

Optimisation and overview of pine liquefaction process

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Energy Engineering and Management

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Abstract

Climate change, depletion of fossil fuels and booming economy of developing countries lead global society to search for new technologies of sustainable fuels and chemical production. There are several methods of changing the energy mix and making the inevitable energy transition process smoother. Biomass as a net-zero emission feedstock may be used to foster a change in energy systems by producing energy, fuels and biocomponents e.g. bioethanol. Nevertheless, an optimisation of the process is needed. Herein, a non-pressurised and acid-catalysed liquefaction was investigated. The usage of 2-ethylhexanol as a solvent and p-toluenesulfonic acid as a catalyst for lignocellulosic biomass (i.e. pinewood) transformation via acid liquefaction was studied. Additionally, the trial of the method to remove alkylphenolic fraction from residues created after bioliquefaction using trimethylamine, acetic anhydride and diethyloaminopyridin was examined. During the process, high ratio of biomass-to-solvent (1:1) was achieved. Fourier Transform Infrared Spectroscopy confirmed the presence of alkoxy group, aromatic groups and organic acids in the obtained solution.

Keywords: Biomass liquefaction, lignocellulosis, alkylphenolic fraction, deacetylation, acid-catalysed

Resumo

As alterações climáticas, depleção dos combustíveis fósseis e próspera economia dos países em desenvolvimento guia a sociedade global para procurar as novas tecnologias de combustíveis sustentáveis e produção química. Existem vários jeitos para mudar a composição de energia e fazer o inevitável processo de transição de energia mais suave. Biomassa como zero-emissão matéria-prima podia ser usada para nutrir a mudança no sistema de energia através produção da energia, combustíveis e bicomponentes como bioetanol. Contudo, uma optimização deste processo é necessário. Neste documento, a liquefacção com catalisador ácido sem pressão foi investigada. O uso de 2-etil-hexanol como o solvente e p-toluenossulfônico ácido como o catalisador para a transformação de biomassa lignocelulosa (pinho) via liquefacção ácida foi estudada. Adicionalmente, a experiência de processo de alquilfenilo fracção de resíduos criados depois a bioliquefacção usando trimetilamina, anidrido acético e dimetilaminopiridina foi examinada. Durante deste processo, alta proporção da biomassa para o solvente (1:1) foi cumprida. Infravermelho por Transformada de Fourier confirmou a presença de alcoxí grupo, grupos aromáticos e ácidos orgânicos na solução obtida.

Palavra-chaves: liquefacção, lignocelulosa, alquilfenilo fracção, deacitilação, catalisado por ácido

Table of contents

Acknowledgements	ii
Abstract	iv
List of Figures.....	vii
List of Tables.....	viii
Nomenclature.....	viii
1. Introduction.....	1
1.1. Classification of biofuels.....	8
1.2. Types and sources of biomass.....	10
1.3. Bio-refineries	11
1.4. Lignocellulosic biomass – resources and composition.....	13
1.4.1. Overview.....	13
1.4.2. Major components	14
1.4.2.1. Cellulose	14
1.4.2.2. Hemicellulose	14
1.4.2.3. Lignin	15
1.4.2.4. Other components	16
1.4.2.4.1. Acetyl groups.....	16
1.4.2.4.2. Minerals and ash components.	16
1.4.2.4.3. Extractives	17
1.4.2.4.3.1. Volatile materials – terpenoids and terpenes.....	17
1.4.2.4.3.2. Non-volatile resinous extractives e.g. resin acids	17
1.4.2.4.3.3. Phenolic extractives – tannins, flavonoids	17
1.4.2.4.3.4. Soluble carbohydrates and other polar extractives e.g. pectines.....	17
1.4.3. Composition of lignocellulosic materials.....	17
1.5. Pre-treatment processes.....	18
1.6. Conversion of biomass through thermochemical processes	20
1.6.1. Direct combustion	20
1.6.2. Gasification.....	20
1.6.3. Pyrolysis.....	21
1.6.4. Direct liquefaction	21
1.6.5. Acidic liquefaction of biomass.....	22
1.6.6. Energy generated in biomass procession.....	24
1.7. Process used in the experimental part.....	24
2. Materials and methods	28
2.1. Feedstock and apparatus	28

2.1.1.	Biomass and its pre-treatment.....	28
2.1.2.	Solvent.....	28
2.1.3.	Catalyst.....	28
2.1.4.	Apparatus	29
2.2.	Overall process procedure	31
2.2.1.	Process parameters.....	32
2.2.2.	Procedure scheme.....	32
2.2.3.	Equations used	34
2.2.3.1.	Yield of the biomass	34
2.2.3.2.	Mass used for further examination.....	34
2.2.3.3.	Moisture	35
2.2.3.4.	Water for alkyphenolic fraction removal	35
2.2.3.5.	Amount of TEA.....	35
2.2.3.6.	Amount of acetic anhydride.....	35
2.2.3.7.	Amount of DMAP	35
2.2.3.8.	Total mass for alkylphenolic fraction removal treatment.....	35
2.2.3.9.	OH number	35
2.3.	Product analysis.....	36
2.3.1.	OH number – hydroxyl value.....	36
2.3.1.1.	Equipment and reagents	36
2.3.1.2.	Procedure	37
2.3.2.	FTIR analysis	37
2.4.	Other research work.....	38
2.4.1.	AutoCAD representation of the process	38
2.4.2.	Process flow diagram	39
2.5.	Other trials to conduct research	39
2.6.	Non-achieved plans inside the Master Dissertation laboratory work	40
2.7.	Aim of the Master Thesis.....	40
3.	Results and discussion.....	40
3.1.	Moisture	40
3.2.	Pine liquefaction.....	40
3.3.	Viscosity.....	42
3.4.	Alkylphenolic fraction removal idea.....	42
3.5.	OH number	45
3.6.	FTIR results analysis.....	45
4.	Conclusions.....	48

5. Future work and recommendations.....	49
6. References.....	50
Appendix 1 – Process flow diagram of bioliquefaction plant.....	55

List of Figures

Figure 1: World total primary energy supply in Mtoe by fuel (A.) and region (B.) [IEA, 2019].....	2
Figure 2: Total primary energy consumption of world by fuel in Mtoe [3].....	3
Figure 3: Primary energy by source in Mtoe/year [4].....	3
Figure 4: Description of possible scenarios according to World Energy Council [5].....	4
Figure 5: Global CO ₂ emission by fuel (A., in Gt of CO ₂) and by region (B., billions of t of CO ₂)	5
Figure 6: Total Final Consumption in Portugal. Compared values of biofuels and waste to total sum ..	6
Figure 7: Percentage of biofuels and waste to Total Final Consumption [8]	7
Figure 8: Total Primary Energy Supply in 2017 [9]	7
Figure 9: Composition of forest cover in Portugal	8
Figure 10: Classification of biofuel sources by different characteristics according to FAO. [20].....	10
Figure 11: Division of biomass types due to its source and origin. [21].....	11
Figure 12: Possible composition of polymers in lignocellulosic biomass [27]	13
Figure 13: Structure of lignocellulose [28]	14
Figure 14: Cellulose structure [31]	14
Figure 15: Structure of hemicellulose [31].....	15
Figure 16: Structure of lignin monomers: a) Coniferyl b) Sinapyl c) p-Coumaryl alcohols [34]	15
Figure 17 : Representation of exemplary acetyl groups found in lignocellulosic biomass (left is a representation of O-acetyl group and right is a representation of Methyl ester group) [35]	16
Figure 18: Pyrolysis process in stages [51]	21
Figure 19: Flowchart of cork liquefaction and adhesive formulation [57].....	23
Figure 20: Cellulose liquefaction reaction scheme in acid-catalysed liquefaction (solvent - ethylene glycol) [56]	23
Figure 21: Phenolic compounds formation from different lignocellulosic compounds in a range of temperatures [61]	25
Figure 22: Possible repolymeration scheme of biodegraded biomass [62].....	26
Figure 23: Esterification reaction scheme of carboxylic acid [65].....	26
Figure 24: Possible polycondensation reaction scheme proposed by [65].....	27
Figure 25: Supplied bio-oils	28
Figure 26: Biomass used for experimentation purposes	28
Figure 27: Liquefaction process montage used in the experimentation	29
Figure 28: Moisture content assessment apparatus - Blue M, Stabiltherm Gravity Oven OV-18C	30
Figure 29: Viscometer REL CPD 2000	30
Figure 30: Filtration apparatus connected to vacuum pump.....	30
Figure 31: Perkin-Elmer Spectrum Two spectrometer	31
Figure 32: Bath oil Huber CC 304	31
Figure 33: Reactor Selecta 6 L. Coil was put on the top of the reactor.....	31
Figure 34: Scheme representation of conducted process.....	32
Figure 35: Mixture of 5% DMAP in acetic anhydride	34
Figure 36: Biomass-to-solvent ration inside the reactor changes.....	41
Figure 37: Evaporation of solvent and water in the function	41

Figure 38: Sample of a residue treated with alkylphenolic removal treatment	44
Figure 39: Perkin-Elmer screenshot of liquid sample filtrated after TEA treatment	45
Figure 40: Liquid sample after TEA treatment FTIR with marked bonds.	46
Figure 41: Perkin-Elmer screenshot of liquid sample filtrated after direct liquefaction (2-ethylhexanol background).....	46
Figure 42: Liquid sample after direct liquefaction FTIR with marked bonds (2-ethylhexanol background).....	47
Figure 43: Perkin-Elmer screenshot of residues after acetic anhydride and DMAP treatment FTIR results with marked bonds (2-ethylhexanol background)	47
Figure 44: Residues after acetic anhydride and DMAP treatment FTIR results (2-ethylhexanol background).....	48

List of Tables

Table 1: Most important figures regarding energy in Portugal.....	6
Table 2: Acetyl contents in lignocellulose from common woody lignocelluloses [35]	16
Table 3: Chemical composition of different lignocellulosic materials used in the liquefaction [39]	18
Table 4: Biomass pre-treatment methods	18
Table 5: Biochemical composition of pine wood [36]	24
Table 6: Typical OH numbers for polyols [72]	36
Table 7: Chemical composition of different lignocellulosic materials used in the liquefaction [73,74]	37
Table 8: Moisture content of examined samples.....	40
Table 9: Viscosity test for Secil bio-oil.....	42
Table 10: Rotary evaporation results of direct pine liquefaction residues treated with TEA	43
Table 11: Statistics from rotary evaporation after alkylphenolic fraction removal	44
Table 12: Functional groups encountered in samples of bio-oils and residues in FTIR analysis.....	48

Nomenclature

UNCCC - United Nations Climate Change Conference

IEA - international Energy Agency

TFC - Total Final Consumption

ICNF - Instituto da Conservação da Natureza e das Florestas

GMO - Genetically Modified Organism

FAO - Food and Agriculture Organization

EU - European Union

US - United States

FTIR - Fourier Transform Infrared Spectroscopy

DME - Dimethyl ether

2EH - 2-Ethylhexanol

PTS - p-Toluenesulfonic acid

TEA - triethylamine

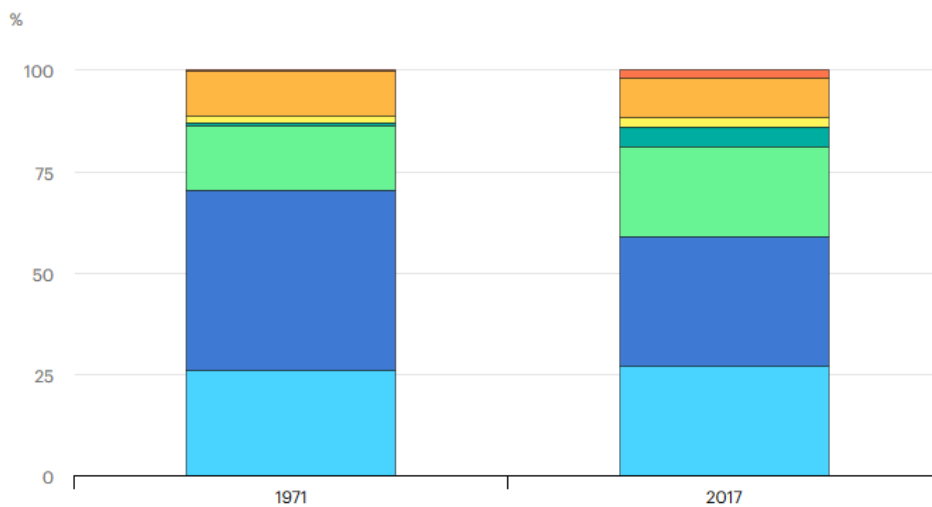
DMAP - 4-Dimethylaminopyridine

THF – tetrahydrofuran

DP – Degree of Polymerization

1. Introduction

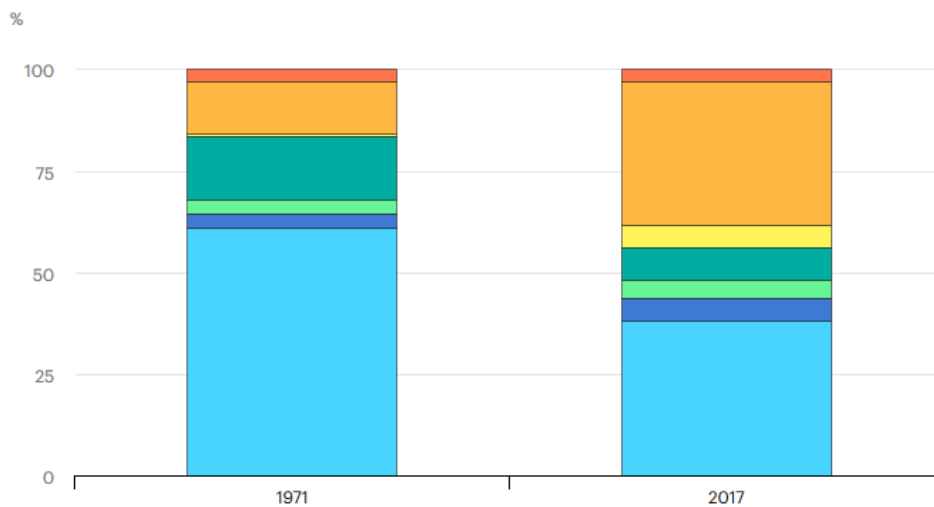
The population of the world as of now is over 7,5 billion people and it is still increasing, especially in developing countries. The increasing population and technological development have made the world to seek new sources of energy. Nevertheless, fossil fuels, has been a base of the industrial revolution and the boost of economies in the 20th century, still get the major part of the energy mix in future energy scenarios for foreseeable future. There is a common consensus among the researchers to search and use the alternative sources of energy in order to halt the climate change caused by anthropogenic factors and to not halt the development of developing countries and the global economy. Global warming is the most detrimental effect influenced by the use of fossil fuels. Paris Agreement 2015 dictates that the governments pursue the long-term goal of keeping the increase in global average temperature below 2 °C in relation to the pre-industrial levels and to aim to limit this increase to 1.5 °C [UNCCC, 2015]. To achieve these goals, it is urgent and inevitable to limit the usage of fossil fuels by accelerating the transition from the aforementioned fuels to renewable energy sources (RES). Figure 1.A. compares the world total energy supply from 1971 and 2017 by fuel type [1] and figure 1.B. – by region [2]. What is worth adding is that the annual supply in year 1971 was 5518 Mtoe and in 2017 – 13973 Mtoe, which is a 253,26% growth in 46 years.



IEA. All Rights Reserved

● Coal ● Oil ● Natural gas ● Nuclear ● Hydro ● Biofuels ● Other renewables

A.



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● OECD
 ● Africa
 ● Non-OECD Americas
 ● Non-OECD Europe and Eurasia
 ● Middle East
 ● Non-OECD Asia
 ● Bunkers

B.

Figure 1: World total primary energy supply in Mtoe by fuel (A.) and region (B.) [IEA, 2019]

In Figure 1 we can notice significant decrease of oil usage along with augmenting of renewables and natural gas share. OECD countries as well as non-OECD countries in Europe and Eurasia lost their shares of energy supply in behalf of, mainly, non-OECD Asia. Coal, natural gas and oil have been the predominant energy sources as shown in Figure 2. What is more, primary energy consumption increases year by year.

Researchers and activists prepared a lot of scenarios showing the possible paths for the global economy fuels usage. A proposal of World Energy Council is shown on Figure 3. The possible scenarios are described in Figure 4. The first scenario from Figure 4, which is depicted on Figure 3, predict share growth in renewables as well as natural gas along with decrease in coal usage as a primary energy source. Scenario called “Unfinished Symphony” projects usage in primary energy source in the same direction as “Modern Jazz”, however, the growth of it is smaller. The last scenario predicts growth in every primary energy source usage. What is worth adding, all of the scenarios claim that in 2040 the amount of energy supply will be bigger than in 2020.

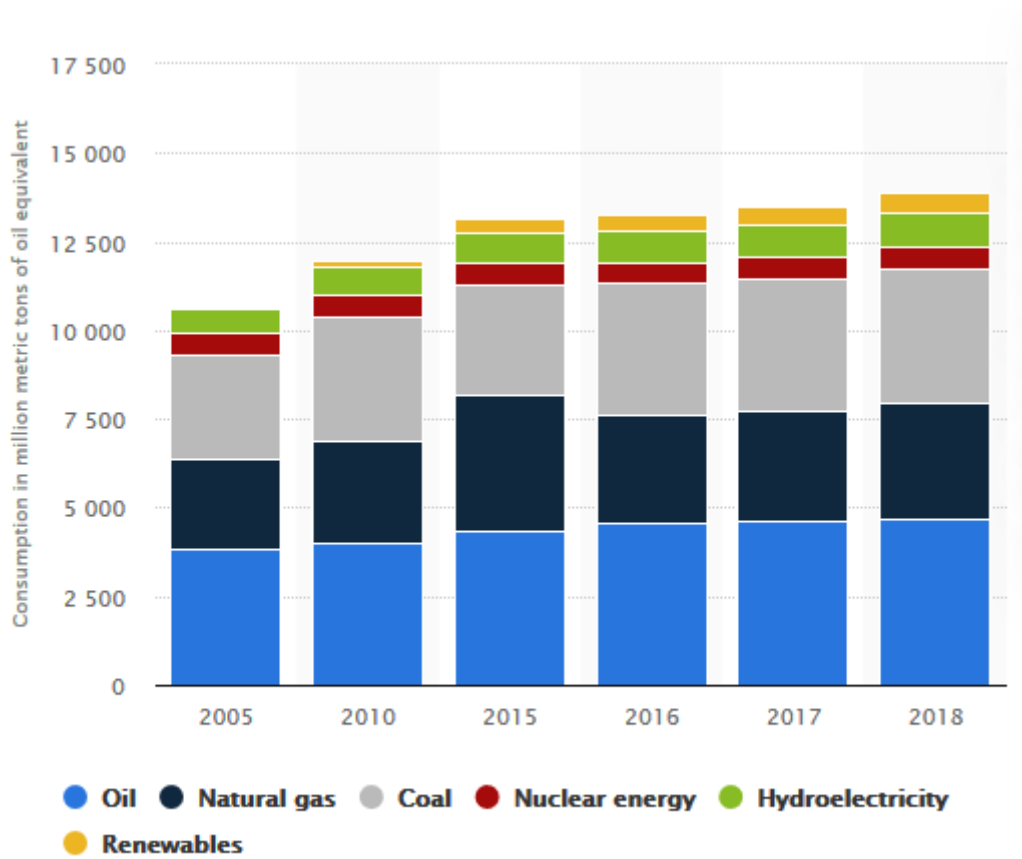


Figure 2: Total primary energy consumption of world by fuel in Mtoe [3]

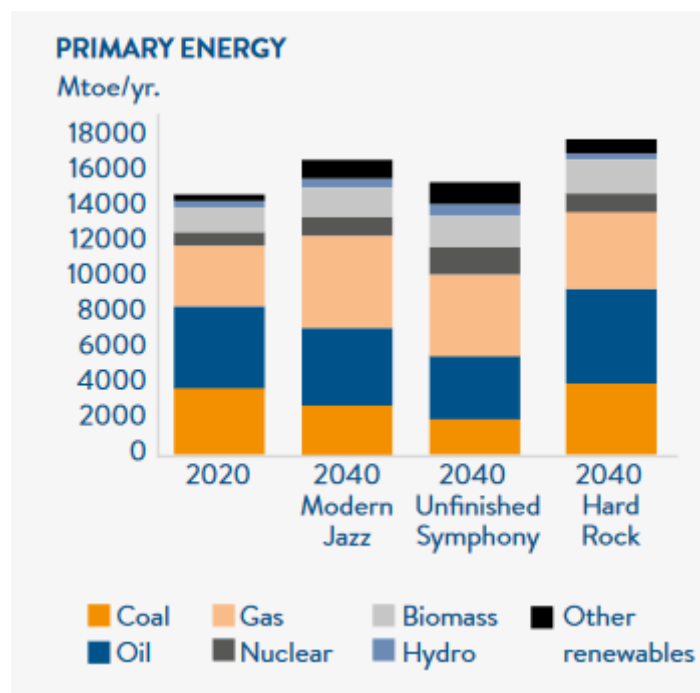


Figure 3: Primary energy by source in Mtoe/year [4]

The 2019 scenarios are summarised as follows:



Modern Jazz. A market-led, digitally disrupted world with faster-paced and more uneven economic growth. Recent signals suggest that this entrepreneurial future might accelerate clean energy access on both global and local scales, whilst presenting new systems integration, cyber security and data privacy challenges.



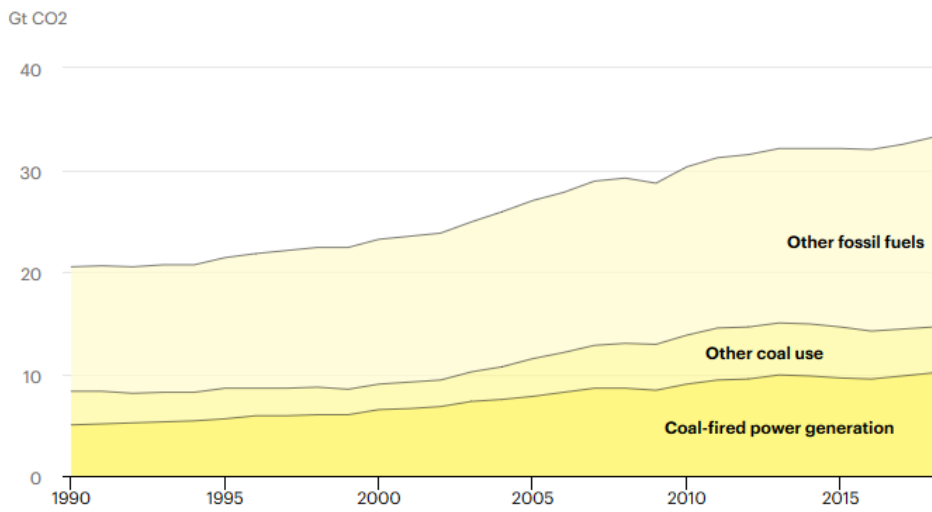
Unfinished Symphony. A strong, coordinated, policy-led world, with long-term planning and united global action to address connected challenges, including inequitable access and affordable decarbonisation. Recent signals suggest increased activism and commitment to addressing climate change at the sub-national level, and an expansion of the focus from climate change mitigation to a broader, socially inclusive and economically affordable sustainable development agenda.



Hard Rock. A fragmented world with inward-looking policies, lower growth and less global cooperation. Recent signals, such as the rise of populist leaders and uncertainty about the outlook for international cooperation, imply that this scenario is also evolving into a story of regionally firmer security foundations rather than total fragmentation and “harder rocks.”

Figure 4: Description of possible scenarios according to World Energy Council [5]

Although the contribution of biomass as a final energy consumption carrier has grown moderately [5], it still is not a great portion of the world energy supply; and without more initiatives in this particular area, it will be hard to redeem the production of energy from coal, lignite, gas or oil using biomass. As an outcome from Figure 5, the huge scale of carbon dioxide emissions comes from fossil fuels compared to other energy sources and by China compared to other countries. Even though the emissions are increasing each year, IEA proposes an optimistic scenario, called Sustainable Development Scenarios (SDS) where the temperature rise is held below 1.8 °C (with 66% probability) and global emissions being less than 10 billion by 2050 and on track to net-zero emission by 2070 [6].

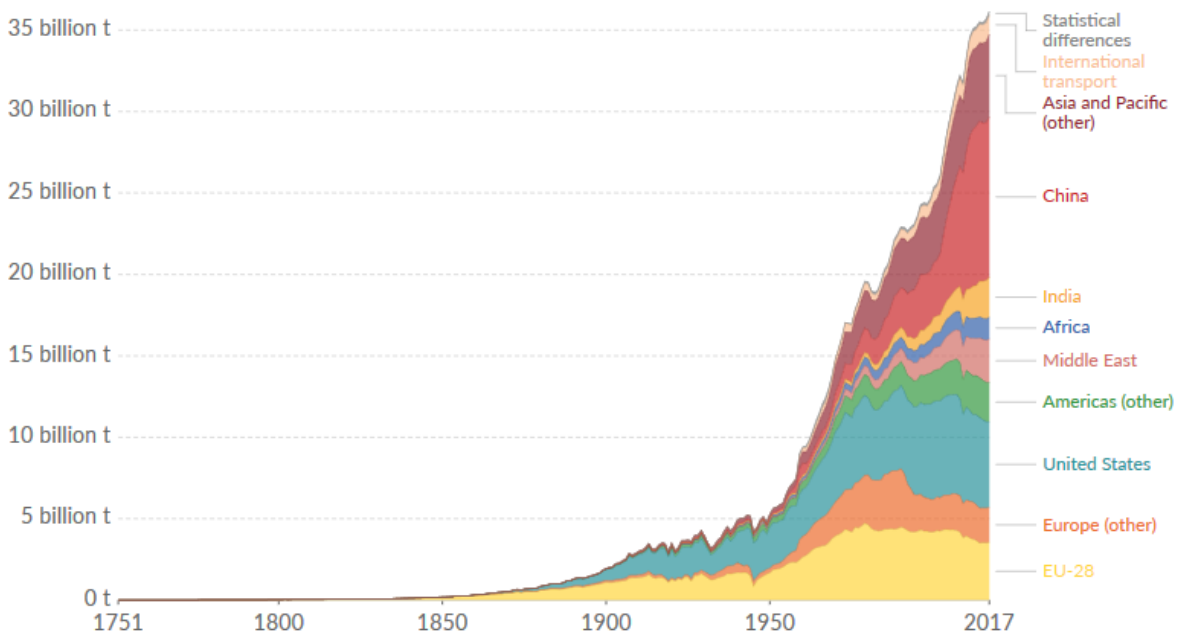


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A.

Annual total CO₂ emissions, by world region, 1751 to 2017

Our World in Data



B.

Figure 5: Global CO₂ emission by fuel (A., in Gt of CO₂) and by region (B., billions of t of CO₂)

As of today, available data indicates the need to adapt solutions such as technologies or fuel sources in order to achieve net zero or negative emission in the long-term future. Thanks to dotation and support programmes, costs of carbon-free renewable energy technologies such as photovoltaics or wind power plants decreased, their intermittency of energy production creates the need to use a stable resource for electricity and fuels generation – biomass. The possibility of utilising locally available biomass and other wastes for energy production purposes is a promising alternative and motivating factor to further explore energy from bio-based materials. Table 1 shows the energy statistics for Portugal and Poland for year 2018 [7].

Table 1: Most important figures regarding energy in Portugal

Country	Energy production (Mtoe)	Net imports (Mtoe)	TPES/capita (toe/capita)	Electricity consumption [TWh]	CO ₂ emissions (Mt of CO ₂)
Poland	62	47	2,8	165,6	309
Portugal	5,841	24,898	2,1	52,05	46

From Figure 6 and 7, it can be concluded that contribution of biomass to total final consumption in Portugal is relatively small. After the period of decline in 2000 and 2005, the percentage of biomass and waste usage now grows steadily. Nevertheless, as depicted in Figure 8, Biomass, Biofuels and energy from waste contributed to less than 15% of Total Primary Energy Supply in 2017.

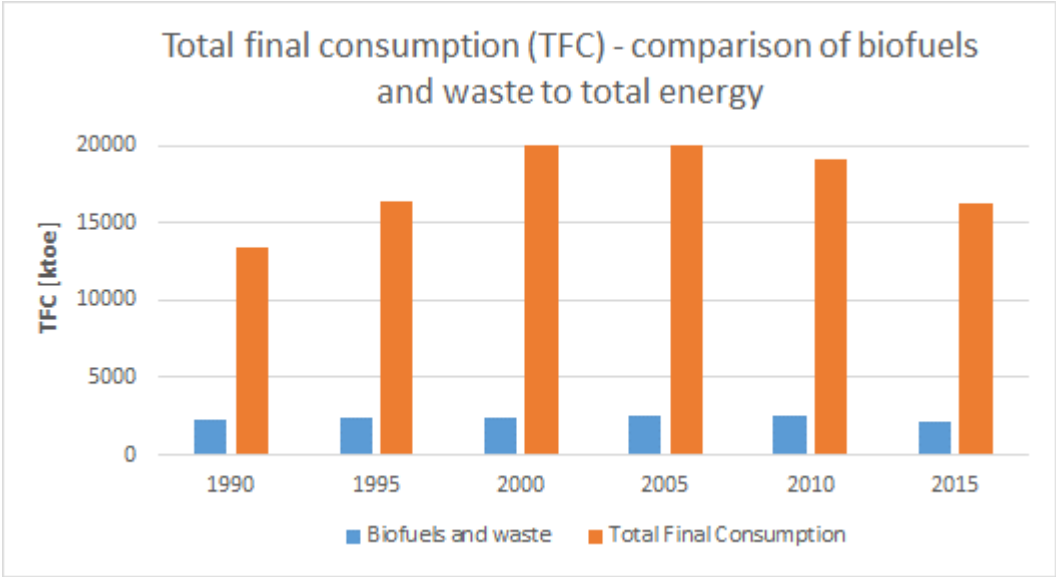


Figure 6: Total Final Consumption in Portugal. Compared values of biofuels and waste to total sum

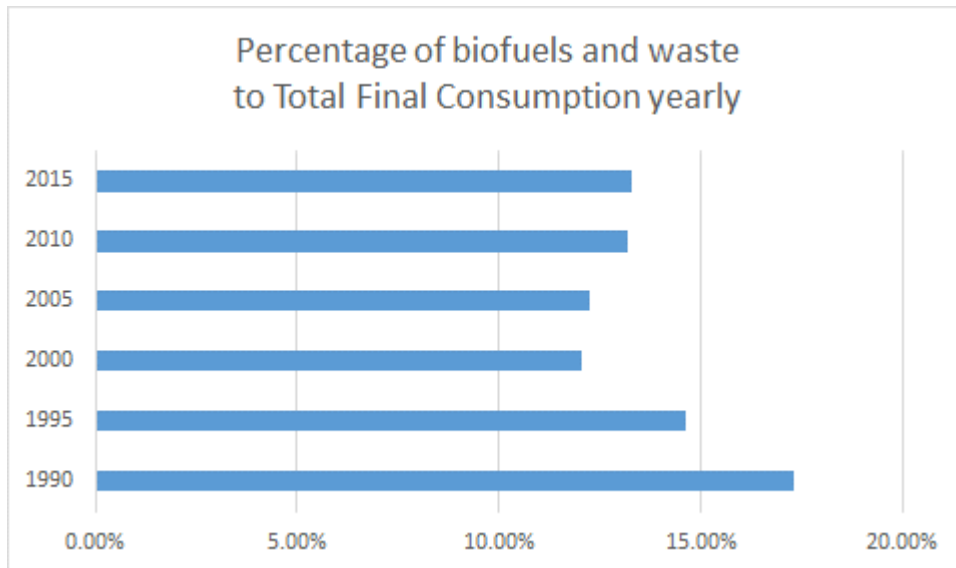


Figure 7: Percentage of biofuels and waste to Total Final Consumption [8]

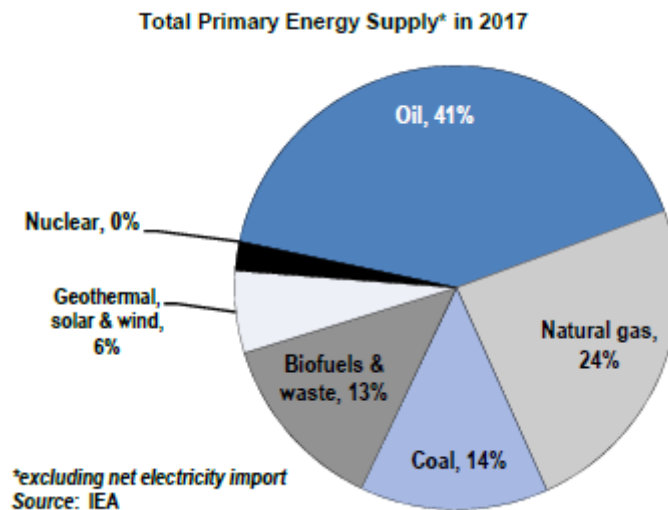


Figure 8: Total Primary Energy Supply in 2017 [9]

Portugal has over 35% of its landmass covered with wooded areas and temporarily deforested areas [10,11]. Due to the variety of forest flora depicted in Figure 9, this country has a great potential in developing energy from forestry residues. This occurs on account of the fact that In Portugal species that are better suited for energy plantations, having such characteristics as: high biomass production in dry weight, good sprouting ability, fast juvenile growth, narrow crowns or large-sized leaves in the upper crown, biomass with high specific energy and quality, adaptability to a wide range of sites, and resistance to biotic and abiotic agents, are grown on larger scale.

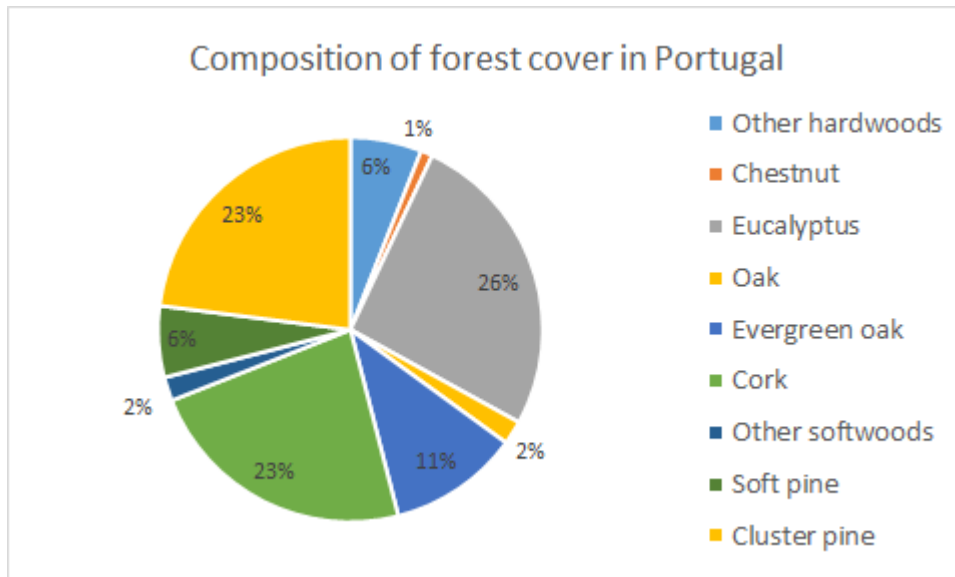


Figure 9: Composition of forest cover in Portugal

Though the wooded area has been more or less consistent throughout many years, quite recently wildfires gained on significance in Portugal. More than 2.5 million hectares of forest cover has been burned due to the aforementioned reason between 1990 and 2012, according to the Institute of Nature and Forest Conservation (ICNF). In June 2017, fire killed 64 people near Pedrógão Grande in Central Portugal in one of the biggest national tragedies of the decade.. During the year 2017, forest fires in Portugal destroyed more than 100000 hectares of forest cover. This puts a big importance on implementation of good forestry management. Establishing a biomass based energy mix and implementation of circular economy in addition to the existing infrastructure could help mitigate this problem and to meet the energy needs of the country. [10,11]

1.1. Classification of biofuels

According to EU legislation [12] biomass is defined as "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste". The most common method of biofuels classification is categorisation into different generations based on their source and production technology.

First-generation biofuels are generated from edible sources and include mainly ethanol and biodiesel. Ethanol is generally produced from the fermentation of C₆ sugars (like glucose) using classical or GMO yeast strains. Only a few different feedstocks, mostly sugarcane or corn, are actually used for the production of first-generation bioethanol. Other more marginal feedstocks include whey, barley, potato wastes, and sugar beets [13].

Second-generation biofuels are produced from non-food crops including waste from food crops, agricultural residues, wood chips and waste cooking oil. This kind of feedstock is the non-edible by-product of food crops. Examples of this generation biofuels would be wheat straw or corn husk. The advantage of using such by-products is that no fertilizer, water or land is needed to produce that kind of feedstock. Even though industry uses some non-edible product to produce animal feed, there is a great amount that could be used for biofuels production [14].

The main component of **third-generation biofuels** are microalgae and microbes. It is currently considered to be a feasible alternative renewable energy resource for biofuel production that could overcome the disadvantages of first and second-generation biofuels. Microalgae can provide several different types of biofuels. This includes methane, biodiesel and bio-hydrogen. There are many advantages for producing biofuel from algae because microalgae can produce from 15 to 300 times more biodiesel than traditional crop on the same area having been used. The harvesting cycle of microalgae is very short and growth rate is very high. Moreover, high quality agricultural land is not required for microalgae biomass production [15].

Fourth-generation uses genetically modified algae to enhance biofuel production. Although genetically modified algae biofuel is a well-known alternative to fossil fuels, the potential environmental and health-related risks are still of great concern due to potential deliberate release of genetically modified algae into the environment. Such release, because of some algae producing toxins, may lead to contamination of human, mammals' and birds' organism. Moreover, horizontal gene transfer is of concern, even though it is a natural mechanism, playing role in evolution [16].

Improving photosynthetic efficiency, increasing light penetration, and reducing photo inhibition are common strategies used in the genetic modification of microalgae [17]. Fourth generation are produced by designer photosynthetic microorganisms to produce photo-biological solar fuels, by combining photovoltaics and microbial fuel production (electro biofuels) or by synthetic cell factories or organelles specially tailored for the production of desired high-value chemicals (whose production is currently based on fossil fuels) and biofuels [18].

However, World Energy Council divides biofuels into two types, which are bioethanol and biodiesel [19]. These are two major biofuel products and they are divided irrespective of their source. The word "biofuel" is often used to refer to either liquid or gaseous biofuels. IEA defines them as 'liquid and gaseous fuels produced from biomass'. However, there are some solid biofuels as well. Therefore, they can also be divided into one of the fourth aforementioned generations. Biofuels are produced in a facility called bio-refinery. It is similar to standard, petroleum refinery, however the feedstock entering the refinery is converted into wide range of products such as fuel, chemicals, plastics, energy, food and feed, taking into account optimisation concept [19].

1.2. Types and sources of biomass

Biomass can be categorised into several types. Food and Agriculture Organisation of the United Nations classified biomass based on the source shown in description of Figure 10.

		woody biomass	herbaceous biomass	biomass from fruits and seeds	others (including mixtures)
		WOODFUELS		AGROFUELS	
Energy crop		- energy forest trees - energy plantation trees	- energy grass - energy whole cereal crops	- energy grain	
By-products*	direct	- thinning by-products - logging by-products	crop production by-products: - straw	- stones, shells, husks	- animal by-products - horticultural by-products - landscape management by-products
	indirect	- wood processing industry by-products - black liquor	- fibre crop processing by-products	- food processing industry by-products	- biosludge - slaughterhouse by-products
End use materials	recovered	- used wood	- used fibre products	- used products of fruits and seeds	MUNICIPAL BY-PRODUCTS - kitchen waste - sewage sludge

Figure 10: Classification of biofuel sources by different characteristics according to FAO. [20]

There is also other classification used by scientists to distinguish different types of biomass from each other. Division, proposed in figure 11, is proposed in Progress in Energy and Combustion Science in 2017 journal:

Biomass type	Examples
Forest products	Wood, logging residues, trees, shrubs and wood residues, sawdust, bark
Biorenewable wastes	Agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes
Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, miscanthus
Aquatic plants	Algae, water weed, water hyacinth, reed and rushes
Food crops	Grains, oil crops
Sugar crops	Sugar cane, sugar beets, molasses, sorghum
Landfill	Hazardous waste, nonhazardous waste, inert waste, liquid waste
Organic wastes	Municipal solid waste, industrial organic wastes, municipal sewage and sludge
Algae	Prokaryotic algae, eukaryotic algae, kelps
Mosses	Bryophyta, polytrichales
Lichens	Crustose lichens, foliose lichens, fruticose lichens

Figure 11: Division of biomass types due to its source and origin. [21]

Another classification was created by the United States Department of Energy.

Dedicated energy crops are non-food crops often grown on marginal non-arable lands grown specifically to harvest biomass. These are further divided into perennial herbaceous crops such as switch grass or elephant grass, and short-rotation woody crops such as hybrid poplar, hybrid willow or sweet gum.

Herbaceous crops are harvested annually after an initial growth period of two to three years while short rotation woody crops are harvested within five to eight years of cultivation. Agricultural crops are crops such as corn or wheat, while agricultural crop residues are parts of crops that are not commercially used for food or food-based products. Aquatic flora such as seaweed or microalgae are also sources of biomass.

Forestry residues, such as pinewood and timber wastes, are the biomass wastes resulting from forest-based industries and management operations. Biomass processing residues such as olive stones or grape seeds, are those which are left after several biomass processing operations. Municipal wastes comprising organic content, such as sewage from residential, commercial and industrial sectors can also be biomass feedstocks. Animal wastes such as poultry wastes, aquaculture wastes, and swine manure sources of biomass as well [22].

1.3. Bio-refineries

IEA proposes the definition of bio-refining: “*Bio-refining is the sustainable processing of biomass into a spectrum of marketable products and energy*”. The bio-refinery concept adopts a wide range of technologies, that are able to separate biomass resources such as wood, corn or algae, into their building blocks, i.e. carbohydrates, proteins or triglycerides, which can be further converted to valuable products - biofuels and chemicals [23].

This concept is analogous to petroleum refinery, which produces multiple fuels and products from crude oil. A forward looking approach is the conversion of greater parts of the global economy and industry into a

sustainable bio-based society using bioenergy, biofuels and bio-based products with bio-refineries as the basis. Such a replacement of oil with biomass requires some breakthrough changes in the production of goods and services. Chemical and biological research will play a leading role in the generation of future industries and new fields combining biological, physical, chemical and technical sciences must be developed. The efficient production of transportation biofuels can be seen as one of the main challenging, but yet rewarding, factors for the future development of bio-refineries. In fact, the transportation sector is growing gradually and the demand for renewable fuels, which can only be, as of today, provided from biomass, grows accordingly. As a consequence, the main challenge for bio-refinery industry development turns out to be the efficient and cost effective production of transportation biofuels. The main bio-based products are today obtained from conversion of biomass to basic products such as starch, oil and cellulose. Other already commercially available bio-based products include adhesives, cleaning compounds, detergents, dielectric fluids, dyes, hydraulic fluids, inks, lubricants, packaging materials, paints and coatings, paper and box board, plastic fillers, polymers, solvents, and sorbents. Most of the existing biofuels and bio-chemicals are currently produced in single production chains and not within a bio-refinery concept, and usually require materials in competition with the food and feed industry, what makes their exploitation limited. In contrast to it, lignocellulosic can be grown on land, which is not suitable for agricultural crops, what creates no competition between it and the food or feed industry [23].

The European Bio-refinery Vision 2030, which is an EU programme that searches possibilities to increase the production of chemical substances from biomass using bio-refineries, defined several aims for year 2030. These ones are:

- 30% of overall chemicals production is bio-based for high added-value chemicals and polymers (specialities and fine chemicals) the proportion is more than 50%, but less than 10% of bulk commodity chemicals are derived from renewable feedstocks.
- 25% of Europe's transport energy needs are supplied by biofuels, with advanced fuels – especially bio-based jet fuels – taking an increasing share.
- The European market for bio-based fibre and polymers such as viscose, carbon fibres, nano-cellulose derivatives and bioplastics will continue to grow rapidly. traditional fibre products such as paper remain 100% bio-based.
- A new generation of bio-based materials and compo-sites produced in bio-refineries allows the production of lightweight, better performing components for industries including automotive and construction.
- 30% of Europe's heat and power generation is going to be from biomass [24].

To expand on this concept, bio-refineries are further classified based on the type of feedstocks used, conversion processes (thermochemical, biochemical, two platform) and the status of technology execution. Thus, bio-refineries are classified into three different types.

Phase I Bio-refinery: This type of bio-refinery utilizes only one feedstock material, has fixed processing capability and produces a single primary product. Examples of this type of bio-refinery are biodiesel from vegetable oil and the production of ethanol from corn grain.

Phase II Bio-refinery: This type is different from Phase I bio-refinery due to its capability of producing various products. Examples of Phase II Bio-refineries are the production of various chemicals from starch and the production of multiple carbohydrate derivatives and bioethanol from cereal grains.

Phase III Bio-refinery: Phase III bio-refineries are advanced bio-refineries being able to utilize various types of feedstocks, processing technologies and produce multiple types of products. These phase can be divided into four bio-refinery classes, being identified as: 1. Whole-crop bio-refinery, 2. Green bio-refinery, 3. Lignocellulosic bio-refinery, 4. Two-platform concept bio-refinery [25].

1.4. Lignocellulosic biomass – resources and composition

1.4.1. Overview

Lignocellulosic biomass such as rice straw, switchgrass etc. is considered as important renewable feedstock and could be utilized to produce biofuels like bioethanol, biodiesel (this process is still in the research phase, with usage of for instance, rice bran [26]), biogas etc. It was estimated that lignocellulosic residues could produce about 80-90 billion gallons of biofuels, which could replace up to 40% of the national US fuel consumption. Composition of lignocellulosic biomass is primarily composed of plant cell wall containing carbohydrates, cellulose, hemicellulose, lignin and heterogeneous phenolic polymers as structural components. Furthermore, its composition differ substantially, dependent on the type and variety of species, weather, soil fertility and fertilization implication. Main components of lignocellulose biomass can be differentiated into hemicellulose (15-35%), cellulose (30-50%), and lignin (10-30) as well as other minor components such as pectines or mineral matter. The potential division of materials inside lignocellulosic material can be seen in Figure 12 and the main components, as well as structure, in Figure 13 [27].

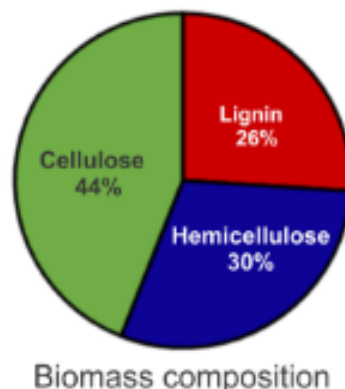


Figure 12: Possible composition of polymers in lignocellulosic biomass. The most common polymer is cellulose, then hemicellulose, then lignin. [27]

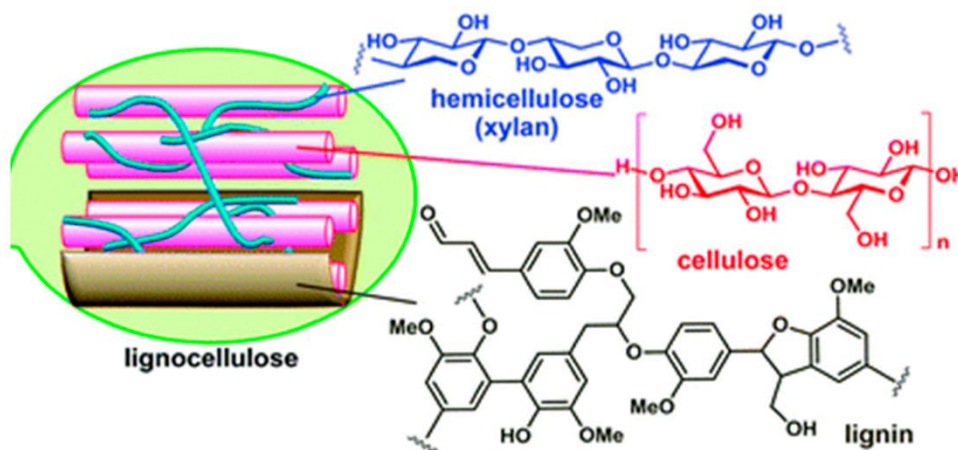


Figure 13: Structure of lignocellulose [28]

1.4.2. Major components

1.4.2.1. Cellulose

Cellulose is the most abundant biopolymer available in nature, because it is one of the major components of the cell walls of majority of the plants. It is a homopolymer of anhydroglucose. Cellulose is the reason of a strengths of plant's cell walls. Moreover, it makes the lignocellulosic matrix very resistant to enzymatic hydrolysis. It owes its structural properties to the fact that it can retain a semi-crystalline state of aggregation even in an aqueous conditions. Thanks to changes in DP (degree of polymerization), which is the number of glucose units in the polymer, we may alter the lignocellulosic biomass' recalcitrance, by causing changes in crystallinity and porosity, however, the exact role is still not clear and needs to be investigated individually [29]. Smaller amounts of cellulose when processed under appropriate conditions, can be converted to a wide variety of derivatives, these can be used in manufacture of few commercial products like cellophane and rayon [30].

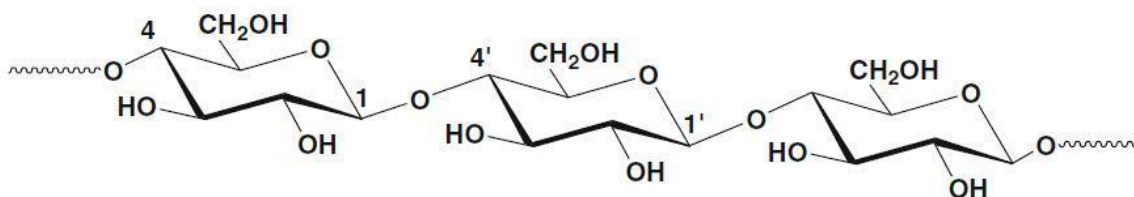


Figure 14: Cellulose structure [31]

1.4.2.2. Hemicellulose

Hemicelluloses are heterogenous group of biopolymers, polysaccharides in plant cell walls. They include xyloglucans, xylans, mannans and glucomannans, and glucans. The DP of it is in the range of 100-200 units, which is much lower in comparison to cellulose. All types of hemicelluloses can be found in the cell walls of all

terrestrial plants, except for glucans and a few other groups. The detailed structure of the hemicelluloses and their availability vary widely between different species and cell types.

The most important biological role of hemicelluloses is to strengthen the cell wall by interaction with cellulose and with lignin, in some cases. Hemicellulose may play this role thanks to its branched structure [32].

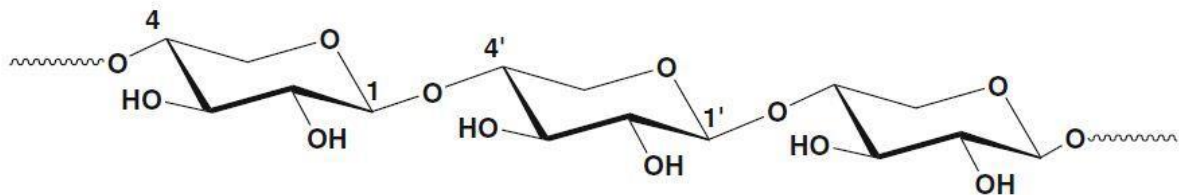


Figure 15: Structure of hemicellulose [31]

1.4.2.3. Lignin

Lignin, making up to 10–30% of lignocellulosic biomass, is the second most abundant natural polymer. Lignin is a very complex, amorphous heteropolymer, insoluble in water and stable in nature, acting as a gluing substance between cellulose and hemicellulose. Lignin is a three-dimensional, highly cross-linked macromolecule composed of three types of phenols, which include: coniferyl, sinapyl, and p-coumaryl alcohols (described in Figure 16) yielding a vast number of functional groups and links. It plays a negative role in the conversion of cellulose, it may physically limit polysaccharide accessibility, blocking the access of the enzymes to cellulose. Therefore, removal of lignin increases the porosity. Lignin substitution potential extends to any product currently sourced from petrochemical substances, because of its chemical and physical properties. The areas in which lignin is applicable include, for instance, emulsifiers, sequestering or fuels to treatments for roadways [33].

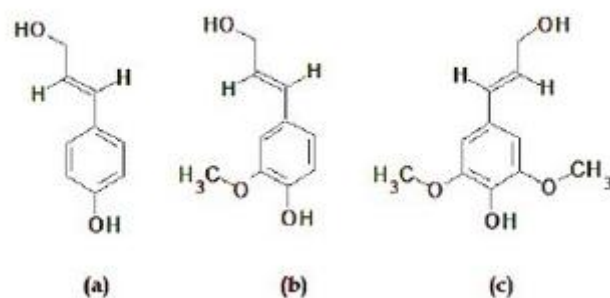


Figure 16: Structure of lignin monomers: a) Coniferyl b) Sinapyl c) p-Coumaryl alcohols [34]

1.4.2.4. Other components

1.4.2.4.1. Acetyl groups

The content of acetyl groups in lignocellulosic biomass affect properties and interactions with other polymers, affecting their possibility of being extracted and solubility. Nevertheless, details of those interactions are still largely obscure. Nowadays, it has been proven that *O*-acetyl groups are a root cause of either enzymatic or chemical de-acetylation, what increases the costs and chemical consumption [35].

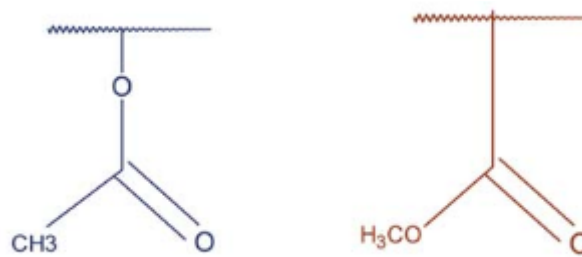


Figure 17 : Representation of exemplary acetyl groups found in lignocellulosic biomass (left is a representation of *O*-acetyl group and right is a representation of Methyl ester group) [35]

Table 2: Acetyl contents in lignocellulose from common woody lignocelluloses [35]

Species	Content in lignocellulosic biomass [%]
Wheat (straw)	2.2
<i>Populus tremuloides</i> Michx. (wood)	3.7
<i>Eucalyptus globulus</i> Labill. (wood)	3.5
<i>Fagus. grandifolia</i> Ehrh. (wood)	3.9
<i>Betula papyrifera</i> Marsh. (wood)	4.4
<i>Picea glauca</i> Moench. (wood)	1.3
<i>Pinus strobus</i> L. (wood)	1.2
<i>Abies balsamea</i> Mill. (wood)	1.5

1.4.2.4.2. Minerals and ash components.

Five most abundant elements in biomass, being a part of ash, which contains mineral content are: silicon, potassium, calcium, sulphur and chlorine, silica having the biggest content. Ash content can make up to 8% of total biomass, for instance, in *Miscanthus*. In case of lignocellulosic biomass' incineration in boilers, it has to be removed and disposed, because of the possible slag formation opportunity, which enhances costs [36].

1.4.2.4.3. Extractives

They are substances removed from lignocellulose cell walls by extraction with natural solvents. They are deposited after cell wall formation and are not considered the structural component of cell walls. Because of diversity of extractives, no generalized procedures for isolation and determination of individual compounds is established. They can be classified as follows [37]:

1.4.2.4.3.1. Volatile materials – terpenoids and terpenes

These are acyclic and cyclic hydrocarbons. They are used in fine chemical, polymer, epoxy and resin industries [38].

1.4.2.4.3.2. Non-volatile resinous extractives e.g. resin acids

The “resins” are a name for a collection of lipophilic extractives soluble in non-polar organic solvents, but not in water. The most abundant example of those are abietic acid and pimaric acid [39].

1.4.2.4.3.3. Phenolic extractives – tannins, flavonoids

Flavonoids are substances having a tricyclic carbon skeleton and are important source of antioxidants [38]. Tannins, on the other hand, are thought to interfere with lignin determinations, because of their insolubility in acids. They, as well, may act as inhibitors of specific enzymes.

1.4.2.4.3.4. Soluble carbohydrates and other polar extractives e.g. pectines

Heterogeneous, polymers that fill in the cellulose–hemicellulose matrix and accumulate in between cells, providing adhesion. They are water-soluble, having a high content of methylated and acidic sugars. They can chelate calcium and form gels. Abundant in waste residues, such as sugar beet pulp or apple pomace, which may be used as feedstocks for biofuel production [40].

1.4.3. Composition of lignocellulosic materials

Composition of lignocellulosic materials can vary mainly from its source. The table with different chemical compositions of biomass various types is presented in Table 3. The conclusion are the following: biomass, which has high content of lignin may require more concentration of enzymes to actively influence cellulose. Nevertheless, lignin may be beneficial to improve biomass’ compatibility with thermoplastic, which together with flame-retardant effect makes it a decent building material. What is more, extractives are the most important in creating essences, therefore grapevine cane may be the most useful for that purpose. Moreover, such biomass as rice straw or date seed may cause problems, when burned in boilers, because of slag formation [41].

Table 3: Chemical composition of different lignocellulosic materials used in the liquefaction [39]

Lignocellulosic material	Chemical composition				
	Cellulose	Hemicellulose	Lignin	Extractives	Ash
Bagasse	49,2	21.7-25.78	19.54-20.1	1.28	1.55-2.38
Rice straw	30.3-38.48	19.8-31.36	6.42-12.8	N/D	7.8-15.6
Cornstalk	42.43	25.75	21.73	3.27	5.80
Wheat straw	40.5-55	15-29.9	20-30	N/D	9.8-9.97
Olive stone	34	25	25	N/D	1
Grapevine cane	50.98	15.32	18.92	13.81	1.88
Date seed	20	55	23	N/D	11
Hazelnut seedcoat	23.4	12.4	41.9	19.6	1.4
Pine	44-46.4	8.8-26	29-29.4	N/D	N/D
Populus	47.6-49.9	27.4-28.7	18.1-19.2	N/D	N/D

1.5. Pre-treatment processes

The presence of lignin and hemicelluloses hinders the efficiency of biomass conversion to useful fuels and materials, because of its barrier functionality. Therefore, pre-treatment is often needed to change the physical and chemical properties of lignocellulosic biomass in order to facilitate the conversion processes. Those processes can be classified in one of five categories.

Table 4 represents the most popular pre-treatment processes and methods along with their advantages and disadvantages.

Table 4: Biomass pre-treatment methods

Name of the pre-treatment process	Chemical	Mechanical/physical	Physico-chemical	Thermochemical	Biological
Overview	It has become one of the most promising methods for improving the biodegradability	This processes convert biomass particles into smaller pieces e.g. fine powder conducting physical changes [43]	They are of importance in dissolving hemicellulose, alteration of lignin structure and improving	Processes relying on heat and chemical catalyst to synthesize useful energy [45]	These methods are mostly associated with fungi action, capable of

	ty of cellulose due to lignin and/or hemicellulose removal. Extensively investigated to be used in pulp and paper industry [42]		accessibility for enzymes. [42]		producing enzymes to degrade lignin, hemicellulose and polyphenols in biomass [42]
Examples of methods	Organic solvents usage, oxidative delignification, ionic liquids, wet oxidations, alkaline/acidic pre-treatment [42]	Milling, chipping, grinding, irradiation [44]	Steam/Ammonia fibre/CO ₂ explosion [38]	Torrefaction [39]	Fungal pre-treatment, Enzymatic hydrolysis, aeration [46]
Advantages	<ul style="list-style-type: none"> • Hydrolyse lignin and/or hemicellulose to sugars • Some methods increase accessible surface area [42] 	<ul style="list-style-type: none"> • Increase the accessible surface area • Increase pore sizes of lignocelluloses • Decrease the crystallinity • Decrease the DP of cellulose 	<ul style="list-style-type: none"> • Improvement of accessibility of the cellulose for hydrolytic enzymes • Increased surface area of biomass • Reduction of cellulose crystallinity • Do not produce excessive amount of inhibitors for downstream processes [42] 	<ul style="list-style-type: none"> • High efficiency • Decent versatility • Wide range of biomass type feedstock may be used [45] 	<ul style="list-style-type: none"> • Can be conducted in low temperatures • Do not require any chemicals • Low energy consumption [46]
Disadvantages	<ul style="list-style-type: none"> • Some methods usage may result in formation of furfurals or 	<ul style="list-style-type: none"> • Energy inefficient [42] 	<ul style="list-style-type: none"> • Energy inefficient • Expensive 	<ul style="list-style-type: none"> • More reactive ashes may be composed 	<ul style="list-style-type: none"> • Very low rate of hydrolysis • Degradation of lignin happens to

	inhibitory compounds <ul style="list-style-type: none"> • Corrosive • Expensive • Some of the methods e.g. alkaline pre-treatment require long residence time [46] 				certain extent [42]
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1.6. Conversion of biomass through thermochemical processes

1.6.1. Direct combustion

The objective of this process is to produce thermal energy and the electricity, possibly in cogeneration.

Combustion processes involve various reactions, which can be classified as devolatilisation and combustions of carbon generated in the process.

During the devolatilisation phase, a mixture of volatile gases is created, such as carbon monoxide, hydrogen, simultaneously with biomass drying. Moreover, devolatilisation causes reactions of decarboxylation and dehydration to happen. Aforementioned gases are then oxidised in the process of combustion, which generates even more energy. The process can be conducted with different raw materials such as residues from forestry and animal residues [47].

However, some pollutants are also liberated during the process such as carbon dioxide, nitrogen oxides and sulphur dioxide. What is more, such problems as raw biomass elevated level of humidity, low energy density, low calorific value causes the pre-treatment process to gain on importance, what may lead as well to cost increase of the whole operation [48].

1.6.2. Gasification

The abovementioned process is based on conducting pyrolysis or thermal cracking under anoxic conditions to biomass as raw material. It is an energy conversion process including a group of complex chemical reactions that large organic molecules degrade into carbon monoxide, methane and hydrogen and other flammable gases in accordance with chemical bonding theory. With temperature increase, biomass goes through dehydration, volatilization and decomposition. Eventually, the produced gases are used for central gas supply and power generation [49]. Currently, biomass gasification is used to produce gas rich in hydrogen through partial oxidation. The quality of final product gas from gasification process varies and depends upon the gasification agent, gasification reactor, residence time and temperature. Oxygen, air and steam are most

frequently used gasification agents. The use of steam as a gasification agent has several advantages over other gasification agents due to air dilution of the product gas final composition, while oxygen makes the process more costly. The main process in the biomass gasification are biomass drying, tar forming and gas releasing. Additionally, biomass gasification is also a valuable technology to produce valuable fuels via Fischer-Tropsch synthesis [50].

1.6.3. Pyrolysis

Pyrolysis process is characterised by solid fuel thermal degradation, involving breaking of C-C and C-O bonds through decarbonylation and decarboxylation. Pyrolysis requires temperatures rising even to 550 °C in neutral atmosphere. Pyrolysis can be achieved by the complete absence of the oxidising agent or by using the oxygen ration below stoichiometric. The products formed during pyrolysis are coal fines, gases, acid extract, and bio-oil. All of them have high calorific value, and can be used further, for instance in chemical industry. Pyrolysis is not only part of the combustion and gasification processes, but the first stage of both of mentioned processes as well.

Figure 18 shows the detailed mechanism of the pyrolysis process. Firstly, feedstock components are decomposed. Then, cracking and condensation takes place that finally lead to obtaining 3 valuable, mentioned in this paragraph, products. [51]

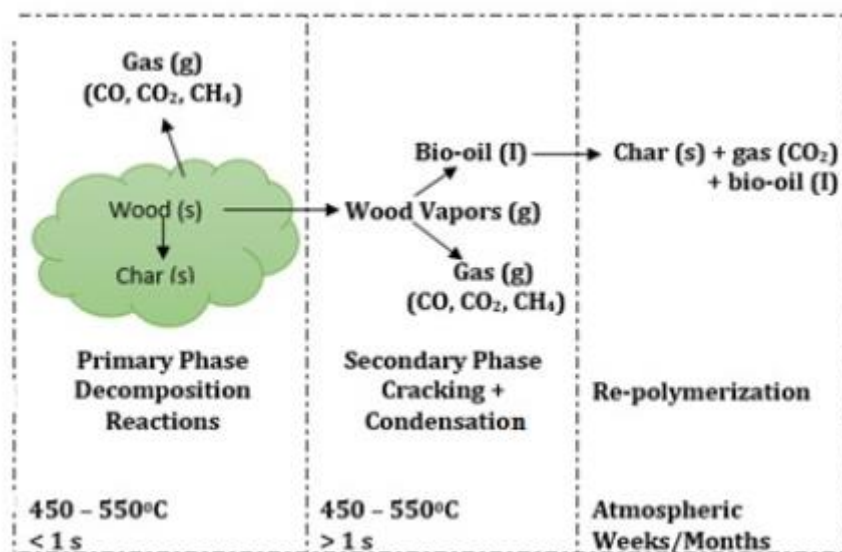


Figure 18: Pyrolysis process in stages [51]

1.6.4. Direct liquefaction

Direct liquefaction is a thermal process of decomposing and hydrogenation which converts biomass into the fuel in a form of oil. Process is conducted in high pressure, up to 25 MPa and temperatures up to 500 °C. The basic reaction mechanisms can be described as depolymerization of biomass followed by biomass

monomers' decomposition by cleavage, dehydration, decarboxylation, and afterwards deamination and reactive fragments recombination [52]. With the disposal of oxygen coming from biomass, secondary products such as water or carbon dioxide are also produced. The process is mainly based on two phenomena:

- Hydrolysis – this process takes role in breaking polysaccharides to sugar monomers [53]
- Solvolysis – dissolution of hemicellulose and lignin due to organic solvent usage [54]

The process is applicable with different types of biomass, including highly moist biomass, even up to 50% [55]. The parameters, that condition the yield of the obtained oil at the end of the process are: temperature, pressure, residential time and concentration of solvent and catalyst.

Nevertheless, direct liquefaction, create some problems, such as increased oxygen content in final product, what hinders the usage of final product as a substitute to gasoline or diesel oil. The interest in this process is driven by promising calorific values of bio-oil produced. Therefore, the process of poly-oils productions has developed, which utilises solvents such as poly-hydric alcohols and phenols. The process can occur in ambient pressure and lower temperature than aforementioned ones. However, this processes were not studied so widely yet [59]. There exist great opportunities for increasing the amount of studies on this subject, that may cause poly-oils produced to be applied in a fuel industry or as wood adhesives.

1.6.5. Acidic liquefaction of biomass

Acidic liquefaction, which was examined in this Master Thesis, is a brand new process among all the biomass processing methods. Thanks to usage of polyhydric alcohols such as 2-ethylhexanol along with acid based catalyst such as p-toluenosulphonic acid, this process can be used to produce polyols and adhesives. As mentioned, the process is quite unstudied yet, but researchers such as prof. Rui Galhano dos Santos or prof. João Bordado examine such processes in their daily work.

The mechanism of the process is similar to the one analysed in [56]. In early stages of reaction glucosides are formed and afterwards , these glucosides subsequently decompose. Cellulose liquefaction in an acidic, non-aqueous medium seem to be analogous to hydrolysis. According to [56] cellulose degradation begins with glycosidic oxygen protonation, followed by formation of carbonium ion and glycosidic bond disunity. After the this bond is broken, cellulose depolymerisation may occur.

Below, in Figures 19 and 20, you may find the flowchart of the acidic liquefaction process along with adhesive formulation and cellulose liquefaction reaction scheme.

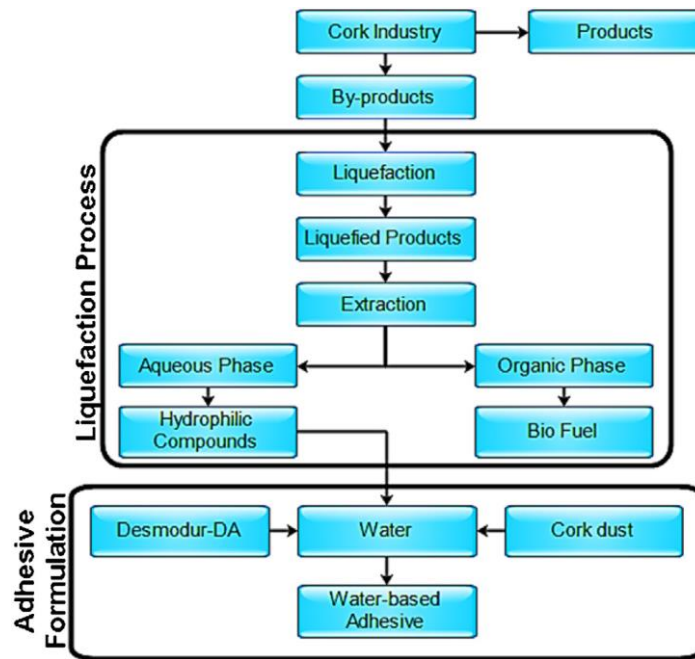


Figure 19: Flowchart of cork liquefaction and adhesive formulation [57]

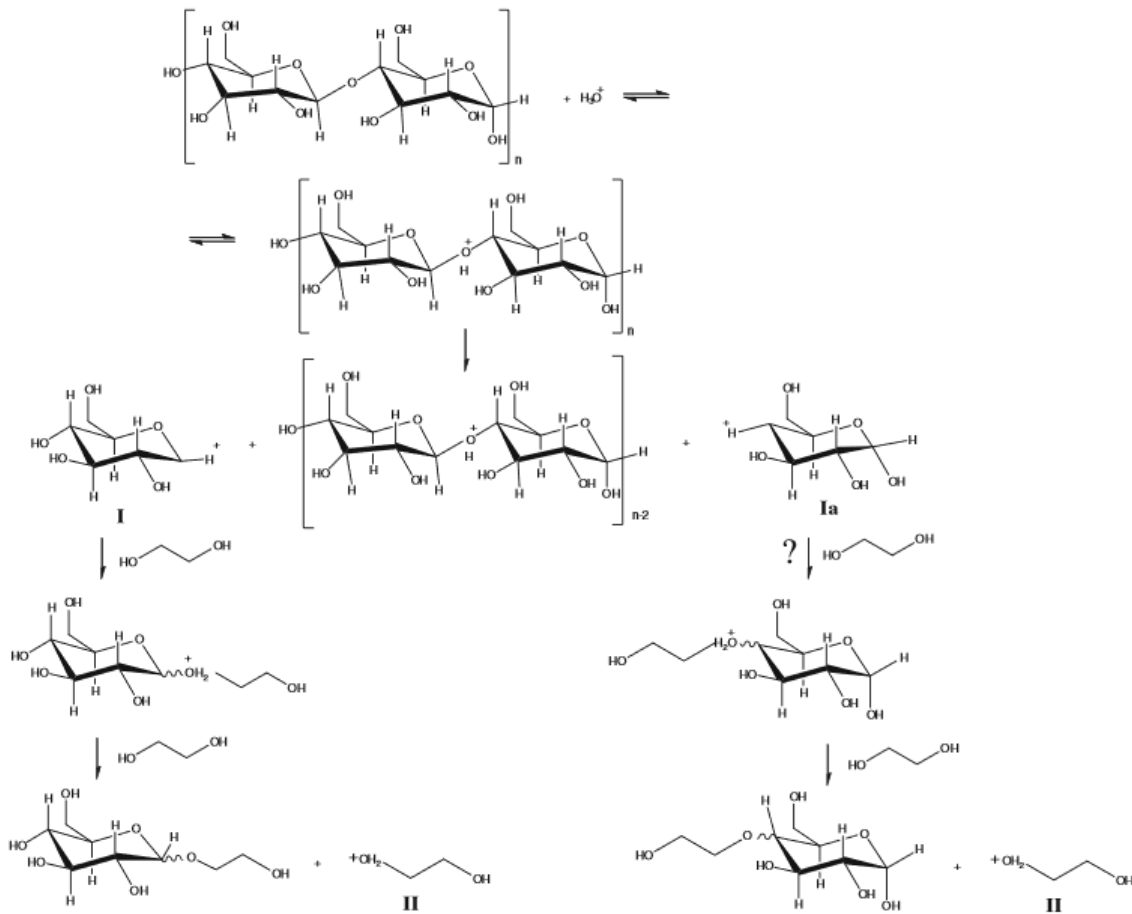


Figure 20: Cellulose liquefaction reaction scheme in acid-catalyzed liquefaction (solvent - ethylene glycol) [56]

1.6.6. Energy generated in biomass procession

During the process of fuels and other chemicals production from biomass, vast quantities of heat and vapours are produced, which may then be used to generate electricity. Some products obtained in the process, such as syngas, can also be used for energy production purposes.

Comparing to the fossil fuels, electric energy generation from biomass is advantageous due to lower price of raw feedstock, secure supply of the materials because of its abundance, low costs of transport the material because of its ability to be gathered from massive quantity of places and neutral carbon dioxide emissions, according to, for instance, European Commission [58]. The range of advantages causes prompts biomass to be a valuable source of bio-fuels, once generated heat and vapours are the secondary products of the reactions. Cogeneration of heat and energy from biomass is a concept known in many industries.

1.7. Process used in the experimental part

In the process of direct liquefaction mostly pine wood was used, though some experiments were conducted using spruce wood. Table 5 represents the chemical composition of pine wood according to [36].

Table 5: Biochemical composition of pine wood [36]

Constituent [%]	Scots pine (<i>Pinus sylvestris</i>)
Cellulose	40
Hemicellulose	28.5
- <i>Glucomannan</i>	16.0
<i>Glucuronoxylan</i>	8.9
<i>Other polysaccharides</i>	3.6
Lignin	27.7
Total extractives	3.5

Liquefaction of lignocellulosic materials involves degradation of polymers into minor polymers or monomers, followed by reactions with solvent.

During liquefaction process, one encounter the presence of big amount of different chemical compounds which react and, in a way, compete with each other for the reaction with the solvent. Some of those reactions are the condensation reactions, which compete with reactions of liquefaction. There is also a part of solid biomass, growing with each biomass addition to the reactor, that creates solid residues, which are, naturally, decrease the possible yield of the liquefaction process. Therefore, it is quintessential to control various parameters of the process such as temperature, pressure, biomass additions to the reactor and ratio between biomass and solvent to maximize the effectiveness of the process.

It was concluded, that usage of acidic catalyst, creating acidic conditions in the reactor, can be favourable

to liquefaction processes of the lignin and cellulose at the cost of condensation.

It was concluded that the step determining the wood liquefaction was the depolymerisation of cellulose.

This may suggest, that the condensation reaction occurred because of the mutual reaction among depolymerized cellulose and degraded aromatic derivatives from lignin part of the biomass [59].

Moreover, it was discovered that amorphous lignocellulosic structures can be broken more easily into monomers or minor polymers than crystalline structure of cellulose [60].

In case of amorphous structures of lignin and hemicellulose, in acidic-catalysed liquefaction temperatures such as 150 °C, structures break into smaller parts, for instance, into oligosaccharides. Solvent used is of importance in the reaction as well, due to the fact, that it determines the products obtained at the end of the process.

The reason why cellulose is harder to obtain monomers of, because of the higher temperature being required, is that it has carbon-carbon bonds, which are harder to break in catalysed reaction than carbon-oxygen bonds, found in lignin.

In Figure 21 there is presented a scheme explaining different temperatures of polymers transformation.

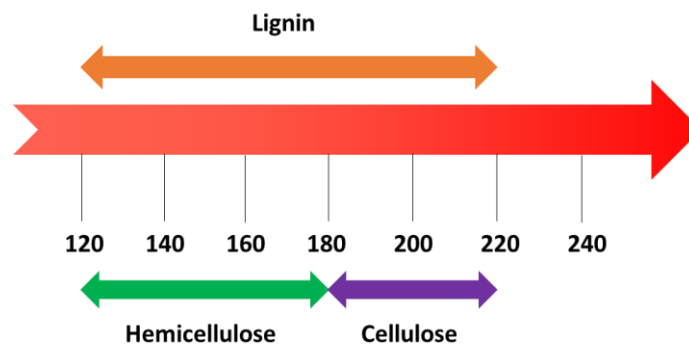


Figure 21: Phenolic compounds formation from different lignocellulosic compounds in a range of temperatures [61]

On the whole bioliquefaction brings several reactions, that occur inside the designed reactor, the main being:

- **Biomass degradation** – In the case of liquefaction, macromolecule compounds in biomass are degraded into small molecules with or without catalyst in the aqueous medium or using organic solvent. Thus, obtained small molecules are unstable and reactive and can repolymerize into oily products with a wide range of molecular weight distribution [62].

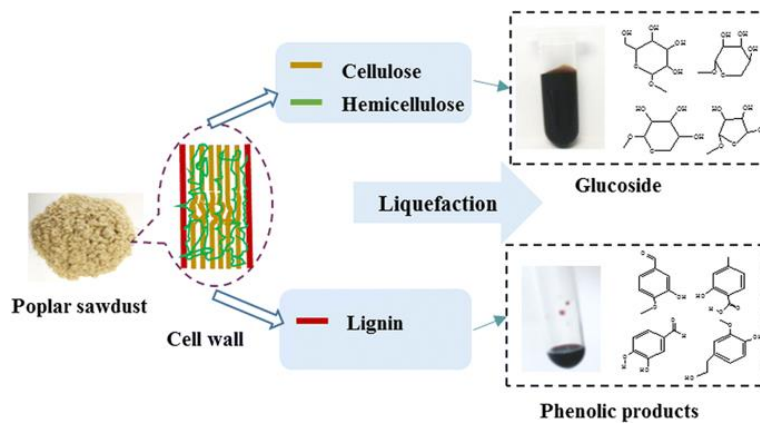


Figure 22: Possible repolymeration scheme of biodegraded biomass [62]

- Esterification** - At atmospheric condition, esterification is a reversible reaction limited by the low equilibrium conversion and slow reaction rate, and has recently been performed with excess alcohol to shift the equilibrium conversion. Heterogeneous or homogeneous acid catalysts are used to achieve acceptable reaction rates. The conventional acid-catalyzed process has been extensively developed; but it suffers from problems associated with the generation of side reactions, corrosion of equipment, expensive purification procedures, long reaction times and discharge of acidic wastes. Various attempts on esterification of carboxylic acids with ethanol have previously addressed important issues concerning product distribution, catalyst activity, and kinetics of acid-catalyzed esterification at lower reaction temperatures, but kinetics of uncatalyzed esterification at elevated reaction temperatures are still very limited. In Figure x there is presented a scheme of carboxylic acid esterification, which is a possible derivative of biomass having been degraded by bioliquefaction [63].

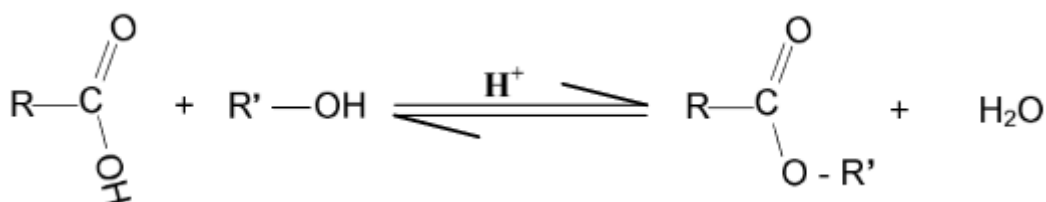


Figure 23: Esterification reaction scheme of carboxylic acid [65]

- Polycondensation** – it is simply stage of residue content rising as a function of time. The formation of residues is due to the condensation between depolymerized cellulose and aromatic derivatives of lignin. The condensation reactions can be mitigated by optimizing the liquefaction parameters (such as temperature and time, selection of acid catalyst and its concentration, and the solvent-to-biomass weight ratio) [64].

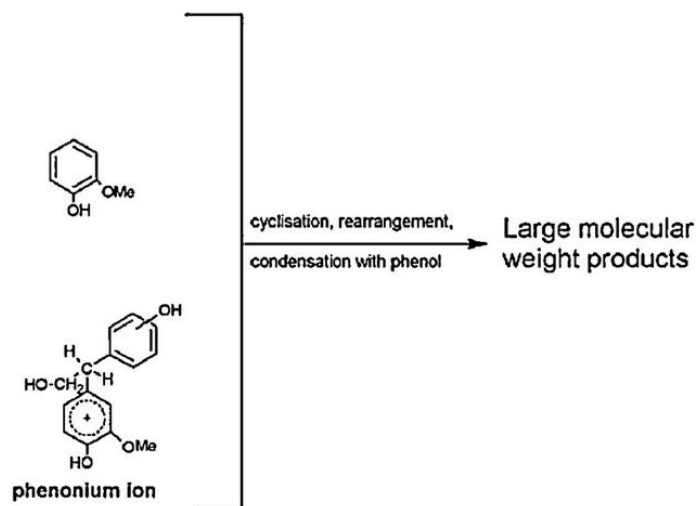


Figure 24: Possible polycondensation reaction scheme proposed by [65]

Even though, the acidic liquefaction process with usage of polyhydric solvent is not yet fully discovered, some researchers bring promising data regarding it.

According to [66] the optimal temperature to conduct acid-catalyzed liquefaction is 160°C. Optimal residence time to acquire the highest yield of liquefied product is about 25 minutes for potato peel and 60 minutes for sweet potato peel. After that, the solid residue content starts to increase and tars and humins content appears. The highest conversion yield was 85% for sweet potato peel and 93% for sweet potato peel.

What is more, [67] checked the possible conversion of *Eucalyptus globulus* in different temperatures (120°C, 150°C and 180°C) and times (20,85,150,185 minutes). The highest conversion yield was achieved in 150°C for a sample residue time being 150 minutes. The increase in temperatures resulted in the higher reaction rates and faster decomposition of sugars.

[56], on the other hand, checked possibilities of wood pulp cellulose liquefaction in ethylene glycol. The achieved yield of cellulose liquefaction was between 72 and 98,9%. The lower molar mass cellulose chains with the higher number of, so called, reducing ends (the free anomeric carbon that is able to reduce another compound), were liquefied and then lesser amounts of residual cellulose were obtained.

The group of [68] compared the usage of different polyhydric alcohols (½ ratio of: glycerol/Diethylene glycol (DEG) or 2-ethylhexanol/diethylene glycol (DEG)) containing a 3% or 1.5% of catalyst, which were sulfuric acid, p-Toluenesulfonic acid and Praseodymium(III) trifluoromethanesulfonate used for cork liquefaction. The conversion rate was the highest using 3% p-Toluenesulfonic acid along with glycerol/DEG (96,6%) and using 3% p-Toluenesulfonic acid along with 2/DEG (96,6%) and p-Toluenesulfonic acid with 2-ethylhexanol/DEG, which conversion rate was 94,5%. The reaction mixture was heated up to 160°C and then controlled.

2. Materials and methods

2.1. Feedstock and apparatus

2.1.1. Biomass and its pre-treatment

For the needs of this Thesis, Versele Laga pine wood chips were used as a biomass feedstock. Material used was crushed, but not milled, due to inability of milling and grinding such big portions of the material on IST. Biomass used in experiment was pre-treated with bio-oil coming from Secil, that can be seen on Figure 26, which is a cement production company. This process was based on pouring portions of aforementioned bio-oil onto the surface of raw biomass as a substitute of pure solvent, which is more expensive than Secil-derived bio-oil. Declared composition was: derived from pine wood, less than 5% of 2EH, less than 2% of ethylene glycol, and 0,4% of acidic catalyst. The left container is a mixture of 70% bio-oil and 30% water, the right one is pure bio-oil, having declared composition.



Figure 26: Biomass used for experimentation purposes



Figure 25: Supplied bio-oils

2.1.2. Solvent

Solvent used during the time of the experiment was 2-ethylhexanol. It has a high boiling point (~ 190 °C), low volatility solvent for fats, waxes, insecticides and dyes. It is a colourless liquid soluble in organic solvents. It is primarily used to manufacture low volatility esters such as and as a key ingredient for manufacturing plasticizers, lubricants and other chemical products [69]. This was the only solvent having been used in the experimental process.

2.1.3. Catalyst

Catalyst used in the process was p-Toluenesulfonic acid (PTS). As mentioned before, acidic catalysts allow for a better performance in direct liquefaction of lignocellulosic materials. It is a non-oxidizing organic acid, white needle or powder crystals, soluble in water, alcohols, ethers and other polar solvents. It is widely used as catalyst agent in the synthesis of pharmaceuticals, pesticides, polymerization stabilizer and organic synthesis, paint intermediates and resin curing agent [70].

Catalyst was added at the beginning of the experiment, as 3% of the total solvent. Then, catalyst constituted as a 3% of every biomass mass in further biomass additions. Used PTS acid was in a form of crystals, that needed to be crushed before adding into the reactor to enable better liquefaction performance and avoid burning the catalyst if it was located next to the heating mantle surface.

2.1.4. Apparatus

Equipment and necessary materials for the research were:

- Agitation motor:
 - Company: Heidolph
 - Model: RZR 2102 control
 - Power: 140 [W]
- Metal agitator
- Heating mantle:
 - Company: J.P. Selecta
 - Power: 410 [W]
- Controller with thermostat:
 - Company: Honeywell
- 2 [L] glass reactor
- O-ring, a closure between the reactor and the lid
- Lid with 4 inserts, 29/32 size
- Thermocouple:
 - Type: J
 - Temperature range: $-40\div 350$ [°C]
- Glass adapters for different inserts
- Dean-Stark apparatus 1 [L] volume
- Condenser
- Caoutchouk blockers of fume evaporations from other inserts that Dean-Stark
- Funnels
- Teflon tape
- Moisture content assessment appliance:
 - Company: Blue M, Stabiltherm

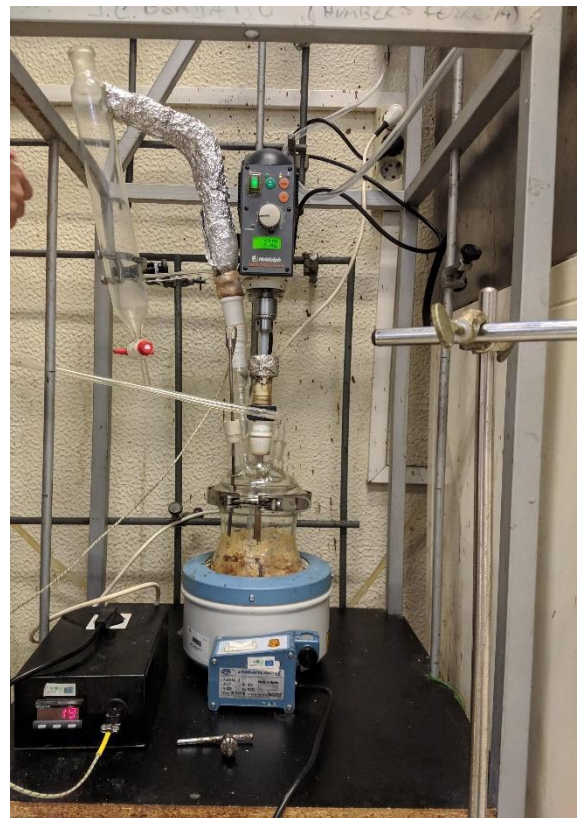


Figure 27: Liquefaction process montage used in the experimentation

- Type: Gravity Oven OV-18C
- Filter paper for filtration process
- Vacuum pump:
 - Company: Ilmvac GmbH
 - Model: OV-18C
- Viscometer:
 - Company: REL
 - Model: CPD 2000 Digital Cone and Plate
 - Range: 0 to 20 Poise [P]
- Rotary evaporator:
 - Company: VWR IKA
 - Model: R 10 control
- Oli bath:
 - Company: Huber
 - Model: CC 304
- Laboratory glass for measurement and containment purposes
- Metal tools such as screwdriver or clamps
- Spectrometer:
 - Company: Perkin Elmer
 - Model: Spectrum Two



Figure 28: Moisture content assessment apparatus - Blue M, Stabiltherm Gravity Oven OV-18C



Figure 30: Filtration apparatus connected to vacuum pump



Figure 29: Viscometer REL CPD 2000



Figure 31: Perkin-Elmer Spectrum Two spectrometer



Figure 33: Reactor Selecta 6 L. Coil was put on the top of the reactor



Figure 32: Bath oil Huber CC 304

2.2. Overall process procedure

Standard procedure, which is a sequence of events, links and conditions having been determined, is described in this subparagraph.

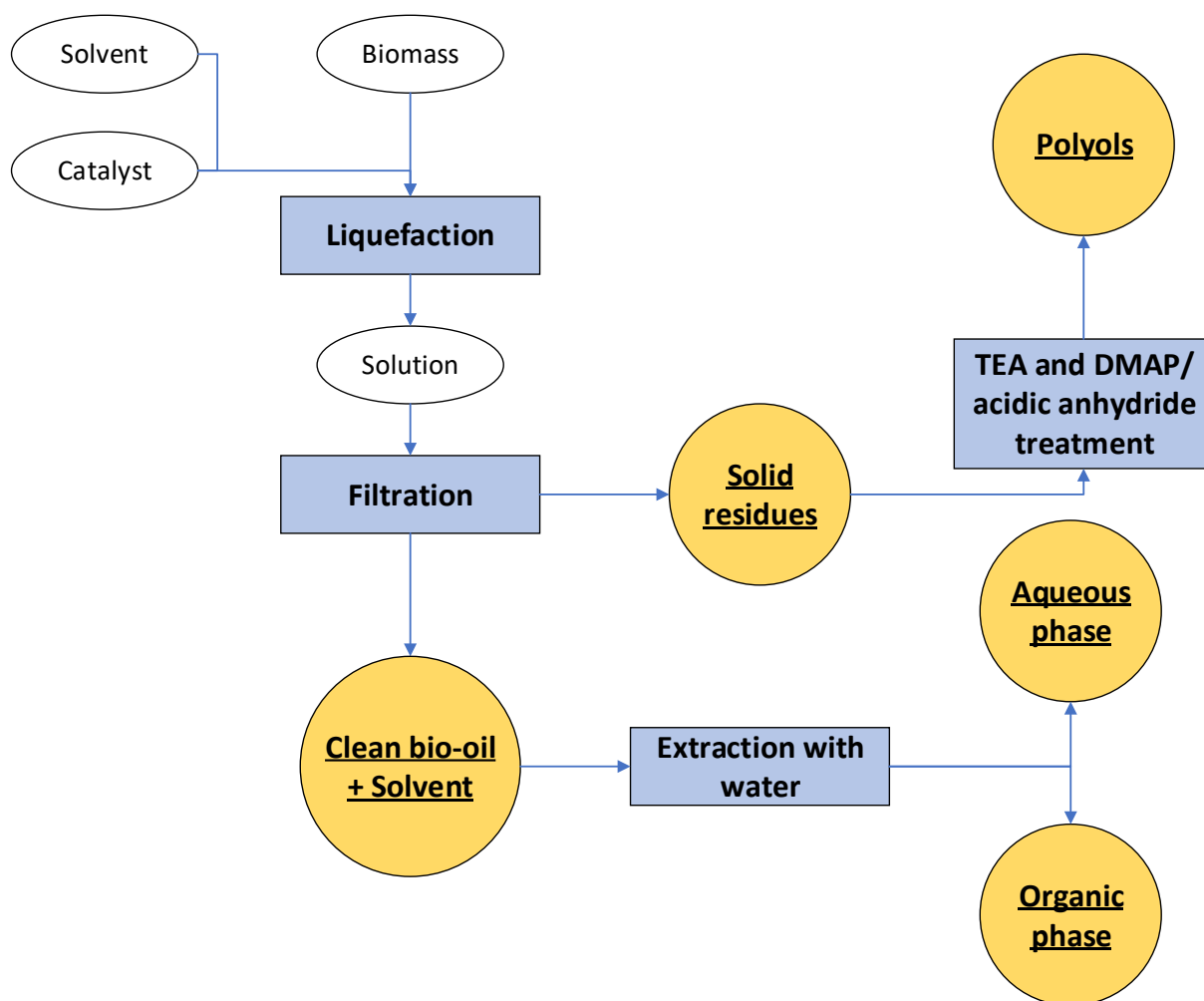


Figure 34: Scheme representation of conducted process

2.2.1. Process parameters

Process parameters were:

- Time of bioliquefaction procedure: 120 [min]
- Set reaction temperature - 160 [°C]. This temperature allow water to evaporate through Dean-Stark apparatus and majority of 2EH to stay inside the reactor.
- Pressure – ambient
- Rotary evaporation parametres:
 - Pressure: 90 [mbar]
 - Radial velocity: 100 [rpm]

2.2.2. Procedure scheme

The procedure was conducted as follows:

- A. Biomass moisture was assessed with usage of two methods:
 - a. Following ISO 18134-1:2015. Description of the procedure:
 - i. A sample of biomass is put onto the glass lid and weighted.
 - ii. Sample is put into the oven for 24 hours, which set temperature was $110\text{ [}^{\circ}\text{C]} \pm 5\text{ [}^{\circ}\text{C]}$.
 - iii. After this time, the sample is put out of the oven and weighted again.
 - b. Blue M, Stabiltherm Gravity Oven OV-18C check
- B. Biomass, solvent and catalyst were inserted into the reactor. The initial composition inside the reactor was: initial ratio of biomass to solvent was 1:5, with 3% of added catalyst, calculated from biomass mass. Such ratio caused the biomass to be dunked in solvent for better agitation in the beginning of the process, when the mixture was not heated to the set reaction temperature level.
- C. Apparatus was assembled:
 - a. Clamps were used to close the reactor
 - b. Inserts were plugged with following equipment
 - i. Agitator
 - ii. Dean-Stark apparatus
 - iii. Thermocouple connected to controller, which was connected to heating mantle
 - iv. Nitrogen flow pipe
- D. Controller was turned on, having been set on set temperature
- E. Temperature rose until met the set condition. Fluctuations of $\sim 10\text{ [}^{\circ}\text{C]}$ were noticed.
- F. Bio-liquefaction is in process for 120 [min]
- G. Dean-Stark apparatus is cleared from evaporated water and 2EH:
 - a. Water is measured
 - b. 2EH is measured and poured back to the reactor, using nitrogen flow pipe input.
- H. Biomass and PTS (as 3% of biomass content) are added to the reactor.
- I. Points [E,F,G] are in loop until the agitator cannot move the content inside the reactor
- J. After bio-liquefaction finish, reactor needed to cool down.
- K. After cooling to room temperature, biomass was moved to the empty container and then filtrated
- L. Solid residues were subjected to the viscosity test. Procedure was as follows:
 - a. Sample was put onto the metal plate at the base of the viscometer in order to completely cover aforementioned plate.
 - b. The handle was put in downright position and the setting the spindle speed on full
- M. Solid residues were subjected to trial of alkylphenolic fraction removal and glycosides hydrolysis in order to break hydrogen bonds, decrease the viscosity and, if possible increase the calorific value. In order to do that, the procedure was as follows:
 - a. Water was added to the residues. The amount of water was equal to 50% of the residues mass obtained from direct liquefaction process
 - b. TEA was added to basify the solution

- i. The amount of TEA depended on pH measurement
- ii. The ideal pH was supposed to be between 8 and 9. To check pH level, litmus paper was used.
- c. Solution was heated in 60 [°C] for 3 hours
- d. Solution was filtrated using paper filter and vacuum pump.
- e. Treated Residues were moved to rotary evaporator to dry under vacuum conditions for 2 [h] in 60 [°C].
- f. Mixture of acetic anhydride and DMAP was added to the residues coming from rotary evaporator. Amounts used:
 - i. Acetic anhydride: 10% (m/m) of biomass used
 - ii. DMAP: 0,5% (m/m) of biomass used
- g. Solution residues in ambient temperature for at least 12 [h].
- h. After that period of time, solution was be heated in 40 [°C] during 4 [h].
- i. Then the solution was put in the rotary for another 4 [h].



Figure 35: Mixture of 5% DMAP in acetic anhydride

2.2.3. Equations used

2.2.3.1. Yield of the biomass

$$Yield = \frac{\text{Mass of solid residue at the end of the experiment}}{\sum \text{Biomass mass from additions}} \times 100 [\%] \quad (1)$$

2.2.3.2. Mass used for further examination

$$m_{total} = m_{biomass,total} + m_{solvent,total} + m_{catalyst,total} - m_{unscraped\ mass\ from\ the\ reactor\ walls} - \sum m_{evaporated\ water} \text{ [g]} \quad (2)$$

2.2.3.3. Moisture

$$Moisture = 1 - \frac{m_{final}}{m_{initial}} \times 100 \text{ [%]} \quad (3),$$

,where:

$m_{initial}$ – biomass mass before drying

m_{final} – biomass mass after drying

2.2.3.4. Water for alkyphenolic fraction removal

$$m_{water} = \frac{m_{biomass,final\ from\ direct\ liquefaction}}{2} \text{ [g]} \quad (4)$$

2.2.3.5. Amount of TEA

$$n_{PTS} = \frac{m_{PTS}}{M_{PTS}} \text{ [mol]} \quad (5)$$

$$m_{TEA} = n_{PTS} \times M_{TEA} \text{ [g]} \quad (6)$$

2.2.3.6. Amount of acetic anhydride

$$m_{acetic\ anhydride} = 0,1 \times m_{biomass,used} \text{ [g]} \quad (7)$$

2.2.3.7. Amount of DMAP

$$m_{DMAP} = 0,05 \times m_{biomass,used} \text{ [g]} \quad (8)$$

2.2.3.8. Total mass for alkyphenolic fraction removal treatment

$$m_{total} = m_{biomass,used} + m_{acetic\ anhydride} + m_{DMAP} \text{ [g]} \quad (9)$$

2.2.3.9. OH number

$$OH\ number = \frac{C \times m_{KOH} \times (V_{white\ sample} - V_{sample})}{m_{sample}} \quad (10),$$

where:

C – is the concentration of the KOH solution, which is 0,5 [mol/L]

m_{KOH} – is the molecular mass of the KOH, which is 56,1 [g/mol]

$V_{\text{white sample}}$ – white sample volume [ml]

V_{sample} – examined sample volume [ml]

m_{sample} – examined sample mass [g]

2.3. Product analysis

2.3.1. OH number – hydroxyl value

The hydroxyl value of a substance is the amount, in milligrams, of potassium hydroxide required to neutralize any acid when combined by acylation in 1 g of the substance under examination [71].

The value is important because it helps determine the stoichiometry of a system for example in polyurethanes. The number of reactive hydroxyl groups on the polyol directly impacts the quantity of urethane linkages, which greatly influences the physical properties of the final polyurethane product, by changing the size and flexibility of its molecular structure. The value may also be used to calculate equivalent weight and if the functionality is known, also the molecular weight also [72]. Table 6 shows typical OH numbers for polyols, having different structure.

Table 6: Typical OH numbers for polyols [72]

Type	Polyether	Polyether	Polyether	Polyester
Structure	Propoxylated propylene glycol	Ethoxylated propoxylated trimethylpropane	Propoxylated glycerol	Ester of adipic acid with diethylene glycol and a small amount off trimethylol propane
OH number	53-59	33-37	53-59	57-63

2.3.1.1. Equipment and reagents

Following equipment and chemicals were used:

- Sample of residual material from liquefaction process
- 2 pipettes, 10 cm³ volume each
- Pipette, 2 cm³ volume

- THF
- pH indicator
- 1% solution of thymolphthalein in THF
- Ethanol solution of 0,5 N of KOH
- Distilled water
- 4-n, n-dimethylaminopyridin

2.3.1.2. Procedure

The procedure was as follows:

- In laboratory glass one should add between 1 and 2 g of sample
- Add from 40 to 50 ml of THF to the laboratory glass.
- Pour 10 ml of 1 % mass solution of 4-n, n-dimethylaminopyridin in THF to the laboratory glass.
- Put the magnetic capsule inside the solution
- Put the sample on an magnetic agitation desk for 10 minutes
- Add 2 ml of distilled water
- Put the sample back to agitate for 30 minutes
- Add a few drops of thymophtalein, as an indicator
- After taking the sample back from agitation, titrate it with 0,5 N solution of KOH until it changes colour.

The same procedure as mentioned above was done, without point [A], which was called a white sample.

2.3.2. FTIR analysis

FTIR technology allows scientists to identify certain functional groups. This method is also beneficial in analysis lignocellulosic materials. Table 7 presents typical values for raw material polymers, that are found in biomass materials.

Table 7: Chemical composition of different lignocellulosic materials used in the liquefaction [73,74]

Lignocellulosic component of empty fruit bunch fibers	Functional groups	Wavenumber [cm ⁻¹]
<i>Cellulose</i>	C-H deformation	1375
	C ₁ O vibration in syringyl derivatives	1330/1320
	C-O-C vibration	1169/1158
	C-O stretching	1048

<i>Hemicellulose</i>	Unconjugated C=O	1738-1734
	C-H deformation	1375
	C-O-C vibration	1168/1158
	C-O stretching	1048
<i>Lignin</i>	Aromatic skeletal	1505/1511
	C-H deformation	1462
	Guaiacyl ring breathing	1268
	C-O stretching	1244

Fourier transform infrared (FTIR) spectroscopy analysis identifies chemical bonds by using an infrared spectrum that is absorbed by the material. Spectroscopy is a powerful non-destructive technique using an electromagnetic radiation interaction effect in order to determine the atomic or molecular structure and the energy level of the substance [75].

FTIR equipment used for the need of this Dissertation was Perkin-Elmer Spectrum Two FTIR spectrometer. Spectra were displayed in the specially designed software made for Perkin-Elmer, allowing to determine the presence of specific chemical groups of the tested samples. Apparatus is presented on Figure 31. The absorption spectrum is primarily determined by the atomic and molecular composition of the material. The frequencies will also be dependent on interaction between molecules and crystal structures in solids. FTIR analysis were conducted for samples of sugars obtained after the filtration of bio-oil into the aqueous and organic phase, biomass residues and biomass residue after experiment leading to removal of alkylphenolic fraction.

The databases used to identify the chemical groups in samples and determine the possible substances in FTIR analysis are listed as [76], [77], [78] and [79]. The programme used to better determine labels was Spectragryph, which is an open-license software. Database was provided by Sigma Aldrich and Chemistry LibreText websites.

FTIR samples, screenshots in Figure 33-36 were examined on the base surface being 2EH. Calibration on 2EH enabled to eliminate this compound from FTIR down-peaks, which also create up-peaks.

2.4. Other research work

2.4.1. AutoCAD representation of the process

Due to the initial interest of Respol Resinas S.A. company, a process was designed using AutoCAD 2D software. The process was designed to help engineers from aforementioned company in order to facilitate their work creating detailed engineering of newly build facility in Fundão Municipality, Portugal. The new bio-oil factory would produce much more bio-oil than the existing one in Leiria, Portugal.

Appendix with bioliquefaction process industrial sketch, which can be found as an attachment submitted to the Thesis, presents the possible process of bioliquefaction in the new factory.

2.4.2. Process flow diagram

Besides 2D representation of the discussed process, process flow diagram was created in VISIO Professional programme. It contains a detailed, visual representation of all the equipment needed for the process and flow of materials.

Appendix 1, which can be found at the end of this Thesis, presents the process flow diagram of bioliquefaction in the new factory.

2.5. Other trials to conduct research

In order to conduct experiment for the bigger scale, a larger, 6 L reactor of Selecta company, which is depicted on the Figure 32 was used to conduct the experiments on bigger scale. The reactor used coil with oil heating system, therefore it was assumed that the carbonisation will not have such a big impact on the experiment in case of the heating mantle system.

The oil was supplied by the Huber CC 304 oil pump and bath, which is presented on Figure 33. The task was to make the oil circulate within a coil and set the oil temperature on 180 – 200 °C in order to compensate thermal losses in the pipes filled with oil. The system was additionally supported thermally with a heating electric belt. Pipes and the reactor with heating belt were covered with aluminium foil as the insulation.

Nevertheless due to several issues with the system such as:

- Maximum coil immersion was equal to 40% of the height of the coil. That cause problems with conducting the heat inside the viscous liquid, consisting of biomass, 2EH and PTS acid. Due to this fact burning the biomass next to the coil occurred,
- Shaft of the agitator needed to be put inside the coil surface from the top of the reactor. Due to the significant difference between the coil diameter and the diameter of the reactor, agitator was unable to effectively stir the biomass all over the reactor, even at border conditions of the motor, constantly causing overload of the motor,
- Due to the excessive temperature, it was often for a hot oil to claw its way out of the pipes, especially in the are close to oil input to the coil, creating leakage and possible hazard for the people and abortion of the experiment. In this case, Teflon tape and better-quality clamps were able to fix the problem,
- Other mechanical problems such as adjustment of thermocouple to not touch the coil inside the reactor because of the small input,

The usage of the aforementioned reactor was aborted.

2.6. Non-achieved plans inside the Master Dissertation laboratory work

Just before the evacuation of the university, due to COVID-19 pandemic restrictions, experiment using 6 L reactor with heating mantle has started. Unfortunately, no sample was retrieved and tested. The initial mass balance was: 600 g of biomass, 1800 g of solvent and 54 g of PTS acid.

2.7. Aim of the Master Thesis

The objective of the experimental work was to try different approaches in order to get the best possible results from direct bioliquefaction with acidic catalyst. Pine chips were used because of the abundance of this material in Portugal, what might have created an impact on future studies regarding the possibility to scale-up the experiments.

What is worth mentioning is the fact that, initially, the experiments were driven by the interest of the Respol Resinas S.A. company, which then resigned from the interest about the Master Dissertation because of security reasons connected with possible threat of copyright.

3. Results and discussion

3.1. Moisture

Moisture of the samples was calculated using the (3) equation. The results are presented in the Table 5 below.

Table 8: Moisture content of examined samples

Sample	Moisture (%)
Pine	10,90%

3.2. Pine liquefaction

The goal of liquefaction was to reach the equilibrium between the biomass added to the reactor and the solvent having been used, so they constitute the same amount inside the solution.

Initial conditions were, as follows: 130 g of biomass, 6500 g of 2EH and 19.5 g of PTS acid.

Figure 36 represents changes of the biomass-to-solvent ratio inside the reactor.

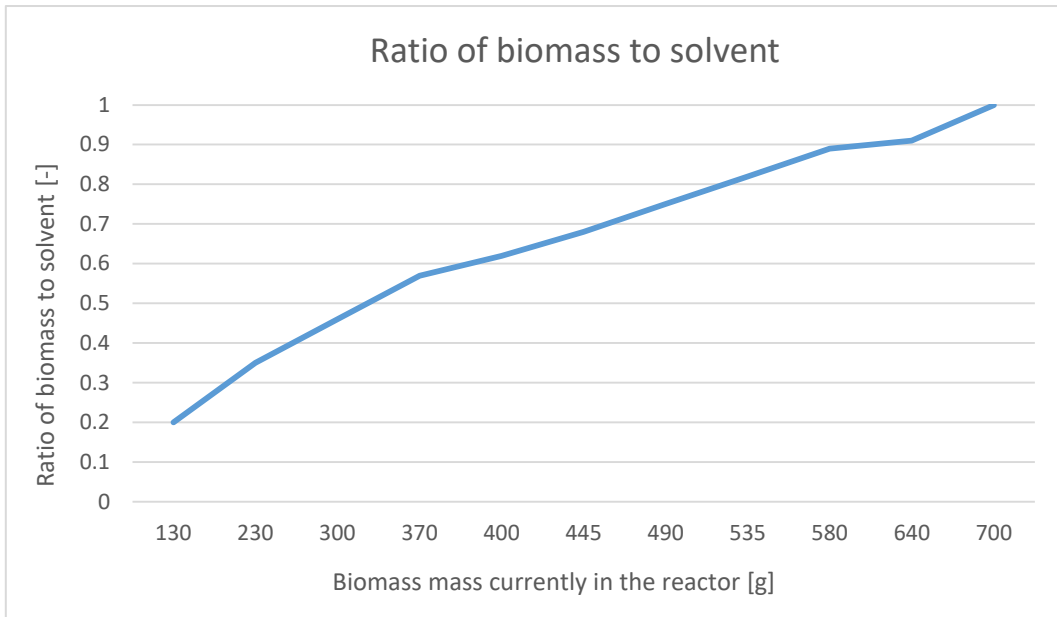


Figure 36: Biomass-to-solvent ration inside the reactor changes

Figure 37 represents the changes of biomass mass inside the reactor and the solvent and water evaporation in [g].

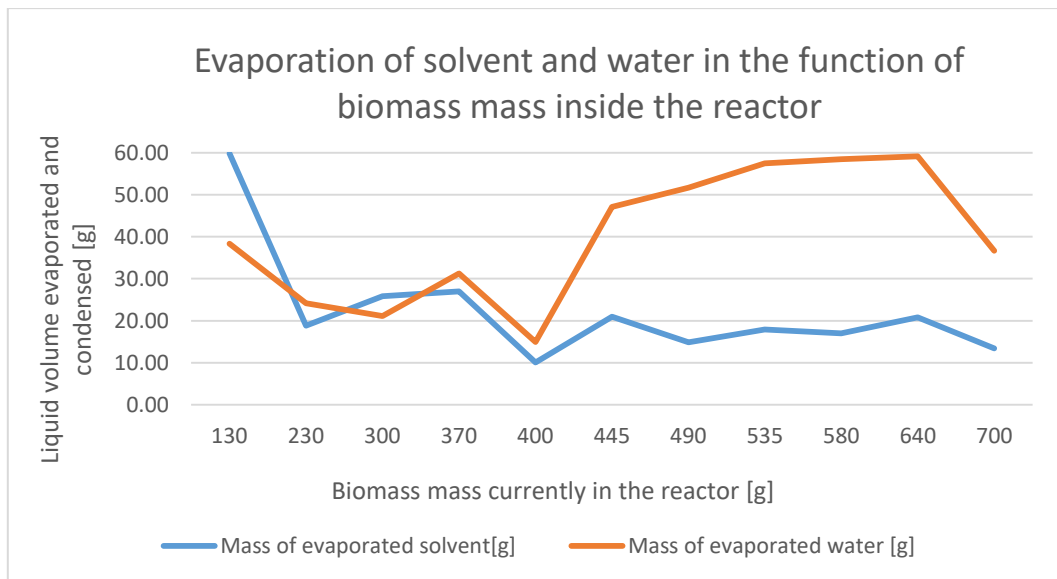


Figure 37: Evaporation of solvent and water in the function

Final mass that went for to be furtherly examined was calculated by formula equation (2):

$$m_{total} = 700 + 700 + 37 - 278,4 = 1158,6 \text{ g (2)}$$

What is worth mentioning, are the facts that:

- Motor was constantly overloaded due to high volume inside the reactor. The power of motor was 140 W, which did not meet the need of the experiment.
- The experiment was stopped for 2 weeks during the university break. Due to this fact, after returning, motor was unable to make the biomass agitate inside the reactor, even at elevated temperatures. Therefore, to aforementioned 500 g of solvent, 150 g more were added to enable the agitator to move and continue the experiment. The reason of inability of the motor might have been secondary aromatization reactions, depolymerisation and oxidation, the last was especially occurring on the surface of biomass.

3.3.Viscosity

The viscosity test was performed for final bio-oils and residues. Unfortunately, the test could not be performed within the range of used viscometer at any temperature within the temperature range of the equipment. The samples of oil had too low viscosity to be examined, and the residues had too high viscosity to be examined. In the case of the second type of samples, coming after acetic anhydride and DMAP treatment, the fumes occurred when there was performed a trial to increase the temperature to lower the viscosity. The only viscosity experiment that gave the results within the range of the equipment was Secil bio-oil viscosity test. The result of this test is given below, in Table 9.

Table 9: Viscosity test for Secil bio-oil

Viscosity [P]	Temperature [°C]
0,3	50

Tests in suggested temperatures such as 25 °C or 75 °C caused the sample to exceed the range of Poise possible to be measured using aforementioned equipment.

3.4.Alkylphenolic fraction removal idea

As derived from equation (2), the amount of biomass used in further experiment is 1158,6 [g].

Amount of water added to a solution was calculated based on the result from equation (4):

$$m_{water} = \frac{1158,6}{2} = 579,3 \text{ [g]} \quad (4)$$

In pH adjustment, the amount of PTS acid used in the experiment needed to be assessed. Therefore, taking into account that:

- $M_{\text{PTS acid, used}} = 37 \text{ g}$
- $M_{\text{PTS acid}} = 172,2 \text{ g/mol}$
- $M_{\text{TEA}} = 101,19 \text{ g/mol}$

from equation (5) and (6) it was found:

$$n_{\text{PTS}} = \frac{37}{172,2} = 0,21 \text{ [mol]} \quad (5)$$

$$m_{\text{TEA}} = 0,21 \times 101,19 = 21,74 \text{ [g]} \quad (6),$$

which was defined as a minimum amount of triethylamine that should be used to make the pH of the solution suitable for further processing.

In the end, in order to get the proper colour on the litmus paper, 23 g of TEA were used to basify the solution.

The mass of residues for rotary evaporation was 1000,25 g.

Due to the small bubble flask volume, rotary evaporation needed to be conducted three times. Table 10 represents the volume of evaporated liquid at each liquefaction and its total sum. Mass difference represents possible losses of material due to suck effect of the vacuum in rotary evaporator, the need to clean the neck of the bubble flask or human error (for instance, caused by bad insertion of the material to the flask)

Table 10: Rotary evaporation results of direct pine liquefaction residues treated with TEA

Evaporation number	Initial material mass [g]	Evaporated water mass [g]	End material mass [g]	Difference [g]
1	365,74	17,56	320,62	27,56
2	318,13	20,87	281,37	15,89
3	275,45	15,38	257,22	2,85
Sum	959,32	53,81	859,21	46,30

The mass that reached the point of experimentation, named as a “end material mass”, was treated with acetic anhydride and 4-Dimethylaminopyridine. From equation (7) and (8), arise that:

$$m_{\text{acetic anhydride}} = 0,1 \times 859,21 = 85,92 \text{ [g]} \quad (7),$$

$$m_{\text{DMAP}} = 0,02 \times 859,21 = 1,72 \text{ [g]} \quad (8)$$

Due to the lack of resource, 2% of 4-Dimethylaminopyridine was used in acetic anhydride instead of 5%.

Total mass of the solution is given by equation (9):

$$m_{total} = 859,21 + 85,92 + 1,72 = 946,85 \text{ [g]} \text{ (9)}$$

During the experiment, the viscosity was too high to move the motor, so it was unable to move the reactor. The temperature was then, in consultation with the supervisor, increased to 50 [°C]. In this conditions, motor could mix the material at the lowest radial velocity possible, which was 12 [rpm] and barely avoiding overload, coming from excessive torque.

Then, sample was punt inside the rotary evaporator again for. Overall mass put inside the rotary evaporator was 912,80 g. Allegedly, the difference of mass came from the fact that there was no possibility to scrap the reactor out of every particle possible.

Table 11 represents the volume of evaporated liquid at each liquefaction and its total sum. Mass difference represents possible losses of material due to aforementioned reasons.

Table 11: Statistics from rotary evaporation after alkylphenolic fraction removal

Evaporation number	Initial material mass [g]	Evaporated liquid mass [g]	End material mass [g]	Difference [g]
1	430,60	6,67	419,9	10,7
2	457,28	1,02	456,1	1,18
Sum	887,88	7,69	876,0	11,88

As mentioned in the previous point, there was an inability of assessing the viscosity of the residues, because of their hardness. Figure 38 represents the sample of the residue after the process on viscometer plate.



Figure 38: Sample of a residue treated with alkylphenolic removal treatment

Final sample was in the end retrieved to FTIR test.

3.5.OH number

The OH number, determined by this experiment, for which the data was:

$$C = 0,5$$

$$M_{\text{KOH}} = 56,1 \text{ g/mol}$$

$$m_{\text{sample}} = 1,88 \text{ g}$$

$$V_{\text{THF}} = 45 \text{ ml}$$

$$V_{\text{white sample}} = 54,4 \text{ ml}$$

$$V_{\text{sample}} = 50,5$$

was calculated from equation (10) cited below:

$$\text{OH number} = \frac{0,5 \times 56,1 \times (54,4 - 50,5)}{1,88} = 58,19 \text{ (10)}$$

3.6.FTIR results analysis

FTIR test was performed 4 times. In the Figures 39-44 below descriptions of the tests with their results can be found.



Figure 39: Perkin-Elmer screenshot of liquid sample filtrated after TEA treatment

In the Figure 34 there is the distribution of peak in liquid sample, obtained after TEA treatment presented. First two peaks (2987 cm^{-1} and 2702 cm^{-1}) might be identified with O-H carboxylic acid's bond stretching. The next group is a stretch of a double bond between the C and O atoms, that comes from carboxylic acid. Bonds with wavelengths 1595 , 1476 and 1395 cm^{-1} are a sign of C-H stretch, indicating the existence or formation of alkane structures [87]. Next identified bond is C-O bond stretching. The one with higher wavelength comes probably

from alcohol group, and the other one – from alkoxy group. The next group comes from C-H bending, probably coming from aromatic groups.

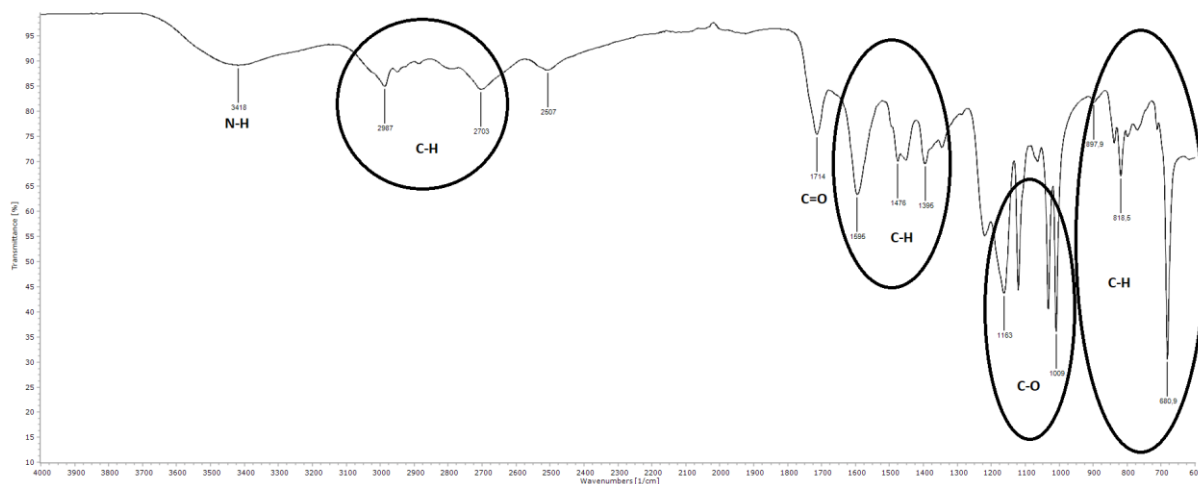


Figure 40: Liquid sample after TEA treatment FTIR with marked bonds.

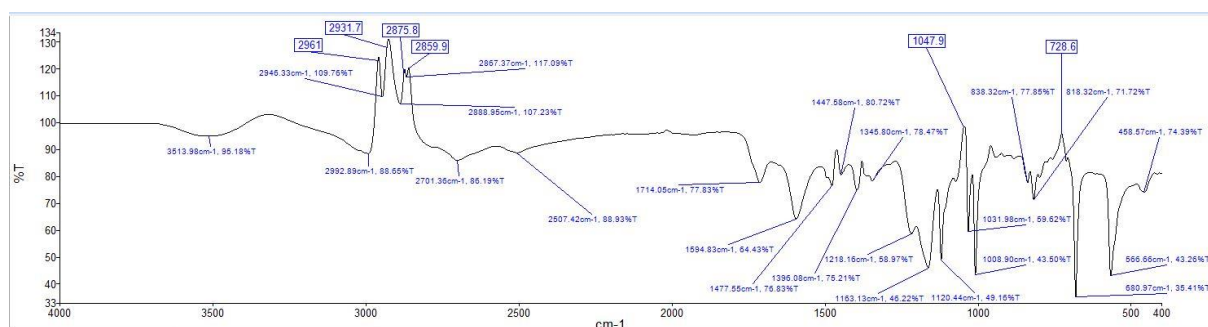


Figure 41: Perkin-Elmer screenshot of liquid sample filtrated after direct liquefaction (2-ethylhexanol background)

In the figure 36, there is a distribution of liquid sample after direct liquefaction presented. First bonding is a O-H stretch, followed by 2EH up-peak, as 2EH was a background for this FTIR experiment.

Then, one can notice C-H bond stretch coming presumably from aldehyde and O-H from carboxylic acid.

However, the O-H stretching is normally centred at $\sim 3000 \text{ cm}^{-1}$, therefore there is a small probability of having a bond stretching there. Afterwards, there is C=O bond stretch from carboxylic acid, followed by C-H bond stretching coming from alkenes and alkanes. After that, peak labelled with 1348 cm^{-1} is S=O strong stretching, probably coming from PTS influence on the reaction as a catalyst. Then, one can see C-O stretching followed by C-H stretching coming from aromatic groups. At the lowest wavelengths C-C bending can be determined.

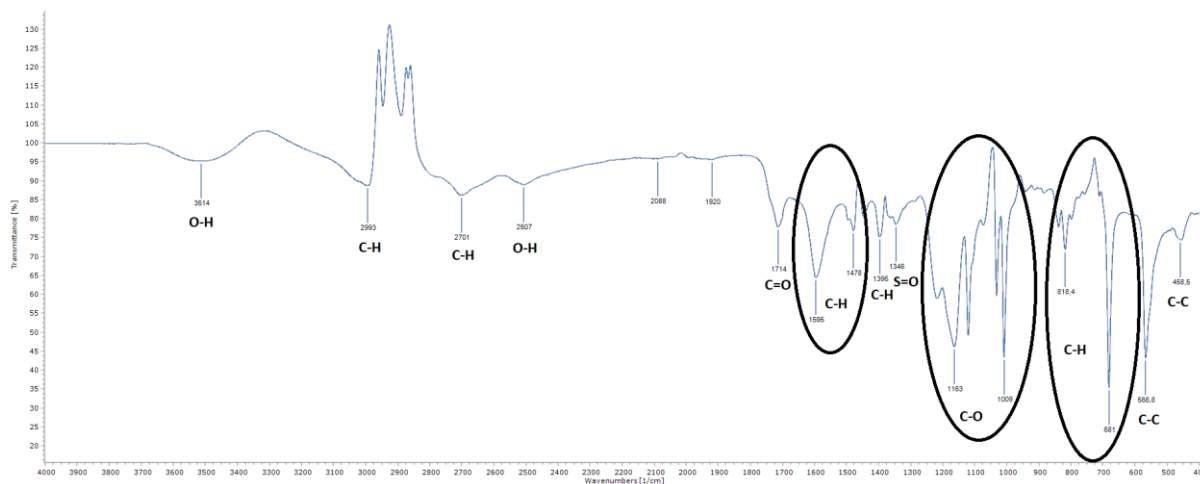


Figure 42: Liquid sample after direct liquefaction FTIR with marked bonds (2-ethylhexanol background)

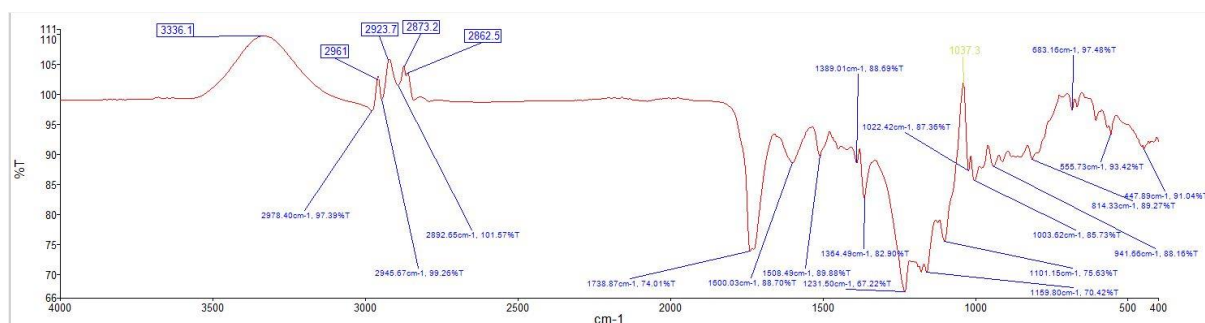


Figure 43: Perkin-Elmer screenshot of residues after acetic anhydride and DMAP treatment FTIR results with marked bonds (2-ethylhexanol background)

In the Figure 38 there is a distribution of residues after DAMP and acetic anhydride presented. Up-peaks are represented by presence of 2EH, because 2EH was used as a background in this experiment. First noticeable down-peak is a C=O peak coming from carboxylic acid followed by C=C stretch. Next one is O-H bond bending coming presumably from alcohol or phenol. From 1232 cm^{-1} to 1101 cm^{-1} C-N stretching can be noticed due to DMAP and TEA activity. Then, C-O stretch can be seen from alkoxy group, followed by peaks generated by alkene and aromatic groups, which caused FTIR to detect C-H stretch from aromatic groups. FTIR analysis lowest wavelengths peak are created by C-C bond bending.

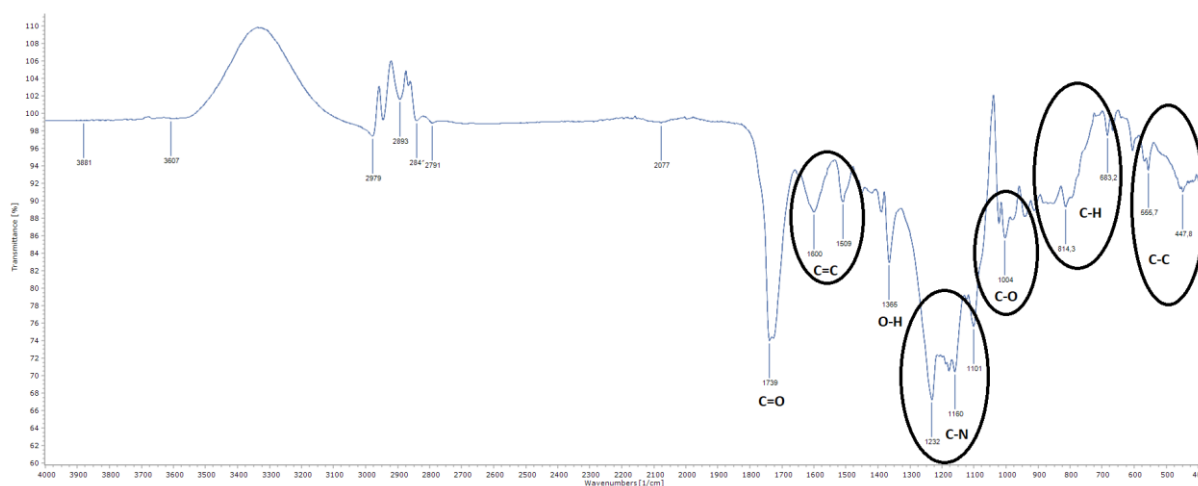


Figure 44: Residues after acetic anhydride and DMAP treatment FTIR results (2-ethylhexanol background)

Below, in the Table 12, there is a list of functional groups normally found in bio-oil and residues, along with their respective wavelengths and components that cause the detection of them in FTIR analysis. All of those groups were found in the experiment.

Table 12: Functional groups encountered in samples of bio-oils and residues in FTIR analysis

Functional groups	Wavelength	Components
O-H stretching	3700 – 3200	Alcohols, phenols
C-H stretching	3100 – 2800; 1465 – 1365	Alkanes, alkenes
C=O stretching	1760 – 1685	Aldehydes, ketons, carboxylic acids
C=C stretching	1678 - 1575	Alkenes, aromatic compounds
C-H stretching	1465 – 1375	Alkanes, aldehydes
C-O stretching	1300 – 1000	Phenols, esters, primary, secondary and tertiary alcohols
C-H bending	900 - 650	aromatic compounds

4. Conclusions

To summarise, in this work, liquefaction of the pine wood was conducted in order to check the ability of the feedstock as a fuel in a direct liquefaction, initially for company Respol Resinas S.A.

New method to increase the number of sugars was involved as well. The liquefaction conditions for pinewood were optimised to reach biomass to solvent ration of 1:1 (m/m). The solvent, that has been used, 2-ethylhexanol, yielded around 55% conversion of initial biomass. To achieve this conversion, ambient pressure, temperature of 160 °C and process time 2 hours for every biomass addition in laboratory scale is required. Study has shown that 1 hour is not enough for full liquefaction, making the system ready

for the next biomass addition, on the laboratory scale. Although, this is a promising technique for biomass conversion, as it does not involve any pressured setting and is an inexpensive process that could decrease both fixed and variable costs of the installation.

The catalyst used, p-toluenesulfonic acid, needed to be applied in concentration 3% of the initial solvent mass and 3% for every biomass addition, which is 2,6% of concentration overall.

Basification using triethyloamine and further experimentation with dimethyloaminopyridine and acetic anhydride led to the creation of a viscous residue that was not able to be examined within the range of viscometer. Used method and the results poses a question whether another method could be used to increase the amount of sugars at the end of the process to satisfactory 60-70% from aqueous phase. Calculation of OH number of final residue sample took place as well. The result obtained lower than usual OH numbers for the bio-oils.

The viscosity was also tested. Due to the low range of the equipment having been used, samples of the bio-oil and residues were either under the range of the equipment or over it.

At the end, FTIR analysis were conducted. FTIR samples proved the formation of new structures, typical for bio-oils such as aromatic compounds, alkanes. In the sample the materials having been used, such as DMAP or PTS acid were also detected at the specific ranges of the wavelength.

In conclusion, the method used for bioliquefaction purposes can be used for further examination in bigger, industrial scale, creating chance of new and sustainable fuel and chemicals creation. Pinewood, which constitutes to 6% of the total wood area in Portugal, can be also used as a valuable feedstock for direct liquefaction and chemicals production.

5. Future work and recommendations

Direct liquefaction in ambient pressure is an extremely promising process and needs to be further studied and optimised. Pine liquefaction in Portugal has a chance to become promising technology of fuels production to be used instead of fossil fuels and sustainable chemicals. Literature indicates the occurrence of reactions between the solvent and lignocellulosic biomasses, however, the exact nature of these reactions, for instance, kinetics, extent and mechanism are unknown [63]. This subject needs to be studied more in order to develop, for instance, ways to recover the unreacted solvents from bio-oil for re-use.

The composition of bio-oils needs to be studied more as well. The optimization of sugars extraction using basification in acidic direct liquefaction and further characterization is also important to achieve more than present ratio of 10 to 15% of sugars in the aqueous phase of the solution in order to, for instance, produce bioethanol without the need of using enzymes. The characterization of the bio-oil remaining fraction to explore the possibilities of upgrading should also be taken under consideration.

6. References

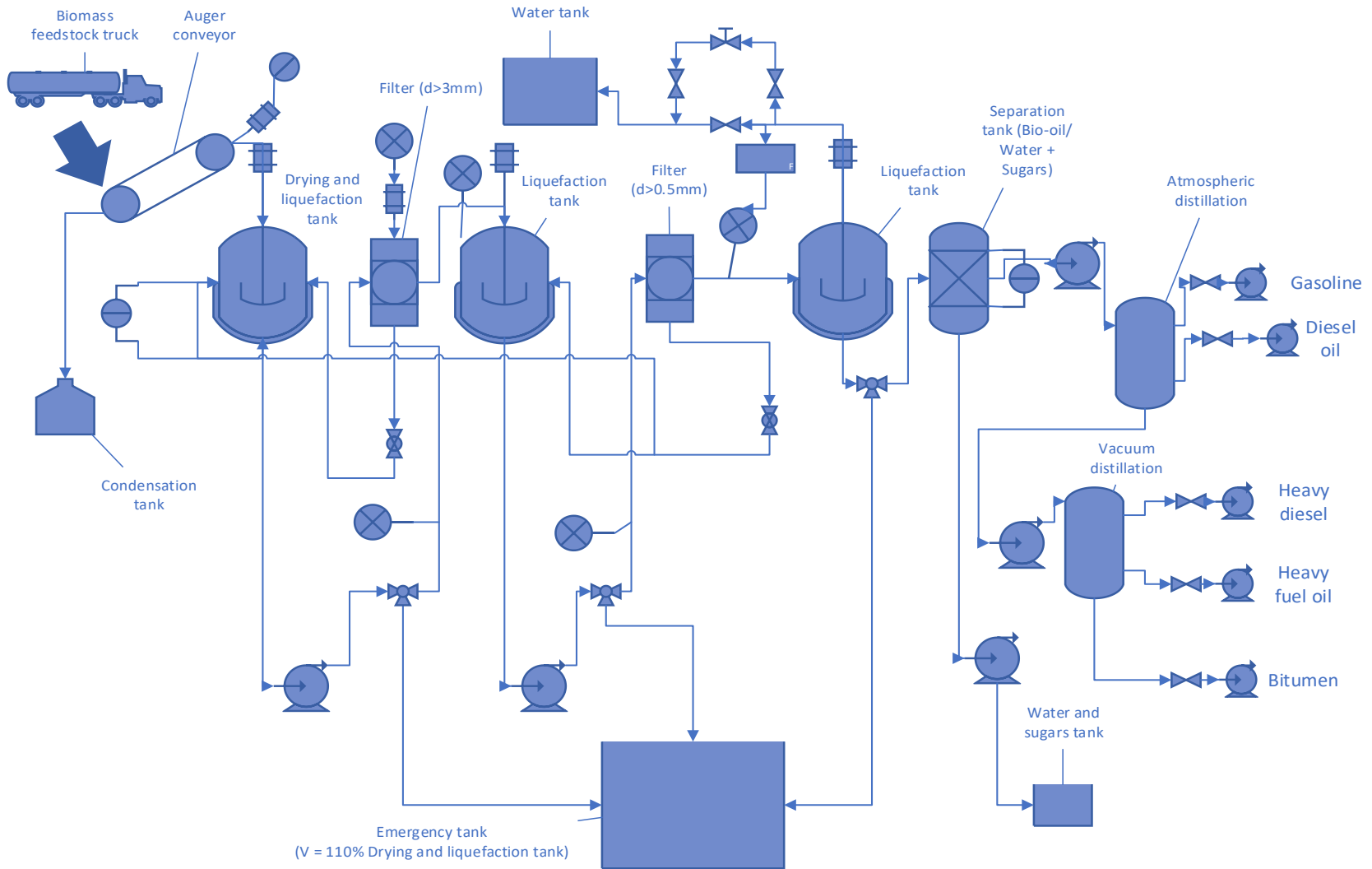
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Appendix 1 – Process flow diagram of bioliquefaction plant