Base	NA	7:1	60	3			

1. Methanol:oil means methanol:FFA in acid esterification reaction; and methanol:triglycerides in base transesterification reaction
2. ✓ indicates advantage and × indicates disadvantage
3. 40:1 methanol:FFAs ratio was used in the second acid esterification reaction when necessary
4. 3–5% after neutralizing the remaining FFA
5. 0.4 grams of Fe2(SO4)3 to an unknown amount of oil

Source: EBMUD

Hydrolysis of Triglycerides Followed by Acid-catalyzed Process

This process first hydrolyzes triglycerides to FFAs (lipid hydrolysis), then the FFAs can be converted to biodiesel through acid-catalyzed esterification reaction. Lipid hydrolysis, traditionally used to produce FFAs from triglycerides, can be catalyzed by acid, base, or lipase.[28]

Table 7: Hydrolysis of Fat and Oil to Free Fatty Acids

Method	Catalyst	Pressure	Temp (^{o}C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
Traditional industrial process	None	50 bar	250	2	96%–99%	(Serri et al., 2008)	✓ Very fast reaction rate × High Pressure × High temp × High cost
Catalytic process	Base or acid	NA	65	2	~100%	(Salimon et al., 2011)	× Base reaction followed by acid reaction
Enzymatic hydrolysis	*Aspergillus niger*, *Rhizopus javanicus* and *Penicillium solitum*	Ambient	45	1.5	97%	(Serri et al., 2008; Murty et al., 2002; Salimon et al., 2011)	✓ Mild reaction conditions ✓ Less solvent ✓ Cleaner products (green) × Sensitive to heat and pH

1. ✓ indicates advantage and × indicates disadvantage

Source: EBMUD

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[28] Salimon, J.; Abdullah, B.M.; Salih, N. Hydrolysis optimization and characterization study of preparing fatty acids from *Jatropha curcas* seed oil. *Chem. Cent. J.* **2011,** *5*(1), 1-9.

Solid Heterogeneous Catalysts

Solid catalysts can potentially replace liquid catalysts used in brown grease biodiesel production. Solid catalysts currently used in lab-scale investigations are zeolites, hydrotalcites, metal oxides, and γ-alumina etc.[29], [30]. The main advantages of the solid catalyst are that: (1) it catalyzes the esterification and transesterification reaction simultaneously thus a solid catalyst is particularly useful for feedstocks with high FFA;[31] and (2) it also simplifies the later product separation step. The disadvantage of the solid catalyst is that the reaction rate is slow compared to that of a liquid catalyst.[32]

Table 8: Heterogeneous Solid Catalysts Used in Biodiesel Process (Lam et al., 2010)

Catalyst Type	Catalyst Loading (wt%)	Methanol /Oil Molar Ratio	Temp (^oC)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
SO_4^{2-}/ZrO_2[2]	NA	NA	230	1	85	(de Almeida et al., 2008)	✓ Two steps occur simultaneously ✓ Insensitive to FFA and water ✓ Easy separation × Slow reaction rate × Expensive catalyst
WO_3/ZrO_2	NA	19.4:1	75	20	85	(Park et al., 2008, 2010)	
Sr/ZrO_2	2.7	29:1	115.5	2.8	79.7	(Wan Omar et al., 2011)	
SO_4^{2-}/TiO_2-SiO_2	3	9:1	200	4	90	(Peng et al., 2008)	

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[29] Lam et al. 2010.

[30] Semwal, S.; Arora, A.K.; Badoni, R.P.; Tuli, D.K. Biodiesel production using heterogeneous catalysts. *Bioresour. Technol.* **2011,** *102*(3), 2151-2161.

[31] Kulkarni, M.G.; Dalai, A.K. Waste Cooking Oil–An Economical Source for Biodiesel: A review.*Ind. Eng. Chem. Res.* **2006,** *45*(9), 2901-2913.

[32] *Ibid.*

Catalyst Type	Catalyst Loading (wt%)	Methanol /Oil Molar Ratio	Temp (^{o}C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
SO_4^{2-}/SnO_2-SiO_2	3	15:1	150	3	97	(Lam et al., 2009)	
$H_3PW_{12}O_{40}$ (PW_{12})	3.7	70:1	65	14	87	(Cao et al., 2008)	
$H_3PW_{12}O_{40}/ZrO_2$	10	50:1	NA	2–16	>90	(Melero et al., 2009)	
Cs_2.5H0.5PW12O^{3}40	0.2	5.3:1	65	0.75	99	(Chai et al., 2007)	
Al0.9H0.3PW12O40	3.7	70:1	65	14	87	(Wang et al., 2009)	
ZrHPW (Zr0.7H0.2PW12O40)	2.1	20:1	65	8	98.9	(Zhang et al., 2009)	
K_3PO_4	4	8:1	60	2	97.3	(Guan et al., 2009)	

Catalyst Type	Catalyst Loading (wt%)	Methanol /Oil Molar Ratio	Temp (^{o}C)	Time (h)	Yield (%)	Reference	Advantage & Disadvantage[1]
CaO[4]	0.85	12:1	60-65	1	66	(Kouzu et al., 2008)	
MgO TiO_2-MgO	NA	NA	180	NA	NA	(Di Serio et al., 2006; Wen et al., 2010)	

NA = Not Available

1. ✓ indicates advantage and × indicates disadvantage
2. Catalyst SO_4^{2-} / ZrO_2. Zirconium oxide is used for heterogeneous catalysis for biodiesel production due to its acidic surface property. If the Zirconium oxide is treated with sulfuric acid to become sulfated zirconia (SO_4^{2-} / ZrO_2), the yield of the transesterification of palm kernel oil can reach 90.3 percent, which is much higher than the yield of 64.5 percent when using unsulfated ZrO_2.
3. Using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as the solid catalyst with a low amount of catalyst (0.00185:1) ratio of catalyst to oil, over a 99% yield can be obtained (Chai et al., 2007). $Cs_{2.5}PW$ is not affected by the FFA and water content. In addition, the catalyst and oil can be easily separated after the reaction. This eliminates the need for neutralization and reduces the amount of washing steps needed as compared with homogeneous catalysis
4. CaO was rapidly hydrated and carbonated in the air

Source: EBMUD

Mass transfer limitations currently prevent application of solid catalysts in industrial-scale biodiesel production. It has been suggested that the use of an oscillatory flow reactor (OFR),microwave reactors, ultrasound application, or addition of co-solvents could help overcome the mass transfer limitation.[33]

Supercritical Alcohol

Supercritical alcohol (such as methanol) refers to alcohol at a pressure and temperature above its critical point, where distinct liquid and gas phases do not exist. When methanol is at a supercritical state, catalysts are not necessary for a successful biodiesel production reaction.[34] It has been demonstrated at industrial scale that supercritical methanol could be used to yield a high conversion of waste cooking oil to biodiesel (99.8 percent) and almost pure glycol without any pretreatment of the oil.[35] A comprehensive review of supercritical fluid technologies for biodiesel production was done by Wen et al.[36]

The advantage of the supercritical method is that it can tolerate FFA and water, whose presence often negatively influences the reaction used by other conversion technologies. In addition, the reaction time of supercritical method is very short at only 2–4 min.

The primary disadvantage of the supercritical method is that it requires high temperature (250– 300 ^{0}C) and pressure (as high as 2000 psi)[37], [38] which makes the operation relatively expensive.[39]

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[33] Lam et al. 2010.

[34] Kusdiana, D.; Saka, S. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresour. Technol.* **2004,** *91*(3), 289-295.

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[39] Banerjee, A.; Chakraborty, R. Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—A review. Resour., Conserv. Recycl. 2009, 53(9), 490-497.

Table 9: Supercritical Methanol Method to Make Biodiesel

Mixing of Feedstock (rpm)	Methanol/ Oil Molar Ratio	Pressure	Temp (^{o}C)	Time (min)	Yield (%)	Reference	Advantage & Disadvantage[1]
500	45:1	20 MPa	335	15	89.91	(Shin et al., 2012)	✓ Very fast reaction ✓ High tolerance of FFA and water × High temperature & high pressure × High methanol to oil ratios × Expensive
Not Available	10:1 –50:1	1450 psi	300	15 30	50–65% ~80%	(Patil et al., 2010)	

✓ indicates advantage and × indicates disadvantage

Source: EBMUD

Enzyme Catalyzed Process

Lipases may be used as enzyme catalysts for biodiesel production.[40], [41], [42], [43] Using lipases potentially avoids issues involving treatment and recovery of byproducts of acid/base catalysts. However, lipases in general are significantly more expensive than acid or base catalysts.

Biodiesel Purification

After chemical reactions, biodiesel produced is contaminated with water, residual catalyst, unreacted methanol, glycerin, soaps, and other unknown chemicals potentially present in the feedstock. Biodiesel purification is necessary to meet the ASTM standards.

For homogeneous-catalyzed processes, washing the ester phase with water or neutralizing with mineral acid is usually performed to eliminate residual base catalyst.[44]

Water washing followed by gravity settling is conducted to remove polar compounds including water, methanol, glycerin, and catalysts. As such, a large amount of wastewater is generated from water washing biodiesel product. During settling, two distinct layers would form: a dense lower layer consisting of water, glycerin, and alcohol, and a light upper layer consisting of ester.

Biodiesel Industry

Table 10 summarizes the companies who are probably producing or produced biodiesel from brown grease; Table 11 lists the related process patents.

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[40] Al-Zuhair, S.; Almenhali, A.; Hamad, I.; Alshehhi, M.; Alsuwaidi, N.; Mohamed, S. Enzymatic production of biodiesel from used/waste vegetable oils: Design of a pilot plant.

Renewable Energy **2011,** *36*(10), 2605-2614.

[41] Chen, Y.; Xiao, B.; Chang, J.; Fu, Y.; Lv, P.; Wang, X. Synthesis of biodiesel from waste cooking oil using immobilized lipase in fixed bed reactor. *Energy Convers.Manage.* **2009,** *50*(3), 668-673. DOI: (http://dx.doi.org/10.1016/j.enconman.2008.10.011)

[42] Li, N.-W.; Zong, M.-H.; Wu, H. Highly efficient transformation of waste oil to biodiesel by immobilized lipase from *Penicillium expansum*. *Process Biochem. (Oxford, United Kingdom)* **2009,** *44*(6), 685-688.

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Table 10: Companies Likely Producing/Produced Biodiesel from Brown Grease

Company	Plant Type	Technology	Production Capacity	Address
BioDiesel Technologies GmbH	Commercial	Compact Production Unit (CPU) 3000[1]	3,000 tons/year	Vienna, 1130 Austria
Novozymes	Not Available	Enzymatic biodiesel process	12.6 kGPD[2]	1445 Drew Ave, Davis, CA
BlackGold	Commercial	FOG is chemically converted into biofuel using acid esterification process	30-250 kGPD[2]	1528 Walnut Street, Floor 21, Philadelphia, PA
Biofuel Box	Commercial	NovoStream process[3], plus an adsorption process for contaminants removal		50 Las Colinas Lane San Jose, CA 95119
Dynamic Fuels	Commercial	Hydro	75 MGY[4]	Geismar, LA
Pacific Biodiesel	Commercial	Not Available	Not Available	Salem, Oregon

1. Feedstocks: oils and fats of vegetable and animal origin, used cooking oils
2. kGPD = 1,000 gallons per day
3. NovoStream is a continuous flow, supercritical process that uses high heat and pressure to convert free fatty acids and triglycerides to biodiesel in one pass with high yields
4. MGY = million gallons per year Biodiesel Magazine (http://www.biodieselmagazine.com/articles/9482/low-cost-biodiesel-production)

Source: EBMUD

Table 11: Summary of Patents on Biodiesel Production from Brown Grease

Patent # (USP#)	Company	Feedstock	Process	Technology	Relevant Parameters	Reference
8052848	Penn State Research Foundation	Vegetable oil, waste oil, biomass, algae, animal tallow	Biodiesel production	Microwave + Ultrasonic	Ultrasonic: 22KHz, 30S Microwave: 85 °C, 220S	(Kropf, 2011)
8039652	Carnegie Mellon University	Plant oil, animal oil, yellow grease, and brown grease	Biodiesel production	Radio frequency microwave energy	Fixed bed with homogeneous/ heterogeneous catalysts	(Portnoff et al., 2011)
7897798	McNeff Research Consultants, Inc.	Vegetable oil, animal fats and oils, yellow grease, and brown grease	Biodiesel production	Supercritical alcohol with catalyst	Mixing feed stock with an alcohol, under supercritical conditions for the alcohol	(McNeff et al., 2011)
7871448	Seneca Landlord, LLC (Ames, IA)	Yellow grease, brown grease, trap grease, tallow, and soybean oil	Biodiesel production	Transesterification followed by distillation separation		(Jackam et al., 2011)
7795460	TDA Research, Inc. (Wheat Ridge, CO)	Raw unprocessed feedstocks and waste grease	Biodiesel production	Solid acid catalyst in packed bed reactors	t = 70–120 °C, 85% conversion, distillation separation	(Elliott, 2010)

Patent # (USP#)	Company	Feedstock	Process	Technology	Relevant Parameters	Reference
7722755	ECR Technologies, Inc. (Dublin, GA)	Vegetable oils, animal fats, bio-oils, and combinations thereof	Biodiesel production	High voltage electrical field to catalyze the reaction	Alcohol mixed with oil	(Baosman and Lawson, 2010)
7619104	Renewable Products Development Laboratories, Inc. (Portland, OR)	Brown grease, trap grease, and sewage plant float grease (high triglyceride feedstocks)	Biodiesel production	Process optimization	Two steps	(Clements, 2009)
7384562	Eco Plus Inc. (Charlotte, NC)	Brown grease		Separate brown grease using polymers	Adjust PH = 3~4 Anionic copolymer Cationic copolymer	(Rogers, 2008)
7982078	UOP LLC (Des Plaines, IL)	Plant and animal fats and oils	Biodiesel production	Hydrogenating and deoxygenating	Hot high pressure hydrogen stripper	(Brady et al., 2011)
7935157	Arisdyne Systems, Inc. (Cleveland, OH)	Feedstock with high FFA and triglyceride	FOG Pretreatment	Flow cavitation apparatuses generating hydrodynamic cavitation zones	Alcohol + acid catalyst 70–120 °C Passing through cavitation reduce	(Kozyuk, 2011)

Patent # (USP#)	Company	Feedstock	Process	Technology	Relevant Parameters	Reference
7943791	McNeff Research Consultants, Inc. (Anoka, MN)	Vegetable oil, animal fats and oils, yellow grease, and brown grease	Lipid feedstock extraction	Fatty acid alkyl ester (FAAE) production process itself; can be used as an effective pretreatment to separate desirable feed stock	Heated FAAE as a refining agent Extracted feedstock + metal oxide to produce biodiesel	(McNeff et al., 2011)
7767839	*Philadelphia Fry-o-Diesel,* Inc. (Philadelphia , PA Blackgold biofuel)	Trap grease, used cooking oil, animal fats, and vegetable oil	Biodiesel production	C1–C4 alcohol Acid catalyst Distilling the reacted mixture (to remove methanol)	T = 80–200 °C P = 80–200 psi	(Berry and Ratigan, 2010)
2008/ 0318763	*(BiofuelBox,* Corp)	Animal fats and oils, vegetable oils, yellow grease, and brown grease	Biodiesel production and desulfurization	An adsorbent medium for absorbing non-fatty acid ester contaminants including sulfur	Not Available	(Anderson et al., 2008)

Source:EBMUD

Comparison of Catalytic Technologies Used for Biodiesel Production

The advantages and limitations of using homogeneous catalysis, heterogeneous catalysis, and supercritical methanol methods for biodiesel production from high FFA feedstocks are discussed in this section.

Table 12: Comparison of Biodiesel Production Technologies (Lam et al., 2010)

Catalyst Type	Advantages	Disadvantages
Solid (acid) Catalyst	✓ Insensitive to water and FFAs ✓ Catalyze esterification and transesterification reactions simultaneously ✓ Simplified biodiesel purification process	× Slow reaction rate compared to homogeneous catalysts (Kulkarni and Dalai, 2006)
Supercritical Alcohol	✓ Fast reaction ✓ High biodiesel yield (may reach 90%) ✓ No catalyst is needed ✓ Insensitive to water and FFAs ✓ Short reaction time (2–4 min) (Banerjee and Chakraborty, 2009)	× High temperature (250–300 °C) and high pressure (2000 psi) required (Balat et al., 2008; Helwani et al., 2009)
Acid Catalyst	✓ Insensitive to water and FFAs ✓ Esterification and transesterification occur simultaneously ✓ Mild reaction condition	× Slow reaction rate × "Corrosive" problem × Catalyst separation and regeneration issues
Base Catalyst	✓ Relatively fast reaction ✓ Mild reaction condition ✓ Catalysts recovery problem	× Sensitive to FFAs and water × Soap formation (decreased biodiesel yield)

Source: EBMUD

As discussed earlier and shown here in Table 12, solid catalyst could be the best option if it works successfully to produce biodiesel from high FFA-containing brown grease, because it can: 1) catalyze the esterification and transesterification reactions simultaneously, therefore is particularly useful for feedstocks with high FFAs; (2) allow easy separation of biodiesel product; and (3) simplify the biodiesel purification process. However, the mass transfer limitation makes solid-catalyzed process difficult to scale-up for industrial production. Ultrasonic treatment is a potential technology that could be used to overcome the mass transfer limitation.

Supercritical methanol may be able to replace the two-step acid-based process for converting brown grease to biodiesel; however, the high pressure and high temperature reaction conditions need to be evaluated for industrial-scale production.

Main Factors Affecting Biodiesel Yield

- Amount of alcohol added for reactions. For acid esterification, the optimum molar ratio range is 15–20:1; for transesterification, the optimum molar ratio is ~6:1 with the use of a base catalyst.
- Catalyst concentration. For transesterification, the yield reaches the maximum when the catalyst concentration is 1.5–2 wt percent. The yield then decreases when the concentration of catalyst is increased, potentially due to increased soap formation from increased amount of catalyst dosed.
- Reaction time. Increasing the reaction time increases the yield. A longer reaction time normally requires a larger reactor and consequently a higher capital cost. Both esterification and transesterification require 1–2 hours of reaction time typically. The reaction time is also influenced by the total mass of catalyst dosed.
- Reaction temperature. Higher reaction temperature can decrease the viscosity of oils, and increase esterification reaction rate. However, when the reaction is conducted at atmospheric pressure, the reaction temperature is limited by the methanol boiling point of 65 0C. Therefore, the optimum reaction temperature is between 50–60 0C to prevent excessive alcohol evaporation.
- Water content. Increasing water content can negatively affect both the reaction rate and the extent of acid-catalyzed esterification. Water content can also reduce the rate of base- catalyzed transesterification by reducing the interaction of base and methanol. As such, water content should be kept to a minimum for both reactions.

Biodiesel Specification

Biodiesel standards (ASTM 6751) identify the requirements that pure biodiesel must meet before it can be sold as a fuel.

Table 13: Specification for Biodiesel (B100) (ASTM 6751-11a)

Property	ASTM Method	ASTM Limit
Calcium & Magnesium, combined	EN 14538	5 ppm max[1]
Flash Point (closed cup)	D 93	93 ºC min[2]
Methanol Content	D 93	130 ºC, min
Water & Sediment	D 2709	0.05 (% vol.) max
Kinematic Viscosity, 40 ºC	D 445	1.9–6.0 mm^2/sec

Property	ASTM Method	ASTM Limit
Sulfated Ash	D 874	0.02 (% mass) max
Sulfur (S 15 grade)	D 5453	15 ppm max
Sulfur (S 500 grade)	D 5453	500 ppm max
Copper Strip Corrosion	D 130	No. 3 max
Cetane	D 613	47 min
Cloud Point	D 2500	Report
Carbon Residue 100% sample	D 4530	0.05 (% mass) max
Acid Number	D 664	0.5 mg KOH/g max
Free Glycerin	D 6584	0.020 (% mass) max
Total Glycerin	D 6584	0.240 (% mass) max
Phosphorus Content	D 4951	0.001 (% mass) max
Distillation	D 1160	360 °C max
Sodium/Potassium, combined	EN 14538	5 ppm max
Oxidation Stability	EN 15751	3 hours min
Cold Soak Filtration	D 7501	360 seconds max

1. Max = Maximum; 2. Min = Minimum

Source: EBMUD

Literature Review on Sulfur in Brown Grease-derived Biodiesel

High sulfur content is a major concern of brown grease being a biodiesel feedstock. Sulfur content in brown grease was measured to be 300–400 ppm, and 200 ppm in the biodiesel made from it.[45] Kim et al. (2010)[46] reported a 640 ppm sulfur in brown grease and 303 ppm in brown grease biodiesel. Jiang (2011)[47] indicated that sewer brown grease has very high sulfur levels, typically well above 10,000 ppm.

Potential Sulfur Compounds in Biodiesel Feedstock

It is important to know the types of sulfur compounds present in biodiesel feedstock, so that effective removal technologies can be selected or designed. However, very limited knowledge is available with respect to sulfur sources and sulfur compounds in brown grease biodiesel. The following are presumed to contribute to the total sulfur present in brown grease biodiesel.

Fat and oil: He et al.[48] investigated sulfur contents in feedstocks, seed meals, oils/fats, and biodiesel made from different feedstocks. Selected data are summarized in Table 14.

Table 14: Sulfur in Biodiesel Made from Different Feedstocks (He et al., 2008, 2009)

Feedstock		Sulfur in Feedstock (ppm)	Sulfur in Biodiesel (ppm)
Vegetable Oil from	Avocado	24.8	6.3
	Candlenut	1.1	0.7
	Canola	5.5	3.0
	Corn	18.6	13.8
	Crambe	11.2	7.2
	Croton	3.4	0.5
	Jatropha	4.9	2.4
	Karanja	22.9	10.4
	Mustard[1]	3.5	2.5
	Palm, Olein	3.2	2.3
	Palm, crude	9.7	7.5
	Rapeseed	11.2	2.4
	Soybean	5.7	1.1

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[45] Chakraparti et al. 2008.

[46] Kim et al. 2010.

[47] Jiang, R. Brown Grease Treatment Processes. U.S. Patent 20110197497 A1, August 18, 2011.

[48] He, B.B.; Van Gerpen, J.H. *Biodiesel Quality Affected by Sulfur Content Originated by Different Feedstocks and a Database for the Same*; KLK432, N08-04; DTRS98-G-0027; Final Report for NIATT, University of Idaho; National Institute for Advanced Transportation Technology, University of Idaho: Moscow, ID, 2008. (http://www.webs1.uidaho.edu/niatt/research/Final_Reports/KLK432_%20N08-04.pdf) (accessed 2012).

Feedstock	Sulfur in Feedstock (ppm)	Sulfur in Biodiesel (ppm)
WVO[2], cook line	21.4	7.2
WVO[2], fryer vapor	15.7	6.3
Fish oil	18.8	10.8
Render	14.7[3]	3.9[3]
Tallow, crude	29.4	12.6

1. Average mustard cultivar of Ida Gold and Pacific Gold
2. WVO – waste vegetable oil
3. Average of render batch #1,2,4,7 and 11

Source: EBMUD

Table 14 shows that sulfur content in biodiesel made from vegetable oil, animal fat or tallow varies with feedstock but falls between 0.5–13.8 ppm, well below what was found in brown grease biodiesel of ~200 or ~300 ppm.[49], [50] Because of this, these feedstocks are unlikely to be a major source accounting for the high sulfur content found in the brown grease-derived biodiesel.

The chemical nature of the sulfur compounds in vegetable oil is not fully understood. The sulfur compounds are suspected to be the hydrolysis products of glucosinolates present in the seeds.

When the glucosinolates undergo enzymatic decomposition, isothiocyanates, thiocyanates and possibly sulfates and sulfides may be produced.

Food (protein): Cysteine and methionine are two sulfur-containing amino acids incorporated into proteins. Cysteine is found in most high-protein foods such as meat, eggs, dairy, garlic, and onions. High levels of methionine can be found in eggs, Brazil nuts, fish, meats, sesame seeds, and other plant seeds.

Detergents: Non-volatile sulfur compounds could also contribute to total sulfur in brown grease biodiesel:

- **Sodium dodecylbenzenesulfonate** ($C_{18}H_{29}NaO_3S$) is a colorless salt commonly used as a surfactant in hand-soaps and detergents in restaurants and households.
- **Sodium lauryl sulphate (sulphuric acid monododecyl ester sodium salt)** ($C_{12+2n}H_{25+4n}NaO_{4+n}S$) is an emulsifying agent used in metal processing, detergents,

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[49] Chakrabarti et al. 2008.

[50] Kim et al. 2010.

shampoos, creams, pharmaceuticals and foods.

Sulfuric Acid: Sulfuric acid used during esterification reaction may also contribute to the high sulfur level detected in the brown grease biodiesel.

Sulfur Testing Methods

High resolution gas chromatography (GC) with sulfur selective detectors provides a rapid means to identify and quantify sulfur compounds in various petroleum feeds and products. The sulfur selective detectors, such as flame photometric detector (FPD) and sulfur chemiluminescence detector (SCD), pulse flame photometric detector (PFPD), atomic emission detector (AED), and FT-ICR-MS etc., have been used for detailed analysis of different types of sulfur species present in diesel.[51] These methods are shown as follows:

ASTM D5623

- GC with sulfur chemiluminescence detection
- Applicable to petroleum liquids with a final boiling point of approximately 230
- ^{0}C (450 ^{0}F) or lower
- Applicable to the determination of individual sulfur species at levels of 0.1 to 100 mg/kg

ASTM D6228

- GC with flame photometric detector or a pulsed flame photometric detector
- The detection range for sulfur compounds is from 20 to 20,000 picograms (pg) of sulfur. This is equivalent to 0.02 to 20 mg/m3 or 0.014 to 14 ppmv of sulfur based on the analysis of a 1-mL sample.

✓ **ASTM D5453** – Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence. This is the specified sulfur testing method in the **ASTM 6751**-11a biodiesel standards.

✓ **ASTM D2622** – Sulfur in Petroleum Products by X-Ray Spectrometry

✓ **ASTM D7039** – Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

✓ **ASTM D3120** – Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

✓ **Others:** ASTM D2784, D3246, D3961, D4468, D6212, D6667

Biodiesel Desulfurization Methods

Limited information was available in literatures on sulfur removal technologies for meeting the ASTM 6751 ultra-low 15 ppm sulfur standard in FOG- and brown grease-derived biodiesel.

In 2008, EBMUD conducted a bench-scale study to investigate sulfur reduction through the biodiesel making process.[52] The total sulfur levels were found to be between 300–400 ppm in the feedstock (brown grease) and approximately 200 ppm in the biodiesel product,

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[51] Stanislaus, A.; Marafi, A.; Rana, M.S. Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. Catal. Today 2010, 153(1), 1-68.

[52] Chakrabarti et al. 2008

corresponding to an approximate 40 percent sulfur reduction, though the removal mechanism is unknown. In the same study, EBMUD also explored several sulfur removal methods; results from these trials are summarized in Table 15.

Table 15: EBMUD Biodiesel Sulfur Removal Tests (Chakrabarti et al., 2008)

Sulfur Removing Methods	Sulfur Removal Efficiency[1]
1-h Air Stripping at 41 °C	13% (from 364 to 318 ppm S)
18-h Air Stripping at 20 °C	33% (from 391 to 261 ppm S)
Biodiesel Distillation into 7 Fractions (ASTM D2892)	Reduced sulfur levels significantly by vacuum distillation (from 251 to 19–25 ppm S in the distillated biodiesel)
Adsorption with Diatomaceous Earth	Not effective
Powdered Activated Carbon Batch Treatment[2]	37–57% (from 182 to 114 ppm for biodiesel) (from 19–48 to 12–23 ppm S in the distillated biodiesel)

1 Sulfur content was determined using either ASTM D5453 (for levels below approximately 50 ppm) or ASTM D4294 method

2 Reaction condition: activated carbon was applied to biodiesel at 25% (w/v of biodiesel), the mixture was heated to 100 ºC and stirred for 21.5 hours, then the mixture was settled, decanted and filtered

Source: EBMUD

Anderson (2008)[53] investigated regeneration of spent metal oxides and metal silicates used in biofuel industry for removing various contaminants including sulfur compounds. He found that by using a "U" shape adsorbent column filled with adsorbent mixture of Davisil silica (15.2g) followed by Camag 507 neutral alumina (84.8 g) (Example 11), sulfur content was reduced from 116 ppm in biodiesel made using supercritical methanol down to 12 ppm.

Berry and Ratigan (2010)[54] reported that the top fraction of distillated biodiesel (at 1.5 torr), made from restaurant trap grease using sulfuric acid catalyzed esterification reaction, had a low sulfur concentration of only 3 ppm, and met the ultra-low sulfur limit of 15 ppm (max).

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[53] Anderson, G. System for Production and Purification of Biofuel. U.S. Patent 20080318763 A1, December 25, 2008.

[54] Berry, W.W.; Ratigan, B.J. Process of Making Alkyl Esters of Free Fatty Acids. U.S. Patent 7,767,839 B2, August 3, 2010.

Kim et al. (2011)[55] investigated the desulfurization method for brown grease and biodiesel at bench-scale, and reported that the sulfur level (640 ppm) in brown grease was reduced to 303 ppm via methanolysis of the ester-sulfates and sulfonates over ZnO/ZrO_2 catalyst. He also showed that an acid wash process could reduce sulfur in brown grease by 33 percent, from 640 to 428 ppm. The acid wash process included brown grease treatment with 1.2 N HCl (1:1 v/v) at 23 ^{0}C for 10 minutes, followed by phase separation and water wash.

Jiang (2011)[56] developed a method to reduce sulfur and free fatty acids in brown grease biodiesel by contacting crude biodiesel with an insoluble base (metal oxide, metal hydroxide, metal silicate) to form adducts of sulfur-insoluble base and FFA-insoluble base for removal by filtration and/or centrifugation. Using this method, the sulfur level in the treated biodiesel was found to be as low as 13 ppm (Example 7). In this example, the brown grease (519 g) extraction included a steam treatment at 134 ^{0}C for 10 min, cooling, filtering, settling and dewatering. The dewatered brown grease was converted to crude biodiesel by a 2-stage solid-catalyzed esterification (Dowex 50W) reaction followed by transesterification reaction catalyzed by sodium hydroxide. The crude biodiesel was first treated by 1 wt percent calcium oxide at 60 ^{0}C for 10 min followed by centrifugation, and the step was repeated one more time. It was then treated by ~1 wt percent zeolite at 60 ^{0}C for 2 hours followed by a series of filtration steps.

In July 2013, the EBMUD project team discovered that RPM Sustainable Technologies (RPM) (http://rpmst.com/) developed a new cost-effective technology for low energy conversion of FOG to ASTM biodiesel (S-15 grade). A full-scale system (0.2 MGY) was under construction at the Torrington Water Pollution Control Authority, CT, and was expected to be operational by June 2014. An EBMUD FOG sample was sent to RPM staff to test their proprietary process, and was told that they were able to successfully remove the total sulfur in biodiesel made from the EBMUD FOG sample down to 16 ppm. With some process modifications, total sulfur was further reduced to 9 ppm. This technology may offer a cost- effective solution for converting FOG to ASTM biodiesel for WWTPs, with an estimated capital cost of $1,000,000 and processing cost of $1/gallon biodiesel produced, based on conversations with the RPM staff.

Diesel Desulfurization Technologies

Because of limited information available on biodiesel desulfurization, literature review for this study was expanded to cover low-cost petroleum diesel desulfurization technologies, for which significant advances had been made over the past decade. This section reviews these recent Ultra-Low Sulfur Diesel (ULSD) technologies, bearing in mind that the types of sulfur compounds present in diesel are likely to be different with those present in biodiesel.

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[55] Kim et al. 2011.

[56] Jiang. 2011.

Organic sulfur compounds in commercial diesel are generally classified as thiophenes, phenyl sulfides, benzothiophenes (BT), dibenzothiophenes (DBT), and alkyl dibenzothiophenes. DBT are usually the most refractory sulfur containing compounds.[57]

Diesel desulfurization can be classified into two main groups based on the usage of hydrogen. In hydrodesulfurization (HDS), hydrogen is used to decompose organosulfurs. HDS is a catalytic chemical process to remove sulfur at elevated temperature ranging from 300 to 400 °C, and elevated pressure ranging from 30 to 130 atm (Stanislaus et al., 2010). The disadvantages of HDS are that it requires high temperature up to 400 °C and high hydrogen pressure up to 100 atm, use of metal catalysts, and large reactors due to long retention times— resulting in higher operational costs (Duarte et al., 2011). Since this study was to research low-cost brown grease- to-biodiesel method, HDS processes were not further considered.

The non-HDS diesel sulfur removal methods found in literatures can be categorized as: (1) Precipitation desulfurization; (2) Extractive desulfurization; (3) Adsorptive desulfurization; (4) Oxidative desulfurization; or (5) Biodesulfurization.

Precipitation Desulfurization

Precipitation desulfurization is based on the formation and subsequent removal of insoluble complexes. Sulfur containing fuel was treated by 2,4,5,7-tetranitro-9-fluorene in a batch reactor, a subsequent filtration step was applied to remove the insoluble complex. The drawback of this method is that the sulfur removal efficiency was only 20 percent.[58]

Extractive Desulfurization

Extractive desulfurization is possible because organosulfur compounds are more soluble than hydrocarbons in an appropriate solvent. At low temperature and low pressure, mixing oil with a selected solvent will allow sulfur compounds to transfer from the fuel oil into the solvent due to their higher solubility in the solvent. Sulfur is then removed when the solvent is separated from the fuel oil. Solvents studied include acetone, ethanol, polyethylene glycols, and nitrogen containing solvents.[59] Solvent selection is critical and dependent on the spectrum of organosulfur compounds possibly present in the feedstock. Extractive desulfurization methods investigated are summarized in Table 16.

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[57] Hanafi, S.A.; Mohamed, M.S. Recent Trends in the Cleaning of Diesel Fuels via Desulfurization Processes. *Energy Sources, Part A* **2011,** *33*(6), 495-511.

[58] Babich, I.V.; Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review☆. *Fuel* **2003,** *82*(6), 607-631.

[59] *Ibid.*

Table 16: Summary of Extractive Desulfurization

Rank	Extraction Media	Operating Parameter	Extraction Media:Oil	Advantage and Disadvantage[1]	Reference
1	Methanol (n = 3)	Room temperature and pressure	25 mL:25 mL (1:1 v/v)	✓ Simple ✓ Cheap × 40% removal efficiency	(Mello et al., 2009)
2	Acetone Acetonitrile	Room temperature and pressure	NA[2]	✓ Simple ✓ Relatively cheap ✓ Relatively low boiling point and easily separated by distillation	(Wan and Yen, 2007)
3	Various solvents and blend of solvents	Low temperature and pressure	NA[2]	✓ Low temperature and pressure ✓ 50–90% sulfur removal efficiency	(Babich and Moulijn, 2003)

1. ✓ indicates advantage and × indicates disadvantage; 2. NA: Not Available

Source: EBMUD

Adsorptive Desulfurization (ADS)

Solid sorbents can potentially remove organosulfur compounds present in liquid fuels. There are two types of adsorption processes considered here: physical adsorption and reactive adsorption. In physical adsorption, the interacting force between sulfur compounds and solid sorbent surface is the relatively weak van der Waals forces.[60] Adsorbents that have been used for physical adsorption are silica-alumina, silica gel, activated carbon, molecular sieves, g-Al_2O_3, zeolites, and ZSM-5.[61] For reactive adsorption, sulfur compounds and the sorbents form chemical bonds. The sorbents such as Cu-ZnO, Ni- Al_2O_3, Ni-ZnO, Ni-SiO_2, Ni-SBA-15, and Ni-ZnO have been used as reactive adsorbents, where Ni-ZnO has been demonstrated to have the best performance.[62]

Adsorption efficiency is determined by the adsorbent capacity, selectivity for organosulfur compounds, durability and regenerability. Table 17 summarizes the current development of adsorptive desulfurization.

Table 17: Adsorptive Desulfurization Test Conditions and Results

Diesel Fuel Type	Sorbent	Test Parameter		Initial Sulfur (ppmw)	Sorbent Capacity	Removal Efficiency	Reference
		Temp (°C)	Time (h)				
Model	Zeolites + transition metals + mixed metal oxides + activated carbon	60		220	3.5 mg S/g- sorbent		(Song, 2003)
Model	Zeolites + activated carbon (fixed bed)	25		687	6.2 g-F/g-A[1]		(Kim et al., 2006)
	Activated alumina ~150 um	25		687	1.4 g-F/g-A[1]		
	$Ni/SiO_2-Al_2O_3$ 150-250 um	25		687	1.6 g-F/g-A[1]		

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[60] Pawelec, B.; Navarro, R.M.; Campos-Martin, J.M.; Fierro, J.L.G. Retracted article: Towards near zero-sulfur liquid fuels: a perspective review. *Catal. Sci.Technol.* **2011,** *1*(1), 23-42.

[61] Stanislaus et al. 2010.

[62] *Ibid.*

Diesel Fuel Type	Sorbent	Test Parameter		Initial Sulfur (ppmw)	Sorbent Capacity	Removal Efficiency	Reference
		Temp (°C)	Time (h)				
Commercial	Activated carbon (fixed bed)	75		400	~2 mL/g-AC[2]		(Bu et al., 2011)
Model	MOF:Basolite F300 ($C_9H_3FeO_6$), 1g/100g	31	72	1724	24 g S/kg	~6 times higher than AC[2]	(Blanco-Brieva et al., 2010)
	Basolite C300 ($Cu_3(C_9H_3O_6)_2$)	31	72	1724	45 g S/kg	~8 times higher than AC[2]	
	Basolite A100 ($Al(OH)(C_8H_4O_4)$)	31	72	1724	38 g S/kg		
Model DBT	Activated alumina Mixing = 120 rpm	30	24	500 (100–1000)	20 g/L adsorbent dose	~58%	(Srivastav and Srivastava, 2009)
Model	Zirconia (ZD383), calcined (ZC893), sulfated and calcined (SZC893), 300 rpm	30–45	22	500 (30–1000 mg/L)	optimal adsorbent dose 10 g/L	~45–55%	(Kumar et al., 2011)
Model	Norit SXRO PLUS AC 300	30–70		27	0.0824–0.1526 mg S /g-sorbent	8.8–12.7 ppmw S (53–63%)	(Muzic et al., 2010)
Commercial ULSD	Ni-sorbent, fixed bed[3]	200		6	2 mg S/g sorbent		(Pieterse et al., 2011)
Commercial ULSD	MCM-48 + Ni-sorbent, fixed bed	220		14.5	2.1 mg-S/g- sorbent		(Sentorun- Shalaby et al., 2011)

1. g-F/g-A = gram fuel per gram of adsorbent;
2. AC = Activated Carbon;
3. Reaction was conducted under high pressure (7 atm)

Source: EBMUD

Oxidative Desulfurization (ODS)

The ODS process includes two steps: (1) oxidation to selectively convert organosulfur compounds into sulfones or sulfoxides by oxidizing agents. This is possible since organosulfurs are slightly more polar than hydrocarbons, oxidizing these sulfur compounds is much easier than oxidizing hydrocarbon fuels, and (2) subsequent sulfur removal to remove sulfones or sulfoxides which are more polar than organosulfur compounds and thus can be removed by distillation, adsorption or solvent extraction.

ODS reaction: ODS is conducted under relatively low temperature (<100 ^{0}C) and ambient pressure with reasonably low cost of operation.[63] Oxidants such as hydrogen peroxide,[64], [65], [66] ozone,[67] t- butyl hydroperoxide[68], [69], and t-butyl hypochlorite[70] are typically used for ODS. Hydrogen peroxide (H_2O_2) is the most environmentally friendly option and has been widely used for sulfur removal from diesel. When handling hydrogen peroxide, its concentration is generally limited to less than 50 percent for safety reasons and concerns over loss of oil quality.[71] H_2O_2 is a slow reacting oxidant but it becomes more efficient when catalysts are added to the reaction. The catalysts used for ODS can be classified as homogeneous and heterogeneous catalysts. The combined H_2O_2/catalyst methods include:

- H_2O_2/inorganic acids[72]

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[63] Duarte, F.A.; Mello, P. de A.; Bizzi, C.A.; Nunes, M.A.G.; Moreira, E.M.; Alencar, Maurício S.A.; Motta, H.N.; Dressler, V.L.; Flores, É.M.M. Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process. *Fuel* **2011,** *90*(6), 2158-2164.

[64] Nanoti, A.; Dasgupta, S.; Goswami, A.N.; Nautiyal, B.R.; Rao, T.V.; Sain, B.; Sharma, Y.K.; Nanoti, S.M.; Garg, M.O.; Gupta, P. Mesoporous silica as selective sorbents for removal of sulfones from oxidized diesel fuel. *Microporous and Mesoporous Mater.* **2009,** *124*(1), 94- 99.

[65] Otsuki, K.; Hirono, T.; Omori, M.; Sakaguchi, M.; Tanigawa, W.; Lin, W.; Soh, W.; Rong, S.-S. Analyses of pseudotachylyte from Hole-B of Taiwan Chelungpu Fault Drilling Project (TCDP); their implications for seismic slip behaviors during the 1999 Chi-Chi earthquake. *Tectonophysics* **2009,** *469*(1), 13-24.

[66] Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction. *Energy Fuels.* **2000,** *14*(6), 1232-1239.

[67] *Ibid.*

[68] Chica, A.; Corma, A.; Dómine, M.E. Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *J. Catal.* **2006,** *242*(2), 299-308.

[69] Wang, J.; Yang, J.; Wan, C.; Du, K.; Xie, J.; Xu, N. Sulfur Composite Cathode Materials for Rechargeable Lithium Batteries. *Adv. Funct. Mater.* **2003,** *13*(6), 487-492.

[70] Stanislaus et al. 2010.

[71] Wu, Z.; Ondruschka, B. Ultrasound-assisted oxidative desulfurization of liquid fuels and its industrial application. *Ultrason. Sonochem.* **2010,** *17*(6), 1027-1032.

[72] Haw, K.-G.; Bakar, W.A.W.A.; Ali, R.; Chong, J.-F.; Kadir, A.A.A. Catalytic oxidative desulfurization of diesel utilizing hydrogen peroxide and functionalized-activated carbon in a biphasic diesel–acetonitrile system. Fuel Process. Technol. 2010, 91(9), 1105- 1112.

- H_2O_2/organic acids[73], [74]
- H_2O_2/heteropolyanion catalysts[75]
- H_2O_2/photocatalysts [76], [77]

In the ODS reaction, the order of S-compound reactivity differs with the different oxidants. For example, when using H_2O_2-formic acid as an oxidant, the order of sulfur compounds reactivity becomes: methyl phenyl sulfide > thiophenol > diphenyl sulfide > 4,6-DMDBT > 4-MDBT > DBT > BT.

According to Wu and Ondruschka[78] (2010), the efficiency of ODS follows the order of H_2O_2–HCOOH > H_2O_2–CH_3COOH > H_2O_2–H_3PO_4 or >CH_3CH_2COOH.

Extraction/Adsorption: After oxidation, formed sulfones or sulfoxides can be removed by subsequent extraction. The solvents used to extract sulfones are methanol, acetone, acetonitrile, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and sulfolane (Stanislaus et al., 2010). Haw et al. (2010)[79] compared acetonitrile and methanol, and concluded that acetonitrile has higher extraction efficiency than methanol.

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[73] Yu, G.; Lu, S.; Chen, H.; Zhu, Z. Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon. *Carbon* **2005,** *43*(11), 2285-2294.

[74] Al-Shahrani, F.; Xiao, T.; Llewellyn, S. A.; Barri, S.; Jiang, Z.; Shi, H.; Martinie, G.; Green, M. L.H. Desulfurization of diesel via the H2O2 oxidation of aromatic sulfides to sulfones using a tungstate catalyst. *Appl. Catal., B* **2007,** *73*(3), 311-316.

[75] Collins, F.M.; Lucy, A.R.; Sharp, C. Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis. *J. Mol. Catal. A: Chem.* **1997,** *117*(1-3), 397-403.

[76] Matsuzawa, S.; Tanaka, J.; Sato, S.; Ibusuki, T. Photocatalytic oxidation of dibenzothiophenes in acetonitrile using TiO2: effect of hydrogen peroxide and ultrasound irradiation. *J. Photochem. Photobiol., A* **2002,** *149*(1), 183-189.

[77] Sachdeva, T.O.; Pant, K.K. Deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst. *Fuel Process. Technol.* **2010,** *91*(9), 1133- 1138.

[78] Wu, Z.; Ondruschka, B. Ultrasound-assisted oxidative desulfurization of liquid fuels and its industrial application. *Ultrason. Sonochem.* **2010,** *17*(6), 1027-1032.

[79] Haw et al. 2010.

The adsorption can also be used after the ODS reaction. The adsorbents used include silica- alumina, silica gel, activated carbon, molecular sieves, Al_2O_3, zeolites, and ZSM-5.[80] Stanislaus also reported that silica-alumina and silica gel were more effective for the adsorption of sulfur compounds based on results of a study conducted by Otsuki.[81].

Table 18: Ultra-Low Desulfurization Technology and Reaction Conditions in Catalyst-Assisted Oxidative Desulfurization Process

Oxidant + Catalyst	Operating parameters				Diesel Type & ppm	Sulfur Removal	Reference	Advantage & Disadvantage[1]
	Mix rpm	Temp (°C)	Time (h)	Extractant				
H_2O_2 + formic acid + activated carbon[2]	750	60	1	Activated carbon adsorption	Model (DBT) 800 ppm	98%	(Yu et al., 2005)	✓ Mild condition[3] × Long hours × PH <2
H_2O_2 + acetic acid + activated carbon[2]	Vigorous stir	50	1 (x3)	Acetonitrile	Commercial 2189 ppm	91.3%	(Haw et al., 2010)	
H_2O_2 + phosphor-tungstic acid	1000	70	2.5	Not available	Commercial 325 ppmw	98%.	(Sachdeva and Pant, 2010)	✓ Highly active and selective × Expensive
H_2O_2 + acid $Q_4W_{10}O_{32}$, etc		60	0.5	DMF[4]	Model DBT 1000 ppm	93.5%	(Jiang et al., 2009)	
H_2O_2 + acetic acid $+Na_2WO_4$	Vigorous stir (300)	70	~1	Methanol	Model 1100 ppm	96.4%	(Al-Shahrani et al., 2007)	

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[80] Stanislaus et al. 2010

[81] Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction. Energy Fuels. 2000, 14(6), 1232-1239.

Oxidant + Catalyst	Operating parameters				Diesel Type & ppm	Sulfur Removal	Reference	Advantage & Disadvantage[1]
	Mix rpm	Temp (°C)	Time (h)	Extractant				
H_2O_2 +H_3PO_4 + Mo/γ-Al_2O_3		60	1.25	1-methyl-2-pyrrolidone	Commercial 320 ppm	97.8%	(Garcia-Gutierrez et al., 2008)	
Air + Tert-butyl hydroperoxide[4] + isobutyl aldehyde	Stirred	60	0.75	Acetonitrile	Model DBT = 403 ppm	96.8%	(Guo et al., 2011)	✓ Simple, efficient ✓ No metal catalysts ✓ Mild condition[3]

1. ✓ indicates advantage and × indicates disadvantage

2. In the ODS reaction with H_2O_2 + formic or acetic) acid + activated carbon (AC), the organic acid provides an acidic medium for ODS processes and stabilizes hydrogen peroxide by forming peroxyacetic acid which is more stable at high temperature (Haw et al., 2010). Activated carbon has a large surface area, a porous nature and is widely used for adsorption. With the existence of organic acid, activated carbon also activates hydrogen peroxide to generate hydroxyl radicals, which is a very strong oxidant to convert the organosulfur compounds to sulfones (Yu et al., 2005)

3. Ambient pressure and moderate temperature (35–60 ^{0}C)

4. DMF = N,N-dimethylformamide; tert-butyl hydroperoxide (organic peroxide)

Source: EBMUD

In summary, ODS, especially catalytic oxidation desulfurization, has been a promising technology for removing organosulfur from diesel oil at relatively low temperature and pressure. The advantages of ODS are: (1) low reaction temperature and ambient pressure; and higher reactivity of the alkyl DBTs compared with HDS process. The main obstacles limiting ODS in industrial applications are: (1) relatively low oxidation activity and low selectivity of organosulfur compounds in oil; (2) difficulty in recovering catalysts; and (3) probability of introducing other compounds that may require removal in order to meet fuel standards.[82]

Ultrasound Assisted ODS (UAODS)

The use of ultrasound can enhance the ODS reaction rate and increase sulfur removal efficiency under mild temperature and pressure. For example, Mei et al. (2003)[83] found the conversion of sulfur to sulfone enhanced when ultrasound was applied. Ultrasound assisted oxidative desulfurization may play an important role in making ultra-low sulfur fuels.

UAODS mechanism: Ultrasonic waves of high intensity in liquids cause acoustic cavitation. Formation and subsequent collapse of cavitation bubbles create extreme local conditions of high temperatures (up to 5000 K) and pressures (up to 1000 atm).[84] Such conditions facilitate the reaction between oxidants and sulfur compounds in the oil.[85] It may also create active chemical intermediates that could generate radicals to break chemical bonds and enhance mass transfer.[86]

Factors influencing UAODS: Factors include: (1) ultrasonic frequency and power; (2) ultrasonic treatment time; (3) oxidizing agent type and amount;[87] (4) catalysts; and (5) extractant[88] and adsorbent types.[89]

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[82] Jiang, R. Brown Grease Treatment Processes. U.S. Patent 20110197497 A1, August 18, 2011.

[83] Mei, H.; Mei, B.W.; Yen, T.F. A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization☆. *Fuel* **2003,** *82*(4), 405-414.

[84] Wu, Z.; Ondruschka, B. Ultrasound-assisted oxidative desulfurization of liquid fuels and its industrial application. *Ultrason. Sonochem.* **2010,** *17*(6), 1027-1032.

[85] Mello, P. de A.; Duarte, F.A.; Nunes, M.A.G.; Alencar, M.S.; Moreira, E.M.; Korn, M.; Dressler, V.L.; Flores, É.M.M. Ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock. *Ultrason. Sonochem.* **2009,** *16*(6), 732-736.

[86] Duarte et al. 2011.

[87] *Ibid.*

[88] Duarte et al. 2011.

[89] Wu et al. 2010.

Table 19: Ultrasound-Assisted Oxidative Desulfurization Reaction Conditions

Oxidant + Catalyst	Ultrasonic		Operation Parameters			Extractant	Fuel Type and Sulfur Conc.	Sulfur Removal Efficiency	References
	Power	Frequency	Time (min)	pH	Temp (°C)				
H_2O_2 + acetic acid	750 W	20 kHz	9	NA	90	Methanol	Commercial 136–249 ppm	75–88%	(Duarte et al., 2011; Mello et al., 2009)[1]
	Ultrasound not applied		9	NA	90	Methanol	Commercial 136–249 ppm	55%	
H_2O_2 + acetic acid + $FeSO_4$ (Fenton's reagent)	200 W	28 kHz	15	2	60	DMF[2]	Commercial 1936.48 ppm 1162 ppm	95.2%	(Dai et al., 2011)
H_2O_2 + acetic acid + $CuSO_4$								89.2%	
H_2O_2 + H_2SO_4/H_3PO_4 + $FeSO_4$	200 W	28 kHz	9	NA	50-60	DMF[2]	1936 ppm	>95%	(Wu and Ondruschka, 2010)
H_2O_2 + phosphotungstic acid	600 W	20 kHz	10–18	NA	75	Acetonitrile	Commercial 1670–1867 ppm	98–99%	(Mei et al., 2003)
H_2O_2 + phosphotungstic acid + tetraoctylammonium fluoride	NA	20 kHz	10	NA	70	Acetonitrile	Model 1710 ppm	>95%	(Wan and Yen, 2007)

Oxidant + Catalyst	Ultrasonic		Operation Parameters			Extractant	Fuel Type and Sulfur Conc.	Sulfur Removal Efficiency	References
	Power	Frequency	Time (min)	pH	Temp (°C)				
H_2O_2 + TiO_2 (photocatalyst)	50 W	45 kHz	0–600	NA	25–80			Varies	(Matsuzawa et al., 2002)

NA = Not Available

1. Duarte et al. (2011) applied an UAODS process to diesel oil and petroleum product feedstock containing model sulfur compounds (benzothiophene, dibenzothiophene, and dimethyldibenzothiophene). The influence of reaction parameters and ultrasound treatment (20 kHz and 750 W, operating at 40%) was investigated in a batch laboratory system. Using the optimized UAODS, high sulfur removal (up to 99% for model compounds in petroleum product feedstock, and 75% for diesel

   oil samples) was achieved using a molar ratio of H2O2 (50 wt%): acetic acid: sulfur of 64:300:1, after 9 min of ultrasound treatment at 90 ^{0}C, followed by extraction with methanol at an optimized solvent:oil ratio of 0.36. Ultrasonic treatment significantly improved the sulfur removal from 55% (without ultrasound treatment) to higher than 75% for diesel oil samples with ultrasound pretreatment.
2. DMF = Dimethylformamide

Source: EBMUD

Diesel ODS and UAODS Patents

There are more than 30 patents on the diesel fuel ODS and UAODS processes, some of which have been commercialized.[90] Table 20 provides a summary of selected patents.

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[90] Stanislaus et al. 2010.

Table 20: Patented Diesel Ultra-Low Desulfurization Technology and Reaction Conditions

US Patent #	Company	Technology	Relevant Parameters	Advantages & Disadvantages[1]	References
6402939 6827844	SulphCo Inc.[2]	H_2O_2 + Ultrasonic	Ultrasonic: 20–50 kHz, 1–10 min T <100 °C	✓ High yield ✓ No catalysts × Sonication cost	(Gunnerman, 2004; Yen et al., 2002)
6402940	Unipure Corporation	H_2O_2 + Formic acid	P = 1 atm, T = 50–130 °C, <15 min 500 ppm -> <8 ppm S	✓ Low cost ✓ Short reaction time	(Rappas, 2002)
7744749	Saudi Arabian oil company	H_2O_2 or other oxidants	T = 50–150 °C, 800 ppm -> <10 ppm S product Continuously	✓ Continuous	(Martinie et al., 2010)
7758745	Not Available	H2O2 + Catalysts (Acetic acid/ trifluoro acetic acid)	Ambient pressure T <200 °C, 99% S removal	✓ Fluidized bed reactor ✓ Ultrasound/mixing × Chemical cost	(Cheng, 2010)
2008-0047875	Lyondell Chemical Process	t-butyl-hydroperoxide	<200 °C, <100 bar, 10 min 500 ppm -> <10 ppm S	× High pressure × High catalysts cost	(Karas et al., 2008)

1. ✓ indicates advantage and × indicates disadvantage
2. The sonocracking process, patented by SulphCo Process, combines ultrasound technology with propriety catalysts to remove sulfur compounds in diesel fuel. The diesel fuel is mixed with a H2O2 solution, treated by an ultrasound probe set at 20 kHz for 1 to 10 minutes.

Source: EBMUD

Biodesulfurization

Biodesulfurization uses bacteria to remove organosulfur compounds present in diesel without degrading the carbon skeleton. The studies that have used biodesulfurization are not included in this review report due to the process's relatively slow reaction rate and high cost. In addition, the crude and diesel desulfurization would need to promote the working of target bacteria.

Only occasionally, new bacteria are developed for oil desulfurization.[91]

Factors Affecting Desulfurization Efficiency

Factors that can significantly influence the extent of desulfurization:

- Feedstock source and quality:[92] Different feedstocks can exhibit different extents of sulfur removal with the same treatment.
- Desulfurization process selection & process parameters
- Catalyst selection

Comparison of Sulfur Removal Technologies Used for Diesel

Table 21 compares the different types of desulfurization technologies reviewed in this section.

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[91] Pawelec, B.; Navarro, R.M.; Campos-Martin, J.M.; Fierro, J.L.G. Retracted article: Towards near zero-sulfur liquid fuels: a perspective review. *Catal. Sci.Technol.* **2011,** *1*(1), 23-42.

[92] Duarte et al. 2011.

Table 21: Comparison of Diesel Desulfurization Technologies

Method	Reaction Condition and Sulfur Removal Efficiency	Advantages & Disadvantages[1]
UAODS (Step 1) Adsorption or Extraction (Step 2)	Oxidants, catalysts, and adsorbents/solvents Sonicator: 50–750 W, 20 kHz T = 25–90 °C Time = 9–10 min Efficiency = 75–95%	✓ Fast reaction ✓ High removal ✓ Mild reaction condition × Separation process needed × Sonication cost
ODS (Step 1) Adsorption or Extraction (Step 2)	Oxidants, catalysts, and adsorbents/solvents T = 50–70 °C P = Ambient Time = ~1 h Efficiency = 90–99%	✓ Mild reaction condition ✓ Higher reactivity × Difficulty on catalysts recovery × Oxidants consumption
ADS	Adsorbents such as activated carbon, zeolite, CaO, etc. P = Ambient; T = Ambient or higher Efficiency: <75%	✓ Reaction at mild condition ✓ Easy separation ✓ Adsorbent regeneration ✓ Removal of other impurities × Adsorbent consumption
Solvent Extraction	Solvents: Methanol, Acetone, etc. T = Room temperature P = Ambient; Time=1 h (3 times) Efficiency = 40% or 50–90%	✓ Simple process × Separation process needed × Relatively low sulfur removal efficiency × Solvent consumption & purification

1. ✓ indicates advantage and × indicates disadvantage

Source: EBMUD

Technology Selection for Testing

Based on technologies reviewed, a rank is given based on the evaluation of reaction conditions (temperature, pressure and time), sulfur removal efficiency and processing cost (Table 22). Technologies that take place at near ambient temperature and pressure and require less toxic chemicals were selected for bench testing in this study.

Table 22: Ranking of Diesel Desulfurization Technologies for Bench Testing

Rank	Desulfurization Method	Reaction Conditions			Removal Efficiency
		Temp (^{o}C)	Pressure	Time	
1	UAODS -> ADS	<100	Ambient	<10 min	75–95%
2	ODS -> ADS	60–70	Ambient	<1 h	90–99%
3	ADS	25–75	Ambient	4–72 h	<75%
4	Extractive Desulfurization	Room temp.	Ambient	1 h (3x)	Various 35–40% 50–90%
5	Precipitation Desulfurization	Room temp.	Ambient	Depends	20%

Source: EBMUD

CHAPTER 4:
FOG to Biodiesel Tests

This section presents the results of bench tests conducted to investigate and evaluate biodiesel production and desulfurization technologies identified in the literature review discussed in Chapter 3. Process steps investigated for improvement included:

- Brown grease extraction from FOG
- Biodiesel production from brown grease
- Sulfur removal from brown grease and brown grease biodiesel to meet the ultra-low sulfur ASTM 6751 (S-15) standards for B100 biodiesel

Approach

The approach employed for testing includes:

- **Brown Grease Extraction:** Bench tests were conducted to evaluate brown grease extraction methods using FOG received at EBMUD Main Wastewater Treatment Plant. The quantity of brown grease recovered and FFA percent in the extracted brown grease were analyzed for comparison.
- **Brown Grease to Biodiesel:** Bench tests were carried out to explore options to optimize the two-step acid-base catalyzed biodiesel production process. Enzyme-catalyzed brown grease-to-biodiesel processes and as well as the use of solid catalysts were also investigated. Other potential process optimizations were also explored.
- **Sulfur Removal:** Sulfur removal tests were conducted with both brown grease and brown grease biodiesel made by EBMUD. Brown grease donated by the San Francisco Public Utilities Commission (SFPUC), as well as brown grease extracted from EBMUD FOG was used. The sulfur removal tests were conducted on a trial and error basis due to unknown sulfur containing compounds in the feedstock and product biodiesel. Total sulfur was analyzed before and after each treatment (ASTM D5453 method), in order to determine the overall effectiveness of each process. Concurrently, a speciation of sulfur compounds present in the produced biodiesel was conducted.
- **FOG-to-Biodiesel Process Assimilation:** Integration of the major process steps of brown grease extraction from FOG, biodiesel production from brown grease, and biodiesel sulfur removal methods were tested. Biodiesel was produced from EBMUD FOG using the processes developed or optimized in this study in quantity sufficient for complete biodiesel testing to evaluate ASTM 6751-S-15 compliance.

FOG to Brown Grease Process Testing

Several brown grease extraction methods were tested; results are summarized in Table 23 and images from the first three tests are shown in Figure 17. Each test aimed to separate brown grease from the aqueous portion and solids in the FOG. Initially, FOG was centrifuged to obtain phase separation and brown grease was only recovered from the upper layer. While the relative amount of brown grease recovered was low in this method (24 percent), the FFA content was high (100 percent). This implies that the triglyceride content likely present in the FOG was not extracted into the brown grease using this method. In the second method test, the FOG was heated to 70 °C, followed by centrifugation for phase separation. In this case, the amount of brown grease recovered was high (55 percent) but the FFA content was lower (76 percent). This indicated a higher efficiency of separation, and possibly a more successful extraction of triglycerides into the brown grease. The third test also heated the FOG prior to centrifugation, but used hot water instead of hot plate, resulting in a high amount of brown grease recovered (68 percent) and FFA content (85 percent). In the final test, FOG was mixed with an equal volume of ethanol, prior to phase separation by centrifugation. In this case both the amount of brown grease recovered (32 percent) and FFA content (29 percent) were low.

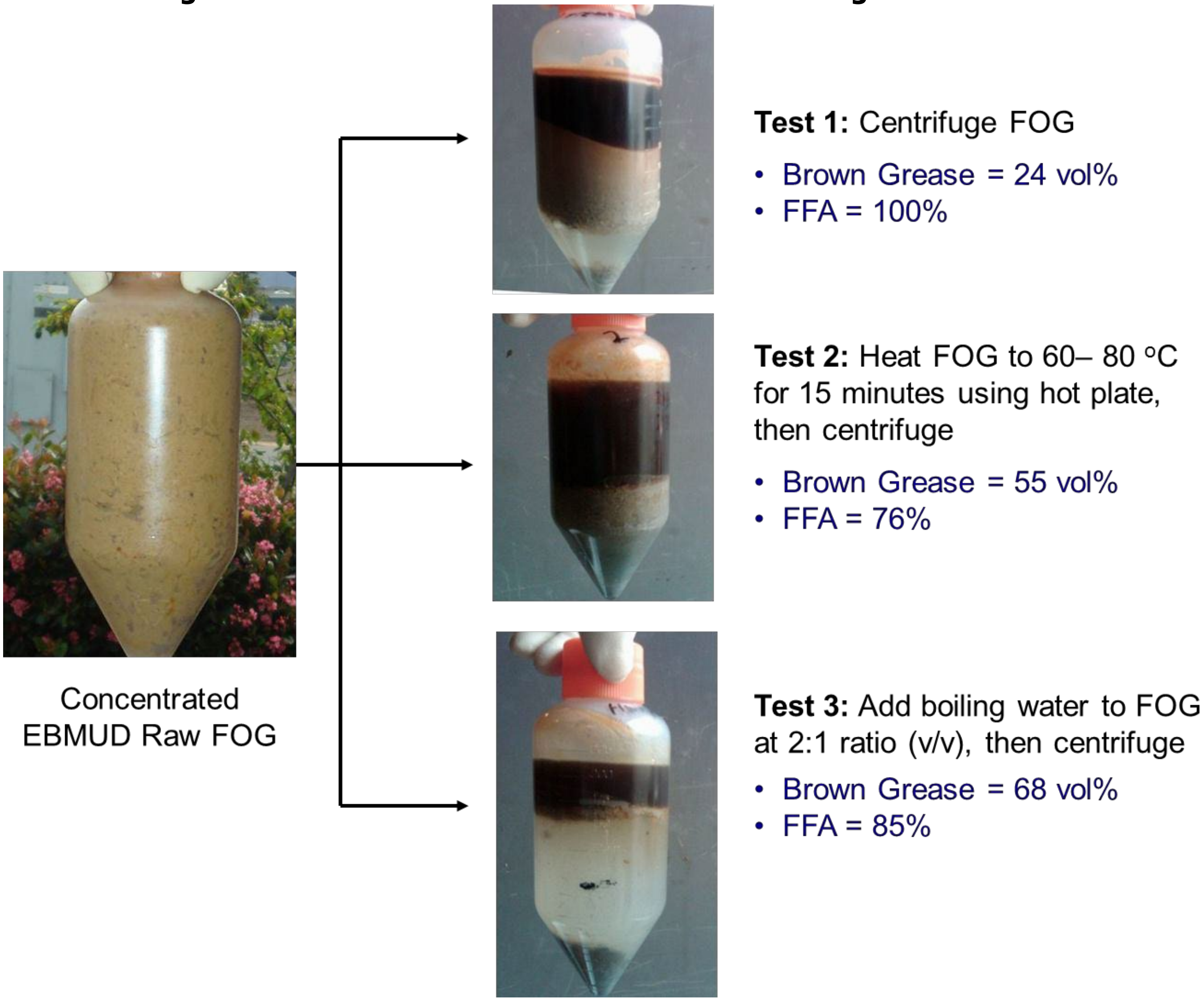
These results implied that simple centrifugation is sufficient to extract brown grease with high FFA content from FOG, albeit with relatively low efficiency. The extraction efficiency could be improved by heating FOG prior to centrifugation.

Table 23: Brown Grease Extraction Results Using EBMUD FOG

No.	Conditions	FFA Content in Brown Grease (%)	Brown Grease Volume Recovered (vol%)
1	Centrifuge only	100	24
2	Heat with hot plate to 70 °C, then centrifuge	76	55
3	Heat with hot water, then centrifuge	85	68
4	Mix with ethanol, then centrifuge	29	32

Source: EBMUD

Figure 18: Brown Grease Extraction Results Using EBMUD FOG



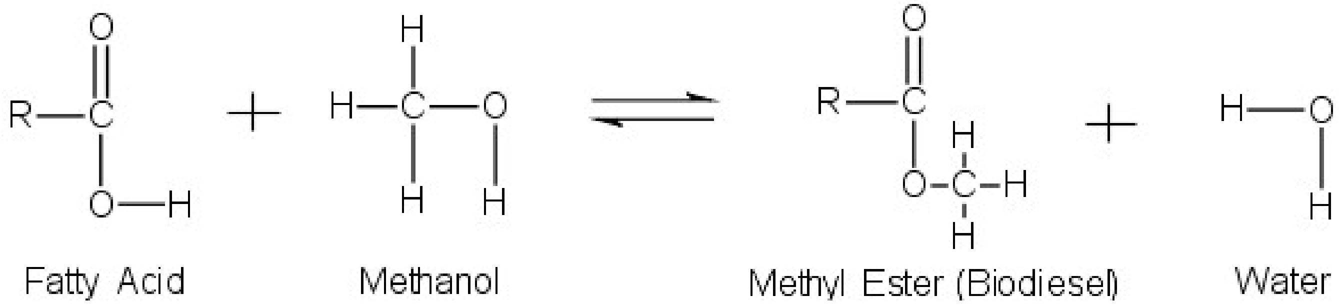
Source: EBMUD

Brown Grease-to-Biodiesel Process Optimization

Two-Step Biodiesel Production

A two-step acid-catalyzed esterification followed by a base-catalyzed transesterification method was used to produce biodiesel from brown grease. Methanol, at a 16:1 molar ratio of methanol:FFA, and 5–10 wt percent sulfuric acid were used in acid esterification to convert FFAs to fatty acid methyl esters (FAME, biodiesel). The high methanol:FFA ratio was necessary to move the reversible esterification reaction towards the product side. The reaction was conducted at 60–65 °C with aggressive mixing for one hour, followed by gravity settling for phase separation of the sulfuric acid and methanol fraction from the biodiesel. The acid esterification process is illustrated in Figure 20.

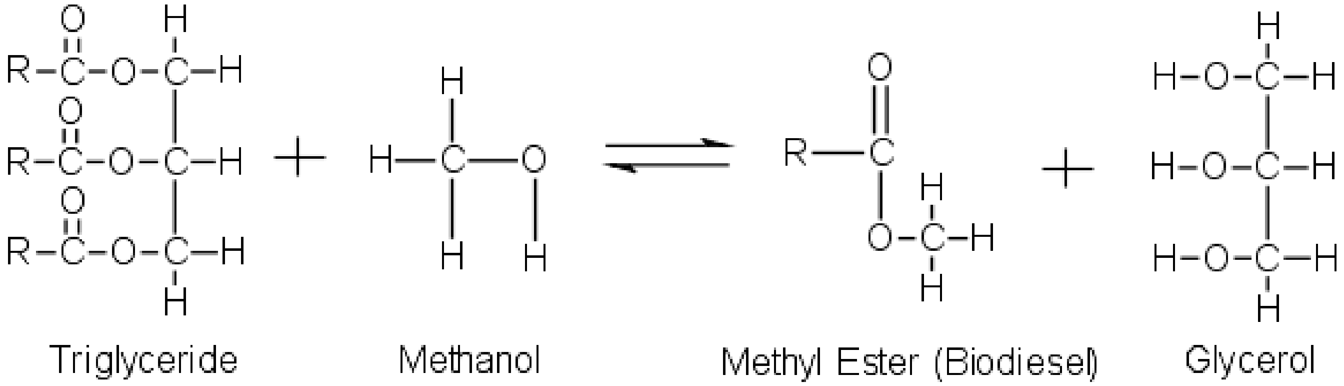
Figure 20: Acid Esterification Process



Source: EBMUD

If necessary, acid esterification was repeated until the FFA level in the biodiesel product was less than 1.0 percent by weight. Esterification was followed by transesterification conducted at 60 °C using 2.5–7.5 wt percent sodium methoxide or potassium hydroxide as a catalyst and providing rapid mixing (1000 rpm) for one or two hours. The transesterification reaction converts triglycerides to methyl esters as shown in Figure 21.

Figure 21: Transesterification Reaction



Source: EBMUD

Esterification Optimization

The esterification reaction conditions, reaction time, and methanol and sulfuric acid concentrations, were tested to identify the optimum process to achieve high FFA-to-biodiesel conversion. Ideally, the concentration of FFA should be reduced to less than 1 percent before base- catalyzed transesterification is carried out, in order to prevent soap formation (saponification) from the remaining FFAs instead of biodiesel.

The reaction time was varied at high temperatures while keeping the amounts of methanol and sulfuric acid constant. The FFA content was measured before and after the reaction. As shown in Table 24, relatively high FFA conversions were obtained with all conditions tested.

Improvements in FFA conversion were negligible with an increase in reaction time from 1 hour to 15 hours.

Table 24: Optimization of Esterification Reaction Time

Initial FFA	Methanol:FFA (molar ratio)	Sulfuric Acid	Time (h)	Temp (°C)	Final FFA
54%	20:1	10%	2	55	1.50%
54%	20:1	10%	15	55	1.20%
82%	20:1	10%	1	58	0.85%
82%	20:1	10%	1.5	58	0.98%
82%	20:1	10%	2	58	0.97%

Source: Internal report by Chakrabarti et al., 2008

When sulfuric acid (catalyst) dose was reduced from 10% to 5% and reaction time was kept constant at one hour, a high conversion of FFA was maintained as shown in Table 25.

Table 25: Optimization of Esterification with Reduced Acid Catalyst Dose

Initial FFA	Methanol:FFA (molar ratio)	Sulfuric Acid	Time (h)	Temp (°C)	Final FFA
82%	20:1	10%	1	64	0.97%
82%	20:1	5%	1	64	0.80%

Source: Internal report by Chakrabarti et al., 2008

The ratio of methanol:FFA was tested at 16:1 and 18:1 molar ratio. As shown in Table 26, high conversion of FFA could be maintained with the lower methanol:FFA ratio.

Table 26: Esterification with Reduced Methanol Dose

Initial FFA	Methanol:FFA (molar ratio)	Sulfuric Acid	Time (h)	Temp (°C)	Final FFA
82%	18:1	5%	1	64	0.85%
82%	16:1	5%	1	64	0.84%

Source: Internal report by Chakrabarti et al., 2008

Tests conducted with a reduced reaction temperature of 22 degrees Celsius from previous tests in the 50–64 degrees Celsius range are summarized in Table 27. Although the FFA was substantially reduced at the lower temperature if given sufficient reaction time, the final FFA concentration was not consistently below 1 percent.

Table 27: Esterification at Ambient Temperature

Initial FFA	Methanol:FFA (molar ratio)	Sulfuric Acid	Time (h)	Temp (⁰C)	Final FFA
86%	18:1	7%	3	22	1.30%
86%	18:1	7%	7.5	22	0.90%
86%	18:1	7%	15	22	1.00%

Source: Internal report by Chakrabarti et al., 2008

Transesterification Optimization

Transesterification reaction tests were conducted to determine the optimal conditions for complete triglyceride conversion. Potassium hydroxide and sodium methoxide were tested as base catalysts where the reaction time as well as the amount of catalyst and methanol used was varied, as shown in Table 28. The potassium hydroxide catalyst resulted in higher overall conversion rates than those of sodium methoxide. Increases in both the reaction time and methanol dose further improved the conversion. To achieve the ASTM total glycerin requirement after transesterification, a 5 percent mass ratio of potassium hydroxide and 12:1 molar ratio of methanol:triglycerides with a 2-hour reaction time was used.

Table 28: Summary of Transesterification Optimization Experiments

Base Catalyst	Catalyst Dose (wt%)	Methanol: Triglycerides[1] (molar ratio)	Reaction Time (h)	Total Glycerin (%)	Pass/Fail ASTM Total Glycerin Limit (0.240% MAX)
Sodium Methoxide	2.5	6	1	0.897	Fail
	2.5	6	2	0.486	Fail
	5	6	1	0.454	Fail
	5	6	2	0.291	Fail
	5	12	2	0.297	Fail
	7.5	12	2	0.381	Fail
Potassium Hydroxide	1.3	6	1	0.334	Fail
	2.5	6	1	0.315	Fail
	5	12	2	0.192	Pass

1. Triglyceride content in brown grease was estimated by (1- FFA%)

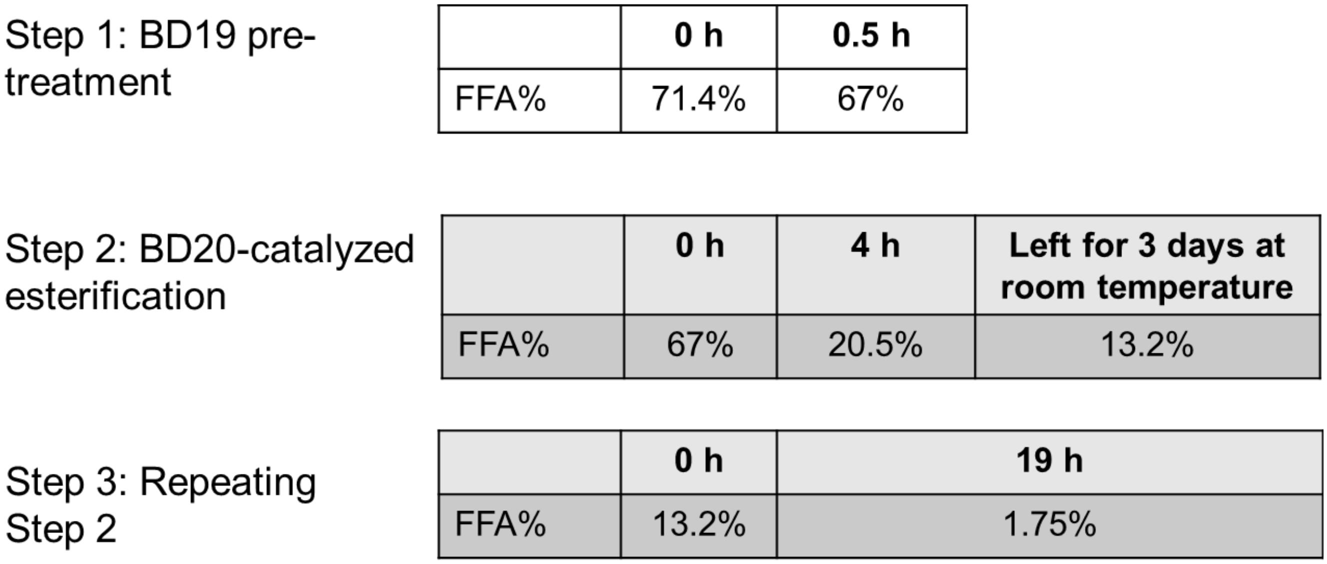
Source: EBMUD

Solid Catalyzed Esterification Process

The water-tolerable solid catalyst, Amberlyst™ BD20, used to convert high FFA feedstocks to biodiesel in a full-scale U.S. biodiesel production plant (name undisclosed), was tested for converting brown grease feedstock to biodiesel in this study.

Batch tests were conducted in 3 steps as illustrated in Figure 18. Results showed that Amberlyst™ BD20, at a dose of 50 grams of BD20 per liter of brown grease or 5 percent (w/v), can successfully convert brown grease FFAs into biodiesel at 60^0 C, ambient pressure, and a methanol:FFA molar ratio of 16:1. However, a significantly longer reaction time (at least 23 hours at 60 ^{0}C with mixing) was necessary at the specified test conditions. This finding is consistent with literature reports of a longer reaction time observed for heterogeneous solid-catalyzed esterification reactions than those catalyzed by homogeneous acid catalysts. For future research, a higher reaction temperature, pressure and catalyst dose should be tested to shorten reaction time, based on findings by Park et al. (2010).[93]

Figure 19: Esterification with Solid Catalyst Amberlyst™ BD20



Step 1: BD19 pre-treatment

	0 h	0.5 h
FFA%	71.4%	67%

Step 2: BD20-catalyzed esterification

	0 h	4 h	Left for 3 days at room temperature
FFA%	67%	20.5%	13.2%

Step 3: Repeating Step 2

	0 h	19 h
FFA%	13.2%	1.75%

Source: EBMUD

Process Simplification from a Two-Step to One-Step Process

Because brown grease typically has high FFAs and low triglycerides, the feasibility of simplifying the two-step acid-base conversion of brown grease to biodiesel into a one-step (acid esterification only) was evaluated.

FFA, free and total glycerin levels were measured in the brown grease feedstock and the resulting biodiesel after the acid esterification and polishing steps. Results are summarized in Table 29. FFA was reduced from 93.5 percent in brown grease to 1.1 percent in the finished biodiesel product, indicating an efficient esterification step. However, with a one-step

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[93] Park, J.Y.; Kim, D.K.; Lee, J.S. Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. *Bioresour. Technol*. **2010**, *101*(1), S62-S65.

esterification reaction alone, total glycerin was not reduced and was not able to meet the ASTM 6751 standard.

Table 29: Summary of One-Step Sulfuric Acid Esterification

Test	ASTM Limit	Brown Grease	After Esterification[1] and Polishing
FFA%		93.5%	1.1%
Free Glycerin	0.020% max	0.010%	0.000%
Total Glycerin	0.240% max	0.562%	0.559%
Monoglycerides		0.105%	0.098%
Diglycerides		1.528%	1.636%
Triglycerides		2.852%	2.779%

1. Esterification reaction condition: methanol:FFA = 16:1 molar ratio, sulfuric acid 10%, batch, stir, 60 ^{0}C, 1 h, settling for 20 hours. Polishing: water wash 10 times, then dry wash with 2.5% magnesol at 65-70 ^{0}C for 30 minutes

Source: EBMUD

BDH Silica Gel (70–230 mesh, 60 Å), which was thought to remove triglycerides in the feedstock and the resulting biodiesel product, was tested for pretreating brown grease feedstock, but proved ineffective.

Lipase Catalyzed Biodiesel Production

Lipases from *Candida antarctica* have been shown to be the most effective for methanolysis among lipases tested by others[94] and is readily available in an immobilized form, lending itself to repeated use. By contrast, limited information is available on the use of lipases from *Aspergillus oryzae* (used in cheese production) in biodiesel production. Nonetheless, its dramatically lower cost when compared with lipases from other sources makes *A. oryzae* a potentially attractive option for biodiesel production. A set of tests was conducted to compare the ability of lipases from *C. antarctica* and *A. oryzae* to catalyze the brown grease to biodiesel conversion process.

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[94] Shimada, Y.; Watanabe, Y.; Samukawa, T.; Sugihara, A.; Noda, H.; Fukuda, H.; Tominaga, Y. Conversion of vegetable oil to biodiesel using immobilized Candida antarctica lipase. *J. Am. Oil Chem. Soc.* **1999,** *76*(7), 789-793. doi: 10.1007/s11746-999-0067-6

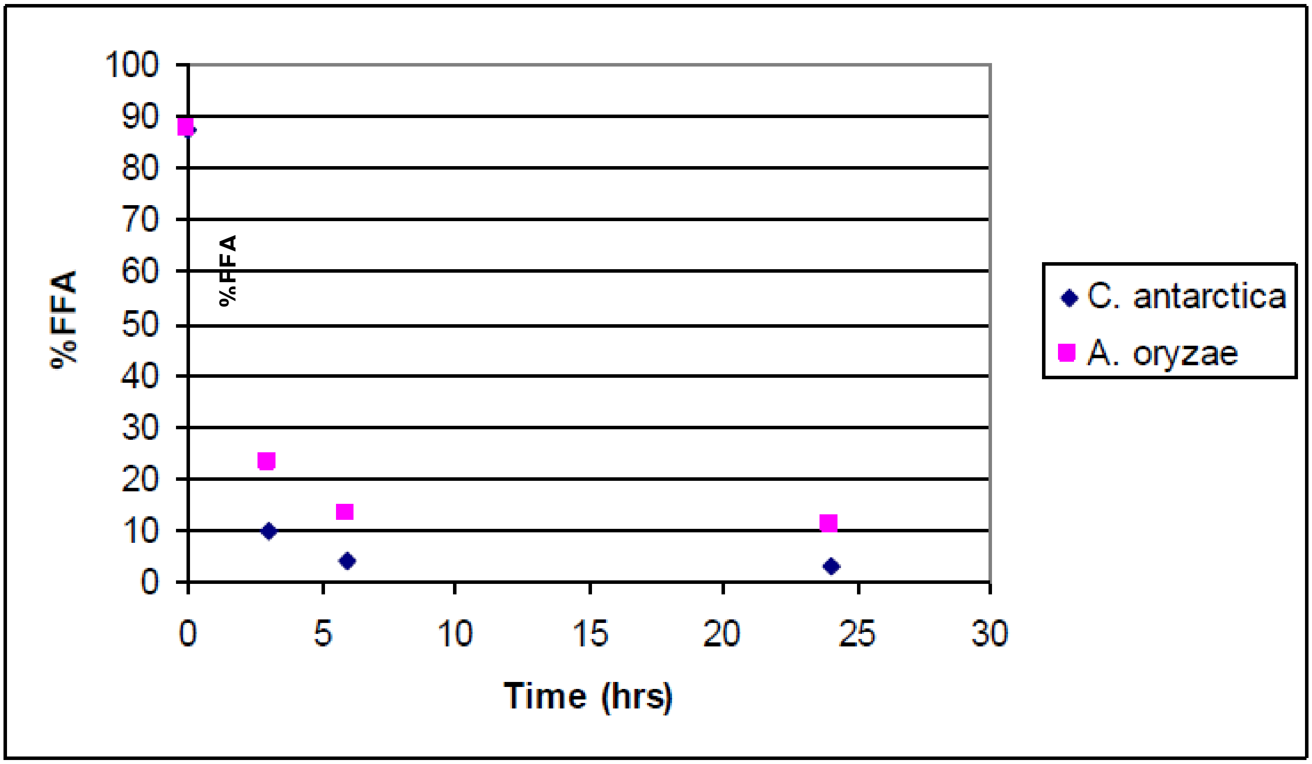
Methanolysis of Brown Grease Using C. antarctica and A. oryzae Lipases

The ability of both *C. antarctica* and *A. oryzae* lipases to catalyze the production of biodiesel from brown grease using methanol is compared in this test. Immobilized *C. antarctica* lipase was used at a 10 percent mass ratio to brown grease. Lyophilized *A. oryzae* was first dissolved in deionized water (1 g enzyme in 5 mL water) and then centrifuged to separate the active enzyme insolution from suspended particles. Then the *A. oryzae* solution was used at mass ratios of 20 percent to the mass of brown grease used. This resulted in the addition of 100 percent by mass of water in the *A. oryzae* reaction. For each reaction, a 3:1 molar ratio of methanol:triglycerides was added in thirds at 0, 3, 6 hours post the start of the reaction. This method was applied in order to reduce the negative effect methanol has on lipase activity. Esterification steps were carried out at 40 °C for 24 hours.

Results are shown in Figure 19. After reacting for 3 hours, over 70 percent of the FFA appeared to be converted in both cases. In 6 hours, FFAs were reduced to 4 percent in the *C. antarctica* catalyzed esterification, but only to 13 percent in the *A. oryzae* catalyzed reaction. Both lipases continued to reduce FFAs after 6-h sampling and showed a further, but modest, reduction when sampled at 24 h after starting the esterification reaction. In general, a higher conversion was obtained using *C. antarctica*. The lower conversion obtained with *A. oryzae* enzyme is presumably due to the fact that significantly more water was present in the mixture. This excess of water could have shifted the equilibrium of the reaction away from the products, leading to less overall biodiesel produced despite a higher amount of enzyme added.

Following esterification, the *A. oryzae* solution was found to be relatively easy to separate from the oil phase. In contrast, *C. antarctica* appeared to form a gelatinous substance with the biodiesel produced. This gel formation may be due to an unanticipated interaction between the biodiesel, methanol, and the Immobead support onto which the lipase was immobilized. While the activity of the enzyme was unaffected by this gel formation, it made the enzyme recovery more difficult.

Figure 23: Methanolysis of FFA in Brown Grease to FAME



Twenty five grams of brown grease (87% FFA) was combined with 10% immobilized *C. antarctica* lipase or 20% *A. oryzae* lipase. Methanol was added in thirds at 0, 3, 6 hours after the start of the reaction. Esterification was carried out at 40 °C. The overall FFA conversion rate was higher using the *C. antarctica* lipase catalyst.

Source: EBMUD

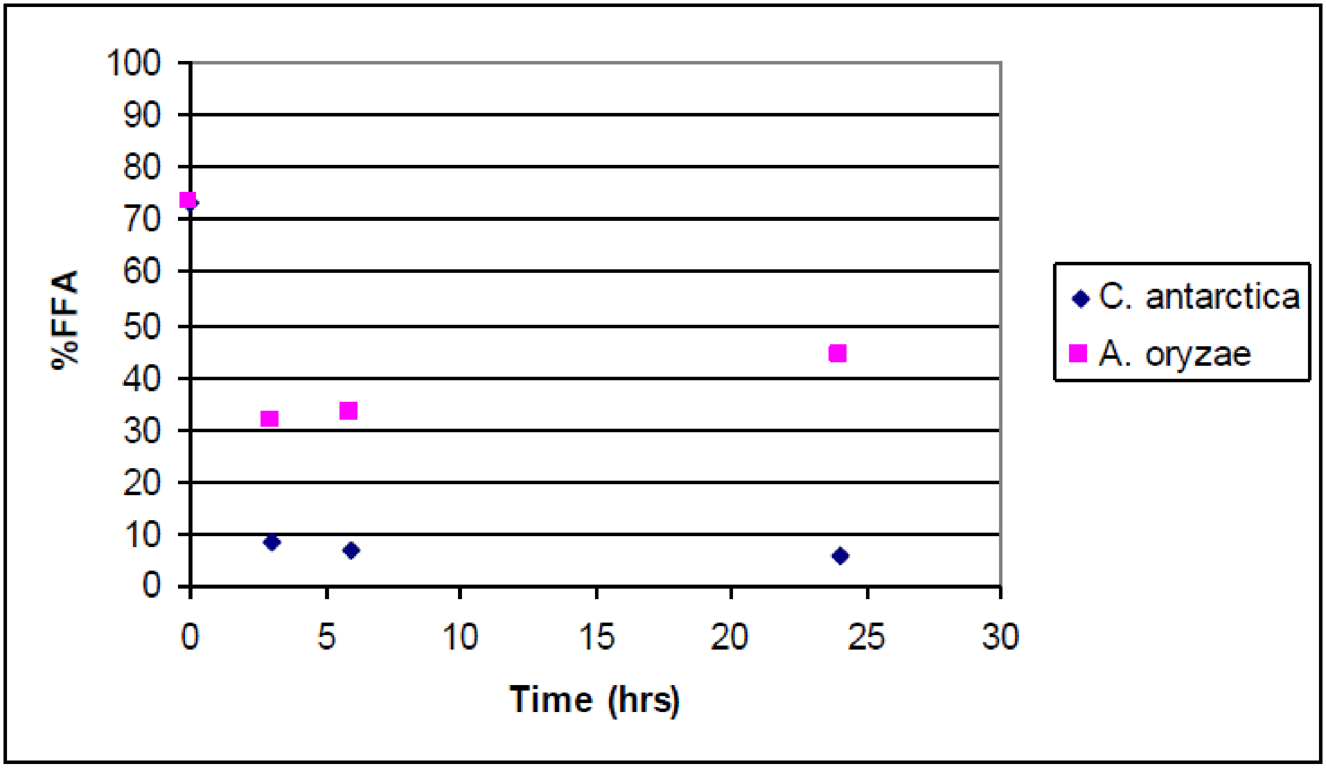
Butanolysis of Brown Grease Using C. antarctica and A. oryzae Lipases

The literature suggests that high FFA could be converted to biodiesel more efficiently using isobutanol instead of methanol. *C. antarctica* and *A. oryzae* lipases were again used to catalyze the production of biodiesel from brown grease, but this time isobutanol was used instead of methanol. Again, 10 percent *C. antarctica*, and 20 percent *A. oryzae* lipases were used. For each reaction a 3:1 molar ratio of isobutanol:triglycerides was added in thirds at 0, 3, 6 hours after the start of the reaction. Esterification steps were carried out at 40 °C for 24 hours. Results are shown in Figure 20.

Overall, a higher FFA conversion was obtained using *C. antarctica*. For *A. oryzae*, the conversion reached a maximum after three hours. However, between 3 and 24 hours, the percentage FFA appeared to slightly increase. This may be due to significant inactivation of the enzyme by isobutanol, and the high concentration of water present in the reaction. With *C. antarctica,* similar overall conversion was observed as when methanol was used as the substrate. However, it was noted that at the end of the reaction, the isobutanol and the biodiesel produced formed a miscible mixture which could not be separated by phase separation. In addition, the formation of the gelatinous substance appeared to be slightly greater than when methanol was used.

These results suggest that isobutanol is less than ideal compared to methanol with either *C. antarctica* or *A. oryzae* lipases.

Figure 24: Butanolysis of Brown Grease FFA to FAME



Twenty-five grams of brown grease (73% FFA) was combined with 10% immobilized *C. antarctica* lipase or 20% *A. oryzae* lipase. Isobutanol was added in thirds at 0, 3, 6 hours after the start of the reaction. Esterification was carried out at 40 °C. The overall FFA conversion was significantly higher using the *C. antarctica* lipase catalyst.

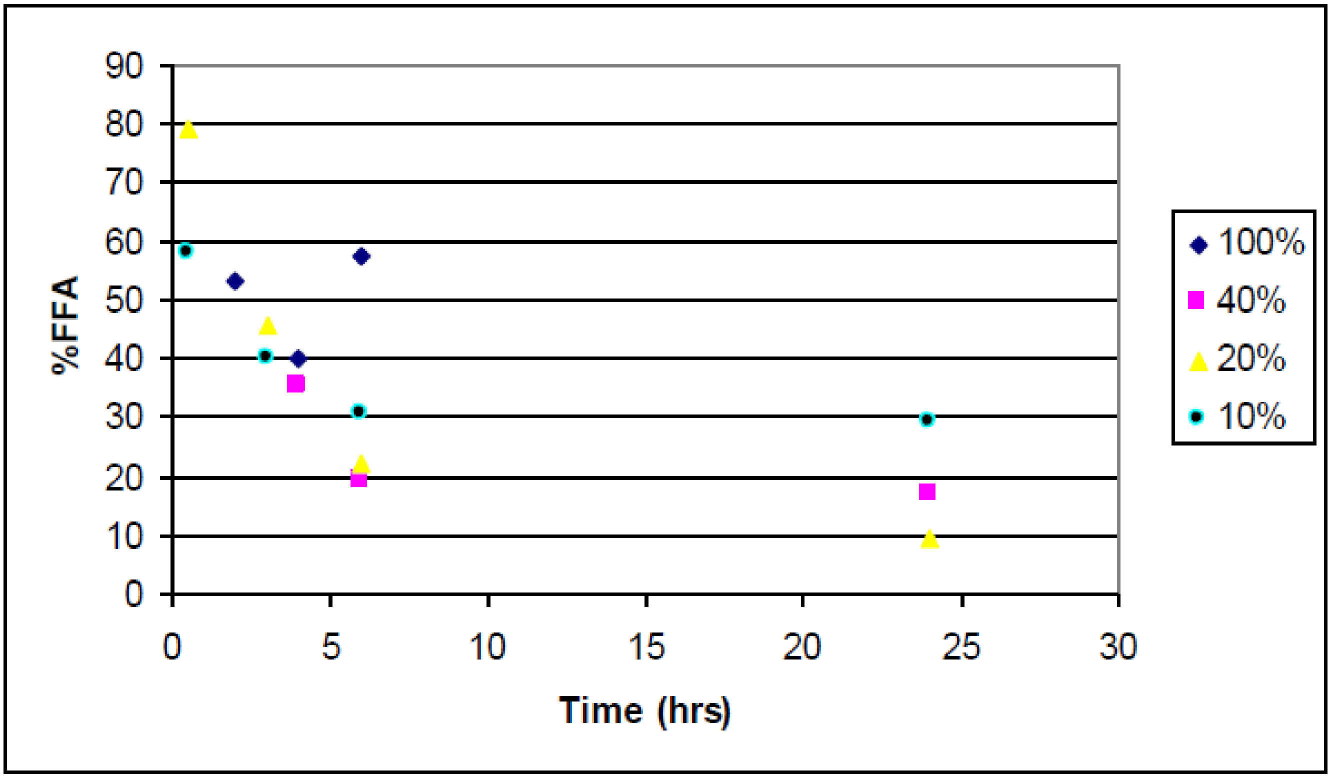
Source: EBMUD

Optimization of Brown Grease Methanolysis with A. oryzae Lipase

Lacking kinetic or equilibrium data for *A. oryzae* lipase-catalyzed biodiesel production (not found in the literature), a test system was set up to determine optimal conditions using this low- cost lipase. Since the brown grease feedstock had relatively high FFA content (~92 percent), only a one-step esterification reaction was conducted to covert the brown grease FFA to biodiesel. Reaction conditions were chosen based on results obtained from previous experiments conducted in this study. Brown grease was combined with lipases from 10 percent (lipase to brown grease) up to 100 percent by mass. Methanol was added in thirds to obtain a final molar ratio of 3:1 methanol: FFA. Reactions were carried out at 40 °C for up to 24 hours. For each condition, FFA concentration was plotted over reaction time in Figure 21.

As expected, the overall conversion of FFA increased as the amount of enzyme solution added was decreased. The exception to this finding occurred with the smallest amount of enzyme solution added. In addition, it was noted that the rate of the reaction slowed most significantly when only 10 percent enzyme mass concentration was used. Since the volume of methanol added in each case was constant, this indicates increased inactivation of the enzyme in solution by the added methanol. This inactivation by high methanol concentrations has been documented by others.[95] The highest overall conversion of FFA in brown grease was observed with the addition of 20 percent by mass of lipase. This corresponds with an equal volume of lipase solution and brown grease. Although the reaction was allowed to continue for 24 hours, it is likely that equilibrium could be achieved in a much shorter time period.

Figure 25: Conversion of FFA in Brown Grease to FAME Using A. oryzae Lipase



Twenty-five grams of brown grease (92% FFA) was combined with indicated amounts of *A. oryzae* lipase. Methanol was added in thirds at 0, 3, 6 hours after the start of the reaction. Esterification was carried out at 40 °C. Using relatively lower amounts of lipase increased the overall conversion of FFA. When 10% enzyme was used, methanol inactivation of the enzyme became more significant, resulting in less conversion than predicted by reaction equilibria.

Source: EBMUD

Lipase Catalyzed Biodiesel Production to Meet ASTM Standards

Biodiesel was produced from brown grease using optimal enzymatic reaction conditions identified earlier and illustrated in Figure 22. These conditions were scaled up in order to produce enough biodiesel for ASTM specification testing. Brown grease was esterified with a 3:1 molar ratio of methanol:FFA and using a 20 percent *A. oryzae* lipase solution as catalyst. The esterification was carried out at 40 °C for 24 hours.The FFA in the sample was reduced to

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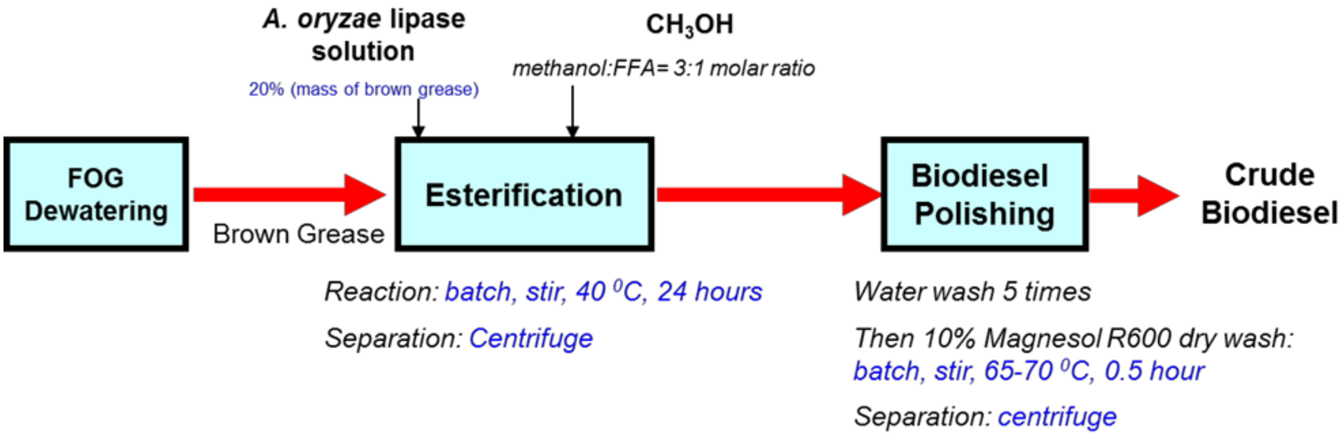
[95] Kaieda, M.; Samukawa, T.; Kondo, A.; Fukuda, H. Effect of Methanol and water contents on production of biodiesel fuel from plant oil catalyzed by various lipases in a solvent-free system. *J. Biosci. Bioeng.* **2001,** *91*(1), 12-15. doi: (http://dx.doi.org/10.1016/S1389-1723(01)80103-1)

15 percent at the end of the reaction. The esterified product was separated from the methanol and lipase solution by centrifugation. The separated lipase- methanol solution can potentially be reused to convert subsequent batches of brown grease. The biodiesel produced was first washed with water, followed by a dry wash with Magnesol® R600. The crude biodiesel produced was further treated for sulfur removal using the combined oxidative and adsorptive desulfurization (ODS-ADS) method developed in this study and discussed in depth in Section 4.6.

Figure 26: Integrated Enzymatic FOG-to-Biodiesel Process



Source: EBMUD

ASTM biodiesel specification tests performed on the biodiesel produced are summarized in Table 30. The FAME content in the biodiesel produced was measured to be 76 percent, similar to what was obtained with the smaller scale production.

The ASTM test results indicated that several standards were not met by biodiesel produced using the lipase catalyzed esterification process.

- The primary parameter not met was the acid number, which at 13.79 mg KOH/g, was significantly higher than the ASTM limit of 0.5 mg KOH/g. This high acid number was due to the presence of unconverted FFAs present in the biodiesel, as expected. The FFA content could have also negatively affected the oxidation stability (Banga and Varshney, 2010). The oxidation stability of the sample (0.4 hours) was significantly shorter than the ASTM standard of 3 hours, despite the addition of an antioxidant (Ethanox 4760R) at 500 ppm. The addition of this quantity of antioxidant increased the stability of biodiesel produced by acid-base catalyzed process from 1 hour to 24 hours (Section 4.7).
- The total glycerin in the sample (0.323 percent) was slightly higher than the ASTM limit (0.240 percent). This was expected because the transesterification step for converting triglycerides to biodiesel was purposely bypassed in this test.
- Total sulfur in the sample did not meet the ASTM requirement. The ODS-ADS treatment removed sulfur levels in biodiesel from 520 ppm to 197 ppm, but sulfur was still significantly higher than the ASTM upper limit of 15 ppm. This was expected since only 10 percent instead of 40 wt percent of silica-alumina adsorbent mixture was used in the

ODS-ADS treatment in order to retain sufficient biodiesel for ASTM testing by minimizing sample loss from this treatment. In addition, the ODS-ADS treatment cannot consistently remove brown grease biodiesel sulfur to meet the ASTM 15 ppm limit, as shown later in Chapter 4.

- The carbon residue in the sample did not meet the ASTM requirement. This was presumably due to the residual activated carbon left in the sample from its use in the oxidative desulfurization treatment as a catalyst.
- Finally, the distillation point (378.5 °C) failed to meet the ASTM requirement of 360 °C (maximum).

Table 30: ASTM Testing Results on Lipase Catalyzed Biodiesel Product

Test	ASTM Method	ASTM Limit	EBMUD Made Brown Grease Biodiesel
Calcium & Magnesium, combined	EN 14538	5 ppm max	0.2
Flash Point (closed cup)	D 93	93 °C min	201.0
Methanol Content, or Flash Point	EN 14110 D 93	0.2% mass max 130 °C min	0.000 201.0
Water & Sediment	D 2709	0.05% vol. max	NM[1]
Kinematic Viscosity, 40 °C	D 445	1.9–6.0 mm /sec	5.924
Sulfated Ash	D 874	0.02% mass max	0.008
Sulfur (S15 Grade)	D 5453	15 ppm max	197.2 (Fail[2])
Copper Strip Corrosion	D 130	No. 3 max	3B
Cetane	D 613	47 min	NM[1]
Cloud Point	D 2500	°C, Report	6
Carbon Residue 100% sample	D 4530	0.05% mass max	0.079 (Fail[2])
Acid Number	D 664	0.5 mg KOH/g max	13.79 (Fail[2])
Free Glycerin	D 6584	0.020% mass max	0.001

Test	ASTM Method	ASTM Limit	EBMUD Made Brown Grease Biodiesel
Total Glycerin	D 6584	0.240% mass max	0.323 (Fail[2])
Monoglycerides	D 6584		0.036
Diglycerides	D 6584		0.618
Triglycerides	D 6584		2.121
Phosphorus Content	D 4951	0.001% mass max	0.000086
Distillation	D 1160	360 °C max	378.5 (Fail[2])
Sodium/Potassium, combined	EN 14538	5 ppm max	0.3
Oxidation Stability	EN 15751	3 hours min	0.4 (Fail[2])

1. NM: Not measured
2. Fail = fail to meet the ASTM 6751 standards

Source: EBMUD

Potential Sulfur Speciation and Source Identification

Sulfur Compounds Speciation

If the sulfur compounds in brown grease and the resulting biodiesel were to be identified analytically, sulfur treatment methods could be designed more precisely to remove them. For this reason, an investigation was conducted by EBMUD to find a suitable analytical method and laboratory for sulfur speciation tests in brown grease and resulting biodiesel. The following three methods were identified for further evaluation, though none had previously been applied to brown grease or resulting biodiesel for sulfur speciation.

Option 1: 33S Nuclear Magnetic Resonance (NMR) Scan by UC Berkeley NMR Spectroscopy Facility

- Per the director of the NMR Spectroscopy Facility, this method has a low chance for identifying sulfur compounds at low concentration of several hundred parts per million. The professional consensus was that identification is difficult to impossible, especially at natural abundance levels.
- Method may require a 100x concentrated sulfur sample to increase the chance of success; in this case a sample would have to be concentrated to boost the sulfur content from about 300 ppm to about 30,000 ppm.

- Method may require a long scan time (overnight) with the NMR system to get a reading
- Costs ~$566+/sample

Option 2: Gas Chromatography with a Sulfur Chemiluminescence Detector (GC-SCD) and/or 2D GC-SCD by Intertek (Westport Technology Center)

- Interferences from other compounds in the samples are minimized as SCD detector will only detect sulfur compounds
- Method has been used for detecting sulfur compounds in petroleum fuels, but not in brown grease or biodiesel
- Method can detect compounds with a carbon chain length up to C28 and a boiling point higher than 376 °C
- Costs ~$800–1,000/sample

Option 3: GC-SCD by Green System's NuGen Desul

Green Systems (http://www.total-compliance.com/greensystems/desulfurization-of-fuels)

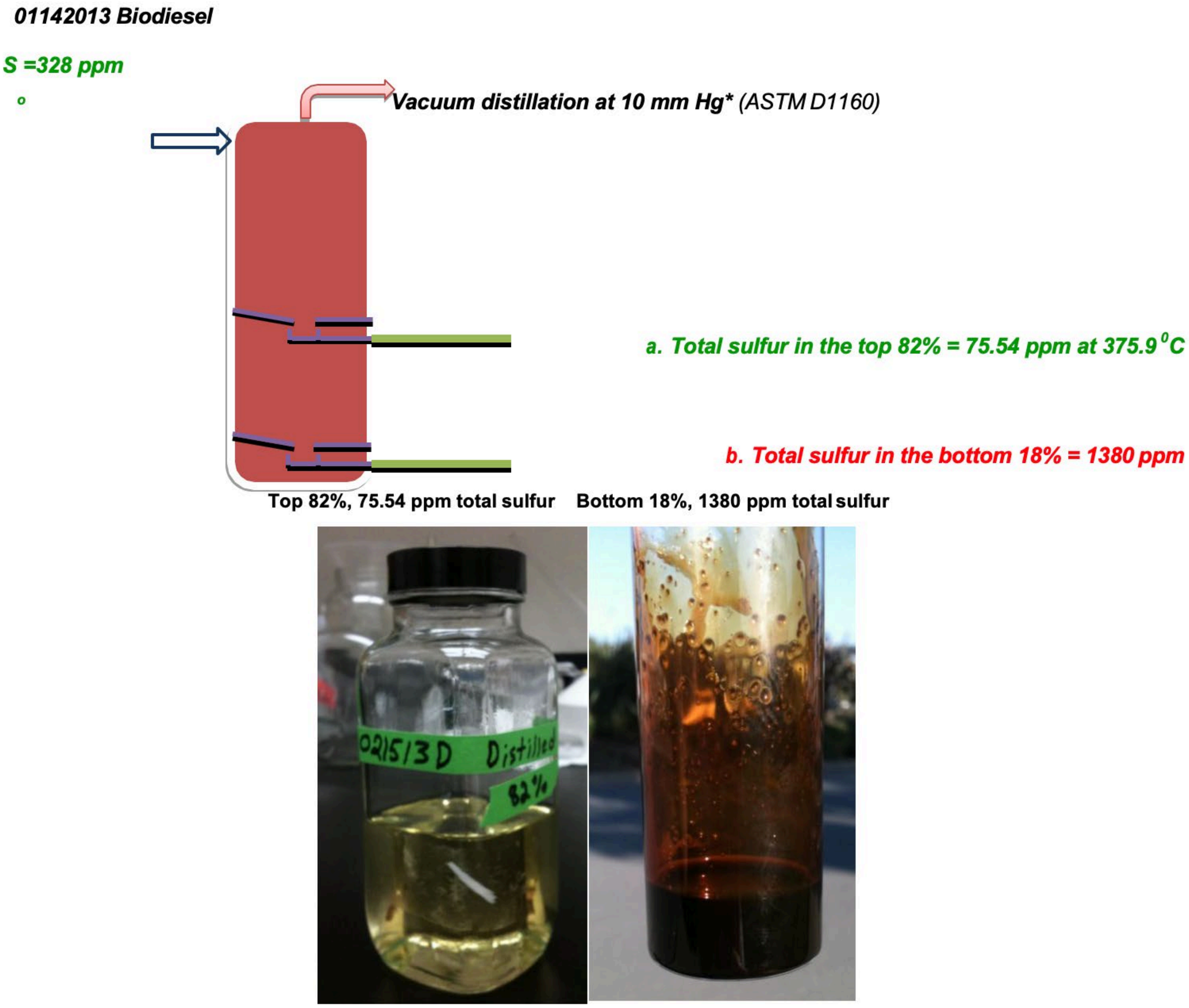
- A library of sulfur compounds present in petroleum diesel has been established from previous research Have experience working on biodiesel made from waste cooking oils and diesel sulfur removal, but not brown grease biodiesel
- Costs $1,200/sample
- NuGen Desul was not responsive to further inquiries by project team

Biodiesel Sample Preparation for 33S NMR Scan

An earlier EBMUD study showed that total sulfur concentration in the distillate bottom from vacuum distillation of brown grease biodiesel can be very high. The distillation method was therefore tried to concentrate biodiesel sulfur sample to prepare for the 33S NMR scan.

However, as indicated in Figure 23, the distillation method was only able to concentrate total sulfur from 328 ppm to 1380 ppm, well below the 100-fold concentration suggested. After repeating the distillation procedure and obtaining similar results, EBMUD decided not to pursue the 33S NMR scan given the low chance of success.

Figure 27: Concentrating Sulfur Compounds in Biodiesel for 33S NMR Scan



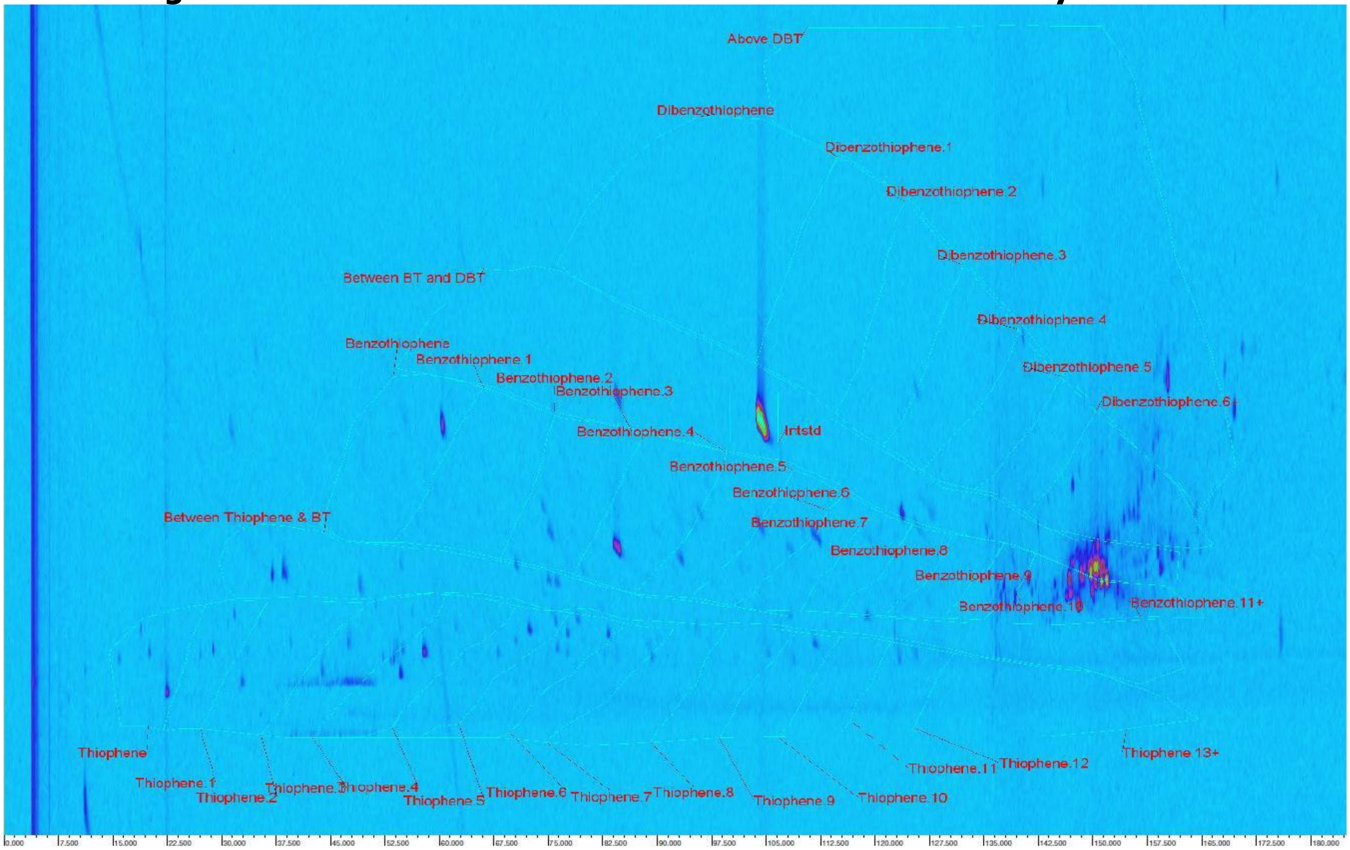
Source: EBMUD

2D GC-SCD by Intertek

Biodiesel made at EBMUD from brown grease was sent to Intertek for 2D GC-SCD analysis. This sample contained 249 ppm of total sulfur as measured by the UV method (ASTM D5453). The 2D GC-SCD analysis detected unknown sulfur peaks, which accounted for 115 ppm of the total sulfur in the sample. Another 41.5 ppm of sulfur had an elution time normally attributed to benzothiophenes (BT) and dibenzothiophenes (DBT) or may be variations of those components types in petroleum. However, per Intertek, since biodiesel may contain sulfur compounds not observed in petroleum, the components could be a different compound family that elutes in this range. Further work is recommended to speciate sulfur in brown grease and brown grease derived biodiesel which may eventually provide needed information for determining more cost-effective methods for removing sulfur from brown grease to meet ASTM standards.

The Intertek report on sulfur speciation is included in Appendix A.

Figure 28: Unknown Sulfur Peaks Shown in 2D-GC-SCD by Intertek



Source: Intertek

Intertek provided evaluation and comment on the sulfur results as follows:

- The structure of the sulfur components cannot be determined based solely on the 2D-GC. The components elute in or near the area for benzothiophenes with approximately 10 carbon substitutions. If the samples had been from standard petroleum, a significant proportion would be expected to have that structure. Intertek has less experience with biofuels and cannot with confidence provide further assessment on the structure, whether it is straight chain or in rings.
- Since the 41.5 ppm of sulfur detected in unknown peaks elutes in the range normally associated with compounds with about 14 carbons, the actual components are likely in the C14 or larger range. The elution time may correspond to the C8–C12 paraffin range, but this analysis has not been benchmarked with the normal paraffins.
- This analysis only measures components that are eluted and detected by the SCD. All sulfur is assumed to have the same response (probably a sound assumption). If the sample contains sulfur components that do not separate well with chromatography and are not eluted during the analysis, they will not be detected. This could explain the difference in total sulfur results measured in the sample when taken (249 ppm) and the 115 ppm measured by 2D GC-SCD

Sulfur Source Identification Effort

Sulfur in Detergents

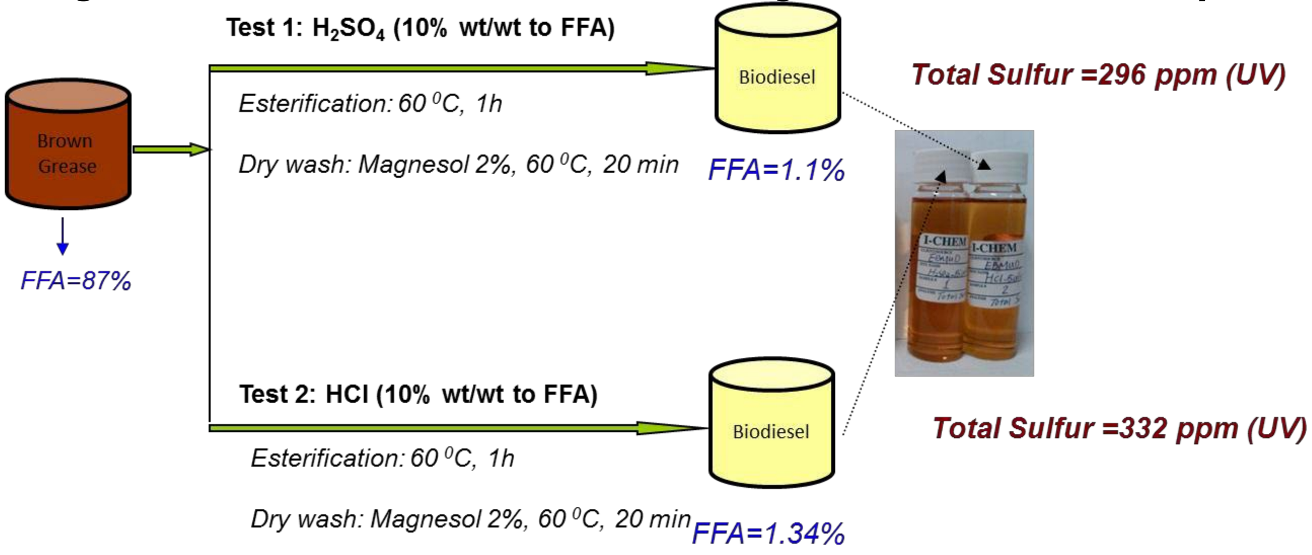
It was hypothesized that household detergents could contribute to the high sulfur in brown grease. To test this, a detergent mixture was made from three off-the-shelf products: Palmolive Concentrated Dish Liquid, Cascade Complete All In One Pack, and Tide Liquid Concentrated Laundry Detergent. The undiluted detergent mixture was found to contain a total sulfur concentration as high as 44,000 ppm measured using the inductively coupled plasma (ICP) method. The correlation of detergent sulfur compounds to brown grease biodiesel sulfur speciation should be investigated in future.

Acid Catalyst (Sulfuric Acid) Contribution to Biodiesel Sulfur

Sulfuric acid (H_2SO_4) used to catalyze the esterification reaction of brown grease was also considered as a possible sulfur contributor to brown grease derived biodiesel.

To investigate this hypothesis, an alternative acid of hydrochloride acid (HCl) was used as the catalyst for esterification as shown in Figure 25. Results showed that total sulfur in the biodiesel produced using these two different acid catalysts was comparable, indicating that sulfuric acid was unlikely to be a significant contributor to the total sulfur measured in brown grease derived biodiesel. Another test using lipase (in lieu of sulfuric acid) to catalyze the brown grease-to- biodiesel reaction supported this finding, as the biodiesel made using that method also contained a high sulfur content (520 ppm).

Figure 29: Total Sulfur in Biodiesel Made using Two Different Acid Catalysts



Source:EBMUD

Brown Grease and Biodiesel Desulfurization Process Development and Optimization

Brown Grease Desulfurization

Brown Grease Adsorptive Desulfurization (BG ADS)

Various adsorbents were selected for the BG ADS trials based on literature findings[96], [97] and industry available adsorption products. The adsorptive performance of the materials was evaluated in 1–hour batch reactions for 10–20 wt percent adsorbent doses, conducted at temperatures ranged from ambient to 80 °C.

The adsorbents showing the most effective performance in this study were: BDH Silica Gel (70– 230 mesh, 60 Å), Fisher Silica Gel (30–70 mesh, S-834-1), PQ® Sorbsil R92 (powder, 80–100 Å, provided by PQ Corporation), and Kite polymer products: Kite No. 2 and Kite No. 4 (polymer dose and application conditions were conducted by the Kite Technology Group). The sulfur removal results by these effective adsorbents are summarized in Table 31. Batch ADS treatment removed 30–55 percent of the sulfur in the BG, however, residual BG sulfur concentration after treatment ranged from 181–264 ppm, which exceeds the ASTM standard of 15 ppm.

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[96] Kim et al. 2006.

[97] Chakrabarti et al. 2008.

Table 31: Summary of Brown Grease ADS Batch Desulfurization Efficiency

Adsorbent	BG-ADS Batch Treatment		Sulfur Removal		
	Adsorbent Dose to BG (wt%)	**Temperature °C**	**Initial S (ppm)**	**Final S (ppm)**	**Removal Efficiency (%)**
BDH Silica Gel (70-230 mesh, 60 Å)	10%	65 °C	340	181	39%
			451	264	41%
Fisher Silica Gel (30-70 mesh, S-834-1)	20%	75–80 °C	451	255	43%
PQ Sobsil R92 (Powder, 80–100 Å)	20%	75–80 °C	451	202	55%
Kite Polymers[1]: Kite No. 2	Not available	Not available	334	264	21%
Kite No. 4			334	235	30%

1. Test conditions and product trials were conducted by the Kite Technology Group

Source: EBMUD

Additional adsorbents tested and proved ineffective for BG desulfurization (less than 30% sulfur removal efficiency) included: Amberlyst® A21, Ambersep™ BD19, bentonite, magnesol, diatomaceous earth, baking soda, sand, and zeolite.

Brown Grease Oxidative Desulfurization (BG ODS)

Hydrogen peroxide at 30 percent by weight was used as the oxidant for the BG ODS tests. A solution containing hydrogen peroxide (1:1 v/v H_2O_2:BG) and acetic acid (27% v/v acetic acid:BG) was added to brown grease samples and rapidly mixed in a 60–65 °C water bath at atmospheric pressure for 1 hour. Two different treatments were applied following the ODS process: (1) ADS using 10 wt percent BDH Silica Gel (70–230 mesh, 60 Å), batch treatment at 65 °C and 800 rpm for 1 hour, and (2) Acid esterification followed by 2 percent magnesol batch treatment at 65 °C and 800 rpm for 1 hour. The results of the oxidative desulfurization of brown grease are shown in Table 32.

Table 32: Summary of Brown Grease ODS Desulfurization Efficiency

Test	Brown Grease ODS Treatment			Post ODS Treatment	Sulfur Removal		
	H2O:BG (v/v)	Acetic Acid: BG (vol%)	Temp. (°C)		Initial Sulfur (ppm)	Final Sulfur (ppm)	Removal Efficiency (%)
Test 1[1] (BG -> ADS)	-	-	-	ADS	424	256	**40%**
Test 2 (BG ODS -> ADS)	1:1	27%	60–65	Same as above	424	188	**56%**
Test 3 (BG ODS -> Biodiesel)	1:1	27%	60–65	Acid esterification followed by magnesol polishing[2]	424	263	**38%**

1. ODS treatment was not applied. ADS treatment was conducted by using 10 wt% BDH Silica Gel in batch treatment at 65 °C, 800 rpm for 1 hour
2. Magnesol polishing comprised a batch treatment with a 2% magnesol dose, 65 °C, 800 rpm for 1 hour

Source: EBMUD

The BG ODS-ADS treatment increased brown grease sulfur removal from 40 percent (Test 1) to 56 percent as shown in Test 2. However, the high residual sulfur concentrations following the ODS-ADS treatment indicates that nearly half of the sulfur in the brown grease could not be removed by oxidative desulfurization treatment.

When ODS was used to pretreat brown grease before biodiesel production, sulfur removal in the resulting biodiesel was 38 percent (Test 3). This indicates that ODS was ineffective as a pretreatment method as the sulfur removal efficiency is comparable to that obtained with the acid-catalyzed esterification brown grease-to-biodiesel process in this study (~30—45 percent).

Biological Sulfur Removal from Brown Grease

Anaerobic digestion has been used to biologically treat sulfate-rich wastewater with demonstrated success. Sulfate reduction occurs in the acidogenic phase of a two-phase digestion process.[98] A bench-scale anaerobic digestion test was conducted to evaluate if significant sulfur reduction could be achieved through anaerobic digestion pretreatment, with minimal loss of brown grease due to anaerobic decomposition.

The test setup is shown in Figure 26. A 2-L flask was operated as a bench scale anaerobic digester run at 52 °C in a temperature-controlled water bath. Sludge taken from an EBMUD full- scale thermophilic anaerobic digester served as the initial seed biomass. A mixture of brown grease and modified Barr's medium, suitable for sulfate reducing bacteria growth, was initially fed to the test digester at a 10:90 v/v ratio (Brown grease: modified Barr's medium) to enrich the sulfate reducing bacteria in the anaerobic biomass. The bench digester was operated in a semi- batch mode with a 3-day mean cell residence time (MCRT). Total sulfur, oil and grease, and chemical oxygen demand (COD) were measured from digester feed and drawoff samples.

Digester gas was collected for hydrogen sulfide and carbon dioxide analysis.

After one month of operation, high H_2S concentrations of 25,000 ppm were detected in the digester biogas, indicating that the sulfur compounds in brown grease had converted to hydrogen sulfide. As a result of anaerobic digestion, the total sulfur was reduced from 995 mg/kg in digester feed to 505 mg/kg in digester withdraw, a 46 percent reduction of total sulfur. However, when the brown grease ratio in the feed was increased from 10 to 50 percent, no sulfur reduction was observed. Even when supplemental lactose was added to the digester feed to maintain a target COD/SO_4-S ratio of 10 (which was reported to be optimal for sulfate reducing bacteria by Mizuno et al., 1997) sulfur remained consistent. It is presumed that the high brown grease load inhibited the sulfur reducing bacteria (similar to inhibiting

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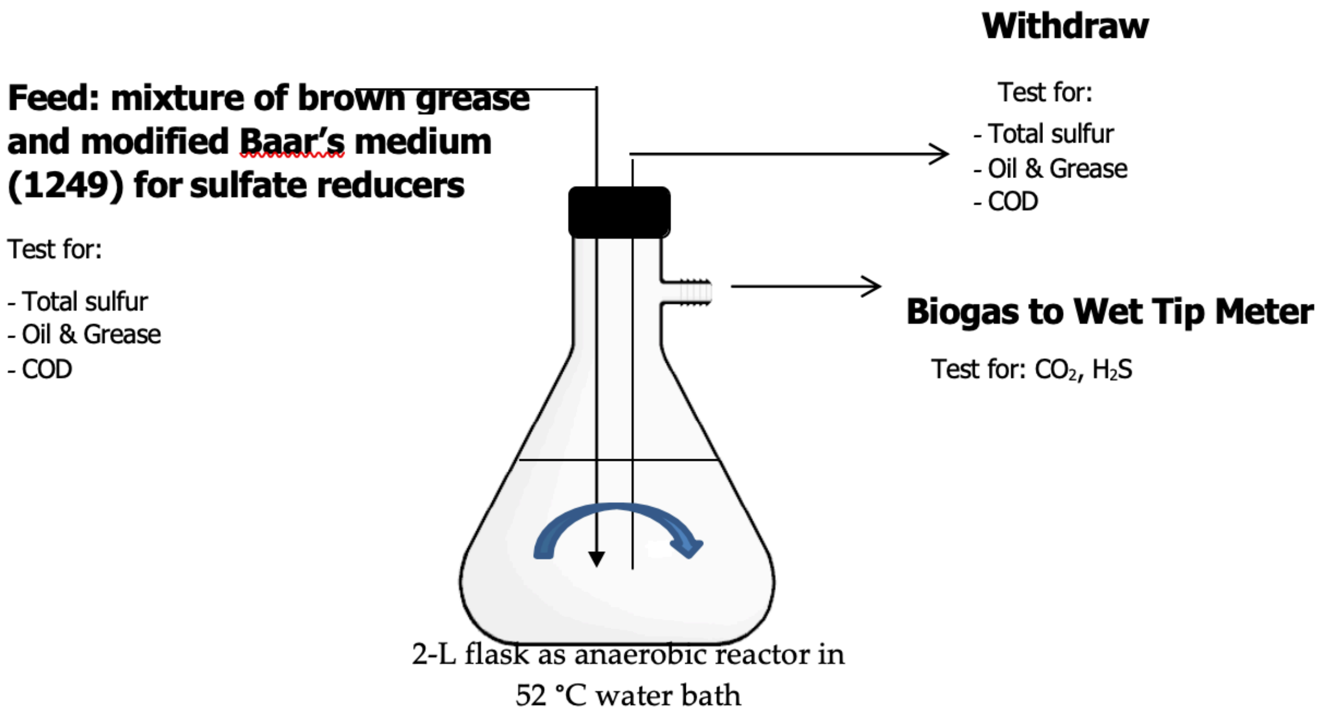
[98] Mizuno et al. 1997.

methanogens with high grease load,[99] and suggests a FOG feed ratio less than 50 percent would be more suitable.

Figure 30: Test Setup of Biological Sulfur Removal from Brown Grease



Source:EBMUD

Biodiesel Desulfurization by Adsorption

Batch ADS

Batch ADS treatments were carried out in 250-mL Erlenmeyer flasks and 400-mL reaction bottles equipped with magnetic stirrers. Biodiesel and an adsorbent were combined at various doses and rapidly mixed during the reaction period. After the reaction was complete, the biodiesel adsorbent mixture was centrifuged at 3600 rpm for 30 minutes to separate the adsorbent from the biodiesel. The top layer in the centrifuge tube was collected and filtered through a 0.45 µm micro-filter as needed. To quantify the ADS removal efficiency, biodiesel samples were collected for total sulfur analysis before and after ADS treatment.

As shown in Table 33, silica gel dosed at 20 wt percent of biodiesel had the highest sulfur removal efficiency (48 percent) of those sorbents tested. A slower mixing speed (300 rpm vs. 500 rpm) and higher adsorbent dose appeared to result in slightly higher sulfur removal

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[99] Suto, P.; Gray, D.M.; Larsen, E.; Hake, J. Innovative anaerobic digestion investigation of fats, oils, and grease. In *Bridging to the Future,* Proceedings of the Residuals and Biosolids Management Conference 2006, Greater Cincinnati, OH, March 12-15, 2006; Water Environmental Federation: Alexandria, VA, 2006.

efficiency, but increasing reaction temperature or time appeared to have negligible effect on removal efficiency when silica gel was used.

Powdered activated carbon provided a higher sulfur removal efficiency compared to silica gel at the same dose (10 wt percent), however it was difficult to separate the biodiesel from the biodiesel- AC mixture afterwards.

PQ® Sorbsil R92 adsorbent required a higher reaction temperature (80 ^{0}C) compared to silica gel (23–60 ^{0}C), and yet the sulfur removal efficiency was slightly lower than silica gel.

Amberlyst® A21 and A26 OH, CaO and zeolite performed poorly under the test conditions providing a less than 15 percent sulfur removal efficiency. Basolite and bentonite (data not shown) also performed poorly in this study.

Table 33: ADS Batch Tests for EBMUD Biodiesel Sulfur Removal

Sorbent(s)	Biodiesel ADS Batch Treatment				Sulfur Removal		
	Dose (wt% to biodiesel)	Temp (°C)	Time (h)	Mixing (rpm)	Initial Sulfur (ppm)	Final Sulfur (ppm)	Removal Efficiency (%)
Amberlyst® A21 followed by A26 OH treatment[1]	5% 5%	60 60	2 2	Not Measured	272	236	13%
Silica Gel[2] Silica Gel[2]	20% 20%	23 23	1 20	300 300	328 328	177 170	46% 48%
Silica Gel[2] Silica Gel[2] Silica Gel[2]	10% 20% 20%	23 23 60	1 1 1	500 500 500	295.8 295.8 295.8	220.3 184.4 174.1	26% 38% 41%
Powered Activated Carbon[3]	10%	23	1	500	295.8	200.8	32%
PQ® SorbSil R92[4] CaO Zeolite[5]	20% 20% 20%	80 60 60	1 1 1	500 500 500	295.8 295.8 295.8	189.1 265.5 265	36% 10% 10%

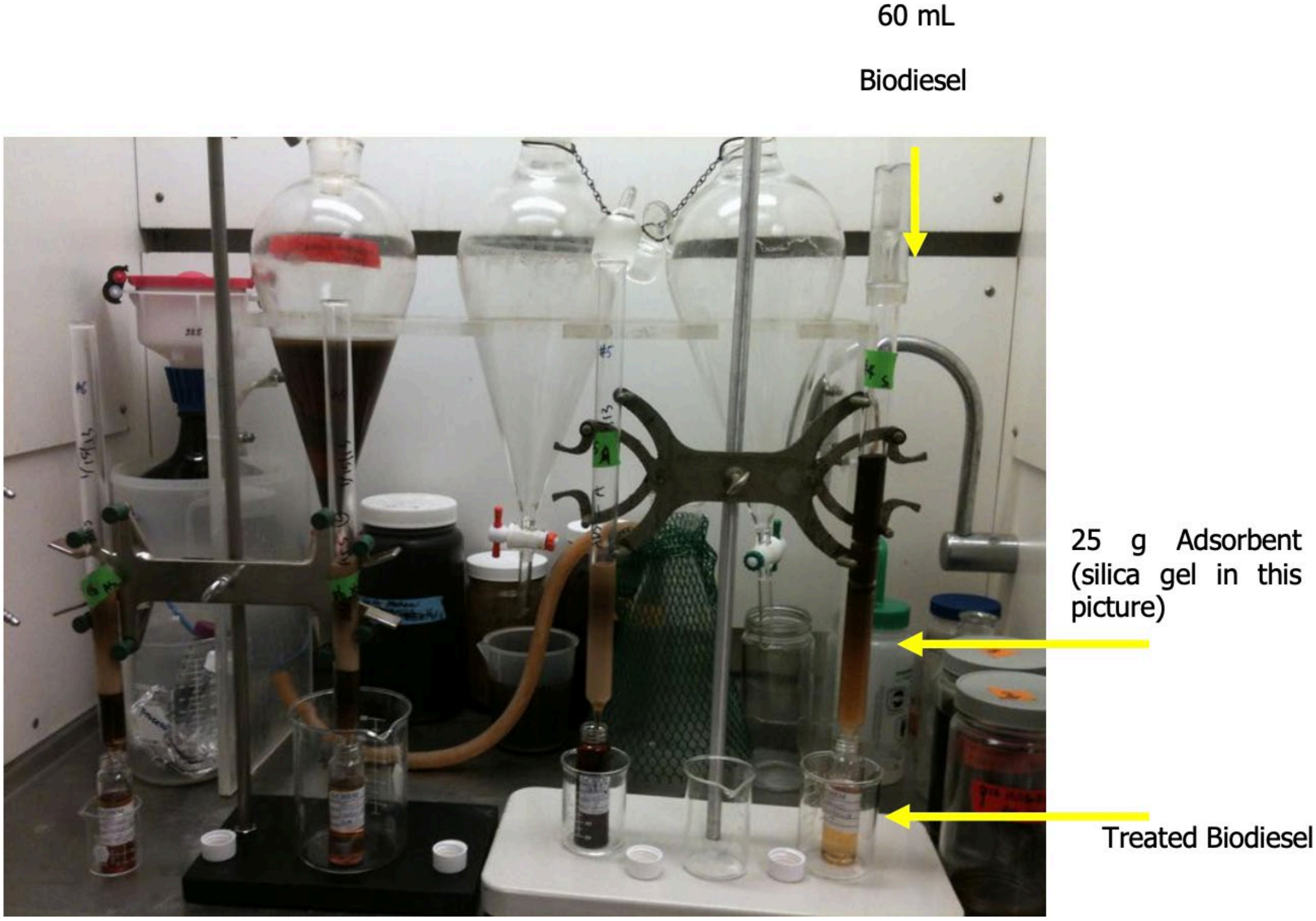
1. Amberlyst® polymers of A21 (weak base resin) and A26 OH (strong base resin) were selected to remove possible sulfur compounds in detergents based on recommendations from the Senior Technical Service Specialist in The Dow Chemical Company.
2. BDH silica gel (70–230 mesh, 60 Å)
3. Supplied by EnviroSupply
4. PQ® Sorbsil R92 (supplied by PQ Corporation) was chosen as an alternative ADS adsorbent to silica gel purchased for laboratory tests due to its
5. Zeolite 13x (AA MS, 13x, powder)

Source: EBMUD

Fixed Column ADS

In addition to the mixed batch reactor, adsorbents were tested in a fixed column as shown in Figure 27. Silica gel and alumina were trialed singularly or in combination, to investigate sulfur removal efficiency for EBMUD-produced brown grease biodiesel samples (Table 33). Filtration columns, with an inner diameter of 20 mm and capacity of 100 mL, were packed with 25 g of the adsorbent or adsorbent mixture and secured vertically to ring stands. Sixty milliliters of EBMUD-produced biodiesel from brown grease was introduced into the column from the top and filtered through the adsorbent media by gravity, over several hours. Treated samples were collected at the bottom of the filtration column using a clean sample vial. The sample volume and total sulfur were quantified before and after filtration and sulfur test results are summarized in Table 34.

Figure 31: Fixed Column ADS Test Setup



Source: EBMUD

Table 34: ADS Fixed Column Tests for EBMUD Biodiesel Sulfur Removal

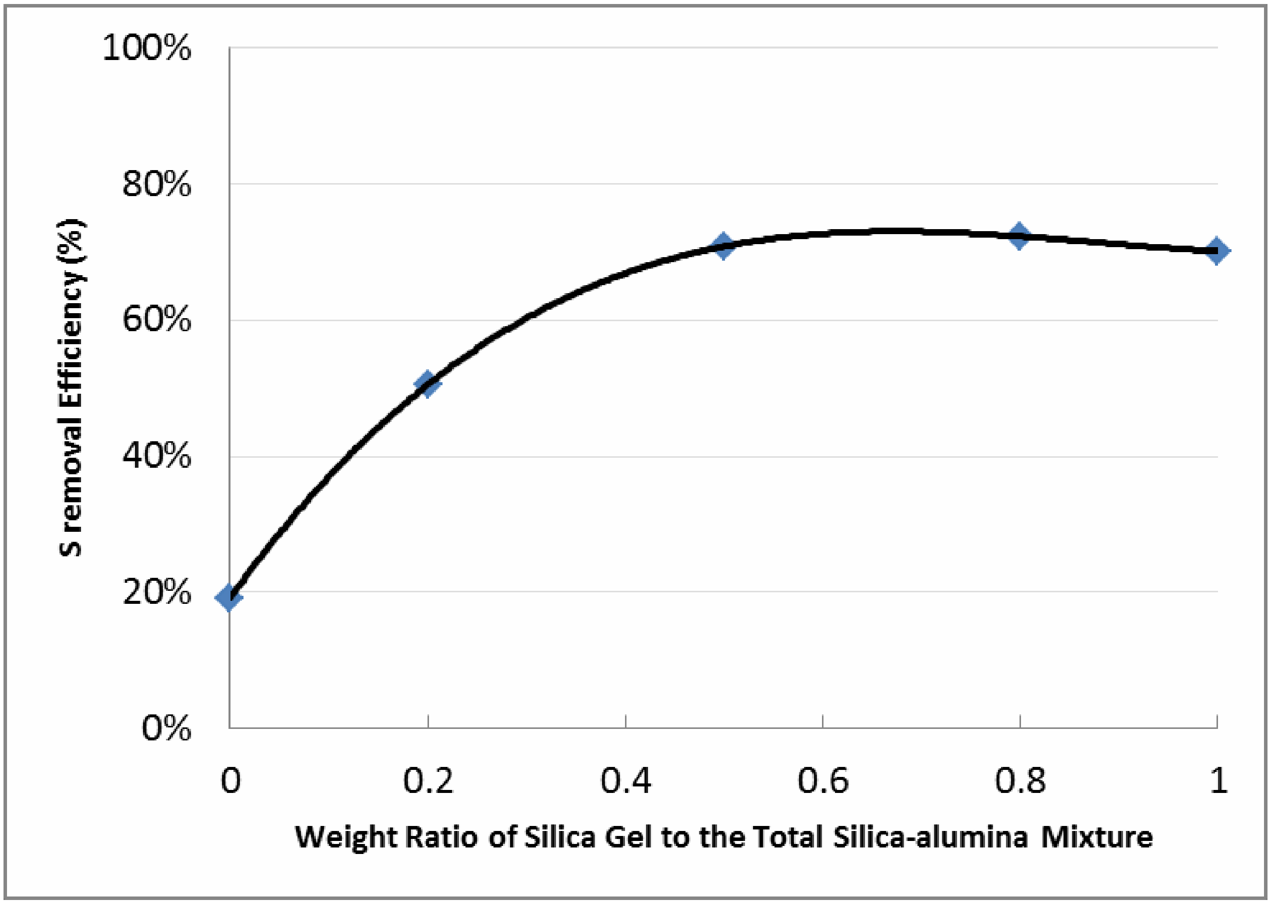
ADS Fixed Column Treatment			Sulfur Removal		
Test	**Adsorbents Packed in Fixed Column**	**Silica Gel:Total Adsorbents (w/w ratio)**	**Initial Sulfur (ppm)**	**Final Sulfur (ppm)**	**Removal Efficiency (%)**
1	Silica Gel 25 g	1	328	98	70%
2	Alumina 25 g	0		265	19%
3	Alumina 12.5 g + Silica Gel	0.5		95.5	71%
4	Alumina 20 g + Silica Gel 5	0.2		162.4	50%
5	Alumina 5 g + Silica Gel 20	0.8	31	86	72%

Source: EBMUD

In Test 1, silica gel was tested in a fixed column. Due to the low bulk density of silica gel, a portion of biodiesel was retained in the silica gel column without passing through. This complication increased the filtration time required and the loss of biodiesel through the filtration column. Incorporating a heavier adsorbent (alumina) with the silica gel uniformly increased the density of the adsorbent mixture and resolved the filtration problem.

As shown in Table 34 and Figure 28, the silica gel column achieved 70 percent total sulfur removal (Test 1) compared to only 19 percent sulfur removal with alumina (Test 2). Interestingly, when a 50/50 mix of alumina and silica gel was tested (Test 3), a similar sulfur removal (71 percent) was achieved to that of silica gel alone (70 percent). In subsequent trials combining the ADS and ODS processes, a 4 to 1 ratio of silica gel to alumina was used due to the higher sulfur removal efficiency and comparable chemical costs between the absorbents.

Figure 32: Biodiesel Sulfur Removal Efficiency by Silica-alumina Fixed Column



Source: EBMUD

Activated carbon (AC) in a fixed column was also evaluated as a potential biodiesel sulfur removal option. As shown in Table 35, the powdered AC column removed 26 percent of the initial sulfur; less than half of that removed by the silica gel and alumina mixture. In addition, it took significantly longer time to filter biodiesel through the AC column, making it less practical for use.

Table 35: Comparison of Biodiesel Sulfur Removal Efficiency by ADS Fixed Columns

Initial Sulfur (ppm)	ADS Fixed Column	Final Sulfur (ppm)	Sulfur Removal Efficiency (%)
296	Silica Gel + Alumina	91.5–112	62–69%
	Activated Carbon (Powder)	220	26%

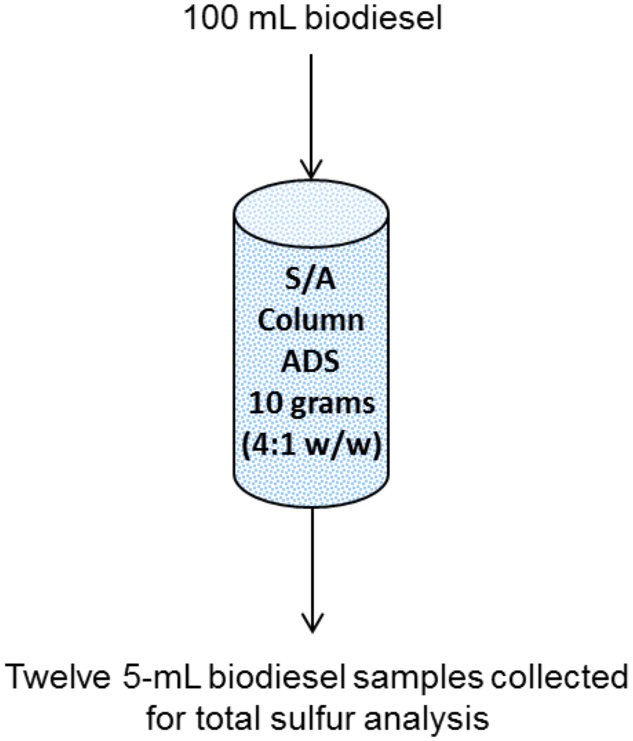
Source: EBMUD

Adsorption Capacity of Silica Gel/Alumina (S-A) Column

The challenge of sulfur removal by adsorption is the limited sulfur adsorption capacity of adsorbent materials. The relationship between the sulfur removal efficiency and amount of biodiesel treated by a S-A ADS filtration column was tested in a set-up as depicted in Figure

29. Ten grams of adsorbent mixture (silica gel to alumina at 4:1 w/w) was packed in the filtration column to treat 100 mL of biodiesel. The treated biodiesel was collected incremental for every 5 mL produced and was stored in separate 40-mL sampling vials. Twelve, 5 mL of biodiesel samples were collected and total sulfur was analyzed for samples 1, 2, 3, 4, 8, and 12.

Figure 33: Test Setup for Silica Gel/Alumina ADS Fixed Column



Source:EBMUD

Total sulfur in the biodiesel sample prior to ADS treatment was 328 ppm. Table 36 and Figure 30 show the reduction of sulfur removal efficiency through the column over the experiment, with the highest sulfur removal of 73 percent obtained in the first 5-mL biodiesel sample (No. 1) and only 32 percent removal for sample No. 12. This indicates that the amount of adsorbent required to achieve a high sulfur removal cannot be reduced, without impacting the sulfur removal efficiency.

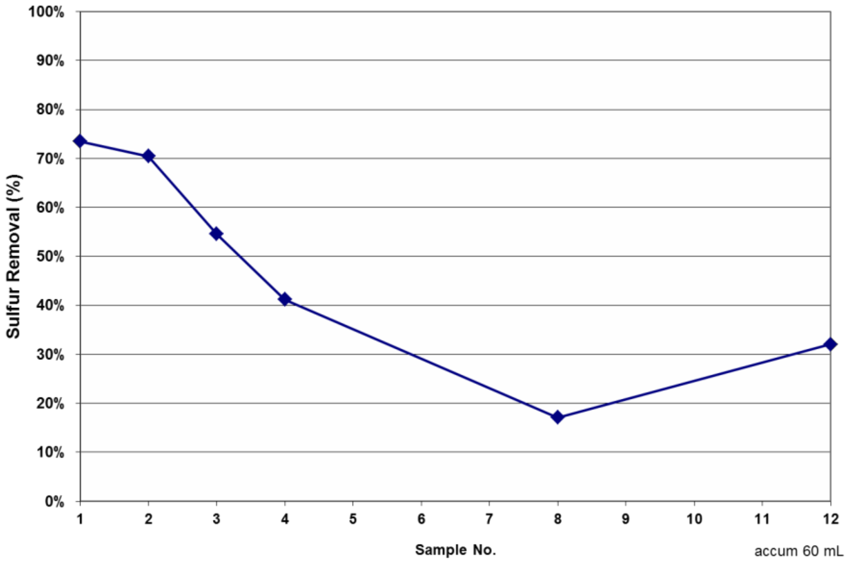
Table 36: Biodiesel Sulfur Removal by Silica Gel/Alumina Fixed Column ADS

Treated Biodiesel Sample No.	1	2	3	4	5-7	8	9-11	12
Final Sulfur (ppm)	87	97	149	193	NM[1]	272	NM[1]	223
Sulfur Removal Efficiency[2] (%)	73%	70%	55%	41%		17%		32%

1. NM: Not Measured
2. Total sulfur in the biodiesel sample prior to ADS treatment was 328 ppm

Source: EBMUD

Figure 34: Biodiesel Sulfur Removal by Silica Gel/Alumina Fixed Column ADS



Twelve 5-mL samples were collected from an ADS column as they emerged, with sample No. 1 being the first, and sample 12 being the last collected. Initial sulfur concentration in the biodiesel prior to ADS was 328 ppm.

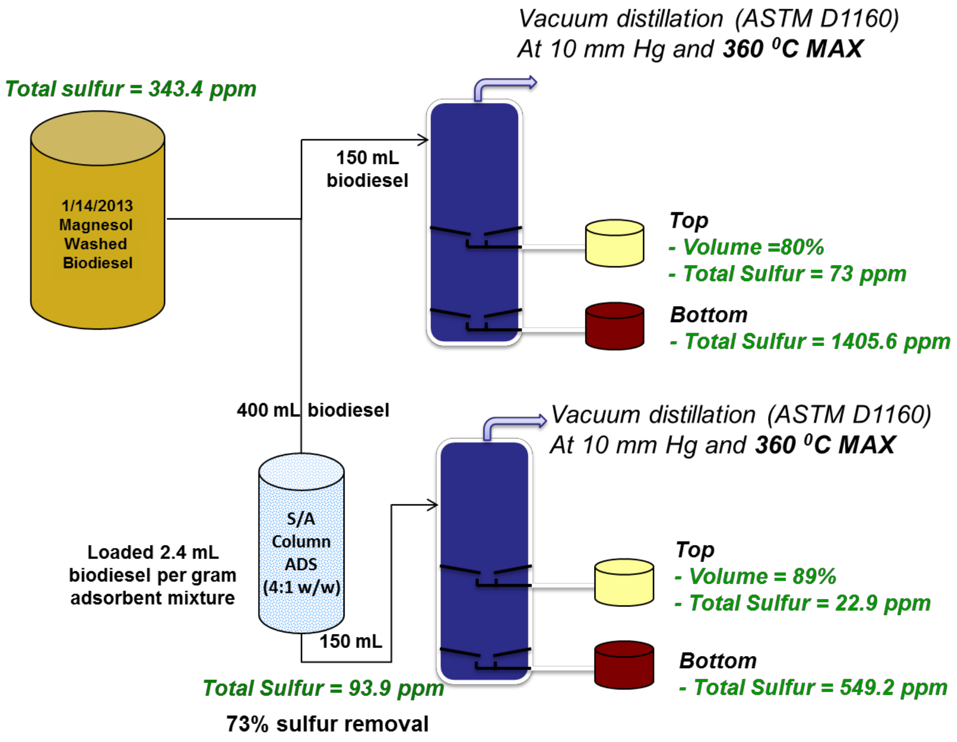
Source: EBMUD

Another consideration for the ADS fixed column is the sizable biodiesel loss in processing. Trials indicate that 30–66 percent of biodiesel could be trapped in the ADS fixed column under gravity flow conditions. Improvements to this process setup to reduce biodiesel loss during filtration need to be made for future testing.

Application of ADS with Biodiesel Distillation for Sulfur Removal

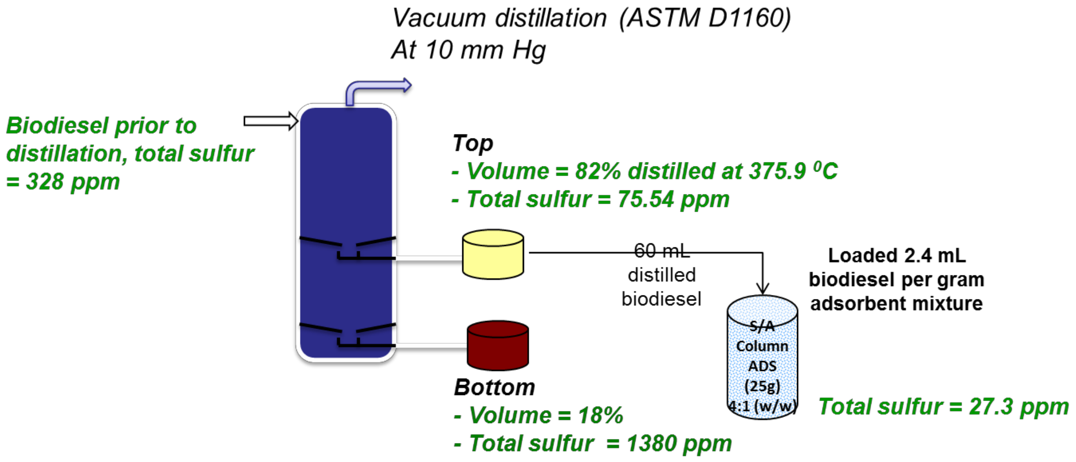
The ADS mixture of silica gel and alumina can reduce biodiesel sulfur by ~70 percent as shown in the previous tests, and may be a beneficial pre- and/or post-treatment process with biodiesel distillation for sulfur removal. Demonstration tests were conducted and showed that the combination of ADS with distillation can reduce biodiesel sulfur concentrations from 328–343.4 ppm to below 30 ppm, as shown in Figures 31 and 32.

Figure 35: ADS Treatment Prior to Biodiesel Distillation



Source: EBMUD

Figure 36: ADS Treatment Post Biodiesel Distillation



S/A represents silica gel mixed with alumina at 4:1 w/w

Source: EBMUD

Regeneration of Spent Adsorbent

Material cost is a consideration for scale-up of any ADS system. Reuse and regeneration of adsorbents have been considered and procedures developed in this study.

Procedures for regenerating spent adsorbents included: Water wash for at least 3 times at 1:1 water:adsorbent ratio (v/v)

1. Methanol wash for at least 3 times at 1 to 1 methanol to adsorbent ratio (v/v)
2. Heating at 104 °C for 2 hours
3. Heating at 550 °C for 15 minutes

Regenerated adsorbents removal efficiency for biodiesel sulfur was measured in the filtration columns. A set of one control and two test filtration columns were compared for side-by-side performance as Test 1 and to simplify the regeneration procedures as Test 2.

Table 37 summarizes regeneration processes and corresponding sulfur removal efficiency. The results indicate that washing the spent adsorbents with methanol, drying at 104 degrees Celsius for 2 hours, followed by heating at 550 degrees Celsius for 15 minutes appeared to be effective in regenerating the spent adsorbents.

Table 37: Regeneration of Spent Adsorbents (BDH Silica Gel and Alumina)

Test	Spent Adsorbent	Water Wash	Methanol Wash	104°C Oven (hours)	550°C Oven (0.25 hour)	Sulfur Removal
1	Mixture of Silica Gel + Alumina at 4:1 (w/w)	No	No	No	No	63% (Control)
		Yes	Yes	2	Yes	72%
		No	Yes	2	Yes	71%
2	BDH Silica Gel from Batch Adsorption Tests	Yes[1]	No	2	No	No Removal

5. Water Wash with a Non-sulfur Containing Detergent

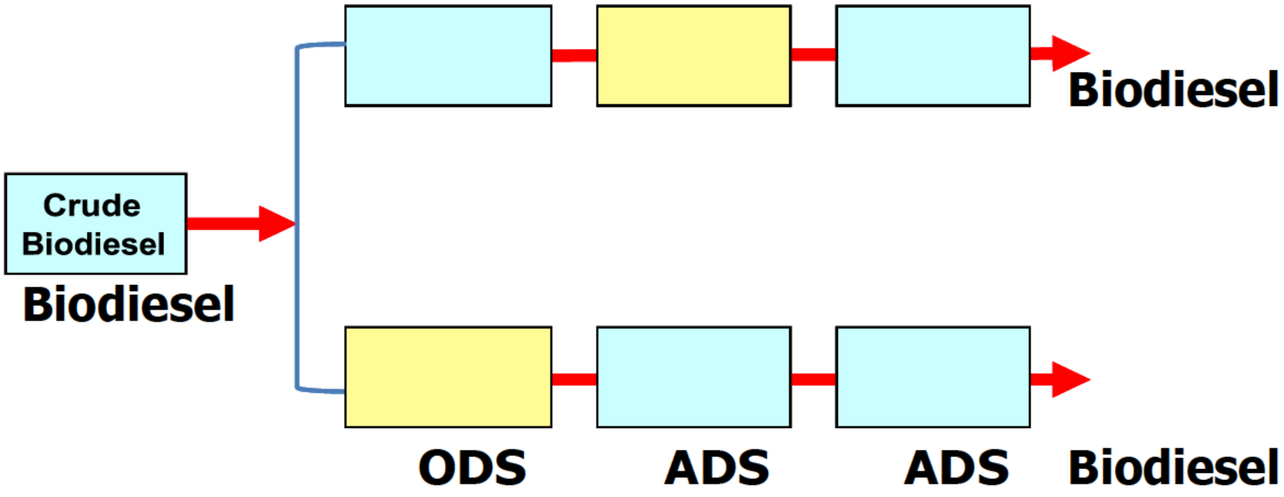
Source: EBMUD

Biodiesel Desulfurization by Combination of ODS and ADS

Results from the ADS tests showed that a maximum of 73 percent of sulfur in brown grease biodiesel could be removed by the ADS fixed-column method, indicating that additional sulfur removal methods are necessary to achieve the 15 ppm sulfur limit.

For this reason, the ODS-ADS combination illustrated in Figure 33 was investigated in this study. In the ODS-ADS combination, ODS is presumed to selectively convert sulfur compounds into more polar compounds that could be removed more easily by the ADS process. An extra ADS treatment step was added prior to- or after- the ODS-ADS treatment process to further enhance sulfur removal to meet the 15 ppm requirement.

Figure 37: Illustration of ODS/ADS Combinations Tested



Source:EBMUD

ADS-ODS-ADS Combination

In the ADS-ODS-ADS trials, biodiesel was treated first through an S-A column to remove a majority of the sulfur compounds before the remaining were oxidized in the ODS reaction. The ODS process used 30 wt percent H_2O_2 in a 1:1 v/v ratio to biodiesel, 0.5% (w/v of biodiesel) phosphotungstic acid ($H_3PW_{12}O_{40}$), and 0.7 percent (w/v of biodiesel) tetraoctylammonium bromide ($C_{32}H_{68}BrN$), serving as a phase transfer agent (PTA). The mixture was heated to 60 °C in a water bath at atmospheric pressure for 1 hour with rapid mixing. Following ODS treatment, the biodiesel was separated by gravity followed by centrifugation at 3600 rpm for 30 min. The separated biodiesel was introduced into a 2nd S-A column for further filtration. Results from the combined ADS-ODS-ADS process are summarized in Table 38.

Table 38: Biodiesel Desulfurization by ADS-ODS-ADS Using H_2O_2, Phosphotungstic Acid and PTA

Initial Sulfur (ppm)	Sulfur After 1st S-A Column (ppm)	ODS Reaction[1]					Sulfur After 2nd S-A Column (ppm)	Sulfur Removal Efficiency (%)
		Test	Ultrasonic	Temp (°C)	Time (min)	Mixing (rpm)		
253	121	Control	-	-	-	-	69	73%
		ODS	-	60	60	1000	7.4	97%
		UAODS[2]	600 W, 20 kHz set at 50%	NM[3]	9[4]	-	8.2	97%
160	80	Control	-	-	-	-	54	66%
		ODS	-	60	60	1000	7.0	96%

- Not applied

1. ODS Reaction: H_2O_2:Biodiesel = 1:1 v/v, 0.5% (w/v) Phosphotungstic Acid and 0.7% (w/v) PTA (tetraoctylammonium bromide $C_{32}H_{68}BrN$)
2. USODS: ultrasonic assisted ODS
3. NM: not measured
4. Ultrasonic treatment was performed 3 times, each at 3 minutes, to avoid high temperature resulting from a consecutive 9- minute treatment

Source:EBMUD

When the ODS process was not applied, the ADS-ADS method alone reduced biodiesel sulfur from 160–253 ppm to 54–69 ppm (Controls), accounting for 66–73 percent sulfur removal efficiency. When the ODS treatment was added between the two ADS processes, the sulfur concentration in the treated biodiesel was reduced to 7.0–7.4 ppm, corresponding to a sulfur removal efficiency of 96–97 percent.

Ultrasonic treatment was applied in selected experiments to test the potential acceleration of the ODS reaction and increase in sulfur removal efficiency. The ultrasonic-assisted ODS (UAODS) experimental procedure was similar to that of the standard ODS process except where a sonicator was used in place of the original mixing system. A TSD-600 Sonic Disruptor, 117 V, 5.5 Amp, 50/60 Hz, with settings maintained at 600 W and 20 kHz at 50 percent was used for all experiments. The reaction was conducted at ambient temperature, with no temperature regulation for the heat generated during the ultrasound-assisted ODS process. The biodiesel ODS solution was sonicated for 9 minutes in total; three 3-minute treatments were applied in sequence with a 1-minute interval between each treatment to avoid high reaction temperature that would result from a consecutive 9-minute treatment.

Incorporation of UAODS between the two ADS processes resulted in a sulfur reduction from 253 ppm to 8.2 ppm, with a corresponding sulfur removal efficiency of 97%. The result demonstrates that ultrasonic assistance has the same effect as the batch ODS treatment conducted at 60 °C with rapid mixing for one hour.

ODS-ADS-ADS Combination

In the ODS-ADS-ADS experiments, crude biodiesel was introduced into the ODS process directly. The ODS process used 30 wt percent H_2O_2 with a 1:1 v/v ratio to biodiesel, with either (1) 0.5 percent (w/v of biodiesel) phosphotungstic acid and 0.7 percent (w/v of biodiesel) tetraoctylammonium bromide, or with (2) 27 percent (v/v of biodiesel) acetic acid with or without the addition of 10 percent powdered activated carbon (w/w of biodiesel). Acetic acid and activated carbon were selected in lieu of the phosphotungstic acid and tetraoctylammonium bromide because they have less environmental impact and are more common resource for wastewater treatment plants.

All ODS reactions were conducted at 60 °C for 1 hour and mixed at 600–1000 rpm. After the ODS reaction, the separated biodiesel was transferred to into the 1st S-A filtration column followed by a 2nd S-A column for another round of adsorption.

The results of the ODS-ADS-ADS experiments are summarized in the Table 39.

Table 39: Biodiesel Desulfurization by ODS-ADS-ADS

Bio-diesel Initial Sulfur (ppm)	ODS Treatment						Sulfur after 1st S/A Column		Sulfur after 2nd S/A Column	
	H_2O_2: Bio-diesel (v/v)	Acid	Catalyst	Temp (°C)	Time (min)	Mixing (rpm)	Final Sulfur (ppm)	Removal Efficiency (%)	Final Sulfur (ppm)	Removal Efficiency (%)
160	-	-	-	-	-	-	80	50%	54	66%
	1:1	Phospho-tungstic acid[1]	PTA[1]	60	60	1000	10.9	93%	10.9	93%
	1:1	Acetic acid[2]	-	60	60	1000	42	74%	16.7	90%
282.4	1:1	Acetic acid[3]	AC[3]	60	60	600	26.1	91%	26.1	91%

- Not applied

1. ODS Reaction: H_2O_2:Biodiesel = 1:1 v/v, 0.5% (w/v) Phosphotungstic acid ($H_3PW_{12}O_{40}$) and 0.7% (w/v) PTA (tetraoctylammonium bromide $C_{32}H_{68}BrN$)
2. ODS Reaction: H_2O_2:Biodiesel = 1:1 v/v, 27% (v/v) acetic acid
3. ODS Reaction: H_2O_2:Biodiesel = 1:1 v/v, 27% (v/v) acetic acid, 10% (w/w of biodiesel) powered activated carbon (AC)

Source: EBMUD

For the phosphotungstic acid assisted ODS-ADS-ADS, the biodiesel sulfur was reduced from 160 ppm to 10.9 ppm (93 percent removal), achieving a higher sulfur removal than ADS-ADS treatment alone (66 percent removal). When the ODS treatment was performed using acetic acid, the ODS-ADS-ADS sulfur removal efficiency was 90–91 percent. These results indicate that ODS-ADS- ADS treatment can significantly reduce sulfur levels in EBMUD biodiesel to lower than 30 ppm, and sometimes less than the 15 ppm ASTM standard.

It should be noted that the 2nd ADS column, in the ODS-ADS-ADS treatment, did not consistently reduce sulfur to the desired level. For example, the sulfur concentrations remain unchanged at 10.9 ppm or 26.1 ppm before and after the 2nd ADS column as shown in Table 4.17.

ODS Process Parameter Optimization

As ODS with ADS treatment was shown to be an effective method for sulfur removal in brown grease biodiesel, tests were conducted to examine various reaction conditions for the ODS process to (1) increase sulfur removal efficiency, and (2) reduce process costs for future large scale applications; by reducing or eliminating chemicals required, employing a lower reaction temperature, or shortening reaction time.

Investigating the Need for Phosphotungstic Acid and PTA in H_2O_2 ODS Treatment

A set of ODS-ADS tests were performed to investigate eliminating the use of phosphotungstic acid and/or PTA required in the H_2O_2 ODS treatment (Table 40).

The control test (ADS in the absence of ODS) showed a 70 percent sulfur removal, while adding ODS treatment with only H_2O_2 (in the absence of an acid and PTA) increased sulfur removal to 78 percent. When phosphotungstic acid was introduced to the ODS process along with H_2O_2, the sulfur removal efficiency increased to 82 percent. When phosphotungstic acid and PTA were incorporated in the H_2O_2 ODS treatment, a 91 percent sulfur removal efficiency was obtained, demonstrating that they are both necessary for the H_2O_2 ODS reaction to achieve maximum sulfur removal efficiency.

Table 40: Investigation of Phosphotungstic Acid and PTA in H_2O_2 ODS Treatment

Bio-diesel Initial Sulfur (ppm)	ODS Treatment						Sulfur after Silica Gel ADS Fixed Column	
	H_2O_2: Bio-diesel (v/v)	Phospho-tungstic Acid (w/v)	PTA[1] (w/v)	Temp (°C)	Time (min)	Mixing (rpm)	Final Sulfur (ppm)	Removal Efficiency (%)
328	-	-	-	-	-	-	98	70%
	1:1	-	-	60	60	1000	70.7	78%
	1:1	0.5%	-				59	82%
	1:1	0.5%	0.7%				30.6	91%

- not applied; 1. Used tetraoctylammonium bromide $C_{32}H_{68}BrN$

Source: EBMUD

Impact of H_2O_2 Dose on ODS-ADS Sulfur Removal

Experiments were conducted for H_2O_2 ODS treatment at various H_2O_2:biodiesel ratios, where all other test conditions were held constant (i.e. acetic acid and AC dose, reaction temperature, mixing rpm, and reaction time). The test results, summarized in Table 4.19, showed that sulfur removal efficiency increased from 88 percent to 92 percent when the H_2O_2:biodiesel dose ratio was increased from 0.5:1 to 1:1. At a higher H_2O_2:biodiesel dose ratio of 2:1, the sulfur removal efficiency reduced to 90 percent.

Table 41: Impact of H_2O_2 Dose on AC-Assisted Acetic Acid ODS Tests

Bio-diesel Initial Sulfur (ppm)	Sulfur after Batch ADS Pre-treatment[1] (ppm)	ODS Treatment						Sulfur after ADS Fixed Column	
		H2O2 :bio-diesel (v/v)	Acetic Acid: bio-diesel (vol%)	AC (w/w)	Temp (°C)	Time (min)	Mixing (rpm)	Final Sulfur (ppm)	Removal Efficiency (%)
285.4	245	-	-	-	-	-	-	80	67%
		0.5:1	27%	10%	60	60	600	34.5	88%
		1:1	27%	10%	60	60	600	24	92%
		2:1	27%	10%	60	60	600	27.9	90%

- not applied; 1. ADS batch treatment using PQ® Sorbsil R92

Source: EBMUD

Impact of Reaction Temperature on ODS-ADS Sulfur Removal

The feasibility of lowering the ODS reaction temperature from 60 degrees Celsius to 40–45 degrees Celsius was tested (Table 42). Sulfur removal efficiency decreased from 91 percent at 60 degrees Celsius (Test 3) to 85 percent at 40–45 degrees Celsius (Test 2), when all other parameters were held constant. Impact of AC Addition on ODS-ADS Sulfur Removal

As shown in Table 42, at reaction temperatures of 40–45 degrees Celsius , an 11 percent increase in sulfur removal efficiency (from 74 percent in Test 1 to 85 percent in Test 2) was observed with the addition of AC to the ODS reaction. The AC-enhanced sulfur removal is likely a result of AC functioning as both a catalyst and an adsorbent that removes sulfur in the biodiesel product as demonstrated in the earlier tests. AC may also have improved the mass transfer between the two immiscible liquid reaction phases: an oil phase containing sulfur compounds and a polar phase that contains H_2O_2.

Table 42: Impact of Reaction Temperature and AC on H_2O_2 ODS Tests

Bio-diesel Initial Sulfur (ppm)	Test	ODS Treatment						Sulfur After ADS Fixed Column	
		H2O2 :bio-diesel (v/v)	Acetic Acid: bio-diesel (vol%)	AC (w/w)	Temp (°C)	Time (min)	Mixing (rpm)	Final Sulfur (ppm)	Removal Efficiency (%)
282.4	Control	-	-	-	-	-	-	115	59%
	1	1:1	27%	-	40–45	60	600	74	74%
	2	1:1	27%	10%	40–45	60	600	42	85%
	3	1:1	27%	10%	60	60	600	26.1	91%

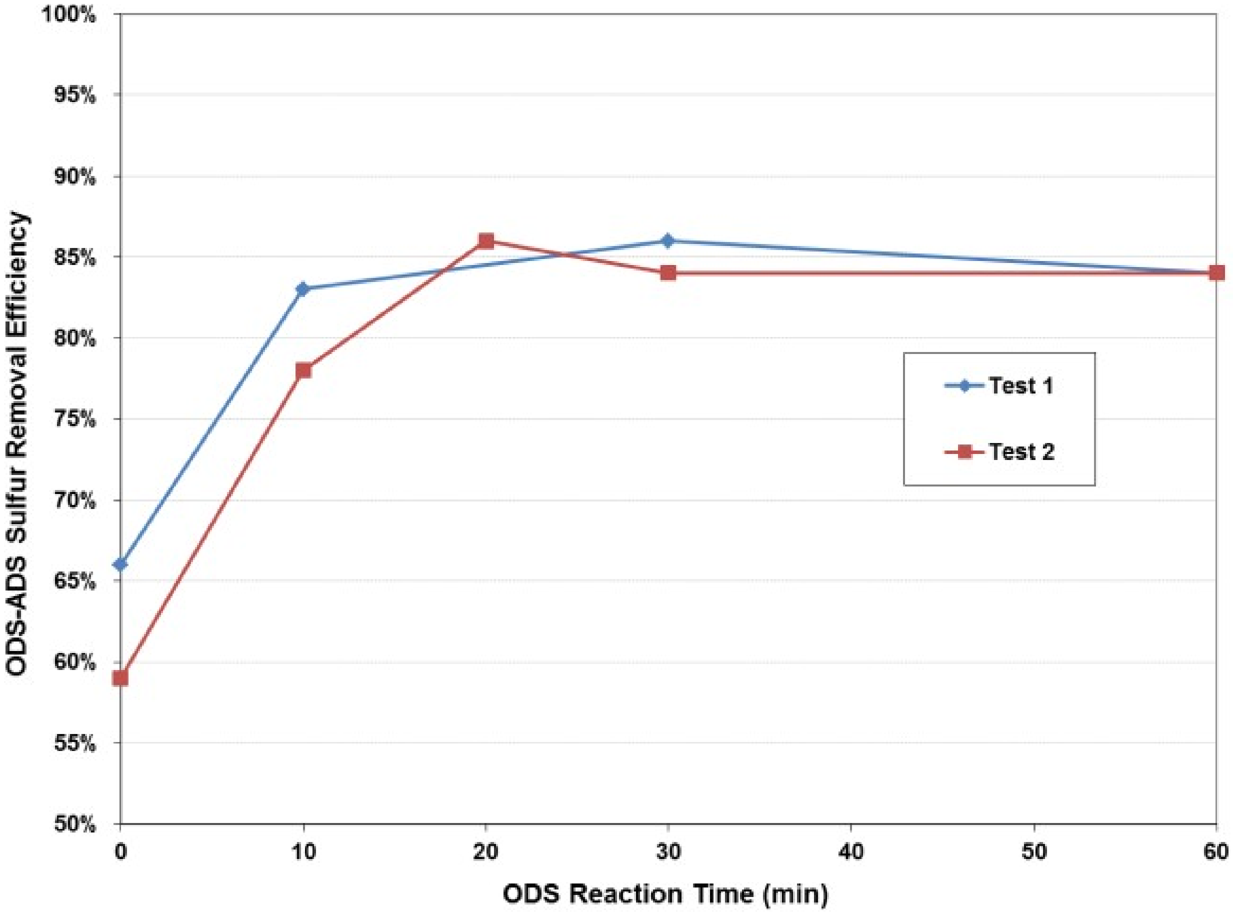
- not applied

Source: EBMUD

Impact of ODS Reaction Time on ODS-ADS Sulfur Removal

Two sets of trials (Tests 1 and 2) were conducted to investigate the impact of ODS reaction time on sulfur removal by ODS-ADS treatment (Figure 34). Tests showed that ODS reaction time has little impact on sulfur removal efficiency after about 20–30 minutes; indicating that ODS reaction time can be reduced from 1-hour down to 20–30 minutes.

Figure 38: Effect of ODS Reaction Time on Sulfur Removal by ODS-ADS



Source: EBMUD

Test 1 ODS Reaction: H_2O_2:Biodiesel = 0.5:1 v/v, 27 percent (v/v) acetic acid, 10 percent (w/v of biodiesel) silica gel, 60–65 degrees Celsius , mixing Test 2 ODS Reaction: H_2O_2:Biodiesel = 1:1 v/v, 27% (v/v) acetic acid, 60–65 degrees Celsius, mixing ADS used for both tests was S/A column (i.e. mixture of silica gel and alumina at 4:1 w/w ratio). At ODS time = 0 min, sulfur was removed by ADS alone (i.e., in absence of ODS treatment).

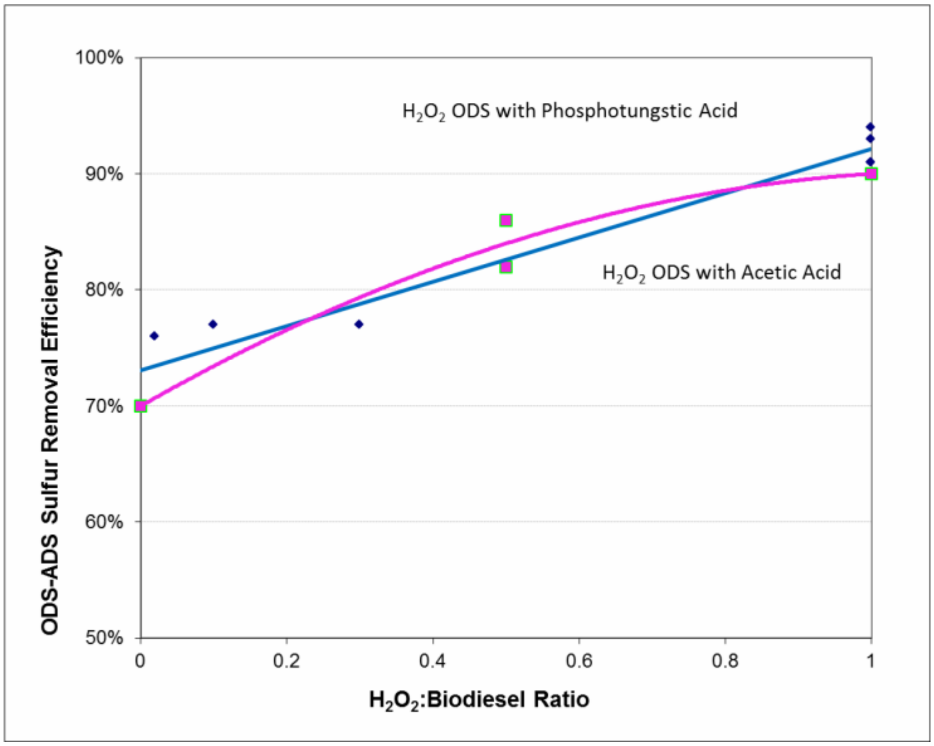
Comparison of Two H_2O_2 ODS Processes

As mentioned earlier, two H_2O_2 ODS processes were evaluated under this study:

- H_2O_2 ODS using phosphotungstic acid and tetraoctylammonium bromide, and
- H_2O_2 ODS using acetic acid with either activated carbon or silica gel

The sulfur removal difference between the two ODS processes for varying H_2O_2 doses was examined by compiling data from several ODS trials conducted over this study (not all data is shown in this report). Results presented in Figure 35 demonstrate that there is no significant difference in sulfur removal between the two processes. The results also show that sulfur removal was improved when the H_2O_2 dose was increased for both ODS processes.

Figure 39: Comparison of Two Different H_2O_2 ODS Processes on Sulfur Removal by ODS-ADS



Phosphotungstic acid ODS reaction: H2O2, 0.5 percent (w/v) Phosphotungstic Acid and 0.7 percent (w/v) PTA, 60–65 degrees Celsius, mixing Acetic acid ODS reaction: H2O2, 27 percent (v/v) acetic acid, 10 percent (w/w of biodiesel) powered activated carbon or silica gel, 60– 65 degrees Celsius, mixing

At ODS time = 0 min, sulfur was removed by ADS alone (i.e., in absence of ODS treatment).

Source: EBMUD

FOG to Biodiesel Production and ASTM-compliance Test

Optimal FOG-to-biodiesel and biodiesel desulfurization processes identified in this study were used to produce biodiesel in quantity sufficient (~1 gallon) for complete biodiesel testing to evaluate ASTM compliance.

As illustrated in Figure 36, first, raw brown grease extracted from EBMUD FOG by centrifuging was esterified with a 16:1 molar ratio of methanol:FFA using 5 percent sulfuric acid as catalyst. The esterification step was conducted at 60 °C for one hour, where a single esterification step typically reduces the FFA in brown grease samples to less than one percent. The esterified product was separated from the methanol and acid catalyst by gravity settling for one hour. Next, the triglycerides in the sample were transesterified using a base catalyst. The sample was combined with a 12:1 molar ratio of methanol:triglycerides using 5 percent potassium hydroxide as catalyst, at 60 degrees Celsius for two hours. The first test was conducted with half the methanol and catalyst, and only a one-hour reaction time.

The crude biodiesel was separated from the methanol and glycerin by gravity settling. The resulting biodiesel was washed with water followed by a dry wash with magnesol (2.5 percent by mass) to remove water, soaps and other impurities.

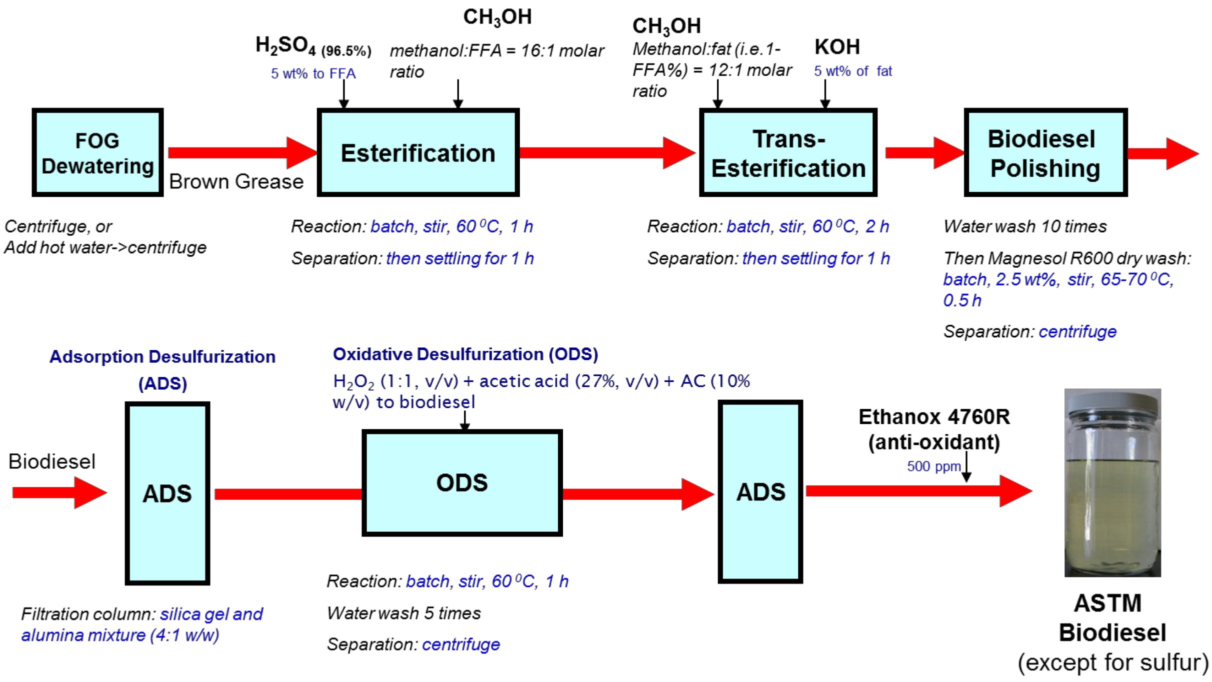
The polished biodiesel was further treated with the ADS-ODS-ADS process for sulfur removal. ADS treatment was done by passing biodiesel through a S-A ADS fixed column and then the ODS process was applied. The ODS process used 30 wt percent H_2O_2 with a 1:1 v/v ratio to biodiesel, mixed with 27 percent acetic acid (v/v of biodiesel) and 10 percent powdered activated carbon (w/v of biodiesel) to assist the ODS reaction. The ODS reaction was conducted at 60 °C for 1 hour. After the ODS reaction, the separated biodiesel was poured into the 2nd S-A column for filtration. The final biodiesel product was tested for ASTM compliance at the Iowa Central Fuel Testing Laboratory, an International Organization for Standardization (ISO)-9001:2008 and BQ-9000 accredited laboratory by the National Biodiesel Accreditation Commission, where the majority of the samples generated during this study were analyzed. Iowa lab was selected after a thorough evaluation by the research team by taking into consideration analytical methods employed, accuracy, cost, turnaround time and willingness to accommodate the research needs of this project.

ASTM test results for each of the three biodiesel batches produced are summarized in Table 43. During the first test, the results indicated that the majority of standards were met except for oxidation stability, total sulfur, and total glycerin. By adding 500 ppm Ethanox 4760R antioxidant to the biodiesel product, the oxidation stability was significantly improved and the ASTM requirement was met in the two subsequent tests (Tests 2 and 3). The total glycerin

ASTM requirement was not met due to a deficient transesterfication reaction in the first test. After doubling the dose of methanol and base catalyst as well as the reaction time, the total glycerin met the ASTM requirement in Tests 2 and 3.

It was noted that in some batches, total sulfur levels in treated biodiesel were significantly higher than those obtained in the earlier, small scale tests (<1 L, typically ~100 mL biodiesel), where less than 50 ppm sulfur was consistently obtained with many repetitive tests of the ADS- ODS-ADS sulfur treatment method (selected results were presented in Section 4.6.3). The increased sulfur levels became an issue as the ODS reaction was scaled up from less than a liter, in the earlier tests, to several liters. Subsequent testing revealed that for larger scale processes, the ratio of H_2O_2:biodiesel must be significantly reduced in order to maintain control of the reaction and to avoid an increase in total sulfur levels measured in the treated samples. The ODS-ADS treatment should not have added sulfur to the biodiesel samples; the reason for the increase in total sulfur results was not determined. Further testing is needed to identify an effective form of ODS that is compatible with large scale biodiesel production.

Figure 40: Integrated FOG-to-Biodiesel Process



AC=Activated Carbon

Source: EBMUD

Table 43: ASTM Testing Results on EBMUD Biodiesel

Test	ASTM Method	ASTM limit	Test 1	Test 2	Test 3
Calcium & Magnesium, combined	EN 14538	5 ppm max	0.1	0.2	0.1
Flash Point (closed cup)	D 93	93 °C min	165.0	165.0	173.0
Methanol Content, or Flash Point	EN 14110 D 93	0.2% mass max 130 °C min	0.000 165.0	0.000 165.0	173.0
Water & Sediment	D 2709	0.05% vol. max	NM[1]	0.000	0.000
Kinematic Viscosity, 40 °C	D 445	1.9–6.0 mm^2/sec	5.503	4.793	4.656

Test	**ASTM Method**	**ASTM limit**	**Test 1**	**Test 2**	**Test 3**
Sulfated Ash	D 874	0.02% mass max	0.002	0.001	0.000
Sulfur	D 5453	15 ppm max	35.3 (Fail[2])	132.3 (Fail[2])	76.4 (Fail[2])
Copper Strip Corrosion	D 130	No. 3 max	1A	1A	1A
Cetane	D 613	47 min	NM[1]	57.6	56.8
Cloud Point	D 2500	°C, Report	7	6	7
Carbon Residue 100% sample	D 4530	0.05% mass max	0.029	0.005	0.005
Acid Number	D 664	0.5 mg KOH/g max	0.01	0.00	0.04
Free Glycerin	D 6584	0.020% mass max	0.000	0.000	0.000
Total Glycerin	D 6584	0.240% mass max	**0.805[3]** **(Fail[2])**	0.124[4]	0.023[4]
Monoglycerides	D 6584		0.019	0.020	0.058
Diglycerides	D 6584		1.274	0.783	0.043
Triglycerides	D 6584		5.840	0.016	0.014
Phosphorus Content	D 4951	0.001% mass max	0.000 09	0.0000 38	0.0000 04
Distillation	D 1160	360 °C max	NM[1]	355.8	352.7

Test	ASTM Method	ASTM limit	Test 1	Test 2	Test 3
Sodium/Potassium, combined	EN 14538	5 ppm max	0.2	0.0	0.0
Oxidation Stability	EN 15751	3 hours min	**1.2 (Fail[2])**	23.8	41.6
Cold Soak Filtration	D 7501	360 seconds max	NM[1]	126	117

1. NM: Not measured
2. Fail = fail to meet the ASTM 6751 standards
3. Transesterification reaction: 6:1 molar ratio of methanol:triglycerides using 2.5% potassium hydroxide as catalyst and the reaction was carried out at 60 °C for one hour
4. Transesterification reaction: 12:1 molar ratio of methanol:triglycerides using 5% potassium hydroxide as catalyst and the reaction was carried out at 60 °C for two hours

Source: EBMUD

Findings

Over a hundred bench tests were completed in this study to identify potential low-cost alternatives for recovering brown grease from FOG, converting brown grease into biodiesel, and removing sulfur and other impurities from biodiesel to comply with the ultra-low sulfur ASTM 6751 standards for B100 biodiesel. Findings are summarized below.

Brown Grease Extraction from FOG

The most efficient brown grease extraction method of those tested was direct heating of FOG on a hot plate or by hot water addition, followed by centrifugation.

Methods tested but determined to be ineffective included: brown grease extraction using ethanol (solvent); addition of ferric chloride, calcium chloride, or glycerol to break FOG emulsions to improve brown grease extractions; use of commercial demulsifiers (trials conducted by Emulsion Control, Inc. using EBMUD FOG); and application of the Abanaki Grease Grabber® (bench unit) to remove floating oil and grease by making the use of the differences in specific gravity and surface tension between oil and water.

FogBusters Inc. was contacted by the EBMUD research team to investigate feasibility of testing its FogBuster™ unit which claimed capable of removing FOG from industrial wastewater streams with higher efficiency and lower cost than comparable systems.

Brown Grease-to-Biodiesel Production Methods

- Two-step acid-base process

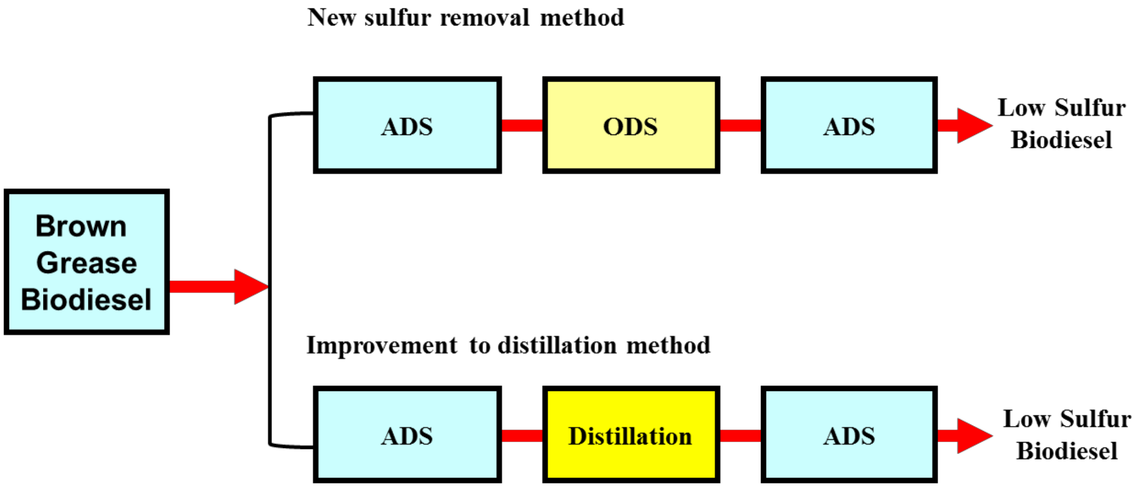
  - Esterification using a 16:1 methanol:FFA ratio and sulfuric acid catalyst at 5% by mass reduced FFA concentrations below 1 percent in one hour.
  - Transesterification using a 12:1 methanol:triglycerides ratio and potassium hydroxide catalyst at 5 percent by mass reduced total glycerin concentrations below ASTM limit of 0.240 percent in two hours.
  - Addition of antioxidants to biodiesel produced using the two-step acid-base process (Figure 4.20) was necessary to meet the ASTM standards for oxidative stability.
    - ✓
- Other potential process improvements explored
  - Utilization of a solid catalyst (Amberlyst™ BD20) in lieu of sulfuric acid in esterification to convert brown grease FFA into biodiesel. A longer reaction time was found to be necessary.
  - Application of a low-cost lipase catalyst (A. oryzae), in lieu of acid-catalyzed esterification process. This method was successful; however, a minimum of 6 hours or longer reaction time was required.
- Methods tested but determined to be ineffective included: ultrasound assistance to reduce methanol:FFA ratio from 16:1 to 10:1 in sulfuric acid-catalyzed or solid-catalyzed (Amberlyst™ BD20) esterification process.

Brown Grease and Biodiesel Desulfurization Methods

- Bench sulfur removal tests, summarized in Table 44, were conducted with both brown grease (~400-500 ppm total sulfur) and brown-grease-derived biodiesel (~300 ppm total sulfur), though many were found ineffective (i.e. 0—30 percent sulfur removal).
- Silica gel proved to be the most efficient sulfur removal adsorbent for brown grease (45 percent) and brown-grease-derived biodiesel (70 percent) of the many adsorbents tested for ADS. It also removes the unsightly brown color often present in brown grease biodiesel. However, biodiesel treated with ADS alone could not meet the total sulfur limit of 15 ppm (max) required by the ASTM standard (S-15 grade).
- ODS treatment in combination with ADS significantly reduced biodiesel total sulfur by more than 90 percent.
- A combination of ADS and ODS maximized biodiesel sulfur removal. ADS-ODS-ADS resulted in brown-grease-derived biodiesel sulfur below 15 ppm for multiple tests and was 20–50 ppm for the majority of tests. While sulfur levels were typically above the ASTM limit of 15 ppm for B100 biodiesel, this method has potential as a low cost sulfur treatment alternative to vacuum distillation, as the ADS/ODS methods' reaction takes place under near ambient conditions.
- Sulfur compounds analyzed in the brown grease biodiesel used for this study, were found to have the following characteristics:
  - Concentrated in the bottom distillate fraction after vacuum distillation per ASTM D1160 method (10 mmHg vacuum and 360 0C max).
  - Removed by silica gel ADS and more by ODS-ADS treatment.

  - Unaffected by many treatment methods tested (i.e. low removal efficiency of 0–30%) for removing sulfur from brown grease or brown grease biodiesel (Refer to Table 44).
- Other findings related to sulfur characterization:
  - Sulfuric acid used in the two-step biodiesel production process is not a significant contributor of total sulfur in brown grease biodiesel.
  - A mixture of kitchen and laundry detergents purchased from a supermarket contained a total sulfur content as high as 44,000 ppm. It is unclear whether this could be a significant source of the high sulfur found in FOG and brown grease extracted from FOG.
- Potential brown grease biodiesel sulfur removal methods developed in this study could be used alone to remove sulfur or used to improve the distillation method, as illustrated in Figure 37. Biological sulfur removal with thermophilic anaerobic digestion may be worth further study as a process step in a larger treatment train.

Figure 41: Brown Grease Biodiesel Sulfur Removal Methods



Oxidative desulfurization (ODS) with or without ultrasound assistance
- H_2O_2+ phosphotungstic acid + Tetraoctylammonium bromide, or
- H_2O_2+ acetic acid + activated carbon catalyst

Adsorptive desulfurization (ADS)
- Silica gel, or silica gel mixed with alumina

Source: EBMUD

Conclusion

- Biodiesel produced from FOG using the processes developed and optimized in this study (shown in Figure 37) met all of the ASTM 6751 standards for B100 biodiesel except to the ultra-low sulfur requirement of 15 ppm maximum total sulfur (S-15).
- This project has made significant progress towards developing a potential low-cost biodiesel production method from FOG and sulfur removal in brown grease derived biodiesel. However, the FOG-to-biodiesel technology has not demonstrated cost

effectiveness and sufficient robustness in meeting the ASTM 6751 ultra-low sulfur standard (S-15) at this stage. Further work is necessary to identify sulfur contaminant sources in FOG waste and to advance processing technology.

Table 44: Brown Grease and Biodiesel Sulfur Removal Tests Conducted in This Study

Test	Brown Grease	Biodiesel Made from Brown Grease
ADS	Batch treatment by various adsorbents: - Silica Gel[1] - Bentonite - Magnesol - Diatomaceous earth - Baking soda - Sand - Zeolite	Both batch treatment and fixed column filtration by individual adsorbent or mixture of adsorbents: - Silica Gel[1] - Bentonite - Magnesol - Diatomaceous earth - Baking soda - Sand - Zeolite - Activated carbon (power)[2] - Activated carbon (granular)[2] - Basolite - Alumina - Calcium oxide
Polymer Treatment	- Amberlyst® A21 - Ambersep™ BD19 - Commercial - polymer - products[3]	- Amberlyst® A21 first then Amberlyst™ A26 - OH - Commercial polymer products[3]
ODS Combined with ADS[4] **UAODS Combined with ADS**[4]	ODS with and without ultrasound assistance - H2O2 - H2O2 with acetic - acid - O_3 with air	ODS with different oxidants and catalysts—with or without ultrasonic assistance Oxidants tested included: - H_2O_2 with acetic acid - O_3 with air - O_3 with air, H_2O_2, and acetic acid - Air - I2[5] Catalysts tested included: - Phosphotungstic acid (with or without tetraoctylammonium bromide) - Activated carbon - Silica gel

Test	Brown Grease	Biodiesel Made from Brown Grease
Precipitation	Precipitation with - $FeCl_3$ (for FOG) - $CaCl_2$ (for FOG) - $BaCl_2$	Precipitation with - $BaCl_2$ - Copper
Other Methods	- Acid wash with 1N - HCL to remove - sulfate-type - surfactant - Biological - sulfur removal - through - thermophilic - anaerobic - digestion	- Acid wash with 1N HCL to remove sulfate- - type surfactant - Biological sulfur removal through - thermophilic anaerobic digestion - Hot water wash - Base wash with NaOH at various concentrations[4] - Extraction with methanol - Vacuum distillation in combination with ADS[4] - Treatment by unknown technologies developed by RPM Sustainable Technologies[4]

1. Silical gel treatment considered effective at conditions tested. Silica gel tested in this study included: BDH (70–230 mesh, 60Å), Alfa Aesar (70–230 mesh, 60Å), Fisher (30–70 mesh, S-834-1), and PQ® Sorbsil R92 (powder, 80–100Å). EMD (70–230 mesh, 60Å) removed <30% of biodiesel sulfur in batch treatment
2. Treatment methods had >30% sulfur removal at conditions tested. Activated carbon was supplied by EnviroSupply
3. Trials conducted by Kite Technology Group
4. Treatment methods had >30% sulfur removal at conditions tested
5. I2 (in ethanol) followed by precipitation of oxidized component (such as protein etc.) with ether.

Source: EBMUD

CHAPTER 5: Investigation of Alternative Biodiesel Feedstocks from Municipal Wastewater Treatment Plants

Approach

Leveraging Wastewater Treatment Plant (WWTP) assets to more cost-effectively produce biodiesel may encourage more WWTPs across the country to produce biodiesel from wastes.

Specifically, this task aimed to:

- Explore the potential for alternative biodiesel feedstocks derived from wastewater or wastewater solids at municipal WWTPs, and
- Evaluate the potential to economically convert methane (produced at WWTPs) into methanol used for biodiesel production at WWTPs (literature review only).

A literature review of alternative biodiesel feedstocks at municipal WWTPs and the methane to methanol process was conducted. Laboratory-scale experiments were used to further investigate and evaluate alternative feedstocks with significant potential at a WWTP. Components of the WWTP sewage sludge, *Nocardia* foam, and raw wastewater were considered for feedstocks in the biodiesel process.

Sewage Sludge to Biodiesel Literature Review Summary

Sewage sludge is organic waste solids generated from municipal WWTP processes. There are two main types of WWTP sludges as a byproduct:

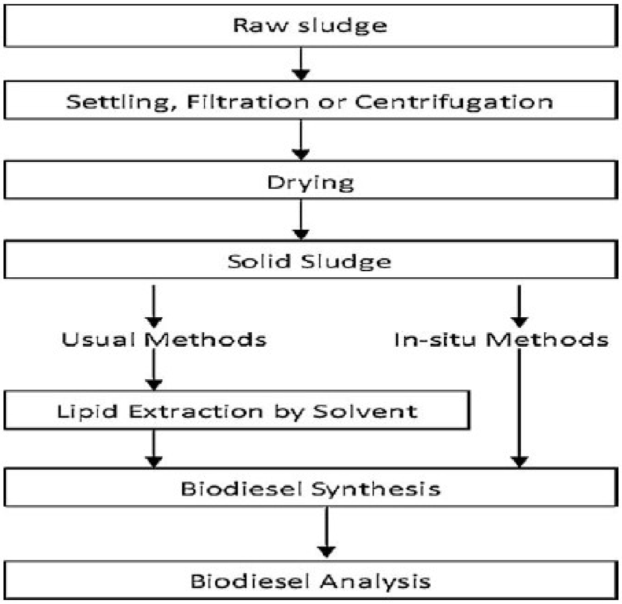
- Primary sludge (Raw Sludge): readily settable material from raw sewage collected in wastewater primary settling tanks
- Secondary sludge (Activated Sludge): predominantly microbial solids produced by the WWTPs biological liquid treatment process

The oil and grease component of these sludges could be extracted as a potential feedstock for biodiesel.

Evaluation of the Sludge to Biodiesel Process

The process of converting sludge into biodiesel requires dewatering or thickening of sludge, removal of water content by drying, followed by lipid extraction and a biodiesel conversion process as outlined in Figure 42.

Figure 42: Overall Biodiesel Production Scheme from Sludge



Source: (Siddiquee and Rohani, 2011)

Processes used to extract oil and grease or lipid components from WWTP sludge were investigated based on the following considerations:[100]

- Quality of biodiesel
- Pretreatment of raw sludge for efficient lipid extraction
- Lipid extraction from the sludge
- In-situ biodiesel production methods from solid sludge
- Process economics

Quality of Biodiesel

Sludge contains triglyceride, fatty acids, phospholipids, bacterial lipids available for extraction, in addition to various chemicals contaminants like wax esters, steroids, terpenoids, polyhydroxyalkanoates, hydrocarbons, pharmaceutical chemicals that could potentially contribute to fuel/gravimetric yield.[101]

The lipid composition of a particular sludge has been identified as 65 percent FFA (C12–C18, mostly palmatic, stearic, oleic acid), 28 wt percent unsaponifiable material (C9–C16 alkane),

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[100] Siddiquee, M. N.; Rohani, S. Lipid extraction and biodiesel production from municipal sewage sludges: A review. *Renewable and Sustainable Energy Rev.* **2011,** *15* (2), 1067-1072.

[101] *Ibid.*

and 7 wt percent glyceride fatty acids.[102] The biodiesel produced from extracted sewage sludge lipids was reported to be similar to biodiesel produced from pure vegetable oil (Dufreche et al., 2007).[103]

Pretreatment of Raw Sludge

Primary sludge typically contains 95–96 wt percent water and secondary sludge can be as high as 98– 99 wt percent water. Pretreatment and drying of liquid sludge is crucial to efficiently extract lipids from sewage sludge. If liquid sludge is used directly for lipid extraction, the process would have an impractical chemical demand and require large-volume processing equipment; due to the viscous or tacky properties sludge has with only a portion of its water content removed.

Successful methods for drying sludge are outlined in Table 45. Various sludge drying technologies have been noted in the literature such as: vacuum drying, fluid-bed drying, freeze drying, and oven drying.[104]

Table 45: Summary of Sewage Sludge Drying Methods

Original Sludge	Process		Reference
Secondary Sludge (~2% solids)	1.	Gravity settling	(Dufreche et al., 2007)
	2.	Centrifugation (3000 rpm, 20 min) [7–8% w/w solids]	
	3.	Adsorption by Hydromatrix	
	1.	Gravity settling	
	2.	Pressure filtration (80 μm, 20 μm nylon filter) [12–14% solids]	
	3.	Adsorption by Hydromatrix	
	1.	Gravity settling (0 °C, 24 h)	

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[102] Boocock, D.G.B.; Konar, S.K.; Leung, A.; Ly, L.D. Fuels and chemicals from sewage sludge: 1. The solvent extraction and composition of a lipid from a raw sewage sludge. *Fuel* **1992,** *71* (11), 1283-1289.

[103] Dufreche, S.; Hernandez, R.; French, T.; Sparks, D.; Zappi, M.; Alley, E. Extraction of Lipids from Municipal Wastewater Plant Microorganisms for Production of Biodiesel. *J Amer Oil Chem Soc.* **2007,** *84* (2), 181-187.

[104] Mondala, A.; Liang, K.; Toghiani, H.; Hernandez, R.; French, T. Biodiesel production by *in situ* transesterification of municipal primary and secondary sludges. *Bioresour. Technol.* **2009,** *100* (3), 1203-1210.

Original Sludge	Process		Reference
Raw Primary & Secondary Sludge	2.	Centrifugation (3000 rpm, 20 min)	(Mondala et al., 2009)
	3.	Freeze drying	

Source: EBMUD

Lipid Extraction

Typically sludge extracted lipids contain about 65 wt percent FFA[105] and are largely palmitic, stearic, and oleic acid. The composition of biodiesel produced from sewage sludge is similar to biodiesel produced from pure vegetable oil.[106]

Solvent extraction is the most commonly used method for separating lipids from waste solids in sludge or other wastewater material. Factors affecting lipid extraction process efficiency and cost include: solvent selection, sludge to solvent ratio, extraction time, temperature, and solvent recovery as shown in Table 46.

Solvents that have been successfully used for sludge lipid extraction are:107

- Methanol
- Ethanol
- HexaneToluene
- Chloroform
- Hexane 60% + methanol 20% + acetone 20%
- Super critical CO2
- Super critical CO2 + methanol

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[105] Boocock et al. 1992.

[106] Dufreche et al. 2007.

[107] Zappi, M.E.; French, W.T.; Hernandez, R.; Dufreche, S.T.; Sparks, D.L., Jr. Production of Biodiesel and Other Valuable Chemicals from Wastewater Treatment Plant Sludges. U.S. Patent 7,638,314 B2, December 29, 2009.

Table 46: Summary of Methods Used for Lipids Extraction from Dried Sewage Sludge

Original Sludge	Technique	Solvent	Dry Sludge to Solvent Ratio	Lipid (wt %)	Reference
Raw Primary Sludge	Soxhlet Extraction	Chloroform	1:6	12	(Boocock et al., 1992)
		Toluene	50 g : 300 mL	17–18	
	Boiling Solvent Extraction	Chloroform	1:6	21.2	
		Toluene	100 g: 600 mL	27.43	
Dewatered Secondary Sludge	Solvent Extraction System (10.3 MPa, 100 °C, 1 h)	HMA[1] – 1x		1.94	(Dufreche et al., 2007)
		HMA[1] – 3x		19.39	
		100% Hexane		1.94	
		100% Methanol		19.39	
		Methanol + Hexane		21.96	
	Supercritical-CO$_2$ Extraction	None		3.55	
		1.96 wt% MeOH		4.19	
		13.04 wt% MeOH		13.56	
Raw Sludge	Basic Extraction	Toluene	1:5	24.8	(Pokoo-Aikins et al., 2010)
		Hexane		24.9	

Original Sludge	Technique	Solvent	Dry Sludge to Solvent Ratio	Lipid (wt %)	Reference
		Methanol		25.5	
		Ethanol		25.5	

6. HMA: 60 vol% hexane, 20 vol% methanol, 20 vol% acetone.

Source: EBMUD

In-situ Biodiesel Production: Esterification without Extraction

Although extraction is most often used to obtain lipids from sludge, it has been reported that WWTP primary and secondary sludge can be converted directly into biodiesel with an in-situ transesterification process, eliminating the need to extract lipid materials separately in a biodiesel conversion process.[108], [109]

In the Mondala et al. (2009) study, sludge was freeze-dried and directly converted into biodiesel with an acid catalyzed in-situ transesterification process. This process was conducted at 75°C, with 5 percent v/v sulfuric acid, 12:1 methanol to sludge mass ratio, and mixed with dry sludge and hexane. A biodiesel yield of 14.5 percent for primary sludge and 2.5 percent for secondary sludge was achieved after a 24-hour reaction time and gravity phase separation.

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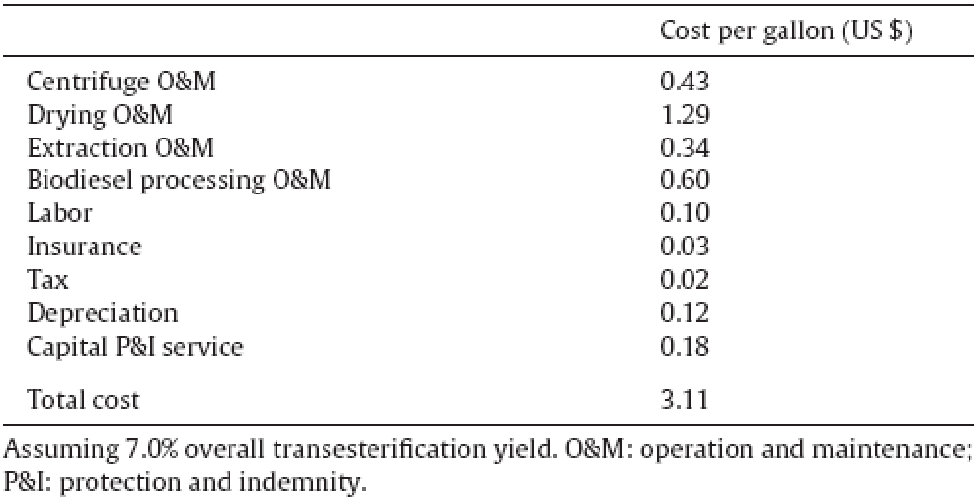
[108] Kim, M.; DiMaggio, C.; Yan, S.; Wang, H.; Salley, S. O.; Ng, K.Y.S. Performance of heterogeneous ZrO2 supported metaloxide catalysts for brown grease esterification and sulfur removal. *Bioresour. Technol.* **2011,** *102* (3), 2380-2386.

[109] Mondala, A.; Liang, K.; Toghiani, H.; Hernandez, R.; French, T. Biodiesel production by *in situ* transesterification of municipal primary and secondary sludges. *Bioresour. Technol.* **2009,** *100* (3), 1203-1210.

Process Economics

A 2009 economic analysis estimated $3.23/gallon for neat biodiesel (B100) produced from the in- situ transesterification process at an assumed yield of 10 percent diesel/dry weight of sludge.[110] Costs for lipid extraction and biodiesel production from the 2011 Siddiquee and Rohani study (Table 47), provide an example of economic breakdown of sludge derived biodiesel at $3.11/gallon for a 7 percent transesterification yield.

Table 47: Production Cost Estimate for Sludge Biodiesel



	Cost per gallon (US $)
Centrifuge O&M	0.43
Drying O&M	1.29
Extraction O&M	0.34
Biodiesel processing O&M	0.60
Labor	0.10
Insurance	0.03
Tax	0.02
Depreciation	0.12
Capital P&I service	0.18
Total cost	3.11

Assuming 7.0% overall transesterification yield. O&M: operation and maintenance; P&I: protection and indemnity.

Source: (Siddiquee and Rohani, 2011)

Nocardia Foam to Biodiesel

Nocardia is a bacterium commonly found in WWTP activated sludge treatment processes, which produces thick surface foam that can be problematic for WWTP operation (Figure 40).

Unlike most other activated sludge bacteria, *Nocardia* produces mycolic acids (40–60 carbons long). These waxy long-chain carbon molecules are associated with bacterial cell walls and likely make *Nocardia* cells lighter and more buoyant. In addition to *Nocardia*'s branch-like structure, mycolic acids are likely a major reason for *Nocardia's* ability to float and form process disrupting foams.

Currently, the two most common *Nocardia* control methods at WWTPs include: operating the activated sludge process at low mean cell residence time (MCRT) around 1 day; or collecting *nocardial* foam for disposal with no reintroduction to the WWTP process flow stream. If *Nocardia* is collected and returned to any of the WWTP process streams instead of disposed, it can cause catastrophic failure in WWTP anaerobic digesters or disruption to activated sludge and other treatment processes.

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[110] *Ibid.*

Nocardial mycolic acids, successfully extracted, could be a potential feedstock for biodiesel production. In addition, removal of the bacteria's mycolic acid component may prevent*nocardial* foam from reforming and allow *nocardial* cells to be returned safely back into the WWTP process train or anaerobic digesters.

Figure 43: *Nocardia* Foaming at WWTPs

Source: EBMUD

Nocardia Foam to Biodiesel Feedstock Bench Tests

Bench tests were conducted to investigate the feasibility of extracting mycolic acids from *Nocardia* foam as an initial step towards converting *Nocardia* foam into a biodiesel feedstock.

Approach

A hexane liquid-liquid-extraction (LLE) based on the EPA 1664 method was used in place of chromatic methods for determination of mycolic acids in this work.

The process was broken down into the following steps:

1. Collect 50–75 g *Nocardia* foam
2. Combine with hexane at 2:1 hexane: *Nocardia* ratio
3. Sonicate three times (600 W, 20 kHz, 50% duty)
    a. Centrifuge sample (3600 rpm, 30 min) to separate hexane phase, and filter hexane over sodium sulphate, after each sonication
4. Transfer hexane containing extracted oil to tared vessel and allow hexane to evaporate
5. Determine mass of extracted oil

Extraction Results

N-hexane was added to 50-gram *nocardial* foam samples at various ratios shown in Table 48. As summarized in Table 48, the hexane to foam ratio of 2:1 with ultrasonic treatment showed the highest yield of extractable material.

Table 48: Hexane Liquid-liquid-extraction of a Wastewater *Nocardia* Foam Sample

Foam Treatment	Hexane:Foam Extraction Ratio (v/v)	Hexane Extractable Oil and Grease mg/kg-*Nocardia* foam
None	0.5: 1	60 mg/kg
None	1:1	1000 mg/kg
None	2:1	1100 mg/kg
Ultrasonic treatment (600 Watt, 20 kHz, set at 50%, treated 3 times, each at 3	2:1	2998 mg/kg

Source: EBMUD

In addition to the extraction tests represented in Table 48, a series of batch extraction tests were conducted using detergents to extract mycolic acids from *Nocardia* foam in an effort to identify a lower cost and safer option to hexane extraction. Due to the limitations of a solid phase extraction (SPE) method employed for oil and grease measurement, results are not presented here; however, detergent-aided extraction might be the subject of future investigations.

Extractions using the ultrasonic process with 2:1 hexane to foam v/v ratio on 75 mg *Nocardia* samples showed production could be as high at 4600 mg oil/kg foam (Table 49).

Table 49: Ultrasonic and 2:1 Hexane to *Nocardia* Extraction Test

Test #	Wet Pellet Mass (g)	Dry Sample Weight (g)	Oil Extracted (mg oil/kg foam)
Nocardia T1	72.0	0.331	4600
Nocardia T2	74.0	0.136	1841
Nocardia T3	80.0	0.058	724
Nocardia T4	75.0	0.277	3693
Nocardia T5	74.2	0.273	3679
Nocardia T6	76.8	0.178	2318

Test #	Wet Pellet Mass (g)	Dry Sample Weight (g)	Oil Extracted (mg oil/kg foam)
Nocardia T7	77.8	0.267	3432
Nocardia T8	152.2	0.448	2943

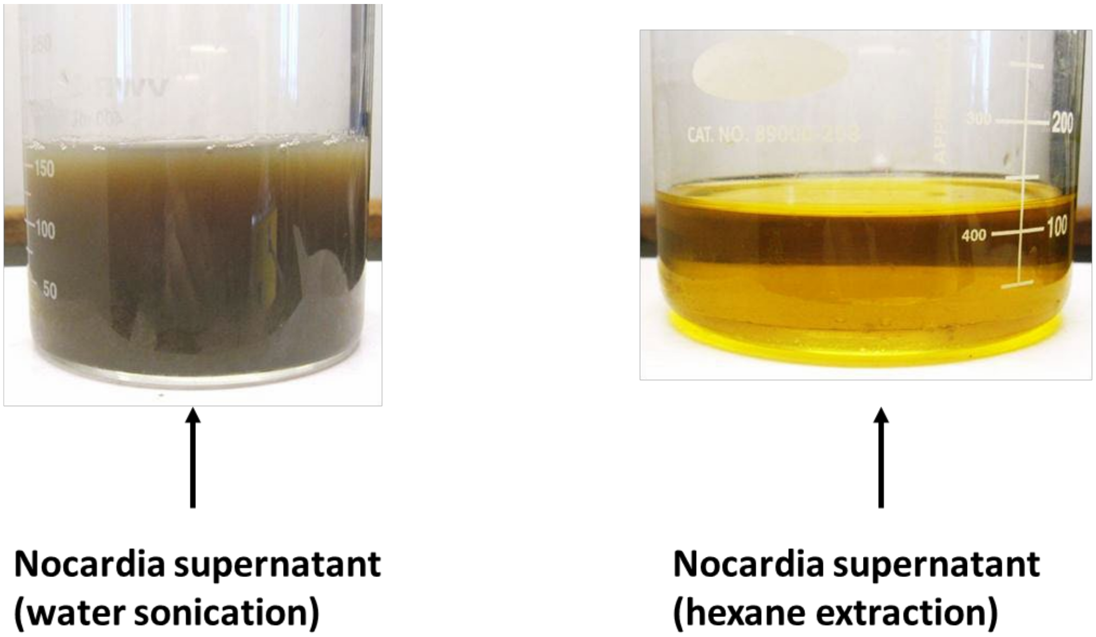
Source: EBMUD

Tables 48 and 49 show that with methods used some hexane-extractable materials can be recovered from *nocardial* foam. Ultrasonic treatment appears to yield more extractable material (almost 3 times as much), suggesting a combination of methods can provide more hexane- extractable material for recovery. These tests, however, should only be considered preliminary. More work is needed to determine process cost effectiveness.

Biodiesel Conversion Results

A sample of oil and grease extracted from *Nocardia* foam was converted to biodiesel using the esterification method optimized for brown grease, as described in Chapter 4 While the mycolic acids appeared to be converted to esters, the noticeably high viscosity of the resulting biodiesel made it unlikely to pass ASTM specifications, as a biodiesel product.

Figure 44: Hexane Extracted Nocardial Oil and Grease Biodiesel Production



Nocardia supernatant (water sonication)

Nocardia supernatant (hexane extraction)

Source: EBMUD

Destruction of *Nocardia* Foaming Potential

Bench tests were conducted to investigate the potential to control *nocardial* foaming and allow for removal and safe return of *nocardial* wastes within the WWTP.

Approach

The investigation into reducing *nocardial* foaming potential was broken down into the following steps:

1. Sonicate 50 g *Nocardia* foam for 3 min, three times in the presence of:
    a. 200 mL hexane, or
    b. 200 mL water
2. Centrifuge at 4000 rpm for 20 min to pellet suspension
3. Weigh out 13 g of *Nocardia* pellet
4. Transfer pellet into 500 mL water in glass beaker
5. Compare floatability of raw *Nocardia* and centrifuged *Nocardia* pellets Four side by side tests were conducted as laid out in Table 50.

Results

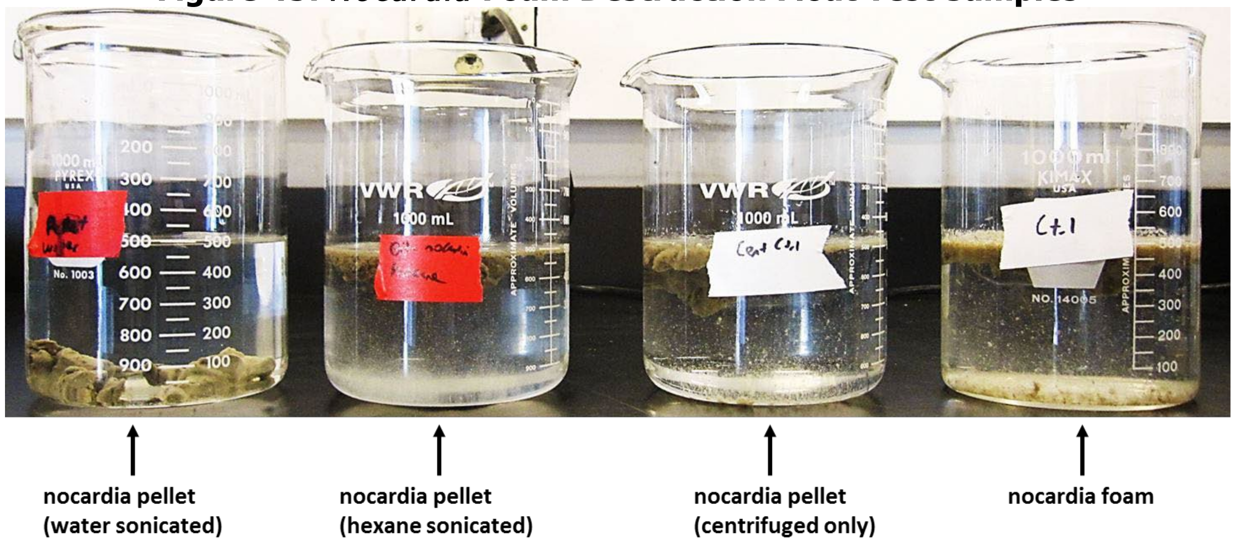
The *Nocadia* pellet from each sample floats except the sample sonicated in water as shown in Figure 42. This suggests sonication of *nocardial* foam at full-scale, without chemical addition, could break up *Nocardia's* branched structure, allowing the *nocardial* foam to compact more and sink. The hexane with sonication tests may have affected the *nocardial* mass in a way where it would still float. More work is necessary, but this experiment offers some indication of a targeted solution for *Nocardia* foaming problems at WWTPs.

Table 50: *Nocardia* Foam Destruction Float Test Results

Test	Centrifuged (4000 rpm, 20 min)	Ultrasonic (600 W, 20 kHz)	Sonication Liquid (200 mL)	Float
Raw *Nocardia* Foam	-	-	-	Yes
No Sonication	x	-		Yes
Hexane Sonicated	x	x	Hexane	Yes
Water Sonicated	x	x	Water	No

Source: EBMUD

Figure 45: ***Nocardia*** **Foam Destruction Float Test Samples**



Source: EBMUD

Wastewater to Biodiesel Using *Corynebacterium*

This study aimed to use bacteria to safely convert organic carbon materials in wastewater that are not suitable for biodiesel feedstock (such as sugars, organic volatile acids, proteins, lignin, etc.) into extractable mycolic acids that could be suitable as a biodiesel feedstock.

Like *Nocardia*, *Corynebacterium* also forms mycolic acids, but at shorter carbon lengths (i.e., 20–38 carbons long). These mycolic acids are closer in size to the free fatty acids commonly used as biodiesel feedstocks. A specific strain of *Corynebacterium glutamicum* (ATCC® 31831™), has previously been shown to grow on a variety of diverse substrates, including lignocellulosic sugars such as arabinose .[111], [112], [113] *Corynebacterium glutamicum* has also been used for many years in the food industry to produce glutamate, making it very safe bacteria to work with.

Corynebacterium Culturing for Mycolic Acid Extraction Bench Tests

To explore the use of bacteria to convert materials not suitable as biodiesel feedstocks, commonly found in municipal sewage, into materials that might be used as feedstocks for

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[111] Kawaguchi, H.; Sasaki, M.; Vertès, A.A.; Inui, M.; Yukawa, H. Identification and Functional Analysis of the Gene Cluster for L-Arabinose utilization in *Corynebacterium glutamicum*. *Appl. Environ. Microbiol.* **2009,** *75* (11), 3419-3429.

[112] Kinoshita, S.; Takayama, S.; Akita, S. Taxonomical study of glumatic acid accumulating bacteria,*Micrococcus glutamicus* nov. sp. *Bull. Agr. Chem. Soc. Jpn.* **1958,** *22*, 176-185.

[113] Abe, S.; Takayama, K.; Kinoshita, S. Taxonomical studies on glumatic acid-producing bacteria. *J. Gen. Appl. Microbiol*. **1967,** 13, 279-301.

biodiesel production (especially those materials that are not easily biodegraded in wastewater treatment plant biological treatment processes, like lignin), *Corynebacterium glutamicum* (ATCC 31831) was cultured and inoculated on different substrates. *Corynebacterium glutamicum* (ATCC 31831 strain) was selected for the following reasons:

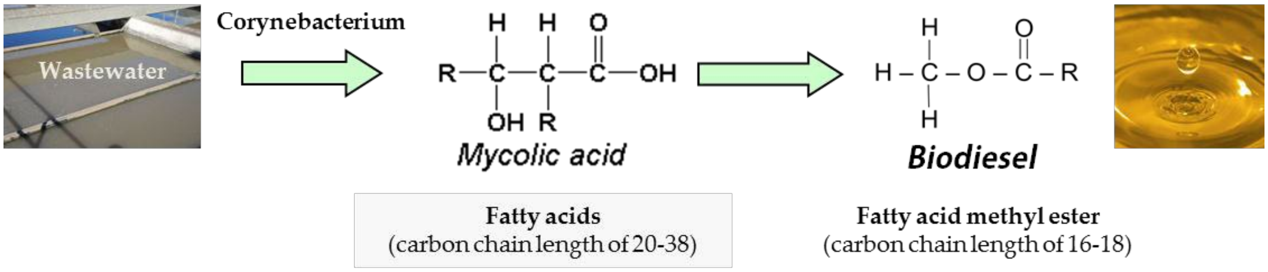
- Safe bacteria used to produce food grade glutamate
- Similar to wastewater bacteria, Nocardia sp., so may grow on wastewater
- Ability to use a variety of local sources, Corynebacterium glutamicum (ATCC 31831) was shown to grow on a variety of substrates, especially relatively refractory organics, such as lignin.
- Produces hexane-extractable materials—namely, mycolic acids
- Well-known bacteria with many references in the literature on many aspects – such as physiology, genome and gene expression, substrate sources, etc.

Bench scale experiments were developed to achieve the following:

a. Phased growth/culturing of *Corynebacterium glutamicum*.
    i. Phase I: Initiate culture of Corynebacterium bacteria in nutrient broth growth media.
    ii. Phase II: Scale up volume of suspended culture to increase microbial mass/densities—Large bench-scale growth for harvesting and extraction work
    iii. Phase III: Extraction of mycolic acids for biodiesel feedstock (conversion of mycolic acids into biodiesel not conducted). A one-step acid catalyzed process could be used as the triglycerides or glycerol are not part of the mycolic acid structure and only free fatty acids would be released from the mycolic acid material; eliminating glycerin formation potential as shown in Figure 43 below.

b. *Corynebacterium* bacteria growth on alternative substrates: wastewater primary effluent and lignocellulosic sugars (lignin).
    ✓

Figure 46: Wastewater to Biodiesel Feedstock Illustration

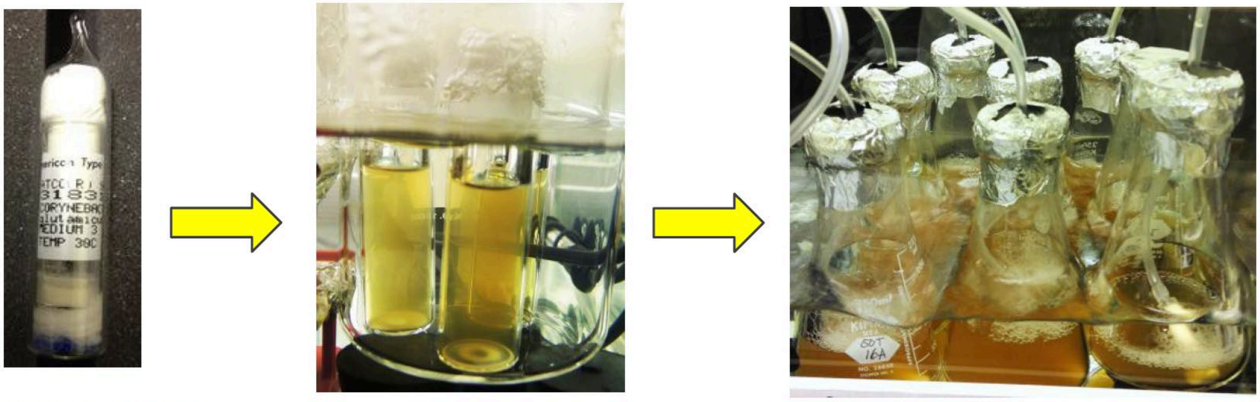


Source: EBMUD

Phase I: Initiate Culture of Corynebacterium

A *Corynebacterium glutamicum* (ATCC® 31831™) culture was propagated from the cryopreserved *C. glutamicum* ATCC 31831 pellet obtained from ATCC. Rehydration of the pellet was conducted under sterile conditions with DIFCO™ #3 Nutrient Broth according to ATCC instructions. Suspended bacteria culture was distributed in 8 drop or 16 drop increments to 20mL sterile Nutrient broth media vials and incubated continuously in a 30 °C water bath (Figure 43).

Figure 47: ***Corynebacterium glutamicum*** **Propagation in Nutrient Broth**



Freeze-dried Culture pellet

Initial bacterial growth in NB

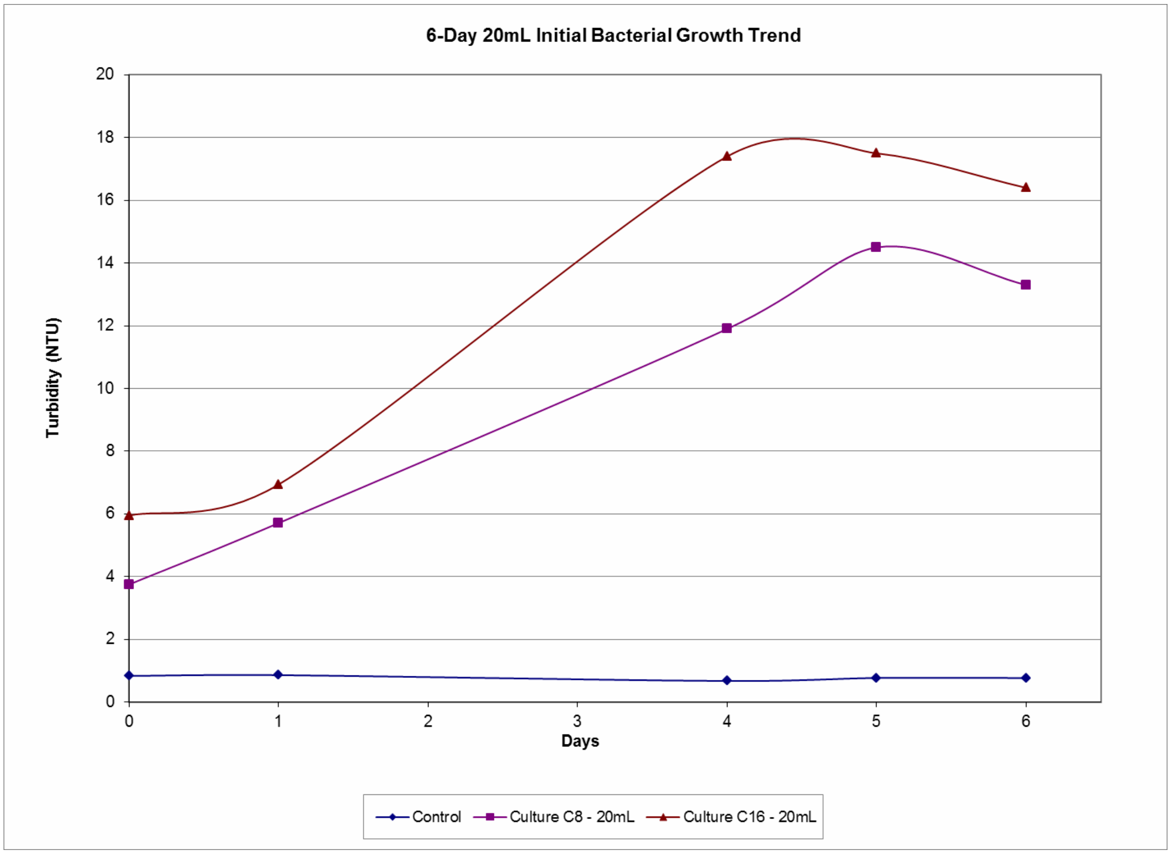
Scale up of Bacterial Culture

Source: EBMUD

Approach

Initial culture growth in each vial was monitored using turbidity measurements, and growth was observed within 24 hours. After a 6-day incubation period and a 3x increase in culture turbidity (as shown in Figure 45 for representative 8 drop (C8) and 16 drop (C16) cultures), cultures from 20-mL tubes were transferred to flasks containing 150 mL sterile Nutrient broth. 150-mL flasks were incubated in 27–30 °C water baths and continuously aerated with ambient air through fine bubble diffusers to maintain aerobic conditions.

Figure 48: Corynebacterium Glutamicum Growth Trend in 20 mL Nutrient Broth

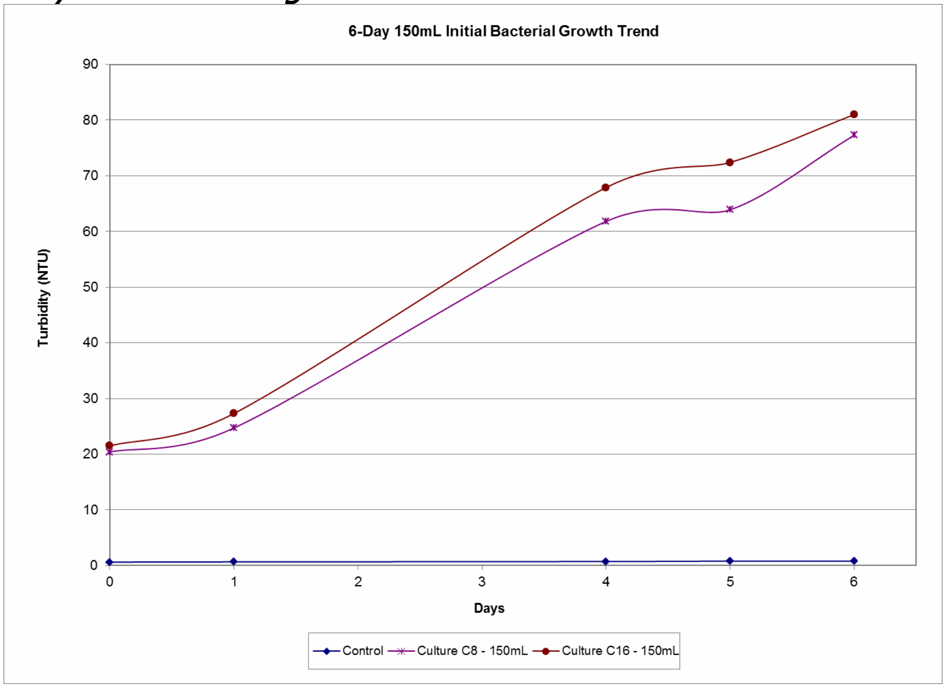


Source: EBMUD

Results

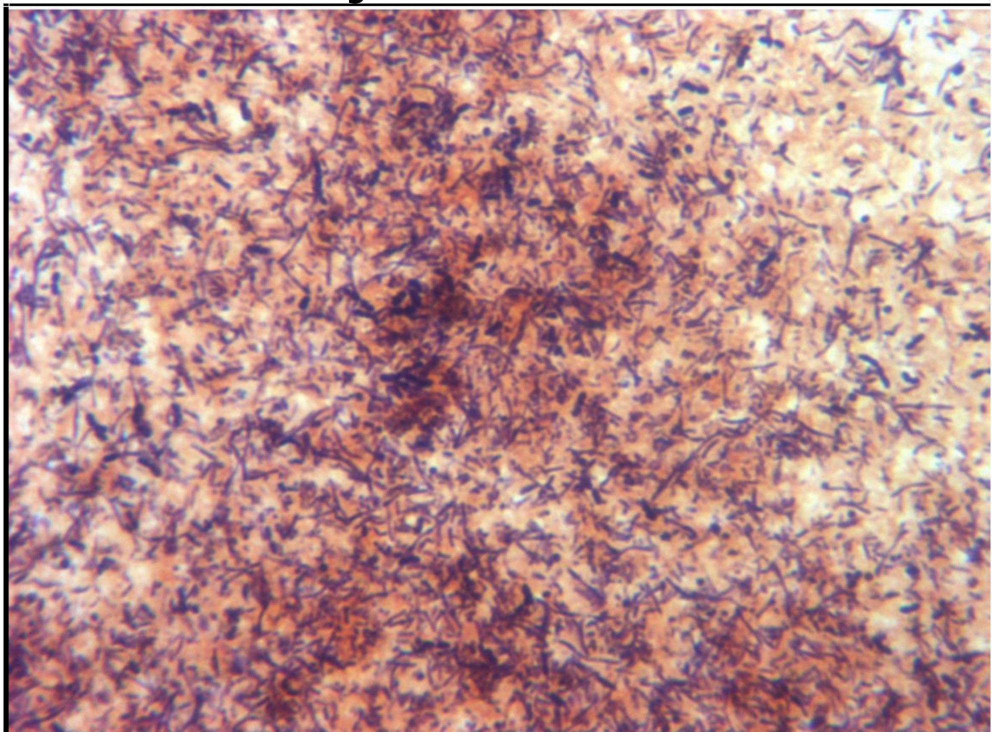
White bacterial growth (confirmed with microscopic observation) in suspension and as fixed mats were visible in each flask after 5–10 days of incubation. Bacterial growth was initially monitored through turbidity measurements. The six-day turbidity trend for cultures C8 and C16 in Figure 44 shows a 4x increase in turbidity for each suspended culture. Culture population density and diversity was confirmed using a gram stain observed with a light microscope at 100X and 1000X. *C. glutamicum* is a gram-positive rod-shaped bacteria showing a blue-purple stain, as shown in Figure 45.

Figure 49: ***Corynebacterium glutamicum*** **Growth Trend in 150 mL Nutrient Broth**



Source: EBMUD

Figure 50: Gram Stain Microscopy Identification of Cultured Corynebacterium glutamicum 1000x



Source: EBMUD

C. glutamicum shown as dark blue-purple, rod-shaped gram positive bacteria

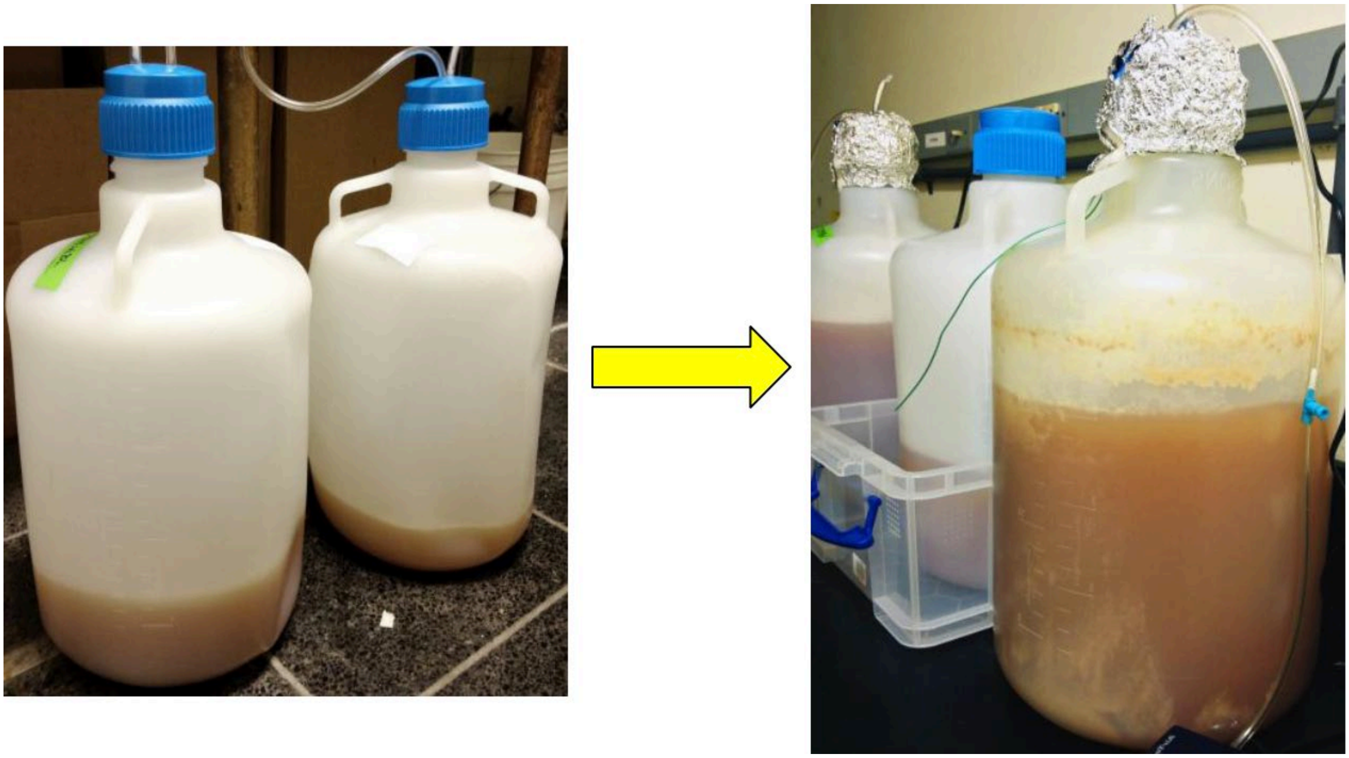
Phase II: Large Bench-scale Growth for Harvesting and Extraction Work

Two 150-mL culture flasks were used to establish two 1-L source cultures in Nutrient broth, to be used as seed for larger scale propagation. The 1-L cultures were incubated at 26–27 °C, continuously aerated (through ambient air with a coarse bubbler), and continuously mixed with magnetic stir bars in suspension cages. After a 15-day stabilization period, 200 mL of culture was removed as 'waste' from each 1-L culture and 200 mL Nutrient broth was fed to each 1-L culture. This practice was continued twice per week through the end of the project.

The 200-mL culture volumes removed from the two base culture flasks were transferred to two sterile 20-L polypropylene carboys and used in large scale propagation efforts. Incremental Nutrient broth volumes were added every four weeks to bring the large scale suspended culture volumes up to 16 liters over a period of 3 months. Large volume cultures were aerated with ambient air through coarse bubbler tubes and maintained at ambient temperature, approximately 21–22 °C.

The bacterial culture was monitored through pH measurements, COD consumption, and light microscopy observation of gram stained slides for *Corynebacterium glutamicum,* gram-positive rod-shaped bacteria, presence and relative density.

Figure 51: Culture Scale-up for Extraction



Source: EBMUD

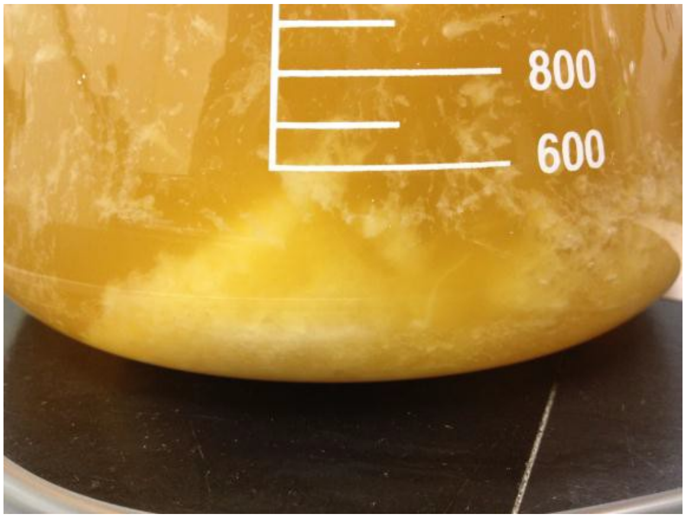
Phase III: Extraction of Fatty Acids for Biodiesel Feedstock

Approach

The ability of cultured *Corynebacterium* to be used as a source of biodiesel feedstock was investigated. As done with *Nocardia* foam, a hexane liquid-liquid extraction method was used.

One liter suspensions of *C. glutamicum* cultures were centrifuged at 3600 rpm for 30 minutes to pellet suspended bacteria. Bacterial pellets were suspended in n-hexane (43:1 hexane: pellet ratio) and subjected to three rounds of ultrasonic treatment for 3 minutes each (600 W, 20 kHz, 50 percent duty). After each sonication, the pellet mixture was centrifuged to separate the hexane phase, and the hexane phase was filtered over sodium sulphate. The final hexane phase containing oil was transferred to a tared vessel and the mass of the extracted oil was weighed once the hexane evaporated.

Figure 52: Bulk Culture Growth Used for Extraction



Source: EBMUD

Result

Up to 97,895 mg oil was extracted from each kilogram of *C. glutamicum* wet cell pellet. As indicated in Table 51, the recovery of oil and grease per gram of *C. glutamicum* pellet is significantly greater than the oil recovered from each kilogram of *Nocardia* foam.

Table 51: Hexane Liquid-liquid-extraction of Corynebacterium glutamicum Pellet

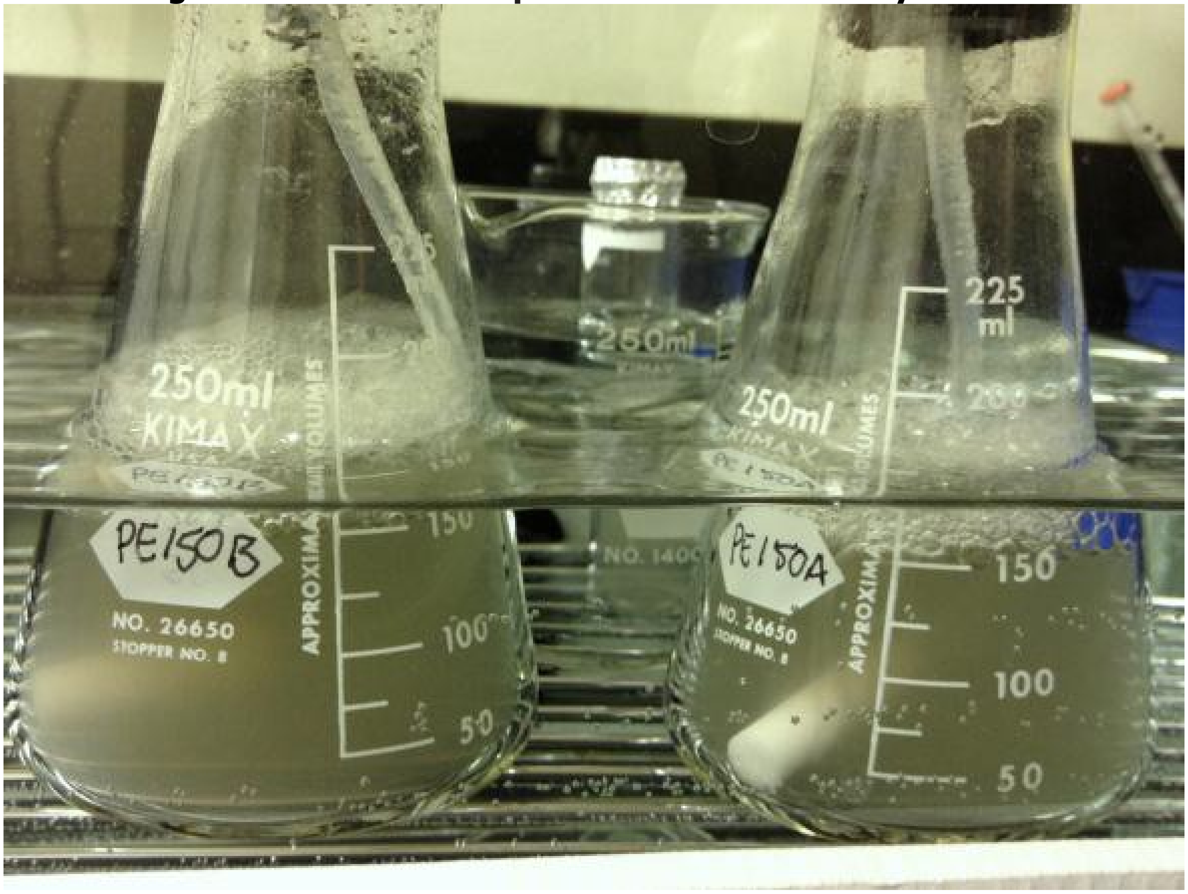
Test #	Wet Pellet Mass (g)	Dry Sample Weight (g)	Oil extracted (mg oil/kg foam)
C.glutamicum 1	4.20	0.203	48,262
C.glutamicum 2	3.60	0.104	44,087
C.glutamicum 3	1.90	0.186	97,895
C.glutamicum 4	2.20	0.160	72,727
C.glutamicum 5	2.20	0.184	83,636

Source: EBMUD

Corynebacterium Growth on Alternative Substrates Bench Tests

This work focused on the growth of *Corynebacterium glutamicum* (ATCC® 31831™) strain on a variety of substrates, including lignocellulosic sugars and wastewater primary effluent .

Figure 53: Culture Setup in Wastewater Primary Effluent



Source: EBMUD

Approach

Growth of *C. glutamicum* was tested using Primary Effluent , collected from the WWTP, as a base substrate/media with supplemental alkaline lignin, dealkaline lignin, or no lignin added (primary effluent alone).

Substrate sources:

Wastewater: Primary Effluent – from the WWTP primary treatment process

Lignin: TCI Lignin (Alkaline) – Product number L0082, sourced from VWR

TCI Lignin (Dealkaline) – Product number L0045, sourced from VWR The three alternative substrate culture tests were set up as detailed in Table 52.

Table 52: Alternative Substrate Test Composition

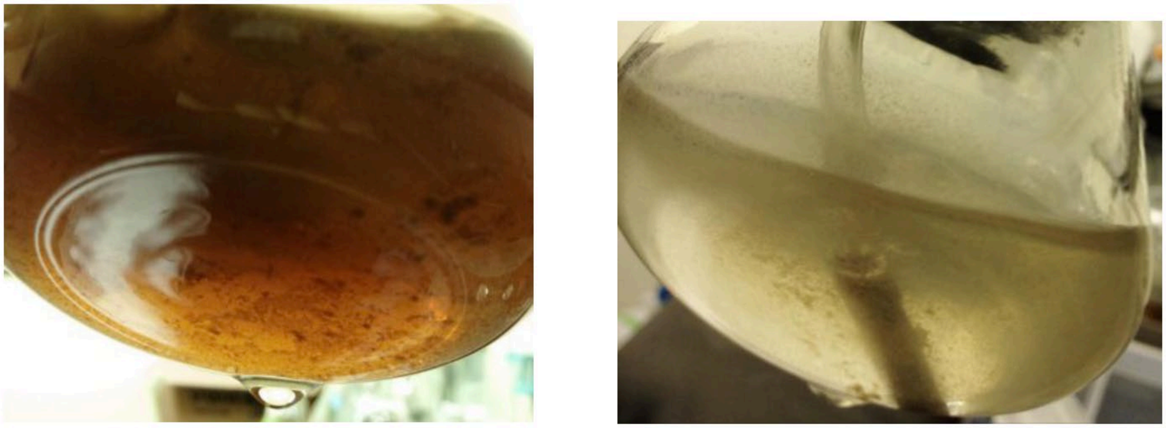
Alternative Substrate Test	Initial Substrate Volume (mL)	Dry Lignin Added (mg)	Initial COD (mg/L)	Initial Lignin Reading (mg)
Primary Effluent	175	-	360	0
Primary Effluent + Alkaline Lignin	175	78.74	957	75
Primary Effluent + Dealkaline Lignin	175	78.72	938	75

Source: EBMUD

All substrates were autoclaved at 121 °C and 1 kg/cm^2 pressure for 15 minutes, and then cooled overnight before inoculation with the source culture. Five milliliter of *C. glutamicum* inoculant was added to each of the three substrate test flasks from the source culture as seed.

Flasks were incubated in a 26–27 °C water bath and continuously aerated to maintain aerobic conditions with ambient air through fine bubble diffusers. The culture was monitored using pH, COD and Lignin (analyzed on a Hach Tannin/Lignin Color Disc Test Kit) measurements. The culture density and diversity was confirmed with light microscopy observation of gram stained slides for the *Corynebacterium glutamicum* gram-positive rod-shaped bacteria.

Figure 54: Bacteria Culturing in Wastewater Primary Effluent and Supplemental Substrates



Growth in Wastewater Primary Effluent with Supplemental Substrate

Growth in Wastewater Primary Effluent without Supplemental Substrate

Source: EBMUD

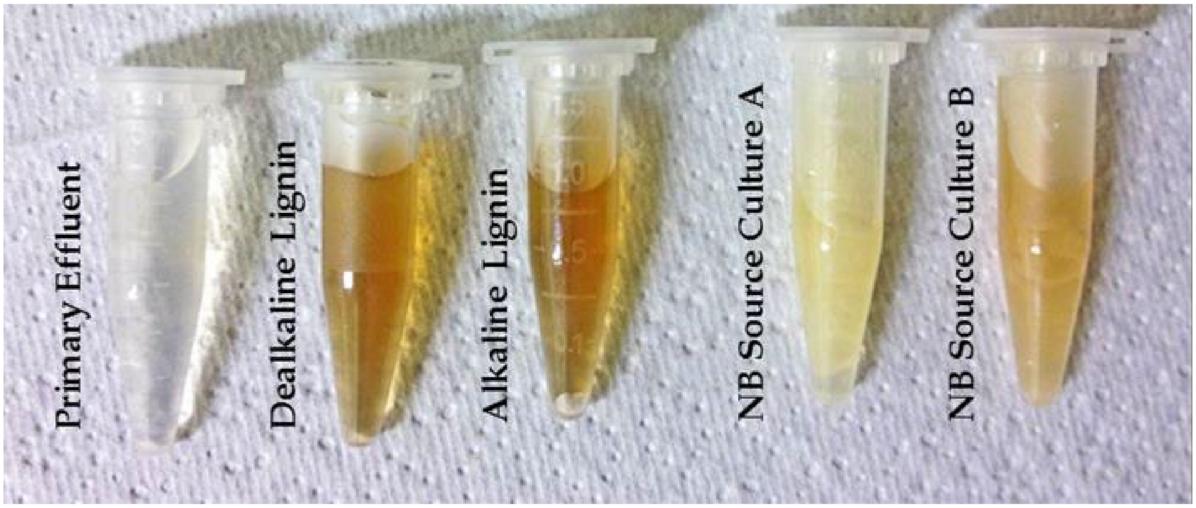
Results

COD in the alkaline lignin and dealkaline lignin substrate cultures was reduced from 957 mg/L and 938 mg/L to 666 mg/L and 601 mg/L, respectively, after 36 days. COD in the Primary Effluent only culture without supplemental substrate dropped from 360 mg/L to 173 mg/L after 36 days. An increase in COD was observed in all samples after 64 days and 92 days. After 105 days, Primary Effluent was added to the Primary Effluent only (20 mL), alkaline lignin (10 mL), and dealkaline lignin (20 mL) cultures to maintain minimum operating liquid levels. COD increased to 247 mg/L in the Primary Effluent only culture at the end of the test. COD dropped to 562 mg/L in the alkaline lignin culture and 408 mg/L in the dealkaline lignin culture after 150 days, as shown in Figure 53.

The lignin concentrations in the supplemental substrate flasks were reduced from 75 mg/L to 50 mg/L for both lignin cultures after 36 days. The final lignin concentrations of each flask after 150 days were 40 mg/L for the alkaline lignin test culture and 35 mg/L for the dealkaline lignin test culture.

The reduction in COD in all test cultures and lignin in the supplemental substrate cultures within the first 36 days suggests that *C. glutamicum* can utilize both WWTP primary effluent and lignin as substrates.

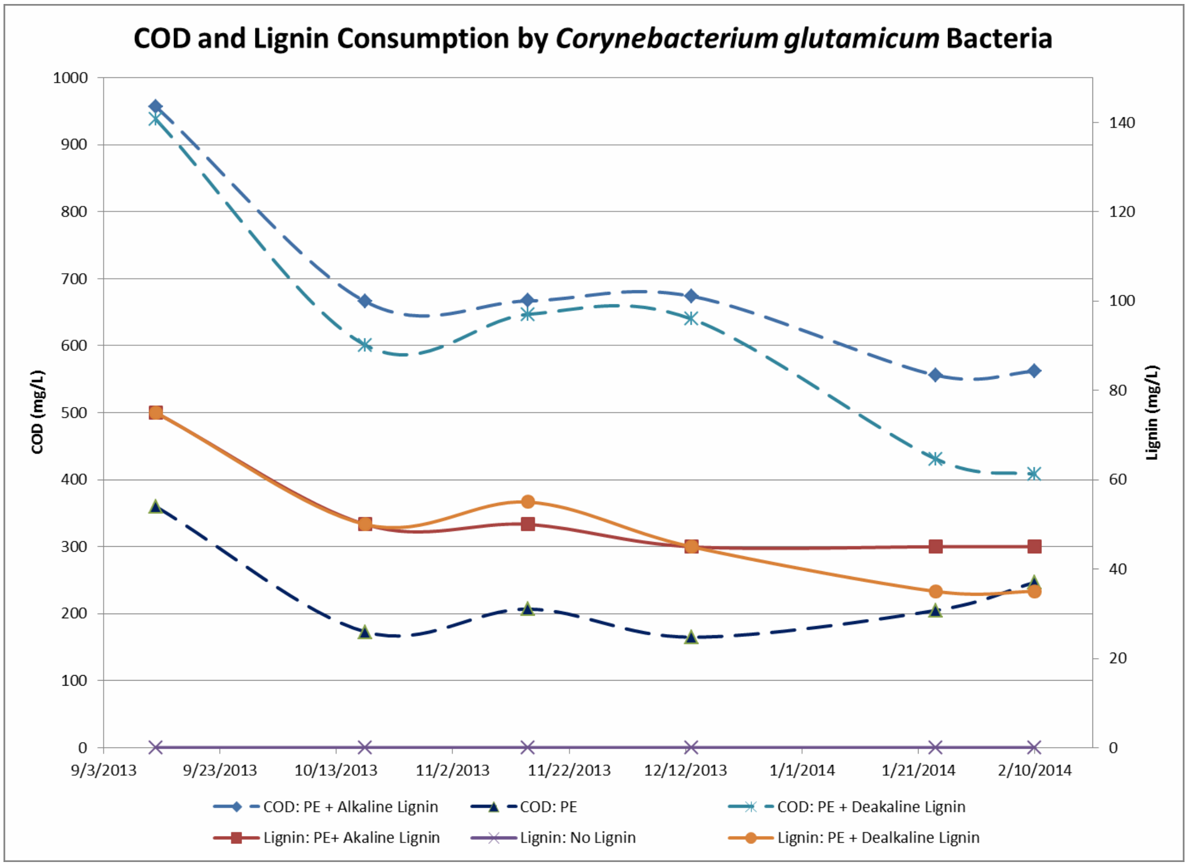
Figure 55: Alternative Substrate Culture Samples for Microscopy Identification



Note: NB Source Culture A&B represent nutrient broth source cultures used to seed the alternate substrate test cultures

Source: EBMUD

Figure 56: *C.glutamicum* COD and Lignin Consumption in Alternative Substrate Tests



Source: EBMUD

Review of Methane to Methanol Technologies

Methane makes up approximately 65 percent of the gas produced by WWTP anaerobic digesters. If this methane can be cost effectively converted into methanol it could be an advantage to WWTPs that produce biodiesel, since methanol is a major chemical cost in typical biodiesel production.

Investigations of methane to methanol technologies for numerous catalyzed oxidation, nano-ionic liquid, and fuel-cell processes, as summarized in Table 53, have shown:

- The most common method for converting methane into methanol has been selective, catalytic oxidation reactions which utilize readily available sources of iron, phosphate, zinc, molybdenum, vanadium, and copper as catalysts.
- Methane is a very inert reactant that requires high reaction temperature.
- Methanol is an intermediate product, which makes it difficult to achieve high selectivity at high methane conversion.

Efforts have been made to improve the efficiency of the catalysts and thereby lower the cost of the process in recent years. Processes, such as those using fuel cells, have been developed for converting natural gas into methanol and have potential applications which might be applied to WWTP anaerobic digester gas.

Table 53: Summary of Methane to Methanol Technology

Technology	Oxidant + Catalyst/Setup	Temp (°C)	Time (min)	Separation process	Performance	Reference
Catalyzed oxidation	- Oxidants:O_2 - Cobalt-containing zeolites	150	25 min	Ethanol, 1h	NA	(Beznis et al., 2011)
	- Oxidants: N_2O, O_2 - Copper iron - Pyrophosphate - Catalysts[1] - Fixed-bed quartz reactor	400–660	3.6 L/h 5h	NA	1.3–6.9%[2]	(Polnišer et al., 2011)
	- O_2+H_2O_2 - Metal mixed catalysts - (Pd–Au–Cu/C) - Proton conductor	250–400	30 ml/min	NA	Higher than fuel cells	(Lee et al., 2010)
Nano-ionic liquid	- Oxidant: $K_2S_2O_8$ - Catalyst: nano-particle - gold - Solvent: ionic liquids	90 (2MPa)	20 h	Distilled	12.6–24.9%[3]	(Wang et al., 2011)
Fuel cell	- Cathode: air - Anode:Methane+H2O - Catalyst: V2O5	50–250	30 ml/min	NA	61%[4] (88%)[4]	(Lee and Hibino, 2011)

NA = Not Available

1. Pyrophosphate catalyst consists mainly of the crystalline $Fe^{II}Fe^{III}_2(P_2O_7)_2$
2. Percent conversion of methane
3. Methanol conversion rate%, yield ranged from 9.0–17.8%
4. Represents current efficiency for methanol production at 2 mA, value in parentheses indicates methanol selectivity

Source: EBMUD

Summary of Findings from the Investigation of Alternative Biodiesel Feedstocks

- Nocardia extraction – a hexane to foam ratio of 2:1 with ultrasonic treatment showed the highest yield of hexane extractable material at 4,600 mg Oil and Grease per kg-Nocardia foam
- Bench-scale testing suggests sonication in water as being a possible solution for managing Nocardia foam
- C. glutamicum extraction: up to 97,895 mg oil was extracted from each kg of C. glutamicum wet cell pellet
- C. glutamicum uptake of the WWTP Primary Effluent and lignin as alternative substrates appeared to occur

These results should be considered preliminary with much more follow-up work needed; however, this work suggests opportunities for the microbial conversion of wastewater and other waste materials unsuitable as biodiesel feedstock into biodiesel feedstock materials. The results also suggest a possible solution for *Nocardia* foam treatment.

CHAPTER 6: Conceptual Design of a Biodiesel Production Facility at a Municipal Wastewater Treatment Plant

Implementation of efficient, cost effective FOG-to-biodiesel facilities once the technology is mature could result in numerous public benefits. This section presents the conceptual design for a full-scale biodiesel production facility at a municipal WWTP, based on findings from this study. Using this conceptual large-scale production of biodiesel from FOG, a number of potential environmental and social benefits have been estimated where biodiesel is used in place of petroleum diesel.

Conceptual Biodiesel Facility Design

The conceptual production facility design based on processes tested in this study, as shown in Figure 54, includes the following process steps:

1. Extraction of brown grease from FOG
2. Brown grease conversion to biodiesel
3. Biodiesel polishing

The facility design has been based on an assumed 50,000 gallons per day of FOG, received with a 5 percent brown grease concentration (3–7 percent),[114], and a 90 percent conversion of brown grease to biodiesel. As the WWTP Biodiesel Facility would produce less than 1 million gallons per year (MGY), a batch process is proposed to be more economical than a continuous flow process due to the small production size expected.

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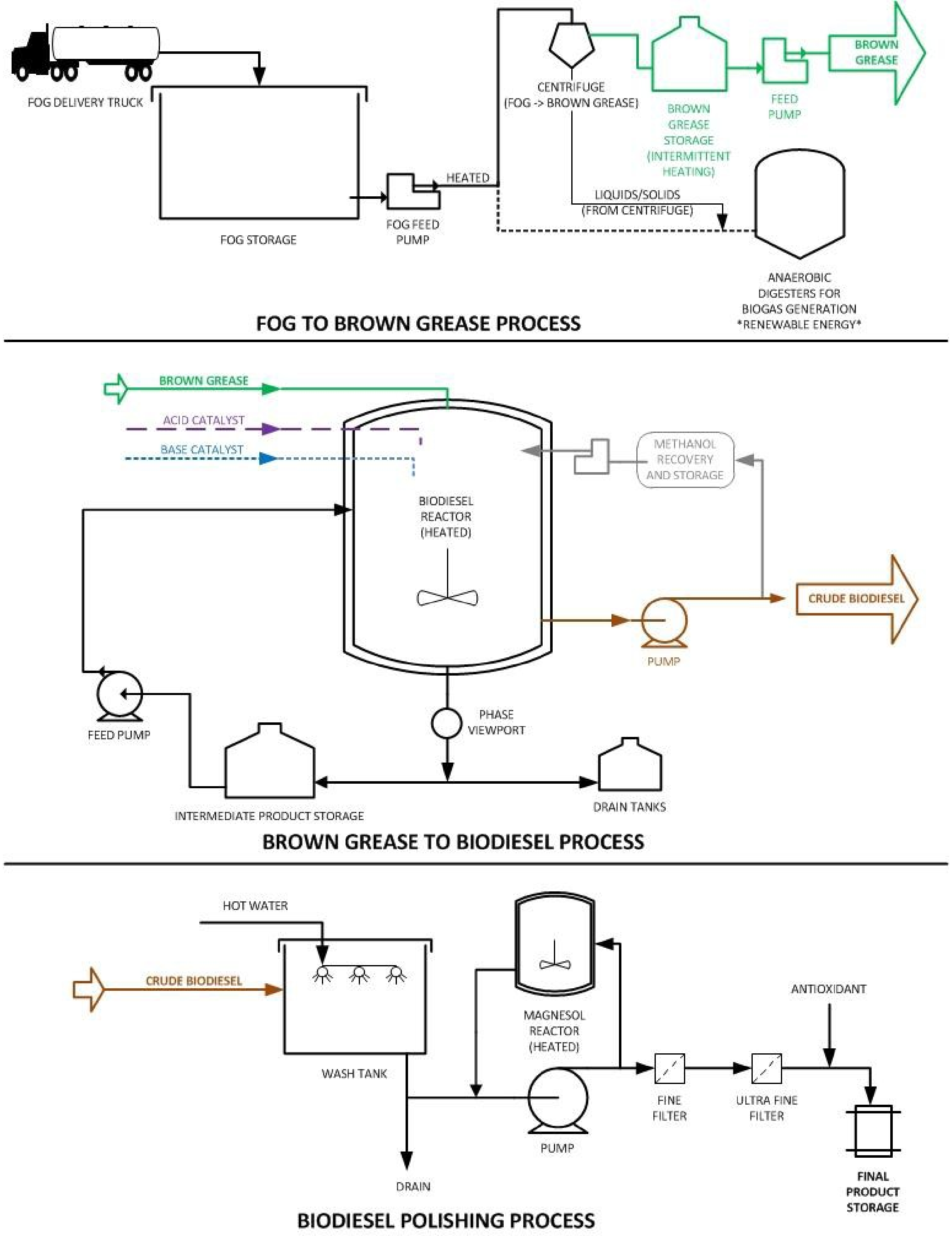
[114] Jolis, D.; Martis, M. *Brown Grease Recovery and Biofuel Demonstration: Oceanside Water Pollution Control Plant Baseline Summary;* Final Report to the California Energy Commission Contract Number PIR-06-001; CEC-500-2013-038; San Francisco Public Utilities Commission and URS Corporation; California Energy Commission: CA, 2013.

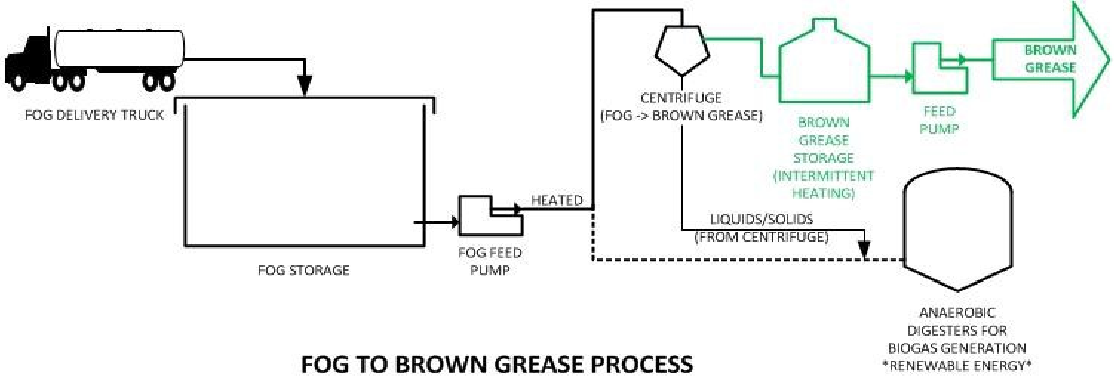
Figure 57: FOG to Biodiesel Conceptual Facility Process Flow Diagram



Source: EBMUD

Production Process Description

Figure 58: Process Step 1: FOG to Brown Grease – Centrifugation



Source: EBMUD

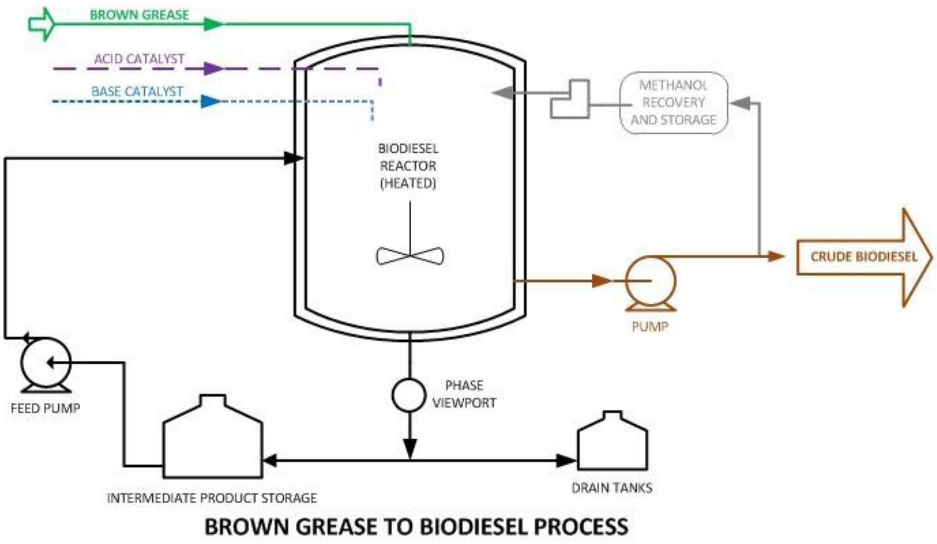
A 3-phase centrifuge (oil, water and solids) technology was selected for extracting brown grease from FOG based on the success of production tests on a bench-scale centrifuge in this study.

Commercial-scale centrifuges have been used successfully in the biodiesel industry for product separation in alternative feed stocks.

Alternative method:

> Brown grease extracted from FOG can also be achieved using heated gravity separation, a process that has been shown effective in this and other studies (Jolis and Martis, 2013).

Figure 59: Process Step 2: Brown Grease to Biodiesel – Two-Step Conversion Process



Source: EBMUD

The two-step (esterification-transesterification) brown grease to biodiesel conversion process has been selected for this conceptual design as it has been successfully demonstrated in this study, as well as earlier studies conducted by EBMUD and others.

The selected two-step conversion process would operate at 60 °C, for 1–2 hours in a batch reactor, using 98 percent sulfuric acid as the acid catalyst, potassium hydroxide (or sodium hydroxide or sodium methoxide etc.) as the base catalyst, and methanol as the reactant.

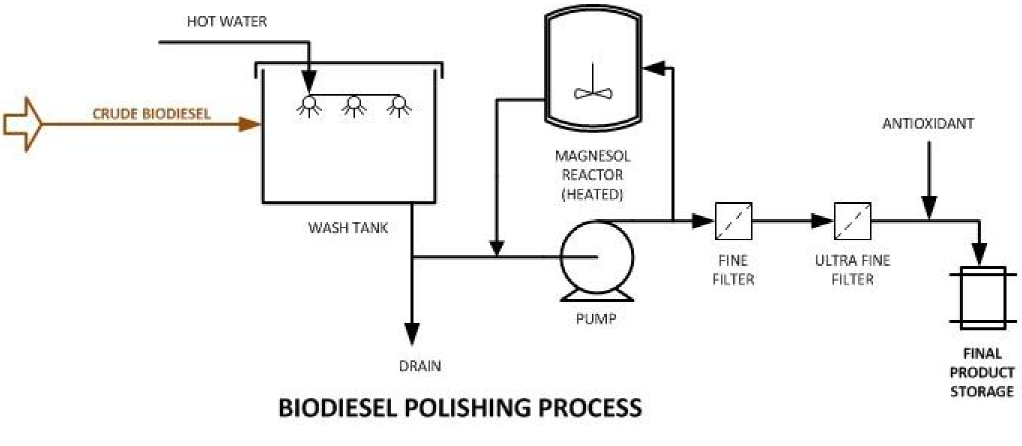
The process presented in Figure 6.1 was adapted from the initial work of Canakci and Van Gerpen (2001, 2003), where biodiesel was produced from high free fatty acid feedstocks using a two-step process: acid catalyzed esterification reaction, followed by a base catalyzed transesterification step. In previous work, EBMUD used a similar pilot system to successfully produce over 1,000 gallons of ASTM 6751-compliant brown grease biodiesel with the exception of the 15 ppm ultra-low sulfur standard (S 15 grade) (Chakrabarti et al., 2008). The biodiesel produced by EBMUD met the then S 500 standard of 500 ppm total sulfur.

Alternative methods:

Based on the results of EBMUD studies, the following modifications can be made to the biodiesel production process if needed:

- If safety or costs prevent the process from operating in the range of 60 °C, bench-scale trials showed that the esterification reaction can be completed at 20 °C with a longer reaction time. Safety considerations may include the close proximity of electrical heaters to methanol (a flammable substance), or the high cost of installing a steam boiler required for the heat exchangers.
- Sulfuric acid at 93% can be used to catalyze the first step esterification reaction if 98% sulfuric acid is not readily available in large quantities.
- If methanol recovery is not possible, the methanol can be reused with no detrimental effect on the product if mixed 1:1 with fresh methanol.

Figure 60: Process Step 3: Biodiesel Polishing and Sulfur Removal Potential



Source: EBMUD

As no one sulfur removal technology has demonstrated sufficient robustness to meet the ASTM 6751 ultra-low sulfur standard at a small scale in this study, potential sulfur removal processes have been discussed but not included in the conceptual design. Although the conceptual design presented does not include sulfur removal; significant removal of total sulfur in brown grease biodiesel can be achieved consistently using silica gel or similar adsorption product(s). Based on research performed in this study, the most promising results were achieved by batch treatment (~40–50 percent sulfur removal) or by filtering biodiesel through an adsorption column packed with silica gel (70 percent sulfur removal). In addition, silica gel treatment removes the unsightly brown color often present in brown grease biodiesel. The combination of oxidative and adsorptive desulfurization can reduce biodiesel sulfur by over 90 percent. Reactors presented in the conceptual design could be used for these sulfur treatment processes.

Environmental Benefit Analyses

The preceding sections described a conceptual design for a theoretical full-scale biodiesel production facility at a municipal WWTP. Implementation of FOG-to-biodiesel facilities in California once the technology is mature could result in a number of public benefits, including:

- Reduced dependence on petroleum-based diesel fuel
- Reduced air pollutants, air toxics and GHG emissions
- Creation of green jobs
- Reduced sewer blockages

Reduced Dependence on Petroleum-based Diesel Fuel

According to a report published by the National Renewable Energy Laboratory, approximately 13.37 lbs/person/year of interceptor grease is produced in urban metropolitan areas of the United States.[115] In California, with a total population of 37 million (US Census Bureau, 2010), almost 250,000 tons of interceptor grease is produced each year. Assuming a 100 percent grease capture rate, up to 61 million gallons of biodiesel could be produced each year (assuming a grease density of 7.3 lbs/gallon and 90 percent conversion rate for grease to biodiesel), or ~4 percent of the 2012 retail diesel sales volume (1,325 million gallons) in the State of California (Energy Commission website).

Reduced Air Pollutants, Air Toxics, and Greenhouse Gas Emissions

Diesel exhaust is a complex mixture of constituents that contains over 40 substances listed by the US EPA as hazardous air pollutants or by the California Air Resource Board (CARB) as toxic air contaminants. These include carbon monoxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx), particulate matter (PM), and hydrocarbons (HC). CO and HC are found in diesel fuel exhaust as a result of incomplete combustion. NOx are present due to combustion of nitrogen gas present in air. SOx result from the combustion of sulfur compounds present in the fuel. PM is an aggregate of extremely small particles and liquid droplets.

Health risks associated with petroleum diesel emissions are well documented by the US EPA. In a 2002 EPA health assessment for diesel engine exhaust, EPA concluded that long-term inhalation exposure was likely to pose a lung cancer risk to humans, as well as other lung damage depending on exposure. Short-term exposures can cause irritation and inflammatory

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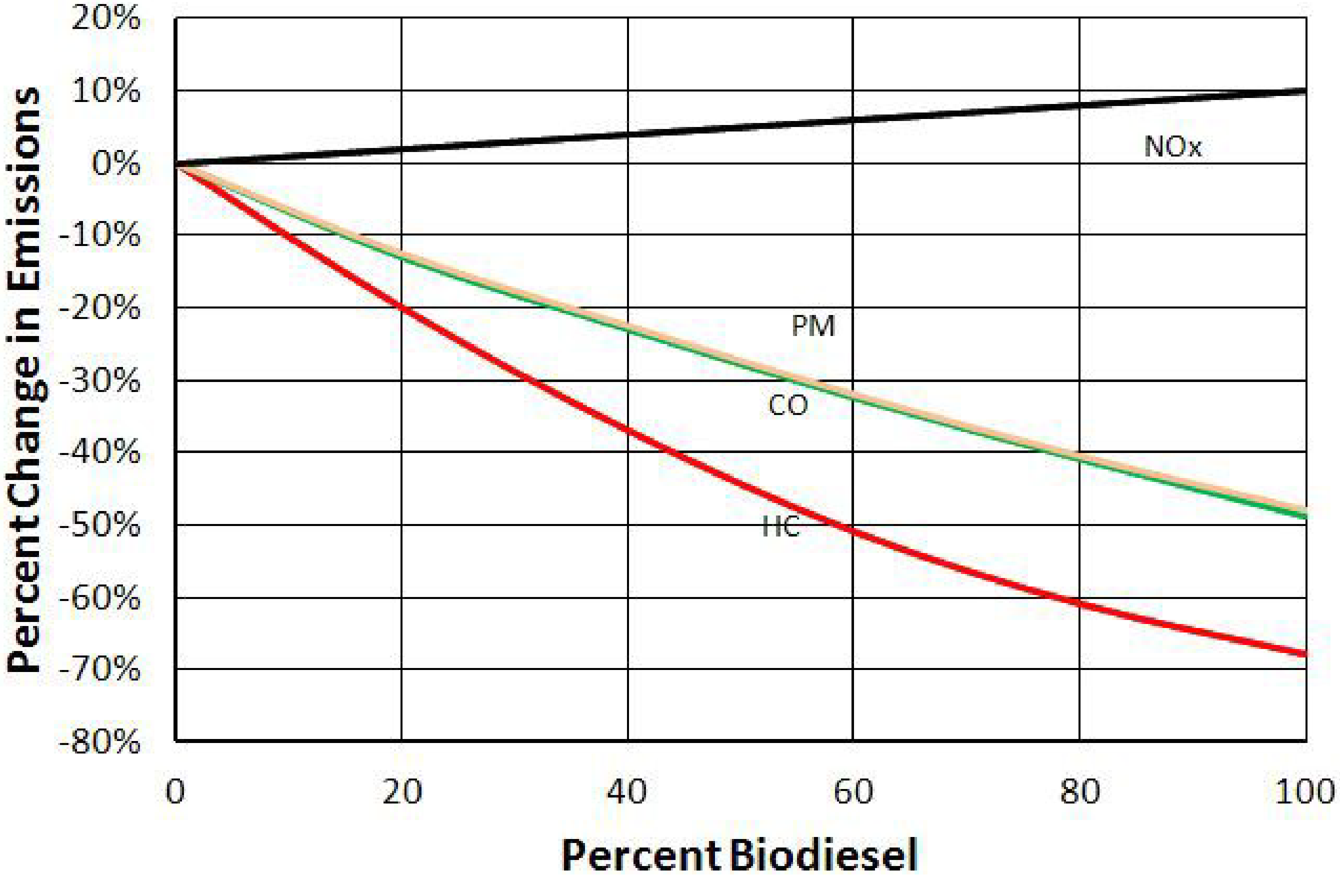
[115] Wiltsee, G. *Urban Waste Grease Resource Assessment;* NREL/SR-570-26141; USDE/ACG-7-17090- 01; Appel Consultants, Inc.; National Renewable Energy Laboratory: Golden, Colorado, 1998.

symptoms of a transient nature. The EPA assessment also indicated that evidence for exacerbation of existing allergies and asthma symptoms was emerging.[116]

Biodiesel use would reduce the release of air pollutants normally found in petroleum diesel engine exhaust. Figure 55 presents a comparison of regulated air toxins from biodiesel emissions to petroleum diesel emissions showing significantly lower PM, HC and CO concentrations in biodiesel emissions.[117]

Figure 61: Average Emissions Impact of Biodiesel for Heavy-Duty Highway Engines (US EPA)



Source: U.S. EPA, 2002

Use of biodiesel would also reduce net GHG emissions. Per California EPA Air Resources Board, the life cycle "Well to Wheel" GHG emissions for biodiesel from waste grease with no "cooking" required (i.e., low temperature process) is 11.76 gCO_2e/MJ, significantly lower (88 percent) than 94.71 gCO_2e/MJ for diesel (see 17 CCR 95480–95490) (EPA, 2009a). In the 2010 finalized Renewable Fuel Standards program known as RFS2, EPA determined that biodiesel produced

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[116] U.S. EPA. *Health assessment document for diesel engine exhaust*. Prepared by the National Center for Environmental Assessment, Washington, DC, for the Office of Transportation and Air Quality; EPA/600/8-90/057F; 2002. (http://www.epa.gov/ttnatw01/dieselfinal.pdf)

[117] U.S. EPA. *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions*; Draft Technical Report for EPA420-P-02-001; 2002.

from animal fats and waste oils reduces GHG emissions by 86 percent (Federal Register, 2010).

To estimate the reduction of air pollutants and GHG emissions by using biodiesel rather than petroleum diesel, an online tool: "Emission Calculator" available at the National Biodiesel Board website (http://www.biodiesel.org/using-biodiesel/handling-use/emissions-calculator) was used. This online tool uses similar or slightly conservative emission reductions for B100 biodiesel (see Table 54) compared to EPA estimates shown in Figure 55 and the GHG reduction (i.e., 86 percent or 88 percent).

Table 54: Average Change in Air Emissions of B100 Biodiesel Compared to Diesel Fuel

Emissions	% Change of B100 Biodiesel
NOx	10.29%
PM	-47.19%
CO	-48.11%
HC	-67.36%
CO2	-76.40%

Source: National Biodiesel Board website

The emission reduction was calculated for two scenarios: (1) a conceptual full-scale 1 MGY biodiesel facility at a WWTP, and (2) capturing and converting all interceptor grease to biodiesel in the state of California. The results are presented in Table 55.

Table 55: Estimated GHG Reduction for Producing Biodiesel from Interceptor Grease

	1 MGY Waste Grease to Biodiesel Facility	California
Biodiesel Production Potential from Waste Grease (gal/year)	1,000,000	61,000,000
Petroleum Reduction (gal/year)[1]	938,000	57,000,000
PM Reduction (metric tons/year)[2]	2	130
CO Reduction (metric tons/year) [2]	24	1,440
HC Reduction (metric tons/year) [2]	2	146
CO_2 Reduction (metric tons/year) [2]	8,007	486,560

1. Represented 93.8% based on the following Btu value: LHV (Btu/gal Biodiesel) 119,550; LHV (Btu/gal ULSD) 127,464
2. Calculated by using an online tool: "Emission Calculator" available at the National Biodiesel Board website (http://www.biodiesel.org/using-biodiesel/handling-use/emissions- calculator).

Source: EBMUD

Creation of Green Jobs

Green collar jobs are defined as jobs that provide services for the renewable energy industry.[118] For a complete consideration of potential green collar jobs, both direct and indirect jobs were estimated; induced jobs are not considered as they are not green collar jobs:

- Direct – jobs directly involved in the construction or operation of the facility
- Indirect – jobs that provide support or services for the operation of the facility
- Induced – jobs not related to the function of the facility but are jobs that provide services to direct and indirect workers within the community

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[118] Jolis, D.; Martis, M. *Brown Grease Recovery and Biofuel Demonstration: Oceanside Water Pollution Control Plant Baseline Summary;*Final Report to the California Energy Commission Contract Number PIR-06-001; CEC-500-2013-038; San Francisco Public Utilities Commission and URS Corporation; California Energy Commission: CA, 2013.

The number of green jobs that could be created from every $1 million spent in capital was determined by SFPUC to be 4.0 job years and 2.7 job years for direct and indirect jobs, respectively. SFPUC derived these numbers after evaluating the number of green jobs estimated by two different organizations: the President's Council of Economic Advisors and Political Economy Research Institute, using two separate methodologies (Jolis and Martis, 2013). Using SFPUC's estimated number of direct (4.0 job years) and indirect (2.7 job years) jobs per $1 million in capital spending, construction of the FOG Receiving Facility at EBMUD's MWWTP (~$2 million capital spent) as part of this project had created 8 direct job years and 5.4 indirect job years.

Construction of a 1 MGY biodiesel facility with an assumed capital cost of $3 million has the potential to create 12 direct job years and 8.1 indirect job years.

More green jobs could be created in the long term for facility operation and management following the construction and start-up.

Table 56: Estimated Green Jobs Creation

	FOG Receiving Facility	**1 MGY Waste Grease to Biodiesel Facility**
Capital Cost ($ million)	$2 million	$3 million
Direct Jobs (job year)	8	12
Indirect Jobs (job year)	5.4	8.1
Total (job year)	**13.4**	**20.1**

Source: EBMUD

Benefits Due to Reduced Sewer Blockages

FOG is the primary cause of 40—50 percent of sewer overflows nationwide and a secondary factor in another 10—25 percent.[119] It could lead to clogged pipes, as brown grease can coat the inside of sewer lines. These clogs can significantly reduce the capacity of sewer lines to transport sewage to the WWTP. With enough brown grease buildup, the sewage could back up into households or restaurants, or even overflow onto public streets. Sanitary sewage overflows can introduce health risks, as well as significant clean-up costs, and costs to clear clogged sewer lines.

Construction of FOG receiving and FOG-to-biodiesel production facilities may encourage increased grease trap use and proper FOG disposal

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[119] Southerland, R. Sewer Fitness: Cutting the Fat. *American City and Country* **2002**, 117(15), 4.

GLOSSARY

ACTIVATED CARBON (AC)- Activated carbon, also called activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions.[120]

ADSORPTIVE DESULFURIZATION (ADS)- Desulfurization by adsorption

ALTERNATIVE AND RENEWABLE FUELS AND VEHICLE TECHNOLOGY PROGRAM (ARFVTP)—Now known as the Clean Transportation Program, created by Assembly Bill 118 (Nunez, Chapter 750, Statutes of 2007), with an annual budget of about $100 million. Supports projects that develop and improve alternative and renewable low-carbon fuels, improve alternative and renewable fuels for existing and developing engine technologies, and expand transit and transportation infrastructures. Also establishes workforce training programs, conducts public education and promotion, and creates technology centers, among other tasks

ALTERNATIVE FUEL VEHICLE (AFV)- A vehicle designed to operate on an alternative fuel (e.g., compressed natural gas, methane blend, electricity). The vehicle could be either a dedicated vehicle designed to operate exclusively on alternative fuel or a nondedicated vehicle designed to operate on alternative fuel and/or a traditional fuel.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)- A non-profit organization that provides a forum for producers, consumers and representatives of government and industry to write laboratory test standards for materials, products, systems and services. ASTM publishes standard test methods, specifications, practices, guides, classifications and terminology.

AMERICAN TYPE CULTURE COLLECTION (ATCC)- a nonprofit organization which collects, stores, and distributes standard reference microorganisms, cell lines and other materials for research and development[121]

ANAEROBIC DIGESTION- Degradation of organic matter by microbes that produces a gas comprised mostly of methane and carbon dioxide, usually under wet conditions, in the absence of oxygen.

ASTM D6571 - The technical specification for B100 biodiesel by American Society for Testing and Materials.

ATOMIC EMISSION DETECTOR (AED)- used in the analysis of gasoline, diesel, oil, environmental pollutants in soil, water and effluent, and Volatile Organic Compounds (VOCs)

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[120] Activated Carbon (https://en.wikipedia.org/wiki/Activated_carbon)

[121] ATCC website (https://www.atcc.org/)

in water. It involves the use of Atomic Emission Spectroscopy to detect elements as they exit the gas chromatograph's column.[122]

BENZOTHIOPHENES (BT)- benzothiophene is a benzothiophene and a member of 1-benzothiophenes.[123]

CALIFORNIA AIR RESOURCE BOARD (CARB)- The "clean air agency" in the government of California, whose main goals include attaining and maintaining healthy air quality; protecting the public from exposure to toxic air contaminants; and providing innovative approaches for complying with air pollution rules and regulations.

CALIFORNIA CODE OF REGULATIONS (CCR) -The official compilation and publication of the regulations adopted, amended, or repealed by state agencies pursuant to the Administrative Procedure Act (APA). Properly adopted regulations that have been filed with the Secretary of State have the force of law. The CCR is compiled into Titles and organized into Divisions containing the regulations of state agencies.[124]

CALIFORNIA ENVIRONMENTAL QUALITY ACT (CEQA)- Enacted in 1970 and amended through 1983, established state policy to maintain a high-quality environment in California and set up regulations to inhibit degradation of the environment.

CARBON MONOXIDE (CO)- A colorless, odorless, highly poisonous gas made up of carbon and oxygen molecules formed by the incomplete combustion of carbon or carbonaceous material, including gasoline. It is a major air pollutant on the basis of weight.

CATALYSIS / CATALYST- A substance that increases the rate of a chemical reaction without being consumed or produced by the reaction. Enzymes are catalysts for many biochemical reactions.

CHEMICAL OXYGEN DEMAND (COD)- A measure of the oxygen-consuming capacity of organic matter present in wastewater. Chemical oxygen demand is expressed as the amount of oxygen consumed from a chemical oxidant in mg/L during a specific test.[125]

DESULFURIZATION- The removal of sulfur from materials using a chemical process.

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[122] Air products website (https://www.airproducts.com/industries/analytical-laboratories/analytical-lab-applications/product-list/gc-with-atomic-emission-detector-gc-aed-analytical-laboratories.aspx?itemId=F63C60220EDA4615903A0FA3243BEAEB)

[123] National Library of Medicine (https://pubchem.ncbi.nlm.nih.gov/compound/benzothiophene)

[124] California Office of Administrative Law (https://oal.ca.gov/)

[125] California State University, Sacramento, Department of Civil Engineering Water Program (http://www.owp.csus.edu/glossary/cod.php)

DIBENZOTHIOPHENES (DBT)- Dibenzothiophene is a sulfur-containing polycyclic aromatic hydrocarbon (PAH) derivate consisting of 3 fused rings with keratolytic activity. Dibenzothiophene is a component of petroleum oils.[126]

DIMETHYL FORMAIDE (DMF)- is a clear liquid that has been widely used in industries as a solvent, an additive, or an intermediate because of its extensive miscibility with water and most common organic solvents.[127]

DIMETHYL SULFOXIDE (DMSO) - is a highly polar organic liquid that is used widely as a chemical solvent and a free radical scavenger. It is readily miscible in a wide range of organic solvents as well as water. [128]

EAST BAY MUNICIPAL UTILITY DISTRICT (EBMUD)- is a public utility district which provides water and sewage treatment services for an area of approximately 331 square miles in the eastern side of the San Francisco Bay.[129]

ESTER / ESTERIFICATION - A compound formed from the reaction between an acid and an alcohol. The process by which esters are produced during chemical reactions between acids and alcohol.

FAT, OIL, AND GREASE (FOG)- Fats, Oils and Grease are also known as FOG which comes from food such as cooking oil, lard, shortening, meat fats, sauces, gravy, mayonnaise, butter, ice cream and soups. Sink, dishwasher, hood and floor cleaning wastewaters and food scraps may also be sources of FOG. FOG can either be liquid or solid and may turn viscous or solid as it cools in the underground sewer.[130]

FATTY ACIDS - A fatty acid is a carboxylic acid (an acid with a -COOH group) with long hydrocarbon side chains.

Fatty acid methyl ester (FAME)- are a type of fatty acid ester that are derived by transesterification of fats with methanol. [131]

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[126] National Library of Medicine (https://pubchem.ncbi.nlm.nih.gov/compound/dibenzothiophene)

[127] National Library of Medicine (https://pubchem.ncbi.nlm.nih.gov/compound/n_n-dimethylformamide)

[128] National Library of Medicine (https://pubchem.ncbi.nlm.nih.gov/compound/Dimethyl-sulfoxide)

[129] EBMUD Wikipedia page (https://en.wikipedia.org/wiki/East_Bay_Municipal_Utility_District)

[130] Fairfax County Government Website (https://www.fairfaxcounty.gov/publicworks/fats-oils-grease)

[131] FAME Wikipedia page (https://en.wikipedia.org/wiki/Fatty_acid_methyl_ester)

FLAME PHOTOMETRIC DETECTOR (FPD)- uses a photomultiplier tube to detect spectral lines of the compounds as they are burned in a flame. Compounds eluting off the column are carried into a hydrogen fueled flame which excites specific elements in the molecules, and the excited elements (P,S, Halogens, Some Metals) emit light of specific characteristic wavelengths. The emitted light is filtered and detected by a photomultiplier tube.[132]

FLUIDIZED BED REACTOR (FBR)- Fluidized bed reactors are heterogeneous catalytic reactors in which the mass of catalyst is fluidized. This allows for extensive mixing in all directions. A result of the mixing is excellent temperature stability and increased mass-transfer and reaction rates. [133]

FREE FATTY ACID (FFA)- Free fatty acids are presented in crude oils but they are removed during refining process. Free fatty acids are more susceptible to autoxidation than esterified fatty acids. Thus, free fatty acids act as pro-oxidants in edible oil (Morales and Przybylski, 2013; Choe and Min, 2006).[134]

GAS CHROMATOGRAPHY (GC)- A chemical analysis instrument for separating chemicals in a complex sample. It uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream at different rates depending on their various chemical and physical properties.[135]

GREENHOUSE GAS (GHG)- Any gas that absorbs infra-red radiation in the atmosphere. Greenhouse gases include water vapor, carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O), halogenated fluorocarbons (HCFCs) , ozone (O3), perfluorinated carbons (PFCs), and hydrofluorocarbons (HFCs). (EPA)

HYDROCARBON (HC)- Compounds containing various combinations of hydrogen and carbon atoms. They may be emitted into the air by natural sources (e.g., trees) and as a result of fossil and vegetative fuel combustion, fuel volatilization and solvent use. Hydrocarbons are a major contributor to smog.

HYDRODESULFURIZATION (HDS)- is a catalytic chemical process widely used to remove sulfur compounds from refined petroleum products such as gasoline or petrol, jet fuel, diesel fuel, and fuel oils. One purpose for removing the sulfur is to reduce the sulfur dioxide emissions resulting from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, or

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[132] Gas Chromatography Wikipedia page (https://en.wikipedia.org/wiki/Gas_chromatography#Detectors)

[133] University of Michigan (http://encyclopedia.che.engin.umich.edu/Pages/Reactors/FBR/FBR.html)

[134] Science Direct website (https://www.sciencedirect.com/topics/food-science/free-fatty-acids)

[135] Wikipedia (https://en.wikipedia.org/wiki/Gas_chromatography)

oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.[136]

HYDROLYSIS - A chemical reaction that releases sugars that are normally linked together in complex chains. In ethanol production, hydrolysis reactions are used to break down the cellulose and hemicellulose in the biomass.

Inductively coupled plasma (ICP) - is a type of plasma source in which the energy is supplied by electric currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields.[137]

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (ISO)- An independent, non-governmental organization with members from standards organizations in 164 member countries. It is the world's largest developer of voluntary international standards and facilitates world trade by providing common standards between nations.[138]

LIQUID-LIQUID-EXTRACTION (LLE)- is a method to separate compounds or metal complexes, based on their relative solubilities in two different immiscible liquids, usually water (polar) and an organic solvent (non-polar).[139]

LIPASE CATALYST- An enzyme that catalyzes the hydrolysis of fats and lipids.

MEAN CELL RESIDENCE TIME (MCRT)-is the amount of time, in days, that solids or bacteria are maintained in the activated sludge system.[140]

METHANOL - An alcohol formed by catalytically combining carbon monoxide with hydrogen in a 1:2 ratio under high temperature and pressure.

METHYL ESTER - An ester that yields methanol during hydrolysis.

NITROGEN OXIDES (NOX)- A general term pertaining to compounds of nitric oxide (NO), nitrogen dioxide (NO2), and other oxides of nitrogen. Nitrogen oxides are typically created during combustion processes and are major contributors to smog formation and acid deposition. NO2 is a criteria air pollutant and may result in numerous adverse health effects.

NOCARDIA- Nocardia is a bacterium commonly found in WWTP activated sludge treatment processes, which produces thick surface foam that can be problematic for WWTP operation

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[136] The American Institute of Chemical Engineers (https://engage.aiche.org/HigherLogic/System/DownloadDocumentFile.ashx?DocumentFileKey=f7300421-4165-4bac-9d5f-ef60751139ac&ssopc=1)

[137] ICP Wikipedia page (https://en.wikipedia.org/wiki/Inductively_coupled_plasma)

[138] International Organization for Standardization (https://www.iso.org/about-us.html)

[139] LLE Wikipedia page (https://en.wikipedia.org/wiki/Liquid%E2%80%93liquid_extraction)

[140] John Wiley & Sons inc. (https://onlinelibrary.wiley.com/doi/pdf/10.1002/0471216682.app2)

NUCLEAR MAGNETIC RESONANCE (NMR)- is a method of physical observation in which nuclei in a strong constant magnetic field are perturbed by a weak oscillating magnetic field (in the near field and therefore not involving electromagnetic waves) and respond by producing an electromagnetic signal with a frequency characteristic of the magnetic field at the nucleus.[141]

OSCILLATORY FLOW REACTOR (OFR)- a specially designed chemical reactor to achieve plug flow under laminar flow conditions.[142]

OXIDATIVE DESULFURIZATION (ODS)- is a two-stage deep desulfurization technology to reduce the amount of organosulfur compounds in fuel oils.[143]

PARTICULATE MATTER (PM)- Unburned fuel particles that form smoke or soot and stick to lung tissue when inhaled. A chief component of exhaust emissions from heavy-duty diesel engines.

PHASE TRANSFER AGENT (PTA) - a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs.[144]

PULSE FLAME PHOTOMETRIC DETECTOR (PFPD) - a relatively new weapon in the arsenal of the analytical chemist. Though it uses a flame like its namesake, the flame photometric detector or FPD invented over 30 years ago, the PFPD is a significant improvement because it can provide better sensitivity and selectivity for sulfur and phosphorus.[145]

SAN FRANCISCO PUBLIC UTILITIES COMMISSION (SFPUC)- provides retail drinking water and wastewater services to the City, wholesale water to three Bay Area counties, and green hydroelectric and solar power to our municipal departments. [146]

SILICA GEL/ALUMINA (S-A)- light yellow, chemically stable, flame-resistant, insoluble except in alkali or hydrofluoric acid. Superficial polarity, thermal stability, performance greater than fine-pored silica gel. [147]

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[141] NMR Wikipedia page (https://en.wikipedia.org/wiki/Nuclear_magnetic_resonance)

[142] Oscillatory baffled reactor Wikipedia page (https://en.wikipedia.org/wiki/Oscillatory_baffled_reactor)

[143] Heilscher Ultrasound Technology (https://www.hielscher.com/oil_desulfurization_01.htm)

[144] Phase Transfer Wikipedia page (https://en.wikipedia.org/wiki/Phase-transfer_catalyst)

[145] Sam Houston State University (https://www.shsu.edu/chm_tgc/primers/pfpd.html)

[146] San Francisco Water, Power, Sewer (https://sfwater.org/index.aspx?page=6)

[147] Silica Gel Wikipedia page (https://en.wikipedia.org/wiki/Silica_gel)

SULFUR CHEMILUMINESCENCE DETECTOR (SCD)- Tool used in gas chromatography

Sulfur oxides (Sox)- Pungent, colorless gases (sulfates are solids) formed primarily by the combustion of sulfur-containing fossil fuels, especially coal and oil. Considered major air pollutants, sulfur oxides may impact human health and damage vegetation.

TRANSESTERIFICATION -A process that includes chemical reactions of alcohols and triglycerides contained in vegetable oils and animal fats to produce biodiesel.

TRIGLYCERIDE (TAG) -A combination of glycerol and three fatty acids. Most animal fats are comprised primarily of triglycerides.

Ultra-low sulfur diesel (ULSD)- is diesel fuel with substantially lowered sulfur content.[148]

ULTRASOUND ASSISTED OXIDATIVE DESULFURIZATION (UAODS) - ultrasonic reactors assist the oxidative deep desulfurization process required to meet the today's stringent environmental regulations and ultra-low sulfur diesel (ULSD, 10ppm sulfur) specifications.[143]

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (U.S. EPA)- A federal agency created in 1970 to permit coordinated governmental action for protection of the environment by systematic abatement and control of pollution through integration or research, monitoring, standards setting and enforcement activities.

WASTEWATER TREATMENT PLANT (WWTP)- may include primary treatment to remove solid material, secondary treatment to digest dissolved and suspended organic material as well as the nutrients nitrogen and phosphorus, and – sometimes but not always – disinfection to kill pathogenic bacteria.[149]

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[148] ULSD Wikipedia page (https://en.wikipedia.org/wiki/Ultra-low-sulfur_diesel)

[149] Waste water treatment Wikipedia (https://en.wikipedia.org/wiki/Wastewater_treatment#Wastewater_treatment_plants)

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APPENDIX B: Intertek 2D-GC-SCD Sulfur Speciation Results

Intertek

Westport Technology Center

Petroleum Geochemistry

WTC-13-003730 **May 2013**

2D-GC-SCD of Biodiesel

Prepared for:

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Introduction

At the request of Yun Shang of East Bay Municipal Utility District (EBMUD), Westport analyzed 1 biodiesel sample (Table 1) for sulfur speciation by 2D-GC-SCD. The results are presented in this report.

Analysis and Processing

Sulfur speciation was measured by 2D Gas Chromatography on a Zoex 2D GC with SCD detector.

Results and Conclusions

The results are presented in Table 2 and Figure 1. The sample exhibits significant sulfur components within the diesel range. The components appear between the ranges normally attributed to benzothiophenes and dibenzothiophenes with about 10 carbon substitutions and may be substitution variations of those components types. However, since biodiesel may contain compound types not observed in petroleum (on which the identifications are based), the components are likely a different compound family that elutes in this range. The concentration values are based on Sulfur only and are calculated based on eluted peaks compared to an internal standard.

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Table 1

Project Samples

Project: WTC-13-003730 - EBMUD - 2D-GC-SCD of Biodiesel Customer: East Bay Municipal Utility District - Yun Shang

Sample	Sample Volume	Login Date	Container	Description	Testing
Biodiesel					
178687	30 cc	5/7/13	Glass Bottle-Jar	2DEK-SCD, Biodiesel	2D-GC-SCD

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Table 2

Sulfur Speciation by 2D-GC-SCD

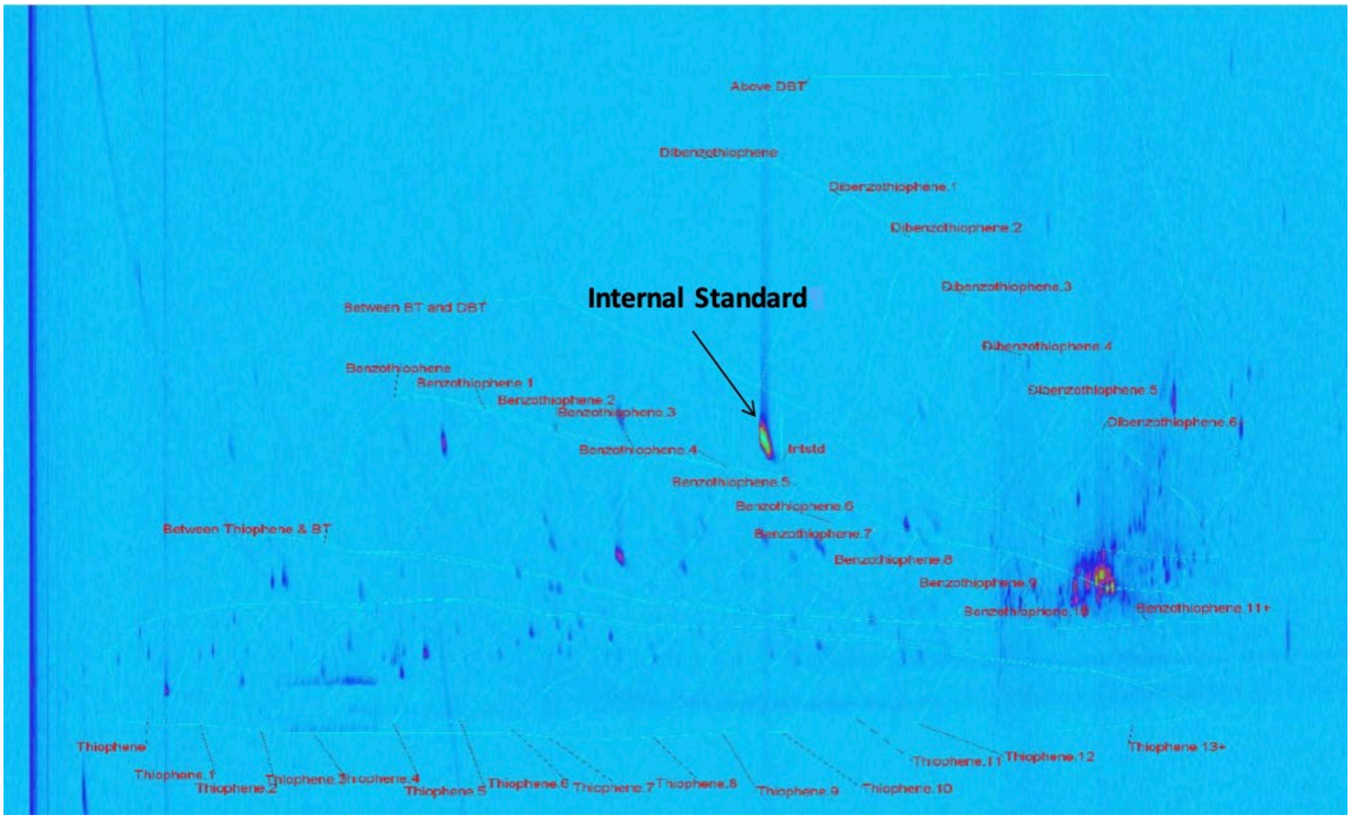
Project: WTC-13-003730 - EBMUD - 2D-GC-SCD of Biodiesel Customer: East Bay Municipal Utility District - Yun Shang

Sample: 178687

Total Sulfur Components

Component	Volum	Sulfur	Blobs
Thiophene	51	1.1	163
Thiophenes.1	34	0.8	138
Thiophenes.2	53	1.2	224
Thiophenes.3	78	1.8	192
Thiophenes.4	86	1.9	196
Thiophenes.5	57	1.3	179
Thiophenes.6	58	1.3	180
Thiophenes.7	43	1.0	142
Thiophenes.8	48	1.1	182
Thiophenes.9	40	0.9	158
Thiophenes.10	41	0.9	117
Thiophenes.11	32	0.7	122
Thiophenes.12	41	0.9	136
Thiophenes.13+	104	2.4	381
Benzothiophene	91	2.1	379
Benzothiophenes.1	63	1.4	372
Benzothiophenes.2	61	1.4	275
Benzothiophenes.3	90	2.0	284
Benzothiophenes.4	47	1.1	201
Benzothiophenes.5	49	1.1	156
Benzothiophenes.6	31	0.7	128
Benzothiophenes.7	26	0.6	111
Benzothiophenes.8	25	0.6	99
Benzothiophenes.9	29	0.7	96
Benzothiophenes.1	53	1.2	72
Benzothiophenes.1	424	9.6	111
Dibenzothiophene	149	3.4	1018
Dibenzothiophenes	67	1.5	518
Dibenzothiophenes	48	1.1	353
Dibenzothiophenes	58	1.3	307
Dibenzothiophenes	60	1.4	217
Dibenzothiophenes	52	1.2	161
Dibenzothiophenes	213	4.8	229
Between T And Bt	233	5.2	783
Between Bt And	1840	41.5	1347
Above Dbt	616	13.9	2507
Total Sulfur	5090	115	12234
Int Std	1050	23.6	1
Units	Total Volume (x 10^3)	ppm as Sulfur	Numb er

Figure B-1: East Bay Municipal Utility District • WTC-13-003730 • 2D-GC-SCD Sulfur Speciation of BiodieselSample: 1786872-D Sulfur Speciation Chromatogramby 2D GC-SCD



Source: EBMUD

5/13/2013