



Analytical evaluation of the performance of pyrolysis-gasification (Py-Gs) combination within hybrid thermochemical-biological biorefinery

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ABSTRACT

Thermochemical treatments like pyrolysis and gasification, were proposed to circumvent hydrolysis bottleneck of conventional 2nd generation biorefineries. Within this big-picture, the target of this article was to establish the type and amount of bioavailable matter that can be obtained through intermediate pyrolysis of biomass followed by gasification of biochar. To establish the amount of "chemical energy" partitioned among different products' chemical oxygen demand (COD), which is proportional to higher heating value (HHV) and often utilized for biological systems, was applied for the evaluation of thermochemical conversion of a lignocellulosic feedstock (fir wood). The most abundant product of intermediate pyrolysis was biochar, which retains from 33 % to 40 % of feedstock COD (with temperatures starting from 450 °C). The yield of water-soluble pyrolysis products (WS) slightly increases from 24 % at 450 °C to 27 % at 650 °C, whereas the yield of WI increases considerably with the same temperature. Pyrolysis temperature showed a minor effect on the composition of WS as revealed by GC-MS analysis of main compounds and size exclusion chromatography. Preliminary gasification experiments, performed at 850 °C under CO₂ atmosphere, provided gasification rates for different biochars, which was equal to 0.004, 0.005, 0.006 min⁻¹ for biochars obtained at 650, 550, and 450 °C respectively. Syngas obtained from gasification of 450 °C and 550 °C biochar was almost tar-free, whereas gasification of 650 °C biochar yielded a detectable amount of tars (0.4 %). Increasing the gasification temperature to 950 °C sharply increases the gasification rate of biochar obtained at 450 °C, allowing to obtain 55% conversion yield. Within the scope of hybrid thermochemical-biological (HTB) processes, the obtained results show that intermediate pyrolysis, when coupled with subsequent 950 °C CO₂ gasification of biochar, can deliver 64% of chemical energy (by COD basis) of the lignocellulosic feedstock as bioavailable constituents, which are defined to syngas and WS based on recent biological studies. Whereas downstream fermentation can process syngas and WS materials in an effective way, such yields could surpass the holocellulose-targeted methods based on hydrolysis.

1. Introduction

Lignocellulose resistance to biological conversion represents one of the main obstacles to the production of biofuels through the exploitation of waste and 2nd generation feedstock. Whether the objective is to obtain methane, ethanol, mixed alcohols, butanol or microbial oils, the main bottleneck of 2nd generation biorefineries is the hydrolysis step, which usually requires severe pretreatment (e.g., steam explosion) and subsequent chemical or enzymatic hydrolysis [1]. However, this approach allows exploiting just the holocellulose portion of biomass and suffers from high capital costs, due to the requirement of high-pressure

equipment and the slow reaction rate provided by enzymes [2].

To address these techno-economic obstacles, an alternative hybrid thermochemical-biological biorefinery (HTB) concept was proposed [3]. This concept suggests depolymerizing biomass using pyrolysis and gasification, instead of hydrolysis. Thus, feeding microbes with CO/H₂ gas [4], anhydrosugars (e.g., levoglucosan) [5] and/or water-soluble organic compounds [6–10]. To compare the performance of different thermochemical coupling, we recently created an approach based on the calculation of COD as a direct measure of chemical energy delivered to the microorganisms [11].

Intermediate or slow pyrolysis, which relies on quite robust

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technology characterized by a limited heat transfer rate, primarily transfers most of the chemical energy to the solid product, known as biochar. In contrast, fast pyrolysis, with its high heat transfer rate allows conversion of finely ground material within an advanced reactor. In this way, fast pyrolysis can yield more than 50% water-soluble (WS) pyrolytic compounds rich in anhydrosugars [12]. Another method, indirect gasification, involves performing the process above 700 °C in a CO₂ or steam atmosphere. This method can deliver up to 80% of the chemical energy as syngas. However, when applied to raw biomass, it produces a significant quantity of tars that, even at low concentrations, can be extremely toxic to microorganism [13].

Starting from the key features of pyrolysis and gasification, there could be some significant synergies between different thermochemical processes. In fact, even a poorly designed pyrolysis reactor allows to volatilize most of the chemical precursor of tars [14] and delivers a moisture-free brittle biochar that can be easily fed into a simplified coal gasifier [15].

As testified by several pyrolysis-gasification schemes previously proposed, the aforementioned approach homogenizes (for chemistry and size) variable biomass feedstock and optimizes the gasification process [15]. Nonetheless, the concept of combining pyrolysis and gasification gains particular significance within the HTB context, given that primary pyrolysis products (resulting from low-temperature pyrolysis) can serve as fermentation substrate, contributing to the overall yield of fermentable products [16]. Although the combination of pyrolysis with gasification is not new in the context of thermochemical conversion, the use of this combination within HTB technology requires establishing yield and composition of products, with particular attention to the bioavailability characteristics, which are usually not important in the context of thermochemical processes. To address this gap, the aim of this work, proposing a new HTB for the conversion of biomass into value-added products through a series of integrated processes (Fig. 1), is to assess a standardized new approach for the combined pyrolysis-gasification of biomass. This approach aims to determine the yield, bioavailability, and composition of the products obtained through the two integrated thermochemical processes applied to a lignocellulosic biomass (fir wood).

2. Material and methods

2.1. Pyrolysis and gasification

Pyrolysis and gasification experiments were performed in a fixed bed reactor system. The apparatus consisted of a quartz cylindrical reactor (710 mm length and 40 mm Ø), where biomass was inserted by a quartz cylindrical sample holder (300 mm length and 27 mm diameter). The

quartz reactor was positioned inside a tubular furnace and followed by a water-containing gas impinger and a small cyclone unit both kept at 0 °C during the experiments. A cotton trap was placed just after the cyclone unit to capture the fine aerosols before to 10 L sized laminated foil gasbag (Supel™ Inert Foil) for storing the produced gas. Besides, a peristaltic pump was positioned before the reactor and a loop line was created for gas flow by using modified polyamide tubing (ø 6 mm OD) laminated with double layer silicone and aluminum foil, for avoiding leaks of highly permeable gasses (e.g., H₂) as explained elsewhere [17]. In addition, an extra gasbag was positioned before the peristaltic pump, to be used as oxidant gas (CO₂) source, only for gasification tests (Fig. 2).

Three different temperature conditions were tested during the pyrolysis of lignocellulosic biomass experiments, namely, 450 °C, 550 °C, and 650 °C (temperature of the furnace wall). For this purpose, sawdust biomass originating from fir tree (*Pinaceae sp.*), were used as feedstock. Before each batch pyrolysis test, the fixed bed system was flushed with excess amount of N₂, for several minutes to strip away atmospheric O₂. Then, 30 g of dried biomass feedstock were compacted inside the biomass holder and inserted into the pre-heated zone (to the target final temperature). Immediately after, gas recirculation was started at 225 mL/min flowrate to sustain the fluids inflow towards to the traps and the gas collection bag. Each temperature condition was tested in triplicates under same operational conditions for 20 min long at the target constant temperature. At the end of each test, heating and peristaltic pump were stopped and the sample was cooled down quickly by moving it to the cold part of the reactor under N₂ flow (<5 min). WS liquid trapped inside the impinger and produced biochar were collected manually and stored at 4 °C until the analysis. Water-insoluble portion (WI) of condensable pyrolysis products (i.e., pyrolytic liquid, or bio-oil), also called condensable tars, dense-oil, or pyrolytic lignin (PL), were scraped away by acetone washing of each glassware unit (namely, quartz reactor, sample holder, gas impinger, cyclone, and cotton-trap) of the apparatus. Later, acetone was evaporated under N₂ from WI fraction and stored in 4 °C until analysis. Produced gases (i.e., syngas, synthesis gas, or pyrogas) were stored inside sealed air-tight gasbags.

Gasification tests were conducted in the same experimental apparatus, with each biochar material obtained at different pyrolysis reaction temperatures tested in duplicate. The pre-heated quartz reactor at 850 °C was purged with an excess amount of CO₂ gas for several minutes before moving the sample holder containing packed biochar into the hot zone. Additional CO₂ was supplied as the oxidant gas, through an extra gasbag connected before the peristaltic pump (Fig. 2). The CO₂/C ratio was set following the methodology of Sadhwani et al. [18]. The moles of CO₂ loaded at the beginning of experiments was set roughly equal to 1.5 the expected (obtained from preliminary experiments) moles of carbon reacted.

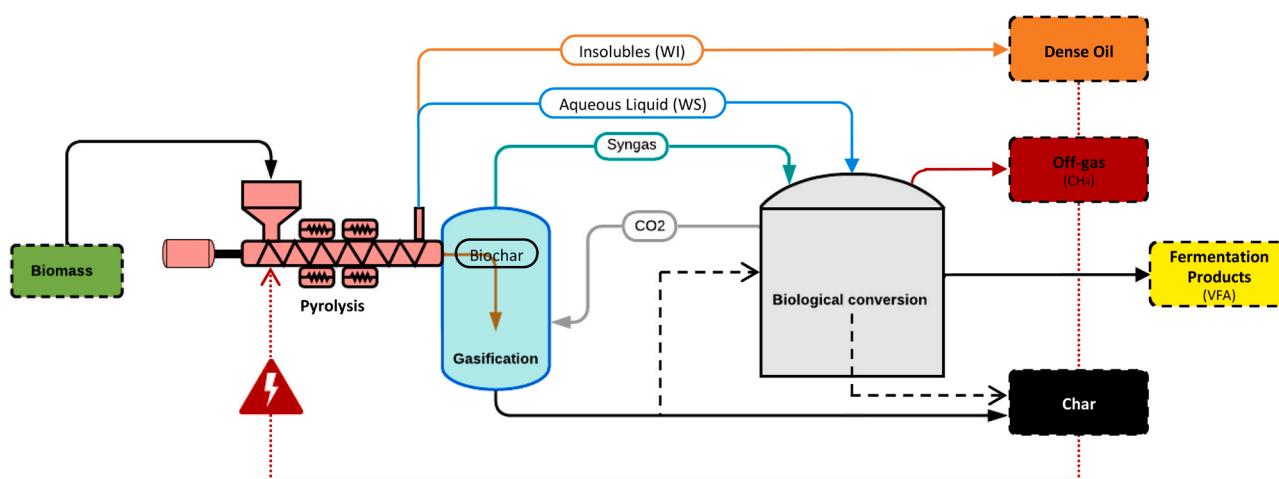


Fig. 1. Scheme of the proposed hybrid thermochemical-biological concept for the biological production of value-added fermentation products.

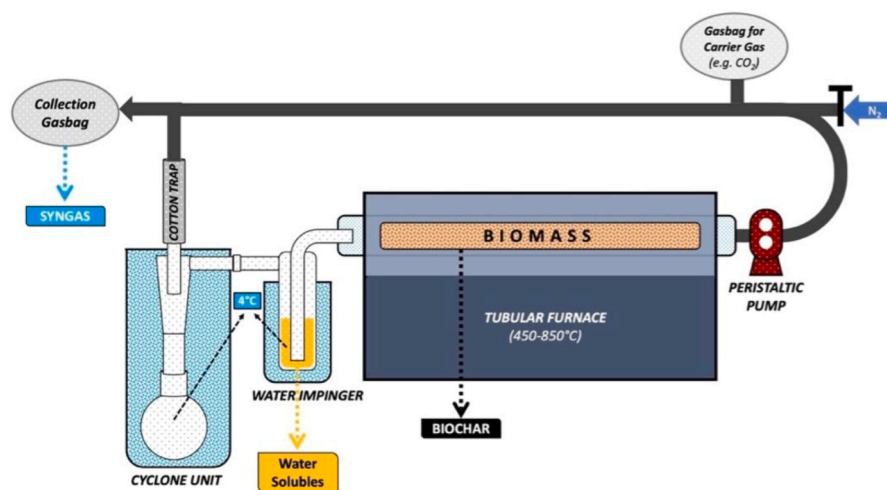


Fig. 2. Flow-diagram and units of the fixed bed pyrolysis-gasification set-up.

2.2. Analytical methods

To establish the COD yield and composition of each pyrolysis gasification product, the overall analytical scheme showed in Fig. 3 was applied. COD content of the WS liquids was analyzed through Quick-COD analyzer (LAR Process Analyzer AG) following the ASTM D6238–98 method based on thermal oxidation at 1200 °C [17]. Gas analysis through GC-TCD, molecular size distributions (MWD) via aqueous size exclusion chromatography-refraction index detector (SEC-RID) and quantification of GC-MS detectable compounds was performed according to methods detailed elsewhere [19]. Quantitation was made by using external calibrations for each target molecule by using pure compounds (Sigma Aldrich). Reactive aldehydes (e.g., hydroxy acetaldehyde) were determined by following Basaglia et al. [20] with a slight modification (DMC used as solvent). Elemental analysis (CHNS) of char and WI materials were conducted using a Thermo Fisher organic elemental analyzer (Flash 2000) with flash combustion technique [21, 17]

2.3. Rationale and calculations

1 mass unit of COD (i.e., gCOD, 1gO, gO₂) is defined as the amount of

organic matter that needs 1 g of Oxygen for complete oxidation. According to the thermodynamic principles, COD of feedstock (e.g., biomass) must be equal to the sum of pyrolysis and/or gasification (Py/Gs) outputs' COD content (given the fact of O₂ has -1.0 gCOD/g and CO₂ has a COD of 0.0, by definition). Here in this study, all concentrations and amounts of organic compounds will be mainly expressed in COD basis of which reliability and theory as initially been demonstrated by Torri et al. [11] and followed by other studies [7,17,19,22,23]. Accordingly, COD yield ($Y_{COD,i}$) of one of the Py/Gs products (e.g., syngas, biochar, WS) is defined as the feedstock's COD amount partitioned into that product. For pyrolysis processes which are conducted without oxidant, overall COD yield (the sum of all $Y_{COD,i}$) should be equal to 1, provided that there are no external COD source (no leakages).

To conduct an overall process evaluation with COD approach, as it is proposed in this study, three main data are required: COD of input ($g_{COD}/g_{feedstock}$), COD of each Py/Gs product (g_{COD}/g_i), mass yield of each Py/Gs products ($g_i/g_{feedstock}$). To be able to calculate the COD of feedstock and each Py/Gs product, several analytical methods were applied depending on the organic matters' physical availability (solid, liquid, or gas) as explained in Fig. 3. Later, mass-to-COD conversions were performed as in compliance with stoichiometry previously explained in Torri et al. [11]. For instance, gas constituents of Py/Gs

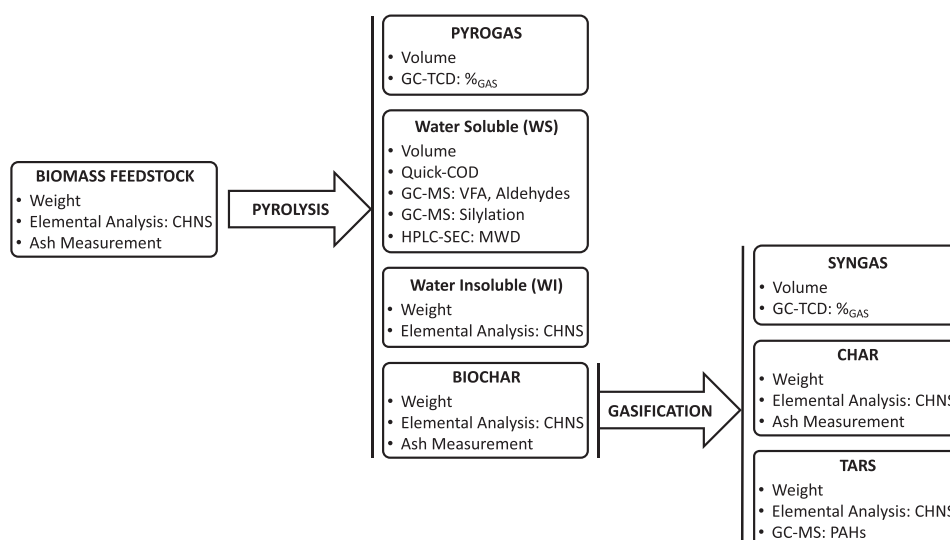


Fig. 3. Analytical characterization scheme of the study.

which are mainly H₂, CH₄, CO₂, and CO, have corresponding CODs values that are 7.9, 4.0, 0.0, and 0.6 g_{COD}/g respectively.

Here in this section, the formulation behind each COD conversion will be shared, unless it was already presented in the previous study [11]. For instance, COD yield of obtained CO gas (Y_{COD, CO}) via gasification process, was calculated according to the following formulations. Initially, mass yield of CO (Y_{m,CO}) was calculated by using the total volume of the obtained gasses (V_{Gas}), volume fraction of CO (X_{CO}) within gas mixture (i.e., syngas) obtained through GC-TCD analysis, theoretical mass density of CO (ρ_{CO} = 1.14 gL⁻¹), and the initial mass of feedstock (M_{Feedstock}). Then, Y_{COD, CO} was obtained through the second formula which is valid for calculating COD yield of any Py/Gs products, where COD_{CO} and COD_{feedstock} are the COD value of CO gas (0.6 g_{COD}/g), and feedstock biomass (for wood ≈1.3 g_{COD}/g), respectively. The full detail of the formulations behind the calculations of COD and mass yields were already presented elsewhere [19].

$$Y_{m,CO} = \frac{V_{Gas} \cdot X_{CO} \cdot \rho_{CO}}{M_{Feedstock}}$$

$$Y_{COD,CO} = Y_{m,CO} \cdot \frac{COD_{CO}}{COD_{Feedstock}}$$

Being biological conversion the target of the study, an estimation of level of toxic compounds was performed through the Toxic Units method as detailed elsewhere [13]. In brief, from the eco-toxicity basics, the amount of pyrolyzed fir that produces 50% inhibition of biological activity (IC_{50,WS}, g_{fir} L⁻¹) was estimated as:

$$IC_{50,WS} \left(\frac{g_{fir}}{L} \right) = \left(\sum_{i=1}^m \frac{Y_i}{IC_{50,i}} \right)^{-1}$$

where Y_i (kg/kg) is the mass yield of a certain pyrolysis product and IC_{50,i} is the corresponding inhibition concentration (expressed as g L⁻¹). For the calculations, IC₅₀ equal 5, 2.5 and 1 g/L was respectively assumed for carboxylic acids, furan derivatives and phenols.

3. Results and discussion

3.1. Pyrolysis at different reaction temperature

Fig. 4 shows the distribution of pyrolysis products (as gCOD_{PyP}/gCOD_{Feedstock}) at different reactor temperatures. All tests provided an acceptable COD balance with an average COD loss around 14 %. Such difference can be due to the loss of a portion of relatively volatile WI compounds due to the WI collection method here used, or incomplete collection of aerosols. The increasing temperature did not significantly affect the yield of WS (around 26±1.5 %), whereas it doubled the gas yield (from 5 % to 12 %) and increased markedly the yield of WI (from 11 % to 18 %) at the expense of the biochar, whose yield decreased from 33 % to 40 %. Such behaviour suggests that, after 30 min at 450 °C, the further increase in severity of pyrolysis mostly affects the completeness of lignin pyrolysis and de-volatilization. This pyrolytic behaviour was previously observed with similar pyrolysis apparatus [24] and fits well

with the different kinetic that characterize the thermal decomposition of holocellulose (which promptly pyrolyzes at a lower temperature) and lignin (whose pyrolysis steps, even at a slightly higher temperature, takes a longer time) [25,26].

Table 1 shows the GC-MS compounds detected in WS from pyrolysis performed at different temperatures. Through direct analysis, silylation and acetalization, the GC-MS allowed identifying above one-third (on COD basis) of the chemical constituents of WS, namely small carboxylic acids (mainly acetic acid), aldehydes and ketones (mainly hydroxyacetaldehyde and hydroxyacetone), furan derivatives, anhydrosugars (mainly levoglucosan) and water soluble phenols. The type and yield of observed chemical constituents were in line with the literature about pyrolysis of fir wood [27,28]. The overall composition is similar at all three tested temperatures, nonetheless as the reactor temperature was increased from 450 °C to 650 °C a significant increase of hydroxyacetaldehyde was detected, as previously observed for auger pyrolysis of fir wood [27] and in line with the temperature dependency of cellulose pyrolysis [29]. The yields of the most powerful inhibitors in WS, namely furan derivatives and phenols [30] were similar at three different pyrolysis temperatures, with a slight decrease from 450 to 650 °C. Considering the overall HTB concept, the evaluation of the quantitative toxicity of the pyrolysis products requires considering both yields and composition of WS. A quantitative indicator of the toxicity of WS generated can be described by the IC₅₀ of pyrolysis products, namely the mass of pyrolyzed biomass that inhibits at 50 % biological activity.

Table 1

Main GC-MS detectable constituents (as % gCOD/gCOD_{WS}) of WS obtained through pyrolysis at different reactor temperatures. The relative standard deviation of repeated analytical procedure was 15 %. ^a13 most abundant phenols detected and identified in WS.

	450 °C	550 °C	650 °C
Carboxylic acids (Σ quantified)	8.4	7.8	6.9
acetic acid	6.9	6.5	5.7
hydroxyacetic acid	0.33	0.05	0.07
propionic acid	0.78	0.81	0.76
butyric Acid	0.37	0.41	0.39
Aldehydes and ketones (Σ quantified)	7.0	9.3	10.7
hydroxyacetaldehyde	2.3	3.9	6.7
hydroxyacetone	1.3	1.3	1.1
cyclopentanone	0.12	0.11	0.10
2-cyclopenten-1-one	0.10	0.11	0.09
2-methyl - 2-Cyclopenten-1-one	0.32	0.32	0.31
2,3-dimethyl-2-Cyclopenten-1-one	0.70	1.64	0.41
1,2-cyclopentanedione	0.81	0.82	1.09
3-methyl-1,2-Cyclopentanedione	1.3	1.2	1.0
Furan derivatives (Σ quantified)	4.6	4.3	3.8
furfural	2.1	1.9	1.7
2-furanmethanol	1.2	1.1	1.0
5-methylfurfural	0.51	0.49	0.41
2-hydroxymethylfurfural	0.78	0.79	0.79
Anhydrosugars (Σ quantified)	2.9	2.4	4.1
1,6-anhydromannopyranose	0.49	0.13	0.69
1,6-anhydroglucopyranose	2.4	2.2	3.5
Phenols (Σ quantified)^a	8.3	7.1	6.6
total GC-MS quantified	31.2	30.9	32.2

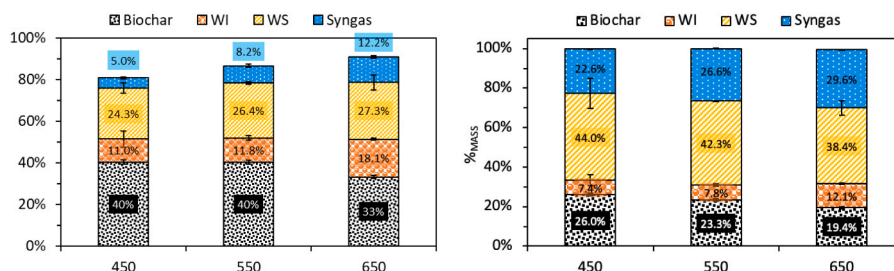


Fig. 4. Pyrolysis products yields at different temperatures by COD (a) and mass (b).

This parameter resulted in roughly identical IC₅₀ for WS, with absolute values in the of 27–30 gFir/L. Interestingly and counter-intuitive, this data is not far from the values that can be calculated for steam explosion [31] with medium severity suggesting that, although pyrolysis intrinsically yields more inhibitors than hydrolysis, the separation of WS and WI phases allows the partition of most of toxic compounds into WI.

To investigate the organic compounds which are not identified and quantified through GC-MS analysis, the WS was subjected to aqueous-phase Size Exclusion Chromatography (SEC) coupled with Refraction Index Detector (RID). Such analysis allows to obtain a non-targeted description of the molecular weight distribution (MWD) of water-soluble material that increases the refraction index of the solution, therefore detecting sugar-like compounds in WS.

The MWD (Fig. 5) of WS shows a bi-modal trend, with two molecular weight groups, hereafter named High Molecular Weight (HMW, > 1.45 kDa) and Low Molecular Weight (LMW, <1.45 kDa) compounds.

From a qualitative point of view, the SEC analysis of WS obtained at different temperatures shows a similar chromatogram, characterized by a HMW tailing peak tipping at 7 min (8 kDa) followed by a group of four LMW peaks centered at 9.6, 10.3, 11.1 and 11.8 min which corresponds to 324, 162, 96 and 60 Da respectively. To the best of the author's knowledge, in most of the previous studies, SEC was performed on whole pyrolysis oil, not solely WS portion, with tetrahydrofuran (THF), N-methyl-pyrrolidone or dimethylformamide as eluent. All the works performed with THF did not detect relevant organics with MW>1.5 kDa [32,33]. On the other hand, the use of N-methyl-pyrrolidone and dimethylformamide mobile phase revealed a bimodal MWD which is quite similar to that found in this work [26,34,35] and the parallel use of Multi-Angle Light Scattering (MALS) detector clearly demonstrated the presence of HMW [36]. As suggested by Hoekstra [33] and Harman-Ware [36] such apparent inconsistency in SEC-RID results could be actually due to specific solubility features of the HMW portion of WS which could suffer significant chemical adsorption onto the stationary phase when working with THF as eluent. This chemical adsorption can produce an artifact shift to lower MW, whereas there are no known artifacts that can shift the SEC peaks to shorter residence time (which means higher MW). Therefore, we could state that organics with MW>1450 Da form a significant portion of WS (about one third of it).

According to the MW and the UVD/RID ratio, the 7 min peak probably consists of random polymeric fragments formed by ejection during pyrolysis [37] and secondary reactions between thereof, whereas the four clearly identified LMW peaks can be identified as anhydro-oligomers (2–3 anhydrosugars units, with MW between 483 and 324), anhydrosugars-like compounds (MW between 204 and 114) and small polar pyrolysis products (e.g. hydroxy acetaldehyde or formaldehyde in the hydrated form). At the end, the comparison between the qualitative composition revealed by SEC-RID and the literature highlights some important differences.

From quantitative analysis (Fig. 6) increasing temperature from 450 °C to 650 °C slightly increases the relative amount of LMW at the expense of HMW constituents, with an almost identical relative MWD within the two groups. Given that HMW are mostly produced by ejection phenomena and LMW are formed upon pyrolytic reactions, such change in the HMW/LMW mass ratio suggests that higher reactor temperature (which also means higher reaction rate) favors pyrolysis reactions over the ejection of polymeric fragments. Nonetheless, on the basis of SEC-RID analysis of WS, we could state that pyrolysis temperature, even influencing the yield of pyrolysis products, doesn't have a large effect on the composition of WS.

Summing up the results obtained from quantification and characterization of pyrolysis products it is possible to state that increasing temperature mainly increases the yield of WI and pyrolysis gas, providing a similar amount of WS with a similar toxicity profile and comparable MWD. 2/3 of the pyrolysis products are low molecular weight compounds which should be considered suitable for biological conversion with a suitable microbial consortium [7], whereas 1/3 of WS is formed by unknown HMW constituents, which could include oligosaccharides and other unknown and scarcely biodegradable constituents.

3.2. Gasification of biochars obtained from pyrolysis

To obtain a reliable estimate of biochar reactivity within the gasification environment, the biochar obtained from intermediate pyrolysis of fir was subjected to bench scale fixed-bed gasification procedure, performed in CO₂ atmosphere at 850 °C for 30 min [39,40]. This procedure, which was optimized to achieve mass and COD balance at a small scale, aimed to evaluate a gasification process that is made using CO₂-rich biogases obtained from anaerobic conversion as described in Fig. 1.

Table 2 shows the detailed input/output balance obtained from the gasification tests performed on biochar materials (obtained at 450, 550 and 650 °C) along with the COD concentrations of each fraction. Consequently, the char materials resulting from biochar gasification were found to have a similar and high chemical energy content of around 37±1 MJ/kg, calculated by Elemental Analysis using the method described elsewhere [38].

As shown in Fig. 7, gasification converts a considerable portion of chemical energy retained in biochar into relatively clean syngas with null (biochar obtained at 450 and 550 °C) or negligible (biochar obtained at 650 °C) amounts of tars. The absence of gasification tars, usually assumed for the gasification of char from high-temperature pyrolysis [15], is noticeable in the gasification of biochar from 450 °C which should contain a significant amount of non-charred organic matter. The composition of produced syngas was not strongly dependent on the temperature used for biochar production, with an overall average among the tested conditions of 18 % (±5), 10 % (±0), 23 % (±6), 3 %

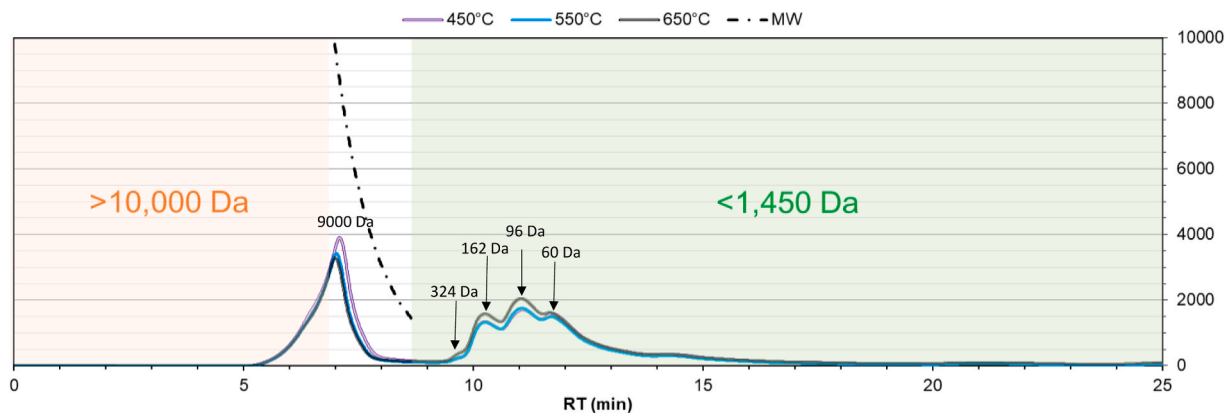


Fig. 5. Molecular weight distribution obtained through SEC analysis of WS obtained by means of pyrolysis at different reaction temperatures.

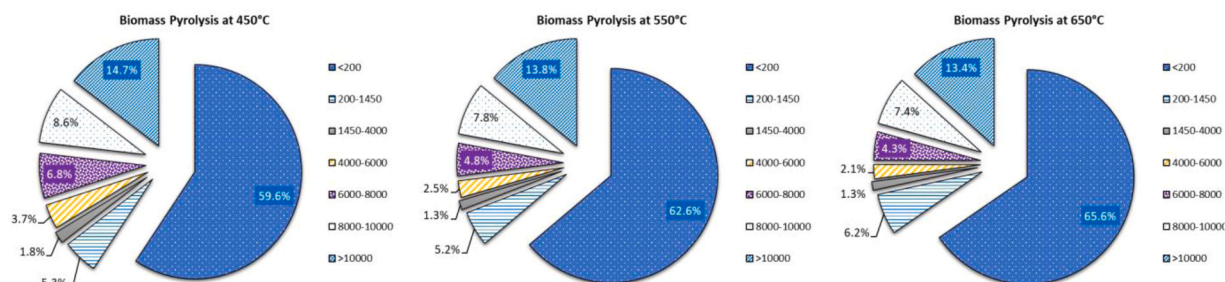


Fig. 6. Quantitative analysis of MWD of WS as obtained with SEC-RID analysis of the samples (as % gCOD/gCOD_{ws}).

Table 2

Summary results of fixed-bed biochar gasification tests under CO₂ atmosphere (30 min). ^a Gasification performed at 850 °C. ^b Gasification performed at 950 °C.

Biochar Synthesis Temperature:			^a 450 °C	^b 450 °C	^a 550 °C	^a 650 °C	
INPUTS	CO ₂	g	14.5	68	16.2	26.9	
	Biochar	g	13.5	19	13.5	23.0	
	C (% w/w)		74	74	82	82	
	H (% w/w)		3.8	3.8	2.8	2.7	
	N (% w/w)		0.2	0.2	0.3	0.3	
	O (% w/w)		22	22	15	14	
	Ash (% w/w)		0.7	0.7	0.8	0.9	
	OUTPUTS	Char	gCOD/g	2.05	2.05	2.27	2.26
			g	10.6	6.8	11.2	19.7
C (% w/w)			94	94	92	91	
H (% w/w)			0.6	0.3	0.6	0.5	
N (% w/w)			0.2	0.1	0.2	0.2	
O (% w/w)			4.4	3.1	6.3	7.5	
Ash (% w/w)			0.9	2.5	1.0	1.0	
Syngas		gCOD/g	2.51	2.50	2.43	2.39	
		g H ₂	0.1	0.03	0.2	0.4	
		g CH ₄	0.9	0.01	1.0	1.4	
	g CO	6.1	37	7.4	10.6		
	g CO ₂	6.8	44	5.1	7.4		
	gCOD/L	0.44	0.43	0.35	0.32		
Tars	g	n/a	n/a	n/a	0.38		

to a biochar conversion rate equal to 0.6, 0.5 and 0.4 % min⁻¹. The observed rate and trend were in line with biochar gasification literature [15,39] and in line with what was experimentally observed by Duman et al. [41]. They observed 0.7–0.6% min⁻¹ conversion with similar feedstock (wood biochar from 500 °C pyrolysis) and identical gasification parameters. Data suggests that low-temperature pyrolysis produces the biochar with the highest reactivity. To evaluate the absolute amount of syngas obtainable from biochar gasification, the gasification temperature was increased to 950 °C and 1 h gasification time was used. This increase of gasification severity sharply increases the COD yield of gas to 56 % (±2) and deeply changes the syngas composition, which becomes dominated by CO (57±5% v/v) with the disappearance of H₂ and CH₄ (0.7 and 0.03% v/v respectively) without any detectable generation of tars. Such results are in line with the literature related to char/coal gasification and highlight the importance of temperature for the kinetic of CO₂ gasification of solid materials.

3.3. Overall evaluation of the Py-Gs for hybrid thermochemical biological pathway

As abovementioned, this paper aims to establish how much bioavailable organic matter can be delivered to an aqueous system for conversion through microorganisms. Fig. 8 provides an adjusted description of all the products obtained using the combination of intermediate biomass pyrolysis and biochar gasification under CO₂.

Intermediate pyrolysis at 450 °C allows the production of 36 % of bioavailable material (30 % from WS and 6 % from gas) with co-production of biochar and WI (i.e., pyrolytic lignin), which retain most of the chemical energy of the feedstock due to high HHVs of 38 and 30 MJ/kg. Low-temperature char (450 °C pyrolysis) provided the higher gasification rate, and it is possible to convert it into a clean syngas, thus providing an additional flow of bioavailable substances (mainly CO). The combination of bioavailable flows from pyrolysis (36 % of feedstock

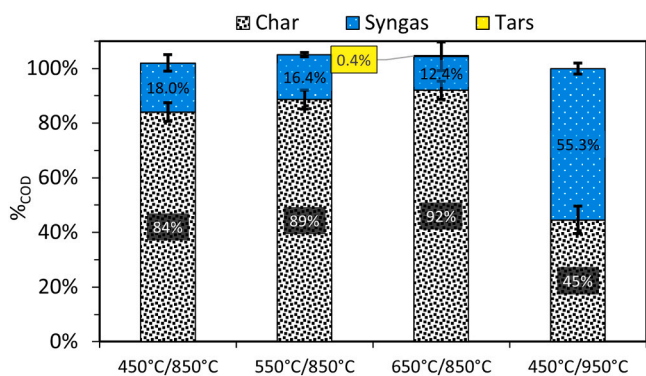


Fig. 7. COD yields of biochar gasification obtained at different pyrolysis and gasification temperature (shown as pyrolysis temperature/gasification temperature).

(±2), and 44% (±1) by volume for hydrogen, methane, carbon dioxide and carbon monoxide, respectively. To evaluate the effect of gasification temperature, 950 °C gasification was tested onto the 450 °C biochar, which was preliminary selected on the basis of early reactivity.

Concerning 850 °C gasification, gas yield slightly decreased for biochar obtained at higher temperatures with gas yields equal to 18, 16, 12 % respectively with biochar obtained at 450, 550 and 650 °C pyrolysis. Considering a gasification time equal to 30 min, this corresponds

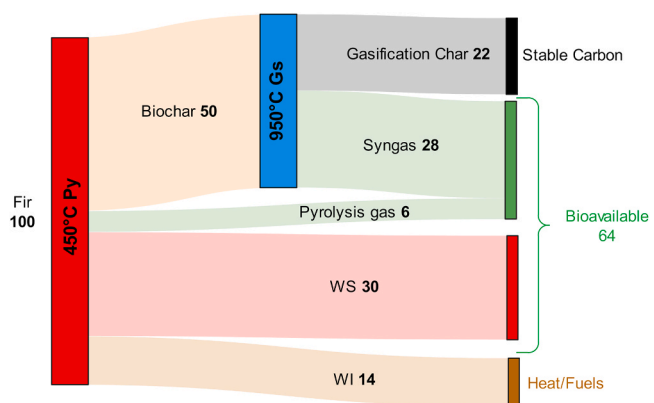


Fig. 8. Sankey diagrams of the Py-Gs pathway for the obtainment of bioavailable organics. All data are shown as %COD respect to initial COD of feedstock (fir wood) and COD balance of Py and Gs were normalized to 100 %.

COD as WS and pyro-gas) and biochar gasification (28 % of feedstock as syngas) sum up to 64 %, whereas 22 % and 14 % of initial COD are delivered as gasification char and WI respectively. The gasification char holds 14 % of feedstock carbon and given its properties (95 % C w/w) can be used for carbon storage or as reducing agent [42], whereas WI (which shows a quite high 30 MJ/kg HHV) could be used to provide the thermal requirement of the process or upgraded to drop-in fuels [43]. Such performance can be compared with conventional hydrolysis-based methods or with conventional gasification (without the pyrolysis step). Concerning hydrolysis-based methods, which are targeted at holocellulose, the maximum theoretical yield obtainable is 60 % if the biomass has 23 % lignin content [11]. Considering the technical limits of hydrolysis, steam explosion and subsequent enzymatic hydrolysis hardly surpass 50 % at reasonable costs (e.g. less than 72 h with moderate cellulase load) [44]. This means that Py-Gs, which partially exploit the lignin portion, provides more bioavailable organics than hydrolysis-based methods, which are targeted just on holocellulose.

Direct gasification of biomass can provide up to 60 % of the COD of biomass as syngas, but this amount is achievable only with proper tar cracking and syngas cleaning [11], and this hinders small-scale applications. In comparison with direct gasification of biomass, it should be highlighted that Py-Gs intrinsically produces null or negligible amounts of tars, which are intrinsically more toxic than WI from low-temperature pyrolysis (which is mainly formed by pyrolytic lignin) and difficult to manage at low scale. Low-temperature pyrolysis can be viewed as a pre-treatment that decreases the amount of tar generated from subsequent gasification and, concurrently, it produces an additional flow of bioavailable organics (WS).

Due to COD-based approach here used it is possible to calculate the yield of products that can be obtained through different biological conversions after Py-Gs, which can be obtained through the following formula:

$$Y_{p,m} = \frac{COD_f}{COD_p} \cdot \sum Y_{i,COD} \cdot \mu_i$$

Where $Y_{p,m}$ is the mass yield of product, COD_f and COD_p are the COD (gO/g) of feedstock and product, $Y_{i,COD}$ is the COD yield Py-Gs product as calculated in this work and μ_i is the biological conversion efficiency of that product. From the literature we know that clean syngas can be fermented to ethanol using single strains [4], WS can be treated/hydrolyzed and fermented to ethanol with single strains [5], or directly fermented to volatile fatty acids or methane using suitable microbial mixed culture (MMC) [6–10]. Just to provide a practical example of direct application of Py-Gs it is possible to calculate the expected yield of ethanol/methane from a process which utilizes clean syngas for the production of ethanol and WS for the production of methane. According to this formula (assuming quantitative conversion of syngas and WS conversion efficiency, equal to 65%), the processing of 1 ton of dry fir through the concept here proposed would allow the co-production of 212 kg of ethanol (with syngas fermentation), 84 Nm³ of CH₄ (with WS biomethanation) and 120 kg of biochar. According to the literature, both Py and Gs require 1600 MJ of thermal energy for fir pyrolysis and (mostly) for char gasification [45,46]. Interestingly this energy requirement matches the ≈2200 MJ/ton which can be obtained by the direct combustion of the 74 kg/ton of WI fraction (≈30 MJ/kg HHV) which is generated by 450 °C pyrolysis step, suggesting that low-temperature pyrolysis can be synergic to CO₂ gasification also considering the heat integration of the processes.

4. Conclusions

The primary aim of this paper was to investigate the amount of chemical energy, evaluated as COD, that can be transformed into potentially fermentable compounds, namely gas and water-soluble substances, from woody biomass (fir) through the coupling of

intermediate pyrolysis with CO₂ gasification. With intermediate pyrolysis (450–650 °C), the total yield of bioavailable compounds was about one-third of the feedstock COD, mostly in the form of complex WS. This performance is lower than that of hydrolysis-based methods and therefore is not satisfactory for HTB schemes. As biochar holds a high chemical energy content (2.1–2.3 gCOD/g) and represents the highest share of COD in pyrolysis products, it was subjected to a model gasification procedure to deliver additional fermentable syngas. Biochar obtained at 450 °C showed the highest gasification reactivity and tar production resulted negligible. Gasification at 950 °C gasification allows to channel 28 % (gCOD/gCOD_{fir}) additional COD toward a clean syngas with null production of tar. The obtained results suggest that Py-Gs scheme can deliver up to 64 % of the COD of the feedstock as bioavailable fractions, namely syngas (34 %) and water-soluble organics (30 %). According to the analytical evaluation performed, the performance of Py-Gs exceeds those achievable with hydrolysis-based methods or direct gasification of biomass. Even considering the established biological conversions for syngas and WS, Py-Gs can be a key tool for 2nd generation HTB. Nonetheless, to confirm the technical feasibility further study should deal with direct Py-Gs coupling with biological conversions, demonstrating the energy balance of the overall system and stability of WS conversion, which is less established than syngas fermentation.

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CRedit authorship contribution statement

Cristian Torri: Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Yusuf Küçükkağa:** Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Serdar Kara:** Writing – review & editing, Supervision. **Andrea Facchin:** Writing – review & editing, Visualization, Methodology, Formal analysis.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yusuf Küçükkağa reports financial support was provided by Scientific and Technological Research Council of Turkey. Cristian Torri reports financial support was provided by European Union. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that has been used is confidential.

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