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Hydrothermal processing of biomass for anaerobic digestion – A review

Fiaz Ahmad[a,*], Edson Luiz Silva[b], Maria Bernadete Amâncio Varesche[a]

[a] Department of Hydraulics and Sanitation, University of São Paulo, Av. Trabalhador São-carlense, 400 Centro – 13566-590, São Carlos, SP, Brazil
[b] Department of Chemical Engineering, Federal University of São Carlos, Rod. Washington Luis, km 235 – 13565-905, São Carlos, SP, Brazil

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ABSTRACT

Price hikes in conventional fuels coupled with sustainability concerns result into growing attraction towards lignocellulosic biomass conversion to biofuels. The hydrothermal pretreatment (HP) impact on structural characteristics of biomass and released inhibitory compounds linked to anaerobic digestion represent a knowledge gap and requires a critical review. In this review, HP chemistry, different hydrothermal processing techniques, inhibitory compounds production mechanism in the hydrolysate, and the impact of pretreatment parameters on biological conversion efficiency in products of biotechnological interest are discussed. Countercurrent flow-through hydrothermal reactor was found a better choice for high carbohydrate concentration in the hydrolysate. Anaerobic digestion is discussed in response to HP and morphological changes in biomass associated with lignin dissolution. Finally, literature previously published for techno-economic and environmental analysis pertinent to HP linked to anaerobic digestion process has been summarized and concluded that it requires much research for the decision makers.

1. Introduction

To reach a sustainable world, many challenges need to be addressed including energy demand, environmental pollution, greenhouse effect, solid waste management, and dwindling fossil fuel reserves. Efficient utilization of available resources is a key to sustainability. Lignocellulosic biomass is the most available carbon resource generated on earth. It is produced by transforming the light energy into chemical energy utilizing atmospheric CO_2 and water in the presence of plants photosynthetic system [1]. It is roughly present in hundreds of billions of tons, with only 3% is being utilized by humans [2]. It is considered a safe alternative to petroleum-based fuels, furthermore, equivalent to zero emission [3]. Lignocellulosic biomass and its derived products are considered the most promising alternatives to petroleum-based commodities [4]. Biomass could address the aforementioned challenges. Furthermore, it attracts the attention on various following grounds; cheap, high availability, renewable, and almost zero competition with food for arable land [5].

Efficient utilization of lignocellulosics into renewable energy production is a challenging task owing to its versatile composition and structural features. To make it ready for the biofuels and biochemical production, it is mandatory to rupture the recalcitrant cell wall to gain access to sugar platforms, thus understanding lignocellulosic composition is of prime importance to utilize this valuable resource at its best. A detailed discussion on lignocellulosic composition and recalcitrance is beyond the scope of this review. Therefore, readers are referred to [6,7] for detailed comprehension of these topics. Various factors govern the chemical composition of lignocellulosics including; soil characteristics, cultivar type, stage of plant growth, and genetic variability [8]. Much research has been conducted to understand its structure and chemical composition. Biomass recalcitrance is the major contributing factor in the utilization of this resource at its optimum potential. Natural factors believed to contribute to recalcitrance are; a) cuticle and epicuticular wax of plant epidermal tissue, b) vascular bundle's density and arrangement, c) relative amount of sclerenchyma tissue, d) degree of lignification, e) plant cell-wall structural complexity and heterogeneity, and f) natural inhibitors present in cell wall to combat fermentation [9]. Plant cell wall modification via genetic means proposed by [10] is an option to minimize its recalcitrance. In short, recalcitrant nature of cell wall is impeding the way of renewable fuel revolution.

It is evident from the above discussion; a preprocessing step is imperative to utilize the lignocellulosic biomass to valorize into methane through anaerobic digestion (AD). Pretreatment is a mandatory approach to fractionate the lignocellulosics [11] into an array of products from a biorefinery perspective, making the process economically viable. A number of pretreatments including physical (comminution, extrusion, irradiation) physicochemical (steam explosion, hydrothermal), chemical (acids, bases, ionic liquids, catalyzed steam explosion,

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* Corresponding author.
E-mail addresses: fahmad14@usp.br, malickfiaz@live.com (F. Ahmad), edsilva@ufscar.br (E.L. Silva), varesche@sc.usp.br (M.B.A. Varesche).

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Nomenclature

AD	Anaerobic digestion
AIL	Acid insoluble lignin
ASL	Acid soluble lignin
°C	Degree celcius
CO_2	Carbon dioxide
CH_4	Methane
EFB	Empty fruit branches
H_2	Hydrogen
H_2SO_4	Sulfuric acid
HCL	Hydrochloric acid
HP	Hydrothermal pretreatment
HTL	Hydrothermal liquefaction
HTC	Hydrothermal carbonization
HTG	Hydrothermal gasification
ISR	Inoculum to substrate ratio
K_w	Water constant
$\log R_0$	Severity factor
NaOH	Sodium hydroxide
PHAs	Polyhydroxyalkanoates
POME	Palm oil mill effluent
RPM	Revolution per minute
SIR	Substrate to inoculum ratio
SRB	Sulfate-reducing bacteria
TS	Total solids
UASB	Upflow anaerobic sludge blanket
VS	Volatile solids

catalyzed hydrothermal, wet explosion, ozonolysis), and biological (fungal, microbial consortium pretreatment) have been developed along the time. A comprehensive overview of the said pretreatments is out of the scope of this work. Therefore, readers are referred to an excellent work of Yi et al. [12] to have an in-depth understanding and comparison of aforementioned pretreatments on lignocellulosic composition, structural changes, and subsequent impact on AD process. Each pretreatment differs significantly from one another on the grounds of reaction conditions, complexity, process efficiency, and subsequent downstream processes. Pretreatment type and conditions are dependent upon the end product of the process [13]. Lignin removal, an oft-cited objective of nearly every pretreatment except physical pretreatment, is much important regarding AD. Pretreatment accounts for 30% of the total cost of a biofuel [14]. A single pretreatment cannot be recommended to different feedstocks considering compositional variability. In addition, pretreatments behave differently on different feedstocks even under the same operating conditions. Biomass undergoes through various physical and chemical changes during pretreatment, thus affecting its chemical constituents; cellulose, hemicellulose, and lignin.

Anaerobic digestion (AD) is an old but ever-evolving topic due to process complexity in addition to microbial growth differences on various substrates. Nearly every organic material could serve as a feedstock to digestion process that adds value to non-valued lignocellulosic feedstock. A number of feedstocks have been reviewed as an option for successful AD process; algal biomass [15], cyanobacteria [16], marine microalgae [17], biodegradable plastics [18], food wastes [19], poultry and livestock waste [20], paper and pulp wastewater [21], giant reed was comprehensively reviewed against miscanthus [22]. Since almost every feedstock needs a pretreatment to make available contained polysaccharides to hydrolytic bacteria to initiate the digestion process, each pretreatment has its impact on the subsequent digestion process, kinetics, microbial flora, biogas yield, and process parameters. Various authors have published reviews comparing different pretreatment strategies for pros and cons of each pretreatment on the digestion process [12,23,24]. However, a review of a specific pretreatment for the AD is scarce.

Some review articles have been published on the hydrothermal processing of lignocellulosic biomass [25,26]. Ruiz et al. [27] published a review on the hydrothermal processing of agricultural residues and marine biomass explaining how hydrothermal processing could be used to fractionate lignocellulosic biomass into an array of products in a biorefinery concept. However, to best of authors knowledge, only one review has been published on the hydrothermal processing of lignocellulosic biomass specifically for the AD by He et al. [28]. But, there is a need to shed light on topics regarding the impact of HP on morphological and structural characteristics linking to the AD and other valuable products. This review paper aims to fill the knowledge gap in this area. In this review, an attempt is made to highlight the recent studies on AD associated with HP, impact on structural components, the chemical composition of substrates, inhibitory products formation, sugar platforms production and techno-economic analysis coupled with life cycle assessment.

2. Lignocellulosic biomass chemical composition

Virtually all biological materials could be converted to biogas, organic acids, alcohol, and other products of biotechnological interest, but chemical composition plays a critical role in the biomass selection and is directly related to products yield and overall process efficiency. For example, lignocellulosics biomass with higher lignin content tends to produce lower methane [29]. To obtain desired results and optimum pretreatment efficiency, it is important to get a clear picture of the lignocellulosic composition to visualize what is going on with lignocellulosic components during pretreatment. ^{31}P NMR (phosphorus 31 – Nuclear Magnetic Resonance) is a direct analysis tool to quantify hydroxyl groups in lignin [30]. Real-time monitoring of lignocellulosic components during pretreatment may pave the way to understand pretreatment impact better and to optimize maximum sugar recovery. Physical properties of the lignocellulosic material; water-holding capacity, specific porosity, specific surface area and crystallinity index change with each kind of pretreatment applied but to a different extent depending on pretreatment type, severity, and lignocellulosic composition.

Lignocellulosic biomass irrespective of their physical appearance shares the same chemical make-ups; cellulose (30–70%), hemicellulose (15–30%), and lignin (10–25%), and extractives [31]. Common components encountered in the lignocellulosic composition of different feedstocks are presented in Table 1. Cellulose, $[C_{6n}H_{10n+2}O_{5n+1},$ n – degree of polymerization of glucose] the most abundant polysaccharide, is a constituent of anhydro-glucan units linked together by β, 1–4 glycosidic linkages in a linear fashion [32]. The hydrogen bonds between glucan units determine cellulose crystallinity. Furthermore, some chains are irregularly arrayed rendering amorphous regions intertwined with crystalline cellulose [33]. Chain length is inversely proportional to hydrolysis efficiency [34]. It is insoluble in water and dilute acid and alkaline solutions at room temperature. Cellulose in its amorphous form is most susceptible to microbial degradation [31].

Hemicellulose $(C_5H_8O_4)_n$ is a linear and highly branched-heteropolymer composed primarily of D-xylose, L-arabinose (members of C5 sugar family), D-glucose, D-mannose, D-galacturonic acid, D-galactose, and glucuronic acid (members of C6 sugar family) and C7 sugar 4-O-methyl glucuronic acid [35]. Individual sugars may be methylated or acylated. This group contains three pentoses (D-xylose, L-arabinose, and D-ribose) and two pentitols (D-arabitol, and ribitol) [36]. The composition is heavily dependent upon the source whether it is derived from angiosperm (hardwood) or gymnosperm (softwood). Xylose is the principle sugar for angiosperms and agricultural wastes while