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Biomass derived chars for energy applications

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ABSTRACT

Biomass-derived chars present energy density values close to those of fossil fuels and therefore they are good candidates in electricity or heat production plants with only minor drawbacks compared to fossil fuels. Even if co-firing seems the most attractive solution for near-term applications, processes based on combustion and gasification (which are competing in dependence of the need of heat or electricity) are receiving renewed attention. Thanks to their high carbon content, and their high specific surface area and developed porous structure, biomass-derived chars can be treated and converted into activated carbons and applied in many different field (as energy storage materials for gaseous fuels, mainly hydrogen and methane, or as electrodes). They can constitute the raw materials for preparing synthetic graphite, which can be used in some types of batteries and fuel cells, and in carbon electrodes for electrochemical capacitors. The performances in terms of capacitance, electrical conductivity, potential, charge and discharge rates, power density, etc. have been reported to be very close to those of commercial devices. The recent progress in the activation protocols brought to higher fuel gas storage capacities, especially in cryogenic conditions and under high pressure, and opened the possibility to apply these materials in new application fields. In catalysis, advances in the use of biomass-derived chars and active carbons have been made thanks to the improvement of the modification techniques. The optimization of the engineering methodologies allows to lower the cost of the activation processes of biomass-derived chars and to tune the char properties to adapt them to the final application. The present paper aims to give a comprehensive survey of already-well-established or future potential energy applications of biomass-derived chars. A critical comparison of their use in different processes is reported and their modification by various catalytic, physical and chemical routes is detailed.

1. Introduction

Biomass-derived chars are stable solid materials with high carbon content, low density, and high porosity. Chars can be shaped into different forms (pellets, briquettes, …) to be easily transported. Although biomass derived chars are primarily used in agriculture as soil amendment, they are recently receiving particular attention in various other fields (Table 1), such as energy production, livestock production, carbon sequestration, wastewater treatment, toxins remediation, etc. [1].

Chars present lower H/C and O/C ratios than raw biomass and consequently a higher energy density. In addition, chars are

Abbreviations: HHV, High Heating Values; HHV_t, High heating value of the product; HHV_0, High heating value of the feed; T_i, ignition temperature; T_f, temperature corresponding to the maximum burning rate; M_t, mass of the product at time t; M_0, initial mass of the feed; db, dry basis; EC, Electric Conductivity; TG, Thermogravimetry; DTG, Derivative Thermogravimetry; V_{max}, maximum burning rate; T_f, temperature of the maximum burning rate; FR, Fuel Ratio; CI, Combustibility Index; VI, Volatile Ignitability; D_i, Ignition index; S, combustion characteristic index; η_M, mass yield ratio; η_E , energy yield ratio; PM, Particulate Matter; HC, hydrocarbons; NO_x, nitrogen oxides; PAH, Polycyclic aromatic hydrocarbons; CSR, Coke Strength after Reaction; CRI, Coke Reactivity Index; VM, Volatile Matter; BF, Blast Furnace; BDF, Biomass Derived Fuel; RDF, Refuse Derived Fuel; CGE, Cold Gas Efficiency; HE, Hot Gas Efficiency; CCE, Carbon Conversion Efficiency; ECE, Energy Conversion Efficiency; SER, Specific Energy Requirements; m_{syngas}, mass flow rate of syngas; M_{syngas}, molar mass of syngas; m_{fuel}, mass flow rate of feedstock; LHV_{syngas} and LHV_{fuel}, calorific values of product gas and feedstock; $Y_{dry\ gas}$, dry gas yield; C_p, specific heat capacity; T_f, temperature at the gasifier exit; T_0, temperature of the fuel (feedstock) entering the gasifier; P, plasma torch power; AC, Activated Carbon; BET, Brunauer-Emmett-Teller; SSA, Specific Surface Area; Vμ, microporous volume; DCFC, Direct Carbon Fuel Cell; MCFC, Molten Carbonate Fuel Cells; PEMFC, Proton-Exchange Membrane Fuel Cells; MFC, Microbial Fuel Cell

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Table 1
Different applications of biomass-derived chars.

Application	Char Precursor	Ref
Reduction of soil contaminant	Broiler litter	[2]
Reduction of nutrient loss	Digested sugar beet tailings	[3]
Improvement of soil properties	Sugar cane bagasse	[4]
Reduction of plant health products	Dairy-manure	[5]
Wastewater treatment	Corncob	[6]
Gas treatment	Olive stones and almond shells	[7]
Carbon sequestration	Corn silage	[8]
Livestock production	Jarrah wood	[9]

hydrophobic, brittle, more easily fluidizable and they agglomerate less. Thanks to these properties the chars present many advantages, when compared to raw biomass, in transportation, storage, milling, densification and feeding. Besides, chars produced from biomass can be co-fired with pulverized coal in already existing large industrial facilities. Indeed, chars, once pulverized, can be added to coal, as their particle size distribution is much more similar to that coal than that of raw biomass. From a process point of view, the oxidation reactivity of biomass-derived chars is higher than that of bituminous coal [10]. The morphology and texture of chars are also positive characteristics for using biomass-derived chars as energy storage systems. Indeed, because chars are good adsorbents for fuel gases (mainly methane and hydrogen) or electrodes in electrochemical devices, the biomass chars seem to achieve higher performances than conventional systems in energy storage [11]. Unfortunately, investments to promote this application of chars are still rare. The reasons of such a reticence is probable connected to the lack of (1) industrial scale plants, (2) to the absence of complete cost analysis studies for the whole chain and (3) to the lack of a global picture of the various already made academic investigations. For this reason, the aim of this review article is to present the state of art, the recent progress, as well as the perspectives of char applications in the energy production and storage fields. This review article is also motivated by the current strong dependence of our society on fossil fuels and by the opportunity that chars give us for developing bioenergy markets.

2. Chars production, characterization and densification

Different chars' production processes (pyrolysis, gasification, hydrothermal carbonization, torrefaction, etc.) can be performed starting from various feedstocks (forestry, agricultural and aquatic biomasses, livestock detritus, industrial and municipal wastes) in a wide range of installations and reactors based on different technologies of various sizes, and operating under different conditions (residence time, particle size, heating rate, final temperature, etc.).

All these parameters lead to the production of a very large panel of chars' types that, depending on their properties, can be chosen for a target final application [12]. The viability of energy related processes based on the use of chars is connected to their high carbon to ash ratio, their developed porosity and their good reducing properties. Besides, many chars are almost smokeless when burned and present relatively low and non-reactive inorganic impurities [13], with the exception of chars derived from sewage sludge, which are very rich in inorganic elements [14,15]. Chars' low water, sulfur and nitrogen contents are very appreciable features that make them promising substitute to commercial coals, especially because no expensive post-treatment equipment is required. Another advantage is the short time required to start the combustion process in the plants, when compared to the time required to start the combustion of raw biomass.

2.1. Chars production

Chars can be produced by various thermal processes (Table 2) with restricted oxygen supply, preferably with slow heating rate (lower than 80 °C/min [16]), which allows long vapor residence time (ranging between 30 min [17] to few hours [18]) and consequently more efficient secondary cracking reactions. The most common production techniques are slow pyrolysis and carbonization that could be carried out in advanced high-tech retorts and/or pyrolysers, as well as in simple traditional pits or kilns. More recently hydrothermal carbonization is increasingly used for char production, even if its application is restraint to specific biomass sources. It consists in treating the biomass with hot compressed water instead of drying it; the resulting product is called hydrochar [19]. Microwave pyrolysis (by dielectric heating) is another technique that has been recently applied at laboratory scale [20,21]. This techniques is characterized by the presence of hot spots in the biomass, and brings to chars with higher HHV and specific surface area than those obtained by conventional pyrolysis [22,23].

Many pilot-scale installations equipped with moving screws, rotary drums, buffers, and other technical solutions, operate in a continuous mode. Usually, the necessary energy is supplied by burning the produced gases and vapors generated during the cracking reaction. Biomass pre-drying reduces the moisture content of biomass and increases the stability of the process in the reactor.

Industrial scale installations (where the integrated processes are represented in Fig. 1) are already operating. Various solutions are proposed by 3RAgrocarbon (Hungary), Premier Green Energy (Ireland), Pyreg (Germany) and Biogreen (France).

Once the biomass collected, it is transported to the pyrolysis facility, where it is crushed, to reduce the particle's size, and dried (pre-processing). The pre-processes material can be then stored or directly fed to the pyrolysis/gasification/carbonization reactor. The generated gases and vapors, as well as the oils, are burned on-site for producing heat. In order to initiate the carbonization process, the humidity accumulated in the raw biomass has to be firstly evaporated. The evaporation step can take from few seconds to few minutes, and its efficiency depends on the temperature, on the installation set-up and on the size of the biomass particles. In a second step, the biomass is degasified at high temperature. Volatiles are here degassed from the biomass. The dry and devolatilized material is then kept in the hot zone of the reactor and the carbonization process can begin. The overall process can be controlled by the biomass feeding velocity, by the biomass humidity content, by the screw rotation, and by the temperature of the reactor walls. The vapors leaving the reactor present high temperature, and, depending from the kind of adopted technology, they can be burned to produce the

Table 2
Thermal processes of char production.

Process parameters	Pyrolysis			Gasification	Carbonization	
	Slow	Fast	Microwave		Torrefaction	Hydrothermal
Final Temperature °C	350–1000	> 400	180–600	> 600	200–320	180-250 (High Pressure)
Heating rate °C/s	< 80	100–1000	5–1000	Few hundreds	< 50	5–150
Oxygen	< 2%	Free	Free	20–45%	Free	Free
Reaction time	Minutes to days	Up to few seconds	Seconds to hours	Up to few seconds	Minutes to days	Minutes to hours

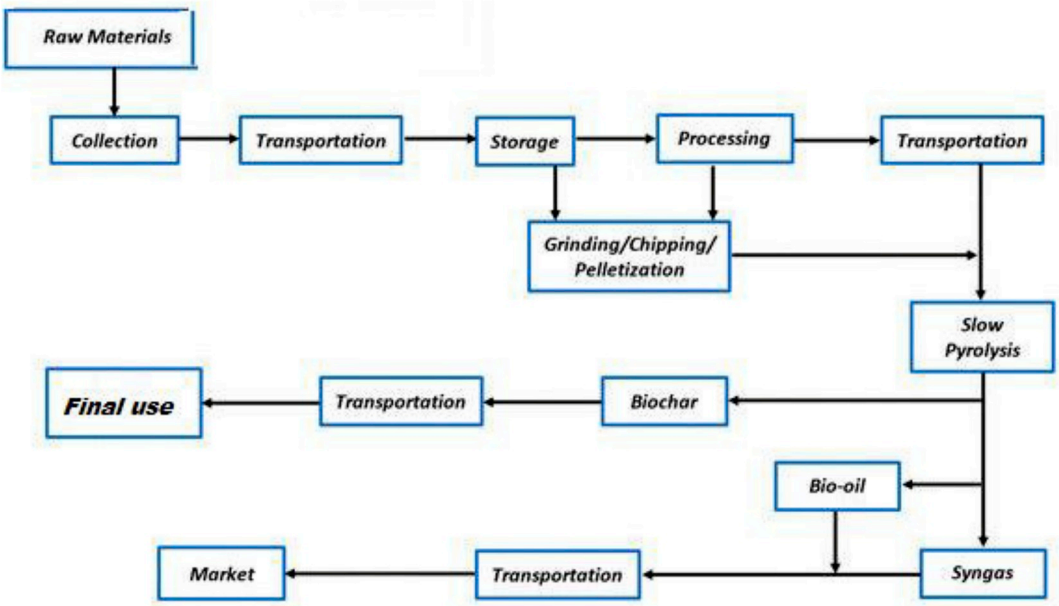


Fig. 1. Industrial biochar system (Adapted from Ref. [24]).

necessary heat for pyrolysis and drying processes, or be sent to a separator (e.g. flash condenser) to produce bio-oil, and non-condensable gas. This last solution provides a fuel that can be used for producing energy or that can be purified and used as feedstock for other applications. Finally, the obtained biochar is cooled down in an absence of oxygen, to prevent auto ignition, and transported to the final destination.

In order to enhance the performances of biochars and adapt them to the various applications, progresses in their engineering are recently being developed. Treatments as surface oxidation, amination, sulfonation, pore structure modification and recombination have been optimized in order to modify the surface functionalities and pore structure of biochar (Fig. 2). The biochars' surface can be modified by adding functional groups, metal nanoparticles and inorganic nanostructures

2.2. Chars' characteristics

The biomass feedstock as well as the production process determines the final characteristics of the obtained char. The physical, chemical, textural and morphological properties of a given char impact significantly its implementation in energy production and storage processes.

2.2.1. Energy contents and chemical composition

Generally, the high heating values (HHV) of chars make them attractive sources for clean energy production instead of fossil-based solid fuels [26,27]. HHVs reported in literature for chars produced from biomass vary between 10 MJ/kg (as for seaweed derived chars [28]) and 33 MJ/kg (for pinewood derived chars [29]), while the HHV for coal vary between 14 and 35 MJ/kg [30].

Ashes are useless and undesirable in energy applications due to several drawbacks, such as a high quantity of fine particles emission, clinker formation, corrosion, etc. The ash content is strongly dependent on the biomass source origin. Chars deriving from slurry (chicken, swine, bovine) have usually high ash contents (up to 43.8% [31]) since the livestock is partially fed with mineral elements, while resinous softwood chars show a very low ash contents (< 1%).

The quantity of volatile organic compounds that accumulate in the gas-phase fraction during pyrolysis and carbonization, and that condensate on the surface and into the pores of the char, are systematically measured by thermo-gravimetric analyses. Condensed volatiles compounds can indeed significantly modify the functionalization of the char' surface. As an example, the high presence of volatile compounds present in cellulosic chars (up to 84%, in Kim et al. (2015) [32]) makes them more suitable for thermal valorization than those obtained from aquatic biomass (27.5% from algae [33]).

As nitrogen-containing compounds are generally decomposed during the char production process, especially during pyrolysis, low concentrations of N (< 6%wt) are found in the final products. Chars, issued from vegetables (potatoes, cabbages, leeks) and slurry, contain even lower amount of nitrogen (1–4%wt) [34]. So, the N-contents do not represent a drawback to the use of biomass derived chars for energy production. Only nitrogen contents higher than 10% can indeed become a problem due to nitrogen oxides production during thermal valorization. Moreover, no or very few sulfur is present in the chars, because it is almost completely released and eliminated during pyrolysis [34].

2.2.2. Electric properties and surface acidity-basicity

Electric Conductivity (EC) is the parameter used to measure the chars' salinity in soil applications. However, it is also considered as an important parameter that has to be probed for chars' used as electrodes or catalysts' supports, since it represents the ability of a solid to conduct the electric current. Furthermore, the surface acidity of a solid is also an important property that needs to be probed for chars' that might be used as electrodes or catalysts' supports [35].

In the same way, pH is another property playing a major role in chars' valorization (Table 3). Indeed, biomass derived chars can be relatively acid (chars derived from fiber materials for instance) or more basic (vegetable and garden wastes derived chars) [36]. In general, the surface chemistry is related to the presence of heteroatoms such as hydrogen, oxygen, sulfur, and nitrogen, that form surface complexes with neutral, acidic, or basic character, and that can strongly influence the chars' adsorption properties. Indeed, anhydrides and carboxylic acids, lactols, phenols, lactones, are acidic; ether groups and carbonyl are neutral functionalities [37]; while quinone, pyrone, chromene, and nitrogen groups show basic features [38]. Moreover, basicity can be also due to the presence of alkali metals, such as sodium and potassium, and alkaline earth metals, such as calcium and magnesium, in the form of carbonates [39,40].

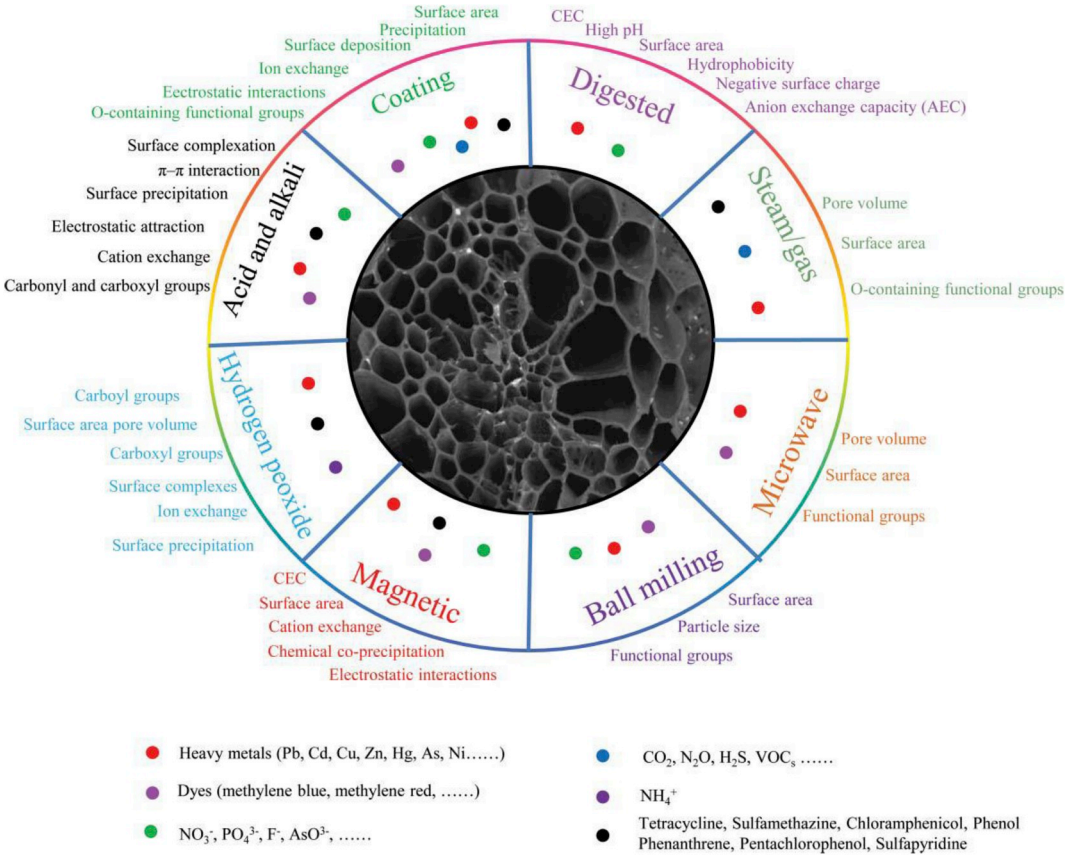


Fig. 2. Biomass derived chars engineering (Reproduced with permission from Ref. [25]).

2.2.3. Morphological, textural and structural properties

Specific surface area and porosity are important parameters since the charges in electrochemical storage systems are accumulated on the surface. The pores size and pores' interconnection facilitate the storage and transport of charges. Biomass derived chars are attractive materials in electrochemical energy storage due to their availability in different forms (as fibers, powders, nanotubes and nanospheres) and their developed porous network. However, carbonaceous materials with average pore size lower than 2 nm are not suitable as supercapacitors materials. To probe the chars specific surface and porosity, N_2-adsorption at −196 °C is commonly performed, even if, due to the presence of micro- and ultra-microporosity in chars, and the presence of high vapor pressure compounds as oils, the results obtained by this method are not always accurate and, too often, do not give reliable values [47].

The identification of the carbon types (organic, inorganic and graphitic) helps in predicting the further transformation during a thermal process. Proportionally to total carbon, graphitic carbon, which is more stable in time, is higher in hardwood chars than in softwood, manure and non-fiber biomass chars [48]. Molar ratios such as H/C_{org} and O/C_{org} are also indicators of the char stability. For energy applications, they should be as low as possible, and never more than 0.7 for the former and 0.4 for the latter (according respectively to DIN 51732 and DIN 51733 test methods). As for the char structure, Raman spectroscopy and X-ray diffraction spectra revealed the presence of ordered and disordered carbon rings, with dominance of highly disordered structure [49].

2.3. Densification

One of the major barriers to the widespread use of carbon materials derived from biomass is their low bulk density. At the expense of new capital and operating costs, densification process could overcome handling, transportation, feeding and storage difficulties. It also helps reaching good thermal conversion efficiencies [50,51]. These thermal qualities are inherited not only from char (the quality of which is itself

Table 3
Properties of biomass-derived chars.

Feedstock	C (%)^{db}	H (%)^{db}	O (%)^{db}	N (%)^{db}	pH	Ash (%)^{db}	VM (%)^{db}	Cfix (%)^{db}	Ref
Pea pod	39.32	4.75	53.3	2.40	na	3.5	78	18	[41]
Cauliflower leaves	31.8	3.2	59.4	4.01	8.84	18.86	51	39	
Orange peel	40.43	4.83	52.90	1.56	9.84	39	70	24.1	
Apple Tree Branches	71.13	4.03	15.05	1.94	11.4	7.85	29.85	62.3	[42]
Noxious weed	51.76	1.65	44.41	2.18	7.83	19.26	26.13	48.41	[43]
Jatropha carcus seed cover	67.48	2.01	28.36	2.15	8.9	16.43	26.52	50.82	
Duckweed	44.4	6.1	36.8	3.7	na	8.2	15.7	76.9	[44]
Poultry litter	51.07	3.79	15.63	4.45	8.7	30.7	42.3	27	[45]
Algae	74.5	4.5	na	na	9.1	68.8	27.5	72.5	[46]

Cfix: Fixed Carbon; VM: Volatile Matter.

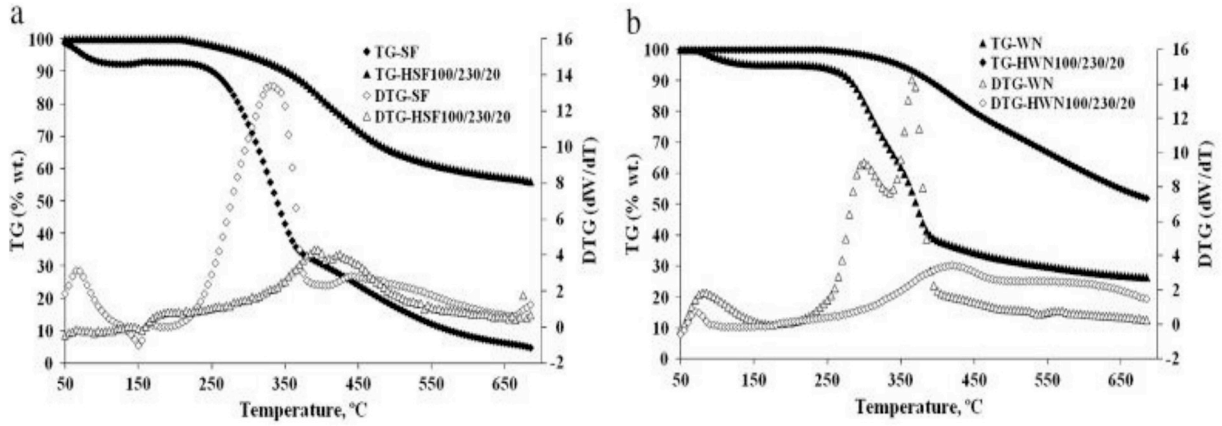


Fig. 3. TG and DTG curves of precursors and respective hydrochars for a) sunflower stem and b) walnut shells under different hydrothermal conditions (Reproduced with permission from Ref. [63]).

depending on the pyrolysis operating parameters), but also enhanced by the operational conditions of the densification process [52]. For example, the net heat output of the pellet/briquette would decrease if the sticking agent is not combustible. This is the reason why materials like starch, lignin, soil, animal dung, waste paper, gum Arabica, etc. are used in binding sawdust and chars [53]. But recently, Wu et al. (2018) successfully prepared very good quality barbecue charcoal from cotton stalks without any binders [54]. During the hydrothermal process, authors have indeed treated the biomass with hot compressed subcritical water (200–260 °C) for a period of time ranging between 5 min and 8 h.

Many technologies are available in a wide capacity range, from very small to very large and with various degrees of mechanization and automation and a wide choice of shapes and sizes of pellets and briquettes, like shown in several companies' internet sites [55,56].

In medium to large scale briquetting technologies, mainly placed in developed countries, up to ten tons per day of medium to high quality char briquettes may be produced and distributed to regular customers, in a well-organized retail network [57]. Oppositely, hand presses and screw extruders (manual or electrical) are scarcely disseminated across rural areas of developing countries lacking electricity supply, despite the low investment needed.

In spite of obvious advantages of char briquettes, such as the relatively low price, the long burning time and the environmental sustainability, their use, instead of solid fuels, is still very limited in Sub-Saharan Africa, even compared to Asian countries, such as India or China. This is probably due to production costs (EUR 0.15–0.25/kg of char-briquettes, without counting purchase, transport and labor costs) [58]. Indeed, the location of the production facility (close or not to the raw material source) and/or the customer type may contribute to more than half of the briquette price.

3. Energy recovery from biomass derived chars

As an energy vector, char based biomass can be used either directly, to produce power and heat, or indirectly, to produce various types of biofuel. Conversion of chars may be achieved mainly by two thermochemical methods: combustion and gasification. Moreover, the output of these two processes might be increased by using biomass-derived char based catalysts. Once densified (in form of pellets or briquettes), the carbonaceous based materials can be perfectly adapted to different reactors (fixed-bed, fluidized-bed, entrained-flow, etc.) for industrial and domestic applications. In addition, the gasification by-products can be valorized by cracking of the tars, to produce additional syngas, or by reforming the hydrocarbon and the oil, to generate hydrogen.

3.1. Combustion of biomass derived chars

3.1.1. Combustion mechanisms

The char combustion process is complex and involves various reaction steps: the oxygen transport into the boundary layer and into the numerous internal voids of the char, by convection and/or diffusion; the adsorption of oxygen on the internal and external surface; the chemical reactions at the surface (reaction involving oxygen, the char, and the various gaseous by-products); the desorption of the combustion by-products from the surface and their diffusion towards the external surface and gas-phase [59,60].

Antal and Grønli (2003) performed a deep investigation on the combustion mechanism and reported that chars, obtained under mild conditions (low temperatures), degrade following two main reactions: the pyrolysis of intact and partially-decomposed glycosyl units, and the decomposition of paraffinic and carbonyl groups. Differently, the degradation of chars obtained at high temperature is realized only by decomposition of paraffinic and carbonyl groups [61]. The same conclusions were reached by Islam et al. (2015) [62] and Roman et al. (2012) [63] for different biomass derived chars (Fig. 3).

3.1.2. Combustion performance

In order to be compared to other coals, chars (densified) can be described by the indicators previously defined to determine the combustibility, the reactivity and their combustion performance. Some of these indicators are experimentally determined, such as the maximum burning rate V_{max} and the corresponding temperature T_f, the ignition temperature T_i, the average combustion rate V_{mean}. Others are calculated, such as the fuel ratio FR, the Combustibility Index CI (MJ/kg), the Volatile Ignitability VI (MJ/kg), the Ignition index D_i (%/(min.°C^2)), the combustion characteristic index S (%^{2}/(min^2.°C^3)), the mass yield ratio η_M, and the energy yield ratio (η_E), on dry basis (db) and according to the following equations:

$$FR=\frac{\text{Fixed Carbon}^{db}}{\text{Volatile Matter}^{db}} \quad (1)$$

$$CI=\frac{HHV^{db}}{FR}x(115-Ash^{db})x\frac{1}{105} \quad (2)$$

$$VI=\left[\frac{HHV^{db}-0.338\text{Fixed Carbon}^{db}}{\text{Total Volatiles}}\right]x100 \quad (3)$$

$$D_i=\frac{V_{max}}{T_i T_{max}} \quad (4)$$

Table 4
Gas emissions of different types of charcoal [77].

Charcoal	CO (g/kg)	CO_2 (g/kg)	NOx (mg/kg)	HC (g/kg)	$PM_{2.5}$ (mg/kg)
China brick-shape	128.2	776.	834.1	3.05	235.3
China spheroid briquette	300.3	986.8	161.6	5.27	368.9
Indonesia sawdust hexagon briquette with hollow core	214.7	878.7	462.1	1.93	153.9
Indonesia Mangrove log	108.5	855.1	277.0	9.30	955.7
Indonesia spheroid briquette	67.7	723.7	413.3	4.05	282.6
Southeast Asian Binshotan log	76.6	1225.2	831.9	3.92	12

$$S=\frac{V_{max}\ x\ V_{mean}}{T_i^2 T_f} \quad (5)$$

$$\eta_M = 100\frac{M_t}{M_0} \quad (6)$$

$$\eta_E = 100\eta_M\frac{HHV_t}{HHV_0} \quad (7)$$

where M_0 and HHV_0 are the mass and the high heating value of the feed, respectively. t-subscript indicates the same variables for the final product.

As widely reported in the literature, the reactivity of chars deriving from lignocellulosic materials is high (for instance it is the double of the reactivity of pyrolytic chars derived from tire derived fuel, ebonite, plastic materials [64], or charcoal [65]). As a consequence, their combustion starts at lower temperatures. As an example, for Hirunpraditkoon et al. (2014), ignition time of commercial coconut shell char briquette was two times longer than that of durian peel charcoal briquette [66]. Such behavior is attributed to the char property (high porosity and disordered structure) that favors short ignition times.

D_i indicates how fast the fuel gets ignited, while S expresses the fuel overall characteristics. The higher are D_i, V_{mean} and S, the better is the fuel combustion behavior. It is usually assumed that when FR values are greater than 2, problems of ignition and flammability may occur. Indeed, a low fuel ratio suggests that the solid fuel easily ignites; degradation is then very fast and difficult to control, resulting in an incomplete combustion of the fuel and in smoke emissions. A suitable value of CI, which is used to evaluate the compatibility of a material for mixed combustion with coal, is 23 MJ/kg [67]. Finally, the minimum for VI should be 14 MJ/kg, which is the available energy provided by the total volatiles, assuming that the fixed carbon constituting the fuel sample is solely made up of pure carbon [67].

With the help of these parameters, many conclusions could be drawn from the numerous investigations [68–70]. To give an order of magnitude, the results published by Wang et al. (2014), concerning the combustion properties of briquettes of maize straw char, obtained at different final pyrolysis temperature, are hereafter presented. D_i values ranged between 0.75 and 1.13%/(s°C^2), while S varied between 0.13 and 0.93 10^{-9}%^{2}/(s^2.°C^3). For chars prepared at 250 °C, as final pyrolysis temperature, the mass yield ratios η_M were of 79.2 and 77.5% and the energy yield ratios η_E were of 83.28 and 86% for Maize straw briquette and torrefied rice husk briquette, respectively. Thanks to these parameters, Conag et al. (2017) were able to predict that torrefaction of sugarcane bagasse at 250 °C would require long time (> 60 min) in order to lower-down the volatile matter content and reach the desired FR, compared to only 30 min for chars prepared at 300 and 350 °C. At the same time, CI was reduced from 82 to 16 MJ/kg and the three final temperatures (250, 300 and 350 °C) could improve the VI to the desired value (from 11 to 16 MJ/kg) [67].

The analysis of these parameters values obtained by Wang et al. (2017) helped to state that blending maize straw char in briquettes with phosphorous additives would not ameliorate the combustion characteristics [71]. Definitively, the assumption that mixing mineral based additive to the char could reduce problems, such as the bed agglomeration, the fouling and the corrosion of the combustion reactors, due to the presence of alkali compounds present in green biomass, is false [72–74].

3.1.3. Combustion emissions

The viability of a combustion process is assessed not only on the bases of the efficiency parameters, but also in terms of emissions. It is widely admitted that during pyrolysis, the majority of inorganic species are retained in the char [75]; consequently, their combustion significantly reduces PM_1 (and the mass of Na, K, and Cl in PM_1), when compared to biomass combustion, as a consequence of volatile and Cl removal from the raw biomass during pyrolysis. At the same time, a considerable increase in the emission of PM_{1-10} as well as of Mg and Ca masses in PM_{1-10} is detected during the char combustion process (Table 4), probably due to the increased ash loading [76]. In any case, comparison among the emission degrees have to be made in the same combustion plant, because the emissions are not only depending by the use of chars or other fuels, but also from the used combustion technology.

In order to obtain a cleaner and more efficient combustion of biomass chars, Qi et al. (2017) added various chemicals to the samples. The presence of calcium oxide and ammonium phosphate together show to reduce the alkali-metals content to different degree, while calcium carbonate promoted the retention of alkali metals. It is well-known that pyrolysis treatment reduces SO_2 emissions during char combustion, but the addition of the three just-mentioned additives during the pyrolysis process, reduces these emissions to almost zero. These additives enhanced the NO emission to 1.2–3.5 mg/g, that are anyway still below the restriction limits. For all these reasons, the three additives were judged economic and suitable for industrial applications [78].

3.1.4. Combustion reactors and applications

It is important to remark that the combustion mechanism, the process efficiency and the emissions level are all influenced by the combustion reactor design and configuration. Many laboratory and bench scale reactors were used in combustion tests; the corresponding main conclusions are reported in Table 5.

The tested reactors are adapted to operate in industrial contexts, but not for domestic applications. Even if cooking and heating needs are still assured by traditional stoves in rural regions, improvements, to reach higher targets of energy efficiency and low emissions, are needed. Indeed, actual concerns are in particular related to hazardous particles and pollutant gases emission (particle matter, black carbon, CO, NO_x, SO_2, PAH), that might cause health risks (indoor air pollution), and environmental problems (greenhouse gases emissions, air pollution, deforestation) [85]. According to Winijkul and Bond (2016), clean-fuel may reduce emissions by 18–25% depending on the pollutant considered [86], while stove improvements, such as adding chimney, retaining heat, plugging fans, etc. may lower emissions by 25–82%, and PM by 95% [87–90]. The stove prices depend by many factors and, for example, they can vary from US $2 in Ethiopia to US $15 in Guatemala [91].

3.1.4.1. Iron and steel production. In the industrial field, the goals in using char feedstock are focused on energy-saving, low emission

Table 5
Combustion of biomass-derived char in different reactors.

Reactor	Char based biomass	Main conclusions	Ref
Drop-tube furnace	Mallee bark	Unimodal particle size distribution of PM_{10}	[76]
Fluidized bed reactor	*Robinia pseudoacacia*	Complete conversion to CO or CO_2 : 50% direct coarse char combustion and 50% during subsequent post-combustion in the bed	[79]
Fluidized bed reactor	Pine seed shells Olive husk Wood chips	Extensive primary and secondary fragmentation of char particles (25–45% of fixed carbon consumption due to percolative fragmentation). The biogenous character of the char fuels: significant role in the afterburning of the attrite fines. Significant particle shrinkage after devolatilization (development of highly porous structure characterized by macropore dominance)	[80]
Fixed bed reactor	Olive wastes	Complete conversion of Carbon	[81]
Laminar flow reactor	Pine Switch grass	Removal of amorphous material and release of oxygen and hydrogen-rich gases Inorganic transformations: vaporization (namely potassium and sodium), surface migration and coalescence, embodiment of metals (such as Ca) into silicate, etc. Shift of amorphous structure of the inorganic compounds to crystalline form	[82]
Chemical looping combustor	Swedish wood Mexican petcoke	High carbon capture rate (93–97% for wood char) High gas conversion (90–95.3%)	[83]
Blast furnace	Sawdust char pellets	Low NOx emissions of torrefied pellets in comparison with raw sawdust explained by the release of volatiles or N-containing volatiles such as HCN and NH_3 during pyrolysis of char it is quickly combusted with the raw cane	[84]

release, and lowering of the energy production cost. The contribution of the transition towards bio-sourced fuels, on the various points of improvement, can be clearly demonstrated in the iron and steel production industries, where sustainable biomass-based chars/charcoals have fully and/or partially replaced the fossil-based coals and metallurgical coke, in the various steps of the process chain (Table 6).

Despite all the advantages that the employment of biomass-based chars can bring to the metallurgic sector (reductions in CO_2 and SO_2 generation, improvements in the quality of hot metal, reduction in slag volumes), some issues have still to be solved (Table 4). Indeed, basic characteristics of solid biomass-based chars are significantly different from those of fossil-based coals and cokes. For example, highly reactive biomass-based reducing agents provide high burnout during blast furnace BF injection, but have also a negative influence on their sintering capacity.

3.1.4.2. Heat and power generation. Another major application of biomass based char, as a renewable fuel, is in the power and heat industry. Characteristics such as “zero balance” of CO_2 emissions, as well as the interesting calorific value, the high carbon content, the low moisture, ash and volatiles contents play in favor of firing and/or co-firing processes in electricity generators. Moreover, the extending generation life assets, the avoiding stranded and the early remediation costs, accompanied to increasing revenues, are other financial benefits that these carbonaceous materials can bring by their use in power plants.

In rural areas, small-scale char-based thermal power plants may solve supply and transmission issues, and small industries, like dairy milk production or cereals milling, can be created [130]. Also larger and consistent fuel demands of bigger industries can be satisfied by biomass-derived chars. As an example, the works of Cunningham et al. (2016) proved that fecal sludge char could potentially be used as a solid fuel in power plants and cement kilns [131].

3.1.4.3. Application in automotive diesel engines. Char can be also used as liquid fuels for potential applications in stationary or nomade transportation diesel engines [133].

The char based fuels are mainly constituted of char-water and char-hydrocarbon mixtures, but an innovative fuel derived from micronized chars has been recently added to the family of liquid biofuels (Fig. 4). These solutions are safe (especially the char-water mixtures), as they are not flammable and eco-friendlier than other fuels usually used for vehicles, ships, agricultural trucks, etc. transport applications and for feeding back-up electricity supply devices [134]. For example, slurry fuels can have a significant advantage as water reduces the flame temperature and NO_x emission, with only a small energy loss due to water vaporization. The char-fuel is easily stored in tanks and pumped, and there is no risk of dust explosions.

Char-water fuel mixtures are obtained by crushing (to a particle size smaller than 70 μm) and suspending the char in water (in presence of a suitable surfactant to guaranty the stability of the suspension). On the other hand, char-hydrocarbons mixtures need to be processed at high pressures. This supplementary cost is regained by the high energy density and to the possibility to use a large panel of configuration of the solid charge (content, particle size, volatility, etc.) [134]. Besides, these systems do not need any pilot fuel injection for lower speed operation. Nevertheless, these aspects should be deeply investigated in order to develop these new automotive fuel systems [135]. Indeed, more target efforts have to be made for reducing the particle sizes, the amount of ash production, and hardening the injectors [136]. A major drawback in the implementation of this kind of fuels for power station applications, is the necessity to produce slurries highly charged in char (to enhance the energy content) with a viscosity compatible to the pumping procedures and atomization of the fuel.

3.1.5. Barriers to biomass char combustion

Despite the high quality of biomass-based chars as fuel in many fields, a barrier to the wider industrial utilization of chars as energy source is the still too high price and the limited number of suppliers, when compared to fossil-based carbonaceous resources [137]. In fact, research is mostly concentrated on woody charcoal, and only little work is performed on other biomass residues, even if they can be less expensive and more widely accessible. To overcome the financial issue, economic analysis suggested that the transition to biomass derived chars would have a higher chance of success if developed as an add-on to existing business, where production facilities (land, building, back office staff, etc.) can be shared.

Moreover, other technical problems related to the use of biomass derived chars can occur in the combustors:

- irregular morphology can complicate operations such as handling or feeding; - vaporization and recondensation of alkali metals that can lead to the release of submicron aerosols and to fouling and corrosion of the burner surfaces [133];
- conversion of calcium and/or alkali metals into silicates that mitigate the ash softening temperature, consequently increasing the ash deposit [82], etc.

Investigations have been performed to find solutions to all these issues. For example, leaching and mechanical separation processes might be key technologies for reducing alkali metal and mineral content

Table 6
Application of biomass-based chars in iron and steel industry.

Biomass based char	Main features/results	Ref
Coke making		
Torrefied: kraft lignin from pulp/paper industry woody components cellulose lignin xylan	Generally lowers the maximum fluidity achieved in the coal-biochar blend: biochars do not pass through the plastic phase during the coking process. The formation and stability of the coke matrix is maintained.	[92–94]
Up to 15% charcoals Up to 10% of highly carbonized biochars	Metallurgical coke with adequate quality (fluidity in the range of 400–1000 dial division per minute (ddpm) Increase in Reactivity attributed to high presence of calcium in the blend.	[95]
Torrefied biomass	Small contraction for coarse torrefied biomass; No contraction for particle sizes < 0.25 mm	[96]
Different concentrations of charcoal added to coal blends	The wall coking pressure decreases significantly (especially for smaller charcoal particles as compared to pure coal blends), due to the gases escaping from the plastic layer in the presence of inert materials. Coarse torrefied biomass particles increase the wall pressure Oven pressure decrease with finer particles.	[97]
Chestnut and pine Sawdust chars (1–5 wt.%)	Post-reaction strength (Coke Strength after Reaction CSR) of coke decreasing and Coke Reactivity Index CRI increasing	[98]
Biochar	For replacement in coke-making, optimal charcoal characteristics: VM < 10%, size < 1 mm, density > 700 kg/m^3 and low alkali content. Net CO_2 emissions saving of 1–5%	[99]
Charcoal	For BF nut coke replacement: VM < 7%, high density, sizes < (20–25) mm. - CO_2 emission savings estimated ~3–7% (in commercial mini BFs and industrial trials in large BFs)	[100]
Iron ore agglomeration and sintering – Reduction and pre-reduction		
20-50% chars from sunflower husks	Sintering time decreases from 440 s (0% husk) to 415 s (20% husk) and 387 s (50% husk); low heat capacity and higher reactivity of the sunflower husk chars No change in combustion efficiency for up to 20% husk replacement	[101]
Red gum charcoal Charcoal prepared from prickly acacia	Satisfactory sinter	[102]
Biomass-based chars	Increasing substitution rates resulted in lower sinter yields and productivity Decrease in maximum temperature and holding time due to higher reactivity	[103]
Charcoals	Low sinter strength along with decreasing of the bulk density, well defined combustion and sintering zones by operating with blast furnaces. The share of charcoal in iron ore sinters limited to 25 wt.%	[104]
Up to 40% Charcoal 20% straw chars	Charcoals provided better results than straw chars, up to 40% bio-charcoals (and only 20% straw chars) could be used to replace Coke breeze without affecting product quality Reduced bulk density of the sinters; Combustion temperatures achieved relatively quickly in these sinters due to rapid heating and lower thermal loads	[105,106]
Waste carbons, Biobased charcoals and chars	Agglomerating fine powders with iron ore fines with the use of binder Higher Iron oxide reduction rates	[107]
Wood straw fiber Sawdust Rice crust chars	Higher Iron oxide reduction rates	[108]
Bamboo char Charcoal	Higher Iron oxide reduction rates	[109]
Charcoal	Replacement charcoal needs to have VM < 3%, densities > 700 kg/m^3, small sizes < 0.3–3 m Net CO_2 emissions reductions of 5–15%. For carbon composites, biochars need to have high strength > 500 N, VM < 5% and sizes typically ~75 μm and could achieve net CO_2 emissions reductions of 3–7%	[110]
Auxiliary fuel injector		
Biochars	Rates can reach up to 200 kg for producing 1000 kg of hot metal Higher rates can seriously impact on furnace stability	[111,112]
Pine, chestnut chips, black poplar torrefied in at 240–300 °C with 11–43 min residence time Pine and birch charcoals produced at 520 °C	Grindability is improved with higher torrefaction temperature and with longer residence time. Flow behavior comparable to that of coals The relative proportion of chars in blends could range between 10 and 50 wt.% without any drawback.	[113] [114,115]
Biochars	CO_2 reactivity of biochars (VM 21.9%) higher than that of a high volatile (38.7%) coal, due to the high porosity and disordered carbon structure of biochars.	[116]
Eucalyptus chars	Higher level of burnout with all levels of VM drop-tube furnace) than injection coals at 1300 °C in a wide range of oxygen levels.	[117]
Biochars	Injection of pulverized biochar particles (< 75 μm) into a BF could reduce CO_2 emissions between 18 and 40% Complete replacement of coals with biochars increases operating costs by 5–16%	[118,119]
Biochars	Biochars need to have high VM 10–20%, low ash content < 5% and low level of alkalis. CO_2 emissions decreased up to 19–25%. In mini and large BFs, physical parameters of biochars, such as porosity, grain size distribution, and specific surface do not have a negative effect on charcoal injection rates.	[120]
Charge carbon and slag foaming agent in electric arc furnace (EAF)		
Biochars from agricultural waste	Fixed carbon, ash content and volatile matter: key parameters to use biochars as a slag foaming agent, either by itself or as coke-biochar blends	[121]
Biochars	High reactivity biochars produce higher levels of slag foaming than coke. Mineral impurities in biochars can affect slag chemistry, slag viscosity and surface tension. For adequate carbon transfer into slag, low density of biochars may necessitate briquetting or pelletizing.	[122]
Agricultural waste (coconut shells and palm shells) chars		[123]

(*continued on next page*)

Table 6 (*continued*)

Biomass based char	Main features/results	Ref
	Strong influence on the combustion performance and carbon/slag interactions including FeO reduction, gas generation and its entrapment within the slag as well as the enhancement of the slag volumes. Extensive reactions in the gas phase and carbon/slag interactions for 100% palm chars. The combustion burnout of coke/agricultural blends higher than the burnout of coke and raw agricultural waste alone. Palm chars: high slag volumes but slow rates for iron oxide reduction. Slower rates of gas generation made it easier for slag to trap gases and to generate sustained levels of slag foaming. A balance between iron oxide reduction and foaming need to be established for optimizing furnace efficiency and operations.	
Biochar fines	No negative impact on steel quality, slag chemistry or slag foaming, but carburization of molten iron below acceptable levels (plant trials), attributed to high combustion rates of biochars in a limited time Possible of control reactivity and combustion behavior of biochars by briquetting with water and molasses	[124]
	No significant differences in metal and slag quality in comparison with coal (industrial-scale trials of charging and injection) Issues of handling, charging, dispersing of low density powders, and intense flame emissions Inadequate and limited slag foaming affected by the penetration of biochar in the slag during injection trials.	[125]
Biochars	Biochars require low VM (2–7%), low moisture content (1–7%), particle size ~0.5–5 mm in industrial trial.	[126]
Pre-reduction		
Biochar based composites	Higher degree of reduction in 60 min attributed to the higher rate of gasification for biochars.	[127]
Biochar based composites	Small effect of particle size on the reduction rate; small enhancement of the reaction kinetics for smaller char particles, attributed to their higher surface area.	[118]
Biomass char	Isothermic reduction of composite briquettes to metallic iron in the presence of H_2–CO gas mixtures. Lower amounts of reduced iron. Iron concentration in biochar-based composite pellets reached 95%, the temperature of the direct reduction increased to 1100 °C. Relative proportion of CO in the gas mixture: negative influence on the overall reduction behavior and metal quality.	[128]
Biochar based self-reducing pellets	Working volumes needed up to 6000 m^3	[129]

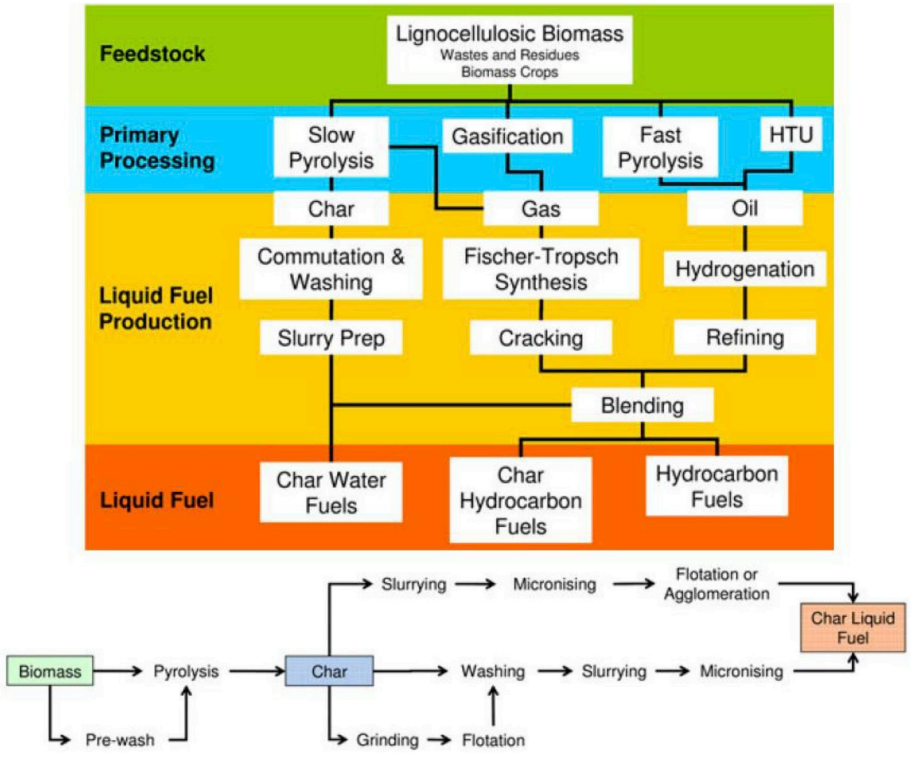


Fig. 4. Pathways from biomass-derived chars to liquid fuels (Reproduced with permission from Ref. [133]).

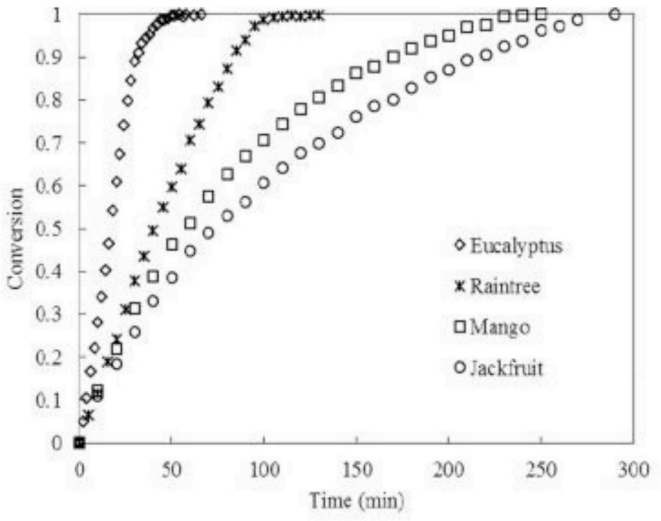


Fig. 5. Conversion of different biomass-based chars for CO_2 gasification at 800 °C (Reproduced with permission from Ref. [139]).

from biomass, in order to produce fuel of higher quality.

3.2. Gasification of biomass derived chars

3.2.1. Gasification mechanisms

Gasification is a thermochemical process that converts carbonaceous materials into useful products, such as gaseous fuels or chemical feedstock. This section focuses on power and biofuel recovery by using already available gasification technologies.

Gasification of biomass char includes several exothermic (methanation, steam-methane reforming) and endothermic reactions (oxidation, reduction) between the char and the gasifying agents (water, CO_2, O_2), in order to convert it into gaseous by-products (mainly H_2 and CO), also called syngas [138] (Fig. 5).

The first step of the process is pyrolysis, during which the char material is decomposed into secondary chars (carbon and ashes), gases (CH_4, CO_2, CO) and tars, at around 300–650 °C in the absence (or very low concentration) of oxidizing agents. The residual solid matrix, obtained after pyrolysis, is then gasified (usually in the 700–1000 °C range) with an external gasifying agent CO_2, H_2O, O_2, air, to produce H_2 and CO (syngas).

Acquiring information on the char reactivity is necessary to optimize the gasifier. Biomass derived chars are more reactive, present a higher content of volatiles, and require lower gasification temperature than other carbonaceous materials, like coals and raw biomass (Table 7).

3.2.2. Gasification reactors and applications

The reactors adapted to the gasification of chars can be classified into 5 main categories (Fig. 6), with specific range of operation conditions:

- Fixed/moving bed (updraft, downdraft and cross-draft bed)
- Fluidized bed (bubbling, circulating)
- Entrained flow
- Rotary kiln
- Plasma gasifier

Such technologies allow to capitalize the use of biomass derived carbon materials. For example, a power plant of 4800 kW electricity generation power, based on wood char gasification technology (temperature range 900–1000 °C), was built in the framework of a sawmill project at Guyana; the objective was to satisfy the power requirements of a sawmill industry (located at Mabura Hill), and the nearby township [148]. Another similar plant was also implemented in Chacco (Paraguay). The capital cost of such power plants was about 15–20% lower than that of a steam power generation plant.

Pellets of corn cobs chars were co-fired with coal in a 17-MW Willmar municipal power plant (by Chippewa Valley Ethanol Company) in Benson with the help of the Agricultural Utilization Research Institute in Minnesota (USA). This procedure succeeded to decrease the power plant emissions and to reach the new emission limits directives [149].

Small updraft and downdraft gasifiers, able to utilize biomass derived char as fuel to operate vehicles, boats, trains, and small electric generators, were developed during the second World War. These gasifiers can also be coupled with diesel engines to produce electricity. The replacement of up to 70% of the petroleum derived fuels with syngas, for operating stationary engines, is a worthwhile investment, especially for isolated areas [150].

Transforming char into fuel gas has been also successfully tested on a pilot scale entrained-flow gasifier by Suncoal Industries GmbH, in cooperation with the Technical University of Munich (Germany), in 2017. Landscape management waste products, garden waste and other similar materials from agriculture, horticulture and food production, were at first converted into char and then into a fuel gas for feeding an engine combining a heat and a power unit [151].

Chemical looping gasification is a promising new technology that can produce high quality and low cost syngas. The economic gain is in particular due to the possibility to avoid the use of pure oxygen and to the limited use of high temperature steam. As a reference, the works of

Table 7
Biomass-based char application in gasification.

Biomass based char	Main conclusions	Ref
Wood char	The increase in heating rate (from 1 to 1000 °C/s) leads to faster gasification rate and to a more reactive solid and higher ash catalytic activity.	[140]
Biomass derived fuel (BDF) produced from rice straw pyrolized at 600 °C Refuse derived fuel (RDF) composed of municipal solid waste and sewage sludge pyrolized at 600 °C	BDF char is more porous and active than RDF char, due to the larger total surface area (around 209.7 m^2/g) and the lower ash content (10 wt.%) Activation energies under gasification conditions were 119.5 kJ/mol for the BDF char and 137.9 kJ/mol for the RDF char. Longer residence time at high temperature during char production may also reduce its reactivity.	[141]
pistachio nut shell (PNS) char	Char gasification reactivity is enhanced in the Na > Ca > Fe > K > Mg > raw char order (in a bench-scale reactor)	[142]
wood char	Steam-gasification: 2–5 faster than CO_2 – gasification and gives a higher calorific value of the produced syngas.	[143]
RDF-derived char	Reactivity is increased by enhancing the partial pressure of steam from 0.333 to 0.667 bar, at 850 °C	[144]
pure corn stover char	The reactivity to CO_2 is affected by temperature and content of CO_2. Char conversion rates increases by increasing the temperature and the CO_2 concentration.	[145]

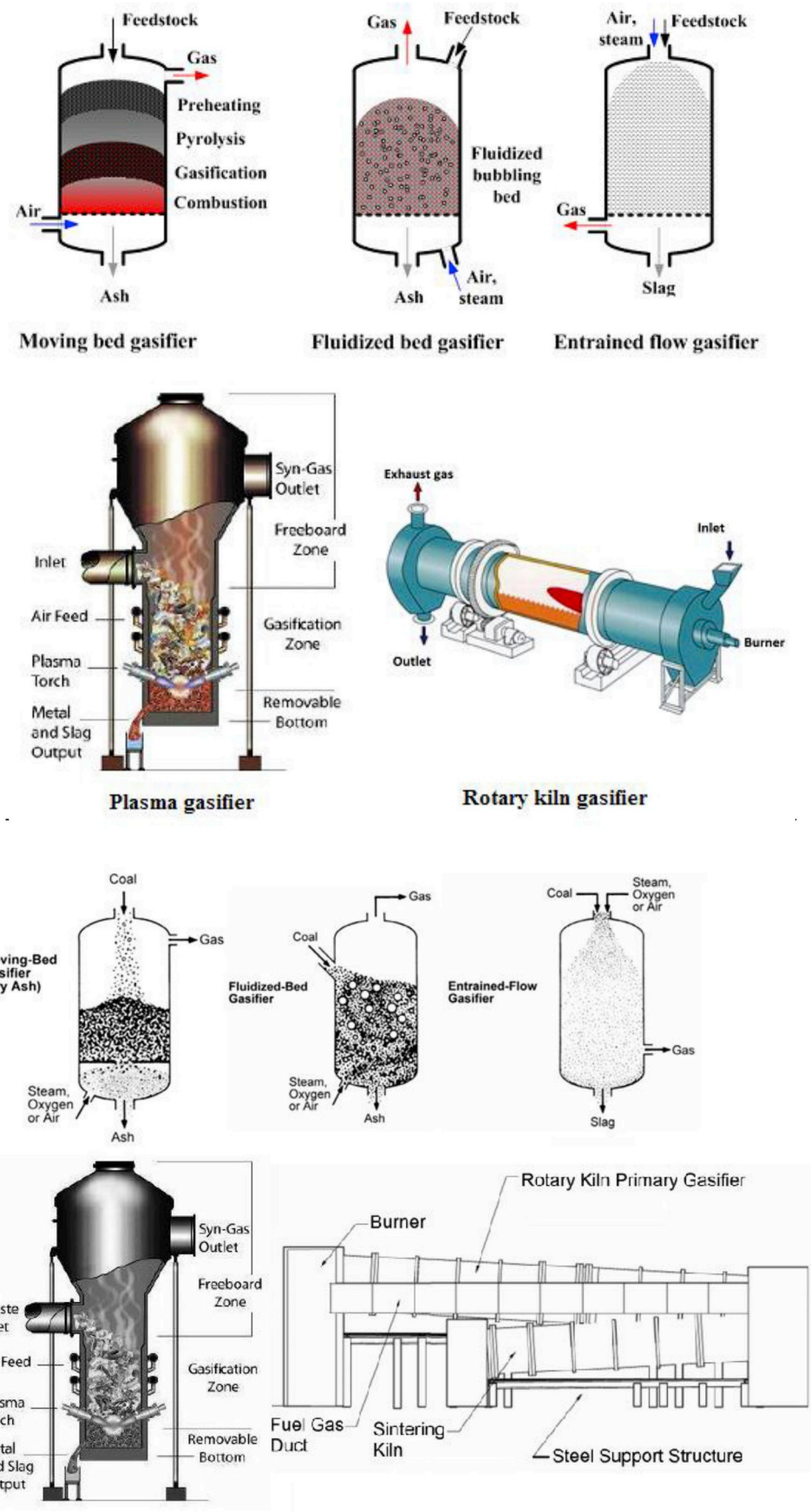


Fig. 6. Types of char gasifiers (adapted from Refs. [146,147]).

Huang et al. (2017) have to be cited; the authors enhanced biomass char conversion by using a highly active Fe—Ni bimetallic oxide ($NiFe_2O_4$), as oxygen carrier. The thermodynamic calculations predicted that the gasification efficiency of the biomass derived char might attain the maximum value at OC/char molar ratio of 0.3 [148]. Using the same technology, CO_2-gasification of char in presence of oxygen carriers significantly increased the conversion rate that was proved to be governed by mass transfer, rather than by kinetic limitations [149].

3.2.3. Gasification performance and emissions

In order to evaluate the performance and the efficiency of gasification systems, the following parameters are commonly used [152,153]:

- Cold gas efficiency

$$CGE = \frac{m_{syngas} \times LHV_{syngas}}{m_{fuel} \times LHV_{fuel}} \times 100\% \quad (8)$$

- Hot gas efficiency

$$HGE = \frac{m_{syngas} \times LHV_{syngas} + m_{syngas} c_p (T_f - T_0)}{m_{fuel} \times LHV_{fuel}} \times 100\% \quad (9)$$

- Carbon Conversion Efficiency

$$CCE(\%) = 12 \times Y_{dry\ gas} \times \left\{ \frac{[CO + CO_2 + CH_4] + 2 \times [C_2H_2 + C_2H_4 + C_2H_6]}{22.4 \times C} \right\} \times 100\% \quad (10)$$

- Energy Conversion Efficiency

$$ECE = \frac{m_{syngas} \times LHV_{syngas}}{P_{plasma} + m_{fuel} \times LHV_{fuel}} \times 100\%, \quad (11)$$

- Specific Energy Requirements

$$SER = \frac{P_{plasma}}{m_{syngas} \times M_{syngas}}, \ [kJ/mol \ or \ kJ/kg \ or \ kWh/kg], \quad (12)$$

where

m_{syngas}, mass flow rate of syngas (mol/s),
M_{syngas}, molar mass of syngas (kg/mol).
m_{syngas} and m_{fuel}, mass flow rates of product gas and feedstock (kg or Nm^3).
LHV_{syngas} and LHV_{fuel}, net calorific values of product gas and feedstock (MJ/kg or MJ/Nm^3).
$Y_{dry\ gas}$, dry gas yield in Nm^3 per kg of dry feedstock (Nm^3/kg).
c_p, the specific heat capacity (J/kg K),
T_f, the temperature at the gasifier exit (K).
T_0, the temperature of the fuel (feedstock) entering the gasifier (K).
P, plasma torch power (W).

The value of CCE gives an indication of the amount of unconverted material, thus providing a measure of the chemical efficiency of the process. ECE is very similar to the CGE, but includes external energy input (all thermal process). In the case of plasma application, SER is the ratio between the input electrical power, used by plasma, and the amount of the produced syngas.

A drawback in the application of gasification are certain negative effects towards environment and human health, such as the release of dust, biomass ash, fly ash/char and hazardous gases. On the other hand, gasification presents environmental and social benefits as enlightened by Evangelisti et al.. The authors showed the lower environmental impact of gasification, when compared to conventional municipal solid waste char treatment technologies, in terms of carbon footprint, global warming, acidification, eutrophication, photochemical ozone creation, and human toxicity potentials [152]. Indeed, by applying gasification technologies, SO_2 emissions were divided by 4 and NOx reduced of 33%. Watson et al. (2018) reported that particulate matter (PM2.5) emissions were 3 times lower for gasification than for combustion, particularly due to the lower NOx emissions. NOx emission were respectively of 0.05 and 0.15 kg PM2.5 eq. for a moving-grate combustor and a gasifier [153].

3.2.4. Barriers to gasification applications

Char gasification systems present various problems as the release of hot gases, that are usually out-streamed with dust, and that contain up to 1 wt. % of tar and particulates (mainly produced by downdraft gasifiers). If the dust is not properly removed, costly problems, connected to maintenance and reliability, can occur. The improper removal of these syngas contaminants is the main cause of gasifier engine system failure. The gas is very dirty during the system starting-up and must be burned in the gasifier until the system reaches the stationarity.

3.3. Chars based catalyst for syngas and hydrogen production

3.3.1. Tar reforming/cracking for syngas production

Catalytic tar reforming is a process used to transform the complex hydrocarbon mixture, deriving from gasification and pyrolysis, into syngas. Once purified, syngas can be used as feedstock in a large variety of reactions to produce chemicals and building blocks.

Expensive catalysts such as zeolites, transition-metal, and alkali-metal based materials are usually used for this process [154], but, recently, biomass derived chars have been taken into consideration due to their high surface area, and their relatively high minerals and metals contain (catalytically active), that are generally well dispersed on the char surface [155]. Structure and morphology also contribute to the reforming catalytic activity of chars. The catalytic behavior of various chars was then related to the presence of weak bonds and of structural defects in the char's structure that can act as catalytic active sites [156].

Biomass derived chars can also be used as catalysts' support. Syed-Hassan et al. (2016), for example, deposited cobalt and nickel on char in order to obtain active catalysts in toluene reforming [157].

Another interesting point for using chars as catalyst or catalyst support is the fact that they can be produced directly in the gasifier. In this configuration, the deactivation is not anymore a concern, since the deactivated char can be easily replaced by fresh char produced inside the reactor (Fig. 7) [158–160]. Besides, they can easily be reused for several runs without significant loss of activity. Tar valorization can also be performed on chars based catalysts issued from adsorption processes of pollutants [161]. In this approach, chars were firstly saturated of heavy metals and then used as char-supported metallic catalysts, for tar conversion.

Several researches, reported in the literature, show the high potential of bare chars in tar reforming [157,162]. Klinghoffer et al. (2015) for example, investigated the influence of the minerals content and inorganics distribution on the char catalytic activity [155]. In another work, Zhang et al. [163] produced chars by pyrolysis of mallee wood and compared the performances of unwashed and acid washed chars, showing, for both samples, a good activity in tar reforming, even if a slighter higher activity for the unwashed catalyst was measured. Syed et al. (2016) prepared char-supported nickel and cobalt catalysts tested in the steam reforming of toluene, used as tar model molecule [157]. The char precursor was constituted of palm kernel shell and its stability was shown to be good up to 850 °C, temperature at which the agglomeration of the metal particles, the loss of alkali and alkaline earth metal, and the coke deposition take part. Shen et al. (2014) performed in-situ tar conversion with very high tar conversion (about 93%), during gasification by using a rice husk char as support for nickel

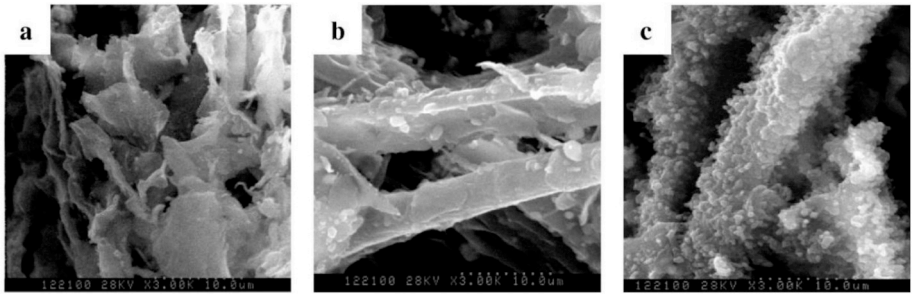


Fig. 7. SEM images of char after the experiment at 700 °C under microwave heating. (a) Fresh char; (b) char from toluene reforming; (c) char from toluene cracking) (Reproduced with permission from Ref. [159]).

and iron species [162].

Although biomass derived chars as catalytic materials showed good performances, their relative low activity and mechanical resistance, compared to conventional catalysts, still restrain their application panel. Indeed, the relocation and agglomerations of metal and inorganic species, dispersed in the biomass derived chars, and the coke deposition, during the reforming process, cause the poisoning of the catalyst active sites, the blocking of the char pores, and the decreasing of the surface, thus lowering the catalytic activity [157,162,164,165]. During reforming, chars can lose oxygenated species due to ring condensation, consequently inorganics and metals can be displaced in the char structure and agglomerate [165].

3.3.2. *Hydrocarbons/oils reforming (hydrogen production)*

Biomass derived chars can be also valorized in the production of hydrogen, a very promising and sustainable alternative to fossil fuels, as energy vector. Hydrogen can be obtained by further reforming of the liquid and gaseous phases produced during the pyrolysis, gasification, and tar reforming processes.

High hydrogen yields, of around 89%, were obtained by bio-oil steam-reforming, using alkali- and alkaline metallic-rich chars as catalyst (Fig. 8) [166]. A hydrochar issued from a macroalgae was used as catalyst in the hydrothermal gasification of the same substrate (the Clodophora glomerata) in order to enrich with hydrogen the gas phase [167]. Various chars, deriving from different biomass sources, have been used as catalyst supports, to prepared Ni-based catalysts [168]. Those prepared on cotton-derived char, presented the highest hydrogen yield (64% H_2 in the gas phase), while rice-derived chars showed lower performances.

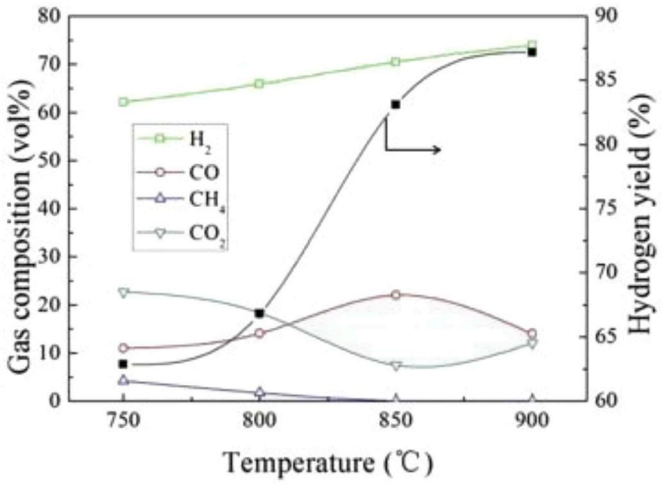


Fig. 8. Effect of temperature on hydrogen yield from wheat straw char gasification (Reproduced with permission from Ref. [166]).

4. Energy storage using biomass based chars

Even though the use of renewable energy sources is an up-to-the-minute solution, security and supply uncertainties, related to their intermittent character, still remain open issues. Storage systems are the solution to these concerns. Whether it is converted, harvested or produced, energy accumulation and supply must be technically and economically feasible and viable.

This section is focused on energy storage systems applying chars and/or activated carbons as adsorbents or electrodes. Among the possible storage systems, gas storage systems (hydrogen and methane) and electrochemical storage devices (supercapacitors, fuel cells and batteries), are here presented.

4.1. *Gas storage by biomass derived chars*

Methane and hydrogen are among the cleanest gaseous fuels. Currently, their storage methods are costly and risky. Indeed, the storage of H_2 and CH_4 in liquid state requires cryogenic devices, and special tanks and pressurized bottles (700 bars), that requires very expensive compression processes, are needed for the storage in gas phase [169].

Storage at low pressure and normal temperature in a solid matrix can be a good alternative, but only if the material presents high volumetric storage density. High specific surface area, high porous volume, tunable pore size distribution, as well as variability in the surface chemistry, are also desired features for gas storage applications.

Several biomass precursors have been explored (Table 8), but simple pyrolysis of biomass does not provide carbon materials with surface area higher enough and, in most part of the cases, an activation step is requested in order to develop the porosity. Activated chars are usually preferred over zeolites and carbon nanotubes in industry, due to their simple synthesis, the possibility of tailoring the pore distribution and to perform chemical functionalization, as well as for their low cost (if produced starting from biomass) [170]. Mainly two types of activation procedures are used: the physical activation by CO_2 or water steam, and the chemical activation by KOH, H_3PO_4, etc. The adsorption isotherms of methane of activated carbons prepared by modification of chars issued from sustainable biomass are reported in Fig. 9 [171].

It is generally accepted that an efficient adsorbent for the storage of methane must have a high specific surface area (from 1000 up to 3000 m^2/g), and a pore size distribution in the 1–2 nm range, with a micropore volume of at least 85% of the total pore volume.

Examples of precursor materials used to obtain the required characteristics are rubber seed coats, olive stones, coconut shell, oil palm fiber, almond shells, sugarcane molasses, and corncobs [172]. Activated carbons can be optimized for methane storage by testing several activation conditions (Table 8).

For H_2 storage targets, parameters, such as the carbon precursor type, the activation agent type and amount, the activation temperature and time, are varied to design efficient adsorbents (Table 9). Chemical

Table 8
Biomass based activated carbons for methane storage.

Adsorbent	Optimal activation conditions	Ref
Corn cobs based AC	Activation of temperature 550 °C for 60 min and impregnation with KOH/char at 1:1 ratio: methane adsorption capacity increased from 25 v/v up to 120 v/v at 25 °C and 3.44 MPa	[173]
Cellulose based AC	150 v/v at 298 K and 3.5 MPa	[174]
Candied chestnut industry waste based AC	Best methane storage capacities for the samples with high BET surface area. Physical activation methods: a higher activation degree resulted in a development of the porosity thus resulting in a higher surface area. Chemical activation: low activation temperature (700–800 °C) and high activation ratio/precursor: higher amount of narrow micropores (< 0.8 nm)	[175]
Synthetic AC	Simulation prediction: maximum storage capacity of AC 209 v/v at 3.4 MPa	[176]

activation with KOH is the most used methodology since it produces highly microporous activated carbons with well-developed surface areas (up to 3700 m^2/g [173]), in shorter time and at lower activation temperatures than those used in physical activation processes. However, as negative point, the treatment with KOH requires a supplementary washing step, in order to remove the impurities introduced during the activation process.

By analyzing Table 9, it can be noticed that, at room temperature, the hydrogen adsorption capacity is very low (the maximum achieved capacity at room temperature and high pressure is only slightly higher than 1 wt%, even when the surface area of the carbon is very high (~3000 m^2/g)). Storage devices working at cryogenic conditions and high pressure (20–209 bars) gave better results, in term of storage capacity (up to 8.1 wt.%), than storage devices working at atmospheric pressure. Further investigations brought to the conclusion that the H_2 storage capacity is more clearly correlated to the presence of ultramicropore volume (volume of pore with size < 0.7 nm) than to the surface area of carbon materials [114,115]. Nevertheless, solutions requiring low temperatures and high pressures cannot be yet applied due to the high costs, when compared to the current available technologies.

4.2. Electrochemical storage by biomass derived chars

The use of different energy storage devices in specific applications is connected to the type of the constituent material of the electrode, generally carbon materials. Carbon electrodes present a high added value (selling price from US $1500 to US $5000 per ton), especially for those used in electric arc furnaces for aluminum production and metal recycling [132].

The use of biomass-derived carbon materials, as electrodes for energy storage devices, is increasing, and many efforts are made in order to improve their specific surface area, their electric and ionic conductivity, as well as their mechanical and chemical stability. Capacitors, batteries (lithium–sulfur; lithium-ion and sodium-ion batteries), fuel cells, etc. may all respond positively to the need of

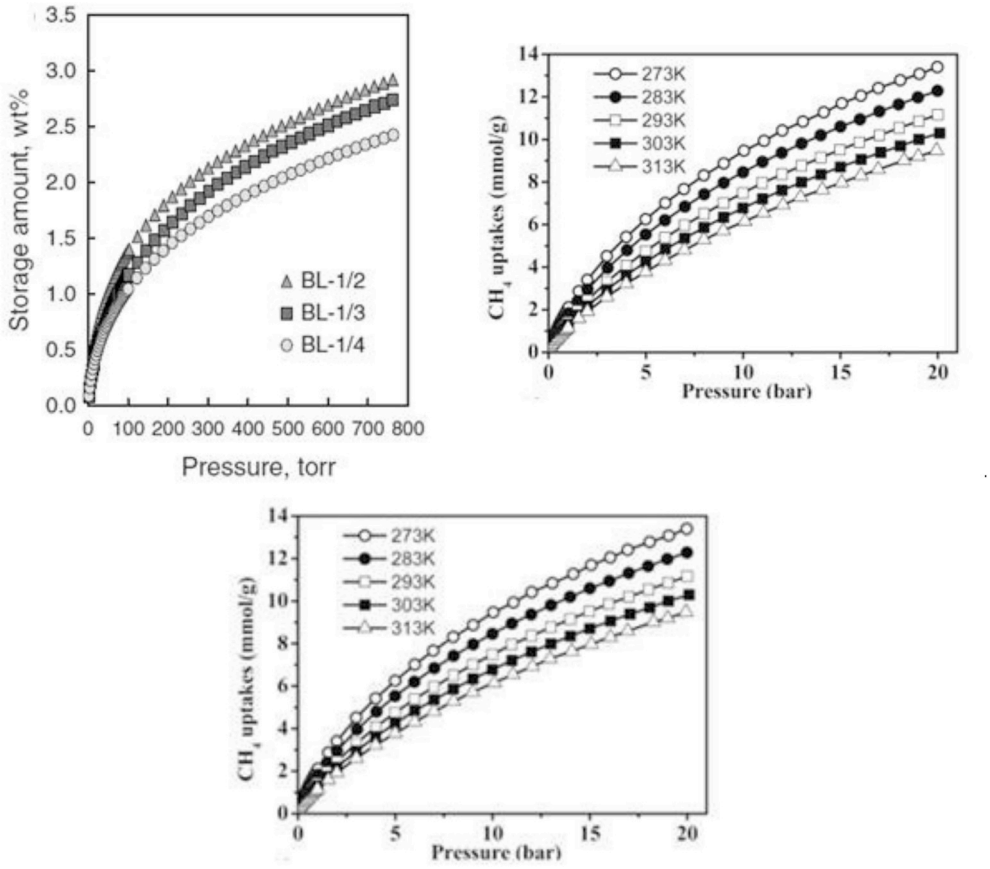


Fig. 9. CH_4 adsorption isotherms on starch chars (CO_2-activated at different temperatures) (Reproduced with permission from Ref. [171]).

Table 9
Hydrogen storage by biomass based chars.

Precursor-Activating agent-T(K)-(bar)	SSA (m^2/g)	Vμ (cm^3/g)	H_2 capacity storage (wt%)	Ref
Cellulose-KOH-298 K-20 bars	3771	–	0.5	[177]
Olive pomace-KOH-298 K-204 bars	1269	0.48	1.22	[178]
Jute fibers-KOH-303 K-40 bars	1224	0.43	1.2	[179]
Tamarind seeds-KOH-303-60 bars	1784	0.64	1.36	[180]
Coffee shell-KOH-298 K-140 bars	3149	–	0.91	[181]
Olive bagasse−CO_2−298 K-200 bars	1185	0.45	0.63	[182]
Fruit bunch−CO_2−77 K-1bar	687	0.297	1.97	[183]
Beer lees-KOH-77 K-1bar	1927	0.70	2.92	[184]
Rice husks-KOH-77 K-1bar	2682	0.792	2.85	[178]
Cellulose-KOH-77 K-1bar	3771	–	3.9	[185]
Starch−CO_2−77 K-1bar	3281	1.1	2.3	[171]
Fungi-KOH-77 K-1bar	2137	0.87	2.4	[186]
Corncob-KOH-77 K-1bar	3708	1.14	3.2	[187]
Chitosan-KOH-77 K-1bar	2919	1.19	2.71	[188]
Hemp Stem-KOH-77 K-1bar	3078	1.13	3.18	[189]
Corncob-KOH-77 K-40 bars	3708	0.59	5.80	[190]
Cellulose-KOH-77 K-20 bars	3771	–	8.1	[177]
Olive pomace-KOH-77 K-25 bars	1269	0.48	3	[191]
Olive pomace-KOH-77 K-209 bars			6.11	
Activated Carbon-KOH-77 K-20 bars	3190	1.09	7.08	[190]
Olive bagasse−CO_2−77 K-25 bars	1185	0.45	2.59	[182]
Starch−CO_2−77 K-20 bars	3281	1.1	6.9	[171]
Fungi-KOH-77 K-20 bars	2137	0.87	5.0	[186]
Corncob-KOH-77 K-20 bars	3708	1.14	5.5	[187]
Chitosan-KOH-77 K-40 bars	2840	1.06	5.01	[188]
Chitosan-KOH-77 K-20 bars	2919	1.19	6.77	
Melaleuca bark-KOH-77 K-10 bars	3170	1.07	3.18	[192]

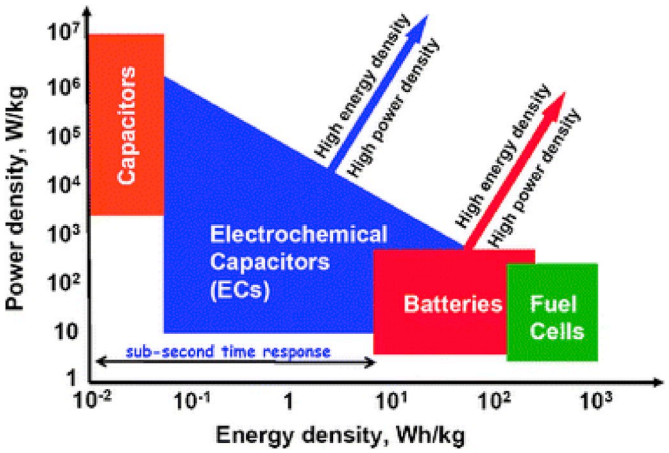


Fig. 10. Common energy storage devices [193] (Reproduced by permission of The Royal Society of Chemistry).

electrochemical energy storage development (Fig. 10).

4.2.1. Supercapacitors

Supercapacitors, also known as electrochemical capacitors or electric double-layer capacitors, are energy storage devices exploiting charge accumulation in the electric double-layer. They can be used as continuous power sources in electric vehicles, digital communication systems, etc. They are different from batteries because the charge is stored in a physical manner, thus limiting the energy density (few Wh/kg). However, the lack of electrochemical reactions ensures very high power density, quick charge/discharge capability, and long cycle life.

Activated carbons are ideal candidates as electrode material for supercapacitors. Different kinds of biomass can be used as precursors for carbon (Table 10), provided that their carbon matrix is microporous (< 2 nm) and mesoporous (2–50 nm) at the same time. Indeed, mesopores facilitate mobility of electrolyte ions, while micropores store the transferred charge.

Table 10
Supercapacitors performance of electrodes made from various biomass-based char precursors.

AC (biomass char-activation agent-activation temperature)	SSA (m2/g)	Capacitance (F/g)	Ref
Waste coffee beans-ZnCl2-900 °C	1019	368	[194]
Sunflower seed shell-KOH-800 °C	2509	311	[195]
Banana fibers-ZnCl2-800 °C	1097	74	[196]
Sugarcane bagasse-ZnCl2-900 °C	1788	300	[197]
Coffee shells-ZnCl2-900 °C	842	158	[198]
Neem dead leaves,-,-	1230	400	[199]
	3404	273	
Corn grains,-,-	3420	257	[200]
oil palm fruit bunches,-,-	1656	111	[201]
Sorghum pith-NaOH−	35	320	[202]
Cotton stalk-H3PO4-800 °C	1481	114	[203]
Coconut kernel-KOH-600 °C	1200	173	[204]
Rice husk-ZnCl2,-	1442	243	[205]
Bamboo-Steam-800 °C	1532	228	[206]
Recycled paper-KOH,-	416	180	[207]
Coconut shell-Steam-800 °C	1532	228	[208]
Pistachio shells-KOH/CO2-780 °C	2145	122	[209]
Waste tea leaves-KOH,-	2841	350	[210]
Water hyacinth-KOH/microwave assisted,-	1010	179.6	[211]
Water hyacinth-ZnCl2,-	579.94	472	[212]
Water hyacinth-KOH-800 °C	1308	273	[213]
Celtuce leaves-KOH,-	3400	273	[204]
Tobacco stem-KOH,-	3326.7	190	[202]
Tobacco rods-KOH-800 °C	–	286.6	[214]
Hemp back-KOH-800 °C	2287	106	[215]
Argan seed shells-KOH,-	2100	335	[216]
Brussel sprouts-KOH-800 °C	2410	255	[217]
Flax textiles-MnO2,-	683.73	46.54	[218]
Kenaf stem-MnO2,-	416	17.3	[219]
Mollusc shell,-,-	1696	8.47	[220]

Although activated carbons are well established in supercapacitors industry, the limit for further improvement as material in the energy accumulators' field is probably attained. In fact, their performance is hindered by the dominance of micropores that slow-down the diffusion of the electrolyte ions. Besides, their preparation is very complex (setting and monitoring of equipment, …), costly (need of high temperature steam, expensive chemicals, …) and hazardous (use of metal chloride salts, …). For this reason, the optimization of the preparation processes of biomass-derived carbon materials, that could substitute the traditional carbons as effective electro-active materials, remains an open issue.

4.2.2. Batteries

Batteries (Lithium−Sulfur; Lithium – ion; Sodium – ion) are well-known energy-storage devices, in particular thanks to their high energy densities. However, each of these batteries present some limitations that can be overcome by substituting them with biomass derived chars.

For example, the low electrical conductivity of sulfur in Li−S batteries is the cause of low cycling stability. It has been demonstrated that incorporating sulfur into different biomass based carbon matrixes could not only improve the conductivity of the sulfur species, but also accommodate the volume expansion of sulfur during cycling [221–224].

As another example, graphite in Li–ion and Na–ion batteries present low capacity and cycling rate, that are not compatible with the use in power advanced systems, such as electric or hybrid vehicles. Anodes technology is demanding of novel hard carbonaceous materials, and biomass chars can act as precursor [225–228]. In particular, biomass-derived carbons with highly-developed surface chemistry, and

especially those containing N-functional groups, could start the redox reactions and consequently boost the specific capacitance (of few orders of magnitude) [228]. To do this, Li et al. (2014) converted N-rich bio-precursor (chicken egg whites) into high-content functionalities and high surface area capacitor electrodes. Knowing that an activation temperature higher than 600 °C can bring to the loss of nitrogen functionalities, the authors proposed an alternative process starting from denatured proteins, which did not require the use of templates. Low-temperature activation under argon flow produced highly microporous material (SSA and total pore volume up to 1405 m^2/g and 0.73 cm^3/g, respectively), containing high amount of N− and O-functional groups. The asymmetric capacitor, assembled with this AC and $NiCo_2O_4$/graphene positive electrode, presented higher energy density (48 Wh/kg) than capacitors prepared starting from commercial activated carbon (23 Wh/kg) [229].

4.2.3. Fuel cells

A fuel cell or Direct Carbon Fuel Cell (DCFC) is an electrochemical energy-storage device in which the chemical energy of carbon is converted to electricity by oxidizing a solid carbonaceous material into carbon dioxide. An innovative application of biomass derived char as a fuel was tested in such kind of device. Chars were integrated in Molten Carbonate Fuel Cells (MCFC) to produce electricity. The chemical energy contained in the char was directly converted to electrical output. At high temperatures, DCFC are able to transform the solid matrix of the feedstock into gases, which represents a thermodynamic advantage. The potential of coupling fuel-cell stack with biomass char was proved for power generation, particularly thanks to the high power density levels achieved on DCFC, 60–70% higher than that of mineral coal, under the same conditions [229].

Dudek et al. (2013) tested charcoal powder (by in-situ produced pyrolytic chars from beech wood and from Carbo medicinalis) as potential fuels for carbon fuel cell equipped with solid oxide electrolyte. The three samples presented graphite-like phases of carbon, although their structure was full of defects and contained amorphous carbon. They provided sufficiently high power density (50–100 mW/cm^2) under loading. The authors concluded that using anode materials with higher activities in C and CO oxidation than those currently used (Ni-YSZ) would improve the performance of such type of fuel cells for long duration of loading [231].

Lim et al. (2014) also found that, palm shell pyrolyzed at 750 °C, with heating rate of 10 °C/min and residence time of 1 h, yielded a highly potential char for DCFC applications [230]. Other researchers investigated biomass chars to support Pt or Fe species in proton-exchange membrane fuel cells (PEMFC) electrocatalysts [231], in microbial fuel cell (MFC) [232] for the oxygen reduction reaction [233], and in alcohols electro-oxidation [234].

5. Costs analysis

The char production performance and costs are closely related to the feedstock characteristics, conversion techniques, logistics (handling, densification, transport) and to the final use. Therefore, each combination of feedstock, conversion process, and application is a unique scenario. These singularities increase the complexity in determining the best strategy for sustainability.

In order to optimize such a strategy, studies on various combinations of biomass resources, conversion technologies, and utilization systems have been reported. Unfortunately, these studies are not very useful for financial analysis, because they deal with too small scale frameworks or they do not take into consideration the feedstock collection and pretreatment, or the char transport and utilization in large pilot facilities.

Anyway, some conclusions can be tentatively reported. For example, biomass residues, farming and agro-industrial wastes have lower financial cost, if compared to energy crops and algae, as the costs of collection are minimized, and those of water consumption, plantation, harvesting, etc. related to crops are suppressed.

Homagain et al. (2016) found that, using as feedstock forest harvest residues, saw mill residues, and underutilized trees, the 25-year average annual cost inventory of 1 MWh pyrolysis plant (k$ 381.5 per year) was the most expensive step of the production process, followed by storage/processing (k$ 237.2 per year including pelleting). The transportation costs varied between $ 98000 and 83000 per year. The average annual cost of operation from all scenarios adopted by the authors was k$ 988.55, with an actual value of k$ 532.8 [235].

As for the charring processes, gasification is probably the technique that cannot yet achieve successful commercialization due to high investing capital and operational costs of the gasification plants (construction sites, biomass pre-treatment units, reactors, producer gas conditioning systems, engines or gas/steam turbines, etc.).

In iron and steel industries, the development of large-scale applications, using chars as reducing agents, faces economic barriers. Indeed, the capital cost of a proposed charcoal plant was estimated to be $111 million, with costs for pyrolysis unit (39%), engineering and construction (21%), storage (18%) etc. Total operating costs were estimated to be $446 per ton and the average charcoal cost at $243 per ton [236].

The use of biomass char as catalyst precursor is motivated by their low cost and the easy recyclability of the supported metal. However, the development of this application is limited by relative low efficiency and low resistance to abrasion, compared with the available commercial catalysts. Moreover, the engineering of the biochar to enhance one or the other of the char properties would increase the cost.

6. Practical implications, challenges and recommendations

Sustainable biomass based chars' production, trade and usage are important means for satisfying the energy demand. The use of biochars contributes also in generating income for individuals (rural), communities (in low and medium income countries), and government (through the issuance, licenses, business permits, etc.). It also saves the country foreign exchange that would otherwise be used to import fuel, even though supply chain is mostly informal [110]. Furthermore, the char production is a labor-intensive process. Indeed, people could be hired in different phases of char making, distribution, marketing and utilization, etc.

Despite of all this, only little attention has been oriented to such industry. Technological improvements in char production and their use in the energy field are in full development and may lead to modernization of this economic segment. This implies to obtain high efficiency processes with low environment impact.

Even if the main challenges for each energy application of chars have been discussed in the related section, a global picture of the more common issues is presented as follows. One of the main drawbacks of char application in energy systems (production and storage) is the parent raw biomass supply. Biomass sources are often available in small batch spread out over a large geographical area, resulting in challenging or/and uneconomic collection systems. Besides, for financially viable operation, the feedstock should present physical and chemical properties suitable to be transformed into char (dry, unmixed, homogeneous, etc.). Non-homogeneous and humid feedstocks require appropriate technologies characterized by high capital investments. The char markets are also weakened by the lack of reliable information.

A recommendation for developing this sector is to involve the society and in particular rural communities for identifying any potential resource that can act as feedstock. Moreover, the performance of small char production systems should be improved, in particular due to their utility in the development of poor countries. These improvements will also indirectly help in establishing eco-friendlier processes. The major progress in the energetic usage of biomass based chars is related to the char engineering (by different modification methods). Finally, an

information database system needs to be put in place and available to all char producers, traders, users, to develop the sector.

7. Conclusions

Energy scarcity, its supply uncertainties and the related environmental issues are concerns that can be solved in a sustainable way by using biomass derived chars. To evaluate the role of chars in future development in the energy field, an overview of the main research studies in the field was presented in order to identify the actual trends and highlight the future challenges.

Various observations can be pointed out from the survey carried out in this review article.

First, char issued from biomass can be used in all industrial applications similarly to other fuel types (whether they are solid, liquid or gaseous), particularly in drying, gasification, steam and electricity generation, firing, etc. At the present, most studies are concentrated in the laboratory scale. Industrial scale production and usage of biomass chars are still in their early days and require more engineering support. Chars' modification and minimizing the processing costs are the keypoints for promoting the biomass-derived chars' industry. A deep understanding of biomass based chars' properties is fundamental to produce biochars with specific features adapted to target applications.

Thanks to their high calorific values, biochars are promising energy vectors that can be used in combustion and gasification processes. Biomass-based char can be used in boilers to produce directly heat and/or steam to generate electricity; but co-firing with more conventional fuels often presents higher efficiency, than when used alone. Moreover, such a solution often decreases the initial investment, since already existing facilities are applied.

Even if the gasification technology is mastered since decades, it needs to be further developed for being implemented in more advanced applications. The energy recovery from gasification, can be in the form of heat, electricity, combustible gas, transportation fuels and chemicals. These outputs can supply small scale units at remote locations, as well as large scale plants.

The quality of the outputs products of thermal conversion processes could be enhanced by purifying the tar, the oil and the hydrocarbon by-products, by reforming or cracking, using sustainable catalyst supported on biomass derived chars.

Chars have attracted also considerable interest in many energy-related applications, such as energy storage (in supercapacitors and batteries), catalysis/electrocatalysis, absorption, and gas separation and storage, due to their abundance, chemical and thermal stability.

More precisely, biomass derived chars show good properties of energy storage thanks to developed pore structure and large specific surface area, which improves the electrode capacitance (up to 250 F/g). Their good electrical conductivity permits to achieve fast charge and discharge rates, as well as potential of about 2 V. Their structure is stable at high-temperature and in corrosive media, and the cycles performance is good. Power density of the char-coated cathode reached 500 mW/m^2, comparable to that of Pt/C-coated cathode. In fuel cell systems, chars could achieve power density of about 60–70% compared to coal-based fuel cells. In catalysis applications, char can be implemented in various processes, such as syngas reforming and conditioning, bio-oils upgrading, etc.

Finally, it is important to carry out technical and economic studies, as well as life cycle assessments, in order to compare all the techniques described in the present review article. The char production performance and costs are indeed closely related to feedstock characteristics, conversion techniques, logistics (handling, densification, transport), and to the final use. Therefore, each combination of feedstock, conversion process, application is a unique case-study and increase the complexity of summarizing the biomass-derived char sector.

Declaration of interest

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