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► **To cite this version:**

Hassan El Bari, Casimir Kalibe Fanezoune, Bogdan Dorneanu, Harvey Arellano-Garcia, Thokozani Majazi, et al. Catalytic fast pyrolysis of lignocellulosic biomass: Recent advances and comprehensive overview. *Journal of Analytical and Applied Pyrolysis*, 2024, 178, pp.106390 (1-24). 10.1016/j.jaap.2024.106390 . hal-04780009

HAL Id: hal-04780009

<https://hal.science/hal-04780009v1>

Submitted on 13 Nov 2024

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Catalytic fast pyrolysis of lignocellulosic biomass: Recent advances and comprehensive overview

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ARTICLE INFO

Keywords:

Catalytic fast pyrolysis
Lignocellulosic Biomass
Bio-Oil
Modelling
Upgrading
LCA

ABSTRACT

Using biomass as a renewable resource to produce biofuels and high-value chemicals through fast pyrolysis offers significant application value and wide market possibilities, especially in light of the current energy and environmental constraints. Bio-oil from fast-pyrolysis has various conveniences over raw biomass, including simpler transportation and storage and a higher energy density. The catalytic fast pyrolysis (CFP) is a complex technology which is affected by several parameters, mainly the biomass type, composition, and the interaction between components, process operation, catalysts, reactor types, and production scale or pre-treatment techniques. Nevertheless, due to its complicated makeup, high water and oxygen presence, low heating value, unstable nature, elevated viscosity, corrosiveness, and insolubility within conventional fuels, crude bio-oil has drawbacks. In this context, catalysts are added to reactor to decrease activation energy, substitute the output composition, and create valuable compounds and higher-grade fuels. The study aim is to explore the suitability of lignocellulosic biomasses as an alternative feedstock in CFP for the optimization of bio-oil production. Furthermore, we provide an up-to-date review of the challenges in bio-oil production from CFP, including the factors and parameters that affect its production and the effect of used catalysis on its quality and yield. In addition, this work describes the advanced upgrading methods and applications used for products from CFP, the modeling and simulation of the CFP process, and the application of life cycle assessment. The complicated fluid dynamics and heat transfer mechanisms that take place during the pyrolysis process have been better understood due to the use of CFD modeling in studies on biomass fast pyrolysis. Zeolites have been reported for their superior performance in bio-oil upgrading. Indeed, Zeolites as catalyses have demonstrated significant catalytic effects in boosting dehydration and cracking process, resulting in the production of final liquid products with elevated H/C ratios and small C/O ratios. Combining ex-situ and in-situ catalytic pyrolysis can leverage the benefits of both approaches. Recent studies recommend more and more the development of pyrolysis-based bio-refinery processes where these approaches are combined in an optimal way, considering sustainable and circular approaches.

1. Introduction

At the current time, the use of fossil fuels poses a major problem for the earth's thermal balance since they emit a huge quantity of carbon dioxide (CO₂), a greenhouse gas (GHG), which results in global

warming. This implies climatic changes, notably extreme phenomena characterized by a succession of periods of drought followed by periods of flooding, implying natural disasters harmful to mankind. In addition, the problem of the depletion of oil and gas reserves is a serious one.

Bioenergy, and in particular the production of biofuel from organic

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waste and residues, appears to be a suitable alternative to these climate and oil depletion problems [1-3]. Indeed, the bioenergy process is carbon neutral since the biomass used emits a quantity of CO₂ equal to that absorbed during its growth. Because of its vast output, elevated organic content, excellent sustainability, lower cost, and minimal GHG emissions, biomass conversion is regarded as a possible replacement for fossil fuels. This is particularly true in the specific situation of lignocellulosic biomasses, which are the most prevalent biomass resources, such as wood, agricultural residues (bagasse, chaff, straw, etc.), waste from processing forest products, and several energy sources [4]; B. [5]; [6].

Fast pyrolysis is a high-temperature method that quickly heats biomass without oxygen. It decomposes as a result, producing mainly vapors, aerosols, and some charcoal [7]. Fast pyrolysis generally encourages the creation of liquid yields, which may account for up to 75% of the total final products. Fig. 1 shows a scheme of input and output of biomass conversion by Fast pyrolysis process. The output is made up of 3 components which are bio-oil, biochar and gases.

The presence of tiny particles in the biomass feedstock makes it easier to achieve a high heating rate and a short residence period during fast pyrolysis [8]. High heating rates are used in fast pyrolysis reactors to increase condensable component (liquid) output and decrease char yield [9]. Heat transport inside the biomass presents a problem for effective pyrolysis to occur, particularly for fast pyrolysis when high heating rates are necessary. Biomass needs to be size-reduced or ground before being fed into the reactor since it has a low heat conductivity [10]. Feedstock particle size is an important parameter that can influence the pyrolysis process in addition to temperature and heating rate. For fast pyrolysis, smaller particles are necessary to increase liquid products [8]. Fast pyrolysis techniques primarily result in the production of bio-oil, whose performance depends on the biomass, process temperature, time that the gas spends inside the reactor, mineral content, size of particle, and heating rate.

Fast pyrolysis of biomass is gaining popularity in Europe due to perceptions that it has considerable logistical and, consequently, financial advantages over conventional thermal conversion techniques. This is so that the liquid product may be carried easily to the location where it will be used most effectively or kept until it is needed [11]. Lignocellulosic biomass is continually transformed into bio-oil, which has an elevated energy density and is convenient to store and transport. It is then delivered centrally to refining plants for large-scale use [12]. The best reactor for fast pyrolysis is a fluidized bed reactor because of its simplicity, stability, scalability, and high bio-oil production (Jahirul et al., 2012). However, poultry litter has undergone a number of fixed-bed investigations, proving its benefits for depollution and energy

valorization. However, the batch pyrolysis reactor case cannot be applied to upscaling and design [13]. The ability of the following pyrolysis reactors to produce significant amounts of bio-oil is outlined in descending order: the rotating cone reactor, the rotating fluidized bed reactor, the auger reactor, the cyclonic reactor, the ablative reactor, and the bubbling fluidized bed reactor [14]. The requirement for pyrolysis reactors that can effectively handle a variety of feedstocks is one of the issues restricting the growth of the bioenergy sector [15].

A promising method that could improve the ability to turn biomass into portable fuels is catalytic fast pyrolysis (CFP) [16]. The CFP is used to produce a valuable hydrocarbon (benzene, xylene, ethene, or toluene) or biofuel while improving expected bio-oil qualities, including acidity, thermal value, and stability. Global trends indicate that biofuel production is projected to increase considerably in the immediate future, leading to an expansion in the size of the bio-oil industries in the ensuing decades. The success of the process with elevated conversion efficiencies and lower operating costs depends critically on the increasing quality of bio-oil using in-situ or ex-situ methods [17]. CFP bio-oils are of higher quality and yield than non-catalytic pyrolysis due to the significantly higher amounts of aromatic hydrocarbons and pH. The H/Ceff ratio, biomass structure, and other process variables all have a significant impact on the CFP bio-oil quality and yield. The majority of studies have concentrated on upgrading bio-oil through condition optimization, catalyst selectivity, and co-pyrolysis with wastes. A promising method that could increase the ability to turn biomass into CFP biofuels [16]. However, due to its characteristics such as high oxygen concentration, high moisture content, and low stability, crude biooil from rapid biomass pyrolysis cannot be directly used in current petroleum-based infrastructure. Adding a catalyst to the fast pyrolysis process, also known as catalytic rapid pyrolysis (CRP), is a convenient and easy way around this obstacle. Dehydration and decarboxylation can be useful to increase biooil yield and quality, respectively, provided that the amount of deoxygenation is constant and no coke is produced [18].

The CFP is to specifically produce hydrocarbons (benzene, ethene, toluene, xylene, and propene) while improving expected bio-oil qualities, including thermal stability, heating value, and acidity. Global trends indicate that biofuel production is projected to increase considerably in the near future, leading to an expansion in the size of the CFP technology and bio-oil industries in the ensuing decades. The total success of the process, which includes improved conversion efficiencies and reduced operating costs, is significantly dependent on improving bio-oil quality through in-situ or ex-situ catalysis [17]. Given the considerably higher quantity of aromatic hydrocarbons and pH, bio-oils from CFP are associated with improved quality and higher production

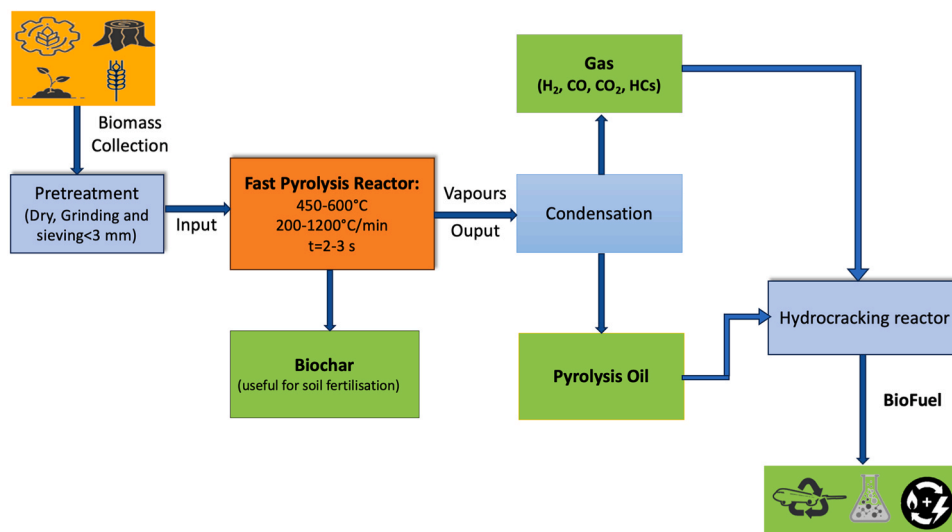


Fig. 1. The scheme of input and output of biomass conversion by Fast pyrolysis process.

but also how to best utilize it by selecting the right catalyst and applying the LCA method to this CFP output.

2. Lignocellulosic biomass as feedstock for fast pyrolysis

Biomass in general and lignocellulosic in particular is the manna of energy of the future, because of its renewable nature and the abundance of exploitable raw materials. It is estimated that it is about 1.3 billion tons per year and can contribute about 14% of the world's energy needs. (Y. [24].

Biomass means, etymologically, a quantity coming from living matter, therefore, organic matter, either vegetable, animal, or fungal, that can be converted by thermochemical or biochemical processes into a profitable source of energy.

2.1. Feedstocks for fast pyrolysis

Biomass is generally grouped into three families according to the conversion processes:

1. Biomass rich in easily hydrolysable carbohydrate substances such as cereals, sugar beets, and sugar cane. The biological conversion pathways (anaerobic digestion and fermentation) are suitable for these kinds of biomasses.
2. Oilseed biomass is rich in lipids such (rapeseed, oil palm, and jatropha) can be used as fuel obtained by pressing or chemical extraction.
3. Biomasses rich in lignocellulosic substances, namely cellulose, hemicellulose, and lignin (wood, green residues, straw, sugar cane bagasse, and fodder), are appropriate for thermochemical conversion (torrefaction, pyrolysis, gasification, and combustion).

Table 1 illustrates some examples of suitable feedstocks for fast pyrolysis including bio-oil, biochar and gas percentage.

The lignocellulosic biomass's structure is formed by a complex matrix encasing its chemical constituents. Two key parts of this matrix are:

1. Structural elements such as lignin, hemicellulose, and pyranose
2. Substances that aren't structured, like mineral extracts.

Cellulose, an organic polymer, is most noticeable by its abundance and greater presence in plant cells, precisely at the level of their cell wall. In cotton fibers, cellulose is almost pure. Also called pyranose, the polymer of cellulose is natural and formed by a chain of repeating units of D-glucose, which is a six-carbon ring (Fig. 2a). The three functional groups of each cellulose unit eventually interact with one another to form intra- and intermolecular hydrogen bonds, which are what give cellulose its characteristic crystal structure, mechanical strength, and chemical stability [28].

The establishment of intermolecular hydrogen bonds between the hydroxyl groups causes the straight cellulose chains made of more than twenty (20) to three hundred (300) glucose units to be rearranged in parallel [29].

Considered an important structural component of lignocellulosic biomass, it forms twenty to thirty percent of the cell wall and is present in small amounts in some annuals[30]. As shown in Fig. 2b,

Table 1
Fast pyrolysis products yield for some suitable feedstocks.

Substrat	Bio-oil (%)	Bio-char (%)	Gas (%)	Reference
Poultry litter	27.62	47-48	22	[13]
Date palm	38.8	37.2	24.0	[25]
Jatropha waste	32.87	29.73		[26]
Sugarcane bagasse	78.07	10-15	5-15	[14]
Leucaena Leucocephala	65.1	19.9	15	[27]

compared to non-catalytic pyrolysis. The H/Ceff ratio, biomass structure, and other process variables all have a significant impact on the quality and yield of bio-oils produced from CFP. The majority of studies have concentrated on upgrading bio-oil through condition optimization, catalyst selectivity, and co-pyrolysis with wastes. Quality enhancement is a major challenge in the production of commercial CFP bio-oil [19, 20].

The catalyst may be located upstream and only in contact with the pyrolysis vapors (ex situ CFP) or directly mixed with the biomass particles (in situ CFP), depending on the catalytic structure. CFP approaches, both in situ and ex situ, may improve bio-oil quality [21]. Therefore, the key to efficiently creating high-quality bio-oil by CFP is to investigate ways to remove the oxygen with less loss in bio-oil output. Generally speaking, throughout the CFP process, oxygen in bio-oil can be extracted as H₂O, CO, or CO₂. Dehydration potentially preserves more carbon elements in biooil, resulting in the highest yield of improved bio-oil, assuming that the CFP process does not result in the creation of coke. [21]. Appropriate use of a catalyst in pyrolysis will increase process efficiency overall by reducing energy input, increasing conversion rate, improving product quality, and boosting product yield. Therefore, it has been determined that the catalytic rapid pyrolysis process using catalysts based on zeolite is an effective method for utilizing biomass [22].

Despite the fact that a range of catalysts have been evaluated in the CFP of biomass and some were found to be relatively useful for upgrading bio-oil, zeolites (ZSM 5 in particular) have been the most problematic catalysts, possibly due to their high efficiency toward oxygen removal. However, their CFP technical growth has been hampered by low aromatic yield and catalyst inactivation. [21]. As a result, the catalytic fast pyrolysis process using catalysts based on zeolite has been recognized as an effective method for utilizing biomass. However, numerous issues and weaknesses must yet be addressed [23]. While zeolite-catalyzed biomass pyrolysis has advanced significantly over the past few decades, numerous problems with conventional zeolite catalysts still exist. These include (i) a lower hydrocarbon yield than anticipated, (ii) a catalytic conversion mechanism that is unclear, including the connection between the structure of the zeolite and the bio-oil composition, and (iii) a catalyst that deactivates quickly from carbonate deposition or water assault [16]. Lignocellulosic biomass CFP is a process that holds promise for making mobile fuels. Although academic and industrial sectors have given biomass CFP considerable attention, its development is still in its early stages, and it has not yet been made available for purchase. CFP biomass has not yet been commercially exploited, despite its advantages in terms of economy and simplicity. One of the major challenges is the precise design of high-yielding zeolite catalysts specifically suited for biomass CFP, as the structure-property relationship of zeolites in biomass pyrolysis is not yet fully understood. [16].

The aim of this study is to explore the suitability of lignocellulosic biomasses as an alternative feedstock in CFP for the optimization of bio-oil production. In this context, the paper aims to provide an up-to-date review of the challenges in bio-oil production from CFP, including detailed discussion for the factors and parameters effects on bio-oil production and the effect of used catalysis on bio-oil quality and yield. These factors start with feedstock selection and analysis, followed by the applied pre-treatment technique moving forward to operating conditions, reactor type, catalyst selection and the applied CFP technology. In addition, this work describes the advanced upgrading methods and applications used for products from CFP that influence the yield and quality of the final products. We also present the modeling and simulation of the CFP process, and process optimization techniques, the application of life cycle assessment (LCA), and the techno-economic analysis of the CFP process. The multifaceted nature of the production of bio-oil using CFP is not discussed in the majority of reviews of research in the literature. The uniqueness of the paper in this context is in the reader's ability to learn not only how bio-oil is made from biomass

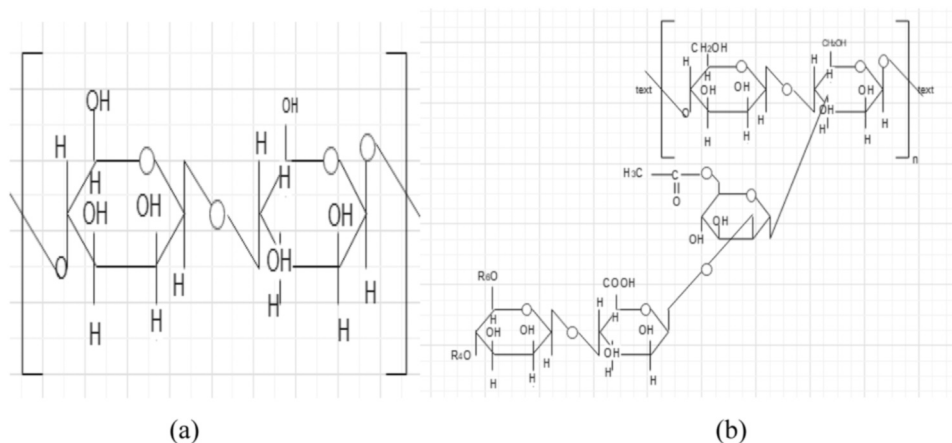


Fig. 2. Cellulose formula (a) Hemicellulose formula (b).

hemicellulose is heterogeneous because of the existence of a short side chain formed by a variety of polymerized monosaccharides, such as:

1. pentoses, which are 5-carbon chains, namely xylose, arabinose, and rhamnose.
2. Hexoses, which are chains with six carbons like glucose, mannose, and galactose
3. Additionally, uronic acids (such as D-gal, 4-O-methylglucuronic, and other D-glucuronic compounds) are also present. Hemicelluloses, which are often generated from the C5 sugar pentose, are in charge of preserving the fibers cellulose and others in plants' cell walls.

Pyranose is less resistant to heat and chemical reactions than the amorphous organic polymer hemicellulose.

Lignin differs from the two previous polymers in two essential traits:

1. First off, it is the only aromatic polymer produced from phenyl-propanoid precursors that make up lignocellulosic biomass.
2. Secondly, lignin is composed of three basic units: coniferyl alcohol (unit G), p-coumaryl alcohol (unit H), and sinapyl alcohol (unit S).

These units are linked by links: carbone-oxygen and carbone-carbone.

Thus forming an amorphous three-dimensional unit that represents a proportion of biomass ranging from 10 to 25% (X. [21]).

Lignin, unlike cellulose and hemicellulose, is less sensitive to thermal decomposition and forms, in the case of decomposition, phenolic substances that will be present in bio-oils.

The proportions of these components can vary considerably depending on the raw material, as shown in Table 2. This difference can have an impact on the yield and quality of the intended product.

Table 2
Proportions of the main components of lignocellulosic biomass for some feedstocks.

Substrat	cellulose	hemicellulose	lignin	Extract	References
Hardwoods (palm wast, olive wast)	43-47%	25-31%	16-24%	2-8%	[7]
Softwoods (rice straw and wood)	40-44%	24-25%	25-31%	1-5%	[23]
average waste composition	30-50%	15-35%	10-20%	1-10%	[31] [32]

2.2. Feedstocks analysis

The proximate analysis and the ultimate analysis are the two easiest and most widely utilized types of analysis.

2.2.1. Proximate analysis

The four key components of biomass are examined using this global analysis: the consistency of the substances that make up the biomass, excluding water, which separates by evaporating at high temperatures; the absence of oxygen, solid carbon, ash, and non-volatile biomass; and the combustion of inorganic residues.

High-volatile matter biomass will convert at the highest rate compared to biomass with a high fixed carbon content. Theoretically, stationary biomass with a high carbon content may be more advantageous for the production of biochar than highly volatile biomass, which may be appropriate for the production of bio-oil.

2.2.2. Ultimate analysis

The ultimate analytical test, on the other hand, produces more complete and accurate results than proximal analysis. Therefore, we shall assess the material's content of carbon, nitrogen, sulfur, hydrogen, and oxygen (CHOSN).

The results of this analysis allow a better comparison between raw materials. The results can also be used to determine the calorific value of the raw material. [33].

In order to determine the higher calorific value (HHV) of biomass utilizing elemental and instantaneous analyses, Chaniwala and Parikh [30] for instance, created the following empirical correlation:

$$\text{HHV, (MJ/kg)} = 0,34910 \text{ C} + 1,17830 \text{ H} - 0,01340 \text{ O} - 0,1 \text{ S} - 0,01510 \text{ N} - 0,02110(\text{A})$$

Regression models were created by Friedl et al. [34] to predict HHV based on the elemental makeup of a portion of 122 samples, all of which were composed of plant matter. The study demonstrates that using least squares and least partial squares regression methods using variables C², C, H, C*H, and N, the models with the best predictive capacity are those generated utilizing carbon content, hydrogen H, and nitrogen N.

$$\text{HHV, (MJ/kg)} = 1870(\text{C}^2) - 144(\text{Carbone}) - 2802(\text{Hydrogen}) + 63,8(\text{CH}) + 129(\text{Azote}) + 20147$$

$$\text{HHV, (MJ/kg)} = 5,22(\text{C}^2) - 319(\text{Carbone}) - 1647(\text{Hydrogen}) + 38,6(\text{CH}) + 133(\text{Azote}) + 21028$$

3. Parameters and factors affecting the pyrolysis of biomass

3.1. Pretreatment of biomass

Pretreatment techniques aim to enhance the physicochemical properties of biomass to facilitate its degradation reactions and to improve the bio-oil. Several types of pretreatments are considered, as depicted in Fig. 3.

3.1.1. Physical pretreatment

This technique reduces the biomass particle size, improving the heat and mass transfer during the pyrolysis and reducing coke formation [36]. It involves mechanical pretreatment (extrusion, densification and milling) and irradiation pretreatment (microwave, γ -rays, electron beam and ultrasonic waves). This method is eco-friendly, and the release of toxic species seldom occurs. However, it consumes a lot of energy [37]. Concerning the mechanical pretreatment, various devices are used, for example mills (ball mill, knife mill, hammer mill, etc), disc refiners and extruders. The type of grinders depends on several parameters, such as the physicochemical properties of biomass (moisture content, density, composition, etc.), the final particle size and the final use (chemical conversion, thermal conversion, fermentation, and enzymatic valorization). Milling is the most widely used technique, especially ball milling [38]. Regarding irradiation pretreatment, it requires high-energy beams with low wavelength such as microwaves where electromagnetic energy is directly transformed into heat at the molecular level. Thus, the energy dissipation throughout the biomass is uniform [39,40]. In lignocellulosic biomass (LCB), this technique decomposes hemicellulose and lignin, and changes the cellulose structure, due to the dielectric polarization, which breaks the covalent bonds between cellulose and hemicellulose [41].

3.1.2. Chemical pretreatment

The key role of chemical pretreatment is to reduce inorganic species such as salts, sulfates and carbonates from biomass [42]. Acid washing with HCl eliminates the inorganic components, especially alkali and alkaline earth metal species (AAEMs), e.g., Ca, K, Mg, and Na [43]. AAEMs have negative effects on the quality of bio-oil by increasing the production of water and organic acids. They act as catalysts for the primary and secondary reactions (volatile-char interactions) of pyrolysis. Consequently, the removal of AAEM increased bio-oil yield, by enhancing the content of anhydrosugars, and decreased the yields of biochar and non-condensable gas. Moreover, Alcazar-Ruiz et al. [44] found that water leaching eliminated potassium and sodium and enhanced the selectivity of guaiacol and syringol.

3.1.3. Thermal pretreatment

Thermal pretreatment aims to reduce the moisture content of lignocellulosic biomass. It takes place in several stages depending on the temperature ranges, between 50 to 300 °C: a primary drying between 50

to 100 °C, allowing a reduction in biomass porosity and the removal of water, post drying (105 to 250 °C), including removal of moisture, softening of lignin (120 to 150 °C), hemicellulose degradation (~200 °C) and removal of volatiles, and the torrefaction (200–300 °C) [45,46]. Torrefaction, also, known as mild pyrolysis, implies a significant degradation of hemicellulose from 200 °C and a little decomposition of lignin and cellulose between 250–300 °C [47]. There are two types of torrefaction technologies: dry torrefaction (DT) and wet torrefaction (WT). WT employs saturated water to solubilize hemicellulose into aqueous phase and conserves cellulose for pyrolysis. Dry torrefaction, the most used pre-treatment, is suitable for biomass with low moisture content, and it produces a higher biochar yield, but of lower quality, compared to wet torrefaction [47]. The chemical composition of bio-oil is also affected, by increasing the oxygenated species. Additionally, numerous reactions may occur during torrefaction, such as deoxygenation reactions (dehydration, decarboxylation, decarbonylation and demethoxylation), decarbonization and dehydrogenation reactions) [48].

3.1.4. Biological pretreatment

Biological pretreatment is the most economical and eco-friendly method. Biomass is treated with microorganisms such as fungi (e.g., white-rot fungi, brown-rot fungi, soft-rot fungi), bacteria and microbial consortia, with low energy input [49]. These microorganisms modify the composition and the structure of biomass, thereby facilitating its pyrolysis by increasing the reaction rate and reducing energy demand (T. [50]. The main aim of this method is the depolymerization of complex biomass species, such as lignin. It can also break down the main links between lignin and hemicellulose or between lignin and cellulose [51]. Recently, Zhang et al. [52] found that white-rot fungus selectively degraded lignin and enriched cellulose, promoting the production of bio-oil during fast pyrolysis. Finally, despite the environmental benefits of biological pretreatment, it is slow and requires a longer pretreatment time and extra space [53].

To sum up, each pretreatment method has its strengths and limitations. Combining techniques could increase the efficiency of the pretreatment and enhance the quality of products. For instance, Gao et al. [54] found that combining acid washing and torrefaction increased the conversion of sugars and reduced the production of phenols, acids and ketones.

3.2. Temperature effects

Temperature is the most interesting factor for biomass pyrolysis. It significantly impacts the quality and yield of degradation products. In this review, we focus on fast pyrolysis, characterized by fast heating rates (10–200 °C/s) and short vapor residence times (< 2 s) [55]. Typically, fast pyrolysis favors bio-oil than char and non-condensable gas. Lower temperatures result in a low reaction rate, high char yield and low liquid yield. Conversely, increasing pyrolysis temperatures generally favor gas production and bio-oil yield which increases at an optimum point, usually between 400 and 650 °C, before declining due to secondary reactions [56,57]. This optimum temperature threshold varies with different biomass types. For instance, Hasan et al. [58] found that beauty leaf fruit husk reached its highest yield of bio-oil (44.2%) at 500 °C during fast pyrolysis. Sugarcane bagasse and wheat straw displayed optimal bio-oil yields at 550 °C, while rice straw peaked at 450 °C [56]. As temperatures increase, the biochar yield decreases due to the thermal cracking of heavy hydrocarbons at high temperatures [59]. In the study of Hasan et al. [58], biochar yield decreased from 41.7 to 32.5%, while syngas production increased from 20.8 to 27.2% due to secondary reactions.

The temperature of the process also crucially affects the composition and quality of the bio-oil because of secondary reactions such as decarboxylation and dehydration [58,60]. For example, Zadeh et al. [61] noted distinct chemical group differences in bio-oil from fast

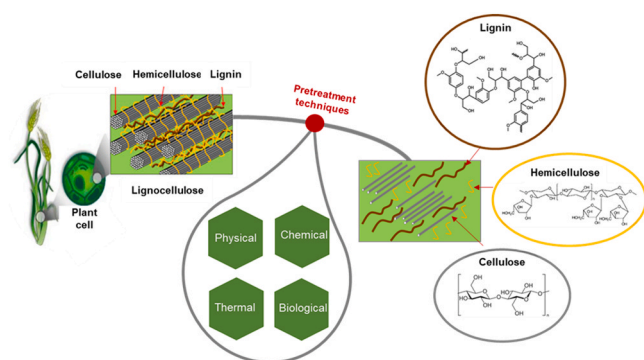


Fig. 3. Schematic of the pretreatment techniques on lignocellulosic biomass, inspired from [35].

pyrolysis of hardwood (Populus) and softwood (Spruce) between 500 and 600 °C. At 500 °C, the bio-oil was composed of phenols, acids, and alcohols, while at 600 °C, furans, sugars, ketones, and aromatics were predominant. This variation in bio-oil composition with temperature relates directly to the decomposition of cellulose, hemicellulose, and lignin, as well as the secondary reactions of tar and char, which are improved by increasing the pyrolysis temperature. Cellulose, which is the main constituent of lignocellulosic biomass, when it is heated below 300 °C, it is depolymerized to levoglucosan and other primary anhydrosugars [62]. It is further defragmented at a temperature of around 600 °C, resulting in the production of hydroxyacetaldehyde and other carbonyls, acids, and alcohols [62]. Hemicellulose, on the other hand, undergoes dehydration at low temperatures, below 280 °C, producing anhydride fragments, water soluble acids, char, gases, and water. At higher temperature, depolymerization takes place, producing volatiles, levoglucosan and other anhydrohexoses, levoglucosenone and furans [63]. Concerning lignin, which is the most stable constituent, dehydration is the dominant process at low temperatures (< 500 °C), and higher temperatures result in the formation of diverse lignin monomers. Primary pyrolysis products like vanillins and guaiacols emerge at 400 °C, and vanillin derivatives transform into a variety of catechols and phenols at approximately 600 °C [63].

3.3. Heating rate effects

Heating rate is a key parameter as it defines the type of biomass pyrolysis: slow, fast, and flash pyrolysis. According to Yang et al. [64], the heating rate is the most important parameter of pyrolysis conditions for the prediction of bio-oil yield and its oxygen content. The heating rate is influenced by the pyrolysis parameters, including the reactor design, biomass particle size, temperature profile, and heat transfer mechanism. For instance, Onay [65] investigated the impact of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed. The study focused on the optimization and characterization of bio-oil and biochar production and found that the optimum bio-oil production was observed at a heating rate of 300 °C/min at 500 °C with a yield of 54% [65]. Typically, a faster heating rate induces rapid fragmentation and reduces the residence time of volatile substances, thereby enhancing gas and bio-oil production, reducing secondary reactions and avoiding char formation [M. [66]. Conversely, the slow pyrolysis process significantly reduces the yield of bio-oil, favoring secondary cracking and increasing char formation [62].

Precise regulation of heating rate and reaction temperature during biomass pyrolysis critically determines the quality and yield of bio-oil and gas. Elevated heating rates and temperature increase bio-oil and gas production, while lower heating rates and lower temperatures increase biochar yield [59]. Additionally, heating rate significantly influences the chemical composition, molecular weight, viscosity, and stability of bio-oil. A recent investigation by Huang et al. [67] examined the effects of high heating rates on the pyrolysis of mushroom bran and corn straw, ranging from 100 to 800 °C/min. Their findings highlighted the decomposition of macromolecules such as nitriles into small molecules occurred at heating rates above 200 °C/min by secondary reactions. Moreover, the synergistic effects of starch and hemicellulose favored the formation of furfural and furan at heating rates exceeding 300 °C/min. Notably, the heating rate can have an impact on the morphological characteristics of biochar, affecting pore structure and surface area. The violent release of volatiles during pyrolysis, attributed to thermal shock, can damage internal porous structures, leading to reduced surface area of the char [59,68].

3.4. Particle size effects

The low biomass conductivity reduces the heat transfer rate, generating a temperature gradient along the particle and thus causing inhomogeneity during pyrolysis. This heat transfer is determined by

particle size (Y. [20]. Recently, Yu et al. [69] investigated the effect of three particle sizes (0.5 ~ 1, 2 and 5 mm) on the pyrolysis of pine wood. They reported that high char and low gas yields were observed for larger particle sizes. However, tar yield depended on temperature. At temperatures below 350 °C, smaller particles produced more tar and inversely at 500 °C, i.e., more tar was generated with larger particles. The mass transfer resistance of larger particles caused a strong intra particle secondary reaction and produced lighter tar. More furans were produced for larger particle size. However, the pyrolysis of smaller particle sizes (0.5–1 mm) produced more sugars, mainly levoglucosan, phenols, ketones, and aldehydes, due to a strong inter-particle secondary reaction [69].

3.5. Moisture and ash in biomass effects

High moisture content has an energetic impact on biomass pyrolysis due to the necessity for added heat. It can also lead to high water content in the bio-oil. A moisture content of more than 10% produces a bio-oil with two distinct phases, water, and an oil phase [70]. The ash content of the biomass is a key characteristic for char quality. It does not degrade or transfer in the pyrolysis reaction but still is in biochar and positively influences its yield. However, it negatively correlates with bio-oil yield, which is explainable as excessive ash content lowers the volatile content [71]. The main part of ash is an inorganic substance, which significantly affects biomass behavior and the pyrolysis product distribution. The presence of ash changes the yields of some chemical substances in pyrolysis liquid, such as a decrease in levoglucosan yield and an increase in the yields of acetic acid [72].

3.6. Pressure effects

High pressure reduces tar production and promotes char and gas yield because of the crosslinking reaction within the molten phase. It can promote the repolymerization of volatiles and produce macrocyclic secondary chars [69]. Product distribution is also affected by pressure. Matamba et al. [73] reported that cellulose and xylan pyrolysis under pressurized conditions favors generation of poly-aromatic hydrocarbons (PAHs) with low molecular weight, such as naphthalene. Meanwhile, lignin pyrolysis was convenient for producing PAHs with high molecular weight. The effect of pressure is more significant at higher temperatures. Cerciello et al. [74] found that increasing pressure increased the formation of phenolic compounds and a network of reactions such as aromatization, charring reaction and crosslinking reaction enhanced char production [69,74].

3.7. Flow rate of carrier gas and residence time effects

The residence time significantly influences the pyrolysis process and product yield in combination with temperatures. A short residence time of pyrolysis vapors (< 5 s) at an intermediate temperature reduces the secondary reactions and improves the production of bio-oil. Conversely, slow removal of vapors from the reactor at high temperatures favors the secondary reactions and lead to the increase of gas yield by cracking reactions [75]. Increasing residence time and temperatures improves the bio-oil yield to an optimum point and then decreases [76]. The effect of carrier gas flow is related to residence time. Faster gas flow through the reactor results in a shorter residence time of the volatiles, preventing secondary reactions. This decreases the char yield and accelerates the decomposition rate of the biomass (C. [77]. Regarding bio-oil yield, Song et al. [78] found that increasing the gas flow rate from 0.1 to 0.3 m³/h during the fast pyrolysis of particle board increased the bio-oil yield but the effect on pyrolysis products distribution is low.

3.8. Reactor type and production scale effects

Various reactor configurations [79] have been used for biomass

pyrolysis, such as bubbling fluidized bed and ablative reactors. The following sub-sections discuss the different reactor types in terms of physical phenomena controlling the pyrolysis reaction.

3.8.1. Fast biomass pyrolysis using bubbling fluidized-bed reactor

Bubbling fluidized-bed reactors are popular due to their advantages of heat and mass transfer and their thermal homogeneity due to bubble motion. The multiphase flow parameters, i.e., the chamber dimensions, the flow rates and particle size dictate the mixing and sub-sequentially the bubble diameters and the reaction rate of the pyrolysis reaction. A degree of control of the reaction can be achieved through the convection motion. In addition, fluidization velocities have a significant effect on pyrolysis process. In fact, higher velocities lead to the formation of larger bubbles and cause a decrease in the efficiency of solid mixing and heat transfer, which decreases the liquid yield [80]. This also induces attrition, erosion, fragmentation and collisions of biomass particles [81].

3.8.2. Fast biomass pyrolysis using fixed-bed reactors

This technology is characterized by its uncomplicated design and ease of use. Typically, reactions are conducted on a solid stationary bed, heated by an external source. An inert gas is needed to remove volatile substances and supply an inert atmosphere [82]. Numerous research studies have been conducted using this configuration [83,84]. In a recent investigation by Muzyka et al. [85], the pyrolysis of biomass was compared using two types of reactors: a fixed bed and a pyrolysis – gas

chromatography – mass spectrometry (Py-GC/MS) setup. The residence time for volatile compounds was observed to be longer in the fixed bed, resulting in the detection of certain products in large quantities in the Py-GC/MS, whereas they were not prevalent in the fixed bed. Conversely, compounds such as anhydrosaccharide and benzene derivatives exhibited different behavior between the two reactor types.

3.8.3. Other reactor types

Ablative reactors lead to a mechanical ablation of biomass surface and the removal of the formed carbon layers [86] as the biomass is in direct contact with the hot reactor walls (less than 600 °C) under high pressure and centrifugal force [87]. There are also small entrained flow reactors which use laminar flow gas to control the pyrolysis reaction within a tube/cylinder configuration. They offer a variety of advantages, such as process control and modelling [88-91]. To sum up, recent studies on biomass fast pyrolysis are summarized in Table 3.

4. Catalytic fast pyrolysis of biomass

Bio-oil from fast pyrolysis offers several merits over raw biomass, such as higher energy density and easier storage and transportation. Bio-oil can be used as fuel for boilers and engines and can be upgraded to premium-grade transportation fuels. However, crude bio-oil faces limitations due to its complex composition, high oxygen and water content, modest calorific value, poor stability, elevated viscosity, corrosiveness,

Table 3

Summary table of the selected studies of this review.

Biomass	Pretreatment method	Reactor	Operating conditions	Products	Reference
Hardwood (Populus) Softwood (Spruce) Pitch pine	Drying (100 °C-12 h)	Fixed bed reactor	T: 500–600 °C Residence time: 2 s Particle size: ~18 mm Nitrogen gas: 500 ml/min	Bio-oil yields: 71.2% (spruce) and 68.4% (populus) Bio-oil Composition: phenolic compounds (spruce); furans, acids and sugar compounds (populus)	[61]
Beauty Leaf Fruit Husk	Knife milling drying in air at 105 °C for 12 h	Bubbling fluidized-bed reactor	T: 400 °C to 550 °C Residence time < 3 s Particle size: 0.35, 0.55, and 0.95 mm	Yields: (at 500 °C, 0.55 mm) Bio -oil: 65.5%; Bio-char: 17.33%; Gas: 17.17% Bio-oil composition: levoglucosan, furfural and guaiacol Gas composition: CO, CO ₂ and a small fraction of hydrocarbon gases (C ₁ –C ₄)	[80]
Macadamia nutshell	-Drying under sunlight (30 days) Physical treatment (hammer shredding)	Pilot auger reactor	T: 400–550 °C Residence time: 2 min and 20 s Particle size: < 1 mm Nitrogen gas: 4 L/min	Bio-oil Yields: 44.2% at 500 °C Bio-oil Composition: Phenols, aromatics, alkanes, ketones, alkenes, alcohols, carboxylic acids	[58]
Mushroom bran & corn straw	-Drying under sunlight (12 days) -Physical treatment (hammer, shredding)	Auger reactor	Particle size: 2 mm, 6 mm, 10 mm T = 350–550 °C Residence time: 40, 120, 200 s	Bio-oil yield: 33.69-42.93%. Biochar yield: 33.98-44.38% Gas yield: 18.54-27.1% Bio-oil Composition: Phenols, aromatics and alcohol	[76]
Coffee Husks	Acid washing	Py-GC/MS	Direct pyrolysis (600 °C, 20 s) Staged pyrolysis (300-600 °C; 50 °C increment / 10 s/ stage)	Composition: CO ₂ , aldehydes, phenols, ketones,	[67]
Pine wood	Grounding Drying in a vacuum oven overnight at 35 °C	Py-GC/MS	T: 400, 500, and 600 °C	Composition: Levoglucosan, Oxygenated Compounds (esters, furans, glycols and ketones)	[92]
Pine sawdust	Drying in an oven at 105 °C for 12 h	Fixed bed reactor	T: 350 – 800 °C Particle size: 0.5-1, 2 and 5 mm Heating rate: 100 °C/min	Bio-oil composition: alcohols, acids, esters, aldehydes, ketones, furans, phenols and sugars.	[69]
Pinewood and poplar	Drying at 105 °C for about 24 h	Fluidized bed	T = 500 °C Oxidative/non-oxidative atmosphere Particle size: 90–180 µm	Bio-oil yield: 36.25% Bio-char yield: 21.03% Bio-oil Composition: anhydro sugars (levoglucosan, ect), phenols/aromatic hydrocarbons light linear compounds (alcohols, carbonyls and acids), cyclopentanones/ cyclohexanones and furan/furfural	[93]
		Vortex Reactor	T = 500 °C Particle size: 2.5–3.5 mm	Bio-oil yields: (Pine-poplar): 70.4- 72.5% Biochar yield: 13.9 - 10.7% Gas yield: 15.7- 16.8% Bio-oil Composition: guaiacols (pine); phenolics, syringols, and catechols (poplar) Gas composition: CO ₂ , CO, CH ₄ , C ₂ H ₆ , C ₂ H ₄ , H ₂	[94]

and insolubility in conventional fuels. To address these challenges, catalysts are introduced in fast pyrolysis to lower activation energy, alter product composition, and produce higher-grade fuels and valuable chemicals [95,96]. Catalytic biomass fast pyrolysis enhances vapor quality by using catalysts with strong deoxygenation activity, enabling control over pyrolysis pathways and enhancing product value [97].

4.1. High-quality bio-oil using catalytic pyrolysis

Throughout catalytic biomass pyrolysis, several chemical reactions take place, including pyrolysis, deoxygenation, catalytic cracking, ketalization, aromatization, and alcohol aldehyde condensation reactions [98]. The applied catalyst and the reaction conditions control the selectivity of these reactions. By adjusting these parameters, the lignocellulose structure can actively contribute to the reaction, resulting in improved desired products selectivity in the bio-oil [99]. Catalysts facilitate additional reactions such as decarboxylation, decarbonylation, cracking, hydrocracking, Diels-Alder reaction, and oligomerization. These reactions breakdown large-oxygenated compounds, thereby reducing the oxygen content and improving the quality of the bio-oil [100]. The selection of catalyst in catalytic fast pyrolysis is of paramount importance as it influences both the product distribution and the overall process efficiency. Various catalysts, including metal oxides, inorganic minerals, zeolites, biomass-derived catalysts, and carbon-based catalysts, have been utilized in biomass catalytic fast pyrolysis. Table 4 provides an overview of these catalyst categories, highlighting their key features and roles in the process. Subsequent sections provide further details on each category along with catalyst

regeneration techniques.

4.1.1. Metal oxides

Metal oxides have found extensive use as heterogeneous catalysts in diverse catalytic processes (B. [105]. They have gained significant prominence in catalytic fast pyrolysis due to their ability to modify the reaction pathways and influence the distribution of bio-oil constituents. They exhibit redox properties owing to their multivalent nature or their possessed acid-base characteristics, which can effectively facilitate the catalytic pyrolysis of biomass, resulting in the formation of more stable products [100]. Metal oxides can facilitate the oxygen removal from biomass-derived compounds, leading to deoxygenation and hydrocarbons formation. They can function as oxygen storage and release agents, promoting the conversion of oxygenated species into less oxygenated products. During the catalytic deoxygenation reactions, oxygen is eliminated from the pyrolysis vapor producing carbon dioxide, carbon monoxide, and water vapor. However, the transfer of carbon within the gas phase and the generation of carbon and water on the catalyst's surface can diminish the overall production of organic and liquid phases [101]. Metal oxides, owing to their distinctive characteristics, can be classified into acidic, basic, and transition metal oxides as presented in Table 4 and discussed in the next sub-sections.

4.1.1.1. Acid metal oxides. SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and other acidic metal oxides are employed as catalysts in the catalytic pyrolysis of biomass feedstocks, in addition to sulfated metal oxides like $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{TiO}_2$ [100]. The utilization of acidic metal oxides has an impact on the pyrolysis products distribution. Employing acidic metal

Table 4
Common catalysts used for catalytic fast pyrolysis, associated features, and role in the fast pyrolysis process.

Catalyst type	Examples	Key features	Role in the fast pyrolysis process	Ref.
1. Metal oxides		<ol style="list-style-type: none"> Redox properties because of multivalent nature Acidic or basic properties based on the oxide type. 	<ol style="list-style-type: none"> Facilitate deoxygenation reactions from biomass-derived compounds leading to hydrocarbons formation. Influence the pyrolysis products' distribution and the bio-oil composition. 	[100,101]
1.1 Acid metal oxides	SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$	<ol style="list-style-type: none"> Acidic properties 	<ol style="list-style-type: none"> Increase the gas and solid yields and decrease the liquid yield. Impede the subsequent breakdown of volatiles into gaseous products, maintaining them in tar. Promote deoxygenation reactions. 	[102,101,103]
1.2 Base metal oxides	CaO , MgO , Ca(OH)_2	<ol style="list-style-type: none"> Basic properties Abundant and cost-effective 	<ol style="list-style-type: none"> Decrease the bio-oil oxygen content. Eliminate the acidic functional groups, thereby diminishing bio-oil corrosiveness. Enhance the bio-oil quality. 	[100,104]; [105]; [106]
1.3 Transition metal oxides	ZnO , V_2O_5 , TiO_2	<ol style="list-style-type: none"> Acidic-basic properties 	<ol style="list-style-type: none"> Decrease the bio-oil oxygen content. Boost biomass depolymerization and catalyze rearrangement reactions. 	[107-109]
2. Inorganic minerals	K^+ , Mg^{2+} , Ca^{2+}	<ol style="list-style-type: none"> Present in the biomass feedstock. Added as inorganic salts. 	<ol style="list-style-type: none"> Facilitate the depolymerization and breakdown of organic matter. Stimulate hydrogen production reactions. Increase the gas and solid yields while reducing the liquid yield. 	[110-112]; [24]; [109]
3. Zeolite catalysts	γ , and β zeolites, ZSM-5, metal-modified zeolites, layered-zeolites	<ol style="list-style-type: none"> Crystalline three-dimensional silicon aluminum salt High porosity Regular pore structure Acidic properties 	<ol style="list-style-type: none"> Superior performance in bio-oil upgrading. Capable of breaking C-O bonds. Boost dehydration and cracking reactions. Zeolite type, pore size and structure play crucial roles in determining the final products distribution. 	[16,113]; [105]; [98];[109]
4. Biomass-derived carbon catalysts	Biochar, activated biochar.	<ol style="list-style-type: none"> High porosity, surface area, and stability. Contains prevalent mineral elements and surface functional groups. 	<ol style="list-style-type: none"> Increase the yield of gas products. Reduce the formation of toxic compounds in the residues. Enhance the process efficiency boosting both conversion efficiency and economic revenues. Impede catalyst deactivation extending the catalyst lifetime. 	[114,115]; [116]; [109];[117]
4.1 Metal-based biomass-derived carbon catalysts	Activated biochar supported by metal (e.g., Fe, Ni, Zn, Mg, K, etc.)	<ol style="list-style-type: none"> Improved pore structure Incorporate metal elements 	<ol style="list-style-type: none"> Promote biomass decomposition. Increase the yields of hydrocarbons, hydrogen, and carbon monoxide gases in the pyrolysis products. Enhance aromatics yield in bio-oil. 	[118-120]

oxides leads to an increase in gas and solid yields and a decrease in the overall liquid yield. For example, [101] reported that using Al_2O_3 in the catalytic fast pyrolysis of commercial wood feedstock reduced the liquid yield to approximately 40 wt% compared to 58.6 wt% for the non-catalytic process. Furthermore, these metal oxides can impede the subsequent breakdown of volatile components into gaseous products, maintaining them in tar. [103] found that using SiO_2 and Al_2O_3 promotes the tar formation in the catalytic pyrolysis of cellulose, lignin, and poplar.

Moreover, the application of acidic metal oxides influences the bio-oil composition and affects the oxygenates' formation according to the acidic nature and the CFP operating conditions. For example, [102] observed that the application of Al_2O_3 as a catalyst during the pyrolysis of sawdust enhanced the breakdown of macromolecular sugar and methoxyphenol. Additionally, using Al_2O_3 nano powders during the catalytic pyrolysis of cellulose resulted in a higher total yield of dehydrated sugars, along with an increased presence of aromatics and polycyclic aromatic hydrocarbons (PAHs) in the organic phase [121]. [101] reported that employing SiO_2 - Al_2O_3 catalysts resulted in the lowest oxygenates concentration in the bio-oil compared to other adopted catalysts in the experiment. Furthermore, SiO_2 with medium porosity and weak acidity demonstrated effective catalytic activity for eliminating oxygenates such as acids, aldehydes, and ketones in the catalytic pyrolysis of *Jatropha* residue. SiO_2 also exhibited the ability to inhibit the coke formation as well as the PAHs, thus improving the bio-oil stability [122].

4.1.1.2. Basic metal oxides. Basic metal oxide catalysts, including salts of calcium, magnesium, sodium, potassium, and others, are primarily characterized by oxide ions acting as bases and the metal cations acting as Lewis acids [104]. These catalysts have gained significant popularity in biomass catalytic pyrolysis due to their abundance and cost-effectiveness. Additionally, basic metal oxides play a crucial role in decreasing the bio-oil's oxygen content via ketylation and aldol condensation of carbonyl compounds and carboxylic acids, as well as eliminating the acidic functional groups, thereby diminishing the corrosiveness of bio-oil. Consequently, they are viable catalysts for bio-oil upgrading [100]; B. [105]; [106].

The introduction of MgO resulted in a decrease in the yield of bio-oil during the fast pyrolysis of cotton seed feedstock, however the bio-oil quality was upgraded with reference to heating value, oxygenated groups removal and hydrocarbon distribution [123]. [124] examined the effects of different basic oxides (MgO , Ca(OH)_2 , and K_2CO_3) on catalytic pyrolysis of palm shell. The findings revealed that Ca(OH)_2 exhibited superior catalytic pyrolysis effects compared to other used catalysts. It boosted bio-oil production and improved the phenols selectivity. The bio-oil produced in the presence of Ca(OH)_2 had a decreased acidic content of 35.2%, when compared to bio-oil produced from conventional pyrolysis without a catalyst having an acid content of 42%, significantly enhancing the bio-oil quality. Similarly, [125] observed that employing CaO and MgO as catalysts lowered the phenols and acid content in bio-oil. Moreover, basic metal oxides facilitated the breakdown of dehydrated sugars, resulting in the production of aromatics, cycloalkanes, and other lighter compounds. As a result, the fuel properties of crude bio-oil were enhanced.

4.1.1.3. Transition metal oxides. Transition metal oxides with distinctive acid-base properties are extensively employed in biomass catalytic pyrolysis. Similar to acidic and basic metal oxides, the application of transitional metal oxides in biomass catalytic pyrolysis also influences the pyrolysis products' yield and composition and decreases the bio-oil's oxygen content. Various transition metal oxides were investigated as catalysts during the catalytic pyrolysis of alkali lignin. The findings revealed that Co_3O_4 substantially enhanced the bio-oil yield and increased the methoxyphenol and methoxybenzene contents in the

produced bio-oil [126]. [127] employed ZnO as a catalyst in the fast pyrolysis of rice husk and observed a decline in the bio-oil yield but an increase in the yield of low molecular compounds. Furthermore, ZnO diminished the presence of oxygenated groups in bio-oil and facilitated hydrogen atoms transfer during the pyrolysis process. [108] performed a comprehensive investigation on the catalytic performances of transition metal oxides. The results demonstrated that the application of transition metal oxides enhanced coke yield and restrained gas formation. Regarding bio-oil production, Co, Mn, V, and Ti oxides exhibited positive effects, while Fe, Cu, Cr, and Ce oxides did not. The study also revealed that transition metal oxides boost biomass depolymerization and catalyze rearrangement reactions. For instance, ZnO , with its high base strength, enhanced the production of phenolic compounds and facilitated hydrogen atom transfer throughout the cracking reactions [107].

4.1.2. Inorganic minerals

The biomass feedstock contains a significant amount of inorganic species, primarily in the form of inorganic salts, comprising more than 85% of its inorganic minerals composition [128]. Inorganic minerals have been found to exhibit catalytic effects in biomass pyrolysis. They facilitate the depolymerization and degradation of organic matter, thereby reducing the activation energy required for pyrolysis and shifting the reactions to lower temperatures (W. [24]; [109]). Moreover, inorganic minerals foster char formation and biomass breakdown, leading to increased solid product yield and decreased gaseous product yield [110,112,129]. Inorganic minerals also stimulate hydrogen production reactions, including water-gas shift and Boudouard reactions, resulting in enhanced production of hydrogen, carbon dioxide, and levoglucosan [111]. Researchers have explored the application of additional inorganic salt solutions to leverage the catalytic activity of inorganic minerals in biomass pyrolysis [130,131]. For example, potassium has been found to catalyze fast pyrolysis and boost the formation of carbon dioxide and carbon monoxide from polysaccharides, methanol from lignin and acetic acid from hemicellulose [112,132]. According to [133], the presence of potassium additives influences temperature profiles, pyrolysis kinetics, and secondary tar reactions, leading to higher yields of gaseous products and light volatiles. The addition of potassium significantly affected conversion time, excursions in exothermic temperature, and gas production, aligning with previous findings of (W. L. [134].

4.1.3. Zeolite catalysts

Zeolites refer to crystalline three-dimensional silicon aluminum salts with uniform pore structure and strong surface acidity that have been widely used in various catalytic pyrolysis [113]. Zeolite catalysts have been reported for their superior performance in bio-oil upgrading [98]. This may be attributed to their capability of breaking C-O bonds, producing bio-oil with excellent stability. Based on their pore size, zeolite catalysts can be grouped into three categories: micropore zeolites (less than 2 nm), mesopore zeolites (2–50 nm), and macropore zeolites (more than 50 nm) [135]. Zeolites have demonstrated significant catalytic effects in boosting dehydration and cracking reactions, leading to the production of final liquid products with high H/C ratios and low C/O ratios [109].

Several factors explain how zeolites function as catalysts in CFP including the presence of acidic sites and their shape-selective properties that make them superior over other catalysts used for CFP. Zeolites possess a significant number of acidic sites due to the presence of aluminum atoms within their crystalline structure. These acidic sites facilitate the breaking of chemical bonds and promote cracking and dehydration reactions of complex organic molecules present in the biomass feedstock [113]. The acidity of zeolites is crucial in influencing the production of bio-oil because the majority of catalytic reactions involved in biomass degradation take place at the acidic sites of zeolites through a carbonium ion mechanism [136]. Within the zeolite

frameworks, there are Brønsted-Lowry and Lewis acid sites essential for cracking and aromatics production. Brønsted-Lowry acidity arises from the presence of hydroxyl groups (Si(OH)Al) in the zeolite, while Lewis acidity stems from tri-coordinated silicon defects [137,138]. Additionally, zeolites' shape-selective properties enable preferential catalysis of desired products based on molecular size and shape. Zeolites have a unique porous structure with well-defined channels and pores of specific sizes and shapes. This shape selectivity property allows zeolites to discriminate between different the molecules of reactants, intermediates and products based on their sizes and shapes, thereby promoting the formation of desired products while restricting the formation of undesired by-products and significantly influences the composition of the resulting bio-oil [138,139].

Moreover, the CFP product distribution is influenced by the interrelationship between zeolite acidity and porosity. The porosity of zeolites plays a role in stabilizing intermediate species derived from biomass, such as phenol alkoxy, by promoting their adsorption and hindering their repolymerization into coke. On the other hand, the acidity of zeolites facilitates the catalytic conversion of these intermediates into aromatic hydrocarbons [140]. Thus, this interrelationship should be considered in zeolites' synthesis and application in the CFP process.

Various zeolites have been applied in catalytic biomass pyrolysis including ZSM-5, γ , and β zeolites. Results revealed that the bio-oil composition depends on the applied zeolite [141-143]. For instance, γ zeolites and ZSM-5 have significantly lowered the oxygen content in the produced bio-oils [144-146]. At lower operating temperatures, oxygen was removed as water vapor, while it was removed as carbon monoxide and carbon dioxide at higher operating temperatures [147]. β zeolites and ZSM-5 enhanced the aromatics selectivity in the produced bio-oil reaching more than 90%, with naphthalenes, xylenes, and toluene being the predominant constituents [148].

Additionally, the pore size and structure play crucial roles in determining the final products distribution. Generally, smaller pores expedite the formation of coke, carbon monoxide, and carbon dioxide, whereas catalysts with large pores have limited enhancements for the aromatics yield along with other value-added chemicals [109]. γ zeolite was reported to exhibit the highest effectiveness in fostering monocyclic aromatic hydrocarbons production during the pyrolysis process due to its acidity and surface area. Meanwhile, β zeolite specifically prompted the naphthalene formation [149]. Among the diverse zeolites, ZSM-5's pore size boosts the selectivity of aromatics production by facilitating the contact of primary vapors with acidic active sites inside the catalyst. As a result, ZSM-5 is respected as a favorable catalyst for selective bio-oil upgrading through adjusting the products distribution [109]. Several modifications have been applied to zeolite catalysts to enhance their catalytic activity in the fast pyrolysis process including metal-modified zeolites, hierarchical zeolites, and dual zeolite catalysts showing superior results in bio-oil upgrading [16]; B. [105]; [109].

4.1.4. Biomass-derived carbon catalysts

The process of biomass pyrolysis yields three primary products: biochar, bio-oil, and pyrolysis gas. Biochar is characterized by its high porosity, surface area, stability, and the presence of prevalent mineral elements and surface functional groups [115,117]. Leveraging these characteristics, biochar has been widely employed in various fields as an adsorbent, catalyst, and catalyst support. The application of biochar as catalyst in biomass pyrolysis increases the gaseous products yield, while decreasing the formation of toxic compounds in the residues. [114] reported that employing biochar catalysts in the fast pyrolysis of woody pellets biomass increased the yields of methane, hydrogen, and carbon monoxide and impacted the product distribution, resulting in an augmented yield of phenols and hydrocarbons. Moreover, the substantial average pore size of biochar acts as a barrier against catalyst deactivation, thereby extending the catalyst lifetime [150]; H. [116]. In addition, biochar application enhances the pyrolysis process efficiency

as it permits recycling boosting both conversion efficiency and economic revenues [109].

4.1.4.1. *Metal-supported biomass-derived carbon catalysts.* The presence of functional groups on the biochar surface provides favorable conditions for the synthesis of metallic-biochar catalysts. Experiments revealed that activating biochar and incorporating metal elements, such as Fe, Ni, Mg, Zn, or K, have a substantial impact on enhancing the biochar pore structure. Numerous studies have proved that loading active metal elements onto biochar can improve its catalytic performance, leading to promoted biomass decomposition, increased production of hydrocarbons, hydrogen, and carbon monoxide gases in the pyrolysis products and increased aromatics yield in bio-oil. [118-120].

Metal-supported biochar catalysts were prepared by [151] using rice husk and various metal salts as activators. The findings indicated that the surface functional groups, structure, and catalytic effects of the used catalysts were influenced by the activator type used in their preparation. Catalysts prepared using KOH and H_3PO_4 exhibited large specific surface area, excellent pore structure and demonstrating high efficiency in catalyzing tar decomposition reactions. $ZnCl_2$ also contributed to the creation of new mesopores, but it tended to aggregate with rice husk, leading to the formation of larger particles that partially blocked some pores. Nonetheless, these catalysts demonstrated favorable catalytic effects on the pyrolytic reactions and exhibited good stability even after five further reactions. In another study, iron-modified biochar surpassed the catalytic performance of commercially available activated carbon. Fe-modified biochar catalyst demonstrated significant improvements in the selectivity and yield of phenol and cresol in the bio-oil when used as a catalyst in the production of phenol-rich bio-oil from corncob feedstock through microwave-assisted pyrolysis and torrefaction [119].

4.1.5. Catalyst Regeneration

Catalytic pyrolysis of biomass enhances the quality of bio-oil, but still causes rapid coking and deactivation of catalysts [152]. There are several deactivation mechanisms including coking, sintering and catalyst poisoning. However, the most common cause of deactivation is the accumulation of coke on the surface and micropores of the catalyst [16, 153]. This is attributed to the breakdown of the oxygenates produced during the pyrolysis of biomass and the phenolic oxygenates re-polymerization [154]. The accumulated coke covers the surface area of the spent catalyst, resulting in the diminution of surface area. The surface area is then restored in the regenerated catalyst due to the combustion of deposited coke. [155] reported that the surface area for the spent catalyst decreased by 24% compared to the value for the fresh catalyst. After regeneration, the catalyst regained 94% of the surface area compared to the fresh catalyst. Thus, the regeneration procedure could be effective in catalyst re-activation. Although the heating value of the produced bio-oil decreased upon increasing the regeneration cycle, it is still higher than the produced bio-oil in non-catalytic experiments even after 6 regeneration cycles.

In the context of industrial implementation, the process of catalyst regeneration offers advantages in terms of managing catalyst expenses and curtailing the production of chemical waste [156]. In comparison to the cost of acquiring a new catalyst, the expense associated with regenerating the catalyst is deemed to be lower. Through catalyst regeneration, the utilization of fresh raw materials is minimized, thereby reducing the requirement for disposal [157]. These factors contribute to the economic and environmental viability of catalyst regeneration in industrial CFP.

The main regeneration techniques for coked catalysts include coke oxidation, hydrogenation and gasification [158,159]. While novel regeneration techniques include plasma applications [160,161]. However, to the best of our knowledge literature discussing the regeneration of costly catalysts used in the CFP process is still limited and further investigation is highly needed to develop cost-effective regeneration

techniques for CFP process to improve the economic and environmental aspects of the process.

4.2. Technology for pyrolyzing biomass to produce high compounds and liquid fuel

Catalytic biomass pyrolysis employs various technologies to obtain high-value green chemicals and liquid fuels. The first approach is direct biomass catalytic pyrolysis, where a catalyst is applied during pyrolysis to enhance the selectivity of bio-oil components, resulting in high-quality bio-oil [98]. The second approach involves non-catalytic biomass fast pyrolysis to produce bio-oil, followed by a catalytic upgrading process for the crude bio-oil to obtain tailored high-quality products. Bio-oil yield depends on the biomass feedstock and operating conditions, reaching up to 70–80% at the optimum conditions by weight and containing 50–90% of the biomass energy (B. [105]). However, the produced bio-oil has low quality and less than half the calorific value of the corresponding petroleum fuels due to its oxygenated compound composition [162,163] that can be further upgraded to higher-value products. Catalytic upgrading schemes include hydrogenation of oxygenates to increase H/C ratio [164], esterification to reduce acidity [98], and cracking to produce chemicals such as alkanes, olefins, and aromatics [165]. Another route involves converting platform compounds obtained through catalytic pyrolysis such as furans, phenols, and ketones into higher-value green chemicals and fuels through various reactions in the presence of a catalyst via aldol condensation, selective hydrogenation, ether reaction, and hydroxyalkylation/alkylation reaction in the presence of catalyst [166].

4.2.1. Direct biomass pyrolysis

Direct biomass pyrolysis is a one-step process that allows to produce high-quality chemicals and liquid fuels. By applying a catalyst during biomass pyrolysis, the quality of the produced vapors can be upgraded. This approach controls the different pyrolysis pathways, selectively modifies component ratios, avoids bio-oil condensation, and increases the value of the end products [17,98]. There are two main configurations for direct biomass pyrolysis based on the contact mechanism between catalyst and biomass: in-situ and ex-situ [162] in addition to their combination [167] as illustrated in Fig. 4.

4.2.1.1. In-situ catalytic pyrolysis. In-situ catalytic pyrolysis configuration relies on the direct mixing of used catalyst and the biomass then placing the mixture into the pyrolysis reactor. This enables the use of a single reactor simple in operation [168] with improved pyrolysis heat management for the upgrading process and less operational costs compared to the ex-situ configuration [17]. It has been extensively studied as direct catalytic pyrolysis configuration [169,170,100, 171-173].

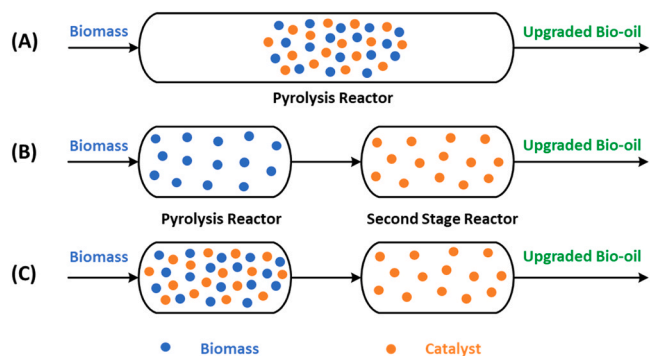


Fig. 4. Schematic diagram of direct catalytic pyrolysis configurations; (A) in-situ, (B) ex-situ, and (C) combined in-situ/ex-situ, inspired from [167] and (X. [18].

The uniform mixing of biomass and catalyst guarantees the early catalyst action during the pyrolysis vapor production phase. This aids in the breakdown of the higher primary products, enhancing the pyrolysis degree and lowering the probability of re-polymerization. Additionally, the immediate active component upgrading lowers the possibility of secondary pyrolysis products reactions. Moreover, [174] and [175] reported that in-situ catalytic pyrolysis reduced the oxygen content of the upgraded bio-oil raising its calorific value.

In-situ catalytic pyrolysis limitations, however, are the increased complexity of biochar formation and catalyst separation which raises the coke content [176]. Moreover, the upgrading capacity of in-situ catalytic pyrolysis is constrained by the short vapor residence times, necessitating greater catalyst/biomass ratios to sustain the quick catalyst and vapor contact compared to ex-situ configuration as reported [177,178]. Furthermore, the pyrolysis and altering processes are conducted at the same operating temperature depriving this configuration of the ex-situ configuration's flexibility and optimization capabilities [17].

4.2.1.2. Ex-situ catalytic pyrolysis. Ex-situ catalytic pyrolysis takes place in two separate reactors, where biomass undergoes pyrolysis in the first reactor producing pyrolysis gas without a catalyst. The pyrolysis gas then contacts the catalyst in the second reactor allowing secondary pyrolysis to occur [179,180].

Ex-situ catalytic pyrolysis allows the pyrolysis and altering processes to be carried out independently at their optimal temperatures. This enables flexible operation and higher control degree for the pyrolysis and upgrading conditions, lower catalyst to biomass ratios, and generally aids in the enhancement of the bio-oil quality (C. [181]; Y. [182]; [183]. Furthermore, ex-situ catalytic pyrolysis produces biochar that is easier to separate using hot vapor filtration which improves the economic viability of the pyrolysis process because of the biochar's high market value [17] and the possibility of using the produced biochar as a source of heat energy for the pyrolysis reactor (Y. [184].

Ex-situ pyrolysis is advantageous over in-situ pyrolysis in enhancing the yield of bio-oil and stimulating the deoxygenation of volatile products at elevated temperatures as reported by [145,185] and [186]. This may be attributed to the different temperature gradients between the biomass and the catalyst in both configurations. The catalyst is pre-heated in the second stage reactor in the ex-situ arrangement while the in-situ arrangement, a significant temperature difference occurs between the catalyst and the biomass (B. [105]). However, the use of two reactors in the ex-situ configuration may lead to economic limitations.

The refined bio-oil composition produced from the in-situ and ex-situ configurations vary significantly. Generally, in-situ catalytic pyrolysis increases the aromatics yield and ex-situ catalytic pyrolysis enhances the alkenes yield [17]. (K. [187] reported that in-situ arrangement enhanced the yield of aromatics and pyrolytic carbon compared to ex-situ arrangement while the ex-situ arrangement showed greater advantages in enhancing the olefins yield. While [186] reported boosted aromatics yield in the ex-situ configuration. The biochar yield under the two distinct catalytic regimes showed no significant variation (B. [105].

4.2.1.3. Combined in-situ and ex-situ catalytic pyrolysis. Combining in-situ and ex-situ catalytic pyrolysis can leverage the benefits of both approaches. Recent research by [167] has applied this combined scheme and achieved higher furans yield compared to individual in-situ and ex-situ systems. Although the specific study focused on furans production, the results may be applicable to direct catalytic biomass pyrolysis. Further research is needed to assess the different configurations and their combinations.

5. Upgrading, applications, and valorisation of the products from fast pyrolysis of biomass

5.1. Fast pyrolysis products

As discussed in the previous sections, the fast pyrolysis of lignocellulosic biomass is a complex process, that depends on various factors such as the biomass type, composition, and the interaction between components such as cellulose, hemicellulose and lignin [188]; [189]; [190], process operation, catalysts, reactor types and production scale (X. [21]; (Z. [191]; [192] or pre-treatment techniques [193];[194]; [195].

The products of this process include bio-char, coke, non-condensable and condensable gases, the latter which are the main source in the liquid product, called pyrolysis oil or bio-oil [196]. Typical product distributions include yields of 60–75 wt% bio-oil, 13–15 wt% gas and 12–15 wt % bio-char, based on the biomass feed weight [188]; [197] [198].

5.1.1. Bio-oil

The objective of the process is to produce large amounts of bio-oil, with relatively smaller quantities of the solid and gas by-products (G. [199]. Pyrolysis oil contains a large number of undesirable compounds

such as aldehydes, acids, ketones, alcohols, phenols, sugars, etc., as well as high amounts (up to 30–40 wt%) of water [200]. Only a small part of these can be detected with the current elemental or chemical composition analysis techniques [201]. Some disadvantages of the pyrolysis oil relate to its moisture content, with detrimental effect on its heating value and flame temperature, low pH values due to organic acid compounds, such as acetic or formic acids, that can cause corrosion during transport and storage, low temperature for polymerization, reactions which can have an adverse influence on its physical properties, the presence of suspended char particles or ash, which can lead to erosion and equipment blockage [28]. Furthermore, the high content of oxygen present in the biomass feedstock is a major obstacle in the production of hydrocarbons (G. [199]. Due to this challenges, application of upgrading techniques is required such that its properties reach the standards required for liquid fuels, i.e., ASTM D7544 or EN16900 [202]. More details on the different approaches for the upgrading of pyrolysis oil to liquid fuels and other high-added value products in the chemical and food and pharma industries will be discussed in Section 4.2.

5.1.2. Biochar

The solid product resulting from the fast pyrolysis of lignocellulosic biomass is a highly carbonaceous material with a content in carbon of

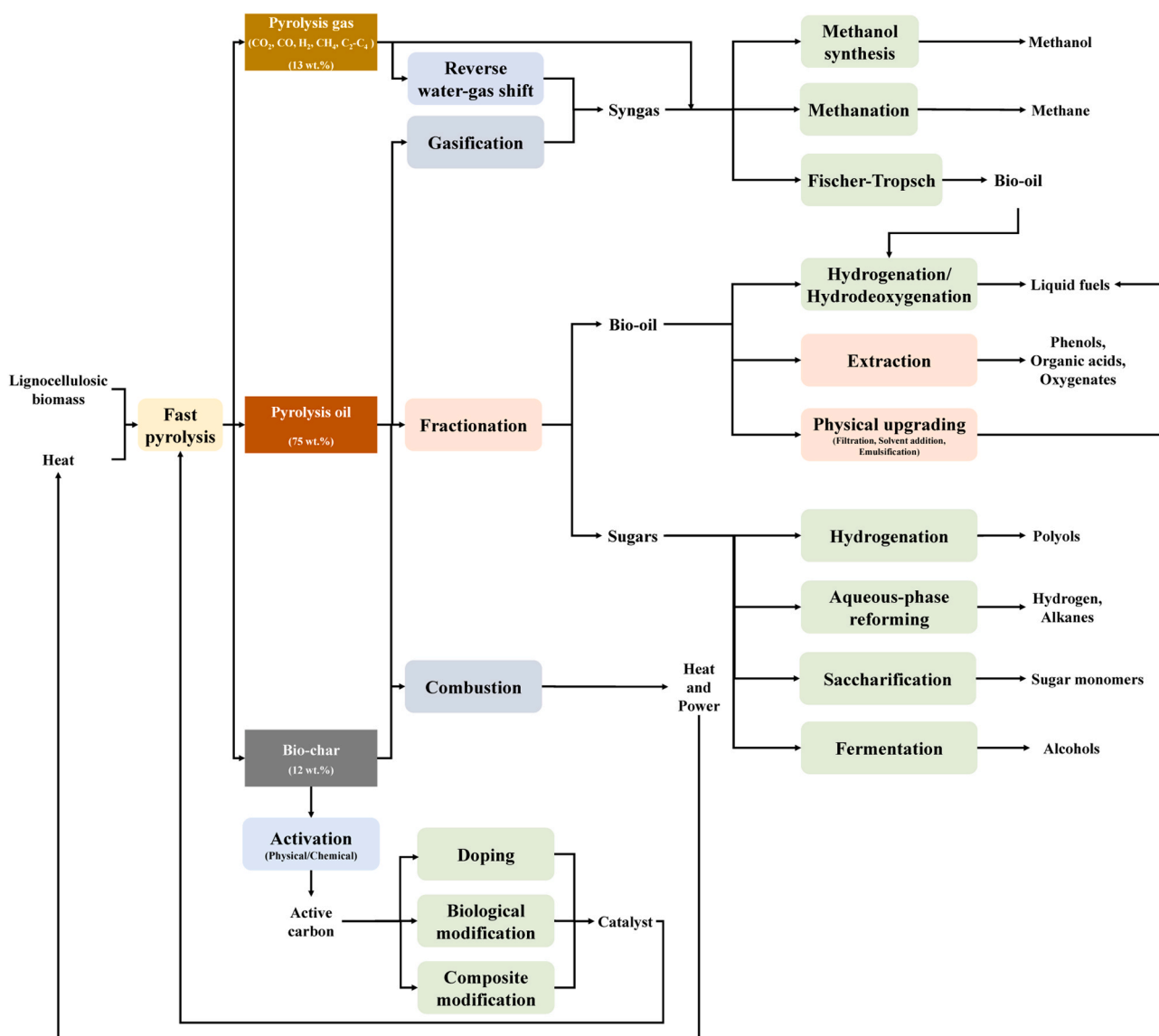


Fig. 5. Pyrolysis-based biorefinery concept.

65–90% [203]. Unlike the biomass feedstock from which it is produced, the bio-char has features such as high surface area or physicochemical stability. Due to its limited porosity and surface functional groups, methods such as porous functionalization, N-doped functionalization, or metal-doped functionalization are often employed to facilitate of the pyrolysis-based bio-char in various use scenarios [204].

Typical applications of the processed pyrolysis biochar include water treatment [205]; [206]; [207], energy storage [208]; [209]; or even in civil engineering [210]. Recently, active carbon-based materials have been employed as catalysts for the fast pyrolysis process [211] or for the efficient and selective conversion of its products into sustainable high-quality bio-oil and platform chemicals [212]; [213]; [214]; [215]; [23]; [216]. These approaches facilitate the development of more integrated approaches for the conversion of lignocellulosic biomass t, by utilizing all its products during the various transformation stages, as illustrated in Fig. 5.

5.1.3. Pyrolytic gases

The pyrolysis gas contains mainly CO₂ and CO, with smaller amounts of H₂, CH₄ and C₂-C₄ fractions, as well as sulfur and nitrogen oxides, and ammonia [217], [218]. As the main objective of the process is the production of the liquid phase, there is a lower focus on the valorisation of the gas fraction, with only a limited number of studies presenting methods to convert it into high-added value products [212]; [219]. The presence of syngas components (CO and H₂) provide potential of utilizing these gases for the production of high-added value chemicals such as bio-oil and advanced biofuels through Fischer-Tropsch synthesis followed by hydrogenation/hydrocracking [220], methanol [221], or fuels such as methane, through the methanation reaction [222]. The presence of CO₂ opens the way to processing towards fuels, via Fischer-Tropsch (X. [223] or syngas through the reverse water-gas shift reaction [224]. The presence of impurities often require further processing, addition of hydrogen from renewable sources or development of reliable catalytic systems that can handle effectively biomass-based syngas types of feedstock [225]; [226]; [227]; [228]. Furthermore, biochar-based catalysts can be developed for the production of hydrogen-rich syngas starting from the pyrolysis of biomass (W. [229], providing further pathways for integration concepts of the process.

5.2. Upgrading of fast pyrolysis Bio-oil

As discussed previously, the liquid product of the fast pyrolysis is the highest and the most desirable fraction of this biomass valorisation pathway. Due to its properties, the pyrolysis oil cannot be used directly as a fuel, but there are plenty of technologies available for its conversion to a wide range of platform chemicals and high-added value products, which are split in physical, catalytic, or non-catalytic upgrading approaches. In the following sub-section, more detail on the current state-of-the-art of these methods will be provided.

5.2.1. Bio-oil physical upgrading

Hot vapour filtration is one of the common approaches for the physical enhancement of the quality of the pyrolysis oil by removing solids (bio-char, ash) and alkali content [230]. Approaches based on membrane separation are often used in its fractionation, especially in specific biorefinery schemes (Paiva [231]. Polar solvents can be added to improve the physico-chemical properties (e.g., heating value, homogeneity, pH, viscosity, water content, etc.) of the bio-oil [232]. Furthermore, advanced approaches based on liquid-liquid (supercritical fluid, water or organic solvent) extraction, as well as molecular distillation, column chromatography, adsorption or crystallization are employed as novel approaches for the separation of the components of the pyrolysis oil [233].

5.2.2. Bio-oil Catalytic upgrading

Although extremely efficient in separating the bio-oil components,

physical upgrading methods do not always maximise the feedstock in terms of the outcomes of the processing. To ensure the production of high quality and high-added value products, advanced catalytic systems are often used for the conversion of the bio-oil into platform chemicals, such as anhydrosugars, furans, phenols, polyols and many others [234]; [235]; [236]. Another significant group of approaches for bio-oil upgrading includes catalytic processes for the production of green liquid fuels via hydrogenation/hydrodeoxygenation processes [237]. This process leads to the breakage and reorganisation of the hydrocarbon chain, the addition of hydrogen to alkenes and aromatics, and the production of naphthenes and alkanes [238]. Green diesel [239] and other sustainable fuels [240]; [241] are some of the upgrading products of significant interest for the decarbonisation of many industrial sectors [242].

5.2.3. Additional technologies for bio-oil chemical upgrading and valorisation

Bioconversion approaches are alternative routes for the valorisation of the pyrolysis oil that are garnering interest in the recent years, ranging from production of biomethane [243] to bioethanol [244]. The main issue in this case related to the presence of inhibitors for the microbial growth, such as phenols, ketones, furans, which must be removed during the pre-processing, such as fractionation or solvent extraction [245].

5.3. Outlook

From the previous sections, it is clear that the effective and selective fast pyrolysis of biomass towards advanced products is a complex challenge, not only in terms of the pyrolysis process alone, where care needs to be taken on the pre-treatment of the biomass, the way the process is operated, but also regarding the extremely diverse set of methods that can be utilized for the valorification and upgrading of the pyrolysis products themselves. Most of the studies available in terms of fast pyrolysis are focused on one type of biomass waste that is being treated, but co-pyrolysis investigations, where biomass is mixed with other types of waste are making their way slowly, to enable some flexibility in the operation [246]. This brings in further challenges in terms of determining the product analysis, process mechanism and kinetics, as well as the design of optimal strategies for the process operation and control [247].

On the upgrading and valorisation side, significant challenges are on the design of efficient and selective catalytic systems that are capable to handle the variety of bio-oil and pyrolysis gas sources coming from the multitude of waste feedstocks available [227]. Furthermore, deciding the best structures for the conversion of the biomass materials into high-added value products is becoming a combinatorial superstructure-type of problem, due to the diverse types of methods that can be included. Recent studies recommend more and more the development of pyrolysis-based bio-refinery processes, where these approaches are combined in an optimum way, considering sustainable and circular approaches [248] [249]; [200]. An example of such a system is illustrated in Fig. 5, where catalysts are produced from bio-char and utilized during the pyrolysis and upgrading processes, and energy input to the system is obtained from various waste streams.

The development of such a system is a multi-scale challenge, which requires development of new modelling approaches for the prediction of the various elements (e.g., kinetics, product distribution, system design) and for capturing all the constituents of the pyrolysis – upgrading system and their interactions at the appropriate scales.

6. Modeling and simulation of biomass catalytic fast pyrolysis

Biomass catalytic fast pyrolysis is a complex process in which biomass is rapidly heated in the presence of a catalyst to create bio-oil, gas, and char. Numerous approaches, including process modelling,

kinetic modelling, and computational fluid dynamics (CFD), may be used to study and simulate this process. The formulation of a mathematical representation of the complete pyrolysis process, including chemical processes, heat and mass transfer, is known as process modelling (Y. [12]). Usually, the goal is to forecast the general behavior of the process and to improve circumstances for optimum effectiveness.

The process of kinetic modelling entails creating an intricate model of the chemical reactions that take place during the pyrolysis process. Based on the kind of biomass and catalyst employed as well as the operating circumstances, the reaction rates as well as the product distribution and composition are defined. The internal gas flow and heat transfer are generally simulated through the use of CFD modelling. When used to improve reactor design and operating conditions, CFD can provide information about the flow patterns, temperature and residence time distributions inside the reactor. The critical interactions that take place throughout the pyrolysis process may be better understood by combining process modelling, kinetics modelling, and CFD. Additionally, CFD is able to provide procedures that are more effective and efficient for turning biomass into useful goods like biofuels [250].

6.1. Recent modeling of biomass fast pyrolysis using computational fluid dynamics

Recent CFD modelling of biomass fast pyrolysis has concentrated on the representation of the phenomena that take place during the pyrolysis process thorough simulations of the intricate flow patterns and heat transfer.

An Eulerian-Lagrangian framework is one method for conducting CFD modelling, in which the solid phase (i.e., the biomass particles) is modelled using the Lagrangian method while the gas phase is modelled using the Eulerian method [251]. This enables a thorough modelling of the interactions between the gas and solid flows that take place inside the reactor.

The use of a two-fluid model is another strategy, in which the solid and gas phases are considered as independent continua, while the interactions between them are modelled using exchange terms that describe the momentum, heat, and mass transfer between the phases.

The complicated fluid dynamics and heat transfer mechanisms that take place during the pyrolysis process have been better understood due to the use of CFD modelling in studies on biomass fast pyrolysis. This has made it possible to create pyrolysis technologies that are more effective and efficient in turning biomass into biofuels and other useful products.

A number of interesting findings have come from the modelling of biomass fast pyrolysis using CFD. Generally, these include the effects of the reactor design, the particle size and the prediction of the temperature and gas composition. CFD simulations have demonstrated that reactor design significantly influences the product yield and quality in biomass fast pyrolysis. For instance, a study by [116] compared a fluidized bed reactor with a straight cylindrical form with a reactor with a conical shape. The results showed that in the first case higher bio-oil production and lower char yield are achieved.

CFD simulations have also demonstrated that the pyrolysis process is significantly influenced by the size of the biomass particles. According to the work of (J. [252]), smaller biomass particles produced more bio-oil and heated surfaces more quickly than bigger ones. Catalysts play a role in the pyrolysis process, and their effects have been studied using CFD models. Adding a ZSM-5 catalyst to the pyrolysis process, for instance, increased the output of bio-oil while decreasing the yield of char, according to the work of [253]; To maximise process efficiency, the process conditions may be improved using these forecasts. For instance, [254] showed that increasing the fluidization velocity resulted in better bio-oil output and lower char yield based on CFD simulations to forecast the temperature and gas composition within a fluidized bed reactor during the pyrolysis of corn stover. Table 6 illustrates the parameters used in the CFD simulations.

Table 6

Parameters used in the simulations of internally circulating fluidized bed (ICFB) [255];[256]; [257].

Parameter	Value
Height of ICFB, mm	1500
Inner diameter of ICFB, mm	290
Height of the draft tube, mm	260, 280, 300, 320
Position of the orifices, mm	10, 15, 20, 25
Inner diameter of the draft tube, mm	75, 100, 125, 150
Area of the draft tube orifices, m ²	0.00753, 0.0147, 0.0226
Thickness of the draft tube, mm	5
Initial bed height, mm	260, 280, 300, 320
Initial solid packing holdup	0.55
Gas density, kg·m ⁻³	1.2
Gas viscosity, Pa·s	1.8 × 10 ⁻⁵
Particle diameter, μm	450, 600, 900, 1200
Particle density, kg·m ⁻³	1000,1520
Frictional angle, °	28.5
Particle packing limit	0.63
Elastic restitution coefficient	0.95

6.2. Kinetic analysis and modelling

Kinetic analysis and modelling play a very crucial part in understanding the biomass pyrolysis. This involves developing mathematical models that describe the reaction kinetics of the process. The yields and compositions of products may be predicted using these models, and process conditions can be improved for optimal effectiveness.

One technique that is often utilized for the kinetic modelling in biomass pyrolysis is the Distributed Activation Energy Model (DAEM) [258] This model suggests that the pyrolysis process may be described by a series of simultaneous events, each with a different activation energy. The underlying premise of the model is that the frequency factor—a measure of how frequently reactant molecules collide—and reactant concentration are correlated with reaction rate. Fig. 6 illustrates the coupling between DEM and CFD.

An alternative approach to studying reaction kinetics is the Chemical Percolation Model (CPM), in which the pyrolysis process may be properly explained by a series of chemical interactions between the solid biomass and the gas phase [259]. In the model, it is assumed that the solid biomass is composed of a network of pores and channels that let the gas phase move through and interact with the solid material.

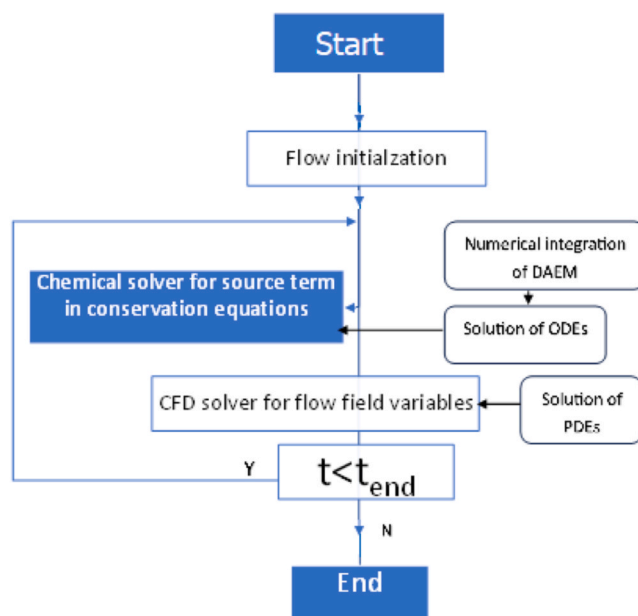


Fig. 6. Flowchart of the coupling between DAEM and CFD.

Kinetic modelling may also be used to anticipate how different process variables, such as temperature, heating rate, and residence time, would affect the pyrolysis process. [260] used kinetics modelling in order to determine how temperature and heating rate might affect product yields and composition during the pyrolysis of several types of biomass.

It was discovered that a novel method called the "Isoconversional Principle" could be utilised to study the kinetics of lignocellulosic biomass pyrolysis [261]. The research, as reported by [261], showed that as the conversion increased, the activation energy for the pyrolysis process decreased, indicating that the reaction became less complicated over time.

(H. [262] explored the Distributed Activation Energy Model (DAEM) to examine the effects of the heating rate on the pyrolysis of maize stover. In addition to a higher yield of bio-oil and a lower yield of char, the study found that increasing the heating rate also caused a decrease in the activation energy and an increase in the pre-exponential factor.

The Chemical Percolation Model (CPM) was used to evaluate the pyrolysis behavior of mixed feedstocks made up of agricultural and forestry wastes (R. [263]. The study found that the CPM model accurately predicted the yields and composition of the mixed feedstocks, and that the addition of forestry residues boosted the output of bio-oil while decreasing the yield of char in accordance with (R. [263].

To explore the pyrolysis of rice straw, [264] coupled experimental observations with kinetic modelling. The study found that the DAEM model could accurately capture the kinetics of the pyrolysis process and that there was high agreement between model predictions and experimental findings.

6.3. Optimization of the process

Process Optimization includes (i) temperature and pressure can significantly impact product distribution and catalyst performance. Fine-tuning these parameters can enhance the selectivity and yield of target products. (ii) Adjusting residence time within the reactor can improve the contact time between the biomass and catalyst, affecting the extent of conversion and product distribution. (iii) Developing methods for in situ catalyst regeneration or recycling can prolong catalyst life, reducing the frequency of catalyst replacement and minimizing downtime. (iv) Pre-treating biomass to remove impurities or modify its structure can enhance the efficiency of pyrolysis and improve the performance of the catalyst. (v) Implementing integrated systems that combine pyrolysis with subsequent upgrading processes (e.g., hydrotreating, hydrodeoxygenation) can increase the overall yield of high-value biofuels or chemicals. Using computational simulations and modeling to predict catalyst behavior, reaction kinetics, and product distributions can guide catalyst design and process optimization [265]. Employing high-throughput screening techniques to rapidly assess various catalyst formulations and identify promising candidates for experimental testing accelerates catalyst development [266].

A statistical technique called response surface methodology (RSM) may be used to identify the best set of process variables for maximizing the yield of desired products. Using statistical analysis, the link between the process variables and the product yield is ascertained by running a number of tests under various process conditions. The RSM approach was investigated by (H. [262] to optimize the process factors for the pyrolysis of bamboo. The research discovered that a temperature of 503 °C, a heating rate of 60 °C/min, and a residence duration of 1.63 s resulted in the highest bio-oil output.

Machine learning techniques based on artificial neural networks (ANNs) may be utilized to predict the complex connections between process factors and product yield (R. [263]. The ideal set of process variables for maximizing the yield of desired products may be predicted using ANNs trained on experimental data. To maximize the yield of bio-oil from the pyrolysis of pine sawdust, an ANN was used to optimize the process variables. According to the study, the ideal process

conditions were 480 °C, an increase in temperature of 80 °C/min, and a residence duration of 0.9 s

In order to identify the ideal combination of process variables, genetic algorithms (GAs), which imitate the process of natural selection, are used as optimization algorithms [267]. This involves the generation of a population of potential solutions using genetic GAs, assessing fitness for each, and then choosing the best ones to move on to the next generation. A temperature of 485 °C, a heating rate of 100 °C/min, and a residence period of 0.6 s were found to be ideal for maximizing bio-oil output.

Finding the best set of process variables to satisfy several goals, such as increasing bio-oil yield while reducing the production of undesirable byproducts, is known as multi-objective optimization. Utilizing optimization algorithms capable of managing many objectives at once is part of this strategy. In order to maximize the output of bio-oil and reduce the production of char, multi-objective optimization was used to determine the ideal process parameters for the pyrolysis of rice straw [268]. This work demonstrated that 540 °C, a heating rate of 40 °C/s, and a residence time of 0.7 s were the ideal process conditions.

Catalytic fast pyrolysis (CFP) of lignocellulosic biomass involves the rapid heating of biomass in the presence of a catalyst to produce valuable bio-oil, which can be further processed into fuels and chemicals. However, there are several challenges associated with this process. During pyrolysis, the catalyst can deactivate due to coke deposition, sintering, or poisoning by impurities present in the biomass feedstock. This reduces its effectiveness over time. Achieving high selectivity towards desired bio-oil components (like aromatic hydrocarbons) and maintaining catalyst stability under harsh operating conditions (high temperature, high pressure) is a challenge. Lignocellulosic biomass feedstock varies in composition based on its source, which affects the reaction kinetics and product distribution [269]. Adapting catalysts to different feedstock compositions is challenging. Advanced catalyst design and process optimization can address these challenges in several ways. Developing catalysts with enhanced resistance to deactivation, improved selectivity, and stability under harsh conditions is crucial. For instance, creating catalysts with better active sites, tailored surface properties, and resistance to coke deposition can mitigate deactivation issues. Employing nanomaterials or nanostructured catalysts can increase the active surface area and enhance catalytic performance. This approach can also improve catalyst stability and reduce deactivation rates. Tailored catalyst composition: Designing catalysts with specific compositions (such as mixed metal oxides or supported metal nanoparticles) optimized for the particular biomass feedstock can improve selectivity and minimize deactivation. Process optimization: Optimizing process parameters like temperature, pressure, residence time, and feedstock pre-treatment methods can improve the efficiency and selectivity of the CFP process. Integrated approaches that involve coupling catalytic pyrolysis with subsequent upgrading steps can also enhance overall product yields. Developing strategies for in situ catalyst regeneration during the pyrolysis process can mitigate catalyst deactivation issues, extending its active lifetime. Utilizing computational modeling and high-throughput screening methods can aid in identifying promising catalyst compositions and structures, accelerating catalyst development. Advanced catalyst design and process optimization can be approached through various strategies to improve the efficiency and effectiveness of catalytic fast pyrolysis (CFP) of lignocellulosic biomass. Some specific methods to address these challenges are (i) Creating catalysts with tailored active sites optimized for the desired reactions during pyrolysis can enhance the selectivity and yield of desired products like aromatics or olefins. (ii) Utilizing nanomaterials or nanostructured catalysts increases surface area and exposes more active sites, improving catalytic activity and stability. (iii) Developing catalysts with mixed metal oxides or supported metal nanoparticles can enhance catalytic performance by synergistic effects between different components. (iv) Modifying catalyst acidity or basicity can influence product selectivity, especially in controlling undesired side reactions and enhancing

the formation of desired compounds [270].

7. Technico-economy analysis and Life cycle assessment of biomass fast pyrolysis

Life Cycle Assessment (LCA) is an evaluation approach used to study the impact of a product or service on the environment. It is a process for assessing the pressure on natural resources and energy consumption. The LCA process involves four main steps (Fig. 7). The first is the definition of the objective of the analysis; this step consists of defining the limits of the system under analysis (e.g., manufacturing or production process stages, components of a value chain, etc.) as well as the functional unit. The second step of the LCA is the life cycle inventory. In this step, an exhaustive inventory of the inputs and outputs of the system delimited in the first step is carried out. The life cycle impact assessment is the third step in the LCA process and is carried out by converting the result of the second step into impact categories. Finally, an interpretation is made to ensure the assumptions used through a sensitivity analysis [271]. LCA provides a comprehensive perspective and is effective for global impact assessment. It determines the potential environmental impacts during the life cycle of a product or service for a defined functional unit, which is a quantified function provided by a product system [272]. In addition to greenhouse gas emissions, LCA examines the potential for acidification, eutrophication, and other indicators related to human health, particularly the potential for toxicity [273].

7.1. Functional unit

The functional unit is a quantification of the product or service that will be the subject of the life cycle assessment. It is a quantification around which the impact analysis will be carried out [274]; [275]. The functional unit can take several forms. In a review of 42 papers on the life cycle assessment of fast pyrolysis of biomass, 52% were based on the feedstock as the functional unit (Fig. 8). Regarding the unit, the tendency is often to use one ton of feedstock, but one can always find one kilogram (J. [276]; [277]) or one hundred kilograms [278]. It should be noted that the area is also used in the functional unit logic [279].

Sometimes a non-quantitative functional unit is utilized; [280] based on an average village household utilizing available cocoa waste. Often if the feedstock does not constitute the functional unit, the final product does. In this sense, we find the final product as energy input (Jens F [281]; [282] as the final product can be found in quantity [283,284]. Another approach to choosing the functional unit is to have two types; [285] have worked on the life cycle assessment of alternative pyrolysis-based transport fuels. They chose as functional unit 1 MJ of energy stored in the fuel produced and 1 Km of distance driven by a light-duty passenger vehicle.

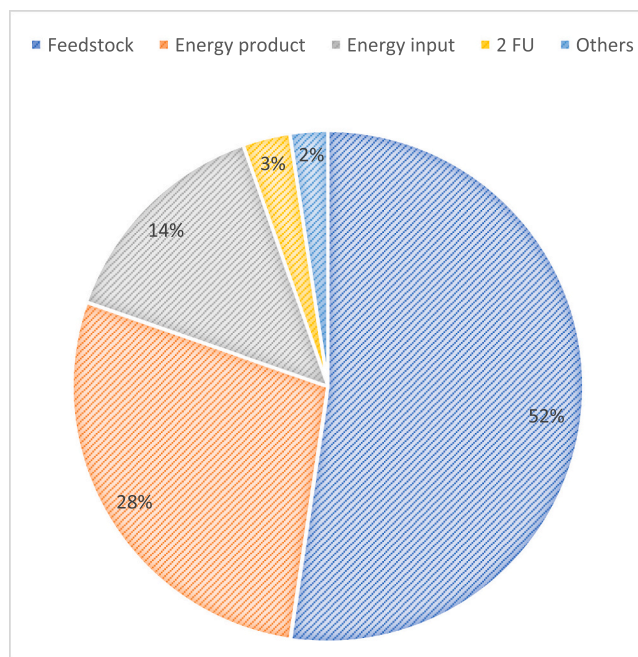


Fig. 8. Distribution of functional unit types used in the LCA of fast pyrolysis products.

7.2. Associated system boundaries

The scientific scope and boundary definition are important to ensure the accuracy of the LCA results. Defining the boundary in LCA is difficult and there are no commonly accepted scientific methods yet. The first block to consider in the limitation of the system is the acquisition of the raw material. In our exercise of analysis of the articles, we found that 37% of the works include the production of the raw material as a part of the system: agricultural production in the case where the material to be pyrolyzed is agricultural waste [286]; [287] or Biomass production for pellet Synthesis [288].

The level of detail in the system limitation differs from one work to another depending on the objectives and the means. One can simply encounter the acquisition of the material, the pyrolysis, and the use of the products [289], as well as a system defined with the maximum possible detail: production of the raw material, biomass pre-treatments, pyrolysis, refining and upgrading of the bio-oil, the use of the bio-char with the inclusion of the transport (Hui. [290].

Detailing as much as possible of the system to be considered in a life cycle assessment is always desirable as it comes closer to the reality in

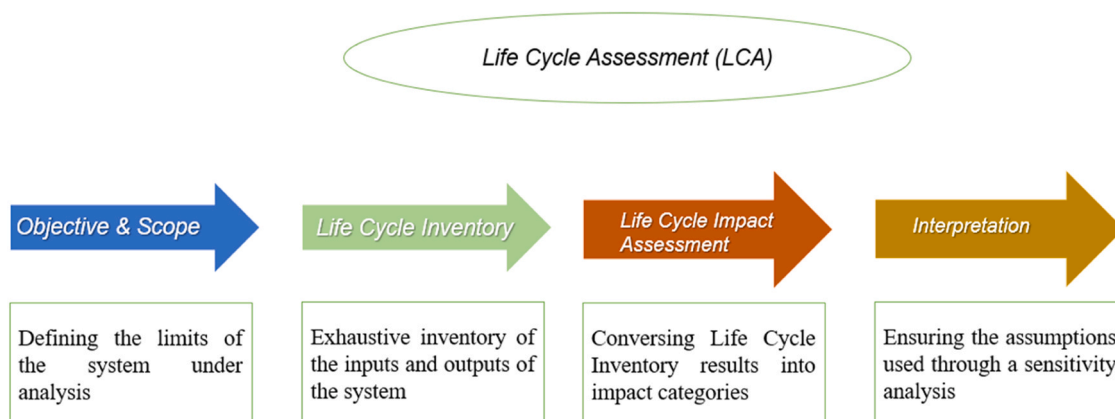


Fig. 7. Life Cycle Assessment main step.

terms of the carbon footprint of the whole process under consideration (Table 7).

7.3. Life cycle inventory

To establish a complete exhaustive inventory of all the flows of the limited system, the data collection is carried out by direct surveys where it is necessary to have the maximum detail and reliability possible on data such as the quantities of energy resources, water, or the number of agricultural inputs (case of agricultural LCA). In case the information is not available, it is recommended to use dedicated databases (e.g., Ecoinvent) [291]. This step is controlled by the determination of the boundary system as it consists of establishing a complete inventory of each process step: quantities of feedstock used, distances travelled, the quantity of energy input, etc.

In comparison, the auxiliary information is characterized as information that is not straightforwardly collected, measured, or assessed, but may be sourced from a third-party life-cycle inventory database. Furthermore, this may incorporate information from distributions and reports. In any case, auxiliary information tends to be less particular and profoundly amassed. A few of the major LCI databases incorporate the Ecoinvent database, United States LCI, World Nourishment LCA, and Plastics Europe databases, respectively [292]. Several studies are based on the use of databases and simulations using software such as "Aspen Plus" to establish the life cycle analysis inventory. Our analysis shows that 47% of articles have followed this approach. The combination of primary information acquisition, via direct collection of information, and secondary information is an approach used; 24% of the articles used this philosophy.

7.4. Life cycle impact assessment

After determining the inventory, the assessment phase comes to estimate the potential environmental impacts arising from the system flows. The impacts are grouped into categories, and it is essential to select the most important ones. Then, a characterization (modeling) and a normalisation of the impacts are carried out to obtain impact indicators. These indicators are grouped and ranked to establish the final assessment. [293].

Regarding potential environmental impacts, pyrolysis produces bio-oil as a sustainable energy product and sequesters biogenic carbon in the form of biochar. For example, authors have found in their work on the production of bio-oils and biochar from various corn stover pyrolysis technologies that fast pyrolysis can achieve a net carbon emission of $-0.33 \text{ kg CO}_2 \cdot \text{kg}^{-1}$ of carbon in the corn stover [294]. Also, Bio-oil obtained through rapid pyrolysis offers better environmental performance than conventional oils. In a comparative life cycle analysis of bio-oil from the fast pyrolysis of whole southern pine trees and residual fuel oil (RFO), authors found that bio-oil outperformed RFO in four of

Table 7

The components to be considered with their different sub-components in the limitation of the system boundaries.

Feedstock	Plant biomass production: technical itinerary (fertilisation, irrigation, agricultural machinery, etc.) Collection and transport of the biomass to be pyrolyzed to the pilot site
Biomass pre-treatment	Physical pre-treatment Chemical pre-treatment Biological pre-treatment
Pyrolysis pathways	Energy input (electricity & heat)
Biochar utilization	Transportation Biochar effects on soil sequestration
Bio-oil	Bio-oil upgrading Bio-oil refinery Transportation and utilization
Waste management	Waste management

the seven impact categories: net global warming, respiratory impacts, ozone depletion and total energy use. The negative emission capacity of pyrolysis resulted in a bio-oil with a net emission of $0.03 \text{ kg CO}_2 \text{ eq. MJ}^{-1}$, which is better than that of RFO ($0.1 \text{ kg CO}_2 \text{ eq. MJ}^{-1}$) [273].

8. Summary and future outlook

The CFP of lignocellulosic biomass is a complex process, that depends on various factors such as the biomass type, composition, and the interaction between components such as cellulose, hemicellulose and lignin, process operation, catalysts, reactor types and production scale or pre-treatment techniques. The substrate pretreatment could improve the quality and yields of the pyrolysis process. Each pretreatment method has its strengths and limitations. However, biological pretreatment is the most economical and eco-friendly method with low energy input. Combining techniques could increase the efficiency of the pretreatment and enhance the quality of the products. The low biomass conductivity reduces the heat transfer rate, generating a temperature gradient along the particle and thus causing inhomogeneity during pyrolysis. This heat transfer is determined by the particle size.

Bio-oil from fast pyrolysis offers several merits over raw biomass, such as higher energy density and easier storage and transportation. It can be used as fuel for boilers and engines and can be upgraded to premium-grade transportation fuels. However, crude bio-oil faces limitations due to its complex composition, high oxygen and water content, modest calorific value, poor stability, elevated viscosity, corrosiveness, and insolubility in conventional fuels. To address these challenges, catalysts are introduced in fast pyrolysis to lower activation energy, alter product composition, and produce higher-grade fuels and valuable chemicals. CFP of biomass enhances vapor quality by using catalysts with strong deoxygenation activity, enabling control over pyrolysis pathways and enhancing product value. The selection of catalyst in CFP is of paramount importance as it influences both the product distribution and the overall process efficiency. Zeolite catalysts have been reported for their superior performance in bio-oil upgrading. This may be attributed to their capability of breaking C-O bonds, producing bio-oil with excellent stability. Zeolites have demonstrated significant catalytic effects in boosting dehydration and cracking reactions, leading to the production of final liquid products with high H/C ratios and low C/O ratios.

The in-situ catalytic pyrolysis simplifies the operation by using a single reactor and improves pyrolysis heat management, resulting in lower operational costs compared to the ex-situ configuration. However, it has limitations such as increased complexity in biochar formation and catalyst separation, which can increase the coke content. It also requires higher catalyst-to-biomass ratios due to shorter vapor residence times. The Ex-situ catalytic pyrolysis allows for independent operation at optimal temperatures, providing flexibility and better control over pyrolysis and upgrading conditions and enables operation at lower catalyst to biomass ratios, and generally improving the bio-oil quality. Combining in-situ and ex-situ catalytic pyrolysis can leverage the benefits of both approaches.

Due to its properties, the pyrolysis oil cannot be used directly as a fuel, but there are plenty of technologies available for its conversion to a wide range of platform chemicals and high-added value products, which are split in physical, catalytic, or non-catalytic upgrading approaches. Hot vapour filtration is one of the common approaches for the physical enhancement of the quality of the pyrolysis oil by removing solids (biochar, ash) and alkali content. Moreover, advanced approaches based on liquid-liquid extraction, as well as molecular distillation, column chromatography, adsorption or crystallization are employed as novel approaches for the separation of the components of the pyrolysis oil. To ensure the production of high quality and high-added value products, advanced catalytic systems are often used for the conversion of the bio-oil into platform chemicals, such as anhydro-sugars, furans, phenols, polyols and many others. Another significant group of approaches for

bio-oil upgrading includes catalytic processes for the production of green liquid fuels via hydrogenation/hydrodeoxygenation processes. Furthermore, deciding the best structures for the conversion of the biomass materials into high-added value products is becoming a combinatorial superstructure-type of problem, due to the diverse types of methods that can be included. Recent studies recommend more and more the development of pyrolysis-based bio-refinery processes, where these approaches are combined in an optimum way, considering sustainable and circular approaches.

Numerous approaches, including process modelling, kinetic modelling, and computational fluid dynamics (CFD), may be used to study and simulate the fast pyrolysis process. The complicated fluid dynamics and heat transfer mechanisms that take place during the pyrolysis process have been better understood due to the use of CFD modelling in studies on biomass fast pyrolysis. This has made it possible to create pyrolysis technologies that are more effective and efficient in turning biomass into biofuels and other useful products.

The yields and compositions of products may be predicted using these models, and process conditions can be improved for optimal effectiveness. A statistical technique called response surface methodology (RSM) may be used to identify the best set of process variables for maximizing the yield of desired products.

Life Cycle Assessment (LCA) is a process for assessing the pressure on natural resources and energy consumption. The functional unit is a quantification of the product or service that will be the subject of the life cycle assessment. One can simply encounter the acquisition of the material, the pyrolysis, and the use of the products, as well as a system defined with the maximum possible detail: production of the raw material, biomass pre-treatments, pyrolysis, refining and upgrading of the bio-oil, the use of the bio-char with the inclusion of the transport.

Data such as the amounts and resources of energy and water, or the number of agricultural inputs, are necessary to establish a complete inventory of all the flows. This step consists of establishing a complete inventory of each process step: quantities of feedstock used, distances travelled, the quantity of energy input, etc. In order to estimate the potential environmental impact of system flows during the assessment phase, these impacts are grouped into categories, and the most significant are selected. Then, a characterization and normalisation of the impacts are carried out to obtain impact indicators.

CRedit authorship contribution statement

Arellano-Garcia Harvey: Investigation. **Majozi Thokozani:** Writing – review & editing, Writing – original draft, Methodology. **Kalibe Fanezoune Casimir:** Writing – original draft. **Dorneau Bogdan:** Writing – original draft. **Hirt Ayoub:** Investigation. **Peixinho Jorge:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Elhenawy Yasser:** Writing – original draft, Investigation. **Bayssi Oussama:** Writing – original draft, Investigation. **Khashaba H. Nourhan:** Writing – original draft, Investigation. **Ashour H. Fatma:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Dhahak Asma:** Writing – original draft, Investigation. **Gadalla Mamdouh:** Writing – original draft, Investigation. **EL BARI HASSAN:** Writing – original draft, Supervision, Conceptualization.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

Acknowledgements

This publication is part of the funding Project titled “Sustainable biomass conversion into bioenergy through pyrolysis” (PyroBioFuel) - LEAP-RE (Europe-Africa Renewable Energy).

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