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Valorisation of Industrial Hemp and Spent Mushroom Substrate with the Concept of Circular Economy

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Development of efficient resource utilization and waste management strategies is highly required to meet ever increasing huge demand and consumption and to avoid reliance on fossil-based sources. Recently, the concept of circular economy has gained more attentions so as to achieve the core sustainable development goals. This study presented initial steps towards total valorisation of biomass with integrated biorefinery approach and the concept of circular economy. Industrial hemp residue (IHR) and spent mushroom substrate (SMS) were considered as a case study in the current research. Different pretreatment methods were employed to hydrolyse individual and/or various mix ratios of IHR and SMS. Finally, analysis of the raw materials, hydrolysates, and residual solids were undergone to gain some insights, identify key research gaps, and forward for future optimization of the process. The results showed that SMS was noticeably more degradable than IHR and co-hydrolysis of mixture of these substrates have provided considerable advantages.

1. Introduction

It is not economically as well as ethical promoted to use resources for the synthesis of chemicals, materials, and biofuels that were allocated for food and other primary products. Then again, generation of waste is certain while producing and consuming these primary products. These wastes could cause detrimental effects including environmental, heath, and socio-economic impacts. Interestingly, enormous efforts and technological advancements have been reported in recent years to transform these resources into value-added products. In connection to this, valorisation of waste biomass resources would provide plethora of advantages such as; avoid the risks associated with their improper disposal, alleviate resource and land competitions, assist to decrease dependence on petroleum-based resources (Dessie et al., 2020). However, the traditional disintegrated approaches limit utilization of waste biomass mainly due to logistics issues, resources loss, inconsistent biomass quality and other challenges (Nguyen et al., 2020). Adoption of an innovative strategy of integrated biorefinery approach (Sangalang et al., 2021) that incorporates the concept of circular economy could address the aforementioned underlying problems. In fact, China has officially accepted circular economy two decades ago, 2002, after the concept has been introduced by environmental economists Pearce and Turner (Su et al., 2013). And it is still globally a hotspot research area.

Commonly, biomass resources subjected to pretreatment to get nutrient rich feedstocks that would intend to support microbial growth for subsequent target product synthesis. Meanwhile, the pretreated materials should be centrifuged and filtered to recover hydrolysates and solid residues. The hydrolysates which are supposed to contain sugars and other nutrients would be used as a fermentation medium, solid residues are usually overlooked. In line with this, the notion of total biomass utilization opts here for sustainable biorefinery implementation (Solarte-Toro et al., 2021) and efficient waste management strategy.

Industrial hemp residue (IHR) and spent mushroom substrate (SMS) are waste biomass resources generated during hemp processing and mushroom cultivation for food, medicine, materials, biofuels, and etc (Figure 1). In the current study, these resources were selected based on their accessibility (specifically in the study area), abundance, applications, potential impacts on disposal, and more. The high recalcitrance nature of IHR limits

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its potential applications. Most of previously implemented hemp pretreatment strategies pose some hindrances such as efficiency, cost (Zhao et al., 2020), and sustainability. Development of feasible, green, and sustainable pretreatment strategy is crucial for realization of circular economy. Here, various pretreatment methods were employed for hydrolysis of IHR and SMS individually or with different mix ratios. The aim of this initial stage of experiment is get some insights for further optimization studies after analysis of the raw materials, hydrolysates, and solid residues. These results will be considered for future implementation of integrated biorefinery approach with circular economy and zero waste concepts (Figure 1). The is the first report to co-utilise IHR and SMS as part of alternative pretreatment strategy which could also increase the economic values of both waste biomass resources.

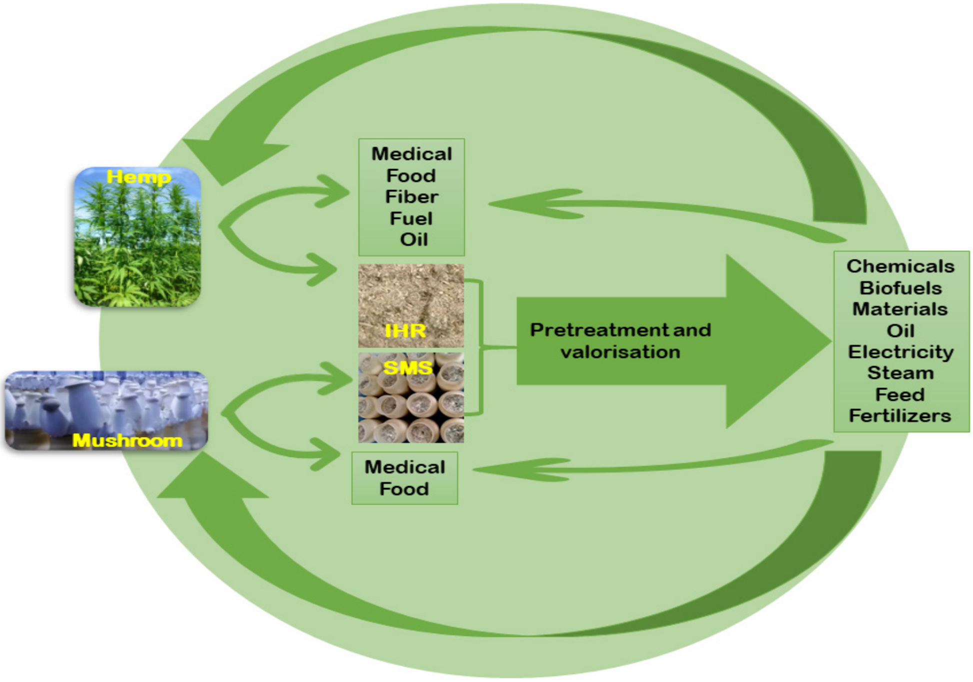

Figure 1: Hemp and mushroom processing with integrated biorefinery approach and the concept of circular economy.

2. Experiments

Raw materials were smashed using stainless steel mini laboratory grinder and sieved into desired particle sizes (0.5 mm) with laboratory wire mesh sieve. In this study, 10 % mass ratio (w/v) of substrates were considered. In the autohydrolysis pretreatment, IHR or SMS was briefly mixed with water at room temperature. Thermal and thermochemical hydrolysis were undergone at 121 °C for 30 min, with the addition of 5 % (w/v) oxalic acid in the latter condition, using individual and various mix ratios (0-100 %) of IHR and/or SMS (Table 1). Hydrolysates were separated from the solid residues through centrifugation (10,000 rpm, 20 min) and filtered by Whatman no. 1 filter paper. The recovered solids were dried in the oven at 50 °C for 24 h. These hydrolysates and solids were then used for further analyses and characterizations. Raw materials and solid residues of the pretreated IHR and SMS were analyzed by scanning electron microscope (SEM) as elucidated elsewhere (Luo et al., 2021) using Hitach SU8010 Cold Field Emission SEM with secondary electron resolution of 1.3 nm.

3. Result and discussion

Raw SMS could contain up to (in %) 48.7 cellulose, 34 hemicellulose, and 39.8 lignin depending on the source of mushroom cultivation medium (Koutrotsios et al., 2014). Likewise, raw IHR content analysis resulted (in %) 44.5 cellulose, 32.78 hemicellulose, and 21.03 lignin (Stevulova et al., 2014). In line with this, different pretreatment methods have been evaluated for valorisation of these bioresources. It is clear that autohydrolysis and thermal hydrolysis pretreatment methods are relatively cost effective and they can also avoid generation of unwanted byproducts due to the absence of chemicals. Oxalic acid (OA) was employed in the thermochemical pretreatment. In recent years, organic acids such as OA have got more attentions in lignocellulosic pretreatment owning some interesting advantages such as high efficiency and selectivity, relatively low cost, and low equipment corrosion (Cheng et al., 2018). More interestingly, OA could be produced from bio-based resources (Jiang et al., 2016) and also it can be recovered and recycled (Cheng et al., 2018) in the pretreatment process, which makes the overall process greener and more sustainable.

Some properties of IHR and SMS hydrolysates and solid residues were studied. Obviously, addition of OA during thermochemical pretreatment resulted enormous drop in the pH of the hydrolysates. The hydrolysates pH generally exhibited the following trend; autohydrolysis > thermal hydrolysis > thermochemical hydrolysis. It is clear that as the temperature rises, dissociation of water generates more H^+ that will lead to decrease in pH value. Besides, the recovered solid residues were decreased after thermal pretreatment as compared with the autohydrolysis and thermochemical hydrolysis counterparts; and as the SMS percentage increases in the mixture with IHR (Table 1). Thermochemical pretreatment of IHR and SMS mixtures apparently increases the hydrolysate volume (Figure 2b, 3-9) as the respective residual solid content keeps decreasing (Table 1). These results explained the partial degradation of polysaccharides in the lignocellulosic biomass. Noticeably, in the case of IHR, the highest solid residues were recovered during thermochemical hydrolysis process. This is probably partly due to the formation of calcium oxalate precipitates (vom Stein et al., 2010) via interaction of OA with calcium from IHR. In general, the current study demonstrated that SMS was more degradable than IHR. The highest reducing sugar production (data not shown) was achieved when SMS was thermally hydrolysed followed by autohydrolysis method. Hence, blending SMS with IHR could provide synergistic effect by taking advantages of each other. Some of the benefits of co-hydrolysis (Lin et al., 2014) of high and low degradable biomass resources include regulate hydrolysis process, enhance degradation efficiency and nutrient contents, dilute inhibitors, improve buffering actions, and etc. (Chakraborty and Mohan, 2019).

Table 1: Experimental setups and pH of hydrolysates and content of recovered solids after pretreatment of IHR and SMS.

Setup	Composition IHR:SMS (%)	Pretreatment	pH	Solid residue (%)
1	100:0	Autohydrolysis	7.56 ± 0.31	88.40 ± 1.45
2	100:0	Thermal hydrolysis	6.85 ± 0.25	82.80 ± 1.08
3	100:0	Thermochemical hydrolysis	0.48 ± 0.01	94.00 ± 1.07
4	90:10	Thermochemical hydrolysis	0.52 ± 0.02	97.20 ± 1.08
4*	90:10	Thermal hydrolysis	6.24 ± 0.15	99.10 ± 0.51
5	75:25	Thermochemical hydrolysis	0.51 ± 0.01	93.20 ± 1.04
5*	75:25	Thermal hydrolysis	6.30 ± 0.11	98.40 ± 0.97
6	50:50	Thermochemical hydrolysis	0.57 ± 0.02	89.80 ± 1.62
6*	50:50	Thermal hydrolysis	6.50 ± 0.30	87.80 ± 0.88
7	25:75	Thermochemical hydrolysis	0.55 ± 0.02	84.80 ± 1.52
7*	25:75	Thermal hydrolysis	6.70 ± 0.23	75.80 ± 1.73
8	10:90	Thermochemical hydrolysis	0.62 ± 0.02	82.20 ± 1.18
8*	10:90	Thermal hydrolysis	7.10 ± 0.32	74.00 ± 1.63
9	0:100	Thermochemical hydrolysis	0.65 ± 0.02	78.40 ± 1.19
10	0:100	Thermal hydrolysis	6.69 ± 0.34	74.20 ± 1.63
11	0:100	Autohydrolysis	6.86 ± 0.33	78.60 ± 1.38

*Various mixtures of IHR and SMS undergone thermal hydrolysis

The colouration pattern of hydrolysates and solid residues unveiled variations with respect to the pretreatment method and the mix ratios of IHR and SMS. Comparatively, thermal hydrolysis resulted the darkest hydrolysates followed by autohydrolysis. Slurries in hydrolysates generated via autohydrolysis and thermal hydrolysis could be undissolved fractions, potentially involved in the dark colouration of lignin (Zhang et al., 2017), that leave the hydrolysates darker and the solid residues brighter (e.g., Figure 2b 1, 2, and 4*). On the contrary, thermochemical hydrolysis removed the colourants from the hydrolysate, make it light coloured while the solid residue remains darker (e.g., Figure 2b; compare 1, 2 and 3, 4 and 4*). The possible reason behind this could be the action of OA. Previous reports (Musiał et al., 2011) revealed that OA can be used as a leaching agent (Salmani Nuri et al., 2019) to eliminate impurities from various materials (Zürner and Frisch, 2019). Remarkably, OA, in the current study, possesses dual-purpose (if not multiple) for depolymerization of lignocellulose materials as well as decolourization of hydrolysates; makes the process even more sustainable and economic. Furthermore, the colour intensity of both hydrolysates and the solid residues get darker as the SMS percentage increases in the mixture (Figure 2b 3-9, 4*-8*). The dark-brown colourations of SMS hydrolysates maybe due to natural colourants from the initial mushroom medium substrates and/or pigmentation during mushroom cultivation stages. Such colourants are usually accompanied with toxic compounds (Korniłłowicz-Kowalska & Rybczyńska-Tkaczyk, 2020) that have antimicrobial effects (Arimi et al., 2014). Even though, SMS contains potentially high nutrients for microbial growth and product formation, the availability of these colourants could limit its applications in this area. Therefore, efficient strategies should be developed to manage these colourants while valorisation of SMS. On the other hand, decolourization processes require additional time, resources and cost. Herein, blending of SMS with IHR and OA pretreatment showed dilution and/or removal colourants; that can be taken as additional novelty of this study.

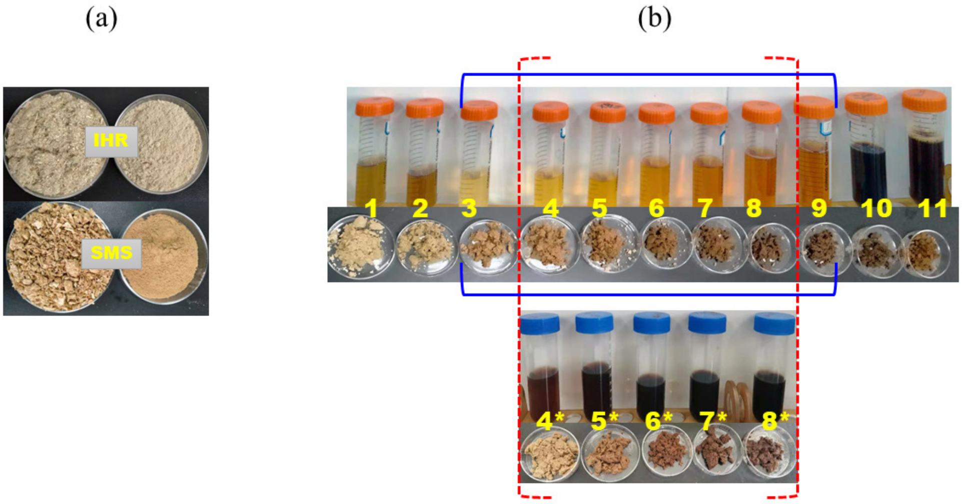

Figure 2: Digital images showing (a) IHR and SMS raw materials, (b) hydrolysates and solid residues after pretreatment.

SEM analysis was performed for both IHR and SMS solid samples. Four samples from each substrate; the raw materials (Figure 2a) and solid residues generated after autohydrolysis (Figure 2b; 1 and 11), thermal hydrolysis (Figure 2b; 2 and 10), and thermochemical hydrolysis (Figure 2b; 3 and 9) were used for comparative surface morphology studies. SEM image showed that IHR is chiefly composed of fibers.

These fibers are characterized as long and intact, shorter and partially degraded, and mostly degraded in raw, autohydrolysed, and thermally hydrolysed solid residues (Figure 3a, b, and c). Compactly bounded fibers began to gradually loosen sequentially and finally, the intact grooves (Figure 3c) disappeared and smooth surfaces were observed in the thermochemically pretreated solid residues (Figure 3d). This is possibly due to degradation of hemicellulose and alternation of lignin structures (Semhaoui et al., 2018). Previous studies (Magro et al., 1984) indicated that OA plays an important role in promoting hydrolysis process though reducing the pH (, creating pH difference between the acidic solution and the plant cell wall) and rendering the calcium-pectate complexes of the cell walls increase susceptibility (Arantes et al., 2009).

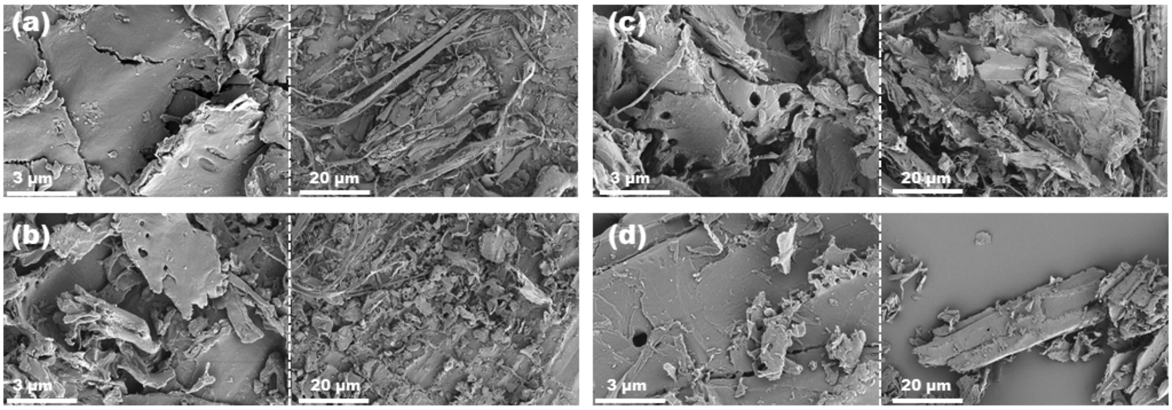

Figure 3: SEM image of (a) raw, (b) autohydrolyzed, (c) thermally hydrolyzed, and (d) thermochemically hydrolyzed solid residues of IHR. Magnification; 3,000 (left) and 500 (right)

Unlike IHR, there were no fibrous structures on the SEM images of SMS samples. This is most likely due to the degradation of lignocellulosic components of the mushroom substrate via fungal enzymes and penetration of mycelium during the previous mushroom cultivation step. Moreover, there were no significant structural changes between the raw and autohydrolysed solid residues (Figure 4a and b). Solid residues of thermally hydrolysed SMS started to disperse (Figure 4c). And, finally, thermochemically pretreated SMS resulted highly fragmented solids (Figure 4d). This step seemingly caused generation of sugars degradation products (Zhao et al., 2020). The high degradable property of SMS may not need high concentration of acid for pretreatment. This assumption was confirmed by the fact that autohydrolysis and thermal hydrolysis of SMS generated lower residual solids (Table 1) and higher reducing sugar than thermochemical hydrolysis of SMS.

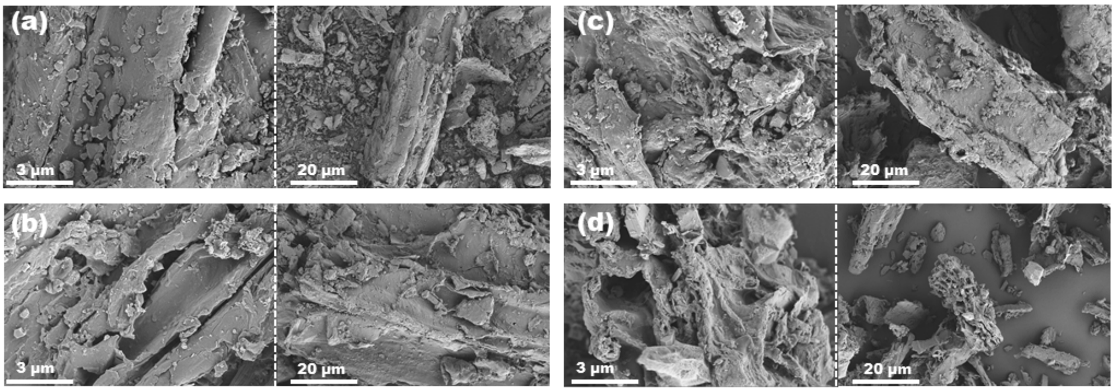

Figure 4: SEM image of (a) raw, (b) autohydrolyzed, (c) thermally hydrolyzed, and (d) thermochemically hydrolyzed solid residues of SMS. Magnification; 3,000 (left) and 500 (right)

4. Conclusions

This early stage of study provided some insights on the degradation effects of autohydrolysis, thermal hydrolysis, and thermochemical hydrolysis against individual and mixtures of IHR and SMS. SMS was found to be highly degradable to the specifically compared with recalcitrant IHR. Co-hydrolysis of these resources complement certain advantages. Results of this study pinpoint future research focus areas. This includes (but not limited); optimization of the pretreatment conditions to establish the most efficient strategy, transformation of hydrolysates into value-added products via microbial fermentation, and implementation of potential valorisation techniques for residual solids. These are some of the steppingstones to accomplish the journey towards full and sustainable utilization of biomass resources via integrated biorefinery approach with the concept of circular economy.

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