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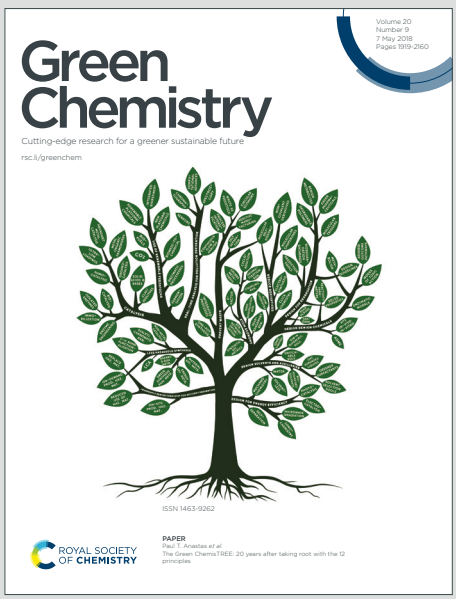




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No primary research results, software or code have been included and no new data were generated or analysed as part of this tutorial review.

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TUTORIAL REVIEW

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# Biomass-derived carbon-based catalysts for lignocellulosic biomass and waste valorisation: a circular approach

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The growing demand for alternative clean energy and environmental crises arose great concerns for humankind. Researchers have devoted effort in finding cheap, eco-friendly, and robust functional materials for future developments of biorefinery process. Among biomass valorisation processes, gasification and pyrolysis are the most explored thermal treatments exploiting biomass-derived catalysts, especially for $H_2$ and bio-oil production, which possess a great potential in the energetical framework proposed by the European Green Deal. While biomass conversion provides intriguing insights, its industrial development has been limited to date. The economic and environmental sustainability of biomass-derived catalyst production is pivotal for reducing pollutant emissions. However, scientists face a bottleneck in synthesizing materials with a high surface area, strong functionalization, and cost-effectiveness to compete with fossil resources. To address this challenge, life cycle assessment emerges as a valuable tool to study process sustainability. This assessment can be coupled with artificial intelligence technologies to predict the properties of biomass-derived catalysts accurately, facilitating comprehensive sustainability analyses.

## 1. Introduction

The intensive use of fossil resources is one of the factors that boosted the human development during the last decades. Progressive depletion, volatile costs and environmental drawbacks have however compromised the current approach of the industry towards the role of non-renewable sources for chemical and energy production, requiring a necessary change of paradigm.[1, 2] As a consequence, stakeholders (policymakers, industries, investors, researchers) are currently working towards the transition from a linear to a circular bioeconomy, able to meet global climate targets set by international agreements and Sustainable Development Goals (SDG).[3,4] Complying with SDG, the main challenges that chemical and petrochemical industries have to face are the replacement of not-renewable with renewable feedstocks, the development of more economically and environmentally sustainable processes and high value increase during process steps.[5] Moreover, in connection with the focus of the development of Science Technology and Innovation towards the Industrial era 4.0,[6] the valorisation of local natural resources represents a research potential aiming to reduce environmental degradation.

Residual Lignocellulosic Biomasses (LB) are the most abundant renewable candidates for the substitution of fossil resources. LB definition encompasses non-edible parts of virgin biomasses (e.g. grass), non-virgin biomasses (e.g. agricultural residues) and energy crops. Along with rapid growth, negative price, carbon neutrality and an esteemed annual production of 170*10^9 t, the complex chemical properties of LB pave the way for a key role as a feedstock in biorefinery processes.[7]

As stated by the European Technology Innovation Platform, a biorefinery can be defined as a "facility for the sustainable and synergetic processing of biomass into marketable products and energy".[8] Though biorefineries can process different types of LB,[9,10] the International Energy Agency suggested a sole distinction between energy-driven biorefineries (high amount of low-value substances) and product-driven biorefineries (smaller amount of high-value products).[11]

The recent trend around the globe is to transform waste into different products useful for various applications, and today agricultural residues are mainly used for the production of second generation bio-fuels,[12] according to a biorefinery approach. Algae have also been recently considered for biofuel production and biorefinery purposes, thanks to rapid biomass productivity and high lipid content.[13,14,15]

LB structure is the result of interactions between cellulose (30-50%), hemicellulose (20-50%) and lignin (10-30%), which are natural polymers also known as LB macro components,[16] having different roles in the plant cells. Cellulose is constituted by chains of 10000 and 15000 cellobiose units, and is organized with a hierarchical structure.[17] Hemicellulose is a heterogeneous polymer constituted by C5 and C6 sugars, possessing a branched structure, that forms a sheath-like coating on cellulose fibrils, acting as a strengthening actor in LB structure and hindering accessibility to cellulose fibrils. Partial removal of hemicellulose is then pivotal to achieve biomass valorisation, and pre-treatment techniques have been developed for this purpose.[17, 18] Lignin is a three-dimensional amorphous polymer with a high molecular weight constituted by hydroxyl- and methoxy-substituted phenylpropane units (*p*-

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coumaryl, coniferyl, and sinapyl). The lignin role is mainly structural, as it gives rigidity to the cell wall and makes the internal components of the LB recalcitrant to degradation due to its hydrophobicity and its resistance to physical agents and micro-organisms (insects, pathogens). The aromatic nature of lignin structure makes this polymer the most viable renewable source for aromatic compounds and polymers production.[19, 20] LB-derived wastes have recently been attracting more attention worldwide as cost-effective source for catalysts synthesis. LB derived catalysts are easily available, biodegradable, non-toxic, and environmentally benign. The presence of minor components in LB can lead to different outcomes. Indeed, the presence of small amounts of lipids is a threat due to catalyst poisoning. On the other hand, the presence of mineral species can both be exploited for catalyst synthesis and cause catalyst deactivation when present in the employed biomass feedstock.[21, 22, 23]

Differently from fossil resources, LB are composed by highly functionalized substances. The general formula of monosaccharides $C_x(H_2O)_y$ implies higher oxygen content than crude oil.[24] This differences brings LB valorisation to be achieved via de-functionalization reactions as hydrogenolysis, decarbonylation, deoxygenation, dehydration and deoxydehydration.[25] The differences between precursor and products for fossil and non-fossil feedstocks are highlighted in the 2004 list of the twelve most promising bio-derived platform chemicals (PC) published by the United States Department of Energy,[26] updated in 2010.[27]

The firstly developed processes for biomass valorisation used concentrated mineral acids (e.g. $H_2SO_4$) as catalysts to promote bonds cleavage (e.g. carbon-oxygen bond) [28]. However, heavy dependence on acids recovery capacity and waste disposal costs (neutralization), along with high E-factor (Environmental factor, that is a simple metric of how "green" a reaction is, defining the amount of waste generated by a process), constitutes a liability for further development of these processes.[29,30] Biochemical processes are considered as another viable option for future developments of biorefinery processes, even though to date, their role in LB valorisation is judged limited by the lack of available literature.[31,32,33] Another option for biomass valorisation is represented by catalytical processes. Historically, heterogeneous catalysis has been mainly used for gas-phase processes;[34] however, recent technological advances allowed to bring out the potential use of these catalysts, thanks to important achievements, such as ease of separation from reaction mixture, a key feature for sustainability.[35] Palkovits et al. have recently labelled catalysis as the most useful instrument to promote biorefinery processes, thus expressing the importance played by an efficient catalytic system.[36,37]

Catalysts world market was estimated to reach 33.9 USD billions in 2019, with an expected 4.4% compound annual growth rate from 2020 to 2027. For the sake of comparison, the corresponding catalysts market size is now nearly six times higher than it was in 1991.[38] The use of catalysts also enables revenues 100-1000 times higher than the catalytic system price, matching perfectly with one of the aforementioned circular bioeconomy goals.[5] Despite the progresses in biomass upgrading by means of metal-supported heterogeneous catalysis,[39, 40] this systems still suffers from drawbacks such as lack of circular aspect, low conversion and low catalytic activity.[41] Process profitability for these catalysts is also severely threatened by the surge of noble metals cost in the early 2020s. Considering that a low E-factor is a condition *sine qua non* for the development of a sustainable process,[30] research has lately been focusing on alternatives to the previously discussed heterogeneous catalysts. In line with the recent tendency to use cheaper green materials for chemical production, biomass-derived catalysts (BDC) have been identified as a key player for the establishment of closed-loop processes. Low cost and carbon neutrality of feedstocks have driven the choice towards BDC, enabling the replacement of coal as a main source for their production and shifting from fossil to renewable resources.[42,43] Despite interesting review works treating roles of carbon-derived materials have been recently been published by Lan, [44] Xia, [45] and Solikhin, [46] a biomass-to-biomass approach has never been described, since commercial cellulose or hemicellulose are often employed as starting material for catalysts' production and model compounds (e.g. phenols and furfurals) constitute the target molecules. These results can be deceiving, given that considerations regarding the direct employment of raw biomass are left out of the equation. To provide a holistic approach to biomass valorisation via BDC, it has been chosen to consider the overall circularity of the described processes as the focus of this review. The catalysts source, the preparation methods and their performances are therefore reported in this tutorial review.

## 2. Biomass-derived carbons for catalysis

Biomass-derived carbons are extremely attractive materials due to the opportunity of tuning their properties for several energy-related applications. Carbon Materials (CM) represent a spread class of substances, which normally possesses a hierarchical porous network as a consequence of a thermal treatment.[47] Generally, pores are classified depending on their diameter (micropores (< 2nm), mesopores (2-50 nm) and macropores (> 50 nm), and different dimensions reflects on different tasks for molecular diffusion in the carbon material.[48] CM normally possess chemical resistance and hydrophilicity/hydrophobicity tuneability via functional groups insertion, features whose exploitation has attracted interest for their catalytic use.[49, 50]

The type of biomass has a significant effect on the properties of the carbon materials produced.[51] Indeed, different biomass sources contain different compositions of cellulose, hemicellulose, lignin, and other organic and inorganic components, which influence the physical and chemical properties of the resulting carbon materials. Moreover, different biomass types have varying amounts of carbon, hydrogen, oxygen, nitrogen, and other elements. This affects the overall chemical structure and functionality of the resulting carbon materials.[52]Customised biochar from agro-industrial waste can effectively enhance the thermochemical conversion of biomass, where precise control of production parameters and post-treatment modifications are crucial to achieve the desired catalytic properties.[53]

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Due to complexity of the topic, a classification of different CM is required and reported herein. It is worth mentioning how in literature, the names defining different CM have sometimes different meanings and often overlap (e.g., activated carbons and sulfonated carbons), making in some cases a classification difficult and contradictory.

### 2.1. Biochar

Biochar is a stable, porous, carbon-rich pyrolysis product, formed along with bio-oil and syngas after the organic feedstock thermal degradation in non-oxidizing conditions.[54] Its production from biomass waste represents a valuable strategy to promote carbon neutrality and circular economy. Biochar is notoriously considered a multi-purpose material for environmental applications and has been studied as a viable solution for environmental issues as greenhouse gases reduction, carbon sequestration and soil amendment.[55, 56, 57, 58] Another promising biochar application encompasses the replacement of coal-derived materials for water treatment and decontamination, that may allow to overcome sustainability and environmental issues related to the use of fossil sources.[59, 60] Literature widely considers surface area and porosity as the most important parameters to optimize during biochar production, thanks to their influence on the number of active sites available. [50, 61] A complete work from Leng et al. [62] grouped the effect of feedstock and pyrolysis conditions on textural properties, while recent updates on biochar modification are discussed in a recent work by Low et al. [63] Despite significant advances in CM research , a standard procedure to tailor CM properties starting from different kind of biomasses and processes has yet to be established.[64] Biochar-based catalysts play a central role in sustainable biorefineries due to their promising characteristics, which include cost efficiency, and thermal behaviour. Advancements in synthesis methods, characterization techniques, and the catalytic performance of biochar in diverse environmental and energy-related applications have recently been discussed.[65] Establishing structure-activity relationships and understanding deactivation mechanisms will provide new insights to overcome technical and economic barriers to optimize performance and commercial viability.

**2.1.1. Biochar from pyrolysis.** Among different biomass thermal conversion processes, pyrolysis represents one of the most promising technologies that enables rapid conversion of biomass into the liquid product termed as bio-oil, biochar as the solid product and the combustible gases.[66]

A comprehensive overview of various biochar production methods and their use as catalysts in biofuel production from algae has been proposed recently, discussing the advantages and limitations of each technique.[67] Additionally, the authors explored the synergistic effects of biochar catalysts in enhancing algal biofuel yields and the sustainability of biofuel production processes. Optimizing the production techniques and understanding the interactions between biochar properties and catalytic performance are essential for practical application. Pyrolysis outcome is mainly controlled by residence time, temperature and heating rate, resulting in pyrolysis classification to be made upon these three parameters. According to recent review works, four pyrolysis types are usually considered: (i) slow pyrolysis, (ii) fast pyrolysis, (iii) intermediate pyrolysis and (iv) torrefaction.[68] For each type, the process conditions have been reported in detail in **Figure 1a**. However, an accurate screening of pyrolysis techniques still remains challenging, due to the relevant influence of other parameters (such as reactor type, biomass type) on the process outcome. Moreover, the temperature strongly affects LB and CM structure,[69] as shown in **Figure 1b**. Depending on the formation temperature, different char typologies made up by mixtures of physical and chemical phases can be produced: unaltered plant material, transition, amorphous, composite and turbostratic char (upper panel). By increasing the temperature, a rapid decrease in char yield, accompanied by a relative increase of fixed-C yield, and a stable ash content are observed between 100 and 700 °C. [69] At these temperatures, a large fraction of ashes is not decomposed. Therefore, the choice of carbonization temperature is important when biomass is employed for catalyst synthesis. In addition, also the pretreatment influences the yield, due to the generation of decomposable aromatic rings and branch chains (e.g., carboxylic acid structures formation). It is then possible to draw a general conclusion implying that the severer the process conditions, the lower the biochar yield. A side effect is the higher yield of bio-oil and syngas.

The effects of heating rate and temperature on the products yields for the different process have been rigorously screened within the literature and represented in a radar diagram shown in **Figure 1c**. The radar diagram effectively combines the influence of each parameter on the different processes: pyrolysis (blue area), gasification (green area) dry torrefaction (orange area) and hydrothermal carbonisation (HTC, red area). Among other pyrolysis techniques documented in literature, worthy of note are the oxidative torrefaction (with agents usually implied for combustion) and the steam torrefaction (steam treatment at <260 °C for 10 minutes).[70] Torrefaction is a thermochemical pretreatment similar to a slow and mild pyrolysis, which is typically conducted at temperatures between 200 and 300 °C in a non-oxidizing atmosphere. During torrefaction, the polymeric structure of biomass –mainly the hemicellulose portion– is partially degraded, leading to a more hydrophobic, breakable, and thermally stable solid. Moreover, pre-treating biomasses by slow oxidative torrefaction increases their surface area and total pore volume (meso-/micropore volume), and the surface chemistry of these materials turns out to have a higher density of carboxyl groups. [71]

Hydrothermal liquefaction is also mentioned as a technique for bio-oil synthesis, and has been recently employed for bio-oil production from algae.[72] Despite the use of sustainable solvents (water) and the relatively mild temperatures used (200-450°C), the high pressures required for this process (10-25 MPa) involve safety improvements before considering an industrial scale-up.[73, 74] For these reasons, hydrothermal liquefaction will not be discussed in this review. The commonly accepted model for biomass pyrolytic degradation implies three steps: i) evaporation of free moisture ii) primary pyrolysis of unstable

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fraction of polymers and iii) secondary pyrolysis involving more stable components.[75] It has been reported that microwave (MW)-assisted pyrolysis of agricultural waste biomass is a promising method for obtaining high-quality biochar, offering improved efficiency and environmental benefits compared to conventional pyrolysis techniques. However, economic assessment is needed before developing any advanced solid waste management technologies.[76]

**2.1.2. Biochar from hydrothermal carbonization/hydrochar.** Also known as wet torrefaction, hydrothermal carbonization is an aqueous process exploiting subcritical water action to produce char, normally referred to as hydrochar.[77] The operating temperature ranges from 180 °C to 250 °C with the mild conditions making it a valid candidate for the development of cost-effective and sustainable methods for biochar production. Hydrochar is usually produced with higher yield than biochar, and possesses lower surface area, lower ash content and lower carbon content (<60%).[78] Other differences between biochar and hydrochar rely in the different moisture degrees allowed in hydrothermal carbonization and pyrolysis. For example, the higher number of oxygenated groups found on hydrochar surface favours the adsorption of metal species, paving the way for an efficient metal dispersion in view of catalytic applications.[79] In general, the low porosity tuneability is the major drawback of this process, indicating that the use of a directing agent is required for the formation of an ordered structure. [44]

**2.1.3. Char from gasification.** CM are also obtained as by-products of other thermal degradation processes.[80] Among others, gasification is a high-temperature and high residence time process used for syngas production, denoted by higher operative temperatures. Despite lower char yields (~10% ), cracking reactions occurring during gasification result in char with higher surface area and non-aligned graphite planes.[43, 81] Gasification could be divided into four phases. After undergoing drying (100-200 °C), and pyrolysis, 800-1200 °C temperatures are reached, causing oxidation (achieved with steam, air, or $CO_2$) and partial combustion reactions. The process is concluded after the gasification step (650-900 °C) of the previously formed volatile substances.[70]

### 2.2. Activated carbon

From a catalytic point of view, low porosity of biochar represents a relevant hurdle for the development of catalysts for biorefinery purposes, which can be solved with activation processes and has attracted great consideration for environmental and catalytic applications.[62, 68, 82] The resulting activated carbon (AC) is defined as an amorphous non-graphitic microcrystalline material.[83] Despite ACs can be derived from a plethora of fossil and non-fossil feedstocks, they will only be considered as the product of physical and chemical activation processes of bio-derived CM.[22, 62, 84, 85, 86, 87]

**2.2.1. AC from physical activation.** Physical activation exploits the action of temperature and oxidizing atmosphere to achieve widening of pores, improve porosity and obtain microporous carbon. Activation can be obtained by means of steam,[88] $CO_2$,[88, 89] and air[90] with a temperature range between 350 °C to 1000 °C and reaction times ranging from minutes to hours,[62, 91] as detailed in **Figure 2a**. The difference between the atmosphere applied for pyrolysis and activation always resulted in the sequential use of these two processes, which means longer times and higher energy consumption. To achieve a one-step activation, atmosphere replacement with oxidizing agent (in the midst of thermal treatment) may constitute a solution.[92, 93] Novel activation techniques using $NH_3$ [94] and gas mixtures (such as $NH_3$+$CO_2$) [94, 95] have emerged in recent years. Moreover, a recent study from Yin et al. reported a smart approach for biochar activation from corncob-derived furfural-rich feedstock implying gasification residue as oxidizing agent, hence providing a circular insight to biochar activation techniques (**Figure 2b**).[96] Biomass self-activation represents a promising alternative to AC production in which biomass precursors can undergo physical self-activation. These techniques are adopted to avoid the addition of outer substances to the system, with eventual disposal problems previously documented.[97] In particular, physical self-activation implies the creation of a porous network through a reaction between pyrolysis gas (in particular $CO_2$ and $H_2O$) and the carbonaceous residues.[98]

**2.2.2. AC from chemical activation.** Chemical activation involves a combination of chemical activating agents and a thermal treatment, milder than physical activation.[99] The penetration of activating agents inside the precursor structure and the consequently promoted oxidation/dehydration processes normally result in a finer and hierarchical structure [22] (**Figure 2a**). Chemical activation can be a one-step (pre-pyrolysis addition) or a two-steps process (post-pyrolysis addition) depending on the activating agent addition. Differently from physical methods, chemical activation can be performed with only one furnace, denoting more easy operativity.[100] Post-treatment procedures usually involve AC rinsing, generating high volumes of wastewater and posing sustainability issues on the process.[97] The nature of LB mixing with the activating agent defines different chemical activation methods. Respectively, wet (mixing in aqueous solution) and dry methods (solid-phase mixing and following grinding) can be carried out.[101, 102, 103] Depending on the nature of the activating agent, AC can be produced via oxidation or dehydration reactions. Oxidation occurs after the precursor treatment with alkali hydroxides (e.g. NaOH, KOH) [104, 105, 106] or alkali carbonates (e.g. $K_2CO_3$).[107, 108] Dehydration is caused instead by the action of activating agents such as $H_3PO_4$ [82, 109, 110] and $ZnCl_2$.[111, 112] Corrosion issues and environmental sustainability caused by these methods are being tackled with the study of benign activating agents made in recent years.[113, 114, 115, 116, 117, 118] When evaluating the effectiveness of a chemical process for AC production, the reported literature considers carbon yield as the most important indicator for AC production. Also, given the different nature of activating agents employed for chemical activation (acid, basic and neutral), two papers by Andas et. al have indicated acid ($H_3PO_4$) [101] and neutral activating agents [119] ($ZnCl_2$) as more capable of achieving higher carbon yield rather than basic agents (KOH). The higher carbon yield observed with $H_3PO_4$-AC is therefore one of the key factors leading to phosphoric acid being one of the most employed activating agents.

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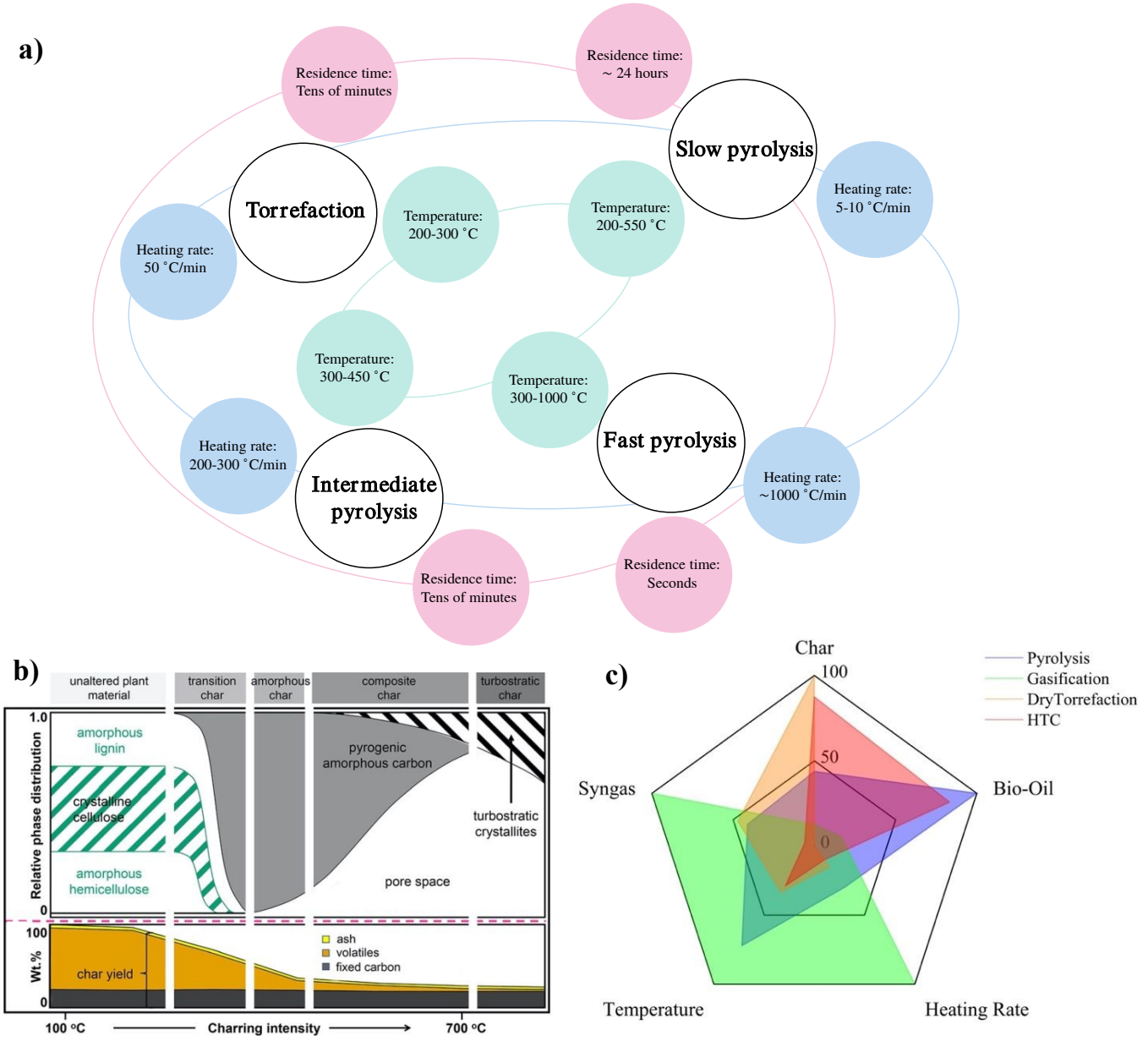


**Figure 1. a)** General parameters of pyrolysis processes. **b)** Temperature effect on LB and CM structure: evolution of the physicochemical structure of biomass (upper panel) and biochar formation during pyrolysis (lower panel), Reproduced from ref. [69] with permission from Elsevier, Copyright 2021. **c)** Representation of the effect of process parameters on LB thermal treatment outcome (built on data from ref. [80]). Every value has been obtained and drawn as a percentage of the highest value in every series. HTC= hydrothermal carbonization.

The presence of $Ca^{2+}$ and $Mg^{2+}$ alkali species can be exploited to perform chemical self-activation. In this specific case a thermal treatment causes the formation of CaO and MgO, which act as templating agents, enabling pores formation.[22, 120]

Chemical activation also plays a pivotal role for CM functionalization, since the presence of functional groups on CM surface is tightly related to their reactivity.[121] Functional groups such as -COOH, -OH and -$SO_3H$ have been found to be the most suitable for biorefinery-related applications.[122, 123] Indeed, the presence of these groups in CM leads similar Brønsted acidity compared to mineral acids, making the former ones good candidates for replacing the latter ones thanks to their low-cost, stability and circular approach.[124, 125] For a comprehensive view of ACs, Gao and Sevilla contributions

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review in detail the formation mechanisms and the different activation techniques adopted for AC production.[22, 126]

## 3. Carbon catalysts for lignocellulosic biomass and waste valorisation

The role of catalysis in the implementation of sustainable technologies for the conversion of non-edible biomass into biofuels and chemicals is of crucial importance. The urge to develop biorefinery catalytical systems facing the sustainability issues has trailed scientific research toward these topics, and to date literature treats almost every aspect of a biorefinery. The number of papers regarding CM used as catalysts for LB and waste valorisation led to consider herein only the processes that solely involve the original feedstock, avoiding model compounds (e.g. glucose) and their specifical reactions.

### 3.1. Biomass-derived catalysts for thermochemical processes

To date, the most relevant and complete paper dealing with LB pyrolysis is a review work published by Sharifzadeh and colleagues, which elegantly discusses pyrolysis-related factors (e.g. feedstock role, process configuration, economic feasibility) and catalysis for bio-oil upgrading.[127] Bio-oil is a liquid mixture containing water (20-30%) and polar organic substances (organic acids, alcohols, phenols, and pyrans/furans). High values of bio-oil yields are obtained from fast pyrolysis, which is consequently the most used pyrolysis technique for its production.

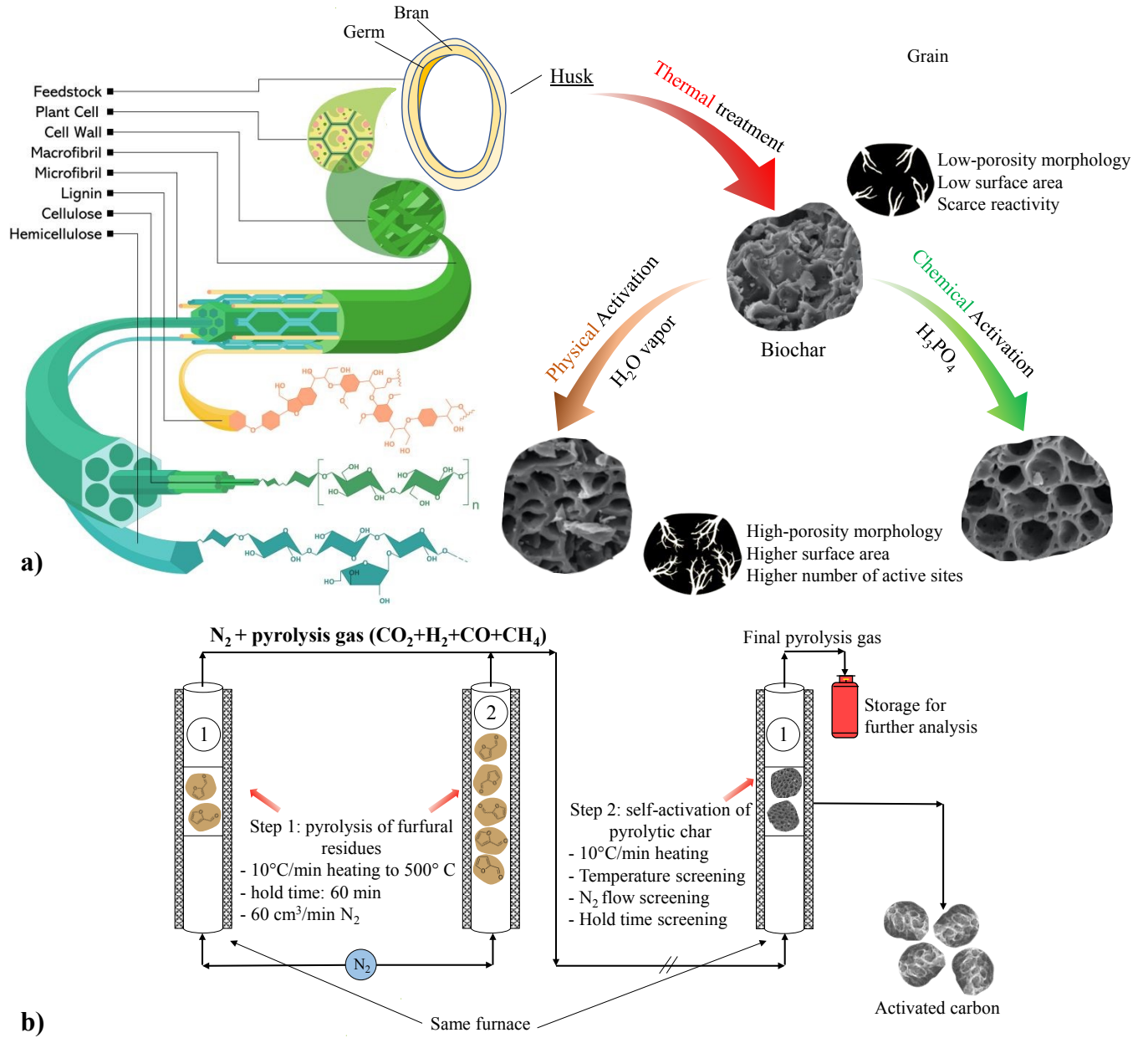


Figure 2. a) AC production from residual biomasses. Reproduced from ref. [86] with permission from Elsevier, Copyright 2021 and from ref. [87] with permission from Wiley, Copyright 2019. b) Scheme of the AC physical activation process for closed-circle biochar activation. Reproduced from ref. [96] with permission from Elsevier, Copyright 2018.

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Despite being evaluated as a substitute for fossil feedstocks, the presence of water, corrosion issues and high viscosity are severe drawbacks affecting bio-oil. Other detrimental features are the lower heating value and the lower flash point, that hurdle direct engine use.[128] The necessary improvement of bio-oil properties involves the development of upgrading processes, that are generally classified as physical, chemical, and catalytic. Due to the considerable oxygen presence, the use of heterogeneous catalysts able to perform deoxygenation is required to upgrade processes.[36] Being phenols the most relevant bio-oil fraction, high yields of this class of substances are often considered by works dealing with bio-oil production from LB as the most important result to achieve.

Due to their aromatic nature, phenols are assumed to arise mainly from lignin. This hypothesis has been confirmed by works studying catalytic pyrolysis of lignin.[129, 130] However, phenols have also been found to derive from catalytic pyrolysis of glucose, cellulose and hemicellulose, and pyrolysis mechanisms were proposed (**Figure 3a**) .[130] More in detail, oligosaccharides and monomeric sugars (4, mainly levoglucosan) were obtained from cellulose depolymerization (1). Dehydration of oligosaccharides took place on the surface acid sites of the bio-based carbon catalyst to form 2-methylfuran, 2(5H)-furanone and furfural (from 1 to 4 or from 1 to 5). At the same time, levoglucosan conversion occurred outside and inside the pores, and only 2-methylfuran and furfural were produced (from 4 to 5). Furans and small hydrocarbon molecules were formed starting from xylan, acids, aldehydes, and ketones (from 2 to 6, 12 and 14). Catalytic lignin depolymerization, followed by deoxidization and demethylation produced phenol (from 3 to 7, 13 and 14).

From a catalytic point of view, the most interesting approach for BDC use to maximise phenols production is achieving precise combinations of functional groups embedded in the CM structure able to promote phenols formation. This scope has been described by Li et al., in their study [130] a bio-based carbon catalyst was prepared from shell dried coconut carbonized at 900 °C for 1 h under $N_2$, then activated with steam at 800 °C for 1.5 h and soaked in 1 M $HNO_3$ solution, at 40 °C for 4 h. High catalytic activity and selectivity in the production of furans and phenols from corncob fast pyrolysis were achieved at 350 °C, therefore improving the bio-oil quality. This was ascribed to the presence of tailored acid sites (with weak acidity and Lewis's acid sites) at the surface of the bio-based carbon catalyst as revealed by XPS characterisation (**Figure 3b**), indicating the presence of mainly graphitic carbon with phenolic, alcohol, ether components. Moreover, C in carbonyl or ester groups was also present. The O1s signal indicated that oxygen species ($O_2^{2-}$ or $O^-$) are adsorbed at the surface of the catalyst and confirm carbonyl groups. Interestingly, also surface OH groups, as well as carbonyl oxygen in ester and anhydrides were detected. [130]

Bamboo waste was efficiently pyrolyzed in the presence of N-doped biochar catalysts obtained as by-products of bamboo N-enriched pyrolysis within a truly circular approach. [131] Catalysts with different nitrogen contents were obtained by adding 10 vol%, 30 vol %, and 50 vol% $NH_3$ solutions, respectively and then performing bamboo fast pyrolysis at 600 °C for 30 min. It was found that the catalytic activity increased by increasing the N content which also enhanced surface area and porosity. As for the mechanism of the catalytic pyrolysis process, it was proposed that the N-doped biochar catalyst acted firstly as an adsorbent for bamboo pyrolysis.[131] Due to its alkaline property, the N-containing groups can adsorb the pyrolytic intermediates (**Figure 3c**). Then N- and O- containing groups catalyse the reaction, pyrrolic-N provide hydrogen to radicals of 4-vinyl phenol, 4-ethyl phenol, p-cresol, phenol adsorbed at the surface of the catalyst and promote the production of phenols. At the same time, –COOH, O–, C=O, and –OH groups react with O-species intermediates to form phenols and aromatics. N-containing groups also catalyse the reaction between adsorbed phenols intermediates and O-species, hence producing large amounts of phenols by dehydration. Moreover, C=O species react with water forming –COOH groups, which decompose by releasing $CO_2$.[131]

As a matter of fact, N-doped biochar catalysts effectively promoted the production of phenols that reached 82%, especially valuable 4-vinyl phenol (31% and 6.65 wt% yield). Aromatics were also formed, whilst the generation of O-species and acetic acid was inhibited, resulting in an enhancement of the bio-oil quality. Interestingly, *N*-containing groups showed good stability during bamboo catalytic pyrolysis, whilst O-containing groups decreased under reaction conditions. The possible formation pathways of the main 4-vinyl phenol product are reported in **Figure 3d**. Firstly, the N-doped catalyst promoted the cleavage of the β-O-4 bond in lignin and of dehydration reactions, leading to the formation of *p*-coumaryl, coniferyl and sinapyl alcohol intermediates, which in turn converted to 4-vinyl phenol with the removal of $–CH_2–OH$ and $–O–CH_3$ groups. [131]

Zhang et al. hypothesized that the presence of -OH, -P-O, -P=O and C-P-O functional groups in a $H_3PO_4$-AC can act as a selective tool for phenols production from sugar-derived molecules.[132] The establishment of the so-called "phenols pool" constitutes then another positive feature deriving from $H_3PO_4$ activation. Pyrolysis is also considered a fundamental tool for the transformation of LB into syngas, $H_2$, CO, $CO_2$ and $CH_4$ mixture, whose employment ranges from industrial applications (e.g. fuel and $NH_3$ production) to heat production via combustion.

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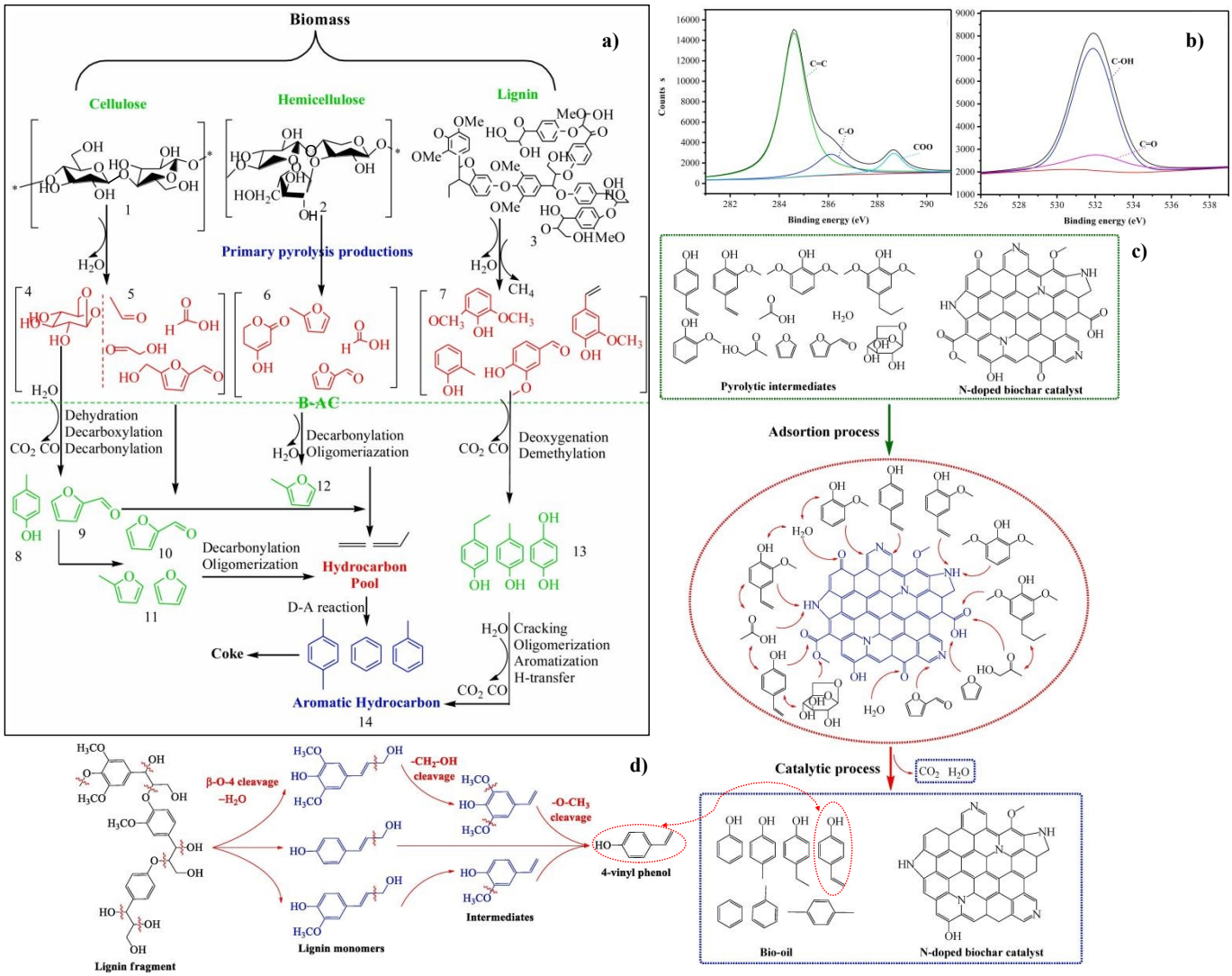


**Figure 3. a)** Proposed reaction pathways of corncob fast pyrolysis for obtaining furans over bio-based activated carbon. Reproduced from ref. [130] with permission from Elsevier, Copyright 2020. **b)** XPS spectra of the bio-based carbon catalyst C1s (left panel) and O1s (right panel. Reproduced from ref. [130] with permission from Elsevier, Copyright 2020. **c)** Proposed mechanism of bamboo waste catalytic pyrolysis over N-doped biochar. Reproduced from ref. [131] with permission from Elsevier, Copyright 2020. **d)** Proposed 4-vinyl phenol formation mechanism during catalytic pyrolysis of bamboo waste over N-doped biochar. Reproduced from ref. [131] with permission from Elsevier, Copyright 2020.

The interest towards syngas is $H_2$ production via biomass gasification has been sparked by the need of establishing a sustainable $H_2$ production as part of the ambitious European Green Deal. A EU report esteems that, by 2050, hydrogen could represent up to 13-14% of the EU energetical mix.[133]

To date, there are few works that deal with both $H_2$ production via gasification and bio-oil upgrading.[131, 134, 135] This is a consequence of the nature of bio-oil upgrading processes, that usually lowers $H_2$ yield in the gaseous fraction. It is then possible to state that one process rules out the other, moreover explaining the mutual absence of bio-oil yields in the relative $H_2$ yields paragraphs of catalytic gasification and catalytic pyrolysis. The development of catalytic thermal processes is usually performed starting from a catalyst that has proved efficient, hence avoiding considering less active, but cheaper solutions. This approach caused economical sustainability issues for the overall process and limited the development of catalytic pyrolysis to the pilot-scale stage. The help to overcome

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economical sustainability issues could then come from solutions distinguished by low-cost and acceptable activity, thus making CM an excellent candidate for catalysis.[136]

**3.1.1. Hydrogen production.** Within the European Green Deal frame, LB gasification-derived hydrogen is listed among other hydrogen streams, since this process can reach up to 85% syngas yield, with high $H_2$ selectivity (~50%), proving its competitiveness with $H_2$ production processes that use renewable energy.[137] However, as discussed in a critical review by You et al., establishing a mass production of syngas should be subordinated to the development of a sustainable procedure for syngas cleaning ($NH_3$ and $H_2S$ removal), which could be achieved with the use of gasification-derived CM, thus allowing a loop closure within the system.[138]

A significant role for LB gasification is played by reactor configuration. *In situ* processes enable the use of the same reactor for catalyst synthesis, gasification, and tar reforming. On the other hand, the lack of general process control and catalyst deactivation are issues affecting this configuration. As for the *ex situ* configuration, pyrolysis vapours are directed towards a reforming unit. This setup guarantees better control on the entire process and reduces deactivation issues. Nevertheless, *ex situ* setup requires higher capital.[139] For the sake of comprehension, recent developments in thermochemical processes have brought the reforming unit to be placed at the end of the pyrolysis layout. This has however caused a lack of uniformity when it comes to *in situ* or *ex situ* definition, because both classifications have been used to describe this setup. In this review, the terminology used by the original articles is maintained. In **Table 1** the use of BDC for catalytic gasification is summarized. Since tar formation is considered, the main drawback affecting LB gasification [140] (negative effect on syngas yield and production of health-hazardous polycyclic aromatic hydrocarbons), tar removal will be indicated, when present. In the presence of a catalyst, tar reforming takes place at lower temperatures than thermal treatments.[58] As a result of promoted tar reforming and enhanced activity, catalytic processes can offer syngas and $H_2$ yields higher than those related to non-catalytic processes.[61, 141] AC effect on tar steam reforming is widely treated in literature, and it could be observed that, when the reforming temperature needs to be optimized, coking-induced pore clogging prevails in AC, compared to biochar. This difference, with the consequential reactivity loss, is due to the AC finer structure.[61] Structural stability and deactivation recalcitrance are other requirements for BDC employed in catalytic gasification, because catalyst reusability is strictly correlated.[43, 140] Contributions by Guo and Zhang described both BDC synthesis and use in catalytic gasification, comparing different physical and chemical activation methods.[86, 142] Both procedures, along with the produced catalysts and a summary of the adopted conditions and catalytic results, are reported in **Table 1**, whereas a selected approach for ACs production from biomass is shown in **Figure 2b**. KOH-AC is the most performing catalyst for $H_2$ yield and tar removal, due to K-species embedded in the matrix. Despite gasification is considered a promising approach, further developments are limited by the endothermic nature of gasification reactions. A novel strategy to overcome this problem is represented by the use of enabling technologies, such as MW, which can provide up to 70% activation energy reduction for gasification related reactions (e.g. the Boudouard reaction), giving higher $H_2$ yields by operating at milder conditions.[143, 144] The high MW-absorbing capacity of CM enables surface hotspots formation, boosting CM reactivity. Limited MW-absorbance by LB hinders the possibility to carry out MW-pyrolysis/gasification processes. However, the progressive carbonization induced by the BDC results in a higher radiation absorption.[144] Nevertheless, strength of MW heating is also weakness. Indeed, hotspot formation exposes materials to a concrete risk of thermal runaway, and MW heating involves a great amount of energy dispensed in short times, requiring adequate facilities.

An integrated process involving MW-assisted acid pretreatment of lignin at 50°c for 60 minutes (AC catalyst) followed by lignin catalytic pyrolysis at 550 °C promoted 98.2% selectivity to phenols as well as syngas formation. [129] The proposed reaction mechanism for the catalytic pyrolysis of MW-assisted pretreated lignin over the AC catalyst is shown in **Figure 4a**. Firstly, the MW-assisted acid pretreatment partially broke the β-O-4 bonds and induced the formation of free radicals and carbenium ions, resulting in the production of mainly phenolic compounds and highly stable depolymerized products. The MW-assisted acid pretreatment resulted preferentially in the formation of monophenols, while promoting demethoxylation and then suppressing guaiacols formation. Up to 7.0 mg/mL of phenol concentration were obtained. FTIR characterisation (**Figure 4b**) revealed that the bands related to the presence of phosphoric groups at the surface of the AC catalyst slightly changed after 4 pyrolysis runs. Moreover, the recycle of the AC catalyst had little effect on the gas composition, while decreasing the $H_2$ concentration and increasing the $CH_4$ and CO concentration. [129]

To achieve the formation of new chemical bonds during gasification related processes, biochar based-nanocatalysts (BBNs) can represent a solution.[140] Metal particle dispersion and tar removal enhancement are undoubted advantages brought by this type of catalysts, that have recently emerged as a consequence of increasing knowledge and expertise on CM production.[63] Indeed, BBNs offer an interesting approach to coking issues (pore clogging and sintering), since metal species can be easily recovered after a thermal treatment, [64] reducing disposal cost and economic impact. The development of synthetic procedures is mainly focused on the improvement of catalyst activity and reusability, while preferentially using sustainable and low-cost resources as precursors, obtaining tailored structure and morphology and proper functionalisation. In this frame, the use of a Ni-BBN catalyst in gasification has been recently reported by Gai et al.,[145] evaluating the calcination temperature effect on the catalytic properties. The authors reported a mild one-step hydrothermal synthesis (see **Figure 5a**) for the preparation of highly dispersed Ni nanoparticles supported on hydrothermal carbon derived from waste biomass.

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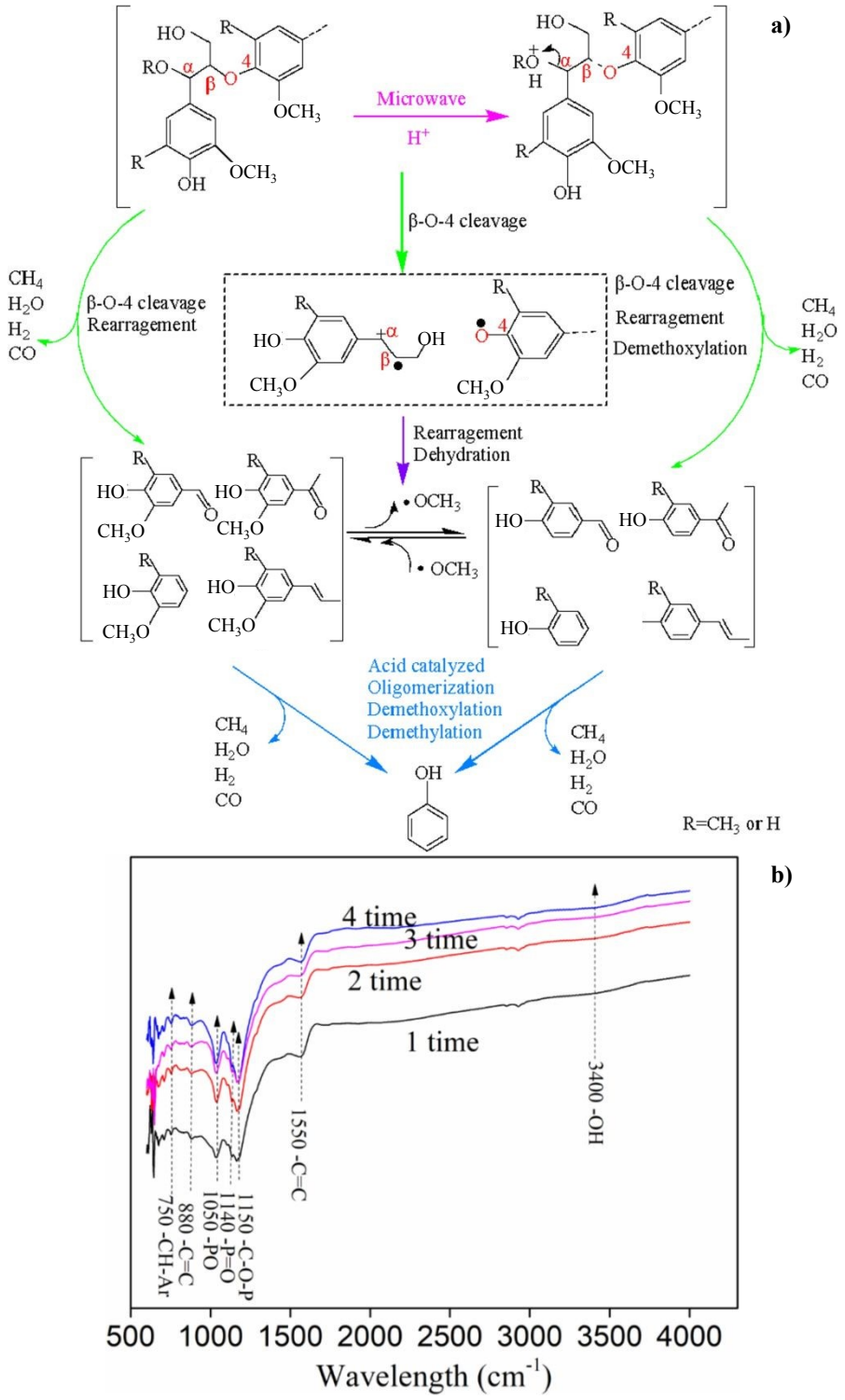


**Figure 4. a)** Proposed reaction mechanism of forming phenol from pretreated lignin pyrolysis over AC catalyst. Reproduced from ref. [129] with permission from Elsevier, Copyright 2019. **b)** FTIR spectra of the AC catalyst after reaction, 1 to 4 runs. Reproduced from ref. [129] with permission from Elsevier, Copyright 2019.

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Although the mechanism of hydrochar formation and growth upon hydrothermal carbonization of the lignocellulosic biomass still remains unclear, the corel-shell LaMer model, composed of a hydrophobic core made up of stable oxygen-containing functional groups and a hydrophilic shell with a -OH and -C=O functionalities was proposed for hydrochar. [145] The $Ni^{2+}$ ions were absorbed via ion exchange interactions with hydroxyl/phenolic, carbonyl, and carboxylic surface groups. The average size of the metallic nanoparticles was tuned between 8–13 nm by varying the preparation conditions (**Figure 5b**). The thermal biomass decomposition in the presence of the metal gave rise to the formation of free radicals in biochar. The derived hydrochar is a redox-active carbonaceous support, and its electron transfer ability is due to the presence of quinone-hydroquinone moieties, conjugated л-electron systems like phenolic hydroxyl.

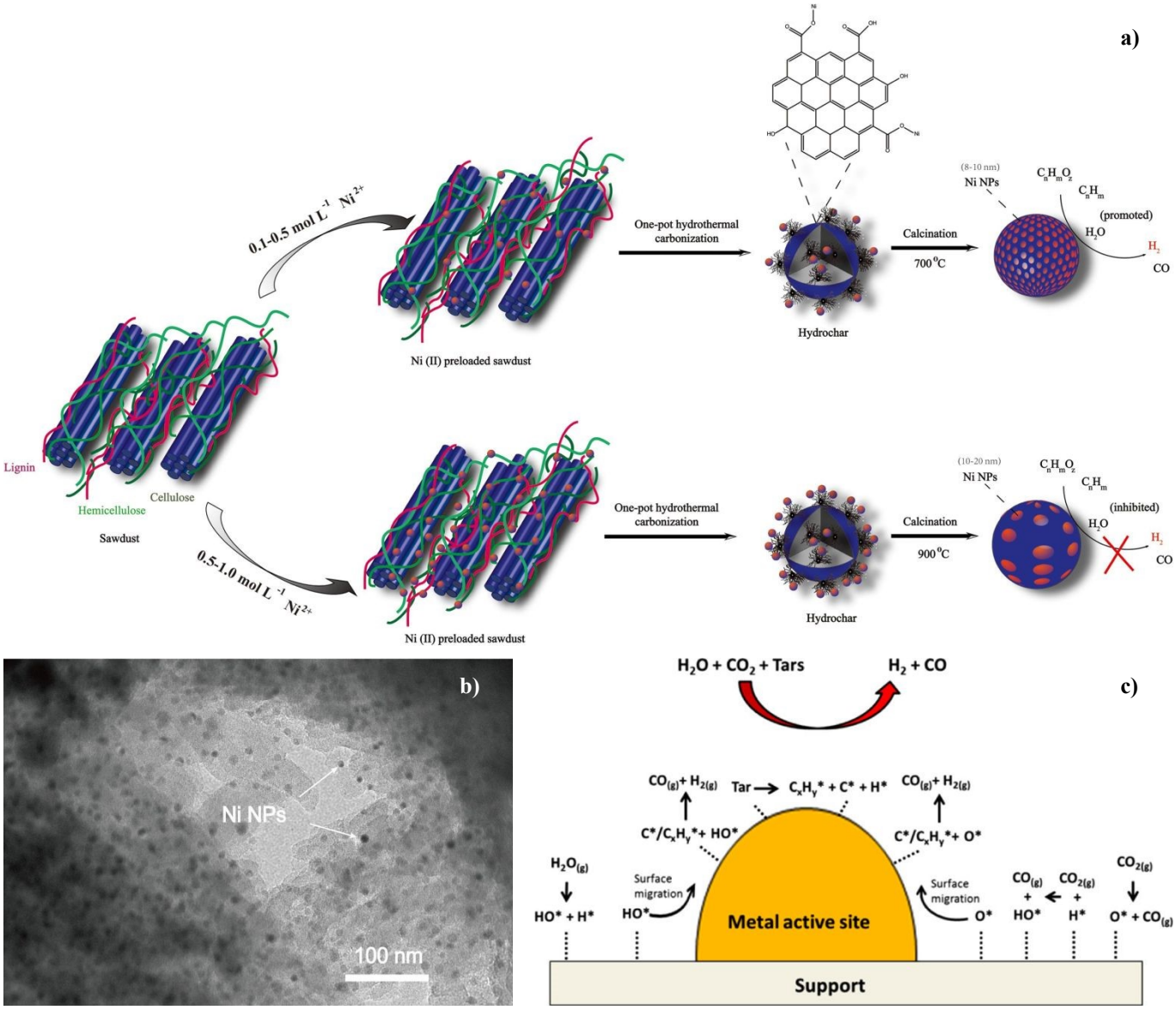


**Figure 5. a)** Synthetic scheme for the formation pathway of metallic nickel nanoparticles supported on hydrochar derived from lignin-rich precursor biomass. Reproduced from ref. [145] with permission from Elsevier, Copyright 2019. b) TEM representative image of the Ni-BBN. Reproduced from ref. [145] with permission from Elsevier, Copyright 2019. **c)** Scheme of catalytic tar steam and dry reforming. Reproduced from ref. [141] with permission from American Chemical Society, Copyright 2016.

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Therefore, the presence of metal ions (as for example $Ni^{2+}$, $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$, etc.) in biomass can enhance the electron-accepting and donating properties of the hydrochar and promote hydrogen-rich syngas production. Optimized calcination temperature (700 °C) that favoured strong metal-support interactions resulted in higher coking resistance of the BDC, while lower and higher temperatures induce respectively lower coking resistance and disordered structures.[145, 146]

The different pathways of catalytic tar steam and dry reforming over a metal supported BBN are proposed in **Figure 5c**. Hydrocracking, catalytic thermal cracking, hydrodealkylation, and hydrogenation reactions can occur on the metallic active sites, resulting in the decomposition of the adsorbed tar into active surface species, in particular, C* and H* species, and $C_xH_y$* fragments.[141] Also water vapour and $CO_2$ are dissociated on the surface of the BBN catalysts at both support and metal sites, which generated H*, HO*, and O* active species. Moreover, $CO_2$ can also react with the adsorbed H* to produce gaseous CO and HO* adsorbed species. Then, the species formed on the surface of the support can spillover on the metallic active sites and decompose the C* species and $C_xH_y$* fragments producing CO and $H_2$. These gases then desorbed from the metallic active sites. The mechanisms presented in **Figure 5c** are not the only mechanisms occurring for example, active surface species (C*, O*, HO*, and H*) can reassemble according to reverse activations to produce again $H_2O$(g) and $CO_2$(g) molecules. Furthermore, H* species can also react to form $H_2$(g) molecules. [141]

Given Ni-similar electronic properties and lower coking, Fe has been co-deposed with Ni,[147] guaranteeing high $H_2$ yield and tar removal, moreover showing reusability and reduced activity loss as reported in **Table 1**. Better performances of Fe-Ni BDC are ascribed to the presence of crystalline $FeNi_3$ alloy particles on the Sargassum chair (SC) support as revealed by X-Ray Diffraction (XRD) (**Figure 6a**), which promote coking resistance and improve deactivation recalcitrance resulting in improved $H_2$ yield from peanut shell catalytic gasification (**Figure 6a**).[148]

Other useful considerations regarding Fe-Ni BDC are reported in an interesting paper by Xie et al., where the bimetallic particles (TEM image in **Figure 6b**) were deposed on wood chips-derived carbon nanofibers showed in the Scanning Electron Microscopy (SEM) image, achieving low decreases of $H_2$ yield and tar removal after 13 cycles (**Figure 6b**). The robustness of the produced catalyst resulted into recalcitrance to deactivation ascribed to t[143]he sacrificial role of Fe, which easily reacts with tar components avoiding tar deposition on Ni particles.[147]

Iron has been employed in gasification as the only deposed metal on BBN. The co-presence of crystalline Fe and $Fe_3O_4$ enhanced $H_2$ yield in the gaseous fraction and provided interesting insights on coking-induced deactivation [149, 150] (**Table 1**, **Figure 6c**). In addition, the one-step copper deposition on a $ZnCl_2$-AC -a rice husk-derived char (RHC) was used- has been reported, showing promising gasification results (according to **Figure 6d**, built on the data reported in the study) and primary tar removal (**Table 1**). [151] Moreover the 1.0Cu1.0Zn/RHC proved to be stable, withstanding five recycle tests (**Figure 6d**). Indeed, it was shown that $Cu^0$ nanoparticles were the active species and formed during biomass pyrolysis. Conversely, the addition of $ZnCl_2$ guaranteed an increase in total pore volume and specific surface area (803.1 $m^2/g$ for 1.0Cu1.0Zn/RHC), resulting in improved dispersion of the nanoparticles (**Figure 6d**). The highest tar conversion efficiency of 94.5% was obtained at 800 °C-1.0Cu1.0Zn/RHC. Interestingly, the results showed that the gas quality was improved in the presence of the catalyst. Oxygenated aromatic compounds and a reduced number of light compounds were obtained after the catalytic cracking. As a matter of fact, the exploitation of metallic species embedded in the carbonaceous matrix following the activation procedure represents an innovative preparation method for mono- and bimetallic BBN.

**3.1.2. Bio-oil production and upgrading.** Bio-oil competitiveness with fossil feedstocks depends on setting up a production able to meet composition and performance targets for engine use. [47] In this field, recent works grouped and analysed the effect of process parameters,[54, 152] process development,[153] and use of different feedstocks,[154] highlighting the complexity of these systems. The use of mathematical models could help in the comprehension of the pyrolysis mechanism, favouring the development of new catalytic systems able to improve the production of bio-oil, even if discrepancies are often observed between the expected and the observed results.[155, 156] Moreover, bio-oil production is affected by a significant bias, since process conditions are often optimized to reach the highest yield, leading to the presence of notable amounts of water and undesired substances.[152, 157] The most interesting BDC used for bio-oil production are listed in **Table 2**, built with an approach similar to **Table 1**. Catalytic upgrading can be achieved via one-step and two-steps processes, the first one being the most viable option, due to higher costs and catalyst deactivation issues of the two-stage approach.[158] *In situ* and *ex situ* configurations are generally considered; the former is deemed more promising due to higher economic sustainability, despite being to date less used.[159]

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**Table 1** Use of BDC for biomass catalytic gasification and tar removal.

| **Feedstock** | Rice Husk (Catalyst); Corn Straw (Substrate) | Rice husk (Substrate and catalyst) | Wood chips (Substrate and carbon nanofibers) | Wheat straw (Substrate and catalyst) | Rice husk (Substrate and catalyst) |
|---|---|---|---|---|---|
| **Gasification** | Dual stage process; fixed bed reactor; 600°C (First Stage), 800°C (Second Stage), 20min | MW-assisted process; Ex situ MW-tubular reactor; 600°C, 30 min, (Conventional heating, pyrolysis unit); 800°C (MW heating, reforming unit) | Dual stage vertical quartz reactor; 550 °C (First stage), 700 °C (Second stage) | Dual stage fixed bed quartz tube; 600°C (First stage), 900°C (Second stage) | Dual stage fixed bed reactor; 600 °C (First stage), 800 °C (Second stage), 20 min |
| **Activating agent/deposed metal** | KOH | Ni10.42 | Fe0.64-Ni0.36 | Fe (5 wt%) | Zn 2.32% + Cu 21.61% |
| **Activation/Production conditions** | Impregnation; Thermal treatment (800°C, 10°C/min, 40 min) | Pyrolysis, 900 W, 15 min; Ni impregnation; Thermal treatment, 800 W, 10 min | Fe-Ni impregnation; pyrolysis (700°C, 1 h) | Fe-impregnation; Calcination, (900 °C, 2 h) | Zn + Cu impregnation; 800 °C, 20 °C/min, 60 min |
| **$H_2$ yield ($mL_{hydrogen}/g_{biomass}$)** | 704.85 | 259 | 300; catalyst retained reactivity for 13 runs | 381.08 | 96.6 |
| **Tar removal (%)** | 91.75 | 98.6 | 85.76, complete aromatic removal | N.A. | 94.5 |
| **Ref.** | 86 | 142 | 147 | 149 | 151 |

The development of one-step processes must then involve multifunctional catalysts able to promote bio-oil upgrading and coke removal.[81, 150 160,]

Considering several factors such as i) the mismatch between global production and global requirement, ii) the high presence in chemical and pharmaceutical industry, iii) the low-yield production from fossil resources and iv) the limited selectivity of inorganic catalysts, the establishment of bio-based phenols production via catalytic pyrolysis is thought to be necessary to lower the dependence from fossil resources. Given the nearly-mature industrial use of BDC for pyrolysis, a steady flow of publications regarding sustainable high-quality bio-oil production has been published in recent years.[159] Uncatalyzed processes are also denoted by low phenols yield, causing the sustainability of LB-derived phenols production to completely depend on the catalytic system. Understanding and ranking the actual yield of phenolic compounds could be challenging, due to the lack of uniformity among results from different authors. Under the name "phenolic substances", in some cases, are only meant phenols and similar molecules (e.g. cresol), while in some works alkyl-phenols are also included. AC-catalysed pyrolysis of LB produced good selectivity towards furanic and phenolic compounds.[130] The improvements brought by BDC to bio-oil yield via pyrolysis are clearly reported in a work by Tahir et al. (**Table 2**), also involving temperature effect on bio-oil composition.[161] In this study, the use of BDC has proved to be effective when adopting mild conditions for the pyrolysis process (500 °C). AC catalytic properties were also coupled with MW-assisted torrefaction on raw biomass, inducing a 4-fold increase in phenols selectivity and showing the importance of combining BDC with pretreatment procedures and enabling technologies (**Table 2**). [157]

*In situ* MW-assisted catalytic pyrolysis is also described in a contribution by Yang et al., where alkyl-phenols production from sawdust was explored.[162] However, given the number of process parameters involved, the adoption of experimental design procedures for pyrolysis has been reported as an efficient optimization tool.

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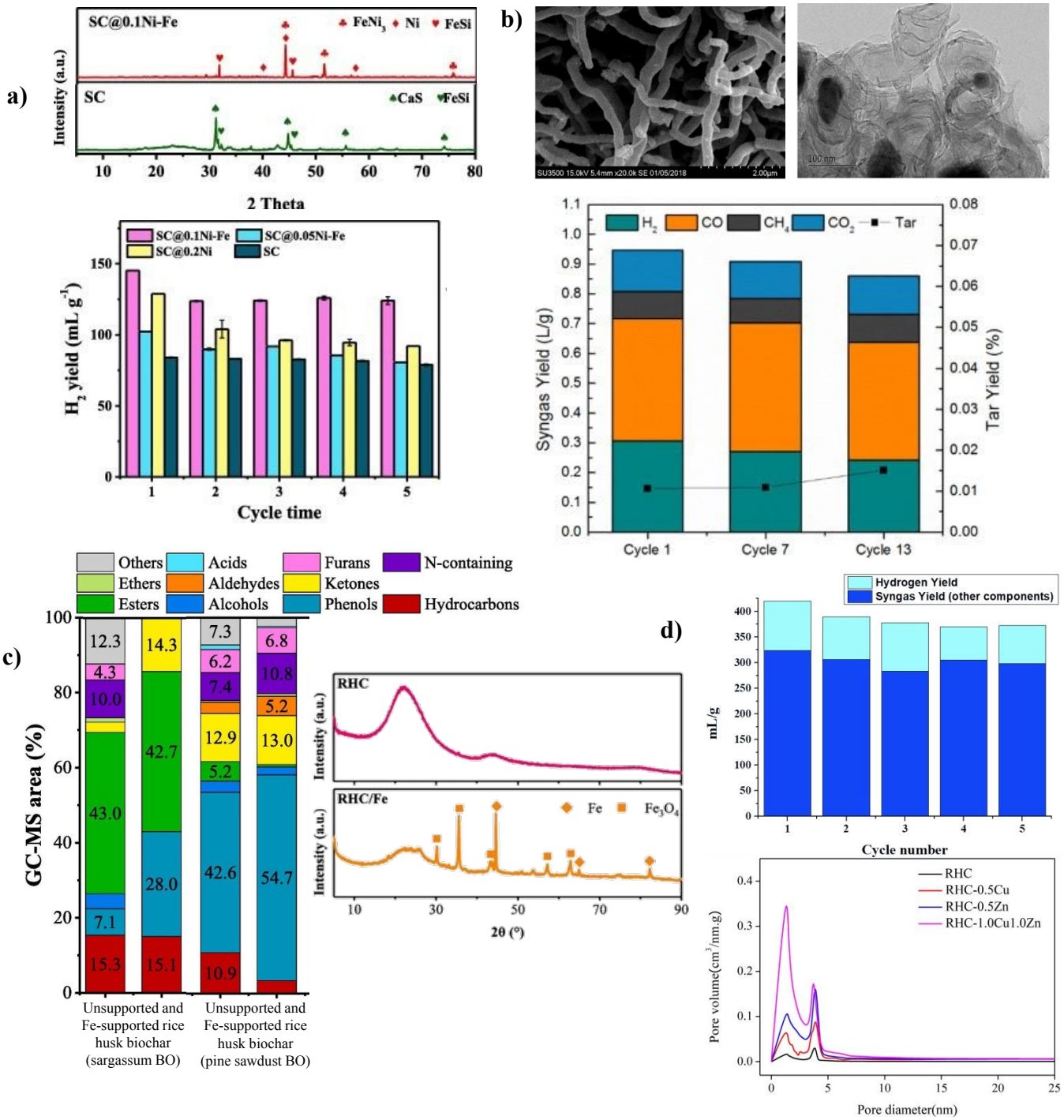


**Figure 6. a)** XRD patterns of Sargassum chair (SC)@0.1Ni-Fe (red curve) and bare SC (green curve) and $H_2$ yield obtained with peanut shell catalytic gasification. Reproduced from ref. [148] with permission from Elsevier, Copyright 2020. **b)** SEM image of wood chips-derived carbon nanofibers and TEM image of Fe-Ni particles supported on wood chips-derived carbon nanofibers) and recyclability up to 13 cycles of Fe-Ni bimetallic catalyst on carbon nanofibers. Reproduced from ref. [147] with permission from Elsevier, Copyright 2018. **c)** CP-derived bio-oil composition from different biomasses obtained in the presence of Fe on rice husk-derived biochar and XRD patterns of rice husk-derived char (RHC) and RHC/Fe. Reproduced from ref. [150] with permission from Elsevier, Copyright 2021. **d)** Recyclability of the 1.0Cu1.0Zn/RHC

BDC (built on data from ref. [151])and pore size distribution obtained by BJH method for bare RHC, RHC-0.5Cu, RHC-0.5 Zn and RHC/1.0Cu1.0Zn fresh catalysts. Reproduced from ref. [151] with permission from Elsevier, Copyright 2019.

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Taguchi design was employed in the paper by Yang et al. while another work by Shahnouri [163] employed response surface methodology to investigate the best conditions for BDC-catalysed catalytic pyrolysis.[162] To tackle AC regeneration issues, it has been suggested to use spent AC as MW-absorber (usually required in MW-assisted processes), thus regenerating the catalyst and achieving another potential loop closure.[132]

Metal-supported catalysts are also employed for catalytic pyrolysis. Specifically, the lack of an activation step and the significative reduction of undesired products (e.g., alcohols, ketones), combined with phenols enhancement, are interesting factors that offer a more complete view on metal-supported catalysts for these processes. For example, Fe-BDC were used in MW-assisted pyrolysis, giving excellent selectivity towards target molecules.[164] By using a higher Fe amount, it was possible to produce a Fe catalyst with core-shell structure, which was however affected by regeneration issues, since a calcination process does not assure the original dispersion of Fe-nanoparticles (**Table 2**). [165] Stability and deactivation were investigated, indicating a decrease (from 75.39% to 59% after 7 cycles) in phenols selectivity. By coupling Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis and Transmission Electron Microscopy (TEM) characterization, the selectivity loss was ascribed to Fe particle coalescence, whereas no significant leaching was observed.

The role of deposed metal on BDC was deeply investigated in a recent paper by Bu et. a, which discussed bio-oil production from MW-assisted peanut shell catalytic pyrolysis with the use of Fe, Co and Zn-BDC.[166] Among the three employed metals, Fe deposition afforded higher surface area (biochar area 154 $m^2/g$ vs Fe-BDC area 258 $m^2/g$), while a possible detrimental role on the carbon matrix of Co and Zn during calcination, leading to a surface area decrease was proposed. Fe deposition also resulted in more acidic sites compared with other transition metals (acidity order Fe>Zn>Co). The properties of the produced $Fe_{10}$ catalyst finally resulted in higher selectivity towards aromatic hydrocarbons (24.57%), showing good aromatization effect of the considered catalyst.[166] Moreover, studies on metal deposed-BDC include the effect of different feedstocks on bio-oil composition. Algal biomasses normally lead to higher esters yield, in the absence of N-containing compounds, that are conversely present in bio-oil from LB, together with a higher quantity of phenols (**Figure 6d**).[150] Differences in the bio-oil composition point out the importance of the production of catalytic technologies able to maintain the same catalytic activity with different feedstocks (**Table 2**, **Figure 6d**).[150] The effect of N-doping on catalytic pyrolysis has been reported, and the hypothesized catalytic pathway favoured in the presence of nitrogen in the biochar structure has been proposed [131, 167] (**Table 2**). Compared with N-free biochar, N-doped BDC lead to an enhancement of phenols selectivity, showing interesting features for what concerns alkyl and vinyl phenols production. *In situ* alkylphenols selective production has been also explored in $H_2$ atmosphere, which was hypothesized to positively influence C=C bond hydrogenation and on C-O bond cleavage (deoxygenation reaction) [168] (**Table 2**). Despite low process development, the production of hydrocarbons for fuel means via catalytic pyrolysis has made recent progresses, given the higher compatibility with direct engine use and lower pollutant production from combustion.

The effect of the employed feedstock on hydrocarbons production is the topic of a recent study by Duan et al. dealing with catalytic pyrolysis of soapstock, where the presence of a lipidic feedstock favours hydrocarbons formation.[134] Other than giving good bio-oil yield, excellent selectivity values towards jet fuel-grade and gasoline-grade hydrocarbons were documented. In parallel, 70% of $H_2$ yield on the gaseous fraction has been achieved, representing an unicum in the literature, due to promising BDC properties for simultaneous bio-oil and syngas production [134] (**Table 2**).

### 3.2. Biomass-derived catalysts for biomass conversion

When developing catalytic systems for LB depolymerization followed by further conversion, the catalyst capability of simultaneously promoting hydrolysis, isomerization and dehydration reactions is pivotal, moreover requiring the presence of both Lewis and Brønsted acid sites.[169] Regarding valorisation processes that require catalysis of a single reaction, several papers have reviewed BDC production and use for biodiesel production via transesterification reaction.[170, 171]

Due to the absence of the biomass-to-biomass approach, biodiesel production has not been considered in this review. Given the limited development of BDC-catalysed direct conversion of LB, most of the studies deals with the conversion of biomass-derived model compounds. An example of the development reached by LB valorisation over BDC is a recent work by Thi and colleagues. Furfural production starting from hemicellulose catalysed by a corncob-derived sulfonated graphene oxide with grafted $Fe_3O_4$ particles has been investigated, affording a 55.05% furfural yield and catalytic stability after 6 cycles.[172] Similar results have been also achieved when working with a $H_2O$- γ-valerolactone mixture, indicating another potential loop closure that could be achieved with the use of biomass-derived solvents. Other approaches involving BDC-mediated conversion of LB involve a first depolymerization step (catalyst: silicoaluminophosphate, SAPO-44) coupled with a second conversion step catalysed by a pine needle-derived biochar deposed with MnO particles.[173]

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| **Feedstock** | Tea waste (Catalyst and substrate) | Corncob (Catalyst and substrate) | Rice husk (Catalyst); Corncob (Substrate) | Rice husk (Catalyst); Sargassum and pine sawdust (Substrate) | Bamboo waste; (Catalyst and substrate) | Rice husk (Catalyst); Sugarcane bagasse (Substrate) | Corncob (Catalyst); Corn oil soapstock (Substrate) |
|---|---|---|---|---|---|---|---|
| **Pyrolysis** | Fast process, fluidized bed reactor (500 °C) | MW-assisted pretreatment (300°C, 40 min); Dual stage tubular reactor (450°C, 10 min) | Torrefaction 240°C, 4°C/min, 1 h; MW-assisted process; Ex situ flask MW-reactor 550°C; 450°C (catalyst bed); time N.A. | MW-assisted process; In situ MW oven. 400°C, 10 min | Dual stage fixed bed reactor; 600°C, 30 min | Fast process; In situ tubular reactor; 330°C, 30 min. $H_2$ atmosphere (few V/V %) | Two stage tubular reactors; 500°C, time N.A. |
| **Activating agent/Deposed metal** | KOH | $H_3PO_4$ | Fe loading N.A. | Fe loading N.A. | $NH_3$ | $H_2O$ | $H_3PO_4$ |
| **Activation/ Production conditions** | Soaking; Thermal treatment (500°C, 10°C/min, 2 h) | Soaking (RT, 24 h); carbonization (550°C, 30 min) | Soaking and hydrothermal carbonization (200°C, time N.A.); pyrolysis 800°C | Soaking (RT, 12 h); Thermal treatment (800°C, 1 h) | Fast process; 600°C, 30 min, 10% $NH_3$ atmosphere | Pyrolysis (500°C, 10°C/min, 1 h, 500 mL/min $N_2$); Activation (First heating 800°C; second heating 800°C, 2 h) | $H_3PO_4$ impregnation (RT, 24 h) MW-assisted pyrolysis (450°C, 1 h) |
| **Product selectivity/Yield** | 40.7 wt% bio-oil yield, 39.72% Phenols selectivity | 79.3% Phenols selectivity | 20.8 wt% bio-oil yield, 75.39% phenolic compounds | Sargassum 28.6% bio-oil yield 42.7% esters, 28.0% phenols, 15.1% hydrocarbons yield on bio-oil; Pine sawdust 54.7% phenols, 10.8% N-compounds yield on bio-oil | 63 wt% bio-oil yield; 82% phenols selectivity; 6.65 wt% 4-vinylphenol yield on biomass | 3.55 wt% 4-ethylphenol yield on biomass; 17.42% 4-ethylphenol selectivity | 41 wt% bio-oil yield, 98.79% jet fuel-grade hydrocarbons 91.03% gasoline-grade hydrocarbons 69.90% V/V $H_2$ fraction in syngas |
| **Ref.** | 161 | 157 | 164 | 150 | 131 | 168 | 134 |

**Table 2** Use of BDC applied to the catalytic pyrolysis of different biomasses.

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This interesting approach by Sarki et. al allowed to achieve an 80 % furfuryl alcohol yield from 2-furfuraldheyde after 4 cycles. The development of lignin-derived catalysts for high-end sustainable applications is extensively reported in the literature, due to promising catalytic performances and stability.[174] Herein, hydrogenation coupled with a 78.8 % 2-furfuraldheyde yield from sugarcane bagasse depolymerization was reported and the activity has been ascribed to good MnO dispersion in the CM structure (6-10 nm), leading to a stable BDC. However, it has been suggested that the production of lignin-derived materials could result in the loss of cellulose and hemicellulose.[175] A more complete LB valorisation may then involve the production of catalysts from the lignin fraction resulting from fractionation, also tackling lignin deposition on the active sites, which is the main cause for deactivation. This approach is well described by Qi et al.,[176] who reported the valorisation of the polysaccharide fraction with a catalyst derived from the lignin-containing black liquor resulting from LB fractionation. According to **Figure 7a**, the substrate is co-ball milled with the black liquor-derived catalyst, and the hydrolysis reaction with dilute acid affords 52.1% glucose and 66.5% xylose yield.

The direct production of a catalyst from biomass is shown in a paper by Kobayashi et al., which is the first to ever be published regarding LB valorisation with a BDC. The effect of a catalyst with slightly acid properties derived from Eucalyptus powder has been combined with the hydrolysing action of a dilute HCl solution. Eucalyptus was also chosen as substrate feedstock and was subjected to a 2-hour co-milling pre-treatment with the catalyst; after hydrolysis, 78% and 94% yields towards glucose and xylose, respectively, were observed.

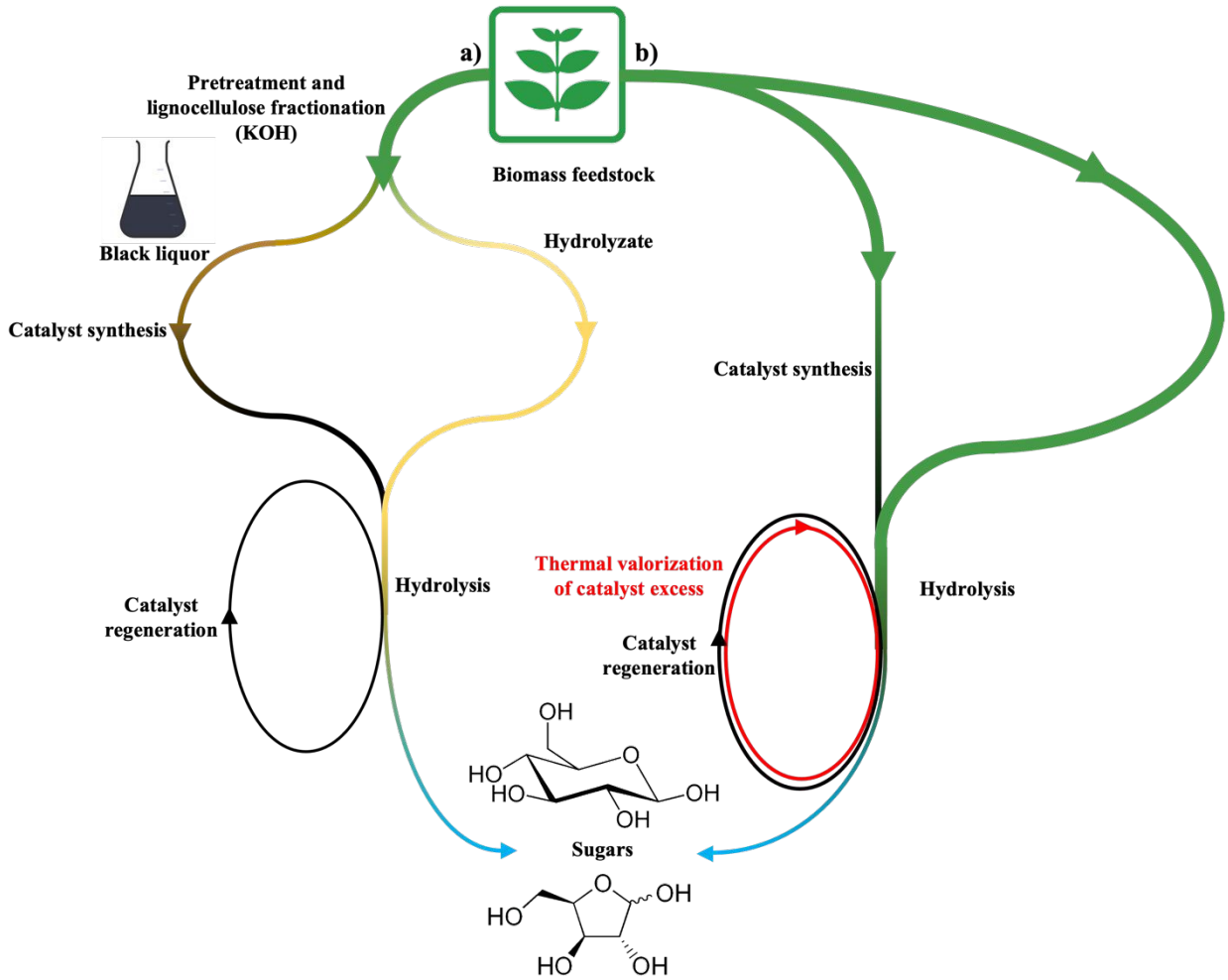


**Figure 7.** BDC role in biomass valorisation according to the approaches followed by a) Qi et al. (fractionated lignin-derived catalyst).[176] b) Kobayashi et al. (biomass-derived catalyst with thermal valorisation of CM excess).[177]

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The most promising feature is however catalyst regeneration, that implied the same activation methodology used for the fresh catalyst. Considering the nearly complete cellulose and hemicellulose conversion, the residue from the first reaction is composed by spent catalyst and lignin. Following regeneration, the obtained catalyst retained activity and did not require further input of fresh catalyst, moreover generating an excess of carbonaceous material that can be subjected to internal energetic recycle [177] (**Figure 7b**). Using a similar strategy, a Eucalyptus-derived catalyst has been obtained via ball milling and gave similar results after hydrolysis.[178] The spent catalyst was milled in the presence of dry ice, showing similar catalytic properties to the fresh one. The sole limitation occurring to a further development of the described approaches is the scarce number of contributions available, probably since the actual technology in not yet mature for valorisation reactions. However, the actual state-of-the-art is denoted by promising features and results achieved, among which are worth to mention:
(i) observation of a synergic effect between catalyst and a dilute acid solution, resulting in a consistent reduction of acid amount required for the hydrolysis process (~98% less than a conventional acid-catalysed hydrolysis).
(ii) use of mild reaction and synthesis conditions.
(iii) use of benign synthesis method (e.g., ball milling).
and (iv) first approach to loop closures regarding catalyst and energy input.

## 4. Sustainability and future green protocols

### 4.1. Life Cycle Assessment procedures

The described advancements in BDC for biorefinery purposes have brought research efforts to mainly focus on finding alternatives to existing processes. This focus has resulted in a lack of systematic consideration regarding the economic and environmental implications of the employed materials. The use of Life Cycle Assessment (LCA) as a standardized tool to evaluate impact on several aspects has recently been common to a great number of biorefinery processes development works. The integration of LCA is, therefore, an essential tool for fostering multidisciplinary understanding and comprehensive considerations. LCA procedure is composed by sequential steps, implying the choice of system boundaries (Life Cycle Inventory), the analysis of the established system (Life Cycle Inventory Analysis), and the final sustainability evaluation (Life Cycle Costing). Given the listed steps, Life Cycle Inventory plays an important role to determine whether a step (gate-to-gate approach) or the entire process (cradle-to-grave approach) can be deemed sustainable. It is also worth noting that catalyst production from LB falls under the cradle-to-cradle framework, which is a crucial step required within the Circular Bioeconomy context.
The most influential parameters on LCA are respectively the chosen software (e.g. GaBi, SimaPro, GREET), the chosen database as data source, the analysed indicators (e.g. global warming, resources depletion effect on human health) and the functional units (e.g. 1 Kg product, 1 hectare used, 1 MJ required).[179, 180] As reported in papers by Ubando [181] and Vuppaladadiyam,[182] biorefinery development lies under a complex scenario, where a multi-criteria decision analysis is needed in order to correlate LCA with techno-economic and social-economic analysis. Given the thermal nature of pyrolysis processes and the emission of potentially pollutant substances, LCA has become a common practice for sustainability evaluation.[179] Global Warming Potential (GWP) has moreover been the most investigated indicator since its ability to provide on-hand comprehension of environmental impact effect/reduction. Given the use of chemicals (e.g. alkali and acid pretreatment of biomasses/activating agents) and heating-related energy, these consumptions are deemed as the main cause for high GWP. [123] It has been suggested that the use of low-emitting energy sources (i.e., nuclear, solar, wind) could effectively tackle the chemicals/heating related environmental burden.
Greenhouse gases emissions derived from not-upgraded and upgraded bio-oil have been discussed, and non-pretreated bio-oil have shown to produce higher greenhouse gases emissions compared to fossil fuels On the other hand, bio-oil subjected to upgrading have demonstrated to cause lower emissions.[183] The consequent lower impact of upgraded bio-oil and the need for upgrading for direct engine use [36] has then determined the incorporation of an upgrading every in almost pyrolysis processes subject to LCA analysis.[182] As another major product of LB pyrolysis, biochar role as a negative emission tool is believed to acquire increasing importance in the following years. Sahoo and coworkers have coupled LCA with a techno-economic analysis of biochar production using forest residues and portable systems for on-site production, with a consistent remediation effect on GWP, usually (-1000 kg $CO_2eq/t_{biochar}$ to -2000 Kg $CO_2eq/t_{biochar}$), and a calculated minimum selling price ranged from 579 $/ton and 3004 $/ton. [184] Similar GWP results have been obtained in another study, which considered two scenarios with different pyrolysis conditions.[185] When employed, severer conditions resulted in a higher energy balance (13,563 $KJ/Kg_{biochar}$) but achieved a nearly 60% increase in carbon sequestration compared to processes with milder conditions. Bio-oil and syngas have been considered for the replacement of fossil fuels employed in transportation and hydroelectricity used during

heating, respectively, lowering the overall impact of the process. [185] A major input of energy reduces the ratio of energy output to energy input (EROI) which is a parameter operating in synergy with GWP for the sustainability evaluation of a process. Considering the main role of biochar for $CO_2$ sequestration and the not-ignorable effect of the catalytic system on the overall LCA (GREET) evaluation of biofuel production,[186] assessing the sustainability of BDC for biomass conversion becomes crucial, in order to understand the necessary steps for future development. Due to the number of BDC used for syngas cleaning (reforming step of catalytic gasification), it is worth mentioning that Frazier and co-workers performed LCA (SimaPro) on a NiO-$Al_2O_3$ catalyst (10%-90%) and a biochar-derived catalyst, finding that the latter outperformed the Ni-loaded catalyst for what concerns the indicators regarding impact on human health (-96.8%), greenhouse gases emissions (-93%) and energy input (-95.7%).[187] LCA (GaBi) was also performed to evaluate $H_2O$-AC production from coconut shells, deeming distillation of the pyrolysis vapours as a required step to improve sustainability of AC manufacturing. This requirement was driven by the detrimental effect towards Freshwater Aquatic Ecotoxicity Potential, Terrestrial Ecotoxicity Potential and Human Toxicity Potential, coming from direct release of pyrolysis vapours in the atmosphere. Coconut shell combustion for internal energy production achieved better result compared with the use of an external energy source, implying the importance of a sustainable energy source for AC production.[188]

LCA tools for LB valorisation with biomass-derived catalysts have been only developed in recent times. Consequently, the first relevant papers performing sustainability, techno-economical and economic analysis regarding $H_2$ and bio-oil production were respectively published by Al-Qahtani et al. [189] and Van Schalkwyk et al.,[190] pointing out that clean energy sources, the presence of externalities and the establishment of an economy-of-scale represent the greatest challenges and opportunities towards commercialization of biomass-derived $H_2$ and bio-oil. The first paper treating LCA evaluation of biomass valorisation with the use of biochar as a catalyst was published in 2021 by Chun Minh Loy and colleagues. Wheat straw was considered a feedstock for both $H_2$ and biochar production, and a gasification process was proposed. Following a multi-factor evaluation (resources depletion, climate change, human health, and ecosystem quality) with a gate-to-gate approach (Impact 2002 + score system), the separation step registered the highest contribute to human health and climate change indicators. Due to the production of hazardous substances and the poor score regarding the effect on health, the discussed paper highlighted that general improvement of the separation step and the LCA investigation of metal-deposed BDC are fundamental to determine the scalability of the proposed gasification process.[191] In a biorefinery context, a LCA (openLCA 1.10.3 and ecoinvent 3.8 database) BDC production (feedstock to catalyst approach) has been published by Cao et al.,[123] representing to date the sole experimental work assessing the sustainability of LB valorisation by means of a LB-derived catalyst. An extended comparison among different biomasses (seaweed, microalga, LB) involving GWP (best performance LB 0.83 Kg $CO_2$eq/$Kg_{catalyst}$) and several midpoint impact categories regarding environmental impact were discussed. Considering the large surface area afforded by KOH activation,[86] chemical activation has been performed with potassium hydroxide, showing however higher environmental impact compared with literature.[192] To improve the environmental impact, the authors have suggested to recover the activating agent after the washing step following KOH activation. Finally, the produced BDC were tested for sawdust catalytic pyrolysis, where the seaweed-BDC allowed to obtain a 54.64% relative content of monophenols in the produced bio-oil, outperforming other BDC. [123] Other than investigating BDC sustainability, the work by Cao et al. has moreover offered a wide characterization of the produced BDC, linking the presence of -OH groups in the active sites to higher monophenols production. Consequently, the authors believe that this work should represent a good example of the multidisciplinary approach required to develop a future BDC employment.

### 4.2. Artificial Intelligence as a green tool

The multitude of parameters influencing the outcome of biomass-related processes (e.g., feedstock properties, process conditions) causes intrinsic issues regarding the development of standardized procedures, upon which basing sustainability assessment.[193] Computational procedures could then represent a powerful tool to achieve process standardization,[194] moreover forecasting yield and properties of the produced materials. Considering the industrial exploitation of BDC, recent studies have discussed artificial intelligence (AI) employment for prediction of biochar role in carbon sequestration,[195] adsorption [196] and yield,[197] furthermore pinpointing to Artificial Neural Network (ANN) [198, 199] and Machine Learning [200] methods as cornerstones for future considerations regarding biochar production.

The use of AI models has also been reported for several biomass-related processes. For example, biomass torrefaction is the subject of a review work by Manatura et al., which highlighted the importance of ANN for process optimization.[201] Hydrothermal gasification (milder gasification with 25 MPa pressure, 600°C temperature and presence of water [202]) was investigated in a review work, where employment of ANN and Machine Learning models were discussed as for process optimization, catalytic screening and biochar yield prediction.[203] Other than demonstrating forecasting reliability of the investigated AI models, these studies clearly highlight that a limited comprehension of the internal mechanisms of the chosen AI models ("black box" problem) leads to a necessary integration with experimental (thermodynamic and kinetic) data. This is then indicated as necessary to assess data quality and have higher homogeneity upon which basing comparison between data collected in different scenarios. Following this approach, a paper by Wang et al. studied the predictive capacity of ANN models regarding AC yield and surface area.[204] Physical ($CO_2$) and chemical (KOH) activation have been explored, observing accurate prediction. An impact analysis has also been

performed, indicating oxygen content in the starting biomass, activating agent /biochar ratio and activation temperature as the most influential parameters on AC production.

Bio-oil produced from biomass pyrolysis contains several oxygenated compounds, therefore compromising its quality. Catalytic hydrodeoxygenation represents a valuable approach to upgrade the bio-oil quality into fuels and chemicals. In this frame, ML has been used for the development of stable and efficient catalysts and selecting optimum operating conditions for the pyrolysis of guaiacol, chosen as a bio-oil model compound. [205] The technology allowed to navigate complex data relationships and optimize process parameters. The flowchart of the research methodology is shown in **Figure 8a**. A screening of the published articles was performed to carefully select eligible publications for in-depth assessment. Pertinent variables of reaction conditions and catalyst requirements were systematically gathered from these chosen papers. Based on the obtained dataset, four ML models were used to model the catalytic pyrolysis process. Then, an optimization algorithm was used to identify the operating conditions and catalyst properties. The use of the best ML model allowed to analyse the importance of the selected features, highlighting the pivotal role of the catalyst surface area and temperature. Through multi-objective optimization, a 92.26% guaiacol conversion was achieved at 365 °C, 2.72 MPa $H_2$ pressure, 37% crystallinity index of the catalyst with surface area of 756.9 $m^2/g$. [205]

The Spearman's rank correlation method was adopted, in which the p-value represents a statistical measure for determining the significance of the correlation coefficient (r) obtained through the method. This correlation method considers the probability that the observed correlation strength may occur by chance, where a value of +1, 0, and – 1 means perfect positive, weak, and complete negative correlation. [205] **Figure 8b** shows the Spearman correlation matrix, built basing on input descriptors and output responses across the dataset. The analysis revealed that guaiacol conversion negatively correlates with temperature ($r= -0.11$, $p< 0.05$) and $H_2$ pressure ($r= -0.19$, $p < 0.001$). By increasing the temperature, phenol selectivity increased ($r= = 0.34$, $p < 0.001$) and hydrogenolysis was preferred over hydrogenation, hence reducing hydrogen adsorption. Interestingly, high $H_2$ pressure negatively affects the gas diffusion rate within the catalyst surface bed and can cause over-hydrogenation, resulting in gaseous product formation. Conversely, low $H_2$ pressure means poor hydrogenation activity and hindered hydrogenolysis. The catalyst BET surface area well correlated with guaiacol conversion ($r= 0.11$, $p < 0.05$).

A positive correlation was also found between guaiacol conversion and the presence of cyclohexane, indicating that an increased surface area promoted cyclohexanol dehydration and cyclohexene hydrogenation. Reaction time slightly positively correlated with guaiacol conversion ($r= 0.093$, $p < 0.05$), nevertheless, prolonged reaction time also enhance carbon deposition and promote gaseous product formation. Finally, reaction time correlates with cyclohexane and cyclohexanol amounts. [205]

As a result of recent parallel development, the synergic action of LCA and AI models have emerged. A work by Cheng et al. employed a Machine Learning method to predict bio-oil ($R^2$=0.80) and Biochar ($R^2$=0.87) properties for hydrothermal treatment of LB. The predicted properties have then been fed into GREET software for GWP and EROI calculation have been compared with the state-of-the-art approach for bioenergy from carbon capture sequestration (biomass burning). Despite achieving higher EROI (but lower $CO_2$ capture), the combined action of AI and LCA offers an interesting point of view on a LB valorisation different from direct combustion.[206] A similar work by the same authors has employed Machine Learning to forecast slow pyrolysis-derived biochar, moreover performing LCA and an economic analysis on the use of different feedstocks.[207] A forecasted minimum selling price 774 – 1256 $/ton (developed market) for the produced biochar has been reported, proving to be competitive and to be able to play a major role in the future innovations regarding this sector. A very interesting practical example of successful LCA-AI coupling is represented by a work published by Fózer et al.[208] Catalytic gasification of a high-moisture biomass (microalgae) for methanol production via syngas has been investigated. Interestingly, ANN models provided simulations of the not-catalysed and catalysed process, while a cradle-to-gate LCA has found excellent decarbonization potential of the designed process (-725 $KgCO_2eq/t_{methanol}$).

Due to the complex framework where BDC are involved, a SWOT (Strengths, Weaknesses, Opportunities, Threats) analysis has been conducted to scrutinize and address the principal features and applications of these materials. On one hand, the SWOT analysis shown in **Figure 9** highlights that BDC leverage renewable feedstocks, contributing to sustainability and reduced dependence on fossil resources. Biomass is abundantly available and diverse, allowing for a wide range of biomass-derived catalysts tailored to specific feedstock compositions. In addition, biomass valorisation can be a carbon-neutral process when considering the carbon dioxide emitted during biomass growth and its subsequent utilization. BDC can be designed with tailored properties to match the unique composition of different biomass feedstocks, enhancing overall catalytic efficiency. Moreover, they can incorporate various active sites, allowing for multifunctional catalysts capable of promoting multiple reactions.

On the other hand, the application of BDC suffers from some weaknesses, as the variability in biomass composition poses a challenge in designing catalysts that can consistently perform well across different feedstocks. BDC are prone to deactivation due to fouling, coking, and other mechanisms, requiring effective strategies for regeneration and recycling. Transitioning from laboratory-scale experiments to industrial-scale production can be challenging, with issues related to preserving catalyst efficiency and optimizing large-scale processes. If the sustainability and properties tuneability represent attracting factors, negative effects on health with necessity to standardize the production and improve the downstream processes are the main drawbacks affecting BDC.

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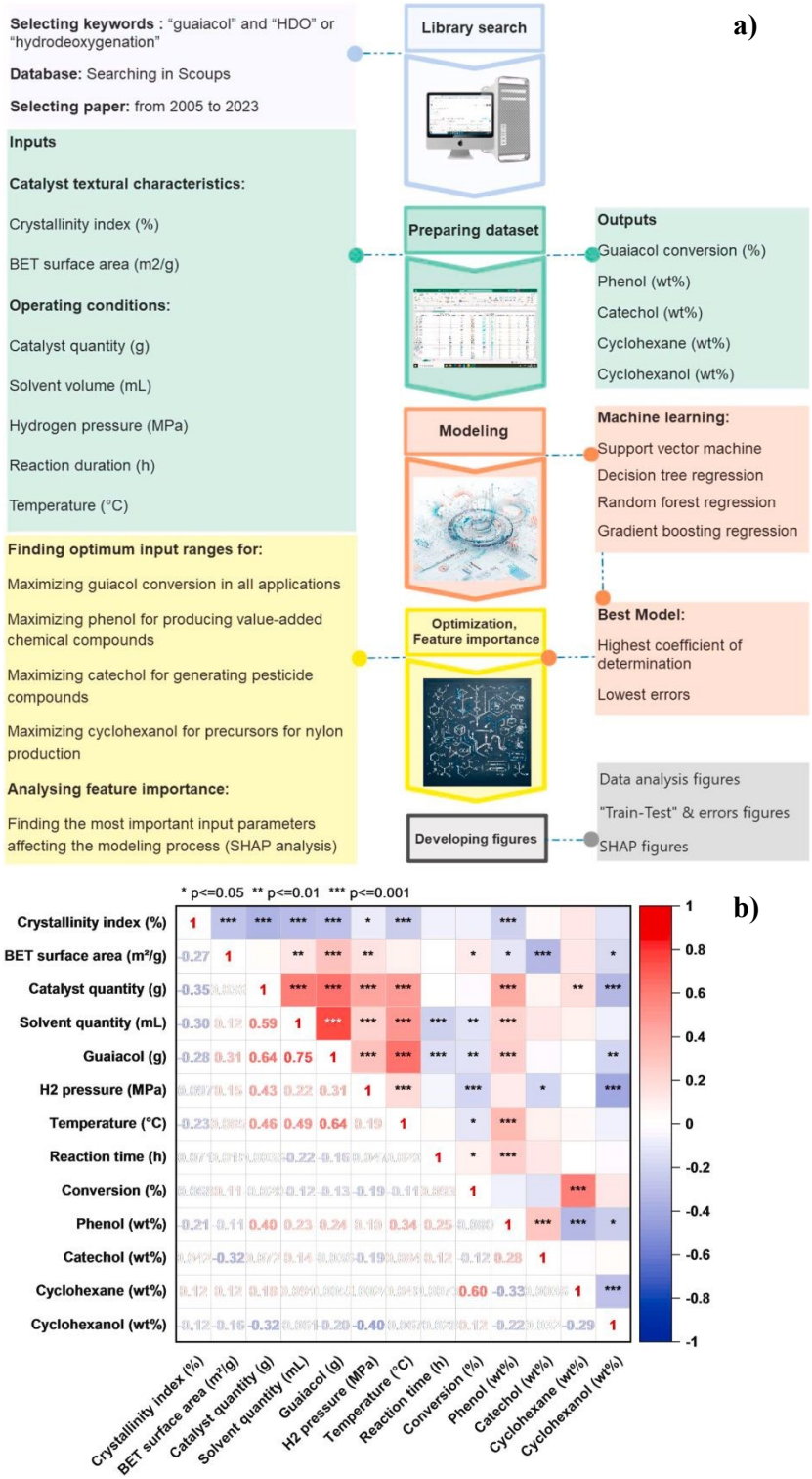


**Figure 8**. **a)** Flowchart of the research methodology. Reproduced from ref. [205] with permission from Elsevier, Copyright 2024. **b)** Spearman's correlation coefficients and p-values among input descriptors and output targets. Positive correlations (red), negative correlations (blue), the intensity of the colours indicates the strength of the link. Reproduced from

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Advances in characterization techniques, such as *in-situ* and *operando* methods, offer opportunities to better understand and tailor catalysts for biomass conversion. Ongoing research and development present opportunities for technological innovations in catalyst design, leading to improved stability, selectivity, and efficiency.

The increasing global focus on sustainability and renewable resources creates a favourable environment for the development and adoption of biomass-derived catalysts. BDC face competition from other technologies, including traditional fossil-based processes and emerging alternatives, which may impact market adoption. Economic factors, such as the cost of biomass feedstock, catalyst production, and process scale-up, can pose threats to the overall economic viability of biomass valorisation. Changes in government policies, regulations, or subsidies may affect the competitiveness of biomass-derived catalysts compared to other energy and chemical production methods. This SWOT analysis provides a comprehensive overview of the internal and external factors influencing the development and utilization of biomass-derived catalysts. Addressing weaknesses, capitalizing on opportunities, and mitigating threats will be crucial for the successful integration of biomass-derived catalysts in the broader context of sustainable and renewable resource utilization. New technologies (e.g., Machine Learning, pollutant capture) could trail the required improvements to achieve competitivity with other processes and health hazard reduction, while the approval of incentives derived from the Green Deal plan could help the industrialization of processes that are to date still limited to the pilot-scale stage. Finally, the main obstacles towards a complete development of BDC could be represented by environmental problems affecting the harvest of LB (lack of regular flows of materials) and technological problems if the limits now affecting BDC would not be overcome.

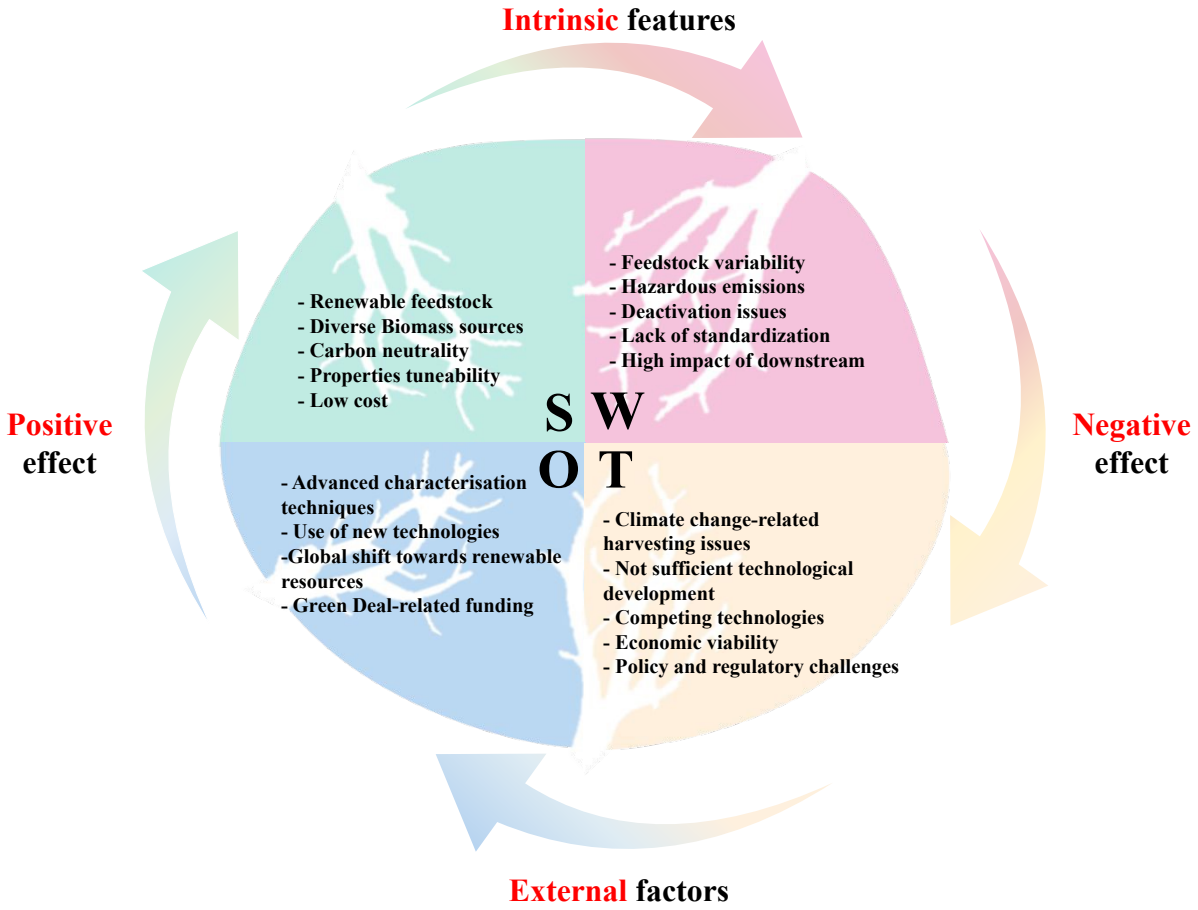


**Figure 9.** SWOT analysis (Strengths, Weaknesses, Opportunities, Threats) regarding BDC properties and use.

## 5. Future perspectives

The exploitation of biomass as a feedstock for catalytic processes presents a set of unique challenges in catalyst development. Unlike traditional fossil-based resources, biomass-derived materials exhibit higher heterogeneity in composition, impurities, and structural complexity. The design of BDC that are both selective and active under such different and variable conditions requires firstly a deep understanding of biomass components and secondly their interactions with catalyst surfaces. However, the development of effective and robust catalysts is hindered by the lack of standardized methods

for biomass characterization and the need for tailored catalysts to accommodate the variability in biomass feedstocks. Indeed, understanding the active sites of BDC is crucial for optimizing their performance in biomass valorisation.

Biomass contains a wide range of components, including cellulose, hemicellulose, lignin, and various impurities. Characterizing active sites on catalyst surfaces that interact with specific biomass constituents poses a significant challenge. Advanced techniques such as spectroscopy, microscopy, and computational modelling are required to unravel the complex interactions between BDC and the biomass components. The precise identification and quantification of active sites are essential for the development of BDCs with improved selectivity and activity. During biomass valorisation, catalysts are susceptible to deactivation due to fouling, coking, sintering, and other detrimental processes. Understanding the deactivation mechanisms and developing strategies for BDC regeneration are critical for ensuring the long-term sustainability of biomass valorisation processes. In this frame, deactivation can result from the accumulation of deposits on the BDC surface, leading to reduced activity and selectivity. Hence, developing effective regeneration methods that restore catalytic activity without compromising the catalyst structure is essential for the economic feasibility of biomass valorisation technologies.

Scaling up biomass valorisation processes from laboratory to industrial scale introduces additional challenges. The transition from small-scale experiments to large-scale production requires adjustments in reactor design, process parameters, and catalyst formulations. Maintaining the efficiency and selectivity of catalysts at an industrial scale while managing heat and mass transfer becomes a non-trivial task. The economic viability of large-scale biomass valorisation relies on overcoming these issues and optimizing the entire process chain.

As a matter of fact, the development of BDC for biomass valorisation faces challenges related to the diverse nature of biomass feedstocks, the need for advanced characterization techniques, scale-up complexities, and the management of catalyst deactivation and regeneration. Overcoming these challenges requires interdisciplinary approaches and continuous innovation in catalyst design and process optimization. Potential future solutions to these challenges entrust firstly advanced catalyst design by developing BDC specifically designed for the unique composition of different biomass feedstocks.

Tailoring catalysts to interact selectively with specific biomass components can enhance overall efficiency. Moreover, the integration of multiple functionalities within a single BDC to address the complexity of biomass components must be explored. This could involve combining acidic, basic, and metal sites to promote a range of reactions. In this context the use of advanced *in-situ* and *operando* characterization techniques to study catalysts under realistic reaction conditions becomes of pivotal importance. This would provide real-time insights into the BDC's behaviour, helping to identify active sites and understand dynamic changes during reactions.

Machine learning algorithms able to analyse large datasets generated from the biomass characterization can aid in identifying catalyst structure-activity relationships, boosting the optimization process. Of course, investigate process intensification techniques to enhance the efficiency of large-scale biomass valorisation would be a successful scale-up strategy. This includes optimizing reactor designs, improving heat and mass transfer, and minimizing energy consumption by adopting, for example, enabling technologies such as MW. In addition, the optimization of modular and flexible process designs would allow for easier scale-up and adaptation to different biomass feedstocks, enhancing the overall versatility and economic viability of biomass valorisation technologies.

Another strategy relies in careful management of BDC deactivation and regeneration. It is worth noting that focusing on designing BDC with improved stability against deactivation mechanisms may involve incorporating self-regenerating features or employing materials with enhanced resistance to fouling and coking. Developing *in-situ* regeneration methods that can restore activity during the reaction without the need for shutting down the process could involve the introduction of specific reactants or treatments during operation.

The exploration of efficient BDC recycling strategies will reduce the overall costs by evaluating the feasibility of recovering and regenerating spent catalysts for multiple cycles, minimizing the environmental impact, and enhancing sustainability. Finally, collaborative interdisciplinary research initiatives will foster collaboration among researchers, industry experts, and policymakers to create interdisciplinary teams addressing the challenges collectively. Sharing knowledge and resources can boost the development and optimization of effective solutions. Encouraging partnerships between academia, industry, and government agencies will facilitate the translation of research findings into practical BDC applications. This collaborative approach can effectively bridge the gap between fundamental research and industrial implementation. As technology advances and research progresses, these future solutions aim to address the challenges in BDC development and enhance the feasibility and sustainability of biomass valorisation processes.

## Abbreviations

AC: Activated Carbon
BBNs: Biochar-based nanocatalysts
BDC: Biomass-derived catalysts
CM: Carbon Materials
LB: Lignocellulosic Biomasses
LCA: Life Cycle Assessment
MW: Microwaves
PC: Platform Chemicals
SC: Sargassum Char

## Author Contributions

**Investigation: M.B.; Conceptualization: M.B., S.T., E.C.G., M.M.; Writing original draft: M.B.; Reviewing and editing: G.C., E.C.G., S.T.; M.M.; Supervision S.T., G.C., M.M.; Project administration: M.M.**

## Conflicts of interest

Authors have no conflicts to declare.

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