Optimization of the production of biodiesel from recycled grease trap waste

by

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fulfillment of the requirements for the degree of
Doctor of Philosophy

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Declarations

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Preface

This doctoral thesis is prepared in “Publication” format according to the “Specifications for Thesis (2017)” of the University of Adelaide. It includes publications that have been published, submitted for publication, or prepared in publication format:

1. Tran, N., McMurchie, E., Ngothai, Y. Production of biodiesel from recycled grease trap waste: a review. (Submitted to Fuel Processing Technology – Under review)
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5. Tran, N., McMurchie, E., & Ngothai, Y. (2018). Biodiesel Production from Recycled Grease Trap Waste: A Case Study in South Australia. Part 2: Optimization of The Transesterification Process. ChemistrySelect, 3(13), 3626-3631.6.
6. Tran, N., McMurchie, E., Ngothai, Y. Co-solvent Applied for the Pre-treatment of High Free Fatty Acid Feedstock for Biodiesel Production. (Submitted to Energies – Under review)

7. Tran, N., McMurchie, E., Ngothai, Y. Scale-up and economic analysis of biodiesel production from recycled grease trap waste. (Submitted to Applied Energy – Under review)

Some relevant components of the project work have been orally presented in international conferences with the following proceeding papers:

1. Tran, N., Ho, P., Tran, C., Chao, L., Curran, P., McMurchie, E., Ngothai, Y. Optimization of the production of biodiesel from grease trap waste (GTW) [online]. In: Chemeca 2016: Chemical Engineering - Regeneration, Recovery and Reinvention. Melbourne, Vic.: Engineers Australia, 2016: [1128]-[1135].
2. Tran, N., Tran, C., Ho, P., Hall, P., McMurchie, E., Hessel, V., Ngothai, Y. Extraction of fats, oils, and grease from grease trap waste for biodiesel production. Proceedings Venice 2016, Sixth International Symposium on Energy from Biomass and Waste, 2016 / Clarke, W., Cassu, R., Diaz, L., Matsuto, T., Nelles, M., Stegmann, R., Liu, J. (ed./s), pp.1-12
3. Tran, N., Ho, P., Hall, T., McMurchie, E., Ngothai, Y. (2017) Optimisation of the Production of Biodiesel from Recycled Grease Trap Waste: A Case Study in Adelaide. The 10th World Congress of Chemical Engineering (WCCE10), Barcelona, Spain.

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My beautiful wife, Linh Doan,

My sons, Hai Tran and Quan Tran,

My sister, Lan Tran,

And all of my family members in Vietnam for their priceless support, assistance, and loves, that enabled me to finish a-4-year PhD study in Australia.

Abstract

This thesis investigated the technical and economic feasibilities of biodiesel produced from recycled grease trap waste (GTW) which accumulates in the wastewater system coming from food outlets and food processing sectors. The study was carried out by performing four principal tasks, these being: (1) extraction of fats, oils and grease (FOG) from GTW and investigation of its characterisation as a potential feedstock for biodiesel production; (2) development of an analytical methodology for the quantitative analysis of free fatty acid ethyl ester profiles; (3) optimisation of the process parameters for the synthesis of biodiesel from the extracted FOG via esterification and transesterification reactions; (4) scaling-up the laboratory-based process using a process simulator, and evaluating the economic feasibility of producing biodiesel from GTW.

The GTW investigated in this study was provided by Peats Soil and Garden Supplies Ltd. Pty., (Adelaide, South Australia). The provided GTW was collected from the floating grease layer in a storage tank in which the lipid content was concentrated due to its lower density (approximately 51 wt%). Lipid extraction was then performed at ambient temperature (25ºC), employing hexane (HEX) and diethyl ether (DEE) as the solvents. A 97% lipid yield was obtained under the optimum operating conditions, these being: 1:1 DEE to GTW ratio (v/w); 300 rpm stirring speed, and 5 hr reaction time.

Due to the high level of free fatty acids (>80 wt%) in the extracted oil, the esterification reaction was then conducted to reduce the FFA level in the feedstock. Two approaches, an esterification reaction with the use of the co-solvent acetone, and an esterification reaction without acetone were investigated and optimized. The optimal conditions for both reactions were determined using response surface methodology (RSM) based on central composite design (CCD). Optimum conditions for the esterification reaction without acetone were found to be 6:1 ethanol to oil molar ratio, 3 hr reaction time, 75ºC reaction temperature, and 3 wt% H_2SO_4 loading per FOG weight. In the presence of acetone, the optimal conditions were 35% v/v acetone to FOG, 6:1 ethanol to oil molar ratio, 3 hr reaction time, and 3 wt% H_2SO_4 loading. The ester yields obtained were 81 wt% and 80 wt%, respectively.

The crude oil obtained from the previous pre-treatment was then subjected to a transesterification reaction to convert the remaining glycerides to ethyl esters. Two approaches, which were specified by the priority of the added components, were investigated to determine the optimal operating parameters. The results showed that a 96.7 wt% ester yield could be obtained under the optimum conditions, which were; 4:1 ethanol to oil molar ratio, 1 hr reaction time, 65ºC reaction temperature, and 1 wt% KOH loading. Importantly, approximately 30% of the excess ethanol could be reduced when ethanol and the base catalyst were heated first, while the extracted oil was added later at a specific rate. It was also found that the characterization of the GTW-derived biodiesel obtained satisfied most of the performance and compositional parameters required by the Australian Biodiesel Standard.

After obtaining the optimal process parameters, two simulation models were constructed using Aspen Plus® V8.8 to generate the equipment and utility data required for the economic evaluation. Those simulation models were classified by the use of the co-solvent acetone in the esterification reaction. The result showed that the minimum production price of GTW-derived biodiesel was US$1,337.5/t, obtained through the process without using acetone. It can be concluded that the production of biodiesel from recycled greases is technically feasible and the economic aspect is also promising, although further studies need to be conducted to produce a biodiesel fuel which all satisfies the current mandatory standards.

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Chapter 1. Introduction

1.1 Project Background

Australia is one of the top ten energy producers and is among the greatest consumers of non-renewable energy resources [1]. According to a recent report, more than 90% of the total energy consumption by Australia was produced from fossil resources, while biofuels only accounted for around 3.3% [2]. In 2015, 130 million liters of biodiesel was produced domestically, making up only 1.4% of the total renewable energy consumption [3]. **Figure 1.1** shows the Australian renewable energy production by fuel type in 2015.

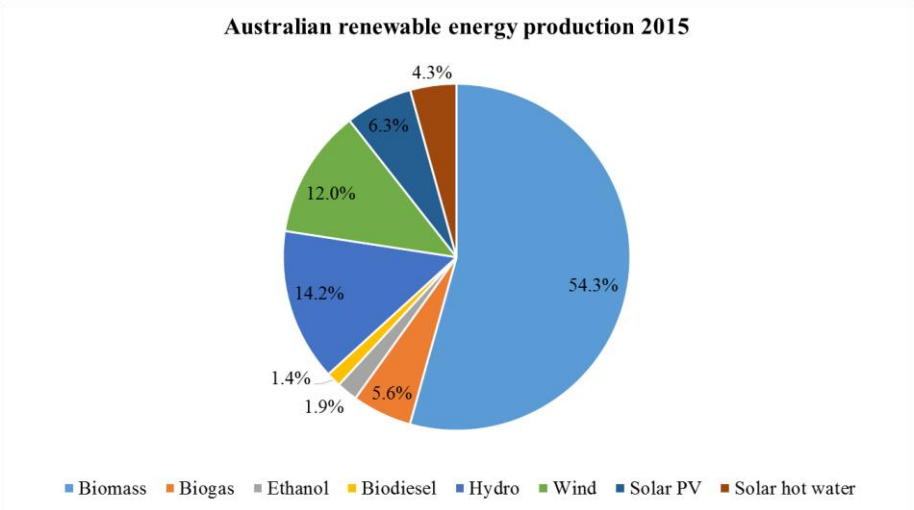

Figure 1.1 Australian renewable energy production by fuel type, 2014-15 [3]

In Australia, biodiesel has been traditionally produced from vegetable oils, animal fats (e.g. beef tallow), and waste cooking oil [3]. Recently, the rapid rise in the cost of such feedstocks, coupled with the unfavorable conditions of limited mandate support, low international oil prices, and insufficient tax relief to offset high feedstock prices to bridge the gap between mineral diesel prices and biodiesel, have forced the biodiesel producers to search for cheaper and more sustainable feedstocks. In October 2016, one of the largest biodiesel production plant in South Australia was closed as a consequence of economic inefficiency, resulting in a significant drop in the annual consumption of biodiesel [3]. Therefore, searching for a more sustainable and cost-effective feedstock is becoming an imperative. Among those, grease trap waste (GTW), which is collected from the interceptors installed in the sewage system of commercial businesses, such as restaurants, fast-food outlets, and food processors, appears to be a potential feedstock since it possesses a very high lipid content which can potentially be used as a feedstock for biodiesel production. In 2015, more than 500,000 tons of GTW was collected national wide in Australia, making it the third highest hazardous waste resource and consequently requiring a costly treatment process before remediation [4]. With approximately 10 wt% lipid content, this corresponds to annual 'brown grease' production of around 2kg per person per year. **Figure 1.2** shows the consumption of GTW collected in six states and two territories of Australia in 2015.

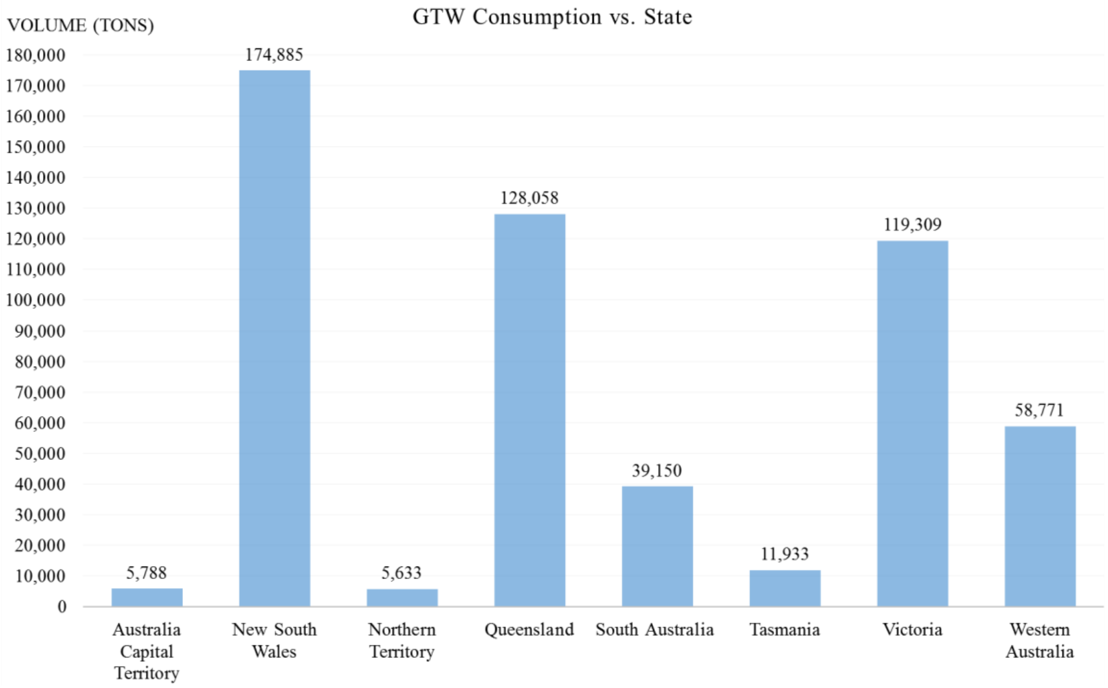

Figure 1.2 GTW consumption in different states and territories of Australia in 2015

Chemically, GTW is a combination of water, fats, oils, and grease (FOG), waxes, soap, and solids with different weight percentage, depending on the location, the season, and the manner in which it was collected [5]. The collection and treatment of GTW are required or enforced by authorities around the world since it is the main cause of sewer pipes clogging, sanitary sewer overflowing, pipeline corrosion, and surface water pollution [5]. Currently, landfill and biodegradation (methane anaerobic digestion) are the two main treatment methodologies for this waste resource [6]. However, due to its high-lipid content of approximately 1 to 40 wt%, GTW has the potential to be utilized as a feedstock for biodiesel production [7].

In Adelaide, the capital city of South Australia, Peats Soil and Garden Supplies Pty. Ltd., one of the major GTW collectors, reported that their company collected annually approximately 10 million liters of GTW essentially free of charge [8]. This represents around 25% of the total GTW generated annually in South Australia, which is estimated around 40,000 tons. Importantly, this amount is predicted to increase significantly in the coming years due to the growth of the population and the increase in industrial activities, resulting in a greater burden for wastewater treatment plants [9]. While the cost of GTW is essentially free of charge, there are associated costs in terms of its collection and transportation. In practice, GTW is pumped from the grease trap installed in the sewerage system of restaurants, cafeterias, and food processing services across Adelaide and then transferred to the treatment site by trucks. Following the environmental service providers, it is then sent to landfill or partially digested to produce methane. Although the company is paid by producers to collect this waste resource, the expenses of transportation and waste treatment still remain significant. Peats Soil and Garden Supplies Pty. Ltd. expect that the use of GTW as a feedstock for biodiesel production could partially cover the cost of GTW collection and transportation. Therefore, there is a need for the development of new technologies for the production of GTW-derived biodiesel in which environmental service providers are considered as the potential producers. Significantly, this can open up an opportunity for such environmental service providers to participate in the biodiesel production market in Australia.

However, the production of GTW-derived biodiesel is technically challenging due to the contaminated nature of GTW, and the very high content of free fatty acids (FFA) found in the feedstock [10]. A large body of research has been developed focusing on both esterification and transesterification reactions between GTW and an alcohol, such as methanol and ethanol, using bases (NaOH, KOH, K_2CO_3), strong acids (H_2SO_4, HCl, H_3PO_4), or solid metal oxides as catalysts, whilst others studies have concentrated on the development of non-catalytic processes to produce GTW-derived biodiesel, such as the use of supercritical or subcritical methanol [11-17]. Most of these studies have been successful at the laboratory scale, but considerable research and development are still required to obtain a feasible economic and commercial production plant. Significant effort has been made into investigating of optimal operating parameters for the production of biodiesel from GTW, however, further research needs to be conducted to clarify the effect of process scale-up on the quality and the yield of biodiesel products. It is essential to determine the appropriate techniques, focusing on the environmental service providers, to maximize the product yield and to produce biodiesel that meets the mandatory standard at an acceptable price.

The aim of this study was to develop a feasible technique for the production of GTW-derived biodiesel utilizing GTW as a feedstock and ethanol as the reactant. The extraction of FOG from GTW using popular industrial solvents, such as hexane and diethyl ether, was first investigated and the optimal extraction conditions were then determined. This was followed by an investigation of the influence of different process parameters on esterification and transesterification reactions between GTW and ethanol, employing strong acids as catalysts. Laboratory-scale reactors were used to conduct the research while multi-objective optimization was performed to determine the optimal parameters and to study the effect of solvent recycling on the quality of the product. Process simulation was also performed based on the results collected through laboratory-based experiments, in conjunction with the data provided by the industrial waste-processing sector, to determine the scale-up effect and the economic feasibility of the project. The properties and quality of GTW biodiesel will also be tested to determine its quality parameters in comparison to the Australian biodiesel standard.

1.2 Research Objectives

The primary aim of this study was to develop a complete GTW-derived biodiesel production process through the optimization of the process parameters of each process stage (i.e. extraction, esterification, and transesterification).

The proposed study was accomplished through the following objectives:

(1) Develop a simple extraction process to extract fats, oils, and grease from grease trap waste.

(2) Develop a quantification methodology to analyze the fatty acid profiles of fatty acid ethyl esters (biodiesel).

(3) Investigate an effective GTW-derived biodiesel production process which would be applicable to the environmental service industry in South Australia.

(4) Evaluate the scale-up effect and the economic feasibility of the GTW biodiesel production process.

Each objective was organized into a main chapter and is summarised in the outline section.

1.3 Thesis Outline

This thesis is presented based on the thesis-by-publication format which consists of seven main chapters which encompass the core findings of the study. Chapter 1 provides some background information about the project in which the consumption of GTW, the collection procedure, and current biodiesel production techniques were addressed. The aims and the main objectives of the thesis are also presented in this chapter.

The second chapter of this thesis is the Literature Review. This chapter discusses the previous studies on biodiesel production from wastewater feedstocks, such as scum sludge and GTW, including FOG extraction processes, feedstock pre-treatment techniques, biodiesel synthesis via esterification and transesterification reactions, catalyst classification, characterization of biodiesel, and economic feasibility of the whole production process. Chapter 3 focusses on the development of a simple methodology for the extraction of FOG from GTW. The required instrumentation, appropriate standards, and chemicals for the analysis of the lipid content and free fatty acid ethyl ester (FAEE) profiles were discussed in chapter 4. This chapter concentrated on the development of a Gas Chromatography using a Flame Ionisation Detector (GC-FID) to quantify the ethyl ester profiles of GTW-derived biodiesel.

Having developed the analytical methodology, the esterification pre-treatment of high FFA feedstock obtained in chapter 3 was presented in chapter 5. Acid-catalysed esterification was performed in order to obtain an FFA level less than 2%, resulting in an optimal operating condition. In chapter 6, a co-solvent approach was applied for the esterification of the GTW-derived feedstock to reduce the total energy consumption. Together with ethanol, acetone was utilized as the co-solvent which enabled the esterification reaction undertaken at ambient temperature, resulting in a potential reduction in the cost of total energy consumption. The sulphur content of the biodiesel was also investigated to evaluate the possibility of this co-solvent approach in the reduction of sulphur levels.

The conversion of the remaining glycerides to biodiesel using the transesterification reaction was introduced in chapter 7. This chapter outlines the various steps required, which were:

a) Conversion of the remaining glycerides to ethyl esters (biodiesel) using the transesterification reaction.

b) Analysis of biodiesel yield and its characterization throughout each process stage.

c) Purification of biodiesel through washing, in concert with a simple vacuum distillation process.

The economic feasibility of the two approaches, esterification when using the co-solvent acetone and esterification without using acetone, was then presented in chapter 8. In this chapter, the process simulator, Aspen Plus® V8.8, was used to construct simulation models that simulated the results obtained in chapter 3, chapter 5, chapter 6, and chapter 7. Economic and cost evaluation methodology was also applied to calculate the total production cost and the break-even price of GTW-derived biodiesel.

The last chapter, chapter 9 (i.e. the conclusion), reiterates the core findings of this study and there are discussed with the view of presenting a number of recommendations which may be further applied for research into the production of GTW-derived biodiesel. A flow-sheet of the thesis outline is shown in **Figure 1.3**.

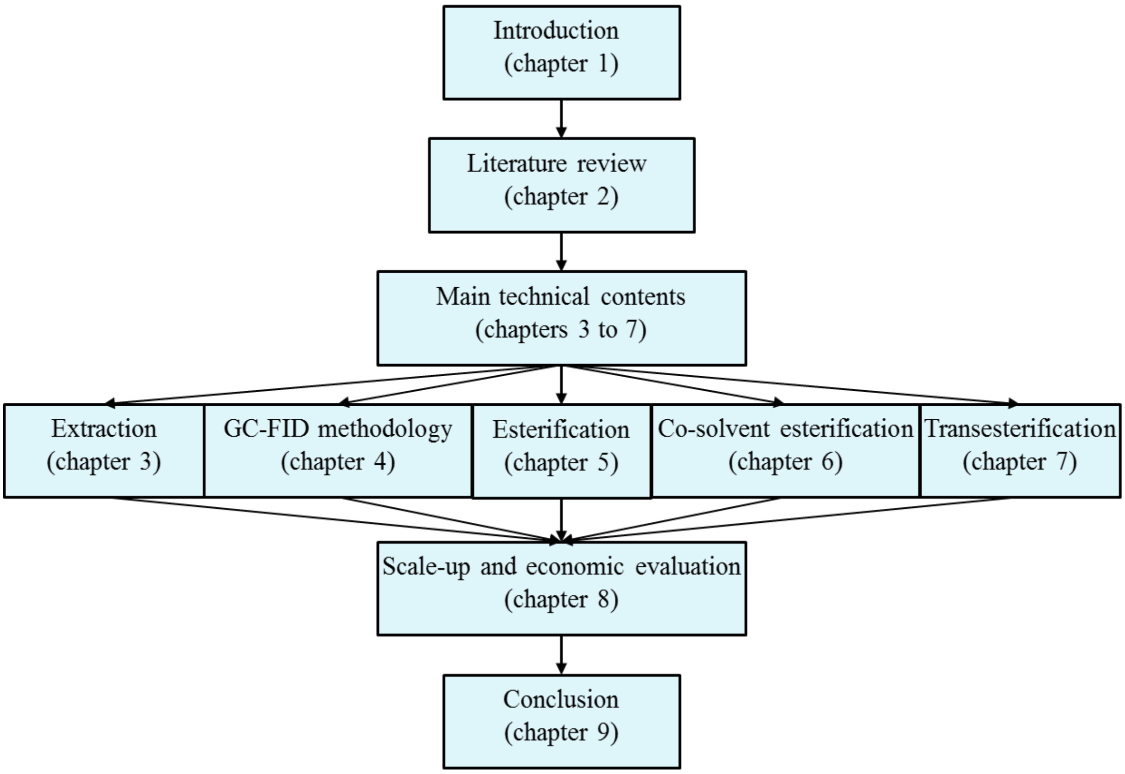

Figure 1.3 Flow-sheet of the thesis outline

References

[1] Hua Y, Oliphant M, Hu EJ. Development of renewable energy in Australia and China: A comparison of policies and status. Renewable Energy. 2016;85:1044-51.

[2] Trainer T. 'Can renewables meet total Australian energy demand: A “disaggregated” approach. Energy Policy. 2017;109:539-44.

[3] Roger F. Australian Biofuels Annual 2017. USDA Foreign Agricultural Service, Canberra, Australia 2017.

[4] Latimer G. Hazardous Waste in Australia 2017. Victoria, Australia 2017.

[5] Wallace T, Gibbons D, O'Dwyer M, Curran TP. International evolution of fat, oil and grease (FOG) waste management–A review. Journal of Environmental Management. 2017;187:424-35.

[6] Hums ME, Cairncross RA, Spatari S. Life-cycle assessment of biodiesel produced from grease trap waste. Environmental Science & Technology. 2016;50:2718-26.

[7] Hums ME. Environmental Impacts of Biodiesel Produced from Wastewater Greases. Philadelphia, United States: Drexel University; 2016.

[8] Curran P. Optimising the Production of Biodiesel from Grease Trap Waste Adelaide: Honours Thesis, The School of Chemical Engineering, The University of Adelaide; 2013.

[9] Lang A, Kopetz H, Stranieri A, Parker A. Australia’s under-utilised bioenergy resources. Waste and Biomass Valorization. 2014;5:235-43.

[10] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology. 2007;98:183-90.

[11] Mardhiah HH, Ong HC, Masjuki H, Lim S, Lee H. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. Renewable and Sustainable Energy Reviews. 2017;67:1225-36.

[12] Mansir N, Taufiq-Yap YH, Rashid U, Lokman IM. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. Energy Conversion and Management. 2017;141:171-82.

[13] Kaddour M. Esterification of free fatty acid by selected homogeneous and solid acid catalysts for biodiesel production. Ontario, Canada: The University of Western Ontario; 2016.

[14] Pastore C, Barca E, Del Moro G, Lopez A, Mininni G, Mascolo G. Recoverable and reusable aluminium solvated species used as a homogeneous catalyst for biodiesel production from brown grease. Applied Catalysis A: General. 2015;501:48-55.

[15] Kellotoay A, Marvin WA, Schmidt LD, Daoutidis P. Process design and supply chain optimization of supercritical biodiesel synthesis from waste cooking oils. Chemical Engineering Research & Design: Transactions of the Institution of Chemical Engineers Part A. 2013;91:1456-66.

[16] Ghoreishi SM, Moein P. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. The Journal of Supercritical Fluids. 2013;76:24-31.

[17] Huynh LH, Tran Nguyen PL, Ho QP, Ju Y-H. Catalyst-free fatty acid methyl ester production from wet activated sludge under subcritical water and methanol condition. Bioresource Technology. 2012;123:112-6.

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Contribution to the Paper	Conducting the literature review and preparing the manuscript		
Overall Percentage	70%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	28/02/2018

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Edward J McMurchie		
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Contribution to the Paper	Supervising the development of the work and approving the manuscript		
Signature		Date	28/02/2018

Chapter 2. Production of Biodiesel from Recycled Grease Trap Waste: A Review

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Abstract

In recent years, the climate changes occurring worldwide have encouraged research into the development of eco-friendly, lower environmental impact, and more sustainable energy sources. This may also be a solution to deal with the rapid decrease in, and depletion of fossil resources. Biodiesel has been considered as a key attribute for effective climate change responses and a potential candidate to substitute for mineral diesel. Even so, the marketability of biodiesel is still very limited due to the lower price of mineral diesel as well as the expensive cost of present biodiesel feedstocks. In this regard, the use of wastewater residuals such as scum sludge and grease trap waste as a cost-effective feedstock appears to be attractive. Many studies have been conducted to investigate the characteristics of grease trap waste in order to develop an appropriate technique for biodiesel production from this low-quality and low-cost resource. However, most of these studies have only focused on a partial process, including the pre-treatment of feedstock, the esterification, and the transesterification processes, without reporting a fully integrated process for biodiesel production from recycled trap grease. Therefore, this study aims to highlight recent achievements in the production of biodiesel from grease trap waste and to consider the potential marketability of this fuel.

Keywords: *Grease trap waste (GTW); Fats, oils, and grease; wastewater sludge; Biodiesel; Renewable energy*

2.1 Introduction

Biodiesel, an alternative fuel for mineral diesel, has attracted worldwide attention due to its biodegradability, low environmental impact, and its ability to be used without modification of the conventional diesel engine. Since biodiesel was first introduced in 1978, the literature has reported many attempts to produce commercial biodiesel from rape seeds, vegetable oils, and animal fats, etc., as feedstocks to substitute for fossil fuels. However, due to the lower price of fossil fuels achieved through technical developments, the total world energy consumption of fossil fuels is still significant [1-4]. In 2016, a report by British Petroleum (BP) showed that the shared market of total renewable energy was only 3.2% [5].

Previous studies have emphasized that the expensive cost of feedstocks is the main impediment to the industrialization and commercialization of biodiesel [1, 6-9]. The production from virgin feedstocks (e.g. edible oils) is plagued by the fact that the feedstock represents up to 70-88% of the production cost, making biodiesel an expensive fuel in comparison with mineral diesel. In addition, the use of farmland for feedstock cultivation has also raised concerns in terms of soil impoverishment and food security. Therefore, searching for a cheaper and more sustainable feedstock has become an imperative for research related to biofuels. Amongst other feedstock choices, the utilization of waste lipids such as those obtained from scum sludge and recycled grease trap waste (GTW), or brown grease has opened a new market for cheaper biodiesel products. Furthermore, the recovery of GTW from wastewater treatment plants can also be beneficial to the environment in terms of reducing sewer pipe clogging, sanitary sewer overflows, preventing pipeline corrosion and avoiding landfill expansion, as well as surface water pollution.

GTW is an abundant lipid resource that can be collected from interceptors installed in the sewer pipes of many restaurants and food processing factories as a mandatory requirement to avoid sewer blockages. Chemically, the composition of GTW generally consists of fats, oils, and grease (FOG), water, soap and other solid contaminations which cannot be processed by rendering plants due to their low quality. GTW also varies in amount and composition depending on seasonal variation affecting the type of food consumed, the location, the hydrolysis process, and the manner by which it is collected. It is estimated that the treatment of sludge accounts for 20-60% of the total operating cost of a wastewater treatment plant [10]. In effect, sludge and GTW are generated in huge amounts worldwide due to the urbanization, industrialization, and growth in population. In the United States, a restaurant can produce an average of about 1,400 to 11,000 kg of GTW per year [11]. Total sludge production in China had an average annual growth of 13% from 2007 to 2013 with around 6.25 million tons of dry solids being produced in 2013 [12]. In Australia, approximately 550,000 tons of GTW was generated in 2014 – 2015 [13]. With an average composition of 10% lipids, approximately 55,000 tons of FOG is potentially available for fuel production.

Canakci and Van Gerpen [14] are among the first to report studies which emphasize the potential of GTW as a feedstock for biodiesel production. They also stated that it is technically challenging to produce biodiesel from GTW due to its high free fatty acid (FFA) content and high levels of other contaminants. Throughout the years, many studies have been conducted focusing on the pre-treatment of GTW as well as on developing more effective techniques to deal with the low quality of the feedstocks. While most of these studies have led to partial success at the laboratory scale, researchers are still striving to develop a feasible economic and commercial production plant to take GTW produced biodiesel to the market. Recently, significant effort has been put into optimizing the operating parameters for the extraction of FOG, the esterification reaction to reduce FFA, and the transesterification process. Results show that GTW-derived biodiesel has great potential to substitute for fossil fuels in terms of both its environmental benefits and economic feasibility [11, 15-29]. However, the low-quality of GTW-derived biodiesel is currently the main obstacle for its marketability since, in the majority of cases, GTW-derived biodiesel cannot satisfy the ASTM D6751 or EN 14214 standards [19, 30]. Further investigation needs to be undertaken to overcome these problems and to clarify the effect of process scale-up on the quality and quantity of GTW-derived biodiesel.

Therefore, the main objective of this review is to summarise studies which focus on the following topics and address the future implications of biodiesel production from GTW:

(1) Lipid extraction processes
(2) Biodiesel production techniques
(3) Fuel properties of GTW-derived biodiesel
(4) Economic feasibility of GTW-derived biodiesel

2.2 Lipid Extraction Processes

2.2.1 Extraction Methodologies

Extraction of fats, oils, and grease (FOG) is the first important step in the production of biodiesel from low-quality feedstocks. Due to the contaminated composition of GTW and sludge, a wide range of techniques have been introduced to extract FOG in order to achieve a useable feedstock for the transesterification process. While the lipid extraction methodology developed by Bligh and Dyer [31] is still applied in many laboratories, research has recently focused on larger scale extraction processes. The simplest lipid separation is based on heating followed by a centrifugal process.

However, this is not effective for the complete extraction of lipid, while heating is also criticized as a high energy consumption process [32, 33]. Importantly, research has also revealed that heating can chemically promote the hydrolysis process resulting in changes to the composition of the GTW [23, 34-36]. In practice, FOG is best extracted in the presence of conventional industrial solvents such as hexane, ethanol, diethyl ether, etc. [10]. The use of such low boiling point solvents for the extraction process offers a simple and affordable separation method that can be applied to industrial production.

Table 2.1 summarizes some solvent types and parameters obtained under optimum conditions during the extraction process. Although the simplicity of solvent extraction is preferred by most of the industrial producers, the recovery of the solvent after the extraction process also requires a huge amount of energy and expensive separation facilities, adding an extra component to the total production cost [37-39]. Recently, attempts have been made to extract FOG from GTW using waste cooking oil (WCO) as a solvent. Tu et al. [37] reported that a 95% extraction yield can be obtained after 240 min, at 70°C, with the ratio between WCO-GTW being 3.2:1 (wt/wt). However, due to the fact that WCO is often contaminated by very high levels of heavy metals, soap and unknown particles in GTW that may lead to a costly refinery process as well as a requirement for a moderate energy consumption, this method has not yet been applied in practical production. Thus, the extraction of FOG from GTW remains attractive but impractical worldwide unless a more efficient process in terms of energy saving and FOG quality is developed.

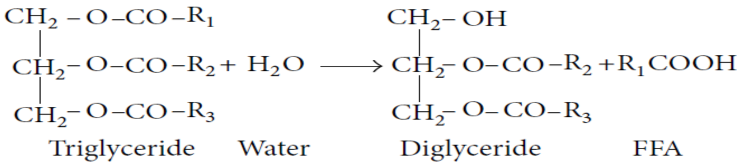
Table 2.1 Summary of oil extraction methods and operation parameters

Feedstock	Methods	Solvent	Ratio	Temp. (°C)	Time	Maximum Yield	Ref.
GTW	heating	none	-	60	At least 6 hr	81 - 93 wt%	[33]
GTW	Solid-liquid extraction	Hexane	100 g of waste, 1.0 ml of concentrated HCl and 100 ml of n-hexane	40	-	-	[17]
Primary sludge	Liquid – liquid extraction	Hexane	2:1 sludge to hexane volume ratio	ambient	Approx. 2 hr	91% after 3 stages liquid – liquid extraction	[40]
Primary sludge	Liquid-solid extraction	Hexane and methanol	10 g of dried sewage sludge to 100 ml and 150 ml of solvent	ambient	2.5 – 4 hr	- Hexane: approximately to 7.5% based on dried sludge - Ethanol: 14 wt% based on dried sludge	[41]
Primary and secondary sludge	Liquid-solid extraction	Methanol and hexane	10-30 ml/g of sample	25 - 75	0.5 – 4 hr	- Primary sludge: 58.85 wt%	[42]

						- 2nd sludge: 51.18 wt% FFA on the basis of lipids	
Dried sewage sludge	Acid hydrolysis	Acid hydrolysis 1 N, petroleum ether, hexane, chloroform − methanol,	10 ml of 1 N hydrochloric acid (36−38%) and 8 ml of distilled water	70 - 80	35 – 50 mins + additional extraction time	85.8	[43]
		ether−petroleum ether, and hexane−ethanol.	20 ml of solvent per 5 g of sample	70 – 80	6 – 8 hr	62.5	
	Soxhlet	Ethanol, methanol, hexane, etc.	75 ml of solvent per 5 g of sample	40 - 50	2 – 3 days	61.7%,	
	Water shaking bath	Acetone, chloroform−methanol, ether−petroleum ether					
GTW	Liquid – solid extraction	waste cooking oil	3.2:1 WCO-SG ratio (w/w)	70	4 hr	95% extraction yield	[37]

2.2.2 Properties of Trap Grease Oil

Characterization of trap grease oil varies depending on the wastewater treatment plant, the season, how the GTW is collected and the extraction processes used. This makes published work related to GTW-derived biodiesel tend to be only of local interest since it is difficult to apply any findings on a global basis. Basically, the oil properties of FOG are mainly based on its fatty acid composition, which is an important criteria used to determine the concomitant biodiesel production techniques required. It is reported that grease trap waste and sludge have very high a fatty acid level in comparison with the other virgin feedstocks [29]. This can be explained by the hydrolysis reaction between the glycerides, the main components of vegetable oils, and the presence of water during the cooking and waste disposal processes [44]. Reaction (1) shows the mechanism of the hydrolysis reaction.



$$\begin{array}{llll} CH_2-O-CO-R_1 & & CH_2-OH & \\ | & & | & \\ CH_2-O-CO-R_2 + & H_2O \longrightarrow & CH_2-O-CO-R_2 + & R_1COOH \\ | & & | & \\ CH_2-O-CO-R_3 & & CH_2-O-CO-R_3 & \\ \text{Triglyceride} & \text{Water} & \text{Diglyceride} & \text{FFA} \end{array} \quad (1)$$

Normally, the FFA content of wastewater feedstock ranges from 8-100% [11, 15, 18-20, 22-24, 26-29, 45, 46]. Many studies reported that the fatty acids C18:1 and C18:2 are the main components found in the composition of grease trap waste [11, 20, 26-29, 32, 33, 40, 47]. **Table 2.2** provides some characteristics of GTW oils obtained from previous studies.

Table 2.2 Characterizations of GTW oils obtained from previous studies

Test/References	**[29]**	**[32]**	**[17]**	**[26]**	**[27]**	**[47]**	**[48]**
Moisture, wt%	0.65	-	1.3–4.7	0.8	1.16		0.19
Acid value, mg KOH/g	1.4 – 83.6	-	4.9–168.2	100±0.02	52.1	16-24	114.0
Molecular weight, g/mol		-	-		846	850.6	443.2
Fatty acid profiles, wt%							
Octanoic (C8:0)	-	-		-	0.4	-	-
Decanoic (C10:0)	-	0.41		-	0.4	-	-
Lauric (C12:0)	-	0.74	3.38	-	3.0	-	-
Tetradecanoic (C14:0)	0.2	2.82	14.61	1.16	1.9	1.3	-
Hexadecanoic (C16:0)	10.92	23.1	20.26	30.38	25.7	38.3	main
Hexadecenoic (C16:1)	0.44	1.84	-	1.42	2.0	1.2	-
Heptadecanoic (C17:0)	0.14	-	-	-	-	-	-
Heptadecenoic (C17:1)	<0.1	-	-	-	-	-	-
Octadecanoic (C18:0)	5.05	10.2	13.82	6.02	5.5	7.2	main
Octadecenoic (C18:1)	33.47	43.8	20.34	38.39	39.4	36.9	main
Octadecadienoic (C18:2)	42.64	11.3	11.12	18.83	19.8	15.1	main
Octadecatrienoic (C18:3)	4.9	0.93	1.52	1.31	1.0	-	-
Octadecatetraenoic (C18:4)	0.21	-	-	-		-	-
Eicosanoic (C20:0)	0.35	0.4	-	-	0.2	-	-
Eicosenoic (C20:1)	0.45	-	-	-		-	-
Docosanoic (C22:0)	0.37	-	-	-	0.08	-	-
Lignoceric (C24:0)		-	-		0.09	-	-
Unidentified acid, %	0.74	4.46	14.96	2.49	-	-	3

Unlike most of the vegetable oils, unsaturated oleic acid and its derived components are the predominant compounds in the fatty acid profiles of the extracted FOG. As such, this requires additional treatment before GTW oil can be taken to the transesterification stage. In addition, extremely high levels of soap, sulphur, and other heavy metals were also found in the content of GTW FOG [20, 34, 44, 49, 50]. Hums [19] reported that the sulphur level found in GTW extracted oil was around 250 – 500 ppm, while the permitted amount in biodiesel is only 15 ppm, when following the ASTM

D6751 standard. Briefly, the GTW oil feedstock can be described as having a very high FFA content which has the additional characteristics of having high viscosity and high heavy metal contamination.

2.3 Biodiesel Production Techniques

Since GTW oil contains very high levels of free fatty acids, which can react with alkaline catalysts to form soap during the transesterification reaction, a pre-treatment is required before any further processes can be conducted [22, 23, 29, 47, 49, 51, 52]. Normally, FOG will first be washed with a strong acid such as sulphuric acid to remove the heavy metals [53, 54]. It will then be converted to alkyl esters via the esterification reaction or converted to the glycerides by the glycerolysis reaction. To continue with the transesterification process, the FFA level in the feedstock should be zero or around 1 to 3% maximum [22, 52, 55-59]. This so-called two-stage reaction is applied widely, with researchers reporting that it has more benefits in terms of wastewater treatment, high production yield, and cheaper production costs in comparison with the single-stage process [10, 60].

2.3.1 GTW Pre-treatment Process

In order to make the GTW extracted FOG well-prepared for the transesterification process, the level of FFA in the FOG should be reduced. Without pre-treatment, the excess FFAs will cause the formation of soap and inhibit the separation of glycerol at the final stage. While many studies have sought to reduce the level of FFA in GTW oil through processes such as distillation, steam stripping, and absorbency, etc., most of them can only be applied to feedstocks having low levels of FFA [53]. There are currently two techniques that appear the most efficient in terms of GTW oil pre-treatment: glycerolysis and esterification. **Table 2.3** summarises some benefits and drawbacks of both these methods.

Table 2.3 FFA levels vs pre-treatment methodologies [53, 54, 61, 62]

Pre-treatment methods	**FFA levels**	**Benefits**	**Drawbacks**
Glycerolysis	15-100%	No alcohol or acid needed Higher yield of biodiesel Lower costs of residue treatment Lower product losses	High temperature, pressure Additional cost for pure glycerol
Esterification	10-100%	Simple process Low energy consumption Heavy metals removal Catalyzed simultaneous esterification Lower consumption of acid for neutralization of the catalyst in the transesterification process	Equipment corrosion Hazardous waste generation High alcohol/oil requirement Catalyst is difficult to recycle

2.3.1.1 Glycerolysis

Glycerolysis is a reaction between FFA and glycerine in which FFAs are converted to mono-, di-, and tri-glycerides, as shown in reactions (2), (3) and (4) [53].

$$\text{Glycerol} + \text{FFA} \Leftrightarrow \text{MAG} + H_2O \qquad (2)$$

$$\text{MAG} + \text{FFA} \Leftrightarrow \text{DAG} + H_2O \qquad (3)$$

$$\text{DAG} + \text{FFA} \Leftrightarrow \text{TAG} + H_2O \qquad (4)$$

Anderson et al. [38] reported that glycerolysis is amongst the most effective method for the pre-treatment of high FFA feedstocks and thus it has been utilized by many industrial companies. The advantage of the glycerolysis process is the reduction in the FFA level in low-grade feedstocks without the use of acid or alcohol. Instead of removing and disposing of FFAs in the waste stream as is done in the treatment of low-FFA feedstock, glycerolysis provides an effective solution for transferring FFAs to glycerides and making them available for the transesterification process, thereby increasing the product yield [38, 62-67]. Another benefit of glycerolysis is the removal of water from the feedstock, avoiding the formation of soaps in the reaction with an alkaline catalyst, since the process is usually conducted at temperatures at above 200^0C [38, 62].

However, the use of extremely high temperatures coupled with the cost of pure glycerol as the reactant for the glycerolysis process, underpin the main concerns of biodiesel producers in terms of process safety and production costs [39, 54, 68]. In terms of the reaction activity, the limited solubility of glycerol in fats is a barrier to achieving a sufficient degree of homogeneity in which the reaction can take place effectively [69]. Kombe et al. [39] have developed a method to conduct the glycerolysis process at a lower temperature, while still maintaining a high conversion rate (up to about 99%). They reported the optimum conditions are 65°C reaction temperature, 73 minutes reaction time, and 2.24 g/g glycerol to oil mass ratio. In another study, Echeverri et al. [66] attempted to recycle glycerol from the transesterification stage of the same biodiesel production process and use it as a reactant for the glycerolysis reaction. Despite some success, the glyceride conversion rate was very low due to the contaminated NaOH and soaps found in the recycled stream. However, this method is still widely applied in the industry when the current facilities have been already designed for conventional feedstocks.

2.3.1.2 Acid Esterification

Acid esterification or pre-esterification is the most prevalent treatment method to deal with high FFA feedstocks. The target of this pre-treatment process is to convert FFA into alkyl esters, employing acid as the catalyst. Reaction (5) describes the esterification of FFA under the presence of an acid catalyst.

$$\text{R-COOH (Fatty acid)} + \text{R'-OH (alcohol)} \Leftrightarrow \text{R-COO-R' (biodiesel)} + H_2O \qquad (5)$$

This method is successful for feedstocks with an FFA level up to 100% [3, 53]. Vitiello et al. [70] indicated that choosing the correct catalyst is the key step to producing biodiesel from the waste oils. Currently, sulphuric acid is widely used since it is a cheap and effective solution in terms of the conversion rate that can be achieved [2, 53, 54, 71, 72]. Importantly, sulphuric acid can act as an agent to remove metallic and non-metallic impurities that may affect the quality of GTW derived biodiesel [19, 49]. Cairncross et al. [49] reported that acidic catalysts can also reduce the amount of sulphur produced during the biodiesel synthesis process. However, concern has been raised concerning the disposal of acidic water, the loss of the excess acid catalyst, as well as the high investment cost for anti-corrosion equipment [55, 73-76]. Furthermore, water, a by-product of the esterification process, not only lowers the reaction rate, but also has a detrimental effect on the next stage of the transesterification process. This method has been criticized by the environmental lobbyists since it may produce more hazardous substances that reduce the environmental benefits of biodiesel.

Research has recently been focused on the utilization of heterogeneous catalysts such as ion-exchanged resins, zeolites and other solid acids to overcome the disadvantages when using homogeneous catalysts [70, 77, 78]. The major benefits of solid catalysts include their ability to be recycled and used in simultaneous reactions, and their insensitivity to water [54, 77]. For example, Keggin heteropolyacids (HPAs) such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ have been reported to be effective for the esterification of waste oils [55, 73, 77]. Chemically, HPAs possesses a stronger oxidative ability than sulphuric acid as they have a very strong Brønsted acidity [77]. Kim et al. [79] studied the effect of zirconia on metal oxide catalysts in relation to the use of high FFA feedstock. They reported that methanolysis was more effective when supported by zirconia, while the level of sulphur could be significantly reduced.

2.3.2 Transesterification

Transesterification is the process used to convert glycerides to free fatty acid alkyl esters in the presence of an alkyl alcohol and a base catalyst. This includes a series of reactions in which triglyceride is converted step-by-step to the esters (biodiesel) and glycerine (by-product) as shown in reactions (6), (7), and (8).

$$\text{Triglyceride} + \text{ROH} \leftrightarrow \text{Diglyceride} + \text{RCOOR1} \tag{6}$$

$$\text{Diglyceride} + \text{ROH} \leftrightarrow \text{Monoglyceride} + \text{RCOOR2} \tag{7}$$

$$\text{Monoglyceride} + \text{ROH} \leftrightarrow \text{Glycerine} + \text{RCOOR3} \tag{8}$$

while R1, R2, and R3 are the long chain hydrocarbons found in the structure of FFA, R is normally a short chain alkyl alcohol. The main reaction includes a series of 3 reversible reactions in which the interaction effect between reactants and products were studied. Methanol was reported as one of the most likely potential reagents since it is relatively cheap and can be recovered at lower temperatures without creating an azeotrope which can occur with the other longer chain alcohols [3, 4, 53, 54]. In addition, it has been reported that methanol has a higher reactivity, does not interfere with the transesterification reaction and can reduce the formation of soap. Typically, the transesterification process can be divided into two reactions: catalyzed and non-catalysed transesterification. There are currently 3 types of catalyst that can be utilized for the process, namely homogeneous, heterogeneous and enzymatic catalysts [10, 11, 80-82]. In terms of the non-catalysed process, the recent introduction of supercritical transesterification has attracted much attention. However, despite the cost-benefit that this process can provide, it has yet to be applied across the industry due to the critical reaction conditions and the relatively high cost of the associated equipment. Currently, homogeneous catalyzed transesterification is the most popular method of dealing with the GTW feedstocks.

2.3.2.1 Homogeneous-catalyzed Transesterification

Homogeneous catalysts are popular for the transesterification of GTW oils following the pre-treatment of FFA. NaOH and KOH are two conventional bases that are widely used for this purpose. There are many factors which determine the reaction rate and the yield of GTW derived biodiesel, however, the type of catalyst and its ratio to the weight of FOG are among the most important. The amount of base catalyst required depends on the glyceride levels, reaction temperature, and reaction time. Varying the amount of catalyst 1-9% resulted in the yield of product to be as high as 96.7 % [16, 17, 24, 27, 29, 47]. Karnasuta et al. [27] studied the production of biodiesel from trap grease collected from cafeterias and restaurants in Bangkok, Thailand via the 2-stage esterification – transesterification processes. They utilized homogeneous catalysts including sulphuric acid and potassium hydroxide for the esterification and transesterification reactions respectively. The final conversion rate was 95.7% while only 1 wt% KOH was consumed by the methanolysis process. These results indicate that the homogeneous catalyst is cheap, exhibits very high catalytic activity, offers a shorter reaction time, and allows the optimal condition for the synthesis process to be determined more easily [80]. Interestingly, the wastewater stream from the process of transesterification with a base catalyst can be used to neutralize the acidic water produced by the previous esterification process [53, 54].

Nevertheless, the use of a homogeneous catalyst also has some drawbacks which need to be taken into account. The sensitivity to FFA levels and the amount of water present are the main parameters to be considered when selecting this technique for GTW-derived biodiesel production since the system requires a costly pre-treatment beforehand. Due to the formation of soap following the reaction between FFA and the base, the process not only used a moderate consumption of catalyst but also inhibited the removal of glycerol, so the FFA levels should be strictly less than 3% and the FOG oils should be dried to reduce moisture. The possible formation of soap is described in the following reaction (9)

$$\text{Fatty acid } (R_1COOH) + NaOH \leftrightarrow \text{Soap } (R_1COONa) + \text{Water } (H_2O) \quad (9)$$

Importantly, the formation of soap as a side reaction also causes problems for the separation of glycerol, and inhibits the main reaction, thereby negatively impacting on the quality of the biodiesel product. Most of the homogeneous catalyst is non-recyclable since the recovery process is complicated and more expensive than that of the brand new catalyst [53, 54]. This leads to a high volume of wastewater which requires treatment, as well as the alkaline water causing a detrimental effect on the durability of the equipment.

2.3.2.2 Heterogeneous-catalyzed Transesterification

Like the use of solid catalysts in the esterification reaction, heterogeneous-catalyzed transesterification was also developed to overcome the stereotype of the homogeneous catalysts. Many solid catalysts under different reaction conditions have been examined, for the production of GTW-derived biodiesel. One of the advantages of the heterogeneous catalyst is the prevention of the formation of soap following the presence of a moderate amount of FFA in the feedstock. A heterogeneous base catalyst such as CaO, MgO, SrO, mixed oxide, and hydrotalcite has been reported as being more effective when used under mild conditions, as in the transesterification process [83].

Ikura et al. [84] and Park et al. [24] investigated the effect of a commercial solid catalyst, amberlyst, on the first stage of the production of GTW-derived biodiesel. They reported that amberlyst, a macro-reticular, polystyrene-based ion exchange resin functioned with a strongly acidic sulfonic group, converted FFA to their alkyl esters. The achieved ester yields were 94.1 % and 63.4% respectively. In another study, Kim et al. [85] investigated the esterification reaction of brown grease oil with various solid catalysts. They found that the order of the catalytic activity was $H_2SO_4 > NiSO_4/SiO_2 >$ zeolite $> SiO_2$. $NiSO_4/SiO_2$, in particular, can be utilized at room temperature to save energy and possibly to reduce the total production cost. Interestingly, Ngo et al. [86] developed a combination enzyme – metal oxide catalyst system that can convert up to 99% of FFA to methyl esters. The reaction was conducted at low temperature (30^0C) using 3 wt% of *thermomyces lanuginosus lipase (TLL)* and *candida antarctica lipase B* immobilized on iron oxide magnetic nanoparticles as a catalyst. Moreover, a solid catalyst also offers a wide range of advantages such as catalyst regeneration and reusability, simple downstream separation and purification, and production of a lower quantity of hazardous wastewater [75-77, 87, 88].

However, the major drawbacks of using heterogeneous catalysts cannot be ignored, including their slow reaction rate in comparison with a homogeneous catalyst; the low FFA level required for the feedstock; sensitivity to moisture; the possible formation of soap; significant high volume of wastewater following the washing of glycerol; and its complexity and expense for synthesis.

Recently, many studies have introduced the use of biomass-derived heterogeneous catalysts such as waste shell, biomass ashes, and activated carbon to reduce the cost of purchasing solid catalysts [77, 89, 90]. Although the application of those green catalysts has been successful at a certain level when dealing with the virgin and the yellow grease feedstocks, the effect of biomass-derived catalysts on the low-quality feedstocks, needs to be investigated further.

2.3.2.3 Enzyme-catalyzed Transesterification

Enzymatic transesterification has recently been investigated as it is more environmentally friendly when compared with homo- and heterogeneous catalysts. The benefits of enzymes were reported in terms of their reusability, stability under mild conditions, and the recovery of the products, etc. *Candida antarctica fraction B* lipase and *Rhizomucor miehei* lipase are among the most highly used enzymatic catalysts. Several studies have confirmed that these lipases are very effective for dealing with the high FFA feedstocks while eliminating the formation of soap during the transesterification process. Furthermore, enzyme catalyzed transesterification produces less hazardous waste than other chemical catalysts.

However, the enzymatic technique has several problems such as slow reaction rates, potential contamination of the product with residual enzymatic activity, as well as the cost [10]. Additionally, the complex mechanism of the enzymatic reaction cannot always guarantee a stable route for synthesis for biodiesel producers. Recently, TransBiodiesel, an Israeli company, has developed and commercialized two different enzymatic catalysts (TransZyme and EsterZyme), for the conversion of low-grade feedstocks to biodiesel [53]. These catalysts can be utilized at relatively low temperatures (20^0C to 30^0C), while the range of FFA levels can range from 3-100%. Nonetheless, the techniques are still being treated as confidential and are currently applicable for commercial purposes only.

2.3.2.4 Other Techniques

In recent years, many technical modifications have been tested to achieve a more efficient route for biodiesel synthesis from low-quality feedstocks. Such research has led to the development of non-catalytic processes that can eliminate the generation of wastewater, reduce the production costs, and provide a higher quality product. Huynh et al. [91] have introduced an *in situ* methanolysis under supercritical conditions in which activated sludge can be converted to fatty acid methyl esters without the need of acid or base catalysts. They reported that a 90% FFA conversion can be obtained after 24 hours of reactions at 175ºC and 3.5 MPa. Despite the authors being maintaining that this can result in a reduction in production costs, the maintenance of high temperatures and sustained (24 hr) high-pressure reaction times, can lead to high energy costs [92-95]. In addition, the application of the critical condition to industrial production is predictably more difficult in terms of equipment design and safety concerns.

At the same time, other techniques such as microwave-assisted heating, direct conversion, etc., have also been reported. Fernandes et al. [45] investigated the effect of microwave irradiation on the esterification of trap grease. They reported that the esterification reaction rate is relatively faster, using microwave heating. A very high conversion (up to 96%) was reported at the optimal conditions which were: a trap grease to methanol molar ratio of 1:6, 1.0% H_2SO_4, 393 K, and 10 minutes. In a very new report, Lee et al. [96] have introduced a direct conversion method to produce biodiesel without the pre-treatment of the GTW. The results show that an 86% yield of fatty acids methyl esters (FAME) can be obtained after only 10s of reaction time. The temperature range was varied from 240ºC to 390ºC and silica was employed as the catalyst. This technique offers two benefits that can overcome the limitations of the previous studies, these being:

(1) elimination the costly pre-treatment step, and (2) reduction in the total required energy consumption to maintain a high reaction temperature over a long period of time.

Table 2.4 summarises the techniques which have been applied to the production of biodiesel from GTW. The maximum biodiesel yield and FFA conversion reported are 99% and 96%, respectively.

Table 2.4 Techniques applied for the production of biodiesel from recycled trap grease

Feedstock source	FFA %	Method	Catalyst	Alcohol	Optimal parameters	yield (%)	FFA Conversion (%)	Ref.
Cafeterias and restaurants in Bangkok, Thailand	26.2	2 stage transesterification	(1) H_2SO_4 (2) KOH	Methanol	0.43 v/v methanol-to-oil ratio, 2.5% v/v H_2SO_4, 4 hr of reaction time, 60ºC 0.26 v/v methanol-to-oil ratio, 1% w/v KOH, 1 hr of reaction time, 60ºC		95.4	[27]
Guangzhou, China	50	Esterification	H_2SO_4	Methanol	35 methanol-to-oil molar ratio, 11.3 wt% H_2SO_4 based on trap grease, 4.59 hr reaction time, 95ºC		89.6	[26]
Guangzhou, China	51.45	2 stage	H_2SO_4 or Amberlyst 15 KOH	Methanol	8.37 methanol to oil molar ratio, 21.0 wt% catalyst/oil, 95ºC. 6:1 methanol to oil molar ratio, 1.2 wt% KOH/oil, 80ºC		94.1	[24]
San Francisco and Atlanta, USA	93.7	Esterification	Diphenyl ammonium triflate salt	Methanol	All reactions were performed at 125ºC for 1 hr, catalyst and methanol to feedstock ratio are varied		95%	
PTT gas service station, Bangkok, Thailand	31.1	Esterification	H_2SO_4	Methanol	Methanol-to-FFA ratio of 5:1, 5 wt% H_2SO_4, and a reaction temperature at 60ºC with a reaction time of 1 hr.		83.5	[23]
Cukurova University, Turkey	65.15	Esterification	H_2SO_4	Methanol	Methanol/oil ratio 9:1, 9 wt% H_2SO_4 catalyst, reaction time 2 hr, 60ºC	93.9		[22]

Singapore’s sewage	21.7	Esterification	*Candida antarctica* lipase B (CALB) (Novozyme 435) and *Thermomyces lanuginosus* lipase (TLL) (Lipozyme TLIM)	Methanol	Methanol/oil ratio is 3:1, 4 wt% enzyme catalyst (CALB:TLL = 1:1), 48 hr reaction time, 30ºC	95	87	[97]
Alpha Synovate Pte Ltd., Singapore.	17	Esterification	*Thermomyces lanuginosus* Lipase (TLL) and *Candida antarctica* Lipase B immobilized on iron oxide magnetic nanoparticle (80 nm)	Methanol	Methanol/oil molar ratio: 7.6:1, 3.3 wt% catalyst, 12 hr reaction time, 30ºC	99		[86]
Brazil	N/A	Microwave-assisted esterification	H_2SO_4	Methanol and ethanol	Methanol/oil molar ratio 1:6, 1.0% H_2SO_4, 393 K, 10 mins		96	[45]
Singapore	21	Biotransformation	*Thermomyces lanuginosus* lipase (TLL)	Methanol	Methanol/oil molar ratio 4:1, 31.3 wt% catalyst, 24 hr, 30ºC	99		[46]
Malaysia	9.8					97		
Brazil	N/A	Esterification	H_2SO_4	Ethanol	Ethanol/oil molar ratio 9:1, 1.5 wt% catalyst, 4 hr reaction time, 70ºC		95.3	[15]

2.3.3 Fuel Properties of GTW-derived Biodiesel

The quality of GTW-derived biodiesel is one of the main concerns that prevents its marketability. **Table 2.5** reviews some of the fuel properties of biodiesel derived from GTW as the feedstock. It can be seen that GTW-derived biodiesel often has a higher viscosity in comparison with mineral diesel, which may cause difficulties in the distribution of liquid fuels in the diesel engine [98]. In practice, biodiesel is blended with mineral diesel in order to reduce its viscosity and adapt it for the conventional biodiesel engines [98-100]. Significantly, the high level of sulphur found in the composition of GTW-derived biodiesel is one parameter hindering its marketability. GTW-derived biodiesel has been reported to exhibit a sulphur content ranging between 160-390 ppm, while the ASTM D6751 standard requires lower than 15 ppm [49, 50]. In Australia, the amount of sulphur permitted in biodiesel is even lower: 10 ppm maximum. Therefore, current research is focusing on techniques that can remove sulphur from the feedstock as well as from the product. In this regard, Ma et al. [50] reported a low sulphur method for the production of biodiesel from scum waste via solvent extraction, acid washing, reflux distillation and adsorptive desulphurization. The results show that approximately 70% of the biodiesel product was obtained with less than 15 ppm sulphur content. In a recent study, Hums [19] has introduced a stripping method in which methanol (as a vapor) was bubbled into the reaction mix at elevated temperature to promote sulphur stripping throughout the biodiesel reaction. The results obtained showed that acid washing and acid esterification can remove 75 to 96% of the sulphur content in the GTW oil. This surpasses the studies conducted by Gardner et al. [101] and Chakrabarti et al. [102] in relation to reducing the final sulphur content.

Table 2.5 Fuel properties of GTW-derived biodiesel

Properties	**Units**	**ASTM D6751**	**[103]**	**[84]**	**[17]**	**[27]**	**[22]**	**[19]**
Viscosity at 40ºC	mm^2/s	1.9 – 6.0	4.2	5.02	5.96	4.84	9.88	4.4
Density at 15ºC	kg/m^3	870 - 900	875	858	878	880	896	-
Flash point	ºC	>130	138	130.2	193.7	165	96.8	153.3
Acid value	mg KOH/g	0.8 max	0.4	0.45	2.9	0.54	3.92	0.73
Cloud point	ºC	-3 to 12	5	19.1	-	7.2	-	3.1 to 3.5
Pour point,	ºC	-15 to 10	3	4	-	-	-	-
Calorific value	Cal/g	-	9036	10105	-	9188	9294	-
Ash content	% mass	0.05	-	-	-	-	-	-
Sulphur content	ppm	15	-	136	-	-	538	25.6
Moisture content	%		-	-	0.03	0.01	-	0.001

With regard to other fuel quality parameters, GTW-derived biodiesel was reported to have higher cloud and pour points compared with mineral diesel. This is a major concern among biodiesel users because biodiesel tends to gel (become frozen) at higher temperatures compared with mineral diesel [104]. The pour point of GTW-derived biodiesel is around 4ºC, which is much higher than that of fossil biodiesel (-40ºC). Fortunately, this problem can be overcome by applying a fractional distillation step to the product to remove the high fraction of saturates, or adding other components to lower the pour and cloud points [84, 104]. As of now, research on high-quality improvements for GTW-derived biodiesel still attracts much interest worldwide.

2.4 Economic Feasibility

While the environmental benefits of GTW-derived biodiesel are promising, the economic aspects appear to be uncertain. Some studies have been conducted to analyze the economic feasibility of biodiesel production from wastewater treatment plants [1, 8, 105, 106]. There are two major which impact on the economic difference between GTW-derived biodiesel and biodiesel produced from other, conventional feedstocks, these being: the cost of the feedstock itself, and the pre-treatment expenses.

In terms of the cost of the feedstock, some studies assumed that GTW can be collected free of charge. This appears to be an important issue since the feedstock cost often accounts for 60 – 80% of the total production cost [7, 8]. Pokoo-Aikins et al. [107] constructed a simulation model to estimate the production cost of biodiesel derived from the dry sludge via a two-step process, these being: solvent extraction, and transesterification. The results show that the cost of biodiesel production was approximately $838 per ton, providing that dry sludge is collected free of charge. The calculated cost was far cheaper in comparison with biodiesel produced from other sources [6, 108, 109]. Hums [19] found that the State of Delaware (USA) charges $0.016 per kg to collect grease trap waste. This contributed to the relatively lower production cost of biodiesel, although they also reported that the economic feasibility was strongly depended on GTW consumption and the lipid content of the GTW oils. The fact remains that only environmental services which cooperate with the wastewater treatment plants have full access to this free, and abundant resource [110, 111]. Thus, there will be a feedstock cost to the primary producers who purchase GTW from those services [1]. Olkiewicz et al. [1] evaluated the economic potential of biodiesel produced from municipal wastewater sludge via experimental data and computational scale-up in terms of the feedstock cost.

The authors recommended the selling price of their biodiesel should be $1,232 per ton, which is still lower than the cost of mineral diesel and biodiesel produced from microalgae.

In terms of the pre-treatment cost, Chesebrough [106] suggested that the addition of a pre-treatment step does not have a significant economic effect on the utilization of a cheaper feedstock. This appears to be a controversial finding, since the other studies revealed that the pre-treatment of low-quality feedstocks is the most expensive step, although the production price of GTW-derived biodiesel may be lower compared with other feedstocks [1, 105].

Finally, future technical developments can also have a significant impact on the economic feasibility of GTW-derived biodiesel. Dufreche et al. [112] estimated the cost of biodiesel would be $3.1/gallon, assuming that a 7.0% overall yield of esters from dry sewage sludge on a weight basis was obtained. They advised that the cost per gallon could drop significantly if techniques are developed to improve the efficiency of the transesterification reaction. In a recent study, Demirbas [113] also reported that it will cost $3.11/gallon to produce biodiesel from municipal sewage sludge, which is higher than the current price of mineral diesel ($3/gallon). The authors emphasized that there are many challenges in terms of sludge collection, lipids separation, process operations, etc., which need to be addressed in order to produce a cheaper biodiesel from wastewater residue.

2.5 Summary Remarks

GTW appears to have the potential to become a vital feedstock for biodiesel production in terms of its environmental benefits and economic feasibility. However, the extremely low quality of this waste resource leads to technical challenges for biodiesel producers particularly with regard to the pre-treatment of the feedstock, and the quality of the GTW-derived biodiesel produced. There are a number of factors that need to be considered carefully when dealing with the wastewater feedstocks. These are summarized below.

Firstly, the pre-treatment of GTW, as well as the other wastewater feedstocks, is relatively expensive and complicated. The extraction of lipid from the GTW via physical (heating, centrifuging) or chemical treatments (solvents), is an energy and time-consuming process. Prior research strongly indicates that this process accounts for the highest expense in utilizing GTW as a feedstock for biodiesel production.

Secondly, the production techniques for GTW-derived biodiesel are complex, due to the high level of FFAs found in the feedstock. Normally, a two-stage process is preferred, starting with the conversion of FFA to its alkyl esters or glycerides via an esterification or a glycerolysis process. This is then followed up with the transesterification of the remaining glycerides to FFA esters employing homogeneous catalysts, heterogeneous catalysts, or enzymatic catalysts. Although attempts have been made to produce biodiesel without using a catalyst, throughout the literature review, it is evident that that choosing the right catalyst is the key to the successful production of biodiesel from GTW.

Thirdly, the quality of the GTW-derived biodiesel is also a concern that needs to be addressed. GTW-derived biodiesel often has a higher sulphur level, viscosity, and cold/pour point in comparison with mineral diesel. This prevents its marketability, since a commercial fuel must satisfy the market standards (ASTM D6751 or EN 14214). As a result, further purification of the crude GTW-derived biodiesel is required, adding an additional fee to the total production cost.

Finally, the economic feasibility of biodiesel produced from GTW and other wastewater feedstocks is influenced by various factors in which the feedstock cost, pre-treatment expense, and production techniques are among the most important parameters. To make GTW-derived biodiesel a competitive fuel, the trade-off across these factors needs further researched.

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References

[1] Olkiewicz M, Torres CM, Jiménez L, Font J, Bengoa C. Scale-up and economic analysis of biodiesel production from municipal primary sewage sludge. Bioresource technology. 2016;214:122-31.

[2] Bi C-h, Min M, Nie Y, Xie Q-l, Lu Q, Deng X-y, et al. Process development for scum to biodiesel conversion. Bioresource technology. 2015;185:185-93.

[3] Erin V. Report outlines global biodiesel production/Erin Voegele. Biodiesel Magazine-2011-August. 2011;31.

[4] Sanford SD, White JM, Shah PS, Wee C, Valverde MA, Meier GR. Feedstock and biodiesel characteristics report. Renewable Energy Group. 2009;416:1-136.

[5] BP. BP statistical review of world energy. London, UK2017.

[6] Canada BB. Biofuel Costs, Technologies and Economics in APEC Economies. In: Report AEWGT, editor. Canada 2010.

[7] Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production costs. Bioresource Technology. 2006;97:671-8.

[8] Haas MJ. Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. Fuel Processing Technology. 2005;86:1087-96.

[9] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology. 2003;90:229.

[10] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: a review. Renewable and Sustainable Energy Reviews. 2011;15:1067-72.

[11] Ragauskas AME, Pu Y, Ragauskas AJ. Biodiesel from grease interceptor to gas tank. Energy Science & Engineering. 2013;1:42-52.

[12] Yang G, Zhang G, Wang H. Current state of sludge production, management, treatment and disposal in China. Water research. 2015;78:60-73.

[13] Latimer G. Hazardous Waste in Australia 2017. 2017.

[14] Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Transactions of the ASAE. 2001;44:1429.

[15] Oliveira J, Antunes P, Mordente T, Santos A, Pinotti L, Cassini S. Biodiesel production from scum of grease traps and sludge from septic tanks. Clean Technologies and Environmental Policy. 2017;19:1231-7.

[16] Demirbas A, Bamufleh HS, Edris G, Al-Sasi BO. Biodiesel production from lipids of municipal sewage sludge by direct methanol transesterification. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2017;39:800-5.

[17] de Oliveira JP, Antunes PWP, Santos AR, Mordente TZ, Pinotti LM, Cassini STA. Transesterification of Sanitation Waste for Biodiesel Production. Waste and Biomass Valorization. 2017;8:463-71.

[18] Urrutia C, Sangaletti-Gerhard N, Cea M, Suazo A, Aliberti A, Navia R. Two step esterification–transesterification process of wet greasy sewage sludge for biodiesel production. Bioresource technology. 2016;200:1044-9.

[19] Hums ME. Environmental Impacts of Biodiesel Produced from Wastewater Greases: Drexel University; 2016.

[20] Nitayapat N, Chitprasert P. Characterisation of FOGs in grease trap waste from the processing of chickens in Thailand. Waste management. 2014;34:1012-7.

[21] Pastore C, Lopez A, Lotito V, Mascolo G. Biodiesel from dewatered wastewater sludge: A two-step process for a more advantageous production. Chemosphere. 2013;92:667-73.

[22] Reşitoğlu İA, Keskin A, Gürü M. The Optimization of the Esterification Reaction in Biodiesel Production from Trap Grease. Energy Sources Part A: Recovery, Utilization & Environmental Effects. 2012;34:1238-48.

[23] Hasuntree P, Toomthong V, Yoschoch S, Thawornchaisit U. The potential of restaurant trap grease as biodiesel feedstock. Songklanakarin Journal of Science & Technology. 2011;33:525-30.

[24] Park J-Y, Lee J-S, Wang Z-M, Kim D-K. Production and characterization of biodiesel from trap grease. Korean Journal of Chemical Engineering. 2010;27:1791-5.

[25] Chan H. Removal and recycling of pollutants from Hong Kong restaurant wastewaters. Bioresource Technology. 2010;101:6859-67.

[26] Wang Z-M, Lee J-S, Park J-Y, Wu C-Z, Yuan Z-H. Optimization of biodiesel production from trap grease via acid catalysis. Korean Journal of Chemical Engineering. 2008;25:670-4.

[27] Karnasuta S, Punsuvon V, Chiemchaisri C, Chunkao K. Optimization of biodiesel production from trap grease via two-step catalyzed process. Asian J Energy Environ. 2007;8:145-68.

[28] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Processing Technology. 2007;88:429-36.

[29] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology. 2007;98:183-90.

[30] Hughes M. GC-MS Characterization of Sulfur Species in Low Temperature Distillates of Biodiesel from Waste Grease: Delaware State University; 2017.

[31] Bligh EG, Dyer WJ. A rapid method of total lipid extraction and purification. Canadian journal of biochemistry and physiology. 1959;37:911-7.

[32] Ngo HL, Xie Z, Kasprzyk S, Haas M, Lin W. Catalytic synthesis of fatty acid methyl esters from extremely low quality greases. Journal of the American Oil Chemists' Society. 2011;88:1417-24.

[33] Kobayashi T, Kuramochi H, Maeda K, Tsuji T, Xu K. Dual-fuel production from restaurant grease trap waste: bio-fuel oil extraction and anaerobic methane production from the post-extracted residue. Bioresource technology. 2014;169:134-42.

[34] Ward PML. Brown and black grease suitability for incorporation into feeds and suitability for biofuels. Journal of food protection. 2012;75:731-7.

[35] Williams JB, Clarkson C, Mant C, Drinkwater A, May E. Fat, oil and grease deposits in sewers: Characterisation of deposits and formation mechanisms. Water Research. 2012;46:6319-28.

[36] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: A review. Renewable & Sustainable Energy Reviews. 2011;15:1067-72.

[37] Tu Q, Wang J, Lu M, Brougham A, Lu T. A solvent-free approach to extract the lipid fraction from sewer grease for biodiesel production. Waste Management. 2016;54:126-30.

[38] Anderson E, Addy M, Xie Q, Ma H, Liu Y, Cheng Y, et al. Glycerin esterification of scum derived free fatty acids for biodiesel production. Bioresource technology. 2016;200:153-60.

[39] Kombe GG, Rajabu HM, Temu AK, Lee KT, Mrema GD. Low temperature glycerolysis as a high FFA pre-treatment method for biodiesel production. 2013.

[40] Olkiewicz M, Caporgno MP, Fortuny A, Stüber F, Fabregat A, Font J, et al. Direct liquid–liquid extraction of lipid from municipal sewage sludge for biodiesel production. Fuel processing technology. 2014;128:331-8.

[41] Melero J, Sánchez-Vázquez R, Vasiliadou I, Castillejo FM, Bautista L, Iglesias J, et al. Municipal sewage sludge to biodiesel by simultaneous extraction and conversion of lipids. Energy Conversion and Management. 2015;103:111-8.

[42] Siddiquee MN, Rohani S. Experimental analysis of lipid extraction and biodiesel production from wastewater sludge. Fuel Processing Technology. 2011;92:2241-51.

[43] Zhu F, Zhao L, Jiang H, Zhang Z, Xiong Y, Qi J, et al. Comparison of the lipid content and biodiesel production from municipal sludge using three extraction methods. Energy & Fuels. 2014;28:5277-83.

[44] Wallace T, Gibbons D, O'Dwyer M, Curran TP. International evolution of fat, oil and grease (FOG) waste management–A review. Journal of Environmental Management. 2017;187:424-35.

[45] Fernandes PS, Borges LE, de Carvalho CE, de Souza RO. Microwave assisted biodiesel production from trap grease. Journal of the Brazilian Chemical Society. 2014;25:1730-6.

[46] Tian K, Li Z. High-yielding, one-pot, and green production of biodiesel from waste grease using wet cells of a recombinant Escherichia coli strain as catalyst. Biochemical Engineering Journal. 2016;115:30-7.

[47] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Applied Energy. 2010;87:3155-61.

[48] Lu P, Yuan Z, Li L, Wang Z, Luo W. Biodiesel from different oil using fixed-bed and plug-flow reactors. Renewable Energy: An International Journal. 2010;35:283-7.

[49] Cairncross RA, Hums ME, Stacy CJ. Acidic methanol stripping process that reduces sulfur content of biodiesel from waste greases. Google Patents; 2016.

[50] Ma H, Addy MM, Anderson E, Liu W, Liu Y, Nie Y, et al. A novel process for low-sulfur biodiesel production from scum waste. Bioresource technology. 2016;214:826-35.

[51] Enweremadu CC, Mbarawa MM. Technical aspects of production and analysis of biodiesel from used cooking oil—A review. Renewable & Sustainable Energy Reviews. 2009;13:2205-24.

[52] Stacy CJ, Melick CA, Cairncross RA. Esterification of free fatty acids to fatty acid alkyl esters in a bubble column reactor for use as biodiesel. Fuel Processing Technology. 2014;124:70-7.

[53] Tafesh A, Basheer S. Pretreatment methods in biodiesel production processes. Pretreatment Techniques for Biofuels and Biorefineries: Springer; 2013. p. 417-34.

[54] Fang Z. Pretreatment techniques for biofuels and biorefineries: Springer; 2013.

[55] Alsalme A, Kozhevnikova EF, Kozhevnikov IV. Heteropoly acids as catalysts for liquid-phase esterification and transesterification. Applied Catalysis A: General. 2008;349:170-6.

[56] Oliveira JFG, Lucena IL, Saboya RMA, Rodrigues ML, Torres AEB, Fernandes FAN, et al. Biodiesel production from waste coconut oil by esterification with ethanol: The effect of water removal by adsorption. Renewable Energy: An International Journal. 2010;35:2581-4.

[57] Jincheng D, Zheng X, Jie L. Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production. Energies (19961073). 2012;5:2683-91.

[58] Boffito DC, Pirola C, Galli F, Di Michele A, Bianchi CL. Free fatty acids esterification of waste cooking oil and its mixtures with rapeseed oil and diesel. Fuel. 2013;108:612-9.

[59] Liu R, Li C, Zhang H, Xiao Z, Zhang A, Chen J. Pilot-scale study of esterification of waste oil for biodiesel production. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2017;39:29-35.

[60] Murugesan A, Umarani C, Chinnusamy TR, Krishnan M, Subramanian R, Neduzchezhain N. Production and analysis of bio-diesel from non-edible oils—A review. Renewable and Sustainable Energy Reviews. 2009;13:825-34.

[61] Voegele E. Biomass Magazine. 2017.

[62] Tu Q, Lu M, Knothe G. Glycerolysis with crude glycerin as an alternative pretreatment for biodiesel production from grease trap waste: Parametric study and energy analysis. Journal of Cleaner Production. 2017.

[63] Islam A, Masoumi HRF, Teo SH, Abdollahi Y, Janaun J, Taufiq-Yap YH. Glycerolysis of palm fatty acid distillate for biodiesel feedstock under different reactor conditions. Fuel. 2016;174:133-9.

[64] Supardan MD, Meldasari Y, Annisa Y. Glycerolysis for Lowering Free FattyAcid of Waste Cooking Oil. Proceedings of The Annual International Conference, Syiah Kuala University-Life Sciences & Engineering Chapter2015.

[65] Costa E, Almeida M, Dias J, Matos A. Glycerolysis of two high free fatty acid waste materials for biodiesel production. WASTES 2015–Solutions, Treatments and Opportunities: Selected papers from the 3rd Edition of the International Conference on Wastes: Solutions, Treatments and Opportunities, Viana Do Castelo, Portugal, 14-16 September 2015: CRC Press; 2015. p. 55.

[66] Echeverri DA, Cardeño F, Rios LA. Glycerolysis of crude methyl esters with crude glycerol from biodiesel production. Journal of the American Oil Chemists' Society. 2013;90:1041-7.

[67] Felizardo P, Machado J, Vergueiro D, Correia MJN, Gomes JP, Bordado JM. Study on the glycerolysis reaction of high free fatty acid oils for use as biodiesel feedstock. Fuel Processing Technology. 2011;92:1225-9.

[68] Nguyen N, Demirel Y. Economic analysis of biodiesel and glycerol carbonate production plant by glycerolysis. Journal of Sustainable Bioenergy Systems. 2013;3:209.

[69] Sonntag NO. Glycerolysis of fats and methyl esters—status, review and critique. Journal of the American Oil Chemists Society. 1982;59:795A-802A.

[70] Vitiello R, Li C, Russo V, Tesser R, Turco R, Di Serio M. Catalysis for esterification reactions: a key step in the biodiesel production from waste oils. Rendiconti Lincei. 2017;28:117-23.

[71] Kaddour M. Esterification of Free Fatty Acid by Selected Homogeneous and Solid Acid Catalysts for Biodiesel Production. 2016.

[72] Diaz-Felix W, Riley MR, Zimmt W, Kazz M. Pretreatment of yellow grease for efficient production of fatty acid methyl esters. Biomass & Bioenergy. 2009;33:558-63.

[73] Talebian-Kiakalaieh A, Amin NAS, Zarei A, Noshadi I. Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: Optimization and kinetic model. Applied Energy. 2013;102:283-92.

[74] Noshadi I, Amin NAS, Parnas RS. Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: Optimization using response surface methodology (RSM). Fuel. 2012;94:156-64.

[75] Dias JM, Alvim-Ferraz MCM, Almeida MF, Méndez Díaz JD, Polo MS, Utrilla JR. Selection of heterogeneous catalysts for biodiesel production from animal fat. Fuel. 2012;94:418-25.

[76] Morales G, Bautista LF, Melero JA, Iglesias J, Sánchez-Vázquez R. Low-grade oils and fats: Effect of several impurities on biodiesel production over sulfonic acid heterogeneous catalysts. Bioresource Technology. 2011;102:9571-8.

[77] Mansir N, Taufiq-Yap YH, Rashid U, Lokman IM. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. Energy Conversion and Management. 2017;141:171-82.

[78] Park J-Y, Kim D-K, Lee J-S. Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. Bioresource technology. 2010;101:S62-S5.

[79] Kim M, DiMaggio C, Yan S, Wang H, Salley SO, Ng KS. Performance of heterogeneous ZrO 2 supported metaloxide catalysts for brown grease esterification and sulfur removal. Bioresource technology. 2011;102:2380-6.

[80] Abdullah SHYS, Hanapi NHM, Azid A, Umar R, Juahir H, Khatoon H, et al. A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renewable and Sustainable Energy Reviews. 2017;70:1040-51.

[81] Pourzolfaghar H, Abnisa F, Daud WMAW, Aroua MK. A review of the enzymatic hydroesterification process for biodiesel production. Renewable and Sustainable Energy Reviews. 2016;61:245-57.

[82] Mythili R, Venkatachalam P, Subramanian P, Uma D. Production characterization and efficiency of biodiesel: a review. International journal of energy research. 2014;38:1233-59.

[83] Mardhiah HH, Ong HC, Masjuki H, Lim S, Lee H. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. Renewable and Sustainable Energy Reviews. 2017;67:1225-36.

[84] Ikura M, Kouchachvili L, Caravaggio G. Production of Biodiesel from Waste Fat and Grease. WSEAS International Conference on Renewable Energy Sources, Arcachon, France: Proceedings of the WSEAS International Conference on Renewable Energy Sources; 2007

[85] Kim HJ, Hilger H, Bae S. NiSO 4/SiO 2 catalyst for biodiesel production from free fatty acids in brown grease. Journal of Energy Engineering. 2012;139:35-40.

[86] Ngo TPN, Li A, Tiew KW, Li Z. Efficient transformation of grease to biodiesel using highly active and easily recyclable magnetic nanobiocatalyst aggregates. Bioresource Technology. 2013;145:233-9.

[87] Torres-Rodríguez DA, Romero-Ibarra IC, Ibarra IA, Pfeiffer H. Biodiesel production from soybean and Jatropha oils using cesium impregnated sodium zirconate as a heterogeneous base catalyst. Renewable Energy. 2016;93:323-31.

[88] Gurunathan B, Ravi A. Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. Bioresource Technology. 2015;190:424-8.

[89] Ngoya T, Aransiola EF, Oyekola O. Optimisation of Biodiesel Production from Waste Vegetable Oil and Eggshell Ash. South African Journal of Chemical Engineering. 2017.

[90] Niju S, Meera K, Begum S, Anantharaman N. Modification of egg shell and its application in biodiesel production. Journal of Saudi Chemical Society. 2014;18:702-6.

[91] Huynh LH, Tran Nguyen PL, Ho QP, Ju Y-H. Catalyst-free fatty acid methyl ester production from wet activated sludge under subcritical water and methanol condition. Bioresource Technology. 2012;123:112-6.

[92] Román-Figueroa C, Olivares-Carrillo P, Paneque M, Palacios-Nereo FJ, Quesada-Medina J. High-yield production of biodiesel by non-catalytic supercritical methanol transesterification of crude castor oil (Ricinus communis). Energy. 2016;107:165-71.

[93] Kellotoay A, Marvin WA, Schmidt LD, Daoutidis P. Process design and supply chain optimization of supercritical biodiesel synthesis from waste cooking oils. Chemical Engineering Research & Design: Transactions of the Institution of Chemical Engineers Part A. 2013;91:1456-66.

[94] Ghoreishi SM, Moein P. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. The Journal of Supercritical Fluids. 2013;76:24-31.

[95] Marulanda VF, Anitescu G, Tavlarides LL. Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. Journal of Supercritical Fluids. 2010;54:53-60.

[96] Lee J, Jung J-M, Park C, Jeon B-H, Wang C-H, Lee S-R, et al. Rapid conversion of fat, oil and grease (FOG) into biodiesel without pre-treatment of FOG. Journal of Cleaner Production. 2017;168:1211-6.

[97] Yan J, Li A, Xu Y, Ngo TPN, Phua S, Li Z. Efficient production of biodiesel from waste grease: One-pot esterification and transesterification with tandem lipases. Bioresource Technology. 2012;123:332-7.

[98] Mahmudul H, Hagos F, Mamat R, Adam AA, Ishak W, Alenezi R. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines–A review. Renewable and Sustainable Energy Reviews. 2017;72:497-509.

[99] Ramalho EFSM, Carvalho Filho JR, Albuquerque AR, de Oliveira SF, Cavalcanti EHS, Stragevitch L, et al. Low temperature behavior of poultry fat biodiesel:diesel blends. Fuel. 2012;93:601-5.

[100] Murugesan A, Umarani C, Subramanian R, Nedunchezhian N. Bio-diesel as an alternative fuel for diesel engines—A review. Renewable and Sustainable Energy Reviews. 2009;13:653-62.

[101] Gardner ER, Shang Y, Yuan Y, Gray D. Producing Biodiesel from Fat, Oil and Grease (Fog) and Other Waste Material at Wastewater Treatment Plants. Proceedings of the Water Environment Federation. 2013;2013:2024-45.

[102] Chakrabarti AR, Hake JM, Zarchi I, Gray D. Waste grease biodiesel production at a wastewater treatment plant. Proceedings of the Water Environment Federation. 2008;2008:2770-89.

[103] Yatish K, Lalithamba H, Suresh R, Arun S, Kumar PV. Optimization of scum oil biodiesel production by using response surface methodology. Process Safety and Environmental Protection. 2016;102:667-72.

[104] Isioma N, Muhammad Y, Innocent D, Linus O. Cold flow properties and kinematic viscosity of biodiesel. Universal Journal of Chemistry. 2013;1:135-41.

[105] Mu D, Addy M, Anderson E, Chen P, Ruan R. A life cycle assessment and economic analysis of the Scum-to-Biodiesel technology in wastewater treatment plants. Bioresource technology. 2016;204:89-97.

[106] Chesebrough EG. From grease traps to bio-gold? An environmental and economic cost-benefit assessment of converting trap grease into biodiesel: University of South Carolina; 2008.

[107] Pokoo-Aikins G, Heath A, Mentzer RA, Mannan MS, Rogers WJ, El-Halwagi MM. A multi-criteria approach to screening alternatives for converting sewage sludge to biodiesel. Journal of Loss Prevention in the Process Industries. 2010;23:412-20.

[108] Balat M. Potential alternatives to edible oils for biodiesel production – A review of current work. Energy Conversion and Management. 2011;52:1479-92.

[109] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: A review. Renewable and Sustainable Energy Reviews. 2010;14:217-32.

[110] He X, de los Reyes III FL, Ducoste JJ. A critical review of fat, oil and grease (FOG) in sewer collection systems: challenges and control. Critical Reviews in Environmental Science and Technology. 2017.

[111] Hajjari M, Tabatabaei M, Aghbashlo M, Ghanavati H. A review on the prospects of sustainable biodiesel production: A global scenario with an emphasis on waste-oil biodiesel utilization. Renewable and Sustainable Energy Reviews. 2017;72:445-64.

[112] Dufreche S, Hernandez R, French T, Sparks D, Zappi M, Alley E. Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel. Journal of the American Oil Chemists' Society. 2007;84:181-7.

[113] Demirbas A. Biodiesel from municipal sewage sludge (MSS): Challenges and cost analysis. Energy Sources, Part B: Economics, Planning, and Policy. 2017;12:351-7.

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Chapter 3. Extraction of Fats, Oils, and Grease from Grease Trap Waste for Biodiesel Production

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Abstract

Fats, oils, and grease (FOG), the main composition of dewatered grease trap waste (GTW), is the major cause of sewer pipe blockage which may require costly treatments required for wastewater treatment plants, councils, and households. To prevent this, grease traps are a mandatory component for sewerage systems for hospitality services such as restaurants, and food processing factories. As a result, a large amount of GTW is being collected which requires downstream treatment for the environmental service providers. This study investigated a potential and a simple solvent extraction method to extract FOG from GTW collected in Adelaide, South Australia. Hexane (HEX) and diethyl ether (DEE) was utilized as the solvents for the extraction process at ambient temperature (approximately 25ºC). Results showed that diethyl ether offered a very high extraction yield, while hexane could prevent the formation of a problematic emulsion phase occurring in the extracted FOG. A yield of approximately 97% of lipid was obtained under the optimum extracting conditions, these being; 1:1 v/w DEE to GTW, 300 rpm stirring speed, and a 5 hr extraction time. In addition, all solvents were recycled

and could be utilized for up to two to three times extractions, which still resulted in no less than approximately 70% FOG extraction yield. The extracted FOG was then tested as a feedstock for biodiesel production.

Keywords: *grease trap waste; FOG; solvent extraction; hexane; diethyl ether; biodiesel*

3.1 Introduction

Grease trap waste (GTW) has been recently considered as a potential and cost-effective feedstock for biodiesel production since it can be collected virtually free of charge from wastewater-sewerage systems associated with the food processing sector [1-5]. While biodiesel producers have had to pay a considerable sum for traditional “high-value” feedstocks such as tallow, canola and other vegetable oils, GTW collectors, in many instances, are paid to remove and to treat the excess flow of waste grease. According to Haas and Foglia [6], the feedstock is responsible for up to 80% of the total operating cost of biodiesel production. This is the main reason that prevents the market growth of biodiesel in comparison to mineral-based fuels, particularly when “high-value” feedstocks. Therefore, finding a cost-effective feedstock is an imperative for the introduction of a competitive biodiesel production in the marketplace.

In the United States, an estimated 1.8 billion kg/year of lipids could be recovered from GTW, which could potentially produce about 1.3 billion kg of biodiesel/year [7]. In Adelaide, South Australia, Peats Soil and Garden Supplies Pty. Ltd., one of the major environmental service providers, collect approximately 10 million liters of GTW annually. According to this company, this represents around 40% of the total GTW generated yearly in South Australia, resulting in an estimated total GTW generation of 25 million liters per year. After water is removed, this corresponds to annual ‘brown grease’ production of around 2.5kg per person per year [8]. This represents a considerable potential feedstock for biodiesel production. **Figure 3.1** shows the partially dewatered GTW obtained from this environmental service provider.

Figure 3.1 Dewatered grease trap waste

Recently, considerable efforts have been focused on research to utilize GTW as a feedstock for biodiesel production to reduce a feedstock cost [1, 3-5, 9, 10]. In practice, it has been reported that biodiesel has been successfully produced from GTW utilizing methanol as the alcohol, resulting in a GTW-derived biodiesel that satisfied the biodiesel quality standards, although these were not at the production scale level, but were pilot studies [11, 12]. There is currently no report concerning the commercial production of GTW-derived biodiesel. Furthermore, there are limited reported studies on the extraction of FOG which is a technically challenging step in order to produce biodiesel from GTW. Chemically, GTW is significantly more contaminated than waste-cooking oil, with much higher levels of non-oil contaminants, making producing biodiesel from these feedstocks more complex and costly [5]. Another major issue with the use of GTW as the feedstock, is the presence of high level of free fatty acids (FFA), resulting from degradation and hydrolysis during storage and collection [9, 13, 14]. Previously, lipid separation from GTW was based only on heating, and this was not an effective process to allow complete lipid extraction. Furthermore, heating promotes the hydrolysis process, resulting in changes to the GTW composition [3, 10, 15, 16]. Recently, non-solvent extraction methodologies have also been reported to extract lipids from GTW. Tu et al. [14] reported that FOG could be extracted using waste cooking oil (WCO) as a solvent. They reported a yield of 95% lipid could be obtained at the optimum conditions, which were: 4 hour extraction time, 70ºC extraction temperature, 3.2:1 w/w WCO to GTW ratio. However, due to the fact that WCO is easily contaminated by GTW, which may lead to a costly refinery process, thereby increasing energy consumption, this method has not yet been applied for practical production.

Therefore, the purpose of this study was to examine the use of the industrial solvents, hexane and diethyl ether, to extract FOG from GTW and utilize such an extract as a feedstock for the production of biodiesel. A simple extraction process, which could be scaled up to significantly higher production output was developed based on the demand of the commercial environmental service provider in Adelaide, South Australia. The benefit of this solvent extraction is that it can be conducted without heating, while a high lipid yield can be obtained. Moreover, hexane and diethyl ether can be recycled at low temperature and re-used a number of times for the extraction process. The extracted FOG was tested as a feedstock for biodiesel production using an esterification process.

3.2 Material and Methodology

3.2.1 GTW Collection and Preparation

GTW was provided by Peats Soil and Garden Supplies Pty. Ltd. It had been collected from food processing services around Adelaide and the grease was then pumped to the storage tanks awaiting further treatment. In this study, GTW samples were taken from the top layer of the storage tanks, which were rich in FOG and contained less water compared with those at the middle or at the bottom of the tanks. The GTW was pumped from the bottom of the tanks, with the first and middle layers going to landfill compost heaps, while the top layer (containing less water to fat) was used in this study. After transferring to the lab, the raw GTW was dried in an oven at 110ºC for 24 hr until the moisture of the sample dropped below 5%.

3.2.2 FOG Extraction and Analysis

3.2.2.1 Experimental Procedure

After being dried in the oven, FOG was extracted from GTW using either hexane or diethyl ether. 500g of GTW was placed in a 2 L-volume Pyrex reaction vessel which was equipped with a mechanical stirrer and a thermometer. The stirrer speed was maintained constantly at 300 rpm. The solvent was then added to the vessel with a different volume to weight ratio based on the weight of GTW. The ratio between solvent and GTW ranged from 1:1 to 2:1 v/w based on previous reports [17-19]. The extraction process was conducted at ambient temperature in order to save energy, targeting at reducing the production cost. **Figure 3.2** shows the extraction procedure undertaken for this study.

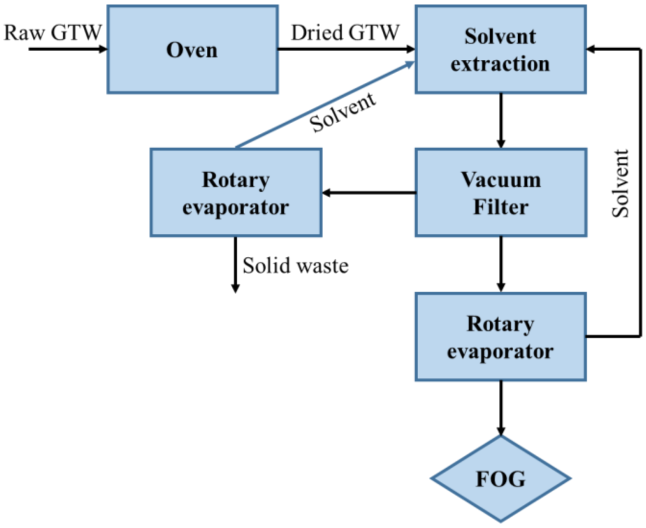

Figure 3.2 Flow-chart of the extraction process

Each experiment was conducted in triplicate and the maximum extraction time was 7 hours. Samples were taken every 1 hour for analysis, using a Pasteur pipette. The ratio between solvent and GTW (volume to weight) and the extraction time were investigated to determine the best strategy for the extraction process. The effect of the volume-to-weight ratio was determined with three levels; these being; 1:1, 1.5:1 and 2:1, while the extraction time was varied from 1 hr to 7 hr.

3.2.2.2 Analysis Methodology

Since FFAs are the main component of FOG, the extraction yield was calculated based on the amount of extracted FFA compared to its initial amount in the raw GTW. The extraction yield was calculated by equation (1) [14].

$$\text{Extraction yield} = FFA_i/FFA_o \times 100\% \qquad (1)$$

where FFA_i is the amount of FFA measured at the sampling time i [g]; FFA_o is the maximum amount of FFA found in the raw, unextracted GTW sample [g].

The amount of FFA was measured based on the standard methodology AOCS Ca 5a-40 (AOCS, 2009) via titration against 0.1N KOH. The following equation was used to calculate the acid number (AN):

$$AN = (a - b) \times N \times 56.1/ w \qquad (2)$$

where a is the volume of KOH solution used for the sample titration [mL], b is the volume of KOH solution used for the blank titration [mL], N is the exact normality of KOH, and w is the amount of the FOG sample [g].

The free fatty acid level (FFA %) was calculated based on the percentage of oleic acid by dividing the obtained acid number by 1.99.

$$\text{FFA\%} = \text{AN}/1.99 \tag{3}$$

The mass of FFA was then calculated using equation (4), while FFA_o was determined by the FFA% obtained from the application of the two-step, Bligh and Dyer extraction methodology [20].

$$\text{Mass of FFA} = \frac{C_{KOH}*(V_{KOH}-V)}{V_S}*V_2*M.W_{FFA} \tag{4}$$

where C_{KOH} is the concentration of KOH used for the titration analysis, 0.1 mol/L; V_{KOH} is the amount of KOH used for the titration of 1 mL of FOG, L; V is the amount of KOH used for the titration of 1 mL of blank solvent, L; V_S is the volume of sample, 1 mL; V_2 is the final volume of the extracted FOG, mL; $M.W_{FFA}$ is the average molecular weight of FFA, 345.5 g/mol based on the composition of the extracted oil.

3.2.2.3 Solvent Recovery

After the extraction process was completed, all solvents were recycled using a rotary evaporator. The solvent in the extracted phase was first removed and then followed by a solvent recovery applied to the solid phase. The amount of recycled solvent was the total obtained from both recycled processes. Based on the solvent boiling points, the recovery temperature was set at 45°C and 75°C for diethyl ether and hexane, respectively. Those solvents were then reused for the extraction of FOG and the recycled effect was determined based on the yield of the extracted FOG.

3.2.2.4 Free Fatty Acid Profiles

Free fatty acids profiles of the extracted FOG were determined using a Perkin-Elmer Clarus 500 GC-FID instrument following a self-developed methodology that has been certified and validated by the analytical service of The University of Adelaide. To study the free fatty acid profiles, all FOG samples were converted into methyl ester (using boron trifluoride in methanol 20% v/v) and diluted as appropriate with hexane before analyzing using GC-FID. The 37 Component FAME Mix standard was purchased from Supelco, while methyl nonadecanoate (C19 methyl ester) produced by Tokyo Industries Pty. Ltd. was utilized as an internal standard.

3.2.2.5 Feedstock Testing for Biodiesel Production

The extracted FOG was converted to free fatty acid ethyl esters (FAEE) via the esterification reaction using ethanol as a reagent in the presence of sulphuric acid. 34.5g FOG (approximately 0.1 mol, based on the composition of the extracted oil) was added to a capped vial heated and stirred by a magnetic hot plate. The magnetic stirrer was set at 300 rpm, while the FOG to ethanol molar ratio was 1:3, 3 wt% H_2SO_4 based on FOG, 3 hr reaction time, and 65ºC reaction temperature [21]. After reaching the required reaction temperature, a mixture of ethanol and sulphuric acid was added. It was noticed that the temperature of the mixture increased by approximately 10 centigrade degrees when sulphuric acid was added. Due to this rise in temperature, the initial reaction temperature was maintained a 10 centigrade degree below the final required temperature. The heating and stirring were stopped after the reaction reached the required reaction time. The temperature of the reactor was then quickly reduced by submerging the reaction vessel in cold water. The mixture was allowed to settle for 1 hr, resulting in the separation of the two phases. While the excess ethanol in the top phase was removed using a separating funnel, the bottom phase containing ethyl esters (biodiesel) and unreacted oil was collected. The biodiesel phase was washed three times with water at 50ºC and was finally heated to 110ºC to remove the remaining water before the weight of the product was measured. The FAEE conversion was then determined by gas chromatography using a flame ionization detector (GC-FID).

3.3 Results and Discussion

3.3.1 The Composition of GTW

Three samples were analyzed for moisture content, glycerides, FFA level, and solid residuals. The results are shown in **Table 3.1**. While the percentage of glycerides is similar to those reported in the previous studies [13, 14, 22], the GTW used in this study had a relatively lower moisture content and a higher FFA level. This higher FFA level could be due to the fact that the GTW had already been concentrated and water was partially removed. Furthermore, the composition of GTW has been reported to be vary depending on the location, the season, and the manner in which it was collected [23-25]. This is a technical challenge for biodiesel production from trap grease since FFAs easily induce saponification, particularly, when a transesterification reaction using base catalyst is performed.

Table 3.1 Properties of GTW

Sample	Moisture (%)	Glycerides (%)	FFA (%)	Residual (%)
#1	43.0	15.4	37.8	3.8
#2	42.1	16.2	34.8	6.9
#3	41.8	12.5	36	9.7
Average	42.3	14.7	36.2	6.8

3.3.2 Extraction of FOG from GTW

3.3.2.1 The Effect of Solvent to GTW Ratio

The volume-to-weight ratio of solvent to GTW is an important factor to determine the efficiency of the extraction process. The more solvent used, the greater are the potential losses, particularly, the additional energy requirement for solvent recovery.

Figure 3.3 shows the lipid yield obtained using various solvent to GTW ratios with both hexane (HEX) and diethyl (DEE) ether during 6 hr extraction time.

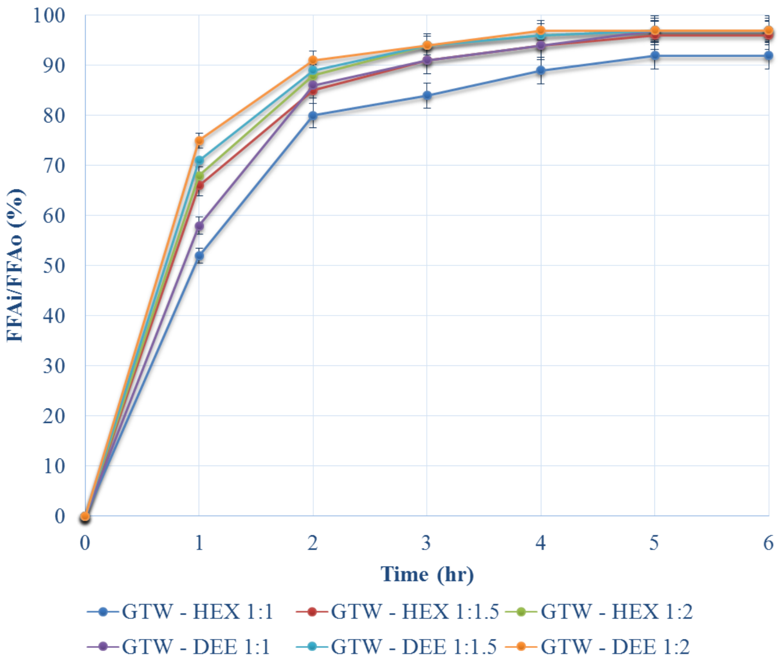

Figure 3.3 The effect of solvent to GTW ratio on the extraction yield

A maximum of approximately 97% of the theoretical extraction yield could be obtained after 5 hr utilizing diethyl ether as the solvent with the DEE to GTW ratio being 1:1 (v/w). However, hexane tends to be a more effective solvent since it provided a higher lipid extraction yield at a shorter extraction time. More than 90% lipid yield could be obtained after 4 hr extraction using hexane as the solvent at the three ratio levels studied. It was also noticed that the FFA extracted yields reached their maximum values after 5 hr extraction with both HEX and DEE. After extraction for 5 hr, increasing the extraction time did not result in a higher extraction yield obtained. The achieved extraction yield surpasses the yields reported in previous studies [18, 26-29], and is in agreement with that reported by Olkiewicz et al. [30]. However, it was observed that an emulsion phase was forming in the mixture of DEE - GTW after 1 hr of settling. This can likely be explained as diethyl ether can dissolve approximately 5 to 10 wt% water at 25ºC, resulting in an amount of water present in the extraction phase [31]. By contrast, no emulsion phase was observed in the oil extracted using hexane. Therefore, to take the advantage of the yield efficiency, while eliminating the formation of an emulsion phase, a mixture of hexane and diethyl ether (1:1, v/v) was tested with the volume ratio was maintained at 1 to 1. The optimum condition obtained using DEE previously was applied to a batch extraction with this solvent mixture. The result is shown in **Figure 3.4**.

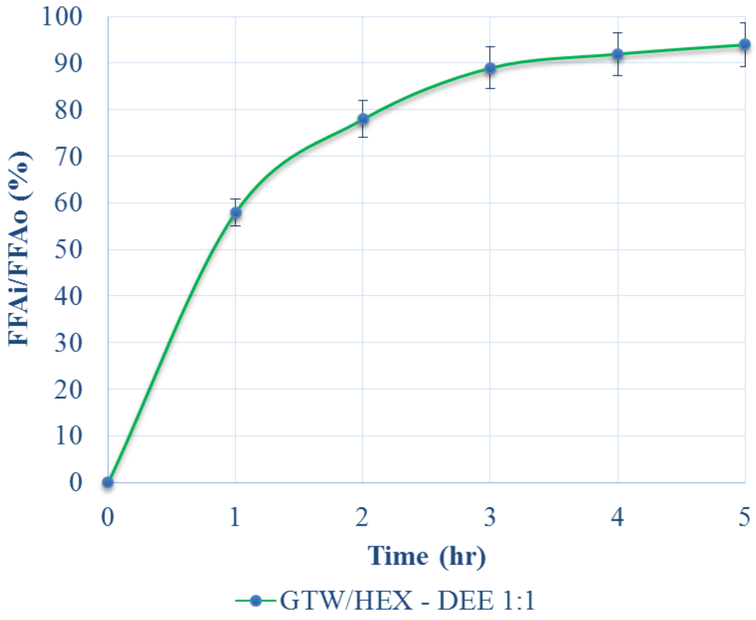

Figure 3.4 The effect of the co-solvent DEE-HEX to GTW ratio (% v/w) on the extraction yield

Utilizing the co-solvent DEE - HEX (1:1 v/v) resulted in a maximum extraction yield of 94% after a 5 hr extraction time. Interestingly, no emulsion phase was observed as the sediment settled down ready for separation after 1 hr. This can likely be explained as diethyl ether tends to extract FFA and dissolve partially in water, while hexane can also extract glycerides and the other unknown components present in GTW [32].

3.3.2.2 The Effect of Recycled Solvents

Since the cost of the solvents is also an important factor which contributes to the total cost of biodiesel production, all solvents were recycled using a rotary evaporator and re-used again to undertake the extractions as previously described in this study. **Figure 3.5** shows the average amount of solvent recovery after the individual and the solvent mixture were utilized up to three times for the FOG extraction process. The volume values of the recycled solvent were based on the original 500ml of solvent used for the extraction.

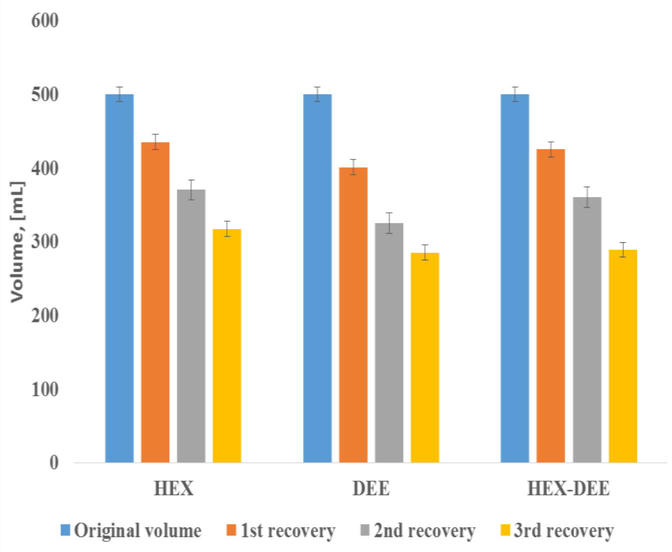

Figure 3.5 Solvent loss via three-time extraction

It can be observed that the loss of diethyl ether was significantly higher than hexane due to its very low boiling point and high volatility. The average loss of hexane and diethyl ether after the three-time recovery were 65% and 58%, respectively. The average amount of recycled hexane was lower than that reported by Siddiquee and Rohani [18]. This loss could be likely explained as the result of solvent evaporation and the absorption of solvent caused by other unknown solid particles present in the GTW. All recycled solvents were utilized for FOG extraction with the same solvent to GTW ratio

(1:1, v/w). **Figure 3.6** shows the efficiency of the extraction process utilizing the recycled diethyl ether (a) and hexane (b) up to 3 times.

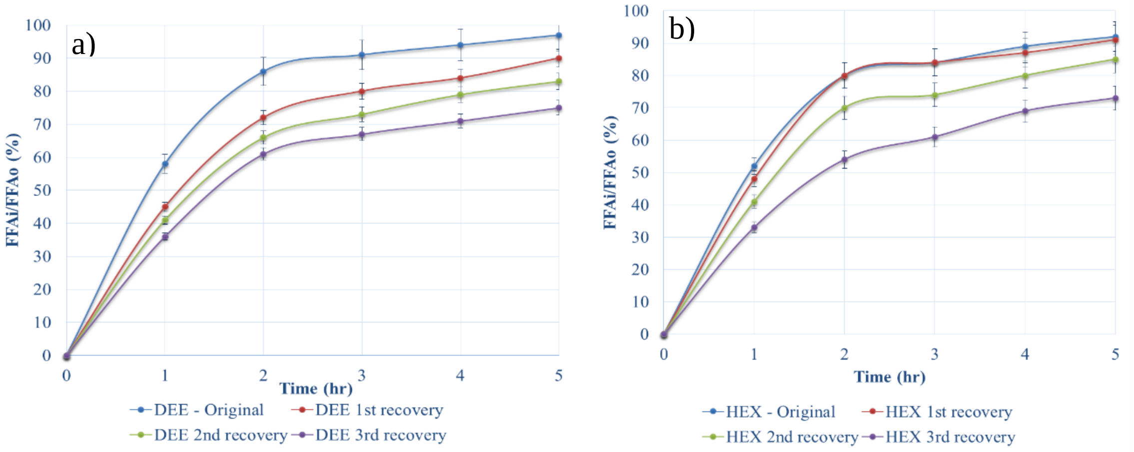

Figure 3.6 Yield efficiency of FOG extracted by recycled solvent

After a 5 hr extraction with DEE, the extraction yield dropped significantly in comparison to that extracted with pure (un-recycled) diethyl ether and hexane. This could be likely explained as the solvent was contaminated which possibly reduced its ability to extract efficiently. Interestingly, the first recycled hexane provided a similar extraction effect to the pure hexane, obtaining approximately 92% FFA yield after 5 hr extraction.

3.3.2.3 Properties of GTW Extracted Oil

The FOGs extracted using hexane and diethyl ether was analyzed by GC-FID to determine the fatty acid profiles. Surprisingly, the fatty acid profiles were not significantly different between FOG extracted by hexane or diethyl ether. Hence, there was no clear evidence of extraction selectivity in terms of lipid profiles when using hexane or diethyl ether as the solvents for the extraction process. **Table 3.2** shows the physicochemical properties of the extracted FOG. C18:1 and C16:0 are the predominant components found in the fatty acid profiles of FOG, accounting for approximately 48% and 22%, respectively. The unsaturated acids accounted for more than 60% of the total composition, and this may have important impacts on the fuel properties of GTW-derived biodiesel [33].

Table 3.2 Characterization of extracted FOG

	Extracted FOG	
Properties	**By hexane**	**By diethyl Ether**
FFA content (%)	>80%	
Water content (%wt)	0.1	
Kinematic viscosity (cSt, 400C)	45.6	
Fatty acid composition (%wt)		
Octanoic acid (C8:0)	0.4	0.3
Decanoic acid (C10:0)	1.3	1.4
Lauric acid (C12:0)	3.4	3.4
Myristic acid (C14:0)	0.4	0.4
Palmitic acid (C16:0)	21.9	20
Palmitoleic acid (C16:1)	1.2	1.1
Stearic acid (C18:0)	7.4	7.3
Oleic acid (C18:1)	47.6	46.8
Linoleic acid (C18:2)	13	12.5
Linolenic acid (C18:3)	1.8	1.7
Arachidic acid (C20:0)	1.0	0.9
Behenic acid (C22:0)	0.3	0.1
Lignoceric acid (C24:0)	0.1	-
Unknown	0.2	0.9
Average molecular weight (g/mol)	345.5	
Density (kg/m^3, 15ºC)	880	

3.3.3 Feedstock Testing for Biodiesel Production

The extracted FOG was tested as a feedstock for biodiesel production utilizing ethanol as the esterifying reagent. The results obtained show that more than 96% of the FFAs in the extracted FOG could be converted to ethyl esters under the operating conditions selected, which were: FOG to ethanol molar ratio was 1:3, 3 wt% H_2SO_4 based on FOG, 3 hr reaction time, and 65ºC reaction temperature.

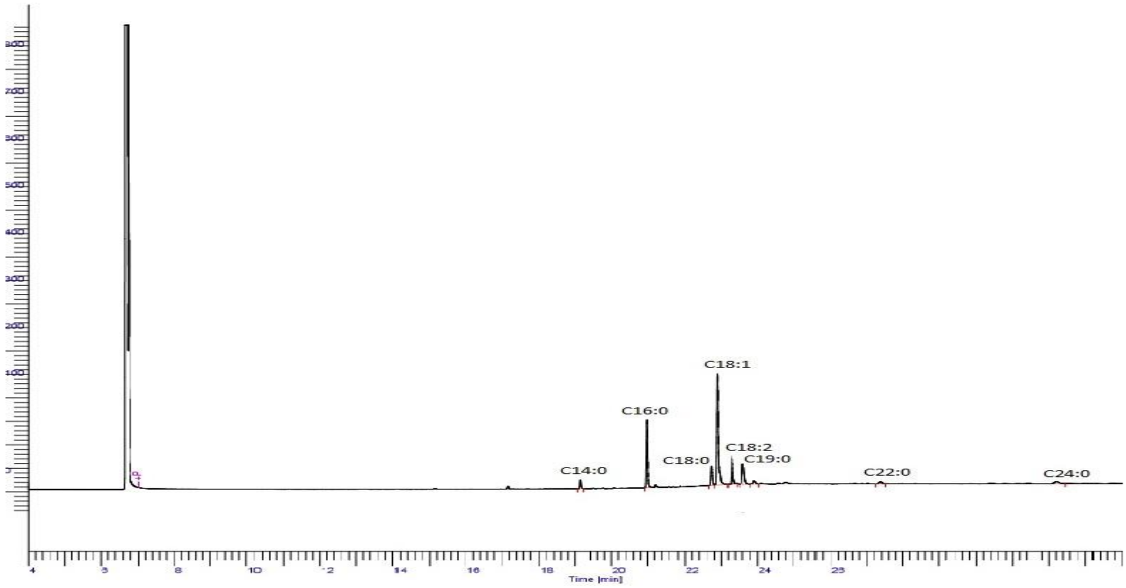

Figure 3.7 Chromatogram of free fatty acid ethyl esters

Figure 3.7 shows the ester composition of GTW-derived biodiesel obtained using GC-FID analysis. It can be seen that C16:0 and C18:1 ethyl esters are the predominant components in the composition of the GTW-derived biodiesel. These results indicate that the GTW fatty acid profile is similar to the extracted FOG fatty acid profile, which in turn correlate well with the fatty acid profile of the FOG-derived biodiesel fatty acid ester profile.

3.4 Conclusion

In the current study, a solvent extraction process has been studied to extract FOG from partially dewatered GTW obtained from an environmental service in Adelaide, South Australia. Diethyl ether and hexane were utilized for all of the extraction processes. A maximum extraction yield of 97% was obtained using diethyl ether as the solvent at the optimum conditions, which were: 1: 1 v/w diethyl ether to GTW ratio, 300rpm stirring speed, and a 5 hr extraction time. A mixture of hexane-diethyl ether with a volume ratio of 1:1 was also studied to prevent the formation of an emulsion phase which was initially observed in the extraction process utilizing diethyl ether. All solvents were recovered by a rotary evaporator based on their boiling points and re-used for the extraction of FOG. The results show that approximately 60% (v/v) of solvents could be recycled after three-time extraction protocol with an extraction yield higher than 70%. Finally, extracted FOG was examined as a potential feedstock for biodiesel production which could provide a potential alternative fuel to substitute for mineral fuels. Further studies will be then conducted to develop full techniques for the production of GTW-derived biodiesel.

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References

[1] Pastore C, Lopez A, Lotito V, Mascolo G. Biodiesel from dewatered wastewater sludge: A two-step process for a more advantageous production. Chemosphere. 2013;92:667-73.

[2] Siddiquee MN, Rohani S. Experimental analysis of lipid extraction and biodiesel production from wastewater sludge. Fuel Processing Technology. 2011;92:2241-51.

[3] Hasuntree P, Toomthong V, Yoschoch S, Thawornchaisit U. The potential of restaurant trap grease as biodiesel feedstock. Songklanakarin Journal of Science & Technology. 2011;33:525-30.

[4] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology. 2007;98:183-90.

[5] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Applied Energy. 2010;87:3155-61.

[6] Haas, Foglia. The Biodiesel Hand Book. 2nd ed. Urbana, Illinois: AOCS PRESS; 2005.

[7] Ragauskas AME, Pu Y, Ragauskas AJ. Biodiesel from grease interceptor to gas tank. Energy Science & Engineering. 2013;1:42-52.

[8] Curran P. Optimising the Production of Biodiesel from Grease Trap Waste Adelaide: The University of Adelaide; 2013.

[9] Reşitoğlu İA, Keskin A, Gürü M. The Optimization of the Esterification Reaction in Biodiesel Production from Trap Grease. Energy Sources Part A: Recovery, Utilization & Environmental Effects. 2012;34:1238-48.

[10] Williams JB, Clarkson C, Mant C, Drinkwater A, May E. Fat, oil and grease deposits in sewers: Characterisation of deposits and formation mechanisms. Water Research. 2012;46:6319-28.

[11] Lee J, Jung J-M, Park C, Jeon B-H, Wang C-H, Lee S-R, et al. Rapid conversion of fat, oil and grease (FOG) into biodiesel without pre-treatment of FOG. Journal of Cleaner Production. 2017;168:1211-6.

[12] de Oliveira JP, Antunes PWP, Santos AR, Mordente TZ, Pinotti LM, Cassini STA. Transesterification of Sanitation Waste for Biodiesel Production. Waste and Biomass Valorization. 2017;8:463-71.

[13] Wang Y, Feng S, Bai X, Zhao J, Xia S. Scum sludge as a potential feedstock for biodiesel production from wastewater treatment plants. Waste Management. 2016;47:91-7.

[14] Tu Q, Wang J, Lu M, Brougham A, Lu T. A solvent-free approach to extract the lipid fraction from sewer grease for biodiesel production. Waste Management. 2016;54:126-30.

[15] Ward PML. Brown and Black Grease Suitability for Incorporation into Feeds and Suitability for Biofuels. Journal of Food Protection. 2012;75:731-7.

[16] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: A review. Renewable & Sustainable Energy Reviews. 2011;15:1067-72.

[17] Lim S, Lee K-T. Influences of different co-solvents in simultaneous supercritical extraction and transesterification of Jatropha curcas L. seeds for the production of biodiesel. Chemical Engineering Journal. 2013;221:436-45.

[18] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: a review. Renewable and Sustainable Energy Reviews. 2011;15:1067-72.

[19] Thiex NJ, Anderson S, Gildemeister B. Crude fat, diethyl ether extraction, in feed, cereal grain, and forage (Randall/Soxtec/submersion method): collaborative study. Journal of AOAC International. 2003;86:888-98.

[20] Bligh EG, Dyer WJ. A rapid method of total lipid extraction and purification. Canadian journal of biochemistry and physiology. 1959;37:911-7.

[21] Tran NN, Ho QP, Tran PC, Chao L, Curran P, McMurchie JE, et al. Optimization of the production of biodiesel from grease trap waste (GTW). Chemeca 2016: Chemical Engineering-Regeneration, Recovery and Reinvention. 2016:1128.

[22] Wang j. Feasibility Study for a Community scale Conversion of Trap Grease to Biodiesel. USA: University of Cincinnati; 2012.

[23] Nitayapat N, Chitprasert P. Characterisation of FOGs in grease trap waste from the processing of chickens in Thailand. Waste Management. 2014;34:1012-7.

[24] He X, Francis L, Leming ML, Dean LO, Lappi SE, Ducoste JJ. Mechanisms of fat, oil and grease (FOG) deposit formation in sewer lines. Water research. 2013;47:4451-9.

[25] Curtis MD, Lanzoni J, Parnas R. High Efficiency Bio-Diesel Production from a Municipal FOG Facility. Proceedings of the Water Environment Federation. 2013;2013:66-72.

[26] Alhassan Y, Kumar N, Bugaje IM, Pali HS, Kathkar P. Co-solvents transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality of fatty acids methyl esters. Energy Conversion and Management. 2014;84:640-8.

[27] Karnasuta S, Punsuvon V, Chiemchaisri C, Chunkao K. Optimization of biodiesel production from trap grease via two-step catalyzed process. Asian J Energy Environ. 2007;8:145-68.

[28] Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A new co-solvent method for the green production of biodiesel fuel – Optimization and practical application. Fuel. 2013;103:742-8.

[29] Wang Z-M, Lee J-S, Park J-Y, Wu C-Z, Yuan Z-H. Optimization of biodiesel production from trap grease via acid catalysis. Korean Journal of Chemical Engineering. 2008;25:670-4.

[30] Olkiewicz M, Caporgno MP, Fortuny A, Stüber F, Fabregat A, Font J, et al. Direct liquid–liquid extraction of lipid from municipal sewage sludge for biodiesel production. Fuel processing technology. 2014;128:331-8.

[31] Vicente G, Martinez M, Aracil J. Optimisation of integrated biodiesel production. Part II: A study of the material balance. Bioresource Technology. 2007;98:1754-61.

[32] Sicaire A-G, Vian M, Fine F, Joffre F, Carré P, Tostain S, et al. Alternative bio-based solvents for extraction of fat and oils: solubility prediction, global yield, extraction kinetics, chemical composition and cost of manufacturing. International journal of molecular sciences. 2015;16:8430-53.

[33] Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies. 2009;2:362-76.

Supporting Data

Table S3.1 Fatty acid profiles and total glycerides of GTW samples

ID	FAT%		**10:0**	**12:0**	**14:0**	**16:0**	**16:1n-7**	**18:0**	**Trans 18:1n-9**	**Trans 18:1n-7**	**18:1n-9**	**18:1n-7**	**18:2n-6**	**18:3n-3**	**20:0**	**20:1n-9**	**22:0**	**24:0**
GTW_1	51.1%	TP	0.5%	1.4%	3.7%	24.1%	1.3%	8.2%	1.1%	1.8%	43.4%	2.2%	9.7%	1.1%	0.5%	0.7%	0.3%	0.1%
		TX	0.2	0.6	1.7	11.4	0.6	3.9	0.5	0.9	20.6	1.0	4.6	0.5	0.2	0.3	0.1	0.1
		GX	ND	ND	0.5	1.3	0.1	0.7	0.1	0.1	2.6	0.1	0.5	0.1	ND	ND	ND	ND
		DX	ND	ND	0.1	0.5	0.0	0.2	0.1	0.1	1.7	0.1	0.3	0.0	ND	ND	ND	ND
		MX	ND	ND	0.2	0.8	0.1	0.3	0.1	0.1	3.3	0.1	0.4	0.0	ND	ND	ND	ND
GTW_2	51.1%	TP	0.5%	1.4%	3.7%	24.1%	1.3%	8.2%	1.1%	1.8%	43.4%	2.2%	9.7%	1.1%	0.5%	0.7%	0.3%	0.1%
		TX	0.2	0.6	1.7	11.4	0.6	3.9	0.5	0.9	20.6	1.0	4.6	0.5	0.2	0.3	0.1	0.1
		GX	ND	ND	0.5	1.3	0.1	0.7	0.1	0.1	2.6	0.1	0.5	0.1	ND	ND	ND	ND
		DX	ND	ND	0.1	0.5	0.0	0.2	0.1	0.1	1.7	0.1	0.3	0.0	ND	ND	ND	ND
		MX	ND	ND	0.2	0.8	0.1	0.3	0.1	0.1	3.3	0.1	0.4	0.0	ND	ND	ND	ND
GTW_3	51.1%	TP	0.5%	1.4%	3.7%	24.1%	1.3%	8.2%	1.1%	1.8%	43.4%	2.2%	9.7%	1.1%	0.5%	0.7%	0.3%	0.1%
		TX	0.2	0.6	1.7	11.4	0.6	3.9	0.5	0.9	20.6	1.0	4.6	0.5	0.2	0.3	0.1	0.1
		GX	ND	ND	0.5	1.3	0.1	0.7	0.1	0.1	2.6	0.1	0.5	0.1	ND	ND	ND	ND
		DX	ND	ND	0.1	0.5	0.0	0.2	0.1	0.1	1.7	0.1	0.3	0.0	ND	ND	ND	ND
		MX	ND	ND	0.2	0.8	0.1	0.3	0.1	0.1	3.3	0.1	0.4	0.0	ND	ND	ND	ND

Notes: results provided by FOODplus Research Centre, The University of Adelaide

FAT% - Crude fat content in sample; TP - fatty acid profiles, expressed as the weight% of individual fatty acid; TX - Total lipids quantitation (unit: gram per 100 gram of sample); MX - Monoglycerides quantitation (unit: gram per 100 gram of sample); DX - Diglyceride quantitation (unit: gram per 100 gram of sample); GX - Triglyceride quantitation (unit: gram per 100 gram of sample); ND - Non detectable

Table S3.2 Fatty acid profile and total glycerides of FOG samples obtained via Bligh and Dyer methodology

ID	FAT%		**10:0**	**12:0**	**14:0**	**16:0**	**16:1n-7**	**18:0**	**Trans 18:1n-9**	**Trans 18:1n-7**	**18:1n-9**	**18:1n-7**	**18:2n-6**	**18:3n-3**	**20:0**	**20:1n-9**	**22:0**	**24:0**
FOG_1	97.1%	TP	0.4%	1.3%	3.4%	22.3%	1.2%	7.4%	1.0%	1.9%	42.6%	2.1%	13.0%	1.8%	0.4%	0.6%	0.3%	0.1%
		TX	0.4	1.2	3.2	20.5	1.1	6.9	0.9	1.7	39.3	2.0	12.0	1.6	0.4	0.6	0.2	0.1
		GX	ND	ND	0.7	2.2	0.1	0.8	0.1	0.1	3.2	0.2	1.0	0.1	ND	ND	ND	ND
		DX	ND	ND	0.2	0.9	0.1	0.4	0.1	0.1	2.2	0.1	0.6	0.1	ND	ND	ND	ND
		MX	ND	ND	0.2	0.9	0.0	0.3	0.1	0.1	2.0	0.1	0.5	0.1	ND	ND	ND	ND
FOG_2	98.5%	TP	0.4%	1.3%	3.3%	22.1%	1.1%	7.4%	1.1%	1.8%	42.2%	2.1%	13.7%	2.0%	0.4%	0.6%	0.3%	0.1%
		TX	0.4	1.2	3.1	20.3	1.1	6.8	1.0	1.6	38.9	1.9	12.6	1.8	0.4	0.6	0.2	0.1
		GX	ND	ND	0.8	3.0	0.1	1.0	0.1	0.1	1.8	0.1	0.9	0.1	ND	ND	ND	ND
		DX	ND	ND	0.1	0.8	0.0	0.4	0.1	0.1	1.6	0.1	0.4	0.1	ND	ND	ND	ND
		MX	ND	ND	0.1	0.7	0.0	0.4	0.0	0.1	1.4	0.1	0.4	0.1	ND	ND	ND	ND
FOG_3	98.5%	TP	0.4%	1.3%	3.3%	22.1%	1.1%	7.4%	1.1%	1.8%	42.2%	2.1%	13.7%	2.0%	0.4%	0.6%	0.3%	0.1%
		TX	0.4	1.2	3.1	20.3	1.1	6.8	1.0	1.6	38.9	1.9	12.6	1.8	0.4	0.6	0.2	0.1
		GX	ND	ND	0.8	3.0	0.1	1.0	0.1	0.1	1.8	0.1	0.9	0.1	ND	ND	ND	ND
		DX	ND	ND	0.1	0.8	0.0	0.4	0.1	0.1	1.6	0.1	0.4	0.1	ND	ND	ND	ND
		MX	ND	ND	0.1	0.7	0.0	0.4	0.0	0.1	1.4	0.1	0.4	0.1	ND	ND	ND	ND

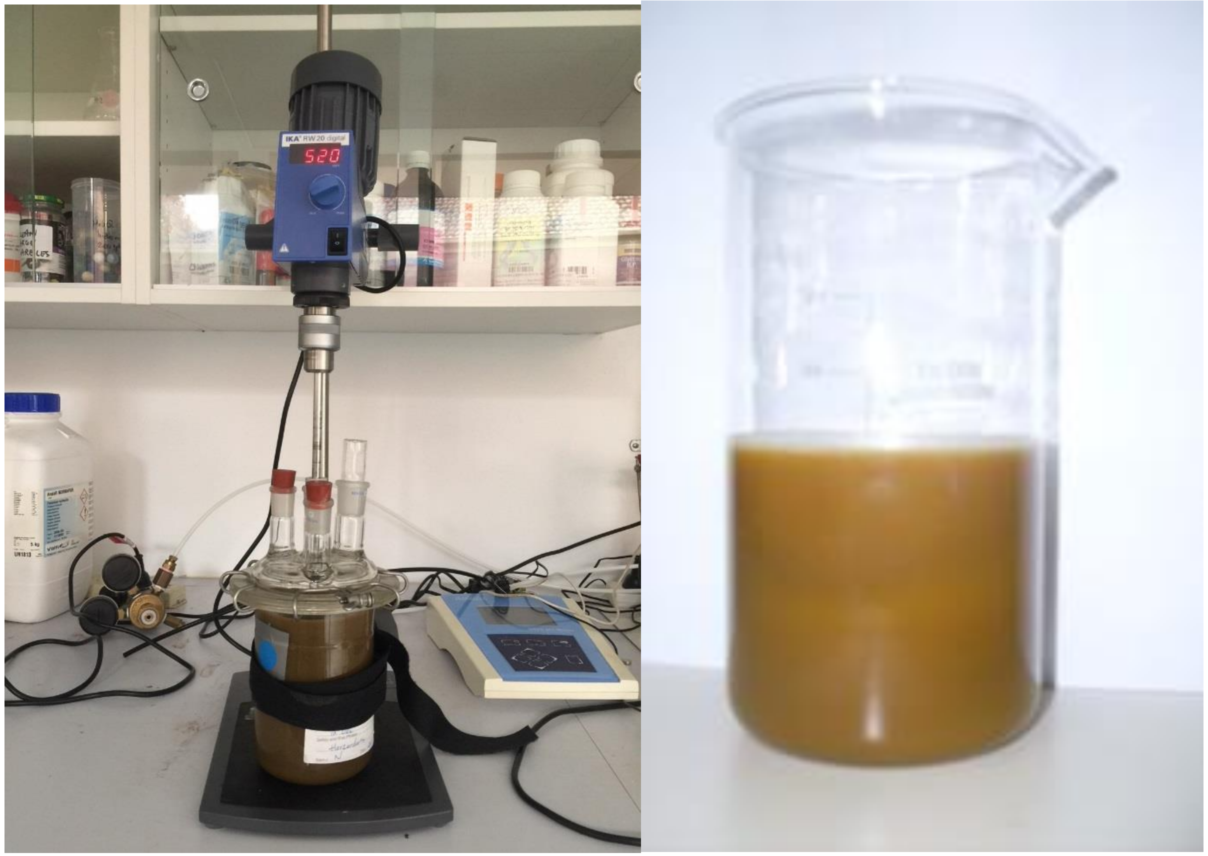

Figure S3.1 Experimental setup for the extraction process and the extracted FOG

Bligh/Dyer extraction of total lipids:

1. Weighing GTW sample.
2. Adding sample to the glass tube and add 3 ml mixture of methanol and chloroform (2:1, v/v).
3. Mixing or stiring for 20 minutes.
4. Adding 1 ml chloroform and 1.8 ml water to the glass tube.
5. Shaking for 10 min
6. Centrifuging at 3000 rpm for 5 min
7. Discarding bottom layer (solid) and middle layer (water)
8. Transfering upper layer (organic phase contains TAGs, membrane lipids, and other neutral lipids) to new tube
9. Drying under nitrogen
10. Dissolving in 200 ul 1:1 chloroform: methanol or 6:1 chloroform:methanol.
11. Analyzing using titration and GC-FID

Table S3.4 The average of FFA extraction yields using hexane

		FFA_i/FFA_0 (%)							
Sample ID	**GTW:HEX ratio (w/v)**	**0 hr**	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**	**6 hr**	**7 hr**
H_1	1:1	0	52	80	84	89	92	92	92
H_2	1:1.5	0	66	85	91	94	96	96	96
H_3	1:2	0	68	88	94	96	97	97	97

Table S3.5 The average of FFA extraction yields using diethyl ether

		FFA_i/FFA_0 (%)					
Sample ID	**GTW to DEE ratio (w/v)**	**0 hr**	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**
D_1	1:1	0	58	86	91	94	97
D_2	1:1.5	0	71	89	94	96	97
D_3	1:2	0	75	91	94	97	97

Table S3.6 The average of FFA extraction yields using recycled diethyl ether

	FFA_i/FFA_0 (%)					
Sample	**0 hr**	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**
Original	0	58	86	91	94	97
1st recovery	0	45	72	80	84	90
2nd recovery	0	41	66	73	79	83
3rd recovery	0	36	61	67	71	75

Table S3.7 The average of FFA extraction yields using recycled diethyl ether

	FFA_i/FFA_0 (%)					
Sample	**0 hr**	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**
Original	0	52	80	84	89	92
1st recovery	0	48	80	84	87	91
2nd recovery	0	41	70	74	80	85
3rd recovery	0	33	54	61	69	73

Statement of Authorship

Title of Paper	Analysis of Fatty Acid Ethyl Ester Profiles in Biodiesel by Gas Chromatography with Flame Ionisation Detector
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Overall Percentage	70%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
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Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate’s stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate’s stated contribution.

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Contribution to the Paper	Supervising the development of the work and approving the manuscript		
Signature		Date	28/02/2018

Chapter 4. Analysis of Fatty Acid Ethyl Ester Profiles in Biodiesel by Gas Chromatography with Flame Ionisation Detector

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Abstract

This paper introduces a simple Gas Chromatography with Flame Ionization Detector (GC-FID) methodology to determine the fatty acid ethyl ester (FAEE) profiles of biodiesel produced from vegetable oils, animal fats or waste resources, utilizing ethanol as a reagent. The procedure is based on the revised EN14103:2011 method which was developed for the analyzing of fatty acid methyl esters (FAMEs). The advantages of this proposed method include:

- Simultaneous determination of FAEE profiles in finished biodiesel, while the existing methods are only applied for FAMEs.
- Use the same capillary GC column that designed for the fatty acid analysis.
- Employment of an internal standard (ethyl nonadecanoate, C19:0) to quantify the concentration of FAEEs in order to achieve an accurate result.

Keywords: *Biodiesel, Fatty acid ethyl esters, GC-FID*

4.1 Backgrounds

Biodiesel or fatty acid alkyl esters is the product of the reaction between a short-chain alcohol and a long-chain free fatty acid or a triglyceride [1]. Depending on the composition of the feedstock, biodiesel can be produced using the esterification reaction, or the two-step esterification and transesterification combined as shown in **Figure 4.1**.

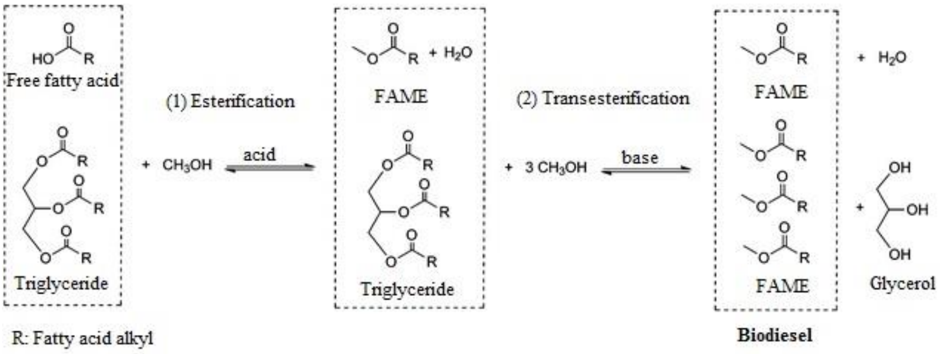

Figure 4.1 Esterification and transesterification reaction with methanol

Previous studies have used methanol as a reagent for the biodiesel synthesis reaction, leading to the development of analytical methodologies which concentrated on the analysis of free fatty acid methyl esters (FAMEs) [2-6]. However, due to the toxicity of methanol, many studies have been carried out to investigate the use of other less toxic alcohols, such as ethanol, propanol, and butanol [7, 8]. Among those potential reagents, ethanol, a bio-available chemical, has been successfully utilized as a solvent for biodiesel production in order to produce a ‘greener’ biodiesel fuel [8-11]. Following the EN14103 standard, the minimum ester content required for an industrial-grade biodiesel is 96.5% wt/wt. Therefore, it is necessary to determine the ester content of biodiesel, with gas chromatography being the most widely used technique [12-14]. Therefore, this method was developed to analyze the fatty acid ethyl ester profiles of biodiesel synthesized from vegetable oils, animal fats, or other waste resources in which ethanol is utilized as a reagent.

4.2 Method Details

4.2.1 Reagent and Standards

SUPELCO C4–C24 even carbon saturated fatty acid ethyl esters 1000 µg/mL of each component in hexane and analytical-grade hexane, were purchased from Sigma-Aldrich (New South Wales, Australia). Since oleic acid ethyl ester (C18:1) and linoleic acid ethyl ester are also the main components of biodiesel, 1000 µg each of those two unsaturated ethyl esters (provided by Nu-Chek-Prep, Elysian, MN, USA) was added to the standard to make a final standard for GC-FID analysis. The list of components is presented in **Table 4.1**.

Table 4.1 List of components and their concentration in the standard

#	Component	Purity (%)	Analytical concentration (µg/mL)	Note
1	Butyric Acid Ethyl Ester, C4:0	99.9	1011.0	standard
2	Caproic Acid Ethyl Ester, C6:0	99.9	994.2	standard
3	Caprylic Acid Ethyl Ester, C8:0	99.6	997.1	standard
4	Capric Acid Ethyl Ester, C10:0	99.9	1003.7	standard
5	Lauric Acid Ethyl Ester, C12:0	99.9	1004.7	standard
6	Myristic Acid Ethyl Ester, C14:0	99.9	901.0	standard
7	Palmitic Acid Ethyl Ester, C16:0	99.7	1001.2	standard
8	Stearic Acid Ethyl Ester, C18:0	99.9	1003.8	standard
9	Arachidic Acid Ethyl Ester, C20:0	99.9	1001.5	standard
10	Behenic Acid Ethyl Ester, C22:0	99.9	1005.2	standard
11	Tetracosanoic Acid Ethyl Esters, C24:0	99.0	1006.3	standard
12	Oleic Acid Ethyl Ester, C18:1	99.0	1003.7	Added
13	Linoleic Acid Ethyl Ester, C18:2	99.0	1004.6	Added

2 mL screw top vials (PTFE septum face) were purchased from Sigma-Aldrich. Ethyl nonadecanoate (C19:0 ethyl ester) provided by Tokyo Industries, was utilized as the internal standard.

4.2.2 Instrumentation

Initial methodology setup was done using a Clarus 500 GC–FID system (PerkinElmer, Waltham, MA, USA) equipped with a BP-20 SGE forte column (30 m x 0.32 mm x 0.25 μm; SGE Forte^{TM}, Australia). The oven was initially set at 60ºC and after injection of the sample, was maintained for 1 min before increasing to 240ºC at a rate of 10ºC/min. After reaching the set temperature of 240ºC, it was then maintained for 12 min. The detector temperature was set at 250ºC, and the flame was maintained with 45 mL/min H_2 and 450 mL/min compressed air. Helium was used as the detector auxiliary gas at a flow rate of 1 mL/min. The total time for each analysis was 30 minutes. The method was then certified by running a comparative sample analysis with an Agilent 5977 Mass Selective Detector (Agilent Technologies, Santa Clara, CA, USA) using the same GC column.

4.2.3 Preparation of Standards

A series of standard mixtures, including all FAEEs listed in Table 1, was prepared in analytical grade hexane. For each level of calibration, all FAEEs were present at an equal concentration, ranging from 10 to 250 μg/mL across the series. As an internal standard, C19:0 FAEE was added to each mixture at a concentration of 100 μg/mL. **Table 4.2** shows the dilution of the standards for the construction of the calibration curve.

Table 4.2 Standard dilution for the construction of the calibration curve

Standard level	C4-C24 standard (µl)	Volume of hexane (µl)	10 mg/mL IS (µl)
50:100:150	250	740	10
20:40:60	100	890	10
10:20:30	50	940	10
5:10:15	25	965	10
2:4:6	10	980	10
0:0:0	0	990	10

4.2.4 Analysis of Standard

To obtain the calibration curves, all standards were analyzed in triplicate using GC–FID. **Table 4.2** shows an example of a standard chromatogram produced by the GC (concentration level 20:40:60). The retention times, peak area and concentration of each component including the standard deviation are shown in **Table 4.3**.

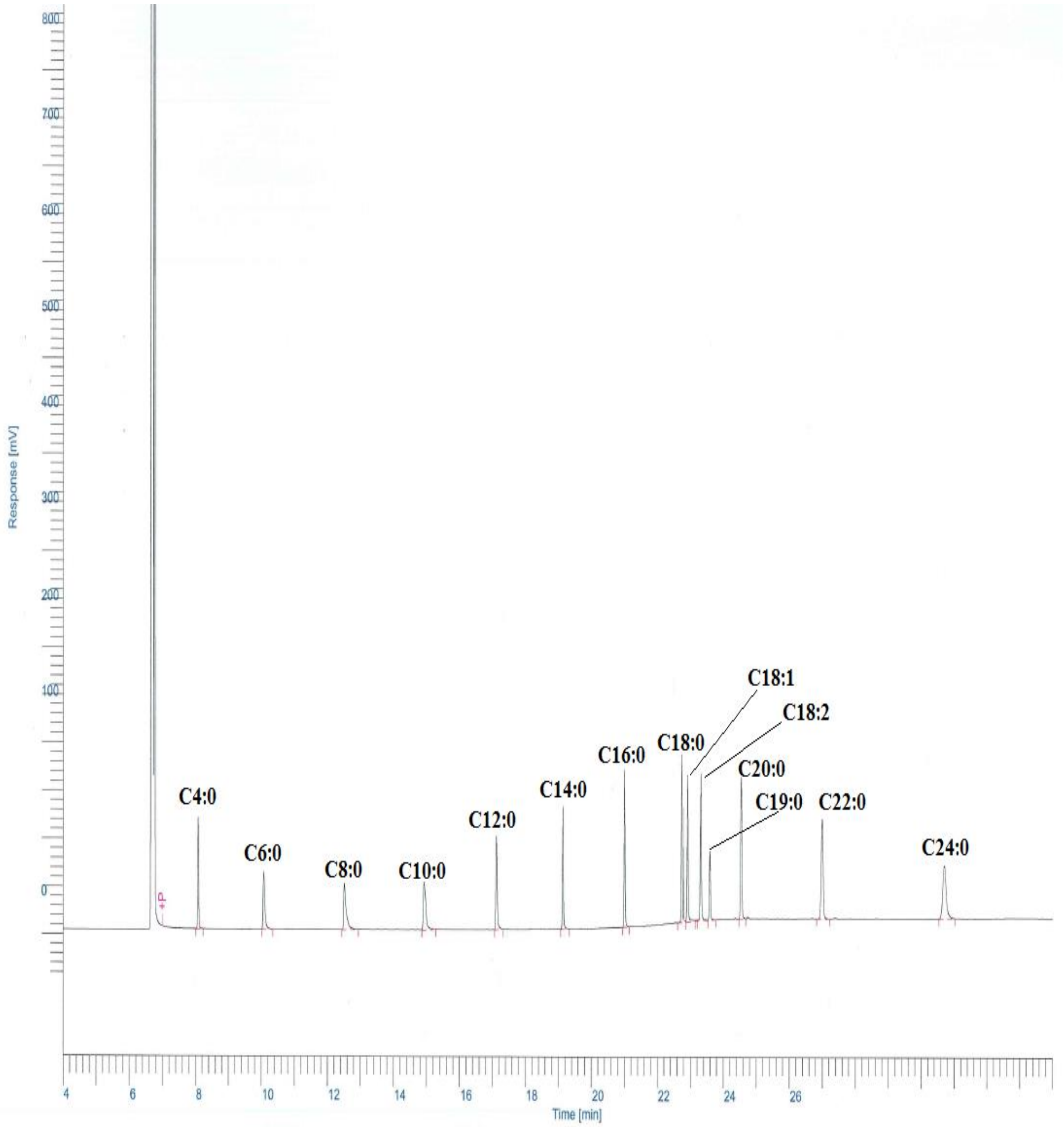

Figure 4.2 Chromatogram of fatty acid ethyl ester profiles

Table 4.3 GC-FID analysis result of fatty acid ethyl esters

Component #	**Compound Name**	**GC-FID**				
		RT (min)	**Area**	**Amount (ug)**	**3SDr**	**RSDr, [%]**
1	C4:0	4.12	75413	96.90	1.34	1.38
2	C6:0	6.13	70384	99.63	1.13	1.13
3	C8:0	8.56	88556	98.63	0.71	0.72
4	C10:0	10.94	95880	96.83	1.35	1.39
5	C12:0	13.15	111936	98.67	1.63	1.66
6	C14:0	15.18	106480	96.37	2.64	2.74
7	C16:0	17.05	123765	95.17	2.44	2.56
8	C18:0	18.79	136369	96.67	0.87	0.90
9	C18:1	18.97	118199	96.03	3.65	3.80
10	C18:2	19.37	130231	99.93	1.39	1.39
11	C19:0*	19.70	153181	98.43	1.27	1.29
12	C20:0	20.61	145859	98.83	0.58	0.59
13	C22:0	23.10	151428	97.20	1.85	1.90
14	C24:0	26.86	153759	98.67	2.11	2.13

**Internal standard*

As shown in **Table 4.3,** all samples were analyzed in triplicate, resulting in an average result. 100% of the relative standard deviation (RSDr) is lower than 5% confirming the reproducibility of the method.

Response Factor (RF)

In GC analysis using an internal standard, it is important to determine the ratio of the peak area of the target components in the sample and the peak area of the internal standard. This ratio is then compared to a similar ratio obtained from the analysis of each calibration standard. The RF is calculated via equation (1).

Response Factor Equation

$$\mathrm{RF} = \frac{\left[{}^{\mathrm{A_x}}/_{\mathrm{m_x}}\right]}{\left[{}^{\mathrm{A_{is}}}/_{\mathrm{m_{is}}}\right]} = \frac{\left[{}^{\mathrm{A_x}}/_{\mathrm{A_{is}}}\right]}{\left[{}^{\mathrm{m_x}}/_{\mathrm{m_{is}}}\right]} = \text{slope of calibration curve} \tag{1}$$

where, A_x, A_{is} are measured by the peak areas of the targeted component and the internal standard; m_x, m_{is} are the amount of the analyte and the injected internal standard in mass.

In general, A_x/A_{is} can be measured from the chromatogram while m_x/m_{is} is calculated for the unknown using equation (1). Since m_{is} is recorded, m_x can be determined.

Calibration curves

Based on the analysis of the standards, a 5 point calibration curve was prepared for each of the components. The calibration curves are presented in **Table 4.3**. For each of calibration curve, R-squared was greater than 99.8%.

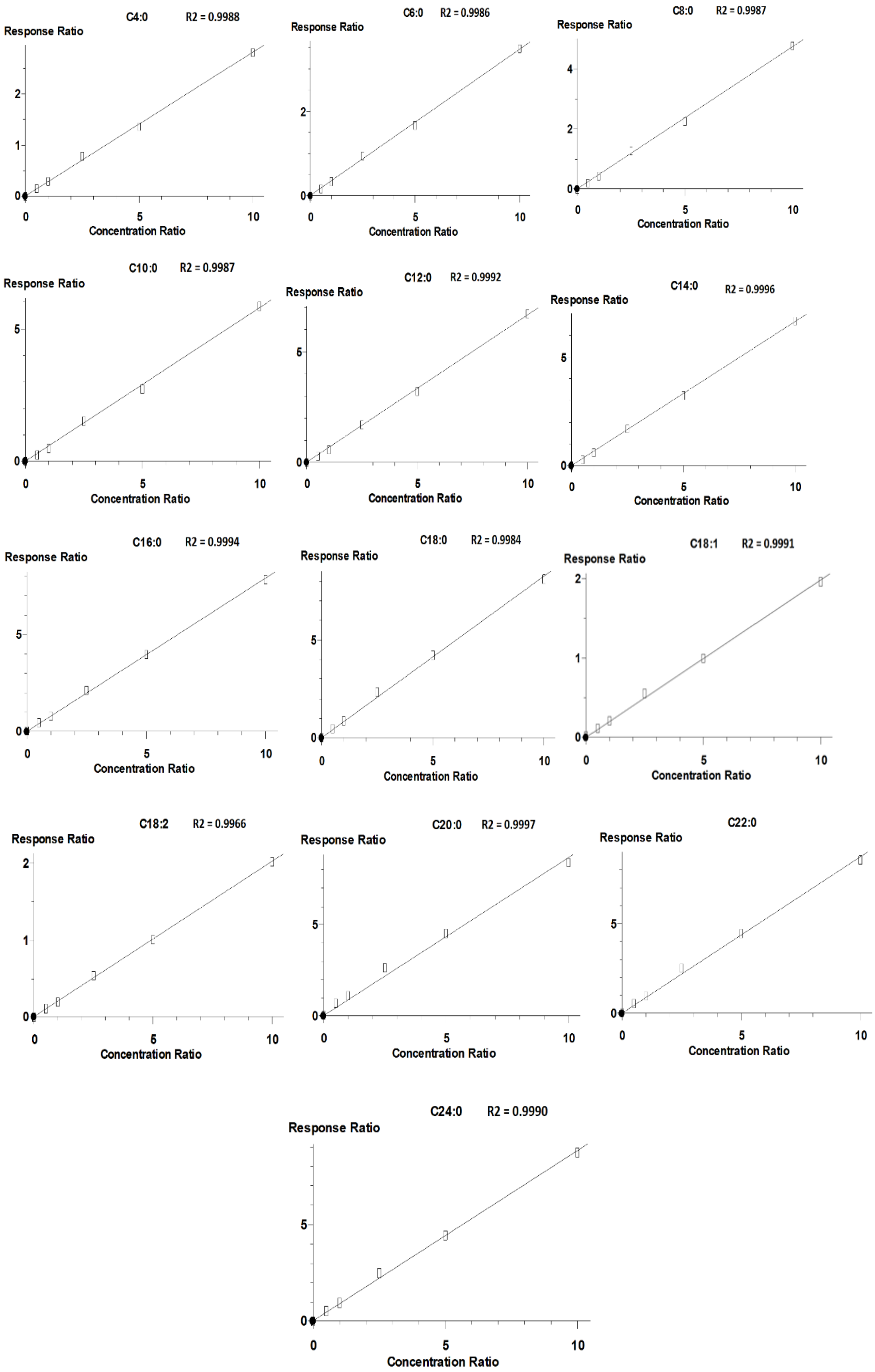

Figure 4.3 Calibration curves of C4 to C24 ethyl esters found in the standard

The calibration curve shows the linear response while the response factor is determined based on the slope of the curve.

4.3 Real Sample Analysis

4.3.1 Procedure

The following section outlining the methodology for the determination of the ethyl ester profile of selected samples is presented as a step-by-step standard operating procedure (SOP).

1. Preparing the sample in hexane (1 mg/mL) in a GC vial using a Pasteur pipette.
2. Vials should be capped prior to every analysis. A silicon septum is recommended to prevent solvent evaporation.
3. Cleaning up and refill the wash solvents as well as the waste vials on the GC. Then, put sample vials in the auto-sampler section. It is recommended that a blank containing only hexane should be run before running the actual samples.
4. Running the samples on the GC-FID with a BP-20 SGE forte column (30 m x 0.32 mm x 0.25 µm; SGE Forte^{TM}, Australia). Following the injection of the sample, the oven was initially maintained at 60ºC for 1 min, increased to 240ºC at a rate of 10ºC/min and was then held for 12 min. The detector temperature was held at 250ºC, and the flame was maintained with 45 mL/min H_2 and 450 mL/min compressed air. Helium was used as the detector auxiliary gas at a flow of 1 mL/min. The total time for each analysis is 30 minutes.

4.3.2 Analytical Results

A biodiesel sample produced by the esterification of extracted oil from recycled grease trap waste using ethanol as a reagent was run on both GC-FID and GC-MSD equipped with the same column. **Figure 4.4** shows the chromatographic results obtained by GC-FID (A) and GC-MSD (B). A comparative quantitative result is displayed in **Table 4.4**. It is observed that GC-MSD has advantages in terms of analyzing components when present at low concentrations, while GC-FID provides a better reproducibility result.

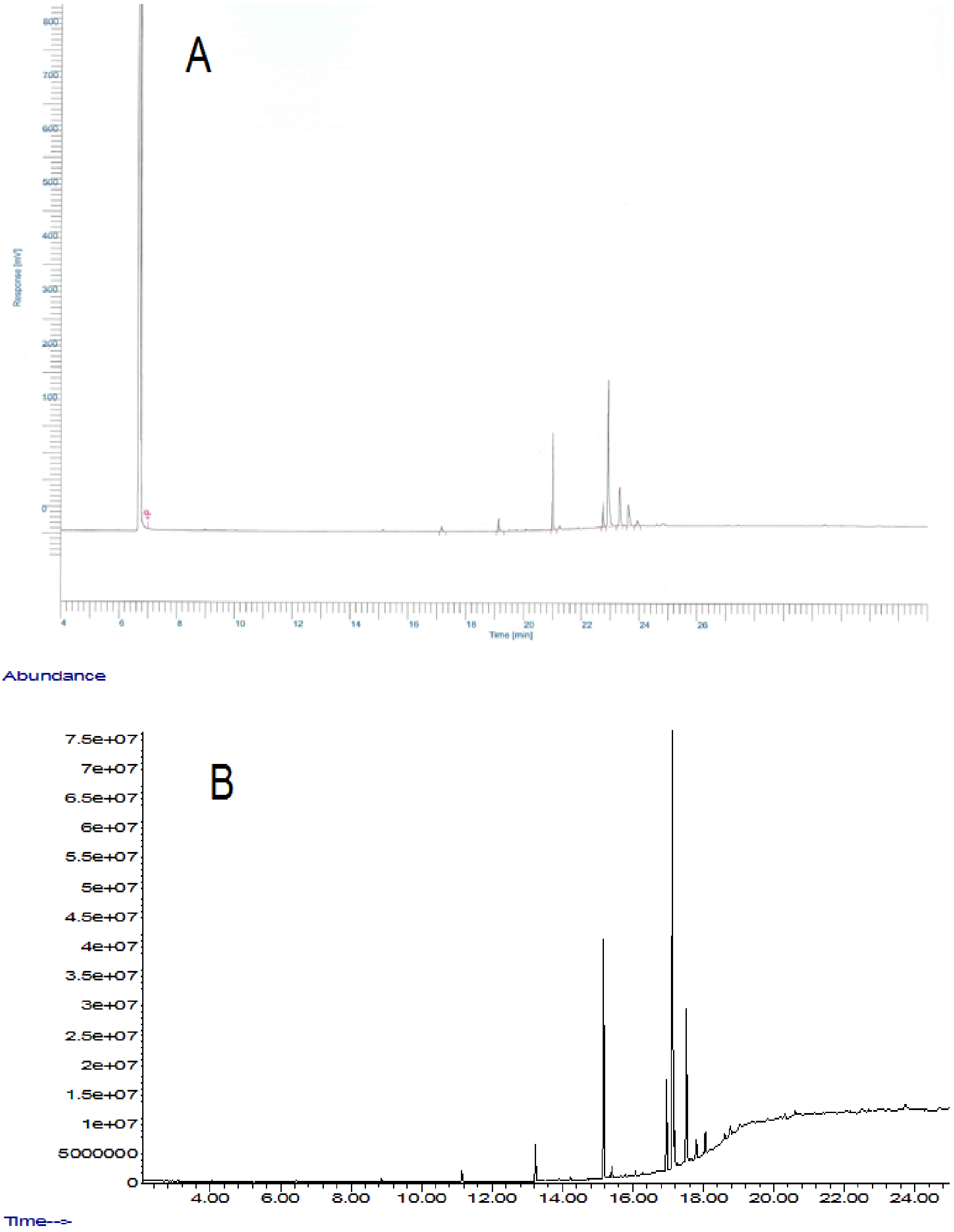

Figure 4.4 Chromatographic results obtained by GC-FID (A) and GC-MSD (B)

Table 4.4 Quantitative results obtained by GC-FID and GC-MSD

#	Name	GC-FID				GC-MSD			
		RT (min)	**Area**	**Amount**	**RSDr (%)**	**RT (min)**	**Area**	**Amount**	**RSDr (%)**
1	C4:0	4.12	75413	0	-	2.352	8215	0.29	10.89
2	C6:0	6.13	70384	0	-	4.067	91966	2.61	11.13
3	C8:0	8.56	88556	0	-	6.44	124787	2.59	17.81
4	C10:0	10.94	95880	0	-	8.869	254920	4.31	15.76
5	C12:0	13.15	11936	13.8	3.57	11.146	772664	11.28	6.77
6	C14:0	15.18	39321	36.7	6.72	13.238	2196672	32.13	8.91
7	C16:0	17.05	193765	173.6	4.17	15.17	13023621	160.40	11.96
8	C18:0	18.79	101368	62.9	4.87	16.949	4984311	58.42	9.55
9	C18:1	18.97	348959	281.7	7.56	17.118	5471291	271.41	18.65
10	C18:2	19.37	193231	154.5	4.38	17.519	3110215	149.61	13.47
11	C19:0	19.70	163181	100.2	6.71	17.813	3089542	97.81	10.71
12	C20:0	20.61	145859	0	-	18.609	397545	4.54	19.80
13	C22:0	23.10	151428	0	-	20.316	275705	3.04	8.91
14	C24:0	26.86	153759	0	-	22.721	105743	1.14	16.73

4.4 Conclusion

A complete method for fatty acid ethyl esters analysis by GC-FID has been introduced in this paper. This method can be applied for the analysis of biodiesel obtained from various resources such as vegetable oils, animal fats, or waste products. A comparative analysis has been conducted on GC-MSD to confirm the validation of the method. The results showed that this method can be well-applied to determine the fatty acid ethyl ester profiles of the biodiesel product.

Acknowledgements

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References

[1] Musa IA. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. Egyptian Journal of Petroleum. 2016;25:21-31.

[2] Chen L, Liu T, Zhang W, Chen X, Wang J. Biodiesel production from algae oil high in free fatty acids by two-step catalytic conversion. Bioresource Technology. 2012;111:208-14.

[3] Ghoreishi SM, Moein P. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. The Journal of Supercritical Fluids. 2013;76:24-31.

[4] Ito T, Sakurai Y, Kakuta Y, Sugano M, Hirano K. Biodiesel production from waste animal fats using pyrolysis method. Fuel Processing Technology. 2012;94:47-52.

[5] Ju Y-H, Huynh LH, Tsigie YA, Ho Q-P. Synthesis of biodiesel in subcritical water and methanol. Fuel. 2013;105:266-71.

[6] Yan J, Li A, Xu Y, Ngo TPN, Phua S, Li Z. Efficient production of biodiesel from waste grease: One-pot esterification and transesterification with tandem lipases. Bioresource Technology. 2012;123:332-7.

[7] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology. 2007;98:183-90.

[8] Likozar B, Levec J. Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition. Applied Energy. 2014;123:108-20.

[9] Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies. 2009;2:362-76.

[10] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Processing Technology. 2007;88:429-36.

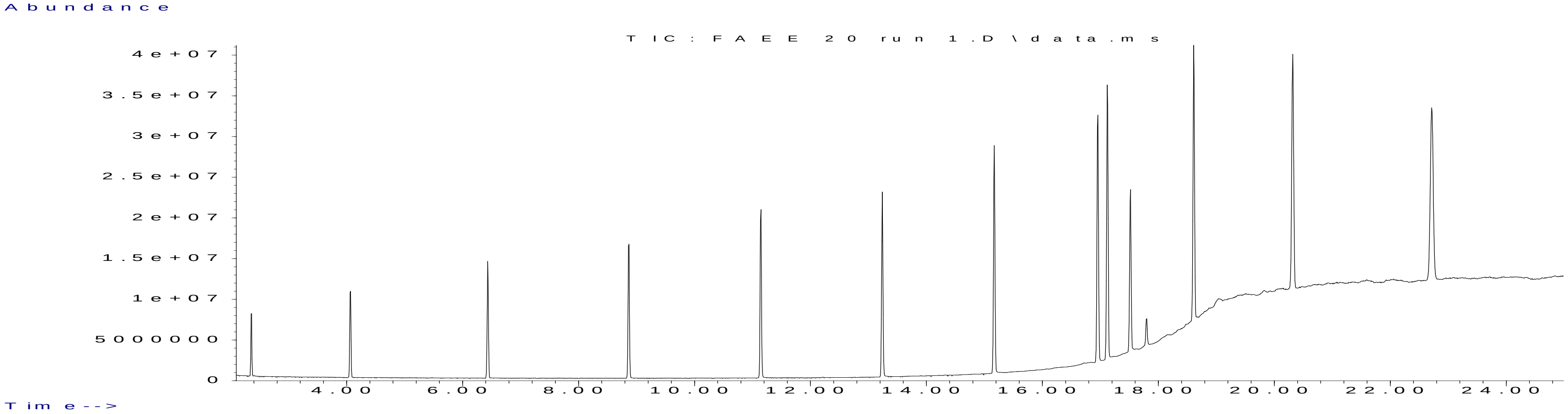
[11] Oliveira JFG, Lucena IL, Saboya RMA, Rodrigues ML, Torres AEB, Fernandes FAN, et al. Biodiesel production from waste coconut oil by esterification with ethanol: The effect of water removal by adsorption. Renewable Energy: An International Journal. 2010;35:2581-4.

[12] Knothe G. Analytical methods used in the production and fuel quality assessment of biodiesel. Transactions of the ASAE. 2001;44:193.

[13] Knothe G. Analyzing biodiesel: standards and other methods. Journal of the American Oil Chemists' Society. 2006;83:823-33.

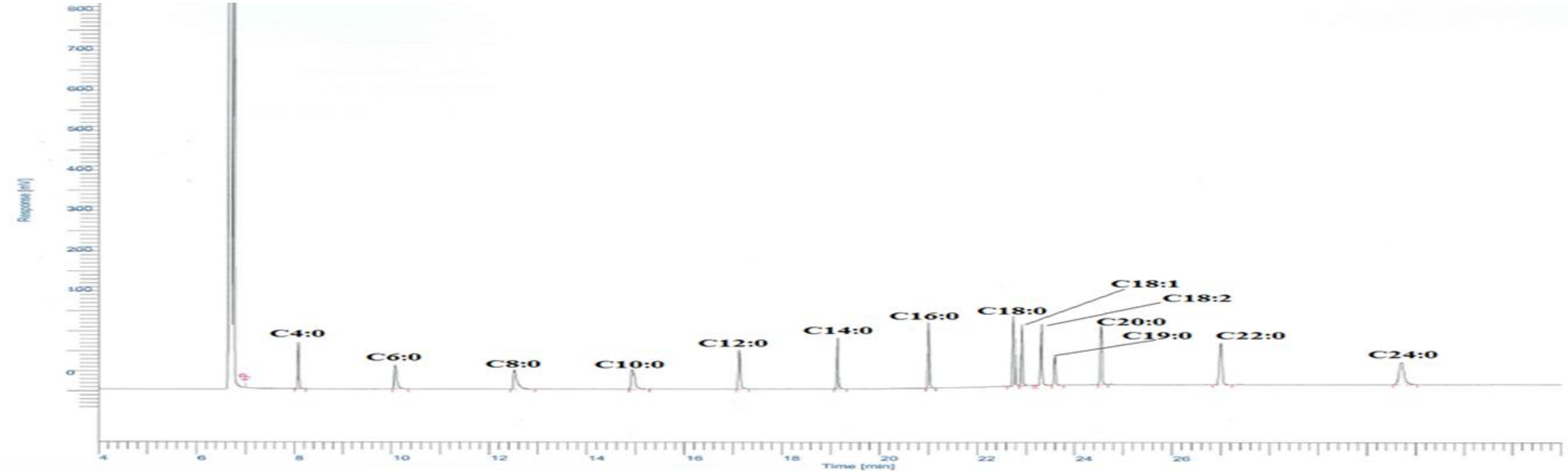
[14] Van Gerpen J, Shanks B, Pruszko R, Clements D, Knothe G. Biodiesel analytical methods. National Renewable Energy Laboratory, Colorado. 2004:37-4

Supporting Data



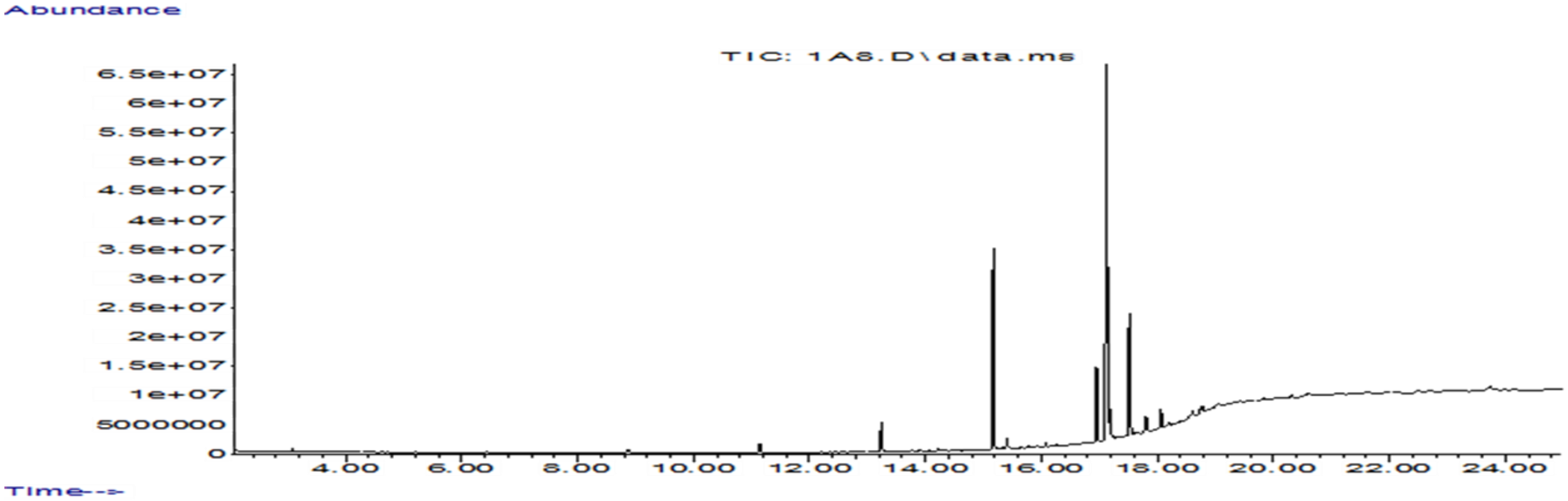
Component	Compound Name	RT (min)	Area	Amount	Units	Q-value
2	C4:0	2.352	3191963	93.9369	ug/ml	99
3	C6:0	4.067	4010229	93.7186	ug/ml	99
4	C8:0	6.432	5488051	93.7591	ug/ml	99
5	C10:0	8.861	6795545	94.44	ug/ml	99
6	C12:0	11.146	7900472	94.8748	ug/ml	98
7	C14:0	13.238	7859697	94.5762	ug/ml	98
8	C16:0	15.17	9343421	94.6711	ug/ml	95
9	C18:0	16.95	9837831	94.8601	ug/ml	98
10	C18:1	17.118	2335660	95.3215	ug/ml	1
11	C18:2	17.519	2404522	95.1572	ug/ml	92
12	C20:0	18.609	10054762	94.473	ug/ml	98
13	C22:0	20.316	10430434	94.5139	ug/ml	96
14	C24:0	22.713	10636038	94.3824	ug/ml	78

Figure S4.1 Chromatogram and calibration data obtained through GC-MSD



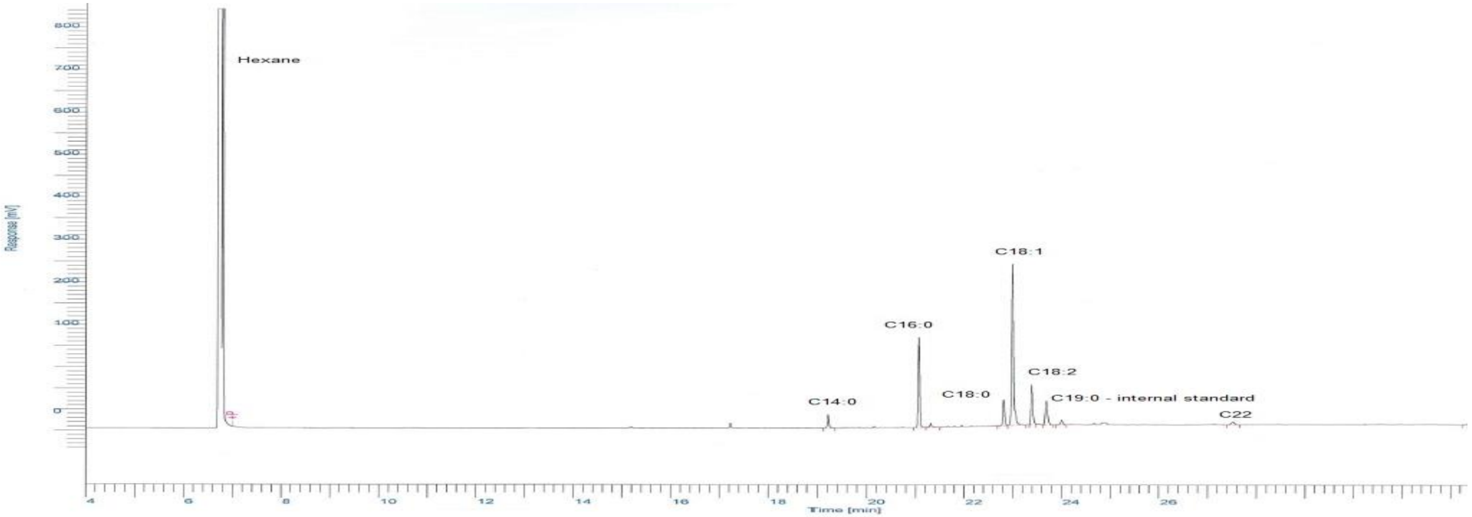
Component	Compound Name	RT (min)	Area	Amount	Units
2	C4:0	4.12	2947657	107.515	ug/ml
3	C6:0	6.13	3721259	107.785	ug/ml
4	C8:0	8.56	5088021	107.735	ug/ml
5	C10:0	10.94	6205800	106.891	ug/ml
6	C12:0	13.15	7145566	106.352	ug/ml
7	C14:0	15.18	7155940	106.722	ug/ml
8	C16:0	17.05	8484806	106.553	ug/ml
9	C18:0	18.79	8900709	106.37	ug/ml
10	C18:1	18.97	2091634	105.798	ug/ml
11	C18:2	19.37	2161173	106.002	ug/ml
12	C20:0	19.70	9175437	106.85	ug/ml
13	C22:0	20.61	9509639	106.8	ug/ml
14	C24:0	23.10	9725404	106.962	ug/ml

Figure S4.2 Chromatogram and calibration data obtained through GC-FID



Component	Compound Name	RT (min)	Area	Amount	Units	Q-value
2	C4:0	2.36	8215	0.29	ug/ml	97
3	C6:0	4.067	91966	2.61	ug/ml	96
4	C8:0	6.44	124787	2.59	ug/ml	100
5	C10:0	8.869	254920	4.31	ug/ml	99
6	C12:0	11.146	772664	11.28	ug/ml	100
7	C14:0	13.238	2196672	32.13	ug/ml	96
8	C16:0	15.17	13023621	160.40	ug/ml	96
9	C18:0	16.95	4984311	58.42	ug/ml	100
10	C18:1	17.118	5471291	271.41	ug/ml	1
11	C18:2	17.511	3110215	149.61	ug/ml	92
12	C20:0	18.609	3089542	97.81	ug/ml	78
13	C22:0	20.316	397545	4.54	ug/ml	95
14	C24:0	22.713	275705	3.04	ug/ml	85

Figure S4.3 Fatty acid profiles of FAEE sample analysed by GC-MSD



Component	Compound Name	RT (min)	Area	Amount	Units
2	C4:0	4.12	75413	0	ug/ml
3	C6:0	6.13	70384	0	ug/ml
4	C8:0	8.56	88556	0	ug/ml
5	C10:0	10.94	95880	0	ug/ml
6	C12:0	13.15	11936	13.8	ug/ml
7	C14:0	15.18	39321	36.7	ug/ml
8	C16:0	17.05	193765	173.6	ug/ml
9	C18:0	18.79	101368	62.9	ug/ml
10	C18:1	18.97	348959	281.7	ug/ml
11	C18:2	19.37	193231	154.5	ug/ml
12	C20:0	19.70	163181	100.2	ug/ml
13	C22:0	20.61	145859	0	ug/ml
14	C24:0	23.10	151428	0	ug/ml

Figure S4.4 Fatty acid profiles of FAEE sample analyzed by GC-FID

Statement of Authorship

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Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	28/02/2018

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate’s stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate’s stated contribution.

Name of Co-Author	Edward J McMurchie		
Contribution to the Paper	Conception design, manuscript review and correction		
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Contribution to the Paper	Supervising the development of the work and approving		
Signature		Date	28/02/2018

Chapter 5. The Pre-treatment of High Free Fatty Acid Feedstock

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Abstract

Grease trap waste (GTW) often has a very high content of free fatty acids (FFA) which requires a pre-treatment step before it can be converted to biodiesel via the transesterification reaction. In this study, the esterification reaction was performed to reduce the level of FFA in the GTW, utilizing ethanol as the reagent in the presence of the catalyst H_2SO_4. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied to determine the optimal conditions for the esterification reaction through four process variables, these being: the molar ratio of ethanol to fats, oils, and grease (FOG), reaction time, reaction temperature, and catalyst loading. A set of 30 experiments were conducted in triplicate to study the interactive effects of the above variables on the reduction of the level of FFAs. An FFA% of 0.84% was obtained at the optimum conditions, which were 6:1 ethanol to FOG molar ratio, 3 hr reaction time, 75°C reaction temperature, and 3 wt% H_2SO_4 loading per FOG weight.

Keywords: *grease trap waste; pre-treatment; esterification; RSM; biodiesel*

5.1 Introduction

While energy plays a vital role in many sectors, such as industry and transportation, the worldwide demand for energy is increasing rapidly, resulting in the diminishment of the fossil resources. Furthermore, the burning of fossil fuels also raises concerns in terms of increasing carbon dioxide emission, which underpin climate change.

This has encouraged research into the development of more renewable and sustainable fuels to substitute for mineral fuels. Among these potential fuels, biodiesel has attracted considerable interest due to its biodegradation, lower environmental impact, and its ability to be used without modification of existing conventional diesel engines [1-3].

Australia is one of the top ten energy producers and is among the greatest consumers of non-renewable energy resources [4]. According to a recent report, more than 90% of the total energy consumption by Australia was produced from fossil resources, while biofuels only accounted for around 3.3% [5]. In 2015, 130 million liters of biodiesel was produced domestically, making up only 1.5% of the total renewable energy consumption [5]. In Australia, biodiesel has been traditionally produced from animal fats (e.g. beef tallow) and waste cooking oil [6-8]. Recently, the rapid rise in the cost of such feedstocks, coupled with the unfavorable conditions of limited mandate support, low international oil prices, and insufficient tax relief to offset high feedstock prices to bridge the gap between mineral diesel prices and biodiesel have forced the biodiesel producers to search for cheaper and more sustainable feedstocks. In October 2016, one of the largest biodiesel production plant in South Australia was closed as a consequence of economic inefficiency, causing a significant drop in the annual consumption of biodiesel [5]. Therefore, searching for a more sustainable and cost-effective feedstock is becoming an imperative. Among those, grease trap waste (GTW), which is collected from the interceptors installed in the sewage system of restaurants and food processing factories, appears to be a potential feedstock since it possesses a very high lipid content which can potentially be used as a feedstock for biodiesel production. In 2015, more than 500,000 tons of GTW was collected national wide in Australia, making it the third highest hazardous waste resource and consequently requiring a costly treatment process before remediation [9].

In Adelaide, the capital city of South Australia, Peats Soil and Garden Supplies Pty. Ltd., one of the major GTW collectors, reported that their company collected annually approximately 10 million liters of GTW essentially free of charge [10]. This represents around 40% of the total GTW generated annually in South Australia, resulting in an estimated total GTW generation of 25 million liters per year in this region. Significantly, this amount is predicted to increase significantly in the upcoming years due to the growth of the population and the increase in industrial activities, resulting in a greater burden for wastewater treatment plants. While the cost of GTW is essentially free of charge, there are associated costs in terms of its collection and transportation. Peats Soil and Garden Supplies Pty. Ltd. expect that the use of GTW as a feedstock for biodiesel production can partially cover the cost of GTW collection and transportation. Importantly, this can open up an opportunity for such environmental service providers to participate in the biodiesel market as the producers.

However, production of biodiesel from GTW is technically challenging due to the very high content of free fatty acids (FFA) found in the feedstock [11-14]. Since FFA can consequently react with the base catalyst to form soap in the transesterification process, the feedstock needs to be pre-treated to achieve an FFA% < 2% before further treatment can be undertaken [12, 15]. There are currently two main techniques applied for the treatment of high FFA feedstocks: (1) esterification, and (2) glycerolysis [12, 15, 16]. While glycerolysis, a reaction in which FFAs are converted to glycerides in the presence of glycerine as a reactant, has been reported to be effective for the treatment of high FFA feedstock, it was criticized in terms of the total energy consumption, as well as process safety due to the requirement of a very high reaction temperature [17-20]. Previous studies have reported that the FFA% could be reduced via the esterification process in which FFAs react with an alcohol in the presence of an acid catalyst to form alkyl esters (biodiesel) [12, 21-23]. Karnasuta et al. [24] reported that the FFA% in trap grease (26.2 FFA%, 846 g/mol molecular weight) can be reduced to less than 2% via acid-catalyzed esterification. The optimum FFA% obtained was 1.3% at 60ºC, 0.43 methanol to oil volume ratio, 2.5% v/v sulphuric acid and 4 hours reaction time. Chai et al. [25] conducted a study to optimize the process parameters for the esterification of vegetable oil with 5% FFA. They found that the methanol-to-FFA molar ratio and sulfuric acid usage should be 40:1 and 10%, respectively. Those parameters worked well with the FFA range of 5%, while the authors reported that the other conditions (19.8:1 methanol-to FFA molar ratio, 5% sulfuric acid) suggested by National Renewable Energy Laboratory (NREL) were not optimized and could only work well with the FFA range of 15-35%. However, the relatively high molar ratio of methanol to FFA (40:1) and sulfuric acid amount (10%) may lead to a costly biodiesel production process. Other high FFA feedstocks, such as animal fat wastes, were also reported in the literature review [26]. In most cases, a two-step trans/esterification process was recommended for the production of biodiesel from feedstocks with high FFA level. In terms of the catalyst, both homogeneous and heterogeneous acids were investigated for the esterification of feedstocks containing high acid contents. Solid acid catalysts (mesoporous silicas, heteropolyacids, acidic polymers and resins, waste carbon-derived solid acids, etc.) appeared to be less sensitive to FFA contaminants, although they possess a poorer activity in comparison to homogeneous acids [27]. However, due to the relatively expensive cost of the solid catalysts, cheaper homogeneous acids (i.e. sulfuric acid) are economically preferred. Dias et al. [28] suggested that a biodiesel purity up to 96.5% could be obtained if the H_2SO_4 concentration was increased from 1 to 3 wt%.

Although several studies have investigated the potential of wastewater feedstocks, the present study investigated the pre-treatment of GTW collected in Adelaide since the composition of GTW varied depending on the location, the season, and the manner by which it is collected. For this purpose, Response Surface Methodology (RSM) has been reported to be a powerful computing tool to optimize the process parameters associated with a particular chemical reaction [29-33]. Furthermore, RSM is effective with multivariable systems, offering an opportunity to study the interactive effects of the process parameters. An additional factor under consideration is the nature of the alcohol used. Methanol, as a reagent for biodiesel synthesis, is very toxic and is a concern in terms of health, safety, and wellbeing. The decision to replace methanol with ethanol is the report that ethanol is an effective reagent in some of the production processes [34-37]. Importantly, Peats Soil and Garden Supplies Pty. Ltd. intend producing ethanol from non-edible plants (e.g. sorghum) cultivated on their waste treatment land utilizing the GTW residues as fertilizer. This will make biodiesel a greener product, while their environmental services will offer the potential to become a self-contained biodiesel producer.

Therefore, the aim of this study is to investigate the pre-treatment of GTW-derived feedstock via an esterification reaction to meet the demand of an environmental service. A total of 30 experiments were designed using Design-Expert Software Version 6.0.8 with five levels and three factors to study the interaction effects of parameters on the response factor. A response surface method based on central composite design was employed to minimize the FFA% in the feedstock, resulting in optimum conditions.

5.2 Experimental Section

5.2.1 Materials

The raw GTW used in this study were provided by Peats Soil and Garden Supplies Pty. Ltd. The composition of GTW consists of water, lipids, soap and other solid organic and inorganic contaminants. The provided GTW was collected from a floating grease layer in a storage tank in which the lipid content had been concentrated to about 51.1%.

For the extraction process, FOG was extracted from GTW using a mixture of n-hexane and diethyl ether. 500 g GTW was mixed with 500 mL n-hexane and diethyl ether (1:1, v/v) in a glass vessel equipped with a mechanical stirrer. The extraction process was performed at ambient temperature (25°C) for 2 hours. The mixture was then centrifuged at 1200g for 5 min to separate the organic phase from water and the impurities. The solvent was then removed via a rotary evaporator before the FOG was vacuum-filtered to discard any remaining solids. FOG was finally analyzed for FFA profiles and acid number via GC-FID and KOH titration, respectively.

5.2.2 Characterization of FOG

The extracted FOG was analyzed for FFA value, density, moisture and glyceride content following the analytical method described by the American Oil Chemists Society (AOCS) [47] and the American Society for Testing and Materials (ASTM) [48].

5.2.3 Experimental Procedure

The experiments were conducted in a 100 mL capped-glass vessel equipped with a magnetic stirrer using a hot plate. 34.5 g FOG (approximately 0.1 mol based on lipid composition) was put into the vessel before ethanol, in a molar ratio defined by the experimental design, and sulphuric acid was added. The amount of sulphuric acid was calculated based on the weight of FOG and was specified in the experimental design section. The temperature ranged from 55ºC to 75ºC, while the reaction time varied from 1 to 5 hours. Following the completion, the mixture was allowed to settle for 1 hour, resulting in two separated liquid phases. The glycerol in the bottom phase was removed via a separating funnel, while the upper phase was washed with water at 50ºC until a clear, colorless water layer was observed. The wastewater stream was then subjected to a rotary evaporator to recover the excess ethanol, while the acidic water was neutralized using a KOH solution. The esterification product was afterward heated at 110ºC to remove the remaining water and ethanol. Finally, the product was weighed, the acid number was examined via titration, and the Free Fatty Acid Ethyl Esters (FAAEs) profiles were analyzed by gas chromatography using a flame ionization detector (GC-FID).

5.2.4 Experimental Design

To examine the effect of process variables on the reduction of the FFA%, four variables were assessed at five levels using response surface methodology based on central composite design. The designed parameters, which are reaction temperature (X_1), ethanol to FOG molar ratio (X_2), reaction time (X_3) and H_2SO_4 loading (X_4), were examined against the response factor, FFA%. The coded and uncoded levels of the independent variables are presented in **Table 5.1**. A set of 30 experiments were conducted in triplicate. The reduction of the FFA% in the feedstock was estimated from the selected independent parameters using a second order polynomial as in equation (1):

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{i-1} \beta_{ij} x_i x_j \tag{1}$$

where Y is the predicted value of FFA% and β_i and β_{ij} are the model coefficients.

Table 5.1 The coded and uncoded variables of experimental design

		Levels				
Independent variables	**Coded Variables**	-α (2)	-1	0	+1	+α (2)
Reaction temperature, ºC	X_1	55	60	65	70	75
Ethanol to FOG molar ratio	X_2	3:1	4.5:1	6:1	7.5:1	9:1
Reaction time, hour	X_3	1	2	3	4	5
H_2SO_4 loading, wt% in FOG	X_4	1	3	5	7	9

5.2.5 *Analysis Methods*

The efficiency of the esterification reaction as a pre-treatment step for GTW-derived biodiesel production was investigated via the reduction of the FFA% in the treated feedstock. The acid number was determined following the ASTM D-664 standard. 1 g of the treated FOG was put in a glass flask and then dissolved in 50 mL of a solvent mixture (1:1 v/v ethanol to diethyl ether). The FOG sample was titrated against 0.1N KOH to the endpoint of the indicator (phenolphthalein). The acid number (AN) was calculated using the following formula:

$$AN = (a - b) \times N \times 56.1 / w \qquad (2)$$

where a is the volume of KOH solution used for the sample titration [mL], b is the volume of KOH solution used for the blank titration [mL], N is the exact normality of KOH, and w is the amount of the FOG sample [g].

Free fatty acid level (FFA %) was calculated based on the percentage of oleic acid via dividing the obtained acid number by 1.99.

$$FFA\% = AN/1.99 \qquad (3)$$

Free fatty acid ethyl ester profiles were measured using a Perkin-Elmer Clarus 500 GC-FID instrument equipped with a BP-20 SGE forte column (30 m x 0.32 mm x 0.25 μm; SGE Forte^{TM}, Australia) and an auto-sampler. The oven was initially started at 60ºC for 1 min, increased to 240ºC at a rate of 10ºC/min and was then held for 12 min. Ethyl nonadecanoate (C19:0) was used as the internal standard. The fatty acid ethyl esters content was calculated using equation (4).

$$C = \frac{\sum A\text{-}A_{SI}}{A_{SI}} \times \frac{C_{SI} \times V_{SI}}{m} \times 100 \qquad (4)$$

where C is the FAEEs content [wt%], $\sum A$ is the total peak area of the ethyl esters, A_{SI} is the peak area of ethyl nonadecanoate, C_{SI} is the concentration of ethyl nonadecanoate solution [mg/mL], V_{SI} = the volume of ethyl nonadecanoate solution [mL], and m is the weight of the sample [g].

5.3 Results and Discussion

5.3.1 Characterisation of GTW and Extracted FOG

Characterisation of GTW and its extracted oil are reported in **Table 5.2**. The FFA content of GTW and FOG are 36.4% and 81% respectively. These numbers are relatively high in comparison to the conventional feedstocks such as vegetable oils, animal fats, and waste cooking oil [35, 38, 39]. Surprisingly, the FOG extracted from GTW collected in Adelaide has a similar composition to the one collected in Philadelphia (USA) reported by Ngo et al. [40], but is different from the ones collected in Guangzhou (China) reported by Lu et al. [41], and Park et al. [42].

Table 5.2 Composition of GTW and the extracted FOG

Composition, (%)	**GTW**	**FOG**
FFA content	36.4	81
Monoglycerides	6.0	7.9
Diglycerides	3.1	4.7
Triglycerides	5.6	4.4
Water content	42.3	0.1
Residual	6.6	1.9

The FFA profiles of the extracted grease trap oil (FOG) were then determined by GC-FID and are shown in **Table 5.3**. Oleic acid is the predominant component of FOG, accounting for approximately 50% of the total fatty acids. Palmitic acid and linoleic acid accounted for 30% and 13% of the total, respectively. The unsaturated FFAs represent more than 60% of the total fatty acid composition which may have a significant effect on the physical properties of fuels prepared from GTW extracts [43].

Table 5.3 Fatty acid profiles of the extracted FOG

Component	**Amount (wt%)**
Palmitic acid (C16:0)	21.9
Stearic acid (C18:0)	7.4
Oleic acid (C18:1)	47.6
Linoleic acid (C18:2)	13
Other fatty acids	10.1
Average molecular weight (g/mol)	345.5

5.3.2 Esterification Reaction Results and Analysis

Statistical analysis of response surface methodology

Based on the experimental design specified in **Table 5.1** in the experimental section, a set of 30 experiments were carried out in triplicate for all of the designed points. The experiments were set up in randomized order and the results are presented in **Table 5.4**, in which the FFA was set as the response. The FFA% obtained varied from 0.84 to 11.56% depending on the particular process parameters. An FFA% of 0.84% was observed at the optimum conditions, which were: 6:1 ethanol to oil molar ratio, 3 hr reaction time, 75°C reaction temperature, and 3 wt% acid catalyst loading. This surpasses the studies conducted by Canakci and Van Gerpen [44] and Karnasuta et al. [24] in relation to reducing the FFA% while using a lower temperature, reaction time, and catalyst loading. This can be likely explained by the use of ethanol as a reactant for the esterification process. In the case of methanolysis, the solubility of oil in methanol is less, causing a limitation in mass transfer [45, 46].

Table 5.4 Experimental parameter setup and results

Run	**Temperature (°C)**	**Reaction time (hr)**	**Ethanol to FOG molar**	**H_2SO_4 loading (wt%)**	**FFA%**	
					Obtained	**Predicted**
1	65.00	3.00	6.00	3.00	3.57	3.40
2	70.00	4.00	7.50	4.00	1.93	2.47
3	60.00	4.00	7.50	2.00	5.92	5.97
4	65.00	1.00	6.00	3.00	5.63	6.07
5	65.00	3.00	6.00	3.00	3.10	3.40
6	60.00	2.00	4.50	4.00	6.20	6.10
7	65.00	3.00	6.00	3.00	3.10	3.40
8	70.00	2.00	7.50	4.00	1.97	1.48
9	70.00	4.00	4.50	4.00	1.95	2.17
10	60.00	2.00	7.50	4.00	2.30	2.43
11	65.00	3.00	6.00	3.00	3.45	3.40
12	60.00	4.00	4.50	2.00	6.42	6.89
13	65.00	5.00	6.00	3.00	3.66	3.27
14	70.00	2.00	4.50	2.00	7.23	7.77
15	65.00	3.00	9.00	3.00	1.97	2.14
16	55.00	3.00	6.00	3.00	3.35	3.80
17	**75.00**	**3.00**	**6.00**	**3.00**	**0.84**	**0.44**[a]
18	60.00	2.00	4.50	2.00	11.25	10.68
19	70.00	4.00	7.50	2.00	4.00	4.28
20	65.00	3.00	6.00	3.00	3.52	3.40
21	60.00	4.00	7.50	4.00	3.38	2.92
22	65.00	3.00	6.00	5.00	4.79	5.00
23	65.00	3.00	6.00	1.00	11.56	11.40
24	70.00	2.00	7.50	2.00	4.23	4.33
25	70.00	2.00	4.50	4.00	4.51	4.43
26	60.00	2.00	7.50	2.00	6.76	6.52
27	70.00	4.00	4.50	2.00	4.53	4.47
28	60.00	4.00	4.50	4.00	3.48	3.35
29	65.00	3.00	6.00	3.00	3.66	3.40
30	65.00	3.00	3.00	3.00	6.32	6.00

[a] The lowest and predicted FFA% are shown in bold

Analysis of variance (ANOVA) was then performed to obtain a polynomial equation and related coefficients. The reduction in FFA% can be estimated by applying the following equation:

$$FFA\% = 3.33 - 0.77X_1 - 0.64X_2 - 0.86X_3 - 1.57X_4 - 0.33X_1^2 + 0.31X_2^2 + 0.13X_3^2 + 1.19X_4^2 - 0.038X_1X_2 + 0.060X_1X_3 + 0.35X_1X_4 + 0.71X_2X_3 + 0.28X_2X_4 + 0.10X_3X_4 \quad (5)$$

where X_1, X_2, X_3, and X_4 were the coded variables defined in the experimental design as previously shown in **Table 5.1**.The coefficient with one factor reveals the effect of that specific factor on the response, while the coefficient with two factors or with factors in 2nd order form represents the interaction between those two factors. Positive or negative (+/-) symbols indicate the synergistic and antagonistic effects respectively [30]. **Table 5.5** displays the variation of the data obtained via the ANOVA analysis.

Table 5.5 ANOVA applied to the quadratic model

Source	**Sum of Squares**	**df**	**Mean square**	**F value**	**p-Value prob>F**
Model	174.09	14	12.43	67.46	< 0.0001
A (X_1)	16.97	1	16.97	92.05	< 0.0001
B (X_2)	11.73	1	11.73	63.64	< 0.0001
C (X_3)	22.39	1	22.39	121.45	< 0.0001
D (X_4)	61.31	1	61.31	332.60	< 0.0001
A2	2.81	1	2.81	15.22	0.0014
B2	2.77	1	2.77	15.02	0.0015
C2	0.77	1	0.77	4.18	0.0587
D2	39.51	1	39.51	214.34	< 0.0001
AB	0.25	1	0.25	1.33	0.2670
AC	0.53	1	0.53	2.85	0.1120
AD	1.54	1	1.54	8.34	0.0113
BC	10.53	1	10.53	57.12	< 0.0001
BD	1.08	1	1.08	5.87	0.0286
CD	0.24	1	0.24	1.30	0.2717
Residual	2.77	15	0.18		
Lack of Fit	2.47	10	0.25	4.21	0.0630 *not significant*
Pure Error	0.29	5	0.059		
Cor Total	176.85	29			

R^2: 0.98; adj R^2: 0.96; pred R^2: 0.91; adeq precision: 36.10; C.V: 9.56

As shown in **Table 5.5**, the model is statically significant with all four factors having an effect on the response factor (p-Value < 0.1). A relatively high value for the correlation coefficient ($R^2 = 0.98$) indicates that the obtained model is capable of explaining the effect of the parameters and their interaction on the reduction of the FFA%. The validity of the model was again supported by high values of adj R^2 and pred R^2 achieved, 0.96 and 0.91, respectively. The lack of fit value is only 0.063, which indicates that it is not significant. **Figure 5.1** shows the linear correlation plots between the observed and the predicted response variables. The convergence of the data verifies that equation (5) is a valid model to estimate the effect of the related factors on the response.

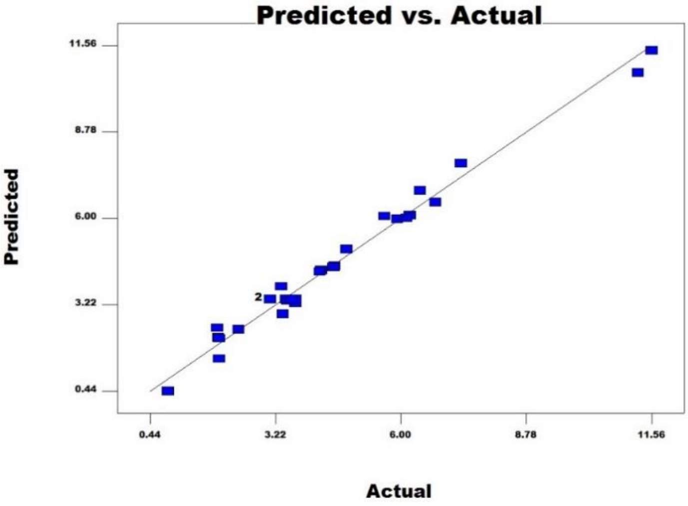

Figure 5.1 Actual yield vs. predicted yield

Figure 5.2 shows the interaction effects of the designed variables on the response. Each plot performs the interaction effects of two specific factors on the reduction of the FFA% as the response, while the other variables were maintained at a constant value. The interaction between the reaction time and the reaction temperature is represented in plot 5.2A. With 6:1 ethanol to FOG molar ratio and 3 wt% H_2SO_4 loading, the FFA% is reduced by increasing both of these factors. Plot 5.2B indicates the reverse effect of ethanol to FOG molar ratio and the reaction temperature on the response obtained with 3 wt% acid loading and 3 hour reaction time. In general, the FFA% falls gradually by increasing both these parameters. The interaction between the acid loading and the reaction temperature is shown in plot 5.2C. With ethanol to FOG molar ratio 6:1 and 3 hr reaction time, this interaction has a significant effect on the FFA%. Increasing both factors resulted in a significant decrease in the FFA content.

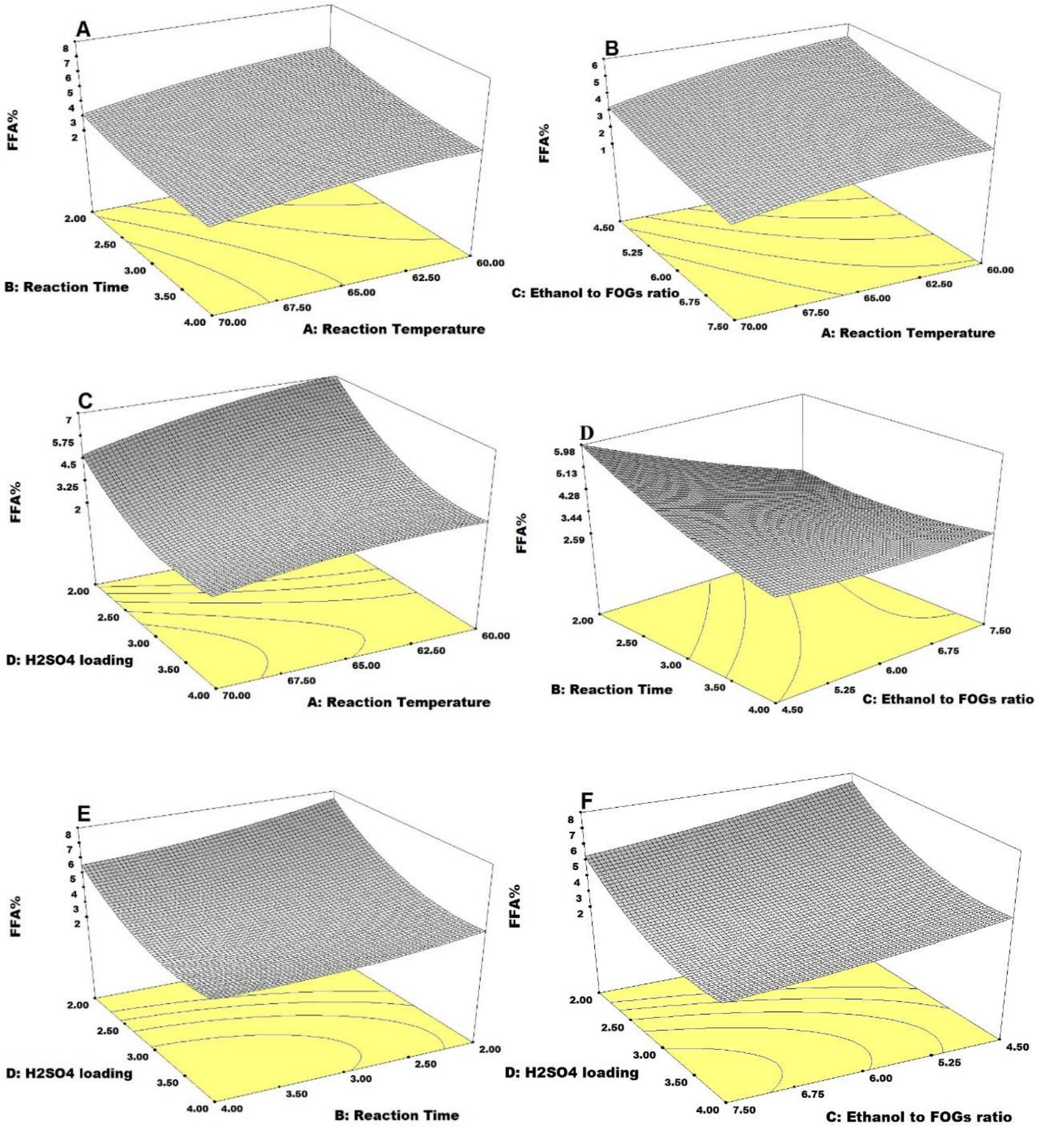

Figure 5.2 Interactive effect of variables on the free fatty acid level

Plot 5.2D shows the combined effect of the reaction time and the ethanol to FOG molar ratio (at 65ºC, 3 wt% H_2SO_4). The FFA% decreases moderately following the increase reaction time and ethanol amount. However, after a 4-hour reaction, the increase of ethanol amount has little impact on the response factor. Plot 5.2E shows the interaction between the acid loading and the reaction time (at 65ºC, 6:1 ethanol to FOG molar ratio), while Plot 5.2F shows the combined effect between the catalyst loading and the ethanol to FOG molar ratio (at 65ºC, 3 hr). Interestingly, catalyst loading has a similar interaction effect with both the reaction time and the ethanol to FOG ratio. Using higher an amount of catalyst resulted in the reduction of the FFA%.

5.3.3 Characterisation of Biodiesel

In order to prepare for the transesterification reaction, the quality of crude biodiesel obtained through the esterification pre-treatment was investigated. **Table 5.6** shows various physio-chemical properties of the biodiesel obtained at the optimum conditions.

Table 5.6 Physio-chemical properties of crude biodiesel

Properties	**Units**	**Crude biodiesel**	**Biodiesel standards**	
			ASTM 6751	**EN 14214**
Density (at 15ºC)	kg/m^3	870*	870 - 900	860 - 900
Kinetic viscosity (at 40ºC)	cSt	6.8*	1.9 – 6.0	3.5 – 5.0
Flash point	ºC	120*	93 min	101 min
Acid value	mg KOH/g	17.1	0.8 max	0.5 max
Ester content	%	80.2	-	96.5 min
Sulphur content	ppm	273*	15	10

[*] Results provided by Advanced Biofuels Laboratory, Northern Oil Refinery, Australia

The results obtained show that the crude biodiesel does not satisfy the ASTM and EN 14214 standards in terms of viscosity, acid value, ester content, and sulphur content. It may likely be the result of there being a significant amount of glycerides remaining in the composition of the produced biodiesel. Therefore, a further transesterification and a final purification process need to be conducted to produce a GTW-derived biodiesel that meets the mandatory Biodiesel Standards.

5.4 Conclusion

In this study, the esterification of the extracted oil from GTW collected in Adelaide, South Australia, was investigated. Response surface methodology based on central composite design was applied to study the interaction effects of the process parameters on the reduction of FFA% in the feedstock, resulting in optimum conditions, which were 6:1 ethanol to oil molar ratio, 3 hr reaction time, 75ºC reaction temperature, and 3 wt% H_2SO_4 loading per FOG weight. The quality of the obtained crude biodiesel was also examined against the ASTM D6751 and EN 14214 standards. Results showed that further treatments would need to be carried out to produce a GTW-derived biodiesel fuel that meets mandatory standards.

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References

[1] Van Gerpen J. Biodiesel processing and production. Fuel processing technology. 2005;86:1097-107.

[2] Canakci M, Sanli H. Biodiesel production from various feedstocks and their effects on the fuel properties. Journal of Industrial Microbiology & Biotechnology. 2008;35:431-41.

[3] Murugesan A, Umarani C, Chinnusamy TR, Krishnan M, Subramanian R, Neduzchezhain N. Production and analysis of bio-diesel from non-edible oils—A review. Renewable and Sustainable Energy Reviews. 2009;13:825-34.

[4] Azad A, Khan M, Ahasan T, Ahmed S. Energy scenario: production, consumption and prospect of renewable energy in Australia. Journal of Power and Energy Engineering. 2014;2:19.

[5] Roger F. Australian Biofuels Annual 2017. USDA Foreign Agricutural Service, Canberra, Australia 2017.

[6] Council AE. Renewable Energy in Australia. How do we really compare. Victoria, Australia Australian Energy Council; 2016.

[7] Azad AK, Rasul M, Khan MMK, Sharma SC, Hazrat M. Prospect of biofuels as an alternative transport fuel in Australia. Renewable and Sustainable Energy Reviews. 2015;43:331-51.

[8] Banković-Ilić IB, Stojković IJ, Stamenković OS, Veljkovic VB, Hung Y-T. Waste animal fats as feedstocks for biodiesel production. Renewable and Sustainable Energy Reviews. 2014;32:238-54.

[9] Latimer G. Hazardous Waste in Australia 2017. Victoria, Australia2017.

[10] Tran NN, Ho QP, Tran PC, Chao L, Curran P, McMurchie JE, et al. Optimization of the production of biodiesel from grease trap waste (GTW). Chemeca 2016: Chemical Engineering-Regeneration, Recovery and Reinvention. 2016:1128.

[11] Nitayapat N, Chitprasert P. Characterisation of FOGs in grease trap waste from the processing of chickens in Thailand. Waste Management. 2014;34:1012-7.

[12] Tafesh A, Basheer S. Pretreatment methods in biodiesel production processes. Pretreatment Techniques for Biofuels and Biorefineries: Springer; 2013. p. 417-34.

[13] Hasuntree P, Toomthong V, Yoschoch S, Thawornchaisit U. The potential of restaurant trap grease as biodiesel feedstock. Songklanakarin Journal of Science & Technology. 2011;33:525-30.

[14] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Applied Energy. 2010;87:3155-61.

[15] Tu Q, Lu M, Knothe G. Glycerolysis with crude glycerin as an alternative pretreatment for biodiesel production from grease trap waste: Parametric study and energy analysis. Journal of Cleaner Production. 2017;162:504-11.

[16] Olkiewicz M, Fortuny A, Stüber F, Fabregat A, Font J, Bengoa C. Effects of pre-treatments on the lipid extraction and biodiesel production from municipal WWTP sludge. Fuel. 2015;141:250-7.

[17] Vitiello R, Li C, Russo V, Tesser R, Turco R, Di Serio M. Catalysis for esterification reactions: a key step in the biodiesel production from waste oils. Rendiconti Lincei. 2017;28:117-23.

[18] Anderson E, Addy M, Xie Q, Ma H, Liu Y, Cheng Y, et al. Glycerin esterification of scum derived free fatty acids for biodiesel production. Bioresource Technology. 2016;200:153-60.

[19] Nguyen N, Demirel Y. Economic analysis of biodiesel and glycerol carbonate production plant by glycerolysis. Journal of Sustainable Bioenergy Systems. 2013;3:209.

[20] Echeverri DA, Cardeño F, Rios LA. Glycerolysis of crude methyl esters with crude glycerol from biodiesel production. Journal of the American Oil Chemists' Society. 2013;90:1041-7.

[21] Mansir N, Taufiq-Yap YH, Rashid U, Lokman IM. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. Energy Conversion and Management. 2017;141:171-82.

[22] Oliveira J, Antunes P, Mordente T, Santos A, Pinotti L, Cassini S. Biodiesel production from scum of grease traps and sludge from septic tanks. Clean Technologies and Environmental Policy. 2017;19:1231-7.

[23] Ragauskas AME, Pu Y, Ragauskas AJ. Biodiesel from grease interceptor to gas tank. Energy Science & Engineering. 2013;1:42-52.

[24] Karnasuta S, Punsuvon V, Chiemchaisri C, Chunkao K. Optimization of biodiesel production from trap grease via two-step catalyzed process. Asian J Energy Environ. 2007;8:145-68.

[25] Chai M, Tu Q, Lu M, Yang YJ. Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. Fuel processing technology. 2014;125:106-13.

[26] Chakraborty R, Gupta AK, Chowdhury R. Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. Renewable and Sustainable Energy Reviews. 2014;29:120-34.

[27] Lee AF, Bennett JA, Manayil JC, Wilson K. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. Chemical Society Reviews. 2014;43:7887-916.

[28] Dias JM, Alvim-Ferraz MC, Almeida MF. Production of biodiesel from acid waste lard. Bioresource technology. 2009;100:6355-61.

[29] Mohamad M, Ngadi N, Wong S, Jusoh M, Yahya N. Prediction of biodiesel yield during transesterification process using response surface methodology. Fuel. 2017;190:104-12.

[30] Yatish K, Lalithamba H, Suresh R, Arun S, Kumar PV. Optimization of scum oil biodiesel production by using response surface methodology. Process Safety and Environmental Protection. 2016;102:667-72.

[31] Hamze H, Akia M, Yazdani F. Optimization of biodiesel production from the waste cooking oil using response surface methodology. Process Safety and Environmental Protection. 2015;94:1-10.

[32] Awad S, Paraschiv M, Varuvel EG, Tazerout M. Optimization of biodiesel production from animal fat residue in wastewater using response surface methodology. Bioresource Technology. 2013;129:315-20.

[33] Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escaleira LA. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta. 2008;76:965-77.

[34] Zenevicz MCP, Jacques A, de Oliveira D, Furigo A, Valério A, Oliveira JV. A two-step enzymatic strategy to produce ethyl esters using frying oil as substrate. Industrial Crops and Products. 2017;108:52-5.

[35] Almeida TA, Rodrigues IA, Estrela TS, Nunes CNF, Machado LL, Leão KV, et al. Synthesis of ethyl biodiesel from soybean oil, frying oil and chicken fat, using catalysts based on vanadium pentoxide. Energy. 2016;97:528-33.

[36] Cunha A, Feddern V, De Prá MC, Higarashi MM, de Abreu PG, Coldebella A. Synthesis and characterization of ethylic biodiesel from animal fat wastes. Fuel. 2013;105:228-34.

[37] Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies. 2009;2:362-76.

[38] Alptekin E, Canakci M, Sanli H. Biodiesel production from vegetable oil and waste animal fats in a pilot plant. Waste Management. 2014;34:2146-54.

[39] Talebian-Kiakalaieh A, Amin NAS, Zarei A, Noshadi I. Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: Optimization and kinetic model. Applied Energy. 2013;102:283-92.

[40] Ngo HL, Xie Z, Kasprzyk S, Haas M, Lin W. Catalytic synthesis of fatty acid methyl esters from extremely low quality greases. Journal of the American Oil Chemists' Society. 2011;88:1417-24.

[41] Lu P, Yuan Z, Li L, Wang Z, Luo W. Biodiesel from different oil using fixed-bed and plug-flow reactors. Renewable Energy: An International Journal. 2010;35:283-7.

[42] Park J-Y, Lee J-S, Wang Z-M, Kim D-K. Production and characterization of biodiesel from trap grease. Korean Journal of Chemical Engineering. 2010;27:1791-5.

[43] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Processing Technology. 2005;86:1059-70.

[44] Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Transactions of the ASAE. 2001;44:1429.

[45] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Processing Technology. 2007;88:429-36.

[46] Santori G, Di Nicola G, Moglie M, Polonara F. A review analyzing the industrial biodiesel production practice starting from vegetable oil refining. Applied energy. 2012;92:109-32.

[47] AOCS A. official method Ca 5a-40: free fatty acids. Official Methods and Recommended Practices of the AOCS (5th ed), American Oil Chemists' Society Press, Champaign, IL. 1997.

[48] ASTM E. Annual Book of ASTM, Section 5 Petroleum Products, Lubricants and Fossil Fuels. West Conshohocken, PA, USA: American Society for Testing and Materials; 2001.

Supporting Data

Table S5.1 Raw data obtained through the experiments based on central composite design

ID	**Run**	**Temp (ºC)**	**Time (min)**	**EtOH to oil molar ratio**	**H_2SO_4 (wt%)**	**Weight of sample (g)**	**Average volume of 0.1 N KOH (mL)**	**Acid Number**	**FFA%**
M1	1	65	180	6	3.00	1.01	1.28	7.10	3.57
M2	2	70	240	7.5	4.00	1.02	0.70	3.84	1.93
M3	3	60	240	7.5	2.00	1.00	2.10	11.78	5.92
M4	4	65	60	6	3.00	1.00	2.00	11.20	5.63
M5	5	65	180	6	3.00	1.00	1.10	6.17	3.10
M6	6	60	120	4.5	4.00	1.00	2.20	12.34	6.20
M7	7	65	180	6	3.00	1.00	1.10	6.17	3.10
M8	8	70	120	7.5	4.00	1.00	0.70	3.92	1.97
M9	9	70	240	4.5	4.00	1.01	0.70	3.88	1.95
M10	10	60	120	7.5	4.00	1.00	0.85	4.78	2.40
M11	11	65	180	6	3.00	1.00	1.22	6.87	3.45
M12	12	60	240	4.5	2.00	1.01	2.30	12.78	6.42
M13	13	65	300	6	3.00	1.00	1.30	7.28	3.66
M14	14	70	120	4.5	2.00	1.00	2.60	14.59	7.33
M15	15	65	180	9	3.00	1.00	0.70	3.92	1.97
M16	16	55	180	6	3.00	1.01	1.20	6.67	3.35
M17	17	75	180	6	3.00	1.01	0.30	1.67	0.84
M18	18	60	120	4.5	2.00	1.03	4.11	22.39	11.25
M19	19	70	240	7.5	2.00	1.01	1.50	8.36	4.20

M20	20	65	180	6	3.00	1.00	1.25	7.00	3.52
M21	21	60	240	7.5	4.00	1.00	1.20	6.73	3.38
M22	22	65	180	6	5.00	1.00	1.70	9.53	4.79
M23	23	65	180	6	1.00	1.00	4.10	23.00	11.56
M24	24	70	120	7.5	2.00	1.00	1.50	8.42	4.23
M25	25	70	120	4.5	4.00	1.00	1.60	8.97	4.51
M26	26	60	120	7.5	2.00	1.00	2.40	13.45	6.76
M27	27	70	240	4.5	2.00	1.00	1.61	9.01	4.53
M28	28	60	240	4.5	4.00	1.01	1.25	6.93	3.48
M29	29	65	180	6	3.00	1.00	1.30	7.28	3.66
M30	30	65	180	3	3.00	1.01	2.19	12.18	6.12

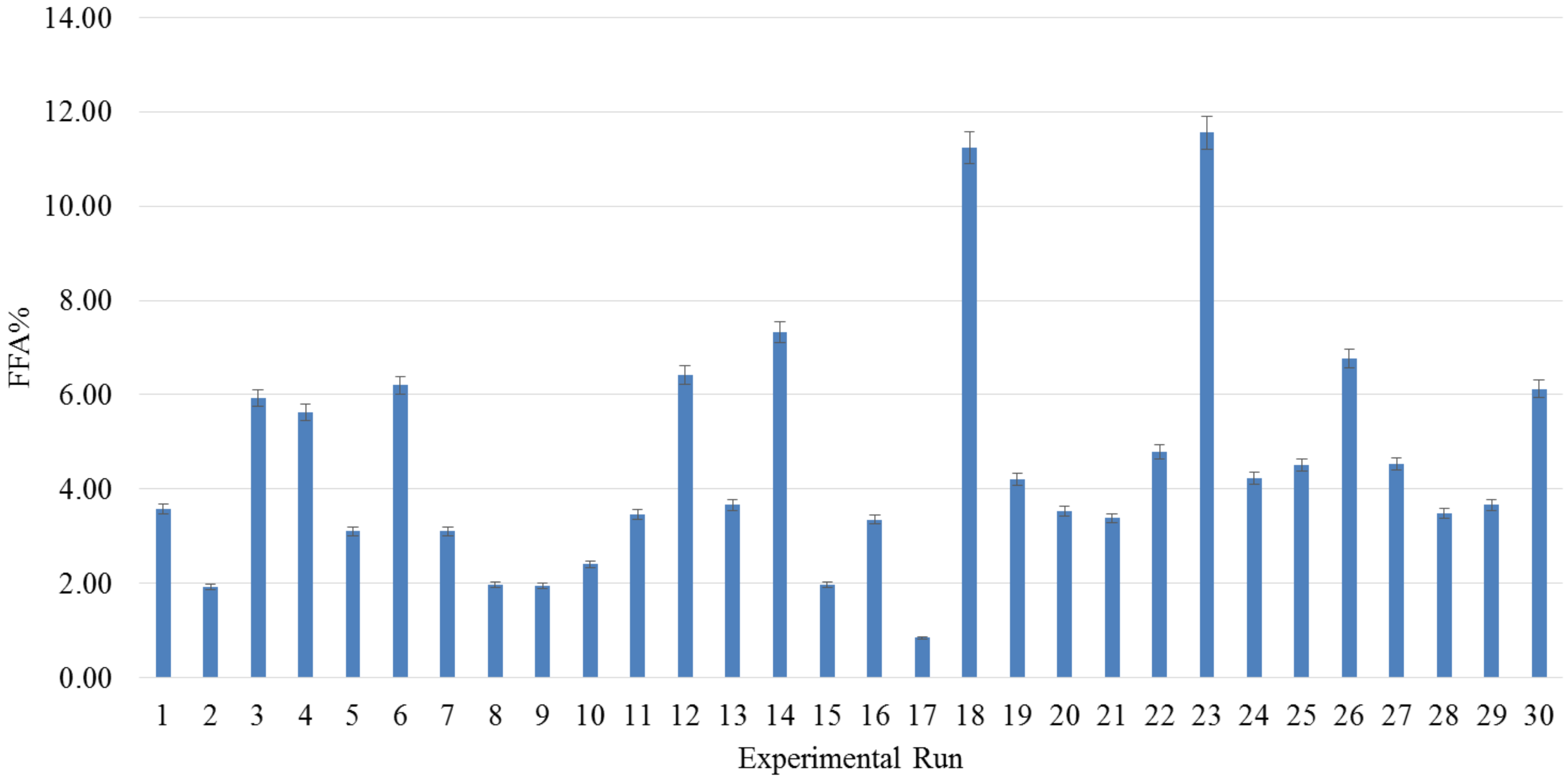


Figure S5.1 Diagram showing error bar of experimental data to confirm the repeatability of the experiments

Table S5.2 Raw data using for the calculation of the molecular weight of FOG

	10:0	**12:0**	**14:0**	**16:0**	**16:1; n-7**	**18:0**	**Trans 18:1; n-9**	**Trans 18:1; n-7**	**18:1; n-9**	**18:1; n-7**	**18:2; n-6**	**18:3; n-3**	**20:0**	**20:1; n-9**	**22:0**	**24:0**	**Total**
TX (g/100g)	0.4	1.2	3.2	20.2	1.1	6.9	0.9	1.7	39.3	2.0	12.0	1.6	0.4	0.6	0.2	0.1	92.1
GX (g/100g)	0	0	0.7	2.2	0.1	0.8	0.1	0.1	3.2	0.2	1.0	0.1	0	0	0	0	8.5
DX (g/100g)	0	0	0.2	0.9	0.1	0.4	0.1	0.1	2.2	0.1	0.6	0.1	0	0	0	0	4.9
MX (g/100g)	0	0	0.2	0.9	0.0	0.3	0.1	0.1	2.0	0.1	0.5	0.1	0	0	0	0	4.1
FFA (g/100g)	0.4	1.2	2.1	16.3	0.8	5.3	0.7	1.4	31.9	1.6	9.8	1.4	0.4	0.6	0.2	0.1	74.6
FFA%	0.4%	1.3%	3.4%	21.9%	1.2%	7.4%	1.0%	1.9%	42.6%	2.1%	13.0%	1.8%	0.4%	0.6%	0.3%	0.1%	100%
MW_FFA	172.3	200.3	228.4	256.4	254.4	284.5	282.5	282.5	282.5	282.5	280.5	278.4	312.5	310.5	340.6	368.6	
MW_MX	554.9	639	723.2	807.3	801.3	891.5	885.4	885.4	885.4	885.4	879.4	873.4	975.7	969.6	1059.8	1143.9	
MW_DX	382.6	438.7	494.8	550.9	546.9	607.0	602.9	602.9	602.9	602.9	598.5	594.9	663.1	659.1	719.2	775.3	
MW_TX	210.3	238.4	266.4	294.5	292.5	322.5	320.5	320.5	320.5	320.5	318.5	316.5	350.6	348.6	378.6	406.7	

Molecular weight of FOG

Average molecular weight of fatty acids, $MW_{FFA} = \sum f_i / \sum (f_i/MW_i)$

Average molecular weight of glycerides, $MW_x = \sum f_j / \sum (f_j/MW_j)$

Where, f_i and f_j are the weight fraction of a reported fatty acid and glyceride, respectively.

The average molecular weight of FOG, $MW_{FOG} = MW_{FFA}*FFA\% + MW_x*(1\text{-}FFA\%)$

$MW_{FOG} = 345.5$ g/mol

TX - Total lipids quantitation (unit: gram per 100 gram of sample); MX - Monoglycerides quantitation (unit: gram per 100 gram of sample); DX - Diglyceride quantitation (unit: gram per 100 gram of sample); GX - Triglyceride quantitation (unit: gram per 100 gram of sample);

<u>GC-FID analysis of the sample obtained at the optimum condition:</u>

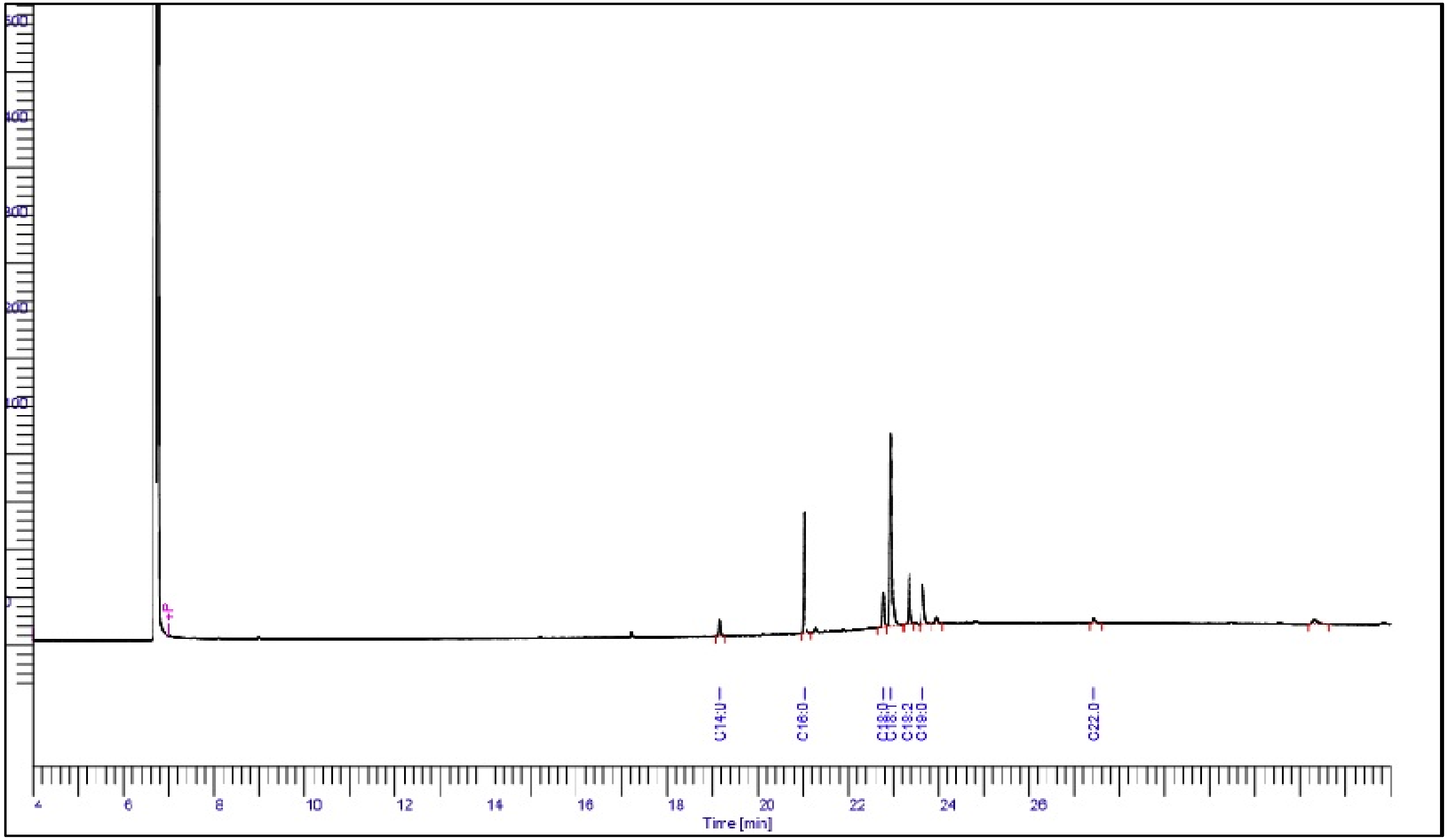
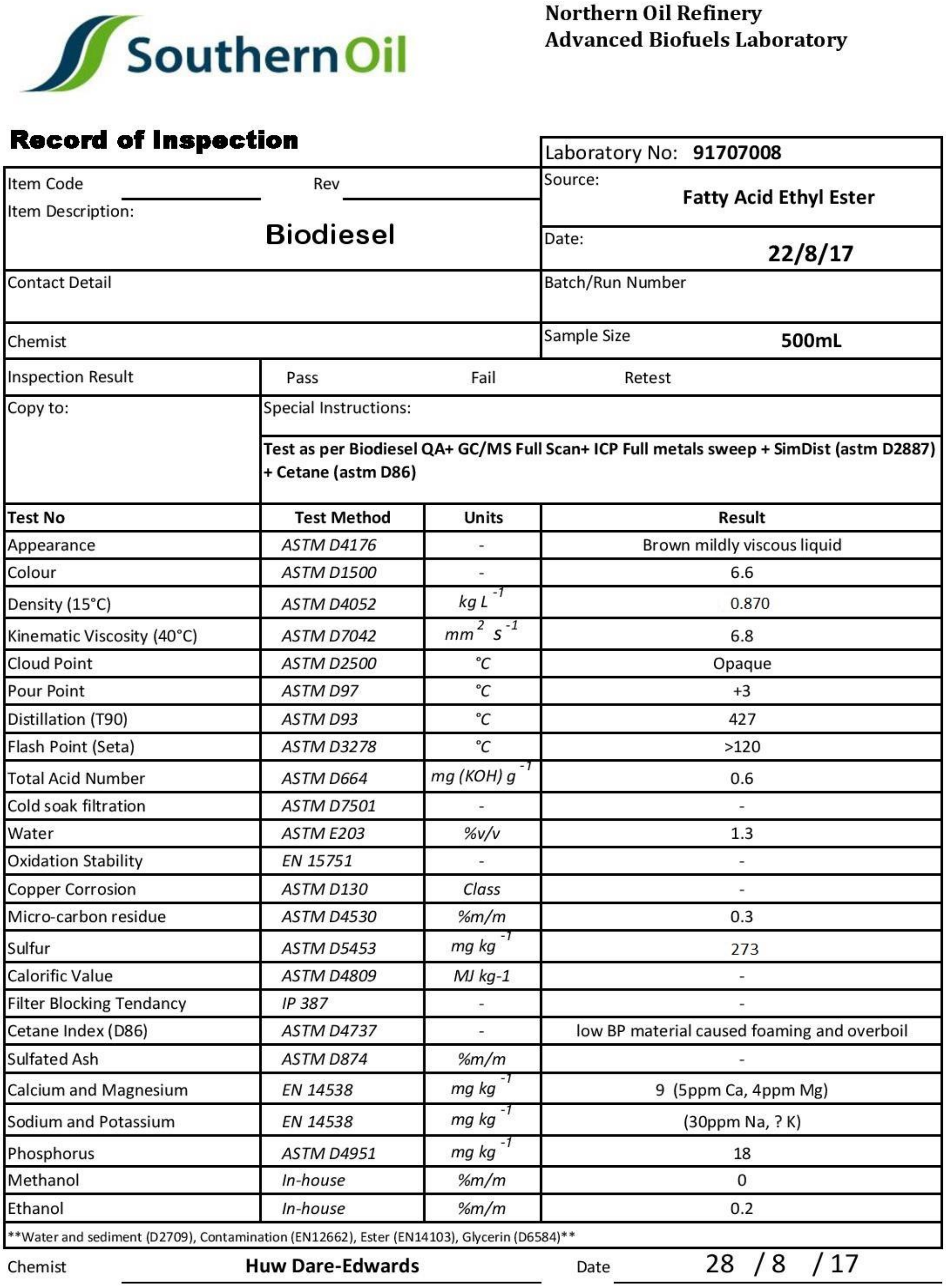


Figure S5.2 Chromatogram of crude biodiesel sample obtained at the optimum conditions



SouthernOil

Northern Oil Refinery
Advanced Biofuels Laboratory

Record of Inspection

		Laboratory No: **91707008**
Item Code	Rev	Source: **Fatty Acid Ethyl Ester**
Item Description: **Biodiesel**		Date: **22/8/17**
Contact Detail		Batch/Run Number
Chemist		Sample Size **500mL**
Inspection Result	Pass Fail Retest	
Copy to:	Special Instructions: **Test as per Biodiesel QA+ GC/MS Full Scan+ ICP Full metals sweep + SimDist (astm D2887) + Cetane (astm D86)**	

Test No	**Test Method**	**Units**	**Result**
Appearance	*ASTM D4176*	-	Brown mildly viscous liquid
Colour	*ASTM D1500*	-	6.6
Density (15°C)	*ASTM D4052*	$kg\ L^{-1}$	0.870
Kinematic Viscosity (40°C)	*ASTM D7042*	$mm^2\ s^{-1}$	6.8
Cloud Point	*ASTM D2500*	*°C*	Opaque
Pour Point	*ASTM D97*	*°C*	+3
Distillation (T90)	*ASTM D93*	*°C*	427
Flash Point (Seta)	*ASTM D3278*	*°C*	>120
Total Acid Number	*ASTM D664*	$mg\ (KOH)\ g^{-1}$	0.6
Cold soak filtration	*ASTM D7501*	-	-
Water	*ASTM E203*	*%v/v*	1.3
Oxidation Stability	*EN 15751*	-	-
Copper Corrosion	*ASTM D130*	*Class*	-
Micro-carbon residue	*ASTM D4530*	*%m/m*	0.3
Sulfur	*ASTM D5453*	$mg\ kg^{-1}$	273
Calorific Value	*ASTM D4809*	*MJ kg-1*	-
Filter Blocking Tendancy	*IP 387*	-	-
Cetane Index (D86)	*ASTM D4737*	-	low BP material caused foaming and overboil
Sulfated Ash	*ASTM D874*	*%m/m*	-
Calcium and Magnesium	*EN 14538*	$mg\ kg^{-1}$	9 (5ppm Ca, 4ppm Mg)
Sodium and Potassium	*EN 14538*	$mg\ kg^{-1}$	(30ppm Na, ? K)
Phosphorus	*ASTM D4951*	$mg\ kg^{-1}$	18
Methanol	*In-house*	*%m/m*	0
Ethanol	*In-house*	*%m/m*	0.2

Water and sediment (D2709), Contamination (EN12662), Ester (EN14103), Glycerin (D6584)

Chemist **Huw Dare-Edwards** Date 28 / 8 / 17

Figure S5.3 Crude biodiesel analytical results provided by Advanced Biofuels Laboratory

Statement of Authorship

Title of Paper	Co-solvent Applied for the Pre-treatment of High Free Fatty Acid Feedstock for Biodiesel Production
Publication Status	☐ Published ☐ Accepted for Publication ☑ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
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Principal Author

Name of Principal Author	Nghiep Nam Tran		
Contribution to the Paper	Conducting the experiment and preparing the manuscript		
Overall Percentage	70%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	28/02/2018

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Phong Quoc Ho		
Contribution to the Paper	Experimental setup and data collection		
Signature		Date	26/02/2018

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Contribution to the Paper	Conception design, manuscript review and correction		
Signature		Date	27/02/2018

Name of Co-Author	Yung Ngothai		
Contribution to the Paper	Supervising the development of the work and approving the manuscript		
Signature		Date	28/02/2018

Chapter 6. Co-solvent Applied for the Pre-treatment of High Free Fatty Acid Feedstock for Biodiesel Production

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Abstract

Grease trap waste (GTW), collected from waste streams of food handling and processing industries, has recently been considered as a cost-effective feedstock for the production of biodiesel. However, due to the high free fatty acid (FFA) content of GTW, additional pre-treatments, such as esterification and glycerolysis, are required to achieve a processible feedstock. Consequently, this results in a higher energy consumption which increases the total production cost, making GTW-derived biodiesel a relatively expensive fuel. This study aimed to investigate the esterification of the fats, oils, and grease (FOG) extracted from GTW using the co-solvent acetone-ethanol at ambient temperature (25ºC ± 1). Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied to determine the optimal conditions through four process variables, which were; acetone to FOG volume ratio, ethanol to FOG molar ratio, reaction time, and catalyst loading. 30 experiments were performed to study the interactive effect of the co-solvent on the reduction of the level of FFAs. A minimum FFA level of 1.62% was obtained at the optimum conditions, these being; 35% v/v acetone to FOG ratio, 6:1 ethanol to oil molar ratio, 3 hr reaction time, and 3 wt% acid catalyst loading based on the weight of FOG. Interestingly, GTW-derived biodiesel prepared using this co-solvent

approach had a lower sulphur content in comparison to those obtained through other processes.

Keywords: *grease trap waste; biodiesel; co-solvent; response surface methods; low energy consumption*

6.1 Introduction

The rapidly increasing demand for fuel and the depletion of fossil fuel reserves are currently the driving forces for alternative fuel sources worldwide [1]. In this regard, biodiesel, a biodegradable, non-toxic and environmentally-friendly product, is considered as an alternative source to substitute for mineral diesel. Biodiesel was first synthesized from vegetable oil and was tested for the diesel engine in the 1890s by Rudolph Diesel [2]. Since then, many attempts have been made to produce biodiesel from a variety of raw materials such as animal fats, vegetable oils (edible and non-edible oils), and micro-organism (yeasts and algae) [3-5]. However, the use of edible oil and related resources have put a negative impact on the commercialization of biodiesel due to the high feedstock cost and the food security concern. It is estimated that feedstock accounts for 60-80% of the total cost for biodiesel production [6]. Recently, research has been focusing on using waste resources such as waste cooking oil (WCO), brown grease, scum sludge, and grease trap waste to produce biodiesel, attempting to produce cheaper biodiesel, as well as to reduce the cost of wastewater treatment [7-13]. In Australia, biodiesel production from waste resources has recently been undertaken to augment mineral diesel. To this regard, GTW appears to be a cost-effective feedstock. Moreover, environmental service providers, i.e. the main GTW collectors, are considered likely potential producers since they can collect GTW at little or no charge [14]. In Adelaide, South Australia, approximately 25 million litres of GTW has generated annually, resulting in a costly wastewater treatment protocol. This corresponding increased cost is expected to be reduced if GTW can be recycled and utilized as a feedstock for biodiesel production.

However, production of biodiesel from GTW is technically challenging. The main challenges include the pre-treatment of the contaminated GTW, the lipid extraction process, the production techniques applied for the high FFA feedstock, and the purification of the low-quality biodiesel product [15]. Since GTW often contains an extremely high level of FFAs, approximately 1-99%, a pre-treatment process is necessary before the base-catalyzed transesterification reaction can be performed. Normally, a 2-step reaction process is required, starting with a pre-treatment to reduce the FFA% to less than 2% before the remaining glycerides are converted to esters through a transesterification reaction [16-18]. There are currently two main techniques for the treatment of high FFA feedstocks namely glycerolysis and acid-catalyzed esterification reaction. Anderson et al. [19] reported the conversion of FFA to glycerides using glycerine as a reactant. While glycerolysis was reported as an effective method to reduce the FFA% in the feedstock [19-22], it was criticized for the enormous energy required due to the extremely high reaction temperature (>200ºC). An acid-catalyzed esterification is preferred for the treatment of high FFA feedstocks since this method can work with the feedstock with an FFA level up to 100% [17, 23]. Oliveira et al. [8] reported the conversion of FFA in scum oil to methyl esters using an acid-catalyzed esterification reaction. They reported that a 95.3% FFA conversion yield could be obtained under the optimal conditions; which were; 4 hr reaction time, 1:9 methanol to oil molar ratio, 1.5 wt% acid, and 70ºC reaction temperature. In another study, Yatish et al. [24] reported that a yield of 93% scum oil methyl ester was obtained at different optimum conditions, which were: 4.5:1 molar ratio of methanol to oil, 75min reaction time, 1.20% catalyst concentration and 62ºC temperature. Despite the high conversion rate that could be obtained through the esterification reaction, the expense for energy still remains significant.

Recently, biodiesel synthesis with the assistance of a co-solvent was reported as a potential solution to lower the energy consumption [25]. Previous studies have applied low-boiling point solvents, such as acetone, diethyl ether (DEE), dibutyl ether (diBE), etc. for the synthesis of biodiesel from *Jatropha Curcus* oil, rapeseed, fish oil, and waste cooking oil [26-29]. The results reported that biodiesel could be produced with a relatively low energy consumption and minimum waste products under the assistance of a co-solvent [25]. Although there is currently no report related to the use of co-solvent for the pre-treatment of low-quality and high FFA feedstocks, such as scum sludge and GTW, the application of co-solvent appears to be promising since it may offer a low-energy consumption method for the production of biodiesel from wastewater feedstocks. In addition, the use of acetone, a less polar solvent, may put a positive impact on the reduction of the significant high sulphur content found in the GTW-derived biodiesel [30-32].

Therefore, the aim of this study was to examine a low-energy consumption method for the esterification pre-treatment of FOG extracted from GTW in the presence of the co-solvent acetone-ethanol. A response surface method based on a central composite design was employed to minimize the level of FFAs, resulting in operational conditions in which four variables including acetone to FOG ratio, ethanol to oil molar ratio, reaction time, and acid catalyst loading, were optimized.

6.2 Materials and Experiments

6.2.1 Materials

GTW was provided by Peats Soil and Garden Supplies Pty. Ltd., which is one of the main environmental service providers in Adelaide, South Australia. Ethanol (100%), acetone (analytical grade), sulfuric acid (98%), 0.1N potassium hydroxide (analytical grade) were purchased from VWR (Australia). GC-FID Clarus 500 (Perkin-Elmer) was employed to determine the fatty acid profile of the extracted FOG, as well as the ethyl ester profiles of the biodiesel product. The C4-C24 even carbon saturated fatty acid ethyl esters (FAEEs) standard was purchased from Sigma-Aldrich, ethyl oleate (>98%) and ethyl linoleate (>98%) were supplied by Nu-chek (USA), while ethyl nonadecanoate (>96%) was supplied by Chem-Supply Pty. Ltd.

6.2.2 FOG Extraction Process

After collection and transfer to the laboratory, the raw GTW was dried in an oven at 110^0C for 24 hr until the moisture of the sample dropped below 5%. GTW was then extracted by using either n-hexane or diethyl ether to produce FOG via a simple solvent extraction process. Following this procedure, GTW was mixed with the solvent in a ratio of 1:1 (w/v) at ambient temperature for 6 hr. The liquid phase was then separated by a vacuum filter before the solvent was recovered via a rotary evaporator. To ensure all of the solvents were recovered, the solid phase was also processed using a rotary evaporator. Finally, raw FOG was heated to 100^oC in a fume hood for 5 min to remove any remaining solvent or water. At this stage, the FOG was ready to be utilized as a feedstock for biodiesel synthesis.

6.2.3 Apparatus and Experimental Procedure

The esterification reaction was carried out in a shaking water bath. 34.5g (approximately 40 mL, 0.1 mol) of FOG was added to a 100 mL capped glass vial before the co-solvent, ethanol-acetone, was added with a specific ratio as defined in the experimental design. A marble ball (0.5 cm diameter) was placed in the vial, acting as a stirrer. After the FOG was totally dissolved in the ethanol and reached the designed temperature, sulphuric acid was added, the shaking function was turned on, and the reaction time calculated. Following the termination of the reaction, the mixture was quickly placed in an ice bath to terminate the reaction. The mixture was then allowed to settle for 1 hr, resulting in two separated liquid phases. The excess ethanol and acetone in the top phase was removed using a separating funnel, while the bottom phase containing ethyl esters (biodiesel) and unreacted FOGs was retained for further treatment. The biodiesel product was washed 3 times with warm water at 50ºC until the water phase was clear. Finally, the mixture was heated at 110ºC for 5 min to remove the remaining water. The weight of the product was then determined and the FFA content was analyzed. To determine the conversion rate, the acid number was analyzed via titration, while the FAEE profiles were analyzed by gas chromatography using flame ionization detector (GC-FID). The acetone and the excess ethanol were separated and recovered using a rotary evaporator.

6.2.4 Experimental Design

Surface response methodology based on central composite design was applied to optimize the reaction conditions in order to achieve a minimum level of FFAs. Previous studies have applied this method to optimize the production of biodiesel from other conventional feedstocks such as sunflower, and waste cooking oil [33, 34]. In this study, RSM was designed with five levels and four factors to examine the effect of the co-solvent acetone-ethanol.

Table 6.1 shows the experimental range and values based on CCD design. A total of 30 experiments were conducted to study the effect of acetone to FOG (X_1, % v/v), the molar ratio of ethanol to FOG (X_2), the acid loading (X_4, wt% based on the FOG weight), and the reaction time (X_3, hr). Each experiment was repeated 3 times and the average FFA level was recorded as the response factor. The reduction of the level of FFAs was estimated from the selected independent parameters using a second order polynomial as in equation (1):

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{i-1} \beta_{ij} x_i x_j \tag{1}$$

where Y is the predicted value of the FFA level and β_i and β_{ij} are the model coefficients.

Table 6.1 Experimental range and values based on CCD

		Levels				
Independent variables	**Coded Variables**	-α (2)	-1	0	+1	+α (2)
Acetone: FOG (% v/v)	X_1	15	20	25	30	35
Ethanol to FOG molar ratio	X_2	3:1	4.5:1	6:1	7.5:1	9:1
Reaction time (hr)	X_3	1	2	3	4	5
H_2SO_4 loading (wt%)	X_4	1	2	3	4	5

6.2.5 Analysis Methodologies

6.2.5.1 Free Fatty Acid Content

To decide whether esterification, transesterification or the 2-step esterification and transesterification combined process should be applied for the synthesis of biodiesel from GTW, the acid number was measured. Feedstock with FFA% > 2% should undergo a pre-treatment process before the transesterification can be processed [17, 35]. The acid number was determined following the ASTM D-664. 1g of extracted FOG was added to a glass flask and then dissolved in 50 mL of the solvent mixture (95% ethanol: diethyl ether, 1:1 v/v). The FOG sample was titrated against 0.1N KOH solution to the endpoint of the indicator (approximately 5 drops of phenolphthalein). The acid number (AN) was calculated by the following formula:

$$\mathrm{AN} = \mathrm{V} \times \mathrm{N} \times 56.1/\mathrm{w} \tag{2}$$

where V is the volume of KOH solution [mL], N is the normality of KOH, and w is the amount of the FOG sample [g].

Free fatty acid level (FFA%) was then calculated based on the percentage of oleic acid by dividing the obtained acid number by 1.99 as shown in equation (3)

$$\mathrm{FFA\%} = \mathrm{AN}/1.99 \tag{3}$$

6.2.5.2 Free Fatty Acid Ethyl Ester Profiles

The composition of free fatty acid ethyl esters was measured using a Perkin-Elmer Clarus 500 GC-FID instrument equipped with a BP-20 SGE forte column (30 m x 0.32 mm x 0.25 µm; SGE Forte^{TM}, Australia). The oven was initially started at 60ºC and was maintained for 1 min before increasing to 240ºC at a rate of 10ºC/min. After reaching this set temperature, it was maintained for the next 12 min. The detector temperature was maintained at 250ºC using 45 mL/min H_2, and 450 mL/min compressed air. Helium was used as the carrier gas at a flow rate of 1 mL/min. The total time for each analysis was 30 min. The internal standard used was ethyl nonadecanoate (C19:0) and the ester yield was calculated using equation (4).

$$\mathrm{C} = \frac{\sum \mathrm{A} - \mathrm{A_{SI}}}{\mathrm{A_{SI}}} \times \frac{\mathrm{C_{SI}} \times \mathrm{V_{SI}}}{\mathrm{m}} \times 100 \tag{4}$$

where C is the FAEEs content, [wt%]; $\sum A$ is the total peak area of the ethyl esters; A_{SI} is the peak area of ethyl nonadecanoate; C_{SI} is the concentration of ethyl nonadecanoate solution, [mg/mL]; V_{SI} is the volume of ethyl nonadecanoate solution, [mL]; and m is the weight of the sample, [g].

The FAAEs yield (biodiesel) was calculated by the following equation as reported by Anastopoulos et al. [36]:

$$\text{Yield} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \text{ x } 100\% = \frac{C_{\text{esters}} * n}{\rho_{\text{FOG}}} \text{ x } 100\% \qquad (5)$$

where m is the mass of ethyl esters, [g]; C is the ester content obtained using GC-FID analysis, [g/mL]; n is the diluted level of the sample; and ρ_{FOG} is the density of the extracted FOG, [g/mL].

6.2.5.3 Sulphur Content Analysis

Three samples obtained at the optimum conditions were sent to The Adelaide Microscopy Centre (Adelaide, South Australia) for sulphur content analysis using an Agilent 7500cx ICP- Quadrupole Mass Spectrometer.

6.3 Results and Discussion

6.3.1 Characteristics of the Extracted FOG

The characteristics of the extracted FOG are shown in **Table 6.2**. The FOG obtained had a very high level of FFAs, accounting for approximately 81% of the total composition. There was also a significant amount of glycerides (approximately 17%) detected in the extracted FOG. Therefore, an esterification reaction would be required to reduce the FFA level before the transesterification could be conducted.

Table 6.2 Characteristics of the extracted FOG

Properties	**Unit**	**Values**
Acid number	mg KOH	161.2
FFA content	%	81
Total glycerides	%	17
Water content	%	0.1
Kinematic viscosity	cSt	45.6
Density	kg/m^3	870
Average molecular weight	g/mol	345.5

6.3.2 Free Fatty Acid Profiles of the Extracted FOG

The FFA profile is an important parameter which determines the characteristic of the fuel produced. FOGs extracted with hexane or diethyl ether were examined for their fatty acid profiles using GC-FID. It was noticed that the fatty acid profiles of FOG extracted by hexane and that extracted by diethyl ether are quite similar in terms of fatty acid composition. In both cases, oleic acid and palmitic acid are the predominant compounds, accounting for approximately 47% and 21%, respectively. The higher amount of the unsaturated acids may also have a significant impact on the fuel properties of the produced biodiesel. Surprisingly, the FOG extracted from GTW collected in Adelaide has a similar composition to the one collected in Philadelphia (USA) reported by Ngo et al. [40], but is different from the ones collected in Guangzhou (China) reported by Lu et al. [41], and Park et al. [42]. **Table 6.3** shows the free fatty acid profiles of the extracted FOG.

Table 6.3 Free fatty acid profiles of the extracted FOG

Fatty acid composition (%wt)	Extracted FOG by hexane	 by diethyl ether
Octanoic acid (C8:0)	0.4	0.3
Decanoic acid (C10:0)	1.3	1.4
Lauric acid (C12:0)	3.4	3.4
Myristic acid (C14:0)	0.4	0.4
Palmitic acid (C16:0)	21.9	20.7
Palmitoleic acid (C16:1)	1.2	1.2
Stearic acid (C18:0)	7.4	7.7
Oleic acid (C18:1)	47.3	46.8
Linoleic acid (C18:2)	13	12.5
Linolenic acid (C18:3)	1.8	1.7
Arachidic acid (C20:0)	1.0	0.9
Behenic acid (C22:0)	0.3	0.1
Lignoceric acid (C24:0)	0.1	-
Unknown	0.2	0.9

6.3.3 Esterification and Statistical Analysis

6.3.3.1 Parity Plot and Analysis of Variance

Based on the experimental design previously specified in **Table 6.1**, 30 experiments were conducted with three replications for all of the design points. All experiments were carried out in a randomized order and the analysis of variance (ANOVA) was performed to obtain the statistical results. The results are shown in **Table 6.4**.

Table 6.4 Experimental Process and results

Run	Acetone: FOG	Molar ratio	Reaction time (hr)	Catalyst loading (wt%)	Biodiesel yield (%)	
					Obtained	Predicted
1	25.00	6.00	1.00	3.00	11.50	11.46
2	20.00	7.50	2.00	4.00	6.88	8.14
3	20.00	4.50	2.00	4.00	10.77	9.89
4	30.00	7.50	2.00	2.00	5.35	5.51
5	25.00	3.00	3.00	3.00	13.85	12.77
6	25.00	6.00	3.00	3.00	2.92	2.84
7	30.00	4.50	4.00	2.00	2.51	2.69
8	30.00	4.50	2.00	2.00	8.59	8.64
9	25.00	6.00	3.00	5.00	2.67	2.2
10	25.00	6.00	5.00	3.00	5.91	4.97
11	20.00	7.50	2.00	2.00	11.18	10.58
12	25.00	6.00	3.00	3.00	3.32	2.84
13	30.00	4.50	4.00	4.00	4.13	4.28
14	20.00	4.50	2.00	2.00	11.66	12.59
15	25.00	9.00	3.00	3.00	10.77	10.87
16	30.00	4.50	2.00	4.00	6.80	7.82
17	25.00	6.00	3.00	3.00	2.27	2.84
18	20.00	7.50	4.00	2.00	7.21	7.63
19	15.00	6.00	3.00	3.00	9.15	8.49
20	20.00	4.50	4.00	2.00	6.24	6.66
21	30.00	7.50	2.00	4.00	5.83	4.95
22	20.00	7.50	4.00	4.00	8.10	7.6
23	30.00	7.50	4.00	2.00	2.11	2.54
24	25.00	6.00	3.00	3.00	2.57	2.84
25	25.00	6.00	3.00	3.00	2.27	2.84
26	**35.00**	**6.00**	**3.00**	**3.00**	**1.64**	**1.32***
27	25.00	6.00	3.00	3.00	3.73	2.84
28	20.00	4.50	4.00	4.00	5.10	6.37
29	25.00	6.00	3.00	1.00	3.56	3.05
30	30.00	7.50	4.00	4.00	3.89	4.39

**The lowest and predicted values of FFA levels are shown in bold*

The FFA% obtained varied from 1.64% to 13.85% depending on the particular parameter values. A minimum FFA% of 1.64% was recorded under the optimal conditions, these being; 3% w/w catalyst loading, 35% v/v acetone to FOG, 6:1 ethanol to FOG molar ratio, and 3 hr reaction time. While the alcohol to FOG molar ratio is similar, the result obtained consumed a higher catalyst loading and longer reaction time in comparison to those reported by Thanh et al. [37] in which methanol was utilized as the alcohol. This could be due to the current feedstock having a significantly higher level of FFAs which require more catalyst and longer reaction time to be converted to ethyl esters. Moreover, the reactive activity of ethanol compared to that of methanol may likely be an important factor which could influence the results. Based on the result of the ANOVA, the following equation can be used to estimate the yield of GTW-derived biodiesel produced using the co-solvent acetone-ethanol protocol.

$$\text{Yield} = +95.35 + 2.18X_1 + 0.59X_2 + 2.00X_3 + 0.26X_4 - 0.72X_1^2 - 2.80X_2^2 - 1.69X_3^2 + 0.034X_4^2 + 0.34X_1X_2 + 6.25\text{exp}^{-3}X_1X_3 - 0.58X_1X_4 - 0.92X_2X_3 - 0.081X_2X_4 - 0.74X_3X_4 \quad (5)$$

where Y is the level of FFAs, while X_1, X_2, X_3, and X_4 were the coded forms of the process variables as previously shown in **Table 6.1**.

Following the results reported by Yatish et al. [24], the coefficient with one factor shows the effect of that particular factor on the response factor, while the coefficient with two factors, or with factors in second-order form, represent the interactive effect between those two factors on the reduction of the level of FFAs. Positive or negative (+/-) symbols indicate the synergistic and/or the antagonistic effects, respectively. ANOVA was also performed to verify the importance of the model.

Table 6.5 ANOVA for the quadratic model

Source	Sum of Squares	df	Mean square	F value	p-Value prob>F
Model	343.60	14	24.54	26.04	< 0.0001 *significant*
A	74.78	1	74.78	79.33	< 0.0001
B	5.43	1	5.43	5.77	0.0298
C	63.25	1	63.25	67.10	< 0.0001
D	1.09	1	1.09	1.15	0.3003
A2	9.22	1	9.22	9.78	0.0069
B2	141.40	1	141.40	150.02	< 0.0001
C2	51.44	1	51.44	54.57	< 0.0001
D2	0.021	1	0.021	0.023	0.8826
AB	1.24	1	1.24	1.32	0.2693
AC	4.101E-004	1	4.101E-004	4.351E-004	0.9836
AD	3.55	1	3.55	3.76	0.0714
BC	8.86	1	8.86	9.40	0.0078
BD	0.069	1	0.069	0.074	0.7900
CD	5.81	1	5.81	6.16	0.0254
Residual	14.14	15	0.94		
Lack of Fit	11.44	10	1.14	2.12	0.2108 *not-significant*
Pure Error	2.70	5	0.54		
Cor Total	357.74	29			

R^2: 0.96; adj R^2: 0.92; pred R^2: 0.80; adeq precision: 21.2; C.V: 0.95

Table 6.5 shows the variation of the data obtained via statistical analysis. The correlation coefficient R^2 was 0.96 which signifies the degree of fitness of the model. A value of R^2 closer to 1.0 indicates that the obtained model is capable of explaining the effect of the parameters and their interactions on the reduction of the level of FFA (the response factor). The validity of the model was again supported by a relatively high value of adj R^2 and pred R^2 achieved, which were 0.92 and 0.80 respectively. The lack of fit value was only 2.12, which indicates that it is not significant. The linear correlation plots between the actual and the predicted response variables are shown in **Figure 6.1**. The convergence of the data was verified by the high value of the correlation coefficient obtained. As a result, equation (5) can be used to estimate the effect of the related parameters on the response factor.

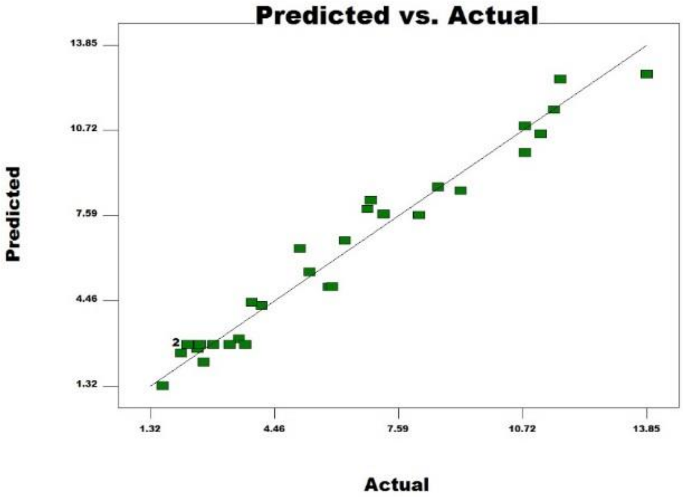

Figure 6.1 Actual FFA levels vs. predicted FFA levels

6.3.3.2 Interactive Effect of the Process Variables

Figure 6.2 shows the interactive effects of the process variables on the FFA level obtained. The interactive effects of two particular variables on the response factor are performed in each plot, while the other variables were maintained at a constant value. The interaction between the acetone to FOG volume ratio and the ethanol to FOG molar ratio is shown in plot 6.2A. After 3 hr reaction and 3 wt% acid catalyst loading, the FFA level significantly reduces by increasing both of those two factors to a particular value. However, the over-use of acetone and ethanol did not result in a lower FFA level. This could likely be due to the excess amount of solvent diluting the reactants and preventing maximum surface contact between the reactants. Plot 6.2B indicates the effect of the reaction time and the acetone to the FOG volume ratio on the response with 3 wt% acid loading and 6:1 ethanol to FOG molar ratio. In general, the FFA level falls significantly following an increase in both the reaction time and the acetone to FOG volume ratio. The interaction between the acid loading and the acetone to FOG volume ratio is shown in plot 6.2C. With 6:1 ethanol to FOG molar ratio and a 3-hr reaction time, the interactive effect of those two factors was not significant.

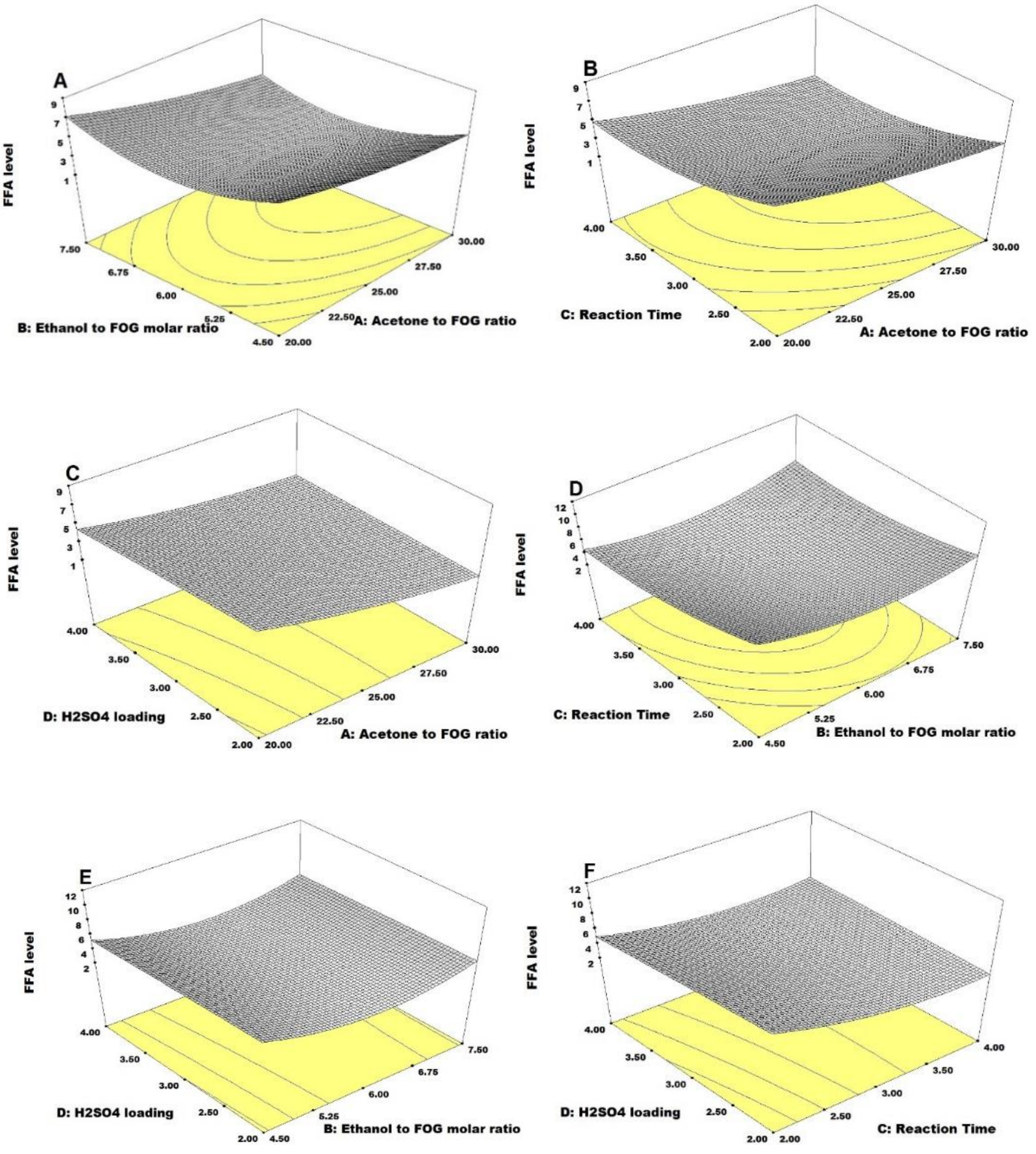

Figure 6.2 Interactive effects of variables on the FFA levels

Plot 6.2D shows the combined effect of the reaction time and the ethanol to FOG molar ratio with 25% v/v acetone to FOG ratio and 3 wt% catalyst loading. Using acetone as a co-solvent, the excess use of ethanol did not lower the FFA%. This result is in agreement with that reported by Ngoya et al. [38]. Plot 6.2E shows the interaction between the acid catalyst loading and the ethanol to FOG molar ratio with 25% v/v acetone to FOG ratio and a 3-hr reaction time. Plot 6.2F shows the combined effect of the acid catalyst loading and the reaction time with 25% v/v acetone to FOG ratio and 6:1 ethanol to FOG molar ratio. Interestingly, increasing the amount of the acid catalyst did not result in a decrease in the FFA level. This may offer an opportunity to reduce the acid catalyst, which is a major concern in terms of process safety and equipment design.

6.3.4 Fatty Acid Ester Profiles of the Pre-treated Oil

The fatty acid ethyl ester profile of biodiesel was examined using GC-FID. **Figure 6.3** shows the chromatogram of the biodiesel product obtained under the optimum conditions. The results indicate that ethyl oleate (C18:1 ethyl ester) and ethyl palmitate (C16:0 ethyl ester) are the main components of the biodiesel product, accounting for 46.5% and 26% of the total content, respectively. The ester profiles were sequenced as follows: C18:1 > C16:0 > C18:2 > C18:0 > C14:0 > C22:0.

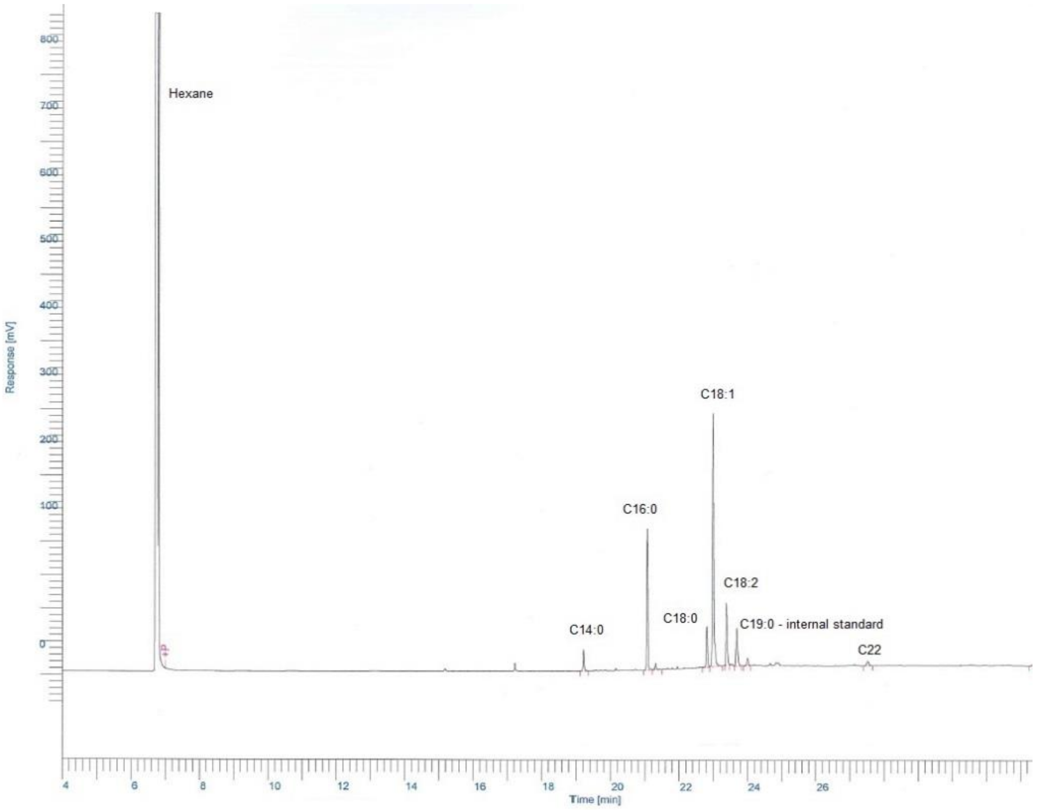

Figure 6.3 Chromatogram of GTW-derived biodiesel

The fatty acid profiles observed in this study match with those reported by Wang et al. [39] and Ma et al. [30]. The results in the present study suggest that the biodiesel produced from GTW may have similar characteristics to the biodiesel synthesized from vegetable oils, although the synthesis process was conducted at ambient temperature, which may provide a significant saving in energy consumption during its production [39].

6.3.5 Sulphur Removal Evaluation

The extremely high sulphur content is currently a significant barrier to the marketability of GTW-derived biodiesel. Due to the contaminated nature of GTW, the sulphur amount found in the raw feedstock ranges from 600 to 1000 ppm [30]. Following the American Society for Testing and Materials (ASTM D6751), the sulphur content of biodiesel should be less than 15 ppm. In Australia, the allowable level of sulphur is 10 ppm maximum. **Table 6.6** shows the sulphur content obtained in this study in comparison to that obtained through the process without the co-solvent protocol, and the results reported in previous studies.

Table 6.6 Sulphur removal effect of different processes

	Sulphur content (ppm)			
Samples	With co-solvent	Without co-solvent	Ma et al. [32]	Hums [33]
Raw GTW	524	524	852.2	307
Extracted FOG	455.3*	455.3*	707.1	-
Esterified products	204.8	273	504.5**	-
Transesterified products	125	180	362.7	171

**FOG extracted with hexane*

***Result obtained through a glycerolysis process*

The obtained results show that approximately 60% of the sulphur content could be removed from the raw GTW feedstock after the esterification reaction when using the co-solvent acetone-ethanol, while only approximately 50% was observed through a process without the co-solvent protocol. This can likely be explained as acetone has both polar and nonpolar properties that can likely dissolve both polar and nonpolar sulphur compounds [40]. The crude biodiesel was then transferred to the transesterification process (4:1 ethanol to oil molar ratio, 1 hr reaction time, 65^0C reaction temperature, and 1 wt% KOH loading per oil weight). The final biodiesel product has a sulphur content of 125 ppm which is lower than those reported by Hums [32] and Ma et al. [30]. An additional fractional distillation may further reduce the sulphur level in order to obtain a GTW-derived biodiesel that meets the mandatory standards [41].

6.4 Conclusion

This study focused on the effect of using the co-solvent acetone-ethanol on the pre-treatment of the high fatty acid containing GTW feedstock. RSM was applied to optimize the esterification reaction in order to obtain a minimum level of FFAs. This minimum level was achieved when the conditions were; 35% v/v acetone to FOG; 3 wt% H_2SO_4; 6:1 ethanol to FOG molar ratio; 3 hr reaction time, and ambient reaction temperature (25ºC). Under these conditions, the FFA level was reduced from approximately 81% to 1.6%. Interestingly, the use of acetone as a co-solvent for the esterification reaction resulted in a biodiesel product with lower sulphur content in comparison to that obtained without the use of the co-solvent. However, an additional purification step needs to be conducted to obtain a biodiesel fuel which satisfies the current mandatory standards.

Conflict of Interest

This article is an original research paper which contains the unpublished material. The corresponding author confirms that there are no conflicts of interest between the authors.

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References

[1] Revellame E, Hernandez R, French W, Holmes W, Alley E. Biodiesel from activated sludge through in situ transesterification. Journal of Chemical Technology and Biotechnology. 2010;85:614-20.

[2] Murugesan A, Umarani C, Subramanian R, Nedunchezhian N. Bio-diesel as an alternative fuel for diesel engines—A review. Renewable Sustainable Energy Rev. 2009;13:653-62.

[3] Tsigie YA, Huynh LH, Nguyen PLT, Ju Y-H. Catalyst-free biodiesel preparation from wet Yarrowia lipolytica Po1g biomass under subcritical condition. Fuel Process Technol. 2013;115:50-6.

[4] Zhou X, Ge H, Xia L, Zhang D, Hu C. Evaluation of oil-producing algae as potential biodiesel feedstock. Bioresour Technol. 2013;134:24-9.

[5] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: A review. Renewable Sustainable Energy Rev. 2010;14:217-32.

[6] Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production costs. Bioresour Technol. 2006;97:671-8.

[7] Chen J, Tyagi RD, Li J, Zhang X, Drogui P, Sun F. Economic assessment of biodiesel production from wastewater sludge. Bioresour Technol. 2018.

[8] Oliveira J, Antunes P, Mordente T, Santos A, Pinotti L, Cassini S. Biodiesel production from scum of grease traps and sludge from septic tanks. Clean Technol Environ Policy. 2017;19:1231-7.

[9] Demirbas A, Bamufleh HS, Edris G, Al-Sasi BO. Biodiesel production from lipids of municipal sewage sludge by direct methanol transesterification. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2017;39:800-5.

[10] Capodaglio AG, Callegari A. Feedstock and process influence on biodiesel produced from waste sewage sludge. Journal of environmental management. 2017.

[11] Urrutia C, Sangaletti-Gerhard N, Cea M, Suazo A, Aliberti A, Navia R. Two step esterification–transesterification process of wet greasy sewage sludge for biodiesel production. Bioresour Technol. 2016;200:1044-9.

[12] Kumar M, Ghosh P, Khosla K, Thakur IS. Biodiesel production from municipal secondary sludge. Bioresour Technol. 2016;216:165-71.

[13] Ragauskas AME, Pu Y, Ragauskas AJ. Biodiesel from grease interceptor to gas tank. Energy Sci Eng. 2013;1:42-52.

[14] Latimer G. Hazardous Waste in Australia 2017. Victoria, Australia2017.

[15] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: a review. Renewable Sustainable Energy Rev. 2011;15:1067-72.

[16] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Appl Energy. 2010;87:3155-61.

[17] Tafesh A, Basheer S. Pretreatment methods in biodiesel production processes. Pretreatment Techniques for Biofuels and Biorefineries: Springer; 2013. p. 417-34.

[18] Olkiewicz M, Fortuny A, Stüber F, Fabregat A, Font J, Bengoa C. Effects of pre-treatments on the lipid extraction and biodiesel production from municipal WWTP sludge. Fuel. 2015;141:250-7.

[19] Anderson E, Addy M, Xie Q, Ma H, Liu Y, Cheng Y, et al. Glycerin esterification of scum derived free fatty acids for biodiesel production. Bioresour Technol. 2016;200:153-60.

[20] Echeverri DA, Cardeño F, Rios LA. Glycerolysis of crude methyl esters with crude glycerol from biodiesel production. J Am Oil Chem Soc. 2013;90:1041-7.

[21] Nguyen N, Demirel Y. Economic analysis of biodiesel and glycerol carbonate production plant by glycerolysis. J Sustainable Bioenergy Syst. 2013;3:209.

[22] Tu Q, Lu M, Knothe G. Glycerolysis with crude glycerin as an alternative pretreatment for biodiesel production from grease trap waste: Parametric study and energy analysis. J Cleaner Prod. 2017;162:504-11.

[23] Fang Z. Pretreatment techniques for biofuels and biorefineries: Springer; 2013.

[24] Yatish K, Lalithamba H, Suresh R, Arun S, Kumar PV. Optimization of scum oil biodiesel production by using response surface methodology. Process Saf Environ Prot. 2016;102:667-72.

[25] Maeda Y, Imamura K, Izutani K, Okitsu K, Van Boi L, Lan PN, et al. New technology for the production of biodiesel fuel. Green Chemistry. 2011;13:1124-8.

[26] Encinar JM, Pardal A, Sánchez N. An improvement to the transesterification process by the use of co-solvents to produce biodiesel. Fuel. 2016;166:51-8.

[27] Fadhil AB, Al-Tikrity ETB, Albadree MA. Transesterification of a novel feedstock, Cyprinus carpio fish oil: Influence of co-solvent and characterization of biodiesel. Fuel. 2015;162:215-23.

[28] Alhassan Y, Kumar N, Bugaje IM, Pali HS, Kathkar P. Co-solvents transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality of fatty acids methyl esters. Energy Convers Manage. 2014;84:640-8.

[29] Encinar J, Martínez G, González J, Pardal AC. Transesterification of rapeseed oil with methanol in the presence of various co-solvents. Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste. 2010.

[30] Ma H, Addy MM, Anderson E, Liu W, Liu Y, Nie Y, et al. A novel process for low-sulfur biodiesel production from scum waste. Bioresour Technol. 2016;214:826-35.

[31] Hughes M. GC-MS Characterization of Sulfur Species in Low Temperature Distillates of Biodiesel from Waste Grease: Delaware State University; 2017.

[32] Hums ME. Environmental Impacts of Biodiesel Produced from Wastewater Greases. Philadelphia, United States: Drexel University; 2016.

[33] Hamze H, Akia M, Yazdani F. Optimization of biodiesel production from the waste cooking oil using response surface methodology. Process Saf Environ Prot. 2015;94:1-10.

[34] Charoenchaitrakool M, Thienmethangkoon J. Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process. Fuel Process Technol. 2011;92:112-8.

[35] Kombe GG, Rajabu HM, Temu AK, Lee KT, Mrema GD. Low temperature glycerolysis as a high FFA pre-treatment method for biodiesel production. 2013.

[36] Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies. 2009;2:362-76.

[37] Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A new co-solvent method for the green production of biodiesel fuel – Optimization and practical application. Fuel. 2013;103:742-8.

[38] Ngoya T, Aransiola EF, Oyekola O. Optimisation of biodiesel production from waste vegetable oil and eggshell ash. South African Journal of Chemical Engineering. 2017.

[39] Wang Y, Feng S, Bai X, Zhao J, Xia S. Scum sludge as a potential feedstock for biodiesel production from wastewater treatment plants. Waste Manage. 2016;47:91-7.

[40] Snyder LR. Classification of the solvent properties of common liquids. Journal of Chromatography A. 1974;92:223-30.

[41] Bi C-h, Min M, Nie Y, Xie Q-l, Lu Q, Deng X-y, et al. Process development for scum to biodiesel conversion. Bioresour Technol. 2015;185:185-93.

Supporting Data

Table S6.1 Raw data obtained through the experiments based on central composite design

ID	Run	Acetone: FOG	EtOH to FOG molar ratio	Reaction time (hr)	H2SO4 (wt%)	Weight of sample	Average volume of 0.1N KOH (mL)	Acid Number	FFA%
C1	1	25	6	1	3	1.00	4.08	22.89	11.50
C2	2	20	7.5	2	4	1.05	2.56	13.69	6.88
C3	3	20	4.5	2	4	1.03	3.93	21.43	10.77
C4	4	30	7.5	2	2	1.01	1.92	10.65	5.35
C5	5	25	3	3	3	1.00	4.91	27.56	13.85
C6	6	25	6	3	3	1.00	1.04	5.81	2.92
C7	7	30	4.5	4	2	1.00	0.89	4.99	2.51
C8	8	30	4.5	2	2	1.00	3.05	17.09	8.59
C9	9	25	6	3	5	1.04	0.98	5.31	2.67
C10	10	25	6	5	3	1.02	2.14	11.76	5.91
C11	11	20	7.5	2	2	1.00	3.97	22.25	11.18
C12	12	25	6	3	3	1.00	1.18	6.61	3.32
C13	13	30	4.5	4	4	1.00	1.47	8.22	4.13
C14	14	20	4.5	2	2	1.01	4.18	23.20	11.66
C15	15	25	9	3	3	1.00	3.82	21.43	10.77
C16	16	30	4.5	2	4	1.01	2.44	13.53	6.80
C17	17	25	6	3	3	1.03	0.83	4.52	2.27
C18	18	20	7.5	4	2	1.03	2.63	14.35	7.21
C19	19	15	6	3	3	1.05	3.41	18.21	9.15
C20	20	20	4.5	4	2	1.00	2.21	12.42	6.24
C21	21	30	7.5	2	4	1.02	2.11	11.60	5.83
C22	22	20	7.5	4	4	1.00	2.87	16.12	8.10
C23	23	30	7.5	4	2	1.00	0.75	4.20	2.11
C24	24	25	6	3	3	1.04	0.95	5.11	2.57

C25	25	25	6	3	3	1.00	0.81	4.52	2.27
C26	26	35	6	3	3	1.01	0.59	3.26	1.64
C27	27	25	6	3	3	1.00	1.32	7.42	3.73
C28	28	20	4.5	4	4	1.01	1.83	10.15	5.10
C29	29	25	6	3	1	1.03	1.30	7.08	3.56
C30	30	30	7.5	4	4	1.01	1.39	7.74	3.89

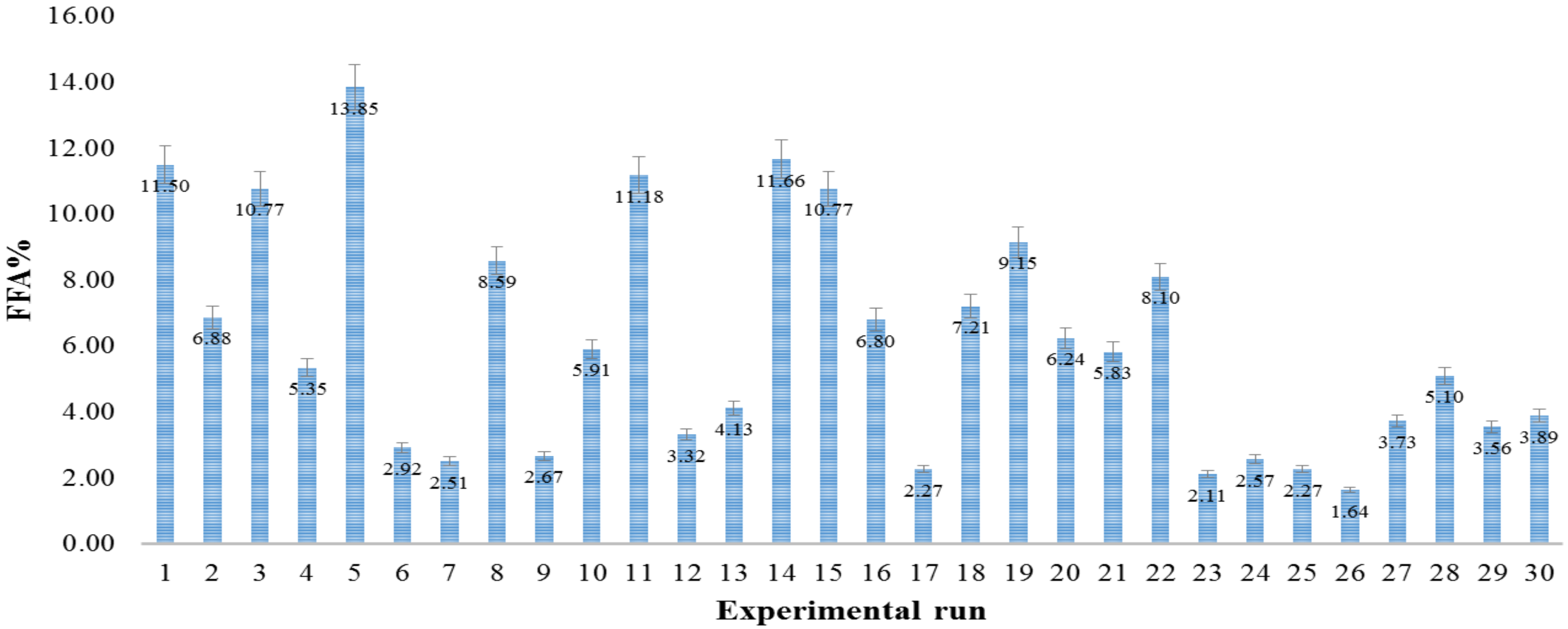

Figure S6.1 Diagram showing error bar of experimental data to confirm the repeatability of the experiments

Figure S6.2 Experimental setup

Table S6.2 Sulphur content measured by ICP-MS

Sample	**ID**	**Biodiesel amount (mg)**	**Standard solution (mg)**	**Total weight (mg)**	**Biodiesel Concentration (mg/g)**	**ICP-MS results (ppb)**	**Sulphur content (ppm)**
Biodiesel standard 1	1	102	4994.5	5096.5	20.01	116	5.8
Biodiesel standard 2	2	103	4902.3	5005.3	20.58	103	5.0
Raw GTW 1	3	100.1	4907.8	5007.9	19.99	372	516.0
Raw GTW 2	4	11.9	4989.7	5001.6	2.38	894	532.0
FOG 1	5	12.6	4995.4	5008	2.52	2054	423.2
FOG 2	6	12.1	5001.1	5013.2	2.41	958	487.4
Ester 1	7	12.6	5000	5012.6	2.51	2438	295.0
Ester 2	8	10.7	5000.5	5011.2	2.14	3179	251.0
Co-solvent 1	9	8.7	5013	5021.7	1.73	900	213.3
Co-solvent 2	10	10.9	4989.1	5000	2.18	1212	196.3
Trans 1	11	12	5000.2	5012.2	2.39	2002	186.2
Trans 2	12	12.1	4993	5005.1	2.42	1294	174.0

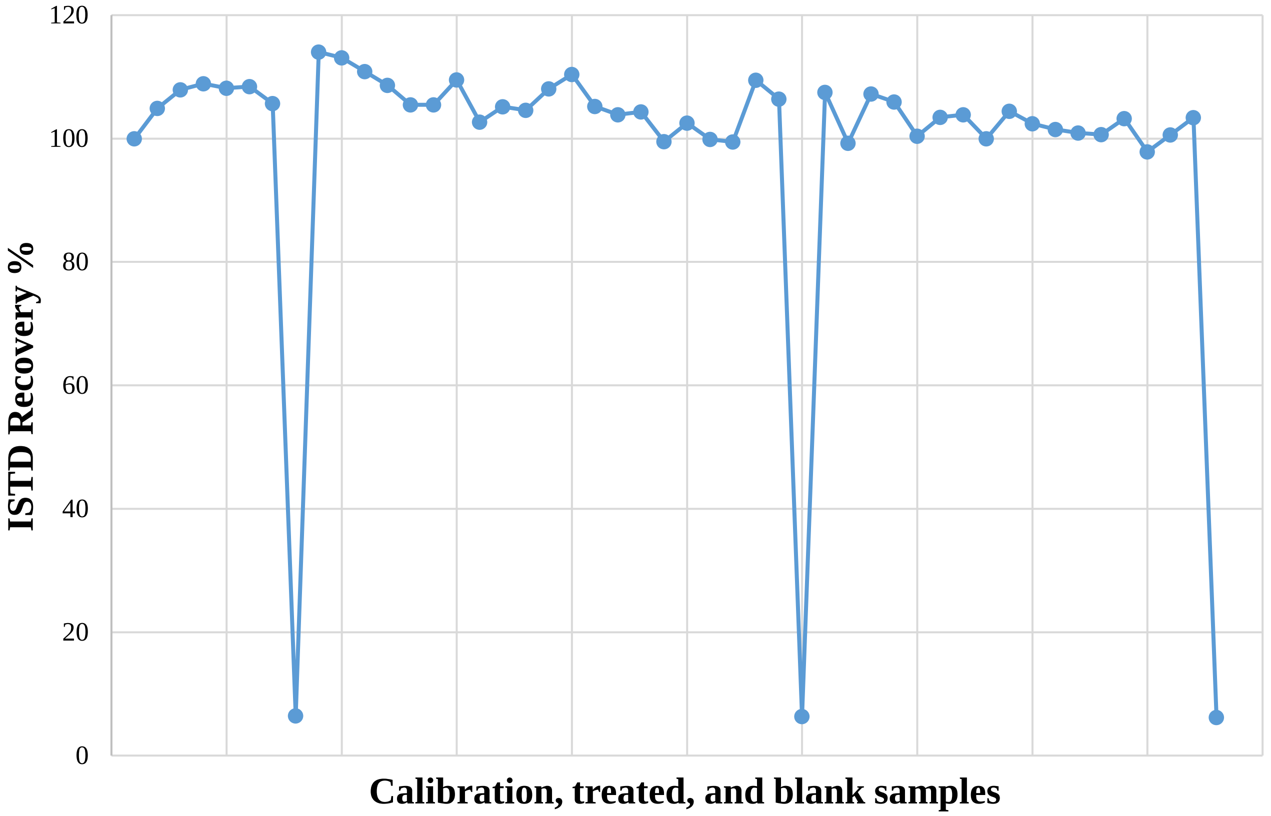

Figure S6.3 Indium recovery by ICP-MS (a consistent recovery resulting in a high fitting to the linear mode

Statement of Authorship

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Principal Author

Name of Principal Author	Nghiep Nam Tran		
Contribution to the Paper	Conducting the experiment and preparing the manuscript		
Overall Percentage	70%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	28/02/2018

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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Chapter 7. Optimization of the Transesterification Process

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Abstract

This study aimed to investigate the conversion of the pre-treated oil, which was originally extracted from grease trap waste (GTW) to biodiesel via a transesterification reaction. The pre-treated oil, which consists of approximately 80% free fatty acid ethyl esters (FAEEs) and 18% of glycerides, was obtained through the esterification of GTW reported in a previous study. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied to determine the optimum conditions for the transesterification reaction through four process variables, these being: the molar ratio of ethanol to oil, reaction time, reaction temperature, and base catalyst loading. A set of 30 experiments were conducted in duplicate to study the interactive effects of the above parameters on the ester yield. A maximum ester yield of 96.7% was obtained at the optimum conditions, which were: 4:1 ethanol to oil molar ratio, 1 hour reaction time, 65°C reaction temperature, and 1 wt% KOH loading per oil weight. In order to reduce the excess ethanol used, a modification was applied to the experimental design of the transesterification reaction, resulting in a 30% reduction in ethanol used, while the same ester yield could be obtained.

Keywords**:** *grease trap waste; biodiesel; transesterification; response surface methods; ethanol*

7.1 Introduction

As an eco-friendly, lower environmental impact, and more sustainable energy source available to substitute for mineral diesel, biodiesel derived from waste resources has recently attracted considerable interest due to the rapid increase in the cost of oil-crop based feedstocks which has been coupled with low international oil prices [1, 2]. Many studies have been conducted worldwide to investigate the potential of low-quality feedstocks such as waste-cooking oil, wastewater sludge, and waste biomass, etc., in order to produce cheaper biodiesel [3, 4]. Amongst these potential feedstocks, grease trap waste (GTW) appears to be a cost-effective feedstock since, in the majority of cases, it can be collected at little or no charge. Recently, attempts have been made to produce biodiesel from GTW-derived feedstock collected in the city of Adelaide, South Australia. However, production of biodiesel from GTW is technically challenging due to the very high content of free fatty acids (FFA) found in the feedstock [5-8]. To overcome this, a pre-treatment technique has been developed to reduce the level of FFAs in the feedstock via an esterification reaction, resulting in a crude oil consisting of approximately 80% ethyl esters and 17% glycerides. Unfortunately, this crude oil failed to meet the mandatory requirement specified by ASTM D6751 and EN 14214 standards, creating a barrier to its usability and marketability. Consequently, it was deemed necessary to conduct a further treatment to convert the remaining glycerides in this crude oil to ethyl esters to increase the ester yield, as well as to remove other contaminants. In this regard, transesterification has been widely used and reported as an effective process to produce biodiesel from glyceride-rich feedstocks, such as vegetable oils [9-11]. It has also been reported that transesterification provided benefits in terms of lowering the viscosity and improving the quality of biodiesel produced from low-quality feedstocks [12, 13]. A combined esterification-transesterification process could significantly reduce wastewater generation produced by neutralization the acidic water stream (generated in the esterification reaction) by the alkaline water stream (generated in the transesterification reaction) [6]. This wastewater generation is a major disadvantage in terms of biodiesel production economics.

In terms of the catalysts used, various studies have reported the use of homogeneous, heterogeneous, and enzymatic catalysts for the transesterification reaction [14, 15]. Recently, heterogeneous catalysts derived from biological wastes, such as waste shell and biomass ashes, have also been reported [16]. However, due to its relatively low cost and high catalytic activity, potassium hydroxide appears from reports as still being the most popular still be reported as the most popular catalyst at industrial level [17, 18]. Nonetheless, potassium hydroxide can react with the remaining free fatty acids in the oil to form soaps which can inhibit the separation of glycerol during the separation stage. This decreases the biodiesel yield as soaps can increase the solubility of esters in glycerol, resulting in a lower yield of biodiesel. Therefore, the amount of free fatty acids in feedstock should be less than 2% to prevent the formation of soaps [6, 19, 20].

With regard to the particular alcohol used, methanol appears to be the one most widely used due to its reactive activity and cost efficiency. However, this alcohol poses particular health concern among industrial producers. In this regard, ethanol has been utilized as a “green” reagent for both esterification and transesterification processes assuming that it can be sustainably produced from biomass resources. Normally, to achieve a high biodiesel yield, an excess amount of ethanol is required. This additional requirement leads to a costly ethanol recovery process that contributes to the relatively high cost of biodiesel.

Therefore the aim of this study was to investigate the transesterification of the pre-treated grease trap oil using ethanol as a reagent. A response surface method based on central composite design was employed to optimize the process parameters of the transesterification reaction, these being: the molar ratio of ethanol to oil, the reaction temperature, the reaction time, and the catalyst loading. A modification to the experimental setup was also performed in an effort to reduce the excess ethanol used.

7.2 Experimental Section

7.2.1 Materials

The crude oil used in this study was obtained from the esterification of GTW oil utilizing ethanol as a reagent. The original GTW was provided by Peats Soil and Garden Supplies Pty. Ltd. The physicochemical properties of this crude oil are presented in **Table 7.1**.

Table 7.1 Physicochemical properties of crude oil

Properties	**Units**	**Crude biodiesel**[a]
Density (at 15ºC)	kg/m^3	870
Kinetic viscosity (at 40ºC)	cSt	6.8
Acid value	mg KOH/g	1.68
Ester content	%	80.2
Total glycerides	%	17.8
Sulphur content	ppm	273

[a] Produced via the esterification of oil extracted from GTW

7.2.2 Experimental Procedure

The experiments were conducted in a 100 mL capped-glass vessel equipped with a magnetic stirrer using a hot plate. Two approaches were applied to the setup of transesterification reaction as seen in **Figure 7.1**.

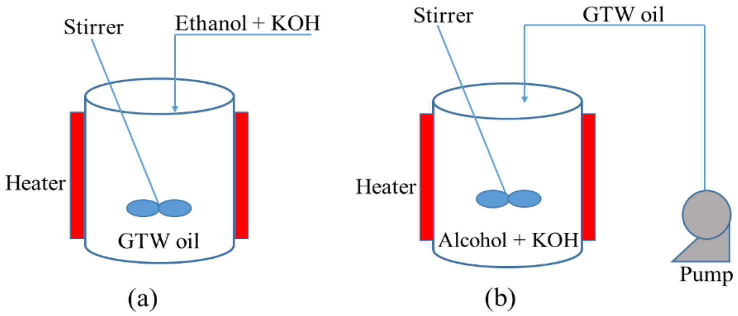

Figure 7.1 Different approaches to fed-batch reactor

Approach 1a: 34.5g oil was initially put into the vessel before ethanol (in a molar ratio defined by the experimental design) together with KOH was added. The amount of KOH was calculated based on the weight of oil and is specified in the experimental design section. The temperature ranged from 50ºC to 70ºC, while the reaction time varied from 0.25 to 1.25 hour as recommended by Karnasuta et al. [28].

Approach 1b: The mixture of ethanol and KOH was firstly heated to reach the specified reaction temperature. To take advantages of the excess ethanol, 34.5g oil was then pumped to the reactor at a rate that did not change the specified reaction temperature. Reaction parameters, such as reaction time, reaction temperature, and base catalyst loading, were tested based on the values obtained at optimal conditions using the approach indicated in 1a, while the ethanol to oil molar ratio ranged from 50% to 100% of the specified experimental values.

Following the termination of the reaction at the specified time, the mixture collected in both approaches was then added to a separating funnel, and allowed to settle for 1 hour. The glycerol in the bottom phase was removed via the separating funnel. The upper phase was then stirred and washed with water three times at 50ºC. To remove any remaining water and ethanol, the product was heated at 110ºC for 5 min. Finally, the product weight was measured and the FAEEs profiles were determined by gas chromatography equipped with a flame ionization detector (GC-FID).

7.2.3 Experimental Design and Statistical Analysis

For approach 1a, a five-level, four-factor central composite design was applied. Four independent variables including reaction temperature (X_1), ethanol to oil molar ratio (X_2), reaction time (X_3), and KOH loading (X_4) were selected to optimize the condition for the transesterification of crude biodiesel oil. It has been reported that these variables have significant effects on the extent of biodiesel production via the transesterification reaction [9, 23, 29, 30]. The experimental range and values of the above-mentioned variables are presented in **Table 7.2**. A total of 30 experiments were conducted in duplicate to study the interactive effects of the process variables on the response factor, i.e the ester yield. The ester yield can be estimated using a second order polynomial as in equation (1):

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{i-1} \beta_{ij} x_i x_j \qquad (1)$$

where Y is the predicted value of ester yield and β_i and β_{ij} are the model coefficients.

Table 7.2 Experimental range and values for approach 1a

		Levels				
Independent variables	**Coded Variables**	-α (2)	-1	0	+1	+α (2)
Reaction temperature (ºC)	X_1	50	55	60	65	70
Ethanol to oil molar ratio	X_2	1:1	2:1	3:1	4:1	5:1
Reaction time (hr)	X_3	0.25	0.5	0.75	1	1.25
KOH loading (wt%)	X_4	0.25	0.5	0.75	1	1.25

After obtaining the values of the process parameters at optimum conditions for the transesterification reaction following the approach 1a, the experimental design for approach 1b was then set up as shown in **Table 7.3.**

Table 7.3 Experimental design for approach 1b

Parameters	**Values**					
Ethanol to oil molar ratio	50%X_2*	60%X_2*	70%X_2*	80%X_2*	90%X2*	100%X_2*
Reaction temperature (ºC)	X_{1*}					
Reaction time (hr)	X_{3*}					
KOH loading (wt%)	X_{4*}					

where X_1*, X_2*, X_3*, X_4* are the values of selected variables obtained at the optimum conditions of the transesterification reaction via approach 1a.

7.2.4 Analysis Methodology

The analysis of the fatty acid ester profiles was done using a Clarus 500 GC–FID instrument (PerkinElmer, Waltham, MA) equipped with a BP-20 SGE forte column (30 m x 0.32 mm x 0.25 µm; SGE ForteTM, Australia). The oven was initially set at 60ºC and was maintained for 1 min before increasing to 240ºC at a rate of 10ºC/min. After reaching this set temperature, it was then maintained for 12 min. The detector temperature was maintained at 250ºC using 45 mL/min H2 and 450 mL/min compressed air. Helium was used as the carrier gas at a flow of 1 mL/min. The total time for each analysis was 30 minutes. The internal standard was ethyl nonadecanoate (C19:0) and the ester yield was calculated using equation (2).

$$C = \frac{\sum A\text{-}A_{SI}}{A_{SI}} \times \frac{C_{SI} \times V_{SI}}{m} \times 100 \qquad (2)$$

where C is the FAEEs content [wt%], ∑A is the total peak area of the ethyl esters, A_{SI} is the peak area of ethyl nonadecanoate, C_{SI} is the concentration of the ethyl nonadecanoate solution [mg/mL], V_{SI} is the volume of ethyl nonadecanoate solution [mL], and m is the weight of the sample [g].

7.3 Results and Discussion

7.3.1 Transesterification Reaction Following Approach 1a

In this present study, a set of 30 experiments were conducted based on central composite design which resulted in a statistical analysis result. The values of all process parameters are tabulated in **Table 7.4**. Results show that a second-order quadratic model was the best fit for the data obtained. The model can be considered statistically significant with 95% confidence with all three independent variables having an effect on the yield, and the fit of the model was checked with the correlation coefficient ($R^2 = 0.97$). This value indicates that the variation of 97% for the ester yield response is attributed to the independent variables. All four independent variables selected had a statistically significant effect on the ester yield. To evaluate the accuracy of the CCD design, the statistical significance of the model was examined through analysis of variance (ANOVA). The ester yield obtained via the transesterification of the crude oil can be estimated using equation (3).

$$\begin{aligned}\text{Ester yield} = {} & 94.88 + 0.67X_1 + 0.8X_2 + 0.8X_3 + 0.12X_4 - 0.1X_1^2 - 0.68X_2^2 - 0.44X_3^2 \\ & - 1.042E^{-3}X_4^2 + 0.33X_1X_2 + 0.069X_1X_3 + 0.26X_1X_4 \\ & + 0.069X_2X_3 - 0.044X_2X_4 + 0.094X_3X_4 \qquad (3)\end{aligned}$$

where X_1, X_2, X_3 and X_4 were the coded variables which are shown in **Table 7.2** of the experimental section.

The coefficient with the single factor shown in equation (3) signifies the effect of that factor on the ester yield response. The interactive effects between process variables were performed via coefficients with two factors or with single factors in second-order form. The synergistic and antagonistic effects are indicated by the (+/-) symbols, respectively [21].

Table 7.4 Experimental parameter setup and results

Run	Temp (°C)	Ethanol:oil	Time (hr)	KOH (wt%)	Ester yield (%)	
					Obtained	Predicted
1	55.00	2.00	0.50	1.00	93.40	93.19
2	60.00	3.00	0.75	0.75	94.70	94.88
3	70.00	3.00	0.75	0.75	96.00	95.82
4	60.00	3.00	0.75	0.75	94.70	94.88
5	65.00	2.00	0.50	0.50	92.20	92.07
6	65.00	2.00	0.50	1.00	93.60	93.49
7	**65.00**	**4.00**	**1.00**	**1.00**	**96.70**	**96.84**[a]
8	60.00	3.00	0.75	1.25	95.10	94.74
9	65.00	4.00	0.50	0.50	94.30	94.29
10	55.00	2.00	0.50	0.50	92.10	92.04
11	60.00	5.00	0.75	0.75	94.20	93.79
12	60.00	3.00	0.75	0.25	91.30	91.52
13	55.00	4.00	1.00	0.50	92.20	92.39
14	60.00	1.00	0.75	0.75	90.30	90.57
15	55.00	2.00	1.00	1.00	93.10	93.19
16	60.00	3.00	1.25	0.75	95.50	95.12
17	60.00	3.00	0.75	0.75	94.80	94.88
18	65.00	4.00	0.50	1.00	95.80	95.99
19	55.00	2.00	1.00	0.50	91.80	91.67
20	60.00	3.00	0.75	0.75	95.00	94.88
21	60.00	3.00	0.75	0.75	95.20	94.88
22	65.00	4.00	1.00	0.50	94.50	94.77
23	65.00	2.00	1.00	1.00	94.20	94.52
24	50.00	3.00	0.75	0.75	93.10	93.14
25	55.00	4.00	0.50	0.50	93.20	92.94
26	60.00	3.00	0.25	0.75	94.40	94.64
27	60.00	3.00	0.75	0.75	94.90	94.88
28	55.00	4.00	0.50	1.00	94.10	94.36
29	65.00	2.00	1.00	0.50	92.90	92.73
30	55.00	4.00	1.00	1.00	94.00	94.19

[a] The highest obtained and predicted ester yield % is shown in bold

Table 7.5 shows the model summary obtained through ANOVA analysis. The Model F-value of 46.63 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to some other random event (i.e noise). Values of "Prob > F" less than 0.05 indicate the model terms are significant, while values greater than 0.1 indicate the model terms are not significant. It can be observed that all four factors have a significant effect on the response factor. The "Lack of Fit F-value" of 3.26 implies the Lack of Fit is not significant relative to the pure error. There is a 10.19% chance that a "Lack of Fit F-value" this large could occur due to some other random event. Non-significant lack of fit is expected since it confirms the fit of the proposed model. The "Pred R-Squared" of 0.88 is in reasonable agreement with the "Adj R-Squared" of 0.95. "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than 4 is desirable, while the value obtained, 28.85, indicates an adequate signal. This model can be subsequently used to navigate the design space.

Table 7.5 Summary of quadratic model obtained through ANOVA analysis

Source	**Sum of Squares**	**df**	**Mean square**	**F value**	**p-Value prob>F**
Model	61.69	14	4.41	46.63	<0.0001 *significant*
A	10.80	1	10.80	114.29	< 0.0001
B	15.52	1	15.52	164.24	< 0.0001
C	15.52	1	15.52	164.24	< 0.0001
D	0.35	1	0.35	3.71	0.0433
A2	0.28	1	0.28	2.96	0.1057
B2	12.54	1	12.54	132.65	< 0.0001
C2	5.28	1	5.28	55.82	< 0.0001
D2	2.976E-005	1	2.976E-005	3.149E-004	0.9861
AB	1.76	1	1.76	18.58	0.0006
AC	0.076	1	0.076	0.80	0.3851
AD	1.05	1	1.05	11.12	0.0045
BC	0.076	1	0.076	0.80	0.3851
BD	0.031	1	0.031	0.32	0.5776
CD	0.14	1	0.14	1.49	0.2413
Residual	1.42	15	0.095		
Lack of Fit	1.23	10	0.12	3.26	0.1019 *not significant*
Pure Error	0.19	5	0.038		
Cor Total	63.11	29			
R^2: 0.97; adj R^2: 0.95; pred R^2: 0.88; adeq precision: 28.85; C.V.: 0.33					

Figure 7.2 compares the difference between the actual yield and the predicted yield based on equation (3). The validity of the model is again verified by the convergence of the data obtained as shown in the figure.

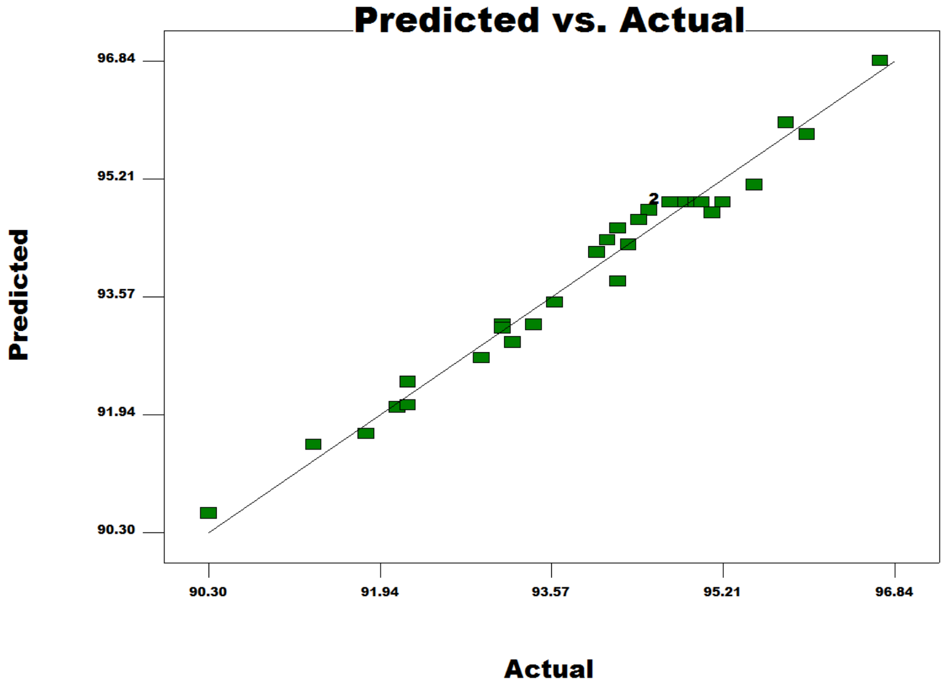

Figure 7.2 Actual yield vs. predicted yield

The interactive effects of the process variables are shown in **Figure 7.3**. The contour plot was reported to be effective for the observance of the interaction between process variables [22]. Plot 7.3A shows the interaction between the reaction temperature and the molar ratio of ethanol to oil. The circular nature of this plot signified the interactive effect between those two factors. A significant increase in the ester yield could be obtained by increasing both the reaction temperature and the ethanol-to-oil ratio. This agrees with the studies conducted by de Oliveira et al. [23] in which GTW-derived biodiesel was also produced utilizing ethanol as a reagent. The interaction between KOH loading and reaction temperature is shown in plot 7.3B. Generally, the ester yield increases gradually by increasing both these factors. Plot 7.3C shows the combined effect of the reaction time and the reaction temperature on the ester yield. It is observed that a significant improvement on the ester yield can be obtained by increasing both temperature and reaction time.

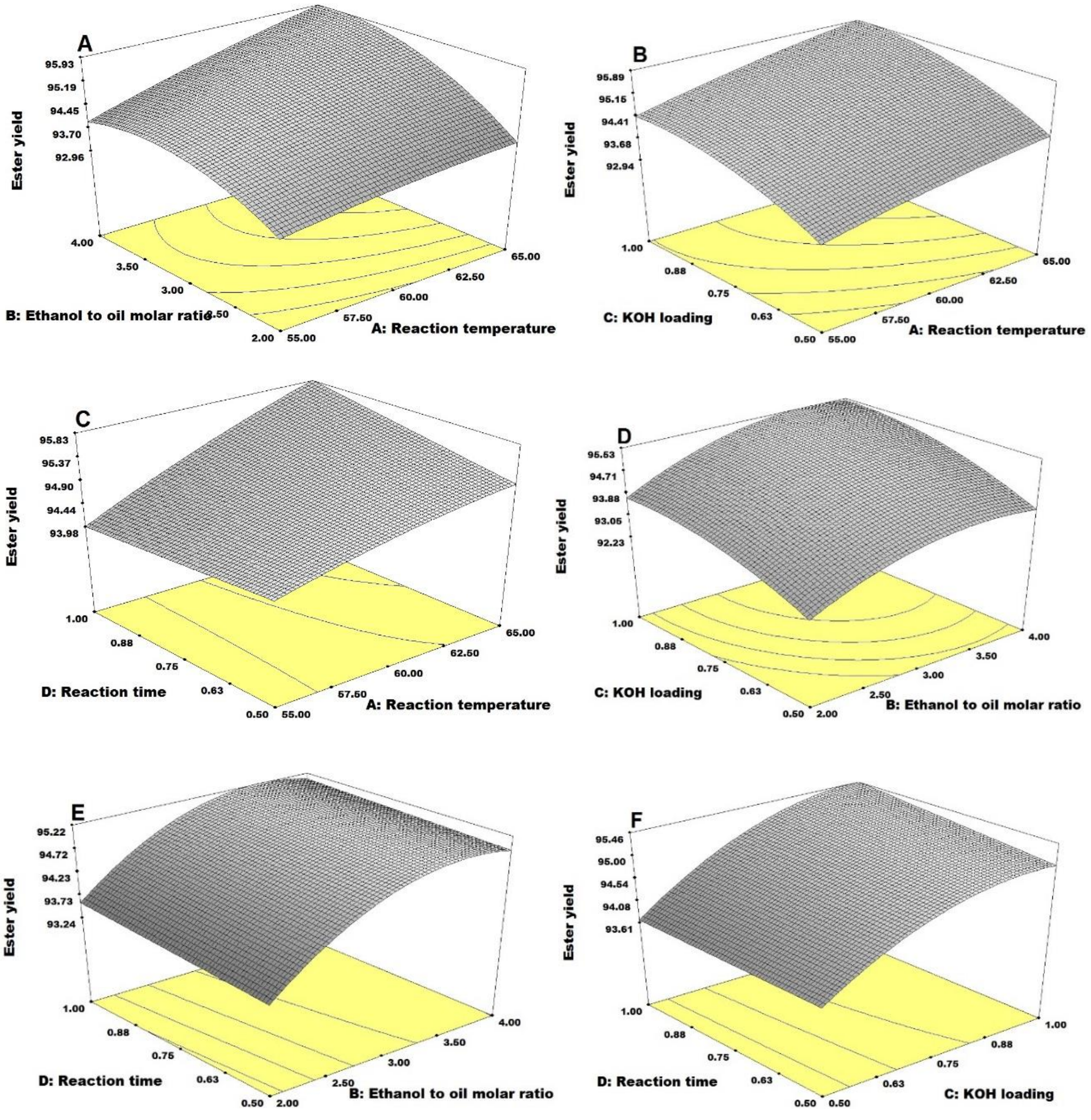

Figure 7.3 Interaction effects of variables on ester yield

The interaction of KOH loading and the molar ratio of ethanol to oil is shown in plot 7.3D. The higher the KOH loading and the ethanol used, the higher was the yield of ester. Plot 7.3E and 7.3F show the interactions between the reaction time and the molar ratio of ethanol to oil, the reaction time and the KOH loading, respectively. It was noted that an increase in both the ethanol to oil ratio and the KOH loading, have positive effects on the response factor when considering of the interactive effects between each of those factors, with the reaction time.

7.3.2 Transesterification Reaction Following Approach 1b

The experimental setup for approach 1b, which is mentioned in **Table 7.3** of the experimental section, was incorporated with the data obtained at the optimum conditions of approach 1a; which were 4:1 ethanol to oil molar ratio, 65ºC reaction temperature, 1 hr reaction time, and 1 wt% KOH loading. The numerical values are shown in **Table 7.6**.

Table 7.6 Coded experiment for approach 1b

Experiments	**A**	**B**	**C**	**D**	**E**	**F**
Ethanol to oil molar ratio	2:1	2.4:1	2.8:1	3.2:1	3.6:1	4:1
Reaction temperature (ºC)	65	65	65	65	65	65
Reaction time (hr)	1	1	1	1	1	1
KOH loading (%wt)	1	1	1	1	1	1

Crude oil was pumped to the reaction vessel at a rate that did not change the specified reaction temperature. The addition of the crude oil was completed in the first 30 min, leaving a further 30 min before the reaction was terminated. Each experiment was conducted in triplicate, and the ester yield results are shown in **Figure 7.4**. The use of this alternate approach could save up to 30% of the ethanol used (experiment C), while the ester yield was as high as that obtained via the traditional synthesis route. This can be likely explained as the advantage of the excess ethanol condition created by approach 1b in which the reaction could be shifted to produce more ester products [6].

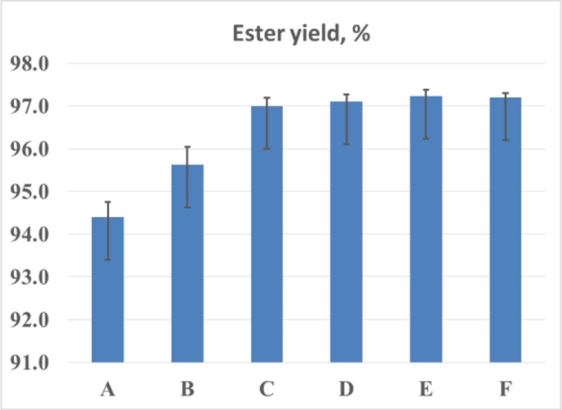

Figure 7.4 The ester yields obtained via approach 1b

7.3.3 Characterisation of Biodiesel

The properties of GTW-derived biodiesel obtained at the optimum conditions were compared to the Australian Biodiesel Standard. The results, tabulated in **Table 7.7**, show that the produced biodiesel satisfies most of the standards required. However, they do not satisfy the kinetic viscosity, water and sediment content, and sulphur content. The achieved results compared well with those reported in previously published studies [23-25].

Table 7.7 Physicochemical properties of crude biodiesel

Properties	**Units**	**Crude biodiesel**[a]	**Australian Biodiesel Standard**		
			min	**max**	**Pass (P); Fail (F)**
Density (at 15ºC)	kg/m^3	879	860	890	P
Kinetic viscosity (40ºC)	cSt	5.65	3.5	5.0	F
Flash point	ºC	>120	120	-	P
Acid value	mg KOH/g	0.65	-	0.8	P
Water and sediment	% (v/v)	0.8		0.05	F
Ester content	% (m/m)	97.1	96.5	-	P
Total glycerol	% (m/m)	0.08		0.25	P
Sulphur content	ppm	180	-	10	F
Pour point	ºC	+3	-	-	-
Calorific value	MJ/kg	9312.6	-	-	-

[a] Results provided by Advanced Biofuels Laboratory, Northern Oil Refinery, Australia

Hums [26] and Ma et al. [27] reported that the sulphur content found in GTW-derived biodiesel could be reduced through the application of a fractional distillation process in which 90% of the sulphur amount could be removed. Furthermore, the distillation which occurs at high temperature can also remove the water, resulting in a biodiesel fuel which goes further in meeting the mandatory standards.

7.4 Conclusion

In this study, the transesterification of the crude oil, obtained via the esterification of the GTW oil collected in Adelaide, South Australia, was investigated. Response surface methodology based on central composite design was applied to study the interactive effects of the process parameters on the ester yield, resulting in the optimum conditions, which were 4:1 ethanol to oil molar ratio, 1 hr reaction time, 65°C reaction temperature, and 1 wt% KOH loading per oil weight. A modification has been applied to the experimental setup which resulted in the saving of 30% of the ethanol used. Finally, the quality of the GTW-derived biodiesel was compared to the Australian Biodiesel Standard. The results showed that GTW could be a potential feedstock for biodiesel production, although further studies need to be conducted to produce a quality fuel.

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References

[1] Rodionova M, Poudyal R, Tiwari I, Voloshin R, Zharmukhamedov S, Nam H, et al. Biofuel production: challenges and opportunities. International Journal of Hydrogen Energy. 2017;42:8450-61.

[2] Martin N, Rice J. Improving Australia's renewable energy project policy and planning: A multiple stakeholder analysis. Energy Policy. 2015;84:128-41.

[3] Skaggs RL, Coleman AM, Seiple TE, Milbrandt AR. Waste-to-Energy biofuel production potential for selected feedstocks in the conterminous United States. Renewable and Sustainable Energy Reviews. 2017:In press.

[4] Wang Y, Feng S, Bai X, Zhao J, Xia S. Scum sludge as a potential feedstock for biodiesel production from wastewater treatment plants. Waste Management. 2016;47:91-7.

[5] Nitayapat N, Chitprasert P. Characterisation of FOGs in grease trap waste from the processing of chickens in Thailand. Waste Management. 2014;34:1012-7.

[6] Tafesh A, Basheer S. Pretreatment methods in biodiesel production processes. Pretreatment Techniques for Biofuels and Biorefineries: Springer; 2013. p. 417-34.

[7] Hasuntree P, Toomthong V, Yoschoch S, Thawornchaisit U. The potential of restaurant trap grease as biodiesel feedstock. Songklanakarin Journal of Science & Technology. 2011;33:525-30.

[8] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Applied Energy. 2010;87:3155-61.

[9] Ngoya T, Aransiola EF, Oyekola O. Optimisation of biodiesel production from waste vegetable oil and eggshell ash. South African Journal of Chemical Engineering. 2017.

[10] Almeida TA, Rodrigues IA, Estrela TS, Nunes CNF, Machado LL, Leão KV, et al. Synthesis of ethyl biodiesel from soybean oil, frying oil and chicken fat, using catalysts based on vanadium pentoxide. Energy. 2016;97:528-33.

[11] Likozar B, Levec J. Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition. Applied Energy. 2014;123:108-20.

[12] Sharma Y, Singh B, Upadhyay S. Advancements in development and characterization of biodiesel: a review. Fuel. 2008;87:2355-73.

[13] Puhan S, Vedaraman N, Ram BV, Sankarnarayanan G, Jeychandran K. Mahua oil (Madhuca Indica seed oil) methyl ester as biodiesel-preparation and emission characterstics. Biomass and Bioenergy. 2005;28:87-93.

[14] Mardhiah HH, Ong HC, Masjuki H, Lim S, Lee H. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. Renewable and Sustainable Energy Reviews. 2017;67:1225-36.

[15] Mansir N, Taufiq-Yap YH, Rashid U, Lokman IM. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. Energy Conversion and Management. 2017;141:171-82.

[16] Abdullah SHYS, Hanapi NHM, Azid A, Umar R, Juahir H, Khatoon H, et al. A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renewable and Sustainable Energy Reviews. 2017;70:1040-51.

[17] Vicente G, Martinez M, Aracil J. Optimisation of integrated biodiesel production. Part II: A study of the material balance. Bioresource Technology. 2007;98:1754-61.

[18] Mahmudul H, Hagos F, Mamat R, Adam AA, Ishak W, Alenezi R. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines–A review. Renewable and Sustainable Energy Reviews. 2017;72:497-509.

[19] Tu Q, Lu M, Knothe G. Glycerolysis with crude glycerin as an alternative pretreatment for biodiesel production from grease trap waste: Parametric study and energy analysis. Journal of Cleaner Production. 2017;162:504-11.

[20] Diaz-Felix W, Riley MR, Zimmt W, Kazz M. Pretreatment of yellow grease for efficient production of fatty acid methyl esters. Biomass & Bioenergy. 2009;33:558-63.

[21] Yatish K, Lalithamba H, Suresh R, Arun S, Kumar PV. Optimization of scum oil biodiesel production by using response surface methodology. Process Safety and Environmental Protection. 2016;102:667-72.

[22] Awad S, Paraschiv M, Varuvel EG, Tazerout M. Optimization of biodiesel production from animal fat residue in wastewater using response surface methodology. Bioresource Technology. 2013;129:315-20.

[23] de Oliveira JP, Antunes PWP, Santos AR, Mordente TZ, Pinotti LM, Cassini STA. Transesterification of Sanitation Waste for Biodiesel Production. Waste and Biomass Valorization. 2017;8:463-71.

[24] Wang Z-M, Lee J-S, Park J-Y, Wu C-Z, Yuan Z-H. Optimization of biodiesel production from trap grease via acid catalysis. Korean Journal of Chemical Engineering. 2008;25:670-4.

[25] Park J-Y, Lee J-S, Wang Z-M, Kim D-K. Production and characterization of biodiesel from trap grease. Korean Journal of Chemical Engineering. 2010;27:1791-5.

[26] Hums ME. Environmental Impacts of Biodiesel Produced from Wastewater Greases. Philadelphia, United States: Drexel University; 2016.

[27] Ma H, Addy MM, Anderson E, Liu W, Liu Y, Nie Y, et al. A novel process for low-sulfur biodiesel production from scum waste. Bioresource Technology. 2016;214:826-35.

[28] Karnasuta S, Punsuvon V, Chiemchaisri C, Chunkao K. Optimization of biodiesel production from trap grease via two-step catalyzed process. Asian J Energy Environ. 2007;8:145-68.

[29] Mohamad M, Ngadi N, Wong S, Jusoh M, Yahya N. Prediction of biodiesel yield during transesterification process using response surface methodology. Fuel. 2017;190:104-12.

[30] Ajala E, Aberuagba F, Olaniyan A, Ajala M, Sunmonu M. Optimization of a two stage process for biodiesel production from shea butter using response surface methodology. Egyptian Journal of Petroleum. 2016:Article in press.

Supporting data

Figure S7.1 Experimental setup: a) approach 1a and b) approach 1b

Table S7.1 RSM raw data based on average values

ID	Run	Temp (°C)	Ethanol:oil ratio	Time (hr)	KOH (wt%)	Average weight of samples (mg)	Average GC-FID results (ug)	Ester Yield (%)
T1	1	55	2	1	0.5	1.00	934.00	93.40
T2	2	60	3	0.75	0.75	1.05	994.35	94.70
T3	3	70	3	0.75	0.75	1.03	988.80	96.00
T4	4	60	3	0.75	0.75	1.01	956.47	94.70
T5	5	65	2	0.5	0.5	1.00	922.00	92.20
T6	6	65	2	1	0.5	1.00	936.00	93.60
T7	7	65	4	1	1	1.00	967.00	96.70
T8	8	60	3	1.25	0.75	1.00	951.00	95.10
T9	9	65	4	0.5	0.5	1.04	980.72	94.30
T10	10	55	2	0.5	0.5	1.02	939.42	92.10
T11	11	60	5	0.75	0.75	1.00	942.00	94.20
T12	12	60	3	0.25	0.75	1.00	913.00	91.30
T13	13	55	4	0.5	1	1.00	922.00	92.20
T14	14	60	1	0.75	0.75	1.01	912.03	90.30
T15	15	55	2	1	1	1.00	931.00	93.10
T16	16	60	3	0.75	1.25	1.01	964.55	95.50
T17	17	60	3	0.75	0.75	1.03	976.44	94.80
T18	18	65	4	1	0.5	1.03	986.74	95.80
T19	19	55	2	0.5	1	1.05	963.90	91.80
T20	20	60	3	0.75	0.75	1.00	950.00	95.00

T21	21	60	3	0.75	0.75	1.02	971.04	95.20
T22	22	65	4	0.5	1	1.00	945.00	94.50
T23	23	65	2	1	1	1.00	942.00	94.20
T24	24	50	3	0.75	0.75	1.04	968.24	93.10
T25	25	55	4	0.5	0.5	1.00	932.00	93.20
T26	26	60	3	0.75	0.25	1.01	953.44	94.40
T27	27	60	3	0.75	0.75	1.00	949.00	94.90
T28	28	55	4	1	0.5	1.01	950.41	94.10
T29	29	65	2	0.5	1	1.03	956.87	92.90
T30	30	55	4	1	1	1.01	949.40	94.00

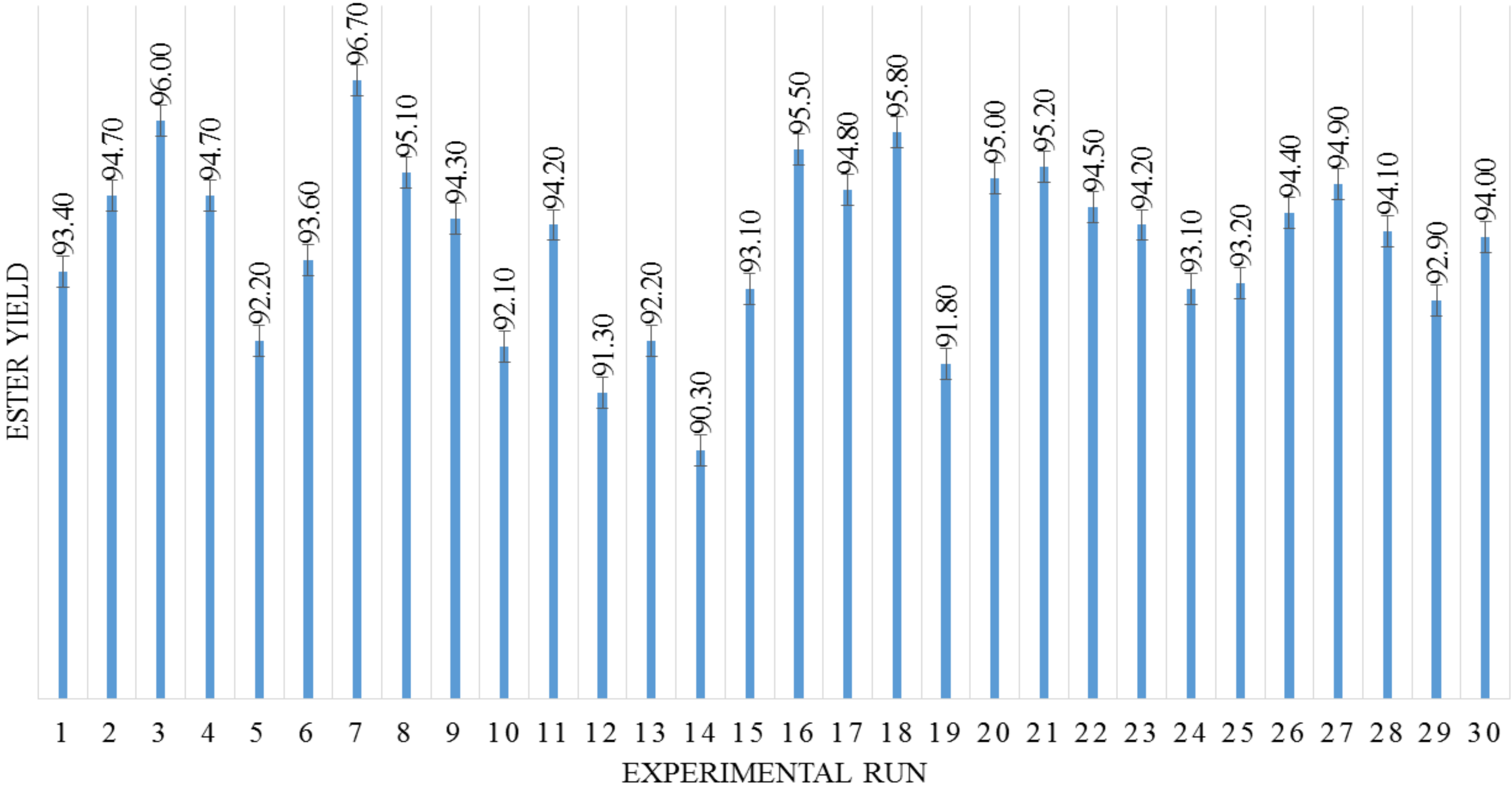
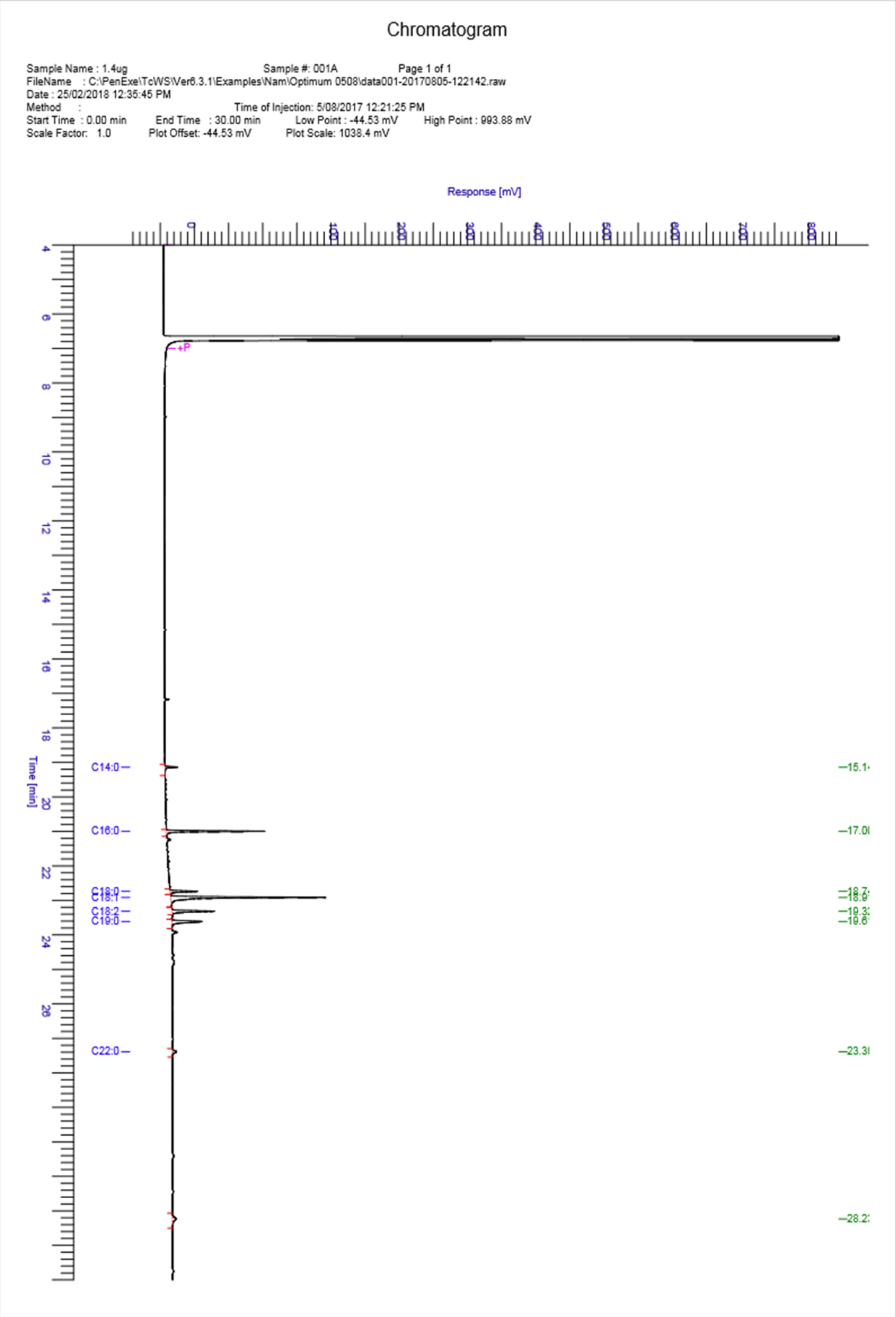


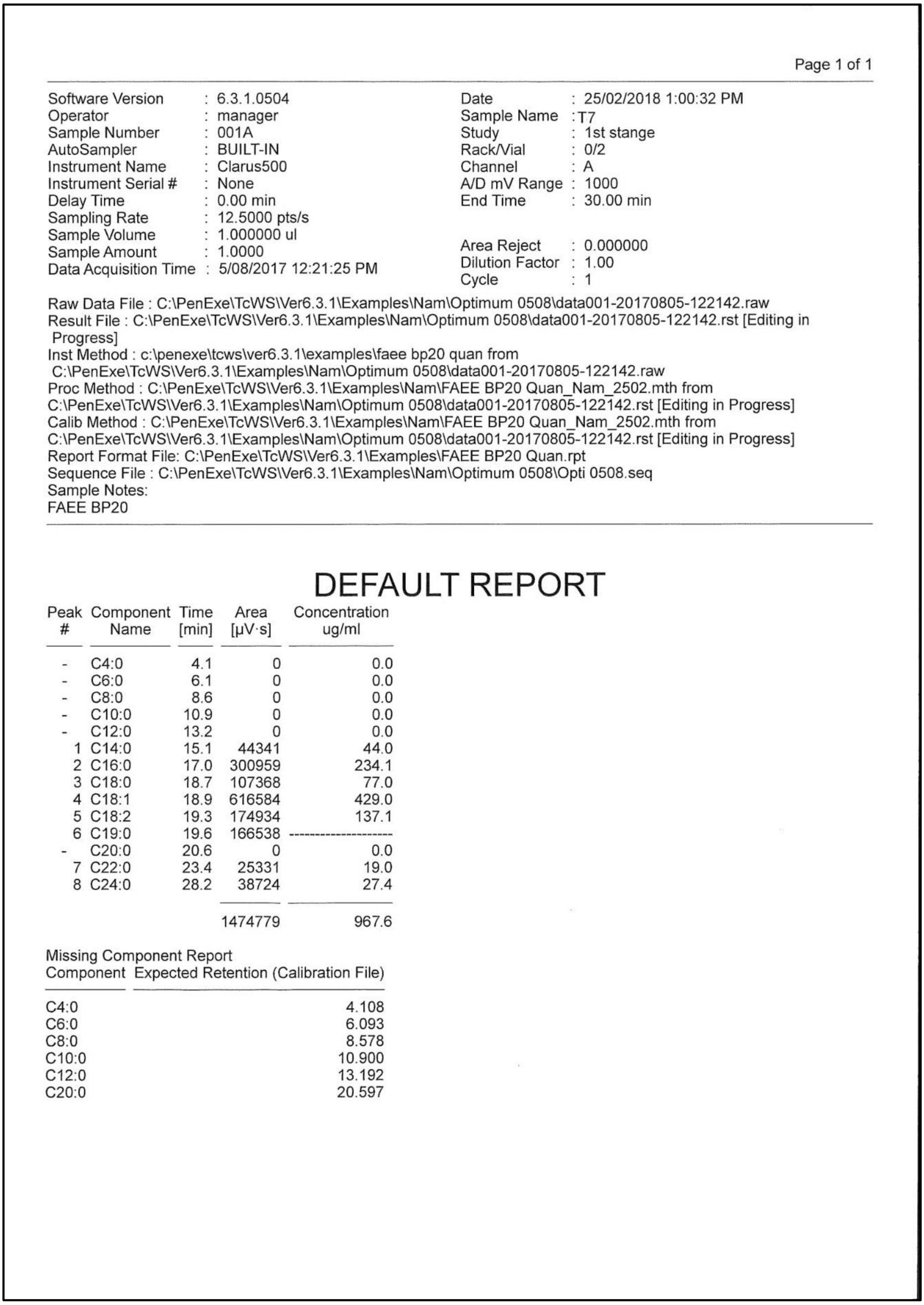
Figure S7.2 Diagram showing error bar of experimental data to confirm the repeatability of the experiments



Chromatogram

Sample Name : 1.4ug Sample #: 001A Page 1 of 1
FileName : C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\data001-20170805-122142.raw
Date : 25/02/2018 12:35:45 PM
Method : Time of Injection: 5/08/2017 12:21:25 PM
Start Time : 0.00 min End Time : 30.00 min Low Point : -44.53 mV High Point : 993.88 mV
Scale Factor: 1.0 Plot Offset: -44.53 mV Plot Scale: 1038.4 mV

Figure S7.3 Chromatogram of the FAEE sample obtained at the optimum conditions



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                                                                                  Page 1 of 1
Software Version      : 6.3.1.0504                     Date            : 25/02/2018 1:00:32 PM
Operator              : manager                        Sample Name     :T7
Sample Number         : 001A                           Study           : 1st stange
AutoSampler           : BUILT-IN                       Rack/Vial       : 0/2
Instrument Name       : Clarus500                      Channel         : A
Instrument Serial #   : None                           A/D mV Range    : 1000
Delay Time            : 0.00 min                       End Time        : 30.00 min
Sampling Rate         : 12.5000 pts/s
Sample Volume         : 1.000000 ul
Sample Amount         : 1.0000                         Area Reject     : 0.000000
Data Acquisition Time : 5/08/2017 12:21:25 PM          Dilution Factor : 1.00
                                                       Cycle           : 1

Raw Data File : C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\data001-20170805-122142.raw
Result File : C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\data001-20170805-122142.rst [Editing in
 Progress]
Inst Method : c:\penexe\tcws\ver6.3.1\examples\faee bp20 quan from
 C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\data001-20170805-122142.raw
Proc Method : C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\FAEE BP20 Quan_Nam_2502.mth from
C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\data001-20170805-122142.rst [Editing in Progress]
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Sequence File : C:\PenExe\TcWS\Ver6.3.1\Examples\Nam\Optimum 0508\Opti 0508.seq
Sample Notes:
FAEE BP20

                              DEFAULT REPORT
Peak  Component  Time    Area    Concentration
 #      Name     [min]  [µV·s]       ug/ml
----  ---------  -----  -------  -------------
 -    C4:0         4.1        0            0.0
 -    C6:0         6.1        0            0.0
 -    C8:0         8.6        0            0.0
 -    C10:0       10.9        0            0.0
 -    C12:0       13.2        0            0.0
 1    C14:0       15.1    44341           44.0
 2    C16:0       17.0   300959          234.1
 3    C18:0       18.7   107368           77.0
 4    C18:1       18.9   616584          429.0
 5    C18:2       19.3   174934          137.1
 6    C19:0       19.6   166538  --------------------
 -    C20:0       20.6        0            0.0
 7    C22:0       23.4    25331           19.0
 8    C24:0       28.2    38724           27.4
                        -------  -------------
                        1474779          967.6

Missing Component Report
Component  Expected Retention (Calibration File)
---------  -------------------------------------
C4:0                                       4.108
C6:0                                       6.093
C8:0                                       8.578
C10:0                                     10.900
C12:0                                     13.192
C20:0                                     20.597
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Figure S7.3 Chromatogram of the FAEE sample obtained at the optimum conditions

Statement of Authorship

Title of Paper	Scale-up and economic analysis of biodiesel production from recycled grease trap waste
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Publication Details	Submitted to Applied Energy

Principal Author

Name of Principal Author	Nghiep Nam Tran		
Contribution to the Paper	Developing the simulation model, evaluating the economic feasibility, and preparing the manuscript		
Overall Percentage	60%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	28/02/2018

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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Signature		Date	27/02/2018

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Signature		Date	28/02/2018

Chapter 8. Scale-up and Economic Analysis of Biodiesel Production from Recycled Grease Trap Waste

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Abstract

Grease trap waste (GTW) has been considered as a cost-effective feedstock for biodiesel production due to its high lipid content and relatively low cost for collection. However, the costly pre-treatment of this resource is currently the barrier to the commercialization of GTW-derived biodiesel due to its many contaminants. This study analyses the economic feasibility of biodiesel production from GTW collected in Adelaide, South Australia, and is based on the results obtained from laboratory-based study together with the data provided by various industrial sectors. Process simulation using Aspen Plus® V8.8 was applied to construct a simulation model in which biodiesel was produced via two different routes, these being; esterification without using acetone as a co-solvent (1); and esterification using a co-solvent of acetone-ethanol (2). Results showed that the use of acetone as a co-solvent could not result in a lower production cost. The best production price of biodiesel obtained was US$1,337.5/t which would indicate that GTW maybe a promising feedstock for biodiesel production.

Keywords: *biodiesel; grease trap waste; economic analysis; simulation*

8.1 Introduction

Biodiesel is currently considered as one of the most potential fuels to substitute for mineral diesel due to its more favorable environmental parameters. It can be produced from a variety of renewable feedstocks, such as vegetable oils, animal fats, waste cooking oil, microorganisms, and wastewater grease. However, current commercial biodiesel production still relies significantly on refined edible and non-edible vegetable oils as the feedstocks. As a consequence, this contributed to the relatively high cost of biodiesel in comparison to mineral diesel, since feedstocks account for 60-88% of the production cost [1]. Moreover, the use of farmland for feedstock cultivation has also been criticized in terms of food security and soil impoverishment. Therefore, the use of waste resources, i.e., wastewater greases, as a cost-effective feedstock has been recently encouraged worldwide [2-11]. Among those feedstocks, grease trap waste appears to have potential since it is currently generated in a relatively large amount, and contains a very high level of lipids. It was reported that up to 30% lipid yield can be extracted from raw grease trap waste [12]. The lipid content can increase to approximately 70% within the top layer of GTW, or after it has been concentrated [9]. Importantly, GTW can be collected at little or free of charge and, in the majority cases, the environmental service providers can also receive payment to collect and to treat this hazardous waste. The recycling of GTW will definitely benefit the environment in terms of solid waste reduction, pipe blockage prevention, and surface water protection.

While evidence has been provided that the environmental benefits of GTW-derived biodiesel are promising, the economic aspects appear to be more uncertain. The economic feasibility of biodiesel produced from wastewater residues has been the subject of numerous studies [6, 11, 13-16]. Due to the contaminated nature of GTW, the pre-treatment of this waste is necessary before further processes can be considered. The extremely high level of free fatty acids within GTW requires a glycerolysis or an esterification pre-treatment step to be performed, adding additional expense to the total production cost. Pokoo-Aikins et al. [17] constructed a simulation model to estimate the production cost of biodiesel derived from the dry sludge using a two-step process, these being; solvent extraction and transesterification. The results showed that the cost of biodiesel production was approximately US$838/t, providing that dry sludge was collected free of charge. The calculated cost was far cheaper in comparison to biodiesel produced from other sources [2, 18-20]. However, the authors did not include the cost of sludge drying in their consideration which may significantly increase the total production cost. In another study, Hums [19] found that the cost of GTW-derived biodiesel production could be partially covered by the fee charged by the State of Delaware, USA (US$0.016/kg approximately). This contributed to the relatively lower production cost of biodiesel, although the author also reported that the economic feasibility was strongly dependent on GTW consumption and the lipid content of the GTW oils. Olkiewicz et al. [15] evaluated the economic potential of biodiesel produced from municipal wastewater sludge using only experimental data and computational scale-up in terms of the feedstock cost. The authors recommended the gate price of their biodiesel should be US$1,232/t, which is also lower than the cost of mineral diesel and biodiesel produced from microalgae. These findings supported the potential for GTW-derived feedstocks in replacing traditional biodiesel feedstocks. Furthermore, future technical developments could also have a significant impact on the economic feasibility of GTW-derived biodiesel. Dufreche et al. [21] estimated the cost of biodiesel would be US$930.7/t (US$3.1/gal), assuming a 7.0% overall yield of esters from dry sewage sludge on a weight basis was obtained. They advised that this cost could drop significantly if techniques were developed to improve the efficiency of the transesterification reaction. In a recent study, Demirbas [22] also reported that a cost of US$933.7/t (US$3.11/gal) to produce biodiesel from municipal sewage sludge, which is higher than the current price for mineral diesel (US$3/gal). The authors emphasized that there were many challenges in terms of sludge collection, lipid separation, process operations, etc., which need to be addressed in order to produce a cheaper biodiesel from wastewater residue.

However, a specific economic model cannot be applied to all wastewater feedstocks due to the fact that the composition of GTW varies depending on its location. Furthermore, such factors as the production and processing of GTW, as well as the prevailing energy policy existing in the region where the GTW is to be utilized, also impact on the economic modeling and gate price estimation. In addition, previous studies have not considered the environmental service sector (the main GTW collectors in Australia) as potential biodiesel producers, resulting in over- or under-estimating the production cost. Therefore, further studies need to be carried out to clarify economic and affordable techniques which could be applied to biodiesel production, focusing on the environmental services as the potential producers. The purpose of this study was to evaluate the economic feasibility of the production of biodiesel from the GTW-derived feedstock, using ethanol as a reactant, based on the results collected from laboratory-based experiments and the information provided by the appropriate industrial sector. Two different production routes, classified by the pre-treatment step, were designed using a process simulator, Aspen Plus® V8.8. Based on the economic analysis, proper techniques will be evaluated which could be introduced to the environmental service sector to produce GTW-derived biodiesel at an affordable price.

8.2 Materials and Methods

Two possible approaches for a production plant with a capacity of around 4,400 t/year (approximately 12,000 tons GTW per year) were studied. The study was conducted based on the data obtained from laboratory experiments incorporated with the data provided by an environmental service provider in Adelaide, South Australia. Based on the experimental data, two production processes were designed using the process simulator, Aspen Plus®, to meet the demand of this environmental service. **Figure 8.1** shows two different routes for biodiesel production plant utilizing GTW as the feedstock.

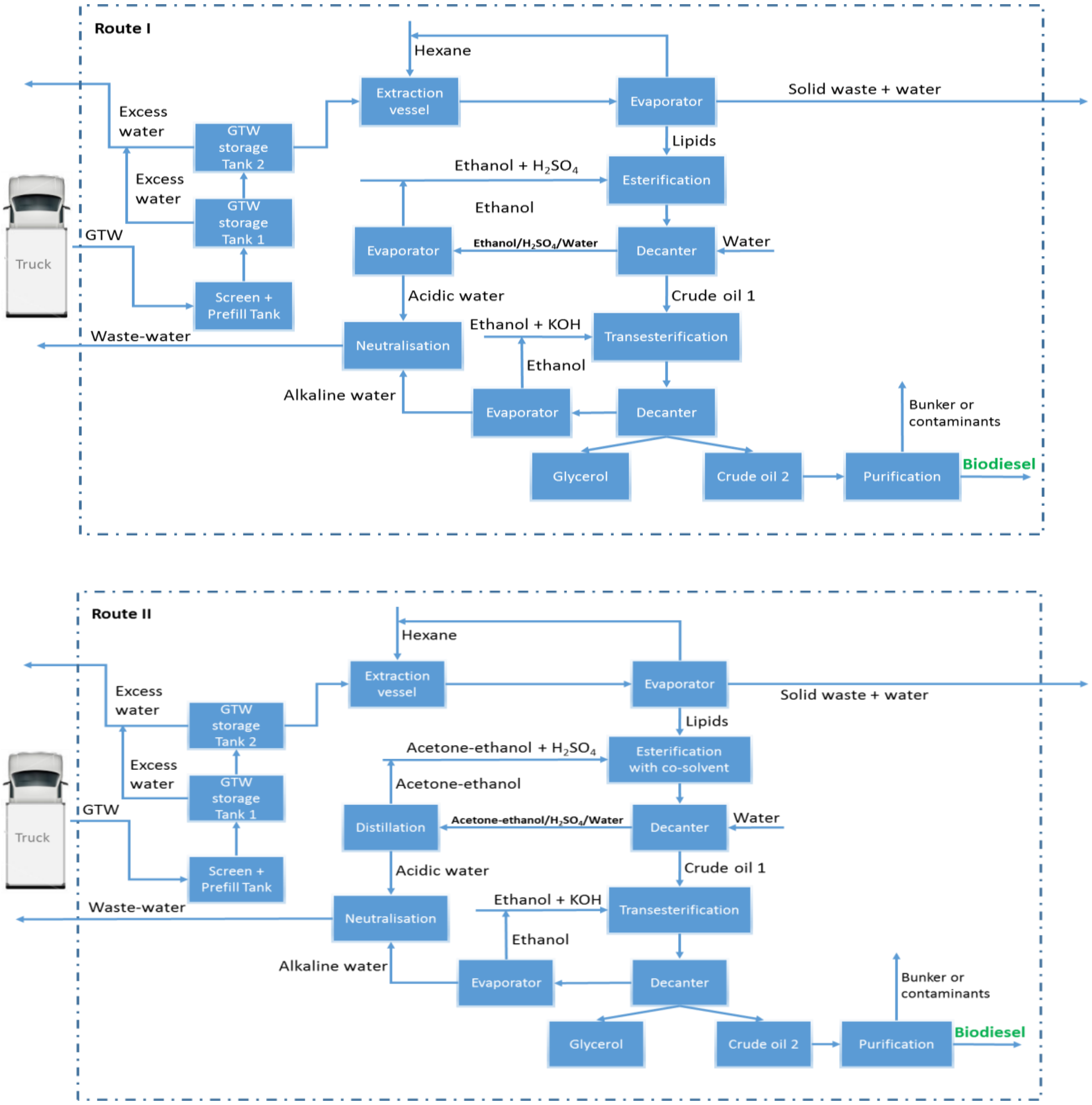

Figure 8.1 Two different routes of a biodiesel production plant

Due to economic factors and the location of the environmental services, the process proposed in this study focuses on two parameters, these being; to simplify the production technique as much as possible (1), and to minimize the energy requirement needed for the production process. A process model was constructed using Aspen Plus® V8.8 to study the scale-up effect and to generate the inventory data for economic calculation.

In route 1, GTW was collected and delivered to the treatment site using a 27-ton truck with three loadings per day. GTW was then concentrated in the storage tanks. The top layer of the tanks, which was rich in lipids, was collected while the middle and bottom phases (rich in water) removed and used for other purposes. Solvent extraction using hexane was then performed to extract the fats, oils, and grease (FOG) from the lipid-rich GTW. The esterification process, using ethanol as an alcohol and H_2SO_4 as the catalyst, was undertaken to reduce the level of FFAs in the feedstock. The crude biodiesel oil, which had an FFA level less than 2%, was processed via a transesterification reaction in which the remaining glycerides were converted to ethyl esters in the presence of KOH as the catalyst. A further purification was also undertaken to remove the remaining contaminants, i.e. mainly sulphur, resulting in a biodiesel product that meets the mandatory standards. All solvents and excess ethanol used were recovered using a rotary evaporator. The acidic water stream generated in the esterification step was neutralized using the alkaline water stream generated in the transesterification step.

In route 2, the use of the co-solvent acetone-ethanol for the esterification process was the main difference. With that co-solvent, the esterification reaction was carried out at ambient temperature, which may result in a reduced total energy consumption.

8.2.1 Approaches and Assumptions

In this study, two assumptions were made to enable a simple simulation of the process using software, these being; the cost of collecting and transporting GTW from around

Adelaide to the treatment site (approximately a 200 km, round-trip) was assumed to be covered by the fee which was charged by the service to collect this hazardous resource (1); and the biodiesel production plant being located on the environmental service provider's site without adding any additional expense for land use (2). The hypothesis integrated the results obtained through laboratory-based experiments in conjunction with the data provided by the environmental service.

8.2.2 GTW-Biodiesel Process Description

8.2.2.1 GTW Feedstock

GTW was collected from an environmental service provider and represented collections from numerous food processing and handling outlets around Adelaide, SA. The composition of GTW is presented in **Table 8.1**. Free fatty acids were the predominant compounds found in GTW. As such, this dictated the production techniques required for the high FFA feedstock.

Table 8.1 Composition of GTW and extracted FOG

Composition (%)	**GTW**	**FOG**
FFA content	36.4	81
Monoglycerides	6.0	7.9
Diglycerides	3.1	4.7
Triglycerides	5.6	4.4
Water content	42.3	0.1
Residual	6.6	1.9

8.2.2.2 Oil Extraction

FOG was extracted from GTW using either hexane or diethyl ether. The results obtained through laboratory experiments showed that the extraction using diethyl ether as a solvent offered a relatively higher lipid yield. However, due to the relatively higher price of diethyl ether in comparison to hexane, the extraction process was undertaken using hexane as the solvent. Following the experimental result, a lipid extraction yield of 92% was obtained under the optimum operating conditions, these being 1:1 v/w hexane to GTW ratio, 300 rpm stirring speed, 6-hr extraction time, and ambient extraction temperature (approximately 25°C). Due to the relatively long extraction time (6 hr) that may negatively impact on the economic feasibility of the process, the simulation model only factored in a 2-hr extraction process in which approximately 80% lipid yield was obtained, based on the laboratory results. Experimental data also showed that approximately 88% of the hexane used initially could be recovered and continuously utilized for the extraction process. **Table 8.2** shows the lipid profile of the extracted FOG. Oleic acid, palmitic acid, linoleic acid, and glycerides were the main components, accounting for 80% of the total composition of the extracted FOG. To simplify the simulation model, only those four components were chosen to represent the composition of GTW, as well as the extracted FOG. In terms of glycerides, triolein was chosen as a single triglyceride for the simulation model.

Table 8.2 Lipid profile of the real extracted and the simulated FOG

Fatty acid profile	**Real value (wt%)**	**Simulation (wt%)**
Palmitic acid (C16:0)	17.6	22
Oleic acid (C18:1)	38.4	48
Linoleic acid (C18:2)	10.4	13
Other fatty acids	20	0
Glycerides	13.6	17 (Triolein)

8.2.2.3 The 2-step Combined Esterification and Transesterification Process

Due to the high level of FFAs in the extracted FOG, the esterification reaction using ethanol and H_2SO_4 (as the catalyst) was first performed to convert FFAs to their ethyl esters. This was followed by a transesterification reaction to convert the remaining glycerides (approximately 17%) to esters. The difference between route 1 and route 2 was the use of the co-solvent acetone-ethanol in the esterification step. **Table 8.3** summarises the process parameters for both the esterification and transesterification processes. Approximately 80% acetone and excess ethanol were recovered and continuously utilized for the esterification reaction, while approximately 87% excess ethanol was recycled during the transesterification process.

Table 8.3 Experimental data for the extraction, esterification, and transesterification

	Route 1		**Route 2**	
Step in process	**Process parameters**	**Yield (%)**	**Process parameters**	**Yield (%)**
Extraction	1:1 v/w hexane to GTW ratio 300 rpm stirring speed 2 hr extraction time 25ºC	80	1:1 v/w hexane to GTW ratio 300 rpm stirring speed 2 hr extraction time 25ºC	80
Esterification	6:1 ethanol to FOG molar ratio 3 hr reaction time 75ºC reaction temperature 3 wt% H_2SO_4 per FOG	99% FFA conversion	35% v/v acetone to FOG ratio 6:1 ethanol to oil molar ratio 3 hr reaction time 25ºC reaction temperature 3 wt% H_2SO_4 per FOG	99% FFA conversion
Transesterification	4:1 ethanol to oil molar ratio 1 hr reaction time 65ºC reaction temperature 1 wt% KOH per oil weight	96.7	4:1 ethanol to oil molar ratio 1 hr reaction time 65ºC reaction temperature 1 wt% KOH per oil weight	96.7
Distillation	300ºC 1 hr	80%	300ºC 1 hr	80%

8.2.2.4 Purification

The crude biodiesel obtained via the transesterification process was first washed with water at 50ºC to separate the crude glycerol and solvent. It was then distilled in a fractional distillation column for 1 hr to remove the remaining FFA, sulphur compounds, and other heavy phases. The maximum temperature was set at 300ºC [9]. Approximately 80% of the transesterification ester yield was collected as B100.

8.2.3 Process Simulation

The economic evaluation of the GTW-derived biodiesel production process was based on the data generated using the process simulator, Aspen Plus® V8.8. This software was reported to be an effective computational tool for chemical process design and has been widely applied in industrial chemical plant control. Haas et al. [1] introduced a simulation model using Aspen Plus to estimate the production cost of vegetable derived biodiesel. They reported that Aspen Plus could be effectively applied to the simulation of biodiesel production process. In another study, Olkiewicz et al. [15] successfully scaled up and estimated the production cost of biodiesel produced from municipal sewage sludge using AspenHysys® as the process simulator. They found that the Peng–Robinson equation of state could be applied for the vapor-liquid systems of the biodiesel production process since it was well-fitted to the non-ideal systems in regard to the rigorous separation for aqueous systems containing ethanol, ester, and other hydrocarbons in the second liquid phases.

In this study, since oleic acid, palmitic acid, and linoleic acid were the predominant compounds present in GTW-extracted oil, they were chosen to represent the composition of the extracted FOG as previously shown in **Table 8.2**. To simplify the simulation model, for the transesterification process, triolein was used to simulate the percentage of glycerides after the esterification process. The Peng–Robinson equation of state was also utilized as the main physical property method for all of the simulation processes. Based on the flow diagram showed in **Figure 8.1**, two simulation models were constructed to perform the production of GTW-derived biodiesel. The detailed flow diagram obtained directly with Aspen Plus® V8.8 simulation package is shown in **Figure 8.2**. **Table 8.4** provides a detailed list of the main equipment simulated by the process simulator. The simulation techniques and parameters were based on the laboratory results that were obtained by our study group. The main difference between the two simulation models is the use of acetone as the co-solvent for the esterification reaction in route 2, which is highlighted in the red color.

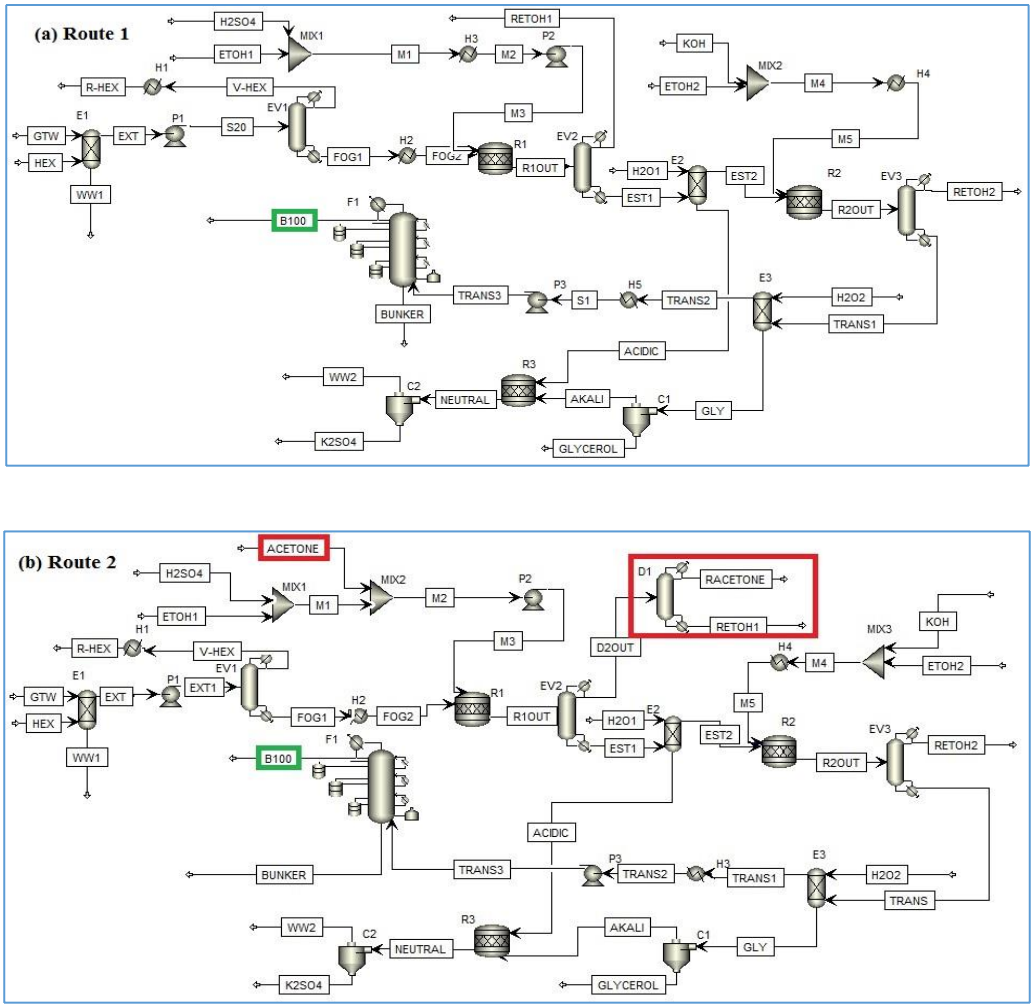

Figure 8.2 Flow diagram for the biodiesel production from GTW

Three groups of equipment including reaction vessels, separation facilities, and other processing equipment were simulated using the available models within the Aspen library. The storage facilities were not simulated in the models; however, they were also taken into account in the calculation of the capital investment.

Table 8.4 List of the main equipment used for the simulation models

Name	Equipment	Purpose
E1, 2, 3	Liquid extractors	Simulation of the extraction of FOG and the washing of ethyl ester
EV1, 2, 3	Evaporator	Simulation of the evaporator to recover solvent
R1, 2, 3	Reactors	Simulation of the esterification, transesterification and neutralization reactors
D1	Separation unit	Representation of the distillation column to recycle acetone
MIX1, 2, 3	Mixing unit	Simulation of the chemical mixers
H1 – H5	Heat exchangers	Simulation of the heater or cooler to control the temperature of material within the product streams
F1	Fractional distillation columns	Purification of the product, removal of sulphur and heavy phases (bunker)
P1 to P3	Centrifugal pumps	Simulation of the centrifugal pumps

8.2.3.1 Lipid Extraction of GTW

The top layer of GTW collected from storage tanks was pumped to the extraction unit E1 with a rate of 1,500 kg/hr. The liquid-liquid extraction was then performed using hexane (1,500 l/hr) as the solvent. The extraction unit was simulated by the extraction column E1, while the lipid yield, as well as the optimal operating parameters, were based on the results obtained through laboratory-based experiments as shown in **Table 8.3**. It was assumed that the feedstock and solvent were pumped to the extraction column with a constant flow rate by centrifugal pumps. After the extraction process was completed, the extract was transferred to an evaporator EV1 where more than 97% of the hexane was recovered and stored in the solvent tank. The raffinate which mainly contains water and the un-extracted lipid was sent to the field for further treatment.

8.2.3.2 Biodiesel Production

The combined two-step esterification and transesterification process was proposed for the production of GTW-derived biodiesel due to the extremely high level of FFA in the feedstock. The acid-catalyzed reaction system was designed for the treatment of the extracted FOG using ethanol as the reactant. The reduction of the FFA level to less than 2% using the esterification reaction took place in reactor R1, while the transesterification reaction in the presence of a base catalyst (KOH) in reactor R2 was targeted to convert the remaining glycerides to their ethyl esters. Based on the experimental results, approximately 99% FFA and nearly 97% glyceride was converted to ethyl esters via the esterification and transesterification reaction, respectively.

In route 1, after the esterification reaction had been completed in R1, excess ethanol was removed using an evaporator EV2, while the remaining mixture was washed with water at 50ºC to remove the acid catalyst. In route 2, due to the use of acetone as the co-solvent in the esterification stage, an additional distillation column D1 was simulated to separate acetone from ethanol. The product stream of the esterification reactor R1 was then fed to the transesterification reactor R2 with the presence of the base catalyst. The reaction was terminated after the designed point was reached, the excess ethanol was then removed by the evaporator EV3, and the heavy phase was washed with water at 50ºC in the extraction column E3 to separate glycerol from the product. The design of both reactor R1 and R2 was based on the stoichiometric model in which the conversion rate of the

FFA and the glycerides were specified. The crude biodiesel was then transferred to the fractional distillation column F1 to remove sulphur, FFA, and other heavy phases. Approximately 80% ester yield was obtained as the B100 biodiesel product.

The by-product, glycerol, was removed using a separating funnel, while the alkaline water was pumped to the reactor R3 where acidic water generated from the esterification reaction was also fed in. K_2SO_4 obtained as the product of the neutralization reaction was then separated using a separating cyclone and the wastewater stream WW2 was sent to the field for further treatment.

It should also be noted that during the design of the process, energy integration strategies were applied in order to reduce the energy consumption in the various stages of the overall process that was specifically energy-consuming. For example, during the hexane recovery and the product purification steps, the streams that leave the separation units at high temperature were used to exchange heat with the input streams so that the heating and cooling requirements were reduced.

8.2.4 Economic Evaluation

The economic model was developed by methods described by Peters et al. [23]. In this study, all materials and parameters of each simulated block were specified based on both the designed capacity of the plant and the experimental results. The simulation models were targeted to generate the energy consumption data as well as to estimate the size of each piece of production equipment involved in the production process. The data was then exported to the Cost and Evaluation Microsoft Excel workbook developed by Nuno et al. [24] in which the Chemical Engineering Plant Cost Index (CEPCI) was modified to 575.1 based on a new release of this value in October 2017. The material cost and energy rate were calculated using quotations obtained from local suppliers, while the installation factor and labor costs were estimated based on the information provided by various industrial sectors.

A depreciation life of 15 years (depreciable factor 0.06) was factored in during the estimation of the production cost. The interest (rate for the financial aspects) was about 5.97% as of October 2017. All of the costs were calculated in Australian dollar before exchanging to US dollar using an exchange rate of 1 US dollar equal to 1.3 Australian dollars. To provide a comparison with the price of mineral diesel, as well as a comparison with the results reported in previous studies, the break-even price (BEP) was calculated using equation (1) which was introduced by Olkiewicz et al. [15].

$$\text{BEP (US\$/t)} = \text{Total product cost (US\$/y)}/\text{Production of biodiesel (t/y)} \qquad (1)$$

The total production cost includes four component costs, which are; variable cost (i.e., raw materials, labour fees, utilities, maintenance and repairs, operating supplies, laboratory charges and patents and royalties), plant overhead, fixed charges (i.e., taxes, financial interest, insurance, rent, depreciation), and general expense (i.e., administration, distribution and selling, and research and development). The total capital investment (TCI) is the sum of the fixed capital investment (FCI) and the working capital cost. To calculate the FCI, the direct costs (equipment purchasing, delivering and installing, instrumentation and controls, piping, electrical systems, buildings, service facilities, etc.) and the indirect costs (construction, legal, engineering and supervision, contractor expenses, etc.), were taken into account. The detailed information is presented in the supplementary data section.

8.3 Results and Discussion

Based on the experimental results together with the data obtained from the industry, two process models were successfully constructed using Aspen Plus® V8.8. The economic evaluation was then performed using the lowest values for materials, equipment, and other supply chain components, provided by local suppliers, and the simulation data was obtained through process simulation. This section compares the total capital investment and the break-even price between the two approaches; i.e. route 1 and route 2. The process with the best BEP will then be assessed against the results reported in recent literature reviews utilizing the same feedstock.

8.3.1 Total Capital Investment

TCI is an important factor when considering a business investment. Depending on the potential TCI, investors can estimate the economic feasibility of the project and then make an informed decision regarding an investment. Based on the process flow diagram shown in **Figure 8.2**, the total capital investment of both route 1 and route 2 was calculated and summarised in **Table 8.5**. The TCI of route 2, the approach using acetone as the co-solvent for the esterification process, is approximately 10% higher than that of route 1. This can likely be attributed to the additional cost of the distillation column which is used for the separation of acetone from ethanol and water. Due to the azeotropic system that would form between acetone-water or ethanol-water, a simple evaporator would not be sufficient for the recovery process. In both cases, the direct costs account for approximately 56% of the TCI, which represent the highest expense for the construction of the production plant.

Table 8.5 Summary of the capital investment cost for a 4,400 t/y biodiesel plant [23]

	Cost (US$, thousands)	
Item	**Route 1**	**Route 2**
Storage tanks (for 25 days)		
GTW tanks (400 m^3)	219.78	219.78
Hexane tank (400 m^3)	219.78	219.78
ETOH tank (300 m^3)	162.44	162.44
KOH tank (5 m^3)	16.58	16.58
H_2SO_4 tank (10 m^3)	21.82	21.82
Acetone (100 m^3)	0	127.30
B100 (150 m^3)	254.60	254.60
K_2SO_4 (15 m^3)	31.02	31.02
Subtotal storage tanks	*926.02*	*1053.32*
Reactors		
Esterification	45.01	45.01
Transesterification	45.01	45.01
Neutralisation	13.31	13.31
Subtotal Process equipment	*103.34*	*103.34*
Separation facilities		
Evaporators	413.60	413.60
Distillation columns	0	137.87
Liquid-Liquid extractors	413.60	413.60
Fractional distillation column	413.60	413.60
Subtotal separation facilities	*1,240.81*	*1378.68*
Other equipment		
Mixing units	27.81	41.71
Heat exchangers	358.06	358.06
Pumps	60.38	60.38
Subtotal other equipment	*446.25*	*460.15*
Total equipment costs	2,720.00	3,000.00
Other direct costs	4,787.00	5,280.00
Total direct costs	7,779.00	8,580.00
Total indirect costs	3,770.00	4,158.00
Working capital (WC)	2,244.00	2,475.00
Total capital investment	*13,793.00*	*15,213.00*

8.3.2 Break-even Price

The total production cost and the break-even price calculated from the production of GTW-derived biodiesel (4,400 t/y) using the two approaches were reported in **Table 8.6**.

Table 8.6 Summary of the total production cost

	Cost (million US$/y)		**Unit cost (US$/l)**	
Items	**Route 1**	**Route 2**	**Route 1**	**Route 2**
Raw materials	0.673	0.983	0.13	0.20
Operating labour	0.346	0.346	0.07	0.07
Operating supervision	0.052	0.052	0.01	0.01
Utilities	0.708	0.728	0.14	0.15
Maintenance and repairs	0.712	0.785	0.14	0.16
Operating supplies	0.107	0.118	0.02	0.02
Laboratory charges	0.052	0.052	0.01	0.01
Royalties (if not on lump-sum basis)	0.059	0.066	0.01	0.01
Variable cost	*2.708*	*3.130*	*0.54*	*0.63*
Taxes (property)	0.237	0.262	0.05	0.05
Financing (interest)	0.692	0.763	0.14	0.15
Insurance	0.119	0.131	0.02	0.03
Rent	0.000	0.000	0.00	0.00
Depreciation	0.712	0.785	0.14	0.16
Fixed Charges	*1.759*	*1.940*	*0.35*	*0.39*
Plant Overhead	*0.666*	*0.710*	*0.13*	*0.14*
Manufacturing cost	5.133	5.780	1.03	1.16
Administration	0.222	0.237		
Distribution & selling	0.294	0.331		
Research & Development	0.235	0.264		
General Expense	*0.752*	*0.832*	*0.15*	*0.17*
TOTAL PRODUCTION COST	5.885	6.612		
Production capacity (t/y)	4,400	4,400		
Break-even price (US$/t)	1,337.5	1,502.7	1.17	1.33

The total production cost of route 2 is approximately 11% higher in comparison to that of route 1. The variable cost contributed to approximately 50% of the total production cost in both cases. Due to the additional expense incurred by the investment of a distillation column together with the utility cost required for the recovery of acetone, the use of acetone as the co-solvent for the production of GTW-derived biodiesel could not result in an economically efficient process. Those expenses were higher than the sum of the savings from the ambient temperature esterification reaction using acetone as the co-solvent. **Figure 8.3** shows the suggested retail price of the GTW-derived biodiesel generated in this study in comparison to the average mineral diesel price obtained from the Australian Institute of Petroleum in 10/2017. The BEP of route 1 and route 2 are US$1.17/l and US$1.33/l, respectively. Those results are higher than the average mineral biodiesel price in Australia reported at the same time (US$1.02/l as of 2017) [25].

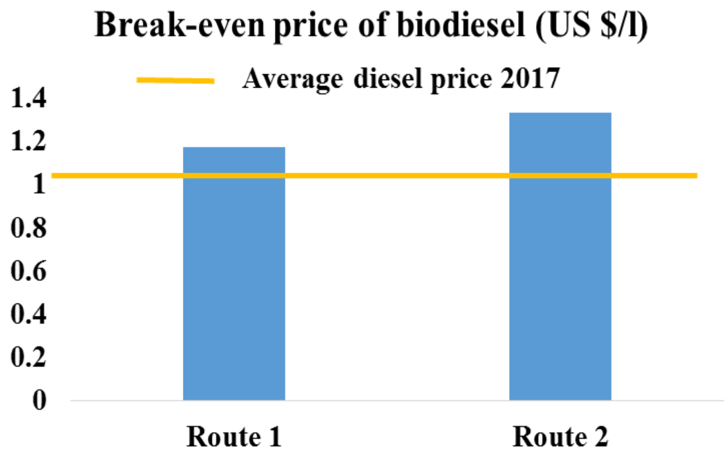

Figure 8.3 Break-even price of GTW-derived biodiesel in comparison to average diesel price

The lowest BEP obtained from route 1 is also higher in comparison to the BEP which has recently been reported by Olkiewicz et al. [15] (US$1,337.5/t vs. US$1,232/t) in which biodiesel was produced utilizing primary sewage sludge as a feedstock without using the sludge drying process. They also used the computational tool, AspenHysys®, to scale up the production process based on the data obtained through laboratory-based experiments. They found that the extraction time and the amount of solvent were the main factors that significantly influence the production cost. Interestingly, although the plant capacities are similar (4,000 t/y vs. 4,400 t/y), the total calculated investment cost is significantly different, US$7,455,447 compared to US$13,793,000 in this study. In another study, Chen et al. [11] reported that biodiesel could be produced from wastewater sludge at an even lower cost of US$670/t for the direct use of sludge as the feedstock, and US$1,070$/t if sludge was employed as medium to cultivate *Oleaginous* microorganism to accumulate lipids and for the biodiesel feedstock. Those relatively lower costs could be likely attributed to the difference in economic evaluation methods, as well as different plant scales, and to the lower production cost associated with labor, materials, utilities, suppliers, etc. Another factor to consider is that methanol, a toxic but relatively cheaper reagent, was utilized in those studies, while this study was undertaken using ethanol (with its relatively lower toxicity compared to methanol). Finally, the longer extraction time (2 hr), and higher solvent extraction ratio used (1:1 w/v GTW to hexane) may partly cause the higher production cost.

To enable the possible reduction of the current BEP, the distribution cost for each route was calculated. **Figure 8.4** shows the distribution cost for both route 1 and route 2 based on the BEP. It can be seen that the variable cost and the fix charges are the main factors dictating the production price of GTW-derived biodiesel, accounting for more than 75% of the BEP in both cases. This can likely be explained by the high material, labor, and utility cost seen in Australia, although the GTW can be collected free of charge. In this regard, the use of bioethanol, a bioproduct produced from sorghum cultivated in tandem to, and on the site of, biodiesel production and which utilizes GTW residues as fertilizer, may be a solution to reduce the BEP.

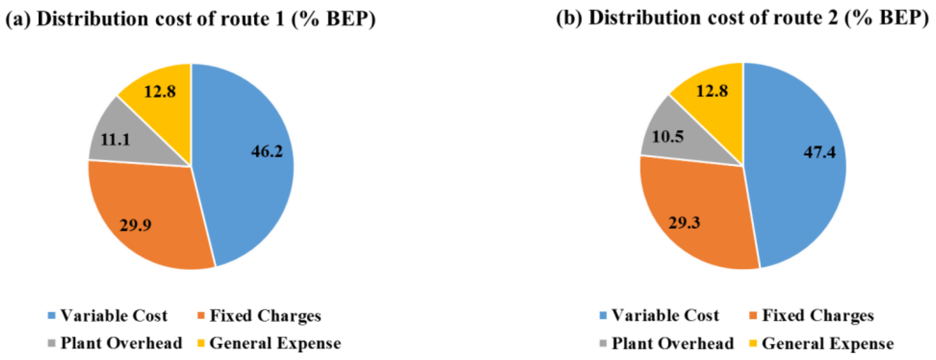

Figure 8.4 Distribution cost of BEP for GTW-derived biodiesel production

In general, despite the difference in economic evaluation methods and the relatively higher BEP obtained in comparison to that of other published data, there is room to improve the economic feasibility of GTW-derived biodiesel production.

8.3.3 Future Prospective

The quality of feedstock contributes significantly to the quality of the biodiesel, but even more, has significant and enabling impact on the implementation of the technological process as also shown in this paper [26]. Here, application of GTW for biodiesel production process was suggested as a promising and cheap feedstock. Ecological improvements are undoubtedly, but still, the selling price of GTW-derived biodiesel is higher than the current cost of mineral diesel due to the need for purifications steps of feedstock and/or final product.

The future improvement using GTW as feedstock in the following directions are foreseen:

a) Search for suitable ionic liquids as solvents for FOGs extraction, instead of hexane.

b) Implementation of environmentally friendlier methods for heavy metals removal from FOG such as e.g. an implementation of mycelial pellets as adsorbents.
c) Application of biocatalytic methods of sulphur removal from feedstock or from biodiesel.
d) Changing the proposed chemical biodiesel synthesis with the enzymatic synthesis.

Regarding the latter one, biocatalytic synthesis is investigated a lot recently, but still, the process was not widely commercialized. Mostly, biotransformations were done with free enzymes in batch systems. However, many research are going in the direction of flow-intensified enzyme-based biodiesel production, such as the use of enzymatic packed-bed microreactors. As highlighted by Budžaki et al. [27], future work should be directed to the search for the cheap and efficient enzyme(s) and carrier(s) as well as suitable immobilization techniques in synergy with cheaper feedstock, such as GTW.

8.4 Conclusions

The detailed technical-economic study indicates that the proposed GTW-derived biodiesel production process is promising and can be practically carried out by the environmental service providers in Australia. Although the proposed selling price of GTW-derived biodiesel was estimated to be US$1,337.5/t, which was higher than the current cost of mineral diesel, this relatively higher cost can likely be reduced if self-produced bioethanol is utilized as a reactant, and further improvement on the lipid extraction process can be obtained. Moreover, a proper tax excise may also encourage the participation of the environmental service providers in the biodiesel production industry.

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References

[1] Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production costs. Bioresource Technology. 2006;97:671-8.

[2] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology. 2003;90:229.

[3] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology. 2007;98:183-90.

[4] Ikura M, Kouchachvili L, Caravaggio G. Production of biodiesel from waste fat and grease. WSEAS International Conference on Renewable Energy Sources. Arcachon, France: Proceedings of the WSEAS International Conference on Renewable Energy Sources; 2007.

[5] Gürü M, Koca A, Can Ö, Çınar C, Şahin F. Biodiesel production from waste chicken fat based sources and evaluation with Mg based additive in a diesel engine. Renewable Energy: An International Journal. 2010;35:637-43.

[6] Yan J, Li A, Xu Y, Ngo TPN, Phua S, Li Z. Efficient production of biodiesel from waste grease: One-pot esterification and transesterification with tandem lipases. Bioresource Technology. 2012;123:332-7.

[7] Cunha A, Feddern V, De Prá MC, Higarashi MM, de Abreu PG, Coldebella A. Synthesis and characterization of ethylic biodiesel from animal fat wastes. Fuel. 2013;105:228-34.

[8] Banković-Ilić IB, Stojković IJ, Stamenković OS, Veljkovic VB, Hung Y-T. Waste animal fats as feedstocks for biodiesel production. Renewable and sustainable energy reviews. 2014;32:238-54.

[9] Hums ME. Environmental Impacts of Biodiesel Produced from Wastewater Greases. Philadelphia, United States: Drexel University; 2016.

[10] Ma H, Addy MM, Anderson E, Liu W, Liu Y, Nie Y, et al. A novel process for low-sulfur biodiesel production from scum waste. Bioresource Technology. 2016;214:826-35.

[11] Chen J, Tyagi RD, Li J, Zhang X, Drogui P, Sun F. Economic assessment of biodiesel production from wastewater sludge. Bioresource technology. 2018.

[12] Zhu F, Zhao L, Jiang H, Zhang Z, Xiong Y, Qi J, et al. Comparison of the lipid content and biodiesel production from municipal sludge using three extraction methods. Energy & Fuels. 2014;28:5277-83.

[13] Demirbas A. Biodiesel from municipal sewage sludge (MSS): Challenges and cost analysis. Energy Sources, Part B: Economics, Planning, and Policy. 2017;12:351-7.

[14] Capodaglio AG, Callegari A. Feedstock and process influence on biodiesel produced from waste sewage sludge. Journal of environmental management. 2017.

[15] Olkiewicz M, Torres CM, Jiménez L, Font J, Bengoa C. Scale-up and economic analysis of biodiesel production from municipal primary sewage sludge. Bioresource technology. 2016;214:122-31.

[16] Mu D, Addy M, Anderson E, Chen P, Ruan R. A life cycle assessment and economic analysis of the Scum-to-Biodiesel technology in wastewater treatment plants. Bioresource Technology. 2016;204:89-97.

[17] Pokoo-Aikins G, Heath A, Mentzer RA, Mannan MS, Rogers WJ, El-Halwagi MM. A multi-criteria approach to screening alternatives for converting sewage sludge to biodiesel. Journal of Loss Prevention in the Process Industries. 2010;23:412-20.

[18] Nguyen N, Demirel Y. Economic analysis of biodiesel and glycerol carbonate production plant by glycerolysis. Journal of Sustainable Bioenergy Systems. 2013;3:209.

[19] Abadi A, Maynard H, Arpiwi NL, Stucley C, Bartle J, Giles R. Economics of oil production from Pongamia (Millettia pinnata) for biofuel in Australia. BioEnergy Research. 2016;9:874-83.

[20] Doshi A. Economic analyses of microalgae biofuels and policy implications in Australia: Queensland University of Technology; 2017.

[21] Dufreche S, Hernandez R, French T, Sparks D, Zappi M, Alley E. Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel. Journal of the American Oil Chemists' Society. 2007;84:181-7.

[22] Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Conversion & Management. 2008;49:125-30.

[23] Peters MS, Timmerhaus KD, West RE, Timmerhaus K, West R. Plant design and economics for chemical engineers: McGraw-Hill New York; 1968.

[24] Nuno L, Fernando G, Paulo dS, Fernando AR. Cost & Evaluation Workbook. Porto, Portugal: University of Porto; 2002.

[25] Ltd ORP. Calendar Year & Financial Year Averages for Petrol and Diesel. Melbourne, Australia: Australian Institution of Petroleum; 2017.

[26] S. Budžaki, G. Miljić, S. Sundaram, M. Tišma, V. Hessel, Cost analysis of enzymatic biodiesel production in small-scaled packed-bed reactors, Appl. Energy, 210 (2018) 268-278.

[27] S. Budžaki, G. Miljić, M. Tišma, S. Sundaram, V. Hessel, Is there a future for enzymatic biodiesel industrial production in microreactors?, Appl. Energy, 201 (2017) 124-134.

Supporting Data

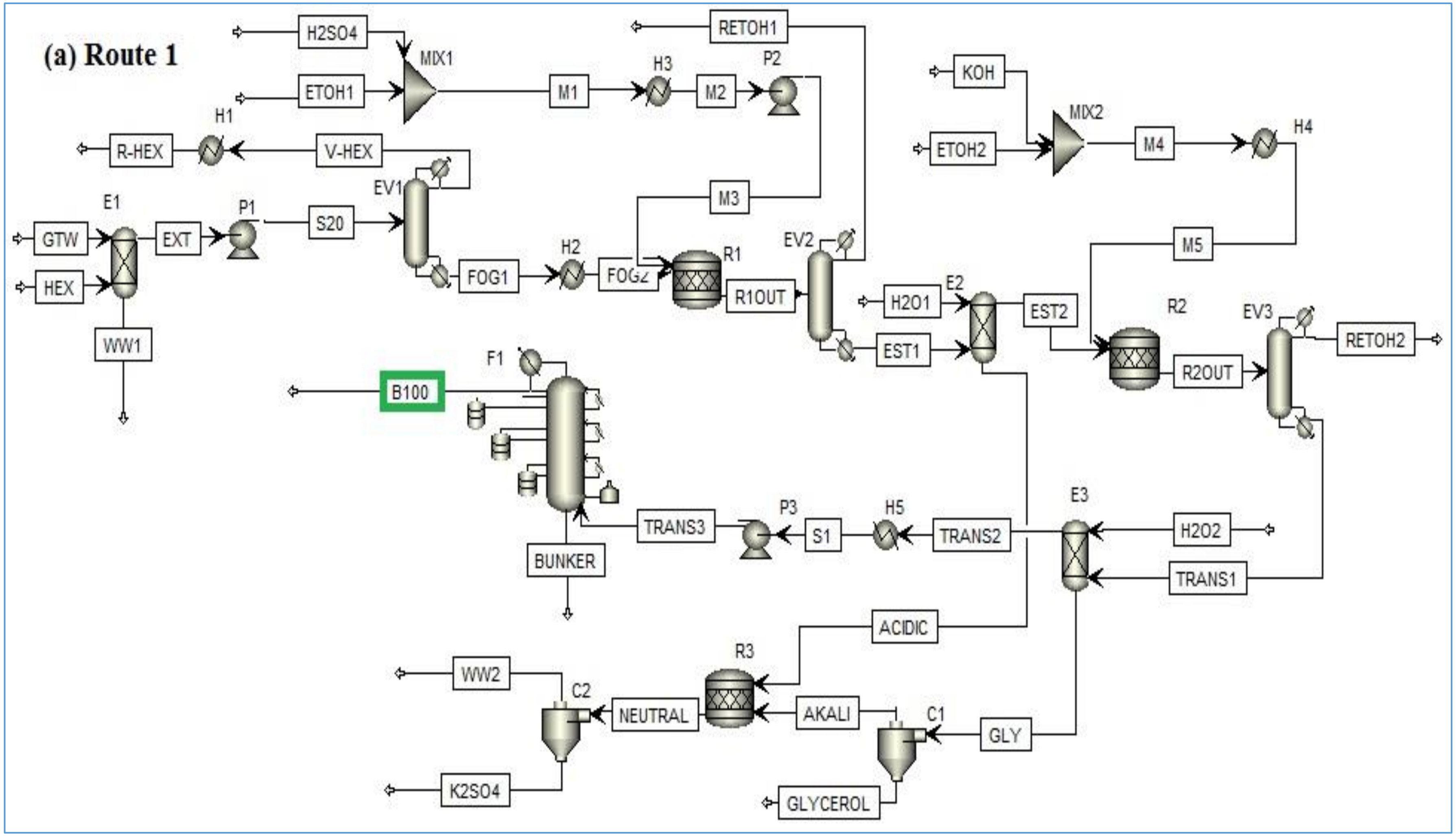


Figure S8.1 Simulation model following route 1: esterification without using acetone

Table S8.1 Some of the product streams obtained through route 1

	GTW	FOG2	R1OUT	EST2	R2OUT	TRANS3	GLYCEROL	ACIDIC WATER	B100	Bunker
Temperature °C	25	75	75	137.6	65	55.1	150	150	42.4	317.4
Pressure bar	1	1	1	1	1	4	1	1	0.5	0.5
Mass Flow kg/hr	1500	600	1135.5	588.9	913.9	592.5	6.8	61.1	550	42.5
Enthalpy MMBtu/hr	-14.6	-1.6	-4.3	-1.3	-3.2	-1.4	-1	-0.8	-1.3	-0.1
Vapor Frac	0	0	0.383	0	0	0	0	0	0	0
Average MW	30.5	315.6	85.3	301	101.2	268.7	92.0	22.9	265.2	325.6
Mass Flow kg/hr										
OLEIC-A	313	295.8	3	2.9	2.9	2.9	< 0.1	< 0.1	2.5	0.4
LINOL-A	84.8	75.8	0.8	0.7	0.7	0.7	< 0.1	< 0.1	0.7	0.1
PALMI-A	143.5	117.5	1.2	1.1	1.1	1.1	< 0.1	< 0.1	1	< 0.1
TRIOLEIN	110.9	110.9	110.9	110.9	3.3	3.3	< 0.1	< 0.1	< 0.1	3.3
E-OLEATE			321.9	300.1	413.3	412.7	< 0.1	< 0.1	383.2	29.5
E-LINOL			82.6	78.6	78.6	78.5	< 0.1	< 0.1	70.3	8.3
E-PALMI			129	89.6	89.6	88	< 0.1	< 0.1	87.1	0.9
GLYCEROL					11.2	< 0.1	6.8		< 0.1	< 0.1
KOH					6	< 0.1	0			
WATER	847.8	< 0.1	31.7	5	5	5.2	0	45	5.2	< 0.1
H2SO4			18	< 0.1				16.1		
K2SO4										

ETOH			436.5	< 0.1	302.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
HEXANE		< 0.1	< 0.1							
Mass Frac										
OLEIC-A	0.2	0.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
LINOL-A	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
PALMI-A	0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
TRIOLEIN	0.1	0.2	0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
E-OLEATE			0.3	0.5	0.5	0.7	< 0.1	< 0.1	0.7	0.7
E-LINOL			0.1	0.1	0.1	0.1	< 0.1	< 0.1	0.1	0.2
E-PALMI			0.1	0.2	0.1	0.1	< 0.1	< 0.1	0.2	< 0.1
GLYCEROL					< 0.1	< 0.1	0.1		< 0.1	< 0.1
KOH					< 0.1	< 0.1	0			
WATER	0.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	0.7	< 0.1	< 0.1
H2SO4			< 0.1	< 0.1				0.3		
K2SO4										
ETOH			0.4	< 0.1	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
HEXANE		< 0.1	< 0.1							

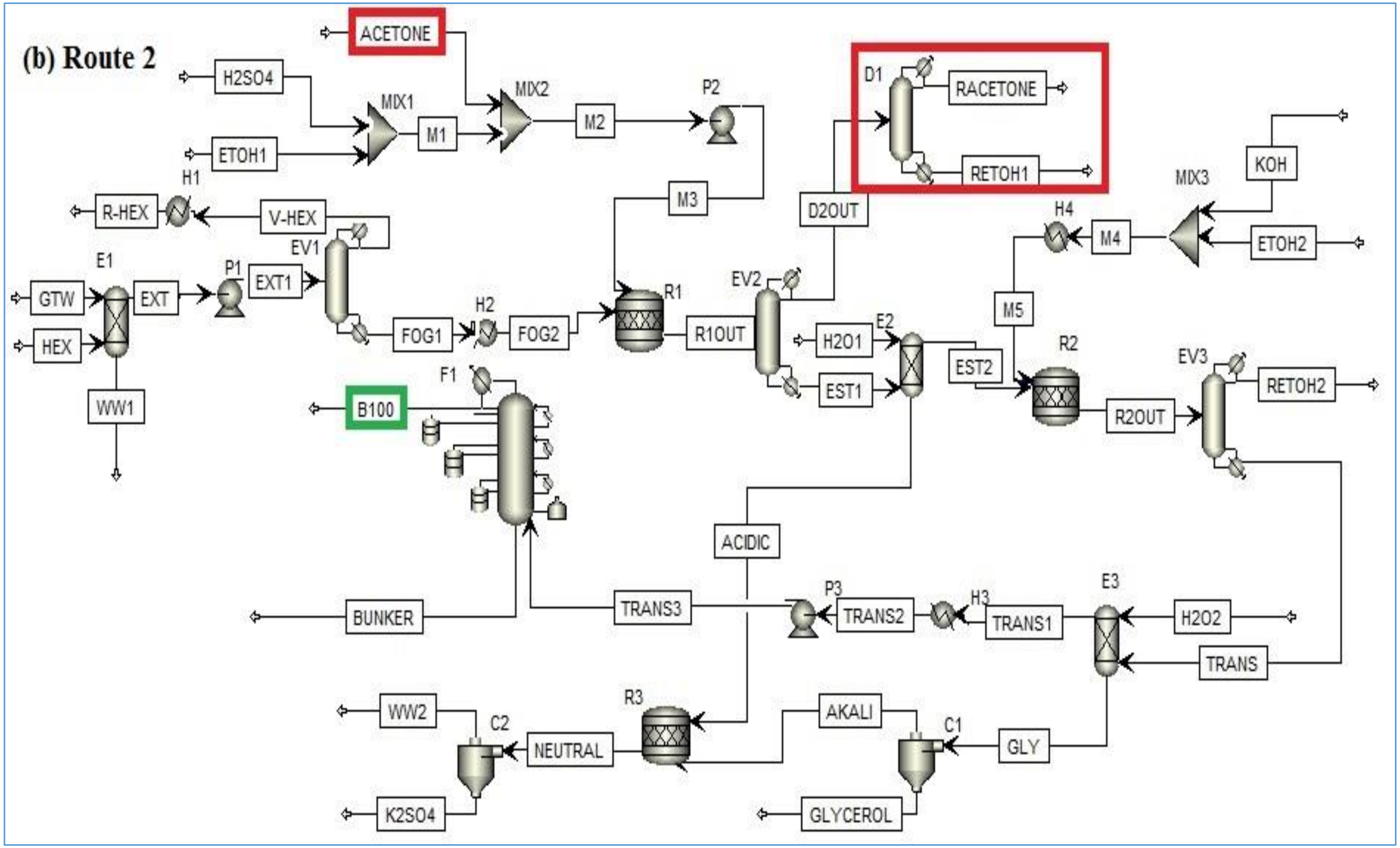


Figure S8.2 Simulation model following route 2: esterification with the presence of acetone

Table S8.2 Some of the product streams obtained through route 2

	ACIDIC	B100	BUNKER	D2OUT	EST2	ETOH1	ETOH2	EXT	FOG1	FOG2	GLYCEROL
Temperature ºC	150	42.4	317.4	66.2	137.6	25	25	24.8	352.4	75	150
Pressure bar	1	0.5	0.5	1	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0	0	0	0	0	0
Mole Flow kmol/hr	2.664	2.074	0.13	15.09	1.955	11.233	6.924	13.757	1.901	1.901	0.075
Mass Flow kg/hr	61.258	550	42.366	745.5	588.742	517.5	319	1642.528	600	600	6.873
Volume Flow cum/hr	0.066	0.656	0.068	0.989	0.801	0.648	0.399	2.418	1.027	0.695	0.046
Enthalpy MMBtu/hr	-0.785	-1.329	-0.067	-3.902	-1.303	-2.961	-1.825	-3.953	-1.133	-1.551	-1.035
Mass Flow kg/hr											
OLEIC-A	0	2.481	0.407	0.07	2.888	0	0	313	295.792	295.792	0
LINOL-A	0	0.672	0.053	0.033	0.726	0	0	84.8	75.823	75.823	0
PALMI-A	0	1.028	0.042	0.104	1.071	0	0	143.5	117.486	117.486	0
TRIOLEIN	0	0	3.327	0	110.899	0	0	110.9	110.899	110.899	0
E-OLEATE	0	384.034	29.445	21.06	300.858	0	0	0	0	0	0
E-LINOL	0	70.495	8.257	3.761	78.813	0	0	0	0	0	0
E-PALMI	0	86.05	0.836	40.551	88.485	0	0	0	0	0	0
GLYCEROL	0	0.001	0	0	0	0	0	0	0	0	6.873
KOH	0	0	0	0	0	0	0	0	0	0	0
WATER	44.997	5.24	0	31.67	5.003	0	0	3.872	0	0	0
H2SO4	16.261	0	0	1.739	0	0	0	0	0	0	0

K2SO4	0	0	0	0	0	0	0	0	0	0	0
ETOH	0	0	0	436.513	0	517.5	319	0	0	0	0
HEXANE	0	0	0	0	0	0	0	986.457	0	0	0
ACETONE	0	0	0	210	0	0	0	0	0	0	0
Mass Frac											
OLEIC-A	0	0.005	0.01	0	0.005	0	0	0.191	0.493	0.493	0
LINOL-A	0	0.001	0.001	0	0.001	0	0	0.052	0.126	0.126	0
PALMI-A	0	0.002	0.001	0	0.002	0	0	0.087	0.196	0.196	0
TRIOLEIN	0	0	0.079	0	0.188	0	0	0.068	0.185	0.185	0
E-OLEATE	0	0.698	0.695	0.028	0.511	0	0	0	0	0	0
E-LINOL	0	0.128	0.195	0.005	0.134	0	0	0	0	0	0
E-PALMI	0	0.156	0.02	0.054	0.15	0	0	0	0	0	0
GLYCEROL	0	0	0	0	0	0	0	0	0	0	1
KOH	0	0	0	0	0	0	0	0	0	0	0
WATER	0.735	0.01	0	0.042	0.008	0	0	0.002	0	0	0
H2SO4	0.265	0	0	0.002	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0	0	0
ETOH	0	0	0	0.586	0	1	1	0	0	0	0
HEXANE	0	0	0	0	0	0	0	0.601	0	0	0
ACETONE	0	0	0	0.282	0	0	0	0	0	0	0
Mole Flow kmol/hr											

OLEIC-A	0	0.009	0.001	0	0.01	0	0	1.108	1.047	1.047	0
LINOL-A	0	0.002	0	0	0.003	0	0	0.302	0.27	0.27	0
PALMI-A	0	0.004	0	0	0.004	0	0	0.56	0.458	0.458	0
TRIOLEIN	0	0	0.004	0	0.125	0	0	0.125	0.125	0.125	0
E-OLEATE	0	1.237	0.095	0.068	0.969	0	0	0	0	0	0
E-LINOL	0	0.229	0.027	0.012	0.255	0	0	0	0	0	0
E-PALMI	0	0.302	0.003	0.143	0.311	0	0	0	0	0	0
GLYCEROL	0	0	0	0	0	0	0	0	0	0	0.075
KOH	0	0	0	0	0	0	0	0	0	0	0
WATER	2.498	0.291	0	1.758	0.278	0	0	0.215	0	0	0
H2SO4	0.166	0	0	0.018	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0	0	0
ETOH	0	0	0	9.475	0	11.233	6.924	0	0	0	0
HEXANE	0	0	0	0	0	0	0	11.447	0	0	0
ACETONE	0	0	0	3.616	0	0	0	0	0	0	0

Table S8.3 Capital investment for route 1 [23]

ESTIMATION OF CAPITAL INVESTMENT BY PERCENTAGE OF DELIVERED EQUIPMENT METHOD					
Project Identifier: GTW-derived Biodiesel Route 1	Fraction of delivered equipment			Calculation values	Calculated values, million $
	Solid-processing plant	Solid-fluid processing plant	Fluid processing plant		
Direct Costs					
Purchased equipment, E'					**2.720**
Delivery, fraction of E'	0.10	0.10	0.10	0.10	0.272
Subtotal: delivered equipment					2.992
Purchased equipment installation	0.45	0.39	0.47	0.47	1.406
Instrumentation&Controls(installed)	0.18	0.26	0.36	0.18	0.539
Piping (installed)	0.16	0.31	0.68	0.16	0.479
Electrical systems (installed)	0.10	0.10	0.11	0.11	0.329
Buildings (including services)	0.25	0.29	0.18	0.18	0.539
Yard improvements	0.15	0.12	0.10	0.10	0.299
Service facilities (installed)	0.40	0.55	0.70	0.40	1.197
Total direct costs	1.69	2.02	2.60	1.60	7.779
Indirect Costs					
Engineering and supervision	0.33	0.32	0.33	0.32	0.957
Construction expenses	0.39	0.34	0.41	0.34	1.017
Legal expenses	0.04	0.04	0.04	0.04	0.120
Contractor's fee	0.17	0.19	0.22	0.19	0.568
Contingency	0.35	0.37	0.44	0.37	1.107
Total indirect costs	1.28	1.26	1.44	1.26	3.770
Fixed capital investment (FCI)					**11.549**
Working capital (WC)	0.70	0.75	0.89	0.75	**2.244**
Total capital investment (TCI)					**13.793**

Table S8.4 Total production cost of route 1 [23]

ANNUAL TOTAL PRODUCT COST AT 100% CAPACITY				
Capacity	4.4	10^6 kg per year		
Fixed Capital Investment, FCI	11.863	million $		
Item	Default factor	Basis	Basis cost, million $/y	Cost, million $/y
Raw materials				0.673
Operating labor				0.346
Operating supervision	0.15	of operating labor	0.346	0.052
Utilities				0.708
Maintenance and repairs	0.06	of FCI	11.863	0.712
Operating supplies	0.15	of maintenance & repair	0.712	0.107
Laboratory charges	0.15	of operating labor	0.346	0.052
Royalties (if not on lump-sum basis)	0.01	of c_o	5.885	0.059
Catalysts and solvents	0	--		0.000
Variable cost =				**2.708**
Taxes (property)	0.02	of FCI	11.863	0.237
Financing (interest)	0.0583	of FCI	11.863	0.692
Insurance	0.01	of FCI	11.863	0.119
Rent	0	of FCI	11.863	0.000
Depreciation	0.06	of FCI	11.863	0.712
Fixed Charges =				**1.759**
Plant overhead, general	0.6	of labor, supervision and maintenance	1.110	0.666
Plant Overhead =				**0.666**
Manufacturing cost =				**5.133**
Administration	0.2	of labor, supervision and maintenance	1.110	0.222
Distribution & selling	0.05	of c_o	5.885	0.294
Research & Development	0.04	of c_o	5.885	0.235
General Expense =				**0.752**
TOTAL PRODUCT COST =				**5.885**

Table S8.5 Total capital investment for route 2 [23]

ESTIMATION OF CAPITAL INVESTMENT BY PERCENTAGE OF DELIVERED EQUIPMENT METHOD

Project Identifier: GTW-derived Biodiesel Route 2	Fraction of delivered equipment			Calculation value	Calculated values, million $
	Solid-processing plant	Solid-fluid processing plant	Fluid processing plant		
Direct Costs					
Purchased equipment, E'					**3.000**
Delivery, fraction of E'	0.10	0.10	0.10	0.10	0.300
Subtotal: delivered equipment					3.300
Purchased equipment installation	0.45	0.47	0.47	0.47	1.551
Instrumentation&Controls(installed)	0.18	0.18	0.36	0.18	0.594
Piping (installed)	0.16	0.16	0.68	0.16	0.528
Electrical systems (installed)	0.10	0.11	0.11	0.11	0.363
Buildings (including services)	0.25	0.18	0.18	0.18	0.594
Yard improvements	0.15	0.10	0.10	0.10	0.330
Service facilities (installed)	0.40	0.40	0.70	0.40	1.320
Total direct costs	1.69	1.60	2.60	1.60	8.580
Indirect Costs					
Engineering and supervision	0.33	0.32	0.33	0.32	1.056
Construction expenses	0.39	0.34	0.41	0.34	1.122
Legal expenses	0.04	0.04	0.04	0.04	0.132
Contractor's fee	0.17	0.19	0.22	0.19	0.627
Contingency	0.35	0.37	0.44	0.37	1.221
Total indirect costs	1.28	1.26	1.44	1.26	4.158
Fixed capital investment (FCI)					**12.738**
Working capital (WC)	0.70	0.75	0.89	0.75	**2.475**
Total capital investment (TCI)					**15.213**

Table S8.6 Annual total production cost of route 2 [23]

ANNUAL TOTAL PRODUCT COST AT 100% CAPACITY				
Project identifier: GTW_derived biodiesel route 2				
Capacity	4.4	10^6 kg per year		
Fixed Capital Investment, FCI	13.084	million $		
Item	Default factor	Basis	Basis cost, million $/y	Cost, million $/y
Raw materials				0.983
Operating labor				0.346
Operating supervision	0.15	of operating labor	0.346	0.052
Utilities				0.728
Maintenance and repairs	0.06	of FCI	13.084	0.785
Operating supplies	0.15	of maintenance & repair	0.785	0.118
Laboratory charges	0.15	of operating labor	0.346	0.052
Royalties (if not on lump-sum basis)	0.01	of c_o	6.612	0.066
Catalysts and solvents	0	--		0.000
Variable cost =				**3.130**
Taxes (property)	0.02	of FCI	13.084	0.262
Financing (interest)	0.0583	of FCI	13.084	0.763
Insurance	0.01	of FCI	13.084	0.131
Rent	0	of FCI	13.084	0.000
Depreciation	0.06	of FCI	13.084	0.785
Fixed Charges =				**1.940**
Plant overhead, general	0.6	of labor, supervision and maintenance	1.183	0.710
Plant Overhead =				**0.710**
Manufacturing cost =				**5.780**
Administration	0.2	of labor, supervision and maintenance	1.183	0.237
Distribution & selling	0.05	of c_o	6.612	0.331
Research & Development	0.04	of c_o	6.612	0.264
General Expense =				**0.832**
TOTAL PRODUCT COST =				**6.612**

Table S8.7 Raw materials, by-product and utilities prices.

Items	**Price, US$**
Raw materials	
Hexane (99.5%)	600 \$/t[a]
Ethanol (99.9%)	0.8 \$/L[b]
Sulfuric acid (99.0%)	110 \$/t[a]
Potassium hydroxide	700 \$/t[b]
Acetone (99.5%)	1000 \$/t[b]
By-product	
Potasium sulfate	150 \$/t[a]
Utilities	
Electricity	108.66 \$/MWh[c]
Natural gas	8 \$/GJ[c]
Cooling water (5-15ºC)	0.25 \$/GJ[d]
Makeup water	0.06 \$/t[d]

[a] *Alibaba.com*

[b] *Chemsupply Ltd. Pty., (bulk buy)*

[c] *Alinta Energy Ltd. Pty., (for small industrial service)*

[d] *SA Water, South Australia*

Chapter 9. Thesis Conclusions

9.1 Conclusions

A detailed technical process for the production of biodiesel from recycled grease trap waste collected in Adelaide, South Australia, focusing on the environmental service provider as a producer, has been studied and developed in this thesis. The results obtained show that the production of biodiesel from recycled greases is technically feasible and the economic aspect is also promising. The overall contribution of this thesis in meeting the objectives laid out in the introduction chapter are summarized below:

1. A simple process applied for the extraction of fats, oils and greases (FOG) from grease trap waste (GTW) using the solvents hexane and diethyl ether, was developed. This process has the potential to be scaled up to significantly higher production output based on the demand of the commercial environmental service providers in Adelaide, South Australia. The benefit of this solvent extraction process is that it can be conducted without heating, and would result in a high lipid yield. In addition, hexane and diethyl ether can be recycled at low temperature and re-used a number of times for the extraction process. Furthermore, the characteristics of the GTW and its extracted oil were also examined and confirmed as a potential feedstock for biodiesel production.
2. An analytical based on a gas chromatography flame-ionized detector (GC-FID) has been developed to quantitatively analyze the fatty acid ethyl ester (FAEE) profiles of the GTW-derived biodiesel. A complete method has been documented which includes the preparation of standards, instrumentation setup, and step-by-step standard operating procedure. This method can also be applied for biodiesel produced from other feedstocks utilizing ethanol as the esterifying reagent. The

advantage of this method is that it offers a reliable and quantitative analysis of FAEE profiles while the processing time for each sample is relatively short (approximately 30 mins).

3. The pre-treatment of the high FFA oil extracted from GTW has been studied using the esterification reaction. Two approaches, these being an esterification reaction using the co-solvent acetone-ethanol at ambient temperature (25ºC), and esterification reaction without acetone at 55 to 75ºC, were conducted. In both cases, the results showed that the FFA could be effectively converted to ethyl esters and the final FFA% was reduced to less than 2%. Furthermore, the use of the co-solvent acetone-ethanol not only resulted in a possible reduction in the total energy consumed by the esterification reaction, but also led to a lower sulfur level in the crude oil.
4. The transesterification reaction of crude oil obtained from the previous pre-treatment steps, utilizing a base catalyst, was investigated using two different approaches. Interestingly, the priority of adding the reaction components had a significant impact on the experimental results. The approach in which ethanol and base were heated first in the reactor while FOG was added later at a specific rate, offered a possible reduction of approximately 30% of the amount of ethanol. In addition, the properties of GTW-derived biodiesel obtained at the optimum conditions satisfied most of the performance and compositional parameters required by the Australian Biodiesel Standard. This strongly suggests that the production of GTW-derived biodiesel is technically feasible, although further improvements are required to produce a biodiesel that satisfies all of the mandatory requirements.

5. A simulation model was constructed using Aspen Plus® V8.8 to study the scale-up effect and to generate data for the economic evaluation of the whole biodiesel production project. The detailed technical-economic study indicates that the proposed GTW-derived biodiesel production process is promising and could be carried out in practice by the environmental service providers in Australia. Although the gate price of GTW-derived biodiesel was estimated to be higher than the current cost of mineral diesel, possible improvements, i.e. using self-produced bioethanol as a reactant and modifying the current extraction process, could be done to reduce this relatively higher cost. This simulation model could provide useful information for the environmental service providers to construct their pilot plants, using the GTW collected in Adelaide as a feedstock.
6. Throughout the project, it is clear that recycled GTW, a hazardous waste resource which possesses a very high lipid content, can be effectively converted to biodiesel which not only reduces the possible environmental impact associated with the combustion of fuels, but also creates added-value for the environmental service providers. However, further research needs to be conducted to both improve the quality of biodiesel, particularly with regard to the levels of sulphur, in addition to producing a commercial GTW-derived biodiesel at an affordable price.

9.2 Recommendation for Future Works

Although this study has introduced a complete process for the production of biodiesel from recycled grease trap waste, there is room for further improvements to be considered in the future.

1. This study only focused on the analysis of GTW samples provided by the environmental service provider, while the design of the whole process was also

based on the analytical results from those samples. However, based on the fact that GTW varied depending on the location, the season, and the manner by which it was collected, a year-long collection of GTW samples would provide statistical data on the lipid content and the available amount of GTW in various regional areas. This would contribute to an optimal process design based on the characteristics of the feedstock, as well as an effective economic evaluation methodology.

2. There is also an opportunity to improve the lipid extraction process which could contribute to a reduction in the biodiesel production cost. The proposed extraction process is relatively long (5 hr) while the amount of solvent used is also quite high (1:1, hexane to GTW v/w). Since the use of solvents is among the main factors that dictate the production price of GTW-derived biodiesel, a cheaper solvent selection, or an extraction methodology without the use of solvent, would significantly reduce the gate price for biodiesel production.
3. Attempts to improve the quality of the GTW-derived biodiesel obtained in this study should also be undertaken in the future. In this regard, the removal of sulphur-containing compounds would be an important step since the significantly high level of sulphur is the main barrier to the commercialization of GTW-derived biodiesel. Results show that there was a significant amount of sulphur-containing compounds in the biodiesel produced. While vacuum distillation at a relatively high temperature could remove a moderate amount of the sulphur, it would be offset by the production price of biodiesel in terms of distillation column investment and associated energy costs. The use of a sulphur absorbent material, such as sulfolane, activated carbon, and graphene, etc. could be a solution for this problem.

4. Kinetic data should also be collected for all of the reactions between free fatty acids, or glycerides, and ethanol. This will enable an effective simulation process with software since such data is not available in the database library of Aspen. Moreover, life-cycle assessment can also be applied, based on both the laboratory-based data and the data generated by Aspen Plus®, to evaluate the environmental impact of the production of GTW-derived biodiesel in comparison to other treatment options, such as landfill and incineration.

Appendix

(Supporting information on published works)

Full Paper | Full Access

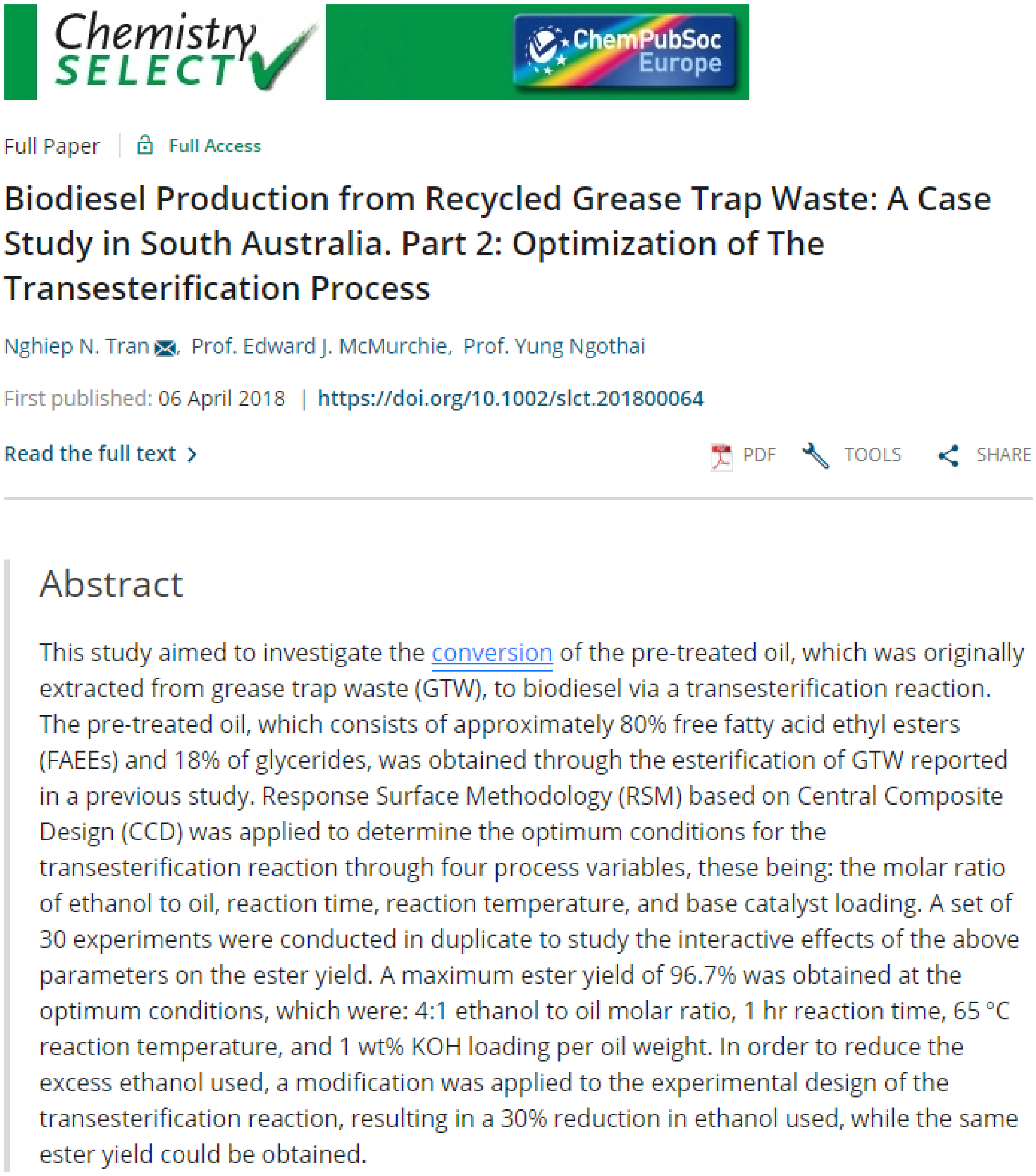
Biodiesel Production from Recycled Grease Trap Waste: A Case Study in South Australia. Part 1: The Pre-Treatment of High Free Fatty Acid Feedstock

Nghiep N Tran, Prof. Edward J McMurchie, Prof. Yung Ngothai

First published: 02 March 2018 | https://doi.org/10.1002/slct.201800065 | Cited by: 1

Abstract

Grease trap waste (GTW) often has a very high content of free fatty acids (FFA) which requires a pre-treatment step before it can be converted to biodiesel via the transesterification reaction. In this study, the esterification reaction was performed to reduce the level of FFA in the GTW, utilizing ethanol as the reagent in the presence of the catalyst H_2SO_4. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied to determine the optimal conditions for the esterification reaction through four process variables, these being: the molar ratio of ethanol to fats, oils, and grease (FOG), reaction time, reaction temperature, and catalyst loading. A set of 30 experiments were conducted in triplicate to study the interactive effects of the above variables on the reduction of the level of FFAs. An FFA% of 0.84% was obtained at the optimum conditions, which were 6:1 ethanol to FOG molar ratio, 3 hr reaction time, 75^0C reaction temperature, and 3 wt% H_2SO_4 loading per FOG weight.



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Biodiesel Production from Recycled Grease Trap Waste: A Case Study in South Australia. Part 2: Optimization of The Transesterification Process

Nghiep N. Tran, Prof. Edward J. McMurchie, Prof. Yung Ngothai

First published: 06 April 2018 | https://doi.org/10.1002/slct.201800064

Abstract

This study aimed to investigate the conversion of the pre-treated oil, which was originally extracted from grease trap waste (GTW), to biodiesel via a transesterification reaction. The pre-treated oil, which consists of approximately 80% free fatty acid ethyl esters (FAEEs) and 18% of glycerides, was obtained through the esterification of GTW reported in a previous study. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied to determine the optimum conditions for the transesterification reaction through four process variables, these being: the molar ratio of ethanol to oil, reaction time, reaction temperature, and base catalyst loading. A set of 30 experiments were conducted in duplicate to study the interactive effects of the above parameters on the ester yield. A maximum ester yield of 96.7% was obtained at the optimum conditions, which were: 4:1 ethanol to oil molar ratio, 1 hr reaction time, 65 °C reaction temperature, and 1 wt% KOH loading per oil weight. In order to reduce the excess ethanol used, a modification was applied to the experimental design of the transesterification reaction, resulting in a 30% reduction in ethanol used, while the same ester yield could be obtained.

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Optimization of the production of biodiesel from grease trap waste (GTW)

Chemeca 2016: Chemical Engineering - Regeneration, Recovery and Reinvention

Tran, Nam Nghiep[1]; **Ho, Quoc Phong**[2]; **Tran, Phuoc Cuong**[3]; **Chao, Lisa**[4]; **Curran, Philip**[5]; **McMurchie, Ted**[6]; **Ngothai, Yung**[7]

Abstract: In this present work, biodiesel production from grease trap waste (GTW), which was supplied by an environmental service company in Adelaide, was carried out employing sulphuric acid and potassium carbonate as catalysts for esterification and transesterification process respectively. The main variables involved in the synthesis of biodiesel, including alcohol types, alcohol/grease trap ratio, amount of catalyst, reaction time, and reaction temperature, were analysed. The complicated two-step process including esterification and transesterification has been applied due to the higher level of free fatty acid in the feedstock. The obtained results showed that average biodiesel yield produced decreased in the following order: isopropanol>propanol>ethanol>butanol. The optimum experimental conditions, which were obtained from the esterification process, were ethanol/oleic acid ratio 3:1, with 5 vol% sulphuric acid catalyst, reaction time 120 minutes, and reaction temperature 65oC. The conversion obtained at the optimum condition is 95.9%.

FULL TEXT PDF (344KB)

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Statement of Responsibility:	Nam Nghiep Tran, Cuong Phuoc Tran, Phong Quoc Ho, Tony Hall, Edward J McMurchie, Volker Hessel, Yung Ngothai