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Reference:

Gracia-Vitoria J., Gandara S. Corderi, Feghali E., Ortiz P., Eevers Walter, Triantafyllidis K.S., Vanbroekhoven K..- The chemical and physical properties of lignin bio-oils, facts and needs
Current opinion in green and sustainable chemistry - ISSN 2452-2236 - 40(2023), 100781
Full text (Publisher's DOI): https://doi.org/10.1016/J.COGSC.2023.100781
To cite this reference: https://hdl.handle.net/10067/1951900151162165141

The Chemical and Physical Properties of Lignin Bio-oils, Facts and Needs.

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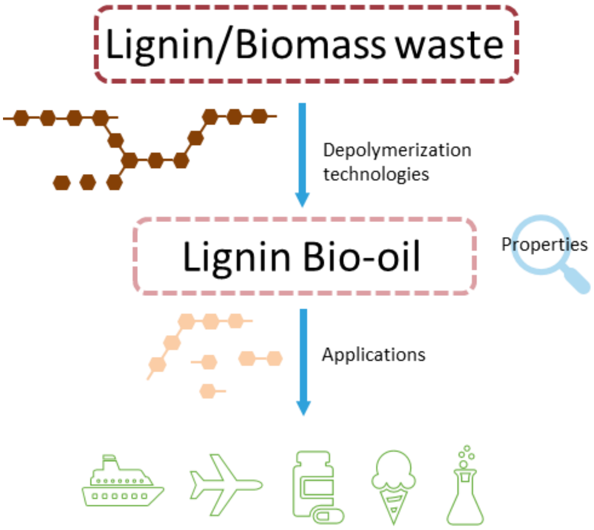
Keywords: Lignin, Lignin depolymerization, Lignin oil, Lignocellulosic biomass

ABSTRACT

Lately, the interest in lignin valorization has notably grown within the scientific community. In the last decade, the number of publications focusing on lignin as an alternative to fossil-based resources has exponentially increased. Different strategies have been employed to valorize lignin as a source of renewable fuel and building blocks for chemicals and materials development. Of these strategies, lignin depolymerization producing lignin oils (bio-oils) has been recently explored on laboratory and pilot scale. The produced bio-oil exhibits unique chemical and physical properties that depend on the type of lignin with regard to the nature of parent biomass and can be further tailored by both the isolation and the depolymerization process conditions. This review aims to group the work done on the production and valorization of bio-oils to provide a common description of the depolymerized lignin oils. This work proposes reporting guidelines of bio-oil properties required to bridge the gap between the depolymerization techniques and chemicals/ materials development using the bio-oils properties.

Graphical Abstract



1. Introduction

Lignocellulosic biomass, being the most abundant organic raw material in the world, will play a central role in the future when it comes to the production of fuels, chemicals and materials. From the three components of lignocellulose, namely lignin, hemicellulose and cellulose, especially the latter, is currently valorized.[1–3] Sadly, less than 3% of the produced lignin is further valorized.[4] However, for a sustainable and profitable biorefinery, the valorization of all three fractions is crucial.[5,6] Thus, the use of lignin (figure 1) as a source of aromatic bio-based building blocks is a must towards a circular and sustainable chemical industry. In this regard, the production of chemicals from lignin has attracted great attention within the scientific community in the last years.[7–11] In fact, the papers mentioning the word lignin underwent a sharp increase in the last thirty years as shown in figure 2.

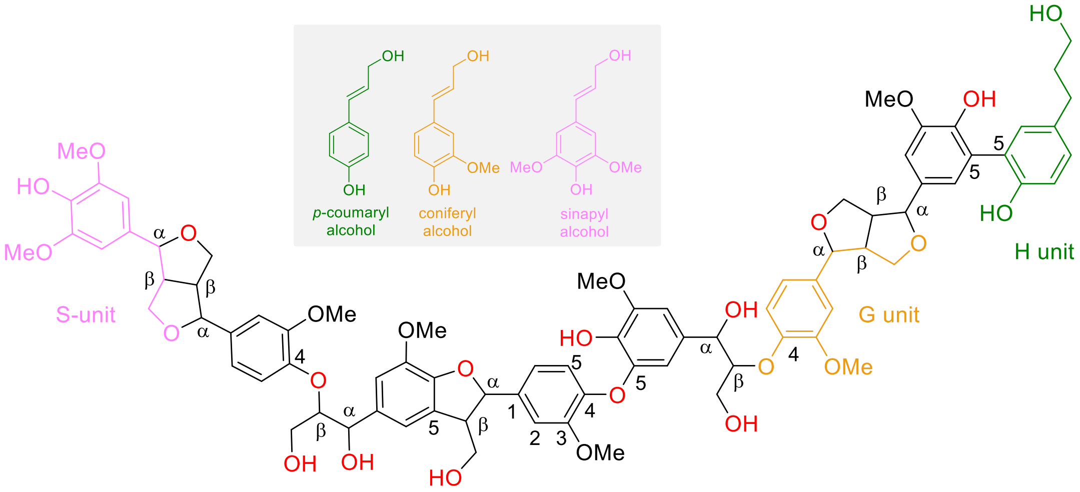


Figure 1. Representative lignin structure, the three monolignols and most frequent interunit linkages.

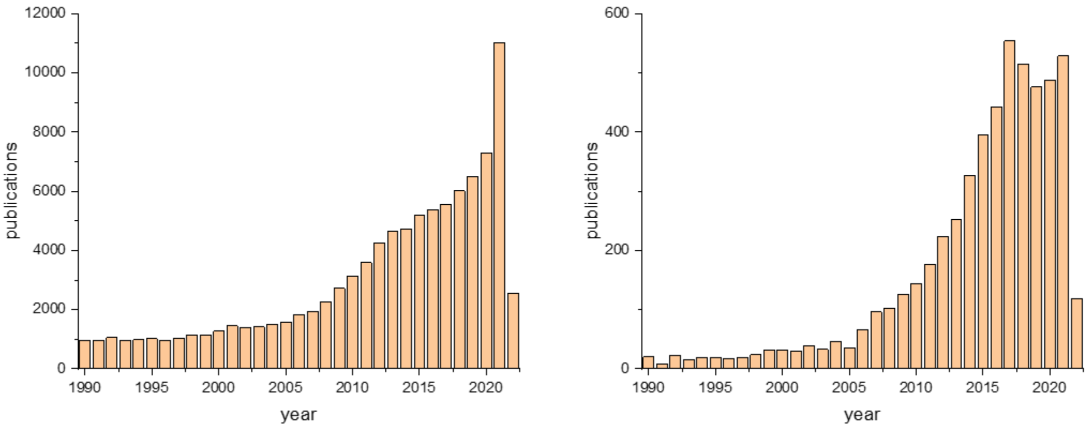


Figure 2. Left: Papers mentioning the word lignin; Right: Papers mentioning lignin oil in the last thirty years. Source: Sci-Finder. (Retrieved of the 1st of April 2022)

It is estimated that around 100 million tons of lignin are produced every year by the pulp and paper industry as a by-product and most of it is burned to provide energy.[12] The small part that escapes the flames is mostly used in low added-value applications such as dispersants, fillers or adsorbents.[13–15] The only exception is the production of vanillin.[16] However, 85% of commercial vanillin is still produced from petroleum, being one of the reasons of this market dominance the premium paid for the “biobased” vanillin.[17] One of the limitations of the lignin-to-vanillin process is the several steps of the process and the low yield, usually ≈5%. [18] Especially needed to purify the mixture obtained after lignin depolymerization. If the process starts from KL the typical yields of vanillin are around 10%.[19] The valorization of industrial (technical) lignins such as Kraft and lignosulfonates is challenging due to their physical and chemical properties e.g., high molecular weight, low functionality, poor solubility in organic solvents and complex molecular structure.[8]

Furthermore, organosolv lignin that results from milder biomass pre-treatment methods, can also engender partially condensed lignin, if strong acids are employed.[20] Accordingly, the depolymerization of isolated lignins is partial and results in low monomer yields and complex product mixtures.[21]

On the contrary, when the biomass fractionation and depolymerization of native lignin are combined in one step, condensation is prevented to a large extent and a narrower product distribution as well as an increased monomeric yield are obtained. After the extraction of the sugar derivatives using liquid extraction, the resultant product is an oil typically formed of aromatic monomers, dimers and oligomers.[22] However, there is no clear definition of lignin oil. In fact, in some publications the term lignin oil refers to the outcome of the lignin depolymerization as such while in others this term accounts for fractionated and in situ depolymerized lignin from the original biomass. In many papers dealing with lignin depolymerization, lignin oil is frequently a solvent-based solution. Therefore, many questions remain unanswered; does the bio-oil have an upper Mw limit? Is it able to flow as such or is it also considered a bio-oil when it is diluted in a solvent? If so, is there a limited concentration of the bio-oil in the solvent? Accordingly, it seems crucial to provide a common definition of the lignin oil, relying on common physical and chemical properties.

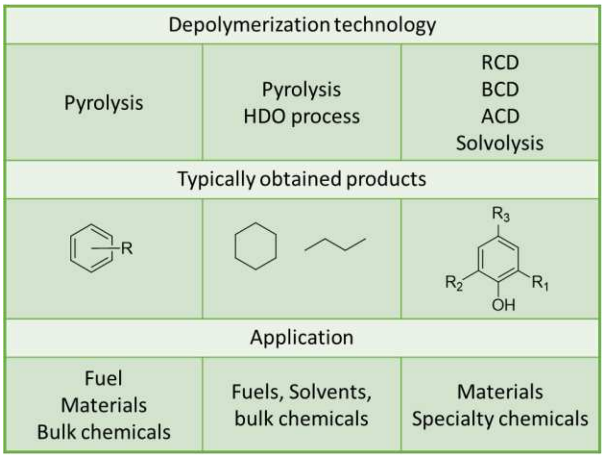
In fact, hundreds of papers and several reviews on lignin depolymerization methods target lignin oils with a focus on process conditions optimization to maximize the conversion or the monomer yield.[23] Nonetheless, researchers usually report different parameters to describe the outcome of the reaction. For example, the comparison between product yield, oil yield and lignin conversion are difficult. Additionally, monomer yield is a common parameter, yet, monomers only represent one part of the bio-oils, and in most cases the minor one. Nonetheless, only few papers, mainly focusing on polymer synthesis, were interested in the determination of the physical and chemical properties of the oils.[24] In fact, the use of lignin derived chemicals in the polymer industry has gained much attention in the last years to reach sustainability and circularity goals. Here, the use of depolymerized lignin oil surpasses technical lignin in terms of compatibility and performance. A full characterization of the physical and chemical properties of the lignin oils is therefore a must in the polymer industry.

A more precise definition of the bio-oils will then be elucidated based on common physico-chemical properties. We believe that these properties are a need to bridge the gap between the depolymerization conditions and the potential applications. The latter were classified under fuels, materials, bulk chemicals, solvents and specialty chemicals. It is to be noted that this work does not cover the upgrading of lignin bio-oils to saturated (cyclo)alkane compounds by means of hydrodeoxygenation (HDO) process.

2. Depolymerization process used for lignin bio-oil production

The interest in lignin depolymerization technologies to produce bio-oils has witnessed an impressive growth in the last 15 years (figure 2). Many depolymerization processes enable the generation of lignin oils, among which, the most developed in terms of technology readiness level (TRL) are: acid catalyzed depolymerization (ACD), base catalyzed depolymerization (BCD), solvolysis, reductive catalytic depolymerization (RCD) and pyrolysis.

The following sub-sections provide an overview related to the most promising depolymerization technologies used to produce lignin oils.



Depolymerization technology		
Pyrolysis	Pyrolysis HDO process	RCD BCD ACD Solvolysis
Typically obtained products		
Application		
Fuel Materials Bulk chemicals	Fuels, Solvents, bulk chemicals	Materials Specialty chemicals

Figure 3. Selection of dep. technology by a product-application approach

2.1 Acid/base catalyzed

Lignins can be depolymerized using acid (ACD)[25,26,35–41,27–34] or base catalysts (BCD) [42,43,52–60,44–51] in aqueous or organic solvents. These depolymerization reactions using both acid (typically at 140 - 400 °C for 0.5 - 6 hours) and base catalysts (usually at 120 – 330 °C for 0.25 - 8 hours) target the cleavage of C-O and C-C interunit lignin bonds leading to monomeric/oligomeric fragments. BCD is usually performed in the presence of soluble base (NaOH) or solid catalysts such as MgO. The monomer yields oscillate from 1 to 35 wt%. ACD is performed in the presence of soluble acid (HCOOH, H_2SO_4) or solid catalyst with monomer yields varying from 3 to 60 wt%.

Unfortunately, these methods promote condensation or repolymerization, especially in the presence of water. The use of hydrogen donor solvents like methanol or ethanol can reduce the condensation reactions and, in this way, generate more stable lignin fragments.[61]

Acid and base catalysts have been combined with strong oxidative or reductive conditions seeking an improvement of monomeric yield.[62]

2.2 Metal catalyzed

Hundreds of papers have been published in the last years regarding RCD,[63,64,73–82,65,83–92,66,93–102,67,103–112,68,113–122,69,123–132,70,133–142,71,143–152,72,153,154][155] which became a popular technology. RCD targets cleavable β-O-4 and α-O-4 bonds present in lignin chains although the process conditions also affect side-chain hydroxyl groups. In this process, hydrolysis of cleavable ether bonds is achieved. An advantage of RCD is that repolymerization is avoided, at least to a larger extent, in contrast to what happens in ACD or BCD processes. Since the most common redox catalysts are not able to cleave the C-C bonds under the applied relatively mild T/P conditions, the limitation of this technology is fixed to the available amount of cleavable ether bonds.

Technically, the reduction is done by a redox metal catalyst and a hydrogen donor, usually hydrogen but it can also be a solvent or chemical.

Lignin powder, wood chips, or even agricultural residues, such as corn stalk or sugarcane bagasse, can be used as feedstock. When lignocellulosic biomass is used, the process is known as lignin First.[22]

Several factors play a role in the success of this depolymerization technology, and the chemical substances obtained.[156,157] Usually, the reactor is pressurized although some examples have been reported at atmospheric pressure.[158] A relevant work discussing the influence of process parameters towards the upscaling of this technology has been published recently.[156]

Alkylphenols and hydroxyalkylphenols are the commonly obtained monomers. Guaiacols/syringols ratio depends on the botanical origin of the biomass feedstock.

It is important to highlight the increase interest in the aldehyde assisted fractionation developed by Luterbacher and co-workers at EPFL. This approach is applied on biomass prior to depolymerization and permits to improve significantly the total monomer content.[159–161]

2.3 Solvolysis

Solvolysis using either a pure solvent or a solvent mixture is characterized by its simplicity compared with other methods. The appropriate selection of an effective solvent, reaction time and temperature (180 to 350 °C) are the most important parameters to control.[162,163,172,164–171] The monomer yields range from 3 to 24 wt%, however, yields around 50 wt% have been reported for organsolv[173] and kraft lignins.[174] A large variety of monomers are obtained including methoxy phenols, catechols and cresols.

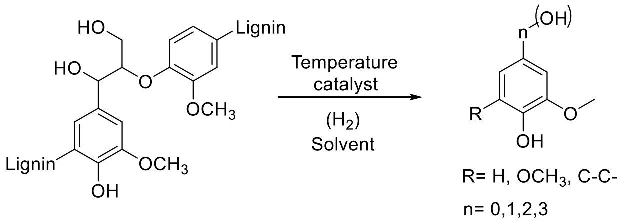


Figure 4. Main products of discussed depolymerization technologies

2.4 Pyrolysis

Typically, pyrolysis is a thermochemical process performed at high temperatures form 400 to 700 °C in the absence of oxygen or air. The process conditions more specifically heating and cooling rates, temperatures, and vapor contact times, have considerable influence on the formation of the bio-oil. In the case of lignin pyrolysis , the bio-oil mainly contains alkoxy-phenols and oxygenated aromatics. In addition, some gases, such as carbon dioxide, carbon monoxide, and methane, as well as solids (char), are also produced in lignin pyrolysis. [23,175–178]

The choice of a depolymerization technology depends mainly on application. For instance, if biomass feedstock is to be used to produce bio-based fuels, a fast (catalytic) pyrolysis strategy[178–181] or HDO upgrading process[182,183] may be a good choice. When the production of high added value chemicals such as vanillin or propyl guaiacol (PG) is targeted, a RCD or an electrochemical oxidative depolymerization strategy would be preferred options.[16] If the aim is to make polymers or materials using hydroxyl functions or phenolic synthons, RCD might be the most promising strategy since it permits a retention of the reactive hydroxyl groups. Maintaining the chemical functionality after depolymerization, is crucial for the replacement of phenol derived building blocks by bio-oils in functional materials.[184] Another aspect of technology selection is related to the technoeconomic assessment (TEA), and the environmental impact evaluated through a life cycle assessment (LCA). Techno-economic, environmental and policy analysis of lignin oils obtained from pyrolysis[185] and RCF[186] have been recently published.

3. Lignin bio-oil properties

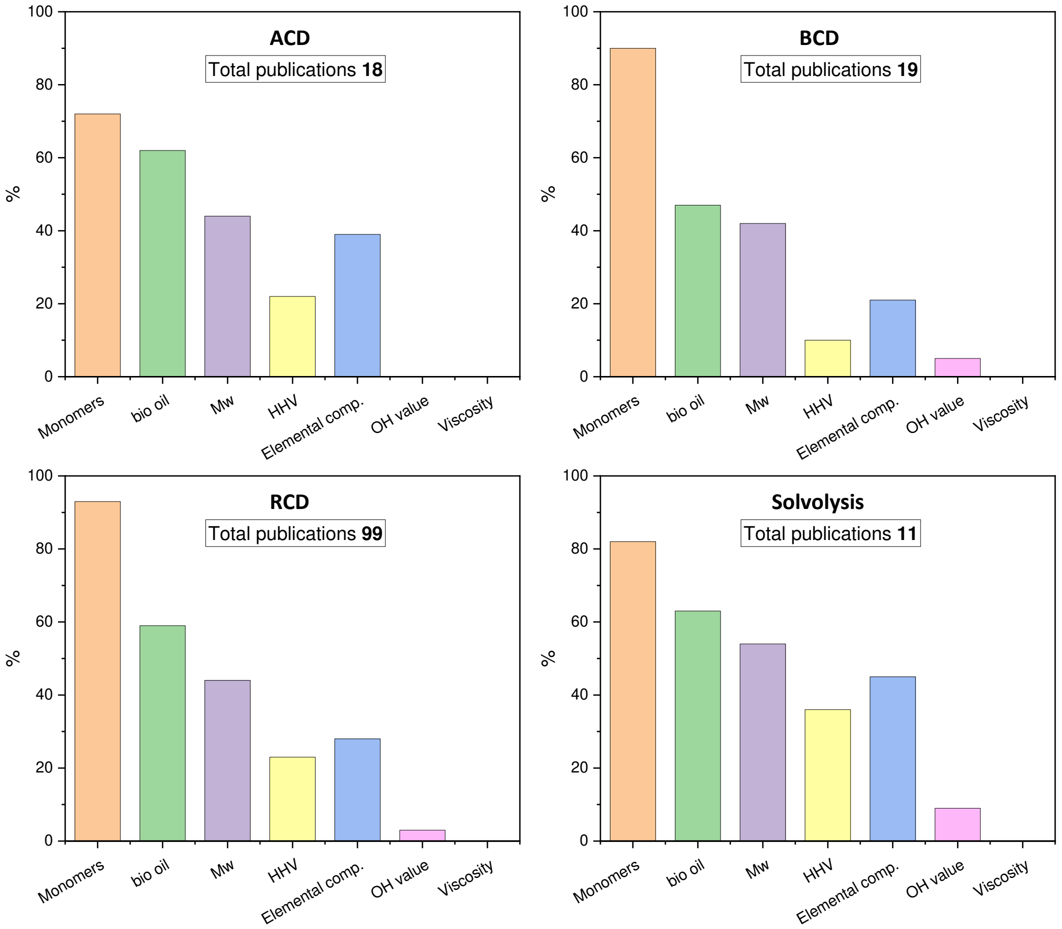
The analytical techniques that are frequently used nowadays to analyze lignin structure and functionality are: gel permeation chromatography (GPC), gas chromatography coupled with mass spectrometry (GC-MS) or with flame ionization detector (FID), gravimetry, calorimetry, elemental analysis, 2D NMR ^{1}H-^{13}C HSQC. However, many of them are performed without a standardized protocol that enables comparison.[187] On other hand, other relevant analyses for applications such as viscosity, density or Karl Fischer determination and even ^{31}P NMR, which is often used to characterize lignins, are scarcely found for the characterization of the bio-oils in the available literature despite their great importance for the further use of such lignin oils.

As mentioned before, both chemical and physical properties of lignin bio-oils are key elements towards full lignocellulosic biomass valorization. Most of the studies dealing with depolymerization of lignin only report the properties and composition of the monomer fraction while neglecting the oligomeric. However, since the oligomeric fraction usually constitutes a significant part in mass of the original lignin feedstock its characterization is crucial when the bio-oils are used in materials development. Recently, some efforts have been made in this sense, a collaboration between KULeuven, UGent and NREL, reported a detailed determination and quantification of oligomers in RCF of pine wood by GCxGC-FID/MS[188] which is in line with their previous work.[189]

Other properties such as viscosity and density are very important parameters for the industrial application of lignin oils, and these are rare to find in the state of the art. For instance, if the lignin oil has a low viscosity and therefore a good flow without adding any extra solvent the energy for mixing and pumping would be reduced. Nonetheless, the impact of the viscosity has to be assessed based on the chosen application.

Some selected parameters reported in the state of the art were plotted and compared in order to get a clear picture of the available data as per the physico-chemical analysis of lignin oils.

From the analytics performed in many published papers concerning those depolymerization technologies (figure 5), it is clear that monomers are the most characterized part of the oil. Indeed, >70% of the papers contain data about abundance and ratios of monomers in the lignin oil. The total lignin bio-oil yield is reported less, which seems quite surprising, accounting for around 60-50% of the papers discussed. Weight average molar mass (Mw) of the monomer or lignin oil is reported even to a lesser extent, which is kind of expected given that some groups only focus on monomers analyses. Elemental composition, which is also a parameter that gives important information about the aromaticity of the fractions, is only reported in 20 to 40% of the works. Higher Heating Value (HHV), which is useful for fuels applications, is given in less than 20% of the papers, except in case of solvolysis which goes up to 40%. HHV is a parameter often determined in lignin pyrolysis studies. Finally, hydroxyl (OH) value is almost never reported even though it is quite important for material developments or further upgrading-chemical modification of the lignin oil fractions. Viscosity and density were never reported in the papers analyzed.



ACD Total publications **18**

BCD Total publications **19**

RCD Total publications **99**

Solvolysis Total publications **11**

Figure 5. % of reported properties in lignin depolymerization papers.

Table 1. Average values and ranges of the lignin oils composition

	ACD		BCD		Solvolysis		RCD	
	Average	Range	Average	Range	Average	Range	Average	Range
Monomers (%)	20	3 to 60	13	3 to 21	19	3 to 48	26	5 to 81
bio-oil yield (%)	68	28-90	47	13-78	56	15-87	71	31-98
Mw (Da)	866	500-1500	1031	300-2600	962	300-1600	636	220-1881
HHV (MJ/Kg)	30,9	29-34	27,9	26-29	28,4	31-25	32,2	22-39
OH (mmol/g)	-	-	-	-	6,5	6,5	7,8	9,3-6,3

On other hand, the stability of the bio-oils during storage, transportation and handling is also a crucial factor for their use in larger volumes.[190] In this concern, Zhu and co-workers recently reported a study dealing with the aging of pyrolysis oil from walnut shells[191] by monitoring the variation of some physico-chemical parameters for 75 days. Recently, a study focusing on the modeling of the aging kinetics of pyrolysis lignin oil has shown to be more accurate[192] and could be very useful to predict the behavior of other lignin oils. Concerning RCD (or RCF) technology, G. Beckham group recently described a storage-stability test of the solvolysis oil of lignin from biomass prior to its depolymerization, being those shelf-stable for 3 months.[193]

However, to the best of our knowledge there is no study on the aging of lignin oils produced using other technologies. This means that efforts must be made in this concern while progress on the further upscaling and use of depolymerized lignin bio-oils in industry are made.

4. Conclusions, gaps and future challenges

We therefore propose to define lignin oil as the depolymerized outcome as such, with a solvent if used, without any further fractionation or upgrading. This bio-oil might be composed of a mixture of monomers, dimers, and oligomers, regardless of the depolymerization technology. The data obtained from the literature show a lot of variations with reference to key parameters that would permit a more specific definition of the bio-oils nevertheless, one can say that in average a bio-oil would have 20 wt% monomers, a Mw < 1000 Da and a HHV of 30 MJ/Kg. It is of great importance to retrieve as much information as possible of the lignin bio-oils to provide a link between the depolymerization conditions and the potentially viable applications. This is still not very well established due to the lack of adequate characterization. Accordingly, and based on the analyzed data we suggest preliminary guidelines for lignin bio-oil characterization. Characterization guidelines include the determination of monomer content, total bio-oil yield, molecular weight distribution, S/G/H composition and remaining β-O-4 an other interlinkages (by 2D ^{1}H-^{13}C HSQC NMR) representing mainly the oligomeric fraction of the bio-oil, OH and COOH content, elemental composition, viscosity and for fuel application HHV. To finish, techno-economic assessment (TEA) and life cycle assessment (LCA) studies should be performed to evaluate the economic viability and environmental impact of the different technologies towards different applications for their potential implementation. Last but not least, there is a very important need for the worldwide spread lignin community not only to agree on the properties of the lignin oils that should be measured but also on the standardization of the methods to analyze them to allow a fair comparison between the many reported publications in the field.

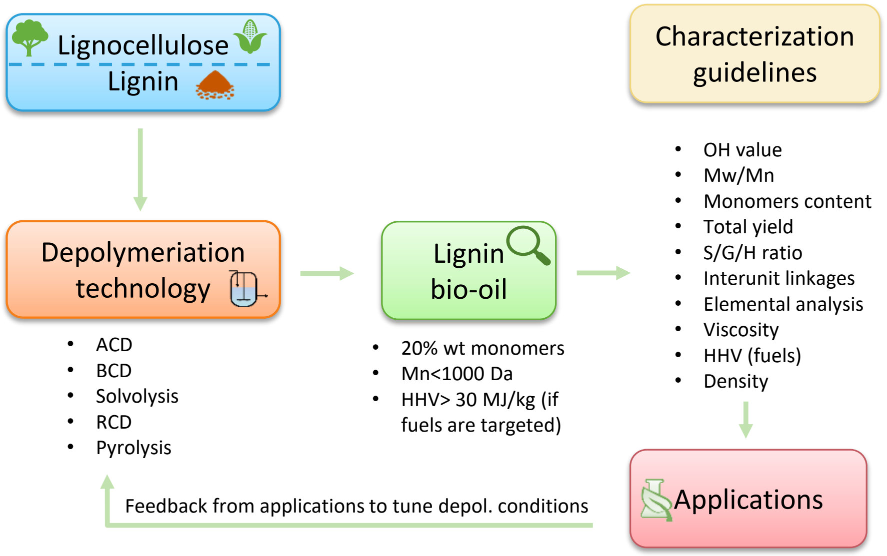


Figure 6. Reasoning and properties to be reported

CRediT authorship contribution statement

Jaime Gracia-Vitoria: Conceptualization, methodology, analysis, writing. **Sandra Corderí-Gándara:** Conceptualization, analysis, writing. **Elias Feghali:** Conceptualization, writing - review & editing. **Pablo Ortiz:** Conceptualization, writing – review. **Walter Eevers:** Conceptualization, review & editing. **Konstantinos, S. Triantafyllidis**: Review & editing. **Karolien Vanbroekhoven:** Review & editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgments

The authors wish to acknowledge COST Action CA17128 “Establishment of a Pan-European Network on the Sustainable Valorization of Lignin (LignoCOST)”. VITO would like to acknowledge the province of Noord-Brabant (The Netherlands) for the financial support in the framework of the activities at the Shared Research Center Biorizon.To the NIBCON project, part of Moonshot, an industry-driven innovation programme of the Flemish Government that supports companies in reducing their CO_2 emissions. JGV and KVB acknowledge the support from the EC LIFE programme for the grant: LIFE20 ENV/BE/000671 “LIFE VIABLE” project.

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