Review

Cellulose Recovery from Agri-Food Residues by Effective Cavitational Treatments

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Abstract: Residual biomass from agri-food production chain and forestry are available in huge amounts for further valorisation processes. Delignification is usually the crucial step in the production of biofuels by fermentation as well as in the conversion of cellulose into high added-value compounds. High-intensity ultrasound (US) and hydrodynamic cavitation (HC) have been widely exploited as effective pretreatment techniques for biomass conversion and in particular for cellulose recovery. Due to their peculiar mechanisms, cavitational treatments promote an effective lignocellulosic matrix dismantling with delignification at low temperature (35–50 °C). Cavitation also promotes cellulose decrystallization due to a partial depolymerization. The aim of this review is to highlight recent advances in US and HC-assisted delignification and further cellulose recovery and valorisation.

1. Introduction

The growing environmental issues and the collateral depletion of global oil reserves and availability have prompted the research towards the utilization of renewable resources as alternatives to the fossil feedstocks. Indeed, the exploitation of biobased materials coming from natural sources was considered as one of the most effective strategies towards sustainability [1]. Among others, lignocellulose biomasses are considered one of the most abundant and yet underutilised bioresources for the production of a broad range of added value products such as green fuels and chemicals [2,3]. Apart from its easy availability and abundance, the fact that 75% of its composition is contributed by polysaccharides (cellulose and hemicelluloses) makes it a valuable raw material for the biofuel [4] and platform chemicals production [5,6]. In 2010, a revised version of the top ten list of the value-added chemicals from carbohydrates (The "Top 10 + 4") was published by the US Department of Energy (DOE), taking into account the extensive newer literature, possibility of direct functionalization, multiple product applicability, suitability for industrial scale-up, etc. [7].

The global increasing demand for alternatives to petroleum-based fuels and chemicals has recently emphasised the stringent need to also diversify and valorise the biobased waste with circular economy strategies [8,9]. Forestry and agricultural crop waste as well as by-products from food processing represent an abundant source of different components for further valorisation. Husk, leaves, seeds, etc. have been reported as extremely low-cost carbon sources for sustainable production of valuable products [10–12]. Additionally, the use of these residues as feedstock does not embody a competition with human nutrition, being a desirable alternative taking into consideration the population growth [13]. The inherent chemical complexity of agri-food waste makes it a very attractive source for the

conversion of crop residues and agro-industrial by-products into value-added chemicals. Moreover, an integrated biorefinery process is more energy efficient in comparison with the current dispose of waste and, despite underutilised, agri-food waste could therefore represent a useful feedstock to establish a more sustainable global society through a biorefinery approach (Figure 1). Cellulose is the world's most abundant natural material that, like starch, is constituted of glucose. It contains hundreds to over ten thousand β-1,4 linked D-glucose monomer units in the form of unbranched straight chains, known as micro-fibrils (present in crystalline and amorphous form), interconnected with van der Waals forces and hydrogen bonds and covered by hemicellulose and lignin [14]. Nevertheless, unlike starch (or sugar), which nature has designed as quickly biodegradable and which has been employed by many pioneering biorefineries as staring material, cellulose as structural plant component is much more difficult to deconstruct (crystalline cellulose is 3–30 times less degradable as compared to amorphous structure). Indeed, its innate close polymeric alignment and its intimate relationship with other lignocellulosic components such as hemicellulose and lignin confer such recalcitrant properties. A delignification process with effective pretreatment to split cellulose and hemicelluloses from lignin is a crucial step and undoubtedly the most challenging [15]. The pretreatment aims to change the supramolecular structure of biomass in which the cellulose, lignin and hemicellulose are closely interconnected to finally release free sugars [16]. Although significant advances have been designed to improve the performances of the hydrolytic enzymes, pretreatment steps are unavoidable.
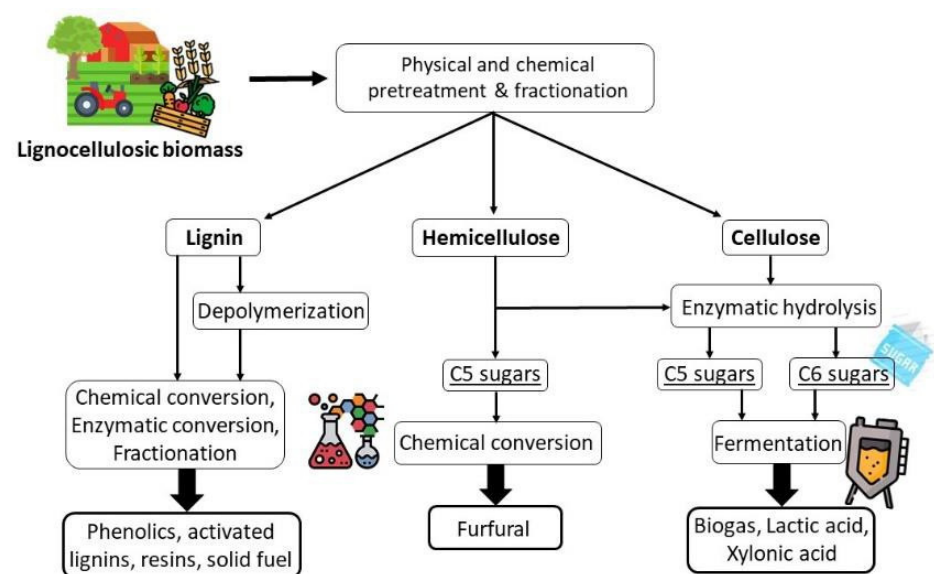
Figure 1. Biorefinery options for lignocellulosic biomass valorisation: a flowchart.

It is common knowledge that hemicelluloses, owing to their branched and irregular structure, are more easily removed compared to other biopolymers forming lignocellulosic biomass and therefore relatively mild treatment such as extraction with hot water may allow their removal. Conversely, lignin stubbornly resists such treatments, as does cellulose; therefore, stronger pretreatments are required [17].

An optimized pretreatment process improves the enzyme accessibility to cellulose, promoting the recovery of the associated hemicellulose and lignin components, without degradation [18–20]. Meanwhile, the formation of inhibitory compounds that could negatively affect the subsequent fermentation step should be avoided. An effective pretreatment process affords: (i) enhanced free sugar production (with a minimum sugar loss and degradation), (ii) low detrimental by-products formation and (iii) sustainable operating cost.

The conversion of agri-food lignocellulosic residues into biofuels or chemicals in integrated biorefineries includes three essential steps: (1) delignification (or pretreatment), (2) conversion of hemicellulose and into C5 and C6 monosaccharides and (3) their fermentation into raw biofuels. Sugars can also be used to produce platform chemicals such as acetone, butanol, ethanol, amino acid, itaconic acid and lactic acid by biological or chemical conversion processes [21]. The conversion of agricultural and forestry waste offers numerous technological challenges, notably in the pretreatment step [16,22] and several processes have been developed for this purpose including mechanical, chemical and biological treatments [15]. During pretreatment, lignin is modified or partially separated and removed from cellulose and hemicelluloses, making them more accessible to hydrolytic enzymes. However, pretreatment process often involves the production of different byproducts such as aliphatic acids (formic and acetic acid), furan derivatives (furan aldehyde, 5-hydroxy methyl furfural "HMF") and several phenolic compounds which inhibit hydrolytic enzymes as well as fermentative microorganisms, thereby decreasing both the overall biomass conversion yields and fermentation capacity [23,24]. For these reasons, pretreatment methods aiming to enhance the enzymatic hydrolysis (EH) of cellulose by reducing the collateral drawbacks should be developed [25,26]. The key factors that should be optimised in the hydrolysis of cellulose are the degree of polymerization, the crystallinity, the surface area as well as the remaining lignin and moisture content. The main pretreatment options historically explored are steam explosion, ammonia fibre explosion, hydrothermal, wet oxidation, alkaline, acidic, organosolv, and, more recently, ionic liquid or deep eutectic solvent pretreatment [27]. However, these current methods are expensive and energy consuming and utilize chemicals which entail special disposal, handling or production procedures. Taking into account biofuel production, it is counterproductive to combine energy severe, wasteful processes. Furthermore, the process required to enhance cellulose accessibility and recovery will be strongly influenced by the nature of the native biomass [28]. Consequently, new technologies must focus on methods with low environmental and economic impacts and high efficiency [29].

In the last few years, the comprehensive utilization of lignocellulosic feedstocks has attracted considerable interest for the development of new sustainable processes established on nonconventional technologies. Although these tools have proven very efficient in biomass fractionation, depolymerization of (hemi)cellulose and lignin or sugar conversion into value-added chemicals, the energy consumption of these processes has to be assessed for a subsequent application on industrial scale [11].

In this context, the disclosure of even more effective delignification processes for the recovery of cellulose from agri-food wastes is desirable, and cavitational treatments could represent the breakthrough. Among them, acoustic (AC) and hydrodynamic cavitation (HC) could provide a harsh physicochemical environment that is hard to achieve with other engineering procedures [30,31], especially in terms of energy efficiency, and could meet the challenges related to the processing of recalcitrant lignocellulosic biomass for cellulose recovery [3].

In this review, the recent advances in the application of acoustic and hydrodynamic cavitation on cellulose recovery from agri-food waste are explored, with a focus on the key parameters that could affect the sustainability of the overall processes.

2. Acoustic and Hydrodynamic Cavitation: Highlights

2.1. Acoustic Cavitation

The term "sonochemistry" is employed to describe the physicochemical processes that occur in solution beyond the energy introduced by ultrasound (US) power [32]. Cavitation phenomena, consisting in the formation, growth and collapse of gaseous microbubbles in a liquid phase (Figure 2) are the consequence of US effects [33]. The powerful local effects (mechanical, chemical and thermal) due to the sudden collapse of those microbubbles and the resulting microjets are the basis of all sonochemical applications.
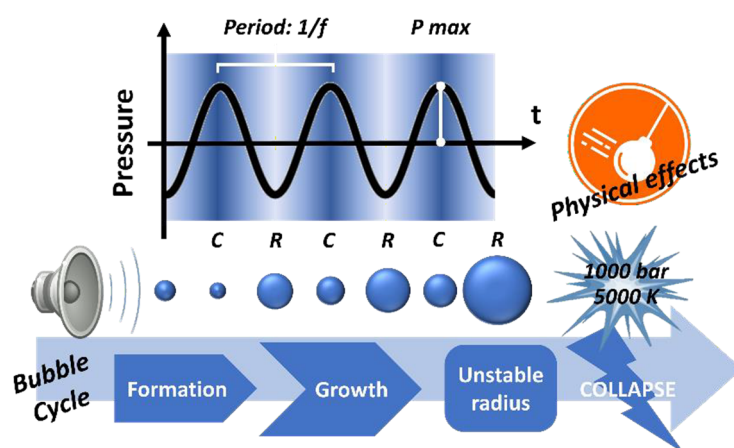
Figure 2. General representation of the acoustic cavitation phenomena.

Even if the full mechanism has not yet been clarified, it is commonly accepted that, in H_2O_2, low frequencies (20–80 kHz) better lead to physical effects (microjets, shockwaves, micro-convection, etc.) [34–36]. On the contrary, high ultrasonic frequencies (150–2000 kHz) mainly cause chemical effects due to the formation of hydroxyl radicals (HO) through local hotspots generated by cavitation. In a broad outline, it is possible to distinguish two large groups of possible US applications in chemistry based either on "sonophysical" or "sonochemical" effects.

The proper choice of all sonochemical parameters (US frequency and acoustic power), as well as the geometry of the used reactor, are strictly connected to US potentiality [35].

For example, in homogeneous systems US are often utilized for their sonochemical effects such as radical formation and bond-breakage to perform chemical reactions. Contrariwise, in heterogeneous systems US are mainly exploited for their enhanced mass transport, erosion and mixing effects.

According to their features, US have been largely applied on biomasses for a large number of purposes. The application of acoustic cavitation for the recovery of secondary metabolites from vegetal matrixes is well known in the literature [37,38]. Furthermore, the acknowledgment of US as a green technique for biomass exploitation has been established by more than 5000 recent papers produced only in the last five years, concerning US-assisted extraction (UAE) [39]. Hence, this technology could play a key role to improve lignocellulosic biomass pretreatment, aiming to subsequent enzymatic and acid hydrolysis: sonochemical and mechanoacoustic effects exerted on the matrix could positively affect the final biomass conversion to added-value products [40,41].

2.2. Hydrodynamic Cavitation

Cavitation phenomena such as the formation, growth and instantaneous collapse of gas- or vapor-filled bubbles, can also be generated by liquid flow in hydraulic systems (hydrodynamic cavitation, HC). In this case, pressure variations in the flowing liquid are generated by the fluid passing through constrictions (Figure 3).

The HC can be generated by Venturi tubes, orifice plates, throttling valves or rotating indentations (See Figure 3) [42].

HC can be explained, according to Bernoulli's equation, based on the relationship between velocity and pressure of the fluid. Bubbles are generated when pressure falls below the vapor pressure of the liquid in correspondence of the constriction. The cavitation bubble generation is described by the cavitation number Cv (Equation (1)):

$$C_v = \frac{P_f - P_v}{0.5\rho U^2} \tag{1}$$

where P_f is the downstream pressure, P_v is fluid vapor pressure, ρ is the fluid density and U is the average velocity nearby the orifice. In theory, cavitation will be formed when $C_v \leq 1$; in practice, it is influenced by other factors than flow velocity, such as the presence of various suspended particles and dissolved gases [43]. A high cavitation number implies that cavitation will not likely take place and vice versa. If cavitation is already in progress, lowering the cavitation number by increasing the flow rate or by decreasing the pressure will boost the cavitation intensity. Increasing the cavitation number may stop cavitation entirely [44].
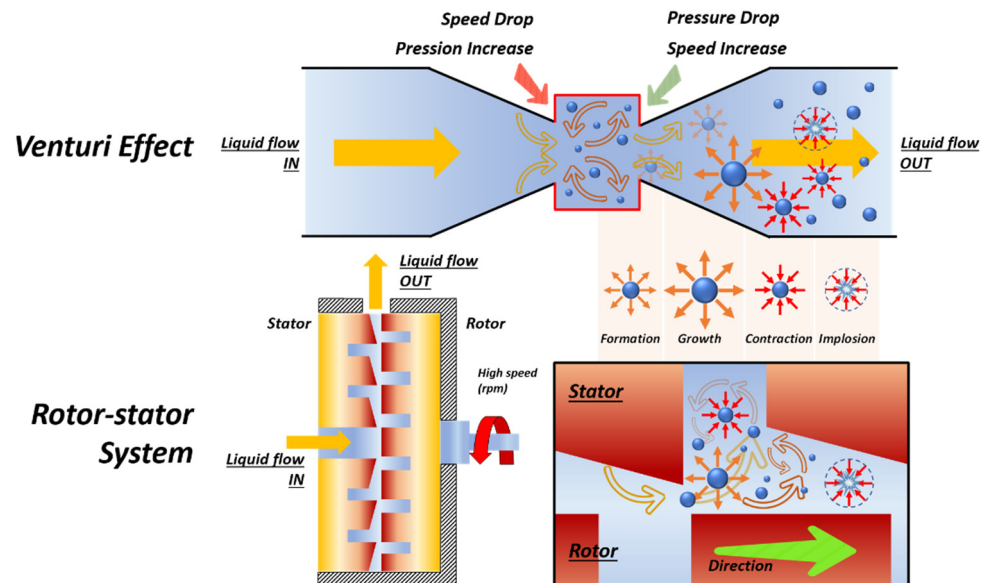

Figure 3. Hydrodynamic cavitation phenomenon in a fluid: Venturi effect and rotor-stator system.

The bubbles' collapse occurs downstream from the constrictions, where the flow decreases and the pressure restores. Under appropriate conditions, the bubbles explosion results in release of large magnitudes of energy which helps the cleavage of the complex biomass structure. Moreover, the copious local low-intensity temperature and pressure impulses generated during HC make it suitable for reactions that require relatively mild pressure and temperature conditions, thus preventing, for example, the formation of degradation products [45].

Bubble dynamics is noteworthy when considering the effects of cavitation. In particular, two main features should be considered: (1) the maximum bubble size and (2) the distance covered by the bubble before downfall, i.e., bubble life. The former defines the cavitation intensity; larger bubbles, formed at high temperature or low pressure [46], collapse with a greater intensity and can produce greater effects on a substrate than smaller ones. For example, they can deeply modify the structure of biomass. Conversely, bubble life is an estimation of the volume where cavitation effects are located, corresponding to the active portion of the system. Commonly, bubble life drops as the region of effective cavitation decreases and vice versa. Many factors affect cavitation, such as the viscosity of the fluids and the vapor pressure. Indeed, to create this phenomenon, highly viscous fluids entail higher energy input, as well as a fluid with a low vapor pressure. Additionally, the geometry and size of the cavitator could deeply influence the process efficiency.

As HC is easier and more economical to scale-up than AC, it is often applied to biomass as a physical pretreatment method for delignification, in order to enhance the enzymatic digestibility of cellulose [47]. Indeed, the high energy-efficiency of HC-assisted processes is useful for scaling up. Moreover, it also allows the reduction of chemical catalysts, still with high lignin removal and high glucose (Glu) yield.

In addition to the physical biomass pretreatment for cellulose recovery, HC can also be exploited as a green process to enhance extraction of bioactive compounds, proteins and lipids from biomass [48–50].

3. Biomass Treatments for Cellulose Recovery

Due to lignocellulose structure, the pretreatment is crucial for getting the fermentable sugars in the hydrolysis step. In fact, one of the main limiting factors to the microbial attack of lignocellulosic materials is their lignin content. Two main reasons have been proposed for the mechanism by which lignin interferes with the hydrolysis of cellulose:

(a) lignin is a structural polymer confined into the plant cell walls and covalently linked to hemicellulose. This configuration prevents carbohydrate exposure to EH [51]; (b) the hydrolytic process of cellulose greatly depends upon the adsorption of enzyme onto the substrate: lignin could irreversibly adsorb enzymes leading to their inactivation.

In this scenario, an effective biomass pretreatment is desirable to reach efficient enzymatic digestion and subsequent production of bioderived compounds [15,52–54]. In fact, one of the major limiting factors to the microbial attack of lignocellulosic materials is their lignin content. A variety of pretreatment processes have been developed in recent decades to enhance the digestibility of lignocellulosic biomass, mainly:

- Physical pretreatment (microwave [55–57], ultrasound [3], mechanical extrusion [58], pulsed electric fields [59]);
- Chemical-with alkali [60]; acid [61]; Oxidative delignification; Ozonolysis [62]; Organosolv process [63]; Ionic liquids (ILs) [64];
- Physicochemical-Hydrothermal pretreatment [65]; Steam explosion [66]; Ammonia fiber explosion (AFEX) [67]; Supercritical CO_2 (SC-CO_2) [68] pretreatment;
- Biological (microorganisms, redox enzymes) pretreatment [69,70].

Each cellulose isolation procedure has a distinct specificity on altering the chemical and physical structure of lignocellulosic materials [71]. The advantages and disadvantages of these pretreatment protocols are reported in Table 1. Among these processes, chemical and physicochemical approaches appear to be the most promising ones for industrial applications. Physical methods (such as chipping, grinding and milling) enable biomass size reduction with a surface area/volume ratio increase [72]. Moreover, thanks to shear forces most of them can decrease cellulose crystallinity. Among other physical methods, microwave (MW) irradiation is a broadly exploited biomass pretreatment [55–57]. It is fast and easy to operate, it requires less energy and it produces a small number of inhibitory compounds [73] even though its scalability is a challenging issue. Recently, pulsed electric fields (PEF) have been investigated in biomass pretreatment [59]. In particular, the high voltages applied on biomass by PEF (5–20 kv/cm for milliseconds) creates pores in cell membranes that enable to the appropriate agents to break down cellulose into free sugars suitable for further conversion.

Table 1. Pretreatment methods for lignocellulosic feedstocks.

Pretreatment for Cellulose Recovery	Processes	Possible Biomass Alterations	Remarks
Physical	Milling	Increases the pore size and the accessible specific surface area	High energy consumption
	Irradiation	Decrease the cellulose crystallinity Decrease the polymerization degrees of cellulose	Cannot remove lignin and hemicellulose
	Steam Explosion	Solubilizes hemicelluloses, alters the structure of lignin	Harsh environment High equipment cost and inhibitors generation
	Hydrothermal Ammonia fiber explosion	Solubilizes hemicelluloses recovering sugars Decreases the polymerization degrees of cellulose	High equipment cost High cost Not effective for biomass with high lignin content

Table 1. *Cont.*

Pretreatment for Cellulose Recovery	Processes	Possible Biomass Alterations	Remarks
Physicochemical and Chemical	SC-CO$_2$	Increases the accessible specific surface area	High pressure requirements Easy CO$_2$ recovery after extraction
	Organosolv process	High delignification Separation and recovery of high-quality cellulose	High price of organic solvents
	Alkali	Decreases the cellulose crystallinity	High pollution and high chemical recovery cost
	Acid	Decreases the polymerization degrees of cellulose Hydrolysis of hemicelluloses	Rapid treatment rate
	Oxidative	High delignification Hydrolysis of hemicelluloses	High cost of bleaching agent
Biological	Fungi	High delignification Degrades lignin and hemicelluloses Decreases the polymerization degree of cellulose	Long pretreatment period Low energy requirement

Multiple physicochemical and chemical approaches are widely used for biomass pretreatmet to increase the accessibility of cellulose to various hydrolytic enzymes (cellulase and hemicellulase), for example, during steam explosion [66] in which biomass are subjected to saturated steam at high temperature (160–240 °C) and pressure (0.7–8.0 MPa) hemicellulose is solubilized while cellulose remains as a solid fraction, becoming more accessible for enzymatic hydrolysis. Although this pretreatment is very effective, the high energy input required and the toxic by-products produced make this process less sustainable. At the same time, liquid hot water treatment process [65] is very close to steam explosion but uses water instead of steam to reach hemicellulose solubilization and lignin transformation. In general, liquid hot water pretreatments are attractive from a cost-savings point of view because no chemicals and corrosion-resistant materials are required for hydrolysis reactors. However, the high energy input required and the production of many toxic products make this eco-friendly method (as no corrosive material is used) less attractive. Furthermore, in the AFEX pretreatment [67], biomass is exposed to liquid NH$_3$ at room temperature and high pressure. AFEX does not require small particle size of biomass, enabling a good cellulose decrystallization and accessibility (by means of a good NH$_3$ induced swelling) to hydrolytic enzymes. AFEX increases the digestibility of lignocellulosic biomass by removing the least acetyl groups by deacetylation process. Drawbacks are the large amount of ammonia required and the ineffectiveness with biomass with high lignin content. The SC-CO$_2$ pretreatment [68] involves the use of supercritical CO$_2$ (1000–4000 psi) that could penetrate the biomass structure, dissolving available water and forming carbonate that could hydrolyse hemicellulose. No inhibitory compounds were produced during SC-CO$_2$ pretreatment, but the required high operating pressure (1000–4000 psi) and the high costs are a big drawback. Among chemical pretreatments, alkali delignification is more effective for low lignin content biomass, especially softwood [74]. Moreover, alkaline delignification is not as energy demanding as some of the other pretreatments being carried out at low pressures and temperatures [60]. Compared with acid pretreatment [61], alkaline delignification has less influence on sugar degradation, but the salts generated are often incorporated into the biomass during the process.

Oxidizing agents, like hydrogen peroxide and ozone, have also been exploited for biomass pretreatment at ambient temperature. Although ozonolysis is one of the few methods capable of breaking down the aromatic structure of lignin without affecting cellulose, it requires a huge amount of ozone.

On the other hand, the use of ionic liquid or the newly introduced (natural) deep eutectic solvent for the agri-food waste pretreatment is a growing practice. These sol-

vents are very effective in the disruption of the hydrogen bonds network among biomass components, facilitating the cellulase access to cellulose but they are very expensive [75].

Biotechnology can contribute to more efficient and greener deconstruction of plant cell wall by providing tailor-made biocatalysts based on the oxidative enzymes responsible for lignin attack in nature. Biological pretreatments performed by means of microorganisms (white rot fungi, brown rot fungi, and soft rot fungi), or a cocktail of enzymes, enable good lignin and hemicellulose degradation with a negligible effect on cellulose but are time consuming (1–2 weeks), making them less attractive for industrial purposes [69,70]. Moreover, the productivity of these methods is affected by environmental factors (temperature) and presence of toxic chemicals in biowaste, which affects microbial growth.

3.1. Acoustic Cavitation (AC) as Effective Biomass Pretreatment

Although a variety of new technologies have been developed at the lab and industrial scale for biomass valorisation, there is still a long way to go to efficiently transform biowaste into biochemicals and bioenergy [76]. In particular, the development and application of even innovative, energy effective, scalable end inexpensive technologies could make the difference. In particular, there is a crucial need to design and develop sustainable cellulose recovery processes.

These criteria are largely addressed by sonication, being a physical treatment that can increase size of pores and accessible surface area and decrease cellulose crystallinity and its degree of polymerization, enhancing the biodegradability or the enzymatic hydrolysis of agri-food residues. Furthermore, the significant decrease in process time and temperature are the most attractive characteristics of US-assisted treatments (UAT). In fact, US could induce fast structure damages due to several mechanisms: local shear stress, erosion, fragmentation, sonoporation and sonocapillary effect.

Recently, many researchers have exploited US to improve biomass delignification, in particular under alkaline conditions. Despite these attempts, the exact physical mechanism of the US-assisted delignification is not yet recognized. Additionally, it can be stated that to date, a single and exhaustive biomass delignification process has not been established to carry out a complete cellulose recovery from agri-food waste in an economic and environment friendly manner.

A comprehensive review of the recent literature on the application of cavitation for delignification has been given in the work of Csoka et al. (2012) [77] reporting the different investigated systems, highlighting reactors features and the important results achieved.

Therefore, extensive research has been carried out for developing various US and HC delignification treatments of biomass. However, after a critical analysis it is possible to claim that pretreatment methods are "tailor-made" processes for every individual matrix which should be carefully chosen and proposed based on the characteristic properties of considered starting material.

In this context, Singh et al. (2014) [78], attempt to give mechanistic insight into UAT delignification of *Parthenium hysterophorus*, commonly known as carrot grass. The approach of their study was to couple simulations of cavitation bubble dynamics to the delignification experiments of this agri-food residue. The best result has been described under US irradiation for 15 min (20 kHz, 500 W) at 30 °C in presence of NaOH (1.5% w/v), starting from a biomass consistency of 2% w/v. They noticed that both physical and chemical effects of transient cavitation contribute to final delignification (90%), that was 2-fold higher compared to mechanical treatment. Furthermore, the lignin depolymerization takes place through homolytic cleavage of phenyl ether $\alpha-O-4$ and $\beta-O-4$ bonds induced by US lignin. The chemical effect of radical generation induces oxidation/hydroxylation of the main lignin aromatic moieties and in addition, side chain elimination phenomena. Due to these exclusive mechanisms, UAT gives efficient delignification at room temperature and with minor requirement of delignifying agents. They finally observed that cavitation also causes decrystallization of cellulose due to its partial depolymerization.

He et al. (2017) [79] also evaluated the UAT effects on biomass structural alterations. Particularly, Eucalyptus wood with a particle size of 0.5 mm was submitted to AC (0.5–1.5 h) with an ultrasonic bath working at 28 kHz and 300 W. The protocol was tested with distilled water, aqueous NaOH solutions or acetic acid. The results of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) on pretreated and untreated wood samples showed that cavitation is indeed effective in altering the physicochemical structure of Eucalyptus wood; the applied protocol reduced the amount of alkali metals (e.g., potassium, magnesium and calcium) in the residual biomass. Compared to the control biomass, the residual char content of NaOH pretreated samples increased by 10%–20%, while the reaction temperature decreased from 361 °C to 341 °C. Conversely, in UAT samples treated in presence of acetic acid or distilled water, the residual char content diminished by 12%–21% and there were no significant discrepancies in reactivity apart from a slight increase in reaction rate. Further results showed that UAT has strong influence on the structure texture of the Eucalyptus wood samples. The acoustic cavitation successfully removed cellulose, hemicellulose and lignin from the substrate, increasing the average crystallinity up to 35.5%; the process also enhanced the exposure of the biomass material to the treatment solutions and broke down sample structure generating pits and microchannels. In addition, US removed and prevented the formation of aggregates and biomass clusters.

When rapeseed straw (RapS) was pretreated by Brahim et al. (2016) [80] either by US, MW or high voltage electrical discharges (HVED) the extraction of reducing sugars and soluble lignin, as well as the delignification, were improved. In terms of energy requirements, HVED induced a significant delignification yield (42.3%) with the lowest energy consumption (in order to achieve the same efficiency, MW and US consumed 9 and 4.5 times more, respectively). Meanwhile, the best EH yields (41.6%) were reached when the RapS were pretreated under US (12 kHz, 400 W, 10–40 min) and HVED in alkaline conditions (at 90 °C). Figure 4 shows the SEM images of RapS pretreated by US and HVED which were related to the greatest delignification yields. Figure 4A–F shows the shredded morphology of the sample, due to the structural damage caused by UAT and HVED. Moreover, there were more rifts and extra fibres appearing in the pulps after US pretreatment than that recorded in the raw material (Figure 4G), where a slick and uniform surface is revealed. Consequently, the lignin recovery (40%) was achieved thanks to an intensified breakdown of polysaccharides-lignin connections, providing better accessibility to enzymes.

Finally, the reported US and HVED were effectively combined with chemical treatments, i.e., NaOH sol. or organosolv (ethanol/water 65% *v/v*, +1% H_2SO_4 20%) for RapS delignification (Brahim et al., 2017) [81].

Best results were noticed for HVED-NaOH and US-organosolv approaches. Both technologies enabled a marginally affected lignin with a higher polymerisation degree (in case of UAT) and damaged ferulates bridges (in case of HVED). The lignin fractions recovered from HVED-organosolv treatment included a lower amount of ferulic acid and *p*-coumaric acid as compared to those extracted by US-organosolv, while the latter showed higher syringyl/guaiacyl (S/G) ratios (1.75) compared to the first (1.31). In addition, pretreatment with HVED and US-under alkali condition induced positive effect on subsequent cellulose recovery.

Brahim et al. also described the successful combination of physical and chemical treatments for the rapeseed hulls extraction of phytomelanins (Brahim et al., 2016a) [82]. Among the reported pretreatments, US and HVED have proven their better activity especially under alkali conditions. The above-mentioned investigation revealed that physical treatment promoted the recovery of the phytomelanin layer and increased the EH of resulting pulps. The results highlighted in particular the effectiveness of US working at 12 kHz with the intensity of 400 W (Figure 5).
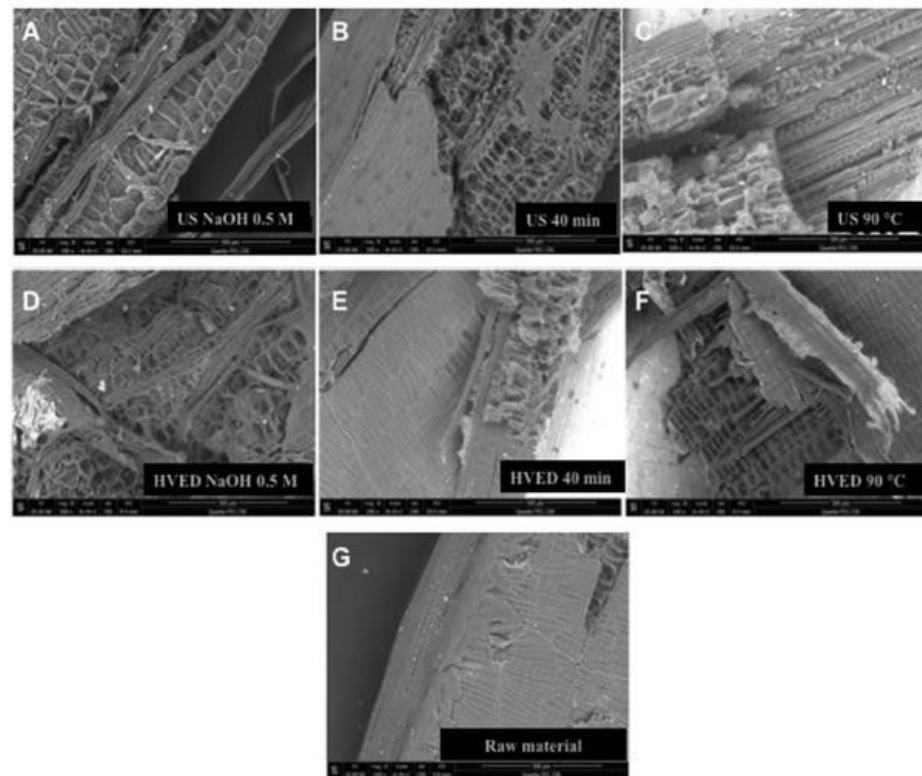
Figure 4. SEM images of pretreated RapS pulps samples: UAT (T = 80 °C, time = 20 min, NaOH = 0.5 M) (**A**); UAT (T = 60 °C, time = 40 min, NaOH = 0 M) (**B**); UAT (T = 90 °C, time = 20 min, NaOH = 0 M) (**C**); HVED (T = 80 °C, time = 20 min, NaOH = 0.5 M) (**D**); HVED (T = 60 °C, time = 40 min, NaOH = 0 M) (**E**); HVED (T = 90 °C, time = 20 min, NaOH = 0 M) (**F**) and raw material (**G**) (magnification 100). Reprinted from *Biomass and Bioenergy*, 95, 92–98, Copyright (2016), with permission from Elsevier.
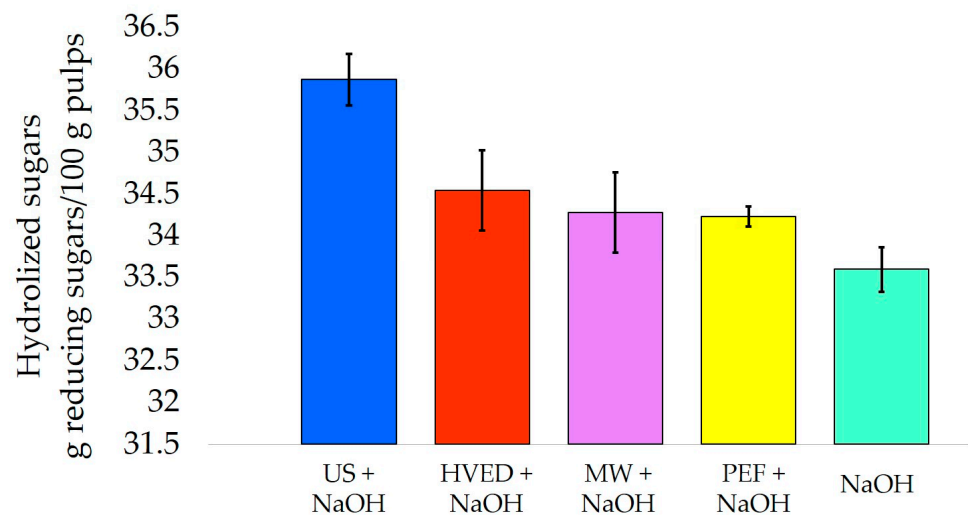
Figure 5. Effect of combined treatment (NaOH sol. (control), Pulsed electric fields (PEF) + NaOH sol., HVED + NaOH sol., US + NaOH sol., MW + NaOH sol.) on sugar recovery after 24 h of enzyme hydrolysis (NaOH sol. conditions: 60 °C, 2 h, 0.3 molL^{-1}, physical treatment condition: 30 min of total solid/liquid contact time (150 kJ kg^{-1} for PEF and HVED, 1500 kJ kg^{-1} for US)).

US-assisted lignocellulosic fractionation proved to be effective also for a typical Mediterranean agri-food waste, *Olea europaea*, as reported by Labidi et al. (2011) [83] UAT (50 Hz, 420 W) enabled the achievement of a high delignification degree and con-

tained cellulose degradation. Moreover, the recovered lignin structure and its thermal properties were not affected by sonication process.

Subhedar and Gogate (2014) [84] examined the application of alkaline UAT on newspaper waste slurry, a substrate containing up to 23.07% of lignin. About 2-fold increase in delignification (around 80%) was achieved by cavitation (20 Hz, 100 W, 70 min) if compared to silent alkaline process (Table 2). The so obtained pretreated biomass could represent a suitable substrate for ethanol fermentation and EH due to its high cellulose content.

Table 2. Effect of US parameters on lignin removal rate.

US Parameters	Delignification (%)	Rate Constant k (min^{-1})
Power (W)		
60	42.77	0.0081
70	50.21	0.0106
80	60	0.0138
90	73.26	0.0197
100	80.16	0.0239
110	82.01	0.0259
Duty Cycle (%)		
40	63.15	0.0148
50	69.97	0.0178
60	75.59	0.0213
70	79.94	0.0242
80	80.92	0.0246

The US pretreatment effect on fibres of oil palm empty fruit bunch (OPEFB) has been evaluated by Yunus et al. (2010) [85] for acid hydrolysis. It has been estimated that the amount of fermentable sugars from OPEFB, namely xylose (Xyl) and Glu account for ca. 70% of the overall composition. This feature makes this substrate extremely interesting for bioethanol production via fermentation. In detail, Yunus et al. applied a US probe operating at 20 kHz and 2 kW power, maintaining the working temperature of 25 °C. A maximum Xyl yield of 58% was achieved when the hydrolytic tests (100 °C, 2% H_2SO_4, 1:25 solid/liquid (S/L) ratio) were performed on fibres treated with US for 45 min. On the contrary, only 22% of Xyl was obtained for raw biomass. A direct exposure of the OPEFB fibres to acoustic power at various amplitudes has a noticeable impact on the effectiveness of acid hydrolysis, estimated on the Xyl yield (Figure 6). This trend has been explained by the increasing removal of silica from the surface of the OPEFB fibres, prior to acid hydrolysis.
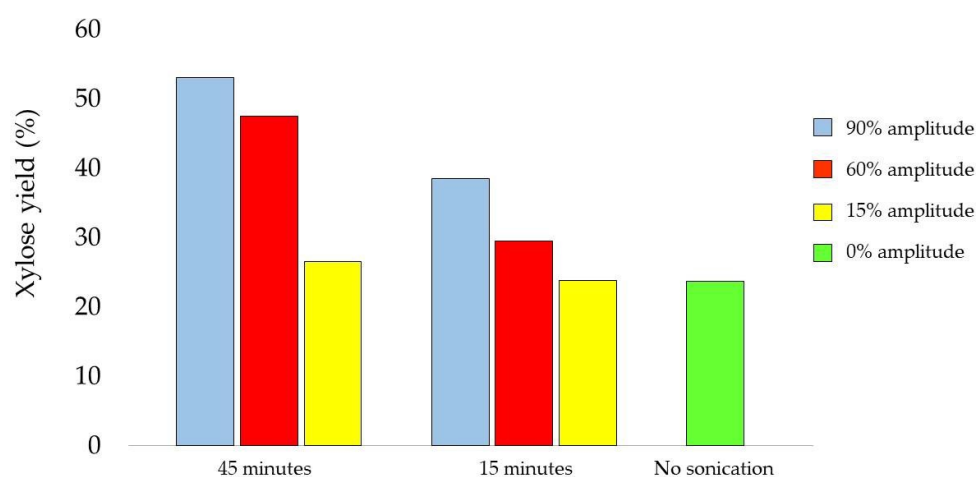

Figure 6. Influence of US amplitude on Xyl yields.

Kandasamy et al. (2017) [86] recently investigated the recovery of cellulosic material from sugarcane bagasse (SCB), an agri-food waste prone to ethanol production without any hydrolytic protocol. The matrix was firstly pretreated under alkali (NaOH 22%–25%), acidic (H_2SO_4 2.5–3.5%) or US condition (20 kHz, 100 W), applied separately or in combination. In addition, SEM analysis showed that the combined acid/UAT was able to destroy the SBC complex structure. The pretreated biomass was then anaerobically fermented without EH. The results indicated higher EtOH production (820 mg/L) when cavitation was combined with acid medium. In addition, 911 mg/L of EtOH was reached when all the pretreatments were utilized, and SCB was treated with US (50 or 109 W) and acid (3%) and then with alkaline (23%) and US (50 or 109 W).

Cellulosic fraction recovered from several biomasses can also be exploited as a fermentation substrate for hydrogen production. The biological dark fermentation represents a more sustainable and less expensive process than lignocellulosic matrix pyrolysis or gasification. Guang Yang et al. (2019) [87] combined US with dilute acid as a pretreatment process to increase fermentative hydrogen production from grass. To evaluate the efficiency of the synergistic process, the two protocols were tested separately as well. In particular, 2 g of grass suspended in 40 mL of distilled water were sonicated with an immersion horn for 30 min with an output power of 260 W, without any addition of chemicals. For the conventional acidic treatment, the same quantity of biomass was added of 40 mL of HCl solution (1% *w/w*) and then refluxed for 30 min.

The same biomass to HCl solution (1% *w/w*) ratio, sonication time and US output power were exploited to investigate the efficiency of US + dilute acid pretreatment towards grass carbohydrate and soluble chemical oxygen demand (SCOD) increase. The combined protocol allowed the increase of SCOD and carbohydrate content, respectively, by almost 99% and 237% if compared to the raw matrix; the SCOD and carbohydrates recovery was 88.5% and 231.5% higher compared to UAT alone, while it was around 17% and 36% higher related to the dilute acid alone. Guang Yang et al. also performed different fermentation batch exploiting raw and pretreated grass as unique carbon source. The highest hydrogen quantity (84.4 mL) was documented for the US + dilute acid pretreatment, which was 190.0% and 35.0% higher compared to US and diluted acid alone pretreatments, respectively (Figure 7). According to the author, this result indicates that combined pretreatment intensified the hydrogen production via fermentation because of the higher carbohydrates availability and the disruption of recalcitrant structure of the lignocellulosic biomass.
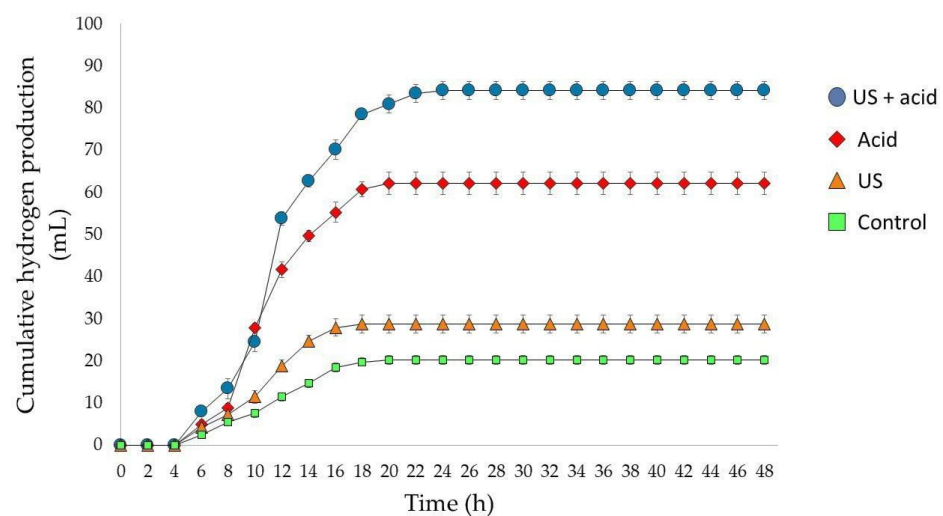

Figure 7. Cumulative hydrogen production for control and pretreated groups.

To improve enzymatic hydrolysis of rice straw (RS), Xiong et al. (2017) [88] have lately exploited the US-assisted cellulose recovery process combined with Fenton's reagent (U/F-RS) by means of a horn type sonotrode, working at 22 kHz in power range of 200–600 W.

The authors confirmed that combination of acoustic cavitation together with the oxidizing agent enabled a reliable and effective pretreatment for RS, suitable for subsequent EH step (Figure 8). Firstly, U/F-RS led to the sample's lowest degree of polymerization and largest specific surface area. Furthermore, this sample had the highest enzymatic activity after 48 h of saccharification, with 4- and 1.5-times higher sugars yield with respect to raw RS and Fenton's reagent alone (F-RS), respectively.
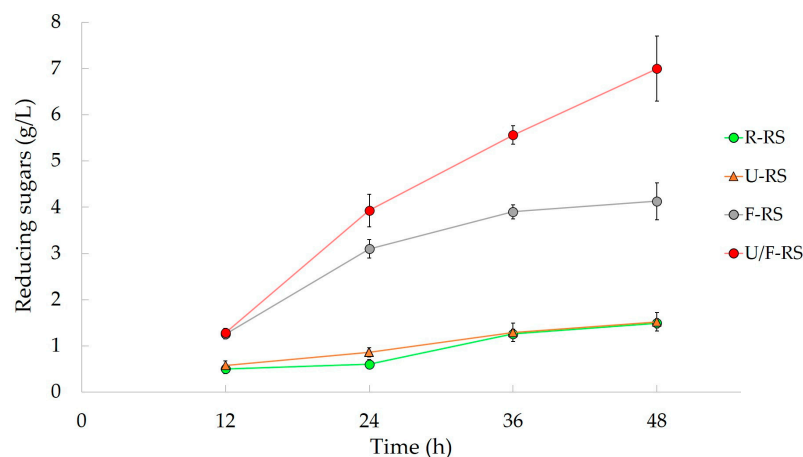

Figure 8. Reducing sugars recovered from pretreated and raw RS samples. U/F-RS = combined US 6Fenton process); F-RS = (conventional Fenton's process); U-RS = (UAT-RS at 400 W); (R-RS = (raw RS).

Post-treated analysis revealed that the application of US did not change the average content of hemicellulose and lignin in comparison with F-RS, hence authors concluded that the rice straw higher specific surface area and lower DP obtained after combined pretreatment led to the higher enzymatic activity observed on U/F-RS. Compared with the conventional Fenton's reagent process which generally takes dozens of hours, the U/F-RS treatment only takes 3 h to obtain similar EH yield.

Since it is well known that cellulose recovery from lignocellulosic matrixes can be improved by means of delignification under alkaline condition at high temperature, the heating generated by US irradiation could be useful to save time and energy. In this context, Wu et al. (2017) [89] showed that the energy dissipated into heat from a horn-type US device working at 300 W and 22 kHz for 70 min, was an effective and reliable method for RS alkali-cellulose recovery. They proved that the alkaline UAT (NaOH) enabled 3.5 times higher concentration of reducing sugar than untreated one, after 48 h of EH (2.91 vs. 0.85 g L^{-1}). These results can be attributed to the US pretreated samples' higher cellulose content as well as their lower hemicellulose and lignin content and to their higher porosity and surface area compared to untreated ones. Nevertheless, it should be stated that the cellulose content of processed straw, together with its surface area and porosity rose with the increasing concentration of used NaOH (0.4%, 0.6%, 0.8% and 1.0%, *w/v*).

A UAT in presence of tetra-butylammonium hydroxide (TBAOH) was recently launched by Zhong et al. (2017) [90] to boost the biodegradability of a largely diffuse agri-food residue: the wheat straw (WS). The synergistic mechanical and chemical effects induced by the combined UAT-TBAOH pretreatment were responsible for both WS surface destruction and internal structure disruption of pretreated samples (Figure 9).

High-efficient lignin removal combined with structural transformation (crystallinity reduction) was accomplished after the process. Experimental screening indicated that sonication time, temperature and US power intensity were pivotal for the pretreatment success of WS in presence of tetra-butylammonium hydroxide.

A 4-fold increased saccharification yield (*ca.* 92.4%) was obtained from residual cellulosic fraction if compared to untreated matrix. In detail, the WS were submitted at 50 °C to 30 min of sonication at 344 W/cm2.
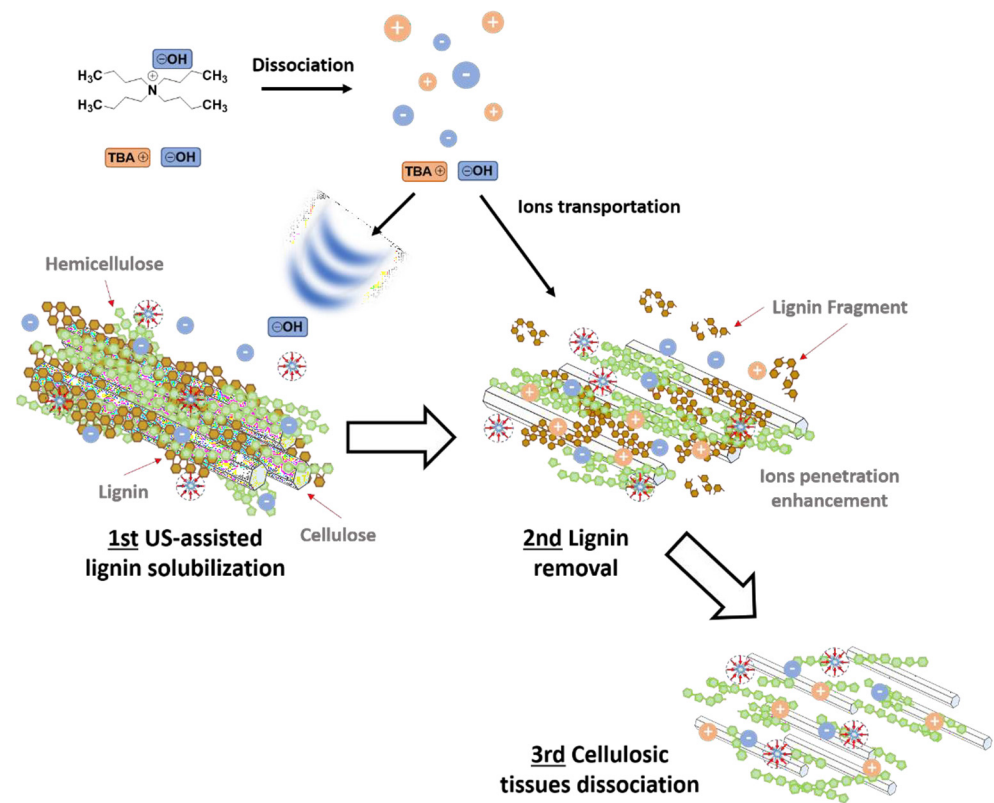
Figure 9. Mechanism of UAT with TBAH.

Moreover, the author pointed out that a certain extent of lignin removal (60–70%) is enough to attain high saccharification efficiency. Meanwhile, an excessive lignin removal achievable under harsher pretreatment conditions may cause cellulose degradation that is not desirable from a biomass valorisation prospective based on cellulose recovery (Figure 10).
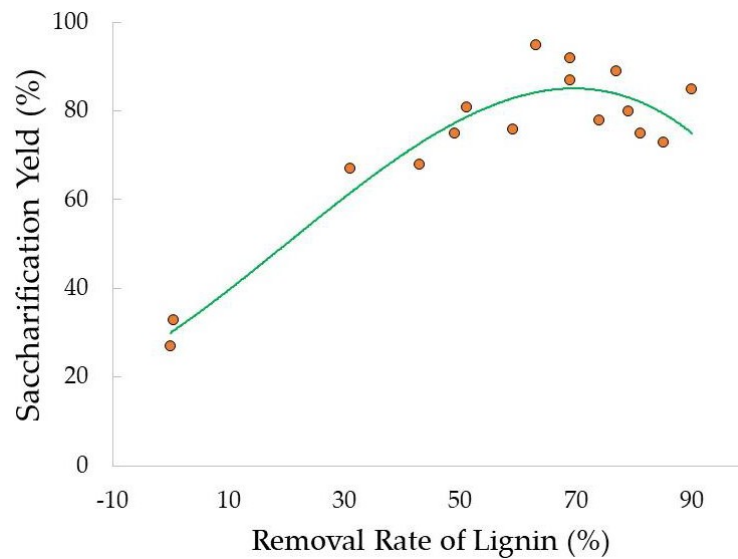
Figure 10. Influence of lignin removal on saccharification yield.

In addition, it was reported that TBAH could be recycled several times without considerable loss of activity.

US technology under different power input (60–540 W) and duration (10–30 min) was successfully applied by Ivetić et al. (2017) [91] as suitable cellulose isolation process for sugar beet shreds biomass (2–4% of solids loading).

In fact, under the tested conditions, US (22–25 kHz), caused up to 28% material solubilization while the recovery of cellulose was approximately 90%. In addition, US provided sugar beet shreds extremely prone to enzymes adsorption (allowing an adsorption capacity of 1.4 to 15 times higher), thus enhancing the EH. The best yield of cellulose EH (approximately 780 mg/g cellulose) was 3.7 times higher than that recorded for the raw substrate, indicating that US could be a good choice to recover from this agri-food waste a cellulosic fraction prone to enzymes conversion.

Coffee silver skin (CSS) is an agri-food processing waste largely produced at almost constant rate in roasting factories over all the year. The CSS could be employed as a fermentable sugars source within a biorefinery approach for its exploitation. Niglio et al. (2017) [92] investigated the effect of the US-assisted dilute acid pretreatment on the effective recovery of cellulose from CSS biomass. The effects of two mainly operating parameters— biomass loading (ranging between 3 and 10% *w/v*) and H_2SO_4 (96% w) concentration (ranging between 0.5 and 2% *v/v*)—were evaluated over sugar yields after EH. A probe type ultrasonic device (20 kHz) was used for the US pretreatment at specific sonication power (energy for dry biomass unit) of 300 W/gDM for 8 min.

In addition, the concentration of fermentation inhibitors (such as furfural, 5-hydroxymethyl furfural (HMF), ferulic and *p*-coumaric acid), was monitored for each US-treated CSS sample after EH step, showing always negligible amounts (less than 1 mg/L). As a consequence, the hydrolysate of US assisted pretreated CSS in presence of diluted acid may be directly fermented without a time-consuming detoxification step.

The same authors also optimized a combined process based on US and mild alkaline conditions for suitable CSS pretreatment (2020) [93]. A central composite design was exploited to identify the best operating conditions for the alkaline UAT tests on CSS aiming at the maximization of reducing sugar yields (YS).

The authors stated that the highest sugar yield (0.6 g/g) was obtained starting from the US pretreated CSS under 5-min sonication at 11% *w/v* biomass loading, and 75-min autoclave in presence of 5% *w/v* of NaOH. Moreover, the alkaline pretreatment alone was exploited as a benchmark, providing a hydrolysis yield higher than that measured for US alone. On the other hand, alkaline UAT produced a slight increase of sugars outcome compared to the conventional protocol. Time screening confirmed that longer sonication treatment (from 5 to 30 min) did not offer any improvement.

All the delignification processes allowed the exposure of cellulose microfibrils resulting in an increased crystallinity index, but the maximum value has been obtained with the alkaline UAT.

According to Niglio et al., some phenolic compounds could be recovered from the pretreated liquor. The alkaline and the alkaline UAT increased phenolic compound release of about 6.5- and 7-fold, respectively, if compared to the raw CSS. In particular, the phenolic content of the recovered liquid after alkaline UAT hydrolysis of CSS was 25 mg GAE g/raw CSS, larger than that reported by Conde et al. (2016) [94] for CSS.

Another effective alkali UAT was reported by Sindhu et al. (2017) [95] starting from chili post-harvest residue. The biomass UAT (80 kHz, 0–60 min) in presence of NaOH, KOH or $Ca(OH)_2$ was followed by a hydrothermal treatment in autoclave for 60 min at 121 °C before EH. Sindhu et al. explored the interaction effects between biomass loading and sonication time on EH. Maximum reducing sugar yield (0.44 g/g) was described for longer sonication time (50–60 min) and middle levels of biomass loading (11.0–15.0% *w/w*). Alkali medium plays a crucial role in delignification, providing reactive hydroxyl ions, acting by means of three major reactions on lignin: (i) fragmentation; (ii) degradation and dissolution; (iii) condensation. The UAT described by Sindhu et al. (2017) could effectively remove lignin and hemicelluloses from chili post-harvest residue, enhancing the cellulose recovery and the final sugar yield. Inhibitor analysis performed on the hydrolysates showed that

furfural, HMF as well as organic acids like citric acid, succinic acid and propionic acid were not present. Hence, fermentation can be carried out without prior detoxification step. Fermentation of the non detoxified hydrolysate yielded 1.9% of ethanol with a fermentation efficiency of 70%.

Acoustic Cavitation Coupled with Alternative Solvents

Considering the hindering effects of lignin on cellulose recovery and conversion, together with the biomass recalcitrance induced by vegetal textures, several studies were conducted investigating new and alternative solvents able to disrupt the matrix network and/or solubilize lignin. In this context, a novel cellulose isolation process based on the use of bio derived γ-valerolactone (GVL) was developed by Li et al. (2017) [96] with the aim to valorise bamboo components into digestible cellulose, fermentable sugars and lignin. Bamboo, as a grassy plant with rigid structure, was pretreated using a GVL/water mixture (60:40) containing 0.05 mol/L of acid (H_2SO_4), resulting in a liquid fraction enriched with cellulose. The recovered liquid fraction was further sonicated (100 W and 35 kHz for 10 min) in presence of NaCl to achieve a water phase rich in degraded sugars and a GVL phase rich in easily recoverable lignin. A cellulose conversion rate of about 90% was reported, 6.7-times higher than the reference sample. The sugars released in water phase were mainly represented by monosaccharides (70–160 g/kg) together with a considerable amount of oligo- and polysaccharides (45–180 g/kg). On the other hand, the lignin fraction recovered from GVL had a high purity degree (less sugar leftovers), a low molecular weight (1820–2970 g/mol) and low polydispersity (1.93–1.98), showing a typical *p*-hydroxyphenyl-guaiacyl-syringyl (HGS) type structure. GVL, as bioderived solvent (Luo et al. 2016) [97,98], could be considered a promising medium for processing lignocellulosic materials, due to its safety and renewability and the above-mentioned study probably established the fundamentals for newly sustainable valorisation process for the conversion of residual Gramineae biomass. In fact, a similar approach was investigated exploiting the ability of ILs to fractionate biomass, efficiently disrupting the complex network of noncovalent connections between biopolymers. It was described as the ILs imidazolium cations [HMIM]+ being able to particularly interact with the lignin aromatic rings by the $\pi - \pi$ interactions to boost lignin solubilization, thus, [HMIM]+ as a small size of cation was efficient in fractionating lignocellulosic biomass. Moreover, lignin solubilization features of ILs could be improved by anions with strong hydrogen bond capability.

At this regard, imidazolium based ILs with different anions (chloride, acetate, sulfate, phosphate, methane sulfonate, *p*-toluenesulfonate) were explored by Zhang et al. (2015) [99] for cellulose recovery by means of biomass fractionation. The Corn stover breakdown into cellulose and hemicellulose and lignin was successfully reported in ILs when combined with US irradiation (3 h, 400 W) at 70 °C. A 60% of original lignin (S-G-H type) was recovered in presence of [HMIM]Cl− and [HMIM]CH_3COO−. Both the acidity and the hydrogen bond capability of utilized ILs contributed to the efficient fractionation. Moreover, smaller anions were desirable, due to their ability to diffuse more easily within the lignocellulosic matrix. Coupled with a small sized cation such as [HMIM]+ the chloride anion, being small-sized and a strong hydrogen-bond acceptor, makes [HMIM]Cl the solvent of choice for biomass splitting and cellulose recovery. EH of recovered cellulose was then accomplished with a 97.77% of reducing sugar yield.

Vishal Sharma et al. (2019) [100] developed, for the first time, a pretreatment process based on ILs and US in association with surfactant PEG-8000 (polyethylene glycol) to enhance SCB (sugarcane bagasse) enzymatic saccharification. Firstly, five different ILs have been tested without US and PEG-800: [Emim][$MeSO_3$] (1-ethyl-3-methylimiazolium methanesulfate), [Emim]Cl (1-ethyl-3-ethylimiazolium chloride), [Emim][CH_3COO] (1-ethyl-3-methylimiazolium acetate), [Bmim]Cl (1-butyl-3-methylimiazolium chloride), and [Emim][Dmp] (1-ethyl-3-methylimiazolium dimethylphosphate). For this purpose, 0.25 g of SCB have been mixed with either of the IL at 0.25 g in an acetate buffer (50 mM, pH 5.0) at a biomass loading of 5%, (*w*/*w*) and then heated at 90 °C for 2 h. The efficiency

of the ILs have been evaluated as resulting maximum sugar yield after pretreated SCB saccharification: [Bmim]Cl resulted the best IL for this biomass with a maximum sugar yield of 130 mg/g biomass. The authors also investigated the effect of [Bmim]Cl load (0.25–1.50 g) in the same pretreatment process; the sugar yield increased with the increase of SCB load and reached the maximum value (168 mg/g) at 1.25 g of [Bmim]Cl after 72 h. The [Bmim]Cl + PEG-8000 pretreatment has been investigated at the same conditions of IL pretreatment alone with the addiction of different surfactant loadings (10–100 mg) and the maximum sugar yield has been reached with 75 mg of PEG-8000. Finally, the combined US, IL and surfactant pretreatment have been performed mixing 1 g of SCB in 19 mL of 50 mM acetate buffer (pH 5.0). The suspension has been sonicated for 60 min (20 kHz, 100 W, pulsing cycle of 59 s off/59 s on) exploiting a titanium probe tip and then pretreated with 5.0 g of [Bmim]Cl and 300 mg of PEG-8000 at 90 °C for 2 h. The maximum sugar yield obtained through enzymatic saccharification of US, IL, surfactant pretreated SCB was 255 mg/g biomass, while it was 177 mg/g biomass for US alone and 192 mg/g biomass for the [Bmim]Cl + PEG-8000 pretreatment. Thus, according to Sharma et al., the use of surfactant coupled to US and ILs improves the delignification process by increasing the SCB surface area with consequential improvement of mass transfer.

Alongside the ionic liquids commonly utilized for biomass pretreatment, an ever-greater interest in natural ILs has recently grown. Completely bioderived ILs such as choline acetate (ChOAc) have been tested in lignocellulose fractionations as new suitable alternative solvents (biodegradable and biorenewable) to even more expensive imidazolium ones. In this context, Ninomiya et al. (2013) [101] exhibited that the UAT of a powdered bamboo waste in presence of bioderived ChOAc could significantly enhanceits cellulose recovery and its subsequent saccharification performance. When thermally pretreated (110 °C) for 60 min in ChOAc, saccharification yields of bamboo powder was around 55%. Conversely, 92% of cellulose was hydrolysed to Glu after UAT (24 kHz and 35 W power) of bamboo powder at 25 °C for 60 min in the same bioderived IL. Furthermore, the crystallinity of cellulose achievable from the matrix was lower in the case of cavitational process than in case of thermal pretreatment in presence of ChOAc.

To deeply explore the pretreatment potential of ChOAc for lignocellulosic substrate, Ninomiya et al. (2015) exploited the cellulosic fraction recovered from the ChOAc UAT of bagasse [102] for subsequent EH. The biomass/IL mixture was sonicated at 24 kHz (35 W power) for 60 min, by using an immersion horn. Saccharification efficiency was evaluated as the percentage of native cellulose in the bagasse hydrolysed into Glu. Likewise, saccharification of hemicellulose was evaluated considering the native percentage of hemicellulose hydrolysed into Xyl. After ChOAc pretreatment, cellulose and hemicellulose saccharifications increased, reaching a maximum of 85% and 100% respectively, after 48 h.

Furthermore, the application of ILs for in situ enzymatic saccharification of cellulose was investigated. For this purpose, the solubility of cellulose and the subsequent cellulase activity on it were tested by Yang et al. (2010) [103] using different alkylphosphate ILs. Moreover, an UAT was exploited to simultaneously enhance the cellulose conversion. Among the screened solvents, the 1-methyl-3-methylimidazolium dimethylphosphate ([Mmim][DMP]), with favourable solubility and biocompatibility, was selected to establish aqueous-ILs system for enzymatic in situ cellulose saccharification.

The conversion of the substrate in aqueous-ILs with US irradiation has an increase of 53% if compared to that recorded for untreated cellulose. Moreover, higher conversions (95%) were documented in aqueous-[Mmim][DMP] by performing a cavitational treatment at 60 °C (45 kHz, 100 W) for 30 min.

The effect of bubbles implosion coupled with the effect of aqueous-ILs appear to decrease the degree of polymerization and crystallization of cellulose, which might contribute to increasing its EH rate.

EmimOAc has been frequently considered the most effective IL for cellulose dissolution and pretreatment aiming to EH (Brandt et al., 2013) [104]. Conversely, pretreatment with ChOAc enhanced the cellulose saccharification to the comparable degree to EmimOAc,

suggesting how the acetate anion has a pivotal role in the reduction of cellulose crystallinity. In general, anions act as hydrogen bond acceptors that interact with the hydroxyl group of polysaccharides, thereby destabilizing their crystalline structure. In contrast, the inhibitory effects of ChOAc on cellulase were much lower than that of EmimOAc, because the cholinium cation was reported to be more biocompatible than the imidazolium one. Hence, ChOAc appear to be a promising option to EmimOAc for the IL based pretreatment and for the in situ saccharification of biomass.

Environmentally friendlier alternatives to ILs are deep eutectic solvents (DESs), which consist in a mixture of a hydrogen bond acceptor (HBA), often a quaternary ammonium salt, and a hydrogen bond donor (HBD), such as alcohols, acids, amines or carbohydrates. In literature, the terms DES and IL have been used interchangeably but it is necessary to point out that these are two different types of solvent. Ong et al. (2019) [105] demonstrated that sequential ultrasonication and DES pretreatment allowed lignin isolation and Xyl recovery from oil palm fronds (OPF). In detail, the UAT was performed in water (70% of amplitude, 30 min, S/L ratio of 1:10 w/v) and then pretreated using DES (choline chloride:urea 1:2, S/L ratio of 1:10 w/v, 120 °C for 4 h). The combined process decreased the lignin content by 36.42% while the DES pretreatment alone reduced the lignin content by 14%.

Moreover, FT-IR confirmed the disruption of lignin C–O–C aryl–akyl ether bonds in the sequential pretreated OPF, while XRD showed that crystallinity index of raw OPF was at 48.92% but the combination of recommended US/DES conditions provided a matrix with a crystallinity index of 59.31%.

Figure 11 reports the samples' images obtained through FE-SEM analysis. In particular, the sequential pretreatment of both US and DES showed the highest OPF structure degradation, where lignin fraction was dissolved and large amount of cellulose fraction was exposed to the surface (Figure 11d).
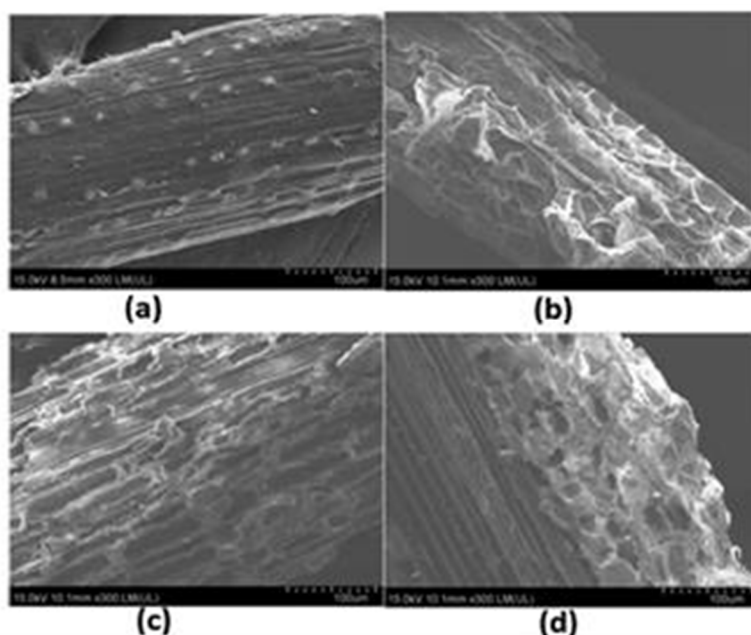
Figure 11. FE-SEM image of (**a**) Raw OPF (**b**) ChCl:urea pretreated only OPF (**c**) US pretreated only OPF (70%, 30 min) (**d**) US-DES pretreated OPF (70%, 30 min ChCl:urea). Reprinted from Ultrasonic Sonochemistry, 58, 104598, Copyright (2019), with permission from Elsevier.

Additionally, the amount of monomeric sugars present in the OPF after the sequential protocol was also evaluated by the authors: HPLC analysis performed on the OPF hydrolysate showed that the two-step pretreatment was able to yield a Xyl recovery of 58%.

Recently, a new class of DES has been synthetized on the basis of binary deep eutectic solvents and applied as a biomass pretreatment process: TDES (ternary deep eutectic

solvents). Jia et al. (2020) [106] developed a US- and MW-assisted TDES process, able to isolate cellulose and to fractionate lignin from the recalcitrant structure of garlic skin (GS). TDES composed by choline chloride (ChCl), glycerol and aluminium chloride ($Al_2O_3 \cdot 6H_2O$) with a 1:2:0.2 mole ratio has been synthetized and used as solvent to evaluate the optimal US frequency for the process. The combined protocol consisted of sequential sonication and MW heating (80°, 2 h) on the mixture of GS and TDES with a 1:10 by weight ratio. The authors firstly investigated the effect of different US function modes of single frequency (20, 28, 35, 40, 50, 60 kHz), dual frequency (20 + 28, 20 + 40, 20 + 60, 35 + 50 and 40 + 60 kHz) and ternary frequency (20 + 28 + 40, 20 + 35 + 50, 20 + 40 + 60 kHz). Compared with the no-ultrasonic pretreatment, the highest lignin removal (73%) and the highest cellulose increase (166%) have been obtained exploiting the 20 + 28 + 40 kHz triple frequency mode. According to the authors, the multi-frequency modes allow one to avoid the formation of ultrasonic barrier (shorter ultrasonic transmission distance and weaker cavitation effect) caused by the increase of cavitation bubbles' number at high frequencies.

In addition, two different metal chlorides ($FeCl_3$ $6H_2O$ and $CrCl_3$ $6H_2O$) and two different hydrogen bond donors (oxalic acid and urea) were used to synthetize TDES, but the best results in terms of lignin removal rate were obtained with the ChCl-Gly-Al DES (Figure 12).
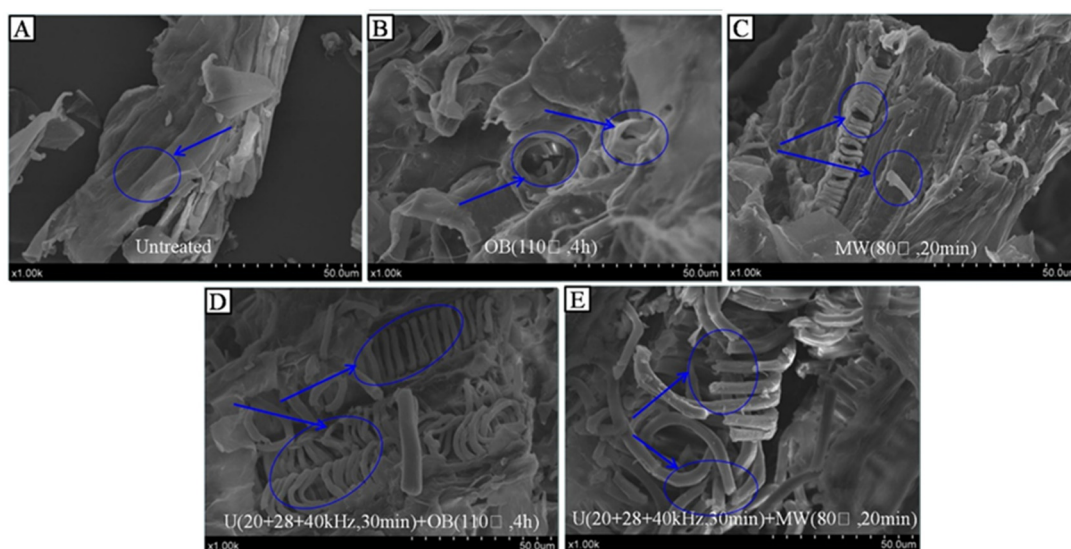

Figure 12. SEM images of GS under different pretreatment methods in TDES (ChCl-Gly-Al). Reprinted from *Ind. Crops and Prod.*, 149, 112357, Copyright (2020), with permission from Elsevier.

Moreover, Qinghua Jia et al. investigated the effect of thermal treatment comparing MW heating and oil bath (OB) heating for each of synthetized DES, after the US treatment (20 + 28 + 40 kHz, 30 min) or alone. Higher lignin removal has been achieved again with the ChCl-Gly-Al DES. The sequential US + MW protocol (80 °C for 2 h) allowed one to obtain a higher lignin removal (90.14%) compared to the ones obtained with the US followed by OB heating at 110 °C for 4 h (87.36%), OB and MW alone (76.10% and 83.71%, respectively).

The pretreated GS has also been characterized by FT-IR, XRD and SEM analysis. While FT-IR confirmed the disruption of chemical bonds between cellulose and lignin (C-O-C aryl–akyl ether bond), XRD confirmed the decreasing of GS crystallinity may be due to the cellulose hydrogen bonds disruption. SEM images obtained on the pretreated GS revealed that US + MW + TDES pretreatment is more effective than both OB and MW alone and US + OB + TDES (Figure 12 b–d, respectively) in terms of surface morphology alteration and inner fibre exposure. As stated by the authors, the TDES combined with US and MW represents a low-cost cellulose isolation process that could improve later stage in biorefinery, especially for the conversion of lignocellulosic biomass into bio-based platform chemicals.

In recent years, especially in the green chemistry area, some special DES that were produced using natural products have been studied and generally called natural deep eutectic solvents (NADES). These new classes of DES and GVL were tested as suitable solvents, coupled to US and MW, in the biomass delignification process by Calcio Gaudino et al. (2018) [107]. In detail, WS (wheat straw) has been treated with both GVL and different NADESs coupled to US and MW technologies for delignification purposes. NADES1 was composed by lactic acid/choline chloride (10:1) while NADES2 was composed by lactic acid/glycerol/choline chloride (1:1:1). The MW-assisted pretreatment was performed in a multimode reactor with a S/L ratio of 1:50 and a variety of GVL/H_2O ratios at 90–120 °C (1500 W-30 min). The UAT has been performed in a high-power ultrasonic bath (40 kHz and 200 W) with a WS/liquid ratio of 1:50 and different GVL/H_2O ratios at 35 and 50 °C for 60 and 120 min. The lignin content of unpretreated and pretreated samples has been determined by Py-GC/MS/FID (analytical pyrolysis coupled with GC/MS/FID). Despite best delignification (45%) being achieved with NaDES2 (lactic acid/glycerol/choline chloride) under MW irradiation at 120 °C in 30 min, all the pretreatment experiments enabled good cellulose recovery.

Moreover, the untreated and pretreated samples of WS have been characterized by nitrogen adsorption-desorption isotherm method to better understand the WS porosity modification. In general, UAT in presence of biobased solvents increased WS porosity both in the GVL and NADES samples. In comparison with conventional extraction, MW and US treatment with green solvents presented significant advantages in terms of sustainability. Furthermore, GVL/water mixtures proved efficiency in reducing the crystallinity of WS' cellulose. As claimed by these findings, NADESs could be utilized for liquid fraction valorisation, whereas GVL could be the solvent of choice for further solid applications.

3.2. Biomass Pretreatment under Hydrodynamic Cavitation

Under alkaline conditions, phenolic hydroxyl groups in lignin dissociate, forming a phenoxy radical stabilised by resonance, which is the initiator of depolymerization reactions. HC in alkaline conditions improves the formation of hydroperoxyl and hydroxyl radicals required for delignification purposes, thus intensifying the overall reaction rates. In addition, shock waves produced during HC are responsible for the breaking of several chemical bonds among lignin and (hemi-)cellulose in the lignocellulosic biomass. Likewise, to US, the key advantages of HC are the local and transient generation of high temperature and pressure (due to the collapse of shock waves) that are necessary for biomass deconstruction and delignification purposes, while the overall batch conditions still remain unaltered, thus preventing the needs of heating (or cooling) devices.

These characteristics make HC a valuable tool for agri-food waste treatment [108], the key step being to recover cellulosic fraction, getting rid of the recalcitrant matrix structure, by means of delignification and detexturization. Polysaccharides resulting from HC-assisted treatment (HCAT), could be furtherly exploited in the lignocellulose pretreatment, the key step in the biochemical processes to biofuels, for instance, an alkaline HCAT (3.0% NaOH) of reed, employed as starting raw material for the bioethanol production [109]. A cylindrical cavitation reactor connected to a centrifugal pump was used, with a radial form of orifice plate, leading to a maximum Glu yield of 326.5 g/kg biomass in 40 min. US treatment was conducted for the sake of comparison in the same conditions at 300 W power and 20 kHz dissolved less lignin (24.5%) than HC (42.3%). The HC highest delignification led to higher digestibility yield of pretreated samples (85.0%) compared to untreated (16%) and US treated ones (73.3%). Furthermore, the HC pretreated samples were used as substrate for batch saccharification and fermentation (SSF) leading to ethanol yield of 90%. An alkaline HCAT exploiting Venturi effect was also employed to enhance the efficiency of alkaline pretreatment of sugarcane bagasse (SCB) for EtOH production (Figure 13) [110]. A cylindrical cavitation reactor with a radial orifice plate with 27 holes of 1 mm diameter was used. Biomass was kept in a cylindrical wire cloth placed within the cavitation zone, in order to aid each particle in fully experiencing the cavitational effect. Under continuous

feeding of 0.48 M NaOH, 60% of lignin removal was reached after 45 min. In addition, 52% of glucan content and 97.2% of enzymatic digestibility were achieved. Furthermore, EH afforded a yield of 82% and 30% higher than the untreated and alkaline-treated controls, respectively. More recently, the same authors reported the alkaline pretreatment of SCB recirculating through an orifice plate having 16 holes at a fluid velocity of 54.49 m/s. With only 30 min of pretreatment, 93% and 95% of cellulose and hemicellulose hydrolysis were achieved at 70 °C using less NaOH (0.3 M) [111]. This result was supplemented by the drastic change of biomass structure created by the dramatically disruptive cavitation effect.
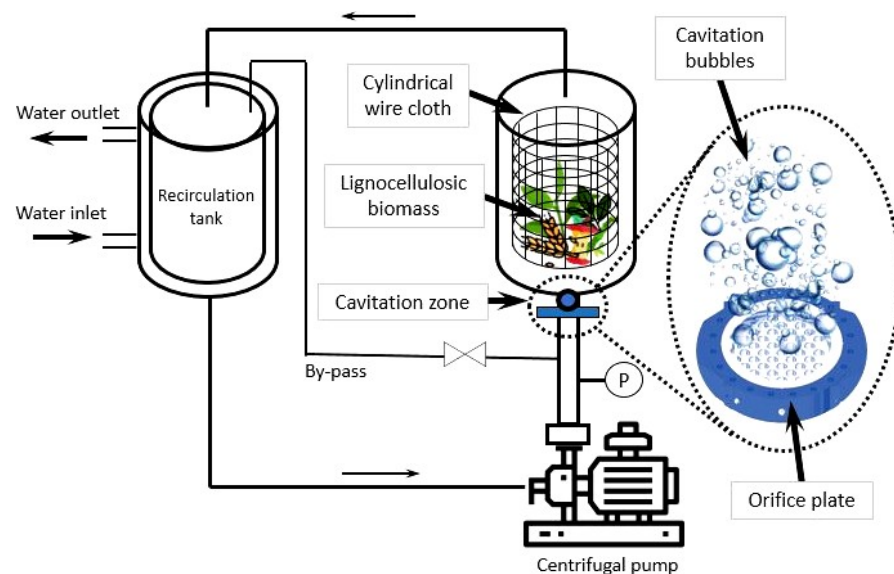

Figure 13. Schematic representation of HC system used for SCB pretreatment.

An alkaline-HCAT of SBC for bioethanol production was also investigated by Hilaresa et al. (2018) [112], which exploited a 3 L HC system composed by a centrifugal pump (1.5 CV), a cavitation zone and a recirculation tank. The system flowrate was adjusted to 5 m^3/h with a resulting cavitation number of 0.017. The process fluid temperature was set to 60 °C thanks to water-jackets while the upstream pressure for cavities generation was set to 3 bar. A Box–Benhken design was utilized to assess the influence of different variables: NaOH concentration (0.1–0.3 M), H_2O_2 concentration (0.2–1.0% v/v) and HC treatment time (2–10 min). For each experiment, 20 g of dry SBC was used.

The highest SCB cellulose increase (40 to 50%) was obtained with the recirculation of the 0.3 M of NaOH, 0.2% (v/v) of H_2O_2 solution in 6 min of process time. On the other hand, the highest lignin removal (27.2 to 14.3%) was reached with a 0.3 M of NaOH, 0.6% (v/v) of H_2O_2 solution and 10 min of time.

The operating conditions have been further optimized to maximize the pretreated SBC hydrolysis yield: the maximum value (95.43% of hydrolysis in 24 h) has been obtained recirculating a 0.29 M of NaOH, 0.78% (v/v) of H_2O_2 solution for 9.95 min and it was quite similar to the one predicted by the model (96.27 ± 7.31%) but higher in comparison to the ones reached with the pretreated biomass with a 0.29 M of NaOH and 0.78% (v/v) of H_2O_2 recirculating solutions, respectively.

The SCB hydrolysate was evaluated in terms of ethanol production exploiting yeast species *S. stipitis* NRRL-Y7124. The highest ethanol yield obtained after the fermentation process into a bubble column reactor was 0.49 g/g biomass (31.50 g/L and 0.68 g/Lh of volumetric productivity) after 46 h. At the same fermentation time Xyl has been completely consumed, contrary to Glu that was completely consumed after only 24 h. The efficiency of HC combined with sodium percarbonate was tested in the degradation of polysaccharides in corn stover, which was treated in a circular flow system, exploiting a Venturi tube (Figure 3) [113].

The SP-UAT of corn stover led to lower digestibility compared to the HC-SP procedure, which was more effective in terms of both Glu and Xyl production. This discrepancy could be attributed to the 50% greater lignin removal during the HCAT. The mild protocol (30 °C) allowed for the avoidance of the generation of inhibitors, such as furfural.

The comparison of energy efficiency during the HC- and US-assisted pretreatments of SCB, reed and corn stover is summarized in the Table 3.

Table 3. Comparison of energy efficiency during various HC-and US-assisted processes UAT and HCAT on different agri-food wastes.

Agri-Food Residue	Pretreatment Process	Conditions	Results (g of Glu/J)
Sugarcane bagasse	NaOH-HCAT NaOH-UAT	NaOH (1.9% *w/v*) 45 min	6.43×10^{-5} 2.61×10^{-5}
Reed	NaOH-HCAT NaOH-UAT	NaOH (3.0% *w/v*) 40 min	6.51×10^{-5} 2.58×10^{-5}
Corn stover	SP-HCAT SP-UAT	$NaCO_3$ (0.4 mol/L) H_2O_2 (0.6 mol/L) 60 min	2.24×10^{-5} 0.11×10^{-5}

The efficiency of pretreatment is reported in terms of cavitation yield, calculated according to Tao et al. (2016) in Equation (2) [114].

$$C_Y = \frac{G_r}{P_m \times t} \qquad (2)$$

where C_Y = cavitation yield (g of Glu/J), G_r = Glu released during EH (g), P_m = power of pump (W) and t = operation time (s). As displayed, HC systems are more energy efficient than UAT.

HC resulted very useful also for other processes requiring a biomass pretreatment step. For example, the delignification of wheat straw in paper manufacturing was improved under HC alkaline conditions [115]. In this case, the hydrodynamic cavitating reactor used for the wheat straw delignification was a rotor-stator type device (Figure 3), with a solid cylinder bearing indentations on its surface [116]. Rotor can be rotated at different speeds of rotation. Due to high speed of the rotor, very high surface velocities are generated at the cylinder surface. Such high velocities (typically 18–20 m/s) are accountable for the formation of elevated turbulence, leading to the breakage/lysis of lignin, cellulose and hemicellulose matrix. After only 10–15 min of alkali pretreatment (0.3 M, KOH), an increasing of the tensile index (50–55%) of the synthesized paper sheets was achieved, suitable for paper board manufacture. HC delignification of WS employed for the manufacture of paper revealed some advantages, such as the reduction of treatment time, energy consumption (nearly 50%) and temperature (25 °C). In addition, the versatility of the process was improved, as different parameters (such as the speed rotation and straw consistency) could be adjusted according to the required properties of the target paper.

A rotor stator type was also employed for the wheat straw pretreatment step in the production of biogas [117]. The design of experiments approach (DOE) helped the optimization of the process conditions. The yield of biogas was increased from 31.8 mL (untreated biomass) to 77.9 mL under HC working at 2500 rpm. Furthermore, the combined pretreatment using KOH and HC gave maximum yield of biogas (172.3 mL).

Garutia et al. (2018) [118] exploited a rotor stator HC reactor to enhance biomethane production from agriculture biomass in a full-scale agricultural biogas plant (ABP) composed by three stirred anaerobic digesters (AD1, AD2, AD3) in series with a total volume of 4200 m³ and an overall hydraulic retention time of 30–35 days to produce electrical energy and heat. The ABP feedstock consisted in agriculture byproducts (beet molasses and corn meal), energy crops (maize silage and triticale silage) and pig slurry. The solid biomass

feedstock was introduced into AD1 on regular time during the day while both AD1 and AD2 were fed with pig slurry. Almost 96% of AD1 effluent was treated only once with the rotor stator type HC system during its transfer to AD2 with an inlet pressure of 2 bar and equal inlet and outlet flow rates as there was no accumulation in the reactor. Three batch experiments with an increasing HC system electrical power (470, 740 and 954 kJ/kg of total solid) have been performed to investigate the effect of the HC rotor speed on the anaerobic biodegradability. All the HCAT set-up enhanced the biomethane yield and degree of degradation (Volatile Solids removed, %) of the digestate from AD1 compared to the same untreated digestate. The highest increase of biomethane yield (+14%) has been obtained with an HC system energy input of 740 kJ/kg while the 470 and 954 kJ/kg experiments allowed for the increase of fermentation yield by 3.5 and 2.9%, respectively. According to Garutia et al. the enhancement of anaerobic digestion with the increasing of HC system energy input can be attributed to an increase of cavitation intensity with consequent increase of biomass surface area. Moreover, the electrical energy used for the ABP operation increases about 100 kWhel/day with the HC reactor implementation. As the total energy production was nearly constant through the whole experimental time, the lower energy consumption has been associated to energy saving in biogas plant (17%).

A further delignification process performed with a rotor-stator HC system was also evaluated by Lauberte et al. (2021) [47]. For this purpose, wheat straw (WS) was pretreated for 30 min at 50 °C in a NaOH solution (10% mass, based on dried biomass) with a 1:50 S/L ratio. The solid fraction was recovered and freeze-dried to evaluate its residual lignin content by wet-chemistry Klason procedure. The HC allowed a delignification removal of 25%, if compared to the untreated WS, and an increase of hexose carbohydrates by up to 16%.

However, the Klason procedure could overestimate the residual lignin content due to the formation of pseudo-lignins, the condensation/coupling reaction product between lignin and other degraded biomass polymer compounds during the analytical procedure. Therefore, the residual lignin of raw WS and pretreated WS was also determined with the Py-GC/MS/FID method. A comparison of the two analytical methods' results confirmed the pseudo-lignin formation during the cellulose isolation process (Figure 14).
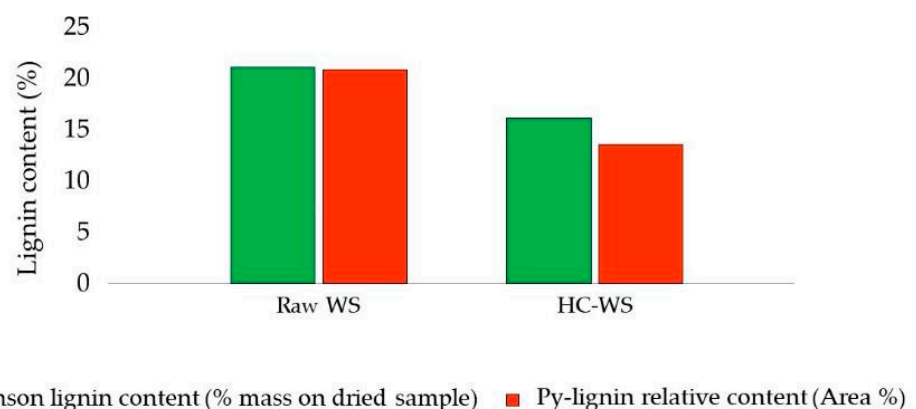
Figure 14. Klason lignin and py-lignin quantification approaches for raw WS and post HCAT WS.

The authors also performed a subsequent sonication of HC-pretreated WS with US (25 and 80 kHz) but no improvements were observed. UAT alone were also performed on the biomass (25–35 °C, 30–60 min, 25–80 kHz, and a combination of them) to compare their efficiencies in cellulose isolation. Overall, the US delignification percentage was higher (30–45%) than the HC alone (25%) but alterations of the lignin aromatic structural units' ratio were observed. According to Lauberte et al., this feature could be a negative factor for further cellulose saccharification, making HC a more suitable process for this purpose. To compare the efficiency of HC and US in the pretreatment of agri-food residues, Zieliński et al. (2019) [119] exploited these two technologies to improve the biogas production in an

agricultural biogas plant (ABP) using a pretreated WS and cattle manure as fermentation substrate. Before UAT and HCAT, the two biomasses were mixed and introduced in a substrate preparation tank (SPT) as follows: 0.2/0.05/0.035 Mg fresh/TS (total solids)/VS (volatile solids) was daily introduced into the SPT, while the cattle slurry was pumped by 10 min with 0.20 m³/d of rate (0.2/0.01/0.008 Mg fresh/TS/VS per day). The UAT was carried out into 5 linked square hollow tubular sections (total volume of 40 L) and located in an US system composed by 60 transducers (24 kHz and 10 kW for each transducer) as shown in Figure 15. The hydrosonic pump used for HCAT was constituted by a cylindrical rotor fixedly connected to the shaft and placed in a tank of 25 L (Patent No PL 214,335 B1). The rotor was powered by a 4 kW electric motor at 2800 rpm (Figure 15).
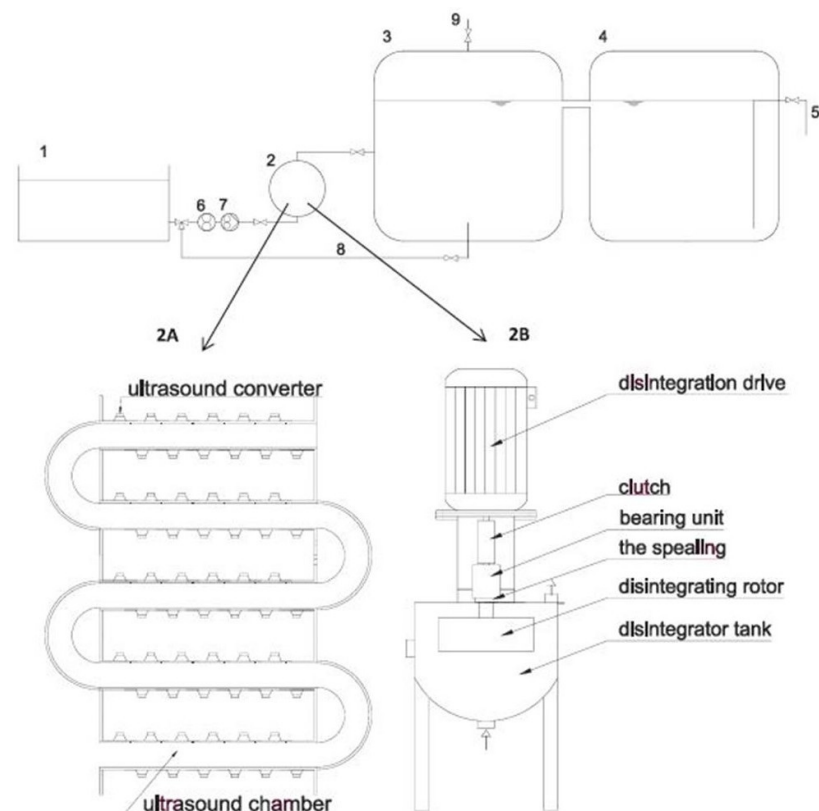

Figure 15. ABP scheme: 1-SPT, 2-cavitation-based pretreatment unit, 2A-US apparatus, 2B-HCP device, 3-MFT, 4-PFT, 5-digestate, 6-shredder, 7-pump, 8-digestate recirculation, 9-biogas outlet. Reprinted from Energy for Sustainable Development, 49, 21–26. Copyright (2019), with permission from Elsevier.

Different experiments have been performed:

- ABP-90 days of operations (without feedstock pretreatment)
- ABP-UAT-90 days of operations
- ABP-HCAT-90 days of operations

To evaluate the efficiency of pretreatment processes, biogas production rate (BPR) and cumulative biogas yield (CBY) have been monitored. In the ABP-90 days the BPR reached 15.9 m³/d, which was lower to the BPR reached with the exploiting of the two pretreated feedstocks. In fact, during ABP-UAT-90 days the BPR maximum value was 19.8 m³/d, while the ABP-HCAT-90 days led to a BPR value of 18.5 m³/d. Collective biogas yield (CBY) during ABP-90 days operation was of 370 L/kg VS, 460 L/kg vs. in the ABP-UAT-90 days and 430 L/kg vs. in the ABP-HCAT-90 days. The authors demonstrated that both UP and HCP improved biogas production by 25% and 17%, correspondingly. Moreover, Zieliński et al. evaluated the energy consumption (to produce 1 m³ of biogas) of the different set-up: comparing the two methods, lower energy demands for HC pump

operation resulted in lower energy requirement per unit of biogas produced in ABP-HCAT (1.65 kWh/m^3 vs. $2.26 \ 1.65 \text{ kWh/m}^3$).

Energy consumption was the lowest in ABP-90 days (1.25 kWh/m^3 of produced biogas). Overall, experiments performed into the small-scale ABP proved that HC offers an energy-efficient method for the treatment of agri-food residues, leading to high biogas productivity.

Thangavelu et al. (2018) [120] also claim that HCAT is an advantageous technology in terms of energy consumption if compared with other pretreatment technologies. In their study, they evaluated the efficiency of combined HC and enzymatic lignin oxidation (HCE) in the reduction of lignin from corncob. In fact, laccase enzyme exploited in this work can oxidize a variety of phenolic subunits of lignin and other aromatic compounds via radical-catalysed mechanism. To determine the optimal conditions for HCE pretreatment, response surface methodology (RSM) was utilized. Three independent variables were assumed to influence the process performed at pH 4.5 (acetate buffer): catalyst loading, biomass to liquid ratio and reaction time. Since the process design consisted in the supply of biomass slurry via holes in the orifice plate to cavitation zone, preliminary studies have been performed to evaluate the proper biomass loading rates to avoid orifice holes occlusion. The range of selected pretreatment variables was: biomass loading of 2.5–5.0% (*w/v*), enzyme loading of $3–10 \text{ U g}^{-1}$ (on dried biomass) and reaction time of 5–60 min. The HC system exploited for the experiments was composed by a 6 L circulation tank, an orifice plate, a centrifugal pump, an electrical motor, gate valves for priming and bypass and pipe accessories. Moreover, two orifice plate configurations have been tested: orifice plate 1 (OP1: 9 holes and 2 mm Ø) and orifice plate 2 (OP2:4 holes and 3 mm Ø). Regardless, the two plates did not influence the tests' outcomes, resulting in common optimized conditions for enzymatic HCAT: matrix loading at 5%, enzyme loading at 6.5 U/g of biomass and a process time of 60 min.

However, the lignin reduction obtained with OP1 set-up (47.4%) was higher than the one obtained with OP2 (35.91%). Thangavelu et al. only reported an increase of cellulose content in treated corncob exploiting OP1, equal to 25.3%. Overall, HCE pretreatment represents a suitable and an "energy saver" technology for cellulose isolation from agri-food wastes but, according to the authors, 5% of biomass loading for scaling up seems to be low and may be increased to achieve an economic output.

Taking into account all the potentiality associated with HC, the disclosure of semi-continuous and continuous HC-based technologies for agri-food residues pretreatment could be a viable alternative. For this purpose, Hilaresa et al. (2019) [121] used HC to perform an alkaline-assisted treatment over a residue of sugarcane bagasse (SCB) in sequential batches (SB-HC), semi-continuous (SC-HC) and continuous (C-HC) approach in presence of H_2O_2. The efficiency of the different pretreatments have been evaluated as biomass cellulose increase and quantity of sugars released after pretreated biomass EH.

For SCB pretreatment in sequential batches process, 25 g of dry SCB was maintained in a cylindrical wire cloth (40 mesh) and an alkaline H_2O_2 solution (0.3 mol/L of NaOH, 0.8% *v/v* of H_2O_2) was recirculated ($2 \text{ m}^3/\text{h}$ flow rate). After first pretreatment (fresh solution), the liquid fraction was collected and recycled in subsequent batches over fresh SCB (at list 14 cycles).

The cellulose recovered from each batch climbed from 40% to 44% and no significant differences were observed by recycling the black liquor. The highest Glu and Xyl recovery after the EH of the fresh solution pretreated biomass are 42.33 g/100 g and 20 g/100 g, respectively, which are 3.5 times higher compared to Glu released in untreated biomass (9.3 g/100 g).

The SC-HC process has been performed in the HC system shown in Figure 16. Three litres of the same solution used for batch process (0.3 mol/L of NaOH, 0.78% of H_2O_2) were placed in the cavitation reactor (N°2 in Figure 16) while 2 L of same solution containing SCB at 1% (S/L ratio) was constantly fed into the HC device (flow rate: 200 mL/min, residence time: 7.5 min). While the cellulose content, on average, after SC-HC process

was slightly higher (48%) than the obtained in the SB-HC with fresh solution (44%), the recovered Glu amount was about 35 g/100 g, which is smaller than that recorded for fresh solution in batch process (42 g/100 g) but greater than that recorded for the untreated SCB (9 g/100 g). To reuse the alkaline solution, the C-HC trials were realized using an alkaline solution (0.5 mol/L of NaOH, 0.78% of H_2O_2) and 1.7% of S/L ratio of SCB placed in the cavitation reactor. Fifteen litres of a 1.7% S/L ratio of SCB suspension were constantly fed to the cavitation reactor (flow rate: 400 mL/min, residence time: 3.75 min).
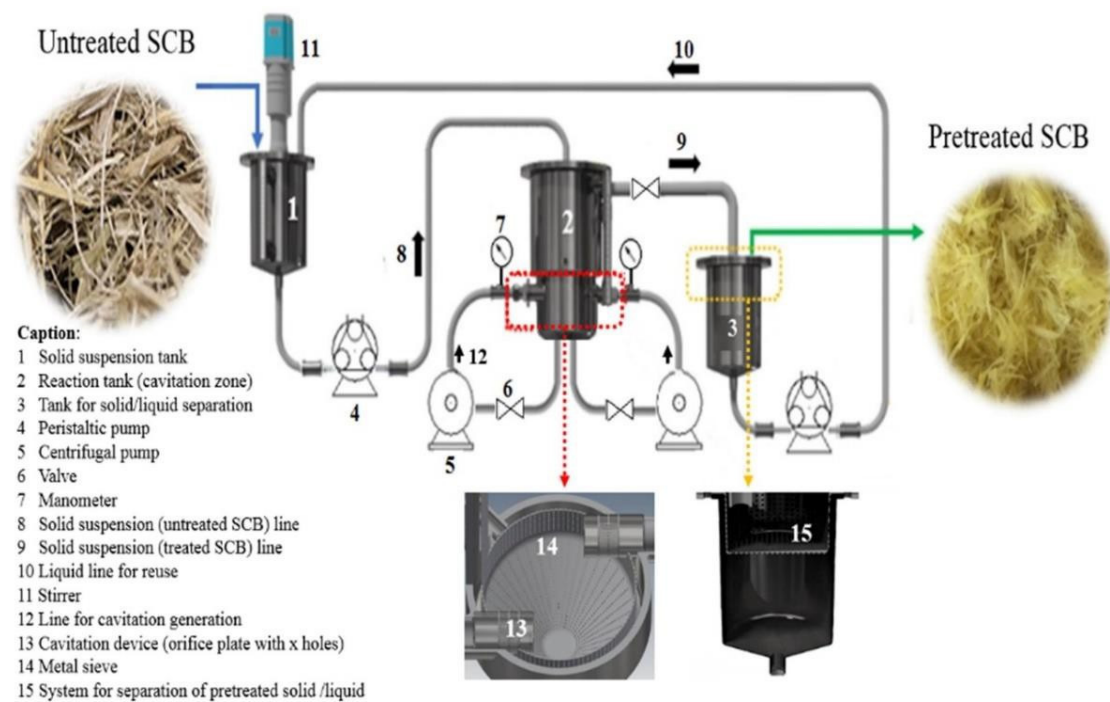

Figure 16. HC devices exploited for semi-continuous pretreatment of sugarcane bagasse. Reprinted from *Bioresource Technology*, 2019, 290, 121,777 with permission from Elsevier.

On average, in the C-HC process, 38–46 g and 32–38 g of Glu per 100 g of SCB were obtained in EH step with an average residence time of 7.5 and 3.75 min, respectively. In SC-HC process, elimination of deadtimes enabled higher amount of biomass to be treated per operation time. In C-HC, the SCB was effectively pretreated recording a high sugars quantity released in the subsequent EH process.

3.3. Cavitational Treatments in Comparison

The effect of acoustic and hydrodynamic cavitation on efficiency of lignocellulosic biomass pretreatment was previously reported in Sections 2.1 and 2.2.

The overall benefits are related to chemical and physical effects of cavitation, which contribute to oxidative degradation and removal of lignin from the biomass in short and mild process conditions. The cavitational-pretreated biomass is more susceptible to cellulases action, which can be associated not only to chemical action of cavitation but also to physical effects as high speed microjets and shockwaves generation during the violent collapse of cavities, which increase the specific surface area, total pore and micropore volumes in biomass, favouring the enzymatic conversion of cellulose and hemicellulose in fermentable sugars. The comparison between the US and HC was summarized in Table 4.

For the sake of comparison, an overview of the results reviewed in this paper was reported in Table 5.

Table 4. Cavitational methods for cellulose recovery from lignocellulosic feedstocks.

Cavitational Pretreatment for Cellulose Recovery	Possible Biomass Alterations	Advantages	Remarks
Acoustic cavitation [3,6]	- Biomass deconstruction - Decreases the polymerization degrees of cellulose	- Low frequencies (20–100 kHz) - High-energy microenvironment - Possible combination with other chemical pretreatment	- Improves mass transfer - low energy requirements
Hydrodynamic cavitation [3,112]	- Enables the oxidative degradation and removal of lignin from biomass - Decreases the polymerization degrees of cellulose - Increases the specific surface area, total pore and micropore volumes in biomass	- Continuous flow process - Short residence time - Mild temperature and pressure conditions - Possible combination with other chemical pretreatment - Scalable at industrial level	- Reactor geometry is crucial to achieve good cavitation number - Physical properties as velocity, pressure, vapor fraction and turbulence through the cavitation device must be carefully considered

Table 5. Agri-Food Residues valorisation by cavitational treatments.

Biomass	Cavitation Technology	Chemical Conditions	Added Value Products	Process yield (Conventional Reference)	Ref.
Carrot grass	US-probe	alkaline	Cellulose recovery [a]	90% (45%)	[78]
Eucalyptus wood	US-bath	alkaline	Biochar	+10–20% (respect to raw)	[79]
Rapeseed Straw (RapS)	US-probe	alkaline	Cellulose hydrolysis	41.60%	[80]
Rapeseed Straw (RapS)	US-probe	organosolv	Lignin recovery	high polymerization degree	[81]
Rapeseed Hulls	US-probe	alkaline	Cellulose hydrolysis	36% (33.5%)	[82]
Olive tree pruning	US-bath	acid	Cellulose recovery [a]	15.87% (6.03%)	[83]
Newspaper waste slurry	US-probe	alkaline	Cellulose recovery [a]	ca. 80% (40%)	[84]
Oil palm empty fruit bunch (OPEFB)	US-probe	acid	Xylose	58% (22%)	[85]
	US-probe	acid	Bio-ethanol	820 mg/mL	[86]
	US-probe	acid + alkaline	Bio-ethanol	911 mg/mL	[86]
	US-probe	IL	Fermentable sugars	177 mg/g biomass	[100]
	US-probe	IL + surfactant	Fermentable sugars	255 mg/g biomass	[100]
Sugarcane bagasse (SCB)	HC (venturi)	alkaline	Cellulose recovery—Cellulose hydrolysis	60–97.2% (67%)	[110]
	HC (venturi)	alkaline	Cellulose—Hemicellulose hydrolysis	93–95%	[111]
	HC (venturi)	alkaline + H_2O_2	Cellulose recovery [a]—Fermentable sugars—Bio-ethanol	27.2–95.4%—0.49 g/g biomass	[112]
	HC (venturi), batch	alkaline + H_2O_2	Cellulose recovery [a]—Glu—Xyl	44%—42 g/100 g (12.1 g/100 g)—20 g/100 g (5.7 g/100 g)	[121]
	HC (venturi), semi-cont.	alkaline + H_2O_2	Cellulose recovery [a]—Glu—Xyl	48%—35 g/100 g (12.1 g/100 g)–23 g/100 g (5.7 g/100 g)	[121]

Table 5. *Cont.*

Biomass	Cavitation Technology	Chemical Conditions	Added Value Products	Process yield (Conventional Reference)	Ref.
	HC (venturi), continuous	alkaline + H_2O_2	Glu—Xyl	46 g/100 g (12.1 g/100 g)–32 g/100 g (5,7 g/100 g)	[121]
	US-probe	ChOAc	Cellulose—Hemicellulose hydrolysis	85–100%	[102]
Grass	US-probe	acid	Hydrogen	84.4 mL (54.9 mL)	[87]
Rice Straw	US-probe	Fenton Reagent	Fermentable sugars	7 g/L (4.6 g/L)	[88]
	US-probe	alkaline	Fermentable sugars	2.91 g/L (0.85 g/L)	[89]
	US-probe	TBAOH	Cellulose hydrolysis—Delignification	92.4 % (23.1% untreated)—70%	[90]
Wheat straw	US-bath	NaDES	Cellulose recovery [a]—Antiox. activity	29.81%—0.2713 mg/mL IC_{50}	[107]
	US-bath	GVL	Cellulose accessibility—Polyphenols from lignin	Total pore volume 10.2 mm^3/g—25 mg GAE/100 mL	[107]
	HC (rotor/stator)	alkaline	Increase in paper tensile strength	*ca.* 55%	[115]
	HC (rotor/stator)	alkaline	Biogas	172.3 mL/g total solids (31.8 mL/g total solids untreated)	[117]
	HC (rotor/stator)	alkaline	Cellulose recovery [a]	25%	[47]
	US	alkaline	Cellulose recovery [a]	30–45%	[47]
	US-bath [b]	-	Biogas	19.8 m^3/d (15.9 m^3/d)	[119]
	HC (not specified)	-	Biogas	18.5 m^3/d (15.9 m^3/d)	[119]
Sugar beet shreds	US-probe	-	Cellulose recovery—Cellulose hydrolysis	90%—780 mg/g cellulose (211 mg/g cellulose)	[91]
Coffee silverskin (CSS)	US-probe	acid	Fermentable sugars	0.190 g/g (0.103 g/g)	[92]
	US -probe	alkaline	Fermentable sugars—Polyphenols	24 g/L (21 g/L)—25 mg GAE/g CSS (23.1 mg GAE/g CSS)	[93]
Chili post-harvest residue	US	alkaline	Fermentable sugars—Bio-ethanol	0.44 g/g—1.94% GC area	[95]
Bamboo components	US	Acid—GVL	Cellulose hydrolysis	90% (12%)	[96]
Powdered bamboo waste	US-probe	ChOAc	Cellulose hydrolysis	92% (55%)	[101]
	US	IL	Lignin recovery—Cellulose hydrolysis	60%–98%	[99]
Corn stover	HC (Venuri)	$Na_2H_3CO_6$	Fermentable sugars	3 mg/mL	[113]
	US-probe	$Na_2H_3CO_6$	Fermentable sugars	2 mg/mL	[113]
Microcrystalline cellulose	US-bath	IL	Cellulose hydrolysis	95.5% (42.8%)	[103]
Oil palm fronds (OPF)	US-cup horn	NaDES	Cellulose recovery [a]	36.42% (14% NaDES only)	[105]
Garlic skin (GS)	US + MW	NaDES	Cellulose recovery [a]	90,14% (76.10%)	[106]
Reed	HC (orifice plate)	alkaline	Delignification—Bio-ethanol	85%—510 mg/g cellulose	[109]
Agriculture biomass mix [c]	HC (rotor/stator)	-	Bio-methane	+14% (respect to raw)	[118]
Corncob	HC (orifice plate)/Enzymes	-	Cellulose recovery [a]	47.40%	[120]

[a] expressed as delignification; [b] hollow tubular sections placed in an ultrasonic equipment made; [c] beet molasses + corn meal + maize silage + triticale silage.

4. Cavitation Processes at Industrial Level

The transposition of UAT at industrial level (applied to one hundred litres of volume) is still slightly challenging, as AC usually is not uniformly distributed through the huge bulk volume, occurring very close to the irradiating surface. Therefore, high power intensities should be required for industrial-scale operations, which can lead to the erosion of sonicator. To overcome these problems, the use of multiple transducers has been investigated for large-scale applications, able to work at multiple frequencies (Figure 17) [6].

Figure 17. Multi-frequency US devices (20–120 kHz) working in flow mode (max. power of 2 kW). Weber Ultrasonics AG [30].

Considering also the economic aspects related to the scale-up of the US processes, the switch from batch to continuous process seems to be the best option for sonochemical intensification at industrial scale because flow-mode US devices are currently commercially available.

HC-based technology seems to be more promising for the treatment of agricultural and food waste on industrial scale, as it can be more easily adapted in semi-continuous and continuous modes, as previously described, saving time, energy and operational costs. Moreover, HC reactors have a simple configuration, easily scalable also in flow mode if compared to acoustic cavitation-based devices. In addition, the chemicals used for the pretreatment could be recycled to improve the economic and environmental sustainability of the process. For example, the rotor-stator device may be easily scaled up, meanwhile preventing the blockage of orifices with particles occurred in conventional HC reactors (Figure 18) [41].

Figure 18. HC rotor stator devices for flowtrought biomass pretreatment in kg scale (max. flow rate 30,000 L/h). E-PIC s.r.l. [115].

5. Conclusions

The high crystallinity of cellulose and its sheathing by hemicellulose-lignin matrix provide the resilient structure of lignocellulosic biomass. Hence, pretreatment is a pivotal step for conversion of agri-food waste biomass to sugars and further valuable bioproducts and biofuels. Extensive research for biomass valorisation has been carried out experimenting with acoustic and hydrodynamic cavitation. This survey shows the effectiveness of cavitation as pretreatment technique for cellulose recovery owing to its potential to simplify the disruption of recalcitrant lignocellulosic matrix. US and HC enhance the mass transfer of the pretreatment process and could enhance the accessibility of lignocellulosic biomass through microjet erosion, cell wall disruption suitable for cellulose recovery.

Despite the promising results reported in lab scale pretreatment for cellulose recovery, US and HC remain underexploited so far. In this innovative field a relevant technical breakthrough is expected in the near future. Nowadays, cavitation activity still strongly depends on the device used, and it is difficult to correlate results obtained with different instrumentation and biomass sources. The efficient design of dedicated cavitational reactors will certainly boost the US and HC application for biomass pretreatment. Cavitation can be described as a complex nonlinear phenomenon, which means that quantitative estimation is a challenging aspect. New capital investments for the scaling up design also require a careful overall economic evaluation (both CAPEX and OPEX).

Following the recent advances in large-scale cavitation technology, we can highlight the easier applicability of HC-based methods that may represent the solution of choice for the efficient pretreatment of agri-foods and forestry waste toward cellulose recovery.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

AC	Acoustic cavitation
ABP	agricultural biogas plant
Bmim	1-butyl-3-methylimiazolium ion BPR: biogas production rate
CBY	cumulative biogas yield
C-HC	continuous hydrodynamic cavitation ChOAc: choline acetate
CSS	coffee silverskin DES: deep eutectic solvent Dmp: dimethylphosphate
DP	degree of polymerization EH: enzymatic hydrolysis
Emim	1-ethyl-3-methylimiazolium ion
FE-SEM	field emission scanning electron microscope
FE-RS	Fenton's reagent process
FTIR	fourier transform infrared spectroscopy GAE: gallic acid equivalent
Glu	glucose GS: garlic skin
GVL	γ-valerolactone
HBA	hydrogen bond acceptor
HBD	hydrogen bond donor
HC	hydrodynamic cavitation
HCE	Hydrodynamic cavitation and enzymatic method
HGS	*p*-hydroxyphenyl-guaiacyl-syringyl
HVED	high voltage electrical discharges
IL	ionic liquid
MAE	microwave assisted extraction
NADES	natural deep eutectic solvents OP: orifice plate
OPEFB	oil palm empty fruit bunch fibers
OPF	oil palm fronds
RapS	rapeseed straw
R-RS	row rice straw
RS	rice straw
RSM	response surface methodology
SB-HC	sequential batches hydrodynamic cavitation
SCB	sugarcane bagasse
SC-CO$_2$	supercritical CO$_2$
SC-HC	semi-continuous hydrodynamic cavitation
SCOD	soluble chemical oxygen demand
SEM	scanning electron microscopy
SPT	Substrate Preparation Tank
TBAH	tetra-butylammonium hydroxide
TDES	ternary deep eutectic solvents
TGA	thermogravimetric analysis
UAE	ultrasound-assisted extraction
U/F-RS	combined US/Fenton process on rice straw
U-RS	ultrasound pretreated rice straw
US	ultrasound
UAT	ultrasound-assisted treatment WS: wheat straw
XRD	X-ray diffraction
Xyl	xylose

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