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ARTICLE

Combining steam distillation with microwave-assisted pyrolysis to maximise direct production of levoglucosenone from agricultural wastes

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The favourable impact of using a wet waste stream of agricultural residues in a biorefinery was studied through a combination of pyrolysis and self-induced steam distillation of hemicellulose depleted barley straw. The results showed that steam distillation provided both selective isolation and higher yields of polysaccharide-derived products such as levoglucosenone (LGO). The acid content of pretreated barley straw had the highest impact on the products selectivity. Both hydrolytic and pyrolytic pathways contributed to the products distribution, with higher selectivity toward pyrolytic products such as levoglucosan and LGO when less than 0.8wt.% acid was used. Interestingly, the increase of water content increased the overall products yields but had no impact on the products selectivity suggesting that the water did not directly impact on the decomposition pathway. In-situ vaporisation of the water generates a microwave transparent steam environment preventing the distilled products for further degradation. The observation of the selective microwave activation of the polysaccharides in the presence of lignin offers significant opportunities for subsequent conversion of lignocellulosic biomass.

Introduction

Lignocellulosic biochemicals are facing critical challenges due to lack of viability, with an over reliance on low-value single product streams such as ethanol for fuels. For decades, many promising lignocellulosic biorefinery models have lacked the flexibility to overcome the recalcitrant nature of lignocellulosic biomass and feedstock heterogeneity, which until now has almost always resulted in loss of product purity and/or yield. Furthermore, significant energy is invested in the pre-treatment of these single stream feedstocks to enable the utilisation of greater proportions of biomass structure and increase product yields; increasing the overall cost of the production process and making the products commercially unviable.[1-3]

One such challenge is the valorisation of lignin-containing waste streams such as fermentation residues. A considerable future increase in the volume of lignin produced as an industrial by-product can be forecast due to the development of processes for the production of second generation biofuels and chemicals from lignocellulosic biomass.[4, 5] This is especially evident when considering that a typical bioethanol plant will likely produce roughly 70,000 tons per year of lignin, based on a 2000 ton per day plant using corn stover as a feedstock. [6] The current biorefinery model consisting of dilute acid pretreatment of lignocellulosic biomass, followed with simultaneous saccharification/fermentation, will produce a significant volumes of residue composed of lignin, unreacted polysaccharides, enzymes and yeast.[7] This intrinsic heterogeneity is one of the substantial problems for the effective utilisation of lignin on a large scale. In many applications of the waste lignin, the sugars are unwanted due to a negative effect on the product properties.[8] Moreover, the presence of water in that residue could be as high as 60wt.%; therefore the majority of upgrading process of this residue will require the complete removal of water, making the whole conversion economically challenging.[9]

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To overcome this, a new approach is required to enable the utilisation of multiple feedstock types, which are heterogeneous and contain significant volumes of water. For example, new process such as self-steam explosion are taking advantage of the inherent moisture content of the biomass.[10] Along with this, a shift in focus from fuels to the co-production of multiple, high value platform molecules should be considered. This will increase the chemical/monetary value gained from the original feedstock and decrease the energy requirement of pre-treatment.[11] We recently reported that, while inaccessible to bioconversion, given the correct processing conditions, the un-utilised polysaccharides found in these materials could be a rich source of highly valuable chemicals, in particular levoglucosenone.[12] Levoglucosenone (LGO) has recently been rated as one of the top 10 platform chemicals with considerable potential for making important chemical products, including the new the green commercial solvent cyrene.[13] It has also been reported as a drugs precursor hydroxylmethylbutenolide (HBO)[14] and for making the polymer feedstock 1,6-hexanediol.[15] According to recent work, LGO is 70,000 times more valuable than ethanol.[16] The production of LGO from cellulose or lignocellulosic biomass has already been investigated and mature technology, such as the Furacell process, has been patented; although the process suffers from low carbon efficiency and difficult waste streams.[17] Based on an intense study of LGO production, there is expert consensus that high yields of LGO could only be achieved in dry pyrolysis (water is considered an inhibitor of this process) or thermal conversion in non-protic solvents under acidic conditions.[18-22]

According to previous work, the selectivity between levoglucosan (LGA) and LGO (two main anhydrosugars produced during cellulose pyrolysis) could be switched using the microwave irradiation that promotes the dehydration of LGA to LGO.[23] This finding is in a good agreement with our recent preliminary report on the conversion of residual saccharides contained in the biorefinery waste lignin paved a new strategy for the valorisation of lignocellulosic fermentation matter and in particular using a microwave heating approach.[12] In this present study, to turn the water content in the lignin waste to our benefit, we investigated the impact of using wet pre-treated lignocellulosic biomass during microwave-assisted pyrolysis. Barley straw, as a more abundent biomass for the UK bio-economy, has been selected as lignocellulosic feedstock model for this study. [24] A combination of microwave assisted pyrolysis with simultaneous steam distillation of polysaccharides-derived products, such as levoglucosenone, was performed on hemicelluloses-depleted barley straw. Impact of the water content, acid concentration, as well as temperature on the products yields and selectivity was studied in order to draw suitable conditions for both efficient production and separation of polysaccharide-derived product levoglucosenone from the lignin enriched residue.

Results and Discussion

The wet pyrolysis study was performed on hemicellulose depleted barley straw (HD-BD) prepared from a MW-assisted hydrolysis procedure described within the experimental section. As illustrated in figure 1, the temperature profile of wet HD-BS pyrolysis in the microwave reactor, showed three phases; starting with a fast increase to around 95°C (i) followed with a plateau (ii), and finally increasing up to the desired temperature (iii). It is interesting to note that the reaction temperature profile depended on the amount of acid present in the impregnated HD-BS (Fig.1). In absence of acid, only phase (i) and (ii) occurred during the first 350 seconds of reaction. On the other hand, increasing the amount of acid reduced the time of phase (i) and (ii) which could be explained by the higher microwave absorbance property of sulfuric acid. Previous work reported that the sulfuric acid loss tangent (tgδ) is 6.5 at 70°C.[25] Compared to 0.05 for the water, the 130-fold increase of the sulfuric acid loss tangent could explain the faster temperature increase even for diluted acid solution (from 0.1 to 1wt.% sulfuric acid solution). However, this explanation should not rule out the fact that the acid catalyses the biomass degradation, producing microwave-active molecules which could improve the heating rate. Unlike phase (i) and (ii), the reaction temperature increase in the phase (iii) was not affected by the increase of acid concentration from 0.4 to 4 wt.%.

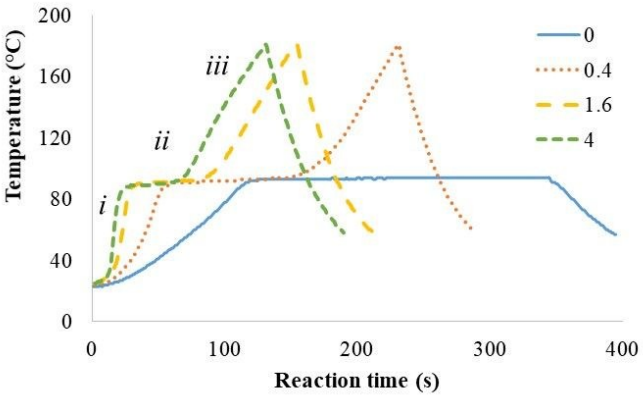

Figure 1: Reaction temperature profiles during microwave assisted pyrolysis/steam distillation of acid impregnated HD-BS as function of the acid concentrations [Experimental conditions: 300W, 20wt.% dry matter (DM), up to 180°C, from 0 to 4g of acid/100g of dry HD-BS]

MW assisted pyrolysis of the wet HD-BS gave two streams of products, split between the water condensate and the residue. The reaction was stopped when the temperature reached 100°C and after substantial water evaporation (see figure 1, end of phase ii). As illustrated in figure 2, nearly half the total LGO was already produced at this early stage of the pyrolysis with an overall yield of 5 mol%. Between 120 and 140°C, the LGO was steam distilled, while the amount in the residue remained constant. After 140°C, the amount of the steam distilled LGO only fluctuated between 6 to 7 mol% while the amount in the residue slightly increased from 3.0 to 4.3 mol%. It is interesting to see that the weight of the water condensate followed the yield of steam distilled LGO. Before the pyrolysis, the biomass water content was 80 wt.%. At 100°C, nearly 75% of that water was evaporated. Between 100 to 180°C, another 18wt.% of the water contained in the wet biomass was evaporated and allowed the steam distillation of levoglucosenone. We can observe that the microwave assisted pyrolysis of cellulose starts to degrade cellulose at low temperature, releasing LGO. Compared to conventional pyrolysis, it has been previously reported that microwave assisted pyrolysis requires lower temperature in order to start degrading biomass components such as cellulose.[26] This allows the water to contribute

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as steam distillation vector. In conventional pyrolysis, the water will be completely evaporated before the pyrolysis starts, cancelling the combined effect of the pyrolysis with steam distillation.

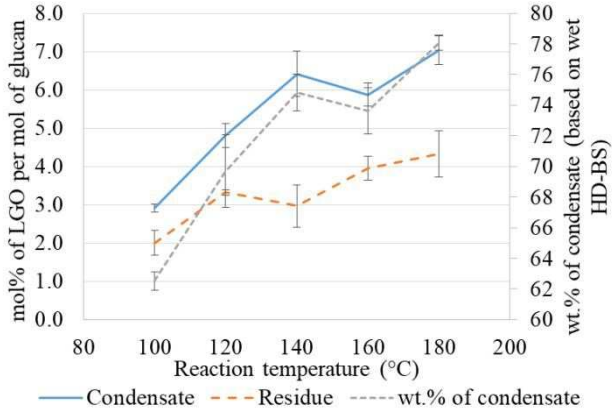

Figure 2: Temperature effect on the yield of levoglucosenone in the condensate and residue as well as the mass of water condensate produced after microwave pyrolysis/steam distillation of HD-BS [Experimental conditions: 300W, 20wt.% DM, 0.8wt.% of sulfuric acid]

Since it was observed that the steam distillation of LGO still occurred after 75wt.% of water had been removed from the sample, the pyrolysis of biomass with reduced water content was studied. Water was partially removed using a rotary evaporator prior to pyrolysis at 140°C. As illustrated in figure 3, the amount of levoglucosenone recovered in the condensate reduced with increasing fractions of added dry biomass matter. More interestingly, the mass of levoglucosenone recovered in the residue did not compensate for the lower LGO yield from steam distillation. As a consequence, reducing the amount of water led to lower overall yield of LGO. This overall decrease of LGO yield was attributed to lower steam distillation of the product, leaving LGO more vulnerable to further degradation/condensation. It is possible that the steam distillation isolated LGO from the MW radiation, preventing further degradation, thus making water beneficial to LGO production. Indeed, the in-situ generation of steam allowed the LGO to be directly distilled from the MW reaction chamber. In the present study, the limited amount of water in the acid impregnated HD-BS did not allow complete steam distillation of the LGO from the residue. However, we could anticipate that all the LGO could be steam distilled from the residue if unlimited supply of steam was provided. As a consequence, the combination of microwave assisted pyrolysis under continuous steam distillation should be an attractive process.

Acid concentration during the pyrolysis is likely to have a great impact on the product selectivity when the hemicellulose-depleted barley straw is submitted to microwave assisted pyrolysis. Previous work reported that conventional steam distillation of levoglucosan from cellulose using superheated steam could be achieved without acid impregnation of the biomass. [27]

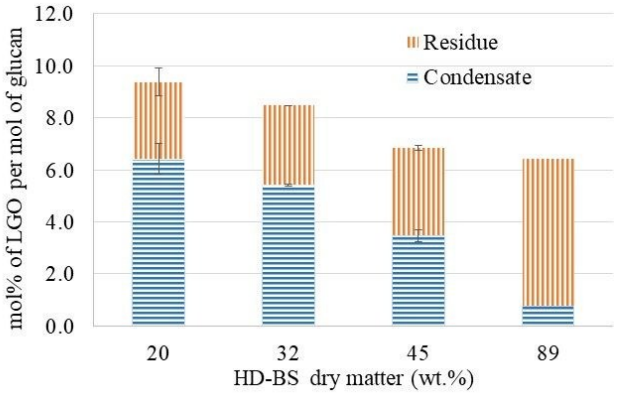

Figure 3: Effect of the HD-BS dry matter on the LGO recovery in water condensate and residue after MW assisted pyrolysis/steam distillation [Experimental conditions: 300W, 140°C, 0.8wt.% of sulfuric acid]

As illustrated in Table 1, LGA and LGO are the main products when a low acid concentration (0.4 wt.%) was used. Then, LGO increased up to 8.3 wt.% (based on the total carbohydrates) at 0.8 wt.% of H_2SO_4. However, higher acid concentration had a negative effect on the levoglucosenone concentration which dropped to 3wt.% of the total carbohydrate when 4 wt.% of H_2SO_4 was impregnated in the straw. The product molar selectivity is greatly affected by the sulfuric acid concentration. At high acid concentration, the furfural became the main hydrolysis product. With the exception of 0.4wt.% of sulfuric acid, the sum of LGO and furfural selectivity is constant at ca. 80 mol%. Importantly, the boiling point of furfural (which is the second main product) is 60ºC lower than the LGO boiling point. Therefore, the LGO purity could be further improved by distillation. Higher selectivity toward levulinic acid, a product of 5-HMF degradation, was observed with increasing sulfuric acid concentration (see Table 1). The dry biomass matter did not have any impact on the product selectivity (Table 1). Previous work reported that the presence of water in an aprotic solvent, such as THF, completely inhibited the production of levoglucosenone and reversed the product selectivity toward 5-HMF.[20] In the present study, the absence of a water effect could be attributed to the fact that in an open vessel, most of the water is vaporised at an early stage of the pyrolysis. At this point microwave radiation will be activating the dry HD-BS surrounded by steam. Levoglucosenone could be produced in these pseudo-dry conditions and subsequently steam distilled once it had diffused into the gas phase. Unlike conventional heating, microwave irradiation does not directly interact with gas.[28] This phenomenon allows the microwave radiation to selectively activate the biomass. As a consequence, steam distillation of the products is beneficial for preventing further degradation.

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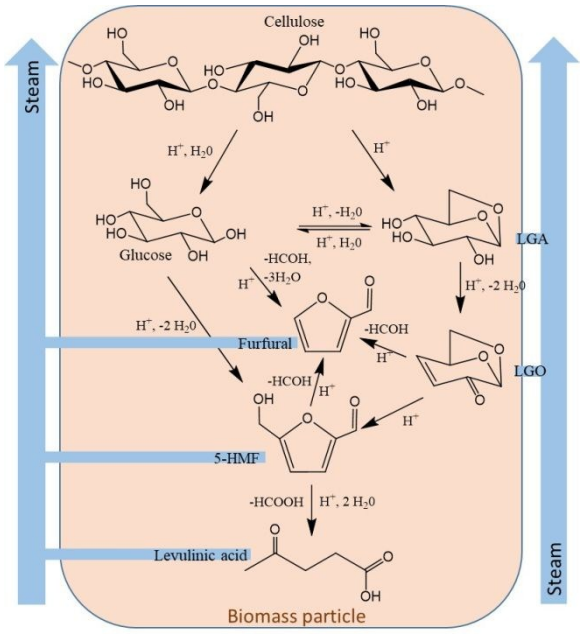
	Mass yields (wt.% of carbohydrates)					Selectivities (mol%)				
	LGO	LGA	LV	HMF	FURF	LGO	LGA	LV	HMF	FURF
(A) Sulfuric acid (wt.%)										
0.4	5.37±0.9	5.73±0.9	0.43±0.0	0.60±0.1	1.66±0.2	41.1	34.1	3.6	4.6	16.7
0.8	8.28±0.7	2.06±0.7	0.85±0.0	0.65±0.2	2.60±0.1	55.7	10.8	6.2	4.4	23.0
1.6	6.54±0.2	0.66±0.0	1.40±0.3	0.29±0.0	3.29±0.0	49.6	3.9	11.5	2.2	32.8
2.4	4.57±0.0	0.40±0.0	1.57±0.2	0.21±0.0	4.09±0.0	37.6	2.6	14.0	1.8	44.1
4	2.95±0.3	0.25±0.0	1.65±0.0	0.15±0.0	3.67±0.2	29.8	1.9	18.1	1.5	48.7
(B) Dry matter (wt.%)										
20	6.83±0.5	2.39±0.4	0.77±0.1	0.50±0.0	2.14±0.1	53.2	14.5	6.5	3.9	21.9
32	6.17±0.0	1.26±0.0	0.74±0.0	0.54±0.1	2.06±0.0	55.1	8.8	7.2	4.9	24.1
45	4.97±0.1	1.36±0.0	0.77±0.0	0.43±0.0	1.43±0.1	54.2	11.5	9.2	4.7	20.4
89	4.67	1.02	0.70	0.76	1.33	53.5	9.0	8.8	8.7	20.0
(C) Temperature (°C)										
100	3.42±0.0	0.41±0.0	0.23±0.0	0.10±0.0	1.30±0.2	59.0	5.6	4.3	1.7	29.5
120	5.74±0.5	1.59±0.1	0.67±0.0	0.38±0.0	1.62±0.0	56.2	12.1	7.1	3.8	20.9
140	6.83±0.5	2.39±0.4	0.77±0.1	0.50±0.0	2.14±0.1	53.2	14.5	6.5	3.9	21.9
160	7.15±0.3	1.93±0.2	0.77±0.0	0.97±0.0	1.92±0.0	55.1	11.6	6.5	7.5	19.4
180	8.28±0.7	2.06±0.7	0.85±0.0	0.66±0.2	2.60±0.1	55.7	10.8	6.2	4.4	23.0

Table 1: Effect of the acid concentration, dry biomass matter and temperature on the yields and molar selectivity of HD-BS pyrolysis products (from condensate + residue extracts), [LGO: levoglucosenone; LGA: levoglucosan; LV: levulinic acid; HMF: 5-hydroxymethylfurfural; FURF: furfural- Experimental conditions: 300W; A: 180°C, 20wt.% DM; B: 140°C, 0.8wt.% acid; C: 0.8wt.% acid, 20wt.% DM]

To visualise the different reactions involved, the cellulose depolymerisation product pathways are shown in scheme 1. According to the product distribution, both hydrolytic and pyrolytic routes occur under the experimental conditions. The hydrolytic route mainly produced glucose, furfural, 5-HMF and levulinic acid.[29] The pyrolytic route favoured levoglucosan and levoglucosenone as the main products.[22] Because only the acid concentration impacts the product distribution towards furfural and levulinic acid (e.g. hydrolysis route), it could be suggested that the hydrolysis of the cellulose starts at a lower temperature when higher acid concentration is used. In this case, the water was not completely vaporised and promoted the hydrolytic pathway leading to greater proportions of furfural and levulinic acid. On the other hand, at low acid concentration, the stability of the cellulose toward hydrolysis allowed the water to be vaporised before pyrolytic degradation occurred, favouring the production of levoglucosenone.



Scheme 1: Cellulose hydrolytic and pyrolytic degradation pathways in presence of steam [LGO: Levoglucosenone; LGA: Levoglucosan] (inspired from Cao and co-worker [20])

Varying the pyrolysis temperature from 120°C to180°C also had no impact on product selectivity (See Table 1). The highest yields of LGO and furfural were 8.6 g and 2.6 g per 100g of polysaccharides obtained using 0.8 wt.% of sulfuric acid at 180°C with 20% dry matter. Under these optimum conditions for LGO, only 15wt.% of polysaccharides derived products were generated. Thus a significant fraction of the cellulose was not converted or degraded. As such a recycling experiment where increasing amount of cellulose is decomposed with relatively good selectivity to LGO in particular can be envisaged.

	Wt.% of dry hemicellulose-depleted barley straw				
	Pyrolysis mass loss	**Acid insoluble residue**	**Glucan**	**Xylan**	**Others**
Hemicellulose depleted barley straw	0.0	25.8	60.7	5.0	8.5
(A) Sulfuric acid (wt.%)					
0.4	42.9	32.3	20.1	1.0	3.8
0.8	40.8	39.9	15.6	1.0	2.7
1.6	41.2	45.7	10.0	0.6	2.4
2.4	43.4	47.5	6.5	0.5	2.2
4	41.1	53.3	4.7	0.3	0.6
(B) Dry matter (wt.%)					
20	38.9	38.4	18.3	1.0	3.4
32	38.4	37.0	20.3	1.0	3.2
45	38.9	38.4	18.3	1.0	3.4
89	41.0	41.6	12.8	0.6	4.0
(C) Temperature (°C)					
100	23.6	28.3	41.1	2.5	4.5
120	34.8	32.4	27.8	1.5	3.4
140	39.0	39.6	16.1	0.8	4.6
160	38.4	38.1	18.6	0.9	4.0
180	38.4	37.0	20.3	1.0	3.2

Table 2: Pyrolysis mass loss and biomass compositional analysis of the HD-BS pyrolysis residue as function of the sulfuric acid concentration, dry matter and pyrolysis temperature [Experimental conditions: 300W; A: 180°C, 20wt.% DM; B: 140°C, 0.8wt.% acid; C: 0.8wt.% acid, 20wt.% DM]

The analysis of residue following pyrolysis and solvent extraction was performed to evaluate the conversion of polysaccharides. As shown in table 2, the mass loss during the pyrolysis of the HD-BS was independent of the acid concentration and the dry matter. A two-step acid hydrolysis of the pyrolysis residue was performed in order to quantify the remaining polysaccharides and the acid-insoluble fraction. From the initial HD-BS, the acid insoluble residue can be assimilated to the lignin content (so-called Klason lignin). However, this assumption is not true for pyrolysis residue. Considering the fate of lignin during the pyrolysis, the absence of GC detectable aromatic monomers in the residue extract and water condensate, suggested that most of the lignin remains in the pyrolysis residue. Only small volumes of aromatic monomers were produced when pyrolysis was performed on lignin-rich barley straw (LR-BS). As illustrated in figure 4, the comparison of GC detectable aromatic products obtained from 30wt.% (see Fig 4.A) or 1wt.% (See Fig. 4.B) glucan containing barley straw shows that the presence of polysaccharides somehow inhibited the production of aromatic monomers.

Even with 25wt.% lignin present in the initial HD-BS remaining after the pyrolysis, the extra weight of the acid insoluble fraction after pyrolysis can be explained by the carbonisation of some of the polysaccharides (See table 2). In order to explain the absence of aromatic monomers produced when pyrolysis was performed on glucan containing barley straw (See Fig. 4.A), it may be that the carbonisation of the polysaccharides prevented the lignin being activated due to the high microwave adsorption of the carbonaceous material. It is well known that the temperature of lignin microwave activation is higher than cellulose decomposition. Therefore one can presume that the cellulose is pyrolysed at a temperature lower than lignin producing volatiles and char. The produced char will scaffold the lignin preventing production of small molecule aromatics. As can be seen (Table 2) this carbonisation was most pronounced at 4wt.% acid concentration, reducing the amount of unreacted glucan in the pyrolysis residue to less than 5wt.% and increasing the acid insoluble residue to more that 52 wt.%. In comparison, the glucan content was still at 20 wt.% and the acid insoluble residue only at 32 wt.% when the HD-BS was pyrolysed with 0.4 wt.% acid.

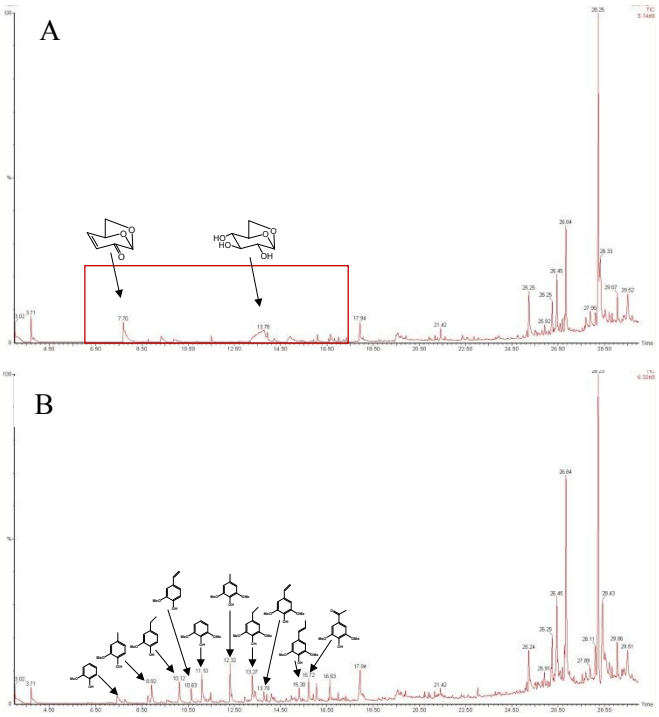


Figure 4: GC/MS of the acetone/methanol extract of pyrolysis residues from LR-BS containing 30wt.% of glucan (A), from LR-BS containing 1wt.% of glucan (B) [Pyrolysis condition: 300W; 200°C, 20wt.% dry matter and 1wt.% acid]

The extent of particle carbonisation as function of the acid concentration can be visualised in Fig. 5. As illustrated in figure 5, it is clear that the pyrolysis heterogeneously affects the acid impregnated HD-BS particles within the same experiment. In microwave assisted conditions, the pyrolysis starts from the centre of the vessel and spreads toward the wall. The pyrolysis residue is then composed of unreacted (light colour) and reacted (dark colour) particles (see figure 5). The FTIR analysis of the pyrolysed HD-BS showed that the light particles (blue) kept the same structural characteristic than the original HD-BS (Figure 6). On the other hand, the dark particles (orange) showed clear depletion of carbohydrate content. Alkali lignin of the HD-BS was prepared for FTIR

comparison purpose. The purity of the lignin was checked using 2D HSQC NMR. As illustrated in Fig.S.1, no peak assignment corresponding to carbohydrates (hemicelluloses) were observed in the HD-BS alkali lignin spectra.[30] However, the grasses lignin-type peak assignments are in accordance with previously reported studies. [30, 31] When the unreacted (light) and reacted (dark) particles FTIR spectra were compared with the HD-BS alkali lignin and Sigmacell cellulose (Figure 6), only characteristic IR bands of the lignin were maintained from the reacted (black) particles while the unreacted (light) particles still showed characteristic IR bands of the cellulose. As seen in figure 5, the higher number of darker particles for HD-BS with 89wt% DM suggested that lower water content slightly increased the carbonisation of the glucan. This is confirmed with the small increase of the acid insoluble residue observed when 89wt.% dry matter HD-BS was pyrolysed (Table 2). This could be attributed to more organic products (furfural, levoglucosenone) remaining in the residue and were vulnerable to condensation. The glucan left in the pyrolysis residue decreased from 100°C to 140°C, but was constant after 140°C (Table 2). It can be concluded that at 0.8wt.% acid impregnation, increasing the pyrolysis temperature from 140°C to 180°C had no impact on the carbonisation of polysaccharides. Visual analysis of the pyrolysis residue confirmed that the temperatures ranging from 140°C to 180°C had no significant effect on the colouration of the particle residue (See figure 5). It could also be suggested that increasing the temperature from 140°C to 180°C had little impact on the conversion of polysaccharides either via carbonisation or depolymerisation. This is explained by the fact that higher temperature is required in order to depolymerise the crystalline region of the cellulose. Previous work reported that temperatures above 220°C were required to activate the crystalline region of the cellulose. [32] Unfortunately, the present setup does not allow us to still have the steam distillation effect while the pyrolysis reaches high temperature (220°C). As we can see in figure 2, almost all water was removed from the sample when the temperature reached 160-180°C. This limits the possibility to combine steam distillation with high temperature pyrolysis at least with our present experimental setup.

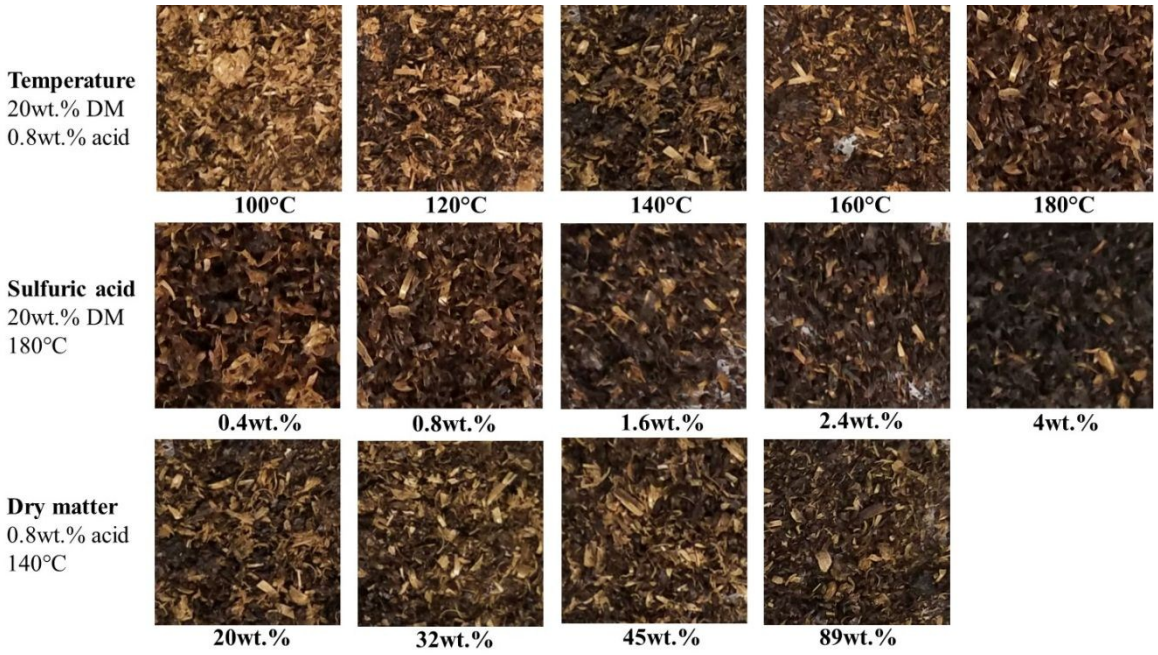


Figure 5. Visual analysis of the temperature, sulfuric acid concentration and HD-BS dry matter effects on the particle carbonisation after pyrolysis

Analysis of pyrolysis residue highlights the negative effect of high sulfuric acid concentrations. However, the pyrolysis temperature from 140°C to 180°C and the biomass dry matter content did not change the carbonization of the polysaccharides, leaving one third of the cellulose unconverted (see Table 2). Consequently, low proportions or even no acid, should be considered to reduce the carbonization of polysaccharides. It is clear that in the absence of sulfuric acid, LGO will be a minor product. However, if the LGA can be efficiently dehydrated to LGO over a solid acid catalyst for example, this could be a more suitable approach for higher LGO yields. Moreover, it is well known that the presence of acid will affect lignin structure, depleting the alkyl-aryl ether linkages, and reducing its potential for catalytic depolymerisation to monomers.[33] The benefit of acid-free conditions on the catalytic conversion of lignin to chemicals has to be considered during the MW pyrolysis of polysaccharides to LGA/LGO. Furthermore, since the presence of water has positive effect on the conversion of polysaccharides to LGO and promote the products steam distillation, performing the pyrolysis under a continuous feed of steam should aid the separation of the products. Product separation is often considered to be the most troublesome aspect of biorefineries. [34] The production of levoglucosan under superheated steam has been recently reported

using a fixed bed reactor and conventional heating at 300°C.[27] The present study using microwave irradiation reduces the pyrolysis temperature to less than 200°C, as well as the reaction time and selectively activates the biomass components.

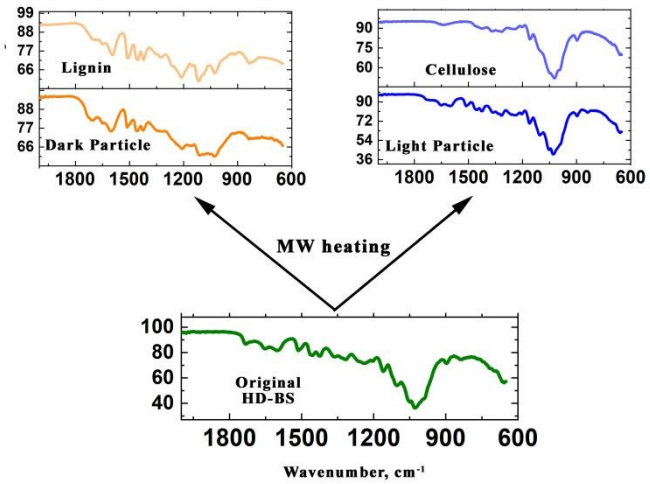


Figure 6. ATR-FTIR spectra of the HD-BS (green), and light pyrolysis particle (blue), dark pyrolysis particle (orange), pure cellulose (pale blue) and alkali lignin of the HD-BS (pale orange) [Experimental conditions: 300W; 20wt.% dry matter, 0.8wt.% sulfuric acid, 180°C]

Experimental

Materials. Barley straw was provided by a local farm (UK, Yorkshire) from 2017 harvest. The straw was hammer milled through a 2 mm sieve. The particles were then sieved over a 250 µm mesh to remove the fines. The moisture content of barley straw was measured at 105°C to be 7.4wt.%. Ethyl acetate, methanol and acetone were HPLC grade solvents purchased from Sigma-Aldrich. D-(+)-Glucose (+99%) was purchased from Fluka. D-(+)-xylose (+99%), L-(+)-arabinose (+99%), levulinic acid (98%), furfural (98%) and octadecane (99%) were purchased from Sigma-Aldrich. Levoglucosan (98%) were purchased from Carbosynth. The 5-hydroxymethylfurfural (98%) were purchased from Acros.Levoglucosenone (95%) was purchased from circa. All reagents were used without further purification.

Preparation of hemicellulose depleted barley straw (HD-BS), lignin-rich barley straw (LR-BS) and alkali lignin of HD-BS. In order to minimize decomposition of the hemicelluloses that could affect the cellulose microwave pyrolysis, removal of hemicelluloses was performed on the barley straw. Flow chart of the barley straw hydrolysis, acid impregnation and steam distillation/pyrolysis is shown on scheme 2. Hemicellulose-depleted barley straw (HD-BS) was prepared using a Milestone Synthwave microwave reactor. Barley straw (20 g) was mixed with 600 mL of 0.2wt.% sulfuric acid solution in a 1L vessel and the reactor was pressurised with 10bar of nitrogen. The barley straw was hydrolysed at 170°C for 20 min. The working temperature was reached after 15 min. After cooling down, the slurry was filtered on a Büchner funnel fitted with filter paper (Fisherbrand, QL100). The residue was washed three time with warm deionised water and stored at 4°C.

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A second hydrolysis step using harsher conditions was performed on the HD-BS in order to partially or completely remove the cellulose. Two Lignin-rich barley straw materials (LR-BS 1&2) were prepared using CEM Discovery SP microwave reactor using similar experimental conditions as previously reported. [35] HD-BS (1g) was mixed with 20 mL of 1%w sulfuric acid solution and hydrolysed at 180°C or 190°C for 10 min. After cooling down, the slurry was filtered on Buchner funnel fitted with filter paper (Fisherbrand, QL100) and the residue was washed three times with warm deionised water, dried at 65°C and stored at room temperature.

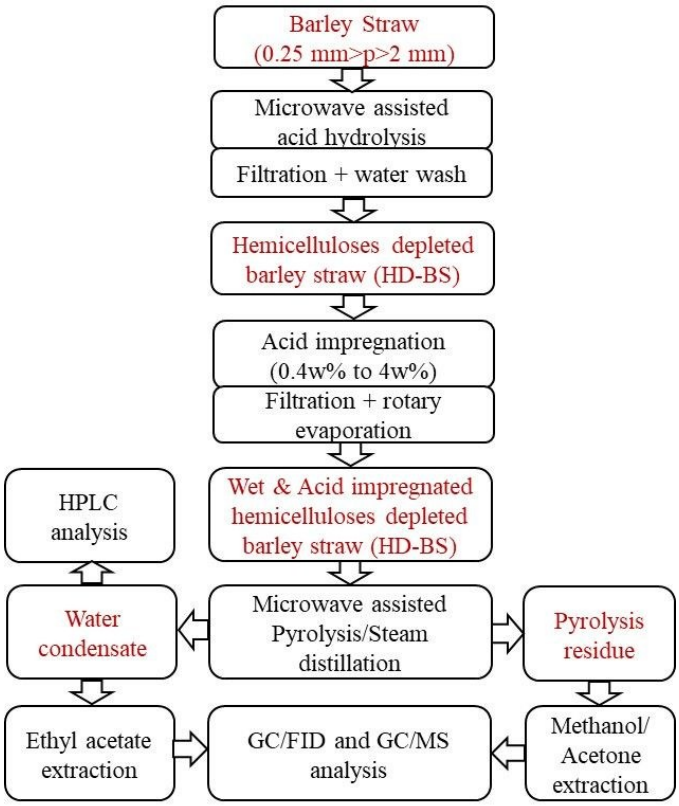
The Alkali lignin of HD-BS was obtained from extraction of the HD-BS with 5N NaOH solution at 80°C (conventional heating) for 2h. After the reaction, the mixture was filtered on a Buchner funnel fitted with filter paper (Fisherbrand, QL100) and the lignin was precipitated after acidification to pH 2 using 6N HCl solution. The alkali lignin was centrifuged, washed with three time with DI water and freeze-dried.

Microwave assisted pyrolysis/steam distillation. The pyrolysis of the hemicellulose-depleted barley straw (HD-BS) was performed in presence of various concentrations of sulfuric acid ranging from 0.4wt.% to 4wt.% (based on the biomass dry matter) and at various water contents ranging from 11wt.% to 80wt.% (based on the wet HD-BS). As illustrated in scheme 2, the HD-BS (15g) was impregnated in 0.1wt.% to 1wt.% sulfuric acid solution (200mL) and filtered on Buchner funnel fitted with filter paper (Fisherbrand, QL100). The water content of the acid impregnated HD-BS was measured at 105°C after sulfuric acid was removed with distilled water to avoid any decomposition during the drying step. The water content of the acid impregnated HD-BS after Buchner filtration was typically 80wt.%. As consequence, the acid content of impregnated HD-BS with 0.1wt.% to 1%wt.% sulfuric acid solution was estimated from 0.4 to 4g per 100g of dry HD-BS. The water content of the impregnated HD-BS was then reduced using the rotary evaporator at 45°C and 50 mbar. After partial water removal, dry matter of the wet acid impregnated HD-BS was calculated from mass difference. The acid impregnated HD-BS materials were stored at 4°C. Same procedure was used for the acid impregnation of lignin-rich barley straw.

The Pyrolysis/steam distillation experiments were performed on the CEM discover SP microwave reactor equipped with a syringe and dean stark device in order to collect the vaporised fraction (water condensate) (See Fig S.1). Typically, from 0.9g to 4 g wet HD-BS (equivalent to 0.8g of dry HD-BS) was placed in a 30mL borosilicate glass vessel. The pyrolysis/steam distillation was performed at a fixed power (300W) until the desired temperature was reached. Following the reaction, the vessel was cooled using compressed air. The mass of water condensate was measured and an aliquot (0.3mL) was quickly extracted with ethyl acetate (2 x 0.8mL). The remaining condensate was stored in the freezer for further analysis. Attempts to quantify the LGO in the water condensate by reverse phase HPLC column underestimated its yield due to the formation of the geminal diol. Alternatively, the geminal diol of LGO (GD-LGO) could also

be analysed in water phase using Hi-Plex H HPLC column only after a complete shift of the equilibrium toward the geminal diol product. This occurred after leaving the sample at room temperature over 3 days. As previously observed by Krishna et al.[36], 1H NMR analysis of LGO in water showed that the ratio GD-LGO/LGO was around 99/1 (See Fig. S.2). However, the co-elution of the hydrated LGO with formic acid limited the use of this HPLC option.

As illustrated in scheme 2, the pyrolysis residue was washed with a mix acetone/methanol (50/50), dry under at 65°C under vacuum and stored at room temperature. The methanol/acetone extract of the pyrolysis residue was concentrated and injected in GCMS and GCFID. Octadecane C18 was used as internal standard for the GC analysis and added to the ethyl acetate (water condensate) and acetone/methanol (residue) extracts.



Scheme 2: Flow chart procedure of the microwave assisted Pyrolysis/Steam distillation of acid impregnated hemicelluloses-depleted barley straw

Biomass Compositional analysis. The two-step acid hydrolysis was used to quantify the amount of glucan, xylan, araban, acid insoluble residue and ash in the initial HD-BS and pyrolysis residues. As described in previous work[37], dry samples were soaked in 72wt.% H_2SO_4 for 2h at 40°C and then refluxed in 7wt.% of H_2SO_4 for 4h. The hydrolysate was analysed by HPLC and the residue was filtered in ceramic porous crucible (porosity 8µm), washed with distillate water and dried at 105°C. The acid insoluble lignin and ash content was measured after calcination of the dry residue at 500°C for 6h.

HPLC analysis of the water fraction. The monosaccharides (*D*-glucose, *D*-xylose, *L*-arabionse), levoglucosan, levulinic acid in the biomass hydrolysates or in the pyrolysis water condensates were quantified using an Agilent 1260 Infinity HPLC system (USA) equipped with a Agilent Hi-Plex H (300 x 7.7mm, 8 µm particle size) column. Samples (5µl) were eluted at 0.4 mL.min^{-1} using an isocratic mobile phase of 5 mM H_2SO_4. The column and refractive index detector temperatures were set at 60ºC and 55ºC, respectively.

GC/FID quantitative analysis. The levoglucosenone, furfural, 5-HMF, levoglucosan, levulinic acid in the pyrolysis residue acetone/methanol extract and the levoglucosenone, furfural and 5-HMF in the condensate ethyl acetate extract were quantified using Hewlett Packard GC 6890 equipped with Restek Rxi-5HT (30 m, 0.25 mm, 0.25 µm film thickness) column and flame ionisation detector. The oven temperature program started at 50°C for 1 min and increased up to 300°C at 30°C/min. Injector and detector temperatures were set at 300 and 340°C respectively. Split mode injection was performed with ratio 1/30. The octadecane C18 was used as internal standard.

GC/MS qualitative analysis. Qualitative analysis of the residue acetone/methanol extract was performed using Perkin Elmer Clarus 500 GC/560S MS equipped with Restek Rxi-5HT (30 m, 0.25 mm, 0.25 µm film thickness) column. The oven temperature program started at 50°C for 1 min and increased up to 330°C at 10°C/min and hold for 1 min. Injector temperatures was set at 280. Split mode injection was performed with ratio 1/5.

Proton NMR of levoglucosenone. 1H NMR of the levoglucosenone in water was acquired at 398 K using a Bruker Avance-700 MHz instrument equipped with a 5 mm inverse gradient $^1H/^{13}C$ cryoprobe. A 2g/L solution of levoglucosenone was prepared and left at room temperature for more than 72h. A drop of D_2O was added to the aqueous solution for locking purpose. Water signal suppression was applied.

2D Heteronuclear Single Quantum Coherence (HSQC) NMR of Alkali Lignin. The Alkali lignin of HD-BS (~60 mg) were mixed with 800 µL DMSO-d_6 and sonicated. The samples appeared to fully dissolve under these conditions. The 13C–1H HSQC NMR spectra were acquired at 398 K using a Bruker Avance-700 MHz instrument equipped with a 5 mm inverse gradient $^1H/^{13}C$ cryoprobe using the q_hsqcetgp pulse program (ns = 64, ds = 16, number of increments = 256, d1 =5.0 s).[31] Chemical shifts were referenced to the central DMSO peak (δC/δH 39.5/2.5 ppm). Assignment of the HSQC spectra is described elsewhere. [38]

FTIR analysis of the hemicellulose depleted barley straw and pyrolysis residue. FTIR analysis of the hemicellulose depleted barley straw and the pyrolysis residue was performed on the PerkinElmer 400 spectrometer using attenuation total reflectance setting. The same pressure was applied on the outer surface of the straw chips. A number of 16 scans were recorded using 4 cm^{-1} resolution.

Conclusion

Microwave pyrolysis was employed on pre-treated wet crop residue (barely straw), with the unique effect of steam distillation observed during the microwave pyrolysis process, due to excess water present.

Key parameters such as the temperature, dry matter and acid concentration were investigated in the microwave assisted pyrolysis of hemicellulose-depleted barley straw. From wet hemicellulose depleted barley straw, nearly 2/3 of the important product levoglucosenone (LGO) were steam distilled and isolated from the microwave irradiation thus providing an important simultaneous production and separation. The acid concentration was the main parameter affecting the product distribution with levoglucosan and LGO dominating at low acid concentration and furfural/levulinic acid becoming the major products at high acid concentration. This suggested that hydrolytic pathways could be more pronounced at high acid concentration while the pyrolytic pathway was favoured at low acid concentration. Surprisingly, an increase of biomass dry matter did not affect the product distribution but reduced the total yield of the LGO and other products. Isolation of the products via steam distillation helps to restrict downstream degradation of the key products. Only partial conversion of the cellulose was observed under all conditions studied leaving 8-30% of unreacted cellulose depending on conditions. Higher temperature or recycling should overcome this issue. High acid concentration leads to a higher amount of carbonaceous material. As a consequence, to maximise the yield of LGO, the pyrolysis of hemicellulose-depleted barley straw should be done in the presence of less than 0.4wt.% of sulfuric acid in the temperature range 180°C to 220°C and under steam flow. We are currently developing a new setup using a MW flow reactor in order to provide a continuous steam while the biomass is treated at various temperature. This new experimental device will allow a combination of higher pyrolysis temperature (220°C) with steam distillation. A combination of microwave assisted pyrolysis/steam distillation of valuable is an attractive approach that can take advantage of sequential microwave activation of various components of the lignocellulosic biomass.

Conflicts of interest

"There are no conflicts to declare".

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