Synthesis of Biofuels and Blended Fuels from Biomass Feedstocks: Strategies for Upgrading Bio-oil

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by
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Authorization to Submit Thesis

This thesis of Samuel B. Hansen, submitted for the degree of Master of Science with a Major in Mechanical Engineering and titled "Synthesis of Biofuels and Blended Fuels from Biomass Feedstocks: Strategies for Upgrading Bio-oil," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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Abstract

Bio-oil upgrading strategies for producing biofuels independently of petroleum-based products exist, though co-processing or refining is considered as the most viable path to commercialization, however remedial upgrading of bio-oil is still required prior to co-processing. Independent methods of upgrading bio-oil can address high oxygen and water content, low hydrogen content, and stability in order to be compatible with existing refineries. Improvements to the initial biomass conversion process (e.g., catalytic fast pyrolysis) can impact some issues, but ultimately falls short of quality goals. Addressing stability and corrosiveness issues of intermediate liquid oil (e.g., bio-oil) to produce cost-competitive and compatible transportation fuels from biomass feedstocks can be accomplished through optimization of existing conversion pathways, as well as the development of new treatment methods for effectively upgrading intermediate products. This thesis constructs and empirically tests various pre-/post-conversion processes for improving pyrolysis-based oil quality and operation yields using new inventions and growing cyber-physical initiatives. In addition, this thesis investigates multiple bio-oil treatments, such as catalytic transfer hydrogenation, ultrasonic cavitation, and emulsification for producing biofuels or blended fuels. The research presented aims to outline the existing state of technology, which is essential in understanding the conversion process intricacies, and provides several approaches and mechanisms for addressing the deficiencies both qualitatively and analytically. Physicochemical treatments (e.g., catalytic transfer hydrogenation and ultrasonic cavitation) preliminarily appear to improve process efficiency and reaction time of catalyst intensive chemical treatment. The critical aspects of upgrading bio-oil are deoxygenation and hydrogenation, since these aspects of refinement address other deficiencies.

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Dedication

I would like to dedicate my work to my wife Courtney, who unwaveringly supported me during school, and my parents, who both financially and emotionally aided my efforts to get a higher education.

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Statement of Contribution

I, Samuel B. Hansen, claim primary responsibility and first author ownership of the work presented herein. The co-authors listed in the articles within this thesis provided some guidance during experimentation, assistance editing prior to submitting and presenting at conferences, and financial support to travel and present the work at the respective conference. The original draft was prepared by myself, Samuel B. Hansen, and initially edited by Amin Mirkouei, further review and editing was completed as a joint effort between Amin Mirkouei, Min Xian, Haiyan Zhao, Michael McKellar, and Luis Diaz. As the primary author of each publication, I claim responsibility for the ideas and published data, which I produced to the best of my ability. Funding for the completion of the project was acquired by Amin Mirkouei through the IDeaL research group and University of Idaho, Equipment and Infrastructure Support Award.

Chapter 1. Introduction

1.1. Research Challenges and Motivation

Energy independence is a key issue in today's economy as the United States vies for cleaner renewable technologies that are less vulnerable to speculation, resilient from foreign conflict, and are safer for the environment. Existing renewable energy resources (e.g., wind, solar, and geothermal) though renewable are not compatible with existing transportation infrastructure which relies heavily on liquid hydrocarbon (i.e., gasoline and diesel). As demand for energy grows, renewable biofuels produced from catalytic fast pyrolysis (CFP) bio-oil present themselves as a frontrunner that can be used as a drop in substitute for traditional hydrocarbon fuel.

Previous work showed bio-oil to biofuel technologies exist, however many are however many failed to comprehensively outline what each effort entailed, thus failing to provide a clear picture of a) what is currently being done as whole, and b) what are the key objectives does each of the technologies accomplish, and c) what are the major drawbacks. Our work investigates the goals of each challenge.

1.1.1. Chapter 2

Concurrent research in biofuel, specifically in bio-oil upgrading causes. Currently, various pathways exist, however a sustainable and effective method for producing hydrocarbons from bio-oil has not been developed at the commercial level. The best remedy can be a consortium of multiple efforts.

1.1.2. Chapter 3

Existing technologies such as hydrotreatments, etc. are effective but inefficient and unsustainable due to hazardous conditions and excess energy requirements. Alternative strategies such as Catalytic Transfer Hydrogenation (CTH) offer a significant advantage when performed under ultrasound treatment which also has independent effects. During the literature review in chapter 2, ultrasound was identified as a nascent technology with potential to aid in increasing the efficiency of other processes such as (CTH). Our efforts herine examine a) the effects of ultrasound alone, b) the effects of ultrasound enhanced by CTH, and c) the effects of a non-exothermic reaction by using a cooled jacket on the bio-oil to reduce the amount of heat imparted on the oil. During our investigating we identified one of the greatest challenges of upgrading bio-oil is characterizing the product inexpensively to validate experiments. Hyperspectral imaging is one mechanism thought to be able to integrate with real time monitoring of bio-oil upgrading to achieve maximum efficiency, though this technology remains undeveloped for use in hydrocarbon production.

1.1.3. Chapter 4

The reviewed literature and experimentation do not yet offer a clear method for producing bio-oil that is market competitive, due to many disadvantages of bio-oil such as high water content, and non-miscibility with transportation diesel. Blended fuel offers some unique benefits to traditional upgrading, such that the need to upgrade bio-oil would be greatly reduced. Additionally, most renewable fuel will be blended with traditional hydrocarbons such as diesel for distribution rather than be sold independently, though, fuel quality issues relating to separation will be greatly reduced. Market demand for bio-oil is currently low, thus interest in commercialization has been stagnant. Ultrasonic Assisted Emulsion offers a means for blending non-miscible bio-oil with diesel into a stable fuel. Ultrasound aided emulsion holds great promise however little has been done to investigate its effectiveness.

1.1.4. Motivation of Thesis

Growing scrutiny of sustainable energy sources (e.g., biofuels, solar and wind energy) and recent policy changes have sparked research and developments in renewable energy sources to reduce dependency on foreign oil, mitigate greenhouse gas (GHG) emissions, and secure energy sources for the future. Particularly, petroleum based transportation fuels have not yet been supplemented with **viable** transportation biofuels due to above-stated challenges. Bio-blend fuels such as E85 rely on subsidies to remain cost-competitive; Ethanol fuel is not considered a viable source of fuel due to inefficiency, high production cost, and negative impact on our nation’s food supply chain [13]. CFP does not compete with existing food sources as do other renewable fuel technologies, such as fermentation, which is a biochemical process for corn-based ethanol production [1,14].

Biomass-derived fuels represent the largest portion of renewable energy in the U.S. (Figure 1.1) [14]. Pyrolysis of biomass with the intent of producing pyrolysis-oil (bio-oil), as one of the promising thermochemical technologies among nascent conversion pathways, is being extensively studied at research institutions and individual corporations [15–17]. Bio-oil, as the major product of pyrolysis, offers a potentially viable means of supplementing petroleum-based fuels due to low-cost and widespread availability of domestic biomass resources (e.g., organic wastes and forest harvest residues). Additionally, the net GHG emissions of burning biofuels are minimized since releasing CO2 from biomass does not introduce new carbon into the atmosphere [18].

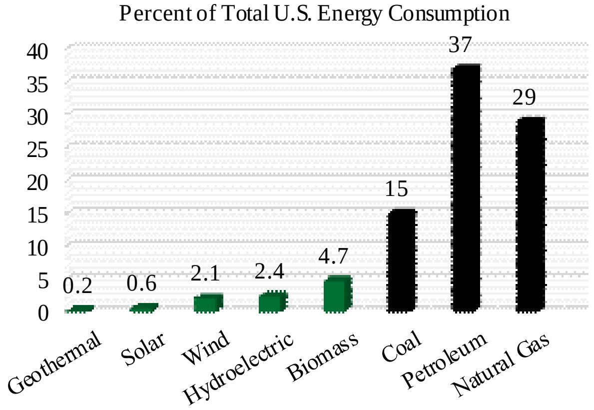

Figure 1.1. 2016 U.S. energy consumption by energy source

The motivation of this thesis is to identify the best technologies for biofuel production from bio-oil produced from CFP, and investigating nascent technologies such as ultrasonic cavitation, catalytic transfer hydrogenation, and emulsion fuel, or blended bio-oil and diesel. The aim of this thesis is to investigate the current state of technology, and contribute results, findings, and proposed future work to progress the field of biofuel produced from bio-oil.

1.2. Research Objectives and Tasks

This thesis is based on the Catalytic Fast Pyrolysis (CFP) system and associated bio-oil upgrading equipment located at the Center for Advanced Energy Studies and the University of Idaho in Idaho Falls, Idaho, USA. The pyrolysis system produces biochar and bio-oil. Our objective is to optimize the bio-oil output and improve the quality of the bio-oil product in order to advance the cost competitiveness of bio-oil based biofuel in general. The tasks associated with the objective include the design and build of the system, optimization of the system through automated control, equipment testing and bio-oil production, experimentational treatment of bio-oil (e.g., ultrasound and Catalytic Transfer Hydrogenation), characterization of treated and untreated bio-oil, and analysis of bio-oil test results.

Reviewing previous literature and pyrolysis reactor designs provided a background framework to design a reactor that could handle our desired feedstock and meet facility requirements relating to safety. A significant amount of trial and error proved most effective to improving the process and increasing bio-oil yield.

Upgrading the base system to automated control via a Human Machine interface was crucial to allowing us to increase the size and accurately control a complex system. All mechanical controls were hardwired to a Programable Logic Controller that interfaced with a laptop. The electronic control of the process is also an important step in allowing the system to be controlled using artificial intelligence algorithms which have not yet been developed.

Bio-oil upgrading technologies, including ultrasonic treatment, catalytic transfer hydrogenation, and bio-oil diesel emulsion were investigated for effectiveness at hydrogenation and de-oxygenation of the bio-oil using a Sonomechanics LSP 500 ultrasound generator and an interfacing treatment vessel made of High Polish Quick Connect Fittings. This apparatus allowed us to investigate various process parameters under mild operating conditions. Samples collected from the tests were carefully labeled and sealed for shipment to Huffman Laboratories in Golden, CO.

Ultimate Analysis was performed on samples to eliminate conflicts with CAES facility requirements, results from Huffman were analyzed in EXCEL by graphing various samples to identify trends between treatment. This data has been shared with Idaho State University as part of a growing effort to correlate traditional results with future analysis techniques such as Hyperspectral Imaging, which currently lacks a large enough database to prove reliable.

1.3. Research Scope

An average of roughly eight million barrels of crude oil are been imported to the U.S. each day and the majority of transportation fuel is petroleum-based (i.e., crude oil). Biofuel contributions to transportation fuel are less than 5% in recent years meaning there is huge potential for a drop in compatible green biofuel that can offset some

Widespread availability of biomass in the form of energy crops, agricultural residues, and forest harvest residues contributes to a low-cost readily sourced carbon resource; associated costs with collection and transportation negatively impact its practicality. Biomass feedstocks can be converted into bio-oil or biochar, using thermochemical processes (e.g., pyrolysis and gasification) and be upgraded to transportation grade fuels, using upgrading facilities (e.g., hydro treating and fluid catalytic cracking. Lignocellulose feedstocks are chosen due to availability in the form of industry residues and underutilized biomass, hence the latter specification has been identified as the primary source of fuel for pyrolysis conversion studies and this thesis. The Catalytic Fast Pyrolysis setup used in this thesis serves as a prototype lab scale piece of equipment that allows for testing of Cyber Physical adaptation of the initial biomass to bio-oil process, as well as a source of bio-oil for subsequent testing of upgrading strategies which forms the basis of the work presented herein.

1.4. Thesis Outline

This thesis is presented in manuscript format and consists of five chapters and three appendices.

Chapter 2 is a review of the existing bio-oil treatment technologies from past successful researchers across the globe. The review identifies key areas of research that are not being addressed, as well as under explored options for upgrading bio-oil that are promising in terms of offering sustainable and novel contributions to the field of biofuel production. This chapter is an article submitted to the Journal of *Renewable and Sustainable Energy Reviews.*

Chapter 3 identifies ultrasound and chemical bio-oil treatments as the most minimally invasive and least expensive upgrading strategies, namely Catalytic Transfer Hydrogenation. Catalytic Transfer Hydrogenation is performed on in house produced bio-oil and reports on preliminary results of analyzed samples.

Chapter 4 explores an alternative to upgrading altogether in the form of blended bio-oil and diesel emulsion. A technical overview of fuel combustion mechanics, and previous work is presented in conjunction with some early testing of bio-oil diesel emulsions using simple time-photo analysis to show effectiveness of Ultrasonic induced emulsions. This chapter is an article published at the *ASME 2019 International Design Engineering Technical Conferences & Computers and Information in Engineering Conference (IDETC/CIE 2019).*

Chapter 5 provides general overall conclusions for this thesis and offers suggestions for future work, and considerations of what has been accomplished.

Chapter 2. A Comprehensive State-of-Technology Review for Upgrading Bio-oil to Renewable or Blended Hydrocarbon Fuels

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Submitted to Renewable and Sustainable Energy Reviews

2.1. Abstract

Bioenergy sources are being advanced as a meaningful environmental solution and a substitute for conventional energy sources. Bioenergy from biomass feedstocks currently comprises the largest portion of renewables in the United States. Thus, more effective process-level solutions can result in scaling-up biomass-derived energy production (e.g., biofuels). Pyrolysis, a thermochemical conversion technology, offers a commercially viable pathway to produce bio-oil from a wide range of biomass feedstocks (e.g., algae and terrestrial). Bio-oil requires further upgrading for producing final bio-products (e.g., transportation fuels and biochemicals). This article focuses on upgrading bio-oil to transportation fuels (liquid hydrocarbons), highlights the critical challenges of existing upgrading technologies, and identifies the potential research directions to meet the market needs. A comprehensive overview and classification of bio-oil upgrading pathways and their competencies are presented through both comparative and systematic literature reviews. It is concluded that the biofuel production cost is highly dependent on post-conversion pathways, particularly their hydrogenation and deoxygenation capacity. Thermochemical treatments are effective, but less cost-competitive due to the intensive process requirements (e.g., heat or pressure). Physicochemical treatments are less effective, however, they operate under mild process conditions and could be integrated with other treatments. Biochemical treatments are inadequate as a standalone process for upgrading bio-oil. It is further concluded that the electrochemical approach can be effective due to the retention of hydrogen from bio-oil water content during deoxygenation.

2.1.1. Highlights

- Overview of existing bio-oil-to-biofuel technologies and recent improvements
- Thermochemical upgrading treatments are effective but less cost-competitive

- Physicochemical treatments are not as effective as thermochemical treatments
- Electrochemical upgrading operates at mild conditions and does not require external H_2
- Ultrasonic cavitation can improve the process efficiency and reaction time of catalyst

Keywords. Biomass; Bio-oil; Hydrogenation; Deoxygenation; Biofuel; Blended Fuels.

List of Abbreviations. U.S., United States; SC, supply chain; ASTM, American Society for Testing and Materials; DOE, Department of Energy; CFP, Catalytic fast pyrolysis; HHV, high heating value; CC, Catalytic Cracking; HDO, Hydrodeoxygenation; EC, Electrochemical; ECH, electrochemical hydrogenation; NPSC, Non-thermal plasma synergistic catalysis; UC, Ultrasonic Cavitation; CTH, Catalytic Transfer Hydrogenation; PHA, polyhydroxyalkanoates; HAME, hydroxyalkanoate methyl ester; SR, systematic review; Mo, Molybdenum.

2.2. Introduction

Increasing global population and standards of living, as well as local economic growth are driving the depletion of international and domestic conventional energy sources (e.g., fossil fuels) [1]. In 2018, renewable energy contribution to the total United States (U.S.) energy consumption was approximately 11% (over 11 QBtu out of 100 QBtu), and have been suggested as part of a comprehensive strategy to address national priorities, such as promoting energy security, creating domestic job, and mitigating global warming (Figure 2.1) [2]. Thus, special attention should be placed on renewable energy sources (i.e., hydroelectric, biomass, geothermal, solar, and wind), particularly on biomass due to compatibility with the existing transportation infrastructure.

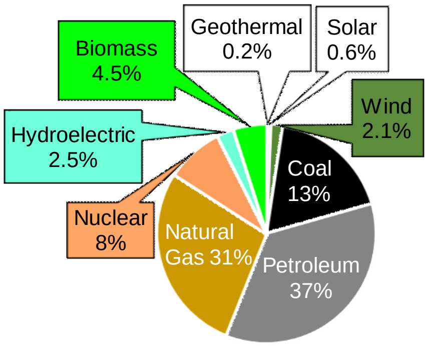

Figure 2.1. U.S. total energy consumption in 2018.

Stationary carbon-free energy sources (e.g., solar, hydroelectric, wind, and nuclear electric power) have limited penetration into the transportation sector, which is the second largest in energy consumption (consumed 28.8% of total) after electric power sector (consumed 38% of total) in 2017 in the U.S. [1]. Current established transportation infrastructures and technologies (e.g., internal combustion engines), and distribution infrastructures favor liquid fuels over other alternative solutions (e.g., electricity and hydrogen) due to numerous technical limitations (e.g., energy densities and fast charging) [3]. Biofuels from biomass can be a promising source of transportation energy due to cheap, renewable resources, and compatibility with existing technologies, engines, and transportation infrastructure [3].

Over the past 30 years, the need has arisen for an efficient bioenergy production process to address major challenges associated with diverse biomass feedstocks, initial conversion strategies, and upgrading processes, which are responsible for high production costs [4,5]. Biomass is a promising renewable resource due to its low price and abundance [6]; over 1.04 dry billion tons per year will be available by 2030 [7]. However, over 45% of biomass is underutilized due to upstream supply chain (SC) challenges (e.g., biomass collection, handling, storage, and pre-treatment processes) and midstream SC challenges (e.g., high production cost and immature conversion technologies) [6,8]. Biodiesel and other renewable fuels (excluding ethanol) consumed at an average rate of 1.2 million barrels per day in the U.S. in 2017 [9]. Therefore, biofuels have been suggested as part of a comprehensive strategy to cut petroleum and coal use in half by 2030 [9]. In the U.S., distributed fuels must meet the American Society for Testing and Materials (ASTM) and the Environmental Protection Agency (EPA) standards prior to distribution. EPA has recently proposed new standards for biofuels, which are detailed in earlier studies [10,11].

The U.S. Department of Energy (DOE) and independent researchers have extensively investigated biomass conversion processes that convert biomass to intermediate energy densified products, such as bio-oil, biochar, and syngas (Figure 2.2) [1,7,12], using thermochemical conversion processes (e.g., hydrothermal liquefaction, pyrolysis, and gasification) [13–16]. Catalytic fast pyrolysis (CFP) has been suggested as one of the promising technologies among nascent thermochemical conversion pathways for bio-oil production due to high process yield and bio-oil quality [17,18]. Other CFP byproducts (e.g., biochar and syngas) have applications in food-energy-water systems as biochemicals, biochar-derived fertilizers, and wastewater filtration systems [14,19,20]. Further details about the CFP are given by [21–24].

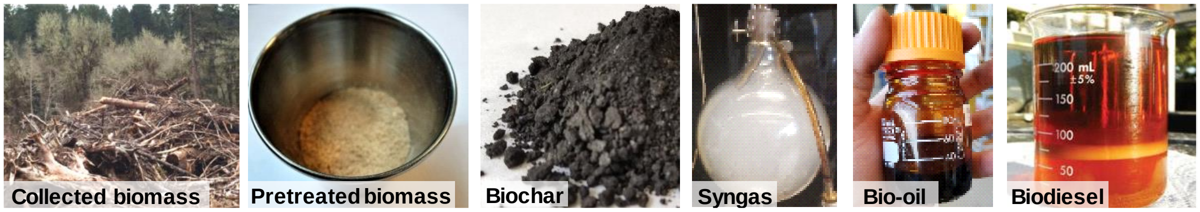

Figure 2.2. Bioenergy products from biomass feedstocks.

The properties and characteristics of bio-oil are extremely variable due to the inherent complexity of biomass’ composition (e.g., furan, hydroxyaldehydes, carboxylic acids, hydroxyketones, anhydrous sugars, and phenols) and lack of control on CFP reactions (e.g., dehydration) that are not entirely understood [25–27]. Table 2.1 presents bio-oil physiochemical properties along with ASTM standards [11,25,26]. Besides variability, bio-oil has several associated issues (e.g., corrosion, viscosity, and instability), which are due to its low pH, high oxygen to carbon (O:C) ratio, and low hydrogen to carbon (H:C) ratio that indicate the quality of liquid product [27–29]. The high water content and oxygenated compounds in bio-oil cause lower high heating values (HHV) of 15-20 MJ/kg compared to 45-51 MJ/kg found in transportation fuels (e.g., gasoline) [30,31], which subsequently increases the resources (e.g., heat and pressure) required for post-conversion treatments [32,33]. Additionally, bio-oil cannot be dried easily because temperatures over 100°C triggers polymerization.

Table 2.1. Bio-oil composition matrix and associated ASTM standards

Property (ASTM Standard)	Value (average)
C	56% wt.
H	6% wt.
O	38% wt.
N	0.2% wt.
S	0.02% wt.
Water content (D95, E203)	25% wt.
pH acidity (D974, D664, D3339)	2.5
Specific gravity (density compared to water)	1.2
High heating value (D240, D4809)	17 MJ/kg
Viscosity (D88, D445, D2170)	40–100 mPa
Solids (char content)	0.1%
Density (D1298, D4052)	1.2 kg/l

Post-conversion treatments attempt to address bio-oil issues by producing market-responsive bioproducts (e.g., biofuels and biochemicals) [34–37]. The treatments for improving bio-oil quality and compatibility are (a) dewatering and deoxygenation (reduces water and oxygen content) and (b) hydrogenation (increases hydrogen content) [38]. Bio-oil can potentially be used in fueling gas turbines and marine engines, however, in order to be used as biofuel in vehicle engines, it requires an energy-intensive upgrading with excessive requirements of hydrogen and catalysts [39–43].

Based on prior techno-economic studies, bio-oil upgrading represents the largest portion of the total biofuel production cost [44,45]. Existing upgrading pathways include thermochemical, biochemical, and physicochemical processes [46]. Thermochemical upgrading processes (e.g., hydrocracking, catalytic deoxygenation, and hydro-deoxygenation) can alter bio-oil characteristics and composition, using heat, pressure, hydrogen, and catalysts [38,47,48]. Thermochemical processes have received the most attention due to prior use in commercialized petroleum refineries, however, the high energy usage and hazardous conditions are considered as the major challenges.

Chemical and biochemical upgrading pathways (e.g., esterification, transesterification, and acid hydrolysis) can alter intermediate products (e.g., low-grade fuels) properties, using chemical solvents or biological treatments without added heat [49,50]. Integrated physicochemical upgrading processes (e.g., electrochemical and ultrasonic cavitation) use electricity as the primary energy source to improve bio-oil quality, using cavitation, electro-deoxygenation, and blending that involve both physical treatments and chemical reactions [9,53–55]. In other words, electricity can be applied directly or converted to mechanical waves that initiate other chemical reactions.

In this study, a literature review is conducted using comparative and systematic techniques to (a) explore the existing challenges, solutions, and advancements, (b) identify the chronological evolution of reported studies, and (c) define research and development gaps on bio-oil upgrading and biofuels production. Upgrading methods are discussed to provide an overview of the current state of existing technologies to identify high potential processes that can address persistent deficiencies and enhance aspects of sustainability in conjunction with smart manufacturing breakthroughs. Additionally, unsustainable or suboptimal strategies and methods are reviewed to gain a better understanding of requirements, intricacies, and opportunities for the future growth of biomass-derived fuels industry.

2.3. Comparative Review

2.3.1. Thermochemical Processes

The most common upgrading technologies utilize heat and pressure to initiate chemical reactions and address bio-oil deficiencies (e.g., energy density and corrosiveness), as well as separate bio-oil into distinctive fractions that can be altered via catalytic treatments and hydrotreating [56,57]. Existing petroleum refinery technologies that utilize high temperature and pressure have shown potential for upgrading bio-oil and other biomass-based intermediate products using various upgrading practices (e.g., hydroprocessing and fluid catalytic cracking) [39,58]. Although the thermochemical upgrading technologies for bio-oil are similar to petroleum refinery approaches, bio-oil is incompatible with existing petroleum infrastructure and requires stabilization due to its high water and oxygen content [36,59].

2.3.1.1. Catalytic Cracking (CC) and Hydrocracking

CC process produces biofuel via the breakdown of bio-oil into low-carbon aromatics and light olefins; alkylation of aromatics with olefins produced C8-C15 hydrocarbons similar to diesel [50,60,61]. Upgraded bio-oils using CC have met ASTM requirements based on the combustion heat, viscosity, and freeze point, which represents a promising substitute for the use in conventional petroleum refineries [62,63]. Gollakota et al. (2016) provided the most extensive review of thermochemical technologies and reported that the average CC temperature was 478°C [48]. Jurulluh et al. (2015) reported that CC used temperatures of 750-850°C, which shows different process configuration strategies between studies [64]. Corma et al. (2007) used CC to treat biomass oxygenates found in bio-oil to reduce oxygen levels, using zeolite catalyst [65]. Zeolite remains as one of the most highly effective catalysts for CC treatment, as reported in recent studies [60,66].

Hydrocracking (a variant CC) uses H_2 in addition to high temperature (400°C+) and catalyst to break longer molecular chains (e.g., carbon-carbon bonds) and achieve conversion yields of up to 20% for gasoline fraction [67]. Bio-oil compounds react with hydrogen through a catalyst at high temperatures to reduce oxygen and water content [68]. During hydrocracking, bio-oil vapor reacts with H_2 molecules to create alkanes (a molecular chain that comprises high-grade hydrocarbon fuels), such as cyclohexane. Hydrocracking approach for bio-oil upgrading is effective, but less cost-competitive due to the intensive process requirements (e.g., heat and hydrogen pressures). Equations 1 and 2 below show hydrocracking, where R_1 and R_2 are arbitrary hydrogen-carbon groups as part of a larger bio-oil molecule [69].

$$\mathrm{CH_{1.4}O_{0.4}\ (Organic\ Phase) + 0.7\ H_2 \rightarrow 1\ CH_2\ (Hydrocarbon) + 0.4\ H_2O} \tag{1}$$

$$\mathrm{R_1 - CH_2 - CH_2 - R_2 + H_2 \rightarrow R_1 - CH_3 + H_3C - R_2} \tag{2}$$

2.3.1.2. Hydrotreatment

Hydrotreatment (e.g., hydro-deoxygenation, hydrogenation, and hydro-desulfurization) refers to conventional processes used in today's petroleum refineries, using high-temperature (310-375°C) in conjunction with H_2 and catalyst to remove oxygen and sulfur in the form of H_2O or hydrogen sulfide (H_2S). Hydrotreating is primarily driven by a reaction between H_2 and phenols by breaking carbon-nitrogen, carbon-oxygen, and carbon-sulfur bonds [69], which produces Benzene and Cyclohexane that have more H_2-C bonds (Eqs. 3 and 4) [30,70,71]. Steam reforming allows for hydrogen production from hydrogen-rich gas (e.g., natural gas, methane, and syngas); thus hydrogen can feasibly be produced during thermochemical processes of biomass feedstocks, further details can be found in earlier studies by [32,72–74].

$$\text{Phenol} + H_2 = \text{Benzene} + H_2O \quad (3)$$

$$\text{Phenol} + 4\,H_2 = \text{Cyclohexane} + H_2O \quad (4)$$

Hydrodeoxygenation (HDO). HDO refers to oxygen removal from oxygen-containing compounds as opposed to H_2 supplementation [48]. Gollakota et al. (2016) reviewed 60 HDO studies for various temperatures and pressures, the average temperature and pressure of HDO was 364°C and 4.42 Mpa (641 psi), respectively [48]. Several metal-based catalysts (e.g., Ruthenium) have been tested for improving HDO, however, high cost and reusability are persistent issues [36,40,75]. Han et al. (2016) reported that Ruthenium showed resistance to deactivation in the presence of water, an issue that typically plagues other catalysts [40]. Primary factors for HDO catalysts are low-cost, reusability, coking resistance, and effectiveness [76]. Catalyst life cycle is currently limited to less than 200 hours as a result of coking [30]. Table 2.2 shows the bio-oil components before and after HDO. Alkanes (e.g., propane, butane, and methane) are products of hydrocracked bio-oil [30,33].

Table 2.2. Bio-oil components before and after treatment

Component	**Untreated (%)**	**Treated (%)**		**Bio-oil component range (%)**	
		HDO	**Hydrocracked**		
Guiacols	34.2	10.3	0.0	Acids	13–16
Acids/Esters	19.8	25.2	0.0	Esters	2–5
Ketones/Aldehydes	13.8	25.1	0.0	*Phenols*	10–18
Furans	11.7	6.8	0.0	Aldehydes	3–9
Phenols	10.3	18.6	0.0	Ketones	8–10
Other	6.8	3.4	5.6	Ethanone	1-2
Alcohols	3.5	5.3	0.0	2-Hydroxy	3-4
Aromatics	0.0	0.9	11.5		
Alkanes	0.0	4.5	82.9		

Traditional hydrocracking and HDO of crude oil results in the formulation of hydrogen sulfide, which poses a significant health hazard and is extremely corrosive [69,77,78]. Earlier studies reported that one of the benefits of producing biofuels from bio-oil is low bio-oil sulfur content (approximately 0.02% wt.) [67,79]. Table 2.3 compares two effective thermochemical treatments based on temperature and pressure range, as well as chemicals and catalysts used in prior studies [32,48,69,80].

Table 2.3. Hydrotreatment comparison

Treatment	**Temperature (°C)**	**Pressure (Mpa)**	**Chemical and Catalyst**
Hydrocracking	500-700 (avg. 478)	0.67-0.70 (avg. 0.00)	H_2/CO; CoMo, HDS, NiMo, and HZSM-5.
Hydrodeoxygenation	300-600 (avg. 364)	< 20 (avg. 4.42)	Ni–Mo and Co–Mo supported on Al_2O_3; Fe/SiO_2 (iron-based catalyst).

2.3.2. Physicochemical Treatments

Physicochemical treatments lack the effects of heat with external chemicals and benefit from low hazards, fewer process inputs, and generally increased sustainable aspects. As emerging technologies, they have not proven as effective as thermochemical or biochemical treatments, however, they could be incorporated as integrated solutions if used in conjunction with other treatments. Physicochemical treatments include electrochemical, plasma, ultrasonic cavitation, and mechanical blending, as described below.

2.3.2.1. Electrochemical (EC)

EC stabilization and upgrading of bio-oil does not require external hydrogen and can be performed at a wider range of temperatures and pressures [9]. As a byproduct, EC upgrading produces H_2 that can be used as a final product or an in-situ supplement for downstream HDO processes [9,76]. EC uses electricity to generate hydrogen protons (H^+) on the anode side of an electrochemical cell (Eq. 5). H^+ is then transferred to the cathode side through a cation exchange membrane, where the hydrogenation of the organic bio-oil molecules proceeds (Figure 2.3) [9,77]. Equations 5 and 6 show chemical reactions occurring at the anode and cathode site, respectively. The net reaction (Eq. 7) combines Eqs. 5 and 6, such as anode and cathode reactions to explain the full EC process [77]. Equations 8-10 use representative C, H, and O composition of bio-oil to show the electrochemical hydrogenation (ECH) process impacts on H-C ratio as reported by Lam et al. (2017) [9]. Equations are based on molar composition, where *n* denotes an arbitrary numerical value.

$$\mathrm{H_2O} \rightarrow \frac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \tag{5}$$

$$\mathrm{RCHO} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{RCH_2OH} \tag{6}$$

$$\mathrm{RCHO} + \mathrm{H_2O} \rightarrow \mathrm{RCH_2OH} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \tag{7}$$

$$\mathrm{CH_{1.99}O_{0.89}} + 0.51\mathrm{H_2} \rightarrow \mathrm{CH_{3.01}O_{0.84}} + \mathrm{O_{0.05}}\text{ (released)} \tag{8}$$

$$\mathrm{CH_{3.01}O_{0.84}} + 0.46\mathrm{H_2} \rightarrow 0.125\mathrm{C_8H_{18}} + 0.84\mathrm{H_2O} \tag{9}$$

$$\text{Bio-oil} + \frac{2\mathrm{n}}{3}\mathrm{H^+} + \frac{2\mathrm{n}}{3}\mathrm{e^-} = \text{Stable Bio-oil} \tag{10}$$

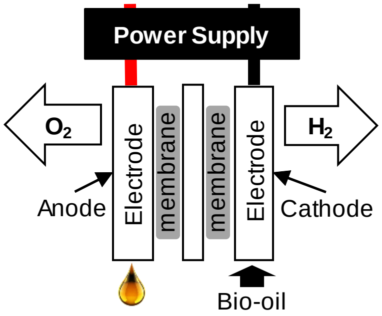

Figure 2.3. Electrochemical setup for bio-oil upgrading, dual membrane systems have been used to remove bio-oil carboxylic acids.

ECH effectiveness depends both on the exact bio-oil composition and the surrounding chemical environment, e.g., conductivity and acidity [78]. Earlier studies reported that hydrogenation of unsaturated C-C bonds is more effective than the hydrogenation of C-O bonds [79–81]. Benzoic acid is one example of a carboxylic group found in bio-oil that can be reduced to alcohol when aided via ECH [82]. Li et al. (2012 and 2014) investigated EHC for upgrading surrogate compounds (e.g., water-soluble fractions of bio-oil and phenolic compounds), using Ruthenium catalyst [78,83]. The high viscosity and low conductivity of bio-oil require the use of membrane electrode assemblies. The ionic membrane acts as the conducting electrolyte for proton transfer. Poor conductivity of bio-oil requires the use of membranes to increase effectiveness, but requires further research prior to actual use, since raw bio-oil has not been tested [9,77,84].

2.3.2.2. Plasma

Non-thermal plasma synergistic catalysis (NPSC) process uses application of an electric field within bio-oil to ionize or energize electrons and radicals [85]. NPSC approach reduces the process heat, energy requirements, and environmental emissions [86]. Catalysts (e.g., HZSM-5 and Pt–Re/Al_2O_3) can improve NPSC, and has been demonstrated as a potential conversion pathway with several benefits, such as in-situ hydrogenation and 47% deoxygenation when tested on surrogate 4methylanisole (i.e., a synthetic bio-oil compound) [85–88]. However, upgraded NPSC products are still considered hydrogen deficient, and catalyst suffered from extensive coking (i.e., deactivation) [86]. Maximum calculated conversion yield and deoxygenation rates were approximately 46% and 19%, respectively [85]. Pulsed NPSC was also used by Mosallanejad et al. (2017) to examine the effects on deoxygenation, and conversion rates of coronal discharge [85]. The highest deoxygenation was observed at 5 kHz and 32W, while greater conversion to phenols occurred at 20 kHz and 54W power. Adjusting pulse frequency impacted distinct bio-oil compounds and electrodes spacing on the test apparatus impacted conversion yield by 10% [85].

2.3.2.3. *Ultrasonic Cavitation (UC)*

Ultrasound generator uses a transducer, amplifier, and probe to convert approximately 60 Hz voltage to high-frequency mechanical energy (~20 kHz). Ultrasound equipment is simple to use and operates under mild conditions, such as low temperature and pressure. Different frequencies may be utilized for different purposes, e.g., high frequency causes cavitation and blending while the low frequency can encourage compound separation [89,90]. High-frequency waves from ultrasound generate micro-scale rise and the collapse of air cavities (e.g., cavitation) within the bio-oil [91]. Energy release from each micro-implosion is minimal, although cumulative effects can be significant [91,92]. Additional effects of UC are thermal scission, free-radical generation, and sonoluminescence, which indicate molecular alterations and other associated phenomena [92,93]. Figure 2.4 shows heavy bio-oil fraction and the cavitation that causes temperatures and pressure to reach 5000°C and 10 Mpa, respectively, via ultrasound treatment [94].

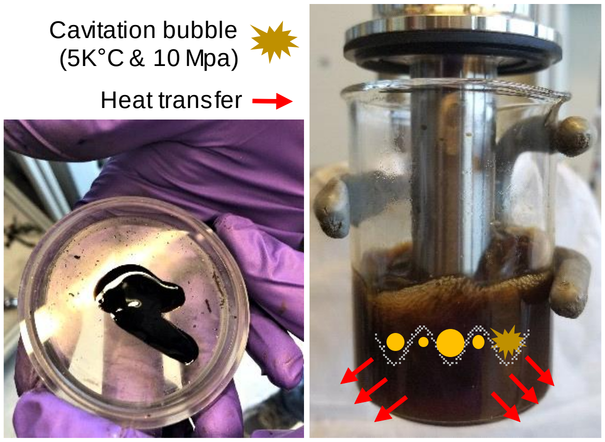

Figure 2.4. Heavy bio-oil (left) and ultrasound cavitation for bio-oil upgrading (right).

Splitting molecules allows to address bio-oil deficiencies (e.g., high oxygen, water content, and viscosity) through the destruction of C-O bonds and forming C-H bonds, using various catalysts and hydrogen donors [91]. Ultrasound-induced cavitation has seen extensive use in food production facilities for its use in reducing long molecular chains; thus, it can also assist in bio-oil corrosion, viscosity, and instability reduction [95,96]. UC treatment can also aid in the fractionation of bio-oil [89] and chemical conversion of muskmelon and vegetable oil to biodiesel [97].

2.3.2.4. *Mechanical Blending*

As an alternative to addressing bio-oil deficiencies, untreated bio-oil may be blended with other hydrocarbons (e.g., diesel and ethanol) in small fractions [98–100]. It should be noted that traditional practices (e.g., mechanically blended biofuels can result in diminished performance (i.e., fuel separation and oxidation). For example, the acidity and corrosiveness of bio-oil resulted in damage to fuel delivery components of a diesel engine during extended testing [101]. However, microscopic fuel blends (e.g., emulsion fuels, Figure 2.5a) can increase blended fuel stability if surfactants (e.g., chemical modifiers) are used for blending and mitigating some fuel issues, such as long-term stability [31,90,100,102–105].

High frequency ultrasound (e.g., 20kHz) can increase biofuel emulsion stability [106]. Examples of bio-oil being used in a biodiesel blend showed that many of bio-oil issues (e.g., acidity, flash point, viscosity, emissions, and low HHV) could be addressed, using bio-oil emulsions [90,107]. The greatest advantage of blended biofuel is the reduction in emissions and reduced or eliminated upgrading requirements [57]. Details regarding combustion of hydrocarbons and their respective emissions can be found in the earlier study by [108,109]. Xiu et al. (2012) discussed thermochemical, chemical, and blending as the primary bio-oil upgrading strategies. The production cost is the major limiting factor for bio-oil upgrading, biochemical extraction and hydrothermal liquefaction (similar to CFP with increased pressure) have been suggested as alternative steps for producing higher quality bio-oil [31].

2.3.3. Biochemical

Chemical and biological processes (e.g., transesterification and esterification) benefit from low capital cost, small-scale suitability, low hazard, and mild operating conditions due to low temperature and pressure in comparison to thermochemical approaches [36].

2.3.3.1. Esterification

Esterification uses alcohol-based solvents for the conversion of carboxylic acids to esters. Addition of alcohols to aldehydes, ketones, and sugars produce acetals [110]. Catalytic esterification (using Co-Zn/HZSM-5 catalyst) reduces acid values, water content, and viscosity at a greater rate than without catalyst [69]. Schulzke et al. (2017) esterified bio-oil using butanol, zinc oxide, and zeolites, which reduced H_2O and viscosity at 90% and 70%, respectively, and increased HHV from 16 to 31 MJ/kg, approximately 45% [111]. They reported that the upgraded bio-oil is compatible with boiler fuels, which have applications in heat and power co-generation plants [111]. Ciddor et al. (2015) provided an extensive review of the esterification process mechanics and chemistry [110]. Equations 11 and 12 shows non-catalytic esterification reaction to form esters from carboxylic acids and the formation of acetals from aldehydes. $R - OH$ and $2(R - OH)$ represent alcohols used in each equation, where R notation indicates a generic carbon-hydrogen group [110].

$$R_1COOH + (R - OH) \leftrightarrow R_1COOR + H_2O \quad (11)$$

$$R_1CHO + 2(R - OH) \leftrightarrow R_1CH(OR)_2 + H_2O \quad (12)$$

2.3.3.2. Transesterification

Transesterification utilizes alcohols to substitute long chains in esters with smaller carbon chains, which separates residual H_2O content, reduces viscosity, and increased pH [114,115]. However, the high solvent (e.g., ethanol or methanol) ratio to bio-oil raises sustainability concerns due to water contamination [113,116]. Biodiesel produced from transesterification requires lower upgrading operations in comparison to transportation gasoline, which is highly dependent on the type of biomass feedstocks used in the pre-conversion segment [51]. Additionally, biodiesel produced via transesterification exhibited higher combustion efficiency and cetane value, as well as lower sulfur content, biodegradability, toxic, and particulate emissions compared to petroleum-based diesel [117].

Zhang et al. (2017) reported on high-temperature transesterification (200°C) with low molecular mass alcohols (such as methanol, 1-propanol, ethanol, 2-propanol, and 1-octanol) for 6-50 hours duration to examine impacts of heat treatment in conjunction with transesterification [115]. For instance, they reported that 1-octanol reduced viscosity by 17%, however, it was less effective for stabilization [115]. Equation 13 outlines transesterification, where esters (acidic compounds present in bio-oil) are converted into hydrogen-rich alkyl groups (an intermediate biofuel component) and R^n notation indicates a generic carbon-hydrogen group [112]. The primary difference between transesterification and esterification is that esterification produces an ester and H_2O as final products, whereas transesterification uses an ester as a reactant, and produced alcohol and modified ester as final products.

$$\text{(Ester) } RCCOR^1 + \text{(Alcohol) } R^2OH \leftrightarrow \text{(Ester) } RCCOR^2 + \text{(Alcohol) } R^1OH \quad (13)$$

2.3.3.3. Catalytic Transfer Hydrogenation (CTH)

CTH uses H_2-rich donors in the presence of catalysts to add hydrogen to bio-oil compounds (Table 2.4) [116–119]. Bio-oil hydrogenation via CTH approach at mild temperature and pressure reduces hazards associated with using pure hydrogen. CTH with physicochemical treatments (e.g., ultrasonic cavitation, Figure 2.5b-h) can effectively increase the chemical reaction rate and improve bio-oil quality and C:H ratio [120,121].

Table 2.4. Catalyst and hydrogen donor candidates for CTH

Catalyst	Hydrogen Donor
Ni-Cu (Nickel and copper)	NH_3 (Ammonia)
Pd (Palladium)	NH_4HCO_2 (Ammonium Formate)
Pd/C (Palladium on carbon)	HCOONa (Sodium Formate)
Ru (Ruthenium)	HCO_2K (Potassium Formate)
Carbon Nanotubes	Furfuryl Alcohol

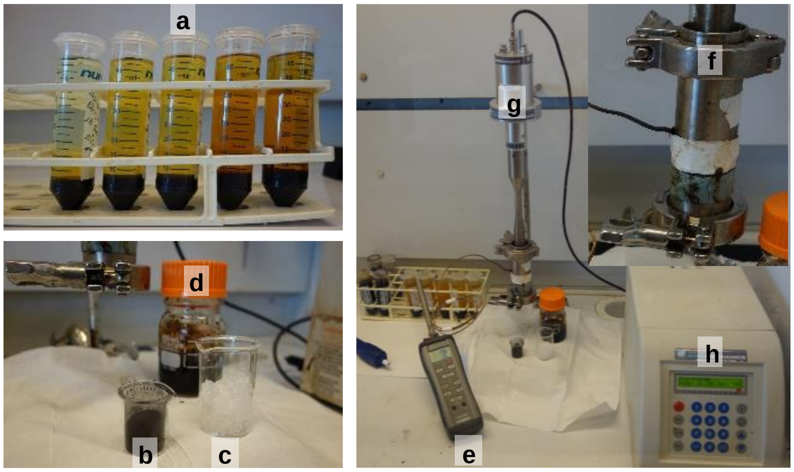

Figure 2.5. Bio-oil upgrading, using catalytic transfer hydrogenation with ultrasound cavitation, (a) emulsion fuels, (b) Pd/C catalyst, (c) NH4HCO2 (Ammonium Formate), (d) untreated bio-oil, (e) digital thermometer, (f) high-pressure/-temperature CTH vessel, (g)

2.3.4. *Biological*

Biochemical conversion pathways (e.g., enzymatic and acid hydrolysis) are designed for conversion of a limited, specific range of biomass to maximize productivity [122,123], which are not suitable for distributed (portable) production due to high capital cost and biomass specificities [122,124]. Although developing processes (e.g., microbial electrolysis) can be used in place of energy-intensive hydrotreatments to produce H_2 from aqueous bio-oil fractions for upgrading as a sustainable H_2 source [125,126]. Aqueous fractions of pyrolysis-based oil were treated, using a bacterial strain (Pseudomonas putida KT2440), which converts Phenols, Guaiacols, Furfural, and other substrates into usable chemicals and decreases post-treatment requirements [54]. Microbial polyhydroxyalkanoates (PHA) produced via bacteria growth in bio-oil can be used to create polyesters and are have been investigated for use in chemical and biofuel production [127]. 3-Hydroxybutyrate methyl ester (HBME) and hydroxyalkanoate methyl ester (HAME) are two biofuel additives resulting from PHA, which have been tested as a substitute for ethanol. The estimated cost for biofuel from HAME was $1200/ton; the U.S. gasoline was roughly $700/ton in 2017 [2,128,129]. Biological processes for upgrading bio-oil have been limited largely due to bio-oil toxicity, which is detrimental to bacteria growth [54]. Consequently, alternative biological pathways are being investigated for suitability for integrated energy systems [130]. Brown et al. (2007) investigated an integrated thermochemical and biological pathway, which fermented bio-oil, however, the upgrading costs were not competitive with conventional upgrading practices [131].

2.4. Systematic Review

Scholars have limited time to maintain an up-to-date knowledge of the state-of-the-science and recent breakthroughs. Literature reviews, therefore, play an essential role to help the investigators identifying the key variables and bridging the research gaps. The conducted systematic review (SR) study herein covers relevant bio-oil upgrading technologies for biofuel and blended fuels production, which are currently being developed as potential conversion pathways to meet market needs. SR aims to reduce bias from the author as opposed to comparative reviews that often reinforce partialities and author's research interest. The SR aids in identifying the major parameters of previous works to guide future studies by exploring the state-of-the-art in existing and next-generation conversion technologies. Two databases are generated in the Web of Science, using the following keyword sets, and a total of 273 papers are reviewed as part of the systematic literature review. It is apparent from the SR that interest in biofuel production from bio-oil is increasing, as shown by increasing publications for each keyword set in the last ten years, from January 2009 to December 2018.

- **Keyword Set 1**: (Bio-oil OR Biofuel) AND (Thermochemical OR Pyrolysis) AND (Hydrogenation OR Ultrasound OR Ultrasonic OR Esterification OR Electrochemical) AND (Renewable OR Sustainable OR Sustainability)
- **Keyword Set 2**: (Biomass OR Feedstock) AND (Bio-oil OR Pyrolysis-oil OR Pyrolysis) AND (Hydrocarbon OR Transportation OR Biofuel) AND (Hydrogenation OR Synthesis) AND (Renewable OR Sustainable)

The primary factors influencing the increased interest in biochemicals and biofuels from biomass are recourse scarcity and GHG emission reduction [132]. Figure 2.6 presents a comparison of the number of publications during the last ten years, using both keyword searches. A consistent increase in publications is an indicator of growing interest in biofuel production from bio-oil with the exception of 2018, showing a slight decrease in keyword set 1. Also, 2009 was the only year both keyword sets yielded an identical number of results.

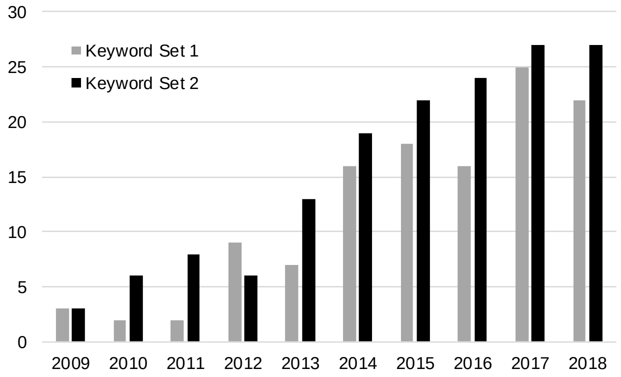

Figure 2.6. Publications by year for both keyword sets.

Gallezot (2012) is the first most-cited article in keyword set 1 that provides an overview of valuable chemicals produced from biomass, but did not focus on bio-oil produced from pyrolysis, which has been shown to be most viable conversion pathway [132]. Wang et al. (2013) also appeared in both keyword sets and the second most-cited in keyword set 1 [133]. They provided a review study on hydrotreatment of bio-oil, including an in-depth discussion of bio-oil composition, and function of noble metal catalysts (e.g., Ru, Pd, and Pt). They also reported that noble metal catalysts provided the best conversion rates and caused fewer deactivation issues. Rhodium (Rh) was shown to be the most effective catalyst, while Molybdenum (Mo) catalyst was shown to be unstable due to sulfide issues. They focused on CFP bio-oil and substituted compounds. In addition to the top two most-cited articles in keyword set 1, Venderbosch et al. (2010) ranked as the third most-cited article and presented stabilization of biomass-derived pyrolysis oils and the issue of rapid polymerization of bio-oil, which inhibits dehydration of the oil. They suggested that bio-oil can be mildly hydrogenated immediately after biomass conversion, in order to reduce overall issues and energy use associated with upgrading later [134]. Demirbas et al. (2011) appeared as the fourth most-cited article and performed a general overview of conversion technologies, pyrolysis-based oil treatments, and various biofuel types, however, many of them lack compatibility with transportation fuels (e.g., diesel and gasoline). They also reviewed biological pathways (e.g., anaerobic digestion), but they did not cover post-conversion and upgrading process mechanics, which are the primary challenges to commercialization [135].

Gallezot (2012) and Alonso et al. (2010) are the most-cited articles in keyword set 2 [132,136]. Alonso et al. provided an overview of biomass feedstock types and subsequent conversion technologies to intermediate bio-oil or ethanol product, however, this study lacks review of post-conversion processes and upgrading technologies to drop-in biofuels [136]. Zhou et al. (2012) ranked as the third most-cited article, and studied chemical and fuels production from lignocellulosic biomass. They also reviewed thermochemical pathways, focusing mainly on biomass pre-conversion technologies, as well as integrated hydroprocessing for producing fuels. They identified CFP as a front-runner for commercialization of sustainable biofuels, but did not extensively discuss upgrading pathways [137]. Donnis et al. (2009) appeared as the fourth most-cited article. They studied rapeseed oil and fatty acid methyl ester (FAME) as two biological-based feedstocks. They extensively covered hydrogenation, chemical reactions, and effects of various hydrotreatments that may be applicable in some ways to CFP bio-oil. However, these treatments are primarily for diesel production as opposed to gasoline, and many differences exist between CFP-based bio-oil and rapeseed oil or FAME, primarily CFP bio-oil is incompatible with many catalysts due to coking [138].

All most-cited articles in both keyword sets are published before 2013, since then, bio-oil upgrading technologies have advanced significantly. Thus, an up-to-date review study is necessary. Keyword set 1 had fewer citations than keyword set 2 since it included fewer thermochemical processes. Recent developments from the DOE showed CFP is one of the front-runners for biofuel production. Table 2.5 presents the top five productive organizations with the highest level of authorship in each keyword set. The National Natural Science Foundation of China has the most publications of any organization, with 11.7% and 13.5% of funding in each keyword set.

Table 2.5. Top five productive organizations based on the number of publications

Keyword Set 1		**Keyword Set 2**	
National Natural Science Foundation of China	14	National Natural Science Foundation of China	22
U.S. Department of Energy	8	Chinese Scholarship Council	5
Chinese Scholarship Council	4	Fundamental Research Funds for Central Universities	5
Canada Natural Sciences and Engineering Research	4	U.S. Department of Agriculture	3
Fundamental Research Funds for the Central Universities	3	National Key Basic Program of China	3

Table 2.6 reports the top ten countries with the most publication records for both keyword sets. The top three countries are identical for both keyword sets (e.g., USA, China, and Malaysia), most likely due to abundant biomass resources. Malaysia, for example, is a top producer of Palm Oil [139]. Chinese interest in biofuel from lignocellulose biomass has been driven in part by recent food shortages and population growth [140]. After USA, China, and Malaysia with a total of 96, 70, and 19 publications, respectively, eight of the top ten countries are identical in each keyword search.

Table 2.6. Comparison of top ten countries based on published articles

Keyword Set 1			Keyword Set 2		
Countries	**Publications**	**Percent**	**Countries**	**Publications**	**Percent**
USA	39	32.5	USA	57	35.0
China	30	25.0	China	40	24.5
Malaysia	7	5.8	Malaysia	12	7.4
Canada	6	5.0	India	10	6.1
England	6	5.0	Canada	8	4.9
Japan	6	5.0	Denmark	7	4.3
Brazil	4	3.3	Germany	6	3.7
India	4	3.3	Italy	6	3.7
Italy	4	3.3	Netherlands	5	3.1
Netherlands	4	3.3	Japan	5	2.1

2.5. Discussion

As of yet, a cost-competitive conversion pathway for biofuels production from CFP-based oil has not been achieved; thus, the opportunity remains for investigating either new or integrated technologies to improve existing approaches. During the past two decades, several technologies and conversion pathways have been presented and integrated (e.g., biological, chemical, electrochemical, and ultrasonic) to maximizing efficiency and profitability of individual entities to maintain competitiveness in the market-place. For example, current biological and chemical technologies can improve some aspects of bio-oil, such as viscosity and acidity, but they are incapable of fully upgrading bio-oil to transportation fuels because they are not able to reduce oxygen content (wt.%) and increase hydrogen content and heating value, which are major biofuel quality parameters.

Integrating various energy systems is one of the promising strategies to address upgrading costs for producing biomass-based transportation fuels and other byproducts, using new inventions and growing initiatives (e.g., low-pressure CFP, flow-through UC, and advanced high-temperature electrolysis), as well as low emission energy from micro-scale reactors [141]. An integrated conversion process can not only reduce capital costs and requirements but also simplify the process as a whole to reduce operational costs [142]. Determination of the most efficient conversion pathway is difficult, however, Xia et al. (2016) showed an increase in conversion efficiency (28% wt.) via integrated HDO with catalysts (e.g., Pt/NbOPO4) [143]. However, Won et al. (2017) performed an analysis between multi-step and single-step processes, showing single step conversion resulted in less energy use and lower operating costs compared to multi-step strategies [142].

Biofuels sourced from bio-oil can be market competitive if upgraded towards a single valuable liquid hydrocarbon blendstock, such as bio-jet fuel [33,144]. According to the U.S. DOE, jet fuel represents approximately 12% of total transportation fuels in the U.S. [145]. Previous work focused on bio-jet fuels, however, elucidation of the complex compounds and commercial viability issues has not been addressed [146–149].

There are several similarities and differences (e.g., temperature and pressure ranges) between upgrading pathways (e.g., hydrocracking, HDO, and hydro-desulfurization) for producing petroleum-based fuels and biomass-based fuels. Thermochemical temperature ranges vary between prior conducted studies, therefore, differentiating the various thermochemical treatments can be difficult. Gollakota et al. (2016) provided a detailed outline of previous researchers who used catalytic cracking, though many listed temperatures well below the accepted threshold (e.g., 350°C) to be considered as a thermochemical operation [46]. Fischer Tropsch synthesis was excluded from this study because it is intended for upgrading the primary products of gasification conversion process (i.e., syngas) rather than the primary product of pyrolysis process, which is bio-oil [150].

Bio-oil produced from CFP in comparison to crude oil must be amended (e.g., thermochemically, physicochemically, or biochemically) prior to integration with existing petroleum refineries or distribution as a hydrocarbon substitute [30,64,142,151]. Meanwhile, existing biofuel production practices cannot meet the energy market needs, however, supplementing biomass with hydrogen-rich fossil fuels (via co-firing waste oil or coal) during the initial thermochemical conversion of biomass-based oil can be an approach to address the stated bio-oil deficiencies and biofuel commercialization challenges [13,47,152–154]. Graca et al. (2013) demonstrated that co-processing of hydrotreated bio-oil with crude oil with ratios up to 20% and 80% could produce gasoline fractions essentially identical to pure crude oil-based fuels although catalysts and hydrogen consumption remained a notable issue. Similarly, non-renewable hydrogen-rich fuel sources that are otherwise considered as wastes (e.g., plastic, tires, and scum) can boost hydrogen content of untreated bio-oil and address other issues when co-processed with biomass [55]. Also, hydrogen can be produced from bio-oil for in-situ hydrogenation, however, the existing conversion technologies are immature and inefficient [42,67]. Regardless of the treatment challenges and profitability, biofuels generally have fewer NO_X and SO_2 emissions and consequently emits less CO_2 eq. and particulate matter (e.g., PM2.5, PM10) when compared to petroleum-based fuels [31,155–158].

Figure 2.7 represents how bio-oil compares with petroleum distillate compounds, which can be separated, using fractional distillation. The fuel distillation curve is an important parameter that can be advantageous for understanding the complex transportation fuel properties and performance. Low distillation temperature indicates the respective molecular size, volatility, viscosity, and combustion temperature of each fraction [41,159]. Traditional processes fractionally distill crude oil into suitable products (e.g., diesel, jet fuel, and gasoline) prior to treatment. However, bio-oil upgrading processes to high-grade fuels via physical and chemical treatments (e.g., HDO, UC, and ECH with catalysts, hydrogen donors, and solvents) can reduce contaminates, O:C ratio, and low-quality components, as well as consequently increase the H:C ratio gradually as opposed to attempting the conversion of the whole fraction.

Figure 2.7. Distillation scale of bio-oil and other liquid hydrocarbon mixtures.

Biochemical pathways (e.g., esterification and transesterification) are enticing due to low capital and operational costs and mild operating conditions. However, the disadvantages of biochemical upgrading approaches are high solvent and catalyst consumption. Chemical treatments are best suited for biodiesel production as opposed to gasoline as a result of less stringent diesel ASTM standards. Esterification and transesterification as batch processes are difficult to upscale. Esterification and transesterification are inadequate as a standalone process for upgrading bio-oil due to high bio-oil oxygen content, which requires higher deoxygenation than chemical upgrading processes have achieved.

UC can impact bio-oil through co-treatment with transesterification and phase separation via hydrolysis, which can separate oil and water fractions. UC treatment can also act as a blending tool for the emulsion of residual water content or combining bio-oil with diesel fuel for the use in combustion engines. UC is advantageous due to mild operating conditions and its lack of toxic chemicals [97]. UC is able to reduce bio-oil viscosity and water content independently and proves effective as a supplementary treatment with other upgrading technologies, such as transesterification. However, tolerances between studies vary due to differences in resources used, equipment, process parameters, and bio-oil composition. In comparison with HDO, UC has not been extensively investigated or proven, however, UC can improve the process efficiency and reaction time of catalyst intensive chemical treatment. Commercial scale UC facilities will require further testing to elucidate the effects of reaction parameters and high capital cost.

EC treatments are newer pathways for improving bio-oil quality that are currently under development to address the associated challenges. Plasma approached used relatively higher voltage

(25V+) than EC (0.1-10V), but an energy analysis for each would need to be performed separately to determine the process efficiency and profitability. For example, the primary issue regarding the EC technology is membrane coking from bio-oil, and low bio-oil conductivity that limits the effectiveness of the reaction [162]. The unique benefit of EC treatment is the retention of hydrogen from H_2O content during deoxygenation, which reduces supplemental hydrogen needed for future upgrading. EC conversion pathways are similar to other non-thermal technologies since operating conditions are mild. Though proven to affect oil quality, EC can be considered effective since it is not capable of producing useable liquid hydrocarbons. Full bio-oil to biofuel conversion process with EC approaches have not been demonstrated as viable pathways due to existing intricacies. However, there is a significant opportunity to advance these approaches from their current state.

Based on the number of published articles from the conducted SR between January 2009 and December 2018, thermochemical technologies have been developed and utilized extensively in comparison to other technologies and published studies combined. The number of studies, using biochemical, physicochemical, and thermochemical technologies have been 315, 48, and 1,889, respectively. There are only nine studies of EC technology during the past ten years. Thus, thermochemical technologies can be regarded as the prominent methodology for investigation since this sector was the primary topic of 84% of all publications discussing bio-oil treatment strategies. Moreover, esterification has received more attention than transesterification based on the results (number of published articles) of conducted SR in this study. Also, the biological methods have received the least amount of investigation due to several issues and could benefit the most from further investigation. Therefore, particular attention should be placed on current and future generation of post-conversion technologies to enhance commercial competitiveness and techno-economic sustainability benefits across the renewable and blended hydrocarbon fuels industry.

2.6. Conclusion and Future Directions

Over the past decade, the need has arisen for more innovative, efficient upgrading and valorizing carbon-based materials in various forms to cost-competitive products, using biomass feedstocks and low-emissions energy sources. The comparative and systematic reviews presented herein provide an overview of existing bio-oil-to-biofuel technologies, process and product challenges, potential science and engineering research paths, and opportunities for future work. The comparative review investigates the prominent conversion processes for bio-oil upgrading based on complexity, efficiency, and profitability. Despite recent improvements, bio-oil upgrading technologies will require further investigation and advancements to overcome process deficiencies (e.g., yields) and product shortcomings (e.g., quality and compatibility) to become commercially viable. The primary bio-oil quality issues are low hydrogen content and high oxygenate content, which impact most other attributes. Existing upgrading approaches are either energy intensive, unsustainable, or ineffective as standalone processes.

This study has determined that upgrading strategies are best indicated by their hydrogenation and deoxygenation capacity, as well as process requirements (e.g., heat and pressure). Thermochemical treatments (e.g., hydrocracking and HDO) for bio-oil upgrading are effective, but less cost-competitive due to the intensive process requirements (e.g., high temperature or pressure). Physicochemical treatments (e.g., UC and plasma) are not as effective as thermochemical or biochemical treatments, but they have mild operating conditions and could be incorporated as integrated solutions in conjunction with other treatments. UC can improve the process efficiency and reaction time of catalyst intensive chemical treatment. Esterification and transesterification are inadequate as a standalone process for upgrading bio-oil. EC approach can be considered minimally effective due to the retention of hydrogen from bio-oil water content during deoxygenation, which eliminates supplemental hydrogen required for producing useable liquid hydrocarbon blendstocks.

This study highlights the gaps and bio-oil upgrading strategies, which are dependent on the end product specification and designation, such as mid-range bio-oil products for co-processing or drop-in biofuels. Biofuels have been most extensively tested for blended fuels production, as this represents the most economically favorable pathway to commercialization. This path still requires remedial bio-oil treatment prior to blending. Co-processing of bio-oil with petroleum as a secondary step utilizes thermochemical upgrading techniques, which are energy intensive and unsustainable. On the other hand, widespread implementation of biofuel blending with petroleum-based fuels may improve emerging technology success in industrial applications. Under-developed technologies (e.g., UC, plasma, and EC) can be promising alternatives, which need further investigation. Additionally, optimization of current technologies, using Industry 4.0 and the Internet of Things can help achieve cost competitiveness and sustainability of each respective technology.

From both comparative and systematic reviews, it is clear that there is an essential need to continue development of biomass-to-biofuel conversion pathways as this represents a major viable solution to various national priorities: energy security, use of diverse domestic natural resources, advanced bio-industries and rural economies, and the dramatic environmental consequences attributed to the use of fossil fuels (e.g., greenhouse gas emissions). Thus, significant research and developments are needed to overcome the drawbacks of traditional bio-oil upgrading and biofuels production practices. Further research to advance bio-oil upgrading technologies and commercialization of biomass-based transportation fuels are as follows:

- Exploration of integrated energy systems (e.g., thermochemical, micro-scale nuclear reactors, high-temperature steam electrolysis) for biofuels production from biomass feedstocks and low-emission energy resources (e.g., nuclear heat).
- Development of blended fuels production from blending bio-oil with petroleum-based fuels, using ultrasound cavitation and emulsification to bring the biofuel industry closer to economical mass production.
- Exploration of tightly coupled existing mild treatments (e.g., EC, CTH, and UC) with commercialized thermochemical practices, using modeling and simulation approaches for input-output analysis to investigate the total resources used (e.g., energy and catalysts) and fuel produced.
- Development of a real-time chemical and spectral characterization of bio-oil and biofuel products to optimize the conversion processes, using cyber-physical advances for diagnostic and prognostic assessments to understand various intricacies of each operation.

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Chapter 3. Ultrasonic-Assisted Catalytic Transfer Hydrogenation for Manufacturing Biofuels: Process Design and Preliminary Results

3.1. Abstract

Existing biofuel conversion processes are energy intensive, and the need for the more efficient process has stimulated research efforts in addressing major challenges associated with process configurations and production costs. Biofuels currently comprises the largest portion of renewable energy sources in the United States. Thus more efficient process-based solutions can result in promoting biofuel production. This research aims to investigate the potential for biofuel production practices from various biomass feedstocks (e.g., invasive plant species, agricultural wastes, forest harvest residues, and algal), using three major technologies, i.e., catalytic fast pyrolysis, ultrasonic cavitation, and catalytic transfer hydrogenation. Existing bio-oil deficiencies, such as low hydrogen content and high oxygen levels necessitate hydrogenation for compatibility with current fuel specifications. Ultimately, the results of this research indicate that the combined – ultrasonic cavitation and catalytic transfer hydrogenation –upgrading pathway can increase the bio-oil energy content and promote bio-oil quality to an extent not done previously.

3.2. Introduction

Global demand for transportation fuels (e.g., biofuels and blended fuels) has increased recently due to a growing standard of living and population, and is projected to grow 40% by 2035 [1,2]. Ethanol represents the largest share of biofuel produced in the U.S.; 379,435 barrels were produced in 2017 [1]. Only 37,993 barrels of bio-diesel were produced in 2017 comparatively, while the US consumes 20.5 million barrels of petroleum product. The transportation industry alone consumes 13,889 barrels of petroleum product daily [1]. Global demand for biodiesel is expected to top 11 billion gallons in 2025, driven by concerns over climate change [3]. Conventional biodiesel and ethanol rely on severely limited feedstocks which negatively influence food production [4]. Furthermore, the Biotechnologies Office (BETO) has set a goal to produce bio-oil priced competitively at \$3/gal. [5]. Biofuel synthesis from pyrolysis derived oil (bio-oil) has advanced recently as a potential source of renewable transportation fuel, however, existing technologies are not able to convert biomass feedstocks to fully equivalent transportation fuels as a result of persistent deficiencies e.g., low hydrogen to carbon (H:C) ratio, high O_2 content, and H_2O content [6]. Table 3.1 shows bio-oil properties, and standards set by the American Society for Testing and Materials (ASTM).

Table 3.1. Bio-oil properties and relevant ASTM standards for testing [5–7]

Chemical Property	**Amount**	**Physical Property**	**ASTM Standard**
C	56% wt.	Density	D1298, D4052
H	6% wt.	Water content	D95, E203
O	38% wt.	Viscosity	D88, D445, D2170
N	0–0.1% wt.	Heating value	D240, D4809, D5865
Water content	25% wt.	Acidic Value	D974, D664, D3339
pH	2.5	Composition	D5373, D5291
Specific gravity	1.2	Specific Gravity	D2274
High heating value	17 MJ/kg	Oxidative Stability	D2274
Viscosity	40–100 mPa		
Solids (char)	0.10%		

Bio-oil from biomass feedstocks is an intermediate product, resulting from various thermochemical conversion technologies, e.g., catalytic fast pyrolysis, liquefaction, and gasification [7,8]. Bio-oil in raw form can potentially be used as heating oil however, bio-oil remains inequivalent to petroleum fuels due to has several issues Oxygen content is the primary inhibitor to upgrading and reacts with H_2 to form H_2O when hydrogen is added [9].

Bio-oil hydrogen to carbon ratio is one of the major parameters that shows bio-oil quality [9]. Quality issues with viscosity, acidity, and thermal instability require remedial treatments prior to storage and or transport [10]. Acidic fuel ruins internal engine components, while thermal instability prevents long-term storage necessary for distribution at the commercial level [11].

Upgraded bio-oil can be used as drop-in biofuels or alternative hydrocarbon fuels that are functionally equivalent and compatible with existing internal combustion engines [12,13]. Several pathways for bio-oil upgrading have been developed, such as biochemical extraction, thermochemical processes, and physical treatments [14].

Biochemical extraction upgrading pathways, e.g., transesterification, esterification, and electrochemical deoxygenation are less effective when compared to high-temperature and high-pressure treatments [15]. For example: electrochemical deoxygenation has only been explored in a limited capacity, early results are not well backed [16]. Other technologies such as transesterification, and esterification are time intensive and considered mild treatments when performed alone [15]. More specifically, they do not address major issues such as hydrogen content.

Thermochemical upgrading processes (e.g., thermal cracking and hydrotreatments) are effective, however, they are unsustainable and suboptimal due to high energy requirements, which must be mitigated as new technologies emerge [17]. Thus, energy reduction strategies and practices are gaining attention in various biofuel conversion processes that can consequently reduce the production cost, promote energy security, using diverse domestic energy resources, and mitigate the dramatic environmental consequences attributed to the use of fossil fuels (e.g., greenhouse gas emissions).

Ultrasonic cavitation is a fairly new approach for upgrading bio-oil which has been used extensively in food pro cessing applications due to the reduced use of toxic chemicals [18,19]. It has also been used to treat crude oil fractions with similar issues as bio-oil, e.g., high viscosity, H_2O, and oxygen content [20–22]. Ultrasonic processors use a transducer to convert 60 Hz voltage to high-frequency (~20 kHz) mechanical vibrations; inducing extreme temperatures on a micro-scale to break heavy-oil fractions into smaller fractions. Figure 3.1 shows a cavitation sequence. Vibration induced waves cause cavitation i.e. the violent rise and collapse of air cavities within the oil [20,23]. Cavity implosions cause phenomena such (e.g., sonoluminescence, thermal scission, rarefaction, radical formation, and bond cleavage)as sonoluminescence and thermal scission [20,23]. Resulting internal temperatures can reach 3700 °C-10000 °C in water and pressures up to 2000 atmospheres [24].

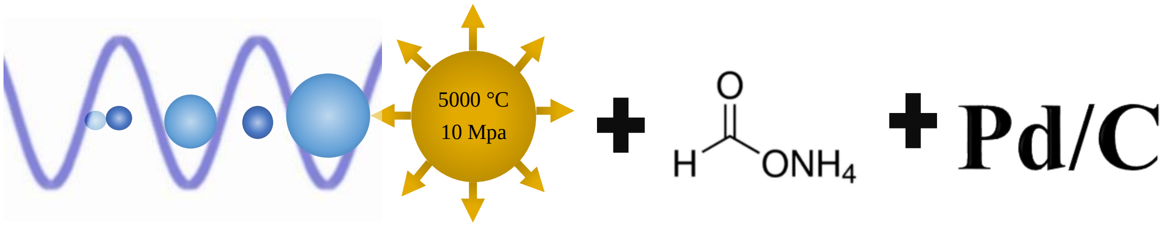

Figure 3.1. Cavitation Sequence in conjunction with Ammonium Formate (HOONH4) and catalyst (Pd/C) for hydrogenation of bio-oil.

Ultrasound treatment has several benefits, such as improved reaction rate, reduced catalyst deactivation, and improved process efficiency, as well as reduce energy consumption during processing, hazards, and feedstock use (Table 3.2) [24,25]. Fewer investigations have been conducted on bio-oil upgrading through ultrasound treatment to reduce oxygen compounds, which plague bio-oil [26]. However, preliminary results of ultrasonication are promising [27–29]. When used in conjunction with other treatments (e.g. transesterification); bio-oil had repeatedly enhanced treatment effectiveness [30,31].

Table 3.2. Ultrasound benefits and studies

Ultrasound Benefit	Study
Reduced catalyst use	[23,26]
Reduce oil viscosity	[19–21]
Hydrogenation	[33]
Deoxygenation	[34]
Dewatering	[35]

Hydrogenation is an approach of increasing hydrogen content of a compound via supplementing H_2 through an external source [31]. Transfer hydrogenation-dehydration reactions are environmentally friendly, and function via transferring H_2 from a H_2 rich donor compound to bio-oil, i.e., a low temperature chemical reaction [32]. Catalytic Transfer Hydrogenation (CTH) employs catalyst for enhanced reactivity [32]. Several catalysts have been used for bio-oil upgrading, such as Ruthenium, Palladium, and Nickel [31]. Porous catalysts allow for greater H_2 transfer. Metallic catalysts allow for reuse of expensive, but effective materials for greater cost efficiency. Palladium (Pd) has been used extensively in the literature for hydrogenation reactions due to exhibiting the qualities discussed [33,34]. Additionally, Pd catalyst is highly active and is widely used since it requires mild conditions [35]. One study explored Pd for Hydrogenation of oil as early as 1983 [36]. Ammonium Formate (NH_4HCO_2) is one commonly known H_2 donor, which is commonly used during CTH [37].

This study is part of a larger effort to enhance sustainability benefits across the biomass-to-biofuel supply chain. Prior studies reported that biofuel production processes represent the largest portion of the total costs, over 60% [38]. Therefore, decision makers (e.g., managers and researchers) should focus on novel midstream segment of biofuel supply chain, i.e., pre-/post-conversion processes to satisfy the stakeholders and maintain competitiveness in the biofuel industry, which is the focus of this study. The proposed approach and an actual case study are detailed in the next section.

3.3. Production and Upgrading Approach

The proposed approach in this study includes two steps: 1) a pre-conversion process, using catalytic fast pyrolysis (CFP), and 2) a post-conversion process, using ultrasonic-assisted catalytic transfer hydrogenation (UCTH) pathway. The CFP pre-conversion pathway is a thermochemical technology that can be designed to be feedstock agnostic and be amenable to the distributed operation, such as portable refinery [39]. Additionally, low capital cost and high-quality bio-oil production achieved at 400-600°C temperature and 10-15 psi pressure within below two seconds residence time are unique advantages that are accessible via a CFP conversion pathway, which is why we considered the CFP technology for bio-oil production.

3.3.1. Pre-conversion Process

The in-house built CFP includes a customized entrained flow reactor, a cyclone, and condensers (Figure 3.2). The CFP production process is a well-explored technology, details regarding process intricacies can be found in the following review [40]. Although the general process is not new, our design is novel as a lab-scale continuously operated design, using an auto feed system, a programmable logic controller, auto flow controllers, and solenoid valves. Our customized CFP reactor utilizes a pre-heated flow, in-line cartridge heater, and an external tape heater to produce bio-oil from various biomass feedstocks. Additionally, a solid copper coil has been used internally for increasing biomass contact with heated elements via direct conduction, induced turbulence, and longer residence time (~ two seconds). The copper coil acts as a catalyst, which reduces O_2 content via an oxidation reaction. The results indicate that the copper coil primarily aided in thermodynamic heat transfer. Compressed nitrogen gas has been used to purge and entrain biomass during the conversion process. Details of pre-conversion process parameters, using the CFP, are outlined in Table 3.3.

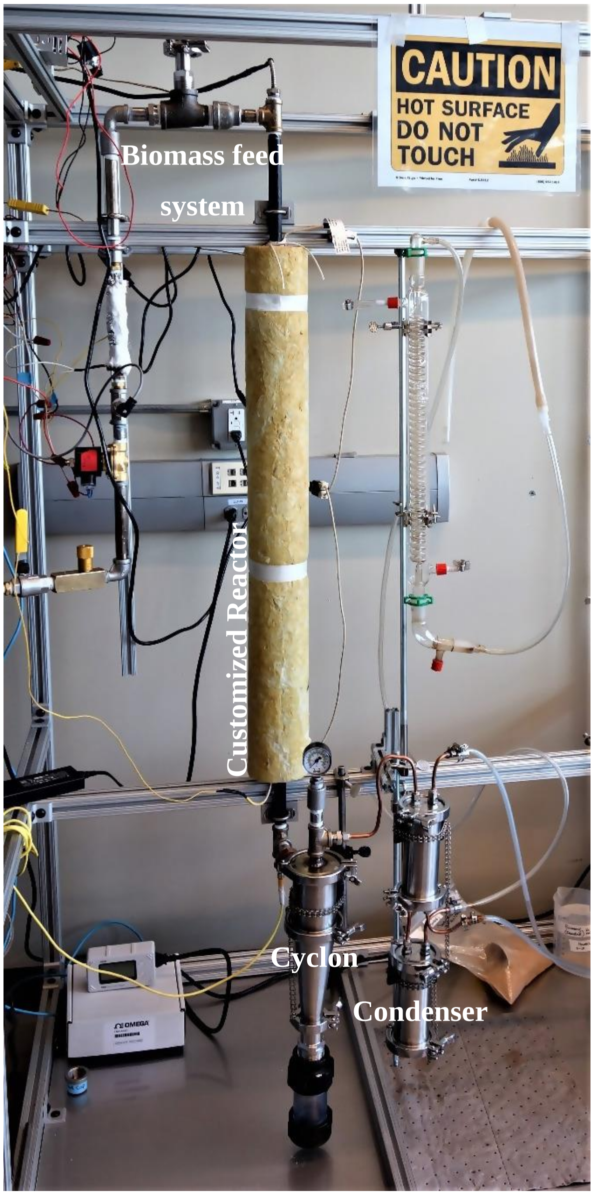

Figure 3.2. Catalytic fast pyrolysis reactor.

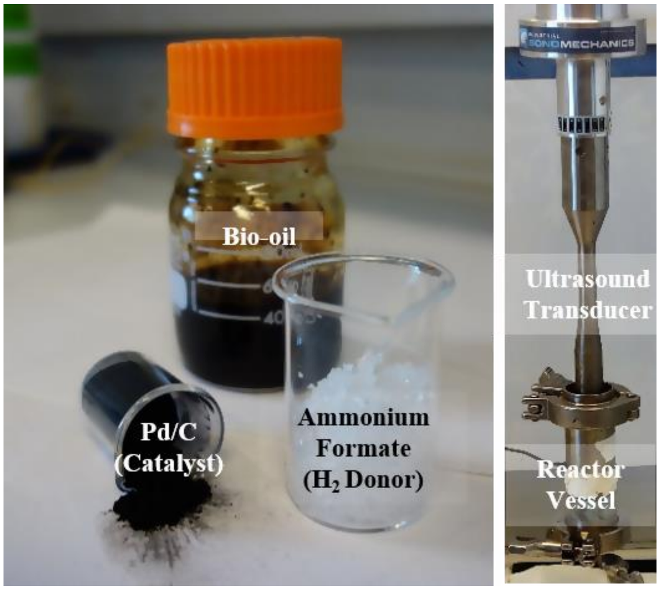

Figure 3.3. Catalytic transfer hydrogenation catalysts, H2 donor, and ultrasound device.

Table 3.3. Process parameters

Process Control	Set point	Average Value
Pre-heater	200°C	
Core Heater	500°-550° C	
Tape Heater	500°-550° C	
Thermowell Probe	N/A	500°C
Flow Rate	15-23 LPM	20 LPM
Pressure	10-15 psi	12.5 psi
Condenser	5° C	5° C
Biomass Size	2 mm	~2 mm
Copper Coil	10 Ft	N/A
Residence Time	1-2 sec.	2 sec.

The developed CFP reactor in this study is unique for its multi-zone heating and adaptability for future modification. Development of a CFP conversion process proved difficult in some instances and confirmed several general findings from prior reported studies [41]. For example, the customized equipment (e.g., auto feed system, CFP reactor, cyclone, and distillation unit) are difficult to outsource and required custom-fabrication [42]. Additionally, existing testing instruments (e.g., gas chromatography-mass spectrometry (GC-MS) and Fourier-transform infrared (FTIR) spectroscopy, Karl Fisher titration and bomb calorimetry) cannot provide real-time information. Therefore, locating a facility and apparatus for bio-oil characterization proved challenging.

3.3.2. Post-conversion Process

A UCTH conversion pathway has been developed to upgrade the produced bio-oil in the pre-conversion process by integrating the ultrasonic processor with a CTH approach (Figure 3.4) for biofuels or blended fuels production.

Figure 3.4. Ultrasonic-assisted catalytic transfer hydrogenation.

Palladium (Pd) on carbon support in 1% loading (Pd/C 1%) was used as a catalyst based on subject matter experts and literature findings. Ammonium Formate ($HCOONH_4$) was added at various (%) wt. samples to investigate the effects of increased H_2 dono alone. Ultrasound treatment was performed at 20kHz and 50% amplitude for a pulse duration of 20 seconds on, 59 seconds off for 10 minutes of total treatment time. Pulse mode operation was used to allow for atmospheric cooling of the ultrasonic vessel and prevent pressurization from occurring.

A duplicate oil sample was withheld from treatment for post treatment analysis and comparison. 60 mg. bio oil was placed in our reaction vessel, catalyst and Ammonium Formate were pre-measured, and introduced to the vessel simultaneously for treatment of 10 minutes. Following treatment a sample from the treated oil was removed, and treated for a longer time duration.

Based on the disparate nature of conversion technologies and inherent complexity associated with various biomass types, it is not surprising that there is little work has been done to integrate the pyrolysis process with ultrasonic cavitation.

To the best of our knowledge, this study is the first pre-/post-conversion pathway, employing CFP and UCTH for biofuels production. The UCTH alters bio-oil molecular structure via cavitation, rarefaction, and hydrogenation, using various catalysts (e.g., Pd/carbon) and solvents (e.g., ethanol). High pressure and temperature peaks are seen during cavitation, and their impacts on the treated medium are similar to intense hydro-treatments. Additionally, this study investigates the effects of ultrasound treatment both independently and in conjunction with CTH.

Upgrading bio-oil requires testing to determine baseline oil qualities for comparison of the effectiveness of bio-oil treatments. Depending on the bio-oil quality, requirements for upgrading may be significant, such that initial conversion process deficiencies should be amended rather than upgrading deficient oil.

3.3.3. Post-conversion Process

Our experiment was designed to investigate the impact of hydrogenation alone, using a single catalyst loading of Palladium on Carbon support (1% Pd/C). Due to intrinsic complexities such as bio-oil composition and unknown reaction kinetics, performing hydrogenation of the bio-oil using Hydrogen donor in loadings ranging from 2.5%-15%. Multiple H2 loading tests are designed to examine the reaction mechanisms and extent of hydrogenation aided by ultrasound. The reaction has been outlined in the experiment matrix Table 3.4. Using a semi-batch model at various levels of hydrogenation allows for an absolute determination of reaction extend during the initial batch, and the opportunity to examine more accurately reaction progression at a smaller resolution.

Table 3.4. CTH experiment plan

No.	Mass	$HCO_2 H_4$	1% Pd/C	Time	Error (% H2)	
1	55	0	0	0	0	N/A
2	55	2.5	0.55	2.5	5	Maximum
3	56.925	5.0	N/A	5	2.6481	Minimum
4	55	7.5	0.55	2.5	10	Maximum
5	59.675	10.0	N/A	5	7.5	Minimum
6	55	12.5	0.55	2.5	15	Maximum
7	62.425	15.0	N/A	5	12.5	Minimum
8	55	0	0	10		N/A

3.4. Discussion and Results

Bio-oil yield from the setup is roughly calculated, since mass balancing of equipment was not possible. The estimated average yield based on the mass of produced oil compared with initial biomass was averaged between separate test runs. Average yield was calculated to be 43% based on prior experimentation. Biomass to bio-oil conversion rates, e.g., yield, was calculated by mass balancing biomass feed with bio-oil collected post condensation. The yield rate of our bio-oil appears lower than other reported results, however due to internal deposition in the reactor, cyclone, and condenser, large scale conversion rates would feasibly be significantly higher. Our group did not attempt to measure syngas since our reactor used a gas feed system which made monitoring syngas difficult.

Optimization of bio-oil yield is not a singular function of temperature and residence time since material feed processes, required downtime for cleanout, and vapor distillation all impact yield and quality. Current literature assumes the optimization of process design has already been achieved, we believe such assumptions are overly optimistic. Our experiments show improvements to distillation (condenser) alone could increase yields. The incompatible nature of bio-oil with laboratory equipment, as well as instruments significantly reduces the accuracy of some results, for example, bio-oil residue/film deposits are lost each time samples are transported, lessening the value of subsequent volumetric and gravimetric analysis.

Produced bio-oil samples have been investigated for preliminary testing of total acid number, viscosity, flash point, and oxidative stability, as well as density, specific gravity, and relative acidity. Table 3.5 reports the results and the corresponding ASTM standards. Preliminary results indicate that the flash point (i.e. ignition temperature) of our produced bio-oil is approximately 114 °C. The flash point of diesel in the U.S. is 130°C (ASTM D6751) [31], which is roughly 12% higher than our CFP-derived bio-oil. Additionally, the viscosity of our bio-oil samples is 32 cSt, which is 92% higher than diesel with 2.5 cSt (ASTM D975) [45] (Table 3.6).

Table 3.5. Catalytic fast pyrolysis bio-oil characterization results

Property	Standard	Description	Result	Units
Acid Value	ASTM D974	Acid and base number by color indicator titration	97	mg KOH/g
Flash Point	ASTM D93	Flash Point by Pensky-Martens Closed Cup Tester	114 ± 2	°C
Viscosity	ASTM D445	Kinematic Viscosity of Liquids	32.4	cSt
Oxidative Stability	ASTM D2274	Oxidation Stability of Fuel Oil (110 °C)	0.02	hr
Density	Lab Measure	Mass Divided by Volume	1133	Kg/m3
Specific Gravity	Hand Calc.	Derived From Density	1.13	ratio
Acidity	pH Test Strip		3	pH

Table 3.6. Bio-oil sample and diesel [43]

Properties	Diesel	Bio-oil
Flash Point (°C)	70°	114°
Viscosity (cSt)	2.5	32
Density (kg/m^3)	837	1133
Acid Value	0.24	97

The presence of H_2O reduced flash point values, thus UCTH can improve flash point via hydrogenation. Viscosity is especially suited for treatment via the ultrasonic processor (Figure 2). Total acid number, though distinctly high, typically results from oxygenated compounds. The proposed CTH can reduce these compounds to some extent. Subsequent esterification, a mild chemical treatment commonly used for biodiesel, could further address the high acid value of our bio-oil samples. Pending further testing and analyses, CTH treatment of bio-oil is a promising approach to address the existing bio-oil deficiencies, e.g., low flash point, high total acid number, and high viscosity.

Figures 3.5 and 3.6 compare H_2O content of bio-oil from Corn and Stover Pine samples, respectively. The marked increase in H_2O % wt. with increased H_2 donor % wt. of both bio-oil sets indicates hydrogenation, since H_2 reacts with oxygen to form water.

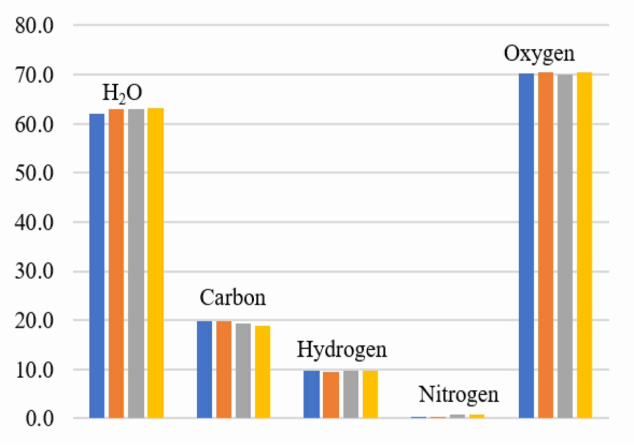

Figure 3.5. Ultimate analysis of corn stover bio-oil.

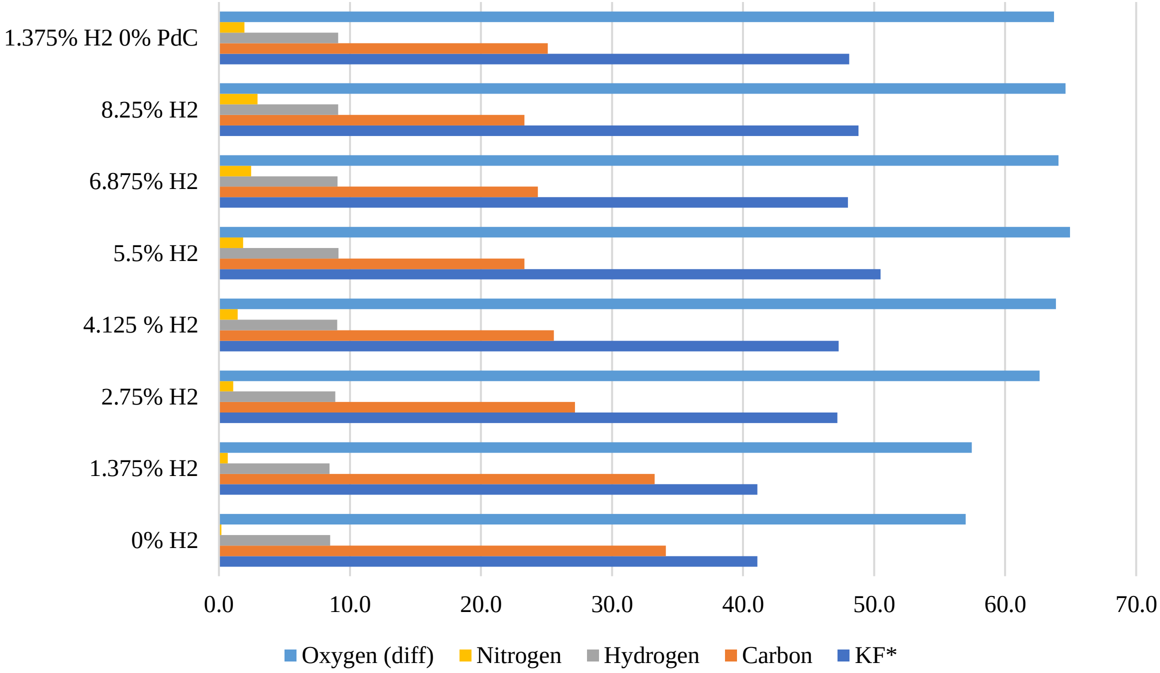

Figure 3.6. Ultimate analysis of pine bio-oil.

Figure 3.7 shows increased H_2 content of Pine bio-oil with increased H_2 donor % wt. The 5.5% wt. sample is an outlier however this may be attributed to testing error. The general trend indicates a positive relationship and successful hydrogenation of the bio-oil. Higher levels of H_2

donor show the optimal H_2 donor can be found at 5.5% of total mixture yielded roughly 7.3% increase in overall H_2.

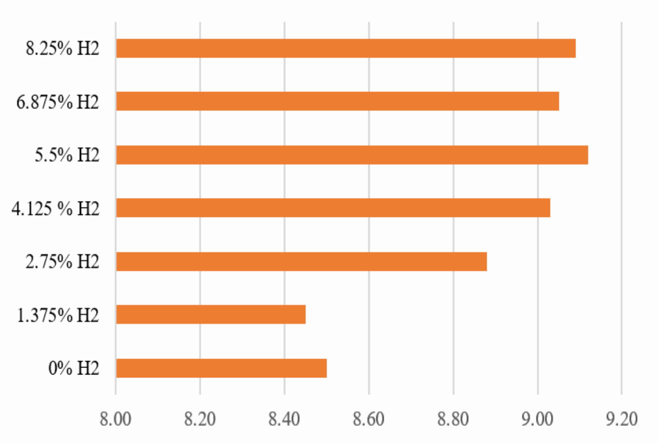

Figure 3.7. Hydrogen analysis of pine bio-oil.

Although the described data indicates a higher level of oxygenation than hydrogenation, the ultimate analysis used calculated oxygen content by difference, which could indicate that other non H-C-N elements were created that were indistinguishable from that of the oxygen estimation. Oxygen that was removed remains indistinguishable from retained oxygen due to the sealed vessel. Thus, our analysis only shows oxygen content as opposed to the deoxygenation of various bio-oil compounds. Gas Chromatography (GC), Mass Spectroscopy, or Thermo Gravimetric Analysis (TGA) could provide greater insight into the changes that have occurred.

A new suggested method of measuring the compounds found in bio-oil would use Hyperspectral Imaging. Figures 3.8 and 3.9 show a comparison of hyperspectral analysis of petroleum and bio-oil samples, e.g., untreated (UT), ultrasonic treatments (UC 1 and 2), and aged bio-oil. Each sample data set is the average of over 60 images taken at each wavelength increment. Bio-oil samples were first placed into a plastic petri dish and homogenized by spreading to uniform thickness of about 1/2” diameter. The ASD probe was then held at a height of 1/2 inch above the sample and 3 separate spectra were collected, each spectra produces an average of 20 spectral readings; our results are the average of 3 separate tests, i.e., 60 spectra. Figure 3.9 shows hyperspectral imaging in a dark room for better results. Ultrasonic treatment showed greater reflectance in every wavelength except for the 1900 nm-2200 nm range, where untreated bio-oil showed the greater reflectance than treated samples respectively. The greatest change was shown by the sample treated with ultrasound for 7.5 minutes (#2) which was obvious from 500nm to 1400nm. Several issues are evident from the initial results: our ultrasound treatment did not attempt to monitor temperature or pressure change as a result of treatment. Therefore, results could be skewed from unintentional loss of volatile compounds that evaporate at lower temperature. Hyperspectral analysis also showed that there were issues with bio-oil imaging, for example, the thickness of bio-oil during imaging varied by an unknown amount, this could impact spectral measurements via contamination from the plastic container spectra. Further research and process refinement is needed to determine the validity of our hyperspectral results using existing techniques (GC, MS, and TGA). Unfortunately, these methodologies were unavailable to our research group due to high cost.

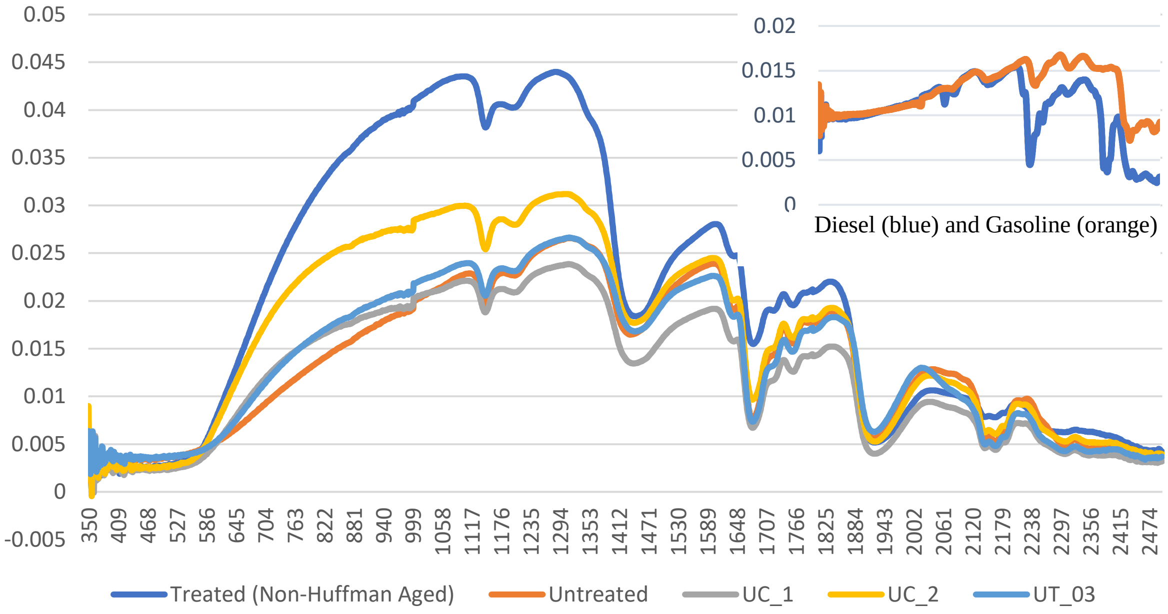

Figure 3.8. Average reflectance treated and untreated bio-oil.

Figure 3.9. Hyperspectral imaging of bio-oil.

3.5. Conclusion and Future Direction

This study aims to demonstrate bio-oil remediation via UCTH. Limited research has been done on these processes thus far, advances in equipment and catalysts which can be used make this an exciting opportunity. The impacts of both ultrasound treatment and transfer hydrogenation serve to address critical issues of bio-oil. The combined technologies offer a more sustainable and manageable means to improve bio-oil and advance biofuel synthesis. With further research, effectiveness could approach that of more intensive processes whose intrinsic functions are similar to that of UCTH.

3.5.1. Future Direction

Hyperspectral Analysis could allow for inexpensive testing of bio-oil, this is one barrier we found that prevented rapid progress. Process parameters that could alter UCTH include pressurized UCTH, high temperature UCTH, and or usage of different unexplored yet sustainable catalyst and hydrogen supplement, both of which affect current pricing negatively. Future work can focus on upgrading bio-oil hydrocarbons using hyperspectral analysis to guide treatments rather than other expensive tests. Our group is presently working on developing in-house bio-oil and biofuel testing system to facilitate real-time analysis, control, and optimization, which will enable smart manufacturing of transportation grade fuels. Smart biofuel production can promote sustainability in biofuel production through improving conversion yields and intermediate/final products quality, as well as production efficiency and productivity [40].

3.6. Acknowledgments

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3.7. References

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Chapter 4. Bio-Oil Upgrading Via Micro-Emulsification and Ultrasound Treatment: Examples for Analysis and Discussion

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4.1. Abstract

Blended fuels allow biofuels (e.g., bio-oil, ethanol, and biodiesel) to be commercialized by mixing them with petroleum-based fuels and address their deficiencies, such as compatibility with existing engine systems. Traditional blends (e.g., B20, E15, and E85) rely on mechanical mixing and use of surfactants (stabilizing chemicals) to prevent mixture separation, however, in many cases bio-blends suffer from reduced performance. Bio-oil, a low-grade liquid biofuel, has high potential in blended fuels production and addresses its deficiencies, such as high upgrading cost due to high oxygen-carbon ratio and H_2O content. Emulsion technology is a relatively immature process, which relies on microscopic H_2O blended with fuel for increased performance and stability. This study explores how residual H_2O in bio-oil may increase performance and compensate for its deficiencies by using bio-oil in diesel emulsion. Our research shows that (a) H_2O emulsion fuel has received little attention yet, which can offer many benefits to reduce fuel consumption and emissions, (b) H_2O content in bio-oil may be significant enough to impact performance in a diesel engine if stability concerns are addressed, and (c) the stability of bio-oil derived diesel emulsions may be increased over conventional practice, using ultrasonic cavitation. It is concluded that emulsified bio-oil in diesel is able to address common upgrading challenges by skipping H_2O removing operation and using H_2O in bio-oil to enhance blended fuel performance. Ultimately, bio-oil can be used to supplement diesel fuel and develop a commercial market similar to the strategy's used earlier with ethanol production from corn.

Keywords. Bio-Oil, Blended Fuel, Emulsion, Environmental Emissions

4.2. Introduction

Vehicle fuel efficiency and hydrocarbon emissions are growing concerns nationally and internationally due to perceived threats from climate change, energy security, and resource scarcity [1]. In recent efforts to reduce emissions resulting from transportation fuels, various conversion technologies and upgrading strategies have been explored to increase fuel economy and efficiency to address environmental emissions [1,2]. According to the U.S. Energy Information Administration (EIA), roughly 47% and 26% of a crude oil barrel can be converted to gasoline and diesel, respectively (Figure 4.1) [3]. On the other hand, renewable and sustainable transportation fuels (e.g., bio-oil derived fuels and biodiesel (Figure 4.1) can address limited resources and increased demand for petroleum-based fuels in compression-ignition engines [4].

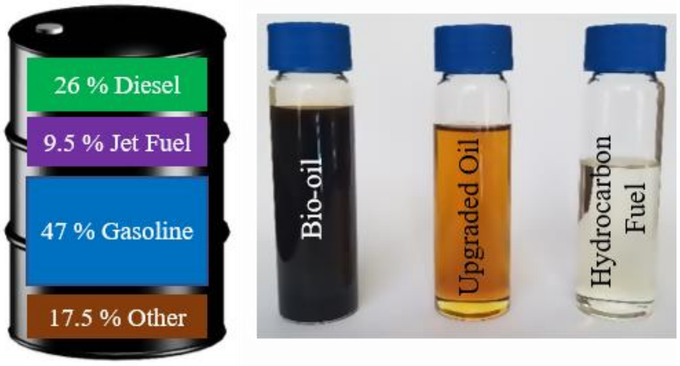

Figure 4.1. Crude oil breakdowns and bio-oil derived fuels.

This study examines the use of blended or modified emulsion fuels, blended fractions of liquid hydrocarbons and H_2O at a microscopic level. Although adding water to fuel appears counterintuitive to the layperson, numerous studies have reported positive results of emulsified fuel with positive benefits [2]. Biofuels, specifically biodiesel blends or emulsions are a potentially feasible way to immediately supplement a significant volume of diesel with several crucial benefits that can impact engine performance and emissions. The goal of this study is to examine ultrasonic induced water in fuel emulsions (WFE) using bio-oil as an H_2O carrier.

Catalytic fast pyrolysis (CFP) derived bio-oil is an intermediate biomass densified product that can be produced from various lignocellulose sources (e.g. forest and agricultural residues), organic wastes (e.g., cattle manure), and advanced feedstocks (e.g., algae) [3]. CFP is currently considered as one of the most prominent thermochemical conversion technologies by the Department of Energy (DOE) due to high quality and process yield, as well as low capital and operational costs in comparison to other thermochemical technologies (e.g., liquefaction and gasification) [4–6]. CFP-derived bio-oil can be improved as a drop-in substitute biofuel or compatible hydrocarbon that is suitable for use in today’s internal combustion engines [7,8]. However, bio-oil contains high water content, which can be difficult and expensive to remove since water is suspended and does not separate easily from hydrophilic compounds present in the oil [9]. The energy required for dewatering bio-oil constitutes roughly 85% of total energy consumption during upgrading of some bio-oil [10].

Thus, elimination of the dewatering step in bio-oil treatment process saves significant costs. Table 4.1 compares properties of water and petroleum fuels that impact WFE performance [21].

Table 4.1. Properties of petroleum-based fuel and water

	Cp (Vapor) J/kg K	**Cp (Liquid) J/kg K**	**Hx of Vaporization kJ/kg K**
H_20	2,009	4,186	2,260
Diesel	1,700	2,050	250
Gasoline	N/A	N/A	305

Emulsion is the combination of two immiscible (non-mixing) fluids, specifically where smaller spherical droplets are dispersed in the larger fluid body (Figure 4.2) [11–13]. Emulsions can be prepared or formulated by the use of chemical additives (e.g., surfactants), mechanical mixing, agitations, high-pressure homogenizers, and ultrasonic vibrations [14]. Sugeng et al. (2017) injected steam into low-temperature diesel fuel in order to form WFE emulsions, though this methodology had limitations, including limited H_2O content [15].

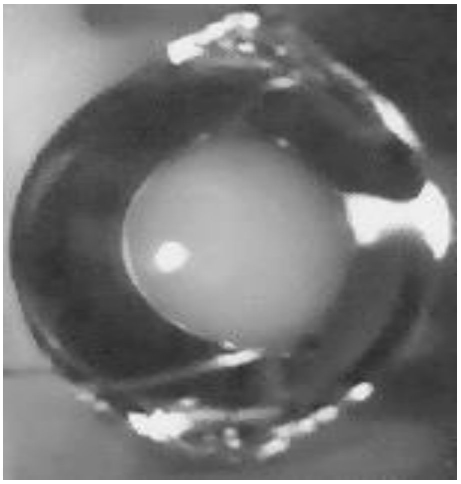

Figure 4.2. Emulsion of H_2O and a combustible oil (adapted from [2]).

Three methods exist that water can be added to the combustion process: (1) direct injection, (2) fumigation of air intake, and (3) emulsion of H_2O in the fuel prior to traditional injection [16]. The last technique is considered as the most viable since fuel treatment prior to distribution remains compatible with existing vehicle engines [16]. WFE for diesel engines are of greatest interest since compression ignition engines require fewer modifications for the use of emulsion fuels and see greater performance and emission benefits [14].

Transportation grade hydrocarbon blendstocks are composed of several fractions and must adhere to the American Society for Testing and Materials (ASTM) to prevent degradation of the product. Depending on environmental concerns and initial composition, some blendstocks (e.g., ethanol blends) are more prone to separation than conventional petroleum-derived products [17]. Conventional fuel treatment relies on standardized mixing of products to address commercialization challenges, however, they are less stable over time since separation an occur [11]. Still, mechanically mixed fuel emulsions show promising results as a temporary alternative to upgrading [18]. H_2O emulsions absorb heat during the evaporation phase of combustion due to a high latent heat of evaporation compared with hydrocarbons, which are 300 kJ/kg vs. 2,254 kJ/kg, respectively [19]. Table 1 outlines petroleum-based fuels (i.e., diesel and gasoline) and water characteristics, including specific heat and latent heat of evaporation. Specific heat (Cp) and latent heat of vaporization are intrinsic material properties, which indicate heat input and absorption during phase change. The rapid phase change of H_2O results in greater diesel fuel dispersion, and a more efficient combustion reaction [20]. Fuel and H_2O evaporation are essential for cooling an engine, a 170°C decrease in temperature was noted using a 50% WFE [19].

Micro-explosion phenomenon is as spontaneous explosion of water vapor droplets during the combustion phase of fuel, where encapsulated H_2O vaporizes and expands more rapidly than diesel (Figure 4.3) [16,19,20].

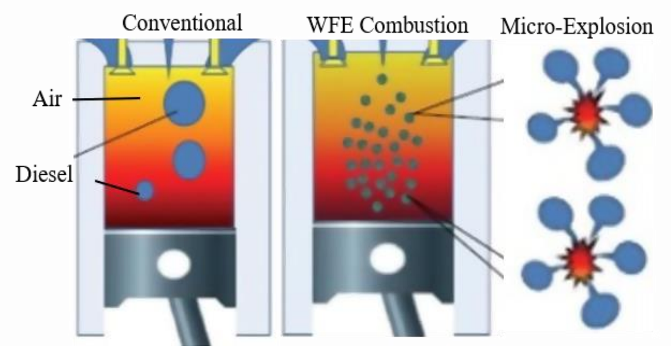

Figure 4.3. Water in fuel emulsion micro-explosion (adapted from [14]).

Ultrasound treatment has seen limited investigation for bio-oil upgrading and producing hydrocarbon fuels, however, few studies examined bio-oil emulsification in diesel, using high H_2O content of bio-oil as WFE [21–23]. Ikura et al. (2003) studied effects of bio-oil blended with diesel as an emulsion, however, ultrasound technology was not used to improve the emulsions [24,25]. Guo et al. (2014) examined bio-oil emulsions produced from ultrasound for long-term stability, however, details regarding the emulsion fuel’s performance were not investigated [26,27]. Emulsion of bio-oil with petroleum-based products offers a short-term approach to utilizing bio-oil in modern engines, though some modifications to injectors, and fuel pumps would be required [18,24,28]. Ikura et al. (2003) suggested that bio-oil in diesel emulsions could encourage bio-oil commercialization if used directly in diesel engines as a substitute or supplement [24]. Markarfi and Ganda (2018) recently referred to emulsification as “bio-blending,” and reported that biodiesel blends reduced engine emissions and improved fuel efficiency and combustion characteristics [29].

Earlier studies reported reduced NOx emissions, but higher particulate matter (PM) 2.5 and 10 emissions when biofuel blends were used [28]. Notwithstanding, low heating value, ash content, and acidity present complications with engine component compatibility [24]. Emulsions of up to 30% bio-oil were tested in a diesel engine resulting in markedly altered combustion, and changed NO_X emissions, though emissions trends were not consistent enough to report in this paper [24,25]. Other issues included separation of fuel and prohibitive surfactant costs, which are necessary to address separation issues [24]. Table 4.2 shows parameters of WFE fuels from previous work, at various blend percentages [24]. For instance, reported high heating value (HHV) shows a linear decrease between hydrocarbon fuel and emulsion fuel, however, this cannot be confirmed without testing the actual HHV of each sample.

Table 4.2. Calculated bio-oil emulsion parameters

Fuel	**HHV (MJ/kg)**	**H_2O (%)**	**Flash Point °C**	**O_2 wt.%**	**Carbon wt.%**
Bio-oil	16.3	29.8%	40-100	51.4	11.1
Ethanol	29.7	<0.1	16.6	35	-
Diesel #2	45.6	<0.1	52-96	9-12	86
Bio-oil Blend	41.2	4.5%	73.4	-	74.7

Conventional fuel blending approaches utilize mechanical methods, such as centrifuge mixers and surfactants, which are inefficient due to low stability and tendency to separate over time [30,31]. Ultrasound treatment allows for blending non-mixing fluids at a microscopic level, also known as ultrasonic emulsification (UEx) [32]. UEx creates a stable emulsion fuel due to the microscopic level of mixing to reduce the tendency of water to separate from fuels [32].

On the other hand, lower levels of ultrasound have been used for demulsification (separation) [33]. Moreover, ultrasonic WFE is able to improve some fuel performance indicators in combustion engines [21]. Emulsions can be categorized by three types based on droplet size, macro (>0.4 µm), micro (0.1-0.4 µm), and nano-emulsions (<0.1 µm) [32]. Complex multi-phase emulsions exist and involve dispersion of oil within emulsions, however, the specifics are beyond the scope of this study. Recent research has focused on single phase emulsions as a result of previous success and simplicity [32].

4.3. Materials and Methods

Since H_2O in bio-oil is inseparable and H_2O can be effective for improving fuel performance, the research presented herein shows a means for introducing water into diesel fuel as an emulsion to offset the effects of the low bio-oil HHV and reduce harmful emissions associated with diesel fuel. Therefore, we hypothesize that blending bio-oil with diesel is shown to increase the longevity of engine components due to higher lubricity, improved performance from WFE, and also reduced carbon emissions as a result of using organic carbon, low-emissions energy resources, and carbon-based feedstocks.

To test the hypothesis and fill the research gaps in mechanisms of bio-oil effects on blended fuels, we used a high-frequency ultrasound processor for blending bio-oil with diesel (Figure 4.4), and subsequently analysis of bio-oil derived fuel properties and characterization. Modern ultrasound technology is capable of producing significantly more stable emulsions that meet ASTM fuel stability standards; that can be accomplished with limited use of surfactants when compared with mechanically mixed compounds. Furthermore, H_2O content of bio-oil would not need to be separated, thus saving a significant amount of energy and cost from refining bio-oil to biofuels. Additionally, WFE can reduce harmful emissions and increase power under load, thus low bio-oil blends could be counteracted and addressed. Bio-oil H_2O composition is roughly 30% when a whole fraction of bio-oil is combined as a 15% fraction of diesel fuel blend, the resulting H_20 content can be calculated to be 4.5% (Equation 1).

$$0.30_{(H_2O\,\%\,in\,Bio-oil)} * 0.15_{(Bio-oil\,\%)} = 0.045_{(Total\,WFE)} \qquad (1)$$

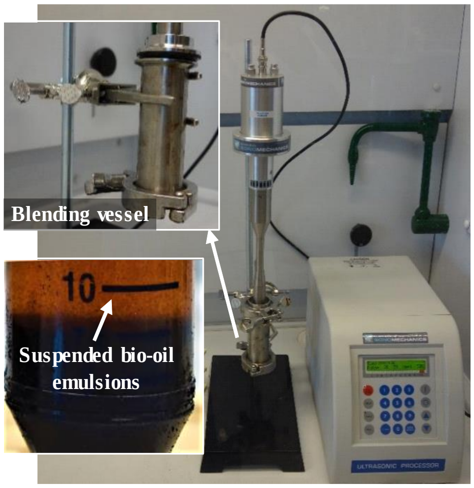

Figure 4.4. Ultrasonic equipment.

A blend of 15% was chosen since previous literature used 10-30% blends. A 15% bio-oil blend results in a WFE ratio of 4.5%, a 5% ratio provided the most positive results in the literature. WFE ratio of 5% was investigated by Khan et al. (2015), which compared engine performance of WFE fuel with B5 biodiesel blend as a commercially available biofuel [11]. Excess blended amounts showed detrimental effects to stability while lower fractions did not utilize enough bio-oil to practicably aid in market development.

In this study, methods examined include non-mixed, mechanically-mixed, and ultrasonic-treated bio-oil (e.g., emulsion). Initial volumes of roughly 50 mL blended fuel were tested. Composition was 42.5 mL diesel and 9 mL of bio-oil were added to a single sealed container for analysis. Ultrasonic emulsions were prepared using an Industrial Sonomechanics LSP-500 in batch mode, using a barbell horn in this study. Sonicated samples were treated using pulsed 20second/59second interval to prevent overheating of the mixture, and loss of volatile matter. Total pulsed time of ultrasonic blending was 5 and 2.5 minutes. Mechanically-mixed samples were prepared using a Baxter Scientific SP Vortex Mixer without pulsed treatment.

4.4. Results

Bio-oil derived fuels separation was monitored, using a high-resolution hand-held camera to collect images of treated bio-oil samples. Clear marked vials were used to estimate separation and stability. Samples were left undisturbed for 60 hours at room temperature and atmospheric pressure conditions. Separation and stability were monitored by measuring the volume of stratified fuel in each respective container in images. A final measurement of stability was given by comparing the separated fuel as a ratio of the initial blended fuels.

Table 4.3. Emulsion energy usage

Treatment	Energy used (Joules)
Mechanical mixing 2.5 (min)	4,248
Mechanical mixing 5 (min)	13,050
Ultrasonic treatment 2.5 (min)	11,359
Ultrasonic treatment 5 (min)	22,718

Table 4.3 presents the energy used during each test. During our tests ultrasound treatment used roughly 267% more power than mechanical mixing at 50% amplitude. Although the ultrasonic treatment is visibly more effective, higher energy requirements may be prohibitive to commercial use. Additional testing is necessary in order to determine the value of higher intensity treatments, such as ultrasound.

Table 4.4. Emulsion fuel properties [24]

Property	Emulsion % of Diesel		
	10	20	30
Density (kg/m^3) at 20°C	871	896	927
Viscosity (cSt) at 40°C	3.3	4.2	6.5
HHV (MJ/kg)	43.2	40.1	36.6
LHV (MJ/kg)	40.6	37.6	34.2
Ash (wt.%)	0.01	-	0.02
Carbon (wt.%)	-	1.6	-
Pour point (°C)	−24	−27	−41
Flash point (°C)	74	-	62

Table 4.4 presents a comparison of the bio-oil and ethanol properties with Diesel #2 and calculated bio-oil blends by taking a weighted average of the respective emulsion component. The calculated blended fuel properties (e.g., HHV and flash point) decrease slightly by around 5-10%. H_2O content of the bio-oil blends was 4.5% as calculated from Equation 1. Also, considering the increased combustion efficiency of 4.5% WFE could compensate for the reduced HHV.

4.5. Discussion

This study is not the first attempt to examine bio-oil emulsions, earlier studies investigated blending bio-oil and diesel, however, they relied on mechanical mixing, surfactants, and bio-oil produced from outdated technology [24,28]. Developing a stable bio-oil emulsion with ultrasonic treatment can be an effective approach to upgrade CFP-derived oil from carbon-based feedstocks, and address national priorities and market needs.

Untreated fuel samples (Figure 4.5) do not show any signs of emulsion, however, mechanically-mixed and ultrasonic-treated samples each shows discoloration from bio-oil mixing with diesel. Ultrasonic treatment was more effective than mechanical mixing at similar treatment time slots in comparison to. The ultrasound-treated samples are clearly darker (Figure 4.6). The 2.5 and 5 minutes treatments could not be visually distinguished for either method. Also, fractionated bio-oil volume was not distinguishable between the different treatment methods, discoloration of samples was used to measure emulsified liquid.

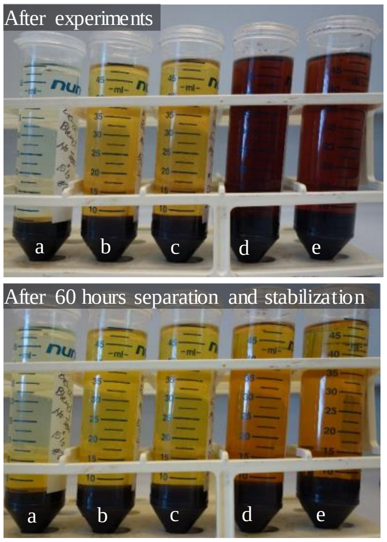

Figure 4.5. Bio-oil and diesel emulsions; (a) untreated mix, (b and c) mechanical mix, and (d and e) ultrasonic-treated mix.

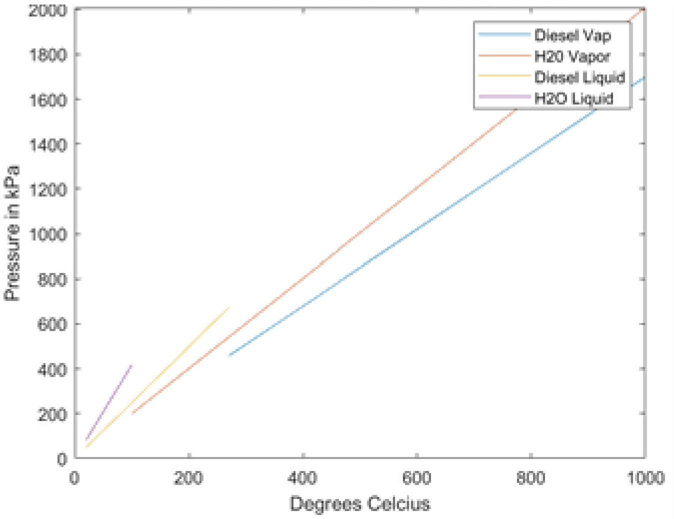

Figure 4.6. Pressure and temperature correlation of H2O and diesel (MATLAB results).

Despite the blended fuels analyses, brake power and torque are thought to increase with WFE as a result of additional force exerted on engine piston and additional vapor pressure from H_2O [34,35]. Water vapor characteristics differ greatly from hydrocarbon fuels, for example, coefficient of expansion of water has a ratio of 1 to 1600. As a result, the force produced during combustion is increased significantly with a small volume of emulsified water. WFE also increases the octane rating of fuel. Octane refers to fuel volatility, and prevents gasoline engines from operating efficiently at high compression, details regarding octane are provided by [36].

Mazlan et al. (2018) reported a decrease of 8.5% fuel consumption using a 6.5% WFE in conjunction with reduced NOx emissions in a light duty truck [20]. Also, thermal efficiency of engines generally increased with WFE, using up to 20% water composition [14,37]. Balancing bio-emulsions between the benefits of octane or cetane increase, fuel dilution, increased combustion rate, and NOx reduction must be achieved prior to commercialization.

Debnath et al. (2015) provided two of the most recent studies reporting increased power output and fuel efficiency of a diesel engine [32,38]. For example, WFE emulsion of 5% improved brake specific fuel consumption (BSFC) 4.6% and increased thermal efficiency of the engine by 11% [32,38]. Czernik and Bridgewater (2004) reported corrosion damage to fuel injectors and fuel pump as a result of bio-oil, both parts are expensive and play a significant role in engine operation [39]. Discrepancies between researchers and experiments indicate mixed results with regards to decreased BSFC, however, most agree that at low engine speeds, BSFC is reduced compared with non-emulsion fuel due to fuel dilution.

Figure 4.7 compares vapor pressure correlation with the temperature on diesel, H_2O, diesel vapor, and H_2O vapor during combustion and across their respective phase change boundaries. The function gradient illustrates the micro-explosion phenomenon, which H_2O lines show a higher gradient than diesel. H_2O concentration, dispersion, droplet size, ambient pressure, and temperature effect micro-explosion strength and subsequently BSFC, power, and emissions.

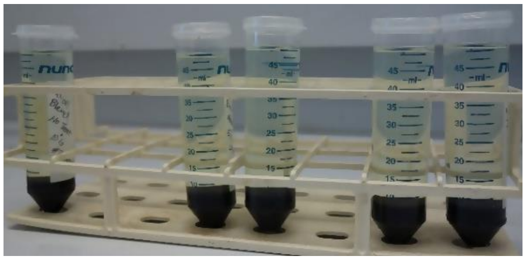

Figure 4.7. Untreated bio-oil and diesel mix.

Engine durability after WFE testing showed no additional signs of wear and damage [40,41]. Observations indicate the decreased carbon deposit on internal components as benefits of emulsion fuels. Diminished fuel stability is a purported negative aspect that may be addressed via surfactants and ultrasonic treatment. Increased performance was noted at some ratios of WFE, 5% WFE ratio resulted in higher engine torque values, the same study reported decreased torque at higher mix ratios [41]. Detrimental aspects of bio-oil emulsions are higher cost, long-term stability, water usage, increased fuel mass, added components, higher CO production, and decreased volatility of diesel (e.g., lower cetane value).

In addition to fuel efficiency, environmental emissions (e.g., carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbon (HC), PM, and nitrogen oxides (NOx)) are other essential factors to consider for today's highway vehicles [42]. Engine operating conditions can affect emissions differently, for example; lean combustion conditions at lower engine loads decrease fuel efficiency but increase NO_x emissions [43]. Details regarding combustion chemistry are given by [36]. The latent heat of evaporation of H_2O results in a reduction of combustion temperature and reduces emissions (e.g., NO_x) [44]. NO_x refers to nitrogen oxide, and nitrogen dioxide, which are partially responsible for acid rain, and is considered a human health hazard [45,46]. Vellaiyan and Amirthagadeswaran (2016) reported 20-35% reduction of NO_x emission due to reduced combustion temperatures from WFE, however, decreased temperature has also been found to result in a less than complete combustion if H_2O content is too high [14]. Further examples of NO_x reduction are provided by [20,47].

WFE can be an effective alternative to reducing NO_x while maintaining fuel efficiency. One side effect of reducing NO_x is increased CO and CO_2 emissions [47]. CO_2 formation occurs at higher temperatures from complete oxidization of fuel and CO forms from incomplete combustion, usually during rich combustion conditions [32]. Debnath et al. (2015) reported that excess WFE above 10% also caused hydrocarbon (HC) emissions to increase as a result of incomplete combustion [32]. HC emissions indicate poor combustion from excessively low temperatures [36]. Decreased HC emission is an example of a less than optimal WFE ratio, and could be addressed in future scenarios. Moreover, Vellaiyan and Amirthagadeswaran (2016) reported that PM was reduced up to 81% using WFE [14].

Distinction should be made between the usage of surfactants and non-surfactant fuels. Surfactants increase cost, but reduce instabilities and produce stable fuels. Additionally, surfactant use can impact combustion mechanics in unintended ways. Inconsistencies in results are thought to originate from differences in engine design parameters, operating conditions, and WFE variances. Performance and emissions tradeoffs exist due to stoichiometric chemistry, thus a decision of which emission to address must be made in order to determine the best WFE ratio for widespread use.

4.6. Conclusion

The effects of micro-explosion and high coefficient expansion of H_2O vapor can increase engine torque up to a certain limit. Emission control of NOx results from the cooling effect of H_2O vapor during lean burning idling conditions (characteristic NOx formation), however, this can simultaneously increase CO_2 emissions by enhancing hydrocarbon combustion. The results of the discussed studies may differ due to the variations in engine design, fuel chemistry, and engine operating conditions. Specific operating parameters, such as ambient air composition and engine design would all impact emulsion fuel performance and need more investigation.

WFE could theoretically compensate for potential losses due to the lower heating value of bio-oil and other fuel performance deficiencies due to low bio-oil quality. Additionally, elimination of the dewatering step in bio-oil upgrading process represents the breakdown of a major prohibitive step in upgrading bio-oil and biofuel production. In a diesel engine, WFE can reduce emissions (e.g., PM and NO_X) and improve fuel efficiency results from a reduction in actual hydrocarbon usage via fuel dilution. For example, supplementing 10% WFE in hydrocarbon fuels can achieve a 10% reduction in hydrocarbon consumption, though volumetric consumption of the mixed fuel remains identical with some benefits to engine power output and emissions. Due to various operating conditions, an ideal emulsion content for best overall performance has not been identified, which can aid to address market needs and national priorities. Furthermore, long-term stability of emulsions is a prohibitive issue along with challenges of mixing fuel prior to final processing and distribution. On the other hand, long-term effects of WFE on engine components have been relatively unexplored, which requires further investigation regarding commercial WFE implementation.

Potential paths for future research include modeling and actual testing of bio-oil derived blends in existing vehicles' engine to confirm the efficiency. Growing initiatives and new analytical instruments (e.g., spectroscopy devices) could be used to real-time characterization of the treated blendstocks, measure actual emulsified content of a fuel, and enable more precise experimentation with ultrasound treatment. Future testing of ultrasonic-treated fuels should be examined for the best intensity, and time duration. Effects of temperature and pressure on emulsions were not observed, but could improve the long-term stability of bio-oil derived blended fuels.

4.7. Acknowledgements

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Chapter 5. Conclusion

5.1. Summary

In chapter 2, a review of existing bio-oil upgrading technologies was performed to identify deficiencies and areas for potential improvement. Although the many of the processes reviewed have been investigated extensively, there are still opportunities to improve upgrading practice through combined technologies since the effective technologies to date are energy intensive and considered by many to be unsustainable.

In chapter 3, Catalytic Transfer Hydrogenation was tested as a method for increasing hydrogen content of bio-oil since it the only non-thermal method that can increase hydrogen content of bio-oil. Ultrasound can increase the effectiveness and speed of the chemical reaction, however our results were not able to show significant differences between samples.

In chapter, 4 bio-oil was investigated as a candidate for a blended fuel with diesel. Some characteristics of bio-oil remain detrimental to engine performance, as shown in previous studies. However, the residual water in bio-oil could enhance blended fuel performance if the bio-oil were blended as an emulsion with diesel. Actual testing is needed to verify real work applicability.

5.2. Conclusions

In chapter 2, we have shown that thermochemical conversion technologies have been more extensively researched when compared to chemical, physical, and biological methods. Although effective, they lack the sustainable characteristics that characterize the motivation to innovate biofuels.

In chapter 3, Catalytic Transfer Hydrogenation was tested on two different types of bio-oil, pine and corn stover. Our results showed an optimal wt %. of 5.5% Ammonium Formate, although Hydrogen content continued to increase in excess percentages our limited experiment size did not allow us to identify the highest hydrogen which could be added. Further testing of the oil would help researchers optimize this process, however testing is expensive. Alternative methods for testing, such as hyperspectral imaging could reduce costs and allow for more rapid turnaround and real time process monitoring of the system.

In chapter 4, we suggested a novel use of residual water in bio-oil diesel blended fuel to overcome detrimental characteristics via water emulsions. Prior research failed to examine this aspect of the bio-oil blended fuel in this manner, this is a crucial factor in determining the success of bio-oil diesel emulsion, since H_2O content can be finely tuned for better fuel combustion when compared with traditional petroleum fuel.

5.3. Contributions

The following contributions have been provided to the research community:

- Created an up to date state of technology review to aid in concentrating the efforts of researchers towards a viable solution for biofuel production from bio-oil.
- Demonstration of Catalytic Transfer Hydrogenation and Ultrasound as a feasible process to upgrade bio-oil through hydrogenation.
- Investigation of blended bio-oil and diesel as a blended emulsion fuel. Use of bio-oil's water content to enhance combustion characteristics in a compression ignition engine.
- Performed the first hyperspectral analysis of bio-oil as a cheaper method for characterizing bio-oil, this will aid in reducing costs, and allow for real time analysis eventually.
- Designed, built, and analyzed a Catalytic Fast Pyrolysis Reactor that successfully produced bio-oil from various feedstock.
- Cyber Physical enabled Catalytic Fast Pyrolysis setups

5.4. Opportunities for Future Research

Future opportunities include implementing AI for control and optimization of cyber-physical enabled bio-oil and biofuel production. The potential for hyperspectral analysis of bio-oil offers a cheap alternative to traditionally expensive testing which is cost prohibitive. Finally, the use of bio-oil as a blended fuel presents what I believe is the most viable pathway to commercialization.

- Supply chain optimization
- CFP optimization of initial biomass to bio-oil via advanced CPS and AI
- Combination of technologies such as biochemical, thermochemical, chemical and physical
- Upscaling production for cost reduction
- Emulsion of bio-oil directly with diesel without upgrading

Biofuel production from biomass sources represents a major challenge for researchers. Upgrading of bio-oil using methods discussed in chapter 2 require further investigation for widespread commercialization and achieve synergy with petroleum based fuels. CTH and Ultrasonic Cavitation were determined as two methods with low capital cost for experimentation and interesting uninvestigated phenomenon, especially when performed simultaneously. Deficiencies of initial conversion processes can achieve greater optimization beyond current state of technology via biofuel

4.0 i.e. CPS and AI integration with CFP. Upgrading strategies such as thermochemical methods are most effective, but remain cost intensive. As of yet, a silver bullet solution to upgrading deficiencies has not been discovered. The best solution is likely a combination of the discussed methods. Widespread implementation of biofuel today such as ethanol relies on blending biofuel with conventional hydrocarbon to compensate for deficiencies. Emulsification offers an alternative to upgrading bio-oil altogether via blending bio-oil with diesel fuel which is not miscible with bio-oil without surfactants or fine blending on a macroscopic scale. Ultrasonic induced emulsification takes advantage of the high water content of bio-oil which can offer beneficial combustion characteristics over conventional fuel. Chapter 4 investigate the potential benefits of bio-oil emulsion practically, it is determined that bio-oil may offset detrimental aspects of untreated or minimally treated bio-oil. The work herein offers an up to date analysis of existing technologies as well as insight into the process intricacies such as reactor component design. As a whole, the following steps can be taken to further commercialization of bio-fuel.