Biocrude Production From Lignin in Hydrothermal Medium: Effect of Rapid Heating and Short Residence Time

Kyoko Hirayama
Old Dominion University, kyokohirayama14@gmail.com

Follow this and additional works at: https://digitalcommons.odu.edu/cee_etds

Part of the Environmental Engineering Commons, and the Sustainability Commons

Recommended Citation
Hirayama, Kyoko. "Biocrude Production From Lignin in Hydrothermal Medium: Effect of Rapid Heating and Short Residence Time" (2023). Master of Science (MS), Thesis, Civil & Environmental Engineering, Old Dominion University, DOI: 10.25777/026t-9k06
https://digitalcommons.odu.edu/cee_etds/123

This Thesis is brought to you for free and open access by the Civil & Environmental Engineering at ODU Digital Commons. It has been accepted for inclusion in Civil & Environmental Engineering Theses & Dissertations by an authorized administrator of ODU Digital Commons. For more information, please contact digitalcommons@odu.edu.
BIOCRUDE PRODUCTION FROM LIGNIN IN HYDROTHERMAL MEDIUM:

EFFECT OF RAPID HEATING AND SHORT RESIDENCE TIME

by

Kyoko Hirayama
B.S. March 2018, Meiji University, Japan

A Thesis Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

ENVIRONMENTAL ENGINEERING

OLD DOMINION UNIVERSITY
August 2023

Approved by:
Sandeep Kumar (Director)
Mujde Erten-Unal (Member)
James W. Lee (Member)
ABSTRACT

BIOCRUDE PRODUCTION FROM LIGNIN IN HYDROTHERMAL MEDIUM:
EFFECT OF RAPID HEATING AND SHORT RESIDENCE TIME

Kyoko Hirayama
Old Dominion University, 2023
Director: Dr. Sandeep Kumar

This study aims to address knowledge gaps in the production of valuable products from waste streams generated during lignocellulosic biofuel production. The primary objective is to develop a process that converts lignin, a byproduct of bioethanol refineries, into a sustainable biolubricant.

The first chapter examines recent advancements in synthesizing biolubricants and investigates their scalability. It explores innovative materials, catalysts, chemical modification approaches, and additives that have emerged in the field. A particular hurdle is the oxidative stability of biolubricants derived from plant oils, which are prone to autooxidation due to their C=C bonds. To overcome this, the study aims to use a three-step approach to produce biolubricant enhancer: hydrothermal liquefaction of lignin, hydrodeoxygenation, and aromatic alkylation. The focus is to economically and efficiently utilize lignin obtained from bioethanol refineries and transform these compounds into high value lubricant improvers.

In the second chapter, the study focuses on the first step, the hydrothermal liquefaction of lignin, with an emphasis on increasing the yield of aromatic hydrocarbons using subcritical water. A new lab-scale batch reactor with an induction heating system is designed. This system enables rapid heating rates of around 100 °C/min, while a conventional electrical heater employs slower heating rates at approximately 5.3 °C/min. The study investigates the influence of heating rate and short residence time on the process. Detailed analysis of the resulting biocrude reveals
that the rapid heating rate improves the selectivity of specific compounds, such as phenol, while the slower heating rate yields a broader range of compounds including anisole and alkyl phenol.

Overall, the developed processes provide an improved conversion rate into value-added products generated from lignin, contributing to greater financial and environmental sustainability.
Copyright, 2023, by Kyoko Hirayama, All Rights Reserved.
ACKNOWLEDGMENTS

I wish to express my sincere appreciation and gratitude to my principal advisor, Dr. Sandeep Kumar, for his guidance, encouragement, and support. I am also very grateful to my committee members, Dr. Mujde Erten-Unal, and Dr. James W. Lee for their valuable feedback. I would like to acknowledge the Department of Civil and Environmental Engineering (CEE) and the very well-equipped Biomass Research Laboratory (BRL) for providing the platform for my research work. I would like to mention CEE office staff Sara Champlin for their administration and timely help. I am forever grateful to all the past and present students working in the BRL for their friendship, collaboration, and training. Again, I thank Dr. Sandeep Kumar for his untiring efforts to acquire research grants and funding my research. I would like to acknowledge the US Department of Agriculture (USDA) for the financial support.
## NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2EH</td>
<td>2-ethylhexyl</td>
</tr>
<tr>
<td>2-NCAR</td>
<td>2-ring non-condensed aromatics</td>
</tr>
<tr>
<td>AlK(SO4)2</td>
<td>Potassium aluminum sulfate</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum System</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose nanocrystals</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CR</td>
<td>Carbon recovery</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative thermogravimetry</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental analyzer</td>
</tr>
<tr>
<td>ER</td>
<td>Energy recovery</td>
</tr>
<tr>
<td>FFAs</td>
<td>Free fatty acids</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectroscopy</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HCL</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>HTHS</td>
<td>High temperature - high shear viscosity</td>
</tr>
<tr>
<td>HTL</td>
<td>Hydrothermal liquefaction</td>
</tr>
<tr>
<td>IA</td>
<td>Isostearic acid</td>
</tr>
<tr>
<td>IH</td>
<td>Induction heating</td>
</tr>
<tr>
<td>ILs</td>
<td>Ionic liquids</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>Potassium carbonate</td>
</tr>
<tr>
<td>KCl</td>
<td>Potassium chloride</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>LBO</td>
<td>Light biooil</td>
</tr>
<tr>
<td>LCA</td>
<td>Life-cycle assessment</td>
</tr>
<tr>
<td>MoDTC</td>
<td>Molybdenum dithiocarbamate</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbone</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NPG</td>
<td>Neopentyl glycol</td>
</tr>
<tr>
<td>PAO</td>
<td>Polyalphaolefin</td>
</tr>
<tr>
<td>SAE</td>
<td>Society of Automotive Engineers</td>
</tr>
<tr>
<td>TEA</td>
<td>Techno-economic analysis</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analyzer</td>
</tr>
<tr>
<td>TMP</td>
<td>Trimethylolpropane</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>TON</td>
<td>Turnover number</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>VPC</td>
<td>Vertical pulsed column</td>
</tr>
<tr>
<td>WCO</td>
<td>Waste cooking oil</td>
</tr>
<tr>
<td>ZDDP</td>
<td>Zinc dialkyldithiophosphate</td>
</tr>
<tr>
<td>ZrOCl₂</td>
<td>Zirconyl chloride</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

## LIST OF TABLES

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
</tbody>
</table>

## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
</tbody>
</table>

## Chapter

1. **RECENT DEVELOPMENTS IN SYNTHESIZING BIOLUBRICANTS— A REVIEW** ......1
   1.1. Introduction ........................................................................ 1
   1.2. Physical and Chemical Properties of Lubricant Relating to Performance .......... 4
   1.3. Vegetable Oil-based Lubricant ................................................ 8
   1.4. Recent Development .................................................................. 17
   1.5. Scale-up and Industrial Feasibility ............................................. 34
   1.6. Summary and Future Prospects .................................................. 39
   1.7. Acknowledgements ...................................................................... 40

2. **BIOCRUDE PRODUCTION FROM LIGNIN IN HYDROTHERMAL MEDIUM:**
   **EFFECT OF RAPID HEATING AND SHORT RESIDENCE TIME** .................. 41
   2.1. Introduction ........................................................................... 41
   2.2. Materials and Methods .............................................................. 48
   2.3. Results and Discussion .............................................................. 54
   2.4. Conclusion .............................................................................. 70
   2.5. Acknowledgements ..................................................................... 71

## REFERENCES ........................................................................... 73

## VITA ....................................................................................... 97
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fresh oil foaming characteristics ASTM D892 [22]</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Summary of 2-step transesterification biolubricant synthesis kinetic models</td>
<td>36</td>
</tr>
<tr>
<td>3.</td>
<td>Various heat sources used in HTL batch studies</td>
<td>44</td>
</tr>
<tr>
<td>4.</td>
<td>Comparison of fast and isothermal HTL setup</td>
<td>49</td>
</tr>
<tr>
<td>5.</td>
<td>Experimental conditions for fast HTL</td>
<td>50</td>
</tr>
<tr>
<td>6.</td>
<td>Loading condition for fast and isothermal HTL</td>
<td>51</td>
</tr>
<tr>
<td>7.</td>
<td>HTL characterization of fast and isothermal HTL</td>
<td>60</td>
</tr>
<tr>
<td>8.</td>
<td>Elemental composition, HHV, and ER of biocrude/hydrochar obtained from fast and isothermal</td>
<td>63</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Three spatially determined lubrication regimes</td>
<td>7</td>
</tr>
<tr>
<td>2.</td>
<td>Plot of average pour points against saturated fatty acid content of different vegetable oils [46]</td>
<td>10</td>
</tr>
<tr>
<td>3.</td>
<td>Common pathways used to synthesize biolubricants from vegetable oils</td>
<td>11</td>
</tr>
<tr>
<td>4.</td>
<td>Schematic representation of the Chauvin mechanism in the presence of a metal alkylidene catalyst. [M] indicates metal</td>
<td>17</td>
</tr>
<tr>
<td>5.</td>
<td>Alternative chemical modification routes in synthesizing biolubricants from vegetable oils</td>
<td>24</td>
</tr>
<tr>
<td>6.</td>
<td>Primary lubricant additive classes</td>
<td>27</td>
</tr>
<tr>
<td>7.</td>
<td>Electrostatic arrangement of ionic liquid lubricants (adapted from [2])</td>
<td>31</td>
</tr>
<tr>
<td>8.</td>
<td>Comparison of heating profile set at 320°C (a) IH reactor, (b) Conventional batch (Parr) reactor</td>
<td>46</td>
</tr>
<tr>
<td>9.</td>
<td>Products separation and analysis steps of the lignin HTL</td>
<td>52</td>
</tr>
<tr>
<td>10.</td>
<td>(a) pH of HTL mixture (b)TOC of HTL mixture (c) biocrude yield as function of time and temperature with fast HTL</td>
<td>56</td>
</tr>
<tr>
<td>11.</td>
<td>Carbon mass balance of products obtained from the fast HTL experiments</td>
<td>58</td>
</tr>
<tr>
<td>12.</td>
<td>Carbon mass balance of products obtained from the fast and isothermal HTL experiments</td>
<td>60</td>
</tr>
<tr>
<td>13.</td>
<td>FTIR spectra for alkali lignin and hydrochar from fast HTL</td>
<td>64</td>
</tr>
<tr>
<td>14.</td>
<td>Relative peak areas of main chemical families in biocrude obtained from fast and isothermal HTL based on GC-MS analysis</td>
<td>66</td>
</tr>
<tr>
<td>15.</td>
<td>(a) TGA curve, (b) DTG curve for biocrude obtained from fast and isothermal HTL at 320 °C for 1 minute residence time.</td>
<td>68</td>
</tr>
<tr>
<td>16.</td>
<td>FTIR spectra for pure phenol and LBOs from fast and isothermal HTL</td>
<td>70</td>
</tr>
</tbody>
</table>
CHAPTER 1
RECENT DEVELOPMENTS IN SYNTHESIZING BIOLUBRICANTS – A REVIEW

Note: The contents of this chapter were adapted from the research article published in the journal ‘Biomass Conversion and Biorefinery’. This is a collaborative work, and my contributions are section 1.1. Introduction, 1.2. Physical and Chemical Properties of Lubricant Relating to performance, and section 1.4.1. Recent advance in feedstocks.


Biolubricants are bio-based compounds that represent a renewable and biodegradable alternative to petroleum-based lubricants. Although biolubricant applications appear promising, their commercial deployment is still limited. Research in the field of biolubricants is continuously developing to improve their properties as well as their production processes, with the aim of overcoming the current limitations and enhancing large-scale application. This review aims at reviewing the most recent developments in the field of biolubricant synthesis, focusing on novel feedstocks and catalysts, as well as new chemical modification routes and additive components. Moreover, techno-economic and life cycles studies aiming at assessing the feasibility of large-scale biolubricant production are also reviewed.

1.1. Introduction

Lubricants are organic compounds used to reduce friction and wear on contact surfaces. Due to the increase in mechanization with growing industrialization and development in recent decades, lubricant consumption has increased drastically [1, 2]. The global lubricants market size reached $125.81 billion in 2020, and it is estimated to grow at an annual growth rate of 3.7% from 2021 to 2028 [3]. On the other hand, it is estimated that over 55% of lubricants consumed annually escape into the environment from spills, improper disposal, accidents, volatility, exhaust fumes in
Engines, and so on [2, 4, 5]. Over 95% of the lubricants entering the environment are petroleum-based lubricants that contaminate soil, drinking water, and air due to high toxicity and low biodegradability [2, 5]. Along with this, they are non-renewable, and depletion of suitable petroleum sources is anticipated in the long term [2, 4].

To address these environmental threats, many researchers have begun investigating renewable sources as potential alternatives to petroleum-based lubricants, and recent researchers estimated that over 90% of all petroleum-based lubricants could be replaced by biolubricants, which are made from bio-based raw materials such as plant oil, animal fats, microalgae oil, or other environmentally friendly hydrocarbon sources as their base component [5]. Renewability and biodegradability are great advantages of biolubricants, and when comparing properties of biolubricants to those of petroleum-based lubricants, the former have higher lubricity, higher viscosity index, and lower evaporative losses in general [2, 4, 5]. Although biolubricants possess many desirable characteristics, they are not widely used currently because of their performance, production scale, and lack of incentives from regulatory entities [2]. The largest drawbacks in terms of biolubricant properties are a poor thermal-oxidative stability and solidification at low temperature [5]. Vegetable oils are composed of triglycerides with various types of fatty acid moieties, and the presence of double carbon bonds (C=C) can act as active sites for many reactions, including oxidation [6-8]. Consequently, vegetable oils need chemical modification processes, such as transesterification or epoxidation, to get rid of the sites that are vulnerable to oxidation and to inhibit the formation of crystals at lower temperature (i.e. the “cloud point” of the oil) [9, 10]. Understanding and controlling oxidation is a major concern for lubricant chemists, since it causes serious problems such as increased viscosity, sludge and sediment formation, additive depletion, base-oil break down, filter plugging, rust and corrosion [8].
Research in the field of biolubricants synthesis and chemical modification of vegetable oils has seen a tremendous development over the past three decades, with many review articles published on this topic [2, 4, 11, 12]. Nonetheless, due to the complexity of lubricant formulations and required properties, which still leave wide margins of improvement, this is an ever-evolving field, and research has been highly prolific in recent years. In this review, we have reviewed the available literature and provided a summary of the recent advances over the last 5 years, focusing on the synthesis of liquid biolubricants (i.e., semi-solid and solid lubricants are excluded), with the aim of highlighting the progress of the research in this field and providing a picture of the up-to-date framework. Specifically, we focus on the development of biolubricants with increased environmental friendliness, covering aspects ranging from alternative synthesis routes and catalysts, as well as novel feedstock and additives employed in the formulations, also analyzing techno-economic and life cycle studies. The review is organized as follows: physicochemical properties of biolubricants relating to performance are initially described, followed by an overview of the main conventional chemical processes utilized to synthesize them. Then, the recent developments regarding novel and more sustainable types of feedstocks, chemical modification processes, novel environmentally friendly catalysts, and additives to improve the lubrication performance are presented. The possibility of using bio-based ionic liquids as novel biolubricants is also discussed. Finally, this review addresses the few works focused on assessing production scale-up and economic feasibility of biolubricant production at industrial scale, to give an overview.
1.2. Physical and Chemical Properties of Lubricants Relating to Performance

In this section, the main physiochemical properties of lubricants in relation to their performances are briefly described. These include viscosity, foam resistance, lubricity, and pour point.

1.2.1. Viscosity

Viscosity is a critical property in determining the quality of lubricants, and it is defined as its resistance to flow [13]. Viscosity of vegetable oil is a major factor in determining end-use application. For instance, low viscosity oils can be applied as automotive transmission oils, while higher viscosity oils can be applied in diesel engine oils [13]. Viscosity has a strong relation with temperature, pressure, and lubricant film thickness. Higher viscosity tends to create thicker lubricant films [14]. Consequently, the viscosity index is a very important property that indicates how lubricants behave with change in temperatures [15]. In particular, high viscosity index indicates less change in viscosity when exposed to different temperatures, so that lubricants with high viscosity index are desirable, since they can create consistent thickness of the lubricant film on the sliding surface in the engine during operation [15, 16].

High temperature - high shear viscosity (HTHS viscosity) is another established indicator to measure the ability to flow within the narrow engine parts at fully warmed temperature (150°C) [17, 18]. The higher the HTHS viscosity, the less amount of wear on the sliding surface, which increases durability in thermal condition. However, a higher HTHS viscosity decreases the fuel economy due to the increase in viscose resistance [17-19]. The Society of Automotive Engineers (SAE) defines current minimum HTHS viscosity for SAE 20 grade oil as 2.6 mPa·s due to a drastic increase in wear at viscosities below this value [19, 20]. Chan et al. [16] described that selection
of viscosity for lubricants for an end-use application is a trade-off between fuel economy and lubrication performance.

In general, vegetable oils are composed of several kinds of fatty acids (oleic, linoleic, linolenic or ricinoleic acid, etc.) and their specific composition differs depending on the kind of oil. The composition affects the key properties of vegetable oils such as viscosity and oxidative stability [6]. The fatty acids in vegetable oils typically have long carbon chain lengths (C18-C24). Fatty acids with longer chain in the nonpolar region tend to create thicker film, and have higher viscosity due to the increase in molecular weight [13, 18]. Normally, bio-based oil derived from plants or animals have a higher viscosity index compared to petroleum-based lubricant and can be desirable for multi-range oil [2, 11].

1.2.2. Foam Resistance

Foaming is an undesirable physical property for lubricants [21, 22]. Stirring motion in mechanical systems such as motor, compressor, and gearbox introduces air in the lubricant and causes air bubbles, whose aggregation results in foam [22, 23]. This foam creates barriers between the liquid and metal surface, and that induces reduction in lubricity, inhibition of heat removal, enhanced oxidation and increased wear to machinery [22, 23]. Consequently, antifoaming agents are commonly used to minimize the foaming properties of lubricants. According to the American Petroleum System (API), ASTM D892 test method is used to measure foaminess, which has several parameters including foaming tendency and stability. This test includes foam measurements at three temperature-based sequences: 1) at 24°C, 2) at 93.5°C 3) again at 24°C. Each sequence has two steps: 1) an air-blowing period for 5 minutes, and 2) a settling period for 1 min. Table 1 indicates the current regulation for passenger car engine oil standard (ILSAC GF-6A) [24].
Table 1. Fresh oil foaming characteristics ASTM D892 [22]

<table>
<thead>
<tr>
<th></th>
<th>Tendency, mL</th>
<th>Stability, mL (after 1-minute settling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequence I</td>
<td>10 (max)</td>
<td>0 (max)</td>
</tr>
<tr>
<td>Sequence II</td>
<td>50 (max)</td>
<td>0 (max)</td>
</tr>
<tr>
<td>Sequence III</td>
<td>10 (max)</td>
<td>0 (max)</td>
</tr>
</tbody>
</table>

In general, vegetable oils have poor oxidative stability, and are more likely to foam compared to petroleum-based oils [8]. In addition, Stojilković and Davidović [25] indicated that although pure vegetable oils have good resistance to foaming, some additives used to improve other poor properties of the oil affect the appearance of foam.

1.2.3. Lubricity (Friction and Wear)

Appeldorn and Dukek described “lubricity” as "if two liquids have the same viscosity, and one gives lower friction, wear, or scuffing, it is said to have better lubricity" [26, 27]. The most significant property in selecting lubricants for end-use application is to meet the requirement that concerns lubricity, friction, and wear [13, 16]. In general, lubricity is related with the formation of the lubrication layer: the higher the lubricity, the lower the friction and energy loss, since the direct contacts of the moving surface are reduced [16]. According to the Stribeck Curve, there are three different types of lubrication regimes observed on systems without an external pumping unit, namely boundary, hydrodynamic and mixed lubrication [28, 29]. Figure 1 illustrates the three different lubrication regimes [28, 30].
Figure 1. Three spatially determined lubrication regimes

Boundary lubrication typically occurs at low speed or heavy load conditions. During boundary lubrication, a thin or unstable tribofilm is formed, which causes rub on the surface and results in high friction and wear [16, 31]. In this regime, the thickness of the film is less than the surface roughness, so that protective additives that reduce sliding damages are required [16]. Mixed lubrication, also known as thin-film lubrication, occurs with the increasing speed of operation, or at lighter load conditions when boundary and hydrodynamic conditions coexist [16, 32]. In this regime, friction and wear rate begin to decrease since asperities of the contact surface will not extend through the film [16, 32]. Lastly, hydrodynamic lubrication, also known as thick-film lubrication, occurs along with further increasing sliding speed and lighter load. In this regime, the film thickness is about three times greater than the roughness of surface, and sliding contact is completely covered. In this condition, there is no serious wear (except fatigue) and friction is caused by only viscose drag and resistance of lubricants [16]. In general, vegetable oils have better frictional properties and wear protection than mineral oils. The frictional properties vary depending on the degree of unsaturation and length of carbon chain. For applications that require thicker fluids such as hydraulic fluids, chemical modification or blending of the vegetable oil is required to obtain higher viscosity [16].
1.2.4. Pour Point

The pour point is an important factor for applications working at lower temperatures [15]. One of the vital properties for lubricants is to remain in the liquid phase over a wide range of temperatures. The lowest temperature limit is called pour point, while the highest temperature limit is called flash point [33]. In lower temperature applications, such as engines, oils should have low pour point, otherwise the wax crystals that are formed can clog filters and cause engine jam [14, 15]. Bio-oil products such as biodiesel have generally higher pour point than petroleum-based diesel, and its value varies remarkably with the fatty acid composition [15, 34].

1.3. Vegetable Oil-based Lubricant

1.3.1. Chemical Processes Utilized to Synthesize Biolubricants

The molecular structure of the triglyceride molecule makes vegetable oils susceptible to oxidation, resulting in cold flow property deficiencies compared to mineral oils which consist of hydrocarbon molecules. It has been established that the unsaturation of the fatty acid moieties in triglycerides, also described as the presence of C=C bonds in the fatty acid chain, influences vegetable oil’s susceptibility to oxidation [34-38]. It is noteworthy, however, to mention that antioxidants (e.g., tocopherols) in vegetable oils can prevent oxidation, thereby improving oxidative stability [39]. Oxidation, specifically autooxidation (i.e. oxidation by introducing atmospheric oxygen) and thermal oxidation (i.e. oxidation at elevated temperatures), degrade vegetables oils during storage and use at high temperatures [36, 38]. Oxidation generally follows a chain reaction mechanism in which intermediates are produced in one step, regenerated in the successive steps, and terminated to undesired but stable products such as aldehydes, ketones, and carboxylic acids [40-43]. These steps are also known as initiation, propagation, and termination steps, respectively. The presence of multiple C=C bonds in a fatty acid chain has been known to
exponentially deteriorate the oxidative stability of vegetable oils. In fact, methyl oleate, methyl linoleate, and methyl linolenate have relative oxidation rates of 1, 41, and 98 hr (OSI, 0°C), respectively [44]. Noteworthy for these selected fatty acid methyl esters is that methyl oleate has one C=C bond, methyl linoleate has two, and methyl linolenate contains three. On the other hand, saturated fatty acid moieties, or the absence of C=C bond, negatively affects the cold flow properties of vegetable oils. Generally, vegetable oil’s pour point temperature increases with saturated fatty acid content as shown in Figure 2. Although, each triglyceride molecule may contain different ratios of saturated and unsaturated fatty acids varying the melting point of each molecule. This leads to a more complex crystallization mechanism, which it has been observed in that high-melting triglyceride molecules crystallizes first, followed by the propagation of crystallization of low-melting point triglyceride molecules in the oil[45]. With the opposing effect of the C=C bond to the oil’s oxidation stability and cold flow properties, hydrogenation or dehydrogenation reactions to saturate or desaturate the fatty acid moiety, respectively, is not adequate to solve vegetable oils’ poor oxidative stability and inadequate cold flow properties simultaneously.
The general approach taken by researchers to improve vegetable oils’ properties for biolubricant application is altering the triglyceride molecule either through substituting the glycerol backbone with another polyol, thereby creating a new polyol ester, or utilizing the C=C bond’s reactivity to create linkages or new molecules. Figure 3 shows the four common pathways studied to synthesize biolubricants from vegetable oils.

Natural triacylglycerides are polyol esters, but can be altered to new polyol esters by transesterification with other polyols beyond glycerol. Triacylglycerides can also be transformed into a complex ester by converting the C=C bond to epoxides, a reactive functional group used to create a branched fatty acid structure. The C=C bond’s reactivity can also be used to either create linkages to form estolides or alter the fatty chain length through alkene metathesis. The following subsections review these reaction pathways used to create biolubricants from vegetable oils.
1.3.2 Esterification/Transesterification

One approach to chemically modify vegetable oils is by altering one of the alkyl components of the ester molecule [47-51]. This is achieved through esterification of fatty acids or transesterification of triglycerides with an alcohol (e.g., methanol) followed by transesterification with polyols, whereby the acyl moieties can be rearranged to form new polyol esters (Figure 3). Polyols that have been tested for this application include 2,2-dimethyl-1,3-propanediol (neopentyl glycol) [47, 50], 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane) [47, 48, 50-53], di-trimethylolpropane[54] and pentaerythritol [47]. The polyol esters that have been synthesized, generally, have improved cold flow properties and increased oxidative stability. For example, palm kernel oil (*Elaeis guineensis*, which solidifies from 20 to 24°C [55], was transformed into di-trimethylolpropane ester with a pour point of −6°C [54]. Similarly, exchanging the glycerol
backbone of palm oil with trimethylolpropane yielded a polyol ester with a pour point of $-1^\circ$C[56]. On average, palm oils have pour points of 7°C [46]. Yunus and co-workers [56] further improved the pour point by separating the methyl oleate from other palmitic fatty acid methyl esters through vacuum distillation. The high oleic fraction was then transesterified with trimethylolpropane. The trimethylolpropane esters was reported to have pour points lower than $-30^\circ$C. Although high-oleic palm oil polyol esters contain unsaturated fatty acid moieties, it was reported that the oxidative stability of palm oil polyol ester and high-oleic polyol ester did not significantly change. Another benefit of exchanging the glycerol backbone with a polyol, such as trimethylolpropane, is it eliminates the $\beta$-hydrogen found in glycerol, which has been reported to contribute to vegetable oil's oxidative stability deficiency [57]. Gryglewicz et al. [50] determined the oxidative stability of rapeseed-based polyol esters by measuring the changes in kinematic viscosity at 40°C and acid number after bubbling air to the esters for 24 h at 100°C. They reported an order of stability of: trimethylolpropane esters > neopentyl glycol esters > 2-ethylhexanol ester $\approx$ rapeseed oil.

1.3.3. Epoxidation – Oxirane Ring Opening

Epoxidation of vegetable oils and their derivatives, followed by an oxirane ring opening reaction gives a complex ester with a saturated and a branched fatty acid moiety. This type of molecular rearrangement often improves oxidative stability and cold flow properties. An oxirane ring is an unstable three-atom ring arranged as carbon-oxygen-carbon and a product of C=C bond epoxidation. Vegetable oil epoxidation is commonly accomplished through the Prileshajev process, in which peracids are used to produce an oxirane ring from the double bonds present in the fatty acid moiety [58, 59]. Peracids are conventionally generated in situ by slowly adding a cold carboxylic acid (e.g., formic acid at $<5^\circ$C) to a cold hydrogen peroxide solution [60-63], as well as mesophilic treatments (between 40 and 60°C) in the presence of strong mineral acids [58,
The order of reactivity of the acids is: $\text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{HNO}_3 > \text{HCl}$ [65]. Heterogenous catalysts (e.g., $\text{SnO}_2$, Amberlite IR-120) [63, 66-68] and lipase enzymes (e.g., Novozymes 435, an immobilized Candida antarctica lipase) [59, 69] have also been used to produce peracids.

Epoxidation using peracids is generally exothermic and slow, requiring between 5 and 16 h for reaction completion [60]. Petrovic et al. [68] reported that the type of peracid used also affects the rate of epoxidation of soybean oil, which the order is: performic acid $>$ peracetic acid.

Epoxidized vegetable oil can be by itself a potential biolubricant as epoxidation improves oxidative stability and increases kinematic viscosity. Sammaiah et al. [62] reported oxidative stability using a rotating bomb oxidative test and kinematic viscosity at 100°C for jatropha oil and soybean oil, resulting in increased oxidative stability following epoxidation. Somidi et al. [66] reported similar trends for epoxidized canola oil. However, the pour point temperatures of the oils increased after epoxidation in both studies. A subsequent oxirane ring opening reaction improves the epoxidized oil’s pour point by adding a branched functional group within the fatty acid while maintain its saturation [70, 71]. The oxirane ring opening reaction is accomplished by reacting the epoxidized oil or its derivatives with a carboxylic acid under an inert gas at 100°C [60] or under atmospheric air in the presence of a catalyst [61, 71, 72]. In some cases, oxirane ring opening reactions can occur with alcohols (e.g., butanol, hexanol, hexadecanol) [63, 70] or with acetic anhydride [67].

1.3.4. Fatty Acid Condensation: Estolide Synthesis

Estolides are oligomers of fatty acids connected at the carboxylic acid group and fatty acid chain by estolide linkages, as illustrated in Figure 3. Estolides are naturally found in trees, such as kamala ($\text{Mallotus philippinensis}$) and Chinese tallow ($\text{Sapium sebiferum}$), flowering plants, mostly $\text{Lesquerella}$ species, and sclerotia of the ergot fungus ($\text{Claviceps purpurea}$) [73]. Most natural
estolides, except for oils from ergot fungus, are found along side with oils containing a hydroxyl group in the fatty acid chain, typically ricinoleic acid (12-hydroxyoctadec-cis-9-enoic acid) [73]. The earliest reported synthetic estolide was produced from fatty acids, extracted from castor oil plant (*Ricinus communis*), via condensation of hydroxyl-containing fatty acid with another fatty acid at 220°C under vacuum [74]. For such applications, castor oil is often chosen as the lipid feedstock since it contains ~90% ricinoleic acid [75]. Synthetic estolides are usually capped by fatty acids (e.g., oleic acid) or by fatty acid alkyl esters [76]. Ricinoleic acid and oleic acid are transesterified with branched alcohols (e.g., 1-ethylhexanol) to provide the alkyl ester capping group [77]. Furthermore, the degree of polymerization is typically kept low (< 5) to avoid creating extremely viscous base oils. Garcia-Zapateiro et al. [76] observed kinematic viscosities of ricinoleic acid estolides at 100°C increased from 51 mm²/s to 232 mm²/s as the degree of polymerization increased from 4.87 to 6.92. Cermak et al. [75] generated a dimer estolide by reacting two capping groups, methyl ricinoleate and oleic acid. For this case, they observed a kinematic viscosity at 100°C of 12.2 mm²/s and pour point of −36°C.

In the 1990s, the U.S. Department of Agriculture: Agricultural Research Service (Peoria, IL) successfully synthesized estolides from unsaturated fatty acids without the hydroxyl functional group in the lipid chain. Using a montmorillonite clay catalyst (e.g., K10), estolides were produced by reacting unsaturated fatty acids (e.g., oleic acid) at temperatures from 180 – 300°C under nitrogen gas [78]. Inherently, the unsaturated fatty acid (e.g., oleic acid) both acts as capping group and base unit where oligomerization can be stopped by using an alcohol, generating the alkyl ester capping group via esterification (Figure 3) [75, 77]. Other acid catalysts were also investigated, and the reactivity order that was observed is: HClO₄ > H₂SO₄ > p-toluenesulfonic > BF₃·Et₂O >
montmorillonite K10 > H₃PO₄ ≈ HNO₃ [79]. Currently, the optimized condition commonly used in the literature correspond to reacting the unsaturated fatty acid at 60°C for 24 h using HClO₄.

Estolides from vegetable oils are currently commercially produced by Biosynthetic Technologies, which was acquired by Calumet Specialty Products in 2018 [80, 81]. The process they use is based on the US Department of Agriculture’s processing technology. One of the estolide-containing oils they manufacture is formulated for a 5W-30 grade engine oil, which is certified to contain 35% bio-based materials.

1.3.5. Olefin Metathesis

Olefin metathesis is the interchange of fragments of alkenes through metal-catalyzed rearrangement of the C=C bonds [82]. The rearrangement involves an alternating [2+2]-cycloaddition, forming a metallacyclobutane intermediate, and [2+2]-cycloreversion of olefins to a metal alkylidene catalyst as illustrated in Figure 4. This sequence of reactions is known as the Chauvin mechanism, named after the Nobel Prize in Chemistry winner Yves Chauvin [82]. There are three basic types of olefin metathesis, namely, ring closing metathesis, ring opening metathesis, and cross metathesis [83, 84]. Ring closing metathesis allows the cyclization of dienes or trienes to cycloalkenes, with generation of a new linear or branched alkene byproduct, while ring opening metathesis performs the reverse reaction. Cross metathesis is the transalkylidenation of either terminal or internal alkenes to form new linear or branched alkenes. Functionalized alkenes, such as methyl esters and triglycerides, can also undergo metathesis as long it contains a double bond. Vegetable oils containing unsaturated fatty acid moieties, like oils from Camelina sativa (camelina) and Carthamus tinctorius (safflower), can produce new esters and alkenes, which can be used as precursors for biolubricant production. These compounds can
be hydrogenated and be used as a blend components of aviation fuels, diesel fuels and base oils as well as precursors for polymers [85-87].

In vegetable oil olefin metathesis, medium-chain alkenes (e.g., C18) are produced from secondary reactions such as homodimerization of terminal alkenes. For example, homodimerization of two molecules of 1-decene will yield a molecule of 8-octadecene and a molecule of ethene, as observed by Chatterjee et al. [88]. Esters with terminal double bonds in the fatty acid chain can also undergo homodimerization resulting in heavy molecules and a restructured polyol ester. Refvik et al. [89] observed an increase in viscosity of the oil product and presence of high molecular weight compounds after conducting metathesis reactions of corn and soybean oils. The results were consistent with the presence of a metathesized material.
Figure 4. Schematic representation of the Chauvin mechanism in the presence of a metal alkylidene catalyst. [M] indicates metal

1.4. Recent Development

1.4.1. Feedstocks

Currently most of the biolubricants are derived from natural oils such as vegetable oil, vegetable seeds, animal fat, algae, and other microorganism [90-92]. However, these feedstocks have some limitations for large-scale production. Crops require large amounts of arable land and operational costs for cultivation, and they typically have a long lifecycle. Also, there is various, competing demands of these oils, since they are used in a variety of applications, including food,
feed, fuel, polymers, and other commodity-scale commercial products (e.g., soaps, detergents, etc.). In this section, we discuss interesting alternative feedstock that has been studied over the last 5 years, and summarized the recent developments.

Borah et al. [91] have investigated a method to use cyanobacteria and a diverse group of algae, including Chlorophyceae, Rhodophyceae, Phaeophyceae, and others, as potential hydrocarbon source for biolubricant production. Compared to microorganisms like bacteria and fungi, these algae do not require special techniques for cultivation; marine microalgae cultivation is possible in sea water, as well as opportunities for using mixotrophism, including treatment of industrial or municipal waste-waters, as well as runoff-derived effluents, as nutritive media to support growth. According to their lab-scale study, the polysaccharides extracted from algae and cyanobacteria have higher molecular weight than typical lubricants, and superior drag reduction properties, as well as good thermal stability as a result of the complexity of the polymorphic molecular structures. Furthermore, it was shown that accumulation of carbohydrates in the cell is improved by simple cultivation stressors, like nutrient starvation. Thus algae biomass production coupled with even dilute nutrient bioremediation in the environment can significantly reduce the production costs [93].

Di Bitonto et al. [94] reported that sewage scum taken from a wastewater treatment plant contains 36%-50% lipids, including a high fraction of free fatty acids (FFAs) (45-60%). The energy content of influent municipal wastewater is 10 times greater than the energy input for the treatment plant, and half of this energy ascribed to suspended solids, which is easy to collect with a simple separation system. The authors reported that 92-99% of lipids can be recovered from sewage scum with thermal centrifugation and a chemical activation process, and more than 96%
of FFAs can be converted in fatty acid methyl esters (FAME) with esterification, based on bench-scale assessment.

Papadaki et al. [95] reported that a neopentyl glycol (NPG) ester derived from microbial oil produced from a confectionery and wheat milling side-stream, have promising physiochemical properties for biolubricant formulation that can be alternative to conventional lubricants. In this case, the authors define ‘microbial oil’ as secondary metabolite produced from algae, yeast, and fungi, which could be used as renewable lipid feedstock. Specifically, the authors reported that NPG esters produced from R. toruloides and C. curvatus have a viscosity value which can be classified as adhering to the ISO VG22 grade. Furthermore, the authors reported a maximum yield of 88% of NPG ester from R. toruloides using enzymatic esterification. However, the cloud point of these NPG esters was 4°C, which is higher than that of biolubricant produced from canola oil (-3°C).

Wu et al. [90] reported that housefly larvae can be used as an alternative feedstock for biolubricant production. Housefly has been reported to have rapid reproduction rate, high resistance to disease, and are capable of converting kitchen waste material to lipids. According to their report, the larvae produced from one cage (0.125 m³) of housefly are capable of converting 2.8 kg of food waste into 200 g of larval lipids within 4 days, with lipid contents of the dried larvae of 15-25% w/w. They have developed a method to produce 2-ethylhexyl (2EH) ester from free fatty acid of housefly larva by esterification with 2-ethyl-1-hexanol, yielding 98.6% conversion. The resulting 2EH ester was reported to have a high viscosity index (< 180 mP·sec) and lower oxidative onset temperature (< 180°C).
1.4.2. Catalysts

Producing polyol esters is typically accomplished in the presence of catalysts. Mineral acids (e.g., H₂SO₄) and alkaline catalysts (e.g., sodium hydroxide) are commonly used to support esterification and transesterification reactions, respectively [54, 56, 96]. However, these conventional catalysts are sometimes challenging to recover during downstream processing, and mineral acids corrode metal reactors over time. Alternatively, enzymes can offer mild reaction conditions (e.g., temperature, neutral pH) and high selectivity, reducing energy inputs and improving conversion yields. Immobilized lipases, such as Novozyme 435, have been proven effective in both esterification and transesterification of fatty acids to alkyl esters and polyol esters [50, 97]. Recent studies on enzymatic synthesis of polyol esters focus mainly on evaluating enzymes from different species and new techniques for enzyme immobilization.

Aguieiras et al. [98] compared Novozyme 435 and Lipozyme RM IM, a lipase extracted from *Rhizomucor miehei*, in transforming soybean and castor biodiesels to NPG. Both enzymes achieved higher than 90% conversion. However, the consumption of NPG, obtained by measuring decay in the presence of the hydroxyl group using gas chromatography, was faster in batches with Lipozyme RM IM than in batches with Novozyme 435, corresponding to rates of 17.2 and 14.6 OH molar consumption/h, respectively. As expected, tribological properties (i.e., kinematic viscosity, oxidative stability and pour point) of the synthesized NPG ester were improved compared to its biodiesel derivative. However, the total acid number increased due to hydrolysis reactions. The authors hypothesized that the presence of water (1% by mass), which was used to increase the solubility of neopentyl glycol, aided the formation of free fatty acids [98] in this case.

In enzymatic production of biodiesel from fatty acids using Novozyme 435 and Lipozyme, solvents (including tert-butanol and isopropanol) are sometimes used to act as a medium for the
enzymes [99]. As an alternative approach, Barbosa et al. [100] utilized solid residues from *Moringa oleifera* oil extraction and SiO\(_2\) to create a solid support for immobilization of *Candida rugosa* lipase. This allowed a solvent-free medium for esterification of fatty acids from *Moringa oleifera* oil with 3-methyl-1-butanol. The authors used a hexane-aqueous interface to promote lipase immobilization via interfacial activation by stirring the enzyme-support solution for 3 hours at room temperature, followed by settling the slurry for 24 h at 4°C. The combined *Moringa oleifera* solid residue and SiO\(_2\) support showed the best conversion among the supported catalysts that were evaluated (i.e., dried *Moringa oleifera* solid residue and SiO\(_2\)). The immobilized lipase esterified 94% mol/mol of free fatty acids to 3-methyl-1-butyl ester.

Carvalho and his co-workers [101], on the other hand, used polystyrene-divinylbenzene beads to immobilize lipases, specifically Thermomyces lanuginosus (Eversa® Transform 2.0 and Lipolase® 100L) and Psuedomonas fluorescens (Amano AK) and Candida rugosa (CRL), via interfacial activation. The immobilized lipases were then evaluated for their activity through esterification of trimethylolpropane and free fatty acids derived from refined and used soybean oil. Like Barbosa’s study [100], Carvalho and his group did not use any solvent to produce the polyol esters. Among the immobilized lipases tested, the immobilized form of Eversa® Transform showed the most activity (83% conversion) and exhibited the highest activity improvement, which its free form only converted less than 15% of the alcohol. The immobilized CRL also showed high activity towards esterification (81% conversion) but it is not due to immobilization rather than the lipase’s activity which in its free form exhibited 79% conversion.

Ghafar et al. [102] reported that calcium oxide derived from waste cockle shell has significant potential as a substitute for the commercial catalyst for production of biolubricant from waste cooking oil. Transesterification is one of the more favorable methods for chemical
modification to improve biolubricant properties, such as oxidative stability and temperature stability, with significant efforts being taken to identify alternative catalyst sources in order to lower the production costs. According to the authors, commercial calcium oxide and waste cockle shell-derived materials have similar FTIR spectra, and TMP triesters-based biolubricant produced with the waste cockle shell catalyst meet the requirement of viscosity and viscosity index for ISO VG32 grade oil.

The discovery of well-defined organometallic complexes allowed olefin metathesis of unsaturated fatty acid esters in vegetable oils; subsequently, using a N-heterocyclic carbene (NHC) ligand as part of organometallic complex, such as the second-generation Grubbs and Hoveyda-Grubbs catalysts, opened new pathways of producing biofuels, biolubricants and chemicals [82, 85]. However, due to the solubility of the current NHC-based catalyst in organic solvents, lifetime and recyclability has been limiting factors for large-scale biofuels and biolubricant production [103].

In catalytic systems, heterogeneous catalysts are favored over their homogeneous counterparts due to added reaction efficiency and reusability. An ideal heterogeneous metathesis catalysts could be easily removed from products, prevent deactivation due to bimetallic bonding of active sites, and yield less heavy metal contamination. Grubbs and co-researchers [104] approached this challenge by creating a triethoxysilyl functionalized N-heterocyclic ligand to mount the NHC to a silica substrate. The heterogeneous NHC catalysts were found to be comparable to its homogeneous counterparts, and retained activity after four reaction cycles. Furthermore, the catalysts were stable in that the ruthenium catalytic site did not leach into the reaction products. As an alternative approach, Renom-Carrasco et al. [105] used a thiolate-coordination chemistry, replacing one of the chloride ligands and retaining the NHC ligand of the
catalyst. The thiolate structure was then tethered to an azidopropyl silica support. The resulting heterogeneous catalyst has a turnover number (TON) of 107, which is comparable to its homogeneous counterparts. It is noteworthy to mention, however, that the TON, defined as the number of molecules converted to products per catalyst molecule, for Grubbs catalysts, exceeds 1,000 [82]. Recently, Ondrusek and Chung [106] used an alternative azobenzene-modified NHC ligand in synthesizing Grubbs catalyst. Even though the resulting structure is a homogeneous catalyst, the azobenzene-modified catalyst can be easily recovered by using a silica-grafted β-cyclodextrin. Azobenzene, specifically in its trans configuration, is known to bind strongly to the hydrophobic inner cavity of a β-cyclodextrin. Mechanistically, the silica-grafted β-cyclodextrin acts as a net for capturing the dissolved Grubbs catalysts, providing >97% successful recovery of ruthenium metal.

1.4.3. Chemical Modification Routes

The complex esters, such as polyol esters and estolides, synthesized via the chemical reaction routes shown in Figure 3 have been demonstrated to be effective pathways in creating biolubricants with suitable tribological properties. In fact, most of the recent studies in modifying vegetable oils for lubricant application focuses on evaluating different feedstocks and reaction conditions, but using similar routes described in Figure 3. Nogales-Delgado et al. [52, 107, 108] used high-oleic safflower (82% oleic acid content) and cardoon (Cynara Cardunculus) oils to synthesize polyol esters with trimethylolpropane, while Bahadi et al. [54] and Chen et al. [109] evaluated kernel oil and Indian mustard (Brassica juncea), respectively. Bashiri et al. [110] transformed used sunflower cooking oil to a biolubricant via successive epoxidation and acid-catalyzed oxirane ring-opening esterification with a palmitic acid. Other authors have introduced alternative routes to restructure the triglyceride molecule to make it suitable for lubricant
Figure 5. Alternative chemical modification routes in synthesizing biolubricants from vegetable oils

It has been established that the fatty acid condensation between ricinoleic acid and oleic acid will yield an estolide with an unsaturated fatty acid capping group. Doll et al. [111] further modified the unsaturated sites by epoxidation followed by oxirane-ring opening reactions using carbon dioxide (Figure 5, Route 1). Epoxidation of the unsaturated estolides was accomplished via the conventional Prileshajev process using performic acid reacted for 24 h at room temperature. The oxirane ring was then opened with 10 MPa of carbon dioxide at 100°C for 45 h, using a tetrabutylammonium bromide catalyst. The presence of the cyclic carbonate group in the estolide,
a product of the ring opening reaction, was confirmed by $^{13}$C NMR. Using the conditions in the study, they observed a carbonate yield of at least 87%. Like epoxidation of vegetable oils, the cyclic carbonate group improved the estolide’s oxidative stability and increased its kinematic viscosity, but negatively affected its cold flow properties. They reported that the pour point of the ricinoleic 2-ethylhexyl ester-oleic acid estolide increased from –42°C to –3°C after ring opening reactions with carbon dioxide.

Hoong et al. [112] synthesized polyhydroxy estolides by reacting oleic acid with hydrogen peroxide at 80°C for 24 h as an alternative approach to estolide production from unsaturated fatty acids. They proposed that the oleic acid is first epoxidized via the Prileshajev process using peroleic acid, produced in situ from oleic acid. The epoxidized oleic acid then undergoes oxirane ring opening with oleic acid creating polyhydroxy estolides (at 77% yield). To reduce the impact of the hydroxyl groups to the molecule’s oxidative stability, they capped the polyhydroxy-estolides by consecutive carboxylic acid and alcohol esterification using excess lauric acid and branched alcohols (e.g., 2-ethylhexanol), respectively. (Figure 5, Route 2). The resulting lauric capped estolides, specifically using 1,3-dimethylbutanol as the alkyl ester capping group, exhibited excellent pour point properties (–41°C) and an oxidative onset temperature (202°C) comparable to commercial mineral oil base lubricant (199°C).

Maglinao et al. [113] utilized oleic acid’s C=C bond reactivity for acid-catalyzed alkylation. Lewis acids, like alumina chloride, are commonly used for lab-scale alkylation of aromatic hydrocarbons with alkenes. Similarly, alkylation of benzene with methyl oleate can be accomplished using similar liquid Lewis acid [114]. However, liquid acids are relatively difficult to separate from the products and pose difficulties for disposal. Maglinao and group [113] used a solid acid catalyst (i.e., montmorillonite) as an alternative to production of phenyl-branched alkyl
esters (Figure 5: Route 3). The phenyl-branched methyl ester was synthesized by reacting methyl oleate and excess toluene at 210°C for 4 h with montmorillonite K30 catalyst. An average yield of 20% mol/mol of phenyl-branched methyl esters was observed. The synthesized product was found to have improved oxidative stability (from 8 min to 17 min using ASTM D7545 method) and cloud point below –19°C. However, the continuous flow reaction studies using canola biodiesel and toluene showed that montmorillonite K30 activity was drastically reduced after 7 h of continuous operation.

1.4.4. Additives

Typical lubricant formulations comprise a base fluid (oil) and small amounts of additives (generally 1% - 5% w/w), which are needed to improve the physical properties and lubricating performances of the former. These include (Figure 6):

- Antiwear additives and friction modifiers: provide protection to the metal surface during moving contact, thus reducing friction and wear;
- Viscosity modifiers: alter the viscosity of the oil, expanding their range of application;
- Pour-point depressants: lower the minimum temperature at which the oil flows;
- Antioxidants: reduce the base-oil oxidation rate, hence extending its lifetime.
Figure 6. Primary lubricant additive classes

Vegetable oil-based biolubricants, due to their relatively narrow viscosity range, higher pour points, and lower thermo-oxidative stability compared to conventional mineral oils, require more and higher amounts of additives to achieve the desired performances. Conventional additives, such as zinc dialkyldithiophosphate (ZDDP) or molybdenum dithiocarbamate (MoDTC), exhibit a multifunctional behavior. However, these metal-based compounds, although present in small amounts, are toxic and extremely harmful to the environment. Hence, recent research is directed towards the development of novel, ecofriendly additives [115].

Among the possible approaches, the use of nanoparticles (NP) as lubricant additives has gained significant interest, and many studies have shown their potential in enhancing tribological performances of base oils. In fact, when boundary or mixed lubrication regimes occur, nanoparticles may carry some load and separate the two contact surfaces, preventing adhesion. Different metals, metal oxides, and carbon-based nanoparticles have been investigated as additives to different base oils. For example, Chaurasia et al. [116] tested the effect of CuO NP on friction and wear behavior of epoxidized Sal oil; Singh and co-workers investigated the addition of SiC NP on a polyol ester of *Moringa oleifera* oil [117] and of TiO$_2$ NP on chemically modified...
Nicotiana tabacum oil [118]. All these studies report an increase in viscosity index and flash point of the base oil, as well as improved friction and wear performances. Similar results were obtained by Talib and co-authors using hexagonal boron nitride NP in jatropha oil, believed to be conferred by the layered structure of this lamellar powder, characterized by strong covalent bonds within layers, and by Van der Waals forces between layers [119]. Nonetheless, the use of inorganic NP as biolubricant additives presents some challenges, related to the high surface energy and density, which causes aggregation and sedimentation of the particles, resulting in low stability of the dispersion. To improve the compatibility, researchers have investigated different approaches. Garg et al. [120] used Cu NP functionalized with long chain fatty acids (oleic acid), acting as surface modifiers to form stable dispersion in karanja oil ester. Sarno et al. [121] proposed a “wet chemistry” approach, synthesizing Cu NP directly in waste cooking oil, which was then dispersed in PAO6 base lube oil. The obtained blends displayed improved tribological performances as well as increased oxidative stability.

Other authors focused on graphene NP as friction reductive agents. This material, thanks to its unique 2-dimensional structure, presents excellent thermal and mechanical properties. Nonetheless, due to Van der Waals forces, it also poses challenges related to the formation of agglomerates and sediments, which hinder the stability of graphene dispersion into bio-oil. Also in this case, surface modification and functionalization of the NP can aid the stability of the dispersion. Del Rio et al. tested the antifriction and antiwear behavior of reduced graphene oxide NP, and reduced graphene oxide modified with octadecylamine NP blended with a biodegradable ester base oil [122]. They obtained good temporal stability of the dispersion, as well as reduced friction coefficients. To further increase the stability of the dispersion, as well as the tribological performances, the authors also investigated a hybrid graphene/ionic liquid additive. Ionic liquids
act as excellent dispersants for graphene nanoparticles, and possess good lubricating properties. In fact, they are also widely employed as additives on their own, or even as neat lubricants (this aspect is better detailed in Section 4). Indeed, the hybrid additive, with 1 wt% ionic liquid and 0.05 wt% graphene NP, showed the best responses among the ones tested. Similar results were obtained by Hasnul and co-workers [123], who found that the hybrid graphene/ionic liquid additive displayed a higher friction reduction compared to graphene and ionic liquid alone.

An alternative to synthesizing novel additives as substitutes to conventional toxic ones, is the possibility of obtaining eco-friendly bio-based additives directly from natural renewable resources, such as chitosan, amino acids, vegetable oils, sugars, or cellulose, among others [124]. For example, cellulose can serve as a multifunctional additive to vegetable oil-based lubricants. Delgado et al. [125] investigated ternary blends of ethyl cellulose with castor oil (which has high compatibility thanks to its polarity) and high oleic sunflower oil, and found an increase in viscosity index (fitting in group III of API classification) as well as a decrease in pour point. Cellulose nanocrystals (CNC) also present interesting properties compared to inorganic NP. CNC’s have high mechanical strength, but lower density, which makes it easier to obtain a stable dispersion in the base oil. Moreover, the high number of hydroxyl groups allows simple functional modifications to further enhance compatibility [126]. Li et al. [127] tested CNC obtained from cotton and subsequently grafted by stearoyl chains, as additives to polyalphaolefin (PAO), and found that 2 wt% of CNC exhibited a good dispersion stability, a high kinematic viscosity, and a reduced coefficient of friction. Rahmadiawan and co-authors [128] used cellulose nanofibers derived from bacteria, thus avoiding acid hydrolysis, as additives to a polyol ester base oil. The nanofibers were characterized by high thermal and mechanical stability, as well as high degree of crystallinity. An addition of 0.6 wt% resulted in high viscosity, with lower friction and wear properties. Besides
cellulose, other bio-based compounds can serve as stabilizing additives. For example, Zhao et al. [129] utilized amidated biophenols as antioxidants in different types of vegetable oils. They registered an increased value in oxidation induction time, with better performances compared to commercial phenols and ZDDP. Kontham et al. [130] found an improvement in thermal, tribological and antioxidant properties of karanja oil esters upon addition of heterocyclic Schiff bases (i.e. furan, pyridine, thiophene, pyrrole), which were derivatized with long chain fatty acids (stearic acid) to improve the solubility. Xu et al. [131] used pentaerythritol rosin ester as a multifunctional additive to rapeseed and soybean oils, obtaining an increase of dynamic viscosity, thermal and oxidative stability of the base oils at 20 wt% content of the additive.

1.4.5. Bio-based Ionic Liquids

Ionic liquids (ILs) are defined as molten salts with a melting temperature $T_m < 100^\circ$C. They are typically composed by an organic cation and an organic/inorganic anion (ionically bonded), arranged in a lamellar structure, with layers held together by Van der Waals forces [2]. ILs possess unique physio-chemical properties that make them appealing for a variety of industrial applications, although their development is still at the early stage. In particular, properties such as broad liquid phase temperature range, high thermal stability, negligible vapor pressure (i.e. non volatility), non-flammability, etc. make ILs very promising candidates for lubricant applications [132, 133]. Additionally, thanks to their polar nature, ILs are easily adsorbed onto metal surfaces, leading to the formation of stable anion-cation monolayer films, which helps in reducing friction and wear issues (Figure 7).
Figure 7. Electrostatic arrangement of ionic liquid lubricants (adapted from [2])

The use of ILs as lubricants was proposed for the first time in 2001. However, most of the early formulations comprised halogen-containing anions (e.g. tetrafluoroborate BF$_4$, or bis(trifluoromethylsulfonyl)imide [Tf$_2$N]), which possess good tribological performances but, besides being toxic and non-biodegradable, are highly sensitive to hydrolysis, producing hydrochloric or hydrofluoric acid that lead to corrosion issues [132, 134]. More recently, the urgent need of shifting towards more sustainable and environmentally benign compounds has driven research towards the development of bio-based and halogen-free ILs. While it has been estimated that potentially up to $10^{18}$ different anion-cation combinations can be obtained for IL production [132], significant R&D investment will be required for realization of IL technology for lubricant manufacture to fulfill all the required properties.
Reeves and co-workers [135] have tested tribological properties of ILs made of phosphonium- or imidazolium-based cations, and several anions, including both bio-based (salicylate, saccharinate and benzoate) and non-bio-based (chlorine, cyclohexane carboxylate and [Tf₂N]). The same authors investigated the thermal stability of these compounds in comparison with bio-based (canola oil, avocado oil and the commercial product SoyGold®) and petroleum-based (SAE 10W-30) lubricants [136]. They found that environmentally friendly ILs outperformed both the vegetable oils and the conventional lubricant in terms of friction and wear properties. Moreover, they showed comparable decomposition temperatures, but being non-volatile and non-flammable, they are intrinsically better suited for uses under high temperature conditions. Sernaglia and co-workers [137] analyzed the physicochemical properties and tribological behavior of two fatty acid-based ionic liquids (FAILs), namely tetrahexylammonium octanoate [N₆,₆,₆,₆][C₈:0] and tetrahexylammonium hexadecanoate [N₆,₆,₆,₆][C₁₆:0]. The study highlighted that a longer anion alkyl chain corresponded to lower density and viscosity, but higher viscosity index and thermal stability, although the latter was overall lower than that of traditional ILs. Nonetheless, none of the two compounds appeared to have corrosion activity on the metal surface. Avilés et al. [138] focused on the behavior of an ammonium-based palmitate IL (DPA) at high temperatures in a stainless steel-sapphire contact vessel. DPA is solid at room temperature, and has two transition temperatures: from crystalline solid to liquid-crystalline mesophase (42°C) and from mesophase to isotopic liquid (105°C). The IL displayed severe wear and high friction when the temperature was in the mesophase range, while significant reduction was observed at a temperature higher than the melting point.

Zhang et al. [139] investigated the lubricating properties as well as the ecotoxicity of completely bio-based ILs, made of choline cation [Ch] and eight different amino acids [AA]
anions, and compared them with a traditional IL, i.e. 1-butyl-3-methyl imidazolium tetrafluoroborate (L-B104). The authors concluded that [Ch][AA] ionic liquids have better or comparable tribological properties but, being non-toxic and biodegradable, are significantly more environmentally friendly than L-B104. In fact, amino acids-based ILs (AAILs) have been extensively investigated as promising biolubricants in the recent literature. For example, Bjorling et al. [140] studied the full film (i.e. elastohydrodynamic) behavior of [Ch][L-proline] ionic liquid. Zhu and co-authors [141] carried out a comprehensive study, investigating the properties of 14 AAILs with tetrabutylammonium cation [N\textsubscript{4,4,4,4}] on various metal contacts (steel/steel, steel/copper and steel/aluminum), and compared them to those of a commercial polyalphaolefin oil (PAO40). Only some of the compounds that were tested were liquid at room temperature, and viscosity increased with increasing carbon chain length. However, viscosity and viscosity index of such compounds were lower compared to those of PAO. All the ILs tested decomposed at 200-300°C. In general, all studies report a reduction in friction and wear coefficients when using IL biolubricants compared to conventional ones.

However, many authors argue that IL biolubricants have significantly higher production costs with respect to conventional, mineral, or natural oils formulations. In this respect, Guo and co-workers [142, 143] proposed the use of protic ILs, which they claim to be significantly cheaper to produce, and investigated the effect of increasing ionicity on wear reduction. They found that a higher ionicity might actually promote corrosion on the steel surface, when the components tested were used as neat lubricants. Indeed, for these reasons, the use of ILs as biolubricant additives, rather than neat lubricants, is widely investigated [122, 123, 133, 134, 142, 144, 145]. Clearly, some of the interesting, even peculiar properties of ILs (such as high thermal stability and non-volatility) are reduced when used as additives. Nonetheless, thanks to their dipolar nature,
employing them as additives improves adsorption on the metal surface compared to the base oil alone. One issue of using ILs as additives is ensuring a good miscibility with the base oil, which is hindered by the ionic forces and hydrogen bonds involved. Typical blends range between 0.5 wt% to 2.5 wt% of IL in the base oil. Zhang and co-authors [144] proposed the use of a polyisobutylene-orthoborate IL (i.e. a polymeric-based compound) to be miscible with non-polar, hydrocarbon oils, and verified that it was soluble up to 10 wt%.

The use of either amino acids or fatty acid anions has proven to be a particularly attractive means for use of bio-based and environmentally benign IL additives. Nagendramma et al. [133] investigated blends of 2 wt% amino acid-based ILs with a polyol ester biolubricant. Kontham and co-authors [115] studied the antiwear behavior of ricinoleate anion-based ILs as additives to two different green base oils, and found that a 0.8 wt% mixture gave the best responses. Rivera et al. [145], instead, tested three fatty acid anion-based ILs (octanoate, laurate and palmitate) in mixtures with an ester-based oil. Gusain et al. [146] analyzed the effect of alkyl chain length and unsaturation of several FAILs (C_{10}-C_{18}) as additives to a mineral lube base oil (SN-150). In particular, the introduction of unsaturation resulted in reduced friction, which is attributed to decreased Van der Waals interactions. As a general outcome, using ILs as additives does not appear to have a marked effect on density and viscosity of the biolubricant (i.e., the elastohydrodynamic behavior was similar), while tribological performances are significantly improved under boundary or mixed lubrication regime.

1.5. Scale-up and Industrial Feasibility

This section summarizes the limited number of articles focused on process scale-up, techno-economic analysis (TEA) and life-cycle assessment (LCA) with the aim of evaluating the commercial viability as well as the environmental impacts of bio-based lubricants. While
experimental investigations have been prolific over the past few years, in order to assess the feasibility of large-scale biolubricant production it is necessary to develop kinetic and process models for reactor design and conceptual process flow sheeting [147].

A few authors conducted experimental investigations with the aim of determining reaction kinetics of various biolubricant compounds obtained through different reaction pathways. Most of these considered a 2-step transesterification route, starting from vegetable oil feedstock [148-151]. More specifically, since the first step consists in obtaining fatty acid methyl esters (FAMEs) from triglycerides and methanol, which has already been widely investigated for biodiesel production, these papers are focused on the second transesterification step, which can be generalized as follows:

\[
R_1COOCH_3 + R_2OH \leftrightarrow R_1COOR_2 + CH_3OH
\]

where \( R_1 \) is the alkyl group of fatty acids and \( R_2 \) is the alkyl group of a long-chain alcohol.

Menkiti et al. carried out transesterification of jatropha oil methyl ester with trimethylolpropane (TMP), and report a second order kinetic rate constant with activation energy \( E_a = 13.57 \text{ kJ/mol} \) [148]. Elmelawy and co-authors conducted a similar study, using oleic acid, and the corresponding methyl ester, as feedstock [150]. The authors considered three reversible reactions occurring in series, to produce the TMP monoester, diester and finally triester. Each reaction was considered as first order with respect to each reactant, i.e., second order overall. Zheng et al. investigated the kinetics of transesterification of palmitic acid methyl ester (PAME) with 2-ethylhexanol over heterogeneous potassium carbonate catalyst, to get 2-ethylhexyl palmitate biolubricant [149]. Over the conditions tested, the authors considered an irreversible reaction of order 0.88 with respect to PAME, and an activation energy \( E_a = 57.04 \text{ kJ/mol} \). Encinar
et al. used 2-ethyl-2-hydroxymethyl-1,3-propanediol as long-chain alcohol for the transesterification of rapeseed oil methyl ester [151]. Since they operated with a large excess of alcohol, the second order reaction rate was simplified to a pseudo-first order, whose activation energy resulted equal to 6.91 kJ/mol. The main results from this analysis are summarized in Table 2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Experimental conditions</th>
<th>Reaction rate</th>
<th>Kinetic parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3FAME + TMP ↔ TMPE + 3M</td>
<td>Calcium hydroxide</td>
<td>FAME:TMP = 4:1</td>
<td>( r = ke^{-\frac{E_a}{RT}}c_{TMPE}^2 )</td>
<td>( k = 0.1) (min °C)^( -1 )</td>
<td>[144]</td>
</tr>
<tr>
<td>FAME + EH ↔ EHE + M</td>
<td>Potassium carbonate</td>
<td>FAME:EH = 1:3</td>
<td>( r = ke^{-\frac{E_a}{RT}}c_{FAME}^a )</td>
<td>( k = 6.79 \cdot 10^5 )</td>
<td>[145]</td>
</tr>
<tr>
<td>1. FAME + TMP ↔ ME + M</td>
<td>Sodium methylate</td>
<td>FAME:TMP = 10:1</td>
<td>( r_1 )</td>
<td>( k_1 = 0.24 )</td>
<td>[146]</td>
</tr>
<tr>
<td>2. ME + TMP ↔ DE + M</td>
<td>Sodium methylate</td>
<td>FAME:TMP = 1:1</td>
<td>( r_2 )</td>
<td>( k_2 = 0.03647 )</td>
<td>( k' = 0.012 )</td>
</tr>
<tr>
<td>3. DE + TMP ↔ TMPE + M</td>
<td>Sodium methylate</td>
<td>FAME:TMP = 1:1</td>
<td>( r_3 )</td>
<td>( k_2 = 0.0268 )</td>
<td>( k = 0.1079 )</td>
</tr>
<tr>
<td>3FAME + A ↔ AE + 3M</td>
<td>Sodium methylate</td>
<td>FAME:TMP = 1:1</td>
<td>( r = k'e^{-\frac{E_a}{RT}}c_{FAME} )</td>
<td>( k' = 0.1151 ) min(^{-1} )</td>
<td>[147]</td>
</tr>
</tbody>
</table>

FAME = Fatty acid methyl ester; TMP = trimethylolpropane; TMPE = trimethylolpropane ester; M = methanol; EH = 2-ethylhexanol; EHE = 2-ethylhexanol ester; ME = monoester; DE = diester; A = alcohol; AE = alcohol ester
Other authors focused on the kinetics of biolubricant production following different reaction pathways [152-154]. For example, Narayan et al. investigated the reaction mechanism and kinetics of esterification of castor oil-derived fatty acids using supercritical methanol [154]. Under supercritical conditions, the formation of esters proceeds without the addition of acid/base catalysts. The authors derived a kinetic model which was able to describe reactant conversions at different temperatures and molar ratios, and report an activation energy of +25 kJ/mol. Tesser and co-authors investigated the synthesis of biolubricants from epoxidized oil with 1-butanol over clays as heterogeneous catalyst [153]. Their findings suggested the existence of two different catalytic active sites with different activities: one with a fast reaction rate, but also fast deactivation, and another with zero-order reaction rate with respect to reactants. Chen and Zhao studied the production of biolubricants equivalent to PAOs starting from lignocellulosic material [154]. In particular, the reaction between hydroxymethylfurfural and 2-alkylfuran obeyed first order kinetics and had an activation energy of +61.2 kJ/mol.

The determination of kinetic parameters is fundamental to develop reactor design and scale-up. Besides kinetics, an efficient reactor design also needs to consider mass transfer and energy efficiency aspects to enhance reaction performances and decrease production costs. For example, Soufi et al. propose the use of a vertical pulsed column (VPC) reactor to increase the interfacial area, thus enhancing mass transfer, between immiscible reactants in the transesterification of waste cooking oil (WCO) methyl ester with TMP [155]. In another perspective, Diaz and co-workers proposed a pervaporation-assisted reactor aimed at in situ methanol removal during transesterification of castor oil methyl ester with TMP, so as to shift the equilibrium towards the direct reaction and increase the biolubricant yield [156].
Ultimately, conceptual process design and mass/energy balances for a large-scale process are necessary to assess the industrial feasibility of a specific biolubricant production technology. Hussein et al. developed a detailed process simulation of dioleoyl ethylene glycol ester biolubricant starting from WCO feedstock, using Aspen HYSYS [157]. The authors carried out an experimental investigation to find optimal operating conditions, and then process simulation to provide material balances for a large-scale process, based on a biolubricant production capacity of 88,700 ton/year, obtained at 87% molar purity. However, the authors did not carry out an economic feasibility assessment. Riazi and co-workers conducted a comprehensive TEA and LCA on the production of isostearic acid (IA) lubricant from both soybean oil and tall oil, using SuperPro Designer process simulator, and considering a production capacity of 4500 ton/year [158]. They found that, considering IA’s market price of 4250 $/ton and revenues from coproducts, the soybean oil pathway had a lower production cost, but also lower profit than tall oil. Both processes appear economically viable, with a relatively brief payback time. In terms of life cycle metrics, the soybean process had a higher climate change impact compared to the tall oil scenario (1.9-3.8 kg of CO$_2$eq/kg of IA vs 1-1.5 kg of CO$_2$eq/kg of IA). However, both perform better than synthetic lubricants on a life cycle basis, considering that the latter releases additional CO$_2$ after its end of use cycle, since it requires disposal. Athaley et al. carried out TEA and LCA for an integrated process producing lubricants and other bio-based chemicals starting from furfural [159]. Specifically, furfural was taken as the byproduct of a previously proposed process for the production of p-xylene from lignocellulosic biomass. The authors conducted detailed process simulation combined with heat integration to minimize energy inputs, using Aspen Plus software. They report a minimum selling price for lubricants in order for the process to be profitable of 4037 $/ton, which is comparable to the current market price of mineral oil-based lubricants (4000-4500
$/ton), considering a production capacity of 98,945 ton/year. The authors highlight the cost of raw materials as the major contribution (83%) to the total OPEX, and high capital costs due to the consumption of large amounts of solvents, which results in the need for large equipment. As for the environmental performance, water depletion, climate change, land occupation, and fossil depletion impacts were analyzed and compared to those of alternative bio-based chemicals production routes.

1.6. Summary and Future Prospects

Biolubricants present several advantages over conventional lubricants derived from mineral oils. They are envisaged to become increasingly important in the transition from fossil sources towards renewable and bio-based products. Although renewed interest in the potential of natural and bio-based oils as lubricants has been observed over the last three decades, their application at commercial scale is still limited. This is due both to deficiencies in their performance properties as well as limitations in the means for production, which currently make mineral oils the preferred choice on the cost basis. For this reason, research in this field is ever-evolving, as testified by the large number of publications produced over the last five years aimed at improving both the properties and the synthesis processes for biolubricants, as well as their renewable content and broader environmental impact. In this regard, finding new sources of renewable oils that do not compete with the food chain in terms of feedstock or land requirements is crucial to develop a sustainable market. In addition, developing more environmentally friendly and efficient catalysts and additives will also promote biolubricants applications. As more countries pledges to zero carbon emissions by 2050, investment on biolubricant research could also increase because it reduces the dependency of the lubricant industry on fossil sources. In North America and Europe, strict emissions standards, which influences the advancement of internal combustion engines that
uses fuels that cannot be efficiently decarbonized by electrification (e.g., industrial diesel engines and marine engines), will drive the development and adaptation of biolubricants. Biobased hydraulic fluids could also enter the hydraulic fluids market, which is projected to grow at 5.54% CAGR in the next 5 years because of the growing concern on the environment impact of petroleum-based hydraulic fluids [160] On the other hand, while a significant quantity of research effort has been devoted to improving biolubricant synthesis, investigating different chemical compounds and reaction pathways, as well as on assessment of the physio-chemical properties of the product in relation to its application, data on industrial scale production feasibility and on overall life-cycle impacts are still lacking. Therefore, more comprehensive process simulations, conceptual process design, TEA and LCA should be developed to guide future directions.

1.7. Acknowledgements

The authors greatly appreciated the financial support from U.S. Department of Agriculture (USDA-NIFA) under award number 2019-67022-29947. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.
CHAPTER 2

BIOCRUDE PRODUCTION FROM LIGNIN IN HYDROTHERMAL MEDIUM:
EFFECT OF RAPID HEATING AND SHORT RESIDENCE TIME

This study investigates the influence of heating rate and short residence time (1-15 min) on the hydrothermal liquefaction (HTL) of alkali lignin, as a function of reaction temperature (280-320 °C). A novel induction heated lab-scale batch reactor was designed and was used for rapid heating rate (~100 °C/min), while a conventional electrical heater was used for slow heating rate (~5.3 °C/min). The rapid heating rate with a short residence time (1 min) resulted in higher yield of biocrude (49.3 ± 1.01 wt%) at 320°C under autogenous pressure. In contrast, a slow heating rate and longer residence time (8-15 min) led to a lower yield of biocrude due to the promotion of gasification and undesired secondary reactions. The detailed characterization of biocrude revealed that rapid heating rate improves the selectivity of compounds in biocrude, such as phenol, while slow heating rate produced a broader distribution of compounds, including anisole and alkyl phenol at 320 °C for 1 min residence time. Furthermore, the usefulness of phenol capping agent during fast HTL of lignin was demonstrated in suppressing char formation and increasing biocrude yield.

2.1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical conversion process using water as the main reaction medium at sub- or supercritical state for depolymerization of biomass into biocrude [161, 162]. HTL has its advantage in terms of using wet biomass or a wide range of organic wastes which would reduce the overall energy need for liquefaction as compared to pyrolysis. Because of its several advantages over other methods, there have been numerous studies
and publications on HTL in recent years [163, 164]. The primary objective of these studies is to investigate the impact of various reaction parameters including temperature, holding time, biomass type, biomass to water ratio, solvent, and catalyst, on the yield of biocrude. The goal is to optimize these parameters to achieve the highest possible yield of biocrude. However, most of the HTL technology mainly focusing in isothermal HTL in batch reactors, where the residence time is typically more than 15 minutes with very slow preheating rate (e.g., 5 to 10 °C/min) [165]. It leads uncertainties in the interpretation of the reaction time and temperature, consequently the depolymerization chemistry due to the slow temperature ramping.

Table 3 lists the reactor volumes and heating rates of HTL batch setups with relatively higher heating rates, using different heat sources as reported in literature. Brand et al. [166] reported that when heating rate increased from 2 to 20 °C/min, biocrude yield increased by 12 wt% at 350 °C for one minute residence time with pine sawdust feedstock. Besides them, positive effect of higher heating rate on biocrude yield has been reported from a variety of biomass including microalgae, wood, corn stover and spent coffee [164, 167-170]. Xue et al. [161] and Akhtar et al. [171] explained that slow heating rate usually leads to the formation of char because of the repolymerization of intermediates, whereas rapid heating rate inhibits the formation of char, avoiding unwanted side reactions. Although positive influence of the higher heating rate to the biocrude yield from different biomass is indicated from several studies, the number of available literatures in this field is still limited due to the difficulty in bringing alternative heating systems that enable fast heating in the laboratory. In general, rapid heating (>100 °C/min) is only enabled with a microreactor (<5 mL) with a sand or tin bath. Despite their advantages, microreactors are limited by their small loading volume, which can make it challenging to obtain precise product yield measurements.
To address this problem, we customized a new laboratory batch reactor equipped with an extremely efficient induction heating system. Unlike conventional heating methods that rely on resistive heating, induction heating (IH) is a contactless heating method that creates a magnetic field and heats any ferromagnetic material within the confinement of induction coils[172]. Figure 8 illustrates a comparison of heating profiles of the fast HTL (IH reactor), a 280 mL batch reactor equipped with induction heating, and isothermal HTL (Parr reactor), a 500 mL batch reactor equipped with conventional electrical heater used in this study. The heating rate of the IH reactor was approximately 100.0 °C /min, while the Parr reactor was 5.3 °C /min to reach 320 °C from room temperature. In addition to its rapid heating capability, induction heating also features high energy efficiency due to its very efficient heat transfer capability compared to conventional heating methods [169, 172, 173]. This means that induction heating has the potential to not only speed up the HTL process, but also improve its economy by minimizing energy usage.
Table 3. Various heat sources used in HTL batch studies

<table>
<thead>
<tr>
<th>Reactor volume (mL)</th>
<th>Heat source</th>
<th>Heating rate* (°C/min)</th>
<th>Cooling method</th>
<th>Feed stock</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>electrical heater</td>
<td>20</td>
<td>water bath</td>
<td>pine sawdust</td>
<td>[166]</td>
</tr>
<tr>
<td>80</td>
<td>microwave</td>
<td>13.5</td>
<td>build in fan</td>
<td>spent coffee</td>
<td>[174]</td>
</tr>
<tr>
<td>20</td>
<td>fluidized sand bath</td>
<td>82</td>
<td>water bath</td>
<td>12commercial polymers</td>
<td>[175]</td>
</tr>
<tr>
<td>10</td>
<td>fluidized sand bath</td>
<td>N.A.</td>
<td>water bath</td>
<td>barley straw</td>
<td>[176]</td>
</tr>
<tr>
<td>5</td>
<td>molten tin bath</td>
<td>ca.300</td>
<td>water bath</td>
<td>woody biomass</td>
<td>[177]</td>
</tr>
<tr>
<td>4.1</td>
<td>sand bath</td>
<td>ca. 416</td>
<td>water bath</td>
<td>5 model compounds</td>
<td>[178]</td>
</tr>
<tr>
<td>1.67</td>
<td>sand bath</td>
<td>ca. 300</td>
<td>water bath</td>
<td>microalgae</td>
<td>[168]</td>
</tr>
<tr>
<td>0.63</td>
<td>sand bath / muffle furnace</td>
<td>179</td>
<td>N.A.</td>
<td>woody biomass</td>
<td>[164]</td>
</tr>
<tr>
<td>ca.0.63</td>
<td>sand bath / muffle furnace</td>
<td>585</td>
<td>water bath</td>
<td>sugar kelp</td>
<td>[179]</td>
</tr>
</tbody>
</table>

N.A.= not available, Ref.= references. *The heating rate indicated is the firstest setup used in their experiments.

Lignin is a naturally abundant aromatic polymer that makes up 15-40% of biomass weight and approximately 40% of biomass heat and energy[180]. It is typically generated as a waste product (black liquor) from the pulp and bioethanol industries. More than 100 million tons of lignin-rich residue is isolated from lignocellulosic biomass annually[181]. Unfortunately, only less than 2% of those lignin is utilized for producing specialty chemicals such as dispersants, adhesives and surfactants, and the rest is just burned for heat and energy[182]. However, its rich in aromatic structure can lend itself as a sustainable source of chemicals and biofuels; a precursor for a variety of value-added products[183]. In recent years, there has been substantial research on the HTL of lignin, with numerous publications exploring its potential for the production of chemicals and
fuels. However, a major drawback when converting lignin into chemical or fuels by HTL is the formation of char and lower yield of biocrude[183]. Also, selective depolymerization of lignin into a few structurally similar aromatic monomers is more attractive for the upgradation process of biocrude such as hydrodeoxygenation to economically produce high-value product. Specifically, we targeted to obtain phenolic monomers in this study due to its high reactivity towards several organic chemical reactions. For instance, Maglinao et al [113], proposed 2-steps conversion (hydrodeoxygenation followed by aromatic alkylation) for the phenolic monomer derived from lignin to produce sustainable lubricant enhancer. Developing ways to use lignin for high-value products such as sustainable lubricant enhancer is crucial because it reduces environmental impact as well as improving the economy of bioethanol production processes.
Figure 8. Comparison of heating profile set at 320°C (a) IH reactor, (b) Conventional batch (Parr) reactor

From those reasons, lignin was chosen as feedstock for this study and to the best of the authors’ knowledge, the influence of heating rate on lignin depolymerization has not yet been reported in the literature [184].
The objective of this work is to study the influence of rapid heating and short residence time (<15 min) on lignin depolymerization, using a newly developed IH reactor. It is important to note that short residence time allows compact (small volume) reactor design which can be scalable and industrially attractive due to the possibility of developing a continuous HTL process. The proposed IH setup enables precise control of reaction temperature and very high heating rate (>100 °C/min) in a medium size reactor (280 mL), thereby reducing the potential for misinterpretation of depolymerization chemistry due to a long preheating time. The recovery rate, quality, and chemical composition of the HTL products are analyzed and discussed. The produced biocrude was analyzed using gas chromatography-mass spectroscopy (GC-MS), elemental analyzer (EA), fourier transform infrared spectroscopy (FTIR) and thermogravimetric analyzer (TGA).

The goal of this study is to increase the yield of phenols in biocrude from HTL of lignin. A higher percentage of phenol in biocrude is desired for converting it to a lubricant enhancer since the hydrodeoxygenation process will maximize the production of aromatics, which can then react with alkyl groups derived from waste cooking oil to produce a sustainable lubricant enhancer. This study is focused on the first step i.e., HTL of lignin to produce a higher percentage of phenol in biocrude.

To maximize the yield of phenols in biocrude, a phenol capping agent and K₂CO₃ was used for all the tested conditions in this study. The presence of phenol as a capping agent in HTL medium was shown to limit the repolymerization reaction and improve yield of liquid product and aromatic monomers [180, 183, 185]. Belkheiri et al. [183], reported that when phenol concentration is lowered from 4 to 2%, they were able to obtain almost the same yield of biocrude. However, the yield of individual compounds was dependent on the phenol concentration. Thus, in this study, 4% of phenol was added to the HTL medium to maximize the yield of phenols in
biocrude, and effectiveness of phenol capping agent to the biocrude yield is also discussed. The addition of K\textsubscript{2}CO\textsubscript{3} was made to maximize the biocrude yield. The effectiveness of K\textsubscript{2}CO\textsubscript{3} during HTL is widely reported to increase the yield of biocrude and suppress char formation[186]. The integrated methods using rapid heating rate and addition of phenol capping agent and K\textsubscript{2}CO\textsubscript{3} could be important for the future of the biorefinery concept in terms of maximizing the phenol yield in biocrude to produce the sustainable lubricant enhancer.

2.2. Material and Methods

2.2.1. Materials

Alkali lignin purchased from the Tokyo Chemical Industry was used as feedstock in this study. Liquid phenol (≥89.0%, Sigma-Aldrich) and potassium carbonate (K\textsubscript{2}CO\textsubscript{3}, >99.0%, Fisher Scientific) were used as received for HTL reaction. Deionized (DI) water was produced from a water purifier (Hydrologix Inc). Hydrochloric acid (37%, Fisher Scientific) was used for the acidification of HTL mixture. Acetone (HPLC Grade, >99.5%, Alfa Aesar), and diethyl ether (technical grade, Acros Organics) were used as received to recover the biocrude after HTL.

2.2.2. HTL Procedure

2.2.2.1. Fast and Isothermal HTL Setup

Table 4 illustrates differences in fast and isothermal HTL setup used in this study. For fast HTL, a 280 mL stainless steel batch reactor (High Pressure Equipment Co, USA) equipped with the IH system (HI-HEATER4020, Dai-ichi high frequency, Japan) was used. The temperature was regulated by a PID controller using two type K thermocouples. One thermocouple measured the outside reactor surface, while the other thermocouple measured the inside reactor temperature from a thermowell that extended into the reactor. Heating rate approximately 100 °C/min was achieved with this setup. Fast HTL conditions cover a range of temperatures (280 – 320 °C) and residence
times (1 – 15 min after reaching the desired reaction temperature) under autogenous pressure (Table 5). At the end of the reaction, the reactor was quickly cooled to room temperature by immersing it in an ice water bath.

For isothermal HTL, a 500 mL batch reactor equipped with an electrical heater (Series 4570, Parr Instrument Company, USA) was used. The temperature is controlled by Parr 4848 controller with a type J thermocouple located in the thermowell inside of the reactor, and heating rate was approximately 5.3 °C/min. Only one condition (320 °C for 1 min residence time) was used to study isothermal HTL. This reaction condition was selected based on the optimal temperature and residence time for lignin depolymerization found by fast HTL experiments. The isothermal HTL was conducted under autogenous pressure, and after a given residence time, the reactor was rapidly cooled by internal cooling coil.

Table 4. Comparison of fast and isothermal HTL setup

<table>
<thead>
<tr>
<th></th>
<th>Fast HTL</th>
<th>Isothermal HTL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heat source</strong></td>
<td>Induction heating</td>
<td>Electrical furnace</td>
</tr>
<tr>
<td><strong>Heating rate (°C/min)</strong></td>
<td>~100</td>
<td>&lt;5.3</td>
</tr>
<tr>
<td><strong>Reactor internal volume (mL)</strong></td>
<td>280</td>
<td>500</td>
</tr>
<tr>
<td><strong>Cooling method</strong></td>
<td>Ice water bath</td>
<td>Internal cooling coil</td>
</tr>
<tr>
<td><strong>Estimated energy consumption for preheating to 320°C (kWh)</strong>*</td>
<td>0.43</td>
<td>1.23</td>
</tr>
</tbody>
</table>

*The estimated energy consumption for the fast HTL was calculated based on the energy output as shown in Figure 1a, where maximum power is 15kW. For the isothermal HTL, the energy usage was estimated assuming the Parr reactor would operate at maximum power of 1.29 kW (from reactor specification of 115V x 11.2 Amps) for the entire pre-heating time (57 minutes).
Table 5. Experimental conditions for fast HTL

<table>
<thead>
<tr>
<th></th>
<th>1 min</th>
<th>8 min</th>
<th>15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>280°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>300°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>320°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

2.2.2.2. HTL Conditions

Table 6 summarizes loading conditions for fast and isothermal HTL. Alkali lignin (10wt %), K$_2$CO$_3$(1.6wt %), liquid phenol (4.0wt %), and DI water (100 mL and 178 mL for fast and isothermal HTL respectively) were added to the reactors. Literatures reports K$_2$CO$_3$ is more effective than other salts catalyst (i.e., CaCO$_3$, Na$_2$CO$_3$, ZrOCl$_2$, AlK(SO$_4$)$_2$, and KCL) and strong basis (i.e., KOH, NaOH) in increasing biocrude yield and suppress char formation[180, 187]. The usefulness of using liquid phenol as capping agent during lignin HTL was explained in the previous section. We conducted additional experiments in absence of liquid phenol to investigate the effect of the phenol capping agent to the biocrude yield at 320 °C for 1 minute residence time using fast HTL. Furthermore, since phenol is also our targeted compound, we performed a blank batch test (without lignin in the feed) using fast HTL to demonstrate the contribution of phenol capping agent to the biocrude yield. The results related to those additional experiments are summarized in section 3.7.
Table 6. Loading condition for fast and isothermal HTL

<table>
<thead>
<tr>
<th>Item</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali lignin</td>
<td>10 wt% (±0.02)</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>1.6 wt% (±0.02)</td>
</tr>
<tr>
<td>Liquid phenol</td>
<td>4.0 wt% (±0.02)</td>
</tr>
<tr>
<td>DI water</td>
<td>100 mL for IH reactor</td>
</tr>
<tr>
<td></td>
<td>178 mL for Parr reactor</td>
</tr>
</tbody>
</table>

2.2.2.3. Product Separation

The procedure for product separation and analysis methods is outlined in Figure 9. Once the HTL reaction was completed, the cooled reactor was slowly opened to release gaseous products, which was not collected or analyzed in this study. The pH of the HTL mixture was measured, and 1.5 mL of the mixture was filtered and saved for total organic carbon (TOC) analysis. The mixture was then transferred to a beaker using DI water and acidified with 1M HCL to achieve a pH of approximately 1-2. This mixture was kept overnight at 4 °C (12 h) to precipitate organic acids and soluble lignin, to improve the separation of the solid and liquid phases[185]. The solid and liquid products in the mixture were then separated by vacuum filtration. The solid portion was dried in an oven at 65 ± 2 °C for four hours, and then left to dry at room temperature overnight. The dried solid was washed with acetone, and the solids were separated from the extract by vacuum filtration. The acetone solution was transferred into a round bottom flask, and the biocrude was recovered using a vacuum rotary evaporator at 48 °C for over two hours until the round bottom flask mass changed by less than 0.05 g. The filter paper with the solid phase was dried in an oven at 65 ± 2 °C overnight and named hydrochar. For the aqueous phase, TOC was measured for all
experiments, and light biooil (LBO) was extracted for selected experiments (320 °C for 1 min residence time in fast and isothermal HTL) using the following procedure. Diethyl ether was added to the aqueous phase, and the mixture was shaken vigorously for about ten minutes. The water-ether mixture was separated using a separating funnel. The ether phase was transferred to a round bottom flask, and the LBO was recovered using a vacuum rotary evaporator at 30 °C for over two hours until the round bottom flask mass changed by less than 0.05 g. The remaining aqueous separated from the ether phase was named aqueous waste, and TOC was measured. All experiments were done in duplicate or triplicate.

Figure 9. Products separation and analysis steps of the lignin HTL
2.2.2.4. Analysis

TOC analysis was carried out with TOC-VCSN (Shimadzu). For HTL mixture, 1.5 mL of sample was taken and filtered with 0.45 µm syringe filter prior to the analysis. The pH of the HTL mixture was measured using an Orion Multifunction Meter (Thermo Scientific). Elemental composition of biocrude, hydrochar and LBO were analyzed with Flash 2000 Elemental analyzer (Thermo Scientific). FTIR analysis of the hydrochar and LBO was carried out with Cary630FTIR (Agilent Technologies). The organic compounds in the biocrude were detected by GC-MS system: a gas chromatograph (7890A GC, Agilent Technologies) coupled with mass spectrometer. The column used was an Agilent HP-5MS 5% Phenyl Methyl Silox (30 m x 250 µm x 0.25 µm). The oven temperature was programmed as follows: begin at 35 °C and hold it for 12 minutes, then ramped to 150 °C at 2 °C/min, followed by another ramp to 270 °C at 10 °C/min, and kept at the final temperature for ten minutes. Thermogravimetric analysis (TGA) of biocrude was performed using TGA-50 (Shimadzu). Biocrude was heated to 900 °C at a heating rate of 10 °C/min with flowing nitrogen gas (purging gas) at 20 mL/min.

The biocrude yield was calculated using Eq. 1. The carbon recovery (CR) of HTL products including biocrude, hydrochar, aqueous phase, aqueous waste, and LBO were calculated using Eq. 2, respectively. The HHVs of the lignin, biocrude and hydrochar were calculated through the Dulong–Berthelot correlation, but without sulfur (Eq. 3) [178]. The energy recovery (ER) of the biocrude and hydrochar was calculated using Eq. 4, respectively.

\[
\text{Biocrude yield (wt%)} = \frac{\text{Mass of biocrude}}{\text{Mass of lignin} + \text{Mass of phenol}} \times 100
\]

Eq. 1
\[
CR \text{ (wt\%) for HTL products} = \frac{(\text{Mass of C in product})}{(\text{Mass of C in lignin} + \text{Mass of C in phenol})} \times 100
\]

Eq. 2

\[
HHV \left(\frac{MJ}{kg}\right) = 0.3414 \times C\text{(wt\%)} + 1.4445 \times H\text{(wt\%)} - \frac{N\text{(wt\%)} + O\text{(wt\%)} - 1}{8}
\]

Eq. 3

\[
ER \text{ (\%) } = \frac{HHV \text{ of product} \times \text{Mass of product}}{(HHV \text{ of lignin} \times \text{Mass of lignin}) + (HHV \text{ of phenol} \times \text{Mass of phenol})} \times 100
\]

Eq. 4

*All the calculation is made based on lignin in dry matter.

### 2.3. Results and Discussion

#### 2.3.1 Effect Temperature and Short Residence Time on Products Yield

The pH of HTL mixture produced immediately after the reaction from fast HTL are shown in Figure 10a. A slight decrease in pH at higher temperatures (300 – 320 °C) was observed with increasing residence time. This can be attributed to the formation of organic acids during the lignin depolymerization process\[188, 189\]. At lower temperature (280 °C), no notable decrease in pH was observed, which is likely due to the less formation of organic acid than higher temperatures. Literature reports that hydrothermal treatment of lignin produces organic acids including formic, acetic, and succinic acids\[190\]. The TOC of HTL mixture was found to be highest at 1 min residence time and further increase in residence time decreased the TOC content at higher temperatures (Figure 10b). This result suggests that lignin depolymerization may occur rapidly at higher temperatures within one minute of residence time. Prolonging residence times may promote
formation of gas and hydrochar, thereby decreasing the TOC content in HTL mixture/water soluble fraction. In contrast, at 280 °C, the highest TOC was observed at 8 min residence time, indicating the depolymerization of lignin appeared to be the dominant process from 1 to 8 minutes of residence time. However, gas and insoluble formation might be more pronounced in case of residence time higher than eight minutes at 280 °C.

Figure 10c presents the yield of biocrude obtained from fast HTL. The highest biocrude yield (49.3 wt%) was obtained at 320 °C for 1 min residence time and extending the residence time to 15 min decreased biocrude yield to 37.3 wt%. A similar trend was observed at 300 °C with biocrude yield decreasing from 44.0 to 37.3 wt%. In contrast, the biocrude yield at 280 °C increased from 23.0 for 40.4 wt% as the residence time increased. It can be inferred that lignin was rapidly depolymerized into biocrude at higher temperatures resulting in high yields within one minute. Moreover, prolonging the residence time at high temperatures may result in undesired secondary reactions and lower the biocrude yield. On the contrary, it is likely that biocrude formation occurs at a slower rate at 280 °C, and biocrude formation dominates over the secondary reaction at this temperature. Our results are in agreement with Brand et al.’s [166] observations, where they concluded that higher heating rate (20 °C/min) results to higher biocrude yields at reaction temperatures between 315 °C and 350 °C in contrast with lower reaction temperatures (250 – 280 °C). Their findings and results in this study indicate that a synergy between temperature and residence time is necessary to obtain higher yields of biocrude from fast HTL. Additionally, higher temperature is preferable to maximize biocrude yield at a short residence time e.g., 1 min.
Figure 10. (a) pH of HTL mixture (b) TOC of HTL mixture (c) biocrude yield as function of time and temperature with fast HTL
*Note: The x-axis in these figures represents the cumulative time, which includes both the pre-heating time (2-4 minutes) and the residence time (1, 8, and 15 minutes, respectively). This approach provides a more precise depiction of the process conditions in our dataset, accounting for the variability in pre-heating time resulting from variations in the initial temperature and the desired set temperature.

Figure 11 illustrates the distribution of carbon within products collected in the fast HTL experiments. The trend in carbon recovery (CR) in the biocrude was consistent with the biocrude yield (Figure 3c), with the highest CR of 52.3 wt% being achieved at 320 °C for 1 min residence time. While the CR in the biocrude decreased with longer residence time, the CR in the hydrochar and aqueous phases remained relatively the same at higher temperatures. However, the CR in the unaccounted phase increased from 1.3 to 11.9 wt% at 300 °C, and 2.2 to 13.7 wt% at 320 °C with increasing residence time. Since the gas phase during HTL was not collected or analyzed in this study, any CR in unaccounted phase is considered a loss from these gas formations. The data suggests that longer residence times of more than 1 minute at higher temperatures promoted carbon loss in gas phase which impacted the biocrude yield. Several studies have reported that the main components of the HTL gas phase are CO₂, and trace amounts of CO, CH₄, and H₂ [191-195]. It is noteworthy to mention that at 280 °C, the CR in unaccounted phase at 1 minute residence time exhibited unexpectedly high which decreased with increasing residence time, contrary to the trend observed in most HTL studies where gaseous product yield increases as reaction conditions become severe [192]. One possible explanation could be that a portion of the lignin rapidly undergoes thermal decomposition, generating volatile intermediate gaseous that react with each other to form non-volatile products as the reaction progresses. However, it should be acknowledged that direct comparisons between studies in HTL are challenging, especially with the application of very high heating rates in this study, and further analysis of the gaseous products is necessary to gain a better understanding of the reaction pathway under these conditions.
The highest CR in hydrochar was obtained at 280 °C and 1 min residence time, which can be attributed to the formation of less carbonized hydrochar with a high yield. At lower temperatures and short residence times, the cracking of lignin molecules is incomplete, resulting in partially carbonized hydrochar. Such hydrochar has a chemical composition comparable to lignin, while hydrochar obtained at higher temperatures and longer residence times (320 °C, 15 min) is more energy dense (high HHV) due to further carbonization.

Figure 11. Carbon mass balance of products obtained from the fast HTL experiments

2.3.2. Effect of Heating Rate on Products Yield

The condition of 320 °C for 1 min residence time was chosen for heating rate comparison as it produced the highest biocrude yield in the fast HTL experiments (Figure 11). A significant decrease in pH of HTL mixture, TOC content in HTL mixture, and biocrude yield was observed
in isothermal HTL (Table 7). This is likely due to many parallel and secondary reactions during the long preheating period, as evidenced by the larger drop in pH observed in isothermal HTL.

Figure 12 illustrates the CR distribution between fast and isothermal HTL. For these two batches, LBO was collected from aqueous phase as per the process described in Figure 9. The carbon distributions (CR) in biocrude, hydrochar, LBO, aqueous waste, and unaccounted are presented. The decrease in CR in biocrude from 52.3 to 38.3 wt% was observed for isothermal HTL. Meanwhile, the CR of the unaccounted phase, which is likely the gaseous product, increased from 4.3 to 16.4 wt%. The slow heating rate may provide enough time for the solvent-lignin mixture to stay in the reactive temperature region, which could lead to gasification or undesired secondary reactions during the preheating stage. This clear trend in CR in biocrude and unaccounted phase indicates that rapid heating rate is beneficial for lignin HTL. The trend of biocrude yield increase with higher heating rate in this study was aligned with the observation reported in the literature [164, 166].

It is interesting to note that the carbon distribution for other products such as hydrochar, LBO, and aqueous waste did not show a significant difference between fast and isothermal HTL. Obeid et al.[196] reported that the reaction pathway of biocrude and aqueous phase to the gaseous products is expected during HTL in many types of biomass. According to their proposed reaction pathway for lignin, the gaseous product is directly converted from biocrude without intermediating the aqueous phase or solid phase. Furthermore, they reported that the activation energy from biocrude to gaseous product was much lower than the one from biocrude to aqueous phase. (7.6 and 39.0 kJ/mol respectively). Hence, the lack of significant difference in CR of hydrochar, LBO, and aqueous waste between fast and isothermal HTL in the present study could be explained by the lignin reaction pathway that directly convert biocrude into gas, and this direct conversion may
proceed during the long preheating time in the isothermal HTL. However, further kinetic studies would be needed to fully explain the reaction pathway in both fast and isothermal HTL of lignin.

Table 7. HTL characterization of fast and isothermal HTL

<table>
<thead>
<tr>
<th></th>
<th>pH of HTL aqueous mixture</th>
<th>TOC of HTL mixture (g/L)</th>
<th>Biocrude yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast HTL (320 °C, 1min)</td>
<td>9.96 ± 0.04</td>
<td>28.4 ± 0.02</td>
<td>49.3 ± 1.01</td>
</tr>
<tr>
<td>isothermal HTL (320 °C, 1min)</td>
<td>9.19 ± 0.03</td>
<td>21.6 ± 0.29</td>
<td>33.2 ± 2.83</td>
</tr>
</tbody>
</table>

Figure 12. Carbon mass balance of products obtained from the fast and isothermal HTL experiments
2.3.3. Elemental Composition of Biocrude and Hydrochar

Table 8 summarizes the elemental composition, higher heating value (HHV), and energy recovery (ER) of biocrude and hydrochar obtained from fast and isothermal HTL. Run 10 (isothermal HTL at 320 °C for 1 min) had the lowest oxygen and highest carbon content in both biocrude and hydrochar, which leading to the highest HHV (29.0 and 27.5 MJ/kg for biocrude and hydrochar, respectively) among all conditions. Whereas the fast HTL generate biocrude and hydrochar had lower carbon content and higher oxygen content, resulting in a slightly lower heating value (26.3-27.9 MJ/kg for biocrude and 22.1-26.7 MJ/kg for hydrochar) compared to isothermal HTL. These outcomes can be attributed by the fact that isothermal HTL favors carbonization due to the long preheating time. The longer preheating time in isothermal HTL may have favored the removal of oxygen through gasification (mainly CO₂), which leads to higher energy content in the products [166, 178]. Also, for runs 1 through 9 (fast HTL), we observed HHV of biocrude and hydrochar increased with increasing residence time and temperature. These trends concur with the study of Brand et al. [166] particularly on the effects of temperature, residence time, and heating rate to the quality of hydrochar.

The ER of biocrude was highest in run 7 (fast HTL, 320 °C for 1 min) at 55.3%, while run 5 (fast HTL, 300 °C for 8 min) had the highest recovery rate in hydrochar at 48%, due to the higher yield of products in these conditions. Thus, it appears to be a tradeoff between product yield and higher heating value (HHV), depending on the HTL conditions. It was also observed that the quality of hydrochar varied widely (ranging from 22.1 – 27.5 MJ/kg), while the quality of biocrude was less varied (ranging from 26.3 – 29.0 MJ/kg) across all tested conditions. In other words, the HHV of hydrochar was more sensitive to the temperature and residence time, as compared to
biocrude across tested conditions in this work. Therefore, fast HTL is apparently advantageous for producing biocrude over hydrochar.

Figure 13 shows the FTIR spectra of alkali lignin and hydrochar obtained from fast HTL experiments. At lower temperatures and shorter residence times, it seemingly the hydrochar primarily consisted of unconverted lignin since no significant chemical changes in the hydrochar were observed. As the temperature and residence time increased, a decrease in the absorbance of various functional groups was observed. These functional groups were identified based on their wavenumbers: 1591 cm\(^{-1}\) and 1508 cm\(^{-1}\) for aromatic vibration in lignin, 1499 cm\(^{-1}\) and 1458 cm\(^{-1}\) for -CH and methoxy groups in the lignin, 1256 cm\(^{-1}\) for the syringyl ring and C-O stretch in lignin, 1204 cm\(^{-1}\) for C-O and C=O stretch in lignin, and 1029 cm\(^{-1}\) for aromatic deformation in-plane and C-O deformation in primary alcohol [197, 198]. This could be attributed to the cleavage of β-O-4 linkage in lignin and polycondensation of fragments during HTL. The decrease in the intensity of O-containing functional groups was consistent with the results of the oxygen component in hydrochar presented in Table 6.
Table 8. Elemental composition, HHV, and ER of biocrude/hydrochar obtained from fast and isothermal HTL

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactor</th>
<th>Temp (°C)</th>
<th>RT (min)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>H/C</th>
<th>O/C</th>
<th>HHV (MJ/kg)</th>
<th>Energy recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkali Lignin in feed</td>
<td>52.3</td>
<td>4.7</td>
<td>0.3</td>
<td>42.7</td>
<td>1.1</td>
<td>0.6</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biocrude</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>IH</td>
<td>280</td>
<td>1</td>
<td>64.9</td>
<td>5.7</td>
<td>0.5</td>
<td>28.9</td>
<td>1.0</td>
<td>0.3</td>
<td>26.8</td>
<td>26.3</td>
</tr>
<tr>
<td>2</td>
<td>IH</td>
<td>280</td>
<td>8</td>
<td>63.5</td>
<td>5.8</td>
<td>0.5</td>
<td>30.2</td>
<td>1.1</td>
<td>0.4</td>
<td>26.3</td>
<td>37.8</td>
</tr>
<tr>
<td>3</td>
<td>IH</td>
<td>280</td>
<td>15</td>
<td>65.2</td>
<td>5.9</td>
<td>1.0</td>
<td>27.9</td>
<td>1.1</td>
<td>0.3</td>
<td>27.3</td>
<td>47.1</td>
</tr>
<tr>
<td>4</td>
<td>IH</td>
<td>300</td>
<td>1</td>
<td>63.3</td>
<td>5.8</td>
<td>0.7</td>
<td>30.2</td>
<td>1.1</td>
<td>0.4</td>
<td>26.3</td>
<td>49.4</td>
</tr>
<tr>
<td>5</td>
<td>IH</td>
<td>300</td>
<td>8</td>
<td>63.3</td>
<td>5.9</td>
<td>0.7</td>
<td>30.0</td>
<td>1.1</td>
<td>0.4</td>
<td>26.5</td>
<td>40.0</td>
</tr>
<tr>
<td>6</td>
<td>IH</td>
<td>300</td>
<td>15</td>
<td>65.9</td>
<td>6.1</td>
<td>0.8</td>
<td>27.3</td>
<td>1.1</td>
<td>0.3</td>
<td>27.9</td>
<td>44.4</td>
</tr>
<tr>
<td>7</td>
<td>IH</td>
<td>320</td>
<td>1</td>
<td>62.9</td>
<td>5.9</td>
<td>0.5</td>
<td>30.6</td>
<td>1.1</td>
<td>0.4</td>
<td>26.3</td>
<td>55.3</td>
</tr>
<tr>
<td>8</td>
<td>IH</td>
<td>320</td>
<td>8</td>
<td>64.8</td>
<td>5.7</td>
<td>0.6</td>
<td>28.9</td>
<td>1.1</td>
<td>0.3</td>
<td>26.8</td>
<td>42.7</td>
</tr>
<tr>
<td>9</td>
<td>IH</td>
<td>320</td>
<td>15</td>
<td>66.1</td>
<td>5.8</td>
<td>0.6</td>
<td>27.6</td>
<td>1.0</td>
<td>0.3</td>
<td>27.5</td>
<td>43.8</td>
</tr>
<tr>
<td>10</td>
<td>Parr</td>
<td>320</td>
<td>1</td>
<td>68.6</td>
<td>6.0</td>
<td>0.3</td>
<td>25.1</td>
<td>1.0</td>
<td>0.3</td>
<td>29.0</td>
<td>41.1</td>
</tr>
<tr>
<td>Hydrochar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>IH</td>
<td>280</td>
<td>1</td>
<td>59.5</td>
<td>4.7</td>
<td>0.6</td>
<td>35.2</td>
<td>0.9</td>
<td>0.4</td>
<td>22.8</td>
<td>33.5</td>
</tr>
<tr>
<td>2</td>
<td>IH</td>
<td>280</td>
<td>8</td>
<td>58.9</td>
<td>4.5</td>
<td>0.6</td>
<td>36.0</td>
<td>0.9</td>
<td>0.5</td>
<td>22.1</td>
<td>44.5</td>
</tr>
<tr>
<td>3</td>
<td>IH</td>
<td>280</td>
<td>15</td>
<td>63.3</td>
<td>4.5</td>
<td>0.6</td>
<td>31.0</td>
<td>0.9</td>
<td>0.4</td>
<td>24.2</td>
<td>38.8</td>
</tr>
<tr>
<td>4</td>
<td>IH</td>
<td>300</td>
<td>1</td>
<td>59.7</td>
<td>4.7</td>
<td>0.2</td>
<td>35.4</td>
<td>0.9</td>
<td>0.4</td>
<td>22.8</td>
<td>39.4</td>
</tr>
<tr>
<td>5</td>
<td>IH</td>
<td>300</td>
<td>8</td>
<td>63.6</td>
<td>4.6</td>
<td>0.1</td>
<td>31.7</td>
<td>0.9</td>
<td>0.4</td>
<td>24.5</td>
<td>48.0</td>
</tr>
<tr>
<td>6</td>
<td>IH</td>
<td>300</td>
<td>15</td>
<td>66.9</td>
<td>4.4</td>
<td>0.2</td>
<td>28.5</td>
<td>0.8</td>
<td>0.3</td>
<td>25.7</td>
<td>30.9</td>
</tr>
<tr>
<td>7</td>
<td>IH</td>
<td>320</td>
<td>1</td>
<td>60.7</td>
<td>4.5</td>
<td>0.3</td>
<td>34.5</td>
<td>0.9</td>
<td>0.4</td>
<td>23.1</td>
<td>31.8</td>
</tr>
<tr>
<td>8</td>
<td>IH</td>
<td>320</td>
<td>8</td>
<td>67.2</td>
<td>4.4</td>
<td>0.1</td>
<td>28.3</td>
<td>0.8</td>
<td>0.3</td>
<td>25.8</td>
<td>39.5</td>
</tr>
<tr>
<td>9</td>
<td>IH</td>
<td>320</td>
<td>15</td>
<td>69.6</td>
<td>4.2</td>
<td>0.1</td>
<td>26.0</td>
<td>0.7</td>
<td>0.3</td>
<td>26.7</td>
<td>30.4</td>
</tr>
<tr>
<td>10</td>
<td>Parr</td>
<td>320</td>
<td>1</td>
<td>70.8</td>
<td>4.3</td>
<td>0.2</td>
<td>24.7</td>
<td>0.7</td>
<td>0.3</td>
<td>27.5</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Note: Oxygen percentage was calculated based on the difference assuming lignin contains only C, H, O, and N elements. RT: Residence time.
Figure 13. FTIR spectra for alkali lignin and hydrochar from fast HTL

2.3.4. Molecular Component in Biocrude

Four biocrude samples (320 °C for 1-15 min with fast HTL and 320 °C for 1 min with isothermal HTL) were selected and analyzed using GC-MS. Figure 14 displays the relative peak areas of main chemical families identified in the biocrude.

The biocrude was mainly composed of phenol, anisole, alkyl phenols, guaiacols, alkane, and 2-ring non-condensed aromatics (2-NCAR) such as xanthene and 2-[(4-hydroxyphenyl)methyl] phenol. Phenol and anisole were found to be the dominant components in all the biocrude samples analyzed. The highest share of phenol (52.1%) was obtained at 320 °C for 1 min residence time, while an increase in residence time to 15 min led to a decrease in phenol share (35.7%) in fast HTL conditions. On the other hand, the percentage of anisole increased from 22.1% to 34.1% as the residence time increased from 1 to 15 minutes. The clear trend of decreasing
phenol and increasing anisole amounts with increasing residence time were likely due to the methylation of intermediate phenol. The increase in alkyl phenol and slight decrease in guaiacol with increasing residence time under fast HTL conditions can be attributed to the typical pattern of lignin depolymerization and conversion process, with an enhancement of demethylation and alkylation reactions[180]. Guaiacol is an intermediate degradation component in the lignin decomposition process and has high reactivity towards catechol and phenols in general [199].

Under isothermal conditions, the shares of phenol and anisole were almost equally distributed at 33.1% and 32.5%, respectively, which was significantly different under fast HTL conditions. Slow heating could have allowed secondary reactions such as methylation and alkylation, to occur resulting in less phenol and more anisole in the biocrude during temperature ramping.

Overall, the results suggest that the dominant conversion of lignin into phenol appears to occur within a very short amount of time (e.g., 1 minute) under fast HTL conditions. Fast HTL was effective in inhibiting undesired secondary reactions and producing more phenol in the biocrude. Longer residence time or slower heating rates resulted in the production of a variety of products including anisole and alkyl phenols, and consequently, the selectivity of phenol was decreased.
Figure 14. Relative peak areas of main chemical families in biocrude obtained from fast and isothermal HTL based on GC-MS analysis

2.3.5. Thermal Properties of Biocrude

Thermal stability of the biocrude obtained from fast and isothermal HTL at 320 °C for 1 minute residence time was evaluated by TGA, as shown in Figure 15a. The residual mass of the biocrude from isothermal HTL was found to be higher (30.9 wt%) than that of the biocrude from fast HTL (25.2 wt%) after heating the samples from room temperature to 900 °C under a nitrogen atmosphere. This result is consistent with the findings reported by Gollakota et al. [200] on chitin-derived biocrude obtained from fast and isothermal HTL.

Figure 15b shows the derivative thermogravimetric (DTG) weight loss curves obtained from the TGA curve. The DTG curve of the biocrude from fast HTL exhibits a distinct peak at
around 88 °C, whereas the biocrude from isothermal HTL shows two broader peaks at 111 – 140 °C and 231 – 240 °C. It should be noted that the moisture content in the biocrude was considered negligible in this study, since the biocrude was extracted from oven-dried solid portion using acetone. The high heating rate during fast HTL may have limited the oligomerization of compounds due to the rapid temperature ramping, leading to the presence of more volatile compounds in the resulting biocrude compared to the biocrude from isothermal HTL.
Figure 15. (a) TGA curve, (b) DTG curve for biocrude obtained from fast and isothermal HTL at 320 °C for 1 minute residence time

2.3.6. Effect of Phenol Capping Agent on Products Yield and Recovery.

2.3.6.1. Effect of Phenol Capping Agent to the Biocrude Yield

Many studies have reported the capping effect of liquid phenol during lignin HTL, which prevents the repolymerization reactions and decreases char formation [183, 185]. In line with these findings, our study showed that adding 4 wt% of liquid phenol in feed increased the biocrude yield.
from 35.9 ± 1.7 to 49.3 ± 1.0 wt% and decreased the char yield from 49.5 ± 2.2 to 19.1 ± 2.93 wt% at 320 °C for 1 min residence time in fast HTL. Studies have shown that addition of phenol in feed promotes the formation of a homogeneous phase during the reaction, entrapping active fragments produced from lignin depolymerization, and thereby preventing the formation of heavier compounds [201, 202].

However, since phenol is one of the target compounds to collect in our project, we conducted a blank batch test (without lignin in the feed) to investigate the effect of using phenol as a capping agent on the biocrude yield. For this test, we added DI water (100 mL), K₂CO₃ (1.6 wt%), and liquid phenol (4.0 wt%) and heated at 320 °C for 1 min residence time with fast HTL. As for the results, only homogeneous aqueous phase was obtained after the reaction, thus the biocrude was not obtained from blank batch test. This result is consistent with the findings from Nguyen et al. [185, 202], and Belkheri et al. [183]. Thus, the biocrude obtained from the other runs in this study is considered to be mainly derived from lignin. However, it is possible for liquid phenol to take part of the biocrude formation reaction when lignin is present in the feed.

2.3.6.2. LBO Characterization

Figure 16 shows the FTIR spectrum of LBOs obtained from fast and isothermal HTL at 320 °C for 1 min residence time, and pure liquid phenol used as capping agent in this study. The stretching vibration of the O-H functional group around 3500 cm⁻¹ and aromatic vibrations at 1593, 1498 and 1471 cm⁻¹ observed in pure liquid phenol were also observed in LBOs from fast and isothermal HTL. Moreover, the FTIR spectrum of the LBOs were almost identical to pure liquid phenol. Nguyen et al. [203] reported that phenol constituted more than 50 wt% of the identified compounds in LBO (diethyl ether soluble fraction of lignin oil), and phenol consumption during HTL process was in the range of 35 – 49% of the input phenol. In our study, the collected LBOs
mass was $78 \pm 1.28$ and $84 \pm 0.46$ wt% of the phenol mass in the feed for fast and isothermal HTL, respectively. Although the molecular composition of the LBOs was not investigated in this study, our findings support the hypothesis that part of the phenol in the feed reacts with the active fragments derived from lignin and contributes to higher biocrude yield while much of the phenol in the feed can be recovered as LBO.

![Figure 16. FTIR spectra for pure phenol and LBOs from fast and isothermal HTL](image)

**Figure 16. FTIR spectra for pure phenol and LBOs from fast and isothermal HTL**

### 2.4. Conclusion

Lignin depolymerization study was conducted in hydrothermal medium and the effect of fast heating rate (100°C/min) and short residence time on the yield of biocrude and phenols from alkali lignin was studied. A biocrude yield of $49.3 \pm 1.01$ wt% along with a high phenol yield (52%
of relative peak area) was obtained from fast hydrothermal liquefaction (fast HTL) of lignin at 320 °C for 1 minute residence time. Increasing heating rate (from ~5.3 to ~100 °C/min) at 320 °C for 1 min residence time increased biocrude yield from 33.2 ± 2.83 to 49.3 ± 1.01 wt% and phenol yield from 33.2 to 52.1 % of relative peak area. In addition, very short residence time (1 min) proved to be effective in increasing phenol percentage in the biocrude, while longer residence time (8-15 min) resulted in a broader distribution of compounds, such as anisole and alkyl phenol.

Additionally, this study showed the usefulness of using a phenol capping agent during fast HTL of lignin. The addition of capping agent in feed increased biocrude yield by 13.4 wt% and suppress char formation by 30.4 wt% at 320 °C for 1 min residence time.

Finally, apart from the product evaluation, a new batch system equipped with induction heating was found to have excellent heat transfer capabilities and precise temperature control. The energy consumption for pre-heating was significantly less (0.425 kWh) than traditional resistance heaters (1.23 kWh) used in isothermal HTL. The combination of fast HTL and induction heating is a significant improvement over traditional isothermal HTL and offers greater scalability and ease of designing a continuous reactor for HTL due to its short residence time and fast heating rate.

2.5. Acknowledgements

The research presented in this paper was made possible thanks to the generous financial support from the Bioprocessing and Bioengineering program (grant no. 2019-67022-29947/project accession no. 1019914) from the United Stated Department of Agriculture -National Institute of Food and Agriculture program.

The authors express sincere gratitude to Dai-ichi High frequency, Japan, for their technical expertise and assistance in the design of the induction heating system used in this project. Special
thanks are extended to Masazumi Takahashi and Isamu Umeda for their invaluable contributions to this work. Their support was instrumental in the success of this study.
REFERENCES


81. *Calumet Specialty Products acquires Biosynthetic Technologies - F&L Asia*.


VITA

Kyoko Hirayama

EDUCATION

Master of Science, Environmental Engineering  
Old Dominion University, Norfolk, USA  
Thesis: Biocrude Production from Lignin in Hydrothermal Medium: Effect of Rapid Heating and Short Residence Time  
August 2023

Bachelor of Science, Molecular Biology  
Meiji University, Japan  
Thesis: Epigenetics regulation of the MAP1LC3 Gene Family in Human Cervical Cancer Cells  
March 2018

RESEARCH PAPERS AND PRESENTATIONS


