COMILLAS
UNIVERSIDAD PONTIFICIA
ICAI

OFFICIAL MASTER'S DEGREE IN INDUSTRIAL ENGINEERING

MASTER THESIS

LIQUEFACTION OF BIOMASS USING SUPERCRITICAL CO2 AS SOLVENT

Author: Carmen Collado Balanzá
Director: Dr. Ashwani K. Gupta

Madrid
July 2024

I declare, under my responsibility, that the project submitted with the title

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Ashwani Gupta

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A mi padre,
Por apoyarme siempre en cada paso que he dado

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LICUEFACCIÓN DE LA BIOMASA UTILIZANDO CO2 SUPERCRÍTICO COMO DISOLVENTE

Autor: Collado Balanzá, Carmen.
Director: Gupta, Ashwani K.
Entidad Colaboradora: University of Maryland

RESUMEN DEL PROYECTO

En el presente Trabajo de Fin de Máster se realiza el estudio del proceso de licuefacción de la biomasa utilizando dióxido de carbono supercrítico (sCO2) como disolvente, así como la optimización de los parámetros que tienen impacto en el rendimiento del bio-aceite y la construcción de un modelo de regresión polinómica con la capacidad de predecir dicho rendimiento.

Palabras clave: Energía renovable, Licuefacción, Biomasa, Bio Aceites, Dióxido de carbono supercrítico, Optimización, Modelo polinómico de regresión

1. Introducción

La creciente preocupación por el cambio climático y la dependencia de los combustibles fósiles ha impulsado la búsqueda de fuentes alternativas de energía. En este contexto, la biomasa se presenta como una opción viable y renovable para la producción de biocombustibles, que podrían ser destinados sobre todo al sector del transporte, donde hoy en día no existe ninguna otra alternativa a los combustibles fósiles.

La licuefacción de biomasa es uno de los procesos más prometedores para la conversión de materia orgánica en bio-aceite. Este proceso implica la descomposición de la biomasa en presencia de un disolvente bajo condiciones de alta temperatura y presión.

El sCO2 es un disolvente que ha ganado atención en los últimos años debido a sus propiedades únicas. A presiones y temperaturas críticas, el CO2 adopta propiedades tanto de líquido como de gas, lo que permite una alta solubilidad y la capacidad de penetrar eficientemente en la biomasa, facilitando su descomposición y extracción de bio-aceite. Este Trabajo de Fin de Master se centra en la utilización de sCO2 como disolvente para la licuefacción de biomasa y la optimización de este proceso para maximizar el rendimiento de bio-aceite.

2. Objetivos

Como ya se ha comentado, el objetivo principal de este proyecto es estudiar la licuefacción de biomasa utilizando dióxido de carbono supercrítico (sCO2) como disolvente para producir de forma eficiente y viable bio-aceite que pueda utilizarse como biocombustible en el sector del transporte. Para ello, en el transcurso de la investigación se pretenden satisfacer los siguientes objetivos más específicos:

1) Conocer el impacto de los parámetros operativos de licuefacción de la biomasa sobre el rendimiento de bio-aceite;
2) Optimizar de la producción de bio-aceite mediante licuefacción de madera de pino blanda utilizando sCO2, optimizar los parámetros operativos, maximizar el rendimiento de bio-aceite;
3) Evaluar la viabilidad técnica y económica del sCO2 como disolvente en el proceso de licuefacción, discutir el efecto de las condiciones de operación;

3. Material y método

El presente Trabajo de Fin de Máster ha sido realizado a partir de un trabajo de investigación científica, combinando tanto el estudio teórico, como la combinación estadística y la experimentación en laboratorio. El proceso seguido para el desarrollo de este trabajo incluye las siguientes etapas:

1) Investigación del estado actual de los métodos de conversión termoquímica en relación con la licuefacción de biomasa mediante la comprensión de las técnicas conocidas, sus ventajas, desventajas y áreas que necesitan mejoras con el fin de comprender las necesidades actuales reales en el campo de la producción de biocombustibles.
2) Análisis y comprensión el impacto de todos los parámetros operativos que afectan al rendimiento de bio-aceite en el proceso de conversión de biomasa (por ejemplo, temperatura, tiempo de residencia, tipo de disolvente, relación disolvente/cosolvente...) con la realización de una extensa revisión bibliográfica de la literatura disponible sobre licuefacción hidrotérmica y solvotérmica de biomasa.
3) Diseño de un modelo de regresión polinómica para la predicción del rendimiento del bio-aceite en el proceso de licuefacción para adquirir un mayor control de dicha técnica.
4) Realización de experimentos a escala de laboratorio para verificar las hipótesis establecidas previamente y determinar el rendimiento real de bio-aceite del proceso de licuefacción de biomasa en las condiciones óptimas previamente establecidas.
5) Evaluación de la viabilidad técnica y económica del sCO2 como disolvente para el proceso de licuefacción, teniendo en cuenta factores como la eficiencia energética, la calidad del biocrudo, el coste de la materia prima, así como las posibles repercusiones medioambientales.

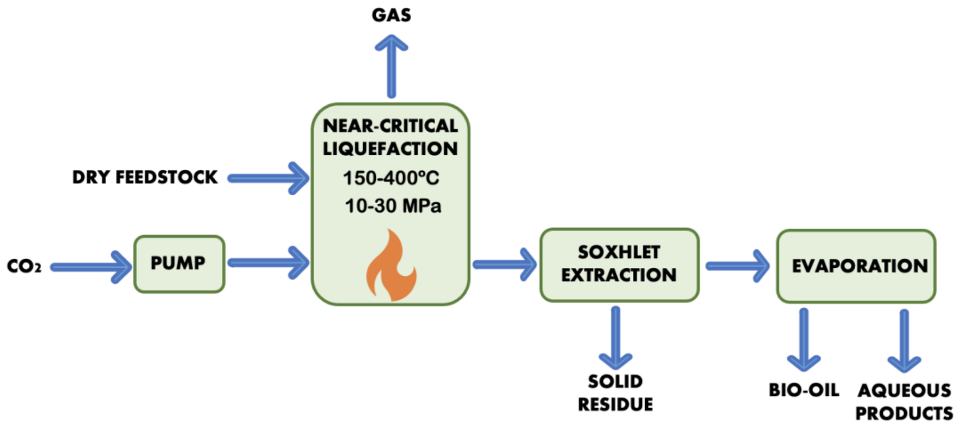
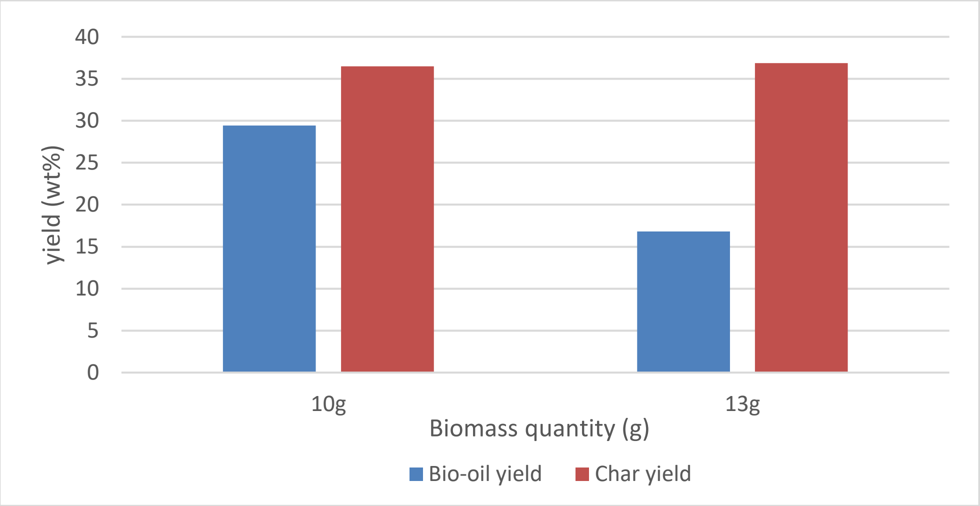


Figure 1: Diagram of biomass supercritical CO2 liquefaction process

4. Resultados

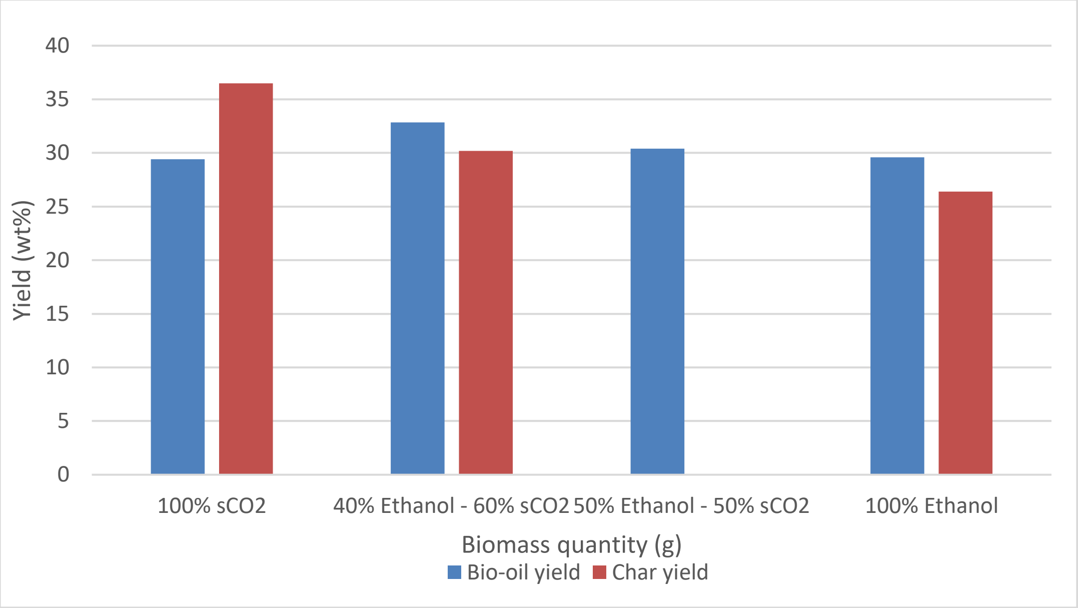
Una vez realizados los dos experimentos planificados para el desarrollo de este proyecto y realizada su correspondiente comparación con los realizados previamente por el Laboratorio de Combustión de la Universidad de Maryland se han obtenido los resultados que han sido representados tanto en el "Graphic 1" como en el "Graphic 2"

Analizando la primera gráfica, puede verse como el aumento de la cantidad de biomasa introducida en el reactor ha provocado una significante disminución en el rendimiento del bio-aceite conseguido. Al analizar los productos obtenidos tras la reacción se pudo ver como en el experimento donde se emplearon 13g de biomasa quedó parte de esta materia sin reaccionar, posiblemente por un exceso de carga en el reactor. Por otro lado, se encontró también parte del catalizador sedimentado en el fondo del reactor sin reaccionar, lo que pudo provocar también esta disminución de rendimiento.



Graphic 1: Effect of biomass quantity added to the reactor on the yield of bio-oil and char

Analizando la segunda gráfica, se puede observar que el porcentaje de rendimiento de bio-aceite obtenido utilizando disolvente 100% etanol y 100% sCO2 es muy similar (29,6 y 29,4 respectivamente). Por otro lado, los resultados muestran que la adición de co-disolvente ayuda a mejorar el rendimiento del proceso, y además, se puede observar que el valor óptimo aproximado en términos de proporciones se aproxima al 40% de etanol y 60% de sCO2. Esto corrobora las afirmaciones realizadas en otros artículos científico sobre la importancia del uso de co-disolventes para la maximización del rendimiento del bio-aceite.



Graphic 2: Effect of solvent/co-solvent ratio on the bio-oil and char yield

5. Conclusiones

El estudio demostró con éxito que el uso de CO2 supercrítico como disolvente para la licuefacción de biomasa puede llegar a convertirse en un método viable para la producción de bio-combustible si se siguen destinando recursos a su investigación y optimización. Las principales conclusiones extraídas son:

Viabilidad y eficacia: El CO2 supercrítico es un disolvente eficaz para la licuefacción de biomasa, capaz de producir cantidades significativas de bio-aceite. El proceso es eficiente, especialmente cuando se optimizan parámetros clave como la temperatura, la presión, la carga de biomasa y el uso de co-solventes y catalizadores.

Viabilidad económica: El análisis económico sugiere que el proceso a escala de laboratorio no puede llegar a ser todavía competitivo debido a su alto coste de producción. Es por ello por lo que se requiere seguir destinando recursos a su investigación para conseguir una mayor optimización del proceso y reducir costes logrando que se comercialización sea viable.

Impacto medioambiental: El uso de CO2 supercrítico, un disolvente relativamente inocuo para el medio ambiente, reduce el impacto ambiental global del proceso de licuefacción en comparación con los métodos tradicionales que utilizan productos químicos más agresivos.

Potencial de optimización: El modelo de regresión polinómica desarrollado en este estudio proporciona una valiosa herramienta para predecir los rendimientos de bio-aceite en función de diversos parámetros operativos, lo que permite una mayor optimización y ampliación del proceso.

Recomendaciones para el futuro: La investigación futura debe centrarse en el rendimiento a largo plazo y la estabilidad del proceso, la exploración de una mayor variedad de materias primas de biomasa, y la investigación del potencial de integración de esta tecnología con los sistemas de producción de biocombustibles existentes para mejorar la sostenibilidad y la eficiencia general.

LIQUEFACTION OF BIOMASS USING SUPERCRITICAL CO2 AS SOLVENT

Author: Collado Balanzá, Carmen.
Supervisor: Gupta, Ashwani K.
Collaborating Entity: University of Maryland

ABSTRACT

In this Master's Thesis, the study of the biomass liquefaction process using supercritical CO2 as solvent is carried out, as well as the optimization of the parameters that have an impact on the bio-oil yield and the construction of a polynomial regression model with the ability to predict this yield.

Keywords: Renewable Energy, Liquefaction, Biomass, Bio-oils, Supercritical Carbon Dioxide, Optimization, Polynomial Regression Modeling

1. Introduction

Growing concern about climate change and dependence on fossil fuels has encouraged the search for alternative energy sources. In this context, biomass presents itself as a viable and renewable option for the production of biofuels, which could be destined mainly for the transportation sector, where today there is no alternative to fossil fuels.

Biomass liquefaction is one of the most promising processes for the conversion of organic matter into bio-oil. This process involves the decomposition of biomass in the presence of a solvent under high temperature and pressure conditions.

sCO2 is a solvent that has gained attention in recent years due to its unique properties. At critical pressures and temperatures, CO2 adopts both liquid and gas properties, providing high solubility and the ability to efficiently penetrate biomass, facilitating its decomposition and bio-oil extraction. This Master Thesis focuses on the use of sCO2 as a solvent for biomass liquefaction and the optimization of this process to maximize the bio-oil yield.

2. Objectives

As already mentioned, the main objective of this project is to study the liquefaction of biomass using supercritical carbon dioxide (sCO2) as a solvent to efficiently and feasibly produce bio-oil that can be used as biofuel in the transportation sector. To this end, in the course of the research, the following more specific objectives are intended to be satisfied:

1) To know the impact of biomass liquefaction operating parameters on bio-oil yield;
2) To optimize bio-oil production by soft pine wood liquefaction using sCO2, optimize operating parameters, maximize bio-oil yield;
3) Evaluate the technical and economic feasibility of sCO2 as a solvent in the liquefaction process, discuss the effect of operating conditions;

3. Materials and methods

This Master's Thesis has been carried out on the basis of a scientific research work, combining both theoretical study, statistical combination and laboratory experimentation. The process followed for the development of this work includes the following stages:

1) Investigation of the current status of thermochemical conversion methods in relation to biomass liquefaction by understanding the known techniques, their advantages, disadvantages and areas in need of improvement in order to understand the actual current needs in the field of biofuel production.
2) Analysis and understanding of the impact of all operational parameters affecting the bio-oil yield in the biomass conversion process (e.g. temperature, residence time, solvent type, solvent/solvent ratio...) by performing an extensive literature review of the available literature on hydrothermal and solvothermal liquefaction of biomass.
3) Design of a polynomial regression model for the prediction of bio-oil yield in the liquefaction process to gain more control of this technique.
4) Conducting laboratory scale experiments to verify the previously established hypotheses and determine the actual bio-oil yield from the biomass liquefaction process under the previously established optimal conditions.
5) Evaluation of the technical and economic feasibility of sCO2 as a solvent for the liquefaction process, taking into account factors such as energy efficiency, biocrude quality, feedstock cost, as well as possible environmental impacts.

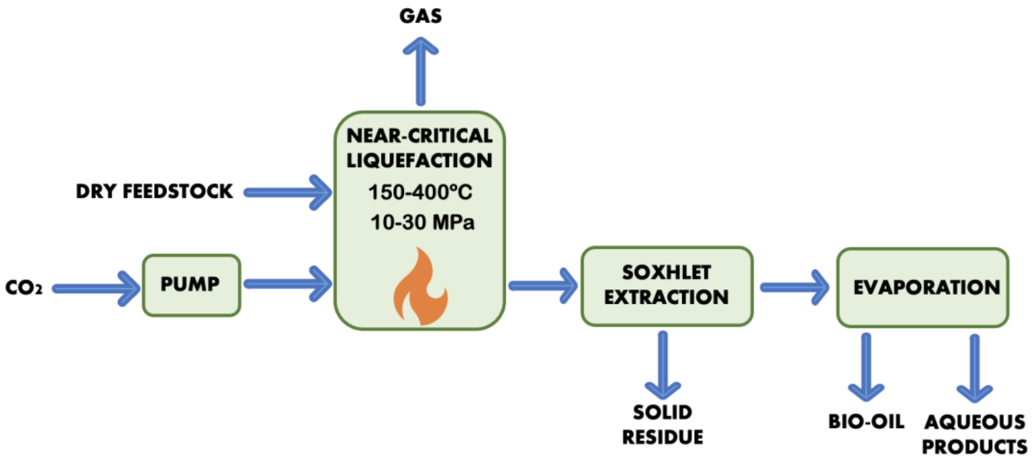
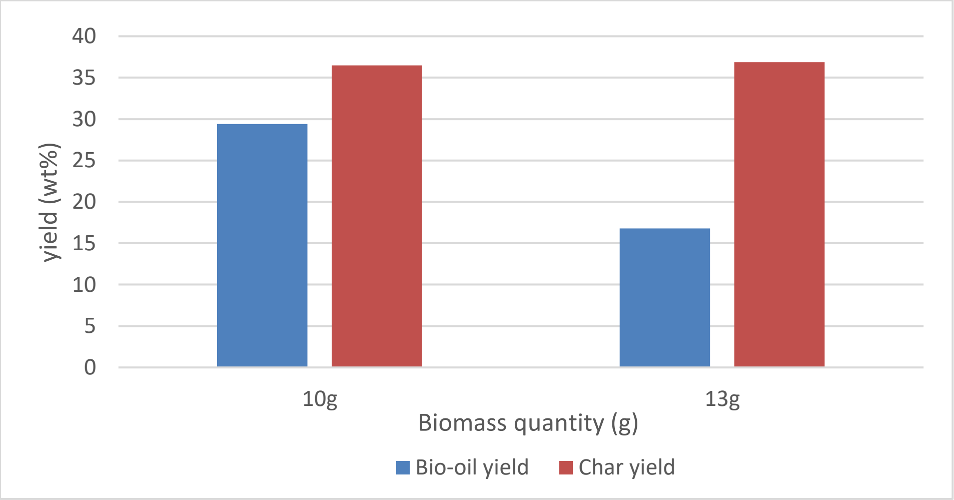


Figure 1: Diagram of biomass supercritical CO2 liquefaction process

4. Results

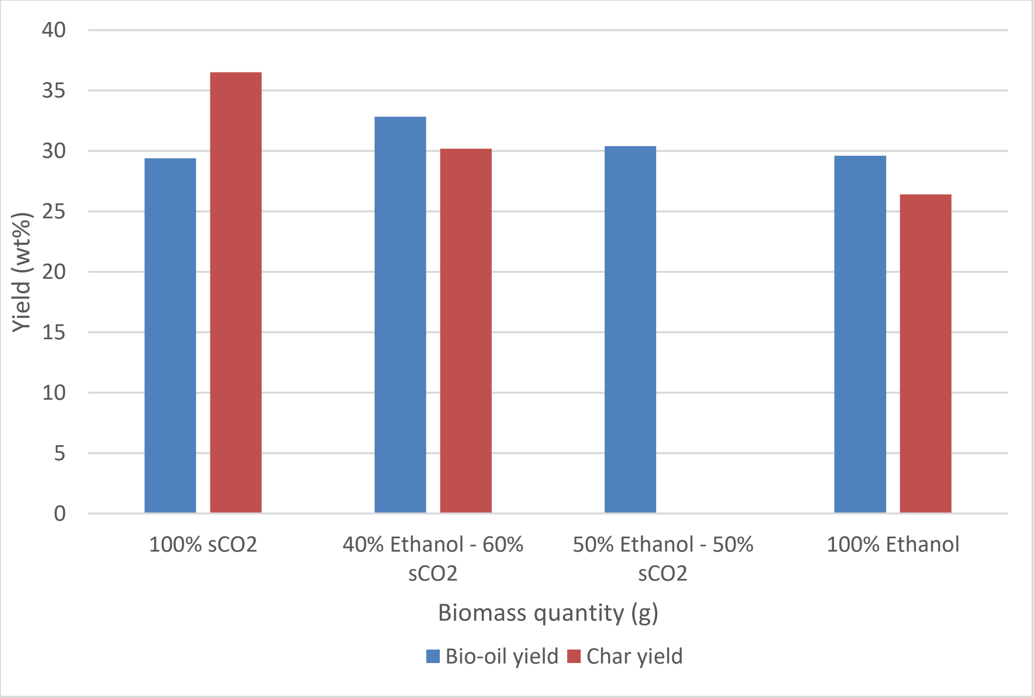
Once the two experiments planned for the development of this project had been carried out and the corresponding comparison with those previously carried out by the Combustion Laboratory of the University of Maryland had been made, the results were obtained, which are represented in both 'Graphic 1' and 'Graphic 2'.

Analyzing the first graph, it can be seen that the increase in the amount of biomass introduced into the reactor has caused a significant decrease in the yield of the bio-oil obtained. When analyzing the products obtained after the reaction, it could be seen that in the experiment where 13g of biomass were used, part of this material remained unreacted, possibly due to an excess load in the reactor. On the other hand, part of the catalyst was also found sedimented at the bottom of the reactor without reacting, which could also cause this decrease in yield.



Graphic 1: Effect of biomass quantity added to the reactor on the yield of bio-oil and char

Analyzing the second graph, it can be observed that the percentage yield of bio-oil obtained using 100% ethanol and 100% sCO2 solvent is very similar (29.6 and 29.4 respectively). On the other hand, the results show that the addition of co-solvent helps to improve the yield of the process, and furthermore, it can be observed that the approximate optimum value in terms of proportions is close to 40% ethanol and 60% sCO2. This corroborates the statements made in other scientific papers on the importance of the use of co-solvents for maximizing bio-oil yield.



Graphic 2: Effect of solvent/co-solvent ratio on the bio-oil and char yield

5. Conclusions

The study successfully demonstrated that the use of supercritical CO2 as a solvent for biomass liquefaction can become a viable method for bio-fuel production if resources continue to be devoted to its research and optimization. The main conclusions drawn are:

Feasibility and efficiency: Supercritical CO2 is an effective solvent for biomass liquefaction, capable of producing significant quantities of bio-oil. The process is efficient, especially when key parameters such as temperature, pressure, biomass loading, and the use of co-solvents and catalysts are optimized.

Economic feasibility: The economic analysis suggests that the lab-scale process cannot yet become competitive due to its high production cost. Therefore, further research resources are required to further optimize the process and reduce costs in order to make it commercially viable.

Environmental impact: The use of supercritical CO2, a relatively environmentally friendly solvent, reduces the overall environmental impact of the liquefaction process compared to traditional methods using more aggressive chemicals.

Optimization potential: The polynomial regression model developed in this study provides a valuable tool for predicting bio-oil yields as a function of various operational parameters, allowing for further optimization and scale-up of the process.

Recommendations for the future: Future research should focus on long-term performance and process stability, exploration of a wider variety of biomass feedstocks, and investigation of the potential for integration of this technology with existing biofuel production systems to improve sustainability and overall efficiency.

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Abbreviations

MSW	Municipal Solid Waste
CFP	Catalytic Fast Pyrolysis
HTL	Hydrothermal Liquefaction
SCF	Supercritical Fluid
VOC	Volatile Organic Compound
AP	Aqueous product
SR	Solid residue
sCO2	Supercritical CO2

Chapter 1. INTRODUCTION

1.1 BACKGROUND

Over the last few years, awareness of the need for carbon-neutral liquid fuels has grown significantly. By far, the main contributor of climate change is fossil fuels, by being responsible for more than 75% of greenhouse gas (GHG) emissions worldwide and about 90% of carbon dioxide emissions overall [1]. The effects of climate change are becoming more and more visible in our daily lives as greenhouse gas emissions are causing the earth to reach record temperatures, what leads into increased drought, loss of species, more health risk, and rising oceans among many other consequences.

Energy consumption can be divided into three main blocks; heat, power and transportation. Being the latter two the sectors that produce the greater amount of CO2 emissions because of combustion of fossil fuels [2].

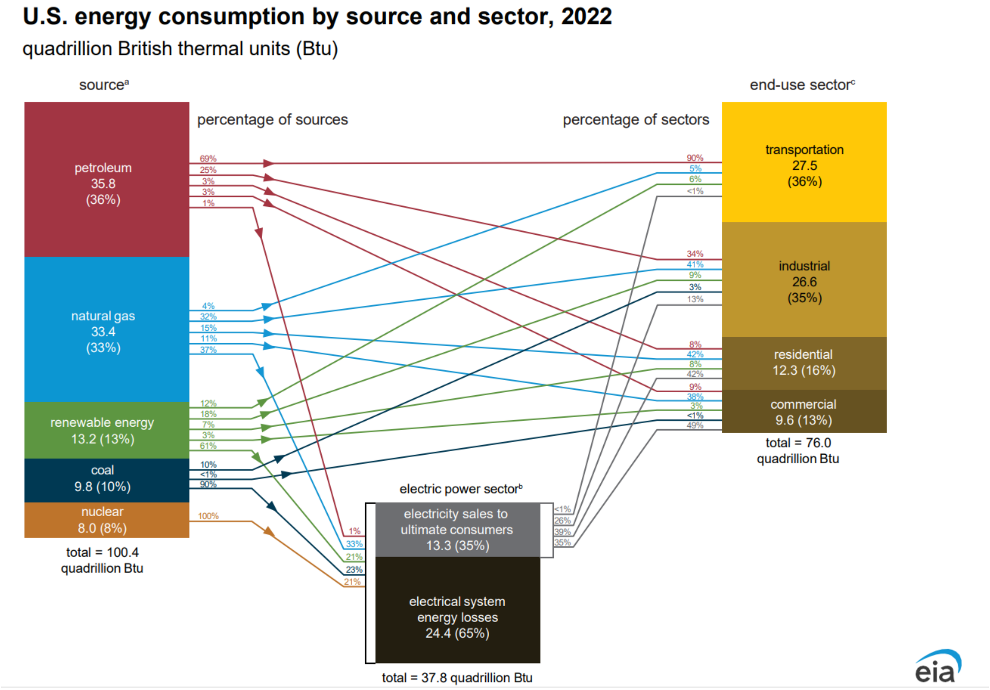


Figure 2: U.S. energy consumption by source and sector, 2022 [49]

While the electric power sector, despite the increase over the years in the electricity demand, has managed since 2000 to significantly reduce energy-related CO2 emissions through increased equipment efficiency and more carbon-free electricity (e.g., photovoltaic and continuous flow) (Figure 3), the transportation sector has continued to emit a similar amount of CO2 emissions over the years. Currently, there is only one viable zero-carbon energy pathway applicable to light-duty motor vehicles, as they are the only ones capable of adapting to the infrastructure that requires the use of electric batteries to reduce the need of combustion vehicles.

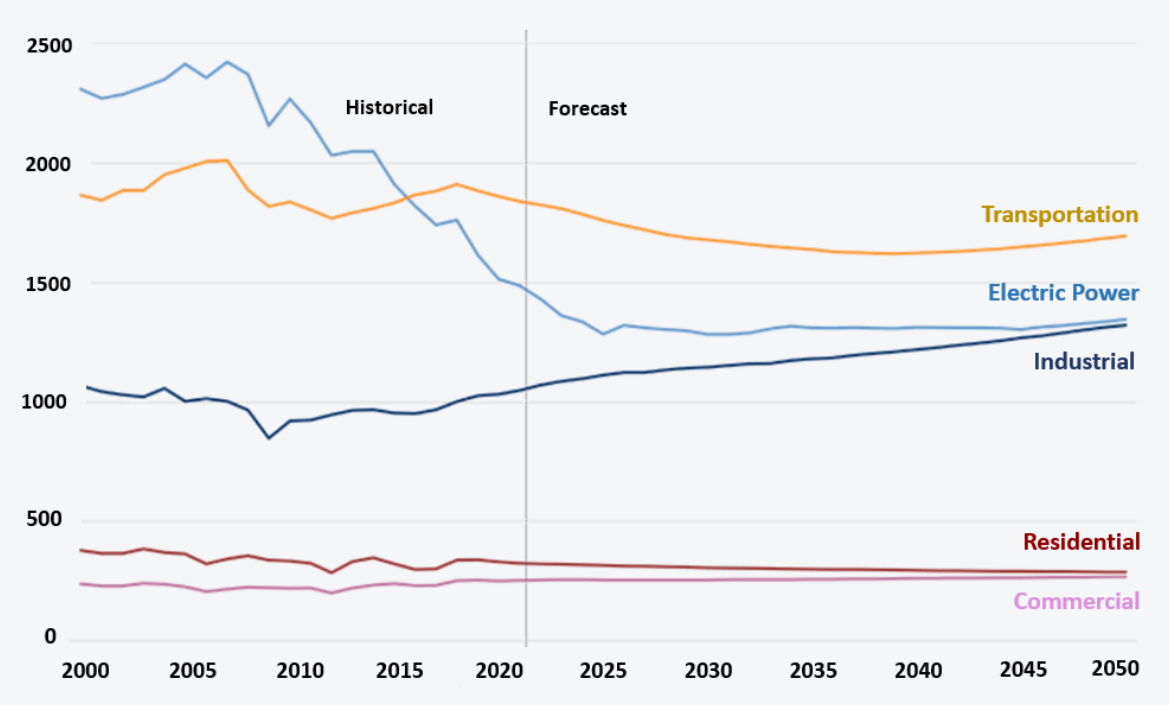


Figure 3: Energy-Related carbon dioxide emissions by sector (MMtCO2), 2000-2050 [3]

Therefore, a societal need arises to investigate new viable ways to produce transportation fuels from renewable sources, as they constitute a large fraction of global consumption, and their demand is expected to grow even more in the coming years due to population increase, industrial growth and massive urbanization. According to the Annual Energy Outlook 2023 the total energy consumption of the transportation sector by 2050 is expected to increase up to 30 quadrillion British thermal units (Figure 4).

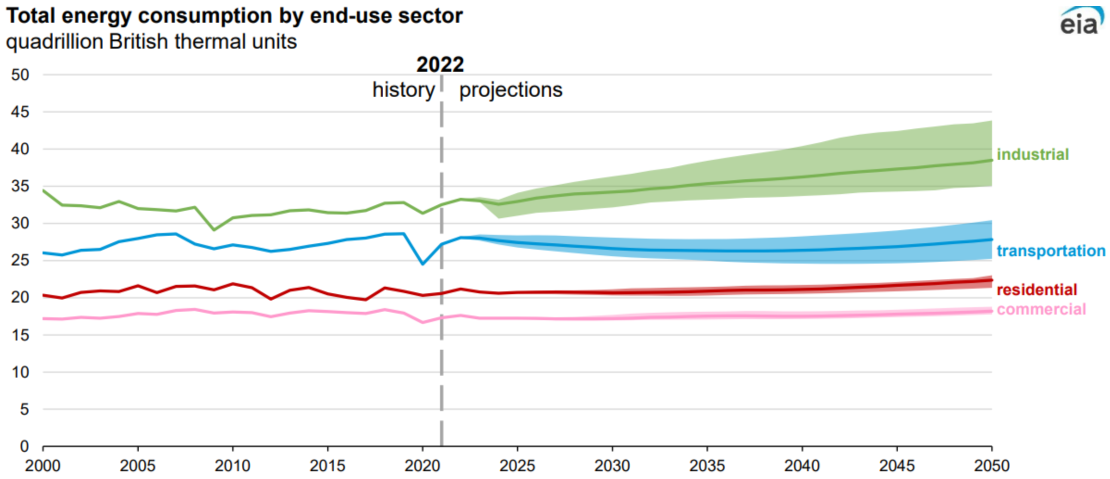


Figure 4: Total energy consumption by end-use sector [3]

Use of renewable energy has become essential in order to develop a long-term strategy to cope with the increase in demand in a sustainable way and reduce the dependence on fossil fuels. Among all the renewable sources, biomass has attracted increasing attention as it is one of the largest sources of energy on the planet, surpassed only by oil, coal and natural gas. In addition, it is also the only renewable carbon source that can be transformed via several processes into useful solid, liquid, and gaseous fuels [4]. The use of this resource for energy purposes not only contributes to reducing the environmental impact of fossil fuels and managing the growing demand for energy, but is also an effective way of managing organic waste [50]. Moreover, it can also be considered a promising option as the biofuels produced through the conversion of biomass do not require changing the existing internal combustion engines or the transportation infrastructure.

For all these reasons, in order to accelerate decarbonization in the transportation sector, it is crucial to advance in the research of the processes capable of converting biomass into biofuel.

1.2 OBJECTIVES

The main objective of this project is to study the liquefaction of biomass using supercritical carbon dioxide (sCO2) as a solvent to efficiently and feasibly produce bio-oil that can be used as biofuel in the transportation sector. To this end, in the course of the research, the following more specific objectives are intended to be satisfied:

1) Understand the impact of biomass liquefaction operating parameters on bio-oil yield;

2) Optimize bio-oil production by soft pine wood liquefaction using sCO2, optimize operating parameters, maximize bio-oil yield;

3) Evaluate the technical and economic feasibility of sCO2 as a solvent in the liquefaction process, discuss the effect of operating conditions;

1.3 MOTIVATION

Finding an alternative route to conventional fuels is increasingly necessary to reduce dependence on fossil fuels and cut the amount of greenhouse gases emitted by the transportation sector. Production of biofuels through thermochemical conversion of biomass seems to be a promising alternative, however, none of the existing processes (e.g. pyrolysis, gasification, hydrothermal liquefaction (HTL)) have yet been industrialized due to their high cost, low efficiency, or difficulty of scalability. Therefore, to solve these feasibility issues, this project focuses on the research and optimization of the sCO2 liquefaction of biomass.

Because the use of sCO2 in this process is relatively new, its research is in the early stages of investigation, and optimization of all its parameters is still necessary in order to maximize the yield and quality of the bio-oil obtained during biomass conversion. Successful development of this technique could have a major impact on the production of renewable fuels, and the promising results it has provided so far are a strong motivator for further research.

If through this process the bio-oil produced from the lignocellulosic biomass achieves an acceptable yield and the quality required to function as a transportation fuel, while being economically viable on a large scale, the full potential of biomass as a renewable energy source will be unlocked, thus taking a major step towards the decarbonization of this polluting sector. The potential offered by this energy source is crucial for the reduction of

GHG and progress toward a more sustainable future, being essential to dedicate resources and effort to this type of research.

1.4 METHODOLOGY

The methodology of this project is based on the Taguchi Method concept. This philosophy advocates that a robust design of experiments reduces the variation in the process. By developing a broad theoretical basis before starting with the design of the experimental part, the use of resources is reduced and the failed experiments that can be avoided with an exhaustive study of the existing literature are prevented.

Since the main purpose of this work is to investigate, develop, and evaluate the SCCO2 liquefaction of soft pinewood for the production of bio-oils, the research project is divided into four main phases.

First of all, the theoretical contextualization of the project is done, by studying the current situation of the existing thermochemical conversion methods and understanding the feasibility issues that need to be covered at the present time.

Then, the optimization of the operating parameters and the design of the experiments is carried out. Followed by the implementation of the laboratory-scale experiments.

Finally, the final phase consists of the evaluation, analysis, and discussion of the obtained results.

1.5 DELIMITATION

The optimization and development of the liquefaction process is limited to the study of the performance of soft pinewood.

The development of the polynomial regression model is a first step with a simple code and without including the full number of input parameters focusing on adding only data from experiments performed with water and without co-solvent or catalyst.

The reaction kinetics in the biomass liquefaction process will not be considered in this project.

1.6 DIFFICULTIES

One of the main limitations of this type of research is that the results vary considerably depending on the type of biomass used. This makes it difficult to compare the results and conclusions of existing research.

On the other hand, the use of SCO2 as a solvent is very recent and the information on it is very limited, which is why the theoretical study and experimental design will be largely based on results obtained through hydrothermal and solvothermal liquefaction processes.

1.7 STRUCTURE OF THE PROJECT

The structure of the project is as follows:

- Chapter 1: Introduction
- Chapter 2: Literature Review
- Chapter 3: Parameter Optimization
- Chapter 4: Liquefaction of soft pinewood in supercritical carbon dioxide
- Chapter 5: Conclusions and Recommendations

Chapter 1 (Introduction) introduces de general view of the project.

Chapter 2 (Literature review) presents a summary of articles and reviews relevant to understanding the current status of biomass liquefaction studies for bio-oil production, introducing also the necessary background information for the right comprehension of the project about biomass, thermochemical conversion technologies, and solvents.

Chapter 3 (Parameter optimization) collects all the parameters that affect the performance of bio-oil, studying their impact and trend through the compilation of data from different scientific articles. It also includes the design of a polynomial regression model for the prediction of bio-oil yield values in order to gain more control of the process.

Chapter 4 (Liquefaction of soft pinewood in supercritical carbon dioxide) includes an experimental and analytical analysis of the liquefaction process carried out in the laboratory, the results and their interpretation of the experiments carried out, and a brief economic analysis of the process of obtaining bio-oil through the liquefaction of biomass using supercritical CO2.

Chapter 5 (Conclusions and Recommendations) presents the final conclusions drawn after the completion of this master's thesis and includes some recommendations for future work along the same lines.

Chapter 2. LITERATURE REVIEW

2.1 BIOMASS

Biomass refers to any biological matter or residue obtained from living organisms [51], and it is considered the only renewable organic energy source in the form of carbon-containing substances that can be used as a potential alternative to fossil fuels. Therefore, this energy source is deemed inexpensive, clean, and environmentally friendly.

A distinction can be made between two different types of feedstocks: dry and wet.

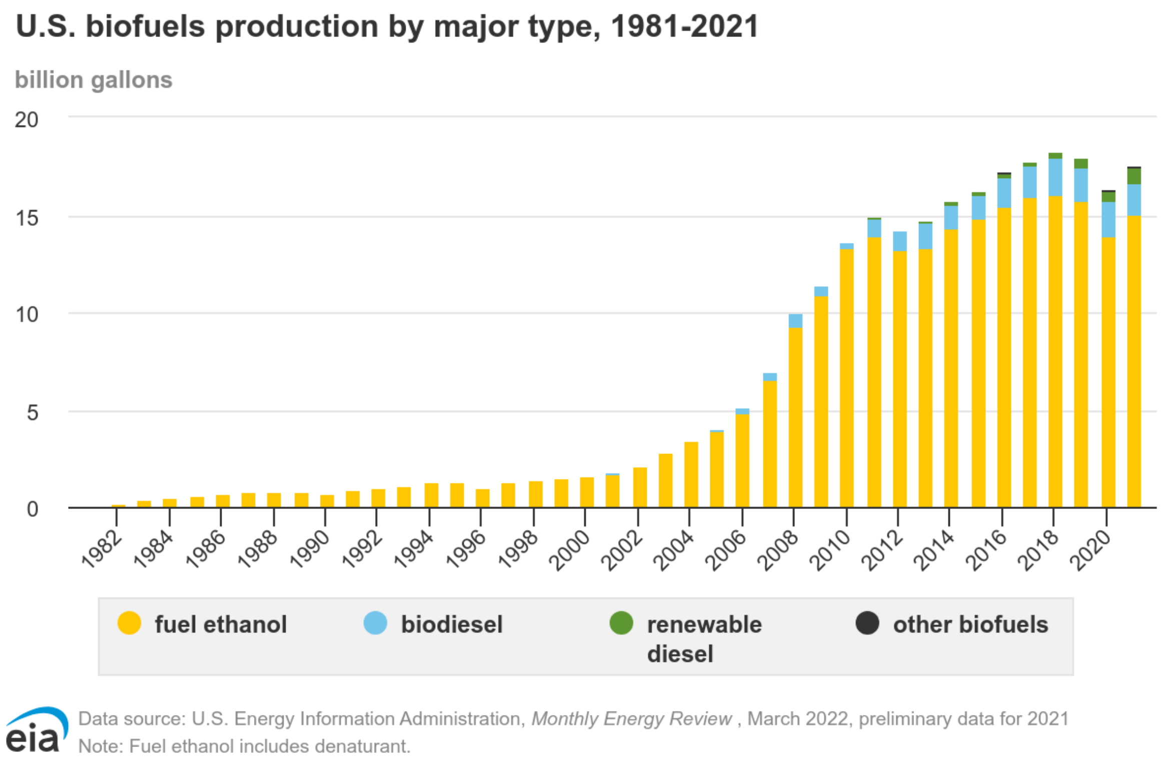
2.1.1 DRY BIOMASS

Dry biomass refers to lignocellulosic materials that have a low moisture content and are often derived from forestry byproducts, agricultural residues, and certain types of municipal solid waste [57].

2.1.1.1 Lignocellulosic

Currently, the most abundant biomass in the world is lignocellulose. According to statistics, 181.5 billion tons are produced annually, out of which only 8.2 billion tons are utilized for different purposes [52]. This natural resource is mainly generated by the sectors of agriculture, forestry, and industry, and its demand has been rising over the past years.

One of the main high-value-added products from lignocellulose biomass is biofuels. In 2021, 17.5 billion gallons of biofuels were produced in the United States (Figure 6). The low-grade and low-cost biomass included in lignocellulose makes it crucial to use it for obtaining renewable fuels, as this facilitates minimizing the final selling price.



Data source: U.S. Energy Information Administration, *Monthly Energy Review* , March 2022, preliminary data for 2021
Note: Fuel ethanol includes denaturant.

Figure 5: U.S. biofuels production by mayor type, 1981-2021 [56]

Lignocellulose (Figure 6a) is the most prevalent biopolymer in nature, responsible for forming the structural basis of the plant's cell walls [4]. It is mainly composed of two hydrocarbon polymers (cellulose, hemicellulose) and one phenolic polymer (lignin), constituting approximately 80% of its dry mass.

- **Cellulose**

Cellulose (Figure 6b) is the primary content of lignocellulose and the most abundant biodegradable polymer on Earth. It is a linear homopolymer of glucose with a crystalline structure composed of a β-1,4 glycosidic linkage of D-glucopyranose units represented by the chemical formula (C6H10O5)n. It has also a high molecular weight due to its substantial polymerization degree of the long polysaccharide chain (approximately 10.000) and its extensive hydrogen bonding and the linear arrangement of glucose molecules make it insoluble in water and most organic solvents [55]. Usually, cellulose constitutes around 40-50% of dry biomass [50].

- **Hemicellulose**

Hemicellulose (Figure 6d) is a low degree of amorphous heteropolysaccharide with a high degree of branching of a straight-chain skeleton, whose basic units are xylan and glucomannan. Typically, hemicellulose constitutes approximately 25-30% of dry mass. Along with cellulose, both polymers have a simple structure, which makes them less stable, facilitating their degradation and liquefaction.

- **Lignin**

Lignin (Figure 6c) is a highly branched, amorphous, and 3-D aromatic polymer composed of phenylpropane units that are linked primarily via ether bonds with hydroxyl and methoxy groups. Unlike the other two polymers, it has a more stable structure that makes it less likely to decay and liquefy to form biocrude. The solubility of lignin in water is very low, and its high thermal stability increases the temperature needed for breakdown. Lignin is mainly situated at the outer layers of the fibers and provides both structural rigidity and impermeability to water. In wood structure, lignin forms a barrier separating the carbohydrate fraction, surrounding the cellulose and hemicellulose fractions. And it usually constitutes 20-35% of biomass.

Each type of dry biomass has different percentages of these components, which affects the yield and composition of the final biofuel. Due to the previously mentioned properties of each polymer, it is known that feedstocks with lower lignin and higher ash content have higher conversion rates and biofuel yields.

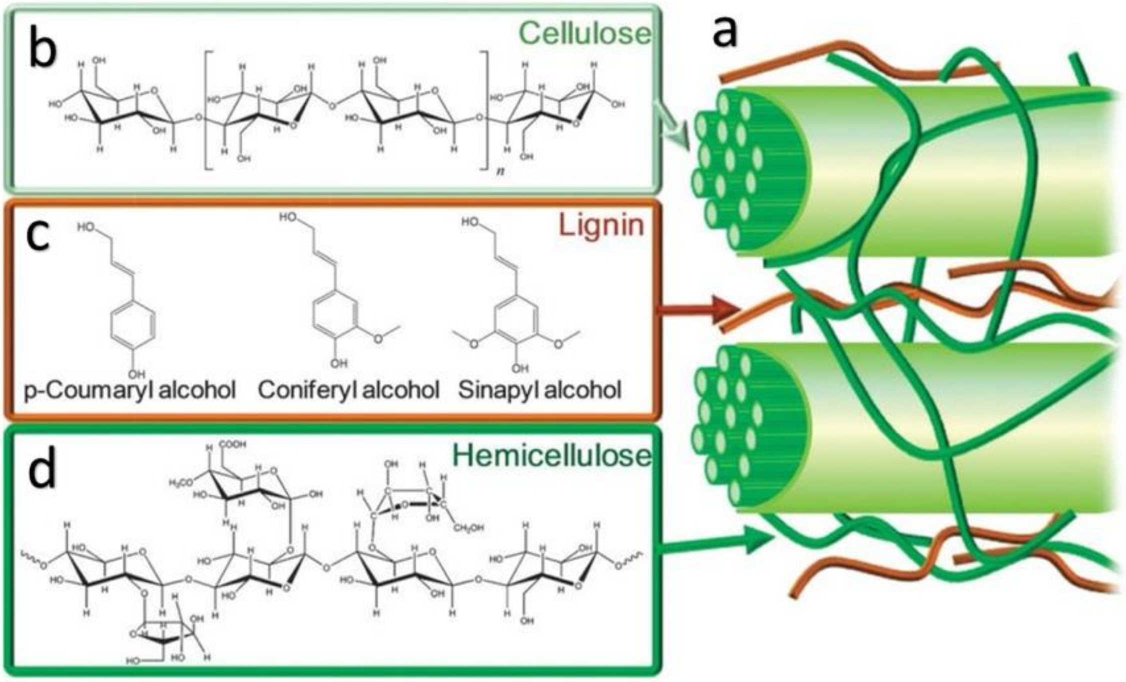


Figure 6: (a) Structure of plant cell wall; (b) Structure of cellulose; (c) Structure of lignin; (d) Structure of hemicellulose [53]

Table 1: Dry feedstocks summary with their elemental compositions and major components (%wt)

Feedstocks	**Components (wt% dry basis)**			**Elemental compositions (wt%)**					**Ref.**
	Cellulose	Hemicellulose	Lignin	C	H	O	N	S	
Pinewood	37	38	22	49.25	6.18	44.17	0.3	0.1	[75]
Red pine sawdust	42.6	29.5	25.2	47.4	6.7	45.9	0.3	0.3	[76]
Corn stover	26.10	29.05	25.32	40.8	6.53	44.8	0.15	0.7	[77]
Rice Husk	33.7	26.2	19.8	38.07	5.24	55.82	0.87	0.1	[78]
Coconut shell	34.1	28.3	26.4	47.14	6.08	46.71	0.06	0.01	
Pine	39.54	20.61	30.15	49.52	6.49	43.89	0.05	0.05	[79]
Pine wood chips	59.37	11.39	29.83	-	-	-	-	-	[80]
Aspen wood	47.14	19.64	22.11	50.39	6.19	43.23	0.19	-	[81]
Corn straw	30.81	25.25	16.76	44.57	5.53	33.7	0.93	0.1	[82]
Peanut straw	36.56	20.27	18.36	41.42	5.51	35.31	1.27	0.15	
Rice straw	46.33	31.09	22.05	41.34	5.33	34.29	1.12	0.14	

Soybean straw	42.39	22.05	18.93	45.99	6.07	39	1.38	0.11	
Beech wood	45.05	31.5	22.25	44.68	6.08	49.24	-	-	[84]
Natural hay	44.9	31.4	12.0	40.6	4.25	54.2	1	-	[85]
Oak wood	38.1	23	32	50.2	7	42.8	-	-	
Walnut shell	23.3	20.4	53.5	45.6	4.3	50.1	-	-	
Soybean straw	35.8	21.24	9.2	41.05	5.52	41.39	2.9	0.28	[86]

2.1.2 WET BIOMASS

Unlike dry biomass, wet biomass refers to organic matter with high water content from sources such as algae, sewage sludge, and food waste. It typically requires processing, like drying or dewatering, before it can be used for different applications including biofuel production or waste management [57].

2.1.2.1 Algae

Algae biomass refers to the organic materials derived from the photosynthetic microorganisms and equipped with chlorophyll found in aquatic environments such as oceans, lakes, and ponds.

Algae biomass can include a wide range of algae species, including microalgae (single-celled algae) and macroalgae (multi-cellular algae or seaweeds). Depending on the type of species the composition can vary significantly. In particular, the high lipid content of some microalgae species makes them great candidates for biofuel production, which is why it is possible to find extensive literature on the processing of this type of feedstock [61].

2.1.2.2 Sewage sludge

The organic material derived from wastewater treatment processes is also known as sewage sludge. It is composed of organic and inorganic matter, including human and animal waste, microorganisms, and suspended solids, among others and its composition consists mainly of proteins (40%), lipids (10-25%), and carbohydrates (14%) [60].

Sewage sludge can be converted through anaerobic digestion. This process breaks down organic matter in the absence of oxygen, producing biogas, a mixture of methane and carbon dioxide. Biogas can be directly used for energy generation or upgraded to biomethane. Additionally, emerging technologies like hydrothermal liquefaction are being explored for converting this type of biomass into bio-oil [68].

2.1.2.3 Food waste

This biomass consists of edible and inedible parts of food that are no longer suitable for human consumption, as well as food residues generated in food preparation and plate waste from kitchens, restaurants, and institutions.

According to the Food and Agriculture Organization of the United Nations (FAO), approximately one-third of all food produced for human consumption (1.3 billion tons) is lost or wasted worldwide each year [58], which is a serious social and environmental problem. Therefore, many measures try to fight against this food waste and propose efficient solutions for the recycling and management of unavoidable food waste. Bioenergy production using this type of biomass as feedstock is one of the most promising solutions due to its rich content of proteins, lipids, and carbohydrates. Through anaerobic digestion, biogas can be generated and through biochemical or thermochemical conversion processes biofuel can be obtained, helping to reduce environmental impacts and promoting the efficient use of resources [59].

Table 2: Wet feedstocks summary with their elemental compositions and major components (%wt)

Feedstocks	**Components (wt% dry basis)**			**Elemental compositions (wt%)**					**Ref.**
	Lipids	Proteins	Carbohydrates	C	H	O	N	S	
Algae species									
Chlorella	11.06	65.32	14.35	47.68	6.73	31.6	10.8	0.87	[86]
C. nivalis	-	-	-	39.94	7.08	44.93	6.64	1.42	[87]
N. gaditana	-	-	-	53.85	8.08	29.32	7.54	1.21	
Dunaliella T.	17.8	50.3	21.7	39	5.37	43.88	1.99	-	[88]
Spirulina P.	6	56.4	20.11	41.36	6.6	43.58	8.46	0.62	[78] [79]

G. gracilis	1.7	13.7	28.6	36.75	5.86	17.51	2.88	1.99	[89]
C. glomerata	2.4	26.3	34.7	31.33	4.99	30.67	4.9	1.99	[81]
Nannochloropsis	45.63	6.20	-	48.41	9.01	33.9	7.38	1.29	[90]
Sargassum sp.	9.95	0.8	-	28.5	2.78	65.4	2.13	1.19	
D. tertiolecta	61.32	2.87	21.69	29	5.37	53.02	1.99	-	[91]
Ulva fasciata	14.3	1.83	46.73	-	-	-	-	-	[92]
Enteromorpha	7.9	5.6	39.9	-	-	-	-	-	[83]
Sargassum	10.75	2.03	30.30	-	-	-	-	-	
Sewage sludge									
Primary sludge	21.2	23.4	29.8	47.81	6.93	40.45	4.81	-	[93]
Municipal s.	5.8	47	47.2	33.2	5.4	28.2	5.4	-	
Paper mill s.	11.8	46.7	41.5	31.5	4.9	29.1	5.3	-	
Agricultural s.	38.5	28.4	43.1	16.3	3	6.2	5.1	-	
Municipal p. s.	21.2	23.4	29.8	36.86	5.34	31.19	3.71	-	[95]
Food waste									
Food waste	19.6	2.9	77.5	-	-	-	-	-	[96]
Pomelo peel	0.7	0.04	-	39.37	5.08	52.72	2.83	-	[97]
Banana peel	5.13	-	45,73	40.24	6.14	52.22	1.3	0.09	[98]
Orange peel	6.5	-	59,4	38.91	6.2	53.64	0.64	0.11	
Citrus peel	-	-	35,8	38.51	6.2	54.55	0.64	0.1	
Lemon peel	7	-	19,5	40.33	5.96	52.25	1.27	0.19	
Jack fruit peel	-	-	-	40.04	5.86	53.08	0.9	0.12	

2.1.3 MUNICIPAL SOLID WASTE AND PLASTIC WASTES

Municipal solid waste (MSW) and plastic waste biomass contain organic and non-organic components that can be converted into valuable products through different technologies. However, they also represent a significant challenge to environmental sustainability and public health, not only for their complex composition but also because of the large amount generated year after year. According to the World Bank, in 2016 the global generation of MSW exceeded 2 billion metric tons [62], and for plastic waste, the journal Science Advances estimated in 2019 that around 400 million metric tons were generated [63].

That is why efforts to improve waste management, promote recycling and circular economy initiatives, and reduce waste generation are essential for addressing the environmental and social impacts of MSW and plastic waste on a global scale, and achieving an efficient way of converting this type of biomass into a useful bioenergy through different processes is so important and needs to be investigated.

2.1.3.1 Municipal solid waste

MSW consists of food wastes, metals, plastics, rubber, paper and paperboard, glass, textile, and yard trimmings usually generated by industries, institutions, and houses. Its composition varies significantly by region and country due to different factors such as economic development, waste management practices, and culture among many others. In China, organic materials represent the largest fractions with approximately 50-60% of the total weight of waste, while in the United States, the most predominant fraction is composed of paper and cardboard [64].

The use of this type of biomass as a renewable energy resource instead of conventional fossil fuels could turn out to be a powerful alternative that would help both greenhouse gas reduction and waste management, as these unused supplies would be reconverted into convenient complementary energy systems using thermal conversion processes. However, the high content of ash and moisture and the low heating value of this type of biomass can be a major challenge to overcome in order to achieve the best possible performance in the conversion [65].

2.1.3.2 Plastic waste

Plastic waste also constitutes a major problem for the environment due to two main factors. As mentioned above, a large amount of plastic waste is generated annually. This added to its slow decomposition rate leads to significant environmental and ecological damage.

Traditional waste management strategies such as landfills and incineration are reaching their limits, encouraging the investigation of alternative solutions. One promising approach, as with MSW, is to use this residue as a source of biomass for biofuel production.

Plastic waste, with its high energy density due to its carbon-rich structure, presents itself as an attractive feedstock for biofuel production. Unlike fossil fuels, plastic waste represents a renewable source of carbon for biofuel synthesis. This approach not only offers a potential solution to manage this growing waste stream but also contributes to the development of renewable energy sources [66].

Conversion technologies like pyrolysis and gasification can break down plastic waste molecules into usable fuels like syngas, diesel, or gasoline. However, only dry biomass can be used in these conversion methods and the rest of the global plastic waste mixes with wet waste usually becomes part of MSW [57].

However, there are still many challenges to overcome to make the use of plastic waste as biomass viable. Firstly, the diversity of plastic types requires efficient classification and pre-processing to ensure compatibility with conversion technologies. Optimizing these processes to maximize biofuel yield and minimize by-product formation is essential for economic viability. Also, an evaluation of the environmental footprint of these conversion processes is crucial to ensure that they are truly sustainable compared to traditional waste management methods. But above all, the biggest challenge lies in the development of cost-effective conversion technologies and infrastructures for large-scale production of biofuels from plastic waste.

2.2 *ACTUAL THERMOCHEMICAL CONVERSION METHODS*

Currently, the most investigated and used thermochemical means are pyrolysis, gasification, and hydrothermal liquefaction. Through them, crude oil is obtained from biomass. This valuable by-product is a dark, viscous liquid similar to conventional petroleum. Biocrude offers an important greener alternative in various sectors, such as transportation, as it can be treated to obtain other even more valuable products, like biofuel, which also makes it a potential renewable resource capable of reducing greenhouse gas emissions and reducing dependence on fossil fuels.

These methods rely on heat, with or without the presence of oxygen, to break down the complex structure of biomass into smaller molecules. The decomposition process that the biomass goes through to obtain the crude oil in a simplified way is as follows.

First, **depolymerization** takes place. As the temperature rises, the long-chain polymers of cellulose, hemicellulose, and lignin begin to break down into smaller molecules like sugars, anhydrosugars, phenolics, and organic acids. Then, these smaller molecules further undergo **fragmentation reactions**, producing even smaller molecules like water, carbon dioxide, and lighter hydrocarbons. Afterward, **secondary reactions**, such as condensation or cracking, occur in the smaller molecules. Finally, it takes place the **char formation**. This by-product is primarily composed of condensed aromatic structures from lignin [69].

Once decomposition is complete, the different components of the biomass have been transformed into more valuable intermediate products such as bio-oil through pyrolysis or synthesis gas through gasification.

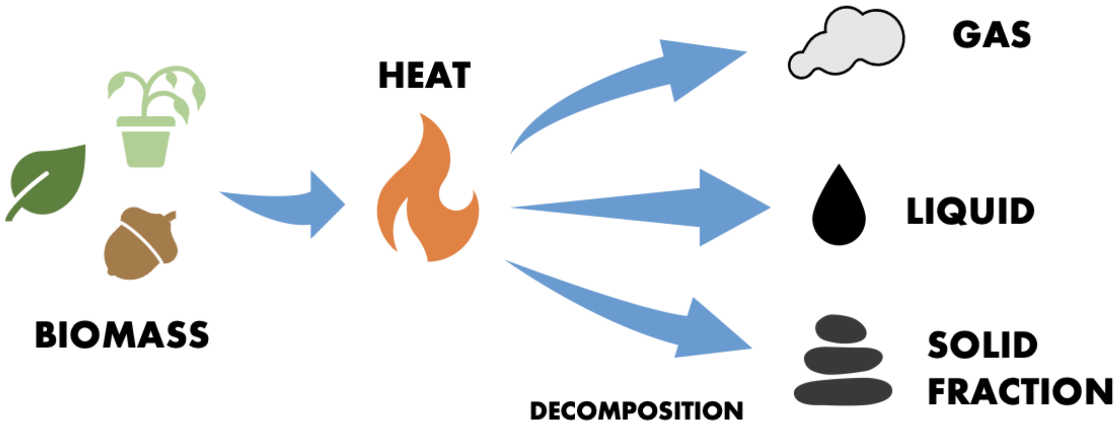


Figure 7: Biomass transformation process

2.2.1 PYROLYSIS

Pyrolysis is a technology where organic compounds are discomposed through the application of heat in the absence of oxygen. In this process, biomass is broken down into biochar, bio-oil, and biogas products, and depending on the operating conditions applied, pyrolysis can be classified into different groups [70].

Nowadays is the most commonly used process for transforming biomass [6] and its research is very extensive. In order to optimize it, different models have been developed simulating the decomposition of the biomass with the aim of studying the reactions that occur in each different component [7]. Numerous studies reveal that to maximize the yield of bio-oil (up to 75wt%) it is necessary to operate at a high heating rate and short residence time, thus occurring fast pyrolysis [9].

Table 3: Pyrolysis processes distinguished based on process conditions [71]

Type	*Temp (ºC)*	*Vapor residence time*	*Char yield (%wt)*	*Liquid yield (%wt)*	*Gas yield (%wt)*
Slow pyrolysis	300-500	5-30 min	35 %	30 %	35 %
Intermediate pyrolysis	500	10-20 s	20 %	50 %	30 %
Fast pyrolysis	500-600	1 s	12 %	75 %	13 %
Torrefaction (partial pyrolysis)	<300	minutes	80 %	5 %	15 %

2.2.1.1 Fast Pyrolysis

Fast pyrolysis stands out for its rapid decomposition of organic matter under a hydrogen atmosphere. In it, rates in the range of 100°C/s are applied to a final temperature of 500-600°C in the reactor [71]. When the biomass is pyrolyzed, the char and pyrolytic vapors are separated. These pyrolytic vapors are cooled down in order to separate the bio-oil from the rest of the gases produced (e.g., CO, CO2, CH4). The main problem of the bio-oil obtained after these first steps is the high level of oxygen content (35-40 wt%) due to the oxygenated polymers in biomass, which leads to a low high heating value (HHV) of approximately 17 MJ/kg. This value is also decreased by the high-water content in the oil (around 25 wt%), which also causes ignition delay. Moreover, its acidity is very high (TAN 100-200), being therefore highly corrosive and immiscible with conventional hydrocarbon fuels. Also, this bio-oil obtained is highly unstable because of the reactive components in it, which causes polymerization over time, thus increasing the viscosity, a process also known as aging [10].

All these unfavorable properties decrease the fast pyrolysis oil demand. Several studies have shown that the oil must be upgraded to compatible transportation fuels by removing oxygen carbons through hydrotreating [11]. This final step consists of re-evaporating the oil at 310-375°C, at high pressure (100-170 bar) and low space velocities (0.1-0.2 LHSV) in the presence of H2 and a sulfide CoMo or NiMo catalyst supported on alumina. This process is extremely critical, expensive, and slow but is essential for the usability of bio-oil [13].

2.2.1.2 Catalytic Fast Pyrolysis

Studies have shown that performing a catalytic fast pyrolysis (CPP) to convert biomass improves the quality of the pyrolytic vapor obtained. This process consists of conducting fast pyrolysis but in the presence of a catalyst, usually based on zeolite or zeolite with noble metal. Depending on when the catalyst is incorporated, there are two types of catalytic pyrolysis: in situ and ex-situ.

In in-situ CFP the catalyst is mixed with the biomass into the pyrolysis reactor. Also, H2 is added simultaneously to perform pyrolysis and deoxygenation at the same time. Dehydration and decarboxylation reactions take place in the reactor to upgrade the pyrolytic gases therefore increasing the bio-oil yield and quality. This method simplifies the reactor needs and avoids the hot-vapor filtration; however, a catalyst with resilience to pyrolysis conditions and ash is needed.

In ex-situ CFP, the catalyst is added only to the pyrolytic vapors in a catalytic deoxygenation reactor after the pyrolysis has been performed and before condensation. As in the in-situ method, H2 is added along with the catalyst for deoxygenation to take place.

Choosing the correct type of catalyst increases the process efficiency by reducing the pyrolysis temperature, enhancing the selectivity of products, improving the quality, and boosting product yield. It has also been found that by increasing the catalytic activity and catalyst mass percentage it also significantly increases deoxygenation, improving then the bio-oil quality in terms of oxygen content. However, only 20-30% of the carbon present in the biomass is transferred to the liquid product, having a significant cost on the bio-oil yield [14].

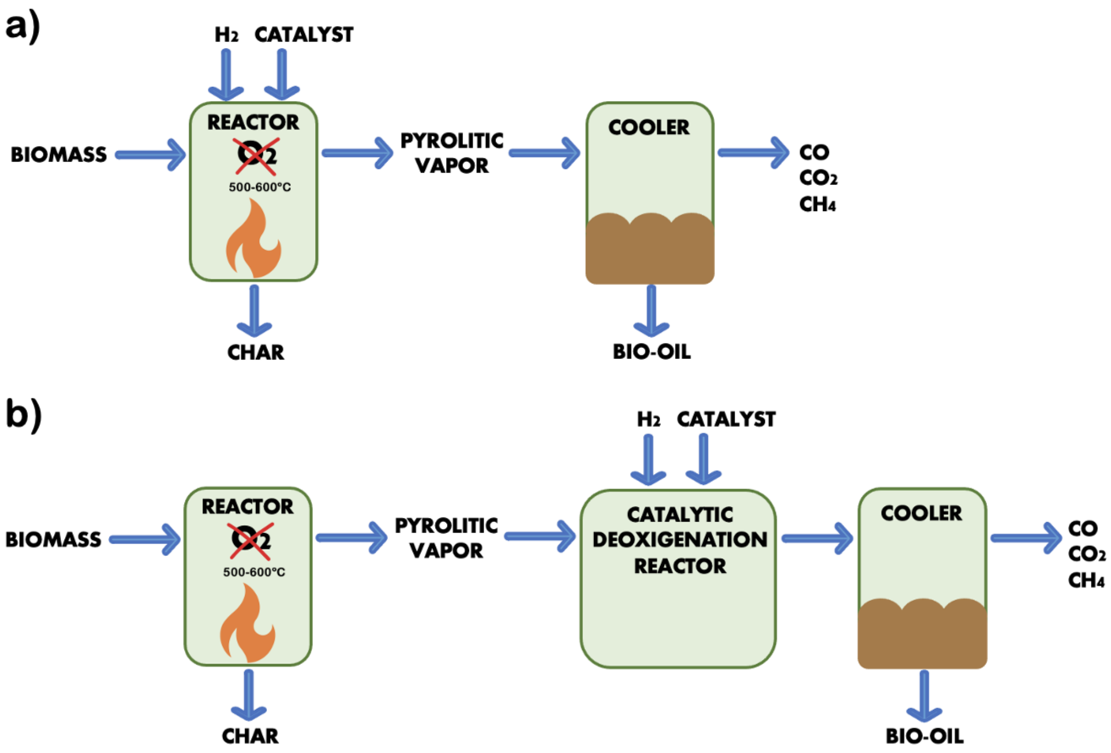


Figure 8: (a) In-situ catalytic fast pyrolysis process; (b) Ex-situ catalytic fast pyrolysis process

2.2.1.3 Hydro pyrolysis

Another process called hydro-pyrolysis is also being developed. In this case, the reaction occurs at 14-34 bars instead of at atmospheric pressures, being the organic matter decomposed in the presence of H2 under high heating rates (500°C/min).

Recent studies show that this thermochemical means is a promising technology for the conversion of biomass into liquid fuels. In the beginning, the research around this method was done for coal treatment [15], but then its feasibility and efficiency to produce hydrocarbons from biomass began to be investigated [16]. The main objective of using pyrolysis under hydrogen pressure is to produce bio-oils with a much lower oxygen content [18]. By this process liquid product with less than 1% oxygen is obtained, and in addition, its total acid number is less than 2, thus achieving better results than fast pyrolysis and CFP [19]. However, this process is still under development and presents some issues such as the large quantity of coke formation, which produces deactivation of the catalyst and clogs the reactor, which implies a higher cost required for catalyst regeneration [21]. Additionally, it also requires extra capital development that is not currently available as it is being developed separately from the existing infrastructure used in fossil fuel refineries [5].

2.2.2 GASIFICATION

Another well-known process is gasification, which has a history extending more than 300 years. To achieve commercialization of the end-products created during biomass transformation, this technology has been extensively researched ever since its first recorded inquiry in 1659 [22].

Gasification takes place when oxygen, air, steam, carbon dioxide, or a combination of these (gasifying agents) come into contact with biomass feedstock at relatively high temperatures and with limited oxidation. This causes a sequence of chemical processes that transform the biomass feedstock into environmentally benign fuels (syngas), chemicals, and char. Several complicated processes, which frequently overlap depending on the gasifier, are involved in the gasification of biomass. These phases are known as reduction, oxidation, pyrolysis, and drying [72]. Through this method conversion efficiencies of over 50% can be achieved, being considered the most effective means of converting lignocellulosic biomass into gas-based energy [73]. The syngas produced has a high heating value and can also be used as an intermediate product for biofuel production [23].

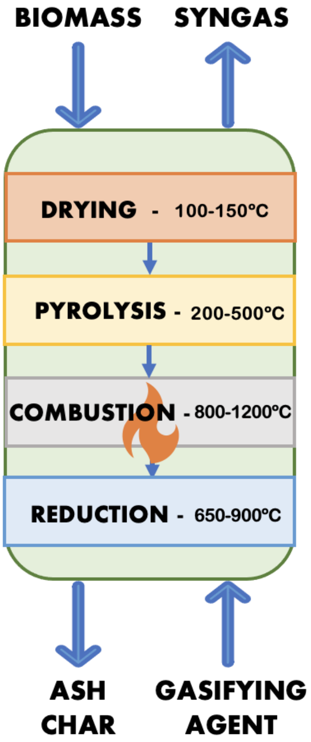


Figure 9: Gasification stages [72]

As in all other processes, the operating parameters, such as temperature or feedstock type, are highly related to the yield and quality of the gas product obtained. According to the existing literature, the yield of syngas as well as the energy output increases by operating at higher temperatures [24]. The use of catalysts during gasification has also been shown to increase significantly syngas production [22], focusing part of the research efforts in this specific direction [26]. Another important pathway being investigated is the use of steam as a gasifying agent. The literature of the last few years shows that the use of this gas produces enhanced hydrogen-rich gas [29]. As a result, it is possible through this process to obtain high-quality syngas, which makes it a promising intermediate product for biofuel production. The most researched way to date is through the Fischer-Tropsch process [31], however, other methods are currently being developed, such as the production of biofuel through ethanol produced from the fermentation of syngas, achieving an improved control of the final fuel range [33].

Therefore, gasification could be a good way to produce energy (electricity generation and biofuel) from renewable sources, but more research efforts are still needed to address the problems that make this technology not yet viable on a large scale. As with pyrolysis, the flexibility of feedstock is very limited. The need to operate at very high temperatures means that biomass with a high moisture and ash content leads to incomplete conversions, corrosion in the reactor, and excessive tarring [5]. This precludes the use of low-grade biomass such as wet agricultural residues, which makes the economic profitability of this process highly dependent on the feedstock price, ranging according to the type of biomass, location, and market conditions [34]. On the other hand, the infrastructural difficulties involved in cleaning syngas of pollutants or recycling the catalyst make system integration the critical point that currently prevents this process from being used on a large scale [5].

2.2.3 HYDROTHERMAL LIQUEFACTION

In response to the problem of feedstock flexibility, **hydrothermal liquefaction (HTL)** appears as a solution. Unlike the previous thermochemical conversion processes, this one stands out for its ability to convert wet biomass into bio-crude oil, which makes it a much more efficient and versatile technology. Not having to remove moisture from the feedstock considerably reduces the energy required, also reducing the economic return of fuel production [35].

This biomass conversion method takes place in the presence of water at temperatures between 250-374 ºC and pressures from 2 to 25 MPa and it has also been tested successfully with different types of feedstocks [74]. However, the biocrude obtained through HTL still has a high oxygen content (10-20%) even though it is lower than the amount present in the biocrude produced through CFP or fast pyrolysis. This results in a more stable liquid product with a higher energy density.

The use of catalysts is not necessary, however, recent studies show that **catalytic HTL** achieves better performance and increases the bio-crude yield, as the hydrodeoxygenation reaction is enlarged and solid waste generation is reduced [36]. Also, the temperature and pressure needed for the conversion can be decreased by choosing the correct type and concentration of catalyst, lowering the total cost of the process [38]. The yield of the bio-oil obtained from HTL usually varies between 10 and 60 wt% [35] and is strongly dependent on the operating parameters. According to the available literature, increasing the amount of solvent concerning the biomass used increases considerably this yield, but also increases the cost of processing the wastewater after the reaction [39]. In the search for ways to treat this water, research has been carried out on the design of a recycling circuit where the wastewater is added into the inlet of the process. However, this alternative is only suitable for dry feedstock as for wet biomass the biocrude yield is affected negatively. Supercritical gasification has been also considered as a solution, but the high pressure required makes it unfeasible as the investment cost of HTL units rises considerably [35]. Other pathways such as synergistically treating aqueous stream with activated carbon produced from HTL char have also been explored, but their viability is still questionable as there is not enough information [5]. Therefore, the water treatment process is one of the most important issues this process suffers and that is why it still needs to be improved so that HTL can be considered viable and integrable.

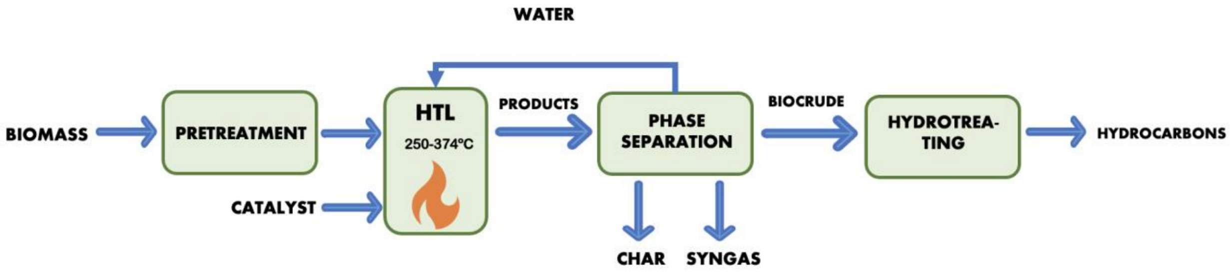


Figure 10: Hydrothermal Liquefaction process

2.3 LIQUEFACTION

In an attempt to tackle all these previous limitations, recent research is trying to open a pathway through the **liquefaction of biomass in presence of organic solvents, supercritical fluids, or ionic solvents** [40,41]. A crucial role in the performance and economic viability of the process is played by the solvent. Until now, water has been the most researched compound (HTL) because it is non-polluting, cheap, and occurs naturally as a component of biomass. However, apart from the issues associated with its treatment after the liquefaction, its properties as a solvent are also limited, resulting in poorer biocrude yields than when the conversion is performed in the presence of other solvents. Wang et al. [42] reported that yields of 29.3%, 27.9%, and 30.8% of bio-oil were achieved when supercritical CO2 (sCO2), acetone, and ethanol were used respectively, while only a 17.3% yield was produced with water. Also, Liu and Zang [75] stated that he use of ethanol, acetone and water as solvents for pine wood liquefaction resulted in bio-oil yields of 26.5%, 20.0%, and 18.6% respectively. This may be due to the fact that lignin, one of the main compounds present in lignocellulosic biomass, is poorly soluble in water owing to its hydrophobic nature and that a fraction of bio-oil was dissolved in the aqueous phase [43]. Also, the lower dielectric constant of organic solvents helps in the dissolution and stabilization of reaction intermediates, and aids in the reactions of alkylation and esterification between solvents and intermediate, enhancing the bio-oil yield [44].

Literature also demonstrates that the use co-solvents during liquefaction helps enhance the bio-oil yield. Cui et al. [99] reported that the presence of a co-solvent solution composed of 50wt% methanol and 50wt% water in the liquefaction of pinecone kraft raised the bio-oil yield to 77.8% in comparison with the 19.2% achieved with a single solution of water or the 69.6% reached with a 100wt% ethanol solution.

In the last years, sCO2 has attracted considerable attention as a powerful solvent due to its unique properties as a supercritical fluid (SCF). When a substance is taken above its supercritical temperature and pressure the phase transition between vapor-liquid disappears, existing a unique homogeneous phase condition in which properties lie between gas and fluid [45]. SCFs have a solvent power similar to liquids, but also a mass transfer of solutes comparable to gases due to their low viscosity and high diffusivity, which makes them excellent solvents.

Injecting sCO2 as solvent into the reactor along with the feedstock for liquefaction shows multiple advantages. Adding a nonpolar solvent increases the solubility of the small nonpolar molecules. Also, the extractability of the biocrude from the by-products is improved and the contaminated water that needs to be processed is minimized, which was one of the main issues that HTL presented. It is also known that with sCO2 the biocrude yield is increased and the process is more energy efficient [42]. The literature available using this solvent is limited but its viability can rely on the literature available for HTL [47,48]. Despite its drawbacks, HTL's successful development for some feedstocks raises the possibility of a sCO2 liquefaction approach. However, there is still a lot of research to be done in this direction so that the scalability and economic viability can be tested.

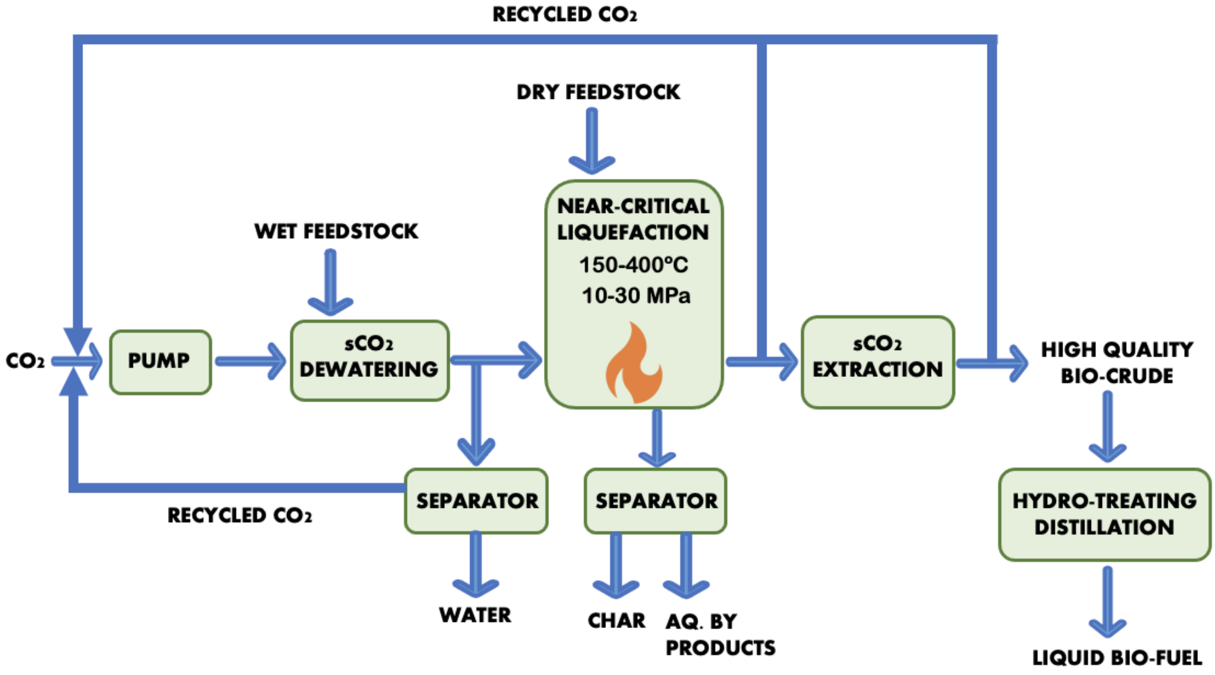


Figure 11: Supercritical CO2 liquefaction process

2.4 SOLVENTS

As seen above, solvents play a fundamental role in the conversion of biomass into biocrude. Depending on the type used, better or worse performances can be obtained without changing any of the other parameters. Achieving better or worse solubility will depend not only on the solvent but also on the composition of the biomass. The different components of the biomass react differently to the same type of solvent, which is why it is crucial to know the type of feedstock that is going to be used in the process as well as the characteristics of each solvent.

2.4.1 WATER

Water is the most studied solvent for biomass conversion to date. Its abundance, low cost, and non-toxicity make it an attractive candidate. Under ambient conditions, water behaves as a polar solvent with good solubility towards polar compounds, like hemicellulose, and salts. However, when it comes to non-polar compounds and gases such as hydrogen or nitrogen, the dissolving capacity of water worsens considerably [100].

As the temperature of this solvent increases, its density decreases, and consequently, the dielectric constant also falls, which in turn decreases its polarity. When water reaches supercritical conditions (550ºC, 20MPa) it becomes a good nonpolar organic solvent, although its molecules are still polar [102].

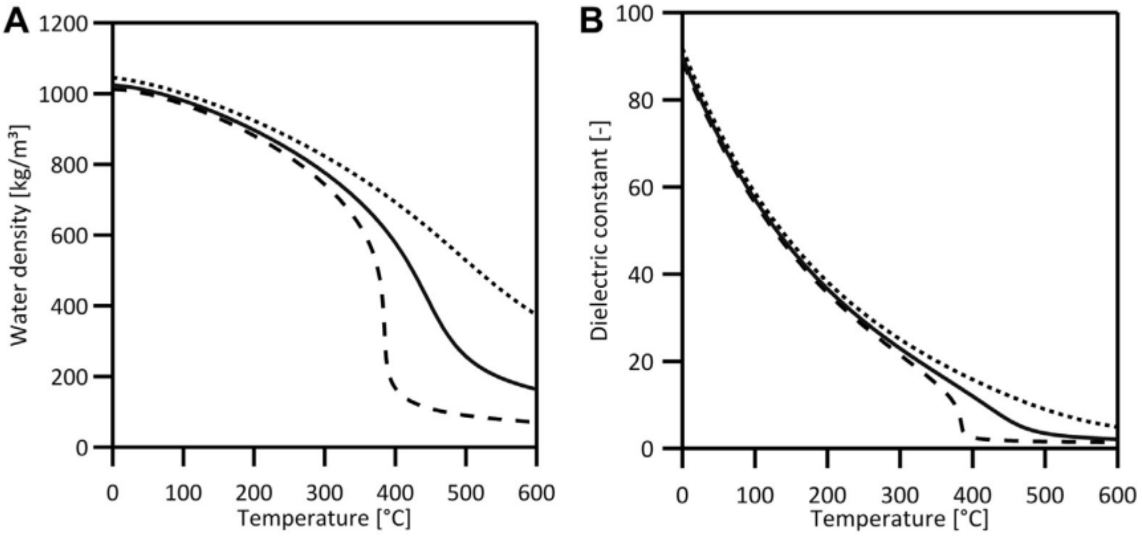


Figure 12: Properties of water as a function of temperature. (A) Density; (B) Dielectric constant [102]

One of the disadvantages of water is that it favors the reactions that produce oxygenated bio-oil, which makes upgrading necessary to achieve better stability and quality of the final product.

Even though its use as a single solvent shows many limitations, its role as a co-solvent does present a much more promising future. Its natural presence in biomass allows this resource to be used without any additional cost and also avoids the need for energy-drying pre-treatment.

2.4.2 ORGANIC SOLVENTS

ACETONE

One of the major advantages of acetone is its ability to dissolve both polar and non-polar molecules. This feature results in the achievement of higher bio-oil yields in comparison with other solvents such as water.

However, one of the main drawbacks of acetone (C_3H_6O) is its low flash point (-18 ºC), which makes it very susceptible to ignition and raises concerns about its safe use. Also, the fact that it is a volatile organic compound (VOC) contributes to solvent losses due to its ability to evaporate at ambient temperature. This also means that it presents risks to both human health and the environment, especially if the level of exposure is very high, and therefore the safety measures and precautions employed must be more stringent [103].

METHANOL

Methanol (CH_3OH), the simplest alcohol of the organic solvent group, is a polar organic solvent capable of dissolving the high molecular weight products of cellulose, hemicellulose, and lignin [104]. Its low boiling point facilitates its recovery, which makes it easily recyclable through distillation. It has also a moderate dielectric constant (32.6 at 20ºC), which indicates its polarity, and facilitates its penetration into the biomass for breakdown and extraction of the valuable components.

However, certain considerations must be taken into account regarding the use of this solvent. Like acetone, it is a flammable VOC with a flash point of 11°C, requiring extra precautions during storage and handling, as well as increasing the amount of solvent lost after each cycle. Its environmental impact must also be considered, as its production involves natural gas reforming, which has environmental implications [107].

Nevertheless, the literature corroborates that the use of methanol in biomass transformation helps to enhance the conversion rate and the bio-oil yield. Fu et al. [106] reported a maximum conversion rate of 95.2% in the supercritical methanol liquefaction of polypropylene.

ETHANOL

Ethanol (C_2H_5OH) has similar solvent characteristics to methanol. Its ability to dissolve a wide range of organic compounds, as well as its relatively low toxicity, and its compatibility with many different types of biomass make it a preferred solvent for biofuel production.

Literature has shown that ethanol can achieve better bio-oil yields than other type of organic solvents. Wang et al. [105] demonstrated that in the liquefaction of cellulose, a maximum of 51.42% of bio-oil yield was achieved with the use of ethanol as solvent meanwhile 23.63% and 42.97% were obtained with methanol and acetones respectively.

2.4.3 CO2

Carbon dioxide stands for being considered a green solvent with many positive impacts. This compound is inert, non-flammable, non-toxic, and economical [46]. It can be regarded as a powerful alternative to replace other cancerogenic and environmentally hazardous solvents such as CCl4, benzene, and chlorofluorocarbons. Another interesting advantage is that the CO2 used can be obtained from other industrial processes and can also be recycled, thus providing a new use for this compound without generating any new greenhouse gases, offering a way of recovering industrial emissions before releasing the CO2 into the environment.

SUPERCRITICAL CO2

The use of this solvent in the supercritical state as a liquefaction solvent is very interesting. When temperature and pressure reach the critical point (304.128K, 73.773 bar), sCO2 can adopt properties midway between a gas and a fluid, which helps to effectively penetrate the biomass matrices. Also, its density and viscosity are easy to adjust by controlling the temperature and the pressure, allowing the solvent properties to be adapted to the specific characteristics of the biomass [115]. It also stands out for its moderate critical point compared to other conventional solvents which makes the processing of sCO2 more energy efficient [114].

Although research on sCO2 applied to lignocellulosic material is not very extensive, the literature on bio-oil extraction from microalgae is much wider. Andrich et al. [120] reported that sCO2 and n-hexane showed comparable values of yield, however, the supercritical fluid extraction was much faster. sCO2 achieved a 90% extraction of the extractable oil after 15 minutes, while n-hexane managed to obtain the same yield but with a time extraction of 6 hours. Its high efficiency as an extractor suggests that using sCO2 as a solvent in biomass liquefaction can also lead to very good results, reason why further research is needed in this field.

Table 4: Summary of critical points of different solvents

Solvent	Critical Point	Ref
CO2	31.1 ºC; 7.38 MPa	[115]
Water	374.4 ºC; 22.064 MPa	[117]
Ethanol	250 ºC; 18.7 MPa	[116]
Methanol	240 ºC; 7.95 MPa	[118]
Acetone	235 ºC; 4.8 MPa	[119]

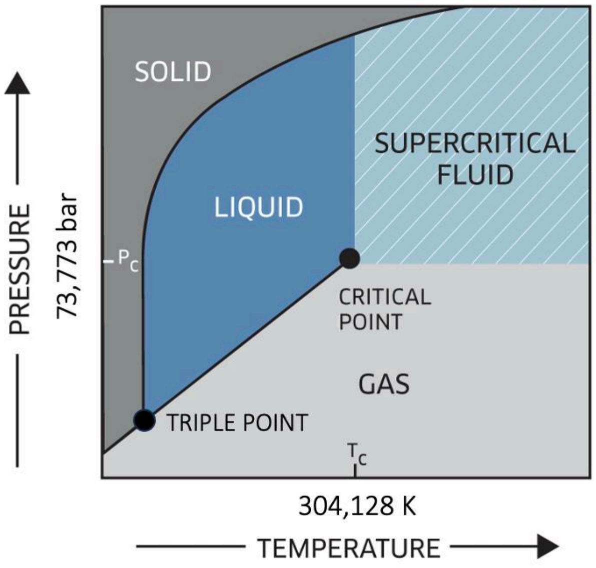


Figure 13: Supercritical carbon dioxide graphic [113]

Chapter 3. OPTIMIZATION OF PARAMETERS

3.1 INTRODUCTION

Optimization of parameters in the biomass liquefaction process is essential in order to maximize the production of bio-oil. However, the large number of input variables, also known as independent variables, makes it necessary in this process to carry out a prior study of the impact that each one of them has on the yield to avoid carrying out a large number of experiments, thus wasting a significant amount of resources and time.

Therefore, this section focuses on first identifying the important process parameters and then, through the study of existing literature and data collection, observing the trend and impact of each parameter on bio-oil maximization. This will make it possible to know the approximate ranges that can maximize each parameter in order to be able to design the experiments to be carried out as close as possible to the desired values. However, as the available literature on sCO2 liquefaction is very limited, an exhaustive compilation of hydrothermal and solvothermal liquefaction studies will be carried out due to the similarity of these processes.

Leveraging the extensive data compilation that was done, a basic version of a polynomial regression model capable of predicting bio-oil yields prior to the experiment results was also done. The objective is that, with further refinement and an expanded dataset (beyond the scope of this project), the model will significantly minimize the resources required for future investigations, providing this predictive capability a total control of the process and its behavior.

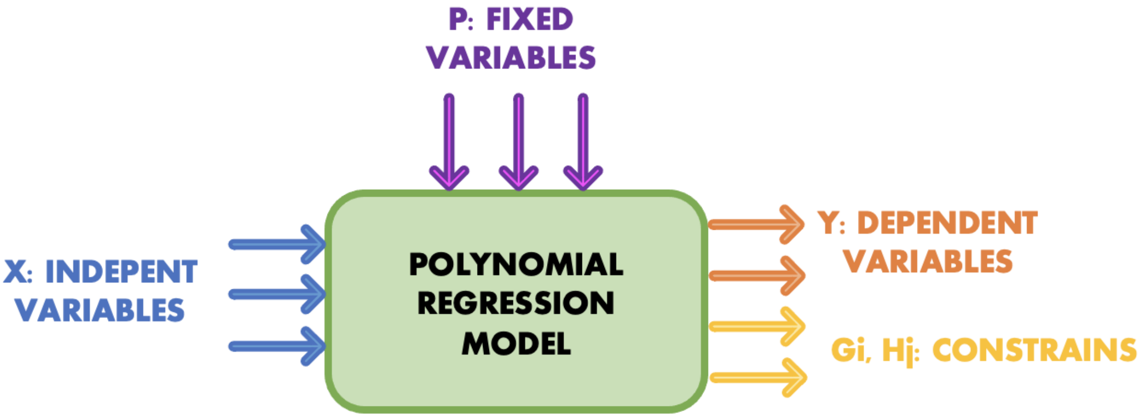


Figure 14: Outline of the polynomial regression model

3.2 DATA COLLECTION

236 bio-oil yield values were collected from different experiments carried out with diverse types of biomasses, solvents, and catalysts.

However, in this section, only a part of the data collected for each parameter is shown in order to see more clearly the trends, always trying that the different experiments shown in each graph are as similar as possible in terms of their parameters, except the one being analyzed, so that they can be compared.

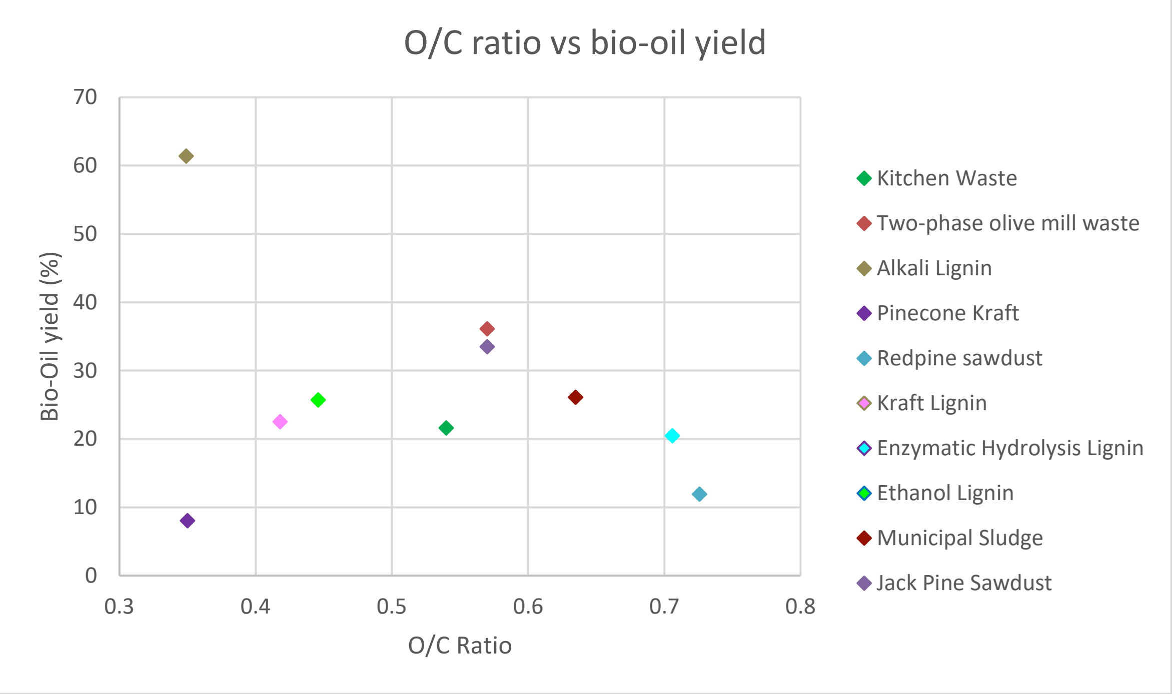
In all the data shown, the use of catalysts will not exist, since the experiments that use them employ different compounds, making it difficult to compare them. The rest of the parameters that have been tried to fix in each section will be indicated below the graph.

3.2.1 BIOMASS

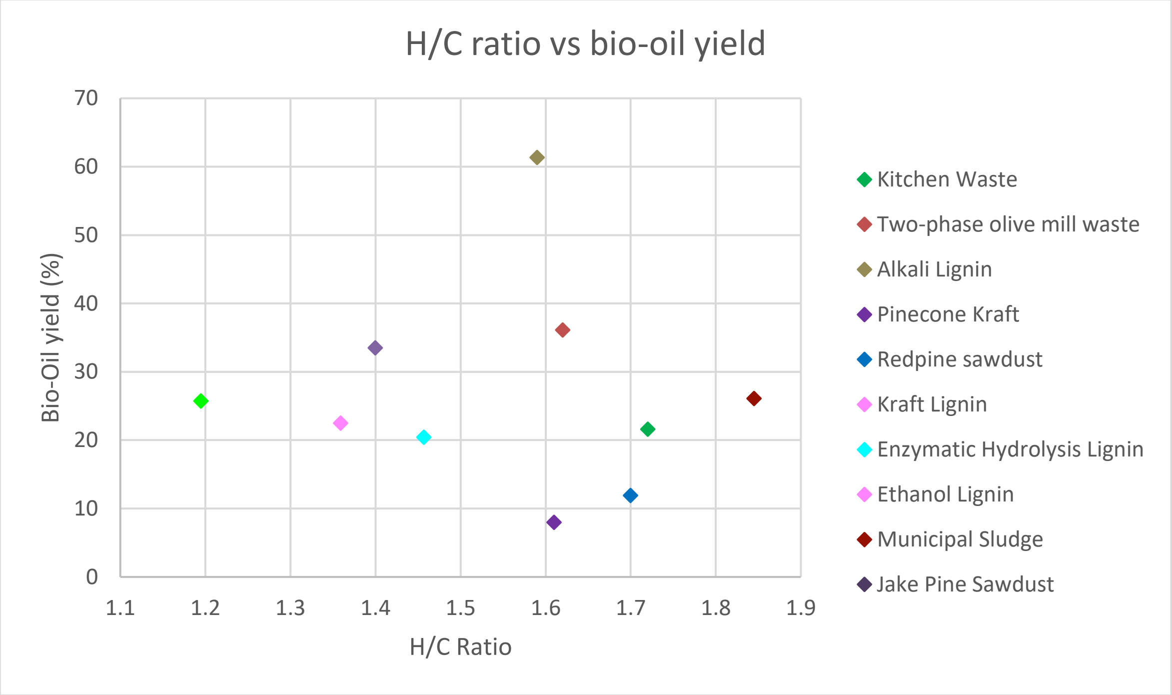
TYPE

The different types of biomasses have diverse compositions depending on their species. These changes affect considerably the yield and distribution of the bio-oil obtained after the liquefaction process. Therefore, in order to compare the different types of biomass, the O/C and H/C ratios have been calculated based on their composition and then represented graphically.

Although no clear trend is observed with the H/C ratio, the graph represented by the O/C ratio does present a polynomial trend, showing that the yield increases as the ratio increases until it reaches a maximum of approximately 0.57, after which the yield begins to decrease.



Graphic 3: O/C Ratio vs Bio-oil yield (%)



Graphic 4: H/C ratio vs Bio-oil yield (%)

Table 5: Fixed parameters O/C and H/C ratio

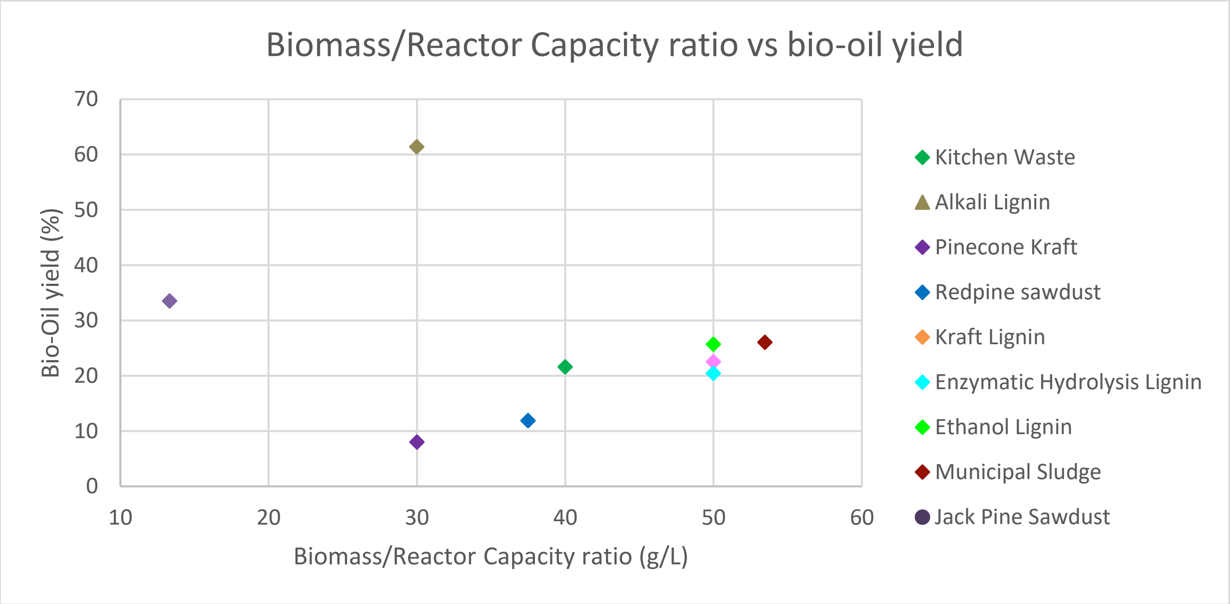
Fixed parameters	
Catalyst	No
Temperature	260-280ºC
Residence Time	30-45 min
Solvent	Water
Co-solvent	No

On the other hand, the literature also shows that feedstock with a lower lignin concentration usually achieves better conversion rates and higher biocrude yields [108]. This is due to the higher resistance of lignin to breakdown compared to cellulose and hemicellulose.

QUANTITY

In order to study the effect of the amount of biomass converted per experiment, the ratio between the amount of biomass (g) and the capacity of the reactor used (L) has been calculated. This standardization allows the comparison between the data collected from different experiments.

The results show a slight trend where the bio-oil yield increases with the loading of the amount of biomass. However, it should be considered that overfilling the reactor can cause problems in maintaining the operating temperature throughout the process (especially in the upper part of the reactor) and should therefore never be overloaded.



Graphic 5: Biomass/Reactor capacity ratio vs Bio-oil yield (%) (g/L)

Table 6: Fixed parameters Biomass/Reactor capacity ratio

Fixed parameters	
Catalyst	No
Temperature	260-280ºC
Residence Time	30-45 min

Solvent	Water
Co-solvent	No

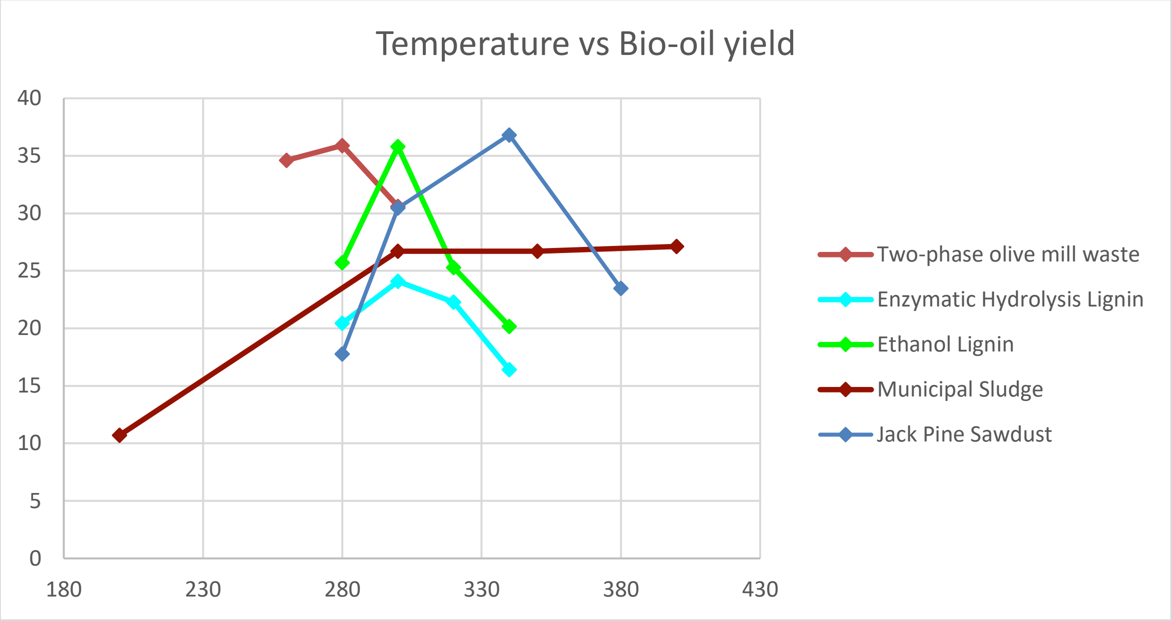
3.2.2 TEMPERATURE

Temperature is the most extensively studied parameter in the liquefaction process because it significantly influences many output parameters of the conversion process, such as the yield of the different products or the total conversion of biomass.

Raising the temperature enhances the fragmentation and degradation of lignocellulosic biomass. In addition, higher temperature also tends to improve the solubility of the biomass components in the solvent, facilitating better interactions and reactions. However, finding the optimal temperature for each process is crucial to achieve the highest possible amount of bio-oil at the lowest energy cost, as very high temperatures tend to promote the cracking of molecules producing more gaseous and solid products at the expense of liquids, as well as requiring higher energy use.

Temperature also affects the composition of the solid residue. By increasing the temperature, the percentage of uncovered components decreases due to the fact that the fractions of cellulose and hemicellulose are more likely to be fully degraded. Also, lignin breakdown is promoted when higher temperatures are reached. However, as said before, excessive temperatures can lead to char formation, increasing then the carbon content of the solid residue while decreasing its overall mass.

All these statements can be verified in the graph below. In the different experiments, it can be seen how the bio-oil yield increases as the temperature rises until it reaches the optimum value where the yield starts to decrease.



Graphic 6: Temperature (ºC) vs Bio-oil yield (%)

Table 7: Fixed parameters temperature

Fixed parameters	
Catalyst	No
Residence Time	30-45 min
Solvent	Water
Co-solvent	No

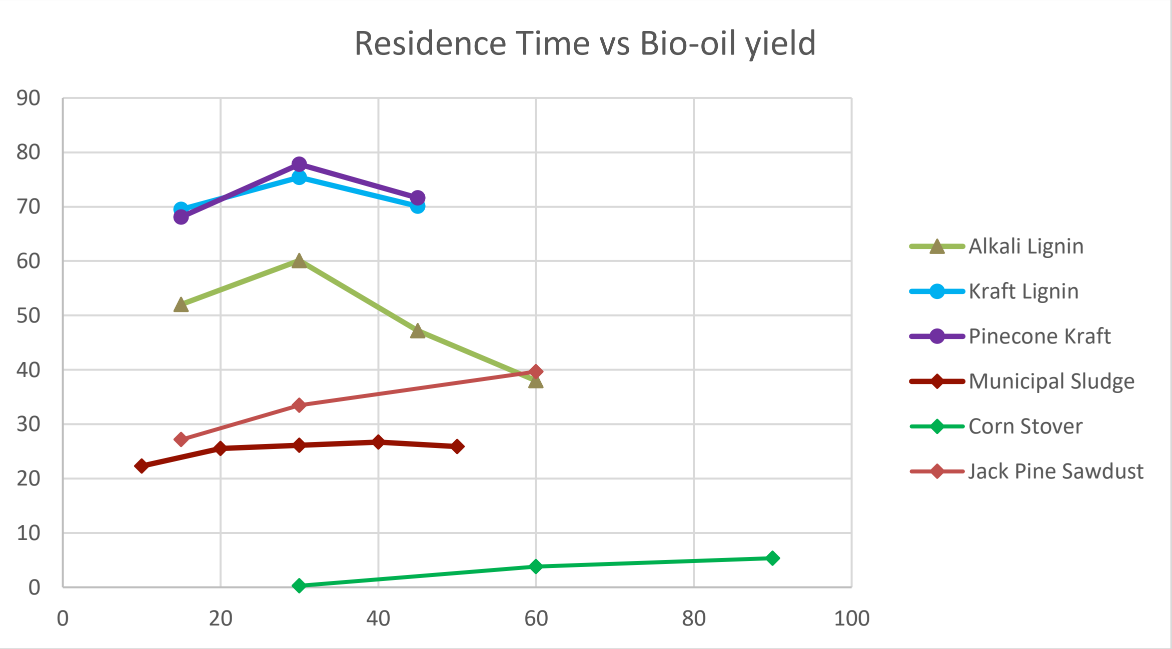
3.2.3 PRESSURE

Pressure is a very temperature-dependent parameter, which is why many scientific articles do not specify its value. However, it does not mean that it is not critical in maximizing the yield of the bio-oil. Higher pressure increases the solubility of the gases and liquid in the reaction medium improving also the interaction between the biomass and the solvent. This increased solubility can accelerate reaction rates and improve the efficiency of biomass breakdown, leading to higher bio-oil yields.

Operating at supercritical conditions (pressure and temperature) can also significantly enhance the liquefaction process. Supercritical fluids have unique properties that improve solvent power, heat and mass transfer, and reaction kinetics, resulting in higher conversion efficiency and product yields.

3.2.4 RESIDENCE TIME

The role played by residence time in the liquefaction process is similar to that of temperature. Longer reaction time generally increases the yield of bio-oil since it provides sufficient time for the degradation of polymers. This may not only increase the bio-oil output but also improve the bio-oil quality with less oxygenated compounds and higher hydrocarbons. However, if the residence time is too long, the bio-oil components undergo secondary reactions giving unwanted products such as gases and char hence decreasing the yield and quality of bio-oil.



Graphic 7: Residence time (min) vs Bio-oil yield (%)

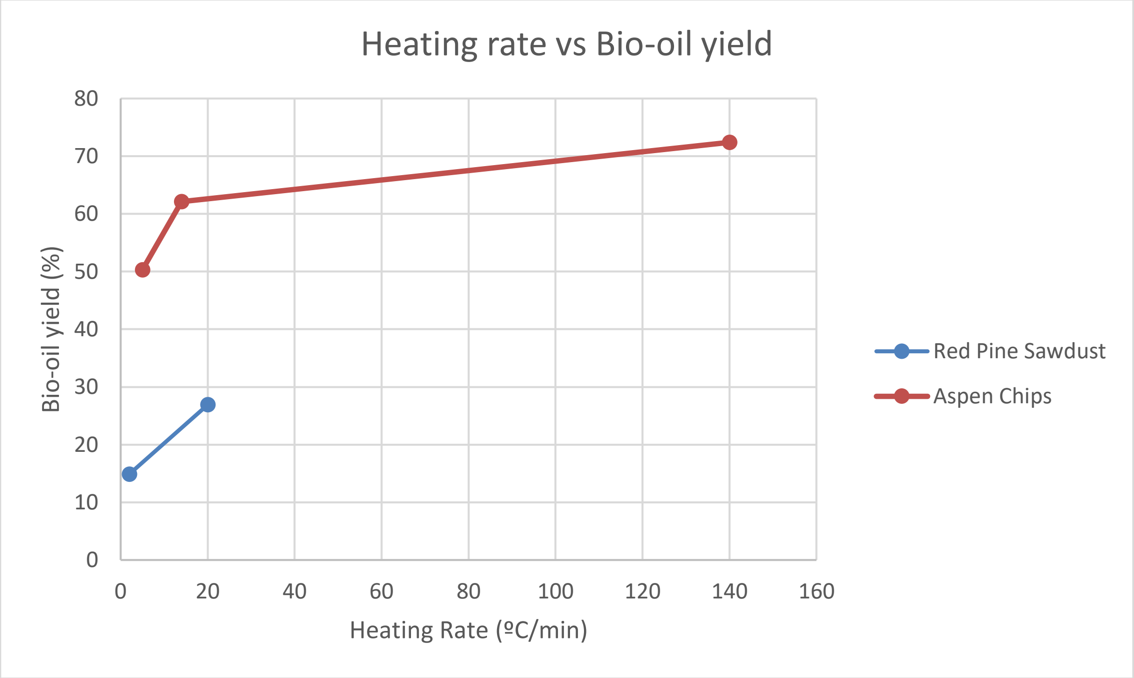
Table 8: Fixed parameters residence time

Fixed parameters	
Catalyst	No

Temperature	270-280 ºC
Solvent	Water: Diamond tag Alcohol: Triangle and Circle tag
Co-solvent	Water: Circle tag

3.2.5 HEATING RATE

The rate at which the temperature is increased during the liquefaction process also plays an important role in both the efficiency of the process and the outcomes of the conversion. A high heating rate promotes the fragmentation of biomass and prevents the formation of biochar [109]. Also, higher heating rates can reduce the degradation and recombination of the initial products [110]. On the other hand, low heating rates can help control and monitor the reaction, but at the cost of increasing residence time, which can reduce throughput and increase operational costs.



Graphic 8: Heating rate (ºC/min) vs Bio-oil yield (%)

Table 9: Fixed parameters heating rate

Fixed parameters	
Catalyst	No
Residence Time	1-10 min
Solvent	Water
Co-solvent	No

3.2.6 SOLVENT

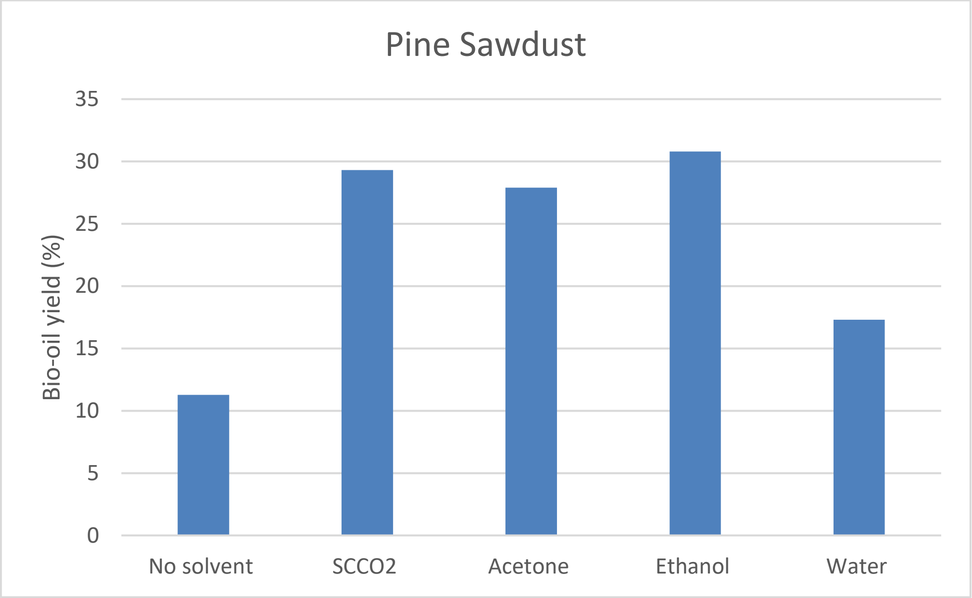
As seen above, the solvent has a significant impact on the liquefaction process. Both the type used and the amount added can vary the bio-oil yield and the overall biomass conversion rate.

TYPE

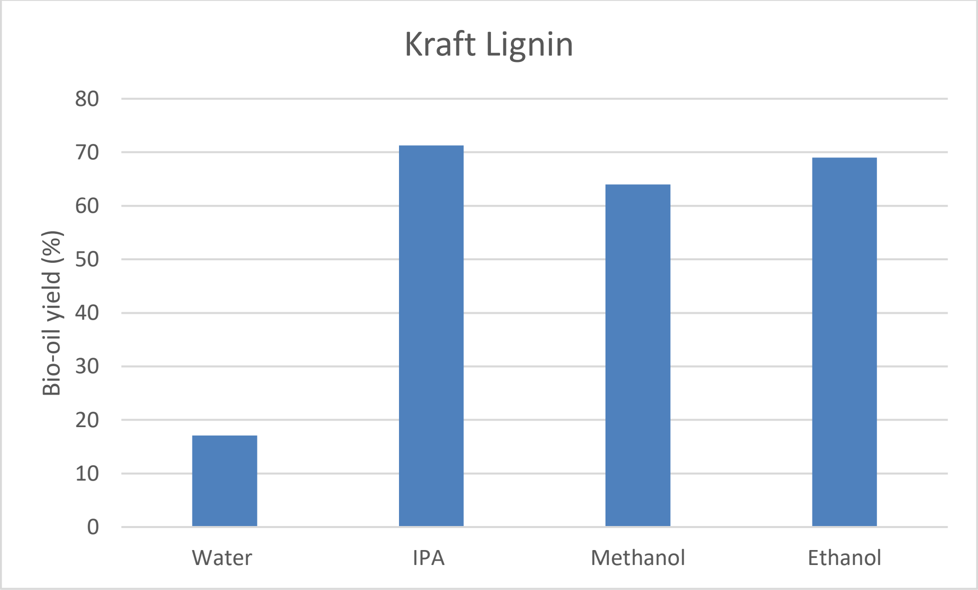
The main role of the solvent is to dissolve the biomass and promote the fragmentation of its components. Solvents with high solubility of biomass elements, such as cellulose, hemicellulose, and lignin, create better contact interaction between the biomass and the solvent, improving liquefaction efficiency. Also, some solvents participate in the chemical reactions enhancing the degradation of biomass into smaller molecules, improving the yield and quality of bio-oil.

Knowing the polarity of the solvents is key to maximizing the process. Polar solvents (e.g., ethanol, methanol) tend to break down biomass components more effectively due to their ability to interact with polar sites on the biomass molecules. On the other hand, non-polar solvents (e.g., water), are more effective in dissolving non-polar compounds from biomass. Although they may not be as effective in degrading polar components, they can be useful in the extraction of lipids and other hydrophobic compounds.

Many scientific articles focus on the comparison of the behavior of different types of solvents with one type of biomass. From them, it can be concluded that water as a single solvent has a limited solubility which prevents it from reaching very high bio-oil yield values. On the other hand, alcohols tend to obtain much more positive results, among which the versatility and efficiency of ethanol should be highlighted.



Graphic 9: Effect in pine sawdust liquefaction of different types of solvents in the bio-oil yield

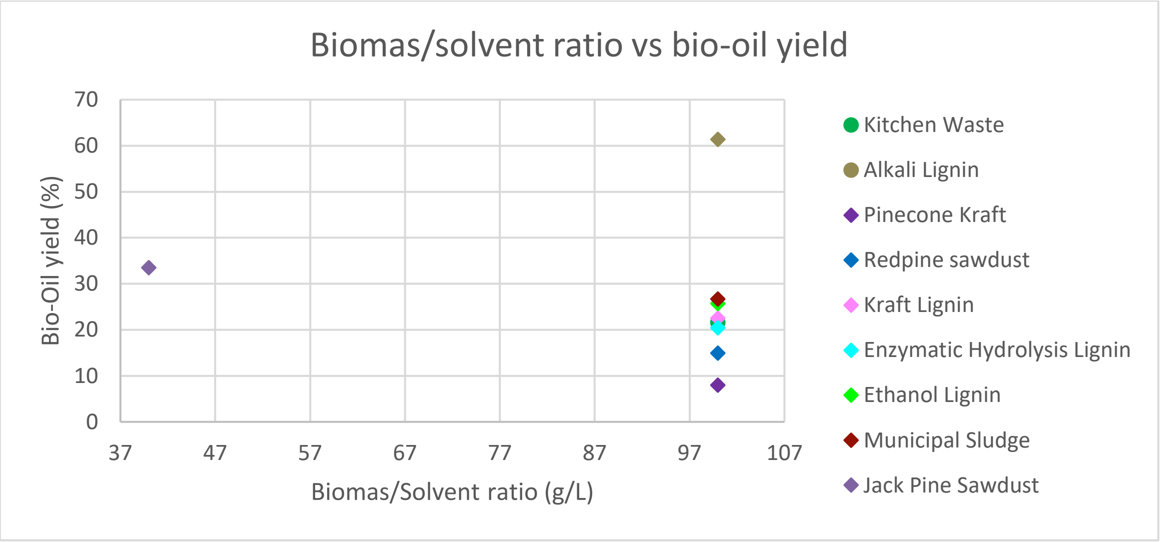


Graphic 10: Effect in kraft lignin liquefaction of different types of solvents in the bio-oil yield

QUANTITY

The amount of solvent used has also to be taken into account when optimizing the process. In order to compare different experiments carried out with different reactors, the data were standardized by calculating the ratio between the amount of biomass (g) and the amount of solvent (L).

Of all the data collected, the parameter with a value of 100 prevails. It can therefore be considered that this variable takes a fixed value as a general rule, as can be seen in the graph below.



Graphic 11: Biomass/solvent ratio (g/L) vs Bio-oil yield (%)

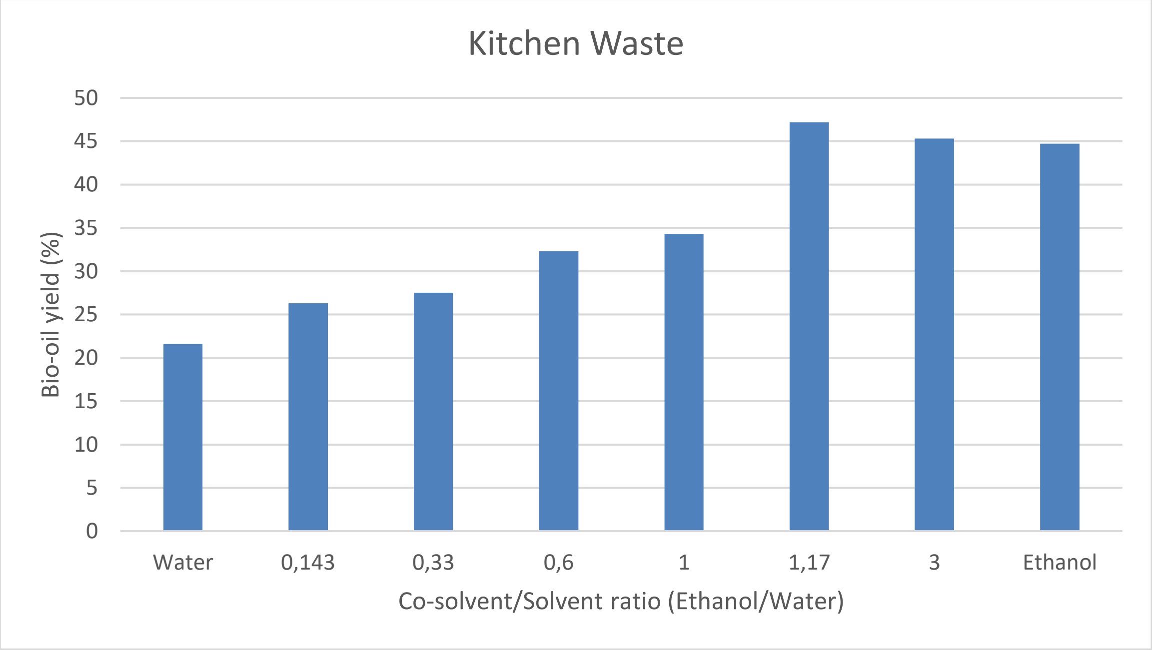
Table 10: Fixed parameters Biomass/Solvent ratio

Fixed parameters	
Catalyst	No
Temperature	260-280ºC
Residence Time	30-45 min
Solvent	Water
Co-solvent	No

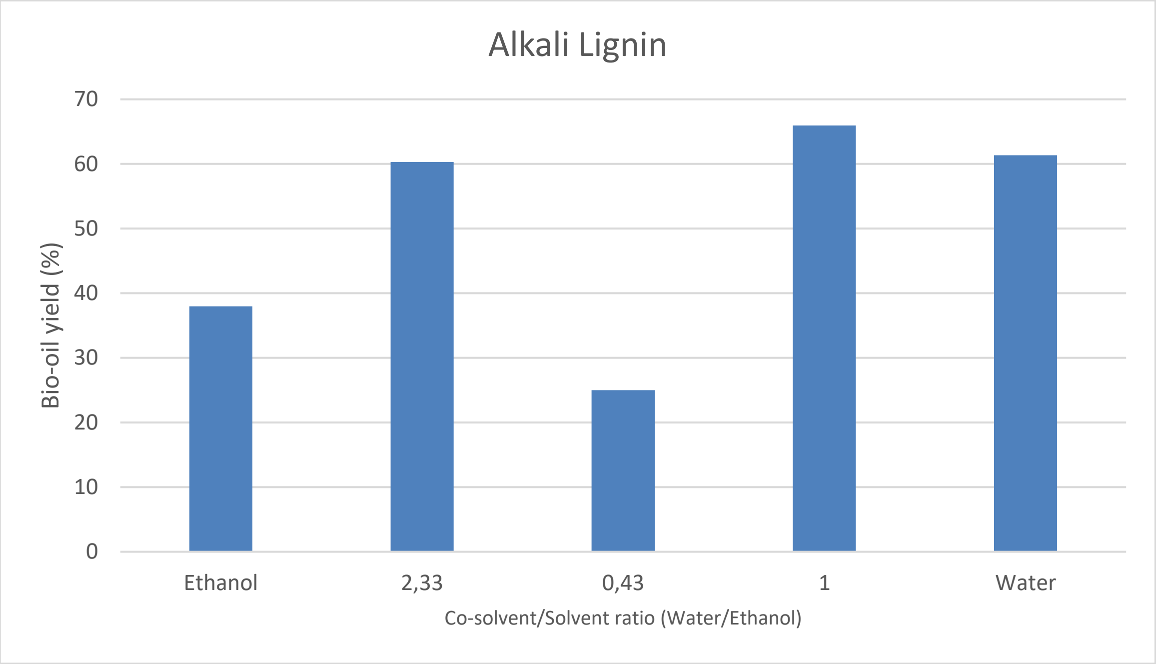
3.2.7 CO-SOLVENT

Co-solvents are used to combine the properties of different solvents to achieve better solubility, reactivity, and overall process performance. Combining solvents with different polarities improves the interaction with both polar and non-polar components of the biomass, leading to more efficient breakdown and conversion resulting in a higher proportion of liquid products.

Some of the most common and studied mixtures are those formed by water and alcohol. Water is excellent for dissolving polar compounds, while alcohol improves the solubility of non-polar compounds. All scientific articles dealing with the effect of the use of co-solvent have shown that there is an undoubted improvement in the process due to the use of these mixtures. Also, the amount of co-solvent added affects the performance of the process.



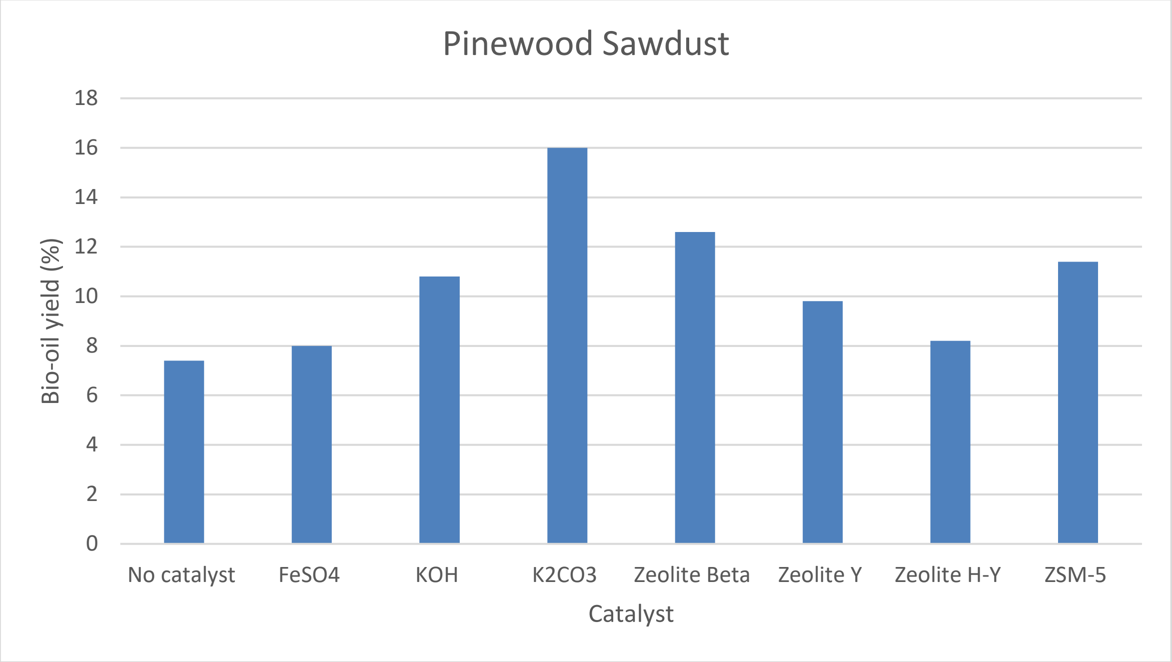
Graphic 12: Effect in kitchen waste liquefaction of co-solvent/solvent ratio in the bio-oil yield (%)



Graphic 13: Effect in alkali lignin liquefaction of co-solvent/solvent ratio in the bio-oil yield (%)

3.2.8 CATALYST

The use of a catalyst in the biomass liquefaction process is essential to enhance the reaction rates, improve product yields, and optimize the overall efficiency of the conversion. These compounds can significantly increase the velocity of the chemical reactions involved in biomass liquefaction by lowering the activation energy required, resulting in a faster conversion of biomass. It also facilitates the breakdown of complex biomass polymers into smaller molecules, enhancing the liquid product proportion in relation to solid residues and gases. They also help to produce bio-oil with fewer impurities and more desirable properties, favoring, for example, deoxygenation to obtain a much more stable bio-oil with a higher calorific value.



Graphic 14: Effect in pinewood sawdust liquefaction of types of catalyst in the bio-oil yield (%)

3.3 POLYNOMIAL REGRESSION MODEL

The use of polynomial regression models represents a powerful and sophisticated tool for predicting the value of a dependent variable. In this case, it will be used to predict the bio-oil yield in the biomass liquefaction process. The model will help to understand the complex relationships between multiple operating variables and bio-oil performance, providing an effective way to optimize and control the process.

In order to build the model, the following steps have to be followed:

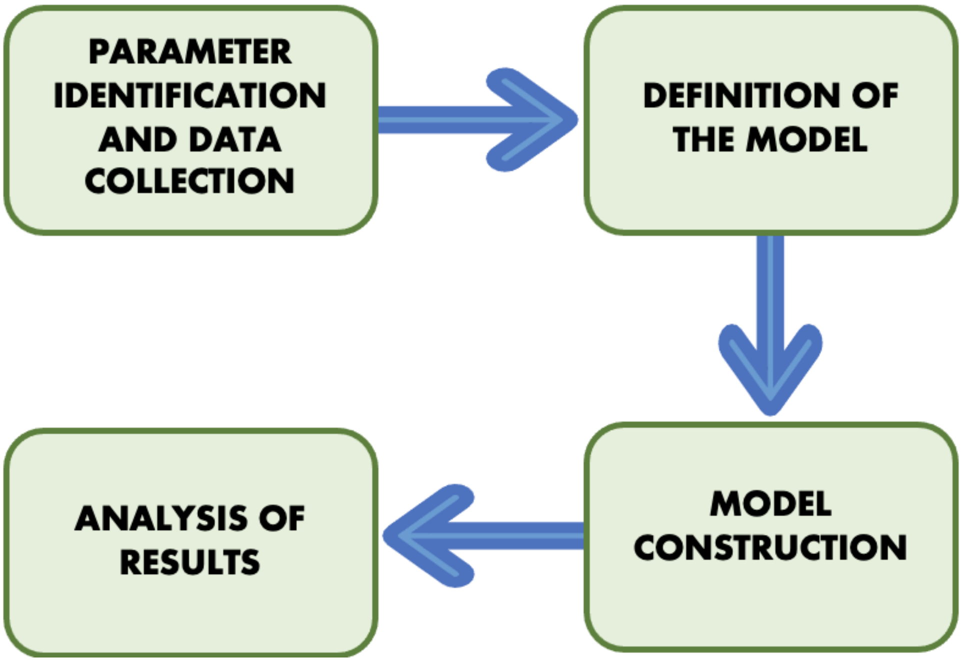


Figure 15: Building process polynomial regression model

PARAMETER IDENTIFICATION AND DATA COLLECTION

To start building a model first it has to be identified the parameters that affect the dependent variable (bio-oil yield). Next, comprehensive experimental data must be collected to reflect the various operating conditions used in biomass liquefaction.

This first step is reflected in the previous section, where the impact of the different parameters was studied through the information found in the scientific literature. In the first iteration of the polynomial model, not all relevant parameters will be included in order to build a simple model that will be further developed and completed in future work. Annex 1 shows the data used for the construction of the model.

DEFINITION OF THE MODEL

The choice of model type depends on a combination of factors related to the available data, the nature of the problem, and the specific objectives of the analysis. In this case, due to the limited amount of data, it is not possible to apply a machine learning model, as this type of complex model requires large volumes of data to work properly. On the other hand, due to the non-linear nature of the independent variables, the best-fitting model is the polynomial.

A polynomial regression model is an extension of linear regression that allows capturing non-linear relationships between the independent variables (process parameters) and the dependent variable (bio-oil yield) [112]. The general equation of a second-degree polynomial model can be expressed as:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 {X_1}^2 + \beta_4 {X_2}^2 + \beta_5 X_1 X_2 + \cdots + \varepsilon$$

Where Y is the bio-oil yield, X_1 and X_2 are process parameters, β are the model coefficients and ε the error term.

As the process parameters considered in the model increase, the number of X variables increases too. The degree of the polynomial equation will be chosen using the cross-validation method to avoid possible under- or over-fitting. Iteration terms, such as $X_1 X_2$, will be taken into account as it is suspected that several independent variables have some dependence on each other.

MODEL CONSTRUCTION

The model designed in Matlab is shown in Annex 2. In the following, a series of comments will be made on the code for its complete understanding.

First, the input data sets X (independent variables) and Y (dependent variables) are defined, where X represents process temperature, residence time, and O/C ratio, and Y the bio-oil yield. These variables are standardized so that their values are within the range [0, 1]. This is important to prevent scale differences between the variables from influencing the regression model.

Next, the cross-validation method is applied to obtain the optimal polynomial degree of our model and assess its performance. It consists of dividing the data set into several smaller subsets, called folds, and then training and evaluating the model multiple times, using different combinations of these folds as training and test data. In this case, a total number of five folds (K) has been defined.

Once the variables storing the cross-validation errors have been initialized and the dataset has been divided into training and test partitions, the polynomial regression model is built. To do this, for each degree of the polynomial, polynomial terms and interactions between variables are constructed, the model is trained on the current training set and evaluated on the test set, and finally, the mean square error is calculated for each partition, and degree of the polynomial. After repeating this process as many times as the maximum polynomial degree has been indicated (in this case 5), the best degree of the polynomial is selected. To do this, the average mean square error is calculated for each degree of the polynomial and the degree with the smallest error is selected.

With the chosen grade according to the cross-validation technique, the final model is built with the provided data of temperature, residence time, O/C ratio, and bio-oil yield.

Since the input data have been normalized, the calculated predictions must be denormalized before the results are delivered. The final results shown are the best polynomial degree, the model coefficients, and the denormalized predictions.

ANALYSIS OF RESULTS

The results obtained with the model constructed and the data provided are as follows:

Best degree of the polynomial:

2

Final model coefficients:

-0.0677
0.6678
0.7277
0.6851
-1.0707
-0.4975
-0.7250
0.2560
0.9565

-0.9505

Deformalized predictions (Bio-oil yield (%)):

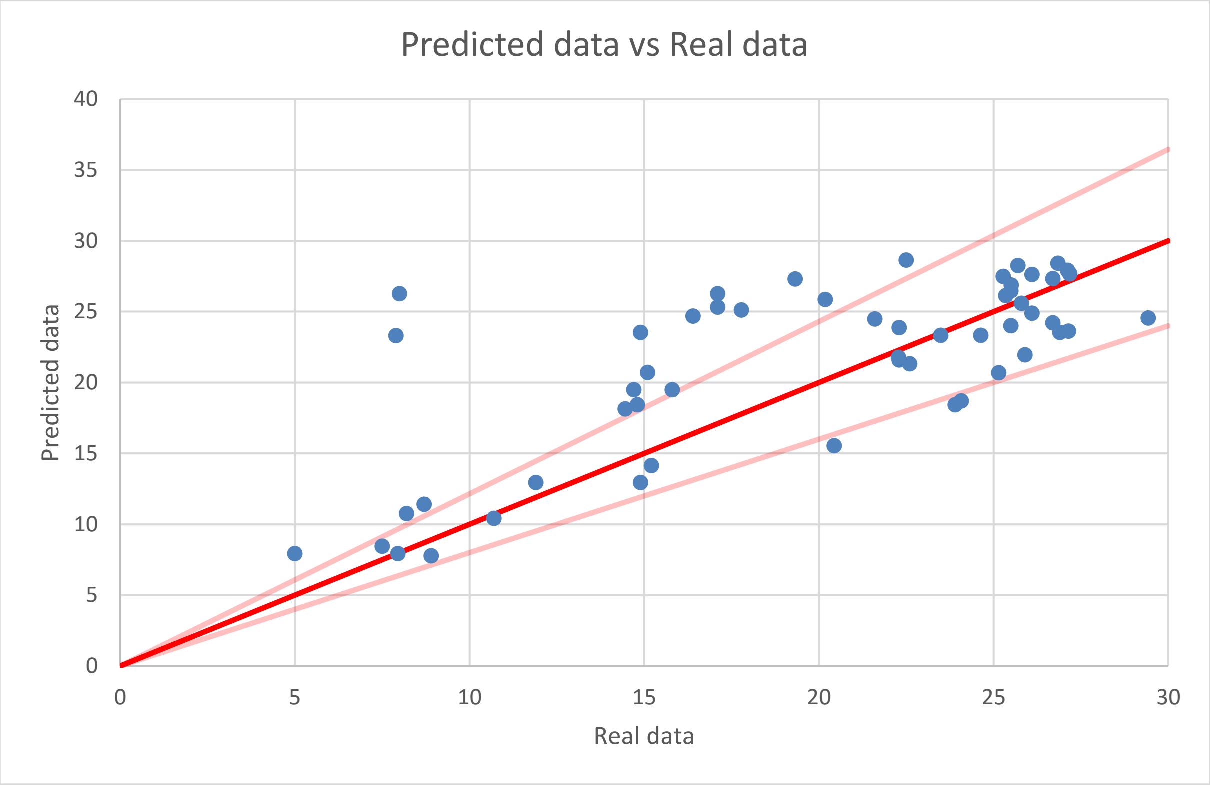
1. 24.4813
2. 26.3234
3. 26.2716
4. 26.2716
5. 7.9435
6. 12.9605
7. 18.4477
8. 23.5406
9. 7.9435
10. 12.9605
11. 18.4477
12. 23.5406
13. 28.6407
14. 28.4241
15. 27.3233
16. 25.3381
17. 15.5383
18. 18.7215
19. 21.7758
20. 24.7013
21. 28.2672
22. 28.2972
23. 27.4978
24. 25.8688
25. 8.4664
26. 10.7681
27. 11.4227
28. 10.4302
29. 7.7906
30. 21.5920
31. 24.0212
32. 24.8944
33. 24.2116
34. 21.9727
35. 23.8879
36. 26.4764
37. 27.6228
38. 27.3271
39. 25.5892
40. 23.3390
41. 26.1508
42. 27.6797
43. 27.9258
44. 26.8892
45. 23.6373
46. 26.2139
47. 22.2942
48. 21.3338
49. 24.5683
50. 23.3416
51. 25.1345
52. 26.2139
53. 26.5838
54. 23.3416
55. 14.1562
56. 18.1426
57. 20.6945
58. 23.3063
59. 19.5001
60. 20.7126
61. 19.5001

Using the cross-validation technique, we obtain that the polynomial degree with which the best results are obtained is 2. The equation obtained with the model would therefore be as follows:

$$Y = -0.0677 + 0.6678X_1 + 0.7277X_2 + 0.6851X_3 - 1.0707{X_1}^2 - 0.4975{X_2}^2 \\ - 0.725{X_3}^2 + 0.256X_1X_2 + 0.9565X_1X_3 - 0.9505X_2X_3$$

Analyzing the results and calculating the average error of all predicted values compared to the actual data has yielded a total error of 21.5%. This error can be decreased by adding the other independent variables that affect bio-oil performance, as well as by adding more new data so that the model can be built with more information to improve its accuracy.

The graph below shows the points whose prediction is closest to the actual data, as well as those that are both inside and outside the mean error of 21.5%.



Graphic 15: Predicted data vs Real data

Chapter 4. LIQUEFACTION OF SOFT PINEWOOD IN SUPERCRITICAL CARBON DIOXIDE

4.1 EXPERIMENTAL AND ANALYTICAL PROCEDURE

4.1.1 MATERIALS

Soft pinewood was sieved to between 40 and 140 meshes and dried in an oven at 105ºC for 20 hours before use. The chemicals used in this study as solvents and catalysts are as follows: CO_2 was purchased from Airgas; Ethyl alcohol (certified ACS/USP reagent grade, 100%) from Pharmco by Greenfield Global, Acetone (certified ACS/HPLC reagent grade, ≥ 99.5%) purchased from Fisher Scientific and Potassium carbonate (certified ACS, anhydrous, 99%) was purchased from ThermoFisher Scientific.

4.1.2 LIQUEFACTION OF SOFT PINEWOOD

All the experiments were conducted in a micro-batch reactor (PARR 4590) consisting of a 100 ml pressurized and stirred 500 rpm vessel. The vessel is equipped with a controlled heater (PARR 4848) to maintain the operating conditions and is connected to a gas cylinder filled with pure CO_2 to be used as a solvent and for removing the air from the reactor by purging before the liquefaction process is started.

For the first run, 13g of soft pinewood (40 – 140 meshes, dry basis), and 1,3g of catalyst were loaded in the autoclave. During the second run, the quantities were reduced to 10g, and 1 g respectively. Once the reactants were completely mixed the reactor was sealed and purged for removing the oxygen. After the nitrogen has been removed, the autoclave starts to be heated with a heating ratio of 10 ºC/min and a stirring speed of 100 rpm until the reaction temperature is reached. After completion of the residence time (2 hours) and thus completion of the liquefaction process, the reactor was cooled down to room temperature using a cooling fan.

4.1.3 PRODUCT SEPARATION

The procedure for the separation of the reactant product is shown in Figure 16. Once the reactor was cooled to room temperature and depressurized until reached atmospheric pressure, the gas was removed from the autoclave, and the reactor was opened. Then, the liquid and solid mixture were collected from the bottom of the reactor by rinsing it with acetone. Once the reactants were collected, the aqueous products were separated from the solid residue using the Soxhlet extraction, which is a technique used to extract compounds from a solid sample using a suitable solvent. This technique is especially useful when the compound of interest has a low solubility in the solvent, and continuous and efficient extraction is necessary. The process is carried out in a specialized apparatus known as a Soxhlet extractor, invented by Franz von Soxhlet in 1879 [111]. The procedure followed to carry out this technique was as follows:

Once the solid-liquid mixture was placed in a filter paper cartridge, the acetone (solvent) in the flask was heated to 80ºC. The acetone vapors raised through the extractor and entered the condenser, where they were cooled and liquefied. The liquid solvent dripped onto the sample, dissolving the compounds of interest. Once the acetone level in the extractor reached a certain point, it was siphoned back into the flask, carrying the dissolved compounds with it. This cycle of evaporation and condensation was repeated until the extraction of the compounds from the solid residue was completed, lasting approximately one hour and a half.

The contents collected in the flask, containing the aqueous products and the bio-oil, were then transferred to a rotary evaporator which was heated to the temperature necessary to evaporate all components except the bio-oil.

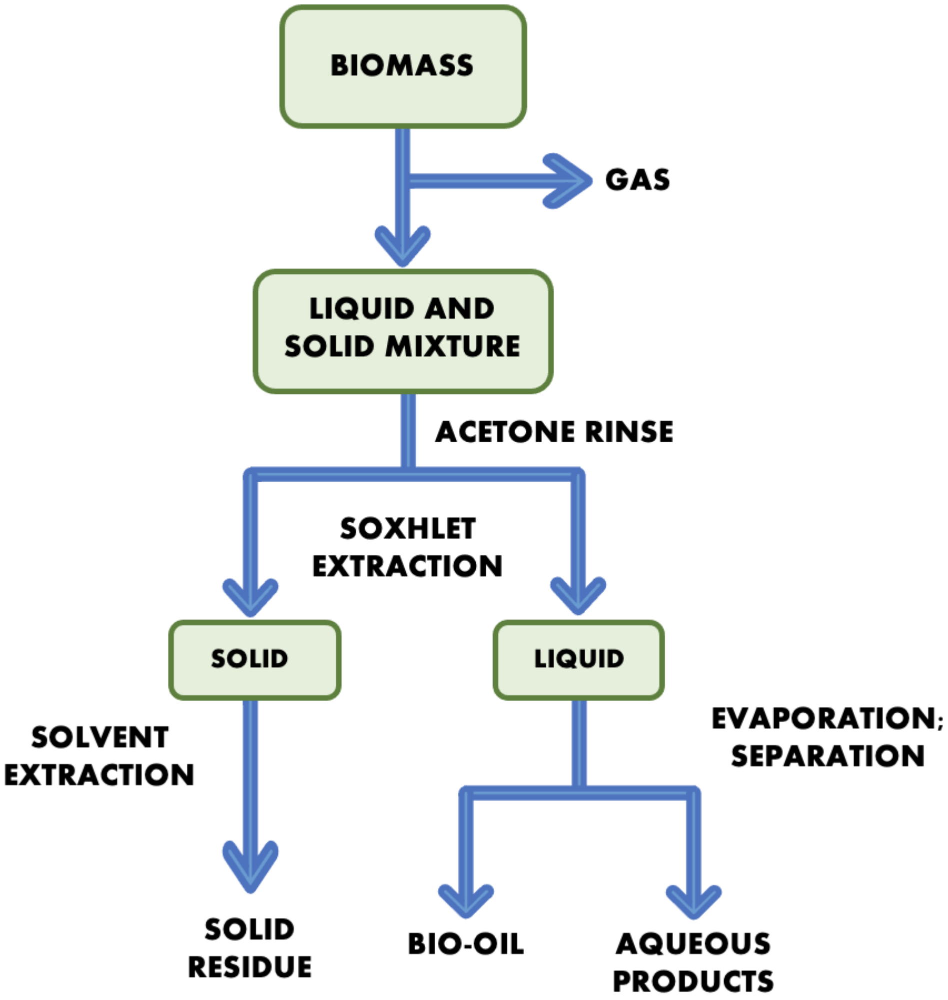


Figure 16: Product separation procedure

4.1.4 PRODUCTS YIELD CALCULATION

After weighing the bio-oil obtained, the yield was calculated with the following expression.

$$Yield\ of\ Bio-oil\ (wt\%) = \frac{W_{bio-oil}}{W_{biomass}} \times 100\%$$

$$Yield\ of\ Char\ (wt\%) = \frac{W_{solid\ residue} - W_{catalyst}}{W_{biomass}} \times 100\%$$

Being $W_{biomass}$ the weight of soft pinewood (dry basis), $W_{solid\ residue}$ the weight of the solid residue obtained, $W_{bio-oil}$ the weight of bio-oil, and $W_{catalyst}$ the weight of the catalyst added to the reaction.

4.2 RESULTS AND DISCUSSIONS

4.2.1 EFFECT OF BIOMASS LOADING IN BIOMASS LIQUEFACTION

In the first experiment, the aim was to test the effect of increasing the amount of biomass loaded into the reactor by 13% compared to previous experiments done in the Combustion Laboratory of the University of Maryland. For this purpose, 13 g of soft pinewood was added on a dry basis together with 1.3 g of catalyst (K_2CO_3) to the reactor. Subsequently, CO2 was gradually introduced until the gas inside reached a density of 0.2 g/ml. This was done by first setting the temperature inside the reactor at 50ºC and then introducing CO2 until the pressure inside the reactor reached 1110 psi, taking into account the isochoric properties of carbon dioxide. Once this pressure was reached, the reactor was heated up to 300 ºC to start the liquefaction process of 2 hours residence time. The reason for setting the density of carbon dioxide at 0.2g/ml is that at this density, at 300ºC (process operating temperature), the pressure reached by the carbon dioxide is 3024 psi. Adding approximately 1000 psi due to the reaction according to previous experiments, the process would reach a maximum pressure of approximately 4000 psi. In this way, it was ensured that, during the liquefaction, excessive pressures that could damage the equipment were not reached as well as too low operating pressures that could decrease the performance of the process.

In order to calculate approximately the amount in grams of CO2 added to the reactor, once the biomass and catalyst were added and mixed, the volume available in the reactor (58.55 ml) was calculated. Therefore, knowing the density of the CO2 (0.2 g/mL), the total amount of solvent used in the process was 11.71 g.

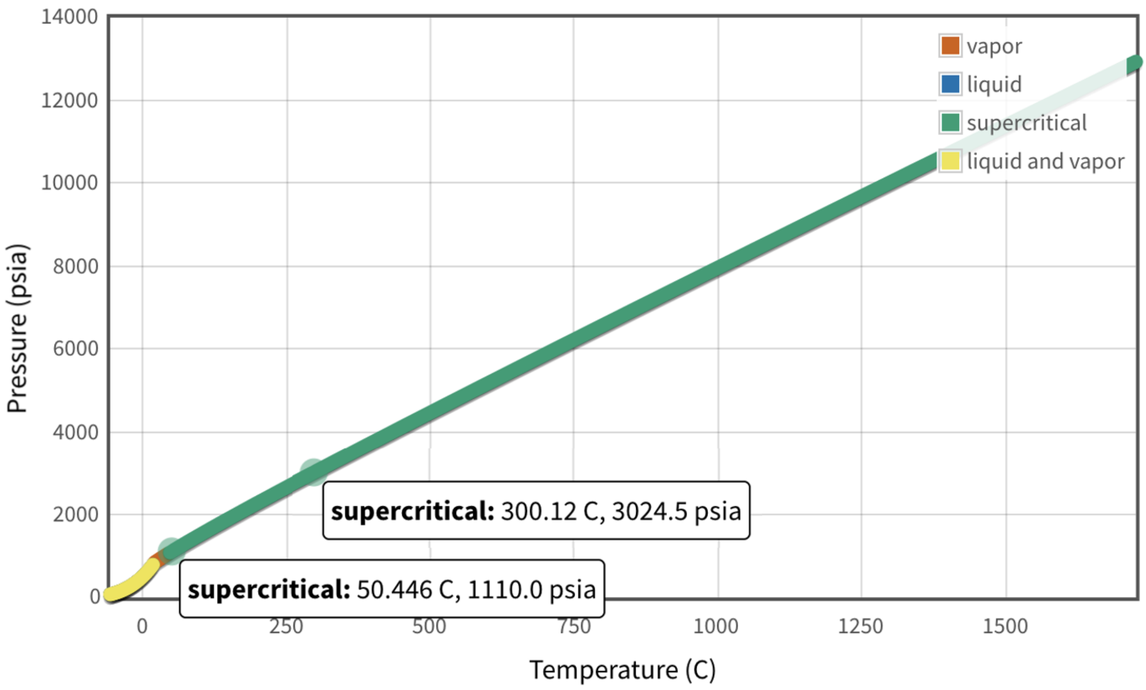
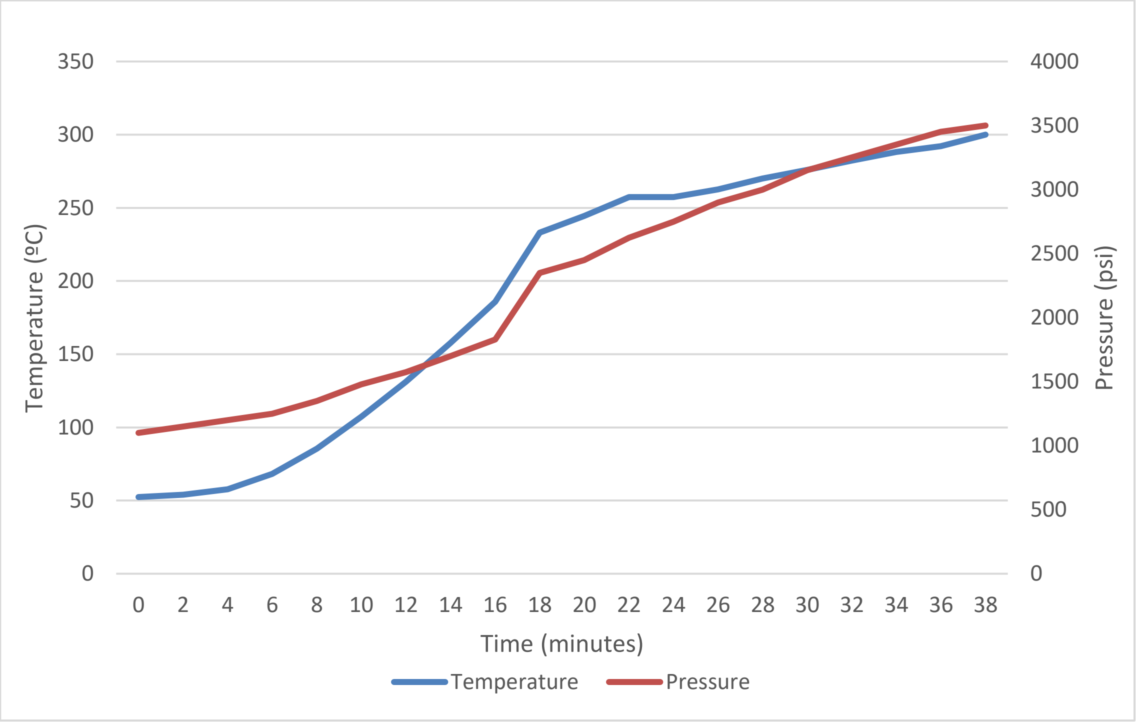


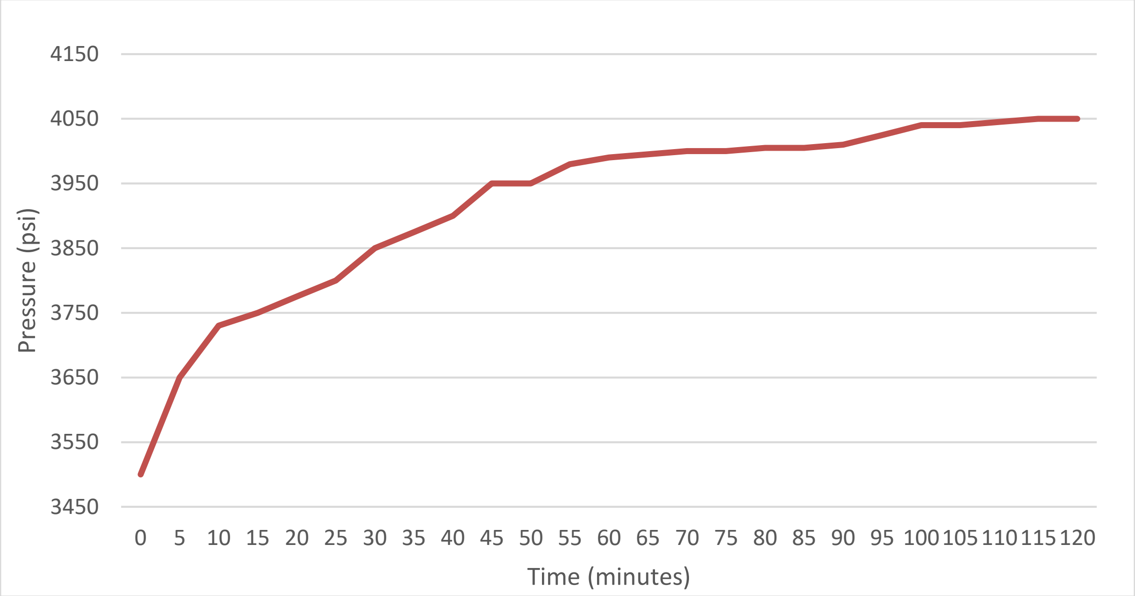
Figure 17: Isochoric properties of carbon dioxide with a density of 0.2 g/mL [121]

Once the reactor started to heat up, it took 38 minutes to reach 300ºC.



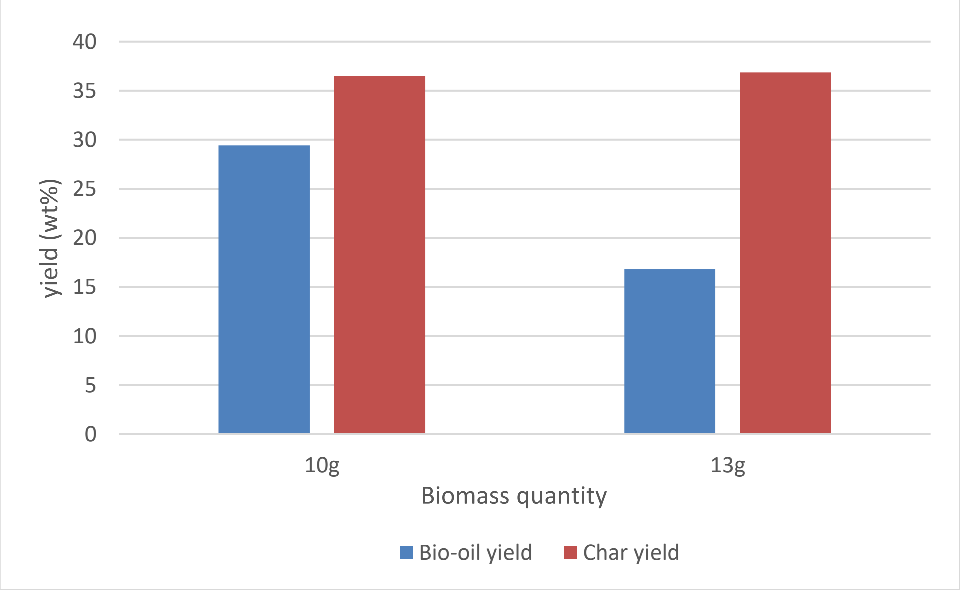
Graphic 16: Heating profile liquefaction process experiment 1

Once the set temperature (300ºC) was reached, the two-hour residence time for biomass conversion began. During this time the maximum pressure reached was 4050 psi.



Graphic 17: Pressure profile during liquefaction process experiment 1

The reactor took about 60 minutes to cool down. After separating the bio-oil from the solid residues and the aqueous products, the bio-oil yield was calculated, obtaining a value of 16.8 wt%.



Graphic 1: Effect of biomass quantity added to the reactor on the yield of bio-oil

Graphic 1 illustrates the evolution of bio-oil yield as the amount of biomass in the reactor increases from 10 to 13g. As can be seen, the yield decreases from 29.4 to 16.8 wt%, which means that, in the first instance, this increase in the amount of biomass is not at all beneficial. Also, the evolution of char yield is shown, and it can be seen how the amount obtained during both experiments is similar (36.5 wt%).

4.2.2 EFFECT OF CO-SOLVENT IN BIOMASS LIQUEFACTION

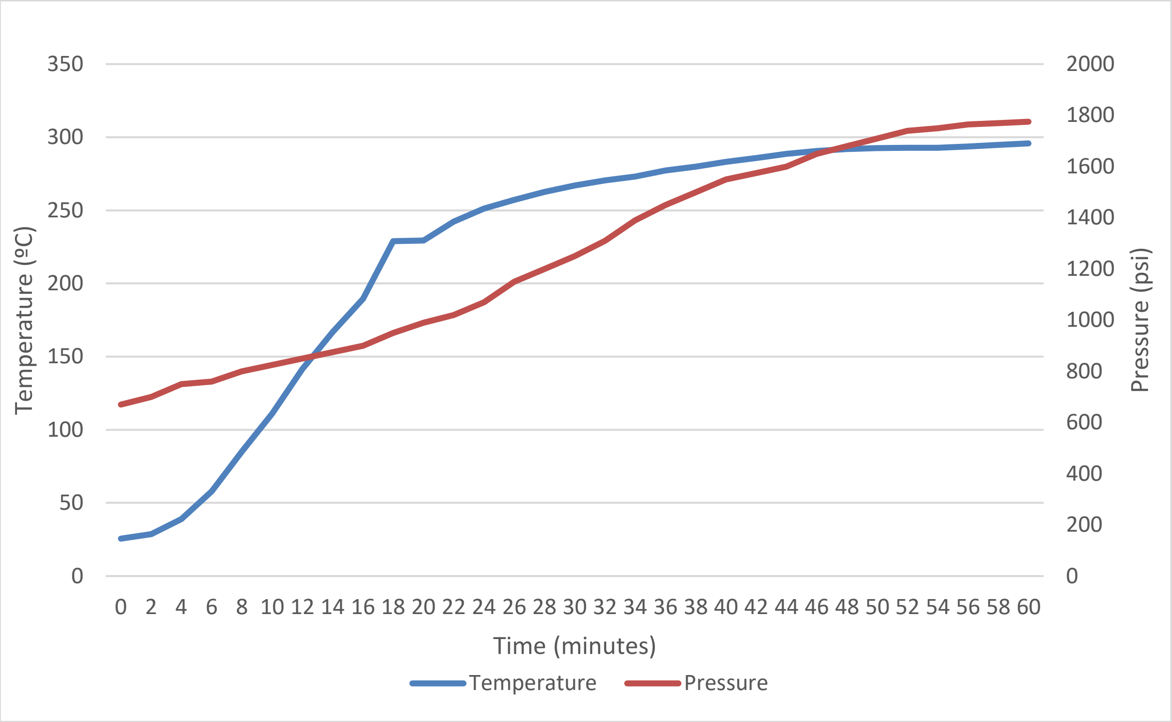
In this second experiment, the objective was to test the effect of the addition of a co-solvent on the bio-oil yield, comparing the results to previous experiments done in the Combustion Laboratory of the University of Maryland. For this purpose, 40% ethanol was added to the amount of biomass used in the process, which in this case was 10 g. Therefore 4 g of ethanol together with 1 g of catalyst (K_2CO_3) were added to the reactor together with the biomass.

To calculate the amount of CO2 to be added in the process so as not to reach too high or too low pressures, the pressure added by the ethanol had to be taken into account. Assuming an ideal gas:

$$p = \frac{nRT}{V} = \frac{\frac{4}{46} \times 8.314 \times 573}{5} = 82{,}85\, bar = \ 1201.63\, psi$$

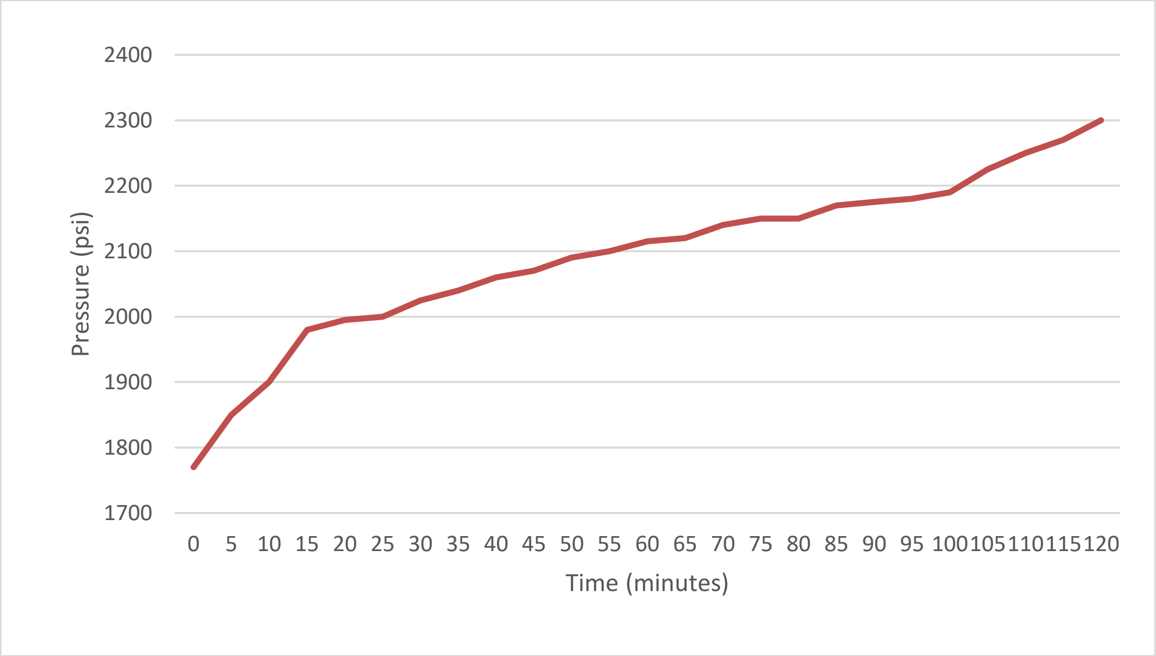
Therefore, the density of CO2 before starting to heat the reactor was set at 0.12 g/mL, since at the temperature of 300 ºC the gas pressure would be approximately 1823.9 psi. For this, by introducing CO2 at room temperature (22 ºC), we tried to obtain an internal pressure of 670 psi, thus obtaining the desired gas density.

The total time to reach 300ºC was 60 minutes.



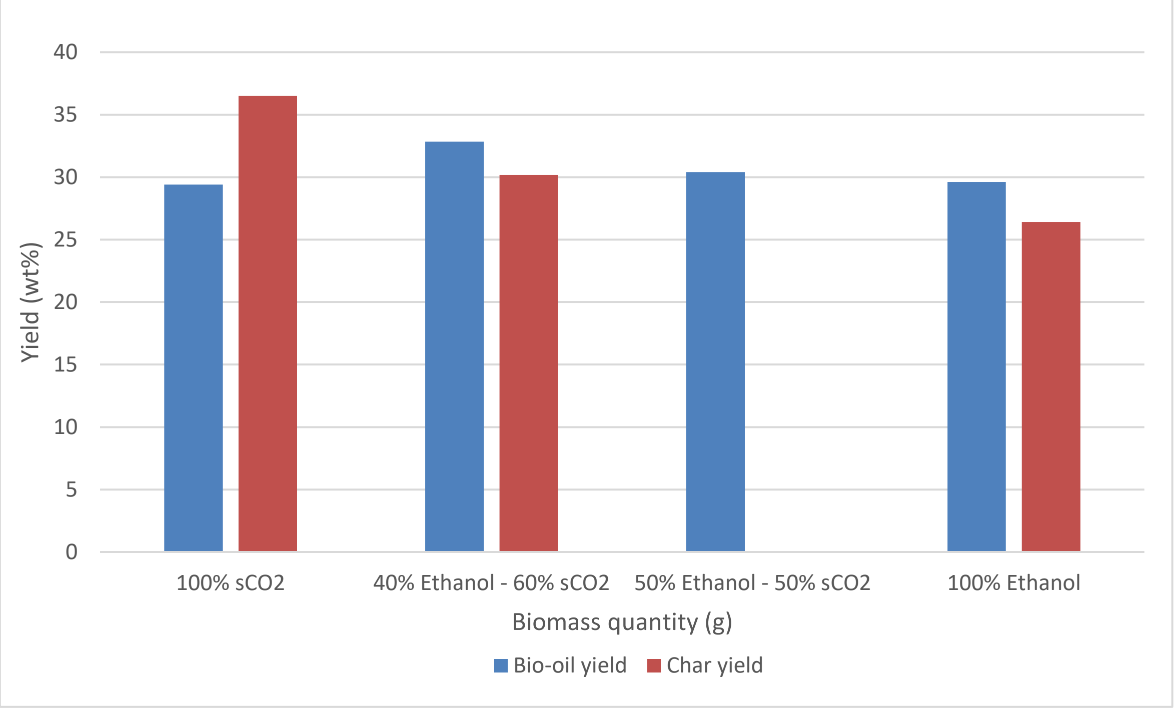
Graphic 18: Heating profile liquefaction process experiment 2

Once the set temperature (300ºC) was reached, the two-hour residence time for biomass conversion began. During this time the maximum pressure reached was 2300 psi.



Graphic 19: Pressure profile during liquefaction process experiment 2

The reactor took about 60 minutes to cool down. After the process of separating the bio-oil from the solid residues and the aqueous products was done, the bio-oil yield was calculated, obtaining a value of 32.84 wt%.



Graphic 2: Effect of solvent/co-solvent ratio on the bio-oil and char yield

Graphic 2 shows the results from previous experiments conducted in the Combustion Laboratory of the University of Maryland and of the experiment corresponding to this section. All of them were performed with the same parameter values, except for the percentage of solvent and co-solvent used so that they can be compared. As can be seen, the percentage yield of bio-oil obtained using 100% ethanol solvent and 100% sCO2 is very similar (29.6 and 29.4 respectively). On the other hand, the results show that the addition of co-solvent helps to improve the performance of the process, and furthermore, it can be observed that the approximate optimum value in terms of proportions is close to 40% ethanol and 60% sCO2.

As for the char yield, it is observed that it decreases as the amount of ethanol used in the reaction increases, varying from 36.5 to 26.4 wt%.

4.3 ECONOMIC ANALYSIS OF BIO-OIL PRODUCTION

An economic analysis of the production of bio-oil through the liquefaction of soft pinewood using sCO2 as solvent has been carried out. For this purpose, the data and times measured in the process conducted in the second experiment will be used.

The economic analysis will be carried out only with the variable costs, without taking into account the cost of the machinery and equipment necessary to carry out the process. On the other hand, the quantities of materials and process times are approximate values that could change depending on the parameters of each experiment.

First of all, the price of the raw material needed to carry out the experiment is calculated.

Table 11: Summary of raw materials needed for the liquefaction process

Raw Material	**Quantity (g)**	**Unitary price ($/g)**	**Total cost ($)**	**Ref.**
Soft Pinewood	10	$0.00022246	$0.00224	[131]
CO2	6	$0.004998	$0.005	[122]
Ethanol	4	$0.0323	$0.13	[123]
Acetone	120	$0.0258	$3.10	[124]
Potassium Carbonate	1	$0.0842	$0.0842	[125]

To estimate the cost of 10g of biomass, taking into account that the price of soft pinewood in the United States varies depending on the market and region, the average price for densified biomass fuel based on recent data was used for the calculations. The prices of the other materials have been obtained from the catalogs of the different brands. With all this, the total price of raw materials to carry out the liquefaction process with the parameters established by the second experiment is 3,321$.

The price of electricity needed for the different processes to obtain the bio-oil is calculated below.

Table 12: Summary of the processes that require electricity in the liquefaction method

Process	Device	Power (W)	Time (min)	Total cost ($)	Ref.
Dry Biomass	Accu Temp-09s	1200	1200	$3.708	[126]
Liquefaction	PARR 4590	700	180	$0.325	[127]
Fan cooler	Holmes, Blizzard	45	60	$0.007	[128]
Soxhlet extraction	IKA C-MAG HS7 digital	1020	480	$1.262	[129]
Evaporation	Cole-Parmer	1050	60	$0.162	[130]

Firstly, in order to carry out the calculations, the average price per kWh in the United States in 2023 (15.47 cents/kWh) was used [131]. On the other hand, the consumption of each device has been obtained from the specifications in the catalogs of each brand. Finally, the time that was taken for each process was measured during the experiment. With all these data, the approximate cost of electricity used to perform the second experiment has been 5.527$.

Therefore, the variable cost of producing 3.28 grams of bio-oil is $8.848, which is equivalent to a unit cost of 2.69 $/g.

4.4 CONCLUSIONS

In this work, soft pine wood was liquefied in sCO2 in order to study the effect of increasing the reactor load by 13% and to test the impact of adding a co-solvent to the process.

In the first experiment, the yield obtained was 16.8 wt%. This is a very low performance compared to previous experiments. The reasons for this may be due to the fact that three different aspects were observed when extracting the solid-liquid mixture from the reactor. Firstly, a small amount of unreacted biomass was found, which could be due to overloading of the reactor. Secondly, it was observed that the catalyst settled low and a large part of it remained unreacted again, this could again be due to the overloading of the reactor. Finally, when cleaning the reactor for the second experiment, it was detected that a considerable amount of liquid and solid mixture was stuck in the reactor depressurization pathway. This could be due to a failure in the procedure where the depressurization was not carried out properly, causing the accumulation of the products in the gas outlet path.

On the other hand, in the second experiment, a higher yield was obtained (32.8%). This confirms the hypothesis that the addition of a co-solvent in the liquefaction process of biomass greatly aids the breakdown of the components, thus achieving a much higher process yield. However, it is crucial to find the optimal ratio that maximizes bio-oil yield, and in this case, this ratio is close to 40% ethanol and 60% sCO2. Furthermore, the results show that a higher proportion of ethanol minimizes the formation of charring. This may be due to the fact that a higher proportion of ethanol in the solvent mixture can improve the solubility of the intermediates and facilitate the stabilization reactions, thus reducing the conditions that favor char formation. However, it should be noted that the extraction process of the aqueous phase and solid residues took 8 hours to complete, which is eight times longer compared to the first experiment. Therefore, a more optimal extraction method that decreases the total process time should be applied for future experiments.

Chapter 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The main objective of the project was to study the liquefaction of biomass using supercritical carbon dioxide (sCO2) as a solvent to efficiently and feasibly produce bio-oil that can be used as biofuel in the transportation sector. To this end, a series of specific objectives were established, which have been met as the project has progressed and whose conclusions are discussed below.

Firstly, after **studying the impact of biomass liquefaction operating parameters on bio-oil yields**, it can be concluded that the bio-oil yield is highly dependent on the operating parameters. Temperature and pressure are some of the most critical factors, especially when operating under supercritical conditions. In order to optimize the performance of the bio-oil, it is vital to know the temperature at which the decomposition process of the biomass is complete without promoting the cracking of molecules producing more gaseous and solid products at the expense of liquids. The other parameters also play an important role in the performance of the process, being evident the variability of results that exists in this process due to the high number of input variables.

Secondly, after trying to **optimize the bio-oil production of the soft pine wood liquefaction using sCO2 as a solvent** it can be concluded that this optimization is essential for maximizing bio-oil yield. Developing a regression model can be an optimal way to know the results before conducting any experiments, thus saving a lot of resources and time. However, the model drafted in this project still requires further study, and a machine learning model could be applied if the data collection is increased, which could provide more accurate results.

Lastly, after **evaluating the technical and economic feasibility of sCO2 as a solvent in the liquefaction process** it can be concluded that this process (sCO2 liquefaction) has a promising future in the world of the transportation sector, as it can be considered as a powerful alternative to fossil fuels. The yields that are being achieved as research progresses give reason to believe that biomass can be considered a renewable and viable energy source for the production of biofuels. However, at the moment this process is at the beginning of a long road of development for which it is still necessary to allocate many more resources and research time. The economic viability at the commercial level cannot yet be considered and for the time being, this method is only under development at the experimental stage.

5.2 RECOMMENDATIONS FOR FUTURE WORK

It is well known that achieving the optimization of all the parameters in this type of process is fundamental in order to make them economically viable and to be able to commercialize their products. For this reason, further development of a more complex and accurate surrogate model may prove to be a significant advance in this optimization, and it is therefore very interesting to continue advancing along these lines in the future.

On the other hand, it would be interesting to try to introduce in the process both the biomass dewatering and the extraction of liquid products using sCO2. These new implementations could improve the efficiency of the process by reducing the amount of time needed to carry out these two steps. Furthermore, it has already been demonstrated how the use of sCO2 can bring great benefits in this type of process, so it would be beneficiail to continue investigating its capabilities.

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ANNEX I

	INDEPENDENT VARIABLES								DEPENDENT VARIBLE	
	Biomass/Reactor capacity ratio	Biomass/Solvent ratio	Temperature (ºC)	Residence time (min)	Heating Rate (ºC/min)	H/C Ratio	O/C Ratio	Moisture content (%)	Bio-oil Yield (%)	Ref
1	40	100	260	30	10	1,72	0,54	5	21,6	[132]
2	30	100	270	30	10	1,59	0,35	4,2	61,35	[133]
3	30	100	280	30	-	1,49	0,35	4,1	17,1	[134]
4	30	100	280	30	10	1,61	0,35	5,2	8	[135]
5	37,5	100	250	1	2	1,7	0,73	0	7,95	[136]
6	37,5	100	280	1	2	1,7	0,73	0	11,9	
7	37,5	100	315	1	2	1,7	0,73	0	14,8	
8	37,5	100	350	1	2	1,7	0,73	0	14,9	
9	37,5	100	250	1	20	1,7	0,73	0	5	
10	37,5	100	280	1	20	1,7	0,73	0	14,9	
11	37,5	100	315	1	20	1,7	0,73	0	23,9	
12	37,5	100	350	1	20	1,7	0,73	0	26,9	
13	50	100	280	45	-	1,36	0,42	-	22,5	[137]
14	50	100	300	45	-	1,36	0,42	-	26,84	
15	50	100	320	45	-	1,36	0,42	-	19,32	
16	50	100	340	45	-	1,36	0,42	-	17,1	
17	50	100	280	45	-	1,46	0,71	-	20,44	
18	50	100	300	45	-	1,46	0,71	-	24,08	
19	50	100	320	45	-	1,46	0,71	-	22,28	
20	50	100	340	45	-	1,46	0,71	-	16,4	
21	50	100	280	45	-	1,20	0,45	-	25,7	
22	50	100	300	45	-	1,20	0,45	-	35,8	

23	50	100	320	45	-	1,20	0,45	-	25,28	
24	50	100	340	45	-	1,20	0,45	-	20,18	
25	53,47	100	200	10	-	1,84	0,63	1,6	7,5	[138]
26	53,47	100	200	20	-	1,84	0,63	1,6	8,2	
27	53,47	100	200	30	-	1,84	0,63	1,6	8,7	
28	53,47	100	200	40	-	1,84	0,63	1,6	10,7	
29	53,47	100	200	50	-	1,84	0,63	1,6	8,9	
30	53,47	100	300	10	-	1,84	0,63	1,6	22,3	
31	53,47	100	300	20	-	1,84	0,63	1,6	25,5	
32	53,47	100	300	30	-	1,84	0,63	1,6	26,1	
33	53,47	100	300	40	-	1,84	0,63	1,6	26,7	
34	53,47	100	300	50	-	1,84	0,63	1,6	25,9	
35	53,47	100	350	10	-	1,84	0,63	1,6	22,3	
36	53,47	100	350	20	-	1,84	0,63	1,6	25,5	
37	53,47	100	350	30	-	1,84	0,63	1,6	26,1	
38	53,47	100	350	40	-	1,84	0,63	1,6	26,7	
39	53,47	100	350	50	-	1,84	0,63	1,6	25,8	
40	53,47	100	400	10	-	1,84	0,63	1,6	24,64	
41	53,47	100	400	20	-	1,84	0,63	1,6	25,35	
42	53,47	100	400	30	-	1,84	0,63	1,6	27,18	
43	53,47	100	400	40	-	1,84	0,63	1,6	27,12	
44	53,47	100	400	50	-	1,84	0,63	1,6	25,51	
45	71,43	100	300	15	-	1,40	0,57		27,15	[139]
46	71,43	100	300	30	-	1,40	0,57		33,49	
47	71,43	100	300	60	-	1,40	0,57		39,67	
48	71,43	100	380	15	-	1,40	0,57		22,6	
49	71,43	100	380	30	-	1,40	0,57		29,43	
50	71,43	100	380	60	-	1,40	0,57		36,42	

51	71,43	100	280	30	-	1,40	0,57		17,78	
52	71,43	100	300	30	-	1,40	0,57		30,47	
53	71,43	100	340	30	-	1,40	0,57		36,82	
54	71,43	100	380	30	-	1,40	0,57		23,49	
55	13,33	40	200	90	7	1,62	0,13	33,08	15,21	[140]
56	13,33	40	225	90	7	1,62	0,13	33,08	14,46	
57	13,33	40	250	90	7	1,62	0,13	33,08	25,15	
58	150	375	320	60	-	1,49	0,57	7	7,9	[141]
59	150	375	320	60	-	1,60	0,64	13,05	14,7	
60	150	375	320	60	-	1,55	0,62	15,1	15,1	
61	150	375	320	60	-	1,58	0,64	4,43	15,8	

ANNEX II

```
% Data
X = [260 30 0.54;
    270 30 0.35;
    280 30 0.35;
    280 30 0.35;
    250 1 0.73;
    280 1 0.73;
    315 1 0.73;
    350 1 0.73;
    250 1 0.73;
    280 1 0.73;
    315 1 0.73;
    350 1 0.73;
    280 45 0.42;
    300 45 0.42;
    320 45 0.42;
    340 45 0.42;
    280 45 0.71;
    300 45 0.71;
    320 45 0.71;
    340 45 0.71;
    280 45 0.45;
    300 45 0.45;
    320 45 0.45;
    340 45 0.45;
    200 10 0.63;
    200 20 0.63;
    200 30 0.63;
    200 40 0.63;
    200 50 0.63;
    300 10 0.63;
    300 20 0.63;
    300 30 0.63;
    300 40 0.63;
    300 50 0.63;
    350 10 0.63;
    350 20 0.63;
    350 30 0.63;
    350 40 0.63;
    350 50 0.63;
    400 10 0.63;
    400 20 0.63;
    400 30 0.63;
    400 40 0.63;
    400 50 0.63;
    300 15 0.57;
```

```
    300 30 0.57;
    300 60 0.57;
    380 15 0.57;
    380 30 0.57;
    380 60 0.57;
    280 30 0.57;
    300 30 0.57;
    340 30 0.57;
    380 60 0.57;
    200 90 0.13;
    225 90 0.13;
    250 90 0.13;
    320 60 0.57;
    320 60 0.64;
    320 60 0.62;
    320 60 0.64];

Y = [21.6; 61.35; 17.1; 8; 7.95; 11.9; 14.8; 14.9; 5; 14.9; 23.9; 26.9; 22.5; 26.84; 19.32; 17.1; 20.44;
24.08; 22.28; 16.4; 25.7; 35.8; 25.28; 20.18; 7.5; 8.2; 8.7; 10.7; 8.9; 22.3; 25.5; 26.1; 26.7; 25.9; 22.3;
25.5; 26.1; 26.7; 25.8; 24.64; 25.35; 27.18; 27.12; 25.51; 27.15; 33.49; 39.67; 22.6; 29.43; 36.42;
17.78; 30.47; 36.82; 23.49; 15.21; 14.46; 25.25; 7.9; 14.7; 15.1; 15.8];

% Standarization dependent variables
X_min = min(X);
X_max = max(X);
X_stand = (X - X_min) ./ (X_max - X_min);

% Standarization independent variables
Y_min = min(Y);
Y_max = max(Y);
Y_stand = (Y - Y_min) ./ (Y_max - Y_min);

% Parameters for cross-validation
K = 5; % Number of partitions for cross validation
degree = 1:5; % Degrees of the polynomial to be considered

% Initialisation of variables to store cross validation results
main_square_error_crossvalidation = zeros(length(degree), K);
% Division of data in training and test set
cross_validation = cvpartition(size(X_stand, 1), 'KFold', K);

% Cross-validation
for k = 1:K
    for i = 1:length(degree)
        % Construction of the polynomial regression model with current degree
        X_poly = [];
        for j = 1:degree(i)
            % Polynomial terms of each independent variable
            for variable = 1:size(X_stand, 2)
```

```
                X_poly = [X_poly, X_stand(:, variable).^j];
            end
            % Terms of interaction
            if j > 1
                for variable1 = 1:size(X_stand, 2)
                    for variable2 = variable1+1:size(X_stand, 2)
                        X_poly = [X_poly, (X_stand(:, variable1).^j) .* (X_stand(:, variable2).^j)];
                    end
                end
            end
        end

        % Training the model on the current training set
        X_train = X_poly(training(cross_validation, k), :);
        Y_train = Y_stand(training(cross_validation, k), :);
        beta = regress(Y_train, X_train);

        % Evaluation of the model in the current test suite
        X_test = X_poly(test(cross_validation, k), :);
        Y_test = Y_stand(test(cross_validation, k), :);
        Y_pred = X_test * beta;

        % Calculation of the root mean square error on the current test set
        main_square_error_crossvalidation(i, k) = mean((Y_test - Y_pred).^2);
    end
end

% Calculation of the root mean square error for each degree of the polynomial
main_square_error_mean = mean(main_square_error_crossvalidation, 2);

% Selection of the best degree of the polynomial
best_degree = degree(find(main_square_error_mean == min(main_square_error_mean), 1));

% Construction of the final model with the best degree of the polynomial
X_poly_final = [];
for j = 1:best_degree
    % Polynomial terms of each independent variable
    for variable = 1:size(X_stand, 2)
        X_poly_final = [X_poly_final, X_stand(:, variable).^j];
    end
    % Terms of interaction
    if j > 1
        for variable1 = 1:size(X_stand, 2)
            for variable2 = variable1+1:size(X_stand, 2)
                X_poly_final = [X_poly_final, (X_stand(:, variable1).^j) .* (X_stand(:, variable2).^j)];
            end
        end
    end
end
```

```
beta_final = regress(Y_stand, X_poly_final);

% Denormalisation of the dependent variable
Y_pred_final = X_poly_final * beta_final;
Y_pred_desnormalized = Y_pred_final * (Y_max - Y_min) + Y_min; % Ajuste de desnormalización
corregido
% Show results
disp('Best degree of the polynomial:');
disp(best_degree);
disp('Final model coefficients:');
disp(beta_final);
disp('Denormalised predictions:');
disp(Y_pred_desnormalized);
```

ANNEX III

ALIGNMENT WITH THE SUSTAINABLE DEVELOPMENT GOALS (SDGs)

The sustainable development goals (SDGs) with which this project is identified are the following:

- ***SDG 7*** *- Affordable and Clean Energy*: The study of conversion of biomass into biocrude bring us closer to a potential pathway with an energy mix that cuts down the use of fossil fuels and improves access to energy that is economical and environmentally friendly.
- ***SDG 9*** *- Industry, Innovation, and Infrastructure*: Optimizing biomass liquefaction processes requires new technology and infrastructure. Through scientific research, the efficiency and viability of these processes are improved, enhancing a more inclusive and sustainable industrialization based on new renewable sources of energy.
- ***SDG 12*** *- Responsible Consumption and Production*: By continuously allocating resources to research on thermochemical conversion processes, maximization of biocrude oil produced from biomass is achieved, what enhances responsible consumption and production patterns on the transportation sector. Also, optimizing these processes helps to achieve sustainable management and efficient use of biomass, reducing waste generation and minimizing the use of resources.
- ***SDG 13*** *- Climate Action*: One of the main motivations of the project is to reduce dependence on fossil fuels and cut the amount of greenhouse gases released into the atmosphere from the transportation sector. Investing resources in research on the production of biocrude oil from biomass is a way to fight against climate change and its impacts by betting on a greater use of renewable energy sources.
- ***SDG 17 -*** *Partnerships for the Goals*: The collaboration between different stakeholders, including educational institutions, the private sector, and government departments is crucial for promoting research and innovation in biomass conversion technologies. Through the establishment of collaborations and knowledge-sharing programs, as the one that has driven the development of this project, the research contributes to the development of means and channels of implementation.