

PROCESS INVESTIGATION AND OPTIMIZATION OF
HETEROGENEOUS CATALYSTIC DECARBOXYLATION OF
FATTY ACIDS AND FATTY ACID METHYL ESTERS FOR
RENEWABLE DIESEL PRODUCTION

A Thesis

Presented in Partial Fulfillment of the Requirements for the

Degree of Master of Science

with a

Major in Biological and Agricultural Engineering

in the

College of Graduate Studies

University of Idaho

by

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Feb 2014

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Abstract

Research and development of biofuels from renewable resources are now expanding from oxygenated transportation fuels into other areas such as renewable diesel. Oxygen removal, or deoxygenation, to produce renewable diesel, is a logical way to overcome the drawback of biofuel's low energy density due to the oxygen presence.

Generally, deoxygenation can be achieved by the following chemical reactions: decarboxylation, decarbonylation and hydrodeoxygenation. This study aims to investigate the effectiveness of catalytic decarboxylation without an external supply of hydrogen. Heterogeneous catalysts, including Pd/C, Pd/Al₂O₃, Pt/C, Ni/SiO₂, Pt/Al₂O₃ and Raney Nickel, were tested on their efficiencies for decarboxylation under different operating conditions, including reaction time, operating temperature and pressure, solvent application, mixing intensity (or stirring rate) and catalyst application rate. Studies on the aforementioned catalysts revealed that the Pd/C was found to be the most reactive catalyst for the decarboxylation of stearic acid, the model fatty acid. Therefore, further studies on the effects of process parameters were conducted using the Pd/C catalyst.

Process parameters were investigated on decarboxylation catalyzed by the Pd/C catalyst systematically. Apparently, the reaction temperature significantly affects the reactant conversion rate and the product yield. The conversion was increased from 54%mol at 265°C to approximately 98%mol at 300°C after one hour of reaction. In general, the decarboxylation rate of stearic acid increases as the concentration of catalyst in the reactant mixture increases. However, this effect levels off when the catalyst concentration is 8%wt or higher. Additionally, as the solvent to reactant mass ratio decreases, the reaction takes longer to complete. Experiments have found that the effects of operating pressure and mixing intensity were negligible under the conditions of investigation, therefore they were kept at constant at 250 *psi* and 500 rpm, respectively.

In optimizing the process conditions for the renewable diesel production, methyl stearate is chosen as the model compound for fatty acid esters. Based on a 2³ full factorial central composite design (CCD) for response surface methodology (RSM), sixteen set of

experiments were performed by varying temperature, solvent to reactant mass ratio (sRatio) and reaction time, which are the most influential operating parameters in decarboxylation of fatty acids. The experimental results were fitted to a second-order polynomial model using multiple regression analysis and examined statistically. The optimum process conditions for maximum product yield were obtained as temperature 355°C, sRatio 62:38, and reaction time 187 min, which corresponds to an experimental heptadecane yield of 82.38 ± 4.62 %mol, and was close to the expected yield of 85.00 %mol.

Acknowledgements

First, I wish to express my earnest gratitude to my advisor, Dr. Brain He, for his advice, support, and patience throughout my study. His professional dedication and meticulousness will influence me beyond my graduate study at UI. I deeply appreciate the time and effort he spent on guiding my thesis work.

My deep gratitude is also extended to my committee members: Dr. Jon Van Gerpen, Dr. Su Ha of Washington State University. They are thoughtful, knowledgeable and generous to offer suggestions and comments when I need help.

I am grateful to Dr. Joe Thompson, Support Scientist, for his great assistance in my experimental work. I would like to thank all of the Lab members, past and present, Zheting Bi, Tushar Jain, Carlo Munoz and Sonam Sherpa, as well as many friendly peer students and great friends from the department, the university and the city.

I would like to thank the Department of Biological and Agricultural Engineering and the National Institute for Advanced Transportation Technology (NIATT) at the University of Idaho for providing the study opportunity, technical support and financial support.

Importantly, I want to thank my family for their continuous and warm support and love. I could never finish my thesis without the constant inspiration and momentum from my husband, Bingwen, and sons, Tony (Changxu) and Taylor (Lele). Special appreciation is also given to my mother and my father in-law for taking care of my sons and me during the busy time I was doing my thesis.

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List of Symbols

| | |
|----------------------------------|--|
| Al | Aluminum |
| Al ₂ O ₃ | Aluminum oxide |
| ANOVA | Analysis of variance |
| ASABE | American Society of Agricultural and Biology Engineering |
| Ba | Barium |
| Ca | Calcium |
| C | Carbon |
| CO ₂ | Carbon dioxide |
| °C | Celsius degree |
| cm | Centimeter |
| Cl | Chloride |
| Cr | Chromium |
| Co | Cobalt |
| Cu | Copper |
| CCD | Central composite design |
| H ₂ PtCl ₆ | Chloroplatinic acid |
| C ₁₈ H ₃₈ | Eicosane |
| FAMES | Fatty acid methyl esters |
| FID | Flame ionization detector |
| GC | Gas chromatography |
| g | Gram |
| C ₁₇ H ₃₆ | Heptadecane |
| H ₂ | Hydrogen |
| Fe | Iron |
| LSD | Least significance difference |
| Ir | Iridium |
| Ru | Ruthium |
| L | Liter |
| Mg | Magnesium |
| TOF | turnover frequencies |
| Mn | Manganese |
| MS | Mass spectrometer |
| m | Meter |
| MeS | Methyl stearate |
| μg | Microgram |
| μL | Microliter |

| | |
|--|---------------------------------|
| μm | Micrometer |
| mg | Milligram |
| mL | Milliliter |
| mm | Millimeter |
| min | Minute |
| Mo | Molybdenum |
| nm | Nanometer |
| Ni | Nickel |
| Ni/SiO ₂ , Al ₂ O ₃ | Ni on silica/alumina |
| N ₂ | Nitrogen |
| C ₁₆ H ₃₄ | Octadecane |
| O | Oxygen |
| Pt | Platinum |
| Pt/C | Platinum on activated carbon |
| Pt/SiO ₂ | Platinum on alumina |
| Pd | Palladium |
| Pd/C | Palladium on activated charcoal |
| Pd/Al ₂ O ₃ | Palladium on alumina |
| Pd/SiO ₂ | Palladium on silica |
| RSM | Response surface methodology |
| Na | Sodium |
| NaOH | Sodium hydroxide |
| sRatio | Solvent to reactant mass ratio |
| SiO ₂ | Silicon dioxide |
| S | Sulfur |
| SO ₂ | Sulfur dioxide |
| m ² /g | square meter per gram |
| SA | Stearic acid |
| W | Tungsten |
| % wt | Weight percentage |
| Zn | Zinc |

Chapter 1 Introduction

1.1 Background

Due to growing worldwide demand for energy and its resulting impact on the environment, biomass-based energy resources are getting more attention (Naik et al., 2010). Plant oils and animal fats have been investigated as a way to provide a renewable source for diesel fuel. Conversion of vegetable oils and animal fats with simple alcohols to biodiesel as a successful approach has been widely studied. Biodiesel is currently an important biofuel for diesel engines. For instance, the United States has increased its production from 2 million gallons in 2000 to nearly 1.1 billion gallons in 2012 (Prater et al., 2013). Biodiesel is comprised of mono-alkyl esters of long chain fatty acids and 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. First, biodiesel can dramatically reduce emissions, such as carbon dioxide (CO₂), sulfur (S), particulate matter emissions, carbon monoxide (CO), hydrocarbon emissions, etc. Secondly, biodiesel can mix readily with petroleum diesel, or it can be blended in any proportion with petroleum diesel fuel, which helps with reducing the world's dependence on diminishing fossil fuel resources. Thirdly, biodiesel can be used in existing diesel engines, requiring little or no modifications (Yusuf et al., 2011). Moreover, biodiesel is a safer fuel due to its high ignition point (175°C/350°F vs. -42°C/-43°F for gasoline). And, it is renewable and has a high cetane number, good combustion properties, low toxicity and excellent lubricity (Narasimharao et al., 2007). However, biodiesel has some drawbacks relevant to its high oxygen content including a high gelling point and lower energy content, limiting its uses in low temperature environments and high energy density requirement.

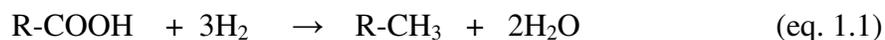
In contrast to biodiesel production, the other way is converting plant oils and animal fats into renewable diesel (or hydrocarbons). Renewable diesel has several potential advantages compared to biodiesel. These advantages include a higher energy content and better cold weather performance. The technology to produce renewable diesel has been developed and commercially accomplished including Neste Oil company, and UOP/Eni Ecofining (NESTE

OIL, 2006). However, it is an energy-intensive process, requiring high pressure and consuming expensive hydrogen feed (Na et al., 2010). Recently, noble metal catalysts supported on activated carbon, due to their high catalytic activity, have been applied in the deoxygenation of triglycerides under inert atmosphere to produce high yields of the corresponding 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 important advantage of this technology is that no hydrogen is required in the process thus it less expensive compared to the hydrodeoxygenation process (Lestari et al., 2009b).

1.2 Renewable diesel

Renewable diesel, also called green diesel, is diesel-like hydrocarbons providing good properties for fuel, such as low viscosity and low cloud point. It is usually produced by hydroprocessing plant oils and animal fats to yield a hydrocarbon fuel that is very similar to petroleum diesel chemically. This process has been studied extensively for its potential as a chemical process for removing oxygen from bio-feedstocks. Various combinational reactions of the deoxygenation of plant oils and animal fats can take place, depending on the feedstocks composition, catalyst choice and reaction conditions. Hydrodeoxygenation and decarboxylation are the most common and universal pathways for deoxygenating oils and fats (Koivusalmi E., 2008; Kubicka, 2008).

Hydrodeoxygenation:



Decarboxylation:



In hydrodeoxygenation, oxygen-containing materials are reduced by hydrogenation while hydrocarbons and water are generated. In decarboxylation, carboxylic acids form hydrocarbons and release carbon dioxide.

1.3 Statement of Problem

Most of the research work on decarboxylation has been done with fatty acids as feedstocks to produce 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). However, it is necessary to have a better understanding and control of the process parameters, such as catalyst types, operating temperature and pressure, solvent application, etc., on the process efficiency as indicated by the product yield, reactant conversion rate and the catalyst activity and selectivity. Biodiesel or mixture of fatty acid methyl esters 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).

1.4 Objective

The goal of this research is to optimize the process conditions for decarboxylation process. This goal is to be achieved by the following objectives. A preliminary study of the decarboxylation reaction is needed with some saturated model compounds (stearic acid, methyl stearate) to identify the major process parameters, e.g. temperature, pressure and catalyst type, etc. and their effects. Next, the optimal operating conditions for maximizing the molar yields of targeted product in the process of decarboxylation of methyl stearate are to be determined. Finally, biodiesel as the feedstock is studied under the optimum process conditions for decarboxylation of methyl esters. The outcome from this research is expected to be a good reference to the current effort in developing feasible technologies for renewable diesel production from plant oils and animal fats.

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Chapter 2 Review of Heterogeneous Catalysts for Hydrogenation and Deoxygenation of Plant Oils and Animal Fats

Abstract

Worldwide declining fossil fuel reserves, increasing energy demand for growing economies and environmental awareness require renewable and sustainable energy sources. Biofuels including triglyceride-based biodiesel and renewable diesel have recently been given much attention. Catalysts play a crucial role in renewable diesel synthesis. This review article primarily presents the catalysts used for both hydrogenation and deoxygenation of plant oils and animal fats to produce renewable diesel. Specific attention is devoted to the preparation, characterization, performance and deactivation of various catalysts used in hydrogenation and deoxygenation. The working mechanisms of catalytic hydrogenation and deoxygenation are also discussed. The review ends with a description of some catalysts that may be simultaneously used for both hydrogenation and decarboxylation.

2.1 Introduction

2.1.1 Background

Plant oils and animal fats are one of the oldest chemical compounds used by humans. They are extensively used to produce many products such as food, paints, candles, lamp oils and soap, etc. (Hasenhuettl, 2005). Plant oils and animal fats, as renewable resources, are mainly composed of triglycerides. A triglyceride, also called triacylglycerol, is a chemical compound formed from one molecule of glycerol and three fatty acids (fig. 2.1). The glycerol molecule has three separate points where a fatty acid molecule can be attached, thus the common reference to fats and oils as triglycerides. Fatty-acid carbon-chain lengths vary between 4 and 24 carbon atoms with up to six double bonds. Carbon chain lengths of 16 and 18 atoms are the most common (O'Brien, 2009).

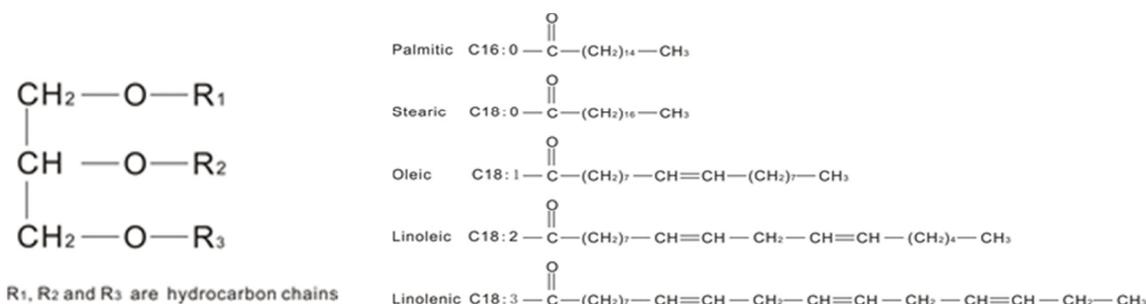


Figure 2.1. Basic structure of a triglyceride molecule and the most common fatty acid chains in vegetable oils.

Physically, triglycerides have lower densities than that of water (they float on water). At normal room temperatures, they may be solid or liquid. When solid, they are called "fats" or "butters", and when liquid, they are called "oils". The different properties are to a large extent determined by the fatty acid composition and the extent of saturation or unsaturation present in the hydrocarbon chains (O'Brien, 2009). These aspects are identified by the carbon chain length and the number and position of the double bonds for individual fatty acids, and their position on the glycerin. Generally, solid fats are indicated by a dominance of saturated fatty acids, while liquid plant oils are evidence of a high level of unsaturated fatty acids (Hui, 2005).

The C=C double bonds and carboxylic/esters functional groups in triglycerides allow these functional groups to be processed via hydrogenation and/or decarboxylation in the presence of heterogeneous catalysts. The hydrogenation of plant oils and animal fats is a very important operation in industrial applications to manufacture various products such as food, pharmacy, cosmetics, plastics, detergents, lubricants, etc. (Nohair et al., 2005). One typical heterogeneous catalytic hydrogenation process is the production of the shortenings and margarine from vegetable oils. The hydrogenation of double bonds in fats and oils aim to get the products with desired melt and texture based on their final use. The hydrogenated oil is more stable and less sensitive to oxidation (Kanhai, 1988).

Due to growing worldwide demand for energy and its resulting impact on the environment, biomass-based energy resources are getting more attention. (Naik et al., 2010; Van Gerpen, 2005). Biodiesel is a promising fuel compound, which is comprised of mono-alkyl esters of long chain fatty acids and typically derived from renewable energy sources, such as plant oils and animal fats (Helwani et al., 2009). Conventionally, biodiesel production is performed by transesterification of plant oils and animal fats with methanol in the presence of homogenous base catalysts (Kalnes et al., 2007; Narasimharao et al., 2007). Compared to petroleum diesel fuel, biodiesel has some attractive advantages. It can help with both reducing the world's dependence on oil and minimizing fossil fuel burning and CO₂ production. Moreover, it has a high cetane number, good combustion property and low toxicity (Narasimharao et al., 2007). However, there exist several drawbacks related to the transesterification reaction. Using the homogenous base catalyst presents problems such as corrosion, downstream separation and waste treatment remains intricate. Although heterogeneous catalysts have been developed for biodiesel production in recent years, they also have other problems. For instance, they always have lower activity compared to the homogenous catalysts and need a higher reaction temperature and pressure (Kunkes et al., 2008). Additionally, high viscosity, high cold point and the low heating value due to their high oxygen content of this kind of biodiesel, limit its use in the modern diesel engines (Naik et al., 2010).

Catalytic cracking or pyrolysis for deoxygenating oils and fats using zeolites was considered as one alternative technology that can overcome the aforementioned issues. However, this

also could lead to a lower energy fuel (Demirbas, 2007, 2008; Lestari et al., 2009a). To improve heating value, the development of renewable diesel has been reported, which can upgrade bio-based feedstocks such as plant oils and animal fats to hydrocarbon middle distillates via hydro-treatment (Huber et al., 2007; Kubicka et al., 2009; Simacek et al., 2009; Zhang et al., 2007). The hydrotreating process has been widely used in petroleum refining to remove sulfur and nitrogen from petroleum-derived feedstocks (Huber et al., 2006). Neste Oil company first introduced this pioneering work to commercialize this new-type diesel production (Neste Oil, 2006). In a similar way, the UOP/Eni Ecofining processed bio-feedstocks through removal of oxygen from triglycerides molecules by a catalytic reaction with hydrogen. This involved decarboxylation and hydrodeoxygenation, and produced aliphatic hydrocarbons referred to as green diesel which is distinguished from the conventional oxygenated biodiesel (John A. Petri; Terry.L. Marker; Brady, 2009; Kalnes et al., 2007). This green diesel, without undesirable oxygen-containing groups such as carboxylic acids, has a high cetane value of 70-90, compared to 50-65 for traditional biodiesel, and good flow properties. It also has excellent storage stability and is completely compatible for blending with the petroleum derived diesel fuels (Naik et al., 2010). Conventional hydrotreating catalysts containing nickel-molybdenum (NiMo), nickel-tungsten (NiW) and cobalt –molybdenum (CoMo) can be used in the process (Simacek et al., 2009). Although hydrodeoxygenation guarantees the main products of linear chains of hydrocarbon, it is an energy-intensive process requiring high pressure and consuming an expensive hydrogen stream (Na et al., 2010).

Recently, the high activity of noble metals supported on activated carbon catalysts were applied in the deoxygenation of triglycerides under inert atmosphere and high yields of the corresponding linear alkanes and alkenes were obtained (Immer et al., 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). The technology for converting bio-based feedstocks based on deoxygenation reaction has been recently developed. An important advantage of this new technology is that no hydrogen is required in the process compared to the hydrodeoxygenation, thus eliminating the additional cost of hydrogen (Lestari et al., 2009a).

2.1.2 Objective of this review

Catalysts are indispensable in biodiesel production. Particularly, for renewable diesel production, many kinds of catalysts have been tested for hydrogenation and deoxygenation of plant oil and animal fats. In order to understand the whole picture of catalysts used in the production of renewable diesel and to help with catalyst screening, this review article will comprehensively review and discuss the most commonly used catalysts.

2.1.3 Scope of this review

This review is composed of two major sections of heterogeneous catalysts for hydrogenation and deoxygenation processes, respectively. Special attention is devoted to catalysis in each process. The mechanism for both catalytic processes is also discussed. Catalyst preparation, properties, performances and deactivation are addressed in detail. Finally, some other catalysts that are not included in the two major sections but have special benefits to simultaneously catalyze both hydrogenation and deoxygenation are discussed.

2.2 Catalysts for hydrogenation of plant oils and animal fats

2.2.1 Hydrogenation

2.2.1.1 Introduction to hydrogenation

Hydrogenation is a process of reaction between a plant or animal species and hydrogen, usually with the aid of a catalyst. The reaction may be one in which hydrogen simply adds to unsaturated carbon bonds in the structure of the molecule or one in which hydrogen addition causes dissociation of the molecule (thus called Hydrogenolysis, or destructive hydrogenation) (Hudlický, 1996).

Hydrogenation can be applied to nearly all organic compounds having unsaturated bonds in the presence of a catalyst. The hydrogenation reaction of organic compounds has shown great industrial importance. For instance, hydrogenation is used in the production of edible fats from liquid oils (Balakos and Hernandez, 1997). In petroleum refining, the hydrogenation of petroleum oil is used in numerous processes to produce gasoline, or

improve lubricating and burning oil, or upgrade heavy oils and residues (Sweeney, 1934). In the last century, coal liquefaction via hydrogenation had become a promising alternative to petroleum processing since the French chemist Paul Sabatier discovered that the introduction of a trace of nickel as a catalyst that facilitated the addition of hydrogen to molecules of carbon compounds (Hook and Aleklett, 2010; O'Brien, 2009). The catalysts mostly used for hydrogenation reactions are the supported nickel catalysts; they are followed by catalysts based on noble metals, while copper chromite and nickel supported on kieselguhr (loose or porous diatomite) are extensively used at high-pressure conditions (Navalikhina and Krylov, 1998).

2.2.1.2 Hydrogenation mechanism of plant oils and animal fats

Not many years after Sabatier demonstrated that the double bonds in organic compounds can be hydrogenated, in 1901 Norman patented the hydrogenation of triglyceride oils (O'Brien, 2009). Hydrogenation of plant oils and animal fats was one of the first commercial hydrogenation processes. It is an important process in production of edible fats, margarine and other food components (Balakos and Hernandez, 1997).

There are two reasons to hydrogenate oils. One is to change naturally occurring fats and oils into physical forms with creaming characteristics, frying stability, sharp melting properties, and the other functional characteristics desired for specific applications. The other reason for hydrogenation is to increase the stability of oils (Balakos and Hernandez, 1997; O'Brien, 2009). Flavor stability is necessary to maintain product acceptability for prolonged periods after processing, packaging, and use as an ingredient in a finished product. A wide range of fats and oils products can be produced with the hydrogenation process, depending upon the conditions used, the starting oils and the degree of saturation or summarization (O'Brien, 2009).

Although the hydrogenation process has been used for about one century, its mechanism is still not fully understood. The Horiuti-Polanyi mechanism is a commonly accepted theory which explains the hydrogenation process of unsaturated fatty acids on the catalyst surface (Bernas et al., 2009; Draguez de Hault, 1984; List, 2011). Hydrogen molecules are adsorbed onto the nickel surface and then dissociated into hydrogen atoms. Simultaneously, molecules

to be hydrogenated are also adsorbed onto this nickel surface by their double bonds. A hydrogen atom H_a reacts with a double bond on the nickel surface and forms a half-hydrogenated intermediate (fig. 2 Absorption). This half-hydrogenated step can follow four different pathways: (1) a second hydrogen atom is added to this intermediate and the original double bond is saturated; (2) The hydrogen H_a returns to the nickel surface and the intermediate dissociate back to the original, because the first addition is reversible; (3) The hydrogen H_b returns to the nickel surface so that the original cis-configuration of the double is changed into a trans-configuration; (4) The hydrogen H_c or H_d returns to nickel surface, so the double bond shifts one position along the fatty acid chain (fig. 2.2) (Draguez de Hault, 1984). Because of containing more double bonds than other fatty acids, highly polyunsaturated fatty acids are the most susceptible to the process of hydrogenation (Gunstone, 2007; Hui, 2006).

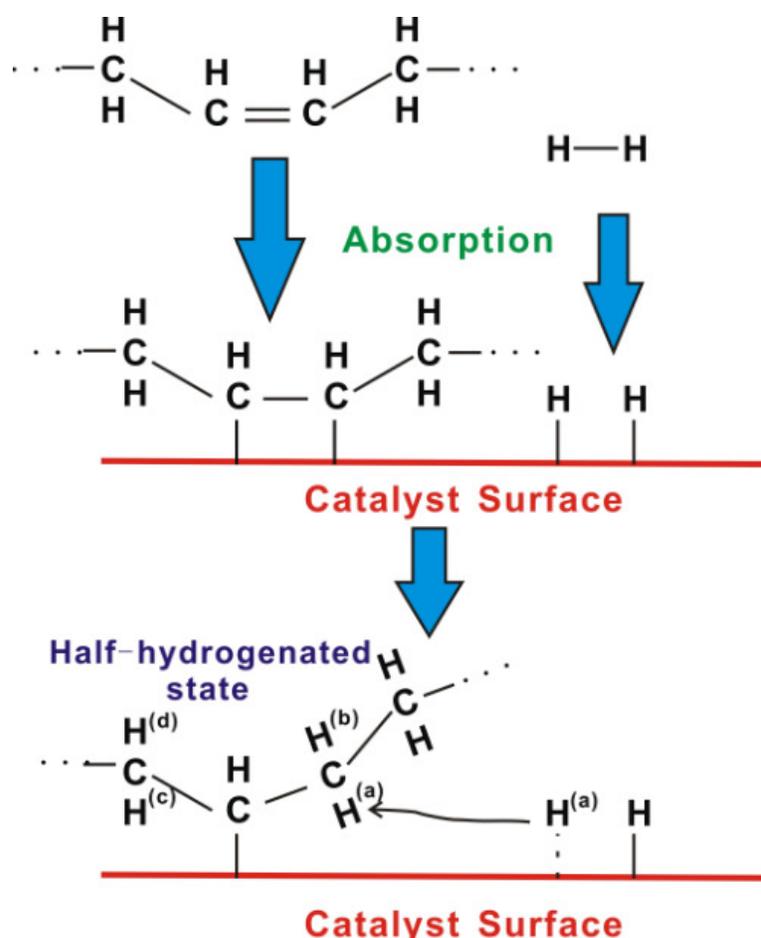


Figure 2.2. Horiuti-Polanyi mechanism for hydrogenating unsaturated fatty acids.

Although the hydrogenation of oils and fats includes a series of side processes, such as the structural reaction (e.g., the formation of *trans* isomers) and positional isomerization reaction (e.g., carbon double bonds shift), the selectivity of process aims to enhance the hydrogenation activity and simultaneously to suppress the isomerization in hydrogenation of edible oil industry (Stankovic et al., 2009). Three different kinds of selectivity are defined (fig. 2.3).



Figure 2.3. Selectivity definition in hydrogenation of edible oil industry.

Here k_1 , k_2 , and k_3 are the rate constants. The rate constant values are used for determining the selectivity relations. The selectivity SL_n for linolenic to linoleic is defined as being the rate constants ratio k_3/k_2 , and the selectivity SL_o for linoleic to oleic acid is defined as being the rate constants ration k_2/k_1 (Draguez de Hault, 1984; Jovanovic et al., 1998). Because fully saturated acids are not easily digested as foodstuffs, the main targets in the commercial hydrogenation process are producing maximum amount of oleic fatty acid and not going too far towards producing the fully saturated steatic acid chains (Hussain et al., 2009). Furthermore, the selective hydrogenation of such vegetable oil must lead to a minimum of 80% toward *cis* oleic acid to meet industrial needs (Nohair et al., 2005).

2.2.2 Heterogeneous Catalysts for plant oils and animal fats

Various heterogeneous catalysts have been applied for the hydrogenation of plant oils and animal fats. Nickel (Ni), copper (Cu), copper-chromite, platinum (Pt) and palladium (Pd) are the most commonly used metals as active species in heterogeneous catalysts for hydrogenation of plant oils and animal fats (table 2.1).

Table 2.1. An overview of reaction conditions and catalysts used for hydrogenation of oils and fats over heterogeneous catalysts.

| reactant | Catalyst | Reaction conditions | Reference |
|------------------------------------|---|--|--|
| Soybean oil | Ni/SiO ₂ | 145°C ;H ₂ , 0.08-0.16MPa; BR | Gabrovska et al., 2006 |
| Sunflower oil | Ni/SiO ₂ | 150, 180, 220°C; H ₂ , 2, 4, 6MPa; SBR | Fernandez et al., 2007 |
| Tallow, Sunflower and soybean oils | Ni/SiO ₂ | 195-200°C; H ₂ , 1.5MPa,(tallow); 150-200°C; H ₂ , 0.08-0.2MPa (oils), | Jovanovic et al., 1998 |
| Canola oil | Mixed catalysts(NiRu/ Al ₂ O ₃ , PdCr/Al ₂ O ₃) | 100,140°C ; H ₂ , 2.7, 5.27MPa (NiRu Al ₂ O ₃) 70,110,175°C; H ₂ , 5.17,3.45MPa (PdCr/Al ₂ O ₃) | Wright et al., 2003 |
| Sunflower oil | Pd/ (Al ₂ O ₃ , TiO ₂ , MgO, ZnO, CeO ₂ , or CeZrO ₂) | 40°C; H ₂ , 1MPa, SBR | Nohair et al., 2005 |
| Sunflower oil | Pt/SiO ₂ | 170°C; H ₂ , 0.3MPa; SBR | McArdle et al., 2010 |
| Soybean oil | Pd/C, Pd/ Al ₂ O ₃ , Ru/C | 150°C; H ₂ , 0.68MPa | Tike and Mahajani, 2006 |
| Vegetable oil | Pd/C | 146-225°C; H ₂ , 0.8MPa; FBR | Simakova et al., 2008 |
| Sunflower oil | Pd/(SBA-15 or MCM-41) | 110°C; H ₂ , 0.5MPa; SBR | Plourde et al., 2004 |
| Sunflower oil | Pd/(α-Al ₂ O ₃ , γ-Al ₂ O ₃ , zeolites), commercial Ni catalysts | 100°C; H ₂ , 0.4MPa; SBR (Pd) 100°C; H ₂ , 0.4MPa; SBR (Ni) | Fernandez et al., 2009 |
| Vegetable oil | Pd/SBA-15, commercial Ni catalysts | 80-130°C; H ₂ , 0.36-9.3MPa; SBR | Belkacemi et al., 2006; Belkacemi and Hamoudi, 2009 |
| Soybean oil | Ru/C | 165°C; H ₂ , 0.2MPa | Cizmeci et al., 2009 |
| Linoleic acid | Ru/C, Ru/Al ₂ O ₃ | 120,165°C; H ₂ , 0.36-9.3MPa | Bernas et al., 2003 |
| Rapeseed oil | Cu/SiO ₂ | 180°C; H ₂ , 0.6,2MPa | Ravasio et al., 2002 |

NOTE: BR is the batch reactor; SBR is the semi-batch reactor; FBR is the fixed-bed reactor.

2.2.2.1 Heterogeneous Catalysts Preparation

Current preparation methods of nickel hydrogenation catalysts typically involve the following techniques:

Impregnation method: Impregnation is the simplest and probably the most common procedure for dispersing a catalytic species on a carrier (Farrauto, 2006). The procedure involves impregnating the pre-dried support to a certain volume of solution containing the precursor of active metal compounds. Two kinds of methods, incipient wetness impregnation and wet impregnation, are distinguished by the volume of solutions. In incipient wetness impregnation, the volume of the solution is equal to the support pore volume, while the excess solution is used in wet impregnation. A subsequent step is drying the support to remove the solvent. Advantages of the impregnation method include its relative simplicity, rapidity and capability of depositing the precursor at high metal loading. However, the main disadvantage is that sometimes material is not uniformly deposited along pores and pellet. (Farrauto, 2006; Navalikhina and Krylov, 1998; Selim and El-Maksoud, 2005).

Precipitation-deposition method: The precipitation-deposition method is one of two precipitation methods considered here. The precipitation method is to precipitate the catalyst precursor in the form of a hydroxide or carbonate in the pores and on the surface of the carrier by adjusting the pH of the metal salt solution and support slurry through addition of a base such as NaOH, NH₄OH etc. Precipitation is a complex process which depends on many parameters, such as pH, solvent, temperature etc. Precipitation is a preferred method when achieving higher metal loadings compared to impregnation, however a possible disadvantage is that some base metal catalyst precursor formed during precipitation, such as Ni silicate or Ni aluminate, are oxidized or reduced to the desired active phase only under severe conditions (Farrauto, 2006). The precipitation-deposition method involves two processes. One is precipitation from bulk solutions, and the other is interaction with the support surface. The advantage of this method is that the precipitation onto the support needs a lower super-saturation than formation of the new phase directly from the liquid

which occurs in the co-precipitation method. For example, nickel hydroxide is precipitated with ammonia from a nickel hydroxide in the presence of a suspension of hydrated alumina. The above precipitate was filtered, washed, dried in an oven at 110°C overnight in air (Gabrovska et al., 2006; Selim and El-Maksoud, 2005).

Co-precipitation method: This is the other precipitation method discussed here. In the co-precipitation method, support and catalyst precursors in bulk solutions are co-precipitated together. Take as an example, nickel sulfate or nitrate solution is added to a boiling solution of sodium silicate. The produced precipitate is filtered and washed. Then the resulting derived paste is dried at 110°C overnight (Selim and El-Maksoud, 2005).

Generally, nickel catalysts prepared by the above methods need to be reduced with pure H₂ gas at 400-500°C prior to their used in reactions. The catalysts prepared by impregnation are the easiest to reduce compared to other methods. The supported catalysts usually have the specific surface of the active nickel of 100 ~120 m²/g. The metal particles on supports have sizes from 2-10 nm. The concentration of nickel in a fresh catalyst ranges from 20 to 22% (Navalikhina and Krylov, 1998).

Monometallic noble based catalysts have been prepared via either simple impregnation or by cationic exchange of the support with precursors in basic medium. Catalyst Pd/SiO₂ can be prepared by impregnation or the cationic exchange method, while the preparation of Pd/ α -Al₂O₃ and Pd/ γ -Al₂O₃ catalysts with impregnation method were reported by using different precursors (Fernandez et al., 2009; McArdle et al., 2010; Nohair et al., 2005; Nohair et al., 2004). Preparation methods and parameters have shown significant effects on the catalyst characteristics such as activity, selectivity, etc. For instance, Pt/SiO₂ catalyst prepared using chloroplatinic acid (H₂PtCl₆) precursor by the impregnation method has slightly higher activity than the catalyst using platinum acetyl acetate [Pt(AcAc)₂] precursor. It is believed that the presence of chlorine on a supported catalyst leads to the increased hydrogen spillover and the improved hydrogenation activity (McArdle et al., 2010).

The bimetal catalysts are always prepared by a catalytic reduction method. For example, Pd-Cu catalyst preparation procedure is carried out by surface redox reaction between hydrogen activated on palladium particles and the copper acetate [Cu(CH₃COO)₂], dissolved in water.

The hydrogen on the palladium catalyst surface is provided by hydrogen bubbling. After 1-hour catalytic redox reaction, the solution is filtered out and the catalyst is dried overnight. Finally, the bimetal catalyst is reduced under hydrogen flow at 400°C for 2 h (Epron et al., 2002).

Copper chromite catalysts are commonly prepared by reacting a water-soluble copper salt with an alkali dichromate and ammonium hydroxide, followed by separating the precipitated copper-chromium-nitrogen formation, washing and calcining the precipitate. For supported copper catalysts, they can be prepared by using conventional incipient wetness impregnation method. However, catalysts prepared by chemisorption-hydrolysis (CH) method showed better performance than those prepared by impregnation method. The CH method is conducted by adding the support to a $\text{Cu}(\text{NH}_3)_4^{2+}$ solution prepared by adding NH_4OH to a $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution until reaching pH9 and slowly diluting the slurry with water. The solids are separated by filtration, washed with water, dried overnight and calcined in ambient air at 673K (Bocuzzi et al., 1999; Ravasio et al., 2002).

2.2.2.2 Nickel-based catalysts

After many tests for triglyceride hydrogenation over many metals, scientists finally found that nickel is one of the most suitable catalysts because of its availability, low cost and inert nature to oils (Balakos and Hernandez, 1997; Draguez de Hault, 1984). Since the catalytic reaction takes place on the surface of the Ni metal it is important to achieve a large specific surface area. The nickel crystallites are typically attached to a porous support. Therefore, Ni nanoparticles are generally supported on silica, alumina, etc. for commercial hydrogenation. The activity and selectivity of the supported nickel catalysts are influenced by the choice and the preparation of the support, nickel and promoter deposition, particle size, pore size and pore size distribution of the support, as well as the activation procedure (Gabrovska et al., 2006). The process variables such as reaction temperature, hydrogen bubbling device, agitation rate and stirrer design also affect catalyst activity and selectivity (Fernandez et al., 2007).

The synthesis of a nickel catalyst supported on diatomite (a natural silicate) has been carried out through a three-stage process: precursor's synthesis, reduction and passivation combined

with impregnation (Jovanovic et al., 1998). The catalyst synthesized above showed good catalytic properties to hydrogenate tallow and fats, while demonstrating a high selectivity in hydrogenation of sunflower and soybean oils (Jovanovic et al., 1998). Nickel catalysts supported on two silica-based supports, diatomite and waterglass (a viscous solution of sodium silicate having a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio ranging from 3.75 to 1.5), usually have been prepared using the precipitation-deposition method, and their physical properties such as texture and structure and catalytic activities are compared in the hydrogenation process of edible oils (Gabrovska et al., 2006). It has been found that, in spite of the differences in the textural and structural properties of the catalysts, both catalysts performed with similar activity and selectivity under the similar reaction conditions.

Usually, calcination of precursors and reduction of nickel are conducted at high temperatures (400-600 °C) (Ermakova and Ermakov, 2003). Selim et al. prepared nano-sized nickel catalysts supported on silica, alumina and zeolite by using different methods such as impregnation, co-precipitation, and precipitation-deposition, followed by a low temperature reduction (160-230 °C). For the hydrogenation of sunflower oil, the catalytic activity was found in the order of impregnation > co-precipitation > precipitation-deposition (Selim and El-Maksoud, 2005).

Raney nickel catalyst is another choice in commercial hydrogenation of oils in an unsupported state due to its economic price (Choo et al., 2001). Raney nickel catalyst typically consists of a Ni-Al alloy and a promoter, such as molybdenum (Mo), chromium (Cr), copper (Cu), iron (Fe) and tin (Sn). Raney nickel has excellent catalytic properties. However, the drawback is its fast deactivation (Mikkola et al., 2000). Furthermore, this conventional catalyst products a significant amount (15%-30%, while recommended level is only 5%) of *trans* fatty acids which have been reported to do harm to people's health (Belkacemi and Hamoudi, 2009).

Although nickel is economically preferred in the hydrogenation of oils and fats, it may contaminate the food product due to its toxicity, either in a batch process or in a continuous reactor (Savchenko, 1999). To replace the supported Ni catalysts, supported noble metals have been considered as substitutes (Choo et al., 2003).

2.2.2.3 Noble metal based catalysts

Nobel metal catalysts are not generally used because of their high cost. However, their high activity in small quantities and the possibility of reuse in fixed bed reactors may compensate for the cost disadvantage (Kitayama et al., 1997).

The catalyst palladium on carbon (Pd/C) has been used for plant oil hydrogenation with sodium formate as the hydrogen donor due to this catalyst's high linoleic and linoleic activity at low temperature (Bernas et al., 2009). This catalyst also has been considered to be cost effective for the production of pure margarine with a novel reactor design which combines the hydrogenation process and the separation of the product and the catalyst (Savchenko, et al., 1999). Despite its high activity, the catalyst Pd/C has low selectivity for producing saturated fat (Hui, 2006). Simakova et al. found using Pd/C catalyst, the monounsaturated products were up to 75%, while saturated ones were only 25% during the hydrogenation of vegetable oils (Simakova et al., 2008).

Activity and selectivity for hydrogenation of linoleic acid (*cis9-cis12-C18:2*) using noble metal platinum (Pt), palladium (Pd), ruthium (Ru) and iridium (Ir) supported on Al₂O₃ catalysts (5 %wt metal content) have been investigated and compared with Ni and Cu on the same support (Kitayama et al., 1997). The catalysts exhibited almost equal selectivity for the stearic acid. However, the hydrogenation activity of these catalysts decreased in the order of Pd >> Ru > Ir >> Pt > Ni > Cu. So the selectivity is not entirely related to the catalytic activity. However, the activity of various noble metals supported on silica decreases in the order of Pd > Pt > Ru under gentle conditions (40°C and H₂ 10 MPa) (Nohair et al., 2004). The palladium catalysts showed highest activity and high selectivity for the double-bond hydrogenation reaction. The selectivity of palladium catalysts for *cis* oleic isomers can be improved by the addition of copper or lead to palladium, but the catalysts are less active than palladium monometallic catalysts. A better method, without loss of activity of these palladium catalysts, was proposed by adding amines in the reaction medium (Nohair et al., 2004).

Ruthenium has also been studied because of its low deactivation behavior. Having higher hydrogen adsorption capacity, was Ru/C shown to be more active than Ru/Al₂O₃ in

isomerization linoleic acid under similar conditions, while Ru/Al₂O₃ Ruthenium also exhibited a different performance in selectivity during the hydrogenation compared to other catalysts such as nickel and palladium. Its high no-selectivity created two times the amount of stearic acid compared to nickel and palladium catalysts at high temperature (165°C) (Bernas et al., 2003; Cizmeci et al., 2009).

A lot of work has been reported on elucidating the effects of supports on the structure and the performance of supported noble metal catalysts. Various oxides, carbon, zeolite, as well as mesoporous materials such as SBA-15, MCM-41 have been used as supports of the noble metal catalyst (Belkacemi et al., 2006; Belkacemi and Hamoudi, 2009; Cizmeci et al., 2006; Fernandez et al., 2009; Nohair et al., 2005; Nohair et al., 2004; Plourde et al., 2004). Nohair et al. used various oxide supports (α -Al₂O₃, γ -Al₂O₃, TiO₂, MgO, ZnO, CeZrO₂) deposited with palladium to investigate the effect of supports. They found that the support effect is not significant by comparing their turnover frequencies (TOF). TOF is defined as the frequency at which molecules react on an active site and the higher TOF value responses to the higher catalyst activity. Although specific surface areas vary from 9 m²/g to 297 m²/g and acid-basic properties of the supports differ, the activity and the selectivity of the catalysts to *cis* C18:1 cannot be improved by changing to other oxide supports compared to Pd/SiO₂ catalyst (Nohair et al., 2005). Fernandez et al. obtained similar results. MCM-22 (one type of Na-zeolite) supported catalysts were found to be slightly more active than other α -Al₂O₃, γ -Al₂O₃ and ZSM5 (another type of Na-zeolite) supported samples. Compared to nickel catalysts, the Pd/Al₂O₃ activity is 375-fold higher under the same operating conditions, while the saturation of C18:1 to C18:0 was more pronounced for the Ni catalyst (close to 30%) and lower for the Pd (18%) catalyst during the hydrogenation of sunflower oil (Fernandez et al., 2009). Cizmeci et al. conducted soybean oil hydrogenation using palladium catalysts supported on carbon and alumina, and claimed that the catalytic activity has a strong dependency on the support materials, while the selectivity is not dependent on support material but mainly catalyst metal type and concentration (Cizmeci et al., 2006).

Rubin et al. have reported that palladium catalysts on narrow porous activated carbon have a lower hydrogenation rate and a higher trans-isomerization rate than palladium oxides with wide pores during the hydrogenation of edible oils (Rubin, 1989). This implies that some

optimal pore structure is required. Recently, palladium over mesoporous material (SBA-15) was considered to be a potential catalyst used for catalytic hydrogenation of vegetable oils (Belkacemi et al., 2006; Belkacemi and Hamoudi, 2009; Plourde et al., 2004; Simakova et al., 2008a). It has been demonstrated that the Pd catalysts using SBA-15 as a nanostructured silica support with less Pd loading (1 %wt) had the same catalytic hydrogenated activity as 21% metal loading Ni-catalysts (Mélanie Plourde, 2004). Furthermore, they revealed a good resistance against structure collapsing and excessive metal sintering.

The bimetal catalysts of Pd-Cu, Pd-Pb and PdFe/Al₂O₃ showed lower activity than palladium monometallic catalysts during the hydrogenation of oils. Compared to the monometallic catalysts, the bimetal catalysts generally take two times as long to get the same conversion (Nohair et al., 2005; Nohair et al., 2004). The more the Cu or Pb additive amount, the more obvious the effect of the activity is. This result is especially in agreement with the low catalytic activity of copper at low temperature (Ravasio et al., 2002). However, the addition of Ni could slightly improve the hydrogenation activity of the Pd catalyst under certain conditions (70°C and 5.2 MPa) where the Ni was inactive (Wright et al., 2003a; 2003b).

McArdle et al. found that the metal precursor used for impregnation also had an effect on the activity and selectivity. The catalytic activity of the catalyst Pt/SiO₂ prepared by precursor chloroplatinic acid, H₂PtCl₆ could be slightly improved by platinum acetyl acetate, Pt(AcAc)₂ by comparing the iodine values. The iodine value determined the amount of unsaturated fatty acids and the higher the iodine number, the more unsaturated bonds are presented in oils or fats. Experiments have shown that the 1.2 %wt Pt/SiO₂ catalyst reached an iodine value of 59, while the 1.5 %wt Pt/SiO₂(Ac) catalyst reached an iodine value of 66 after 5 hours reaction time. It is reasoned that the presence of chlorine on a supported catalyst raises the hydrogen spillover, which may improve the hydrogenation activity. It is also thought that the Pt loading from 0.7% to 4.6% correspondingly decreased the metal dispersion and increased the metal particle size (McArdle et al., 2010). The results coincided with the previous research by others (Choo et al., 2001; Simakova et al., 2008b).

2.2.2.4 Supported Copper, Copper-chromite catalysts

Copper-chromite is a universally employed commercial catalyst for the selective hydrogenation of soybean oil (Tike and Mahajani, 2006). Although the copper-chromite is most selective for hydrogenating the linolenic acid in soybean oil and other vegetable oils (Koritala, 1984), copper catalyst has shown lower activity at low hydrogen pressure (0.3 MPa or less) and studies have demonstrated that high pressure (3 MPa or more) could increase the rate and the degree of the hydrogenation of soybean oil (Mounts, 1978). However, the high cost batch equipment for high-pressure hydrogenation have impeded their commercial use in the hydrogenation of oils (Koritala, 1984). Copper-chromite promotes formation of the highest amount of trans-isomers than that by palladium and nickel catalysts, while Copper-chromite catalysts pose spent catalyst disposal problems due to the Cr content (Tike and Mahajani, 2006).

Supported copper catalysts only attract the attention of a few researchers due to the catalysts' lower activity compared to other metal catalysts. Ravasio et al. in 2002 patented a series of pre-reduced 8% Cu/SiO₂ catalysts which showed two times higher activity compared with unreduced catalysts and a different selectivity towards formation of high oleic derivatives (up to 88%) in the selective hydrogenation of rapeseed oil. They continuously investigated the performance of various supported copper catalysts which were prepared by chemisorption-hydrolysis (CH) and incipient wetness (IW) methods for selective hydrogenation of rapeseed oil, and found that copper on silica catalysts by IW showed no activity even after a very long reaction time, while the catalyst prepared by CH exhibited very low activity (Ravasio et al., 2002).

2.2.2.5 Catalyst deactivation

Considerable research has found that catalyst poisoning by sulfur or other components present in oil and fat is the main cause for catalyst deactivation with time (Edvardsson et al., 2001; Klimmek, 1984; Semikolenov, 1996; Twigg and Spencer, 2001). Although all poisons in feedstocks are removed, catalyst deactivation may still happen because of side reactions during the hydrogenation. Those reactions generate intermediates or by-products, such as carbon monoxide or carbonaceous deposits (coking), which may lower the activity of catalysts. Coke leads to catalyst activity decay by blocking the active sites or plugging the

pores in the supports, which is typically associated with high-temperature gas-phase reactions. For instance, although palladium supported on wide porous titanium dioxide and alumina shows high initial activity, it is prone to fast deactivation due to the activity of metal blocking by impurities from the feed and water adsorbing on its hydrophilic surface (Semikolenov, 1996). Edvardsson et al. examined the stability of supported palladium and platinum catalysts during the hydrogenation of vegetable oils and investigated the role of coke in the deactivation process using a temperature-programmed oxidation method (Edvardsson et al., 2001). They found that the deactivation of the catalyst and the coke accumulation occurred simultaneously on the Pd/ γ -Al₂O₃ catalyst and the mechanism for deactivation by coke formation should include both the types of metal and support. Palladium catalysts allowed both faster formations of trans-isomers and higher selectivity compared with platinum catalysts for linoleate hydrogenation. These were attributed to the large-molecule formation of conjugated dienes which are also suggested to be coke precursors on the catalyst surface. The large coke molecules condensed on metal surface causing the loss of activity.

2.3 Heterogeneous Catalysts for deoxygenation / decarboxylation of plant oils and animal fats

2.3.1 Deoxygenation / decarboxylation

2.3.1.1 Introduction to deoxygenation/decarboxylation: General concept

Deoxygenation in processing plant oils and animal fats refers to the chemical reaction for removing oxygen from bio-feedstocks. Formats of deoxygenation include the Barton-McCombie deoxygenation (the replacement of hydroxyl group by hydrogen), Wolff-Kishner reduction (the replacement of oxo group by two hydrogen atoms), decarboxylation, etc. (Barton, 1975; Wade, 1999). Decarboxylation is a standard organic synthesis method by eliminating the –COOH group as CO₂. since the time when Bertram studied a homogeneous

catalyst over selenium to decarboxylation stearic acid to heptadecane (Bertram, 1936). Various decarboxylation reactions have been investigated (King, 1992).

2.3.1.2 Deoxygenation / decarboxylation mechanism of fatty acids of plant oils and animal fats

Various combinational reactions of the deoxygenation of plant oils and animal fats can take place, depending on the feedstocks composition, catalyst choice, and reaction conditions. Hydrodeoxygenation and decarboxylation are the most common and universal pathways for deoxygenating oils and fats. In hydrodeoxygenation, oxygen-containing materials are reduced by hydrogen, while hydrocarbons and water are generated. In decarboxylation, the reaction is only restricted to carboxylic acids and their esters, resulting in the formation of hydrocarbons and the release of CO₂. In the presence of hydrogen, the alkene resulting from CO₂ elimination is hydrogenated to generate the corresponding alkane, which is called hydrodecarboxylation (Koivusalmi, 2008; Kubicka, 2008).

Kubicka and Kaluza investigated the pathways involved in the transformation of triglycerides into hydrocarbons by collecting the experimental data over three sulfided catalysts (Ni/Al₂O₃, Mo/Al₂O₃ and NiMo/Al₂O₃) under certain hydrogen pressure conditions (260-280 °C and 3.5 MPa). The double bonds in triglycerides, the main component of the oils and fats, are first saturated. Then they are converted into fatty acids via hydrogenation. The fatty acids can undergo several parallel reactions, either a further hydrogenation to yield fatty alcohols and ultimately saturated n-alkanes with an even carbon atoms number, namely hydrodeoxygenation, or a direct decarboxylation yielding hydrocarbons with odd numbers of carbon atoms (Kubicka and Kaluza, 2010).

Supported noble metal catalysts, specially a commercial palladium supported on activated carbon, have been recently investigated for converting triglycerides to hydrocarbons based on decarboxylation reaction (Lestari et al., 2009a; Smith et al., 2009). Because catalytic decarboxylation requires lower hydrogen consumption compared with catalytic hydrodeoxygenation, it is a potential technology for converting plant oils and animal fats to hydrocarbons. Snare et al. comprehensively studied catalytic decarboxylation of stearic acid

without hydrogen over a variety of supported catalysts, especially over Pd/C. It is found that there exist several plausible reaction pathways (table 2.2) in the deoxygenation of stearic acid which is a typical reaction intermediate in deoxygenation of triglycerides (Snare et al., 2006).

Table 2.2. Plausible liquid-phase reaction pathways reaction.

| Liquid-phase Reaction | | |
|-----------------------|---|--|
| Hydrodeoxygenation | 1 | $R-COOH + 3H_2 \rightarrow R-H + 2H_2O$ |
| Decarboxylation | 2 | $R-COOH \rightarrow R-H + CO_2$ |
| Decarbonylation | 3 | $R-COOH \rightarrow R'-H + CO + H_2O$ |
| | 4 | $R-COOH + H_2 \rightarrow R-H + CO + H_2O$ |

R =Saturated alkyl group R = unsaturated alkyl group

From this table, fatty acids can be directly decarboxylated or decarbonylated without hydrogenation. Direct decarboxylation produces paraffinic hydrocarbon by eliminating the carboxyl group and releasing carbon dioxide. Direct decarbonylation produces olefinic hydrocarbons by removal the carboxyl group to form carbon monoxide and water. Fatty acids can also be deoxygenated by adding hydrogen. Therefore, the production of hydrocarbons can be carried out via direct hydrogenation or indirect decarboxylation. Apart from the liquid-phase reactions, a number of gas-phase reactions are involved during decarboxylation and/ or decarbonylation, specifically those reactions including methanation and water-gas shift reactions (table 2.3)(Lestari et al., 2009a).

Table 2.3. Plausible gas-phase reaction.

| Gas-phase Reaction | | |
|--------------------|---|--|
| Methanation | 1 | $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ |
| | 2 | $CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O$ |
| Water-gas Shift | 3 | $CO + H_2O \leftrightarrow H_2 + CO_2$ |

Deoxygenation and decarboxylation can be studied by using a wide range of model molecules such as stearic, oleic, linoleic acids etc. The reaction mechanism and reaction rate depend on the type of oxygen compound. Since fatty acids are formed in the initial step of triglycerides conversion, fatty acids and their esters can be used as model compounds in

order to clarify the reaction mechanism of deoxygenation/decarboxylation of plant oils and animal fats (Mikulec et al., 2010).

Based on a comprehensive analysis of gas and liquid products, Han et al. proposed a plausible mechanism involving two kinds of bond cleavage as shown in Figure 2.4. One is the cleavage of the alkyl-oxygen bond, and the other is the cleavage of the acyl-oxygen bond. Aliphatic esters were converted into alkanes with one less carbon atom than aliphatic acid counterparts of methyl esters through a decarboxylation route accompanied by decarbonylation reaction. This is contrasted with alkanes with the same number carbon atoms as aliphatic acid counterparts of methyl esters might can be derived by complete hydrodeoxygenation (Han et al., 2010).

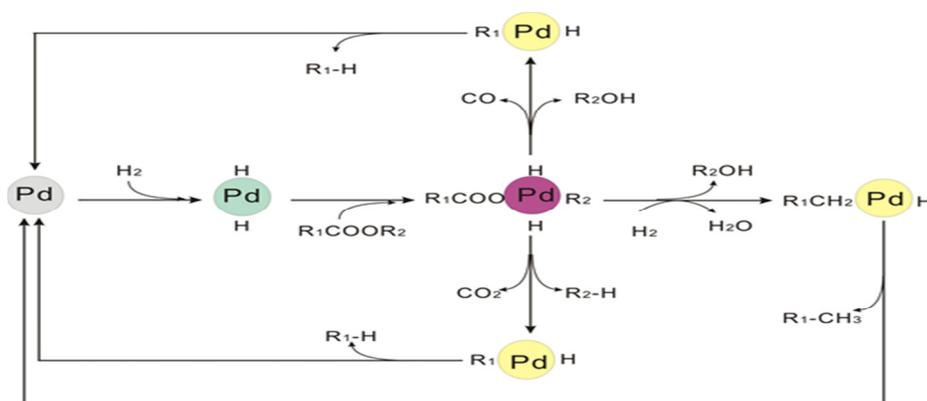


Figure 2.4. Plausible decarboxylation mechanism of aliphatic esters.

2.3.2 Catalysts for deoxygenation / decarboxylation of fatty acids, plant oils and animal fats

2.3.2.1 Supported metal sulfides catalysts

There are many reasons that make supported metal sulfide catalysts to be suitable for deoxygenation of oils and fats. On one hand, supported metal sulfides catalysts are the important industrial catalysts which have been well developed and widely used in the

hydrosulfurization of petroleum feedstocks to remove sulfur and nitrogen (Thomas Weber, 1998). On the other hand, they are the first hydrotreating catalysts developed for upgrading coal-derived liquids that contain large amount of oxygenated compounds (Weisser, 1973). In addition, recent research on supported metal sulfides catalysts has demonstrated that they are suitable catalysts for deoxygenation, especially hydrodeoxygenation of oils and fats (table 2.4). Moreover, they are the only industrial application catalysts used in the deoxygenation of triglycerides so far (Abhari, 2011; Jakkula, 2007).

2.3.2.1.1 Catalyst Preparation

Generally as a rule, the major components of sulfide metal catalysts for deoxygenation oils and fats are Co (or Ni) and Mo (or W) (Navalikhina and Krylov, 1998). These catalysts are usually prepared by the impregnation method. Taking a conventional NiMo/Al₂O₃ catalyst as an example, the support Al₂O₃ is impregnated sequentially by solutions of nickel acetate and sodium molybdate. Following drying at 120 °C, it is calcinated under nitrogen with a flow of 2.5 L/h at 400 °C under atmospheric pressure for 2 hours. The catalyst is sulfided under 5 %vol H₂S/H₂ mixed gas with a flow of 2.5 L/h under atmospheric pressure for 4 hours (Senol et al., 2005b).

Table 2.4. An overview of reaction conditions and catalysts used for deoxygenation of oils and fats over supported metal sulfides catalysts.

| Model compound | Catalyst | Reaction conditions | Reference |
|---|--|--|---------------------------|
| Decanoic acid | NiMo/Al ₂ O ₃ | 280°C ;H ₂ , 7 MPa; FBR | Laurent and Delmon, 1994b |
| Rapeseed oil | CoMo/MCM-41 | 300,320°C; H ₂ , 2-11 MPa | Kubicka et al., 2010 |
| Aliphatic fatty acid esters | NiMo/Al ₂ O ₃ , CoMo/Al ₂ O ₃ | 250°C; H ₂ , 1.5 MPa | Senol et al., 2005a |
| Sunflower oil | NiMo/Al ₂ O ₃ /F | 300-360°C ; H ₂ ,2-4 MPa | Kovacs, 2011 |
| Rapeseed oil | NiMo/Al ₂ O ₃ , Ni/Al ₂ O ₃ , Mo/Al ₂ O ₃ | 260-280°C; H ₂ ,3.5 bar, FB | Kubicka and Kaluza, 2010 |
| Rapeseed, palm, sunflower oils and lard | NiMo/ γ -Al ₂ O ₃ , NiMo/TiO ₂ , NiW/TiO ₂ , NiMo/ZrO ₂ , NiMo/NaY | 320-360 °C; H ₂ , 4.5MPa; FBR | Mikulec et al., 2010 |
| Waste vegetable oil | NiW/Al ₂ O ₃ , NiMo/Al ₂ O ₃ , CoMo/Al ₂ O ₃ | 250-350°C; H ₂ , 7MPa; FBR | Makoto Tobaa, 2011 |
| Sunflower oil | CoMo/Al ₂ O ₃ | 300-380 °C; H ₂ , 2-8 MPa | Márton Krár, 2010 |

NOTE: BR is the batch reactor; SBR is the semi-batch reactor; FBR is the fixed-bed reactor.

2.3.2.1.2 Catalyst Characterization and performance

Sulfide metal catalysts have been studied extensively in hydrodeoxygenation due to their well-known and wide industrial application in the hydrosulfurization of fossil-based oils (Crocker, 2010). Generally bimetallic aluminum oxide supported catalysts in sulfided form (usually NiMo/Al₂O₃, occasionally CoMo/Al₂O₃) were investigated for deoxygenation of oils and fats (Donnis et al., 2009; Kubičková, 2010; Liu et al., 2009). Triglycerides present in plant oils and/or animal fats 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 mainly n-alkanes which have 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, CO₂ and water (Darocha et al., 1993; Donnis et al., 2009; Gusmãoa.J.; 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 / hydrodecarboxylation (Mikulec et al., 2010). The reaction conditions affect product distribution, or the operating temperature and reaction pressure affect all parallel reactions. Hydrodecarboxylation prevails over hydrodeoxygenation with increased temperature and decreased reaction pressure. These findings not only can be proved by experimental data (Kubicka et al., 2009; Mikulec et al., 2010) but also have been proved by thermodynamic calculations (Smejkal et al., 2009). Different catalysts also have led to significantly different product distributions (Kubicka and Kaluza, 2010). Promotion of hydrodecarboxylation over hydrodeoxygenation has been found more NiMo than CoMo catalysts. NiW catalysts showed stable hydrogenation activity and that they were more efficient in decarboxylation than NiMo and CoMo catalysts because nearly twice the quantity of hydrocarbons formed via decarboxylation or decarbonylation by NiW catalysts than the other two kinds of catalysts. (Makoto Tobaa, 2011). In addition, early studies have shown that the yield by decarboxylation from carboxylic acids is more than that by hydrodecarboxylation from esters with the corresponding acids (Laurent and Delmon, 1994c).

Several studies have analyzed the impact of deoxygenation products on the catalyst activity and selectivity. They concluded that the impact originated from heteroatoms, mainly H₂S, NH₃ and water. The effects of hydrogen sulfide on deoxygenation of various oxygenated compounds have been investigated in detail (Laurent and Delmon, 1994a; Senol et al., 2007a; Senol et al., 2005a). Hydrogen sulfide can help in preserving the activity of sulfide metal catalysts during deoxygenation (Senol et al., 2007a). It is explained that coordinately unsaturated Mo atoms and sulfhydryl (-SH) or hydride (-H) contribute to hydrogenolysis sites, responsible for the cleavage of the heteroatom-carbon bonds. These sulfhydryl groups can be generated by H₂S absorption on the sulfur vacancies associated with the MoS₂ phase (Ferrari et al., 2001). On the sulfided catalysts, the support shows Lewis acid characteristics. The surface of the sulfided catalyst also includes groups such as S²⁻, SH⁻ and H⁺ (Berhaut et al., 1998; Topsoe and Topsoe, 1993). The SH⁺ and H⁺ groups exhibiting Bronsted acid characteristics are formed by dissociative adsorption of H₂S on the vacancies. The dissociation also turns the S²⁻ groups into SH⁻ groups. The Bronsted acidity of the catalyst increases and the Lewis acidity decreases at the same time when H₂S was added (Petit et al., 1997). The SH groups might be involved both in supplying hydrogen for the hydroprocessing reactions and providing Bronsted acidity for the acid-catalyzed reactions (Topsoe and Topsoe, 1993). But the addition of H₂S does not protect the catalysts from deactivation (Senol et al., 2007b). The effect of water cannot be ignored. Water inhibited the rate of hydrodeoxygenation and hydrodecarboxylation of esters only slightly, but it can improve hydrolysis of esters (Laurent and Delmon, 1994a). In the hydrodeoxygenation of aliphatic esters, water also decreased the conversion of the esters, specially suppressed the decarboxylation on the catalysts. Another interesting result is that hydrogenation reactions only inhibit with the NiMo catalysts, but not with the CoMo catalysts. The addition of H₂S cannot only effectively compensate for the water inhibition, but also shift the product distribution to decarboxylated hydrocarbons (Senol et al., 2005a). Ammonia also showed strong inhibition with both hydrodeoxygenation and decarboxylation (Laurent and Delmon, 1994b).

Kubicka et al. studied standard bimetallic hydrotreating catalyst (NiMo/Al₂O₃), compared the monometallic catalysts (Ni/Al₂O₃ and Mo/Al₂O₃), and further investigated to understand

the role of individual components of the kind of catalysts on their activity and selectivity. They found that there are significant differences between bimetallic and monometallic catalysts. The activity of the catalysts increased in the order of $\text{Ni}/\text{Al}_2\text{O}_3 < \text{Mo}/\text{Al}_2\text{O}_3 < \text{NiMo}/\text{Al}_2\text{O}_3$ (Kubicka and Kaluza, 2010). Actually, this result agrees with the trends reported for hydrodesulfurization (Kubičková, 2010; Weisser, 1973). It is proposed that Ni acts as a promoter in the bimetallic catalyst as it only present in a lower concentration than Mo (the atomic ratio $\text{Ni}/(\text{Ni}+\text{Mo})$ is 0.3). Final hydrocarbon products are mainly n-heptadecane over $\text{Ni}/\text{Al}_2\text{O}_3$ and are only n-octadecane over $\text{Mo}/\text{Al}_2\text{O}_3$, and n-heptadecane and n-octadecane on $\text{NiMo}/\text{Al}_2\text{O}_3$. Furthermore, it can be inferred that the hydrodecarboxylation step over Ni sulfide catalyst is significantly faster than the hydrogenation step as none of the hydrogenation products such as fatty alcohols or n-octadecane are found in the reaction products. In contrast, Mo sulfide catalysts are more favorable for hydrodeoxygenation because there are only minor concentrations of decarboxylation products (Kubicka and Kaluza, 2010). Other literature also confirms that Ni and Co sulfide catalysts generally have higher selectivity than Mo sulfides (Thakur and Delmon, 1985; Zakharov et al., 1997). The results can be attributed to inherently different electronic properties of the Ni and Mo sulfide phases. These electronic properties affect the adsorption of triglycerides and the preferred deoxygenation pathways. Different Ni/(Ni+Mo) atomic ratios were not found to significantly affect the catalyst selectivity. The catalysts with higher atomic ratios have only slightly more efficiency than the lower ones (Kubicka and Kaluza, 2010).

The support as the main component of catalyst mechanism plays an important role in the activity of sulfide metal catalysts (Yang et al., 2008). The role of the support has been investigated by many researchers (Kubicka et al., 2010; Kubicka et al., 2009). Multiple literature reports have shown that $\text{NiMo}/\text{Al}_2\text{O}_3$ has the activity on both decarboxylation and hydrodeoxygenation and the activity can be affected by the reaction conditions (Kovacs, 2011; Kubicka and Kaluza, 2010; Kubicka et al., 2009). By comparing different supports of NiMo catalysts during the catalytic conversion of jatropha oil, Liu and his co-workers found that the $\text{NiMo}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst had the highest isomerization (*iso*-alkanes) activity and high cracking activity (Liu et al., 2009). In former research, sulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ and

CoMo/Al₂O₃ catalysts have been active for decarboxylation, but they are prone to be deactivated by coke deposition due to the acidity of alumina support (Laurent and Delmon, 1994a). Mesoporous materials have been investigated and shown great potential as a catalyst support for deoxygenation of triglycerides. Selective conversion of triglycerides into hydrocarbons over CoMo supported on mesoporous nanoparticles of alumina, show a better performance than the conventional alumina supported catalyst at temperature 310°C and reaction pressure 7 MPa (Kubicka et al., 2009). However, CoMo supported on MCM-41 (all-silica-based) catalyst was significantly less active than alumina-based catalysts (Kubicka et al., 2009). David et al. further have studied CoMo modified MCM-41 catalysts with different Al content. These catalysts still showed worse performance in complete deoxygenation of triglycerides into hydrocarbons than alumina catalysts due to different composition of supports (Si versus Al), whereas Al incorporated in the MCM-41 support could partially improve the catalyst performance (Kubicka et al., 2010).

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, storage tank and sulfur left-over in the product, etc. Marton and his co-workers further studied non-sulfided form bimetallic catalysts (CoMo/Al₂O₃) (Márton Krár, 2010; Senol et al., 2005b). They found that the process parameters were milder when the reduced catalyst is applied (340°C-360°C; 2-4 MPa; 1.0 h⁻¹; 600Nm³ H₂/sunflower oil ratio), while using pre-sulfided catalyst can result in a 5-8% higher yield. They further concluded that the decarboxylation/decarbonylation have a higher rate than hydrodeoxygenation by reduction when using either reduced or pre-sulfided catalyst. Therefore, the reduced CoMo/Al₂O₃ catalyst is also a good choice for conversion oils and fats (Márton Krár, 2010).

2.3.2.1.3 Catalyst deactivation

It has been known that coke formation and desulfurization are the main causes of the deactivation of sulfided catalysts (Furimsky, 2000; Furimsky and Massoth, 1999). The changes in the carbon and sulfur contents of the catalysts might explain the deactivation. The formation of sulfur-containing product compounds is likely associated with the catalyst desulfurization (Senol et al., 2007b). It has been reported that sulfide NiMo/Al₂O₃ and

CoMo/Al₂O₃ catalysts can be deactivated by coke deposition due to the acidity of alumina support (Laurent and Delmon, 1994a). So the application of a neutral support, such as activated carbon, probably could limit the formation of condensation products which act as coke precursors, and also assist the elimination of oxygen from the molecules which are involved in coke formation (Rodriguez-Reinoso, 1998). Low-quality feedstocks always have impurities such as alkalis and phosphorus, which would induce deactivation of deoxygenation catalysts. Alkalis and phosphorus can accelerate catalyst deactivation due to their deposition on the catalyst surface leading to poisoning of active sites (Kubicka and Horacek, 2011).

2.3.2.2 Supported noble metal catalysts

As discussed above, decarboxylation is a potential technology for converting plant oils and animal fats to hydrocarbons. Supported noble metals, such as Pt, Pd, and Ru, are a class of catalysts that are applied in various industrial processes, mainly including selective hydrogenation, naphtha reforming, 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 specially Pd and Pt are the more active catalysts for decarboxylation of oils and fats (Snare et al., 2006).

Several groups have studied comprehensively the activity and selectivity of some supported noble metal catalysts, such as Pd/C, Pt/C, Pt/Al₂O₃, Pt/TiO₂, etc. (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 group first tested a series of commercial supported noble metal catalysts in decarboxylation of triglycerides. They used stearic acid as the model compound because it is a typical reaction intermediate in decarboxylation of triglycerides. Through a catalyst screening, they found better results were achieved than palladium and platinum supported on activated carbons than other catalysts. Decarboxylation is profound over Pd/C by gas phase analysis, while decarbonylation is evident over the same catalyst (Snare et al., 2006). This group further studied Pd/C catalyst using other model compounds including unsaturated model chemicals.

At the same time, other noble supported catalysts were investigated under a series of decarboxylation conditions (table 2.5) (Kubičková, 2010). Those catalysts included Pt/Al₂O₃, Pt/TiO₂, Pd/SBA-15, Pd/BaSO₄, and so on.

2.3.2.2.1 Catalyst Preparation

Generally, the preparation of supported catalysts includes the approaches of: impregnation, adsorption, ion-exchange, or precipitation followed by washing, drying, calcinations, and activation (Farrauto, 2006). Most of the supported noble metal catalysts used for decarboxylation of oils and fats, such as Pd/C, Pt/C, Ir/Al₂O₃, Ir/SiO₂, Ru/SiO₂, Ru/MgO, Pd/BaSO₄, and Pd/BaCO₃, are prepared by impregnation with chlorine containing precursors, such as H₂PtCl₆, H₂PdCl₄, etc. (Chiappero et al., 2011; Do et al., 2009; Lestari et al., 2009b; Lestari et al., 2009c; Maki-Arvela et al., 2007; Snare et al., 2006). Pt/Zeolite is prepared by the ion-exchange method (Sotelo-Boyas et al., 2011). For example, preparation of 5 %wt Pd/C follows these steps. Support carbon was crushed and sieved to get a required particle size. Palladium chloride was dissolved in hydrochloric acid to synthesize the precursor H₂PdCl₄. The carbon support was immersed in demineralized water into which an aqueous of NaOH was added in double-molar excess. This slurry was stirred overnight to achieve the complete wetting of the carbon pores. The amount corresponding to the nominal loading of 5 %wt Pd on the catalyst was added dropwise under the flow of nitrogen. Then, the catalyst was filtrated, washed and dried at 70°C. At last, the dry catalyst was reduced by molecular hydrogen at 150°C for 1 hour (Lestari et al., 2009c).

The catalyst of Pd nanoparticle supported on SBA-15 used for deoxygenation is made by direct synthesis method. (Han, 2007; Lestari et al., 2010) First, an appropriate amount (based on Pd metal loading) of palladium chloride was added to a homogeneous mixture containing Pluronic P123 triblock copolymer (EO₂₀PO₇₀EO₂₀) and tereaeethyl orthosilicate (TEOS) in hydrochloric acid solution. Then the resulted gel goes through hydrothermal process at 100 °C for 48 hours, washing, filter and drying processing. At last, the catalyst is synthesized by calcining the obtained powers at 550°C (Lestari et al., 2010).

Table 2.5. An overview of reaction conditions and catalysts used for deoxygenation of oils and fats over supported noble metal catalysts.

| | Catalyst | Reaction conditions | Reference |
|-----------------------------------|--|---|--|
| Stearic acid | Various catalysts | 300°C ;N ₂ , 600kPa; SBR | Snare et al., 2006 |
| Stearic acid | Pd/C | 300-350°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°C; Ar-H ₂ , Ar, 10 bar; FBR; Dodecane | Lestari et al., 2009b |
| Stearic acid | Pd/SBA-15 | 360°C ; H ₂ -Ar,1.7MPa; SBR; Dodecane | |
| Stearic acid, palmitic acid | Pd/C | 260-300°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 °C; He, H ₂ , 15 bar; SBR; Dodecane or Heptadecane | Immer et al., 2010; Immer and Lamb, 2010 |
| Oleic, linoleic acids | Pd/C | 300-360°C; Ar, H ₂ -Ar, 1.5-4.2 MPa; SBR and FBR; Mesitylene | Snare et al., 2008 |
| Caprylic acid | Pd/C | 300-400 °C; H ₂ -He, 2.1 MPa; FBR | Boda et al., 2010 |
| Methyl octanoate, methyl stearate | Pt/Al ₂ O ₃ , Pt/TiO ₂ | 300-350°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 °C ; H ₂ , 11 MPa; BR | Sotelo-Boyas et al., 2011 |

NOTE: BR is the batch reactor; SBR is the semi-batch reactor; FBR is the fixed-bed reactor.

2.3.2.2.2 Catalyst Characterization and Performance

Effect of physical characteristics

Physical properties of catalysts include particle size, density, pore volume, porosity, BET surface area, etc. These properties play an important role in the development of the reaction. Considering that oils and fats exist as the big molecules, the pores of the support should be sufficiently large enough to make the active metal access the molecules of oils and fats. Furthermore, since the reaction takes place on the surface of the catalyst, a large surface area is fundamental to achieve a good performance for the catalyst. A thorough catalyst screening including supported noble metal catalysts, such as Pd/C, Pd/Al₂O₃, Pt/Al₂O₃, Pt/C, Ru/MgO, and Ru/SiO₂ and bimetallic catalysts PdPt/C, NiMo/Al₂O₃, as well as other catalysts such as a skeletal nickel catalyst, supported nickel catalysts Ni/Al₂O₃, Ni/Cr₂O₃, NiSiO₂ has been done by Snare et al (Snare et al., 2006). The surface areas of these catalysts varied from the large surface area carbon supports (>1000 m²/g) to low surface area metal oxide supports (<100 m²/g). A series of 1%, 5% and 10% Pd/C catalysts have the larger surface areas than other determined catalysts. By comparing the initial reaction rates over these different catalysts, the highest rates were obtained over supported carbon catalysts, especially Pd/C, Pt/C. They concluded that the catalyst structure such as the larger specific surface areas are presumably the main reason of the higher initial reaction rate over this kind of catalysts (Snare et al., 2006).

Effect of support

Metal-supported carbon catalysts were found to be very selective to deoxygenation and all catalysts of palladium and platinum on carbon could arrive >90% selectivity to produce hydrocarbons (Snare et al. 2006). Catalytic deoxygenation of stearic acid was found dependent on the type of the support and the surface properties of carbon support material (Lestari et al., 2008). In a 4 %wt Pd/C catalyst, Sibunit (a carbon support material) has a system of wide pores of 50-80 nm and volume 0.2 cm³/g which provide efficient transport of reactants to and from palladium particles.

It is observed that the selection of this carbon support is beneficial for production of longer chain paraffins from stearic acid. In addition, the acidity of supports is also an important

factor to determining the product distribution in decarboxylation of ethyl stearate (Maki-Arvela et al., 2007).

When stearic acid was used as the model compound to study deoxygenation, a byproduct, the symmetrical ketone, was formed over several catalysts including Pt and Pd supported on alumina (Do et al., 2009; Snare et al., 2006). At opposite poles, the deoxygenation products over Pt and Pd supported on active carbon consisted almost exclusively of a mixture of C₁₇ hydrocarbons. Do et al. related this byproduct formation to the catalysts deactivation. (Do et al., 2009) Especially, the selectivity of the symmetrical ketone over Ru/MgO was above 99%. Other catalysts including Ir/Al₂O₃, Pd/Al₂O₃, Pt/Al₂O₃, Ru/SiO₂, Rh/SiO₂ also have high selectivities to ketone formation (Snare et al., 2006). Interestingly, those catalysts have the same feature that they are all supported on oxide materials. In addition, after Do et al. probing the catalytic deoxygenation of methyl-stearate over Pt/Al₂O₃ and Pt/TiO₂ catalysts, ascertained that the oxide support under hydrogen-deficient environment is crucial in the formation of condensation products. The support of TiO₂ can contribute more oxygen vacancy sites than Al₂O₃ and makes Pt/TiO₂ more favorable in the formation of ketones compared than Pt/Al₂O₃ under similar conditions (Do et al., 2009).

Effect of reaction conditions

According to the reaction stoichiometry, the deoxygenation / decarboxylation occurs via CO₂ removal without requiring hydrogen for saturated model compounds, such as stearic acid and its esters, methyl-octanoate, tristearine etc. (Do et al., 2009; Immer et al., 2010; Kubickova et al., 2005; Snare et al., 2006). Although catalyzing those model compounds eventually resulted in high conversion under inert reaction atmosphere conditions, such as N₂ and He, it was also observed that the main product n-heptadecane is initially high, but it decreases with time (Maki-Arvela et al., 2007). Other researchers also found that when a small quantity of hydrogen is present in liquid phase, the reaction rate of fatty acids was faster than that under an inert atmosphere. It is indicated that hydrogen is able to preserve the catalyst activity for a longer time (Lestari et al., 2009b) which is also demonstrated by Kubickova et al. (Kubickova et al., 2005). They found that under low partial pressure of

hydrogen condition (5% H_2 , 95% He), TOF values obtained in the experiments was the highest compared to inert atmosphere (He) or purity hydrogen reaction conditions.

Effect of metal dispersion

Murzin group also investigated the effect of metal dispersion (D) on decarboxylation (Simakova et al. 2009). Pd/C with 1% Pd (wt.) catalysts having four different metal dispersions were used to study deoxygenation of a palmitic (59 %mol) and a stearic acid (40 %mol) mixture. Different metal dispersions were achieved by changing the pH of the palladium hydroxide solution and varied in a range of 18-72% according to CO chemisorption. Under the normal decarboxylation conditions (260-300°C; 1.75 MPa H_2 - He ; solvent: dodecane), the effect of Pd dispersion was significant. The conversion levels (C) after 300 minutes of reaction decreased over different Pd/C catalysts as follows: $C_{47\%} > C_{65\%} > C_{72\%} > C_{18\%}$. The reason that highly dispersed sample (Pd/C $D=72\%$) seemed to be not sufficiently active probably was attributed to its strong interaction with the support. According to Temperature Programme Reduction method (TPR), although the average particle sizes for samples Pd/C ($D=65\%$) and Pd/C ($D=72\%$) is close, the sample Pd/C ($D=65\%$) is more uniform and performs more actively. The sample Pd/C ($D=18\%$) that is expected to have large metal particles is not so active due to small surface area. All these results suggest the importance of metal dispersion in catalysts (Simakova et al., 2009).

2.3.2.2.3 Catalyst deactivation

Supported noble metal catalysts are effective catalysts for the hydrogen-free decarboxylation of fatty acids. However, the catalysts suffer severe deactivation after one use. Less than 5% conversion to n-heptadecane can be achieved for the one time use of the catalyst, which is significantly lower than the over 80% conversion for the fresh catalyst (Ping et al., 2011). High surface coverage of reactant acids in non-reactive binding configurations is hypothesized to be responsible for the catalyst deactivation as the catalyst can be regenerated by solvent extraction to remove the organic species. Catalyst deactivation during the deoxygenation of fatty acids and their derivatives have also been reported to originate from coking and poisoning by CO and CO_2 (Maki-Arvela et al., 2007). When the reaction atmosphere H_2 was replaced with helium, this deactivation was accelerated. At the

beginning, the conversion under He was 40% compared to 61% under H₂. After 2 hours, the conversion dramatically dropped to 15%. This indicates that the catalyst activity significantly decreases. At the same time, unsaturated hydrocarbons and heavy substances (i.e., symmetrical ketone) are observed in the product distribution (Do et al., 2009). Those results were also confirmed by other researchers (Immer et al., 2010; Simakova et al., 2010; Snare et al., 2006). Furthermore, research has also shown that using low-boiling-point solvents, e.g. decane and mesitylene, can improve the catalyst stability (Maki-Arvela et al., 2007). However, the catalyst deactivation and regeneration have not been well studied so far (Lestari et al., 2009a).

2.3.2.3 Other catalysts

Although the use of precious metals such as palladium and platinum provides some promising results, an economical drawback is apparent. Some studies have transferred to use cheaper catalysts, such as hydrotalcite catalysts, activated carbons, and nickel catalysts.

Obtaining hydrocarbon fuels also can be achieved by the decarboxylation of oil and fats over the hydrotalcite catalysts. Na et al. have investigated a series of hydrotalcite catalysts and found that the hydrotalcites showed some activities of decarboxylation without hydrogen and could produce pure hydrocarbons. MgO ratio in hydrotalcites and reaction temperature play key roles in decarboxylation reaction. Higher MgO concentration and higher temperature are preferred. They also found that the cracking and decarboxylation occurred simultaneously during the reaction catalyzed by hydrotalcites. However, the production of heptadecane by direct decarboxylation is not very high while almost oxygen in oleic acid has been removed (Na et al., 2010). Other investigators also found that the MgO-supported catalyst promoted the decarboxyl-cracking of triglyceride to make middle-distillate range hydrocarbons (Tani et al., 2011).

A poorer conversion of carboxylic acids in the ketonic decarboxylation process has been obtained over Ni/Al₂O₃ than over supported Pd catalysts (Maier, 1982) and similar results have been obtained in the hydrodeoxygenation of waste fat for producing renewable diesel have also presented by Madsen et al (Madsen et al., 2011). Ni supported on MgO-Al₂O₃

catalysts are influenced by the temperature of the catalyst calcination. At 300°C of calcination temperature, the catalysts performed the highest catalytic decarboxylation of oleic acid than the catalysts from other calcination temperatures (400°C and 500°C) (Roh et al., 2011). Compared Pd/C to Ni/C catalysts, catalysts containing Ni shows higher activities for both cracking of fatty acid chains and for triglyceride deoxygenation (Morgan et al., 2010).

Investigation on whether the only activated carbon support could be an effective catalyst for hydrothermal decarboxylation of fatty acids was conducted by Fu et al. They found that the activated carbons could convert saturated and unsaturated fatty acids to fuel-range hydrocarbons under supercritical water and H₂-free conditions. From the research of kinetics of palmitic acid decarboxylation, they recorded the apparent activation energy of 125 kJ/mol by activated carbons as catalysts. The result is higher than the activation energy of 79 kJ/mol observed with a 5% Pt/C catalyst (Fu et al., 2011).

2.4 Summary

2.4.1 Current status

Deoxygenation of plant oils and animal fats is a potential process for the production higher quality hydrocarbon-based fuels. The process includes both hydrogenation of the carbon double bond and decarboxylation.

Hydrogenation of oils and fats has been a subject of extensive research for more than one hundred years. Although Ni based catalysts are generally used as the commercial catalysts in the hydrogenation of oils and fats, high cost noble metal catalysts are being given more attention because of their high activity and small quantity requirement.

Supported metal sulfide catalysts as hydrotreating catalysts have been widely applied in the petroleum industry. There is considerable preferential experience using these catalysts for the development of deoxygenation processes. But deoxygenation by full decarboxylation of -COOH function groups in fatty acids is the ideal way to make green diesel because the

utilization of expensive hydrogen is not required. Supported noble metal catalysts show greater potential than other catalysts due to their high selectivity to paraffin hydrocarbons. Catalysts of Pd on active carbon for decarboxylation have been investigated intensively. Research on other noble metals such as platinum and on other supports is being gradually launched. Pt/Al₂O₃, Pt/SiO₂, PtSnK, etc., all show good promise for converting oils and fats to hydrocarbons.

Some hydrogenation catalysts, particularly the supported noble metal catalysts, are also capable of catalyzing decarboxylation and/or hydrogenation of the plant oils and animal fats to remove oxygen. Moreover, these catalysts perform higher activity compared to other catalysts in both hydrogenation and decarboxylation reactions. Supported metal sulfides catalysts can also promote simultaneous hydrogenation and deoxygenation of oils and fats.

2.4.2 The need and trend of R&D activities

Catalysis is still regarded as a state of art, although it is evolving from an art to a science due to the introduction of powerful instruments into this field. Catalyst screening or even the trial and error method is still needed to select an optimum catalyst for a specific catalytic process. The pathways of deoxygenation of bio-feedstocks show a complicated reaction network, which requires catalysts to have high selectivity to the desired products. However, some catalysts show high selectivity to side-products, like symmetric ketone. Some catalysts have high selectivity to the desired products, but their stability is quite low and regeneration may need additional cost.

For the recently catalytic production of renewable diesel, model components are usually used. Although they represent some characteristics of real feedstocks used in industry, there are still many differences between them. For instance, many types of impurities exist in real feedstocks. When applying the catalysts and operational parameters to large-scale production, adjustments are definitely needed, which implies the importance of pilot testing before industrialization.

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Chapter 3 Investigation of Catalytic Decarboxylation of Fatty Acids and Esters

Abstract

Research and development of biofuels from renewable resources are now expanding from transportation fuels into other areas such as jet fuels. Oxygen removal, or deoxygenation, to produce jet fuels, is a logical way to overcome the drawback of biofuels' low energy density.

Generally, the process of deoxygenation includes the following chemical reactions: decarboxylation, decarbonylation and hydrodeoxygenation. This study aims to investigate the effectiveness of catalytic decarboxylation without an external supply of hydrogen. The following heterogeneous catalysts were tested on their efficiencies for decarboxylation under different operating conditions, including reaction time, pressure, temperature, solvent application, stirring rate and catalyst application rate: Pd/C, Pd/Al₂O₃, Pt/C, Ni/SiO₂, Pt/Al₂O₃ and Raney Nickel.

Pd/C was found to be the most reactive catalyst for the decarboxylation of stearic acid. Although the Pt/C catalyst has a similar selectivity as the Pd/C catalyst, the Pt/C catalyzed reaction is slow. Since it was the most reactive, further studies were conducted using the Pd/C catalyst. It was found that increasing the temperature caused an increase in the conversion rate of the reactant to heptadecane and therefore increased the product yield. The conversion was increased from 54% at 265°C to approximately 98% at 300°C after one hour. In general, the decarboxylation rate of stearic acid increases as the concentration of catalyst in the reactant mixture increases. However, the effect of catalyst concentration levels off when it is 8% or higher. Additionally, as the solvent to reactant mass ratio decreases, the reaction takes longer to complete. The effects of pressure and mixing intensity were found to be negligible.

3.1 Introduction

Declining fossil fuel reserves, increasing energy demands from growing economies and environmental awareness all contribute to the demand for renewable and sustainable energy sources. Second-generation biofuels provide promising replacements for traditional petroleum-derived transportation fuels (i.e. diesel, jet fuel and gasoline). Fatty acids and their esters are potential raw materials for producing long chain, diesel-like hydrocarbons which are considered to be renewable diesel. Renewable diesel has many advantages over conventional biodiesel, such as better cold flow properties and higher energy density.

Hydrodeoxygenation and decarboxylation are the most common and universal processes for renewable diesel production. In hydrodeoxygenation, oxygen-containing materials are reduced by hydrogenation while hydrocarbons and water are generated. In decarboxylation, carboxylic acids and their esters form hydrocarbons and release carbon dioxide. In the presence of hydrogen, the release of carbon dioxide leads to the formation of corresponding alkanes in a process called hydrodecarboxylation (Koivusalmi, 2008; Kubicka, 2008).

Most of the research work on decarboxylation has been done using fatty acids as the feedstock to produce 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). However, better control of the parameters (e.g. the product yield, reactant conversion rate and the catalyst activity and selectivity) is necessary. The operating conditions, such as temperature, pressure and catalyst type, have various effects. This study aims to investigate the effectiveness of catalytic decarboxylation in the absence of a hydrogen supply under different operating conditions.

3.2 Methodology

3.2.1 Materials

Stearic acid (95%), FCC (food chemical codex) grade, was purchased from Sigma-Aldrich (St. Louis, MO.). Methyl stearate (>95%) was purchased from Tokyo chemical industry Co., Ltd (Tokyo, Japan). Dodecane (100%) was purchased from Acros Organics (Geel, Belgium). Various commercial catalysts were obtained from Sigma-Aldrich (St. Louis, MO.) which include: 5 %wt palladium on activated charcoal (Pd/C), 5 %wt platinum on activated carbon (Pt/C), 5 %wt palladium on alumina (Pd/Al₂O₃), 65 %wt Ni on silica/alumina (Ni/SiO₂, Al₂O₃), and Raney Nickel.

All of the following reagent grade standards were bought for identifying the product and calibrating the gas chromatography system. The reagent grade standards included: hexadecane (C₁₆H₃₄), n-heptadecane (C₁₇H₃₆), octadecane (C₁₇H₃₄), eicosane (C₁₈H₃₆), N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) supplied by Acros Organics (Geel, Belgium), stearic acid obtained from Nu-Chek Prep company (Elysian, Minn), methyl stearate purchased from Tokyo chemical industry Co., Ltd (Tokyo, Japan). High purity gases, nitrogen (99.9999%) and helium (99.999%), were used for the reaction and were provided by Oxarc (Lewiston, Idaho).

3.2.2 Experimental Procedure

All the decarboxylation experiments were performed in a 300 mL Parr pressure batch reactor (model 4560, PARR Instruments, Moline, Ill.) equipped with a 4857 controller which includes a pressure transducer to monitor the operating pressure, an agitation system to adjust the agitation motor speed by a tachometer and a temperature control unit to enable the temperature adjustment of the system. The reactor is also equipped with a shut-off mechanism to prevent a high temperature and/or high pressure over-shoot.

Prior to the experiment, a-specified amount of the catalyst was measured out and put into the reactor. The catalyst was reduced by 99.999% hydrogen at 1.38 MPa (200 *psi*) in situ at 200°C for one hour. After the reduction, a specified amount of dodecane solvent was added to the reactor, in the presence of hydrogen, before the reaction, either stearic acid (SA) or methyl stearate (MeS) put in the reactor. Thereafter, the reactor was flushed thoroughly with nitrogen for one minute to remove any traces of hydrogen and oxygen. While being agitated, the reactor was then heated to the desired temperature and the pressure was adjusted to the

desired level with nitrogen. The reaction typically lasted between two and four hours, starting from the moment when the temperature reached desired value. Upon the completion of the reaction, the reactor was cooled down to room temperature by the cooling unit inside of the reactor. Samples were taken at one-hour intervals during the operation and saved for further analysis by gas chromatography.

3.2.3 Product Analysis

Agilent 6890N Gas Chromatograph (GC) was used for analyzing the reactants and the liquid products. It 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 μ m). The GC oven temperature program was set as follows: 110°C, 1°C/min to 126°C, 30°C/min to 185°C, 1°C/min to 200°C, 5°C/min to 300°C, holding for two min. The entire procedure takes approximately 55 min. The carrier gas (helium) flow rate was 170 mL/min. Samples, 1 μ L in size, were injected onto the column inlet with a 60:1 split ratio and the concentrations were determined relative to an eicosane internal standard.

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 five percent, 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 the process evaluating parameter. The experimental data were processed and analyzed according to the following definitions.

Molar yield of a product from a special chemical reaction is typically defined as the moles of the actual desired product in the product mixture to that of the theoretical moles formed stoichiometrically. For the study of heterogeneous catalytic decarboxylation of SA or MeS, provided that the density change of the liquid mixture is minimal thus negligible during the reaction, the yield of the desired product (i.e., heptadecane), Y_{hep} , is defined as:

$$Y_{hep} (\%mol) = \frac{C_{f,hep}}{C_{i,react}} \times 100\% \quad \text{-----} \quad (3.1)$$

Where:

$C_{i,react}$ is the molar concentration of reactant (SA or MeS) before the reaction, which is equivalent to the theoretical molar concentration of desired product heptadecane after stoichiometric reaction, *mmol/mL*

$C_{f,hep}$ is the molar concentration of heptadecane in the products after the reaction, *mmol/mL*

Similarly, the conversion of reactant SA or MeS (C_{react}) and the selectivity of the targeted product heptadecane among the total products (S_{hep}) are defined, respectively, as:

$$C_{react} (\%mol) = \frac{(C_{i,react} - C_{f,react})}{C_{i,react}} \times 100\% \quad \text{-----} \quad (3.2)$$

Where:

$C_{i,react}$ is the molar concentration of reactant (SA or MeS) before the reaction, *mmol/mL*

$C_{f,react}$ is the molar concentration of reactant (SA or MeS) after the reaction, *mmol/mL*

$$S_{hep} (\%mol) = \frac{C_{f,hep}}{\sum C_{f,prod}} \times 100\% \quad \text{-----} \quad (3.3)$$

Or, it can be expressed by the ratio of product yield to reactant conversion (Towler and Sinnott, 2012):

$$S_{hep} (\%mol) = \frac{Y_{hep}}{C_{react}} \times 100\% \quad \text{-----} \quad (3.3')$$

Where:

$C_{f,hep}$ is the molar concentration of product heptadecane, *mmol/mL*

$C_{f,prod}$ is the molar concentration of product *i* in product mixture, *mmol/mL*

Y_{hep} is the yield of the desired product (heptadecane), *mmol/mL*

C_{react} is conversion of reactant SA or MeS, *mmol/mL*

3.3 Results and Discussion

3.3.1 Catalytic Activity

The experimental results of the catalyst screening for SA deoxygenation are summarized in Table 3.1. Pd/C and Pt/C exhibit relative higher activity and selectivity in the decarboxylation of SA than the other catalysts. When using the Pd/C catalyst, SA was completely converted and the highest yield of the desired product, heptadecane, was obtained after three hours of reaction. When using the Ni/SiO₂ catalyst, the SA conversion rate was 48.1% and the yield of the targeted product was only 14.4%. Other catalysts such as Raney Nickel, Pt/Al₂O₃ and Pd/Al₂O₃ showed mediocre catalytic activity in the decarboxylation of SA.

Table 3.1. Experimental Results of Catalyst Screening for SA Deoxygenation.

The reaction conditions: 300°C, 1 MPa, reaction time: 3 h, catalyst concentration: 20 %wt, sRatio: 9:1, and stirring speed: 1000 rpm.

| No. | Catalyst | C_{react} (%mol) | Y_{hep} (%mol) | S_{hep} (%mol) |
|-----|-----------------------------------|-----------------------|---------------------|---------------------|
| 1 | Raney Nickel | 10.5 | 2.7 | 25.71 |
| 2 | Pd/Al ₂ O ₃ | 18.9 | 8.0 | 42.33 |
| 3 | Pt/Al ₂ O ₃ | 29.3 | 4.2 | 14.33 |
| 4 | Ni/SiO ₂ | 48.1 | 14.4 | 29.94 |
| 5 | Pt/C | 83.5 | 78.2 | 93.65 |
| 6 | Pd/C | 100 | 88.6 | 88.60 |

Table 3.1 clearly shows that Pt/C and Pd/C performed well, with high conversion rates, product yields and selectivities, making them feasible catalysts for the deoxygenation of SA and MeS. A comparison of C_{react} and Y_{hep} at the same sampling intervals for Pt/C and Pd/C (fig. 3.1 and 3. 2) reveals that Pd/C performs better than Pt/C. It took more than three hours to reach completion when the Pt/C catalyst was used. While using Pd/C as the catalyst, the reaction was almost complete in one hour. The high catalytic activity of Pt/C in SA deoxygenation is in agreement with the findings by Snare et al. (2006). In addition, the Pt/C catalyst favors the undesirable decarbonylation pathway around 360°C, and the carbon monoxide generated from decarbonylation inhibits the decarboxylation pathway (Snare et al., 2006). Based on these experimental results and the information gathered from related literature, Pd/C is the most active and selective catalyst for SA and MeS decarboxylation. Therefore, further decarboxylation studies will focus on the Pd/C catalyst.

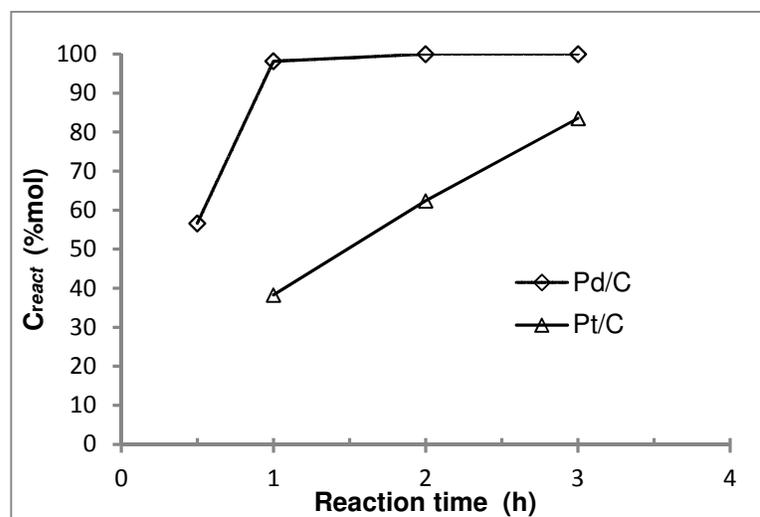


Figure 3.1. Conversion of SA as a function of reaction time.

Reaction conditions: 300°C, 1 MPa, sRatio: 4:1, catalyst concentration: 20 %wt and stirring speed: 1000 rpm.

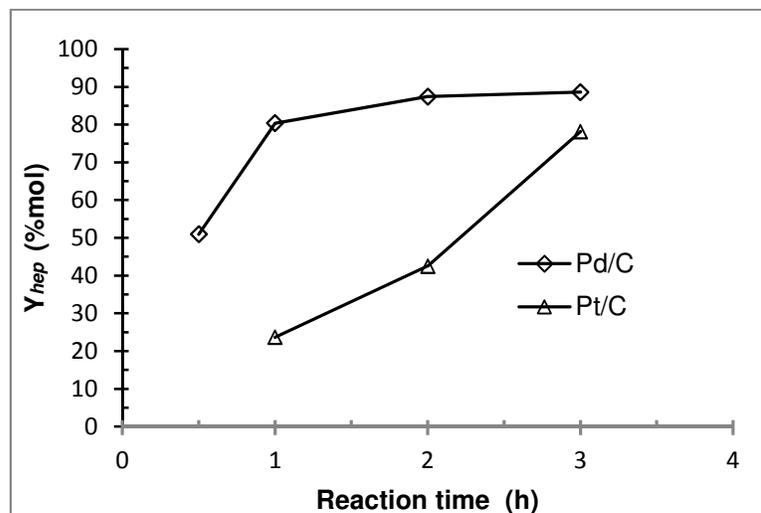


Figure 3.2. Targeted product yield as a function of reaction time.

Reaction conditions: 300°C, 1 MPa, sRatio: 4:1, catalyst concentration: 20 %wt and stirring speed: 1000 rpm.

Visual observation of the samples after three hours of reaction time can also give us some information on the level of reaction completion. Before reaction, the reactant SA is in solid form and cannot dissolve in the solvent dodecane at room temperature. When the mixture of SA and solvent dodecane is heated to approximately 60°C, the mixture becomes a homogeneous solution. After three hours of reaction time, the product mixtures show different visual appearance once cooled to room temperature when different catalysts were applied (fig. 3.3). When the catalyst is relatively active, such as Pd/C, the product mixture is much more transparent at room temperature, indicating a higher conversion to the product. On the other hand, less active catalysts, such as Ni/SiO₂, can only produce turbid mixtures since the SA has barely reacted. The more the heptadecane forms, the clearer the sample turns. Therefore, turbidity of the reaction mixture allows us to visually estimate the extent of reaction completion and catalyst activity. The sample from the Pd/C catalyzed reaction resulted in a much clearer solution, thus indicating a more complete reaction. It's worth noting that the first sample catalyzed by Pd/C turned clear when the temperature reached 300°C, indicating that at temperatures lower than 300°C, the decarboxylation reaction has begun. This result is consistent with those reported by Simakova et al. (2009).

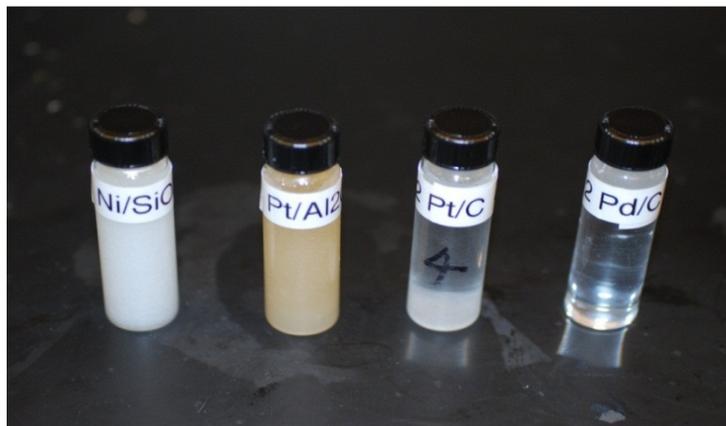


Figure 3.3 Selected samples of product mixtures after three hours of reaction time.

Reaction conditions: 300°C, 1 MPa, sRatio: 4:1, catalyst concentration: 20 %wt and stirring speed: 1000 rpm. Catalyzed by (from left to right): Ni/SiO₂, Pt/Al₂O₃, Pt/C and Pd/C.

3.3.2 Effect of Reaction Time

Using Pd/C as the catalyst, the SA decarboxylation was analyzed at three different reaction times: half an hour, one hour and two hours. Table 3.2 presents the experimental results of the SA conversion rate and the heptadecane yield at these varying reaction times. When there is a higher concentration of reactant, a longer reaction time is preferred for a complete conversion of SA and a higher heptadecane yield. The Pairwise comparisons, using Fisher's Least Significance Difference test (LSD) at 95% confidence level by SAS software (SAS Institute Inc., Cary, N.C.), were applied to statistically analyze the effect of different reaction times when sRatio is 4:1. The results of these comparisons showed that the p-value was greater than 0.1, which suggested that there was no significant difference in the conversion of SA from 1 to 2 hours.

Table 3.2. Experimental results of SA conversion and the targeted product heptadecane yield at different reaction time and sRatio.

Other operating conditions: 300°C, 1 MPa, Pd/C at 10 %wt, and stirring speed 1000 rpm.

| Reaction Time (h) | sRatio | Catalyst Concentration (% wt) | C _{react} (% mol) | Y _{hep} (% mol) |
|-------------------|--------|-------------------------------|----------------------------|--------------------------|
| 0.5 | 4:1 | 10 | 41.8±3.8 | 33.2±2.1 |
| 1 | 4:1 | 10 | 97.0±0.5 | 85.1±3.3 |
| 2 | 4:1 | 10 | 97.9±0.9 | 91.0±1.1 |
| 1 | 9:1 | 20 | 98.6±1.0 | 81.6±2.7 |
| 1 | 1:1 | 10 | 36.2±4.1 | 22.6±3.4 |
| 2 | 1:1 | 10 | 94.0±1.7 | 70.7±4.6 |

In the reaction with an sRatio of 4:1 and 10 %wt catalyst, the concentration of the product, heptadecane, gradually increased with time as the concentration of the reactant, SA, decreased (fig. 3.4). SA almost completely converted to heptadecane after 2 h. GC analysis showed that less than 5% of the byproduct, C₁₆H₃₄, was present in the mixture.

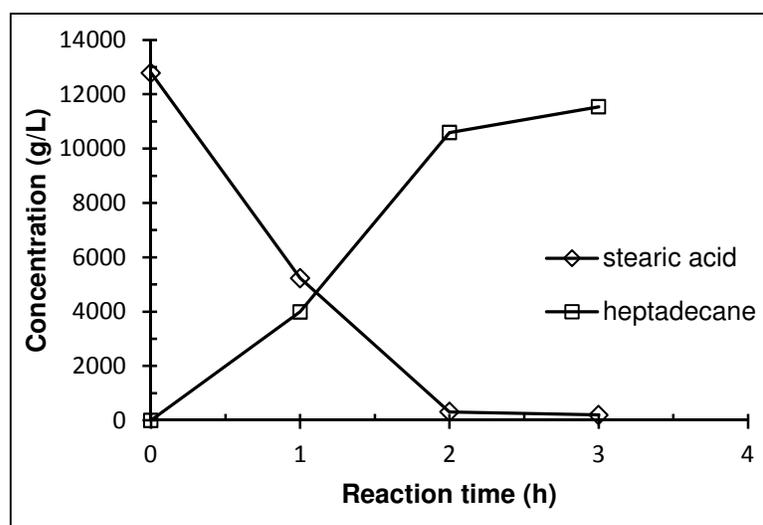


Figure 3.4. Concentrations of SA and heptadecane in the mixture as functions of reaction time.

Reaction conditions: 1 MPa, sRatio 4:1, catalyst concentration 10 %wt, and stirring speed 1000 rpm.

3.3.3 Effect of Solvent to SA Mass Ratio

The sRatio was varied while the concentration of the catalyst (Pd/C) was kept constant at 9 %wt. Other reaction conditions, such as the temperature, pressure and stirring speed, were kept constant at 300°C, 500 psig and 1000 rpm, respectively.

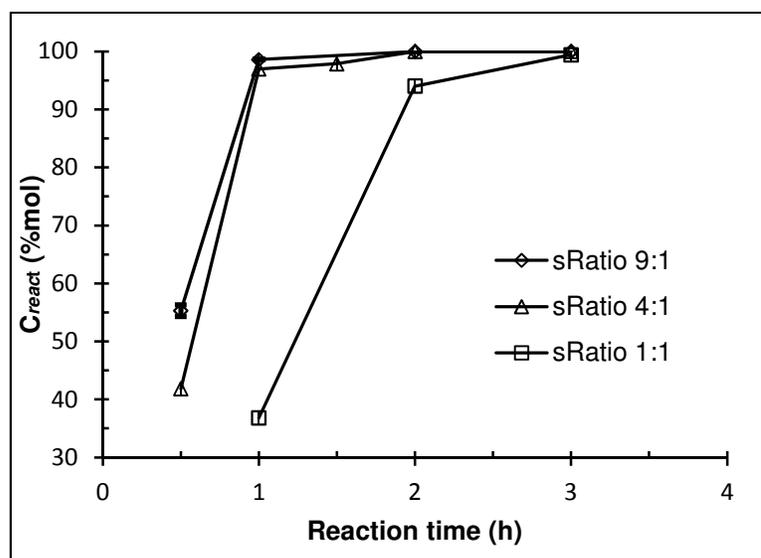


Figure 3.5. Conversion of SA as a function of reaction time at different sRatio.

Reaction conditions: 300°C, 1 MPa, catalyst concentration 10 %wt and stirring speed 1000 rpm.

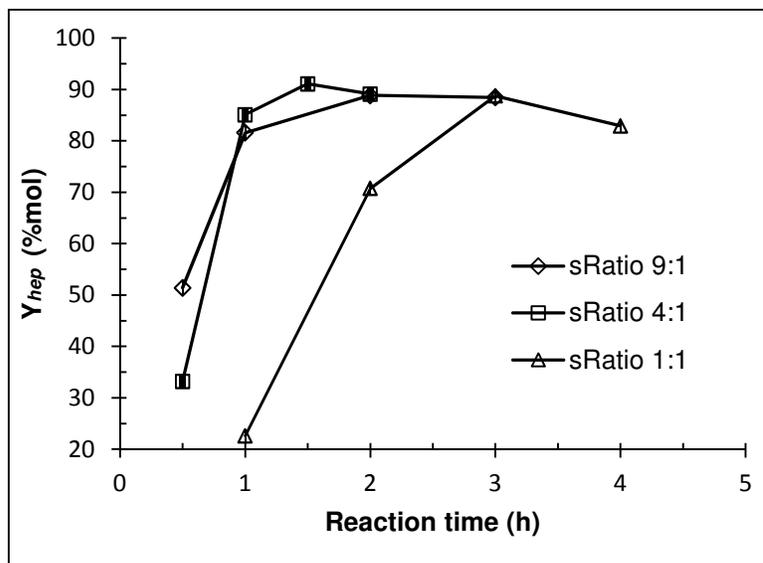


Figure 3.6. Yield of heptadecane as a function of reaction time at different sRatio.

Reaction conditions: 300°C, 1 MPa, catalyst concentration 10 %wt and stirring speed 1000 rpm.

Figures 3.5 and 3.6 show that at an early stage in the reaction (30 – 60 min), the SA conversion and the heptadecane yield steadily increased. After approximately 2 h of reaction, the complete conversion of SA, at different solvent to SA mass ratios, was achieved. However, with an sRatio of 1:1, (i.e., less solvent application), a slower SA conversion rate was observed (fig. 3.5). When reaction time was further extended, the yield of heptadecane dropped slightly for all sRatio values (fig. 3.6). This slight drop in product yield could be due to a small portion of the heptadecane cracking into shorter hydrocarbons over the Pd/C catalyst.

3.3.4 Effect of Reaction Temperature

Three different reaction temperatures, 265°C, 285°C and 300°C, were investigated in the decarboxylation of SA while using Pd/C as the catalyst. At 265°C, the SA conversion was 54% after 1 hour of reaction time, while at 300°C the conversion rate was approximately 98% after 1 h of reaction time (fig. 3.7).

Temperature strongly affects the conversion of SA and the heptadecane yield. According to the laws of kinetics, raising the temperature increases the kinetic energy of the molecules. The higher the temperature, the larger the number of molecules which have enough energy to overcome the activation energy of the reaction, therefore the reactivity is higher. However when the reaction time is sufficient, the product yields will be similar regardless of the temperature. After 3 hours of reaction, the product yield at 285°C is almost the same as that at 300°C, although the product yield at 265°C is still lower compared to those at the other two temperatures (fig. 3.8).

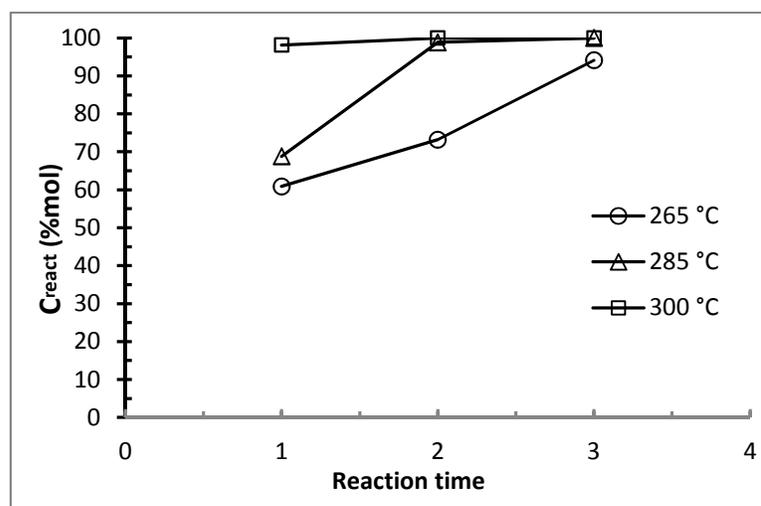


Figure 3.7. Conversion of SA at different reaction temperatures.

Reaction conditions: 1 MPa, sRatio: 9:1, catalyst concentration: 10 %wt and stirring speed: 1000 rpm.

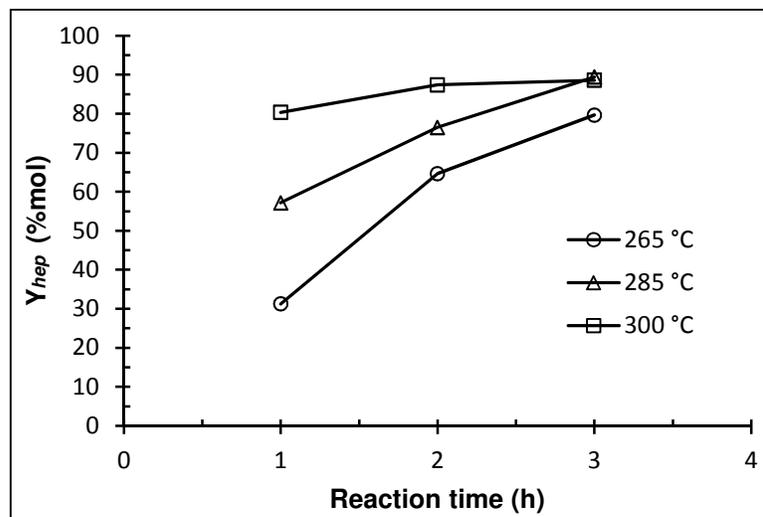


Figure 3.8. Yield of heptadecane at different reaction temperatures.

Reaction conditions: 1 MPa, sRatio: 9:1, catalyst concentration: 10 %wt and stirring speed: 1000 rpm.

3.3.5 Effect of Catalyst Concentration

Figure 3.9 shows the overall conversion of SA and the heptadecane yield after one-hour of reaction time using different catalyst concentrations. The overall SA conversion is significantly affected by the amount of catalyst applied. Over the range of 0-8% catalyst concentration, the higher concentration the catalyst, the faster the decarboxylation of SA occurs. However SA conversion levels off and the yield of heptadecane almost levels off when the catalyst application rate is 8 %wt or higher under the studied conditions: 300°C, 1MPa, sRatio: 9:1 and stirring speed: 1000 rpm.

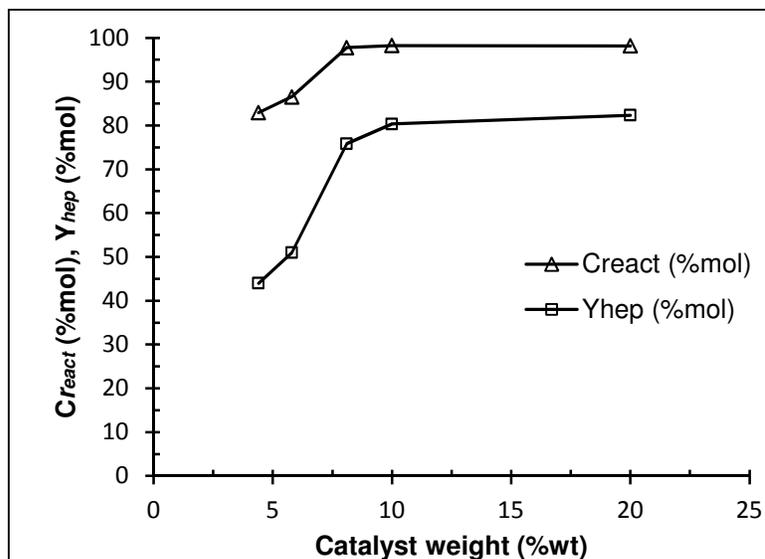


Figure 3.9. Conversion of SA and yield of heptadecane vs. Pd/C catalyst application rate after 1 hour of reaction time.

Reaction conditions: 300°C, 1 MPa, sRatio: 9:1 and stirring speed: 1000 rpm.

3.3.6 Effects of Reaction Pressure

The decarboxylation of SA is a liquid phase reaction. Theoretically, pressure is not an important factor in the reaction. To examine its possible effect, operating pressure was varied by adding nitrogen gas at different levels, such as 1.03 MPa, 3.44 MPa. As shown in Figure 3.10, the pressure impacted the reaction slightly and only at the beginning of the reaction. The experimental data were analyzed by the statistical analysis system software (SAS Institute Inc., Cary, N.C.). After the least significant difference test (LSD test) at 95% confidence level, pairwise analysis suggests that there are not significant differences under selected various pressures. Therefore, operating pressure is not considered as an important process parameter for the decarboxylation of SA.

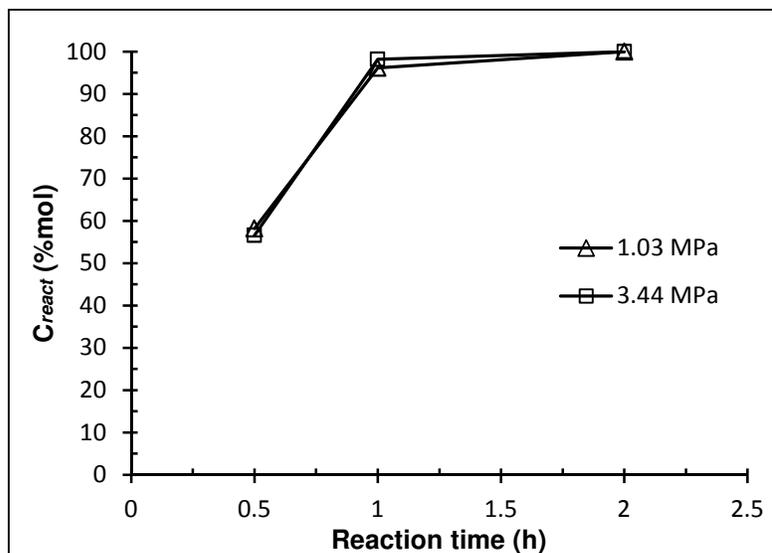


Figure 3.10. Conversion of SA at different pressures and reaction times.

Reaction conditions: 300°C, catalysts concentration: 10 %wt, sRatio: 9:1 and stirring speed: 1000 rpm.

3.3.7 Effect of Mixing Intensity

In order for the reactant to make better contact with the solid catalyst, a certain mixing intensity has to be provided. To avoid mass transfer limitations in a heterogeneous catalyst system, high stirring speed (approximately 1000 rpm or higher) is typically used (Do et al., 2009). However, such high stirring speed is difficult to achieve in commercial processes. In order to determine the effect of mixing intensity, three different stirring speeds, i.e., 100 rpm, 500 rpm and 1000 rpm, were investigated. Figures 3.11 and 3.12 show that the stirring speed significantly affected the reaction at in the first half hour of reaction, however after one hour of reaction time the stirring speed did not significantly affect the reaction. The experimental data were also analyzed statistically by the Pairwise comparisons using an LSD test at a 95% confidence level by SAS software (SAS Institute Inc., Cary, N.C.). The results showed that all of the p-values were greater than 0.1, which suggested that there are no significant differences in the yield of heptadecane and the SA conversion under different stirring speeds.

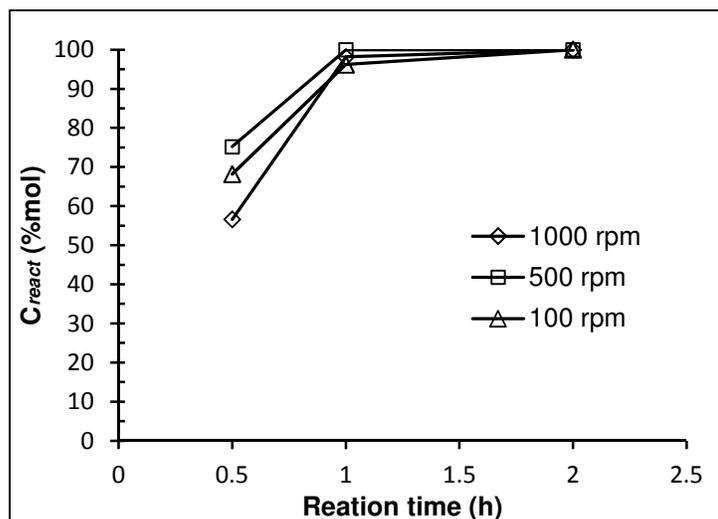


Figure 3.11. Conversion of SA at different stirring speeds.

Reaction conditions: 300°C, catalysts concentration: 10 %wt and sRatio: 9:1.

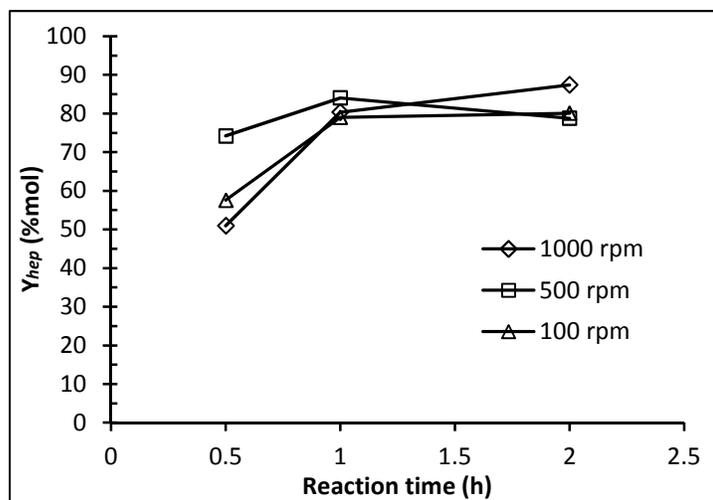


Figure 3.12. Yield of heptadecane at different stirring speeds.

Reaction conditions: 300°C, catalysts concentration: 10 %wt and sRatio: 9:1.

3.3.8 Methyl Stearate as the Feedstock

The decarboxylation of methyl stearate, MeS, over a Pd/C catalyst was also studied in the absence of an external hydrogen supply. The only difference between the molecules of MeS and SA is their terminal group. Therefore the targeted product of MeS decarboxylation should also be heptadecane while carbon dioxide, carbon monoxide and methane are the possible gas phase products. Figures 3.13 and 3.14 compare the conversion of reactants and the yield of target product when using MeS and SA as the feedstock. Under the same operating conditions, the decarboxylation rate of MeS was much slower than that of SA. At 300°C and with a reaction time of one hour, the conversion of SA and the yield of target product were high, 97.3% and 82.9%, respectively, while the conversion of MeS was only 31.0%, and the yield of target product was less than 10% under the same reaction conditions. When given a longer reaction time, conversion and yield still did not improve significantly for MeS. Therefore it seems that the decarboxylation of MeS needs a higher temperature than that of SA.

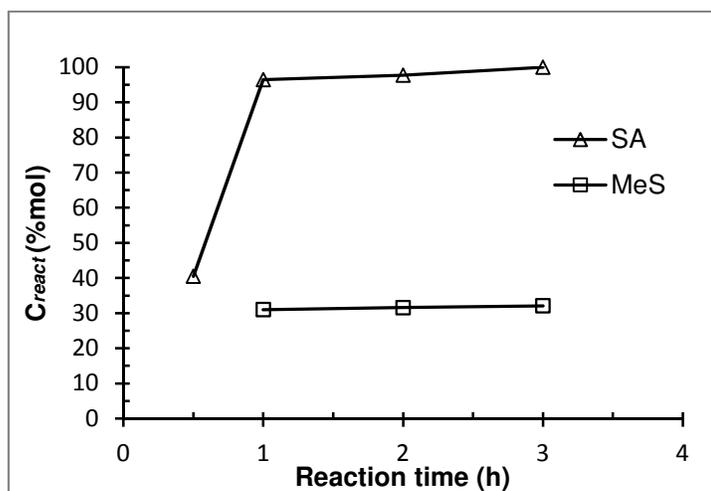


Figure 3.13. Conversion of reactants when using different feedstocks.

Reaction conditions: 300°C, catalysts concentration: 10 %wt, sRatio: 4:1 and stirring speed: 500 rpm.

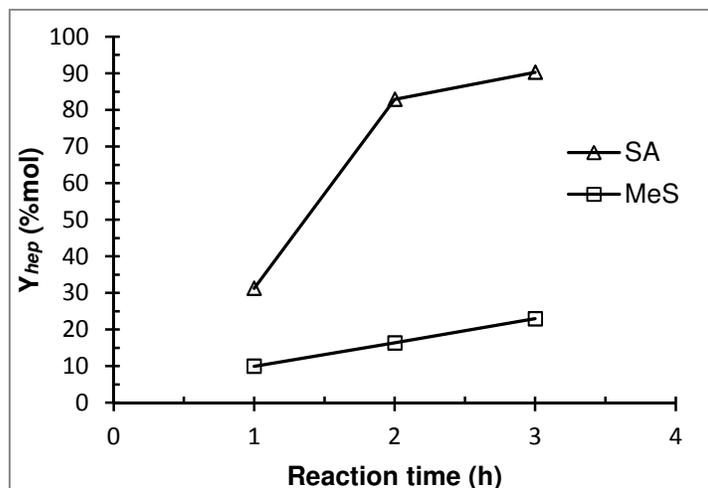


Figure 3.14. Yield of targeted product from different feedstocks.

Reaction conditions: 300°C, catalysts concentration: 10 %wt, sRatio: 4:1 and stirring speed: 500 rpm.

The decarboxylation of MeS is affected by specific operating conditions, such as temperature, solvent to reactant ratio and reaction time, in a similar manner as the decarboxylation of SA. Figure 3.15 shows that when high temperature was applied, the reaction rate increased and a high conversion and yield were also obtained. As the temperature increased from 300°C to 350°C, the conversion of MeS increased from 26.8% to 81.2% and the yield of heptadecane increased from 14.1% to 69.7% after 3 hours of reaction time. Figure 3.16 compares the conversion of MeS at different solvent-to-MeS ratios. The amount of solvent influences the conversion rate of MeS and the yield of heptadecane considerably. As compared to SA, a higher concentration of MeS (or low sRatio) requires a longer time for the reaction to complete.

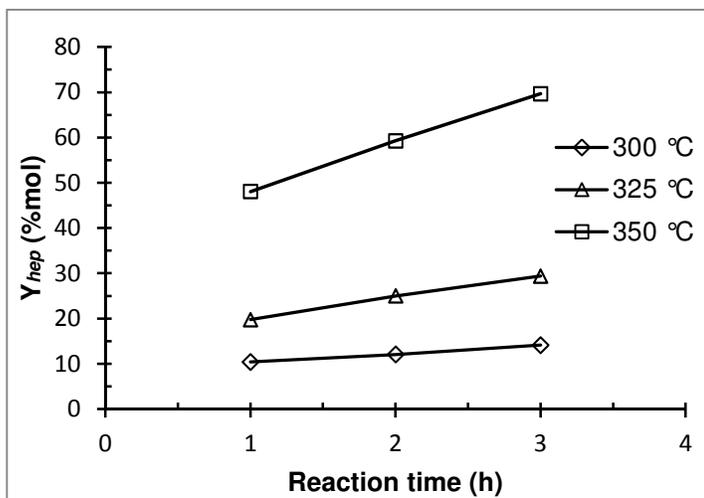


Figure 3.15. Yield of targeted product at different reaction temperatures.

Reaction conditions: 1 MPa, sRatio: 3:2, catalyst concentration: 10 %wt and stirring speed: 500 rpm.

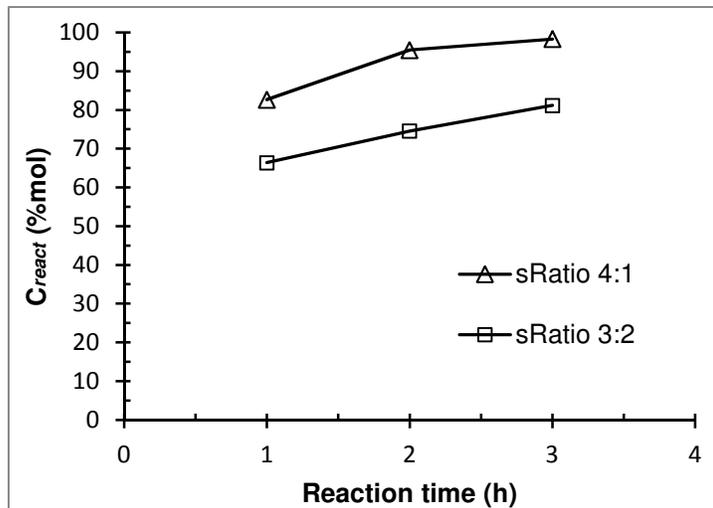


Figure 3.16. Conversion of MeS as a function of reaction time at different sRatio.

Other operating conditions: 350°C, catalyst concentration: 10 %wt and stirring speed: 500 rpm.

3.5 Conclusion

Based on the experimental results discussed previously, the catalytic decarboxylation of stearic acid (SA) over some heterogeneous catalysts, such as Pd/C and Pt/C, was successfully achieved with high activity and selectivity to the desired product, heptadecane. Pd/C was found to be the most reactive catalyst for the decarboxylation process of stearic acid. Although the Pt/C catalyst has a similar selectivity as Pd/C, the conversion rate of the reactant on Pt/C is slow.

Further studies were conducted using the Pd/C catalyst to test other operation parameters. 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 amount 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; the conversion was increased from 54% at 265°C to approximately 98% at 300°C after one hour. The lower the amount of solvent that is applied, the longer the reaction time that is required. The decarboxylation rate of stearic acid generally increased as the catalyst concentration in the reactant mixture increased. However, the effect of the catalyst concentration becomes constant when the concentration is 8%wt or higher. Solvent application affects the reactions. When the solvent to reactant ratio increases, a longer time is need 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 the decarboxylation process were found to be similar. However, MeS requires a higher temperature, a longer reaction time and a higher solvent to MeS mass ratio in order to be converted to the target product, heptadecane.

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Chapter 4 Process Optimization for Decarboxylation of Methyl Stearate Using Response Surface Methodology

4.1 Introduction

Liquid biofuels will play a major role in a more sustainable energy system of the future due to the fossil fuel limitations and their environmental burden (Ahmad, 2010). Conversion of vegetable oils and animal fats to biodiesel as a successful approach has been widely studied. However, biodiesel has some undesirable fuel properties, high viscosity, high cold point and the low heating value (Naik et al., 2010). Producing long chain diesel-like hydrocarbons or renewable diesel has recently caught much attention. Because of its lower or no hydrogen consumption compared to catalytic hydrodeoxygenation, catalytic decarboxylation is a potential technology for converting plant oils and animal fats to hydrocarbons (Do et al., 2009; Maki-Arvela et al., 2007). Research has been done on decarboxylation of fatty acids as feedstocks to produce renewable diesel (Maki-Arvela et al., 2007; Simakova et al., 2010; Simakova et al., 2009; Snare et al., 2006). These previous studies suggest that biodiesel can be selectively deoxygenated to improve fuel properties. Research on process parameters, e.g., product yield, reactant conversion, catalyst activity and selectivity, etc., is needed. Also, little work has been done with methyl esters (Do et al., 2009). Moreover, there are only some research efforts that focused on the process development or process optimization on such hydrocarbon-based biofuel production (Na, 2012).

Response surface methodology (RSM) is a powerful and efficient mathematical approach widely applied in the optimization of various operating processes, e.g., in biodiesel production process (Mumtaz et al., 2012) and fermentation process (Kim et al., 2011; Tellez-Mora et al., 2012). RSM can give us not only valuable information about the interaction between process variables, necessary information for design and process optimization, but also multiple responses at the same time.

In our previous study on process parameters, we used stearic acid as the principal model compound to produce renewable diesel by catalytic decarboxylation over heterogeneous catalysts, including Pd/C and Pt/C. It was found that the operating conditions have strong effects on the decarboxylation process of stearic acid. Comparing the operating conditions for the decarboxylation process of stearic acid, more rigorous conditions are required for methyl stearate decarboxylation. To the best of the author's knowledge, there is not much information available on thorough investigation of MeS decarboxylation for heptadecane via decarboxylation of methyl stearate nor on the process optimization for producing renewable diesel purpose. The objective of this work is to explore the optimum operating conditions for maximizing the molar yields of heptadecane in the process of MeS decarboxylation. Therefore, successful conduction of this study will contribute to a better understanding and improvement of the process which can direct the next step research for conversion of unsaturated fatty acids and esters as renewable diesel. To achieve a process optimization, an RSM was used for the analysis of multiple response variables on the effects of reaction temperature, solvent to reactant ratio (*sRatio*) and reaction time, the most influential process parameters according to our previous study (see Chapter 3).

4.2 Methods

4.2.1 Experimental Procedure

In total, 16 sets of experiments were performed in the Parr pressure batch reactor. Palladium catalyst on activated carbon (Pd/C) loaded with a constant mass ratio 0.12:1 to the reactant was adopted in all experiments. This catalyst loading rate was selected based on the results of Pd/C catalyst activity as presented in Chapter 3. The reactor system is a 300 mL pressure vessel equipped with a 4857 controller to monitor the operating pressure, an agitation system to control agitation speed, and a temperature control unit to enable the system temperature adjustment.

In a typical experiment, a certain amount of the catalyst was weighed in grams and put into the reactor prior to the experiment. The catalyst was reduced by 99.999% pure hydrogen at pressure 1.38 MPa (200 *psi*) *in situ* at 200°C for one hour. After the reduction, a certain

amount of solvent dodecane was added under hydrogen environment before reactant methyl stearate (Kunkes et al.) was put in the reactor. Thereafter, the reactor was flushed thoroughly with nitrogen for one minute to remove hydrogen and possible oxygen in the head space. The reactor was then heated to a desired temperature, and the pressure was adjusted to a desired level with nitrogen while being agitated. The reaction lasted typically 2~3 hours from the moment when the temperature reached 300°C. Upon the completion of the reaction, the reactor was cooled down to room temperature by the equipped cooling unit. Samples were taken at one-hour intervals and saved for analysis by gas chromatography.

Agilent 6890N Gas Chromatography (GC) was used for analyzing reactants and liquid products. It 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 GC oven temperature was programmed as: 110 °C, 1 °C/min to 126 °C, 30 °C/min to 185 °C, 1 °C/min to 200 °C, 5 °C/min to 300 °C and holding for 2 min. The whole procedure takes approximately 55 min. The carrier gas (helium) flow rate was 170 mL/min. Samples (1 µL size) were injected onto the column inlet with a 60:1 split ratio, and the concentrations were determined relative to an eicosane internal standard. See Appendix A for details.

This study aimed to investigate the optimum reaction conditions of catalytic decarboxylation in the absence of hydrogen supply. The operating conditions, such as temperature, reactant to solvent ratio and reaction time, which may significantly affect the process of heterogeneous catalytic decarboxylation, were studied. Generally, final liquid products from decarboxylation of methyl stearate include heptadecane (C₁₇H₃₆, the dominant product), octadecane (C₁₆H₃₄), eicosane (C₁₈H₃₈), etc., and the desired product is heptadecane. Byproducts took typically up to a very small fraction (<5%). Therefore, the yield of heptadecane was used in this study as a main indicator for determining the decarboxylation efficiency. The reactant conversion and product selectivity were also used as process evaluating parameters. The experimental data were processed and analyzed according to the following definitions.

Molar yield of a product from a special chemical reaction is typically defined as the moles of the actual desired product in the product mixture to that of the theoretical moles formed stoichiometrically. For the study of heterogeneous catalytic decarboxylation of SA or MeS, provided that the density change of the liquid mixture is minimal thus negligible during the reaction, the yield of the desired product (i.e., heptadecane), Y_{hep} , is defined as:

$$Y_{hep} (\%mol) = \frac{C_{f,hep}}{C_{i,react}} \times 100\% \quad \text{-----} \quad (4.1)$$

Where:

$C_{i,react}$ is the molar concentration of reactant (SA or MeS) before the reaction, which is equivalent to the theoretical molar concentration of desired product heptadecane after stoichiometric reaction, *mmol/mL*

$C_{f,hep}$ is the molar concentration of heptadecane in the products after the reaction, *mmol/mL*

Similarly, the conversion of reactant SA or MeS (C_{react}) and the selectivity of the targeted product heptadecane among the total products (S_{hep}) are defined, respectively, as:

$$C_{react} (\%mol) = \frac{(C_{i,react} - C_{f,react})}{C_{i,react}} \times 100\% \quad \text{-----} \quad (4.2)$$

Where:

$C_{i,react}$ is the molar concentration of reactant (SA or MeS) before the reaction, *mmol/mL*

$C_{f,react}$ is the molar concentration of reactant (SA or MeS) after the reaction, *mmol/mL*

$$S_{hep} (\%mol) = \frac{C_{f,hep}}{\sum C_{f,prod}} \times 100\% \quad \text{-----} \quad (4.3)$$

Or, it can be expressed by the ratio of product yield to reactant conversion (Towler and Sinnott, 2012):

$$S_{hep} (\%mol) = \frac{Y_{hep}}{C_{react}} \times 100\% \text{-----} \quad (4.3')$$

Where:

$C_{f,hep}$ is the molar concentration of product heptadecane, *mmol/mL*

$C_{f,prod}$ is the molar concentration of product *i* in product mixture, *mmol/mL*

Y_{hep} is the yield of the desired product (heptadecane), *mmol/mL*

C_{react} is conversion of reactant SA or MeS, *mmol/mL*

4.2.2 Experimental design and optimization by response surface methodology

Response surface methodology (RSM) was used for the optimization of decarboxylation of methyl stearate 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), ratio of solvent to reactant (*sRatio*; x_2 , dimensionless) and reaction time (x_3 , min) were chosen for the independent variables. Temperature range was from 286 to 355 °C; the *sRatio* range was from 87:13 to 53:13, and reaction time range was from 49 to 251 min. These values were chosen on the basis of the results of preliminary experiments (see Chapter 3). Suitable coded levels for independent variables are presented in Table 4.1.

Table 4.1 Levels of the variables tested in CCD.

| Coded levels | -1.682 | -1 | 0 | 1 | 1.682 |
|-----------------------|---------------------|-----|-----|-----|-------|
| Variables | Levels of variables | | | | |
| Temperature, x_1 | 286 | 300 | 320 | 340 | 355 |
| <i>sRatio</i> , x_2 | 87:13 | 4:1 | 3:7 | 3:2 | 53:47 |
| Reaction time, x_3 | 49 | 90 | 150 | 210 | 251 |

For the purpose of statistical analysis, the variables, x_i , are coded as X_i , according to the following equation (4.1).

$$X_i = \frac{x_i - x_0}{\Delta x_i}, i = 1, 2, \dots, K, \dots\dots\dots$$

(4.1)

Where X_i is coded value of the real variable, x_i and x_0 are the real values of X_i at the center point (zero) and Δx_i is the step change.

The coded variables, i.e., X_1 for temperature, X_2 for ratio of solvent to reactant and X_3 for reaction time, are defined as

$$X_1 = (x_1 - 320)/20; \quad X_2 = (x_2 - 30)/10; \quad \text{and} \quad X_3 = (x_3 - 150)/60.$$

To save time and cost on running the experiments, small response surface design is preferred in this study. Replication of center points was chosen in order to improve the accuracy of the experiments in small response space design. Sixteen conditions composed of six axial points and a duplication of the center points are listed in Table 4.2. The yield of the desired product heptadecane as the dependent response variable was the focus of interest and will be thoroughly discussed, while the other two response variables, i.e., the conversion of reactant and the selectivity of heptadecane product, will be also addressed in the optimization of MeS decarboxylation.

The second-degree polynomials [equation (4.2)], which include all interaction terms, were used for the predicted responses,

$$Y_i = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^{n-2} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \dots\dots\dots$$

(4.2)

Where Y_i is the predicted value, X_i and X_j are the coded values of the factors (temperature, sRatio and reaction time), β_0 is a constant coefficient, β_i is the linear coefficients, β_{ij} is the interaction coefficient, and β_{ii} is the quadratic coefficient.

Table 4.2 Experimental design and corresponding experimental results.

The 2^3 full factorial design was composed with six axial points and two replicates in the central point matrix for three independent variables, i.e., temperature, sRatio and reaction time.

| No. | Variables and coded levels | | | | | | Experimental results | | |
|-----|------------------------------|-------|--------------------------|-------|---------------------------------|-------|----------------------------|------------------------------|----------------------------|
| | Temperature (x_1 , °C) | | sRatio (x_2 , m/m) | | Reaction time (x_3 , min) | | Yield | Conversion | Selectivity |
| | Levels | Coded | Levels | Coded | Levels | Coded | (Y_{hep} , %mol) | (C_{react} , %mol) | (S_{hep} , %mol) |
| 1 | 300 | -1 | 4:1 | -1 | 90 | -1 | 24.02 | 30.52 | 81.83 |
| 2 | 340 | 1 | 4:1 | -1 | 90 | -1 | 50.02 | 61.02 | 85.24 |
| 3 | 300 | -1 | 3:2 | 1 | 90 | -1 | 19.80 | 40.24 | 50.55 |
| 4 | 340 | 1 | 3:2 | 1 | 90 | -1 | 51.82 | 67.10 | 77.93 |
| 5 | 300 | -1 | 4:1 | -1 | 210 | 1 | 44.32 | 47.86 | 92.61 |
| 6 | 340 | 1 | 4:1 | -1 | 210 | 1 | 73.34 | 72.92 | 100.00 |
| 7 | 300 | -1 | 3:2 | 1 | 210 | 1 | 26.54 | 49.29 | 49.89 |
| 8 | 340 | 1 | 3:2 | 1 | 210 | 1 | 63.88 | 78.48 | 83.29 |
| 9 | 286 | -1.68 | 7:3 | 0 | 150 | 0 | 5.67 | 18.67 | 47.15 |
| 10 | 355 | 1.68 | 7:3 | 0 | 150 | 0 | 92.39 | 99.96 | 92.65 |
| 11 | 320 | 0 | 87:13 | -1.68 | 150 | 0 | 73.10 | 78.98 | 92.55 |
| 12 | 320 | 0 | 53:47 | 1.68 | 150 | 0 | 21.47 | 39.53 | 63.90 |
| 13 | 320 | 0 | 7:3 | 0 | 49 | -1.68 | 21.61 | 27.23 | 78.84 |
| 14 | 320 | 0 | 7:3 | 0 | 251 | 1.68 | 39.64 | 47.92 | 80.59 |
| 15 | 320 | 0 | 7:3 | 0 | 150 | 0 | 28.01 | 42.27 | 75.05 |
| 16 | 320 | 0 | 7:3 | 0 | 150 | 0 | 28.15 | 34.99 | 84.95 |

4.3 Results and discussion

The yield and the selectivity of product heptadecane, and the conversion of reactant MeS depend on the reaction conditions as shown in Table 4.2. Preliminary observations showed that increased reaction temperature and time resulted in high conversion rate of reactant and high yield of products. The higher the reaction temperature is, the higher the selectivity. It is also noticed that high solvent to reactant ratio improved the reaction conversion, product yield and selectivity. This observation was in agreement with the findings from preliminary experiments (see Chapter 3). The highest yield of 92 %mol with a conversion rate of 100%mol was obtained under the condition of 355°C, 7:3 sRatio and 150 min reaction time. To find the optimum condition for maximizing the yield of heptadecane, a multiple-variable regression analysis was performed by fitting the response function with the experimental results. Generally, before a regression analysis, experimental data are tested for homogeneity and normal distribution of residuals in order to ensure the normality assumptions of the model to be satisfied. An ANOVA of the significant values for Student's distribution was performed (tables 4.3-4.5) to determine if the quadratic polynomials for the heptadecane yield, the MeS conversion and the selectivity of heptadecane were statistically significant. The coefficient determination, R^2 , was calculated to evaluate the performance of the regression equation.

4.3.1 Statistical analysis and the models fitting

The experimental data (table 4.2) was submitted for the analysis of variance by the Design Expert software (Stat-Easy, Minneapolis, Minn.). The fitted regression models were given as

$$Y_{hep} = 31.35 + 19.76X_1 - 8.5X_2 + 6.76X_3 + 6.48X_1^2 + 5.86X_2^2 \quad \dots\dots\dots (4.3)$$

$$C_{react} = 39.24 + 18.21X_1 - 3.20X_2 + 6.22X_3 + 7.74X_1^2 + 7.71X_2^2 \quad \dots\dots\dots (4.4)$$

$$S_{hep} = 77.83 + 10.84X_1 - 10.71X_2 + 6.26X_1X_2 \quad \dots\dots\dots (4.5)$$

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, and X_1 , X_2 and X_3 are the coded levels for temperature, sRatio and reaction time, respectively.

ANOVA table is used to summarize the tests for the significance of fitted regression model for product yield, for the individual model coefficients, and for the lack of fit. Goodness of fit was evaluated from R^2 and the lack of fit test in order to check the reliability of the model. Tables 4.3 through 4.5 reveal that quadratic models are statistically significant for the selected responses, i.e., the yield of heptadecane, conversion of reactant MeS and the selectivity of heptadecane. And the p -values were less than 0.001, which shows that all models are strongly significant at 99% of confidence level. From the summary outputs of the yield and selectivity models (tables 4.3 and 4.5), their p - values for the lack-of-fit test are 0.1132 and 0.7829 (insignificant) respectively, implying that these two quadratic models adequately describes the observations. However, summary output for conversion of MeS (table 4.4) shows that the lack of fit for the quadratic model is significant (p -value = 0.0236), indicating that a more complex model might be needed. It is noticed from the analysis of variance for the model that the test for the sRatio variable is not significant (p -value = 0.2846), which is probably the reason causing the significance of the lack of fit. Additional experimentation is probably required to obtain appropriate data for specifically estimating the variable sRatio effect. The R^2 value is high and close to one, which is desirable. It is suggested that for a good fit of a model, R^2 should be at least 0.80. For the model of heptadecane yield (table 4.3), the value of R^2 is 0.8781, implying that 87.81% of the variations could be explained by the fitted model.

Tables 4.3-4.5 also show that the main factors (i.e., temperature, sRatio and reaction time) are significant at a 95% confidence level. Table 4.3 indicates that temperature is the most effective variable, followed by sRatio, reaction time, the square of temperature and the square of sRatio for the model of heptadecane yield. And there are no interacting effects of temperature, sRatio and reaction time on the yield of heptadecane. The experimental results also well fit with the model on the MeS conversion (table 4.4). However, the reaction time is not a significant variable for the model of heptadecane selectivity, while there are interaction effects between temperature and sRatio (table 4.5).

Table 4.3 ANOVA for the fitted quadratic model of heptadecane yield (Y_{hep}) for the individual variables.

| Source | Sum of squares | Degree of freedom | Mean square | F value | p-value |
|----------------------------------|----------------|-------------------|-------------|---------|---------|
| Model | 7963.69 | 5 | 1592.74 | 20.17 | <0.0001 |
| X₁ (Temp.) | 1606.09 | 1 | 53333.04 | 67.54 | <0.0001 |
| X₂ (sRatio) | 986.33 | 1 | 986.33 | 12.49 | 0.0033 |
| X₃ (Time) | 623.98 | 1 | 623.98 | 7.90 | 0.0139 |
| X₁² | 611.41 | 1 | 611.41 | 7.74 | 0.0147 |
| X₂² | 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 | | | |

$$R^2=0.8781$$

Table 4.4 ANOVA for the fitted quadratic model of the reactant MeS conversion (C_{react}) for the individual variables.

| Source | Sum of squares | Degree of freedom | Mean square | F value | p-value |
|----------------------------------|----------------|-------------------|-------------|---------|---------|
| Model | 6791.48 | 5 | 1358.30 | 16.13 | <0.0001 |
| X₁ (Temp.) | 4530.55 | 1 | 4530.55 | 53.80 | <0.0001 |
| X₂ (sRatio) | 140.23 | 1 | 140.23 | 1.67 | 0.2846 |
| X₃ (Time) | 527.62 | 1 | 527.62 | 6.27 | 0.0253 |
| X₁² | 872.46 | 1 | 872.46 | 10.36 | 0.0062 |
| X₂² | 864.51 | 1 | 864.51 | 10.27 | 0.0064 |
| Residual | 1178.95 | 14 | 84.21 | | |
| Lack-of-fit | 1090.63 | 9 | 121.18 | 6.86 | 0.0474 |
| Pure error | 88.32 | 5 | 17.66 | | |
| Total | 7970.43 | 19 | | | |

$$R^2=0.8521$$

Table 4.5 ANOVA for the fitted quadratic model of heptadecane selectivity (S_{hep}) for the individual variables.

| Source | Sum of squares | Degree of freedom | Mean square | F value | p-value |
|-----------------------------------|----------------|-------------------|-------------|---------|---------|
| Model | 3483.51 | 3 | 1161.17 | 22.88 | <0.0001 |
| X₁ (Temp.) | 1606.09 | 1 | 1606.09 | 31.65 | <0.0001 |
| X₂ (sRatio) | 1565.18 | 1 | 1565.18 | 30.84 | 0.0033 |
| X₁X₂ | 312.25 | 1 | 312.25 | 6.15 | 0.0246 |
| Residual | 1105.47 | 16 | 50.75 | | |
| Lack-of-fit | 937.21 | 11 | 41.74 | 0.59 | 0.7829 |
| Pure error | 168.26 | 5 | 70.59 | | |
| Total | 4295.55 | 19 | | | |

$$R^2=0.8110$$

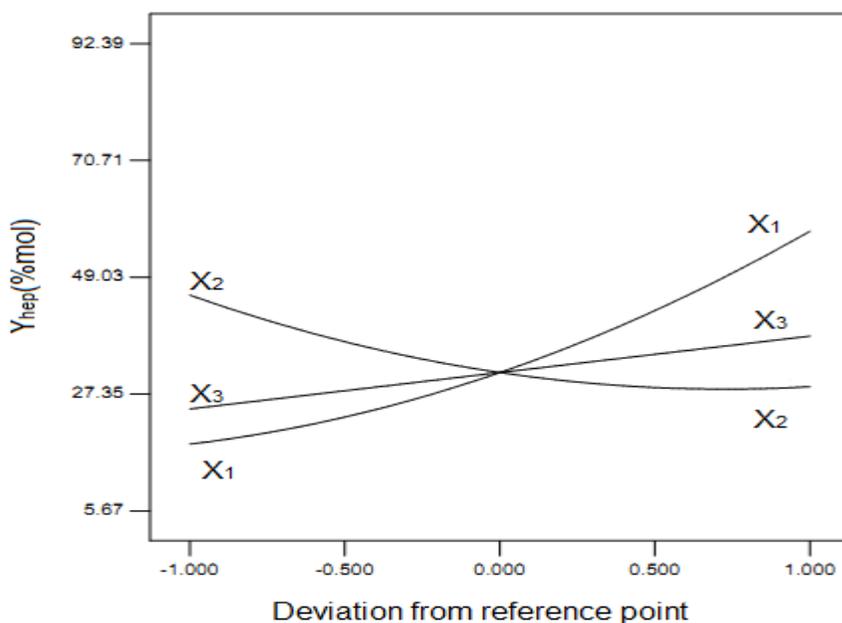


Figure 4.1 Perturbation plot of heptadecane yield showing the effects of temperature (X_1), sRatio (X_2) and reaction time (X_3) deviation from the reference point ($X_1=X_2=X_3=0$).

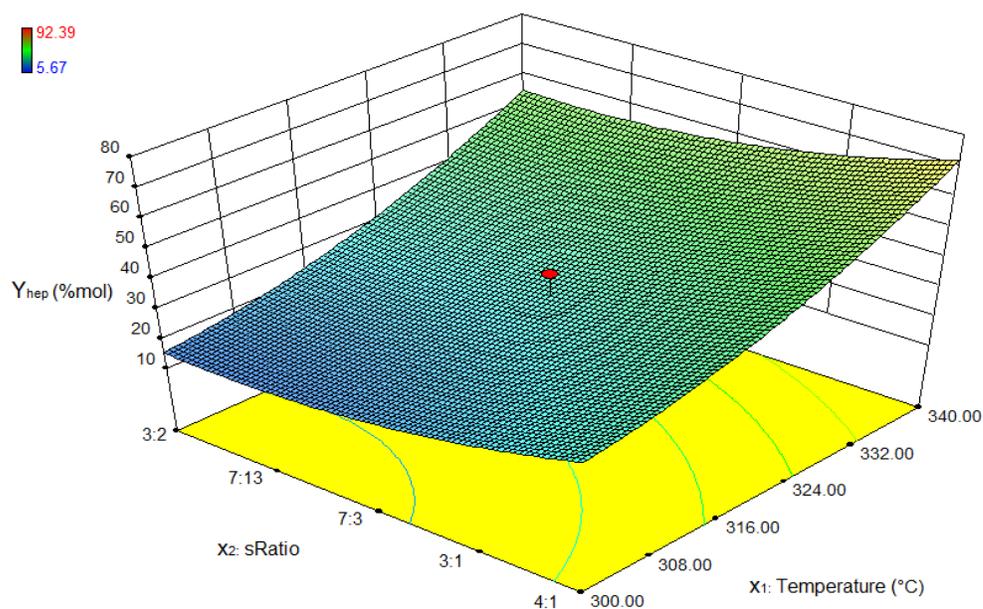
A Perturbation plot was used to assess the effect of each factor graphically. Figure 4.1 shows how the yield of heptadecane changes as each factor changes from the chosen reference point, with all other factors being held constant at the reference values. It can be seen that

each of the three variables used in the present study has its individual effect on the response variables. We can see that reaction time (X_3) has a relatively small effect as it changes not much from the reference point, while temperature (X_1) and sRatio (X_2) have more effect on the yield of heptadecane, although their effects are opposite.

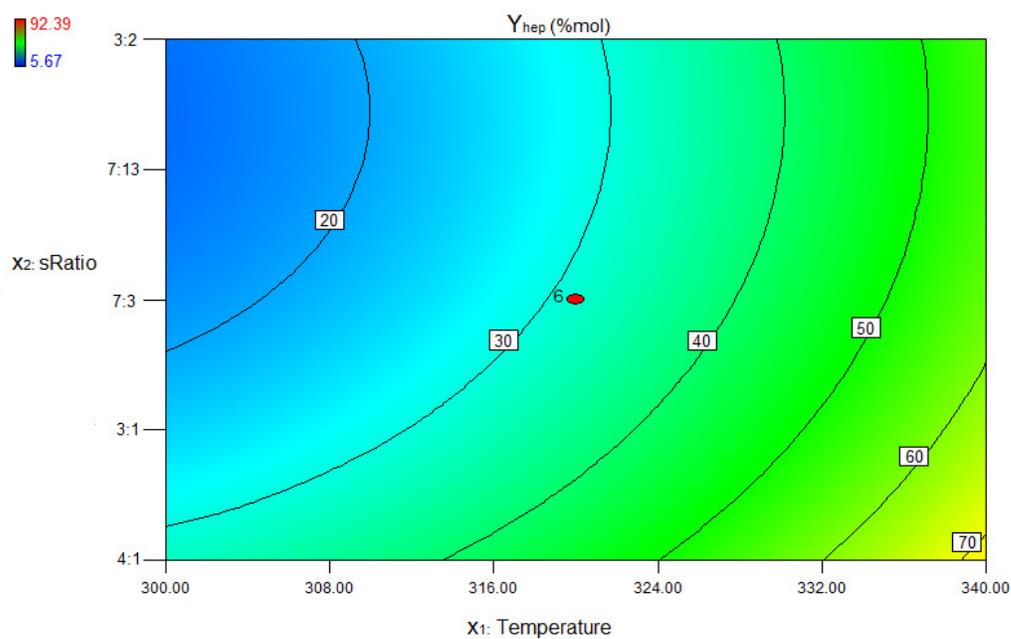
4.3.2 Optimization for the yield of heptadecane from decarboxylation of methyl stearate

A numerical optimization technique based on a desirability function was carried out to determine the workable optimum conditions for the process of MeS decarboxylation. This method can optimize any combination of one or more responses. Here three response variables: heptadecane yield, selectivity and the conversion of reactant MeS, will be separately optimized.

Response surface [Figure 4.2(A)] was plotted using Design Expert 8.0.1 software to study the effects of parameters and their interactions on the yield of heptadecane. This response surface is a three-dimensional plot of two factors (i.e., temperature and sRatio) while the reaction time was kept constant at 150 min. Figure 4.2(B) depicts a projected two-dimensional contour plot of the response surface in Figure 4.2(A). It is found that temperature and solvent to reactant ratio have significant effects on the response surface. The highest value of temperature (coded as +1) and the lowest value of sRatio (coded as +1) under the specified reaction time (coded as 0) tend to enhance the conversion towards the product heptadecane. It is noticed that increased temperature leads to increased heptadecane yield. It is possibly that the response values have a trend of slow growth and the response surface finally appears a saddle graph at a higher temperature (above the operating temperatures used in current experiments). However, due to the operating temperature limit of the reactor, we could not increase reaction temperature to any higher value. It is inappropriate to use the highest point as the optimal condition because too high of a ratio of solvent to reactant is not recommended in the practical production process.



(A) 3D plot of response surface



(B) 2D contour plot of response surface

Figure 4.2 Plots of experimental results of response surface method on the yield of heptadecane with respect to the reaction conditions. Reaction time fixed at 150 min and coded as level 0.

In searching for the optimum reaction condition, proper consideration should be given to obtain the reasonable outcomes within the range of experimental operation. Therefore, it was decided to set the maximal goal for the yield of heptadecane at 85% or higher. The optimum conditions should also be in the experimental design ranges of reaction temperature, sRatio and reaction time.

With these set conditions set, the experimental data were processed using the Design Expert software to perform the numerical optimization and generate solutions for the optimized operation conditions (table 4.6). It was found that high temperature (above 350°C) is required to obtain an 85.00% or better yield of heptadecane. The results suggested the optimum conditions for maximizing heptadecane yield as approx. 350°C, 2:3 sRatio, and 180~210 min reaction time. It should be noted that the desirability value of all solutions showed satisfactory values. The values are over the range from zero to one and they should only be assessed based on the upper and lower limits that are chosen for the responses and variables. In this case, upper and lower limits of all variables were chosen according to the practical ranges of study while the yield of heptadecane was set to be at maximum of 85.00%.

Table 4.6 Selected numerical optimization solutions for heptadecane yield.

| No. | Predicted Optimum Reaction Parameters | | | Predicted Y _{hep} (% mol) | Desirability |
|-----|---------------------------------------|-----------------|------------------------|---------------------------------------|--------------|
| | Temperature (°C) | sRatio (m/m) | Reaction time (min) | | |
| 1 | 354.62 | 62:38 | 187.19 | 85.00% | 1.00 |
| 2 | 353.77 | 61:39 | 192.07 | 85.00% | 1.00 |
| 3 | 352.38 | 3:2 | 218.35 | 85.00% | 1.00 |

As seen in fig. 4.3 that apparently, there was not an exact condition peak under the operation conditions for MeS decarboxylation. What we could suggest is to use these solutions as references according and to determine optimal conditions based on the practical production process. The suitability of the model equation for predicting the optimum response values was tested using the selected optimal conditions. Additional three sets of independent experiments were conducted to test the model using the following conditions: temperature 355°C, ratio of solvent to reactant 62:38, and reaction time 187 min, as the optimum

operation conditions. Under the selected operation conditions, the yield of heptadecane was 82.38 ± 4.62 %mol, which was close to the predicted yield of 85.00 %mol by the model. The model fitted the experimental data well described the region studied.

Table 5.6 Experimental values according to optimized operation conditions.

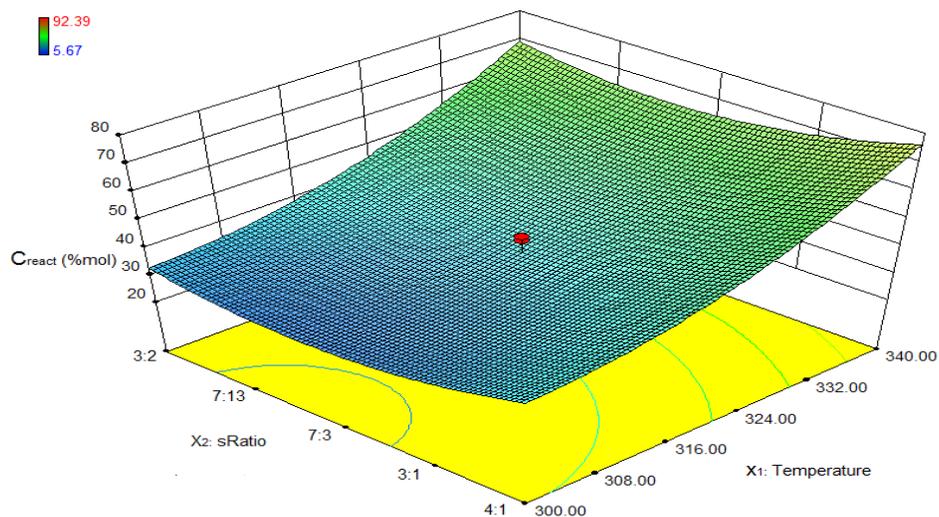
| Independent trials | Experimental values | | |
|--------------------|--------------------------|----------------------------|--------------------------|
| | Y_{hep} (% mol) | C_{react} (% mol) | S_{hep} (% mol) |
| Trial 1 | 80.11 | 92.91 | 86.22 |
| Trial 2 | 85.06 | 96.49 | 88.15 |
| Trial 3 | 81.97 | 93.86 | 87.33 |

4.3.3 Optimization for the MeS conversion and the heptadecane selectivity in decarboxylation of methyl stearate

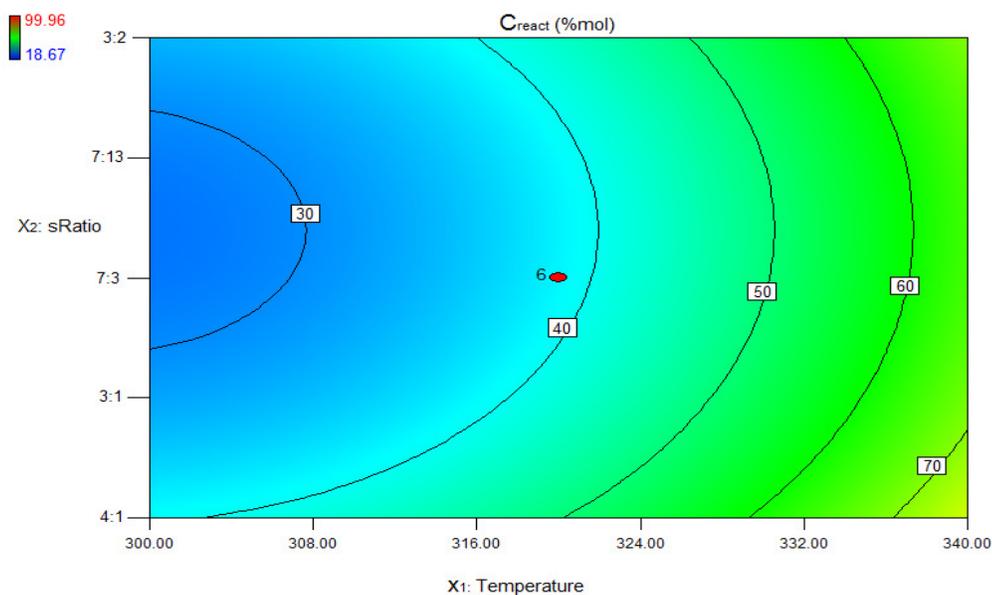
Two other optimizations for the conversion of MeS and the heptadecane selectivity based on the results shown in Table 4.2 were also carried out using regression models (Eq. 4.4 and 4.5). The results are shown in the three-dimensional plots [fig. 4.3(A) and 4.4(A)] and the detailed two-dimensional contour plots [fig. 4.3(B) and 4.4(B)]. These response surfaces [fig. 4.3(A) and 4.4(A)] show mostly the same common features as the response surface in fig 4.2(A). For example, temperature and sRatio have significant effects on the response surfaces of the MeS conversion and heptadecane selectivity. Similar to the optimization of heptadecane yield, a numerical optimization method was used to determine the optimum conditions for MeS conversion of and heptadecane selectivity. The optimum condition for the MeS conversion was 354°C, sRatio 61:39, and reaction time 166 min. The MeS can be completely converted to products under these reaction conditions. A predicted selectivity of 90.00% can be achieved under the following condition: 353°C, sRatio 65:35, and reaction time 205 min.

It is noticed that the three quadratic models showed different optimal conditions. However, when the optimal condition for the MeS conversion was adopted for the model of heptadecane yield in Eq. (4.3) and the heptadecane selectivity in Eq. (4.5), their predicted

responses were 84.41 %mol and 85.42 %mol, respectively. Likewise, the optimal condition for the heptadecane selectivity was applied the other quadratic models, the predicted heptadecane yield and selectivity were 86.32 %mol and 97.46 %mol. Therefore, there were no significant differences in these optimal conditions.

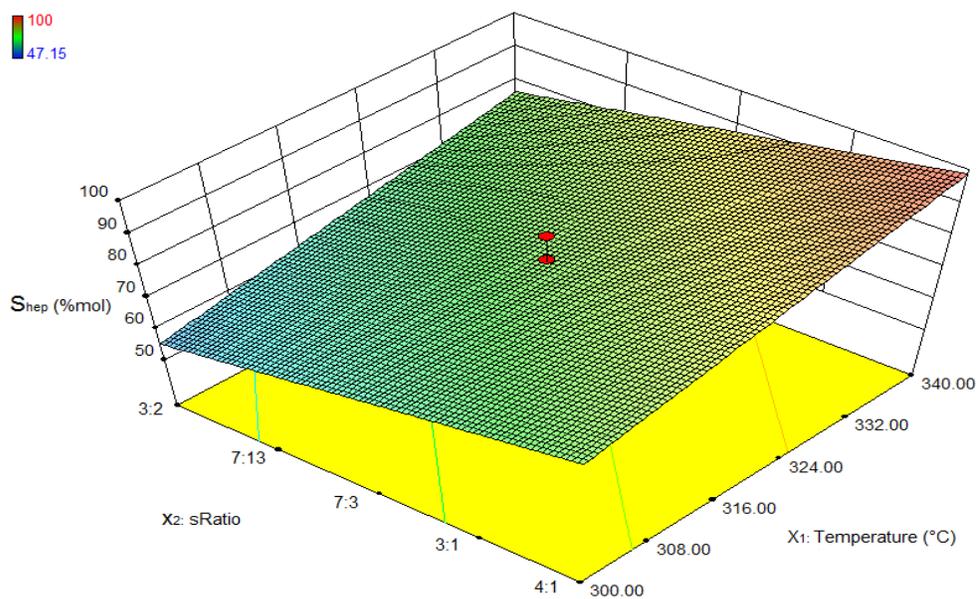


(A) 3D plot of response surface

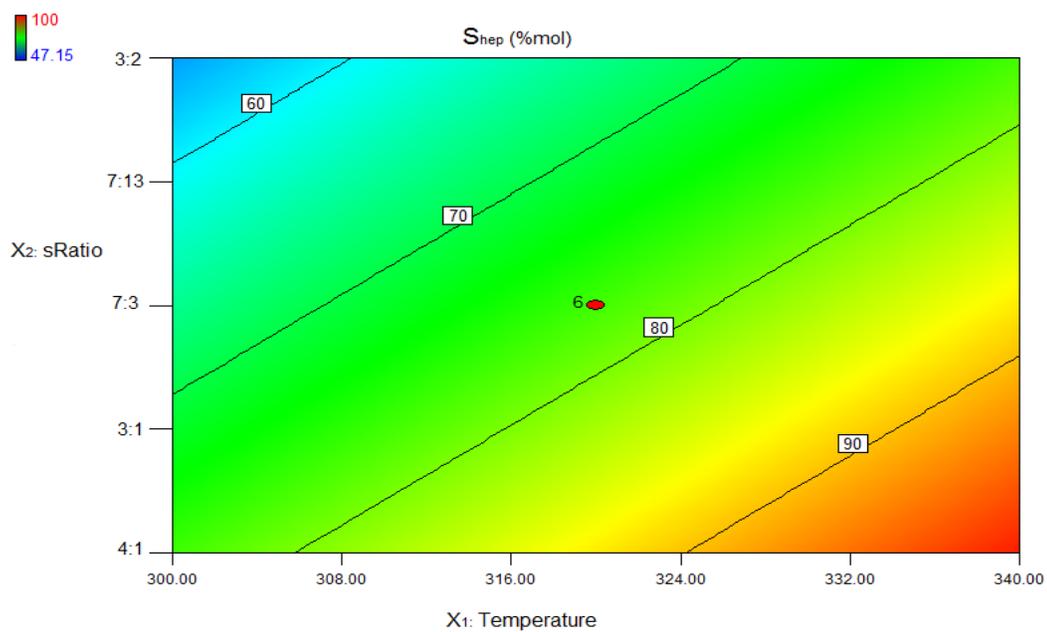


(B) 2D contour plot of response surface

Figure 4.3 Plots of experimental results of response surface method on the conversion of methyl stearate with respect to the reaction conditions. Reaction time fixed at 150 min and coded as level 0.



(A) 3D plot of response surface



(B) 2D contour plot of response surface

Figure 4.4 Plots of experimental results of response surface method on the selectivity of heptadecane with respect to the reaction conditions. Reaction time fixed at 150 min and coded as level 0.

4.3.4 Decarboxylation of mixed methyl esters (or biodiesel) of mustard oil

Biodiesel, a renewable diesel fuel, consisting of fatty acid methyl esters (FAMES), has been paid much attention in recent years due to its environmental benefits and the fact that it is made from renewable resources, such as vegetable oils and animal fats. The common method for biodiesel production is transesterification of triglycerides with methanol, which is efficient and well understood. However, there is growing concern about the compatibility of these fuels with conventional petroleum-derived diesel due to the oxidative and thermal instability. Another concern is the lower energy density of biodiesel due to its higher oxygen content (usually 10-12%) than petroleum diesel. Lowering oxygen content in the fuel would improve the stability of biodiesel and therefore increase its utilization potential. The objectives of this part of the research were to evaluate the decarboxylation of mixed methyl esters or biodiesel for the renewable diesel production and to optimization of the decarboxylation process conditions.

The experiments of biodiesel decarboxylation were also conducted in the 300 mL high pressure batch reactor under the optimized conditions (temperature 355°C, ratio of solvent to reactant 38:62, and reaction time 189 min) in the absence of hydrogen supply. The same experiment procedure was used as previously presented in Section 4.2.1. Samples were analyzed by Anatek Labs (Moscow, Idaho) and using gas chromatograph-mass spectrometer (GC-MS) to identify the product composition.

Table 4.7 FAME profile of biodiesel and the major components after decarboxylation.

| Biodiesel feedstock | | Decarboxylated biodiesel | |
|-----------------------|--------|--|-------|
| Methyl esters | % wt | Formula | % wt |
| Myristate C14:0 | 1.01 | Total paraffin | 29.13 |
| Palmitoleate C16:1 | 1.92 | C ₇ H ₁₆ | 1.61 |
| Palmitate C16:0 | 23.50 | C ₁₀ H ₂₂ | 1.58 |
| Linoleate C18:2 | 62.17 | C ₁₅ H ₃₂ | 3.81 |
| Stearate C18:0 | 6.74 | C ₁₇ H ₃₆ | 22.13 |
| Arachidate C20:0 | 1.40 | Esters or acids | |
| Eicosonate C20:1 | 2.27 | C ₁₇ H ₃₄ O ₂ | 10.00 |
| Behenate C22:0 | 1.04 | C ₁₉ H ₃₈ O ₂ | 30.56 |
| <i>Sum =</i> | 100.50 | C ₁₈ H ₃₆ O ₂ | 8.24 |
| | | Aromatics (C ₁₇ H ₂₈ , C ₁₅ H ₂₄ , etc.) | 16.36 |
| | | Others (C ₁₉ H ₃₀ O ₂ , C ₁₃ H ₂₀ O ₂ , etc.) | 5.69 |
| | | <i>Sum =</i> | 99.98 |
| Oxygen content | 11.08% | Oxygen content | 5.09 |

Table 4.7 shows the mass based FAME profile of biodiesel which has 11.08% oxygen content. After reaction, decarboxylated biodiesel has 29.13% of paraffin content and 5.69% oxygen content. From our earlier work on the deoxygenation of saturated fatty acids or esters, the dominant reaction pathway was decarboxylation. However, the biodiesel is a complex mixture of both saturated and unsaturated methyl esters. Multiple kinds of products were detected, including alkane, aromatic products, methyl esters and fatty acids, etc., as shown in Table 4.7. The decarboxylation of biodiesel was found to be more complicated than only using saturated model compound, MeS, as the feedstock. Many reactions have simultaneously happened, such as decarboxylation, decarbonylation, cyclization, hydrolysis, cracking, hydrogenation and some gas-phase reactions (Snare et al., 2006; 2008). It was reported that deoxygenation of unsaturated feedstocks products is difficult under hydrogen deficit conditions (Snare et al., 2008). Alkane products, mainly pentadecane (C₁₅H₃₂) and heptadecane (C₁₇H₃₆), 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 C₁₇H₂₈ and C₁₅H₂₄, were also found in the deoxygenated products (Appendix B). Despite the inert atmosphere, hydrogenation still happened as no unsaturated methyl esters were found among the products, which may not be a negative thing. The source of hydrogen for the hydrogenation process could be from a

simultaneous, hydrogen re-distribution reaction (Snare et al., 2008). Short chain hydrocarbons (such as C_7H_{16} and $C_{10}H_{22}$) were produced via cracking reactions.

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. Under optimized reaction conditions, the yield and selectivity of decarboxylation product, i.e., heptadecane, both reached 85% when methyl stearate as the reactant. However, unsaturated carbon double bonds have strong effects on the decarboxylation reaction, which makes decarboxylation more complicated. Many side-reactions, such as cyclization, may happen, making products less unpredictable.

4.4 Conclusion

In this study, a central composite response surface design was performed to optimize the operation conditions including temperature, sRatio and reaction time for decarboxylation of methyl stearate. The experimental results showed the effects of these process parameters. Temperature is the most influential variable, followed by the sRatio, and reaction time. A maximum of 82.38 ± 4.62 %mol heptadecane yield could be achieved at the optimum temperature, solvent to reaction ratio and reaction time of 355°C , 62:38, and 187 min, respectively. Meanwhile, the complete conversion of MeS was predicted at the optimum condition of temperature 354°C , ratio of solvent to reactant 61:39, and reaction time 166 min, respectively. The predicted selectivity is 90.00% at the following conditions: temperature 353°C , ratio of solvent to reactant 65:35, and reaction time 205 min, respectively.

Biodiesel as the feedstock was also tested for decarboxylation. The experimental results showed that it is difficult to directly convert the mixture of unsaturated and saturate methyl esters to renewable diesel without other undesired reactions such as cracking of the unsaturated feedstock. The unsaturated carbon double bonds strongly affected the reactions and decarboxylation was not the dominant reaction anymore. Many side reactions simultaneously happened and lead to low efficiency of deoxygenation of mixture methyl esters.

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Chapter 5 Summary and Recommendations

5.1 Summary

The conversion of vegetable oils and animal fats to biofuels is currently one of the strategies to obtain transportation fuel from renewable sources. Biodiesel from vegetable oils and animal fats contains high the oxygen content. Lowering oxygen content of the fuel would improve the fuels properties, such as stability, energy density, etc. This thesis presents an important renewable diesel production technology of decarboxylation which can lower oxygen content by catalytic removal of carboxyl groups of the esters / fatty acids to make alkane-like compounds. Saturated compounds, stearic acid and methyl stearate were chosen as model compounds. This study investigated the process of decarboxylation without hydrogen supply for potentially producing renewable diesel from fatty acids and methyl esters. The process conditions and their optimization, including catalyst selection, and reaction conditions including temperature, pressure, solvent to reactant ratio, catalyst content and different feedstocks, were systematically studied.

Catalysts play a crucial role in renewable diesel synthesis. Therefore, catalyst screening for stearic acid deoxygenation was first conducted. Using a 300 mL PARR 4560 pressure reactor, several catalysts including 5%wt palladium deposited on activated charcoal (Pd/C), 5%wt platinum on activated carbon (Pt/C), 5%wt palladium on alumina (Pd/Al₂O₃), 65%wt nickel on silica/alumina (Ni/SiO₂/Al₂O₃), and Raney nickel, were tested. The experiment results showed that that Pt/C and Pd/C performed best in high conversion rates (83.5%mol and 100%mol, respectively), product yields (78.2%mol and 88.6%mol, respectively) and selectivities (93.65%mol and 88.6%mol, respectively). Further comparison between Pt/C and Pd/C indicated that Pd/C performs better than Pt/C because Pt/C took more than three hours to complete the conversion, while, using Pd/C as the catalyst, the reaction was almost complete in one hour. Then all the further decarboxylation studies used Pd/C catalyst.

The experiments of the decarboxylation of SA and MeS were set up to determine the effects of reaction temperature, reaction time, pressure, sRatio, catalyst dosage, and stirring speed.

Three reaction temperatures, i.e., 265°C, 285°C, and 300°C, were investigated in decarboxylation of SA using Pd/C as the catalyst. Temperature strongly affects the SA conversion, which is further confirmed by the response surface experiment analysis. The solvent application also affected the reaction. The solvent to reactant ratio ranged from 9:1 to 1:1 and results showed that the lower the solvent is applied, the longer the reaction time is for the reaction to complete. Under the reaction condition of 300°C, 1 MPa, and sRatio 9:1, SA conversion rate increases with increased catalyst dosage up to 8 %wt, then the effect becomes to level off when the catalyst dosage was over 8 %wt. There were no significant effects of pressure and mixing intensity in the process of decarboxylation of SA, therefore, they were kept as constants.

Response surface methodology (RSM) was employed to determine the suitable conditions for renewable diesel production. Based on the preliminary results, three parameters, which affected the decarboxylation process significantly, were identified as temperature, reaction time and sRatio. Based on central composite designs of RSM, sixteen operations were performed on the three parameters. The yield and selectivity of product heptadecane and the conversion of reactant MeS were set as the response variables. The optimal condition for the process of MeS decarboxylation was 355°C, sRatio 62:38, and reaction time 187 min, respectively, with a predicted heptadecane yield of 85.00%.

The decarboxylation of biodiesel was also conducted at the optimum conditions as discussed above. Experimental results showed that the oxygen content of biodiesel changed from 11.2% to 5.09%, a decarboxylation efficiency of approx. 50%. The degree of oxygen removal with decarboxylated biodiesel was lower than that with saturated model compounds stearic acid and methyl stearate. The results indicated that unsaturated carbon double bonds affected the reactions dramatically.

5.2 Recommendations

In this research, saturated fatty acids and methyl esters have been successfully converted to diesel-like hydrocarbons (i.e., renewable diesel) by directly decarboxylation reaction on

Pd/C catalyst. However, the ultimate goal of this research is to deoxygenate biodiesel. However, the results for deoxygenation of biodiesel were not satisfactory. At this point, the conditions for successful decarboxylation of unsaturated esters are not clearly known.

In order to achieve the goal, I suggest further research on:

- Investigation of the process of decarboxylation of unsaturated fatty acids or methyl esters
- Study of continuous decarboxylation system, and
- Further scale-up would be of interest before applying the process to industrial production for hydrocarbons from plant oils and animal fats.

Appendices

Appendix A

Methodology of Heterogeneous Catalytic Decarboxylation of Fatty
Acids and Esters

A.1. Experimental Procedures

A.1.1 Catalyst preparation

Generally, before each experiment, the heterogeneous catalysts need to be pre-treated to ensure the catalytic activity.

- 1) Weigh the empty reactor vessel.
- 2) Using a piece of weighing paper, weigh a certain amount of catalyst and put it into the reactor vessel.
- 3) Cover the reactor cap by uniformly tightening screws.
- 4) Place the reactor on its stand, connecting interfaces to gas sources, cooling water, thermometer, and pressure gauge.
- 5) Turn on the computer and initiate the computer-based control and data acquisition system. Open the reactor control software “CALGRAFIX” to set temperature, pressure, and stirring speed.
- 6) Flush reactor with N₂ for 1 min to remove the oxygen in the headspace.
- 7) Adjust the pressure to 500 psig with hydrogen.
- 8) Heat reactor to 200 °C and maintain for one hour to activate the catalyst.
- 9) Weigh approx. 100 g solvent dodecane in a 250 ml beaker on a digital scale.
- 10) Put the beaker with dodecane on a hot plate to warm the solvent to approx. 45°C to reduce viscosity.
- 11) Weigh a pre-determined amount of stearic acid (SA) or methyl stearate (MeS) in a 50 mL beaker. Typically, 5 ~ 75 g SA or MeS was used according to experimental plan.

A.1.2 Preparing the decarboxylation experiments

- 1) After the one-hour catalyst activation, cool the reactor to room temperature, then release the pressure.
- 2) Introduce the solvent dodecane into the reactor through the sampling port on the reactor using a syringe.

- 3) Bubbling hydrogen through solvent and maintain 5 min with a hydrogen pressure of 200 psig to avoid any air trapped in the solvent.
- 4) Release hydrogen and flush the reactor with N₂ for 1 minute.
- 5) Disassemble the reactor and weigh the reactor vessel with solvent and catalyst on a digital scale.
- 6) By subtracting the weights of the empty reactor vessel and the catalyst from this total, the solvent mass is known. Add additional dodecane if needed to bring its total to the desired quantity.
- 7) Add a pre-determined amount of reactant into the reactor.
- 8) Reassemble the reactor by closing the reactor by uniformly tightening screws, placing the reactor on its stand, connecting interfaces to gas sources, cooling water, and computer.
- 9) Flush the reactor with nitrogen gas for one minute.
- 10) Heat the reactor to 300°C. When the temperature reaches 300°C, adjust the reactor pressure to the desired levels with N₂, and initiate stirring.

Experiments typically lasted for 3 hours. Start the time from the moment when the temperature reaches 300°C and take samples at 0, 30, 60, 120, and 180 minutes.

A.2. Analysis of Samples

A.2.1 Apparatus

Agilent 6890N Gas Chromatograph (GC) was used for analyzing hydrocarbons and residual stearic acid or methyl stearate. 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 dimension of 60 m x 0.32 mm x 0.5 μm). The column was installed according to the requirements of the manufacturer and was conditioned before analyzing the samples. After conditioning, analytical conditions summarized in Table A.1 was set up in the Agilent ChemStation.

Table A.1. GC operating conditions

| | |
|----------------------|---|
| Inlet temperature | 265 °C |
| Injection volume | 1 µL |
| Split ratio | 60 : 1 |
| Carrier gas | Helium (flow rate 170 mL/min) |
| Head pressure | 172.4 kPa for 60min and increased at 34.48 kPa/min to 221 kPa |
| Over temperature | Start at 110°C to increase at 1°C/min to 126°C, 30°C/min to 185°C, 1°C/min to 200°C, 5°C/min to 300°C and hold for 2 min. Total operating time is 55 min. |
| Detector temperature | 290°C |
| Detector gas | Hydrogen at 40 mL/min; Air at 450 mL/min |
| Make up gas | Nitrogen |

A.2.2 Sample preparation and analysis

In order to analyze MeS using the same non-polar DB-5 column, samples were first silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA). Eicosane (C₂₀H₄₂) was used as an internal standard for calibrating and quantifying the sample analysis. Typically, a 100 µL (approx. 80mg~100 mg) of liquid-phase sample was taken to a 10 mL vial and 100 %wt excess of BSTFA was added to make sure the sample was completely silylated. Thereafter, the mixture was kept in an oven at 60°C for one hour. Then the sample was injected to GC under the aforementioned analytical conditions.

A.2.3 Construction of calibration curves

Before the preparation of calibration curves, a known amount of each chemical standards, including stearic acid (SA) silylated with 100 %wt excess of BSTFA, n-heptadecane, octadecane, eicosane diluted by dodecane, was analyzed by GC to determine the retention time. Then the following three steps were used for constructing the calibration curves.

1) Estimated concentration range

The actual reactant solutions contain approximately 30-50 %wt MeS and 50-70%wt solvent. Assume the initial concentration of MeS was 0.4 g/mL and the sample to be diluted by 100 times before analyzing. Then the concentration of MeS for GC was 0.004 g/mL. In calibration, the maximum concentration of MeS was prepared at 0.005 g/mL.

2) Preparation of stock solutions

The standard stock solutions for calibration were prepared using reagent grade compounds listed in Table A.2. The weighed compound (to the nearest 1 mg) was added into a volumetric flask and diluted to the mark line with solvent dodecane. The standard stock solutions for calibration were stored in a refrigerator when not in use.

Table A.2. Compounds for standard stock solutions.

| No. | Compounds | Sample size (mg) | Total solution volume (mL) |
|-----|---------------------------------|------------------|----------------------------|
| 1 | MeS | 500 | 10 |
| 2 | C ₁₆ H ₃₄ | 500 | 10 |
| 3 | C ₁₇ H ₃₆ | 500 | 10 |
| 4 | C ₁₈ H ₃₈ | 500 | 10 |
| 5 | C ₂₀ H ₄₂ | 1,000 | 1,000 |

3) Standard solution for calibration

Five standard solutions as shown in Table A.3 were prepared from the stock solutions. After transferring specific volumes of the standard stock solutions to 10 mL septa vials with microliter syringes, 100 μ L of BSTFA was added. Then the vials were covered and shaken for 5 min. The vials were kept in an oven at 60 °C for one hour to make MeS completely silylated. Dodecane was added to the vials to the marked line of the volumetric flask. The solution was shaken for 5 min to ensure complete mixing of the compounds.

Table A.3. Preparation of the standard solutions

| Standard solution | Stock solutions | | | | | BSTFA (μL) |
|-------------------|--|----------|--------------------------------------|--------------------------------------|--------------------------------------|------------|
| | C ₂₀ H ₄₂ (Internal standard) (μL) | MeS (μL) | C ₁₆ H ₃₄ (μL) | C ₁₇ H ₃₆ (μL) | C ₁₈ H ₃₈ (μL) | |
| #1 | 100 | 1000 | 100 | 200 | 100 | 100 |
| #2 | 100 | 800 | 80 | 400 | 80 | 100 |
| #3 | 100 | 600 | 60 | 600 | 60 | 100 |
| #4 | 100 | 400 | 40 | 800 | 40 | 100 |
| #5 | 100 | 200 | 20 | 1000 | 20 | 100 |

4) Calibration curve

The standard solutions for calibration were analyzed by GC under the same analytical conditions for actual samples. For each standard solution, a chromatogram and a peak integration report were obtained. For each chemical compound, a calibration curve was obtained by plotting the area ratios (y-axis) versus the concentration ratios (x-axis). A calibration function was obtained through regression in the form of:

$$\frac{A_i}{A_s} = m * \left(\frac{C_i}{C_s}\right) + b$$

where:

$\frac{A_i}{A_s}$ = ratio of the area of tested compound (A_i) to the area of internal standard (A_s)

$\frac{C_i}{C_s}$ = ratio of the concentration of tested compound (C_i) to the concentration of

internal standard (C_s)

m = slope of the calibration equation, and

b = intercept of the calibration equation.

The correlation coefficient r^2 value for each compound can be calculated by the equation and the r^2 should be at least 0.99 or greater. For example, Figure A.1 shows the heptadecane (C₁₇H₃₆) calibration curve.

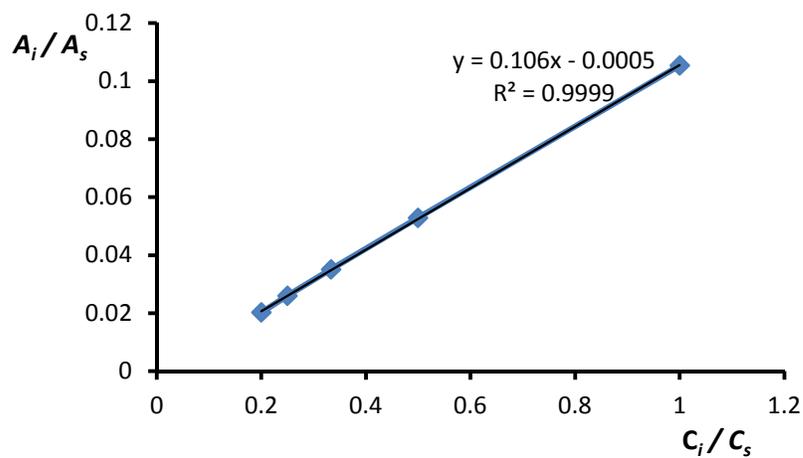


Figure A.1 Calibration curve for heptadecane ($C_{17}H_{36}$).

To analyze the samples with unknown heptadecane concentrations, the ratio of the heptadecane area to internal standard ($C_{20}H_{42}$) area was determined from the chromatogram. The corresponding ratio of heptadecane concentration to internal standard concentration was determined from the calibration function. The concentration of heptadecane in the unknown sample can be obtained by multiplying the known concentration of internal standard in the sample to the area ratio.

Appendix B

Selected GC-MS Analysis Results for Decarboxylation of mixed esters (or Biodiesel) of mustard oil

B.1 Raw data of reactant (biodiesel) GC-MS analysis results**(see next page)**

Library Search Compound Report

File : T:\DATA1\SEMIVOC\2013SVOC\SEP\0906\2701030.D Vial: 27
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 Quant Method : T:\DATA1\S...\BNA0906CC.M (RTE Integrator)
 Title : EPA 8270C/625 Calibration
 Library : T:\DATA1\NIST129K.L

 Peak Number 1 Tridecanoic acid, 12-methyl- Concentration Rank 11

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.43 | 1994.59 ppm | 2519860 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | Tridecanoic acid, 12-methyl-, me... | 242 | C15H30O2 | 005129-58-8 | 95 |
| 2 | Methyl tetradecanoate | 242 | C15H30O2 | 000124-10-7 | 87 |
| 3 | Methyl tetradecanoate | 242 | C15H30O2 | 000124-10-7 | 81 |
| 4 | Undecanoic acid, methyl ester | 200 | C12H24O2 | 001731-86-8 | 70 |
| 5 | Decanoic acid, methyl ester | 186 | C11H22O2 | 000110-42-9 | 70 |

 Peak Number 2 9-Hexadecenoic acid, methyl... Concentration Rank 7

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 12.16 | 3800.71 ppm | 4801620 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | 9-Hexadecenoic acid, methyl este... | 268 | C17H32O2 | 001120-25-8 | 99 |
| 2 | 7-Hexadecenoic acid, methyl este... | 268 | C17H32O2 | 056875-67-3 | 99 |
| 3 | 9-Hexadecenoic acid, methyl este... | 268 | C17H32O2 | 001120-25-8 | 98 |
| 4 | 9-Hexadecenoic acid, methyl este... | 268 | C17H32O2 | 001120-25-8 | 96 |
| 5 | 9-Octadecenoic acid (Z)-, methyl... | 296 | C19H36O2 | 000112-62-9 | 76 |

 Peak Number 3 Hexadecanoic acid, methyl e... Concentration Rank 2

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.25 | 46590.50 ppm | 58859900 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------|-----|----------|-------------|------|
| 1 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 98 |
| 2 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 98 |
| 3 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 94 |
| 4 | Pentadecanoic acid, 14-methyl-, | 270 | C17H34O2 | 005129-60-2 | 93 |
| 5 | Tridecanoic acid, methyl ester | 228 | C14H28O2 | 001731-88-0 | 93 |

 Peak Number 4 10,13-Octadecadienoic acid,... Concentration Rank 1

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.90 | 54730.00 ppm | 69142900 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | 10,13-Octadecadienoic acid, meth... | 294 | C19H34O2 | 056554-62-2 | 99 |
| 2 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 99 |
| 3 | 9,12-Octadecadienoic acid, methy... | 294 | C19H34O2 | 002566-97-4 | 99 |
| 4 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 99 |
| 5 | 9,15-Octadecadienoic acid, methy... | 294 | C19H34O2 | 017309-05-6 | 99 |

Peak Number 5 10,13-Octadecadienoic acid, ... Concentration Rank 3

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.90 | 28665.80 ppm | 36214800 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | 10,13-Octadecadienoic acid, meth... | 294 | C19H34O2 | 056554-62-2 | 99 |
| 2 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 99 |
| 3 | 9,12-Octadecadienoic acid, methy... | 294 | C19H34O2 | 002566-97-4 | 99 |
| 4 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 99 |
| 5 | 9,15-Octadecadienoic acid, methy... | 294 | C19H34O2 | 017309-05-6 | 99 |

Peak Number 6 9,12-Octadecadienoic acid (... Concentration Rank 5

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.97 | 15609.20 ppm | 19719800 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 99 |
| 2 | 9,12-Octadecadienoic acid, methy... | 294 | C19H34O2 | 002462-85-3 | 99 |
| 3 | 10,13-Octadecadienoic acid, meth... | 294 | C19H34O2 | 056554-62-2 | 98 |
| 4 | 8,11-Octadecadienoic acid, methy... | 294 | C19H34O2 | 056599-58-7 | 98 |
| 5 | 9,15-Octadecadienoic acid, methy... | 294 | C19H34O2 | 017309-05-6 | 98 |

Peak Number 7 9,12-Octadecadienoic acid, ... Concentration Rank 4

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.99 | 24202.90 ppm | 30575600 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | 9,12-Octadecadienoic acid, methy... | 294 | C19H34O2 | 002462-85-3 | 99 |
| 2 | 10,13-Octadecadienoic acid, meth... | 294 | C19H34O2 | 056554-62-2 | 98 |
| 3 | 9,12-Octadecadienoic acid (Z,Z)-... | 294 | C19H34O2 | 000112-63-0 | 98 |
| 4 | 9,17-Octadecadienal, (Z)- | 264 | C18H32O | 056554-35-9 | 98 |
| 5 | 9,15-Octadecadienoic acid, methy... | 294 | C19H34O2 | 017309-05-6 | 97 |

Peak Number 8 Octadecanoic acid, methyl e... Concentration Rank 6

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 13.04 | 13354.10 ppm | 16870900 | Phenanthrene-d10 | 11.89 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------|-----|----------|-------------|------|
| 1 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 98 |
| 2 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 97 |
| 3 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 96 |
| 4 | Heptadecanoic acid, 16-methyl-, | 298 | C19H38O2 | 005129-61-3 | 95 |
| 5 | Heptadecanoic acid, 14-methyl-, | 298 | C19H38O2 | 057274-45-0 | 94 |

Peak Number 9 11-Eicosanoic acid, methyl ... Concentration Rank 8

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.56 | 2942.44 ppm | 3604160 | Chrysene-d12 | 14.34 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|----------------------------------|-----|----------|-------------|------|
| 1 | 11-Eicosanoic acid, methyl ester | 324 | C21H40O2 | 003946-08-5 | 99 |
| 2 | Eicosanoic acid, methyl ester | 324 | C21H40O2 | 027070-40-2 | 64 |
| 3 | Cyclopropanoic acid, 2-hex | 282 | C18H34O2 | 010152-61-1 | 53 |
| 4 | 9-Octadecanoic acid (Z)-, methyl | 296 | C19H36O2 | 000112-62-9 | 47 |

5 Cyclododecanemethanol 198 C13H26O 001892-12-2 46

Peak Number 10 11-Eicosenoic acid, methyl ... Concentration Rank 12

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.57 | 1695.06 ppm | 2076260 | Chrysene-d12 | 14.34 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|------------|-------------|------|
| 1 | 11-Eicosenoic acid, methyl ester | 324 | C21H40O2 | 003946-08-5 | 99 |
| 2 | Elaidic acid, isopropyl ester | 324 | C21H40O2 | 022147-34-8 | 53 |
| 3 | 1,1'-Biphenyl, 4,4-bis(1-pyrroli... | 292 | C20H24N2 | 000000-00-0 | 35 |
| 4 | Dibenzimidazole[1,2-c | 292 | C15H8N4OS | 000000-00-0 | 32 |
| 5 | 2-(4-Fluorophenyl)-5-methoxy-2H- | 292 | C18H13FN2O | 000000-00-0 | 30 |

Peak Number 11 Eicosanoic acid, methyl ester Concentration Rank 10

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.62 | 2097.78 ppm | 2569550 | Chrysene-d12 | 14.34 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------|-----|----------|-------------|------|
| 1 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 98 |
| 2 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 98 |
| 3 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 98 |
| 4 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 97 |
| 5 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 97 |

Peak Number 12 Eicosanoic acid, methyl est... Concentration Rank 13

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|------------|--------|------------------|-------|
| 13.63 | 753.13 ppm | 922499 | Chrysene-d12 | 14.34 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------|-----|----------|-------------|------|
| 1 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 98 |
| 2 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 95 |
| 3 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 95 |
| 4 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 94 |
| 5 | Eicosanoic acid, methyl ester | 326 | C21H42O2 | 001120-28-1 | 93 |

Peak Number 13 Docosanoic acid, methyl ester Concentration Rank 9

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 14.23 | 2122.46 ppm | 2599770 | Chrysene-d12 | 14.34 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------|-----|----------|-------------|------|
| 1 | Docosanoic acid, methyl ester | 354 | C23H46O2 | 000929-77-1 | 99 |
| 2 | Docosanoic acid, methyl ester | 354 | C23H46O2 | 000929-77-1 | 99 |
| 3 | Docosanoic acid, methyl ester | 354 | C23H46O2 | 000929-77-1 | 98 |
| 4 | Docosanoic acid, methyl ester | 354 | C23H46O2 | 000929-77-1 | 97 |
| 5 | Docosanoic acid, methyl ester | 354 | C23H46O2 | 000929-77-1 | 96 |

Quantitation Report (Not Reviewed)

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 Sample : UI-1 Inst : SEMIVOC1
 Mass : Multiplier: 100.00

MS Integration Params: rteint.p

Quant Time: Sep 09 08:22:06 2013

Quant Results File: BNA0906CC.REG

Quant Method : T:\DATA1\SEMIVOC\BNA0906CC.M (RTE Integrator)
 Title : EPA 8270C/625 Calibration
 Last Update : Fri Sep 06 14:46:07 2013
 Response via : Initial Calibration
 DataAcq Meth : BNASV1

| Internal Standards | R.T. | QIon | Response | Conc | Units | Dev (Min) |
|---------------------------|-------|------|----------|-------|-------|-----------|
| 1) 1,4-Dichlorobenzene-d4 | 7.62 | 152 | 312836 | 20.00 | ppm | 0.00 |
| 19) Naphthalene-d8 | 8.88 | 136 | 1023090 | 20.00 | ppm | 0.00 |
| 35) Acenaphthene-d10 | 10.53 | 164 | 701052 | 20.00 | ppm | 0.00 |
| 60) Phenanthrene-d10 | 11.89 | 188 | 1013892 | 20.00 | ppm | 0.00 |
| 74) Chrysene-d12 | 14.34 | 240 | 954322 | 20.00 | ppm | 0.00 |
| 82) Perylene-d12 | 15.87 | 264 | 895129 | 20.00 | ppm | 0.00 |

| System Monitoring Compounds | R.T. | QIon | Response | Conc | Units | Dev (Min) |
|-----------------------------|------|------|----------|------|-------|-----------|
| 3) 2-Fluorophenol | 0.00 | 112 | 0 | 0.00 | ppm | |
| Spiked Amount 50.000 | | | Recovery | | | 0.00% |
| 4) Phenol-d5 | 0.00 | 99 | 0 | 0.00 | ppm | |
| Spiked Amount 50.000 | | | Recovery | | | 0.00% |
| 20) Nitrobenzene-d5 | 0.00 | 82 | 0 | 0.00 | ppm | |
| Spiked Amount 25.000 | | | Recovery | | | 0.00% |
| 39) 2-Fluorobiphenyl | 0.00 | 172 | 0 | 0.00 | ppm | |
| Spiked Amount 25.000 | | | Recovery | | | 0.00% |
| 64) 2,4,6-Tribromophenol | 0.00 | 332 | 0 | 0.00 | ppm | |
| Spiked Amount 50.000 | | | Recovery | | | 0.00% |
| 76) Terphenyl-d14 | 0.00 | 244 | 0 | 0.00 | ppm | |
| Spiked Amount 25.000 | | | Recovery | | | 0.00% |

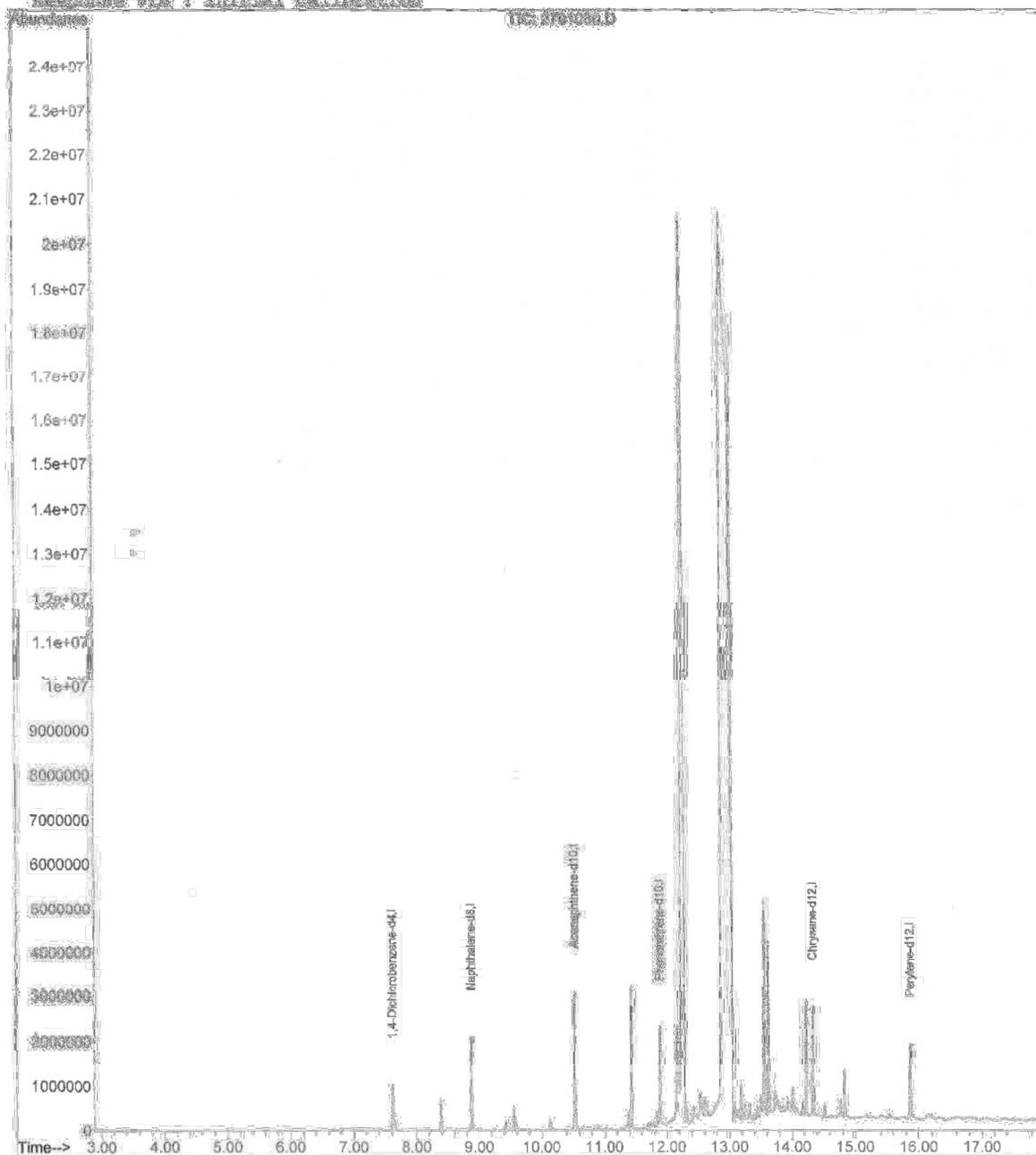
Target Compounds Qvalue

 (#) = qualifier out of range (m) = manual integration
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Quantitation Report (Not Reviewed)

Data File : T:\DATA1\SEMIVOC\2013SVOC\SEP\0906\2701030.D Vial: 27
Acq On : 6 Sep 2013 8:42 pm Operator: EMP
Sample : UI-1 Inst : SEMIVOC1
Misc : Multiplr: 100.00
MS Integration Params: nteint.p
Quant Time: Sep 9 8:22 2013 Quant Results File: BNA0906CC.RES

Method : T:\DATA1\SEMIVOC\QUANT2013\BNA0910CC.M (RTE Integrator)
Title : EPA 8270G/625 Calibration
Last Update : Wed Sep 11 11:27:40 2013
Sample Via : External Calibration



B.2 Raw data of decarboxylated biodiesel

(see next page)

Library Search Compound Report

Data File : F:\DATA1\SEMI\VOCA\2013\VOCA\SEP\0906\2901032.D Vial: 29
 Acq On : 6 Sep 2013 9:34 pm Operator: EMP
 Sample : III-2 Inst : SEMI\VOCA1
 Misc : Multiplr: 100.00
 MS Integration Params: Lscint.p
 Quant Method : F:\DATA1\S...\BNA0906CC.M (RTE Integrator)
 Title : EPA 8270C/625 Calibration
 Library : F:\DATA1\NIST129K.L

Peak Number 1 Heptane, 2,2,4,6,6-pentamet... Concentration Rank 1

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|---------------|-----------|------------------------|------|
| 7.55 | 139568.00 ppm | 147611000 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|---------|-------------|------|
| 1 | Heptane, 2,2,4,6,6-pentamethyl- | 170 | C12H26 | 013475-82-6 | 83 |
| 2 | Tetradecane, 2,2-dimethyl- | 226 | C16H34 | 000000-00-0 | 64 |
| 3 | Heptane, 2,2,4,6,6-pentamethyl- | 170 | C12H26 | 013475-82-6 | 64 |
| 4 | Decane, 2,2-dimethyl- \$\$ 2,2-Dim... | 170 | C12H26 | 017302-37-3 | 64 |
| 5 | Heptane, 2,2,4,6,6-pentamethyl- | 170 | C12H26 | 013475-82-6 | 64 |

Peak Number 2 2,2,4,4,-Tetramethyloctane Concentration Rank 4

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|--------------|----------|------------------------|------|
| 7.79 | 24074.70 ppm | 25462100 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|---------|-------------|------|
| 1 | 2,2,4,4,-Tetramethyloctane | 170 | C12H26 | 062183-79-3 | 64 |
| 2 | Nonane, 2,2,4,4,6,8,8-heptamethyl- | 226 | C16H34 | 004390-04-9 | 64 |
| 3 | Nonane, 2,2,4,4,6,8,8-heptamethyl- | 226 | C16H34 | 004390-04-9 | 50 |
| 4 | Nonane, 2,2,4,4,6,8,8-heptamethyl- | 226 | C16H34 | 004390-04-9 | 50 |
| 5 | Octane, 3,6-dimethyl- \$\$ 3,6-Dim... | 142 | C10H22 | 015869-94-0 | 40 |

Peak Number 3 Decane, 2,6,7-trimethyl- Concentration Rank 5

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|--------------|----------|------------------------|------|
| 7.85 | 14054.30 ppm | 14864200 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|---------|-------------|------|
| 1 | Decane, 2,6,7-trimethyl- | 184 | C13H28 | 062108-25-2 | 72 |
| 2 | Octane, 2,6-dimethyl- | 142 | C10H22 | 002051-30-1 | 59 |
| 3 | Octane, 3,5-dimethyl- \$\$ 3,5-Dim... | 142 | C10H22 | 015869-93-9 | 56 |
| 4 | Undecane, 2,5-dimethyl- | 184 | C13H28 | 017301-22-3 | 53 |
| 5 | Dodecane, 2,7,10-trimethyl- | 212 | C15H32 | 074645-98-0 | 50 |

Peak Number 4 Decane, 2,6,7-trimethyl- Concentration Rank 7

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|--------------|----------|------------------------|------|
| 7.94 | 10906.60 ppm | 11535100 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|---------|-------------|------|
| 1 | Decane, 2,6,7-trimethyl- | 184 | C13H28 | 062108-25-2 | 78 |
| 2 | Undecane, 2,6-dimethyl- \$\$ 2,6-D... | 184 | C13H28 | 017301-23-4 | 64 |
| 3 | Octane, 2,6-dimethyl- \$\$ 2,6-Dim... | 142 | C10H22 | 002051-30-1 | 53 |
| 4 | Undecane, 2,5-dimethyl- | 184 | C13H28 | 017301-22-3 | 53 |
| 5 | Decane, 2,6,9-trimethyl- | 184 | C13H28 | 062108-22-9 | 53 |

Peak Number 5 Nonane, 3-methyl- Concentration Rank 20

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|-------------|---------|------------------------|------|
| 7.97 | 2581.27 ppm | 2730020 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|----------|-------------|------|
| 1 | Nonane, 3-methyl- | 142 | C10H22 | 005911-04-6 | 42 |
| 2 | Heptanoic acid, 2-methyl-2-butyl- | 200 | C12H24O2 | 000000-00-0 | 40 |
| 3 | Hexane, 3-methyl- | 100 | C7H16 | 000589-34-4 | 38 |
| 4 | 4-Octene, (E)- \$\$ (E)-4-Octene \$ | 112 | C8H16 | 014850-23-8 | 27 |
| 5 | 4-Octene, (E)- | 112 | C8H16 | 014850-23-8 | 27 |

Peak Number 6 Hexane, 3-methyl- Concentration Rank 19

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|-------------|---------|------------------------|------|
| 8.01 | 2616.80 ppm | 2767590 | 1,4-Dichlorobenzene-d4 | 7.67 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|--|-----|---------|-------------|------|
| 1 | Hexane, 3-methyl- | 100 | C7H16 | 000589-34-4 | 64 |
| 2 | Decane, 2,6,7-trimethyl- | 184 | C13H28 | 062108-25-2 | 59 |
| 3 | Hexane, 3,3,4-trimethyl- | 128 | C9H20 | 016747-31-2 | 56 |
| 4 | Undecane, 3,3-dimethyl- | 184 | C13H28 | 017312-65-1 | 53 |
| 5 | Hexane, 2,3,4-trimethyl- \$\$ 2,3,4-trimethyl- | 128 | C9H20 | 000921-47-1 | 50 |

Peak Number 7 Pentadecane \$\$ n-Pentadecane... Concentration Rank 10

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 10.45 | 4336.36 ppm | 6557640 | Acenaphthene-d10 | 10.53 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|---------|-------------|------|
| 1 | Pentadecane \$\$ n-Pentadecane \$\$ | 212 | C15H32 | 000629-62-9 | 97 |
| 2 | Pentadecane | 212 | C15H32 | 000629-62-9 | 96 |
| 3 | Pentadecane | 212 | C15H32 | 000629-62-9 | 95 |
| 4 | Pentadecane | 212 | C15H32 | 000629-62-9 | 93 |
| 5 | Heptadecane \$\$ n-Heptadecane \$\$ | 240 | C17H36 | 000629-78-7 | 90 |

Peak Number 8 Heptadecane \$\$ n-Heptadecane... Concentration Rank 3

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 11.36 | 26751.80 ppm | 38048300 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---|-----|---------|-------------|------|
| 1 | Heptadecane \$\$ n-Heptadecane \$\$... | 240 | C17H36 | 000629-78-7 | 99 |
| 2 | Heptadecane | 240 | C17H36 | 000629-78-7 | 95 |
| 3 | Heptadecane | 240 | C17H36 | 000629-78-7 | 95 |
| 4 | Octadecane | 254 | C18H38 | 000593-45-3 | 91 |
| 5 | Heptadecane | 240 | C17H36 | 000629-78-7 | 91 |

Peak Number 9 Benzene, (1-methyldecyl)- \$... Concentration Rank 8

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.41 | 4695.20 ppm | 6677860 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|----------|-------------|------|
| 1 | Benzene, (1-methyldecyl)- \$\$ Und... | 232 | C17H28 | 004536-88-3 | 47 |
| 2 | Benzene, (1-methyldecyl)- | 232 | C17H28 | 004536-88-3 | 38 |
| 3 | 2-Phenyl-5,6-dihydro-4H-1,3-oxazine | 161 | C10H11NO | 000000-00-0 | 38 |
| 4 | Heptane, 2,6-diphenyl-3-methyl- | 266 | C20H26 | 000000-00-0 | 32 |

5 Benzene, (1-methylpentyl)- 162 C12H18 006031-02-3 27

Peak Number 10 Nicotinonitrile, 1,4-dihydr... Concentration Rank 9

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.45 | 4536.56 ppm | 6452220 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|----------|-------------|------|
| 1 | Nicotinonitrile, 1,4-dihydro-1-p... | 148 | C9H12N2 | 019424-17-0 | 43 |
| 2 | Benzene, (1-methyldecyl)- \$\$ Umd... | 232 | C17H28 | 004536-88-3 | 43 |
| 3 | Benzene, (1-methyldecyl)- | 232 | C17H28 | 004536-88-3 | 37 |
| 4 | Benzene, (1-methylbutyl)- | 148 | C11H16 | 002719-52-0 | 35 |
| 5 | Nopyl acetate \$\$ Bicyclo[3.1.1]h... | 208 | C13H20O2 | 000128-51-8 | 32 |

Peak Number 11 Benzene, diethyl- \$\$ Diethy... Concentration Rank 12

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.50 | 4208.29 ppm | 6985330 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|------------------------------------|-----|------------|-------------|------|
| 1 | Benzene, diethyl- \$\$ Diethylbenz | 134 | C10H14 | 025340-17-4 | 38 |
| 2 | 2-Methyl-3,5-dinitrophenyl .beta | 330 | C16H14N2O6 | 000000-00-0 | 37 |
| 3 | Benzene, 1-methyl-3-propyl- \$\$ T | 134 | C10H14 | 001074-43-7 | 30 |
| 4 | Benzenemethanol, ar-ethenyl- \$\$ | 134 | C9H10O | 030584-69-1 | 30 |
| 5 | Benzene, 1-methyl-4-propyl- \$\$ T | 134 | C10H14 | 001074-55-1 | 27 |

Peak Number 12 Ether, 3-hydroxy-2-butyl 1-... Concentration Rank 13

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.61 | 4003.63 ppm | 5694260 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|--------------------------------------|-----|----------|-------------|------|
| 1 | Ether, 3-hydroxy-2-butyl 1-(p-to... | 208 | C13H20O2 | 000000-00-0 | 53 |
| 2 | Benzene, 1,4-dimethyl-2-(2-methy... | 162 | C12H18 | 055669-89-0 | 50 |
| 3 | Benzene, 2-ethyl-1,4-dimethyl- \$... | 134 | C10H14 | 001758-88-9 | 47 |
| 4 | Benzene, 1-methyl-3-(1-methyleth... | 134 | C10H14 | 000535-77-3 | 43 |
| 5 | Benzene, 1-ethyl-3,5-dimethyl- \$... | 134 | C10H14 | 000934-74-7 | 43 |

Peak Number 13 Hexane, 2-phenyl-3-propyl- Concentration Rank 11

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 11.75 | 4261.04 ppm | 6060360 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|------------------------------------|-----|------------|-------------|------|
| 1 | Hexane, 2-phenyl-3-propyl- | 204 | C15H24 | 000000-00-0 | 50 |
| 2 | Benzene, (1,2,2-trimethylpropyl)- | 162 | C12H18 | 019262-20-5 | 43 |
| 3 | Benzene, (1,3-dimethylbutyl)- \$\$ | 162 | C12H18 | 019219-84-2 | 40 |
| 4 | Benzene, (1-cyclohexylethyl)- | 188 | C14H20 | 004413-16-5 | 38 |
| 5 | 3-[(4-Aminobenzoyl)hydrazono]-N- | 338 | C19H22N4O2 | 000000-00-0 | 23 |

Peak Number 14 Hexadecanoic acid, methyl e... Concentration Rank 6

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.24 | 12085.20 ppm | 17188500 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|--------------|----|---------|------|------|
|-----------|--------------|----|---------|------|------|

| | | | | | |
|---|---------------------------------|-----|----------|-------------|----|
| 1 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 99 |
| 2 | Pentadecanoic acid, 14-methyl- | 270 | C17H34O2 | 005129-60-2 | 97 |
| 3 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 96 |
| 4 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 93 |
| 5 | Hexadecanoic acid, methyl ester | 270 | C17H34O2 | 000112-39-0 | 91 |

 Peak Number 15 Octadecanoic acid, methyl e... Concentration Rank 2

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|--------------|----------|------------------|-------|
| 12.98 | 36938.70 ppm | 52336900 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------|-----|----------|-------------|------|
| 1 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 99 |
| 2 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 98 |
| 3 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 97 |
| 4 | Heptadecanoic acid, 16-methyl- | 298 | C19H38O2 | 005129-61-3 | 97 |
| 5 | Octadecanoic acid, methyl ester | 298 | C19H38O2 | 000112-61-8 | 90 |

 Peak Number 16 Nonanoic acid, 9-(o-propylp... Concentration Rank 17

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.02 | 2873.75 ppm | 4087250 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|------------|-------------|------|
| 1 | Nonanoic acid, 9-(o-propylphenyl... | 290 | C19H30O2 | 017670-86-9 | 14 |
| 2 | Heptanoic acid, 7-(o-pentylpheny... | 290 | C19H30O2 | 013397-97-2 | 14 |
| 3 | (2,2-Diethyl-1,3-dioxo-butyl)-be... | 248 | C14H20N2O2 | 000000-00-0 | 4 |
| 4 | Isoxazole, 3-ethyl-5-phenyl- | 173 | C11H11NO | 004211-90-9 | 4 |
| 5 | Borane, diethyl[1-ethyl-2-(trime... | 302 | C12H27BSn | 087184-06-3 | 4 |

 Peak Number 17 Octadecanoic acid Concentration Rank 14

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.10 | 3900.89 ppm | 5548130 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|----------|-------------|------|
| 1 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 70 |
| 2 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 70 |
| 3 | Octadecanoic acid \$\$ Stearic aci... | 284 | C18H36O2 | 000057-11-4 | 85 |
| 4 | Octadecanoic acid, 2-(2-hydroxye... | 372 | C22H44O4 | 000106-11-6 | 22 |
| 5 | Isopropyl stearate | 326 | C21H42O2 | 000112-10-7 | 12 |

 Peak Number 18 Octadecanoic acid Concentration Rank 16

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.11 | 3309.45 ppm | 4706940 | Phenanthrene-d10 | 11.90 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|----------|-------------|------|
| 1 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 99 |
| 2 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 95 |
| 3 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 94 |
| 4 | Octadecanoic acid \$\$ Stearic aci... | 284 | C18H36O2 | 000057-11-4 | 93 |
| 5 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 93 |

 Peak Number 19 Octadecanoic acid Concentration Rank 15

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|------|---------|------|------------------|------|
|------|---------|------|------------------|------|

13.12 3784.16 ppm 3897050 Chrysene-d12 14.33

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|---------------------------------------|-----|----------|-------------|------|
| 1 | Octadecanoic acid | 284 | C18H36O2 | 000057-11-4 | 53 |
| 2 | Phosphorin, 2,6-bis(1,1-dimethyl... | 284 | C19H25P | 017420-27-8 | 38 |
| 3 | 4-p-Hydroxyphenyl-2,2,4-trimethy... | 284 | C18H20OS | 000000-00-0 | 37 |
| 4 | 5,19-Cyclo-5.beta.,7.androst-6-ene... | 284 | C19H24O2 | 033585-88-5 | 27 |
| 5 | 3-Methoxyestra-1,3,5(10),8-tetra... | 284 | C19H24O2 | 006733-79-5 | 27 |

 Peak Number 20 3-Pyridinecarbonitrile, 1,4-dihy. Concentration Rank 18

| R.T. | EstConc | Area | Relative to ISTD | R.T. |
|-------|-------------|---------|------------------|-------|
| 13.26 | 2855.36 ppm | 2940540 | Chrysene-d12 | 14.33 |

| Hit# of 5 | Tentative ID | MW | MolForm | CAS# | Qual |
|-----------|-------------------------------------|-----|---------|-------------|------|
| 1 | 3-Pyridinecarbonitrile, 1,4-dihy... | 120 | C7H8N2 | 019424-15-8 | 46 |
| 2 | Benzene, 1,4-dimethyl-2-(2-methy... | 162 | C12H18 | 055669-88-0 | 43 |
| 3 | Benzene, 1,4-dimethyl-2-(2-methy... | 162 | C12H18 | 055669-88-0 | 43 |
| 4 | 7-Methoxymethyl-2,7-dimethylcycl... | 164 | C11H16O | 073992-48-0 | 38 |
| 5 | Phenyl 2-phenylisopropy sulfide | 228 | C15H16S | 004148-93-0 | 38 |

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