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Abstract

This research sought to demonstrate the potential of biodiesel and softwood derived Fast Pyrolysis Oil (FPO) blends as an alternative low-carbon drop-in diesel fuel. FPO was supplied from an in-house fluidized bed reactor as well as a commercial source. Separate FPO-biodiesel blends from both FPO sources were prepared using initial volumetric ratios of 80:20 and 60:40 (biodiesel:FPO, by volume). Upon blending each performed volumetric ratio, mixing and a 24 hour settling period, two layers formed and the top, biodiesel-rich layers containing about 5 and 10 vol % FPO were decanted and characterized on the basis of a thermogravimetric analysis, viscosity, acid number, water content, elemental analysis, and heating value. Significant decreases in viscosity, acidity, and water content from the original FPO validated blending as means of extracting compounds suitable for use as fuels from pyrolytic liquids in biodiesel.

A single cylinder, direct injection diesel engine was used to analyze the combustion performance of the FPO fuel blends against neat diesel and biodiesel. Fuel performance was characterized on the basis of a thermodynamic analysis and corresponding exhaust measurements for CO₂, CO, unburned hydrocarbons, particulate matter, and NOx. Two thermodynamic measurement campaigns were performed in order to provide insight into FPO fuel performance across various engine conditions. In addition to the thermodynamic measurements, in-cylinder high-speed photography was implemented to support the interpretation of thermodynamic combustion data.
Engine testing revealed similar indicated efficiencies for biodiesel and diesel at all considered engine-operating modes, while blend fuels showed indicated efficiencies between 75 and 95% of diesel values. FPO fuels exhibited increased ignition delays and shorter combustion durations with greater FPO blend concentrations, though this could be partially compensated for using a pilot injection strategy. The longer ignition delays of the blend fuels resulted in overly lean regions of the cylinder, which produced largely premixed combustion events contributing to brake specific CO and uHC emissions up to 1.5 and 3.5 greater than diesel, respectively. Specific PM emissions were 41-62% lower for blend fuels than diesel. Both blends of in-house FPO showed similar PM emission performance, however at higher concentrations than low blend commercial fuel.
Preface

As primary author, I performed the majority of the development of the fast pyrolysis production facilities in the Clean Energy Research Centre and Pulp and Paper Center at the University of British Columbia. I was supported in the production and characterization of biomass fast pyrolysis oil by Katharina Kirsch and Dr. Chang Soo Kim. Upgrading of biomass fast pyrolysis oil was performed by myself along with Katharina Kirsch. The auxiliary common rail fuel system and emissions measurement systems were designed and assembled by myself in conjunction with a single cylinder diesel engine test facility developed by Jeremy Rochussen and Jeff Yeo. Combustion measurements were the result of a team effort including Jeremy Rochussen, Jeff Yeo, Mahdiar Khosravi, and myself. I performed all resulting data analysis under guidance of Dr. Patrick Kirchen and Dr. Naoko Ellis.

The data presented in Sections 4.2, 4.3.1, 5.4 relevant to the production, blending, upgrading, and use of FPO derived compounds in the third engine testing campaign was prepared in a manuscript and submitted for review to Elsevier FUEL under the title, *Production, Analysis and Combustion Characterization of Biomass Fast Pyrolysis Oil - Biodiesel Blends for use in Diesel Engines* with Dr. Patrick Kirchen and Dr. Naoko Ellis as co-authors. I performed the majority the writing and data analysis, with insight and revisions provided by the co-authors.

UBC Ethics Board Approval was not required.
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<th>Abbreviation</th>
<th>Meaning</th>
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<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>aTDC</td>
<td>After Top Dead Center</td>
<td></td>
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<tr>
<td>C</td>
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<td>CAD</td>
<td>Crank Angle Degree</td>
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<td>DTG</td>
<td>Derivative Thermogravimetric Analysis</td>
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<td>GIMEP</td>
<td>Gross Indicated Mean Effective Pressure</td>
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<td>HHV</td>
<td>High heating value</td>
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<td>Volume</td>
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<tr>
<td>W</td>
<td>Mass flow rate</td>
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<td>Indicated Work</td>
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<td>( \frac{dQ_n}{d\theta} )</td>
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Though I take authorship of this thesis, the development of this project was guided by those whose supervision, support and encouragement allowed me to enhance my understanding of engineering sciences in mechanical and chemical engineering.

My supervisors, Dr. Patrick Kirchen and Dr. Naoko Ellis, whose vision, countless hours of guidance, and encouragement are responsible for the leadership which directed the project for the past two and a half years.

Dr. Steven Rogak, Dr. Chang Soo Kim, and Dr. James Butler have all shared a wealth of knowledge and information that provided valuable insight during critical times and led to a greater understanding of combustion science, reactor design, and fuel characterization.

Katharina was not only a valuable peer, but also a wonderful friend during her time in Vancouver. Jeremy and Jeff selflessly offered their time and sweat during the midst of their own research to help integrate new fuel measurements into the engine lab while also being great friends.

Beyond the laboratories, I am indebted to my friends who take me to the mountains to clear my mind, and to Sonia for her encouragement and devotion.

Ultimately it is my family to whom I am most grateful; for their sacrifices, support, and compassion which have allowed me to unreservedly pursue my goals.
Dedication

Für Anne, Joy, Arno

Jennie and Frank

und Oma
Chapter 1 Introduction

Biomass pyrolysis processes and products have been researched for several decades as feedstock in sustainable energy systems and renewable materials; however, their application remains limited. The following prefatory section offers an introduction to the development of biomass resources for energy generation, specifically in reference towards the application of fast pyrolysis oil in internal combustion engines. A framework for the research objectives and outcomes discussed in this body of work will be presented within context to the project scope.

1.1 Background and Project Motivation

In the field of research motivated by developing technical solutions to mitigate global greenhouse gas emissions, the transition from fossil fuels for energy generation in mobile and transportation systems has often been considered with biologically derived fuels due to their inherent carbon reducing potential. Low carbon, biogenic fuels have demonstrated feasibility in modern combustion infrastructure including existing fuel distribution systems and vehicle powertrains. Solid biofuels have shown feasibility in stationary power systems such as gasifiers, boilers, and furnaces. Liquid biofuels have already been adopted by several industries for application in vehicle engines and aviation turbines[1].

Pyrolysis oil is a product from the thermal degradation of a feedstock, traditionally from a waste stream such as residuals from forestry or agricultural products. There is extensive research in the literature detailing pyrolysis oil production in a variety of reactor configurations and operating conditions[2–4]. The application of crude pyrolysis oil and derivative products as fuels has been researched, primarily in compression ignition engines, as well in single flame burners and
stationary furnaces. A general overview of applications of fast pyrolysis products is presented in Figure 1-1.

![Figure 1-1 Overview of applications for fast pyrolysis products. Used with Permission. [5]](image)

Early testing of biomass pyrolysis oil for power generation often emphasizes the need for product upgrading due to poor material compatibility from high water content, residual solids, high viscosity, and high oil acidity (often as a result of carboxylic acid groups formed in the pyrolysis production process [6]). Testing of crude pyrolysis oils in traditional combustion engines has resulted in failure of fuel pumps, injectors, and other engine hardware as a result of significantly longer fuel ignition delay[7]. As a result, there exists a need to develop low-cost upgrading strategies of biomass fast pyrolysis oil in order to develop a more appropriate fuel for modern combustion infrastructure. Specifically, addressing fuel corrosiveness by neutralizing acidic groups may enhance material compatibility, reducing pyrolysis oil viscosity to match flow and spray dynamics of traditional fuels could reduce wear on fuel supply systems, and removing char and ash content could reduce coking in the engine and exhaust systems.
Various upgrading methodologies have been investigated with varying degrees of complexity and success. It is the purpose of this thesis to develop research in biomass fast pyrolysis production, upgrading, and performance as a drop in fuel for internal combustion engines. Ultimately, the work presented here should contribute to the understanding of biomass pyrolysis oil application in a future low-carbon energy mix.

1.2 Advancement of Biofuels

North American fuel economy standards, regulated by Corporate Average Fuel Economy (CAFE) regulations, were first introduced as a result of the oil crisis in the 1970s. Since their introduction, increasingly stringent regulations on fuel economy have reduced individual passenger vehicle fuel consumption and inherently, reduced individual passenger vehicle carbon dioxide emissions. In 2005 the United States passed the Energy Policy Act which enacted Renewable Fuel Standards (RFS), requiring conventional petroleum derived transportation fuel sold in the United States to be blended with biofuels that demonstrate lower greenhouse gas emissions in order to reduce the dependence of non-domestic sources of oil, while reducing greenhouse gas emissions. Since the RFS mandates, the biofuel economy has seen continuous growth in order to meet the demands of gasoline and diesel blends, specifically from ethanol and biodiesel, respectively. As the production of biofuels advanced, feedstock markets that traditionally supplied food distribution saw increased competition, which impacted food prices as a result of increased demand. The increased demand from 2011-2014 and projected E85 consumption to 2025 under variations of proposed CAFE standards is shown from Whistance et al., 2014 [8] in Figure 1-2.
Not long after the initial growth of the biofuel industry, a debate of food vs fuel emerged which brought to light ethical concerns of devoting food resources for transportation fuels. These biofuels quickly became known as first generation biofuels, classified as fuels derived from resources in direct competition with food production such as corn and sugarcane for ethanol, and soybeans, rapeseed, and palm oil for biodiesel. To address the ethical debate implied with first generation biofuels, second generation biofuels were promoted with intent to mitigate land use changes and competition in food markets from biofuel production required for RFS mandates. Second generation biofuels are derived from non-food derived feedstock such as lignocellulosic biomass and waste resources [9]. Lignocellulosic biomass, often referred to as woody biomass, is composed of cellulose, hemicellulose, and lignin. Carbohydrates available from cellulose and hemicellulose have been successfully used as feedstock for renewable ethanol and butanol production as drop in fuels in internal combustion engines. The aromatic polymer structure of lignin is considered to be a renewable feedstock more appropriate for diesel fuels, however is less developed as a potential second-generation biofuel source.
One potential second generation biofuel is pyrolysis oil produced from lignocellulosic biomass. Pyrolysis oil is a thick brown liquid with a strong smoky aroma and water content traditionally between 15 and 35%. Pyrolysis oil is a product of pyrolysis reactions, along with solid bio-char, and non-condensable vapours including syngas. Softwood timber industries are an excellent feedstock for second-generation biofuels due to the waste sawdust and woodchips, commonly processed into wood pellets. In 2013 it was estimated that over 14 Mt (million metric tonnes) of wood pellets were produced globally for commercial heating and industrial co-firing [10]. Pellets are produced from agricultural waste as a densification step to reduce material volume and transportation cost. Softwoods (gymnosperms) account for the majority of timber resources and primarily include Spruce, Pine, Cedar, and Fir.

Current non-food based biofuel development includes waste streams such as as timber sawdust and sugarcane bagasse; algae harvesting for lipid generation, and biologically engineered organisms producing lipids or carbohydrates. While it is unlikely that biologically derived feedstock can entirely supply current global petroleum demand, the continued development of biomass energy resources could contribute to offset traditional fuels in future carbon economies.

1.3 Thesis Objectives

This thesis has three primary research objectives: 1. Pyrolysis oil production from softwood biomass 2. Pyrolysis oil upgrading and characterization 3. engine testing of fuels for drop-in performance against reference fuels. Exhaustive reviews of each research objective exist in the literature; however, a limited number discuss the operations to manage the entire waste-to-energy processes, from pellet to piston. The goals were addressed sequentially; first developing fast pyrolysis oil production facilities, assessing the pyrolysis products against commercially
available pyrolysis oil for potential upgrading techniques, and ultimately engine system design and operation with pyrolysis derived fuels.

A literature review of the three project areas is presented in the Chapter 2. A discussion of Experimental facilities, conditions, and results of Production, Characterization and Upgrading, and Engine testing are presented in Chapter 3, Chapter 4, and Chapter 5, respectively. A summary of the thesis conclusions is given in Chapter 6 and Future research recommendations are discussed in Chapter 7.
Chapter 2  Literature Review

Pyrolysis oil and its applications have been studied for over two decades and as such, the available research is imperative to review in order to establish procedures in agreement with established knowledge for production, upgrading, and energy generation of pyrolysis oil. While many of these sections are addressed in published review articles that summarize a collection of works [2,3,5,7], individual publications that were found to offer more specific details relevant to the project were referenced for stricter guidance.

2.1 Pyrolysis Oil Production

Pyrolysis generally denotes the process of the thermal decomposition of a material, biomass being of interest in this work, in an inert atmosphere. Resulting biomass fast pyrolysis oil (FPO) products are formed as solid, liquid and gas. Gases include CO, CO$_2$, H$_2$, CH$_4$, and trace amounts of larger alkanes. [3] Produced liquids include water, carboxylic acids, aldehydes, ketones, phenolics, furans, and alcohols. The formation of molecular ring structures is attributable to the abundance such structures in the feedstock relative cellulose and lignin fractions [3]. Produced solids are in the form of residual char and ash. A breakdown of the composition of typical pyrolysis products is shown in Figure 2-1.
The relative distribution of solid, liquid and gas pyrolysis products have been shown to be a function of several production factors, most notably impacted by feedstock composition, particle size, heating and quenching rates, and reaction and quenching temperatures [2]. In efforts to develop biomass pyrolysis oil production for energy generation, three primary production factors were considered to be most effective in maximizing pyrolysis oil yield and heating value: reactor heating and cooling rates, feedstock particle size, and reactor temperature [3].

To provide the heat transfer in anoxic environments for pyrolysis to occur, a variety of reactor systems have been reviewed for pyrolysis oil production in the literature. In addition to maximizing pyrolysis oil yield and caloric value, a major objective to this research project was the development of a continuous reactor system to supply greater quantities of pyrolysis oil than batch reactors might provide. Pyrolysis systems are often classified into two groups, slow and fast pyrolysis. Largely in reference to the heating rates and residence times, slow pyrolysis reactors exhibit feedstock residence times between 5-30 minutes by subjecting pyrolyzing
material to much slower heating rates. Conversely, fast pyrolysis systems exhibit feedstock heating rates between 0.5 and 10 °C/S and have been shown to exhibit greater yields and faster pyrolysis oil generation from accelerated thermal decomposition mechanisms [2]. Fast pyrolysis liquid yield is often reported in the range of a 60-85% feedstock conversion rate [2,3,12]. Three primary methods of achieving fast pyrolysis are outlined with ablative, fluidized bed, and vacuum pyrolysis reactors. Ablative reactors press feedstock against a heated surface, however are largely limited in heat transfer capability of the reactor which results in limited reactor surface areas. Fluidized bed reactors incorporate convection and conduction heat transfer to the feedstock particles which allow for more heat transfer and greater liquids yields, however require significant carrier gases for proper fluidization conditions [3]. Vacuum pyrolysis reactors rely on vacuum pressure to quickly remove vapours from slow heating rate reactors in order to simulate fast pyrolysis vapour quenching. Vacuum pyrolysis reactors are shown to exhibit slightly higher char and gas formation, with pyrolysis liquid yields 15-20% lower than the fluidized bed and ablative reactors [3]. As such, Fast Pyrolysis Oil (FPO) is considered a more favourable product over conventional pyrolysis products. Due to their superior for pyrolysis oil yield capacity and the available hardware during the research project, fluidized bed reactors were chosen for the in-house pyrolysis oil production development.

The report of Salehi et al., 2011[13] sought to develop a fluidized bed reactor for FPO generation from softwood particles. The research objectives were to investigate the effect of particle size and heating rates on FPO yield with a pilot scale fluidized bed reactor. Given the similarities to the UBC pyrolysis production research objectives the report proved to be a valuable resource in developing production procedures. Through a series of optimizations, production conditions for
FPO were optimized for yield and heating value based on feedstock particle size and reactor temperature from a pine wood feedstock.

Salehi et al. showed the effect of particle size on theoretical particle heating rate. Particle size ranges were determined through collected ground biomass separated with sieves and theoretical heating rates were determined from the reactor volume and volumetric gas flow rate. Overlaid on the experimental data of bio-oil, gas, and char conversion, the effect of feedstock particle size seen on pyrolysis product yield in Figure 2-2.

![Figure 2-2 Effect of feedstock particle size on pyrolysis product yield. Salehi et al. Used with Permission. [13]](image)

Particle sizes greater than 590 µm are shown to have constant particle heating rates with increasing size, from which one can conclude that the limitations of heating rates are limited by the internal conduction of the particles. As heating rates increase with decreasing particle size, the heat transfer limitations are shifted from the internal conduction to the external convection
mechanisms. The mechanisms of the particle heating rate rely on steady reactor flow, solids fraction, and Reynolds numbers within the system. The resulting increase in bio-oil yield at higher heating rates as a result of smaller particle sizes highlight an important factor in optimizing pyrolysis reactor systems and was used to determine the particle sizes for in-house FPO production development. The effect of reactor temperature on pyrolysis product yield as solid chars, non-condensable gases, and bio-oil liquids is seen in Figure 2-3.

![Figure 2-3 Effect of reactor temperature on pyrolysis product yield. Salehi et al. Used with Permission. [13]](image)

A mass balance of the products at set reactor temperatures showed agreement with the general pyrolysis trends of increasing solid char yields at temperatures below 400 °C and increasing gaseous product yields at temperatures above 600 °C [2]. The optimal recovered mass fraction of FPO was shown to occur at reactor temperatures of 500 °C with FPO, gaseous, and solid char mass yields of 62%, 23%, and 15% respectively. The reported temperature of ~500°C for optimal FPO production is also reported for other biomass feedstock [2].
An optimization of the product higher heating value (HHV) was performed and is shown in Figure 2-4. The peak HHV of FPO is demonstrated at reactor temperatures of 500 and 525 °C with 15 MJ/kg for the bio-oil products. From these findings reported by Salehi et al. and in agreement with other literature reviews [14,15], reactor conditions were prepared for in-house production using similar residence time and particle sizes to achieve analogous heating rates and thus maximum FPO yields ~500 °C.

2.2 Upgrading Fast Pyrolysis Oil

ASTM D7544 specifies the characteristics for commercial pyrolysis oil to be used in stationary energy generation such as furnaces or kilns [16]. In absence of a suitable standard for pyrolysis oil use in combustion engines [17], these properties can be compared to the characteristics of modern transportation fuels of diesel and biodiesel through ASTM D675 and ASTM D975, respectively. Table 2-1 below summarizes key characteristics of the three fuel standards. The
reduced heating value, substantial water content, high viscosity, and high total acid number (TAN) distinguish the pyrolysis liquids from the characteristics of biodiesel and diesel.

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<tr>
<td>Gross Heat of Combustion, MJ/kg</td>
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<td>38</td>
<td>44</td>
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<tr>
<td>Water Content, % mass, max</td>
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</tr>
<tr>
<td>Ash Content, % mass, max</td>
<td>.25</td>
<td>.01</td>
<td>0</td>
</tr>
<tr>
<td>TAN, (mg/g KOH)</td>
<td>72</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

To upgrade FPO for use as a transportation fuel, physical and chemical strategies have been presented to more resemble properties of traditional transportation fuels [20]. Physical upgrading often entails emulsions or blends of FPO with biodiesel, diesel, or solvents in order to effectively reduce water content, viscosity, acidity, all while maintaining similar heating values to the mixing agents [5]. Physical upgrading has been shown to have significant effect on fast pyrolysis oil stability and homogeneity however at high cost of solvents and energy input from emulsion processes [5]. Chemical upgrading implements techniques such as catalytic cracking, esterification, and hydrotreating for deoxygenation. Using advanced chemical upgrading techniques often requires energy intensive procedures with hydrogen for deoxygenation, elevated pressures, and expensive catalysts in order to produce upgraded FPO derived fuels [5,21]. As a result of these implications, the development of chemical upgrading processes on scales large
enough to provide the quantities of fuel required for experimental engine testing were not economically feasible for the development of UBC in-house FPO upgrading.

Due to the simplicity and promising results, the upgrading methodology of Jiang and Ellis, 2010 was used [22]. This investigation found optimal emulsion stability of biodiesel and FPO with an octanol surfactant. Through varying mixture fractions of biodiesel, FPO and octanol; varying stirring intensities; and emulsion temperatures, an optimal emulsion stability was determined. This offered a novel method for extracting fuel appropriate compounds from crude FPO. The method was initiated with a mixture of biodiesel and FPO that were combined and agitated to facilitate the transfer of compounds from FPO into the biodiesel phase. Following the agitation period, the liquids were allowed to settle for a 24 hour period, forming two distinct immiscible layers. Changes in volumetric mixture fractions were observed as increases in the top biodiesel layer and were attributable to the transfer of compounds from FPO into the biodiesel. Figure 2-5 below demonstrates the change in volume from initial mixture fractions of biodiesel and FPO, and the resulting distribution of layers of the top biodiesel rich, and lower FPO rich phases.
The upper FPO layer was decanted and analyzed. The initial blend fraction of 40 vol. % FPO and 60 vol. % biodiesel resulted in stable volumetric distributions of 73 vol. % biodiesel rich upper layer and 27 vol. % bio oil layer. This lower layer was found to have a water content of 0.46%, TAN of 14.01 mg KOH/g, HHV of 35.8 MJ/kg, and viscosity of 4.67 Pa•s. The increased acidity of the upper blend fraction over biodiesel was attributed to the transfer of acidic groups from the bio oil. The water content increased by almost a factor of three from neat biodiesel, however remained < 0.5% in the upper layer. The higher heating value of the upper layer was reduced by 13.7% from neat biodiesel, which was attributed to the increased overall oxygen content of the fuel [22].

While the characterization of the upper emulsion layer proved to offer significantly more desirable fuel properties than crude FPO, the values remained well above several ASTM limits for commercial diesel and biodiesel reviewed in Table 2-1. Nonetheless, significant upgrading of
the upper layer emulsion from crude FPO was evident and due to the relatively inexpensive and simple upgrading procedure, the methodology was adopted for UBC in-house upgrading of FPO for combustion testing.

2.3 Pyrolysis Oil and Derivatives in Internal Combustion Systems

The largest barrier towards implementing biomass fast pyrolysis oil as a transportation fuel remains the incompatibility of hardware found in internal combustion engines. Crude and upgraded derivatives of biomass FPO has been tested in a variety of internal combustion engines, however with varying degrees of success. One of the first accounts of FPO combustion testing in a diesel engine was by Shihadeh and Hochgreb, 2000 [23]. Their findings reported similar indicated thermal efficiencies of FPO to diesel, however found that the long ignition delay of FPO fuels required air preheating for reliable engine performance. Through means of a three zone model, the investigation also concluded that while diesel is predominantly mixing limited in combustion, pyrolysis oil was predominantly kinetically limited throughout the combustion processes [23]. The investigation also remarked on significant hardware modifications required to perform the combustion testing on the diesel engine, such as in-line fuel switching to allow ethanol flushes between experiments to prevent gumming and scaling, and additional in-line fuel filters to reduce in situ particulate growth which caused abrasion to the fuel pump assembly and the fuel injector nozzle. These findings are in agreement with other investigations highlighting significant wear on fuel delivery systems [7,11]. Chiaramonti et al., 2003 [24] determined similar failures of a diesel injector and imaged the fuel injector needle after 6.5 hours of engine operation with a 25 wt% FPO-diesel emulsion. An image of the needle corrosion is seen below in Figure 2-6.
A review of FPO compatibility in compression ignition engines by Mueller, 2013 concluded that the sensitivity of diesel fuel delivery systems, in particular high pressure common rail direct injection systems, is not yet suitable for the application of FPO crude and upgraded fuels [11]. Investigations into FPO characteristics and experimental engine in testing allude to the understanding that crude FPO is not a suitable transportation fuel. To address the shortcomings of FPO, progress has been made towards upgrading FPO to more closely resemble modern transportation fuel properties such as viscosity, acidity, water content, and heating value. Investigations of FPO upgrading strategies often are limited to lab-scale systems that would be cost prohibitive to produce the fuel quantities required for experimental engine testing. As a result, few combustion studies have been performed on upgraded FPO and are often limited to non-engine research. It is the purpose of this thesis to investigate FPO as a potential drop-in fuel from production, upgrading and characterization, to combustion in a research engine. The scope of this work should provide insight into a broader evaluation of FPO products as suitable transportation fuels with respect to production yield, extent of upgrading, and assessment of engine performance with reference to reference fuels.
Chapter 3  Pyrolysis Oil Production Facilities

The development of in-house biomass FPO production facilities ultimately resulted in modifying two reactors through efforts to optimize product quality and maximize FPO availability. The first reactor was developed in the Clean Energy Research Centre (CERC) High Head Lab at the University of British Columbia. While this reactor was fully assembled and operational, it was decommissioned shortly after initial FPO production for alternative purposes due to non-ideal performance of several reactor subsystems such as the biomass screw feeding system and system and condenser units. A secondary reactor was reworked from an existing pilot scale fluidized bed biomass gasifier in the Pulp and Paper Centre (PPC) High Head Lab at the University of British Columbia. Through a series of FPO productions performed in order to verify optimal reaction conditions gathered from literature, a standardized biomass FPO production procedure was developed. Ultimately, the in-house FPO production facilities were developed in order to provide the quantity softwood derived FPO required for experimental engine testing, about 15L, and any future research objectives requiring crude FPO.

3.1  CERC Reactor Production

The CERC reactor had previously been used as a gasifier for coal and biomass in previous studies [25] and was thought to be a viable system to reform into and pyrolysis reactor. The reactor was 707mm in length with an inner diameter of 76mm. Silica sand with mean particle diameter \(d_p = 469 \, \mu m\) was used as a fluidizing media. The bed material rested on a perforated distributor plate with 95, 3mm holes covered in 400 \(\mu m\) stainless steel wire mesh, preventing bed solids from the preheater area. Silica sand was fed manually into the reactor to a calculated static height of 375mm determined from the bulk density of \(\rho = 2400 \, \text{kg/m}^3\). Nitrogen provided from Praxair was used as a fluidizing gas, supplied via external pressurized tanks through regulators.
and rotameters. The system was heated by four clam-shell heaters. Two heaters surrounded the
preheater, and two heaters surrounded the upper bed area. A ceramic fiber material was used
around the heaters in order to insulate the system heat. Heaters were independently controlled
through two programmable logic controllers and monitored using K Type thermocouples.
Thermocouples were mounted in the radial center of the fluidized bed along the several axial
locations below, within, and above the bed. A cyclone with an inlet of 50mm inner diameter
removed chars from the entrained gas flow exiting the heated reactor area. The reactor process
diagram and operating conditions are seen in Figure 3-1, and Table 3-1 respectively.

Figure 3-1 Process Diagram of CERC Reactor. (1) Feedstock hopper, (2) steam generator, (3)
preheater, (4) fluidized bed 500 °C, (5) internal cyclone, (6) condenser, (7) condensate
collection, (8) particle filter, (9) mass flow meter, (10) Agilent 4900 micro-GC, (11) afterburner,
(12) 5 micron particle filter 500 °C, (13) tar sampling impinger bottles, (14) APEX XC-60 gas
sampler. Adapted from Butler, 2013. Used with Permission. [25]
### Table 3-1 CERC FPO reactor operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Feedrate (kg/hr)</td>
<td>0.5</td>
</tr>
<tr>
<td>Gas velocity (m/s)</td>
<td>0.34</td>
</tr>
<tr>
<td>Nitrogen flow (LPM @ ambient)</td>
<td>6.60</td>
</tr>
<tr>
<td>Hopper N₂ purge (LPM)</td>
<td>0.11</td>
</tr>
<tr>
<td>Fluidizing bed temperature (ºC)</td>
<td>500</td>
</tr>
<tr>
<td>Max Bed Pressure drop (kPA)</td>
<td>30.0</td>
</tr>
</tbody>
</table>

In total, five pyrolysis productions were attempted using the CERC reactor. In each attempt a multitude of failures prohibited more than 50ml of FPO to be collected from the reactor. Fatigue in the feed hopper assembly resulted in failures to pressurize the hopper as seen in Figure 3-2. Due to inability to sufficiently cool the feeder inlet pipe, significant clogging occurred within the feeder tube as a result of feedstock pyrolysing too quickly as shown in Figure 3-3. Furthermore, from what feedstock was able to reach the fluidized bed, significant bed agglomeration was evident which disrupted the fluidizing conditions of the reactor and impaired production. An example of an agglomerated particle is shown in Figure 3-4.
Figure 3-2 Torn Feedhopper in CERC FPO Reactor

Figure 3-3 Clogging at exit of feeder tube in CERC FPO Reactor

Figure 3-4 Agglomerated biomass and silica bed material in CERC FPO reactor.
The issue of particle agglomeration was found in other literature accounts [26] to be a result of produced sticky molten particles from partially pyrolysed feedstock interacting with produced char and bed material. The partial pyrolysis of feedstock was indicative of undesirable heat transfer conditions within the reactor [26,27]. Given the multitude of technical challenges facing the CERC FPO reactor, the hardware was decommissioned and the development of a more robust system was initiated.

3.2 PPC Reactor Development

A small pilot scale fluidized bed reactor in the Pulp and Paper Centre of the University of British Columbia was determined to be suitable for the project needs in developing a continuous production system of FPO. The reactor system was previously used for biomass and coal gasification in a temperature range of 0-1000°C [28]. To operate the system as a FPO reactor, several changes were made in the upstream hardware, the feed hopper, the screw feeder and the nitrogen supply to the reactor. A particle entrainment system as a means to introduce ground particles into the fluidizing gas from a remote screw feeder was developed. Figure 3-5 illustrates the reactor systems as a process and instrumentation diagram. The core of the pyrolysis system was a fluidized bed reactor operated in the bubbling flow regime with a reactor inner diameter of 72 mm and a length of 1.45 m. A bed heat transfer medium of silica sand with an average particle diameter of 425 µm and particle density of 1955 kg/m³, as reported by the silica supplier, was used as an energy carrier. The bed formed a static height of 31 cm above the supported gas distributor plate at the reactor bottom. The reactor system was heated by a pair of semi circular electrical heaters installed the reactor area with refractive material encasing the exterior or the heater system. The heater temperature settings were set such that the temperature in the bubbling regime (thermocouple T2a) measured the idealized 500°C operating conditions. The temperature
of the volatile compounds above the bed was measured by thermocouple T3b, whereas the
temperature of the reactor wall was measured from T13 and T1.

Softwood pellets were used as raw material and crushed and sieved to a desired particle size
similar to optimal values from the literature [2,13] of Sauter mean particle diameter of 410 µm.
The crushed and sieved biomass was placed in the feed hopper with a maximum storage capacity
of about 10 kg of loosely packed material. The feed hopper was purged under 35 kPag nitrogen
supply to ensure an atmosphere void of oxygen. The nitrogen purge served as a safety measure
against the explosive nature of sawdust inside the storage bin and to prevent back pressure from
the reactor to the hopper. The sawdust was transported via a mechanical screw feeder from the
hopper to the tube where it was entrained by the conveying nitrogen gas (NF2) into the bottom of
the reactor. This gas was provided by liquid nitrogen (LN₂) provided by Praxair. The flow rate of
the nitrogen and thus the relative residence time of the volatiles could be controlled by the
rotameters seen in . The particle entrainment system had to be continuously leak tested to prevent
clogging. The pressure inside the feed hopper (P10) was maintained greater than the pressure in
the reactor (P11) before starting to feed the system with sawdust.

Downstream of the reactor, the hot gas stream was separated from entrained char particles in two
sequential cyclones. The upper flanges of the cyclones had a diameter of 72 mm, a height of 75
mm and a conical section of 105 mm. The inlet of the cyclones had a height of 30 mm and a
width of 20 mm. Beneath the cyclones were separated storage compartments with a diameter of
26 mm for measuring collected char.

Following the sequential cyclones, pyrolysis vapours were condensed through two double pipe
heat exchangers. The first pair of the condensers was cooled by ambient air to an outlet gas
temperature (T7) of about 120 °C, while the second pair was cooled by water to an outlet gas
temperature (T6) of about 20 °C. The system pipes between the reactor and the condensers, as
well as the top of the cyclones were wrapped with electrical heating tape and fiberglass isolation
to prevent premature volatile condensation. From the water-cooled condenser, the liquid product,
FPO, was directed into a glass vessel for collection. The non-condensable gases were passed
through a knock-out drum filled with water to remove remaining entrained particles and vapours.
The residual pyrolysis oil in the gas was separated by a filter with a polycarbonate bowl and was
collected in a bin. Non-condensable gases were directed to an afterburner and ignited with
natural gas. The system thermocouples and pressure transducers recorded the temperature and
pressure distributions during experimental campaigns using LabVIEW.
Figure 3-5 PPC FPO P&ID
3.3 PPC Reactor Operating Conditions

The PPC FPO operating procedure was developed in accordance with the initial fluidizing and heat transfer conditions determined from the most relevant literature sources as discussed in section 2.1. An investigation of the reactor performance quantified by FPO product yield, was performed by a visiting researcher and summer student which concluded that the reactor conditions determined to optimize FPO yield by Salehi et al., 2011, including reactor temperature and reactor pressure drop were in agreement with the performance characteristics of the PPC reactor [29] A summary of the PPC reactor operating conditions is seen in Table 3-2.

<table>
<thead>
<tr>
<th>Table 3-2 Operating conditions of PPC Reactor for FPO production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Feedrate (kg/hr)</td>
</tr>
<tr>
<td>Gas velocity (m/s)</td>
</tr>
<tr>
<td>Nitrogen flow (LPM @ ambient)</td>
</tr>
<tr>
<td>Hopper N₂ purge (LPM)</td>
</tr>
<tr>
<td>Fluidizing bed temperature (°C)</td>
</tr>
<tr>
<td>Max Bed Pressure drop (kPA)</td>
</tr>
</tbody>
</table>

Furthermore, the reactor system optimization resulted in the determination of the reactor settings such as nitrogen flow rates, heater settings, and service intervals for continuous FPO production procedures. A summary of the of findings is presented as the PPC FPO Production.

3.4 Reactor FPO Yield

Before and after each experimental run, the mass of the bio-oil in the collection vessel (m_{bio-oil, collector}), the filter bin (m_{bio-oil, filter}), the char collection bag (m_{char}), and the sawdust were measured (m_{biomass}). Because values of the noncondensable gases, and the system residue (
m_{\text{residue}} + m_{\text{NCG}} \) were not measured, a mass balance (equation 3.1) could not be completed. Instead a collection efficiency was determined, \( Y_{\text{bio oil}} \) (equation 3.3).

\[
m_{\text{biomass}} = m_{\text{bio-oil}} + m_{\text{char}} + m_{\text{residue}} + m_{\text{NCG}} \tag{3.1}
\]

\[
m_{\text{bio-oil}} = m_{\text{bio-oil, collector}} + m_{\text{bio-oil, filter}} \tag{3.2}
\]

\[
m_{\text{NCG}} = W_{N2} \cdot t \cdot \frac{x_{\text{NCG}}}{x_{N2}} \tag{3.3}
\]

\[
Y_{\text{bio oil}} = \frac{m_{\text{bio-oil}}}{m_{\text{biomass}}} \cdot 100, [%] \tag{3.3}
\]

Throughout the production period of FPO in the PPC reactor, an average collection efficiency of \( Y_{\text{bio oil}} \) was determined to be 31%. This value, much lower than the values reported in the literature, traditionally ranging between 65-85 wt% [3], was explained by a large fraction of residual material found to have been built up over time in the pipe walls between the cyclones and the condensers.

3.5 Procurement of Commercial FPO

From literature accounts [3,5,16] as well as observations from the PPC system, it was obvious that significant variability in the properties of produced pyrolysis oil existed as a result of variability in feedstock composition, reactor heating and quenching rates, residence times, and ultimate storage conditions. For comparison of the in-house FPO product, a commercial source of FPO was procured from the Biomass Technology Group, BTG, in the Netherlands. BTG reactor specifics and feedstock were not disclosed; however, it was communicated upon purchasing that the product was produced in a fast pyrolysis reactor from a general softwood feedstock. 30L of the fuel was purchased and stored in a 4°C storage area under a nitrogen purge.
until needed for characterization and upgrading.
Chapter 4  Upgrading Fast Pyrolysis Oils

Having developed the facilities and procedures for producing in-house FPO and procuring a commercial standard FPO product, two methodologies were explored for FPO product upgrading. Literature studies offered several accounts detailing the incompatibility of FPO with modern internal combustion systems that emphasize the need to improve FPO characteristics to more closely resemble those of traditional transportation fuels [5]. To explore simple upgrading methods for implementing FPO products as drop-in fuels in internal combustion engines, various upgrading techniques were considered with particular attention given to minimize complexity of the upgrading process and avoid higher costs. Continuing the work outlined in Jiang and Ellis, 2010 [22] a blending technique of FPO with biodiesel and a 4% total volume octanol surfactant was adopted as an upgrading method.

4.1  Upgrading Procedures with Surfactant

Jiang and Ellis, 2010 report the optimal conditions for emulsion stability of FPO and biodiesel are achieved with initial 40:60 volumetric ratios of FPO:Biodiesel and 4% volume 1-Octanol. Mixing was achieved with a stirring intensity of 1200 rpm and preparation temperature of 30°C, after which the blend was allowed to settle for 24 hours resulting in two distinctive layers. A visualization of the resulting volumetric distributions is seen below in Figure 4-1 FPO-Biodiesel volumetric product distribution. The top biodiesel rich layer showed an increase in volume from the initial biodiesel fraction, which confirms the transfer of compounds from FPO to the biodiesel. The exact volumetric distribution is not representative of the experimental results, rather a simplified visual aid to show the process.
To prepare the fuels for engine testing, initial FPO upgrading entailed blending 20:80 and 40:60 FPO:biodiesel by volume using neat biodiesel and pyrolysis oil produced in house (FPO-IH) and commercially obtained (FPO-C). Each blend was stirred at room temperature in atmospheric conditions at 300 rpm for 180 minutes with an orbital shaker and allowed 24 hours to settle. The upper layer of the blends was decanted and stored at 4°C until they were required for further characterization and engine fueling. These decanted upper layers are referred to as LB - Low Blend (20:80) and HB High Blend (40:60), depending on the initial volume fractions of biodiesel and FPO. The high blend ratio was selected due to the findings of Jiang and Ellis, 2010 reporting the specified blend fraction to exhibit the optimal stability. The lower blend fraction was selected in order to consider a median value between neat biodiesel performance and the high blend fuel.

The reproduced procedure deviated from the literature methodology in stirring intensity quantified as the rotational speed of the mixer, however were otherwise representative of the upgrading technique. Due to the large volumes of fuel required for engine testing (10L) in
comparison with bench scale experiments in the literature (0.1L), the maximum stirring intensity achieved was the maximum rotational speed of the orbital shaker used to prepare the required fuel quantities, 300 rpm. Biodiesel was sourced from a commercial supplier, New World Energy in Bellingham, WA and Octanol was sourced from Sigma Aldrich (99.5% purity).

Biodiesel, FPO, and Octanol were measured in graduated glass cylinder and combined in a sealed mixing vessel where they were mixed in an orbital shaker at 300 rpm. The liquid was allowed to settle over a 24 hour period, after which the top biodiesel rich later was decanted and stored at 4 ºC. Table 4-1 below depicts the volumetric distribution of the initial and final fuel blends. The blend volumetric ratios were investigated in 200ml sample volumes and were performed in triplicate.

<table>
<thead>
<tr>
<th>FPO Source</th>
<th>Initial Volume Biodiesel (%)</th>
<th>Initial Volume FPO (%)</th>
<th>Upper Layer Volume (%)</th>
<th>Lower Layer Volume (%)</th>
<th>Increase Biodiesel Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB - In House</td>
<td>80</td>
<td>20</td>
<td>85</td>
<td>15</td>
<td>6.3</td>
</tr>
<tr>
<td>LB - Commercial</td>
<td>80</td>
<td>20</td>
<td>84</td>
<td>16</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The resulting volumetric distributions from the low blends (20:80) resulted in an increase in biodiesel layer volume by about 5%, while the high blend (40:60) showed an increase of about 8% volume. Jiang and Ellis, 2010 reported that the top layer was primarily composed of nonpolar species, leaving the lower layer to contain most of the lignin and water compounds. Though direct analysis was not performed during the in-house blends, the immiscibility of water
and octanol was thought to have led to the transfer of octanol primarily into the biodiesel rich phase.

4.2 Upgrading Procedure without Surfactant

A second round of upgrading was performed without the use of octanol as a surfactant. Internal research from other graduate students ultimately determined that the use of octanol did not have an impact on the quantity of volume transferred from FPO to biodiesel, or on the quality of the biodiesel rich FPO layers [30]. As the goals of the project were to consider simple and low cost solutions to FPO upgrading, a second fuel batch was prepared without a surfactant however under the same procedure used as the initial fuel blends. Table 4-2 shows the relative volumetric percentage of biodiesel and FPO and resulting fuel blends from high and low blend fractions with in-house and commercial FPO.

<table>
<thead>
<tr>
<th>FPO Source</th>
<th>Initial Volume Biodiesel (%)</th>
<th>Initial Volume FPO (%)</th>
<th>Upper Layer Volume (%)</th>
<th>Lower Layer Volume (%)</th>
<th>FPO transferred to Biodiesel Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB - In House</td>
<td>80</td>
<td>20</td>
<td>85</td>
<td>15</td>
<td>6.3</td>
</tr>
<tr>
<td>LB - Commercial</td>
<td>80</td>
<td>20</td>
<td>84</td>
<td>16</td>
<td>5.0</td>
</tr>
<tr>
<td>HB - In House</td>
<td>60</td>
<td>40</td>
<td>67</td>
<td>33</td>
<td>11.7</td>
</tr>
<tr>
<td>HB - Commercial</td>
<td>60</td>
<td>40</td>
<td>66</td>
<td>34</td>
<td>10.0</td>
</tr>
</tbody>
</table>

The resulting volumetric transfer of compounds from FPO into the biodiesel rich fuel-blend layers without the addition of octanol proved to be similar to the performance of the octanol blends reported in. Table 4-1 and in agreement with the alternative motivating research.
4.3 Characterization of Products with respect to ASTM Standards

Through a series of analytical tests, blend fuels were characterized in order to quantify the changes from the initial biodiesel and crude FPO feedstock. Select properties were used as metrics in order to consider the relevant effects of product upgrading. In particular the following metrics were analyzed: acidity, viscosity, water content, heating value, elemental composition, and volatility of blend fuels from traditional neat diesel and biodiesel commercial fuels. Fuel acidity represents the relative corrosivity of a fuel, which may interfere and ultimately degrade engine components. Due to the high viscosity of crude FPO and the incompatibility of injector systems with high viscosity fuels [7], fuel viscosity is important to quantify relative changes from the upgrading process. Water content, heating value, and elemental composition measurements provide insight into the relative energy density of the fuel and are useful for combustion performance analysis. Fuel volatility measurements provide insight into fuel behavior during in-cylinder direct-injection processes.

Two standards were referenced for comparison of blend fuel properties against existing commercial fuels for diesel engines, ASTM-D6751 [31] and ASTM-D975 [19] for biodiesel, and diesel, respectively. A select list of properties comparing the two fuels is seen below in Table 4-3, below. Most notable are the lower heating value of biodiesel in relation to diesel, the greater viscosity of biodiesel, and the higher boiling point of biodiesel. Variations in property standards such as the range presented in Boiling Point, Flash Point, and Cetane Number is the result of varying molecular composition of the fuels, which may impact the overall property [32].
### Table 4-3 Select ASTM biodiesel and diesel standard property values as reported by ASTM D6751 and ASTM D975

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel ASTM D975 [19]</th>
<th>Biodiesel ASTM D6751 [31]</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value</td>
<td>~40</td>
<td>~33</td>
<td>kJ/l</td>
</tr>
<tr>
<td>Viscosity @ 40° C</td>
<td>1.3 - 4.1</td>
<td>1.9 - 6.0</td>
<td>mPa•s</td>
</tr>
<tr>
<td>Specific Gravity @ 60° C</td>
<td>0.85</td>
<td>0.88</td>
<td>kg/l</td>
</tr>
<tr>
<td>Density</td>
<td>7.079</td>
<td>7.328</td>
<td>lb/gal</td>
</tr>
<tr>
<td>Water and Sediment</td>
<td>0.05 max</td>
<td>0.05 max</td>
<td>% vol</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.0015</td>
<td>0.0 - 0.0024</td>
<td>wt. %</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>180 - 340</td>
<td>315 - 350</td>
<td>°C</td>
</tr>
<tr>
<td>Flash Point</td>
<td>60 - 80</td>
<td>130 - 170</td>
<td>°C</td>
</tr>
<tr>
<td>Acid Number</td>
<td>0.05 max</td>
<td>0.05 max</td>
<td>g KOH/g</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40 - 49</td>
<td>42 - 89</td>
<td></td>
</tr>
</tbody>
</table>

#### 4.3.1 Analytical Characterization Methods

Several analyses were performed in-house; including acidity which was quantified through titration to determine total acid number, water content through Karl Fisher titration, dynamic viscosity using a rotary viscometer, and thermogravimetric analysis which offered insight into mass loss rates from constant heating. Heating value and elemental analysis were measured in a third party lab, (Econotech Services in Delta, B.C.) due to UBC laboratory limitations. For all characterizations, tests were performed at least in triplicate and the resulting mean values are presented.

#### 4.3.2 Water Content

The water content investigations were carried out with a volumetric Karl Fischer Titration method in accordance to ASTM D6304, Standard Test Method for Determination of Water in
Petroleum Product. A Metrohom 794 Basic Titrino was used in conjunction with Sigma Aldrich Hydranal Composite 5 titrant and dry Methanol ($\leq 0.01\%$ Water) as a solvent medium.

4.3.3 Total Acid Number

The Total Acid Number (TAN) was measured with an automatic titration system HI902 from Hanna Instruments using aqueous potassium hydroxide (0.1 M) standard titrant and acetone supplied by Sigma Aldrich (99.9%) as the titration solvent. ASTM D664 is traditionally implemented in determining of acid number; however a rapid aqueous method was used in order to conserve solvents more often needed with petroleum analysis [33]. A sample mass of 0.10 – 0.25 g was dissolved in 100 ml acetone before every titration. After titrating the sample solution, the titration system reported the end-point titrant volume.

4.3.4 Dynamic Viscosity

The dynamic viscosity was determined using an Anton Paar rheometer MCR 501 in rotational mode. 20 ml of a fuel sample was filled into the device and heated to 40°C, the temperature ASTM viscosity values are measured, using an external circulating temperature controlled bath. Measurement time was kept constant to 100 seconds with constant shear ramping rates. The geometry of the sample device was a cylindrical couette piece.

4.3.5 Heating Value and Elemental Analysis

The elemental composition and heating value of the samples were determined by Econotech, Richmond, BC. The reported values of carbon, hydrogen and nitrogen content were measured used ASTM D5291, and the balance was assumed to be oxygen because ash was not quantified. The heating value was measured using bomb calorimeter in accordance with ASTM D4809.
4.4 Analytical Results

The results of the characterization of test fuels and crude FPO feedstock is presented against the standard ASTM values of biodiesel and diesel below in Table 4-4.

<table>
<thead>
<tr>
<th></th>
<th>Water Content ±0.01 (%)</th>
<th>Acid Number ± 0.3 (mg KOH/g)</th>
<th>Dynamic Viscosity (40º C) ±0.2 (mPa*s)</th>
<th>Gross Heating Value (kJ/kg)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>∆O</th>
<th>Stoichiometric Air-Fuel Ratio</th>
<th>Estimated Cetane Number Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>0.05</td>
<td>-</td>
<td>3.4</td>
<td>44.8</td>
<td>14.7</td>
<td></td>
<td></td>
<td></td>
<td>40-49 [18]</td>
<td></td>
</tr>
<tr>
<td>Biodiesel</td>
<td>0.18</td>
<td>0.6</td>
<td>4.6</td>
<td>39.9</td>
<td>77.6</td>
<td>11.9</td>
<td>&lt;0.1</td>
<td>10.5</td>
<td>12.5</td>
<td>42-89 [18]</td>
</tr>
<tr>
<td>FPO IH</td>
<td>24.8</td>
<td>110</td>
<td>63.3</td>
<td>13.8</td>
<td>23.5</td>
<td>8.54</td>
<td>&lt;0.1</td>
<td>68.0</td>
<td>-</td>
<td>0-35 [11]</td>
</tr>
<tr>
<td>FPO C</td>
<td>22.6</td>
<td>79.8</td>
<td>66.5</td>
<td>15.6</td>
<td>39.5</td>
<td>7.89</td>
<td>0.11</td>
<td>52.5</td>
<td>-</td>
<td>0-35 [11]</td>
</tr>
<tr>
<td>LB IH</td>
<td>0.36</td>
<td>13.3</td>
<td>4.5</td>
<td>39.4</td>
<td>76.3</td>
<td>11.2</td>
<td>&lt;0.1</td>
<td>12.5</td>
<td>12.1</td>
<td>-</td>
</tr>
<tr>
<td>LB C</td>
<td>0.34</td>
<td>9.9</td>
<td>4.5</td>
<td>40.0</td>
<td>76.9</td>
<td>11.9</td>
<td>&lt;0.1</td>
<td>11.2</td>
<td>12.2</td>
<td>-</td>
</tr>
<tr>
<td>HB IH</td>
<td>0.55</td>
<td>16.4</td>
<td>4.1</td>
<td>30.0</td>
<td>76.3</td>
<td>11.7</td>
<td>&lt;0.1</td>
<td>12.0</td>
<td>12.4</td>
<td>-</td>
</tr>
<tr>
<td>HB C</td>
<td>0.64</td>
<td>9.0</td>
<td>4.3</td>
<td>26.0</td>
<td>77.7</td>
<td>11.9</td>
<td>&lt;0.1</td>
<td>10.4</td>
<td>12.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Though a majority of the water from FPO remained in the lower lignin-rich layer, the blended fuels exhibited higher water content than the neat biodiesel. Water content in the low blend fuels (LB-IH, LB-C) doubled from neat biodiesel values while high blend fuels showed nearly three times the neat biodiesel water content. The acidity of the fuels increased as well with increasing FPO blend concentrations. Higher water content and acid number in FPO IH than FPO C also translated to high water content and acid number in the respective blend. The dynamic viscosity of FPO blends was slightly lower than that of biodiesel for high blend fuels, though no change was observed for the low blends, relative to biodiesel. In agreement with other experimental work [34], the heating values of the low blend fuels were unchanged from neat biodiesel, likely as a result of compounds with similar heating values as the blend fuel being transferred to the biodiesel phase. High blend fuels showed a significant decrease in heating value for both FPO
blends relative to the biodiesel, though this reduction does not seem to be related to the water content.

The elemental analysis of C-H-N mass distribution yields the oxygen content by difference with an assumption of negligible ash and sulfur content. LB-IH, LB-C, and HB-C exhibit an increase in oxygen content relative to neat biodiesel; however, HB-IH showed a slight decrease in oxygen content.

Despite the findings of relatively consistent C/H content from the elemental analysis, there is inconsistency in the expected heating values of the fuels, particularly with respect to the high-blends. Because the heating value and elemental analysis investigations were performed by a third party, comments on the experimental procedures or datasets cannot be made. It could be hypothesized that incomplete combustion of the high-blend fuels occurred in the calorimeter which reduced the measured heating value of the fuels.

4.5 Thermogravimetric Analysis

A TA Instruments SDT Q600 was used to perform a thermogravimetric analysis (TGA) to provide insight into fuel evaporation rates. Samples were heated at a constant rate of 10°C/min from room temperature to 500°C. The furnace is continuously purged with a nitrogen flow of 100 mL/min to prevent oxidation of the sample. The resulting mass loss and derivative mass loss provide insight into fuel evaporation characteristics. Figure 4-2 shows the derivative thermogravimetric (DTG) mass loss rate for a constant furnace heating rate of 10°C/min under a Nitrogen purge for diesel and biodiesel, crude FPO feedstock, and the four fuel blends.
The TGA measurements of fuel were performed in triplicate to verify that the trends were repeatable. The diesel analysis indicates a peak mass loss rate half of that of biodiesel or FPO blends; however, across a temperature range roughly 50ºC broader than compared biodiesel and FPO fuels. LB-IH and LB-C fuels showed little deviation from neat biodiesel DTG curves with the exception of a slightly lower peak mass loss value. HB-IH and HB-C exhibit similar, albeit slightly higher mass loss rates until around 220ºC. At temperatures above this, HB-IH continues to increase to a maximum mass loss at a temperature below that of biodiesel but greater than all other fuels tested. The HB-C mass loss follows the same qualitative trends as that of the biodiesel, but at lower temperatures.

At low temperatures (50-100ºC) the crude FPO samples indicated mass loss rates consistent with previous literature highlighting the release of highly volatile compounds and water fractions [22]. The predominant peaks in both crude FPO samples from 100 - 150ºC also correspond to other findings which have been attributed to the decomposition of organic acids, phenols, and
furans [34]. Ultimately, the DTG characterization revealed that the volatility of the blend fuels showed similar trends to that of neat biodiesel. DTG analysis was performed in triplicate to assure the repeatability of the analysis.

4.6 Assessment of Fuel Characteristics

Characterizing relevant properties of crude FPO and upgraded blends offers insight into the relative fuel quality of biodiesel:FPO blends in relation to commercial biodiesel and diesel fuels. Significant reductions in acid number from crude FPO suggested that fuel corrosivity might not be as severe as with crude FPO. Reductions in water content from the original crude FPO contributed to increasing the fuel heating value by a factor of two. The dynamic viscosity of the fuels also showed values similar to neat biodiesel, greatly reduced from original FPO values.
Chapter 5  Combustion Testing

To evaluate combustion and emission characteristics of FPO – biodiesel prepared fuels as drop-in fuels, a single cylinder research engine in the Clean Energy Research Centre was commissioned with commercial OEM based fuel supply hardware. The measurement campaign utilized thermodynamic analysis as well as high speed photography in order to measure fuel performance against neat biodiesel and diesel fuels. The combustion analysis was meant to compliment the analytical characterization of pyrolysis oil derived fuels as a means of comparing the fuel performance against other investigations of FPO derived fuels. Three measurement campaigns were performed. The initial engine test was performed with one prepared fuel blend ratio at two engine-operating points. The following campaign utilized the engine in optical mode in order to observe visible combustion phenomena from the first campaign. The final testing round included two fuel blend ratios measured at six different engine operating conditions.

5.1  Engine Facilities

The experimental facilities utilized for combustion testing included a single cylinder research engine, a Mustang dynamometer, an AVL emissions bench, and particulate matter measurement system. The engine used was a naturally aspirated, single-cylinder, heavy-duty four-stroke diesel engine (Ricardo Proteus) attached to a SP800 Mustang Dynamometer. Due to potential fuel system failure caused by pyrolysis oil combustion testing [7], extra precaution was taken to ensure material compatibility. A high-pressure direct-injection common rail fuel delivery system was assembled using production components from Bosch. The fuel supply components are commercially used in LLY Chevrolet Duromax Diesel V8 engines. The common rail fuel injection system was upgraded to use stainless steel compression fittings where possible and flexible fuel lines were replaced with biodiesel resilient elastomer hoses for low-pressure
applications (e.g., fuel injector return line). No modifications were made to the fuel injector or high-pressure pump. Table 5-1 details the research engine specifications.

| **Displacement** | 1998 cc |
| **Bore** | 130 mm |
| **Stroke** | 152 mm |
| **Compression Ratio** | 14.25:1 |

Table 5-1 Test Engine Specifications

| **Block** | Ricardo Proteus |
| **Fuel Pump** | Bosch CP3.3 |
| **Injector** | Bosch CRIN2 |
| **ECU** | Custom based on NI Powertrain Control Modules |

Figure 5-1 provides the process control and instrumentation components of the engine test facility. K-type thermocouples were implemented in the intake and exhaust manifolds, fuel supply line, oil pan, and engine coolant to monitor the system temperature. Fuel temperature was monitored and limited to 55°C in the fuel pail in order to minimize potential thermal degradation of the FPO blended fuels, while the fuel mass flow rate was gravimetrically determined with a scale to measure the change in fuel mass throughout the duration of the measurement period. In-cylinder pressure was measured in-situ with a piezo-electric pressure transducer (Kistler 6125C) and was used for heat release rate analysis. Low-pressure fuel supply pressure was monitored through an Omega pressure transducer and high-pressure fuel supply was measured from the Bosch rail-mounted pressure transducer. A mass airflow sensor provided the airflow rate to the engine. Two heated sampling lines were mounted in the exhaust line for sampling emissions of gasses and particulate. Gaseous exhaust emissions were measured from a heated sampling line and filter and directed to an AVL Emissions Bench, (CEB II) to characterize the exhaust stream \( \text{O}_2, \text{CO}_2, \text{CO}, \) unburnt hydrocarbons (uHC), and NOx concentrations. The \( \text{O}_2 \) concentration was measured using a paramagnetic detector; \( \text{CO}_2 \) and CO were measured through a non dispersive infrared sensor (NDIR); uHC were measured with a flame ionizing detector; and NOx was measured through chemiluminescence. Diluted particulate matter was sampled using a
separate heated exhaust line in conjunction with an eductor dilutor, driven by bone dry air from a compressor (Ingersoll-Rand IRN50H-CC). The diluted particulate matter (PM) sample line was directed through a low range CO\(_2\) analyzer to determine the dilution ratio, typically in ranging 15-20:1, as well as a TSI DustTrak 8533 to measure PM mass concentrations.

Figure 5-1 Process and Instrumentation of Engine Test Facilities. P: Pressure Transducers. T: K-Type Thermocouple. 1-Low Pressure Fuel Pump. 2-Fuel Filter. 3-Bosch CP3 High Pressure Fuel Pump. 4- Fuel Return Heat Exchanger 5-Fuel Rail and Injector Return Line
5.2 Combustion Testing Round 1

The primary motivation of the initial engine testing campaign was to ensure steady engine operation with FPO derived fuels, assess the performance, and ultimately develop a more robust testing strategy. Conservative measures were taken in this first attempt of running FPO fuels in an engine to prevent hardware failures. These measures included relatively low engine loads and speeds, low blend ratio fuels, and fuel system inspections after every measurement in order to observe changes in the fuel supply system. Thermodynamic and emission measurements were made with two FPO blends of equal mixture ratios at two engine operating modes with constant engine speed and varied fuel injection timing.

Throughout the test campaign of the emulsion fuels, several hardware failures were observed which resulted in temporary engine shutdowns and redesigns of fuel supply systems. Low-pressure fuel supply hoses initially routed with chemically resilient Viton fluoroelastomers were replaced with stainless steel compression fittings. A low-pressure diaphragm pump that used to prime the high pressure pump failed after 2 hours of engine operation. Remaining engine tests required the high-pressure pump to be manually primed before engine startup.

5.2.1 Test Fuels

The first round of pyrolysis fuel testing was performed using the fuels described in section 4.1. The fuels were of lower blend fractions and were prepared with a 4 % vol. 1-octanol surfactant. Though the ultimate fuel fractions were not quantified for emulsion stability, as referenced in Jiang and Ellis, 2010, they are referenced as emulsions within the context of the engine testing due to the use of the surfactant. Table 5-2 summarizes the FPO test fuels. FPO 1 sourced in-
house derived FPO and FPO 2 sourced a commercially available FPO. In addition to the emulsions, neat biodiesel and diesel were tested as well at the specified engine test modes.

<table>
<thead>
<tr>
<th>FPO Source</th>
<th>Initial Volume Biodiesel (%)</th>
<th>Initial Volume FPO (%)</th>
<th>Upper Layer Volume (%)</th>
<th>Lower Layer Volume (%)</th>
<th>Increase Biodiesel Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- In House</td>
<td>80</td>
<td>20</td>
<td>85</td>
<td>15</td>
<td>6.3</td>
</tr>
<tr>
<td>2 - Commercial</td>
<td>80</td>
<td>20</td>
<td>84</td>
<td>16</td>
<td>5.0</td>
</tr>
</tbody>
</table>

5.2.2 Test Points

Engine testing was performed over a series of five days. Two test points were chosen for a low load and high load operating condition. A pilot injection was kept constant between the two loads starting a -17 CAD aTDC lasting 0.48 ms. High and low engine load points were achieved through varying the main injection length. Both points began their main injection at -6 CAD aTDC, with the low load point lasting 0.65 ms and the high load lasting 1.08 ms. The diesel referenced gross indicated mean effective pressure (GIMEP) is included and represents the indicated work $W_i$ normalized by the swept volume of the engine as seen in equation 5-1.

$$ \text{GIMEP} = \frac{W_i}{V_s} \quad (5-1) $$

The indicated work represents the work done by the combustion gases on the piston ($\int p dV$), but does not consider parasitic losses such as engine friction.

During initial load testing, mode 1 and mode 2 values resulted in a gross indicated mean effective pressure (GIMEP) of 400 kPa and 570, respectively. Fuel injection pressure of 1000 bar, engine speed of 1000 rpm, and valve timing were kept constant. When taking engine
measurements, engine temperature was found to have significant impact on the thermodynamic performance of the fuels, as well as the relative emissions. Each measurement was taken after the engine had reached an exhaust temperature not varying by more than 2 °C as measured by a thermocouple 35cm downstream of the exhaust valve. A summary of the engine operating modes including fuel timing is seen below in Table 5-3.

Table 5-3 Summary of engine operating modes during first engine testing

<table>
<thead>
<tr>
<th>Test Mode</th>
<th>$\square_{\text{Pilot}}$ (CAD aTDC)</th>
<th>$\tau_{\text{Pilot}}$ (ms)</th>
<th>$\square_{\text{Main}}$ (CAD aTDC)</th>
<th>$\tau_{\text{main}}$ (ms)</th>
<th>GIMEP Diesel (kPa)</th>
<th>Engine Speed (rpm)</th>
<th>Injection Pressure (Bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-17</td>
<td>0.45</td>
<td>-6</td>
<td>1.08</td>
<td>700</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>-17</td>
<td>0.45</td>
<td>-6</td>
<td>0.65</td>
<td>430</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

5.2.3 Testing Procedures

The fuels were maintained in an oxygen-free environment at 4 °C until system fueling. As needed, the fuel was brought into the engine facilities and filled into the fuel pail. For each fuel measurement campaign, the engine was allowed to warm to a standard repeatability point, mode 2. Measurements were recorded only after exhaust and coolant temperature had a variation of less than 2.0 and 0.5°C, respectively, over a period of 5 minutes. The procedure was replicated for each fuel at each test condition. During each fuel change, the fuel supply system was purged, rinsed with biodiesel and flushed with the next fuel to be tested.

5.2.4 Thermodynamic Performance

From the in-cylinder pressure, a first law analysis provides the net heat release rate $\frac{dQ_n}{d\theta}$, as seen in Equation 5-2 below [35]. P is the measured in-cylinder pressure in kPa, V is the cylinder
volume \((m^3)\) defined by the crank position \(\theta\), and the specific heat ratio is taken to be constant at \(\gamma = 1.37\). The net heat release rate indicates the rate at which energy is converted by combustion and lost from the cylinder by heat transfer.

\[
\frac{dQ_n}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta}
\]  \(\text{(5-2)}\)

Below in Figure 5-2 the low load (mode 1) heat release indicates two noticeable trends in the fuel performance. Emulsion 2 and diesel show very similar combustion patterns throughout the premixed combustion phases. Similarly, emulsion 1 and biodiesel have similar premixed and mixing control combustion phases. During high load (mode 2) operation seen in Figure 5-3 the combustion mechanisms of all four fuels appear similar, with the exception of diesel showing elevated heat release during premixed combustion stages and relatively elongated mixing controlled combustion. The short plateau of heat release rate near 0 CAD of all four fuels likely corresponds with the end of the main fuel injection. Similarly seen in the low load performance of the fuels, the variation in heat release trends correlates with the duration of the main fuel injection event.

![Figure 5-2 Mode 2 heat release rate of four test fuels](image.png)
The extent to which the fuel energy was converted to work was quantified using the gross indicated thermal efficiency. Gross indicated thermal efficiencies of the fuels at various operating modes were calculated according to Equation (5-3) and are shown below in Figure 5-4.

\[ \eta_{th, i} = \frac{W_i}{m_f \cdot LHV} \]  

(5-3)

It is generally reported that the thermal efficiency of biodiesel is comparable to engines running with mineral diesel with some reports suggesting slightly greater efficiency [36]. The mode 1 indicated thermal efficiencies show relatively similar fuel performance amongst all the fuels, while there is a significant decrease for both FPO emulsions at mode 2. This finding agrees with other investigations that examined blended FPO fuels in internal combustion engines [7,37,38]

*Figure 5-3 Mode 1 heat release rate of four test fuels*
Ultimately, the initial thermodynamic analysis of low blend ratio FPO fuels in relation to neat biodiesel and diesel performance in a compression ignition engine showed similar results to reported FPO performance with respect to thermodynamic efficiency [23], however the trends quantified in the heat release rates, specifically the similarities between diesel and emulsion 2 and biodiesel and emulsion 1 suggested further analysis of fuel performance was required.

5.2.5 Emissions Performance

To compliment the thermodynamic measurements from the engine during each operating point, emission measurements were recorded with an AVL exhaust bench in ppm and normalized to specific indicated engine power. The normalized exhaust emissions provide another means of comparing the performance of FPO fuels against the tested commercial diesel and biodiesel.

Figure 5-5 depicts specific CO emissions of the four test fuels at both operating points. High load CO emissions do not show significant variation amongst the four fuels, while there exists
substantial differences at lower loads. In a previous study, CO emissions from pyrolysis oil and pyrolysis oil derivatives are shown to be greater than traditional fuels, potentially as a result of incomplete combustion [23,39]. At low loads, emulsion 2 shows 40% greater specific CO emission in relation to Emulsion 1, while Emulsion 1 and biodiesel both fall below the specific emissions of diesel.

![Specific CO Emissions](image)

*Figure 5-5 Specific CO emissions of four test fuels at two engine operating points. Error bars denote measurement standard deviation.*

Specific total hydrocarbon emissions were significantly higher for diesel at both operating points in comparison to the other three fuels in Figure 5-6. Biodiesel has been shown to reduce engine hydrocarbon emissions potentially due to the limited aromatic content of biodiesel fuels [40,41] which is also reflected in this data. The specific THC emissions of biodiesel against emulsions 1 and 2 show little variation, again not reflecting traditional trends of higher CO and THC emissions expected from lower combustion efficiency.
NO$_x$ measurements of the four fuels operating at two loads are shown in Figure 5-7. It has been reported that fuel bound oxygen in biodiesel can lead to higher NOx emissions than diesel [42,43] however this was not distinguishable between biodiesel and diesel at the high load points, and biodiesel produced only greater specific NOx emissions at lower loads. Emulsion 1 and biodiesel show similar performance at both operating modes; as do the emulsion 2 and diesel, following the similarities in heat release rate profiles.
Particulate matter emissions shown in Figure 5-8 indicate specific PM emissions from diesel fuel are 2-3 times greater than the emission from the other fuels. Biodiesel and both emulsions perform similarly, with emulsion 1 having slightly less specific PM than emulsion 2 at both engine operating modes. The effect of oxygenated compounds on fuels in diesel engines is well known to reduce particulate matter through oxidizing carbon during traditional soot formation pathways [44–46]. A similar trend is observed in other studies of biodiesel based FPO blends in diesel engines [37,40].
Overall the results presented from the analysis of emissions data showed trends in agreement with observations in the literature of FPO fuel PM and THC emission reductions from diesel values, while an increase in low load specific CO emissions correlates with the lower thermal efficiency observed in emulsion 2.

5.3 Combustion Testing Round 2 - Optical Analysis

Following the thermodynamic engine analysis, an optical investigation was performed to compliment the thermodynamic measurements and provide greater insight into the trends observed in the low load combustion performance seen in Figure 5-4. The engine used for initial thermodynamic testing is capable of operating with an alternative piston, and cylinder head which allows for the combustion chamber to become optically accessible through the implementation of a quartz window in a Bowditch piston as demonstrated in Figure 5-9. A Phantom CMOS high speed camera was synchronized to record with the combustion phasing of
the engine. Various camera settings were applied to capture the combustion events, however the images with the clearest exposure and composition were captured at 10000 frames per second, 100µsec exposure times, and an aperture of f/8.0.

Due to the design limitations of the optical engine assembly, continuous operation was not achievable because the optical head assembly impeded oil and coolant supply. As a result of the limitations, each operating mode effectively was a cold start. This was partially mitigated by adjust an engine oil preheated heater system to the maximum output which resulted resulting in a block coolant temperature of 72 °C, as well as preheating the intake runner in order to intake charge air temperature to ~45 °C.
Limitations in engine lubrication from the lack of continuous oil supply prevented engine operation for more than 2 minutes. On average, about 20 combustion events were observed for each optical measurement before the assembly required maintenance to lubricate piston rings and clean the optical surfaces. The engine operating point chosen for the optical analysis was mode 2, the lower engine load point from the thermodynamic campaign discussed in section 5.2.2.

5.3.1 Optical Combustion Results

Observations of the combustion patterns of the four fuels throughout the four stages combustion at -12 CAD, -6 CAD, 0 CAD, and 12 CAD aTDC offer insight into the results observed from the thermodynamic combustion analysis due to their phasing showing the pilot fuel, main fuel injection, approximate peak heat release rate, and late combustion events, respectively. Figure 5-10 below summarizes the findings of the optical investigations. To better visualize the combustion chamber at during periods of relatively low light (without intense incandescence from combustion), images at -12 CAD aTDC were batch processed to increase image gain by 50% equally for each fuel. Similarly, gain was increased by 20% on all photos from -6 CAD aTDC. The images taken at 0 CAD and 12 CAD aTDC were not altered. In the image sets, the intake and exhaust valves are partially seen in the cylinder head through the bore of the cylinder block, as well as the fuel injector mounted in the center of the frame.
In the earliest image set at -12 CAD aTDC, the pilot fuel injection has occurred and the ignition of fuel is most evident in the biodiesel case. Similarly in both emulsions, evidence of pilot fuel ignition is evident in the lower portion of the images, however with less light intensity than that which is observed in the biodiesel fuel. Ignition of the fuel is not evident in the diesel image likely as a result of the lower cetane number of diesel fuel relative to biodiesel [31]. At -6 CAD aTDC the beginning of the main fuel injection event is seen and the ignition of the fuel spray is visible in each image. While the biodiesel and emulsions only appear to be partially ignited, each
fuel branch of the diesel is burning, potentially as a result of the greater fuel volatility as observed in the TGA characterization. The intensity, an effect of the luminosity of the soot which are heated to incandescence, of both emulsions is lower than that of the commercial fuels. At 0 CAD the diesel fuel again exhibits the greatest light intensity with each fuel branch fully ignited. In comparison, liquid fuel jets of the biodiesel and particularly in both emulsions are evident near the fuel injector while the ignited fuel is most intense closer to the cylinder walls. Adequate mixing of the biodiesel and emulsions with oxygen is potentially inhibited by either lower volatility, or higher viscosity in contrast to the trends of the diesel fuel. In the final image at 12 CAD aTDC, again the diesel remains the brightest combustion image in agreement with the thermodynamic data showing longer heat release trends from the diesel engine operation. Fuel drops from the injector dribble are evident near the fuel injector tip during the late diesel combustion, however are not seen in the biodiesel or emulsions.

Ultimately the visible light observed in the images is a result of the incandescence of soot particles. While the oxidation processes of the reacting species was not measured or quantified, an overall greater and longer combustion event seen in the diesel fuel also resulted in the greatest PM generation.

5.4 Combustion Testing Round 3

Following the initial thermodynamic measurements and the subsequent optical combustion investigations, a secondary thermodynamic measurement campaign was established to further assess the characteristics of FPO derived fuels. To further quantify fuel performance, the test engine-operating load range was increased to 5 test to include a larger load range than the initial thermodynamic investigations. In addition to the five test modes using pilot injection strategies,
one single fuel injection test was also added in order to observe the impact of pilot injections on low FPO fuels. Additionally, higher FPO:biodiesel blend ratio fuels were developed to further discern the trends of FPO fuels in diesel engines. In total, the second thermodynamic testing operating-map included 6 fuels which were measured at 6 different engine operating modes.

5.4.1 Test Fuels

Six engine operating points were chosen to compare the combustion and emission characteristics of the four FPO blended fuels against neat diesel and biodiesel. Five operating points utilized pilot injections, consistent with modern fuel injection strategies. A sixth test point utilized a single injection event (no pilot injection), to contrast the differences in the auto ignition characteristics of the fuels.

Table 5-4 summarizes the injection criteria of each test point. $\theta_{\text{Pilot}}$ and $\theta_{\text{Main}}$ are the commanded crank angle for fuel injection for the pilot and main fuel injection, respectively. $\tau_{\text{Pilot}}$ and $\tau_{\text{Main}}$ are the commanded injection duration for the pilot and main fuel injection, respectively. For all operating points, the engine speed was 1000 rpm and fuel injection pressure was 1000 bar.
Table 5-4 Injection Command Criteria for Fuel Test Campaigns

<table>
<thead>
<tr>
<th>Test Mode</th>
<th>θ&lt;sub&gt;Pilot&lt;/sub&gt; (CAD aTDC)</th>
<th>τ&lt;sub&gt;Pilot&lt;/sub&gt; (ms)</th>
<th>θ&lt;sub&gt;Main&lt;/sub&gt; (CAD aTDC)</th>
<th>τ&lt;sub&gt;main&lt;/sub&gt; (ms)</th>
<th>GIMEP Diesel (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-20</td>
<td>0.45</td>
<td>-6</td>
<td>1.20</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>-20</td>
<td>0.45</td>
<td>-6</td>
<td>1.00</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>-20</td>
<td>0.45</td>
<td>-6</td>
<td>0.65</td>
<td>450</td>
</tr>
<tr>
<td>4</td>
<td>-17</td>
<td>0.45</td>
<td>-6</td>
<td>0.65</td>
<td>430</td>
</tr>
<tr>
<td>5</td>
<td>-20</td>
<td>0.45</td>
<td>-6</td>
<td>0.45</td>
<td>240</td>
</tr>
<tr>
<td>Single</td>
<td>Ø</td>
<td>Ø</td>
<td>-6</td>
<td>0.65</td>
<td>275</td>
</tr>
</tbody>
</table>

5.4.2 Test Fuels

The test fuels used in the second thermodynamic engine test campaign are those described in Section 4.2. From each FPO source, in-house and commercial, two blend ratios were implemented, 80:20 and 60:40 biodiesel:FPO. In this strategy an octanol surfactant was not included in the fuel preparation. Because of the lack of added surfactant, the fuels for the second thermodynamic testing are referenced as fuel blends rather than emulsions, despite all other preparation techniques being equal.

The engine used was naturally aspirated without a throttle. As such, the variable fuel oxygen content influenced the effective equivalence ratio for operating with each fuel blend at a given operating mode under fixed injection parameters. The equivalence ratios reported are determined using Equation (5-4), where the stoichiometric air-fuel ratio is affected by the fuel composition.

\[
\phi = \frac{m_{\text{fuel}}/(m_{\text{ox}})}{(m_{\text{fuel}}/m_{\text{ox}})_{\text{stoich}}} \tag{5-4}
\]
A summary of the diesel normalized oxygen equivalence ratios for the operating modes with pilot injections is shown in Figure 5-11. The values are calculated according to Equation (5-5).

\[
\phi_{i,\text{norm}} = \frac{\phi_i}{\phi_{\text{diesel}}}
\]  

(5-4)

Ultimately, the equivalence ratio will have a strong impact on combustion performance and exhaust emissions [44,46]. Blended fuels generally have lower overall equivalence ratios than that of biodiesel due to their oxygenated nature. The general trend of the oxygenated fuels showing increasingly lower global equivalence ratios relative to diesel at higher loads points is a function of greater injected fuel mass with relatively constant cylinder oxygen mass from the charge air.
Figure 5-11 Normalized equivalence ratios for five fuels at operating points with pilot injection. Equivalence ratios are normalized by the corresponding diesel equivalence ratio at the same operating point. Error bars denote measurement standard deviation. For a given operating mode, the same injection parameters were used for all fuels.

5.4.3 Testing Procedures

The fuels were tested in increasing potential of component failure (neat diesel and biodiesel, followed by lower blend fuels, and then higher blend fuels). Before testing with new fuel, the fuel filter was replaced and the system was drained and rinsed with biodiesel. Lower blend fuels did not exhibit any issues with material compatibility. Despite these efforts, it was not possible to carry out tests with HB-C as the fuel supply system was unable to provide the requisite pressure, likely due to fuel related damage. Further investigation is required to elucidate the mechanisms of this failure.
5.4.4 Thermodynamic Performance

The normalized indicated efficiencies are compared in Figure 5-12. A trend is seen here with biodiesel efficiencies no more than ±2% from the indicated efficiency of diesel combustion. At higher loads (modes 1 and 2) the thermal efficiencies of the blend fuels are generally lower than biodiesel. At lower loads, (modes 3-5) a significant decrease in the efficiency of the blend fuels is noted, relative to diesel. In particular, the indicated efficiency for HBIH fuel in modes 3-5 is lower than the diesel efficiency by 25%.

![Figure 5-12 Diesel normalized gross indicated thermal efficiency of tested fuels for pilot injected test modes 1-5.]

The coefficient of variation (COV) of GIMEP is presented in Figure 5-13 which is an indicator of engine stability, such that a lower COV represents a more repeatable steady operating condition. For operating modes with pilot conditions, the COV increases with decreasing load. Across all piloted engine modes, biodiesel and diesel perform very similarly and show roughly half the COV values as the blend fuels. The GIMEP COVs of both low blend fuels were
consistently within 2% of one another. The greatest GIMEP COV is seen in the single injection case of the high blend in-house fuel, which is likely due to the very low load and long ignition delays. A comparison of the single injection operation with lower load setting of mode 5 indicates that the pilot injection for the high blend fuel reduces GIMEP COV by 62%.

![Graph](image)

*Figure 5-13 Coefficient of Variation of GIMEP for test fuels at all engine operating conditions.*

The heat release rate histories of two operating points using a pilot injection (Modes 1 and 3, GIMEP 700kPa and 580 kPa, respectively) are shown in Figure 5-14 and Figure 5-16. Figure 5-14 indicates a significant variation in the pilot ignition delay of the different fuels, which can be attributable to the differences in cetane number. Previous work has estimated the cetane number of crude pyrolysis oil to be in the range of 5-25 [47]. As such, increasing blend fractions of low cetane number pyrolysis oil with high cetane biodiesel would result in a lower cetane number, and longer ignition delay, for blended fuels (relative to diesel) with increasing FPO content. Using the peak heat release rate during the pilot combustion as an indicator of the
ignition delay (and CN), an increase in the ignition delay (and associated decrease in CN) is noted for increasing FPO fractions (-7.5, -6, and -4.5 CAD aTDC for biodiesel, low blend, and high blend, respectively).

Figure 5-14 Mode 1 Heat Release Rate of 5 Test Fuels. High load (GIMEP diesel 700 kPa)

After the pilot combustion, the subsequent combustion process is generally assumed to be mixing controlled. During the early phases of mixing controlled combustion (here, 0-2 CAD), biodiesel and diesel have similar heat release rate slopes, as do the blended fuels. These similarities are present approximately until the end of the main fuel injection. Due to the mixing controlled nature of combustion, the heat release rate during the injection is expected to be dependent on the fuel injection rate. Figure 5-15 indicates the fuel energy injected during each operating mode cycle and, due to the constant injection duration, indicates the average energy addition rate during injection. The higher fuel-energy injection rate for diesel and biodiesel results in higher mixing controlled heat release rates during the injection process observed in.

Figure 5-14
The distinctive heat release trends during early mixing controlled combustion are attributable to the differences in injected fuel energy between the neat and blend fuels. The overall trend of all fuels show well defined premixed and mixing controlled combustion stages. While the premixed combustion varies as a result of varying fuel ignition delays (i.e., cetane number), the main heat release profiles are similar. The differing peak heat release rates during the mixing controlled combustion are a result of varying fuel injection quantities and heating values. The variation in fuel injection quantity – despite constant injection pressure and duration for all fuels - is due to the differing fuel viscosities of each fuel.

Though all fuels exhibited a similar heat release behaviour for mode 1, this was not the case for the higher blend fuel at the medium load condition (mode 3). As shown in Figure 5-16, a distinct heat release is not evident for the pilot combustion event for the HB-IH fuel. Furthermore,
operation with HB-IH exhibited a delayed and higher peak heat release rate than other fuels, likely because the pilot injected fuel was well premixed and converted during the main heat release event. Due to the pilot fuel not igniting, the HB-IH peak heat release is delayed by 2 CAD from all other fuels and results in a 16% and 32% greater peak heat release rate relative to diesel and biodiesel, respectively. While low blend fuels still exhibit a pilot heat release an increase in the ignition delay from that of neat biodiesel is evident. For mode 3, this significant premixed combustion fraction may be the result of a quenched pilot flame, as indicated by the “flattened” heat release rate trace of HB-IH at approximately the same crank position as the fuel injection command.

Engine operation with a single injection event (vs. pilot followed by a main injection) was considered for each fuel to evaluate the ignition behaviour of the fuels without a pilot ignition. Figure 5-17 displays the heat release rates of the single injection measurement test points. The shorter ignition delay of biodiesel, attributed to a greater cetane number than diesel, is seen in

![Figure 5-16 Mode 3 Heat Release Rate of 5 test fuels. (GIMEP diesel 450 kPa)](image-url)
the earlier heat release profile [41,48]. Furthermore, an extended ignition delay from increasing FPO blend fractions matches the trend of extended ignition delay with increasing FPO blend concentrations observed in modes 1 and 3. The two low blend fuels (LB-IH, LB-C) show very similar heat release profiles to that of biodiesel, but with peak heat release rates retarded by 1 CAD. HB-IH had a longer ignition delay than biodiesel and the LB fuels, as well as lower and retarded peak heat release rate (52% that of biodiesel and 5 CAD later). This very retarded combustion timing is likely the reason for the very high COV noted in Figure 5-15 for the single injection operating mode. The neat diesel fuel exhibited the longest ignition delay with a peak heat release rate 3 CAD after that of the HBIH fuel, leading to the conclusion that the cetane number of the HBIH fuel was substantially reduced from the original neat biodiesel, through the addition of FPO derived compounds, and was more similar to that of the presumed lower diesel value. Ultimately, the extended fuel ignition delays suggest that optimized use of the blended fuels would require modified injection timing if a single injection event strategy were to be used. Such a strategy may be relevant for older, non-common rail injection system applications.
Figure 5-17 Heat release histories for neat diesel and biodiesel, and blended fuels, using a single main injection strategy (no pilot).

An overview of the ignition delay for single and piloted injection strategies (modes 1-5) is presented in Figure 5-18. Here the ignition delay is characterized as the change in crank position from the commanded start of injection to 5% integral heat release (CA5). At higher engine loads, the ignition delay generally decreased for all of the fuels. Biodiesel consistently displayed the shortest ignition delay in agreement with reportedly higher cetane numbers than diesel [49]. Low blend fuels, generally had a similar ignition delay as biodiesel at lower loads, including the single injection case. At high load (mode 1), the biodiesel ignition delay was significantly shorter and the FPO blends exhibited ignition delays similar to those of diesel. The increased ignition
delay of the high blend fuel in modes 3-5 is in agreement with delayed premixed combustion noted in the heat release rate for mode 3 (Figure 5-16). Increasing fractions of pyrolysis oil (estimated cetane number 5-25 [47]) in biodiesel (estimated cetane number 60-89 [18]) result in longer ignition delays (and lower cetane numbers). This phenomena is observed between the low blend and high blend fuels in this work, as well as other FPO emulsion investigations in compression ignition engines [50,51]. It should be noted that the in this work the cetane number was not explicitly determined, in light of fuel volume limitations.

A previous review of crude pyrolysis oil performance in compression ignition engines attributes the extended ignition delay to the high water content of pyrolysis oil (between 15-30%) [11]. In the current work, the water content of the low and high FPO blends was < 1% (though higher than that of biodiesel), suggesting that ignition was also inhibited by other factors. This conclusion is supported by other investigations indicating that the molecular composition of the crude pyrolysis oils, and not just the water content are primary governing factors of pyrolysis oil ignition kinetics [51].

While the different fuel compositions resulted in significant differences in the ignition delay, the subsequent combustion process was less variable between the fuels. To characterize this, the combustion duration is quantified as the crank rotation between 10% and 90% integral heat release and is shown in Figure 5-19. The FPO blends have shorter combustion durations in comparison to biodiesel and diesel. A study of diesel-FPO emulsions concluded that combustion duration decreases with increasing FPO fractions which was attributed an increased premixed combustion fraction and shorter mixing controlled combustion fraction than diesel fuel [50]. This
trend is also seen in Figure 5-16 and may be attributable to larger premixed combustion fractions of the blend fuels, as well as the delay in mixing controlled combustion to diesel and biodiesel.

Figure 5-18 Ignition delay (CA5-SOI) of all considered operating modes for all fuels at 1000 rpm. Error bars denote measurement standard deviation.
5.4.5 Emissions Performance

For each of the operating points, the CO, uHC, NOx, and PM emissions were characterized for operation with each of the fuels. The FPO-blend fuels had an increased oxygen content over biodiesel, which has been linked to lower PM, uHC emissions, and CO tailpipe emissions [39,41,44,45]. Previous publications reported that biodiesel combustion tests result in increased NOx emissions in the majority of engine tests compared to diesel performance, though the survey found this to not be universally conclusive [42].

Figure 5-20 presents the indicated specific uHC and CO emissions of biodiesel and the tested fuel blends, normalized with respect to diesel emission levels. The uHC emissions of blend fuels are generally greater than biodiesel across, in contrast to a study reporting emulsified biodiesel-FPO blends to have significantly lower uHC emissions than neat biodiesel and diesel [39]. A
study of diesel-FPO blends reported that the uHC emissions of emulsions were higher than that of diesel, potentially attributed to overly lean regions formed during extended ignition delay periods [50]. This hypothesis of locally lean regions contributing to incomplete fuel combustion, particularly in the case of modes 3-5 of high blend fuels, is supported by high CO emissions (1.5 – 3.3 times greater than that of the diesel), as well as decreased indicated efficiency (75-85% that of diesel). A similar trend of increased CO emissions and poor thermal efficiency is observed for the low blend fuels at lower loads as well, however to a lesser extent with specific CO emissions only 1.5-2.5 times the diesel levels. Previous studies show increased levels of CO emissions from diesel from biomass pyrolysis derived fuels in compression ignition engines. [37,39,50]

![Figure 5-20 Specific uHC and CO emissions normalized to diesel for piloted injection operating modes. Error bars denote measurement standard deviation.](image-url)
Specific NOx and PM emissions of biodiesel and the blend fuels, normalized to diesel emission values, are shown in Figure 5-21. Thermal NOx formation dominates NOx formation in diesel engines [42]. The formation of NOx in biodiesel fuels has been heavily researched with varying conclusions; however, elevated NOx emissions over diesel engines are often attributed to fuel bound oxygen creating more stoichiometric flame autoignition zones, and thus elevated local in-cylinder temperatures [42]. In this study, biodiesel shows greater NOx emissions than diesel only in the highest load operating mode, potentially as a result of the fuel bound oxygen and the greater in-cylinder temperatures achieved at the highest engine operating load. Despite heating values similar to biodiesel and greater fuel oxygen content, low blend fuels show lower NOx emission (85% of diesel). A study on biodiesel–FPO emulsions similarly reported 7-16% lower NOx emissions from biodiesel-FPO emulsions containing 5-15% wood pyrolysis oil [39]; while, a separate investigation with wood pyrolysis oil-biodiesel blend reported a 17% reduction in specific NOx emission at high load from neat biodiesel [52].
The specific PM emissions from neat biodiesel ranged between 70-85% of diesel emissions. It is reported that the addition of oxygenates in biodiesel fuels help to oxidize carbon to CO and CO₂, thereby inhibiting PM formation and promoting oxidation [44]. Studies reviewing similar FPO-biodiesel blend performance also report significant decreases in PM relative to diesel and biodiesel [39, 52]. The PM emissions from the commercially derived FPO show 30-80% emission levels of diesel. In comparison, blend fuels derived from in-house pyrolysis oil performed similarly to one another producing 50-98% of the specific PM emissions of diesel (i.e., 33-50% than the commercially sourced FPO blend fuel). Due to the similarities of the LBIH and LBC fuels in heating value, water content, viscosity, and volatility, it is proposed that differences in extracted compounds from the respective FPO feedstock, potentially including aromatic compounds, may attribute to the variances in PM formation. While beyond the scope of this investigation, a comprehensive characterization of the FPO composition is the focus of
future work. Differences in fuel composition are evident in the relative oxygen content in the fuels. While oxygenated species in diesel fuels result in lower PM emissions [44,45], the LBC fuel produced the lowest PM emissions, yet had the lowest oxygen content of the pyrolysis FPO derivative fuels. This indicates that the fuel oxygen content alone is not a sufficient metric for characterizing the PM formation propensity of FPO-biodiesel blends.
Chapter 6  Conclusions

To investigate the application of pyrolysis compounds from waste biomass as drop-in fuels, FPO was produced in a continuous fluidized bed reactor system and compared to commercially produced FPO. The in-house production system developed here resulted in an FPO collection efficiency of 31%. Collection efficiencies cited in literature reviews of biomass fast pyrolysis oil production in fluidized bed reactors are often above 75% [2]. The PPC BFB reactor collection efficiency was ultimately limited by tar deposition in the reactor. In spite of the variation in collection efficiency, the in-house and commercial FPO did not show significant deviation within the standards for ASTM FPO characteristics for use as heating fuel in industrial furnaces.

In total, three fuel batches were produced using both in house FPO and commercial FPO. The first blend batch utilized an emulsion stabilizer, 1-Octanol mixed into 80:20 biodiesel:FPO at 4% total volume. For subsequent blends a stabilizer was not used and biodiesel was blended with FPO in initial volumes of 80:20 and 40:60 to produce fuel blends with ~5 and 10 % (by volume) of FPO derived compounds, respectively. The volatility of the blend fuels remained unchanged relative to the neat biodiesel, regardless of the stabilizer. The FPO-Biodiesel blends had 200-350% greater water content than neat biodiesel, a large increase in acid number, and a 2%-10% decrease in dynamic viscosity. The gross heating value for the low blends was not impacted, however it was reduced by 25 and 35% for HB-IH and HB-C, respectively.

In efforts to reduce the variability in engine operating conditions, fuel performance was measured at constant engine speed, fuel injection pressure, and in a set of constant fuel injection timing modes to achieve a range of engine loads. This strategy was used to minimize the
variables during engine operation and also served to reduce fuel requirements due to limited FPO supply.

Engine testing of emulsions showed very similar heat release characteristics between biodiesel and emulsion 1 (in house) as well as diesel and emulsion 2 (commercial). At low loads the FPO derived fuels showed almost 10% reduction in indicated thermal efficiency from higher loads. This finding is in agreement with literature reports that FPO fuel performances suffer at low engine loads due to incomplete combustion. At higher engine loads the fuels performed relatively similar with respect to heat release rate and indicated thermal efficiency. Exhaust emissions analysis showed relatively similar PM and uHC emissions for both blends as biodiesel, however drastically reduced from diesel values. To further assess this performance, a high speed camera was implemented to record the combustion events of the four fuels at the low load point using the engine in an optically accessible configuration. The optical images show the suppressed ignition of the FPO fuel pilot injection in comparison to that of the diesel.

Following the initial round of thermodynamic and optical combustion testing, neat diesel, biodiesel, and the two ratios of FPO fuel blends were tested in a single cylinder research engine to observe their combustion performance across five operating modes using a piloted injection strategy and one operating mode with a single injection strategy. All fuels exhibited well defined premixed and mixing controlled combustion profiles at higher loads (mode 1 and 2). The relative phasing of the premixed combustion peaks indicated that an increase in FPO resulted in longer ignition delays, which agrees with an expected reduction in Cetane number, though Cetane numbers were not explicitly determined in the current work. Lower heat release rates were
observed during the initial phases of the mixing controlled combustion for the blended fuels during high load operation. This was attributed to a lower average fuel-energy addition rate during injection, due to the lower heating values of the blended fuels. For medium to low loads (modes 3-5), only a weak pilot combustion event was noted for the high blend fuel, which resulted in large single event heat release rate profiles. This was likely the result of the pilot combustion being quenched by main injection fuel. Single injection testing showed a slight retardation of the heat release rate profiles for the low blend fuels from biodiesel, while the high blend fuel had a similar heat release profile to diesel. In general, the FPO fuels showed increasing ignition delay and shorter burn duration with greater FPO blend concentrations; however, the use of a pilot injection resulted in a relatively similar heat release behavior for all test fuels at all but the lowest load (mode 5).

The indicated efficiency of biodiesel was within 5% of diesel values, while the blended fuels resulted in a reduced indicated efficiency relative to diesel at lower engine loads (80% the efficiency of diesel in modes 3-5). The extended ignition delays of the blend fuels, particularly at low loads, likely resulted in overly lean regions of the cylinder, which in turn resulted in large, delayed, premixed combustion events. The large premixed combustion fractions produced elevated CO and uHC emissions, and associated low fuel conversion and indicated gross efficiencies. Similar trends of elevated CO and uHC emissions from pyrolysis derived fuels are in agreement with previous work [37,39,50]. The PM emissions were consistently lower for blend fuels with the exception of the lowest load operating mode, where absolute PM emissions were minimal for all fuels. Both blends of the in-house FPO showed similar PM emission performance, however these emissions were higher (33-55%) than the blends of commercial
obtained FPO. It is suspected that the variability in pyrolysis-derived compounds, evident in the
distinctive elemental compositions of the FPO derivative fuels, can be attributed to the variable
PM emissions.

Throughout the characterization and engine testing research portions, the high blend fuels
showed unexpected results. The C, H, and N elemental composition concentrations of the high
blend fuels were similar to those of the low blend fuels, however the calorimetry results
reported heating values of the high blend fuels up to 35% lower than values for the low blend
fuels. It is hypothesized that the measured heating value may have been affected by incomplete
combustion in the calorimeter. The poor heating value of the high blend fuel consequently
resulted in definitively lower indicated thermal efficiency. This incomplete combustion was
attributed to the obvious differences in combustion heat release trends such as poor pilot
injection ignition, and was also thought to explain the increased CO and uHC exhaust
concentrations. Because of the discrepancies in the heating values of the high blend fuels with
respect to the relatively consistent elemental composition, the low indicated thermal efficiency of
the high blend fuels may be invalid and must be addressed in future studies.

FPO-biodiesel fuel blends offer a low cost solution to improve crude FPO fuel quality by
selectively extracting biodiesel soluble compounds. Promising reductions in the biodiesel NOx
effect and reductions in PM emissions may contribute to future solutions to further reduce
tailpipe emissions in the advancement of renewable fuels. In spite of this, challenges with
modern fuel hardware compatibility and long ignition delays, which impair low load
performance, must be addressed to optimize FPO blends for consideration as appropriate drop-in fuel alternatives.
Chapter 7  Recommendations

The purpose of this thesis was to provide a broad experimental project of biomass fast pyrolysis oil production, upgrading, characterization, and engine testing to determine the potential of FPO derived products as drop in diesel fuels. Due to logistical constraints or limitations in resources encountered throughout the research process, several recommendations can be made to improve the pursuit for understanding FPO production, upgrading, and combustion.

7.1 Future FPO Production

Lessons learned from the development of the CERC reactor proved useful in the buildup of the PPC reactor, such as removing the screwfeeder from the reactor heat source, and implementing an entrainment system for feedstock delivery into the reactor. Nonetheless, the development of the production procedures of FPO in the PPC fluidized bed reactor remained an arduous process stemming from utilizing equipment designed for gasification for pyrolysis oil production. The FPO production procedures outline the methodology required for further FPO acquisition, however there exists significant opportunity to optimize the reactor hardware in order to address poor FPO collection yield. Implementing a more robust heating system after the cyclones would prevent early condensation of the FPO vapours and contribute to a higher collection efficiency. Furthermore, installing heat quenching system in a singular condenser has shown to be effective in homogenizing FPO product [5]. Beyond simple system hardware upgrades, FPO quality and yield could be enhanced through the implementation of catalytic beds or in-situ hot filters. [5]

7.2 Future FPO Upgrading and Characterization

The properties characterized in this thesis: viscosity, water content, acid number, elemental analysis and thermogravimetric analysis proved to be valuable to quantify changes in FPO products before and after upgrading with biodiesel. The discrepancy in heating values of the
high-blend fuels requires further investigation. The significant reduction in heating value of the high-blend fuels is reported to have occurred from and increased FPO content of ~5% vol. over the low-blend fuel. This 5 % vol. change of the fuel compounds should not impact the value of the heating value of the fuels by 25-35% as reported by the calorimeter. To address this, retesting of the fuels in a calorimeter should be performed and cross-referenced with theoretical heating values from calculated elemental analysis data.

Throughout the investigations the molecular composition of the upgraded fuels was often deliberated. The upgrading methods promoted an obvious transfer of compounds of FPO material into the biodiesel, however the molecular composition of the fuels remained unknown. In order to better understand the differences in fuel chemistry, determining the molecular composition of FPO, biodiesel, and the resulting blend’s upper and lower layers would provide insight into the mechanisms behind the upgrading processes. This could be done in conjunction with a TGA and FTIR to correlate fuel volatility with molecular species, or other spectroscopy tools such as GC/MS.

7.3 Future FPO Engine Testing

From the engine testing campaigns in this thesis, a major observation was the kinetically limited combustion of FPO fuels, particularly in higher blend ratios and lower engine loads. Fundamental combustion tests could be performed to investigate the phenomena observed from engine testing. Specifically of interest would be to experimentally determine equivalent cetane numbers of upgraded fuels using a rapid compression machine. Experimental cetane numbers in conjunction with a molecular composition of the test fuels could provide insight into optimizing FPO products as drop in fuels through known performance metrics of equivalent fuel surrogates.
(i.e. phenolics, organic acids, etc.) The deviation of cetane numbers of upgraded fuel blends from neat biodiesel could be considered a function of the calculated carbon aromaticity index of crude FPO feedstock. Understanding this relationship would be a useful metric when considering FPO blends as drop-in fuels and would allow for further optimization of engine operating strategies based on analytical fuel chemistry-combustion correlations.
Bibliography


918–930.


## A1 Data and Results of Pyrolysis Processes

### I. Process Conditions

> **Table A3.1: Process conditions of all experiments**

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Nitrogen and non-condensable gas mass flows

Table A3.2: Data and results of nitrogen and non-condensable gas mass flow calculations

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<td>Q\textsubscript{N2, C0}</td>
<td>m\textsuperscript{3}/h</td>
<td>1.92</td>
<td>1.94</td>
<td>2.20</td>
<td>2.11</td>
<td>2.15</td>
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<tr>
<td>volume flow of N2 fluidization stream</td>
<td>Q\textsubscript{N2, F2}</td>
<td>-</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>3.00</td>
<td>2.00</td>
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<tr>
<td>volume flow of N2 fluidization stream</td>
<td>Q\textsubscript{N2, F1}</td>
<td>CFM</td>
<td>2.05</td>
<td>2.05</td>
<td>2.05</td>
<td>3.06</td>
<td>2.05</td>
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<tr>
<td>volume flow of N2 fluidization stream</td>
<td>Q\textsubscript{N2, F1}</td>
<td>m\textsuperscript{3}/h</td>
<td>3.49</td>
<td>3.49</td>
<td>3.49</td>
<td>5.21</td>
<td>3.49</td>
</tr>
<tr>
<td>volume flow of N2 fluidization stream</td>
<td>Q\textsubscript{N2, F0}</td>
<td>m\textsuperscript{3}/h</td>
<td>3.78</td>
<td>3.81</td>
<td>3.94</td>
<td>6.21</td>
<td>3.86</td>
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<tr>
<td>mass flow of N2 fluidization stream</td>
<td>W\textsubscript{N2, F0}</td>
<td>kg/hr</td>
<td>4.3</td>
<td>4.4</td>
<td>4.5</td>
<td>7.1</td>
<td>4.4</td>
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<tr>
<td>total N2 volume flow</td>
<td>Q\textsubscript{N2, total}</td>
<td>L/min</td>
<td>78.17</td>
<td>79.33</td>
<td>84.76</td>
<td>110.82</td>
<td>82.70</td>
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<tr>
<td>total N2 volume flow</td>
<td>Q\textsubscript{N2, total}</td>
<td>m\textsuperscript{3}/h</td>
<td>4.64</td>
<td>4.67</td>
<td>5.04</td>
<td>6.59</td>
<td>4.94</td>
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<tr>
<td>total N2 mass flow</td>
<td>W\textsubscript{N2, total}</td>
<td>kg/hr</td>
<td>5.37</td>
<td>5.45</td>
<td>5.82</td>
<td>7.61</td>
<td>5.68</td>
</tr>
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</table>

NCG content (see GC analysis) | 0.02 | - | 0.03 | 0.02 | 0.04 | 0.07 |
| total NCG mass flow       | W\textsubscript{NCG, total} | 0.12 | 0.00 | 0.15 | 0.12 | 0.22 | 0.41 |
## II. Product distribution

<table>
<thead>
<tr>
<th></th>
<th>Symbol</th>
<th>Unit</th>
<th>≈ 450 °C</th>
<th>≈ 500 °C</th>
<th>≈ 500 °C</th>
<th>≈ 500 °C</th>
<th>≈ 525 °C</th>
<th>≈ 550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>biomass mass</td>
<td>( m_{BM} )</td>
<td>kg</td>
<td>4.24</td>
<td>1.90</td>
<td>2.78</td>
<td>3.56</td>
<td>5.32</td>
<td>7.52</td>
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<tr>
<td>char mass</td>
<td>( m_{Char} )</td>
<td>kg</td>
<td>0.11</td>
<td>0.22</td>
<td>0.08</td>
<td>0.14</td>
<td>0.80</td>
<td>0.37</td>
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<tr>
<td>bio-oil mass</td>
<td>( m_{Bio-oil} )</td>
<td>kg</td>
<td>0.58</td>
<td>0.22</td>
<td>0.70</td>
<td>0.40</td>
<td>0.87</td>
<td>1.26</td>
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<tr>
<td>bio-oil/filter mass</td>
<td>( m_{Bio-oil/filter} )</td>
<td>kg</td>
<td>0.62</td>
<td>0.00</td>
<td>0.16</td>
<td>0.56</td>
<td>0.46</td>
<td>0.56</td>
</tr>
<tr>
<td>residue in system</td>
<td>( m_{residue} )</td>
<td>kg</td>
<td>2.44</td>
<td>1.36</td>
<td>1.99</td>
<td>2.35</td>
<td>3.69</td>
<td></td>
</tr>
<tr>
<td>total biomass mass, dry</td>
<td>( m_{BM, dry, total} )</td>
<td>kg</td>
<td>3.99</td>
<td>1.79</td>
<td>2.62</td>
<td>3.35</td>
<td>5.01</td>
<td>7.08</td>
</tr>
<tr>
<td>total bio-oil (incl. filter) mass, dry</td>
<td>( m_{Bio-oil, dry} )</td>
<td>kg</td>
<td>0.67</td>
<td>0.18</td>
<td>0.45</td>
<td>0.25</td>
<td>0.49</td>
<td>0.76</td>
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*Table A3. 3: Yield of products*

<table>
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<tr>
<th></th>
<th>Symbol</th>
<th>Unit</th>
<th>≈ 450 °C</th>
<th>≈ 500 °C</th>
<th>≈ 500 °C</th>
<th>≈ 500 °C</th>
<th>≈ 525 °C</th>
<th>≈ 550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of char</td>
<td>( Y_{char} )</td>
<td>%</td>
<td>2.59</td>
<td>11.58</td>
<td>2.88</td>
<td>3.93</td>
<td>15.04</td>
<td>4.92</td>
</tr>
<tr>
<td>Yield of NCG</td>
<td>( Y_{bio-oil} )</td>
<td>%</td>
<td>28.30</td>
<td>11.58</td>
<td>30.94</td>
<td>26.97</td>
<td>25.00</td>
<td>24.20</td>
</tr>
<tr>
<td>Yield of residue</td>
<td>( Y_{NCG} )</td>
<td>%</td>
<td>11.62</td>
<td>0.00</td>
<td>17.25</td>
<td>13.18</td>
<td>15.74</td>
<td>21.84</td>
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<tr>
<td>Yield of bio-oil</td>
<td>( Y_{residue} )</td>
<td>%</td>
<td>57.48</td>
<td>0.00</td>
<td>48.94</td>
<td>55.92</td>
<td>44.22</td>
<td>49.04</td>
</tr>
<tr>
<td>Yield of bio-oil, dry</td>
<td>( Y_{char} )</td>
<td>%</td>
<td>2.59</td>
<td>11.58</td>
<td>2.88</td>
<td>3.93</td>
<td>15.04</td>
<td>4.92</td>
</tr>
</tbody>
</table>
A2 Table A.1 Summary of Experimental Data Presented

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Mode</th>
<th>COV GIMEP (%)</th>
<th>Indicated Power (kW)</th>
<th>Fuel Injected grams/cycle</th>
<th>Equivalence Ratio</th>
<th>CA5-SOI (CAD)</th>
<th>CA90-CA10 (CAD)</th>
<th>PM (g/kWh)</th>
<th>uHC (g/kWh)</th>
<th>NOx (g/kWh)</th>
<th>CO (g/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel 1</td>
<td>0.50%</td>
<td>11.67</td>
<td>0.14</td>
<td>0.50</td>
<td>15.7</td>
<td>26.6</td>
<td>0.55</td>
<td>0.31</td>
<td>7.92</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>Diesel 2</td>
<td>0.62%</td>
<td>9.23</td>
<td>0.13</td>
<td>0.40</td>
<td>14.9</td>
<td>25.5</td>
<td>0.71</td>
<td>0.39</td>
<td>6.73</td>
<td>1.35</td>
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</tr>
<tr>
<td>Diesel 3</td>
<td>0.89%</td>
<td>7.17</td>
<td>0.09</td>
<td>0.33</td>
<td>14.2</td>
<td>20.6</td>
<td>0.33</td>
<td>0.72</td>
<td>5.97</td>
<td>3.98</td>
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<tr>
<td>Biodiesel 1</td>
<td>0.53%</td>
<td>10.49</td>
<td>0.15</td>
<td>0.45</td>
<td>12.3</td>
<td>27.4</td>
<td>0.32</td>
<td>0.16</td>
<td>8.57</td>
<td>0.91</td>
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<tr>
<td>Biodiesel 2</td>
<td>0.69%</td>
<td>8.40</td>
<td>0.12</td>
<td>0.37</td>
<td>13.7</td>
<td>24.7</td>
<td>0.44</td>
<td>0.43</td>
<td>6.54</td>
<td>1.76</td>
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<tr>
<td>Biodiesel 3</td>
<td>0.75%</td>
<td>6.22</td>
<td>0.09</td>
<td>0.31</td>
<td>14.2</td>
<td>21.5</td>
<td>0.26</td>
<td>0.71</td>
<td>5.66</td>
<td>5.30</td>
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</tr>
<tr>
<td>LBIH 1</td>
<td>1.48%</td>
<td>9.33</td>
<td>0.13</td>
<td>0.41</td>
<td>14.4</td>
<td>24.5</td>
<td>0.49</td>
<td>0.28</td>
<td>6.52</td>
<td>1.13</td>
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<tr>
<td>LBIH 2</td>
<td>1.40%</td>
<td>8.03</td>
<td>0.10</td>
<td>0.36</td>
<td>15.3</td>
<td>21.4</td>
<td>0.34</td>
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<td>6.25</td>
<td>2.34</td>
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<td>LBIH 3</td>
<td>1.80%</td>
<td>5.26</td>
<td>0.07</td>
<td>0.28</td>
<td>15.4</td>
<td>19.4</td>
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<td>0.91</td>
<td>4.83</td>
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<tr>
<td>LBC 1</td>
<td>0.56%</td>
<td>9.35</td>
<td>0.13</td>
<td>0.41</td>
<td>14.5</td>
<td>24.6</td>
<td>0.30</td>
<td>0.26</td>
<td>6.58</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>LBC 2</td>
<td>0.54%</td>
<td>8.15</td>
<td>0.11</td>
<td>0.37</td>
<td>14.0</td>
<td>23.9</td>
<td>0.21</td>
<td>0.39</td>
<td>6.61</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>LBC 3</td>
<td>0.95%</td>
<td>5.94</td>
<td>0.09</td>
<td>0.29</td>
<td>15.2</td>
<td>20.0</td>
<td>0.13</td>
<td>0.77</td>
<td>5.34</td>
<td>7.70</td>
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</tr>
<tr>
<td>HBIH 1</td>
<td>1.63%</td>
<td>9.31</td>
<td>0.13</td>
<td>0.41</td>
<td>14.9</td>
<td>24.1</td>
<td>0.42</td>
<td>0.25</td>
<td>6.75</td>
<td>1.39</td>
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<td>HBIH 2</td>
<td>0.53%</td>
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<td>0.37</td>
<td>14.6</td>
<td>23.2</td>
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<td>0.35</td>
<td>6.72</td>
<td>2.24</td>
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</tr>
<tr>
<td>HBIH S</td>
<td>3.75%</td>
<td>2.92</td>
<td>-</td>
<td>-</td>
<td>15.5</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Start Heating Up the Reactor

1. Check that
   a. All valves are closed.
   b. There is a blind flange between the gasifier and the pyrolysis system
      (3rd floor) to separate the two units.
   c. The filter and knock-out drum are connected to the exhaust gas pipe.
   d. The biomass for the run has been loaded in the storage hopper.

2. Switch on (main floor):
   a. The main power box.
   b. The steam superheater control box.
   c. The reactor heater control box and set (*) the temperature of the
      heater 1&2 to 500 °C and the heater 3 to 450°C.
   d. The power strip which is connected to the heating tapes in the 2nd
      floor.
   e. (Make sure that the heating tape on the top of the cyclones is
      connected to the voltage controller. The voltage controller and the
      other heating tape have to be plugged in the power strip on the 2nd
      floor.)
   f. The CO-analyzer.

3. Open the red valve of the natural gas pipe (2nd floor).

4. Turn on (main floor):
   a. The after burner control box (press “START”) and wait until the
      “flame on” light appears.
   b. 24VDC power supply (ON position).

III. Start data acquisition

1. Turn on the computer.
2. Initiate the final version of the LabVIEW program (Biomass Pyrolysis Highbury).
3. Press the “Run” bottom to constitute the temperatures and pressures of the unit.
4. Press the “collect T data” and “collect P data” bottom and save the data with the actual date.

IV. Start Cooling Water flow stream
1. Open the valve of the building water which is located at the wall next to the liquid nitrogen storage tank.
2. Turn on the water control valve WV0 and raise the flow to Q=4 L/M at WF1.

V. Start Purging and Bed Fluidization
1. Open the valve NVB0. (NVA0 must be closed)
2. Turn on the liquid nitrogen cylinder valve in front of the pressure controller (PC1).
   (Make sure that the pressure of the pressure controller is set around p=100 psi.)
3. Switch the heater purge valve NV7 to the open position.
4. Open the green valve GV4 in front of the knock-out drum (3rd floor) in the same time as opening slowly the flow control valve NV1 to increase the fluidization flow stream to Q=3 CFM at the rotameter NF1.
5. Keep the fluidization flow constant until the system almost reached T5=300 °C, T6=200 °C and T2a the pre-defined reactor temperature.

VI. Start Analyzing the gas flow stream through GC
1. Make sure the Micro-GC is connected to the gas flow stream after the filter and the valve GV5 is switched to GC.
2. Turn on the vacuum pump.
3. Open on the galaxy workstation program at the computer. Choose the sequence: File → Open → Open sequence: DFB-HTAS.SEQU and press the run bottom at the data tab.

VII. Start the Conveying Flow and pressurizing the feed hopper
1. Decrease the fluidization flow to Q=2 CFM.
2. Open the flow control valve NF2 of the conveying flow a little bit.
3. Switch the bypass valve NV3 to the open position.
4. (The pressure P11 should increase very fast and drop down to almost the same value as P2 → the sand in the tube of the bottom of the reactor is pushed out).
5. Increase the conveying flow to Q=1 CFM.
6. Open the valve NV6 and set the pressure to a value which is a little bit higher than P2 by the pressure regulator. If everything is leak tight P10 should reach the same value than the setting.
7. When P10>P2 switch the nitrogen flow from the bypass to the feeding line:
8. Close NV3 at the same time as opening NV4 and NV5.
9. If there is no clogging in the feeding line P10 should drop to the same pressure as P11 and P2.
10. Set the nitrogen flow to the feed hopper to 2-3 L/min. by NF3.
11. Check all the pipes to the reactor for leaks.

VIII. Start feeding biomass
1. Check if:
   a. The temperatures T2a and T10 reached the desired pyrolysis temperature.
   b. The temperature T5>300 °C and T6>200 °C.
   c. The pressures P2 and P3 are stable and P2<20 kPa.
   d. The pressure drop dp1 is fluctuating in a stable range.
2. Set the speed on the feeder control box to 10 % and switch it on.
3. (Make sure that the pressure P10 is not increasing otherwise there’s building up a clog.)

4. After 10 minutes increase slowly the speed to 15%.

5. (After feeding for a few minutes the pressures P2 and P3 should drop down.)

6. While feeding observe the pressure P10. If it raises more than P2 there will be a clog in the feeding line:
   a. Switch off the *feed hopper* on the *feeder control box*.
   b. Switch the nitrogen flow stream from the feeding line to the bypass line:
      Open NV3 at the same time as closing NV4 and NV5.
   c. Close the valve NV6 and release slowly the pressure of the *feed hopper*.
   d. Open the feeding tube and remove the clog.
   e. After reassembling test all connections for leaks and start again with point vi

IX. Empty the Cyclones every 30 minutes
   1. Put on a respirator or safety mask.
   2. Knock on the outside wall of the cyclones with a rubber hammer.
   3. Close the upper valve CSV1/ CSV2 and open slowly the bottom valve CSV3/ CSV4.
   4. Collect the char with the *bag house filter bag*.
   5. Close the bottom valve CSV3/ CSV4 and open the upper valve CSV1/ CSV2.

X. Shut-down Procedure
   1. Switch off the *feeder control box*.
   2. Set the temperature of the *Heater 1&2* and *Heater 3* to T=0 °C.
   3. Switch off the power strip with the heating tapes (Main floor, next to Liquid nitrogen tank).
   4. After a few minutes purging the feeding line with N₂, switch the nitrogen flow stream from the feeding line to the bypass line:
   5. Open NV3 at the same time as closing NV4 and NV5.

7. Purge the Reactor and the downstream equipment with nitrogen for about 15 minutes.

8. Close the valve NV3 in the same time while turning off the conveying flow stream through the valve NV2.

9. Switch off the fluidization flow stream through the valve NV1 and close the valve NV7.

10. Close the liquid nitrogen tank valve and NVB0.

11. Press the “Stop” bottom of the after burner control box and close the natural gas valve NGV1 in 2nd floor.


13. Switch off the vacuum pump in front of the GC.

14. Save the data of the GC:
   a. File→Open→Open the last summary report: Delete all files in the last summary report and add new chromatogram (right mouse button)→data
   b. Switch to the tab variables: Method File: DFB-Syngas.METH
   c. Switch to the tab export: Export File: MS-Excel 97/2000 (Filename: Actual date)
   d. Press the bottom: Export report

15. Close LabVIEW and save the data in the folder data test.

16. Switch off:
   a. The 24VDC power supply (OFF position).
   b. The reactor heater control box
   c. The steam superheater control box.
   d. The main power box.
   e. Cooling water control valve WV0 and the building water valve.

XI. Preparation Procedure

1. Fill up the feed hopper with biomass sawdust.
2. Exchange the filter with a new one.
3. Clean the U-tube of the air-cooled condenser with acetone after each run.
4. Clean the U-tube of the water-cooled condenser with acetone after every second run.

5. Collect the bio-oil soonest 24 hours after the last run and clean the collector with acetone.