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Could Pyrolysis Substitute Hydrolysis in 2nd generation biomass valorization strategies? A Chemical Oxygen Demand (COD) approach.

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Abstract

Pyrolysis converts a wide array of feedstock into a mixture of products which can be used by microorganisms in hybrid thermochemical-biological (HTB) processes. Such approach can be very efficient in the valorization of lignocellulosic waste streams. In this study, a method based on calculation of Chemical Oxygen Demand (a measure of chemical energy) was proposed in order to assess the maximum potential of HTB process from lignocellulose. A deep literature survey on papers dealing with pyrolysis of lignocellulosic feedstock ended up with a database of bioavailable matter (e.g. water-soluble product and gas) obtained under different reactor configurations and various biomass pre-treatment methods. Such evaluation suggests that, at the present state of the research, intermediate and non-optimized fast pyrolysis is able to deliver bioavailable products with 30-40% yield. Considering the downstream processes typical of HTB (e.g. detoxification or use of specific microorganisms), this depolymerization performance is attractive only using a feedstock that is not already suitable for biological process. Innovative combination of pre-treatment and fast pyrolysis can transform more than 60% of the feedstock chemical energy into bioavailable products. This value, higher than those obtained through conventional hydrolysis-based strategies, confirms the great promise of HTB processing of lignocellulose into valuable intermediates or final bioproducts.

Nomenclature

ABE: Acetone-Butanol-Ethanol

AS: anhydrosugars

BOD₂₈: biological oxygen demand

COD: Chemical Oxygen Demand

EA: Elemental Analysis

ER: Equivalence ratio, for a thermochemical process (e.g. gasification) the amount of oxygen with respect of theoretical oxygen demand.

HHV: Higher Heating Values

HTB: Hybrid Thermochemical-Biological

MMC: Mixed Microbial Cultures

PyP: Pyrolysis Products

SSC: Single Strain Culture

VFAs: Volatile Fatty Acids

WI: water insoluble fraction of condensable PyP

WS: water soluble fraction of condensable PyP

Y: Yield

1.Introduction

To date, most of the efforts to obtain drop-in biofuels or chemicals from second and third generation feedstock were spent only on biological or thermochemical approaches [1]. At the interface of these compartmented approaches, hybrid thermochemical-biological (HTB) processes are an interesting, although immature, field of research. Although HTB represents a relatively new research domain, the potential of biology to alleviate, or even solve, specific technical issues related to thermochemical process and, more specifically, pyrolysis, was demonstrated by several groups [1–5].

In pyrolysis, biomass is heated without (or with minimal) oxygen at 350-600°C. Heat easily breaks polymers resulting in the production of a vapor stream enriched in pyrolysis products (PyP) and a carbonaceous residue (char or biochar). The stream of PyP is subsequently cooled down, yielding a gas and a liquid product (pyrolysis liquid, formed by water and organic substances). Being a relatively simple process, pyrolysis allows the treatment of a large array of different feedstock, representing one of the most reliable pathway for depolymerizing the slowly biodegradable fractions of biomass [6]. Although pyrolysis is a high rate method to depolymerize biomass, the high temperature used in the process implies a lower selectivity of the reaction, especially when complex feedstock is considered [7]. HTB approaches aim to exploit microorganisms as a sort of “biological funnel” [8], to decrease the complexity of PyP and unlock advanced utilization of thereof [9]. Different HTB schemes based on pyrolysis and gasification have been proposed and investigated during the last two decades [1–4,10,11] Although some challenges (mainly related to low volumetric productivity) remains relevant [12], Syngas fermentation by single microbial strains (or single strain culture, SSC) is the most mature HTB approach, with two commercial exploitation attempts (Coskata and INEOS Bio, finally

2

bankrupted) and one commercially available process (Lanzatech) in 2021 [13–16]. HTB processes based on pyrolysis can address some of the limitations of syngas fermentation, but poses two additional challenges: toxicity and bioavailability [17]. Toxicity is influenced by pyrolysis process (feedstock and pyrolysis conditions), PyP detoxification strategies and by adopted microorganisms (or consortia in microbial mixed culture, MMC) with their own tolerance levels towards PyP. On the contrary, bioavailability depends solely on feedstock and pyrolysis conditions. Before going into details about HTB feasibility and to put efforts into HTB experimental work, it is important to establish what is the “prize up for grabs” for HTB, and to compare it with standard 2nd generation approaches (e.g. lignocellulosic ethanol based on hydrolysis of holocellulose). Within this context, this paper proposes a versatile method to establish the maximum yields so far obtained by HTB processes. Such a method aims to provide a common playground for researchers involved in developing HTB processes, namely chemists, biologists and chemical engineers.

The assessment of yields obtainable by HTB methods, and their comparison with second-generation technologies, require the definition of a common unit of “chemical energy”, which can be easily applicable in both aqueous biological systems and thermochemical processes. To date, tons of oil equivalent (toe), corresponding to 41.85 GJ, is the most widely used chemical energy unit to compare oil, biomass fuels and power sources in energy systems. Although helpful, such a measure is intrinsically related to oil and requires analyses (namely HHV, Higher Heating Value, or elemental analysis) that are difficult or inaccurate if performed in aqueous solutions. As such, relying on toe is quite difficult in HTB processes, whereas the use of chemical oxygen demand (COD) or theoretical oxygen demand, usually adopted in many biotechnological approaches [18], could be of great importance in comparing different HTB systems. This paper specifically proposes COD as a useful direct measurement of chemical energy in biomass, pyrolysis products and solutions. Such approach allows to evaluate the performance of pyrolysis as a way to depolymerize biomass into compounds within 2nd generation biomass valorization scheme.

2. Methods

2.1 Rationale of the chemical oxygen demand (COD) method

For the scope of this paper, 1 kg of COD (otherwise named as kgCOD, 1 kgO, or kgO₂) is defined as the amount of organic matter in a given volume that needs 1 kg of oxygen to be completely oxidized. The Highest COD is that of hydrogen (8 kgCOD/kgH₂), whereas the COD of organic materials ranges between 0.2 (oxalic acid) and 4 (methane) kgCOD/kg. Natural occurring substrates typically shows a narrow COD range between that of glucose (1.07 kgCOD/kg) and lignin (2.3 kgCOD/kg_{feedstock}). Due to the stoichiometry of redox reactions, 1 kg of COD corresponds, by definition, to 0.125 kmol of electrons packed into the energy-rich bonds of organic

compounds by photosynthesis or electrosynthesis [19][20]. For instance, 0.125 g of H₂ (1 g of COD) through water electrolysis requires an electric current equal to 12 kC/gCOD against an electric potential of more than 1.23 V. If the reaction is reversed, the maximum stored chemical energy that can be recovered as electric power is:

$$\frac{MJ}{gCOD} = \frac{12440 C \cdot 1.23 V}{gCOD} = 15.3 \frac{kJ}{gCOD} \cong \mathbf{15} \frac{MJ}{kgCOD}$$

15 MJ/gCOD can be obtained by several independent approaches as the typical “energy content” of 1 kg of COD. In fact, due to stoichiometry, both COD and HHV are correlated to elemental compositions [21]. This is because both COD (exactly) and HHV (empirically) are proportional to the number of bonds that are broken during combustion to form the stable bonds of H₂O and CO₂. Even considering that the different chemical bonds are characterized by slightly different bond energy, this amount of energy released by oxidation of 1 kg of COD range in a quite narrow range between 12 MJ/kgCOD (graphite) and 18 MJ/kgCOD (carbon monoxide). This slight variability in HHV/COD ratio of organic compounds is actually the driver which can support the anaerobic processes (e.g. anaerobic digestion of glucose to CH₄, anaerobic fermentation of glucose to ethanol) feasible with net energy gain. In fact, according to thermodynamic principles, biocatalysts allow to exploit paths that are within limits of two fundamental rules extensively elucidated elsewhere [10]:

- (i) the COD of reagents should be equal to the COD of products. Given that oxidants have negative COD (e.g. oxygen -1 gCOD/g, by definition) this assumption is valid in both anaerobic and aerobic systems;
- (ii) Organism can exploit just favorable “COD pathways”, which are those that foresee a decrease in HHV/COD ratio or oxidize a part of COD [22].

From the above, it is possible to establish that 1 kg of COD as PyP can theoretically be transformed in 1 kg of COD of fermentation products, such ethanol, butanol or Volatile Fatty Acids (VFAs). It follows that maximum mass yield is equal to COD of PyP (e.g. 1.2 gCOD/g_{WS} for water-soluble PyP) divided by the COD of the product (e.g. 2.09 gCOD/g_{EtOH} for ethanol).

2.2 Calculation of COD yield of thermochemical processes

According to the above considerations, COD yield of a pyrolysis product *i* ($Y_{COD,i}$, gCOD_{PyP}/gCOD_{in}) is defined as the amount of feedstock’s COD partitioned into a certain pyrolysis product: namely pyrolysis gas, WS (water-soluble compounds), WI (water-insoluble compounds), char. COD yield of certain fraction is then equal to the mass yield multiplied by the ratio between COD of products and COD of feedstock:

$$Y_{COD,i} = Y_{m,i} \frac{COD_i}{COD_{feedstock}}$$

Where $Y_{m,i}$ is the mass yield (g/g) of the pyrolysis product, COD_i is the COD (gCOD/g) of that pyrolysis product and $COD_{feedstock}$ is the COD (gCOD/g) of the feedstock. For instance, if wood (1.3 gCOD/g) pyrolysis produces 20% mass yield of char (2.5 gCOD/g), the corresponding $Y_{COD,char}$ is

$$Y_{COD,i} = 0.2 \cdot \frac{2.5}{1.3} = 38\%$$

In absence of oxidant and without losses, the sum of all $Y_{COD,i}$ should be equal to 1, within a partially oxidative process (e.g. autothermal pyrolysis or gasification) the sum of Y_i should be equal to:

$$\sum_i Y_i = 1 - Y_{CODloss} - ER$$

Where $Y_{CODloss}$ is the loss of COD due to leakage of some pyrolysis products or unintended oxygen entrance into the system, and ER (equivalence ratio) is the ratio between oxygen used in the process and the stoichiometric amount of oxygen required for the complete oxidation of the feedstock (usually between 0.1 and 0.3 in direct gasification).

To calculate COD yield of HTB processes, two main data are therefore needed: mass yield (which is available for almost all available pyrolysis studies) and COD of each PyP (COD_i) and feedstock ($COD_{feedstock}$). In this paper, the COD values were obtained in different ways according to available data, namely:

- Directly measure using COD analyzer or chemical procedure for the COD determination;
- Back calculating from Elemental Analysis (EA) of bulk pyrolysis fraction;
- Back calculating from the Higher Heating Value (HHV) of pyrolysis fraction
- Back calculating from detailed molecular composition and COD of each PyP constituent.

Using EA, the COD of a PyP or feedstock can be calculated through stoichiometric assumptions with the following formula:

$$COD = \frac{gCOD}{g} = \frac{32}{12} \cdot C + 8 \cdot H + 1.5 \cdot S - O$$

As described above (section 2.1) COD and HHV are both correlated to EA [23] [21] with, on average, 15 MJ every kg of COD for most common PyP. This means that, given a substance or a mixture with a certain HHV expressed in MJ/kg, its COD can be calculated as follows:

$$COD \left(\frac{gCOD}{g} \right) \cong \frac{HHV \left(\frac{MJ}{kg} \right)}{15 \left(\frac{MJ}{kgCOD} \right)}$$

Whereas just Lower Heating Value (LHV) values are available, it is possible to convert LHV into HHV knowing the hydrogen content or the amount of water produced during the combustion.

When the molecular composition of a PyP product (e.g. pyrolysis liquid) is known, the COD of that fraction is given by the sum of COD of all constituents namely:

$$COD \left(\frac{gCOD}{g} \right) = \sum_{i=1}^n X_i COD_{x,i} + X_{uk} COD_{uk}$$

Where X_i is the mass fraction of the i -th constituent, $COD_{x,i}$ is the COD of that constituent and COD_{uk} is the average COD of non-quantified compounds. $COD_{x,i}$ can be obtained from the general chemical formula $C_aH_bS_cN_dO_e$ as follows:

$$COD_{x,i} = \frac{gCOD/Mol}{g/Mol} = \frac{16 \cdot (2a + b/2 + 3c - e)}{12a + b + 32c + 14d + 16e}$$

In which a, b, c, d, e are the number of atoms respectively of carbon, hydrogen, sulfur, nitrogen and oxygen in the i -th molecule. Since most of papers report an incomplete molecular characterization, in absence of any other information, it is assumed that COD_{uk} is equal to the average COD of detected constituents.

These methods allowed to calculate COD yield from most of literature studies concerning pyrolysis. For the vast majority of studies, COD of feedstock and biochar can be calculated from HHV or elemental analysis, which are available in most of papers. Concerning pyrolysis gas, the molecular composition (usually % of gas volume) or HHV are usually provided. For pyrolysis liquid, the characterization strategy is highly variable and, depending on author's aims, can provide HHV, EA and/or molecular composition.

Whereas more than one approach can be used for calculation of COD yields, the more accurate approach was chosen as follows. Beyond direct COD measurement, which is not yet common in the pyrolysis field, EA is intrinsically the best approach because of exact correlation. When EA is not available, HHV is usually more accurate than molecular characterization. Given the assumption about COD_{uk} described above, it was assumed that molecular characterization provides accurate results only if a significant (>70%) portion of the analyzed fraction is identified and quantified.

3. Results and discussion

3.1 Classification of PyP in term of bioavailability

To establish the maximum yield of target products (e.g. chemical or drop-in fuel) obtainable from HTB approaches, it is hallmark to evaluate how the COD of the feedstock (as a package of chemical energy) is

partitioned by pyrolysis into PyP characterized by different properties in term of biological utilization, namely bioavailability, biodegradability and toxicity, which are a function of the composition PyP and their chemical structure. PyP composition is, in turn, a function of the feedstock and process conditions. Pyrolysis (and subsequent condensation) splits the organic matter into char, gas and condensable products. Within the aqueous suspension required for the life of microorganisms, condensable PyP are further partitioned in two different fractions: water-soluble (WS) and water-insoluble (WI) compounds. In the case of wood and lignocellulose, pyrolysis gas is typically composed of carbon monoxide, hydrogen, methane and small hydrocarbons. WS comprises up to 500 constituents from pyrolysis holocellulose and, to lesser extent, lignin (e.g. acetic acid and WS phenols). This fraction is relatively biodegradable and, by definition, bioavailable [24]. On the contrary, WI mainly originate from lignin and are mostly (more than 80% wt/wt) formed by pyrolytic lignin, less polar phenolic and hydrocarbon derivatives from resins/waxes pyrolysis [25].

Pyrolysis gas is biodegradable and can be used anaerobically or aerobically by a large number of microorganisms. The main issue related to pyrolysis gas conversion is the low water solubility of CO and H₂ as well as the eventual presence of highly toxic contaminants (e.g. hydrogen cyanide or NO_x) [26], which are typically less relevant in pyrolysis than in gasification [27]. Equilibrium contacting of 1 atm H₂ or CO in 40°C water would transfer just 11-12 mgCOD/L into the liquid. Nonetheless solubilization can occur quite rapidly when the reactor is characterized by high mass transfer coefficient (K_LA , 1/h). Taking experimentally achieved volumetric mass transfer coefficients (K_LA) [28], which can be up to 600 1/h, the resulting volumetric productivity (VP) of gas conversion can be, in principle, higher than that obtainable with highly fermentable soluble substrates (e.g. glucose). Although fermentation of CO/H₂ mixture is known by more than 30 years [29], fermentation of “real syngas” obtained from gasification/pyrolysis was studied in six papers (performed with SSC with *Clostridia* class). Such works demonstrated the fermentation of different gaseous mixtures derived from gasification/pyrolysis of biomass, yielding alcohols and VFAs with COD yields in 55%-89% range [30–35], product concentration up to 81 gCOD L⁻¹ and maximum VP up to 4.6 gCOD L⁻¹ d⁻¹ [30–35]. Such figures suggest that pyrolysis gas, although sparingly soluble, should be considered almost entirely bioavailable with moderate to low mass transfer rate.

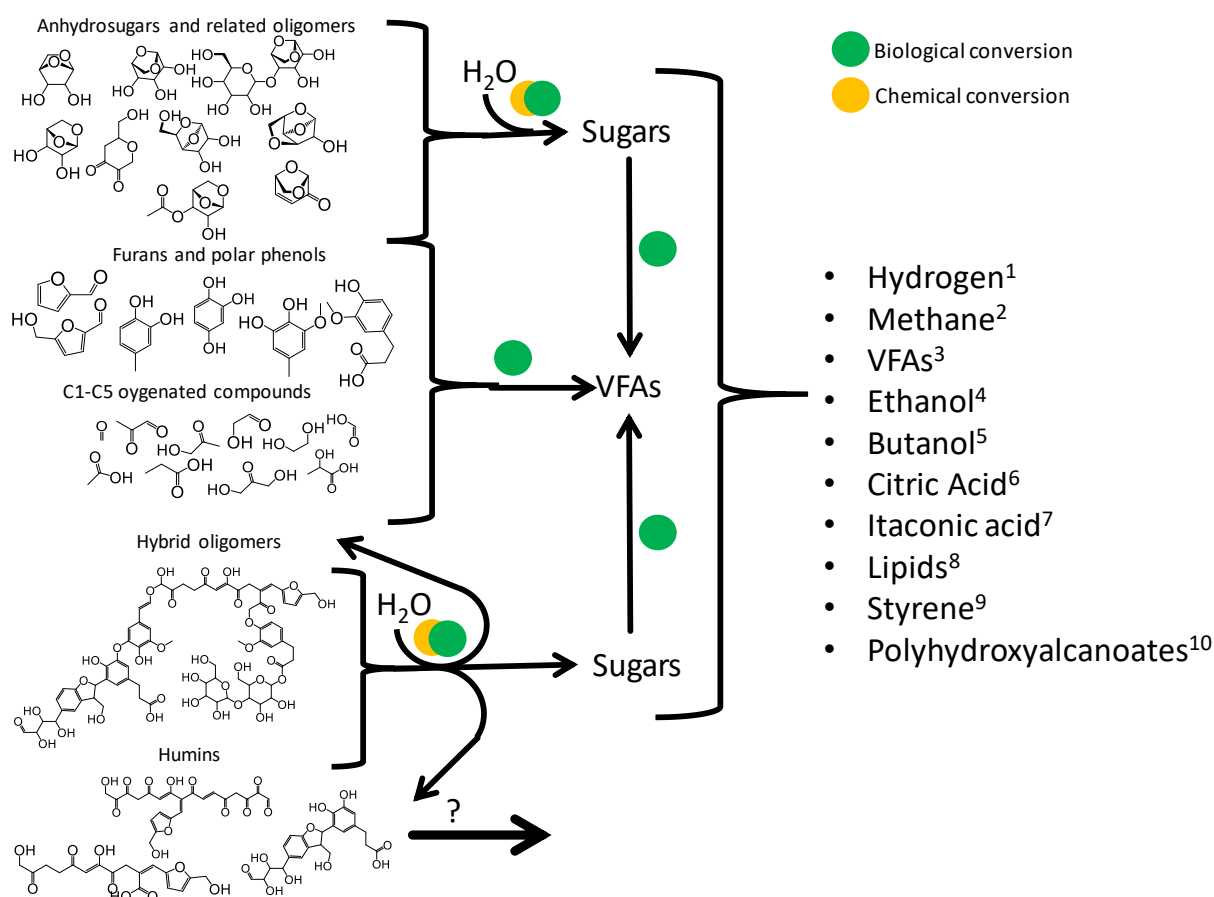


Figure 1. Constituents of Water soluble fraction of PyP (WS) and potential pathways for biological conversion. ¹with MMC in a microbial electrolysis cell(MEC) [36–38]; ² with MMC[39–46]; ³ with MMC [40,43–45]; ⁴ with SSC [5,47–54]; ⁵ Acetone-Butanol-Ethanol (ABE) fermentation with clostridia [55]; ⁶ with SSC [56,57]; ⁷ with SSC [58]; ⁸ with SSC [59–62]; ⁹with genetically modified microorganism [63].¹⁰with anaerobic/aerobic MMC [64,65]

Composition of WS, graphically depicted in figure 1, is a highly debated topic. About one third of WS is GC-MS detectable, like VFAs, AS, hydroxyacetaldehyde or polar phenols (e.g. di or tri-hydroxybenzenes)[66]. The remaining share is typically represented by anhydro-oligosaccharides formed by cellulose ejection [67] and complex water soluble substances whose exact molecular description could range between humin-like matter and hybrid oligomers formed by lignin cellulose and lignin PyP [68]. WS or some selected portions of WS (e.g. AS, oligomers or WS without most toxic constituents) was used in the fermentative production least 10 products (listed in figure 1). AS are the most peculiar (and sometimes the most abundant) pyrolysis product of WS. In principle, AS can be directly fermented by various natural [56,69,70] or engineered [52,53] single strain microorganisms, or chemically hydrolyzed to easily fermentable glucose [71]. The latter conversion is the most investigated one, mainly because it enables the use of “biotechnological workhorses” (e.g. *Saccharomyces cerevisiae*), which are characterized by higher yields and productivity. At now, several authors demonstrated the use of AS-rich pyrolysis fraction to produce a large array of chemicals, namely Methane, Ethanol, Acetone-Butanol-Ethanol (ABE), VFAs, Citric Acid, Itaconic Acid, Styrene and Lipids. [5,47,57–63,71,48–50,52–56]. The yield and VP obtained from hydrolyzed AS are actually close to that observed with glucose, therefore there is a large consensus that AS can be a reliable source of sugars for

second generation fuels and chemicals [4]. Beyond AS, few studies focused on SSC fermentation of other chemical classes of WS, namely hydroxyacetaldehyde [72,73] and carboxylic acids [61,62]. Concerning WS as a whole, few aerobic and anaerobic biodegradation studies performed after large dilution to overcome their toxicity suggest that WS from fast/intermediate/slow pyrolysis are definitively bioavailable and biodegradable even exploiting natural microbial consortia [10]. For instance, in the case of aerobic biodegradation studies on pyrolysis liquid from woody feedstock, WS was found to be easily biodegradable using, as inoculum, sludge from wastewater treatment plant. Promptly biodegradable fraction of WS, namely 28 days Biological Oxygen Demand (BOD_{28}), corresponds to 68-83 % of the COD, with higher biodegradability observed for slow pyrolysis WS [24,74].

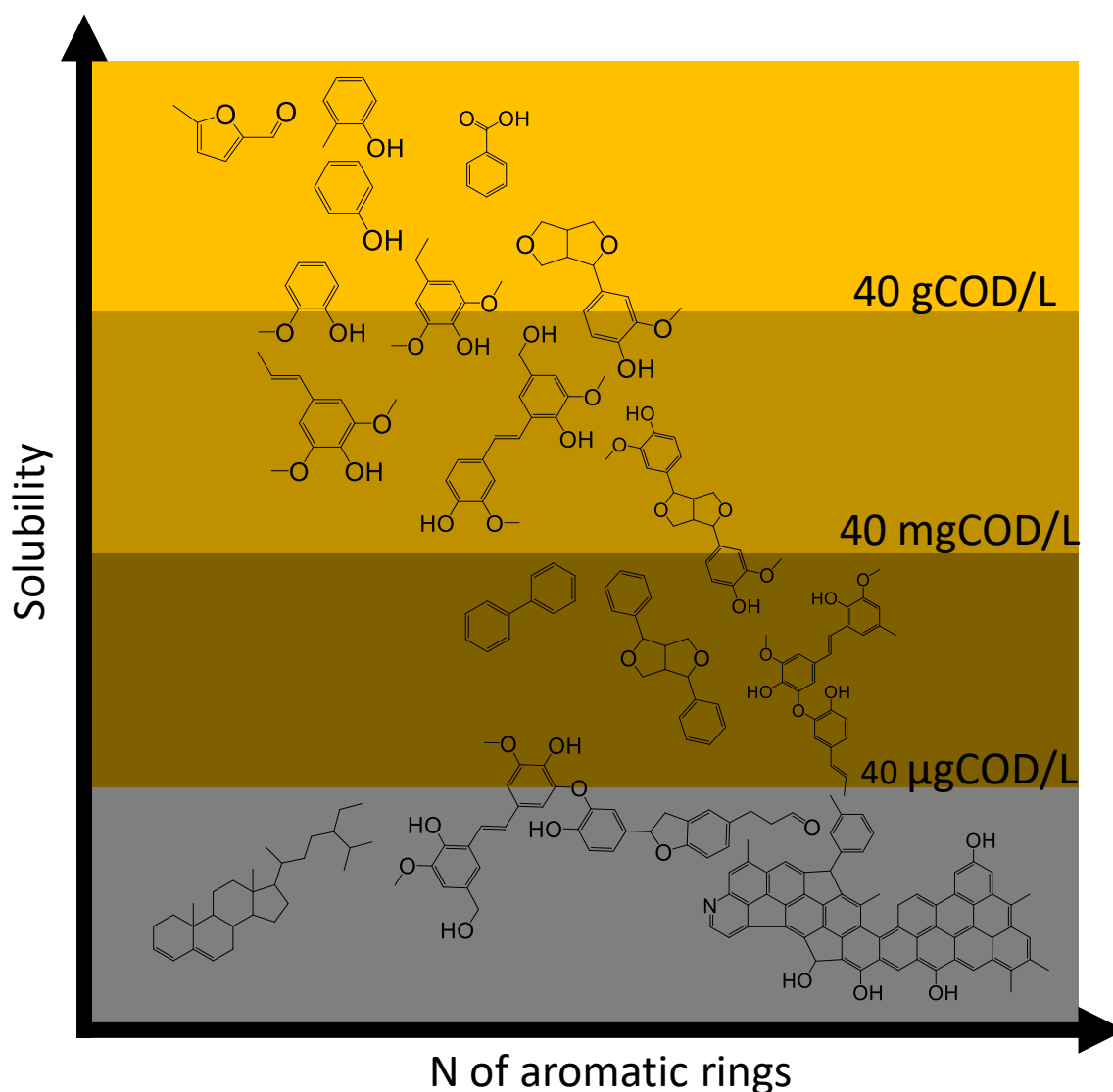


Figure 2. Example of molecular structures of Water Insoluble fraction of PyP (WI).

Whereas WS is mostly derived from holocellulose, WI (figure 2) is mostly formed by lignin derivatives, with variable amount of oligomers and monolignols and resin derived hydrocarbons. Such mixture is typically less

biodegradable (<30% in 28 days respirometric tests [24]) and characterized by high partition coefficient. The latter characteristic hampers bioavailability and, given the higher toxicity usually described for phenols and carboxylic acids [75–77], suggests an intrinsic high toxicity [78,79]. According to chemical structures present in WI, which are analogous to those of native lignin but with higher bioavailability, partial biodegradation of WI is theoretically feasible with specifically adapted microbial consortia or upon specific pre-treatment of WI (e.g. ozonolysis or further chemical depolymerization) [80,81].

Several authors demonstrated the potential conversion of lignols and lignin oligomers frequently generated through oxidative cleavage, into biochemical intermediates [81,82]. So far, there is only a limited number of studies about the use of WI in biological processes, mostly focused on monolignols [83,84]. Nonetheless, low solubility and toxicity issues suggest that the biological conversion of WI with adequate rate is still far to be achieved. For this reason, WI is the most challenging fraction and it is not yet suitable to enter into the so called biological funneling of PyP into valuable compounds where single and/or mixed microbial strains can be adopted to produce added value products such as enzymes, organic acids and alcohols.

3.2 Evaluation of maximum Yield of Bioavailable PyP

Aim of this paper is to compare the depolymerization efficiency of pyrolysis as alternative to conventional 2nd generation hydrolysis processes. A novel method based on COD was developed and used to quantify the capability of pyrolysis to deliver bio-available compounds to microorganisms. COD yields of char, pyrolysis gases, WS and WI for different pyrolysis configurations were calculated (Figure 3). Average inter-laboratory results were obtained for slow and fast pyrolysis of woody biomass in 400-550°C range, considering different types and scales of reactors.

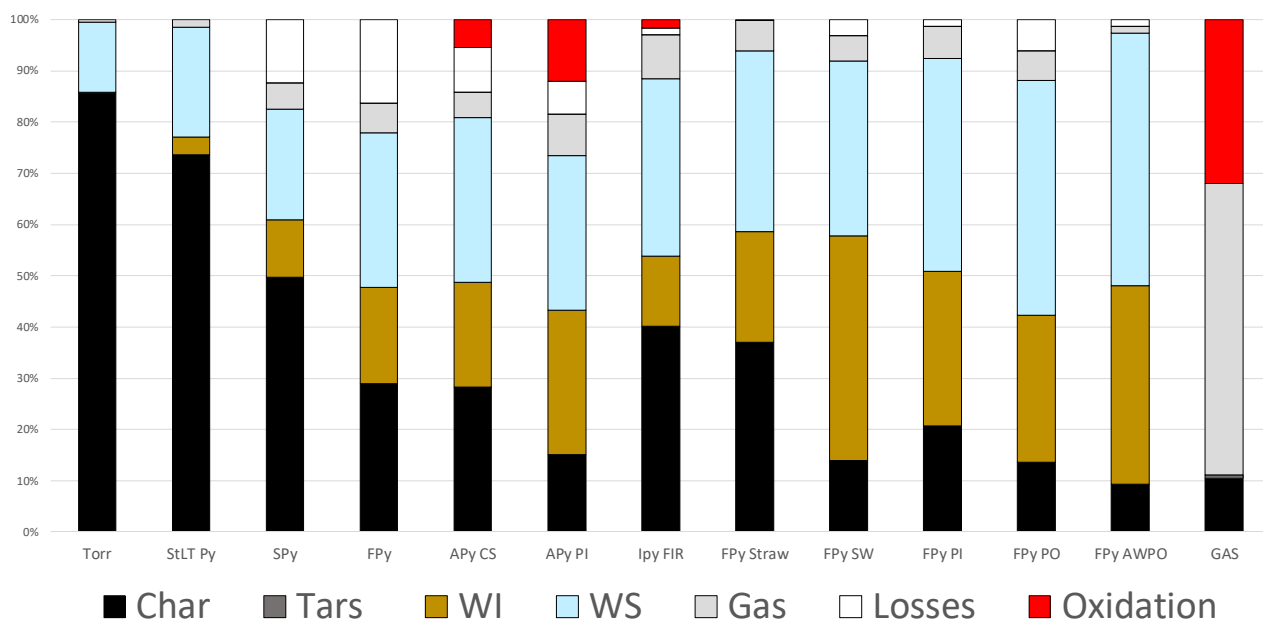


Figure 3: COD yield ($gCOD_{fraction}/gCOD_{feedstock}$) obtainable with pyrolysis of different feedstock and different composition. Torr: torrefaction of willow at 300°C [85]; StLT Py: staged 280°C and 350°C pyrolysis of beech wood; SPy: slow pyrolysis, average data from selected literature; FPy: fast pyrolysis, average data from selected literature; APy CS: autothermal pyrolysis of corn stover [86]; APy PI: autothermal pyrolysis of pine wood [87]; IPy FIR: Intermediate pyrolysis of Fir wood from unpublished data from author's laboratory; FPy Straw: fast pyrolysis of straw in fluidized bed [88]; FPy SW: fast pyrolysis of switchgrass in fluidized bed [89]; FPy PI: fast pyrolysis of pine in fluidized bed [88]; FPy PO: fast pyrolysis of poplar in fluidized bed [90]; FPy AWPO: fast pyrolysis of acid washed poplar [90]; GAS: yields calculated from performance of downdraft gasifier operated with sawmill residue [91];

Torrefaction, namely anoxic thermal treatment below 350°C, leaves 85% of chemical energy in the solid material. In terms of mass, the most relevant effect is the production of water and carbon dioxide, which originated from holocellulose reactivity at low temperature, while in COD basis the most relevant feature is the β -elimination of acetic acid and methanol from hemicellulose and lignin thermal degradation. Considering the yield and composition of volatile organic compounds, torrefaction converts just 15% of the chemical energy of the feedstock into few small organics, which consists mainly of acetic acid, methanol, small hydroxy-acids and minor amount of carbon monoxide.

As shown by de Wild and coworkers [92], when temperature is slowly increased to the lower boundary of cellulose conversion, namely 350°C, volatile products yield increases to 26% but most of the chemical energy (74%) is still retained in the solids [92]. Besides low yield, analysis of pyrolysis products obtained at 350°C shows that 86% of condensates consists in WS and they are potentially biodegradable.

Conventionally, slow pyrolysis is characterized by slow heating rate, but final pyrolysis temperature exceeds the decomposition temperature of all biomass biopolymers (e.g. 500°C). To obtain a general description of the COD flow determined by slow pyrolysis, a representative selection of the available literature on slow pyrolysis [93–101] was used to calculate COD yields. This process (Figure 3:SPy), on a COD basis, converts the feedstock mainly into char (50% COD yield), where the yields of volatilized compounds were found to be

5, 22 and 11% for gas, WS, and WI, respectively. Feedstock type mainly influences the ratio between yields of WS and WI, which is fairly correlated to the holocellulose/lignin COD corrected ratio in the biomass.

It is important to notice that there is a large variability among different studies and most experimental apparatuses do not allow to close the mass and elements balances (the latter relevant for COD balance). Inter-laboratory relative standard deviation values (with respect to global average) are limited for char (7%), significant for condensable products (30 and 10% for WS and WI, respectively) and high (60%) for gas yield. Concerning the accuracy of the global average, there is a 2-10% COD difference between feedstock and products and it is not clear if slow pyrolysis missing COD is due to undetected gas (e.g. few studies analyze small hydrocarbons), oxygen leaks or other losses due to small scale experiments.

In the case of fast pyrolysis, a selection of literature was merged to obtain an “average” COD distribution of this process [102–111]. The mean value confirms that higher heating rates typical of fast pyrolysis disclose higher yield of semi-volatile compounds, [112] namely: $5.7 \pm 3\%$ pyrolysis gas, $30 \pm 5\%$ WS, and $19 \pm 3\%$ WI at the expense of char, whose COD yield drops to a lower but still significant 29%. Again, in most of studies the elemental balance is far from being closed, revealing on average a 16% gap between the COD that enters in the process and total COD collected in PyP. To highlight the maximum yields obtainable, a selection of articles dealing with relatively large-scale equipment and with reliable mass balance analysis was considered. Oasmaa et al. pyrolyzed sawdust in fluidized bed within a process development unit, providing detailed analysis of products obtained [88]. Back calculating the COD balance starting from elemental analysis and products composition provided by the authors, it is possible to obtain a reasonable COD balance with the following COD yields: 21% char, 30% WI, 42% WS, and 6% gas (Figure 3: FPy Straw). A similar fluidized bed was also used by fast pyrolysis on finely grinded poplar, obtaining an extremely low COD yield of char (14%), 46 % WS, 29% WI, 6% gas, and 6% losses [90] (Figure 3: FPy PO). When applied to herbaceous crops (straw), characterized by lower lignin and ash content, fluidized bed pyrolysis yielded less WS (to 35%), probably due to high ash content, and a decrease in WI yield to 22% [88]. This suggests that, even if herbaceous crops have higher holocellulose content than wood, the WS yield is less than that observed for woody biomass. This effect can be due to the higher ash content of herbaceous biomass, which is known to catalyze the char formation [113]. The adverse effect of high ash levels on depolymerization yields is even clearer considering the work of Scott et. al. related to de-ashed poplar [90] (Figure 3: FPy AWPO) where the removal of K and Na, triggered by acid washing, allowed to obtain an outstanding COD yield, namely 49% and 39% of WS and WI, with almost negligible biochar yield (9%). Noteworthy, beyond the extraordinary increase in levoglucosan yield (from 3 to 17 %), such procedure was able to increase both WS and WI shares and provided the largest depolymerization yield of the literature concerning fast pyrolysis. Biomass hydrothermal treatment temperature higher than 150°C [114] with water or solvents [115] where found effective in dissolving a portion of hemicellulose (providing it in bioavailable form) and most of K and Na in biomass. The main

conclusion that can be drawn from the literature is that the maximum COD yield of WS obtainable through fast pyrolysis of alkali-free cellulose within biomass could be close to that obtainable from pure cellulose under optimized conditions, which can be almost quantitatively (96%) converted into WS PyP, in which levoglucosan represents more than 80% of COD [116,117].

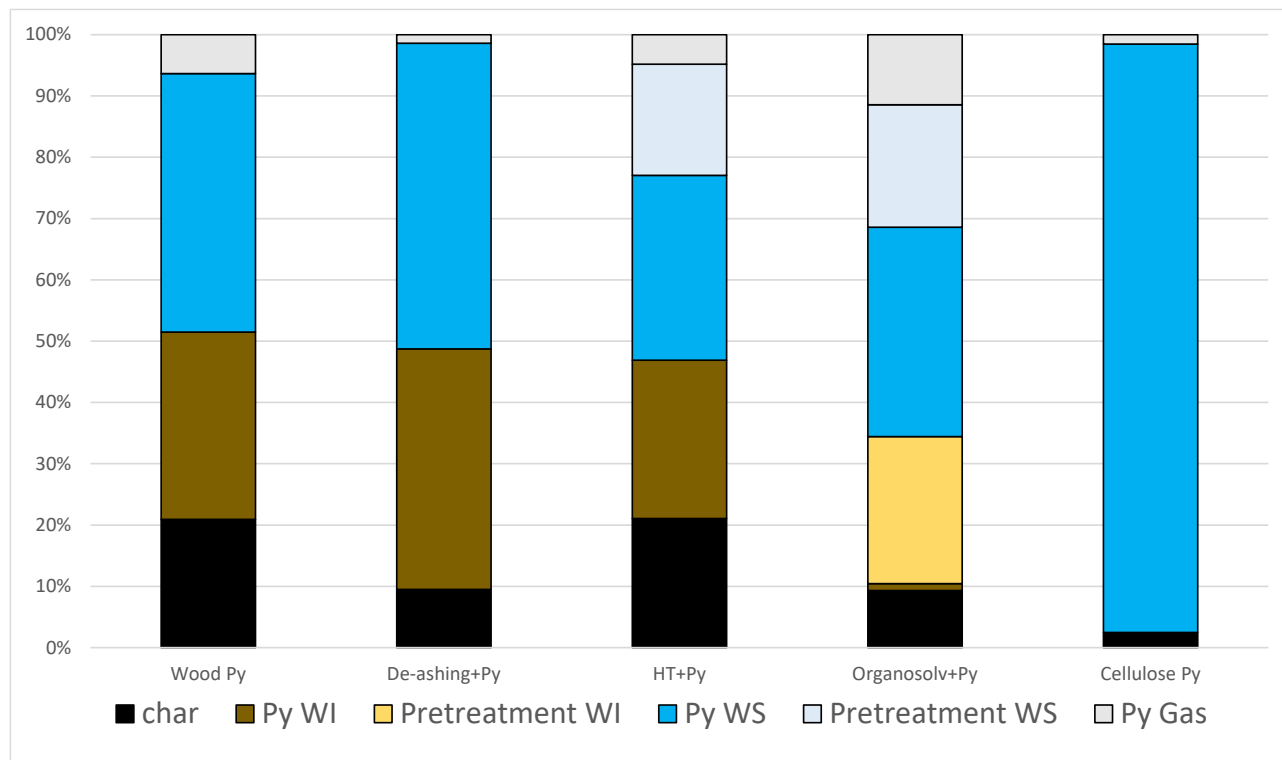


Figure 4: COD yield ($\text{gCOD}_{\text{fraction}}/\text{gCOD}_{\text{feedstock}}$) obtainable with pyrolysis of different feedstock and different pre-treatment/pyrolysis combination. Wood Py: fast pyrolysis of pine in fluidized bed [88]; Deashing+Py: 0.1% nitric acid treatment followed by fast pyrolysis; HT+Py: hydrothermal treatment followed by fast pyrolysis (data on WS/WI where back calculated from C-NMR data through assumption on molecular structures) [114]; Organosolv+Py: Microwave assisted organosolv pretreatment followed by fast pyrolysis [115]; Cellulose Py: Optimized Vacuum pyrolysis or cellulose in optimized reactor [117]; Black: Char; Brown: pyrolysis WI; Beige: pretreatment WI; Blue: Pyrolysis WS; Light blue: pretreatment WS; grey: Pyrolysis gas.

Besides the increase of WS and AS obtainable with pre-treatment, the latter can also produce bioavailable organic matter (e.g. dissolved hemicellulose) that can be provided as carbon source to the microorganisms. Figure 4 shows the back-calculated COD balance of some interesting pre-treatment/pyrolysis combinations, compared with fast pyrolysis and simple de-ashing. Combination of 190°C hydrothermal pre-treatment with fast pyrolysis allows to obtain 18% COD yield as dissolved hemicellulose, 29% WS and 5% gas, thus delivering 54% of COD as bioavailable [114]. Analogously, if fast pyrolysis is used within organosolv lignin-first biorefinery allows to obtain 20% COD yield as dissolved hemicellulose 34% WS and 11% gas, with 60% total yield of bioavailable products [114].

3.3 Can pyrolysis substitute hydrolysis?

Literature analysis through the COD method was useful to assess the real promise of pyrolysis as depolymerization strategy within HTB processes. According to calculated values, slow pyrolysis is not

effective, delivering less than one third of chemical energy as WS and gas. Intermediate-fast pyrolysis of raw biomass was found to support up to half of chemical energy, which can be considered satisfactory if the WI and char co-products can be valorized. Best performances were obtained when fast pyrolysis is coupled with upstream pretreatments that involve hemicellulose dissolution and de-ashing, COD yield of bioavailable compounds can be equal or even higher than the maximum obtainable with 100% efficient conversion of holocellulose (e.g 60% if the biomass has 23% lignin content). This suggests that, besides cellulose conversion, lignin significantly contributes to production of bioavailable compounds (e.g. gas). Noteworthy, most of the chemical and enzymatic processes target only holocellulose, and hardly surpass 90% yield of fermentable substrates [118]. Therefore, if pyrolysis co-products (biochar and water-insoluble fraction) can have a value equal or higher than that of lignin, we can consider pyrolysis, and in particular, fast pyrolysis as an extremely interesting route to depolymerize biomass. Besides such promising absolute yields, a critical evaluation suggests two key aspects of pyrolysis as pre-treatment biological conversion:

1. Pyrolysis is effective in depolymerization although it can be energy demanding. High yield (>50%) of bioavailable constituents (WS and gas) are indeed obtained only with extremely high heating rates and high quality, finely grinded biomass feedstock. The heat and electrical energy requirements of the overall process, if expressed as primary energy consumption, can be more than one third of the chemical energy in biomass [119].
2. Pyrolysis is intrinsically non-selective, therefore a small but significant part of bio-available compounds are characterized by extremely high toxicity and/or require enzymes which are not readily available in most of the microbes so far exploited for their biotechnological funneling [10].

To partially overcome the first issue, autothermal pyrolysis was recently proposed [86,87,120]. Once biomass is pyrolyzed with sub-stoichiometric oxygen input, (equivalence ratio up to 12%) thermal energy production required by pyrolysis reaction is obtained through the oxidation of char and only minor amount of bioavailable PyP. Such approach produces the reaction energy in direct contact with biomass, allowing to obtain a bioavailable PyP yield close to that obtainable from fast pyrolysis, but without the strict requirement of conventional fast pyrolysis. Nonetheless it provides the advantage of eliminating the external energy input of pyrolysis, which can range between 5-25% of the feedstock energy content of feedstock according to the scale and system configuration [121,122].

Considering now the second disadvantage, no efficient approach has been proposed so far to increase the pyrolysis selectivity towards bioavailable compounds. Since WI consists of lignin oligomers or WI hybrid lignin-carbohydrates oligomers, a promising route would be to minimize the oligomers formation. Water solubility of oligomers increases as molecular weight and methoxylation degree decreases. As such, the following approaches can be in principle beneficial:

- Back cycling WI and/or gasification of WI portion of PyP: WI oligomers can be returned to the pyrolyzer, thus obtaining an increased yield of monomeric phenols [123]. Gasification with equivalence ratio up to 0.4 or thermal decomposition of PyP onto hot char bed typically produces gas as main product (up to 60% feedstock COD), converting most of WI into gas and minor amount of tars. The main drawback of such approaches is the production of relevant amounts of completely non-biodegradable tars (xylenes and polycyclic aromatic hydrocarbons) whose toxicity effects could overcome the advantages related to increased fermentable gas output.
- Optimized pyrolysis atmosphere: vacuum/steam/hydrogen/sub-stoichiometric air pyrolysis should be adopted as a strategy to increase water bioavailability of lignin derived PyP, through the increase of the i) monomer/oligomer ratio, ii) hydroxyl groups through demethoxylation, or iii) carboxyl groups through partial oxidation [124,125].
- New concepts of catalytic pyrolysis: given that most of research was so far focused on de-functionalization and production of WI (e.g. fossil fuel substitute) PyP, research about catalysts increasing the production of WS PyP represents a quite interesting and unexplored topic. Changing selectivity of pyrolysis from WI, formed by large phenolics and lignin oligomers, to WS fraction (non-aromatic or simple phenols) could represent a “silver bullet” to concurrently increase the PyP bioavailability and reduce their toxicity.
- Increasing the bioavailability of WI by stable nanodispersions or emulsions: WI of PyP can be considered as extremely small lignin particles, which can be metabolized by microorganisms; if adequate contact is provided, such oligomers can be gradually introduced in the “biological funnel” by means of various lignin and lignols degrading microorganisms [8,84]. This approach, even with low quality biomass, can dramatically increase the yield of bioavailable compounds provided to microorganisms. Nonetheless, this approach must consider that either SSC or MMC should be tolerant to chemical functionalities typical of WI, which are more toxic and can be slightly different from that of native lignin.

4. Conclusions

Pyrolysis was evaluated as depolymerization strategy in order to deliver bioavailable products to microorganisms in a HTB scheme. Despite the greatly heterogeneous nature of experimental conditions, feedstock and values available in the huge number of investigated papers, the method proposed in this paper was useful to draw few considerations. Slow and intermediate pyrolysis can transfer up to half of the feedstock COD into bioavailable PyP, namely gas and water-soluble fractions. Such performance suggests that HTB processes can be complete when the starting feedstock is not suitable for biological process. De-ashing and higher heat transfer rate (fast and flash pyrolysis) are the main drivers that leads to highest yields,

namely 65% of chemical energy of initial biomass. This performance, which can be actually obtained by combining innovations on pyrolysis and fermentation sides, is actually higher than that obtainable from any existing 2nd generation hydrolysis based process, and even more interesting if the co-production of valuable byproducts (e.g. biochar and WI) is accounted. Further advances in research and development of HTB will support even higher yields and productivities which can increase HTB competitiveness in the wider industrial context of 2nd generation biomass processes.

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