PRODUCTION OF RENEWABLE DIESEL FUEL FROM BIOLOGICALLY BASED FEEDSTOCKS

FINAL PROJECT REPORT

By

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16. Abstract

Renewable diesel is an emerging option to achieve the goal set by the Federal Renewable Fuel Standard of displacing 20% of our nation's petroleum consumption with renewable alternatives by 2022. It involves converting readily available vegetable oils and animal fats to alkane hydrocarbons that can be considered to be drop-in replacements for petroleum-based fuel components. The objective of the project was to develop a model process to produce renewable diesel from triglyceride feedstocks, such as vegetable oils, in a bench scale facility. Specifically, this study was to investigate the process conditions that affect the catalytic decarboxylation of fatty acids and esters without an external supply of hydrogen.

Several heterogeneous catalysts were tested for their effectiveness of oxygen removal via decarboxylation. Palladium on activated carbon (Pd/C) was found to be the most reactive catalyst, and hence was used in further investigations on the effects of process conditions, including reaction time, operating temperature and pressure, solvent application, mixing intensity and catalyst application rate.

Studies revealed that the reaction temperature is the most influential process parameter affecting the reactant conversion rate and the product yield. When the operating temperature was increased from 265°C to 300°C, the reactant conversion was increased from 54%mol to approximately 98%mol after one hour of reaction. The catalyst application rate also affects the decarboxylation rate. However, this effect levels off when the catalyst concentration is 8%wt, i.e., further increase in catalyst application beyond 8% by weight did not increase the process efficiency of decarboxylation significantly. The solvent to reactant mass ratio is also important because it affects the process productivity. It was found that the effects of operating pressure and mixing intensity were negligible under the conditions of investigation.

Once the most influential process parameters were identified, an optimization of the process conditions for renewable diesel production from methyl stearate, the model compound for fatty acid esters, was attempted based on a 2^3 full factorial central composite design (CCD). Experimental results revealed that there were no true optimal points on reactant conversion or desired product yield in the range of operating temperature (300°C - 340°C). Therefore, a conditional set of optimum process parameters were obtained instead. Under the pre-set targets of 85% product yield, the process parameters are a temperature of 355°C, a solvent to reactant mass ratio of 62:38, and a reaction time of 187 minutes. Experimental verification showed that this set of operating conditions led to a targeted product yield of 82.38±4.62%mol, very close to the expected 85%mol level.

Experimental results showed that decarboxylation of mixed fatty acid methyl esters yielded a complex product mixture due to the presence of unsaturated methyl esters. Besides decarboxylation, other reactions, such as cracking of the unsaturated feedstock, also occurred. Further systematic investigation is needed to fully understand the chemical reactions and process parameters on the composition of the final product mixture.

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List of Abbreviations

Al_2O_3	Aluminum oxide		Ru	Ruthium
ANOVA	Analysis of variance		L	Liter
Ba;	Barium		Mg	Magnesium
Ca	Calcium		Mn	Manganese
C	Carbon		MS	Mass spectrometer
CO_2	Carbon dioxide		m	Meter
cm	Centimeter		MeS	Methyl stearate
Cl	Chloride		µg	Microgram
Cr	Chromium		µL	Microliter
Co	Cobalt		µm	Micrometer
Cu	Cupper		mg	Milligram
CCD	Central composite design		mL	Milliliter
C_{react}	Yield of desired product		mm	Millimeter
	heptadecane		Mo	Molybdenum
FAME	Fatty acid methyl esters		Nm	Nanometer
FID	Flame ionization detector		Ni	Nickel
GC	Gas chromatography		Ni/SiO_2	Ni on silica
g	Gram		Ni/Al_2O_3	Ni on alumina
H_2	Hydrogen		N_2	Nitrogen
Fe	Iron		O	Oxygen
Ir	Iridium		Pt	Platinum

Pt/C	Platinum on activated carbon	S	Sulfur
Pt/SiO$_2$	Platinum on alumina	SO$_2$	Sulfur dioxide
Pd	Palladium	SA	Stearic acid
Pd/C	Palladium on activated charcoal	S_{hep}	Selectivity of desired product heptadecane
Pd/Al$_2$O$_3$	Palladium on alumina		
Pd/SiO$_2$	Palladium on silica	Y_{hep}	Yield of desired product heptadecane
RSM	Response surface methodology		
Na	Sodium	Zn	Zinc
NaOH	Sodium hydroxide	%mol	Percentage on molar basis
sRatio	Solvent to reactant mass ratio	%wt	Percentage on mass basis
SiO$_2$	Silicon dioxide		

Acknowledgments

Executive Summary

Renewable diesel is an emerging option to achieve the goal set by the Federal Renewable Fuel Standard of displacing 20% of our nation's petroleum consumption with renewable alternatives by 2022. It involves converting readily available vegetable oils and animal fats to alkane hydrocarbons that can be considered to be drop-in replacements for petroleum-based fuel components. The objective of the project was to develop a model process to produce renewable diesel from triglyceride feedstocks, such as vegetable oils, in a bench scale facility. Specifically, this study was to investigate the process conditions that affect the catalytic decarboxylation of fatty acids and esters without an external supply of hydrogen. Heterogeneous catalysts, including Pd/C, Pd/Al$_2$O$_3$, Pt/C, Ni/SiO$_2$, Pt/Al$_2$O$_3$ and Raney Nickel, were tested for their effectiveness on decarboxylation under different operating conditions. It was found that Pd/C is the most reactive catalyst for the decarboxylation of stearic acid, the model fatty acid. Hence Pd/C was used in subsequent investigations on the effects of process conditions, including reaction time, operating temperature and pressure, solvent application, mixing intensity and catalyst application rate for decarboxylation, a means of oxygenation removal.

Studies revealed that the reaction temperature is the most influential process parameter affecting the reactant conversion rate and the product yield. When operating temperatures increase from 265°C to 300°C, the reactant conversion was increased from 54%mol to approximately 98%mol in one hour of reaction. The catalyst application rate also affects the decarboxylation rate. However, this effect levels off when the catalyst concentration is 8% by weight. Further increases in catalyst application beyond 8% by weight did not increase the process efficiency of decarboxylation significantly. As the decarboxylation of fatty acids/ esters is a liquid reaction, careful selection of the solvent to reactant mass ratio is important. Too high

of a solvent to reactant mass ratio will reduce the process productivity while too low will extend the processing time toward completion. It was also found that the effects of operating pressure and mixing intensity were negligible under the conditions of investigation.

Once the most influential process parameters were identified, an optimization on the process conditions for renewable diesel production from methyl stearate, the model compound for fatty acid esters, was attempted based on a 2^3 full factorial central composite design (CCD). Experimental results revealed that there were no true optimal points on reactant conversion or desired product yield in the range of operating temperature (300°C - 340°C). Therefore, a conditional set of optimum process parameters were obtained instead. Under the pre-set targets of 85%mol product yield, the process parameters are 355°C, solvent to reactant mass ratio 62:38, and reaction time 187 minutes. Experimental verification showed that this set of operating conditions led to a targeted product yield of 82.38±4.62%mol, very close to the expected 85%mol level.

Mixed fatty acid methyl esters (FAME or biodiesel) as the feedstock was also tested for decarboxylation. Experimental results showed that the process yielded a complex product mixture due to the presence of unsaturated methyl esters. Besides decarboxylation, other reactions, such as cracking of the unsaturated feedstock, also occurred. Further systematic investigation is needed to fully understand the chemical reactions and process parameters on the composition of the final product mixture.

Chapter 1 Introduction

The biodiesel industry has been a rapidly growing industry. Production in the United States has increased from 2 million gallons in 2000 to 1.1 billion gallons in 2012 (Prater et al., 2013). Biodiesel is comprised of mono-alkyl esters of long chain fatty acids that are typically derived from renewable energy sources, such as plant oils and animal fats (ASTM, 2012). Compared to petroleum diesel fuel, biodiesel has a number of attractive advantages, such as reduced emissions, high cetane number, low toxicity and excellent lubricity (Narasimharao et al., 2007). However, biodiesel has some drawbacks. One of them is its high oxygen content which leads to lower energy content, limiting its uses in applications that require high energy density.

1.1 Renewable Diesel

Renewable diesel, also called green diesel, is a diesel-like hydrocarbon fuel. It possesses good fuel properties such as lower viscosity, better fuel stability and higher energy density than biodiesel. Renewable diesel, which is chemically similar to petroleum diesel, is usually produced by hydro-processing plant oils and animal fats to remove the oxygen from a biobased feedstock.

Producing renewable diesel is really about oxygen removal or deoxygenation. Various combinational reactions of the deoxygenation of plant oils and animal fats can take place, depending on the feedstock composition, catalyst choice and reaction conditions. Hydrodeoxygenation and decarboxylation are the most common studied pathways for deoxygenating oils and fats (Koivusalmi E., 2008; Kubicka, 2008). For example, hydrodeoxygenation of fatty acids involves external hydrogen supply:

$$R\text{-COOH} + 3H_2 \rightarrow R\text{-CH}_3 + 2H_2O \qquad\qquad (1.1)$$
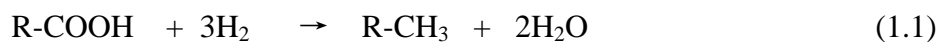
In hydrodeoxygenation, oxygen-containing materials are reduced by hydrogenation to form hydrocarbons and water, retaining the original carbon structure with a cost of external hydrogen. While decarboxylation is about removing oxygen as a CO_2 group chemically:

$$R\text{-COOH} \quad \rightarrow \quad R\text{-H} \quad + \quad CO_2 \tag{1.2}$$

Carboxylic acids are reduced to form hydrocarbons while releasing a carbon dioxide.

The technologies to produce renewable diesel have been developed and commercially explored by the Neste Oil Company, UOP/Eni Ecofining, and others. Current technologies are mainly hydrodeoxygenation which is energy-intensive, requires high pressure, and expensive hydrogen feed (Na et al., 2010). Recently, new research using noble metal catalysts supported on activated carbon has been studied on the decarboxylation of triglycerides under inert atmosphere to produce linear alkanes and alkenes (Immer, 2010; Immer and Lamb, 2010; Lestari et al., 2010; Lestari et al., 2009c; Lestari et al., 2008; Maki-Arvela et al., 2007; Morgan et al., 2010; Simakova et al., 2010; Simakova et al., 2009; Snare et al., 2008; Snare et al., 2006). An advantage of this chemical pathway is that no hydrogen is required in the process and is therefore less expensive compared to the hydrodeoxygenation process (Lestari et al., 2009b).

1.2 Statement of Problem

Most of the research on decarboxylation was done with fatty acids as feedstock in producing renewable diesel (Maki-Arvela et al., 2007; Simakova et al., 2010; Simakova et al., 2009; Snare et al., 2006). These previous studies suggest that decarboxylation is a potential process for the conversion of plant oils and animal fats to hydrocarbons (Do et al., 2009; Maki-Arvela et al., 2007). It is necessary to have a better understanding and control of the process parameters, such as catalyst type, operating temperature and pressure, and solvent application, on the process

efficiency as indicated by the product yield, reactant conversion rate and the catalyst activity and selectivity. A mixture of fatty acid methyl esters or biodiesel can also be selectively deoxygenated for improved fuel properties. However, little work has been done with methyl esters (Do et al., 2009). Moreover, there are only few research efforts focused on the process development and optimization of the hydrocarbon-based biofuel production (Na, 2012).

1.3 Objective

The objective of this project was to develop a model process to produce renewable diesel from triglyceride feedstocks, such as vegetable oils, on a bench scale. Specifically, this study was to investigate the process conditions that affect the catalytic decarboxylation of fatty acids and esters without an external supply of hydrogen. A study on the decarboxylation reaction using saturated model compounds (e.g., stearic acid, methyl stearate) was conducted to identify the most influential process parameters, including operating temperature, pressure and catalyst type, and their effects. Next, the optimal operating conditions for maximizing the molar yields of the targeted product in the process of decarboxylation were examined. Studies on mixed fatty acid esters as the feedstock under the optimum process conditions for decarboxylation are necessary and were included in this study.

The outcome from this research contributes to the current effort and knowledge base in developing feasible technologies for renewable diesel production from plant oils and animal fats.

Chapter 2 Literature Review

Deoxygenation of plant oils and animal fats refers to the chemical reaction of oxygen removal from biomass-feedstocks. Various deoxygenation reactions of plant oils and animal fats can take place depending on the feedstock composition, catalyst choice, and reaction conditions. Many kinds of catalysts have been tested for hydrogenation and deoxygenation of plant oil and animal fats for renewable diesel production.

2.1 Catalysts for Deoxygenation of Plant Oils and Animal Fats

2.1. 1 Metal Sulfides Catalysts

Sulfide metal catalysts have been studied in conjunction with hydrodeoxygenation due to their well-known industrial applications in the hydrosulfurization of fossil-based oils (Crocker, 2010). Bimetallic aluminum oxide catalysts in sulfide form, usually $NiMo/Al_2O_3$ and occasionally $CoMo/Al_2O_3$, have been investigated (Donnis et al., 2009; Kubičková, 2010; Liu et al., 2009). Triglycerides in the presence of hydrogen and sulfide metal catalysts are transformed and converted to hydrocarbons at about 300-360°C and at least 3 MPa of hydrogen. The hydrocarbons are either the same number of carbon atoms (i.e., products of hydrodeoxygenation) or one carbon atom less than the original acid (i.e., products of hydrodecarboxylation/ decarboxylation). The side-products include propane, water and/or CO_2 (Darocha et al., 1993; Donnis et al., 2009; Huber et al., 2007; Kubicka et al., 2009; Simacek et al., 2009). The appropriate selection of the catalyst and technological condition is the key factor for successful hydrodeoxygenation and/or hydrodecarboxylation (Mikulec et al., 2010). The reaction conditions affect product distribution and all parallel reactions. Hydrodecarboxylation prevails over hydrodeoxygenation with increased temperature and decreased reaction pressure. These findings

have been explored by experimental study (Kubicka et al., 2009; Mikulec et al., 2010) and by thermodynamic analysis (Smejkal et al., 2009). Different catalysts have also led to significantly different product distributions (Kubicka and Kaluza, 2010). It was found that a NiMo catalyst promotes hydrodecarboxylation while a CoMo catalyst promotes hydrodeoxygenation. NiW catalysts showed stable hydrogenation activity and more efficient in decarboxylation than NiMo and CoMo catalysts (Makoto Tobaa, 2011). In addition, studies have shown that the yield by decarboxylation from carboxylic acids is higher than that by hydrodecarboxylation from esters with the corresponding acids (Laurent and Delmon, 1994c). Although sulfide metal catalysts are efficient for the deoxygenation of oils and fats, they also have disadvantages such as additional cost of the sulfidation agent. Reduced $CoMo/Al_2O_3$ catalyst was also considered as a good choice for deoxygenating oils and fats (Márton Krár, 2010).

2.1.2 Noble Metal Catalysts

Noble metals, such as platinum (Pt), palladium (Pd), and ruthenium (Ru), supported on various porous materials are a class of catalysts that are used in various industrial processes, including selective hydrogenation, naphtha reforming, and hydroformylation reactions (Kubičková, 2010). Therefore, it is not surprising that they are also potential catalysts for deoxygenation of oils and fats. Moreover, recent research has shown that supported noble metal catalysts, especially Pd and Pt, are the more active catalysts for decarboxylation of oils and fats (Snare et al., 2006).

The activity and selectivity of some supported noble metal catalysts, such as palladium on activated carbon (Pd/C), platinum on activated carbon (Pt/C), platinum on aluminum oxide (Pt/Al_2O_3), platinum on titanium oxide (Pt/TiO_2), etc., have been studied by many researchers (Chiappero et al., 2011; Immer et al., 2010; Kubickova et al., 2005; Lestari et al., 2008;

Simakova et al., 2010; Simakova et al., 2009; Snare et al., 2008; Snare et al., 2006). Murzine et al. found that better results were achieved with Pd and Pt supported on activated carbons. Decarboxylation catalyzed by Pd/C proceeds significantly while decarbonylation is also observed over the same catalyst (Snare et al., 2006). Although supported noble metal catalysts are effective for decarboxylation of fatty acids, the catalysts suffer severe deactivation after multiple uses (Ping et al., 2011). Further examples of studies are summarized in Table 2.1).

Table 2. 1: Summary of reaction conditions and catalysts for deoxygenation of oils and fats over supported noble metal catalysts

Model compounds	Catalyst	Reaction conditions	Reference
Stearic acid	Various catalysts	$300^{\circ}C$;N_2, 600kPa; SBR	Snare et al., 2006
Stearic acid	Pd/C	$300\text{-}350^{\circ}C$; He, H_2-Ar,H_2,1.7 MPa; SBR	Kubickova et al., 2005; Maki-Arvela et al., 2007; Maki-Arvela et al., 2011
Stearic acid	Pd/C	$360^{\circ}C$; Ar-H_2, Ar, 10 bar; FBR; Dodecane	Lestari et al., 2009b
Stearic acid	Pd/SBA-15	$360^{\circ}C$; H_2-Ar,1.7MPa; SBR; Dodecane	
Stearic acid, palmitic acid	Pd/C	$260\text{-}300^{\circ}C$; H_2/Ar, 17.5 bar; SBR; dodecane	Lestari et al., 2009c; Lestari et al., 2008; Simakova et al., 2009
Stearic, oleic, linoleic acids	Pd/C	$300\,^{\circ}C$; He, H_2, 15 bar; SBR; Dodecane or Heptadecane	Immer et al., 2010; Immer and Lamb, 2010
Oleic, linoleic acids	Pd/C	$300\text{-}360^{\circ}C$; Ar, H_2-Ar, 1.5-4.2 MPa; SBR and FBR; Mesitylene	Snare et al., 2008
Caprylic acid	Pd/C	$300\text{-}400\,^{\circ}C$; H_2-He, 2.1 MPa; FBR	Boda et al., 2010
Methyl octanoate, methyl stearate	Pt/Al$_2$O$_3$, Pt/TiO$_2$	$300\text{-}350^{\circ}C$; H_2-He, 0.7 MPa; SBR, FBR	Do et al., 2009
Methyl octanoate, methyl laurate	Pt/Al$_2$O$_3$, Pt/SiO$_2$, PtSn/SiO$_2$, PtSnK/SiO$_2$	593-623K; He, 0.31-2.41MPa; SBR	Chiappero et al., 2011
Rapeseed oil	Pt/Zeolite	$380\,^{\circ}C$; H_2, 11 MPa; BR	Sotelo-Boyas et al., 2011

Chapter 3 Method

3.1 Materials

Food grade stearic acid (95%) was purchased from Sigma-Aldrich in St. Louis, Missouri. Methyl stearate (>95%) was purchased from Tokyo Chemical Industry Company, Tokyo, Japan. Dodecane (100%) was purchased from Acros Organics (Geel, Belgium). Various commercial catalysts were obtained from Sigma-Aldrich including 5% by weight palladium on activated charcoal (Pd/C), 5% by weight platinum on activated carbon (Pt/C), 5% by weight palladium on alumina (Pd/Al$_2$O$_3$), 65% by weight nickel on silica/alumina (Ni/SiO$_2$, Al$_2$O$_3$), and Raney nickel.

Standard chemicals for calibrating the gas chromatography system were all reagent grades. These reagent chemicals included hexadecane (C$_{16}$H$_{34}$), n-heptadecane (C$_{17}$H$_{36}$), octadecane (C$_{17}$H$_{34}$), eicosane (C$_{18}$H$_{36}$), N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (products of Acros Organics, Geel, Belgium), stearic acid from Nu-Chek Prep Company (Elysian, Minnesota), methyl stearate (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan). High purity nitrogen (99.9999%) and helium (99.999%) were supplied by Oxarc (Lewiston, Idaho).

3.2 Experiments

3.2.1 Batch reactor operation

All experiments to evaluate process parameters of decarboxylation were performed in a 300 mL Parr pressure batch reactor (model 4560, PARR Instruments, Moline, IL) equipped with a 4857 controller.

Prior to each experiment, a specified amount of the catalyst was measured and transferred into the reactor. The catalyst was activated by 99.999% hydrogen at 1.38 MPa (200 psi) *in situ* at 200°C for one hour. After the activation, a specified amount of dodecane solvent was added, in

the presence of hydrogen, to the reactor to cover the catalyst from exposure to air before the reactant(s) was added to the reactor. Thereafter, the reactor was flushed with nitrogen for one minute to remove any traces of hydrogen and oxygen. The reactor was then heated to the desired temperature, while being agitated, and the pressure was adjusted to the desired level with nitrogen. The reaction typically lasted 2-4 hours, after the temperature reached the desired level. Upon the completion of the reaction, the reactor was cooled to room temperature by the cooling unit inside of the reactor. Samples of the reaction mixture were taken at 1-hour intervals during the operation and saved for further analysis.

3.2.2 Continuous-flow Testing

Continuous decarboxylation of MeS was studied in a continuous-flow tubular reactor packed with catalyst of Pd/Al_2O_3 in pellet form. The catalyst was activated in the same way as in the batch reactor. The reaction was maintained at a constant temperature of 355°C. Solutions of the reactant in the solvent dodecane were continuously pumped through the reactor at a feeding rate of 1.1 mL/minute. Samples of the finished product stream were taken at 6-hour intervals.

3.3 Product Analysis

An Agilent 6890N Gas Chromatograph (GC) was used for analyzing the reactants and the liquid products. The GC is equipped with a flame ionization detector (FID), split/splitless injection system and a non-polar column (DB-5MS, Agilent J&W capillary, with dimensions of 60 m x 0.32 mm x 0.5 μm). The temperature of the GC oven was programed as follows: after reaching 110°C, 1°C/minute to 126°C, 30°C/minute to 185°C, 1°C/minute to 200°C, 5°C/minute to 300°C, holding for two minutes. The entire procedure took approximately 55 minutes. The flow rate of the helium carrier gas was 170 mL/minute. Samples, 1 μL in size, were injected onto

the column inlet with a 60:1 split ratio. Concentrations of the products in the samples were determined in reference to the internal standard of eicosane.

Generally, the final liquid products from the decarboxylation of SA and MeS included the desired product, heptadecane ($C_{17}H_{36}$), as well as the byproducts octadecane ($C_{16}H_{34}$) and eicosane ($C_{18}H_{38}$). These byproducts typically represented a small fraction, less than 5%mol, of the overall product. Therefore, the yield of heptadecane was used in this study to determine the decarboxylation efficiency. The conversion rate of reactants was also used as a process evaluating parameter.

3.4 Response Surface Methodology

Response surface methodology (RSM) was used in the process optimization of MeS decarboxylation to find suitable conditions for renewable diesel production. This statistical approach was based on a 2^3 full factorial central composite design (CCD) for RSM and processed by the Design Expert software (Stat-Easy, Minneapolis, MN). Temperature (x_1, °C), solvent to reactant mass ratio (sRatio; x_2, dimensionless), and reaction time (x_3, minutes) were chosen as the independent variables as shown in Table 3.1. The explored ranges of these parameters were 286-355°C, sRatio from 87:13 to 53:13, and reaction time from 49 to 251 minutes. These values were chosen based on the results of preliminary experiments. The yield and the selectivity of desired product heptadecane, and the conversion of reactant MeS were chosen as the response variables.

Table 3.1: Experimental design for optimization of MeS decarboxylation

No.	Temperature (x_1, °C)		sRatio (x_2, m/m)		Reaction time (x_3, minutes)	
	Levels	Coded	Levels	Coded	Levels	Coded
1	300	-1	4:1	-1	90	-1
2	340	1	4:1	-1	90	-1
3	300	-1	3:2	1	90	-1
4	340	1	3:2	1	90	-1
5	300	-1	4:1	-1	210	1
6	340	1	4:1	-1	210	1
7	300	-1	3:2	1	210	1
8	340	1	3:2	1	210	1
9	286	-1.68	7:3	0	150	0
10	355	1.68	7:3	0	150	0
11	320	0	87:13	-1.68	150	0
12	320	0	53:47	1.68	150	0
13	320	0	7:3	0	49	-1.68
14	320	0	7:3	0	251	1.68
15	320	0	7:3	0	150	0
16	320	0	7:3	0	150	0

Chapter 4 Results

4.1 Reaction Conditions for Catalytic Decarboxylation of Fatty Acids and Esters

4.1.1 Catalytic Activity

The catalysts Pd/C, Pd/Al$_2$O$_3$, Pt/C, Ni/SiO$_2$ and Raney nickel were evaluated in this study. While these catalysts showed insignificant catalytic activity in stearic acid (SA) decarboxylation without external hydrogen supply, Pt/C led to a satisfactory SA conversion rate of 83.5%mol and the heptadecane yield was only 78.2%mol. However, Pd/C showed the highest activity. When Pd/C was applied, SA was completely decarboxylated with the highest heptadecane yield of 88.6 %mol after 3-hours of reaction.

4.1.2 Effect of Reaction Time

In the reaction with a sRatio of 4:1 and 10% by weight catalyst application, the concentration of heptadecane gradually increased with time. SA almost completely converted to heptadecane after 2 hours. GC analysis showed that less than 5%mol of the byproducts, mainly octadecane (C$_{16}$H$_{34}$), was present in the mixture.

4.1.3 Effect of Solvent to Reactant SA Mass Ratio

Solvent concentration also affects the reactions. In the early stage of the reaction, after 30 to 60 minutes, the SA conversion and the heptadecane yield steadily increased. With solvent to reactant SA mass ratios (sRatio) of 9:1 and 4:1 (i.e., high solvent application or low reactant concentrations), complete SA conversion was achieved in 2 hours. Although a complete SA conversion can be achieved with a sRatio of 1:1, (i.e., less solvent application or high reactant application), a slower SA conversion rate was observed.

4.1.4 Effect of Reaction Temperature

Three different reaction temperatures, 265°C, 285°C and 300°C, were investigated in the decarboxylation of SA using Pd/C as the catalyst. At 265°C, the SA conversion was 54%mol after 1 hour of reaction time, while at 300°C the conversion rate was approximately 98%mol after 1 hour of reaction time. Temperature strongly affects the SA conversion and the heptadecane formation.

4.1.5 Effect of Catalyst Concentration

The overall SA conversion is significantly affected by the amount of catalyst applied. Over the range of 0-8% by weight catalyst application, it was found that the higher the catalyst concentration the faster, the SA decarboxylation. However, there was no significant effect on SA conversion and the heptadecane yield when the catalyst application rate was 8% by weight, or higher.

4.1.6 Methyl Stearate as the Feedstock

The decarboxylation of methyl stearate (MeS), the model ester compound, was also studied in the absence of an external hydrogen supply. Similar to SA decarboxylation, the decarboxylation of MeS is also affected by operating conditions. It was observed that under the same operating conditions the decarboxylation rate of MeS was much slower than that of SA. With the same reaction conditions (300°C, 10% by weight catalyst, 4:1 sRatio, and 1 hour reaction time), the SA conversion was as high as 97.3%mol while the MeS conversion was only 31.0%mol. To achieve better MeS conversion and product yield, a higher temperature was applied. As the temperature increased from 300°C to 350°C, the MeS conversion was significantly improved from 26.8%mol to 81.2%mol. The corresponding yield of heptadecane increased from 14.1%mol to 69.7%mol after 3 hours.

4.2 Process Optimization for Decarboxylation of Methyl Stearate

Preliminary observations showed that increased reaction temperature and time resulted in higher reactant conversion and product yield. To determine the best combination of operating parameters for high MeS decarboxylation a process optimization was attempted based on a 2^3 full factorial central composite design (CCD).

An analysis of variance (ANOVA) on the experimental results was conducted using the Design Expert software (Stat-Easy, Minneapolis, MN). The regression models obtained from the ANOVA analysis are:

$$Y_{hep} = 31.35 + 19.76X_1 - 8.5X_2 + 6.76X_3 + 6.48X_1^2 + 5.86X_2^2 \qquad (4.1)$$

$$C_{react} = 39.24 + 18.21X_1 - 3.20X_2 + 6.22X_3 + 7.74X_1^2 + 7.71X_2^2 \qquad (4.2)$$

$$S_{hep} = 77.83 + 10.84X_1 - 10.71X_2 + 6.26X_1X_2 \qquad (4.3)$$

Where Y_{hep}, C_{react}, S_{hep} are the response values for the yield of heptadecane, the conversion of reactant MeS and the selectivity of heptadecane respectively. The X_1, X_2 and X_3 are the coded levels for temperature, sRatio and reaction time, respectively.

Table 4.1 shows a summary for the significance of differences of the regression model for product yield, individual model coefficients, and the lack of fit. It can be seen that with a probability (p-value) of less than 0.0001, this model was statistically significant for the heptadecane yield. The p-value for the lack-of-fit test is 0.1132, implying that this quadratic model adequately describes the observations. The main factors (temperature, sRatio and reaction time) are significant at a 95% confidence level. Temperature is the most effective variable, followed by sRatio, and reaction time. It is also seen that the interacting effects of temperature, sRatio and reaction time on the yield of heptadecane are not significant.

Table 4.1 ANOVA for the fitted quadratic model of heptadecane yield (Y_{hep})

Source	Sum of squares	Degree of freedom	Mean square	F value	*p*-value
Model	7963.69	5	1592.74	20.17	<0.0001
X_1 (Temp.)	1606.09	1	53333.04	67.54	<0.0001
X_2 (sRatio)	986.33	1	986.33	12.49	0.0033
X_3 (Time)	623.98	1	623.98	7.90	0.0139
$X_1{}^2$	611.41	1	611.41	7.74	0.0147
$X_2{}^2$	500.55	1	500.55	6.34	0.0246
Residual	1105.47	14	78.96		
Lack-of-fit	937.21	9	104.13	3.09	0.1132
Pure error	168.26				
Total	9069.16	19			

To study the effects of parameters and their interactions on the yield of heptadecane, the response surface of the model to the independent variables of temperature and sRatio was plotted as shown in Figure 4.1. Experimental results indicated that there were no optimal points on desired product yield in the range of operating temperature (300°C - 340°C). Therefore, a conditional set of optimum process parameters were obtained instead. Under the pre-set targets of 85 %mol targeted product yield, the optimum conditions for maximizing heptadecane yield as approximately 350°C, 2:3 sRatio, and 180~210 minute reaction time.
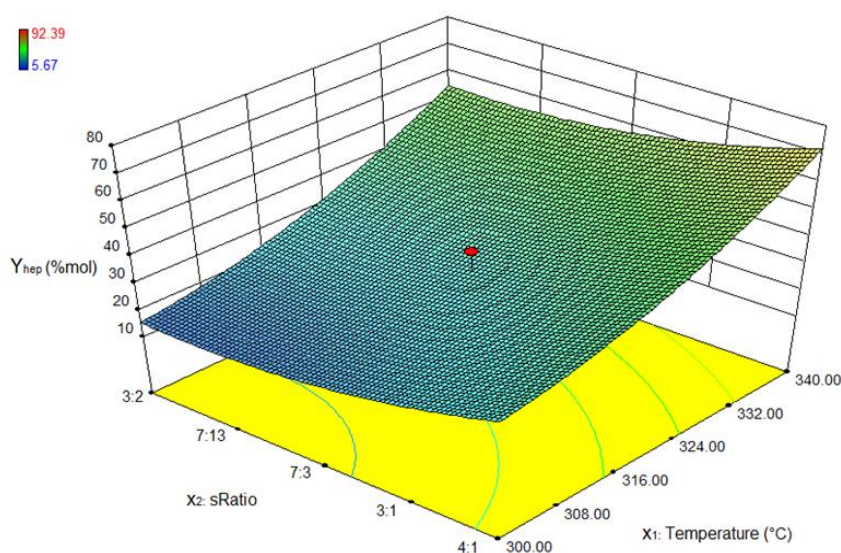

Figure 4.1: 3D plot of response surface for the yield of heptadecane.

Similar to the optimization of heptadecane yield, conditional optimizations were performed to obtain the suitable process conditions for MeS conversion and heptadecane selectivity. The results were 354°C, sRatio 61:39, and reaction time 166 minutes, for MeS conversion and 353°C, sRatio 65:35, and 205 minutes reaction time for product selectivity. It is noted that these operating conditions are not significantly different from those for the desired product yield discussed above.

4.3 Decarboxylation of Mixed Fatty Acid Methyl Esters (FAME)

Analysis on the mass profile of mixed fatty acid methyl acid esters (FAME) showed that the specific FAME feedstock contained 11.08% by weight oxygen content. After processing under similar operating conditions as those for the model ester MeS, multiple types of products were detected, including alkane, aromatic products, methyl esters, fatty acids and aromatics. Samples of the decarboxylated FAME contained 29.13% by weight of paraffin content and 5.69% by weight oxygen content. Therefore, besides decarboxylation, other side reactions, such as cracking of the unsaturated feedstock, also occurred. Further systematic investigation is needed to fully understand the chemical reactions and process parameters on the composition of the final product mixture.

4.4 Catalytic Decarboxylation of Methyl Esters in a Continuous Flow Reactor

The decarboxylation of methyl stearate was also tested in a continuous-flow reactor. A tubular continuous flow reactor (300 mL) was packed with Pd/Al_2O_3 catalyst in the absence of external hydrogen supply. The decarboxylation reaction was maintained at 355°C, solvent to reactant mass ratio 62:38, and reactant feeding rate 1.1 mL/minute. The system was run for 7

days or longer continuously and samples were taken at 6-hour intervals. Preliminary experimental results showed that the MeS could be converted completely. However, the yield of desired product heptadecane was low and many undesired products were detected, including compounds of C_7H_8, C_8H_{10}. Additionally, after a period of reaction time, the system showed less conversion efficiency and the reaction appeared to stop. Due to some unexpected difficulties in running the continuous flow reactor, and the time constraint, this part of the testing was not completed. Further testing is still under way as this report is drafted.

Chapter 5 Discussion

5.1 Reaction Conditions of Decarboxylation

The experimental results showed that the operating conditions, especially the operating temperature, strongly affected the decarboxylation process. In order to increase the conversion rate of SA and to obtain a higher yield of heptadecane in a shorter period of time, a higher temperature is preferred. It was found that increasing the temperature increases the conversion rate of reactant and the yield of heptadecane significantly. For example, the conversion was increased from 54 %mol at 265°C to approximately 98 %mol at 300°C after one hour. The lower the amount of solvent applied, the longer the reaction time that is required due to the limited solubility of SA in the solvent dodecane. The decarboxylation rate of stearic acid generally increased as the catalyst concentration in the reactant mixture increased. However, the effect of the catalyst concentration levels off when its concentration is 8% by weight or higher. Solvent application affects the reactions. When the solvent to reactant mass ratio increases (i.e., less solvent application), a longer time is needed for the reaction to complete. The effects of pressure and mixing intensity were found to be insignificant.

When methyl stearate (MeS) was used as the reactant, the effects of the operating conditions on its decarboxylation were found to be similar. However, MeS requires a higher temperature (e.g., 350°C), a longer reaction time (e.g., 3 hour) and a higher solvent to MeS mass ratio (e.g., 3:2) in order to be converted to the target product heptadecane.

Generally, an optimization process is to find a point of maximum or minimum response. However, in our attempt to obtain an optimal condition for MeS decarboxylation, it was found that increased temperature leads to increased heptadecane yield but no optimal points were identified. It is possible that the response values have a trend of slow growth and the response

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surface finally appears as a saddle point at a much higher temperature beyond the operating

temperatures (i.e., higher than 350°C) used in this study. As seen in Figure 4.1, there was not a

well-defined peak under the operating conditions explored for MeS decarboxylation.

Unfortunately, further explorations could not be attempted since the reactor system could not be

operated above 350°C for safety concerns.

From this optimization exercise, we had a better understanding on the decarboxylation of

MeS. The finding is a good reference for the further research on the details of renewable diesel

production.

5.2 Decarboxylation of Mixed Fatty Acid Methyl Esters (FAME)

Our previous experimental results have demonstrated that saturated feedstocks, such as

stearic acid and methyl stearate, are prone to be deoxygenated and yield diesel-like hydrocarbons

over Pd/C without hydrogen supply. The dominant reaction pathway was decarboxylation.

However, the FAME is a more complex mixture of both saturated and unsaturated methyl esters.

Decarboxylation of FAME leads to more complex products. Many reactions, such as

decarboxylation, decarbonylation, cyclization, hydrolysis, cracking, hydrogenation and some

gas-phase reactions, have possibly happened simultaneously. It was reported that deoxygenation

of unsaturated feedstocks products is difficult under hydrogen deficit conditions (Snare et al.,

2008). Alkane products, mainly pentadecane ($C_{15}H_{32}$) and heptadecane ($C_{17}H_{36}$), were expected

to be generated by directly decarboxylation / decarbonylation of saturated methyl esters, such as

palmitate or stearate. However, some amounts of aromatics products, such as $C_{17}H_{28}$ and $C_{15}H_{24}$,

were also found in the deoxygenated products. Short chain hydrocarbons, such as C_7H_{16} and

$C_{10}H_{22}$, may be produced via cracking reactions. Despite the inert atmosphere, hydrogenation

still happened as no unsaturated methyl esters were found among the products. This may not be a negative result for renewable diesel production. The source of hydrogen for the hydrogenation process could be from a simultaneous, hydrogen re-distribution reaction (Snare et al., 2008).

5.3 Continuous Decarboxylation of MeS

Our previous experimental results showed the Pd/C was the most active catalyst for the decarboxylation process of stearic acid and has led to satisfactory deoxygenation efficiency in the batch operation system. However, the Pd/Al$_2$O$_3$ did not perform as well as expected in the process of decarboxylation of stearic acid. The SA conversion rate was low, approximately 18.9%mol and the yield of the targeted product was only 8.0%mol. Preliminary experimental results also suggested that the Pd/Al$_2$O$_3$ in powder form may not be a feasible catalyst for MeS decarboxylation in a continuous flow operation. A pelletized Pd/C catalyst might be a better choice.

To improve the means of catalyst application, we re-shaped the power Pd/C catalyst, as it was purchased and used in batch mode testing to the 40~60 mesh particles. Then the Pd/C particles were uniformly mixed with the inert SiC particles (~200 mesh) as a catalyst support which can make the catalyst homogeneous distributed in the catalyst holding cages and provide uniform contact well with the reactant solution through the reacting volume. Testing using this improved form of Pd/C catalyst was conducted, however, analytical analysis on the samples are in progress as this report is drafted.

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

This research studied an important method for renewable diesel production via decarboxylation. An advantage of the technology explored in this research is that the decarboxylation was achieved without a requirement of external hydrogen supply.

The choice of catalysts plays a crucial role in renewable diesel production. Therefore, the best catalyst screened from this study for stearic acid deoxygenation was palladium supported on activated carbon (Pd/C), with platinum supported on activated carbon (Pt/C) as the second best. A 100 mol deoxygenation rate on stearic acid Pd/C can be achieved with Pd/C catalyst with an 88.6%mol product yield.

The experimental results showed that operating temperature strongly affects the SA and MeS deoxygenation, which was further confirmed by the response surface experimental analysis. The solvent application also affects the reaction in such a way that a solvent to reactant mass ratio of 3:2 or higher is preferred. Increased rate of catalyst application positively affects the deoxygenation efficiency. However, a catalyst application rate of 8% by weight or higher does not significantly increase the process efficiency.

Process optimization was attempted but results showed that no optimal conditions existed. Instead, the efficiency strongly depends on the operating temperature. To achieve a reactant conversion rate of 85%mol or higher, a suitable set of operating conditions are suggested as 355°C, sRatio of 62:38, and a reaction time of 187 minutes.

Decarboxylation of mixed fatty acid methyl esters (FAME) can be achieved but was not thoroughly investigated due to the time constraints. Further research is needed to understand the decarboxylation process of this complex feedstock.

6.2 Recommendations

In this research, saturated fatty acids and methyl esters, with stearic acid and methyl stearate as the model compounds, respectively, were successfully converted to diesel-like hydrocarbons by directly decarboxylation on Pd/C catalyst. However, the ultimate goal of this research is to deoxygenate FAME or even straight plant oils and/ or animal fats. Challenges still exist before this ultimate goal is achieved. Further research is recommended on the following items:

1. decarboxylation of unsaturated fatty acids or methyl esters
2. decarboxylation of straight plant oils and animal fats
3. continuous decarboxylation of mixed FAME and plant oils/ animal fats, and
4. scale-up of such a process for potential industrial application.

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