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Advances in the Pyrolysis Process and the Generation of Bioenergy

Vittor Rodrigues Santos Alves

Abstract

The reduction of environmental impacts caused by emissions of greenhouse gases has become an internationalized goal. In this context the development of technologies capable of producing energy from clean or renewable sources has gained broad prominence, among them the fast pyrolysis is a type of thermo-chemical process capable of converting biomass and agroindustrial waste into a liquid product called bio-oil that has a wide range of applications in the bioenergy scenario. For this type of technology to be consolidated as an alternative source of renewable energy, economic, political and environmental incentives are necessary, as well as research development to improve the conversion processes, such as reactor types, logistics in obtaining and pre-treating potential biomass, improvement and conversion routes for bio-oil obtained in renewable biofuels or chemicals with higher added value. This chapter covers the fundamentals of thermal conversion of biomass into bio-oil and the most studied processes to convert bio-oil into a product with better properties, such as deoxygenation and energy densification.

Keywords: biomass, fast pyrolysis, bio-oil, bioenergy, environmental

1. Introduction

The demand for clean energy sources and the accompanying reduction in greenhouse gas emissions have gained increasing emphasis on environmental policy agendas around the world. One of the current portraits of these discussions was in 2021, when the Climate Summit was promoted, in which the political leaders of each nation set social, technological and political goals for the coming years in order to mimic the agents causing natural and climate changes. Among the most discussed measures, mainly by countries in the northern hemisphere, is the attack on the consumption of fossil fuels such as diesel, gasoline and mineral coal.

Biomass, urban and agricultural waste have great potential to be converted into products with added energy value. Although there are several routes for converting biomass into fuels (biological, thermal and physical-chemical), most of them, as biological, are highly selective, offering little variability of the final product. In thermal processing there is the possibility of producing a range of complex products such as chemicals, advanced biofuels and integrated electrical energy. Although the production of charcoal, through the carbonization process, is an old and well-known process, it was during the oil crisis in the 1970s that research was directed towards obtaining renewable fuels from lignocellulosic materials, where fast

pyrolysis stood out. In this process, the carbonaceous material is subjected to moderate temperatures (in the range of 500°C) at high heating rates and in the absence of oxygen, thus, the release of organic vapors and gases occurs at low residence times in the reactor, in addition to the formation of a char fraction [1, 2].

The biomass pyrolysis process in general can be understood as a thermal fractionation of the lignocellulosic complex into three predominant fractions: char, gases and liquids (condensable vapors). The greater or lesser yield of each of these fractions is adjusted according to the input parameters and adjustment of process variables such as temperature, reactor type, biomass composition, biomass physical properties and so on. In the fast pyrolysis process, all these parameters are conditioned in such a way as to provide low residence times in the vapor phase reactor. When being condensed, these vapors form a liquid phase composed of a variety of organic compounds called bio-oil.

Bio-oil has a wide range of applications. Due to its varied composition (alcohols, organic acids, sugars, phenolic aromatics, etc.) it can be used to obtain chemical species through refining and extraction, raw material for obtaining advanced bio-fuels, in addition to liquid biofuels for processes of direct burning of biomass is not possible. In addition, as it is a liquid product, its handling and transportation are facilitated in relation to solid biomass. Finally, bio-oil can have its quality improved by modifications directly in the pyrolysis process such as downstream upgrading processes.

Thus, this work presents an overview of the fast pyrolysis of biomass for bio-oil production, the properties of bio-oil and its general application, showing the main processes (reactors) developed and new trends for the improvement of the pyrolysis process aiming to obtain more efficient bioenergy sources.

2. Fast pyrolysis: general aspects

Thermochemical processes have by their nature the conversion of raw materials into products that have greater added energy value. These processes occur having heat as the agent of transformation, either by release or demand of the process. **Figure 1** shows a summary of the main endothermic processes [3–9].

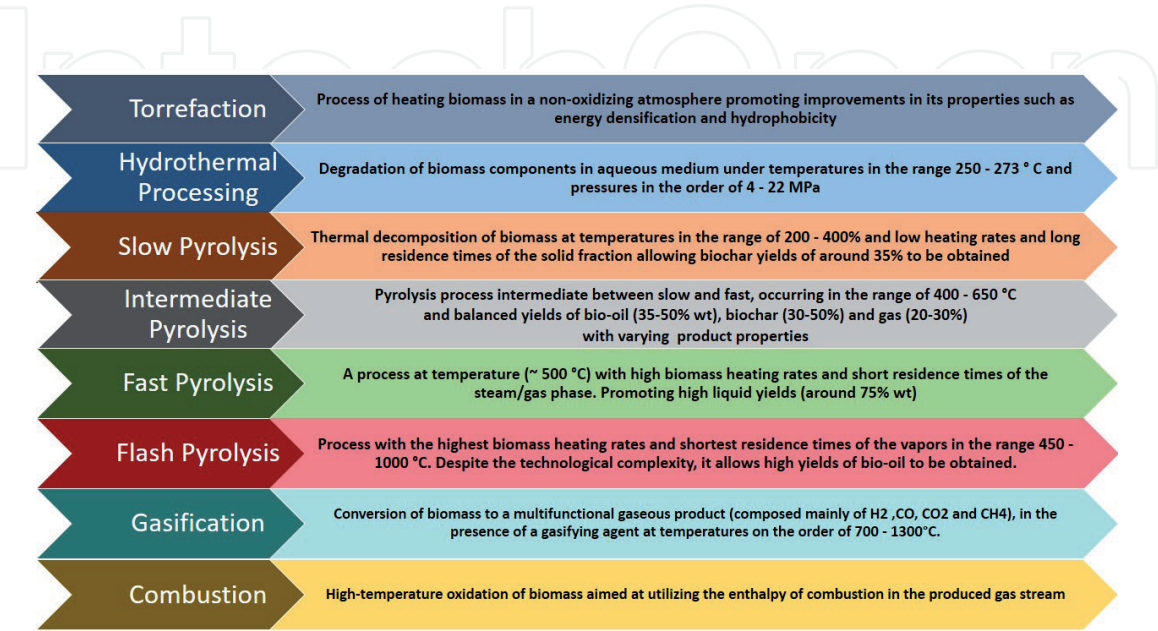


Figure 1.
Diagram showing the main characteristics of the most conventional thermochemical processes.

Property		Heavy oil fuel	Biomass feedstock			
			Mahogany waste wood	Oak/ maple	Birch	Pine wood
Elemental analysis (dry basis), % wt	C	83–86	50.2	—	44.0	45.7
	H	11–14	6.6	—	6.9	7.0
	N	<1	<0.4	0.2	<0.1	<0.1
	O	<0.1	42.6	—	49.0	47.0
	S	<4	<0.06	<0.01	0.00	0.02
	Ash	0.03	0.15	0.01	0.004	0.03
Moisture, % wt		0.1	21.4	22.0	18.9	17.0
pH		—	5.64	2.5	2.5	2.4
Density, kg/L		0.94	0.95	1.18	1.25	1.24
HHV, MJ/kg		44	29.52	17.0	16.5 ^a	17.2 ^a
Viscosity (40°C), cSt		5.5–24	4.6	50 ^b	28 ^b	28 ^b
Solids (char), % wt		—	—	0.045	0.06	0.03
Distillation residue, % wt		<1	—	not distillable	—	—
Flash point, °C			68.0	55	62	95
Pour point, °C		–18	13.5	–25	–24	–19
Ref.		[10–13]	[14]	[15]	[16, 17]	[16, 17]

^aas LHV.
^bat 50°C.

Table 1.
Main properties of bio-oil from different feedstock compared to heavy fuel oil.

During the fast pyrolysis process, the lignocellulosic structure of the biomass is degraded and converted mostly under specific reaction conditions, generating a main product called bio-oil. **Table 1** shows an overview summary of the main physical–chemical properties of a typical bio-oil compared to a heavy fuel oil.

In order to quantitatively obtain organic products in the form of bio-oil in an expressive way, it is necessary to maintain some parameters and variables in an essential way during fast pyrolysis.

- High heating rates of the particle, for this it is necessary that the feed is in reduced particle size and moisture [18, 19].
- Good temperature control, allowing the process to occur in temperature ranges close to 500°C [18, 19].
- Low residence times of the vapor phase (below 2 s) as well as a fast cooling of these [18, 20].

By carefully following these parameters, it is possible to obtain bio-oil yields of up to 75% on a dry basis depending on the technology (reactor type) employed and the nature of the material. Moreover, depending on its composition and the way it is collected, the bio-oil can form two phases, a lighter one with a higher presence of water and a heavier one with a higher concentration of organic fraction.

3. Bio oil properties and its applications

In general, biomass is composed essentially of three organic components: cellulose, hemicellulose and lignin. Besides these there is also an inorganic fraction (ash) and the water associated with the structure of the material in the form of moisture. The composition of these fractions is an important reference in the quality of bio-oil to be obtained. **Table 2** shows a general summary of the lignocellulosic composition of various biomasses.

During the pyrolysis process these three polymers decompose at virtually the same time, however each has different thermal decomposition kinetics [21], which can lead not only to different yields of bio-oil and its sub products (biochar and gas) but also generate a variation in the distribution of organic functions that make up the bio-oil [22].

Due to the different physicochemical properties of cellulose, hemicellulose and lignin, they tend to produce different products. While cellulose tends to contribute to higher bio-oil yields, higher lignin concentration contributes more significantly to biochar formation [20, 23, 24]. The organic composition of bio-oil is extremely variable and presents several classes of organic composts. **Figure 2** shows a deviation map of these organic functions that typically compose the pyrolysis bio-oil in relation to the thermal reactivity of cellulose, hemicellulose and lignin [25].

In addition, the inorganic fraction of biomass (ash) can also influence the characteristics of bio-oil. Some studies show that biomasses with alkali rich ash, such as potassium (K), and phosphorus can exhibit catalytic properties and alter the distribution of organic compounds present in bio-oil [26]. A number of other characteristics of bio-oil can be described to assess its quality, such as appearance, typically characterized by a dark brown or reddish color; odor, which is characteristic of acidic flavors and can even cause airway and visual irritation upon prolonged exposure; and miscibility, which is a complex factor as it is not miscible with petroleum fuels due to the large presence of polar and oxygenated compounds,

Biomass	Composition, % wt				Ref.
	Cellulose	Hemicellulose	Lignin	Other	
Softwood	41	24	28	7	[9, 20]
Oakwood	34.5	18.6	28	—	
Birchwood	35.7	25.1	19.3	—	
Hardwood	39	35	20	7	
Leaves	15–20	80–85	0		
Olive husk	24	23–24	48–49		
Miscanthus	24	44	17		
Sugarcane bagasse	19–24	32–48	23–32	—	
Willow plant	50	19	25	—	
Rice straw	30	25	12	33	
Wheat Straw	40	28	17	15	
Nut shell	25–30	25–35	30–40		
Walnut shell	25–26	22–23	52–53		
Corncob	50.5	31	15		

Table 2.
Lignocellulosic composition of various biomasses.

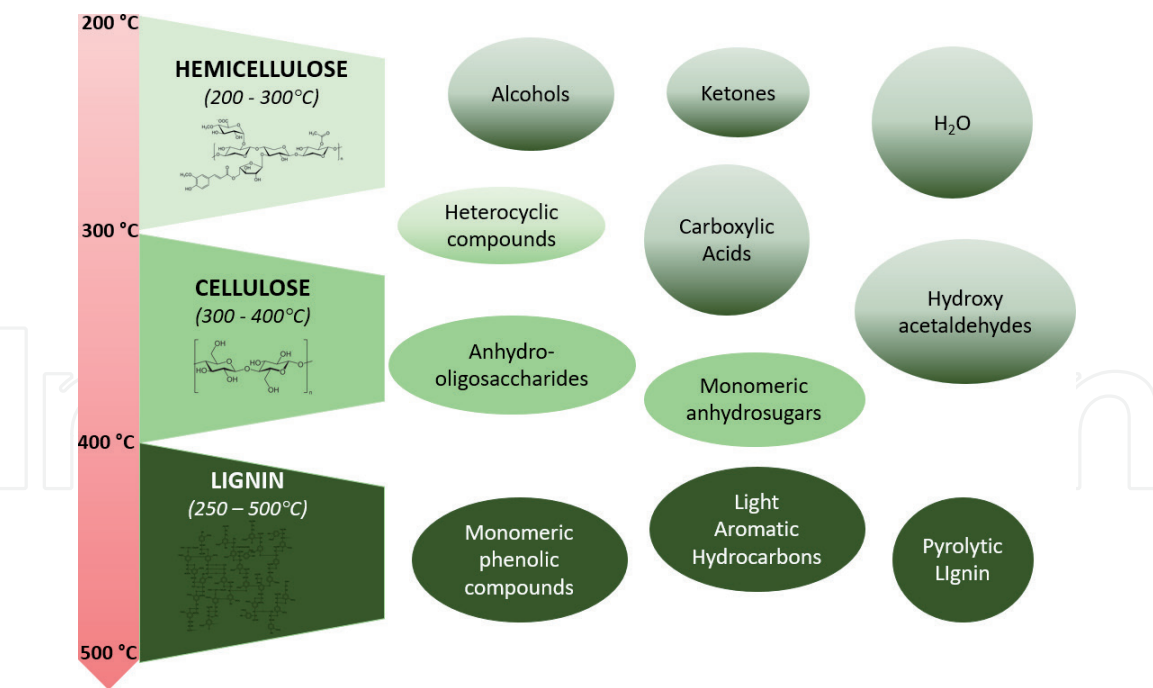


Figure 2.
Thermal decomposition of lignocellulosic compounds and their products (adapted from [25]).

and is not water soluble as excessive addition can lead to the formation of two liquid phases [19, 20].

Due to its varied composition, a number of applications have been attributed to bio-oil. **Figure 3** illustrates some of the main applications.

The pyrolysis bio-oil presents compounds in high concentrations such as phenols, guaiacs, acetic acid among others and with the advancement of separation techniques, such as liquid–liquid extraction, with the addition of solvents (hexane, chloroform etc.) has allowed the recovery of fractions with high concentrations of these compounds that have high added value for the industry, production phenolic resins, organic acids among others [27–30]. In addition, the greatest potential for use of bio-oil is in its use for the production of biofuels, being necessary, firstly, the application of upgrading steps to improve its properties.

Bio-oil can also be used in combustion or co-combustion systems with other fuel oils to obtain heat in industrial processes. However, the applications of bio-oil in these combustion systems are traditional for combustion of heavy or

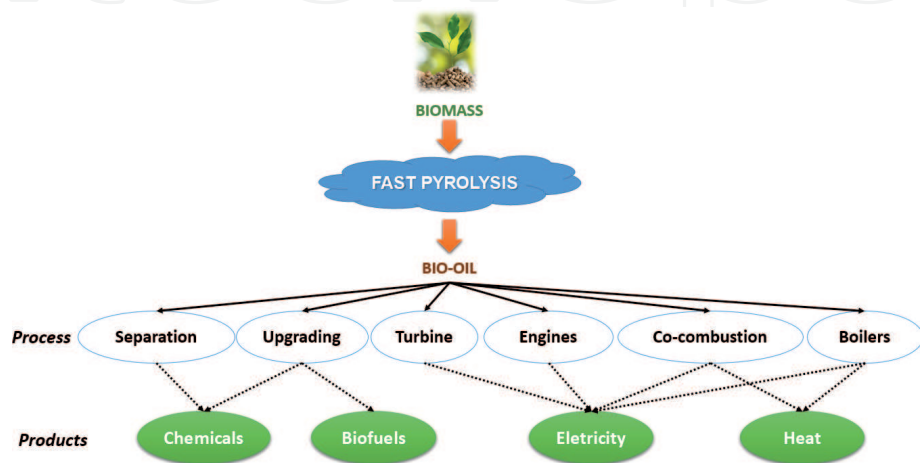


Figure 3.
Bio-oil applications.

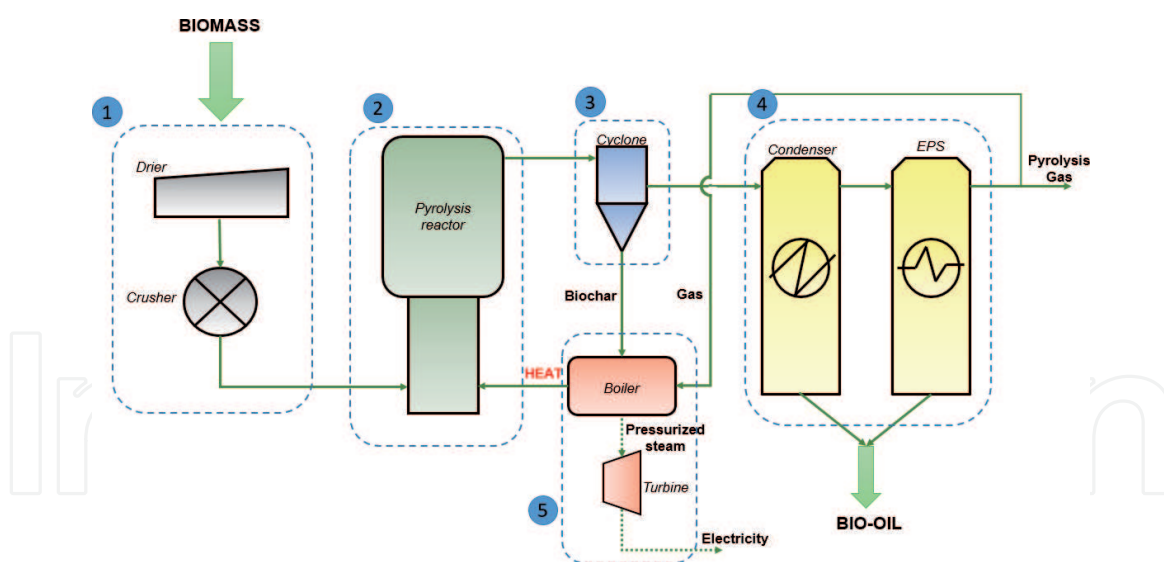


Figure 4.
General system to biomass fast pyrolysis.

mineral oils due to their physical–chemical characteristics completely different and their instability that can impact on essential parameters for a quality combustion of oil as the quality of atomization, ignition, tendency to coke formation, vaporization rate of drops, clogging among others. However, having a good understanding of the properties of the bio-oil used and the ratio some benefits are reported in co-combustion operations such as the reduction of SO₂ and thermal NO_x emissions [27–30].

4. Reactors to fast pyrolysis

The design of a fast pyrolysis process has at its core the reactor where the appropriate heat and mass transfer conditions will be provided for the thermo-chemical processing of the material. In general, a fast pyrolysis process consists of a biomass fitting unit (1) to fit the required particle size and moisture conditions, the pyrolysis reactor (2) where the bio-oil (vapors) and by-products (biochar and non-condensable gases) are formed, cyclone(s) and/or particulate removal systems (3), condensation unit and bio-oil collection (4) and finally a thermal energy conversion and integration system in the system (5) as illustrated in **Figure 4**.

The pyrolysis is an endothermic process, as the goal of fast pyrolysis is to obtain higher yields in liquids, the other by-products (biochar and gas) can be used as fuels in the thermal energy generation unit providing the necessary entapia, to perform the pyrolysis reactions. Fast pyrolysis reactors in general can be separated into those that use a gaseous agent for heat transfer in the reactor and those that do not use gas as a fluid, and most of them are already in commercial scale. A **Table 3** mostra um resumo dos principais reatores utilizados nos processos de pirólise dos principais características e seu status comercialização.

5. Pyrolysis and bio-oil improvement strategies

Bio-oil obtained from lignocellulosic feedstock with fast pyrolysis has many disadvantages in front of fossil fuels such as high water content, presence of small particles of coal and alkaline ash, acidity, low calorific value and thermal stability that make it difficult to application of bio-oil in the power system such as

Reactor type	Main features	Limitations	References
Circulating fluidized bed	Easy scale-up. Efficient heat and mass transfer. Flexibility in system design.	Low solid phase residence time (similar to gases) leading to higher coal yields. Complex hydrodynamics.	[1, 31–39]
Bubbling fluidized bed	Good heat and mass transfer, easy control, operational simplicity. High bio-oil yields.	High pre-treatment accuracy of biomass, requiring low particle sizes	
Rotating cone	It uses centrifugal force to move the particles. Uses little carrier gas. Yields in bio-oil in the range of 60–70%.	A more complex in-grid system is required with cone pyrolysis reactor, riser for transport and recycle of the sand particles, fluidized bed combustion chamber.	
Auger or screw	The process takes place during mechanical conveying. The heat carrier can be the walls or ceramic/sand particles. Suitable for heterogeneous biomass/waste or waste that is difficult to transport and handle.	Longer residence time of the vapors. Lower bio-oil yield compared to fluid bed reactors.	
Ablative	Heat transfer is via reactor part contact, allowing the use of larger diameter parts and without the need for carrier gas.	Limitation in the scale-up mainly concerning the reactor surface.	
Spouted bed	Very high heat and mass transfer coefficients. Short residence times. High liquid yields (up to 70%).	Complex scale-up accompanied by high pressure drop.	

Table 3.
Description of the main fast pyrolysis reactors and their characteristics.

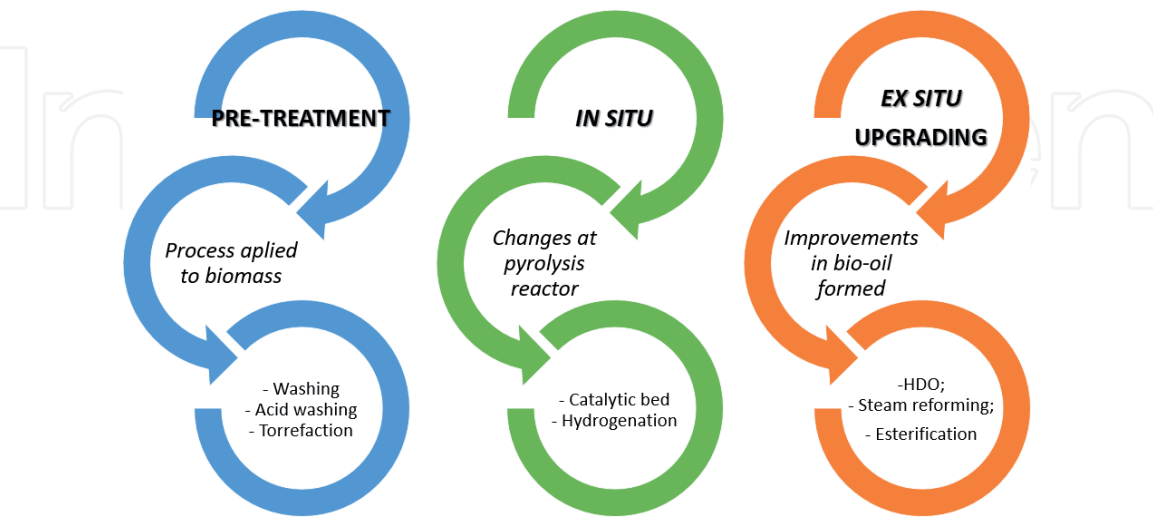


Figure 5.
Different processes and strategies to improve the fast pyrolysis of bio-oil quality.

engines [40]. The currently technological research shows that there are basically three ways to improve the performance of the fast pyrolysis and the quality of the obtained bio-oil. The **Figure 5** shows these deferments strategies.

5.1 Pre-treatment

Several authors have already reported the effect of physical treatments (i.e. treatments that do not alter the chemical composition or chemical structure of biomass) of biomass on pyrolysis processes. The most relevant one reported is the biomass grinding aiming at its particle size reduction, which has a positive impact on all fast pyrolysis reactors, providing an increase in the bio-oil yield [41].

The washing (or leaching) it's a process used to remove or modified inorganic compounds of the biomass or modified the lignocellulosic complex. The H_2O washing it's a simple and low cost process able to remove mainly alkalis (K, Ca), Cl and S [42, 43]. The Acid washing it's a more complete but expensive kind of washing with (organic or inorganic) acid diluted, this process its able to remove near all components (alkalis, halogens, heavy metals etc) found in biomass ashes promoting the complete demineralization [42, 44]. In addition to these effects, the acid treatment of biomass (washing and acid infusion) can lead to the formation of bio-oil rich in sugars [45, 46]. Studies have pointed out [46] showed that there is considerable enrichment in sugars, especially levoglucosan (up to 55% of cellulose) during the acid infusion of corn stover. These results were mainly attributed to the catalysis of the decomposition of the cellulose structure.

Another process considered a pre-treatment of biomass for fast pyrolysis is Dry Torrefaction. This process is like mild pyrolysis; occurring in the range of 200–280°C and in an inert atmosphere, it promotes a thermal pre-degradation of lignocellulosic polymers, generating a biomass with the potential to produce a bio-oil with better quality [47, 48]. In parallel, the Wet Torrefaction (WT) process can also qualitatively improve the biomass properties for the fast pyrolysis process. It occurs in aqueous phase and ambient to moderate pressures, with water at high temperatures it removes alkalis, carbonates and halogens. Research shows that bio-oil produced from biomass pre-treated with WT produced bio-oil with less phenols, ketones, furans and richer in sugar, especially levoglucosan. However, in addition to energy consumption, this process generates a biomass with high water content [46, 49–52].

The process of acid treatment and torrefaction of biomass can be combined to improve the performance of fast pyrolysis both quantitatively (higher bio-oil yield) and qualitatively (bio-oil with better properties) as shown in **Figure 6**. Studies showed that the coupling of acid washed with acetic acid (1% wt) and

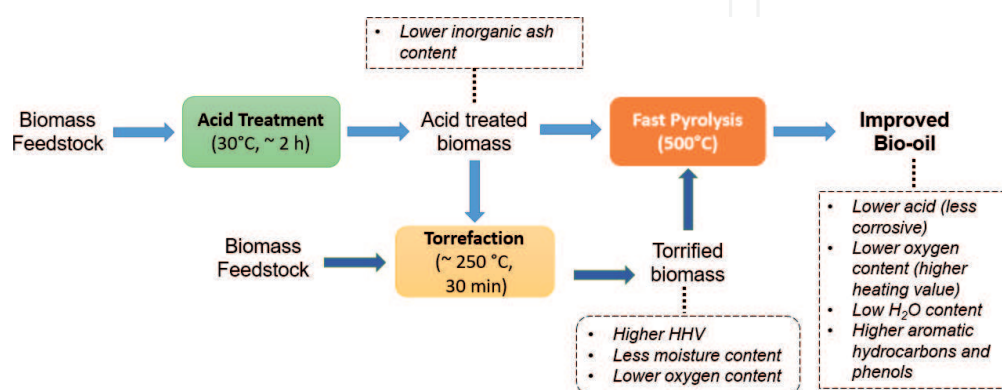


Figure 6.

A combination of acid treatment and dry torrefaction to improve the fast pyrolysis process performance (adapted from [53]).

dry torrefied (270°C) in the pretreatment of *P. radiata* allowed achieving 57.8% of bio-oil yield and improving the quality of bio-oil with low H₂O and organic acids content [54].

5.2 In situ upgrading

Other strategy to improve the properties of the bio-oil obtained by pyrolysis process is the modification in situ, i.e., inside the own reactor by change of the variables and the parameters. Two strategies that have gained prominence and show good results in obtaining a bio-oil with good qualities are hydrogenation and catalytic pyrolysis, and the hybrid process with both.

The addition of H₂ as a pyrolysis gas agent in the absence of catalysts promotes hydrogenation reactions mainly with the volatiles released and may have various effects such as increased formation of less oxygenated species, greater selectivity in phenolic compounds among others. For example, the effect of adding hydrogen in the carrier gas (up to 15% vol) in the pyrolysis of food waste in a downdraft reactor promoted the formation of a bio-oil more selective in aromatic, phenolic compounds while reducing the amount of heterocyclic nitrogenous species such as (quinoline) [55]. Other biomasses, such as poplar wood showed the same behavior upon pyrolysis in H₂ atmosphere (6% vol) compared to pure N₂ atmosphere obtaining higher yield and selectivity in phenolic species [56]. Another important effect of the addition of H₂ in the pyrolysis process is that, regardless of the presence of catalysts, it can promote the production of bio-oil with higher H/C ratio which is highly beneficial for the use of bio-oil as liquid fuel [57].

Recycling the pyrolysis gas to the reactor as a reactive atmosphere is a potential alternative, although its effect is not yet clear. When fast pyrolysis of biomass takes place under a N₂ atmosphere, the main gaseous products of pyrolysis are CO, CO₂, H₂, CH₄ and low levels of light hydrocarbons, therefore, when this gas is recycled to the reactor, it can promote a reactive atmosphere and not more inert. Studies in fluidized bed reactors, in the temperature range of 430–500°C, show that the increase in gas recycling rates can lead to a decrease in the production of organic liquids, but some biomasses, such as oak and switch grass, show good results. Deoxygenation effect and HHV increase in your bio-oil with gas recycling rates of up to 80%. However, other biomasses, such as *Pennycress Presscake* and pine wood, had no effect on the yield and composition of bio-oil with the pyrolysis gas recycled in the reactor [58, 59].

Among all the in situ alternatives to improve the obtainment of higher quality bio-oil, catalytic pyrolysis stands out as the most promising. The process basically consists of the insertion of a solid catalyst in the pyrolysis reactor capable of acting in the set of pyrolysis reactions, promoting the formation of bio-oil with better properties and selectivity in the components of interest of interest. Several authors have already published works testing different catalysts, in different process configurations, attesting to diverse improvements in obtaining bio-oil. Among these improvements in the use of catalysts in the fast pyrolysis process, it is worth mentioning: [60].

- The use of some catalysts can provide lower temperature operation. Considering that the pyrolysis process is endothermic, this would lead to a reduction in energy costs [61, 62].
- Reduction of bio-oil acidity and possible corrosion problems due to less formation of acidic compounds.

- High degree of deoxygenation, increased H/C ratio and associated energy densification [63].
- Considerable increase in the selectivity of bio-oil products, reducing the molecular weight range of the hydrocarbons obtained (C₅–C₁₂) [64].
- Depending on the catalyst(s) selected, there may be a significant increase in aromatic compounds (up to 50%), giving greater stability to the bio-oil and providing a potential use as a fuel [60, 65].

Despite promising experimental results, the fast pyrolysis process using catalysts still needs to overcome some obstacles to reach the industrial level. The basis for these challenges is the development of catalytic reactors capable of supporting the pyrolysis atmosphere without expressive rates of catalyst deactivation, expanding the selection of desired products in bio-oil, in addition to efficient developments in the recovery and regeneration of catalysts [41, 60]. **Table 4** below shows a set of

Feedstock	Process parameters	Catalyst	Yield	Deoxygenation	Ref.
Loblolly pine	Circulating fluidized bed 36 kg _{biom} /h 520°C	γ-Al ₂ O ₃	—	13–6–24.2% wt O	[66]
Forest pine woodchips	Auger reactor 450°C 2 kg _{biom} /h	CaO CaO.MgO	48–50%	24.2–25.4% wt O	[67]
Pine wood	Auger reactor 500°C 0,2 kg _{biom} //h	ZSM-5 based acidic catalys	50,3%	—	[68]
Pine wood	Bubbling fluidized bed reactor	Sspray-dried 40% ZSM-5	45.5–50.0%	—	[69]
Microalgae (Enteromorpha prolifera) + HDPE plastics	Fixed bed reator 550°C EP:plastic:catalyst ratio 1:1:2	HZSM-5	71.4%	13.5% wt O	[70]
Miscanthus	Conical spouted reactor 400–600°C 1–5 catalyst/biomass	ZSM-5	37.5% [500°C]	1,7% of phenols and 5,5% wt other oxygenates [500°C]	[71]
Waste tires + pistachio seeds	Fixed bed 500°C 5% wt catalyst	Ni-Mo/ Al ₂ O ₃	63%	5.3% wt (oxygen)	[72]
Lingnin	Fixed bed reactor 450°C	K ₂ CO ₃	29%	O/C=1,40	[73]
L. japonica + polypropylene	Fixed bed reactor 500°C	Al-SBA-15	50,32%	~ 10% of oxygenate compounds	[74]
Pine wood	Fluidized bed reactor	H-MOR-20	17,6% (free water)	—	[75]

Table 4.
Some research about catalytic pyrolysis.

works on catalytic pyrolysis of biomass at different scales, the characteristics of the catalysts used as well as the yield in bio-oil.

5.3 *Ex situ* upgrading

Ex situ processes are carried out outside the pyrolysis reactor, ie outside the main reaction zone. Esses processos podem ser de natureza física ou físico-química, promovendo alguma melhoria na qualidade do bio-óleo bruto gerado na pirólise. Dentre esses, pode se citar: [76–78].

- Physical methods
 - Solvend addition
 - Emulsification
 - Hot vapor filtration
- Chemical
 - Catalytic hydrodeoxygenation (HDO)
 - Steam reforming
 - Esterification
 - Supercritical fluids

Although there are several strategies to improve the quality of bio-oil, the most studied processes, aiming at the industrial potential, are hot vapor filtration (HVF), catalytic hydrodeoxygenation (HDO) and steam reforming.

HVF is one of the most common and simple able to improve some properties of bio-oil. It consists of passing the pyrolysis vapors through a filtering medium, even at higher temperatures. This method, in addition to being more efficient than traditional cyclones for removing small particles of coal and ash, can add better properties to the condensed bio-oil later on [48, 79].

Some types of filter (fixed bed glass wool, ceramic candles) and biomass raw material (sugarcane, rice and cassava waste) for pyrolysis were tested in the configuration: reactor + hot filter. In short, the addition of the filter introduces a longer residence time of the bio-oil organic vapor at high temperatures, promotes cracking reactions of organic molecules and causing a loss in bio-oil yield (around to 5%), increase in yield of the gas in addition to the higher content of H₂O in the bio-oil. But the condensed bio-oil tends to present a series of improvements such as: practically free of char and ash, less viscous. There may also be a certain deoxygenation of the bio-oil (decrease in the O/C molar ratio) but this effect is not fully understood, depending on the type of hot filter, biomass and operating conditions of the pyrolysis [79–81].

Another upgrading process, of the great highlighted is the hydrodeoxygenation (HDO) of the bio-oil. The HDO it's a particular case of hydrotreatment process, where the bio-oil is its reacted with H₂ under specific conditions of temperature, pressure, catalytic, and fluidynamis (**Figure 7**). In this way, the organic compounds of the bio-oil are submitted to a set of reactions, mainly hydrogenation and hydrodeoxygenation, providing an improvement in properties, forming less oxygenated and more stable compounds.

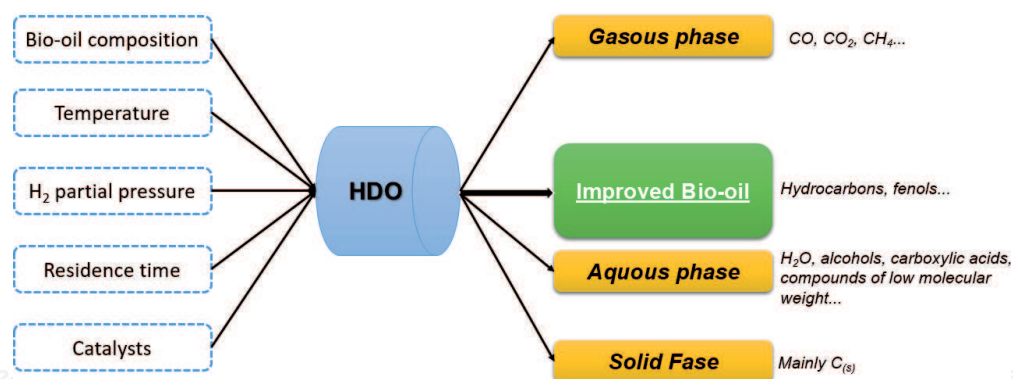


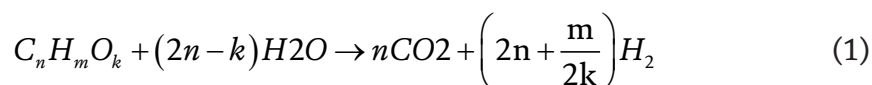
Figure 7. Schematic of the catalytic hydrodeoxygenation process, its variables and products.

Good control of the variables and parameters is essential to obtain a bio-oil with a high degree of deoxygenation and with lower H₂ consumption. The process occurs in the range 200–450°C and higher temperatures, in general, increase the degree of deoxygenation but at the expense of a decrease in the yield of improved bio-oil due to higher gas production. The partial pressure of H₂ is a variable of great relevance in the process and a minimum value of around 80 bar is required for good solubilization of the bio-oil, increased catalytic activity and minimization of adverse effects such as repolymerization of the bio-oil forming unwanted solid products [82, 83].

Finally the selection of the catalyst, jutanly with the support, is fundamental. The first catalysts tested in this process were CoMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ due to their use in oil refineries for nitrogen and sulfur removal processes. About these a number of sulfide, noble metal, and transition catalysts have been studied, each presenting different advantages with respect to higher catalytic activity, selectivity, and deactivation rates upon the presence of inorganic elements such as sulfur and ash present in the bio-oil [83]. The catalytic hydrodeoxygenation becomes a promising alternative for obtaining a bio-oil of higher quality and opening the possibility for the production of biofuels from it.

The steam reforming process emerges as another alternative of great potential for the valorization of lignocellulosic currents and hydrogen production. H₂ is a gaseous fuel with high added value due to its energy density and its combustion is free of carbon emissions. In this process, bio-oil, as well as fossil fuels, react with H₂O vapor at temperatures in the range of 700–1000°C, in the presence of a catalyst (usually nickel-based) offering as main product the H₂-rich syngas, along with CO₂ [76–78]. The main advantage of this process is the simultaneous production of high value-added fuel (H₂), and it allows the assimilation of CCSU (Carbon Capture Storage and Utilization) technologies. But one of the major disadvantages is the high energy demand to carry out the process.

The overall balance of this process can be given by Eq (1): [77, 78].



Where the coefficient expresses the maximum possible H₂ yield per mole of carbon fed. The steam reforming of bio-oil can be performed mainly in fixed bed, fluidized bed or staged bed reactors. The process can be carried out using a wide range of catalysts (Dolomite, Ru, Ni, Co, Rh) and supports (Al₂O₃, ZrO₂, MgAl₂O₄, etc.) but Ni based catalysts are the most active but also have the highest deactivation rates due to coke formation. However, changes in the processes, mainly concerning

the Vapor/Carbon ratio, besides the temperature and the catalytic support, can minimize the impact of the decay of the catalytic activity by coke formation in the steam reforming process [84, 85].

6. Conclusions

The process of fast pyrolysis is an alternative of great potential for the conversion of biomass and waste into renewable fuels and chemicals of high added value contributing to the reduction of emissions of greenhouse gases, with potential for application and integration in biorefinery projects. Technically some technologies such as fluid bed and rotating cone reactors are emerging for commercial applications and the main product generated, bio-oil, has a variable and complex composition requiring stages of improvement and stabilization. In this sense, several studies point out routes to improve the quality of bio-oil obtained from the pre-treatment of biomass (such as washing and torrefaction), in situ improvements and downstream processes such as HDO and steam reforming capable of converting bio-oil into a stream with higher added value.

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