Aqueous extraction of Levoglucosan from fast pyrolysis bio-oils: A comparative study between solvent extraction and extraction during quenching condensation of hot pyrolysis volatiles, aided by phase equilibria modelling.

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1   Abstract

The production of Levoglucosan (LG) from biomass has gained attention recently as it represents a major precursor for the production of monomeric sugars such as glucose and subsequently biofuels such as bioethanol. This study investigated the efficiency of applying a novel recovery method of LG from fast pyrolysis vapours during condensation. The method employed quenching the hot pyrolysis volatiles with water in a single step condensation process such that the condensed organic-rich condensate (ORC) fraction of the fast pyrolysis bio-oil (FPBO) is recovered together with the water quench on a single stage. A mass flowrate ratio of the water quench to the hot pyrolysis volatiles of 2.0 was utilised. Of the two-phased products recovered, 100% LG ended up in the extracted water quench phase. Compared to the liquid-liquid (solvent) extraction of LG from already condensed ORC, this technique demonstrated to be highly efficient for LG extraction from FPBOs, as it requires significantly lower solvent to feed ratio for optimum LG recovery and it eradicates the need for downstream liquid-liquid extraction systems. Interestingly, the aqueous pyrolysis condensate, a side-stream product that is usually recovered during fractional condensation of hot pyrolysis vapours has shown promising characteristics over fresh water in its utilisation as solvent for LG extraction, which proves to be a favourable addition towards

attaining a sustainable pyrolysis biorefinery. Model predictions of both techniques also showed that the modified UNIFAC Dortmund (UNIFAC-DMD) model in addition to its huge prospects in predicting vapour-liquid equilibrium behaviour of fast pyrolysis vapours also has huge capabilities in accurately handling liquid-liquid equilibrium behaviour of water and FPBOs.

1. Introduction

Sugars happen to be one of the vital platform chemicals (generated during the conversion of biomass to biofuels) that can readily be converted into several compounds [1]. Conversion pathways of biomass into sugars that serve as substrate for fermentation remain a key decider for their application. One of the most commonly exploited pathway to extract sugar from biomass is enzymatic or acid hydrolysis [1,2]. The catalytic effects of enzymes or an acid break down cellulose and hemicellulose down into glucose and xylose. Although the enzymatic conversion pathway has proven to be promising, it is limited in terms of economic feasibility and commercial scale-up applications as a result of high costs of enzymes, comparatively low product concentration and slow hydrolysis rate [1,2]. Also, the adventure of using acids and the associated challenges in regenerating the spent acids also discourages the application of acid hydrolysis at industrial scale [1]. Thermochemical conversion pathways such as fast pyrolysis have been identified as an alternative conversion pathway to overcoming these challenges [1,3]. Fast pyrolysis bio-oils (FPBOs) contain considerable amounts of anhydrosugars [1,4]. Levoglucosan, LG (1,6-anhydro-β-D-glucopyranose) is the major anhydrosugar component present in FPBOs [5]. It is predominantly formed from the depolymerisation of cellulose during fast pyrolysis [6]. Up to 70 wt.% of LG can be obtained when microcrystalline cellulose is pyrolysed [1]. Interest in the production of LG is based on

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the fact that it serves as a major precursor for the production of monomeric sugars such as glucose, which also can further be utilised for the production of biofuels such as ethanol and butanol [5,7].

Solvent extraction is one of the widely explored methods used for the recovery of LG from FPBOs as the differences in polarities, solubilities and densities of the diverse compounds present in FPBOs are advantageous for the process [8–11]. A number of solvents have been employed for extracting various compounds present in FPBOs, some of which include, water, ethyl acetate, n-butanol, hexane, chloroform, dichloromethane, methanol, toluene and petroleum ether [1,9–11]. Of all these solvents, water is readily available, green and cost-effective to use [1,12]. Phase separation may occur when a certain threshold amount of water is added to FPBOs [13]. This typically occurs when water in the range of 30 to 45 wt.% is added [12]. Following phase separation, the aqueous phase, which normally remains atop is mostly characterised by polar carbohydrate-derived compounds whereas the organic dense bottom phase is mostly enriched with less polar lignin-derived components [14]. LG is one of the major components that can primarily be extracted into the aqueous phase. A study by Vitasari et al. [12] demonstrated that compared to other compounds that are also easily extracted into the aqueous phase (such as acetic acid, acetol, glycolaldehyde, etc.) LG has the highest distribution coefficient. This was attributed to the hydrogen bond interactions that occur between LG and water.

The amount of water added to the FPBO (water-to-oil-ratio) is a key factor that defines optimum recovery of LG from FPBOs. A number of studies investigated this. Vitasari et al. [12] investigated the effects of water-to-oil ratio and stirring rate on the extraction of LG with water from forest residue and pine-derived bio-oils. For the water-to-oil ratios in the ranges of 0.3:1 to 0.8:1 (for forest-derived oil) and 0.4:1 to 0.9:1 (for pine-derived oil)

investigated, water-to-oil ratios of (0.6 - 0.7):1 and 0.5:1, respectively were recommended for maximum LG extraction. They also concluded that stirring rate determines the time to reach equilibrium, but does not influence the equilibrium composition. Chan and Duff [15] investigated the water extraction of LG from bio-oil. A water-to-oil-ratio within the range of 0.1:1 to 20:1 was studied. They reported that phase separation first occurred when 9.86 wt.% of water (about 0.1:1 water-to-oil ratio) was added. 100 wt.% of water addition (1:1 water-to-oil ratio) resulted in the optimal recovery (4.98 wt.%) of LG from bio-oil. Bennet et al. [5] investigated the effects of temperature, contact time and the water-to-oil-ratio (within the ranges of 0.5:1 to 2:1) on the optimum extraction of LG from bio-oil obtained from Scots pine. They concluded that a water-to-oil-ratio of 0.62:1 was enough to yield optimum extraction of LG together with optimum contact time and temperature of 22 min and 34 °C, respectively. Li et al. [16] also investigated the effects of water-to-oil-ratio (in the ranges of 0.25:1 to 4.5:1) on the extraction of LG from FPBO obtained from loblolly pinewood. They established that a water-to-oil-ratio of 1.3:1 was enough for the optimum extraction of LG. They also ascertained the fact that contact time and temperature had no significant effects on LG yield and the minimum figures investigated (20 min and 25°C) were enough for maximum isolation of LG. Sukhbattar et al. [17], Wang et al. [18], Chi et al. [19], Lian et al. [20] and the studies of Rover et al. [2,21] all employed a 1:1 water-to-oil-ratio to optimally isolate LG from FPBOs. The extracted LG was further utilised as substrate for fermentation into ethanol.

It is evident from the trends that a water-to-oil-ratio of 1:1 (w/w) is generally enough to optimally isolate all LG present in FPBOs. Nevertheless, the optimum ratio is also dependant on the initial water content of the FPBO in question. It has also been established that temperature and contact time of mixing hardly influences the yield of LG extracted.

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Nonetheless, contact times of at least 20 min and ambient temperatures are just enough to optimally extract LG from FPBOs.

The aqueous condensate (AC) is a consequent product of the fractional condensation of hot pyrolysis volatiles. It is primarily made up of about 85 wt.% water and traces of organic compounds such as carboxylic acids, ketones and furans [22]. Owing to its low organic content and calorific value, it has seen only limited applications as compared to the ORC and in most situations, it is discarded following costly treatment methods to remove organics. For most industrial-scale processes, condensation of the AC is avoided and instead, the vapours are combusted along with non-condensable pyrolytic gases and char to supply heat to the process. Alternatives are however currently being developed to valorise AC as gasifier feed after mixing with char [23,24] and as carbon source for microbial cultivation and anaerobic digestion [22,25–27]. With the high solubility of LG in aqueous systems, using the AC as solvent to extract LG for subsequent application as substrate for microbial conversion and anaerobic digestion tends to be stimulating towards realising a sustainable biorefinery concept as it eliminates the need for using fresh water as solvent.

Optimum recovery of LG from FPBO has received abundant attention and has been widely investigated, which has uncovered more room for further extensive process developments [9]. One of such instances was the studies of Li et al. [7], who introduced a water spray injection system just before the condensation train to rapidly cool the hot pyrolysis volatiles. Consequently, it was noted that this spray effect lowered the temperature of the vapours from 400 to below 300 °C. However, a critical evaluation of their results revealed that impact of this spray system essentially had no significant effects on the yield of LG recovered. The increased yield of LG reported in their study was notably influenced by the acid pretreatment of the biomass feedstock. These observations are

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contrary to their claims that pyrolytic spray increases LG production during fast pyrolysis. The direct spray quenching technique limits cracking reactions, which are known to inhibit LG production [9]. However, the spray system of Li et al. only cooled the pyrolysis vapours to temperature regions of around 300 °C, a temperature range high enough for cracking reactions to still occur. Also, subsequent fractionation of their resulting product also meant that water and the organic-rich fraction (within which LG is mostly recuperated) are recovered on separate stages and hence no avenue for mixing and consequent extraction of LG. To mitigate this, it is paramount that the volatiles are cooled down intensively to temperatures where the likelihood of cracking occurring is minimal. Additionally, as LG is highly soluble in water, a single step condensation setup such that the recovered organic-rich fraction together with sprayed and condensed water are all collected on the same condensation stage will enhance efficient extraction of LG. The recovery of LG by this technique if effectively implemented could exclude the need for further downstream solvent extraction processes, limiting costs and opening up prospects towards attaining a sustainable pyrolysis-based biorefinery.

Phase equilibria model prediction of condensation systems facilitates the understanding such systems devoid of the time and effort required in investigating such systems in actual setups. It also aids in ascertaining key unexplained phenomenon that are usually associated with such processes. These have been successfully revealed in previous studies [22,28], when the modified UNIFAC Dortmund (UNIFAC-DMD) was used to predict the yields and composition of FPBOs, detailing how crucial modelling such processes can be. In view of this, extending this to the extraction of LG from FPBOs tends to be stimulating.

In this study, a single stage quenching condensation water spray system was designed and developed and was used to optimise the recovery of LG from hot pyrolysis volatiles

generated from *miscanthus* and wheat straw. The extraction efficiency of this setup was compared to conventional liquid-liquid water extraction of LG from already condensed FPBOs. In addition to water, the use of the aqueous condensate (AC) fraction (which is usually recovered as a side stream product following fractional condensation of pyrolysis vapours) as solvent for LG extraction was also probed. Finally, the phase equilibria model prediction of both processes were explored and likened to their corresponding experimental data.

2   Materials and methods

2.1   Materials

ORC and AC used for solvent extraction were obtained from the fast pyrolysis of wheat straw and *miscanthus* on the bioliq® fast pyrolysis plant [29]. Physicochemical properties, particularly water content of these products have been reported elsewhere [29,30]. For these previously reported data, it is important to highlight that wheat straw (2018 campaigns) and *miscanthus* (2019 campaigns) were used for this study.

Demineralised water at ambient temperature was supplied by the facilities management of Karlsruhe Institute of Technology (KIT) at ambient temperature and 4 bar pressure.

2.2   Bench scale solvent extraction of Levoglucosan.

Two solvents (water and the AC) were investigated for LG extraction from the respective ORCs. Six different solvent-to-oil-ratios (STORs) of 0.2:1, 0.5:1, 1:1, 2:1, 5:1 and 10:1 were investigated. 50 g of ORC was mixed with corresponding amount of solvent as per the STOR in Schott bottles. Following mixing of solvent with ORC, the mixture was vigorously shaken by hand and then placed on a CERTOMAT® shaker table set at a rotation speed of

250 min^{-1} for about 4 hours for thorough mixing towards equilibrium. It takes at least 20 min to reach phase equilibrium. Hence, 4 hours affirms that equilibrium has been attained.

Following mixing, the mixture was left undisturbed overnight at room temperature to allow for suspension of the raffinate (mostly containing heavy phenolic fraction) from the extract phase. The extract phase was then gently decanted and analysed for LG. Knowing the mass of LG originally contained in the ORC ($mass\ of\ LG\ in\ ORC$) and that deduced from the characterisation of the extract ($mass\ of\ LG\ in\ extract$), the percent fraction of LG transferred into the extract phase is calculated using eq. (1.

$$\%\ LG\ extracted = \frac{mass\ of\ LG\ in\ extract}{mass\ of\ LG\ in\ ORC} * 100\% \tag{1}$$

2.3   Levoglucosan extraction during direct contact condensation.

LG extraction during quenching followed similar procedure employed elsewhere [28], where water was used as quench. Except for this instance, the first condensation stage was set to a lower temperature of 40 °C to allow for the optimal recovery of almost every condensate together with the spent water quench on this stage. This facilitates a single step condensation of both ORC and solvent (water) on the same condensation stage, which enhances the transfer of water-soluble compounds such as LG into the spent water quench phase. The single stage condensed product of the fast pyrolysis bio-oil (FPBO) and water are collected and separated using a separating funnel following which both phases are characterised for LG.

2.4 Products characterisation.

For bench scale experiments, only the water extract phase was analysed for LG. This was conducted by use of a compact IC Flex Amperometric system equipped with 945 Professional Amperometric Detector and a metrosep Carb 2 250/4.0 column. The column has dimensions of 250×4 mm with a styrene-divinylbenzene copolymer that acts as a stationary phase, which is best suited for the characterisation of carbohydrates and anhydrosugars. The mobile phases, which comprise of NaOH (100 mmol/L) and CH_3COONa (10 mmol/L) are diluted with pure water with resistivity greater than 18 MΩ.cm at 25 °C. The 838 Advanced Sample Processor injects 20 µL of the sample into the mobile phase, pumped by an Ion Chromatographic (IC) pump at a 0.5 ml/min flow rate. The temperature of the column is maintained at 35 °C by an oven and the system pressure is maintained at 11.5 MPa. The measurement span is 100 ms. Prior to injection into the amperometer, samples were first filtered using a 0.2 µm CHROMAFIL Xtra PA-20/13 disposable syringe filters. Thereafter, the filtered samples were diluted to concentrations that fall within the calibration range (2-20 mg/L) of the amperometer.

With the concentration of LG in hot pyrolysis volatiles being virtually impossible to quantify, it is important to characterise LG concentration in both the extract and raffinate phases of products recovered from the single step condensation process to enable calculations of LG distribution in both phases. As the raffinate fraction could not be characterised using amperometry, both products were subjected to GC-MS/FID characterisation. Method description of the GC-MS/FID process has been elucidated elsewhere [31] and results for all products have been presented in Tables S1 to S6 in section 1 of supporting information.

The water content of all products was determined by volumetric Karl-Fischer-titration. Hydranal methanol was used as solvent and the titration was conducted using Hydranal Composite-V as titrant. An automated titration equipment, Metrohm 841 Titrando/800 Dosino was utilised. All reagents were supplied by Sigma Aldrich.

2.5   ASPEN Plus model simulations.

2.5.1   Bench-scale solvent extraction.

The phase equilibrium at given conditions during solvent extraction at bench scale was simulated in ASPEN Plus® V12 to predict how STOR influences LG extraction from the ORC. The simulation was discretely conducted for water and AC solvents at ratios that were investigated experimentally.

Surrogate mixtures for ORC (feedstock) and AC (one of the solvents investigated) derived from wheat straw and *miscanthus* (Table S7 in section 2 of supporting information) were first defined. Thereafter, simulation of solvent extraction was setup as per the ASPEN flowchart depicted in Fig. 1. The mixing of solvents (water and AC) with the ORC both at ambient temperature was modelled as a mixer operating at 1 bar.
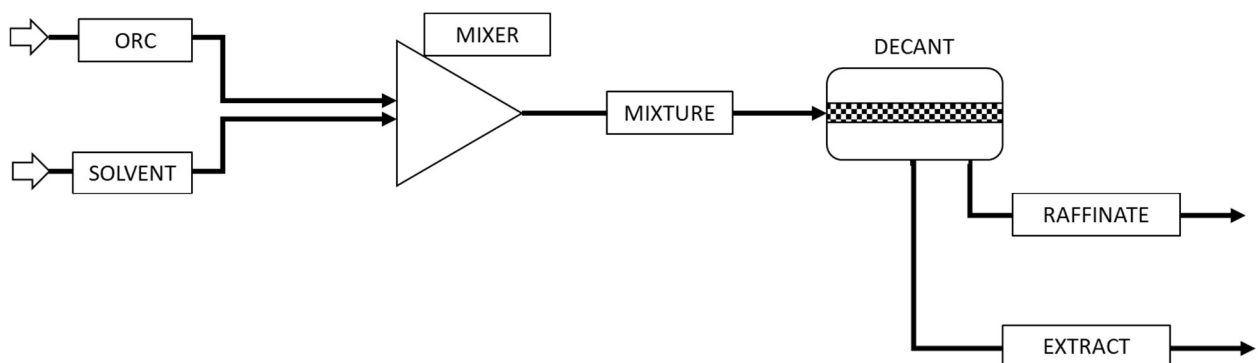

Fig. 1. ASPEN flowchart of bench-scale solvent extraction of LG from ORC using water and AC as solvents.

Following mixing, the mixture was decanted to separate the extract from the raffinate. Root Mean Square Error (RMSE) (eq. (2)) was used to quantify the extent of deviation of model predictions from experimental data.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}$$

(2)

Where:

n represents the number of observations of the dataset.

y_i represents the experimental value for observation i.

$\hat{y}_i$ represents the model predicted value for observation i.

2.5.2 Extraction during direct contact condensation.

Simulation of phase equilibrium conditions during direct contact condensation followed same exact procedures described elsewhere [28]. Except that, condensation temperature on the first condensation stage was set to 40 °C to allow for a single-step condensation as was implemented for the experimental investigation. A mass flowrate ratio of water quench to hot pyrolysis volatiles (m_q/m_v) of 2.0 was utilised. In effect virtually, no product ended up on the second condensation stage.

3 Results and discussions

3.1.1 Bench scale solvent extraction
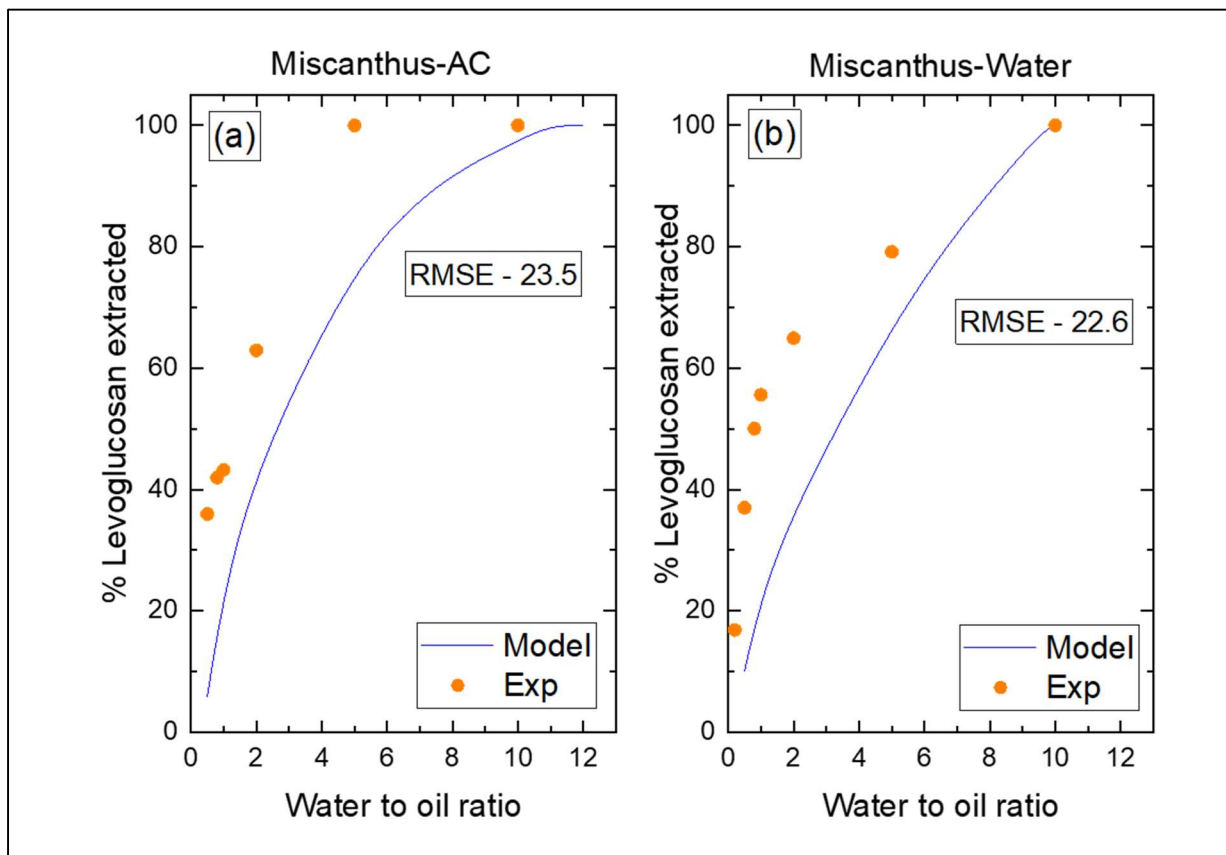
3.1.1.1 Experimental investigations

Fig. 2. Experimental data and model predicted effects of STOR on fractions of LG extracted, showing RMSE data for *miscanthus*: (a) AC as solvent and (b) water as solvent.

The evolution of LG concentration in the extract phase with increasing STOR for the ORC derived from *miscanthus* using both water and the AC solvents has been depicted in Fig. 2. Employing water as solvent saw a steady increase in the concentration of LG extracted from a little below 20 wt.% and climaxing at 100 wt.% as the STOR increased from 0.2 to 10 (Fig. 2b). Unlike the studies of Bennett et al. [5], Chan and Duff [15], Sukhbattar et al. [17] and Vitasari et al. [12] who all recorded optimum LG at ratios of within the ranges of 0.5:1 and 1:1, optimum water-to-oil ratio in this study was only attained at a ratio of 10:1. This is

attributable to the conspicuously lower water content (ca. 14 wt.%) originally present in the ORC used in this study as compared to those recorded for these studies, which ranged between 21 to 34 wt.%. With the high water content associated with these ORC feedstocks, it is expected that only lower amounts of water addition will be required to induce phase separation and subsequently facilitate the optimum extraction of LG. Hence, with the lower water content associated with the ORC used in this study, the higher water-to-oil ratio of 10:1 recorded as optimum is not surprising.

Similar observations were made for the AC as solvent scenario, where a steady increase in concentration of LG extracted was noted with the rise of STOR from 0.5:1 to 10:1 (Fig. 2a). For the AC, no phase separation occurred at the lowest STOR of 0.2:1 investigated. With the AC already saturated with some trace amounts of organic compounds, ratios as low as 0.2:1 might not be enough to create a concentration gradient enough to trigger phase separation.

For wheat straw, employing water as solvent saw a rather sharp increase in extracted LG from about 40 to 75 wt.% when STOR rose from 0.2:1 to 10:1 (Fig. 3b). Similar trends were observed for the investigation that employed the AC as solvent (Fig. 3a). For wheat straw, only about 80 to 85 wt.% of LG was extracted at the maximum STOR investigated as compared to the nearly 100% recorded for *miscanthus*. This is attributable to the comparatively lower concentration of LG originally present in the wheat straw derived ORC, which implies comparatively lower diffusion gradients.
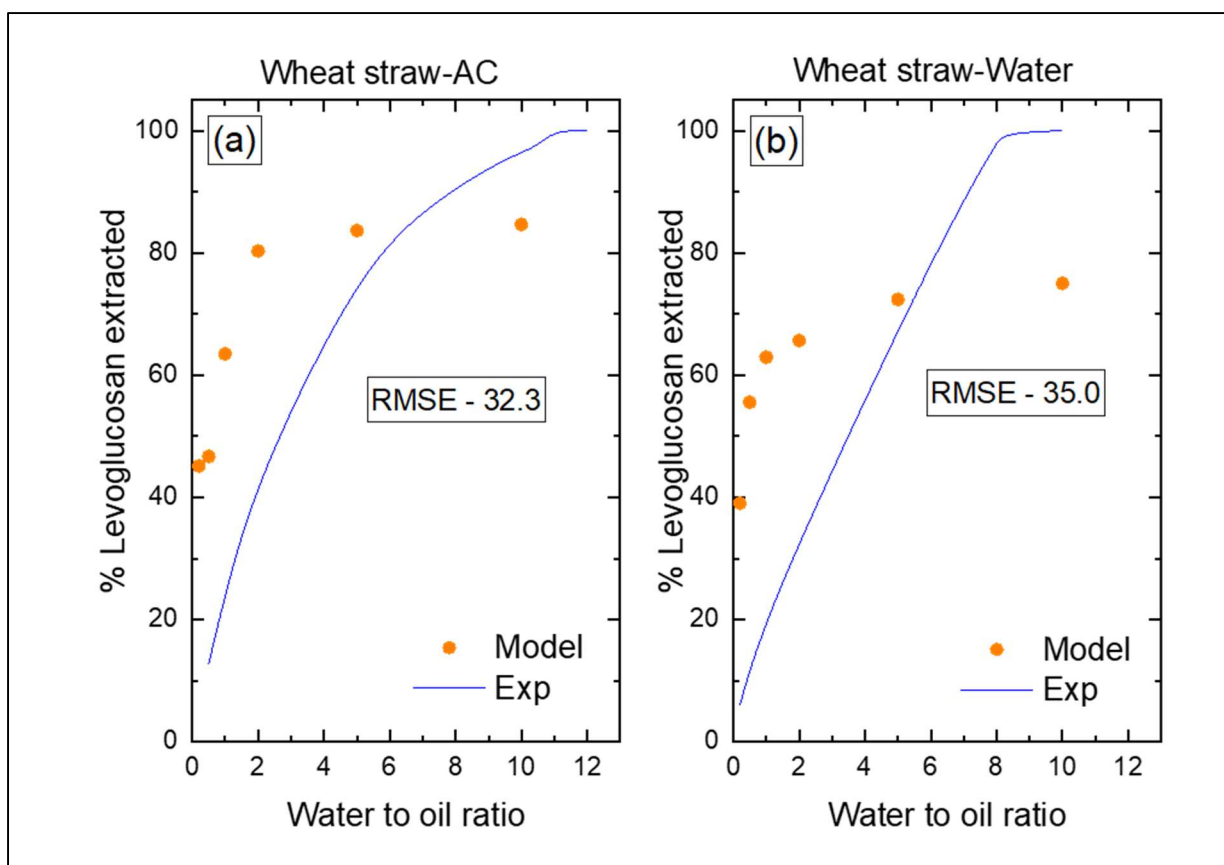
Fig. 3. Experimental data and model predicted effects of STOR on fractions of LG extracted, showing RMSE data for wheat straw: (a) AC as solvent and (b) water as solvent.

Remarkably, for both *miscanthus* and wheat straw cases, it was noted that peak extraction of LG was attained at lower STORs for the AC solvent as compared to water. For the case of *miscanthus*, peak LG extraction was even now attained at a STOR of 5:1 and for the case of wheat straw, percent LG extracted was relatively higher when AC was employed as solvent at STOR ratios of 5:1 and beyond. This is particularly interesting because, with the AC already saturated with some trace amounts of organic compounds, it is to be expected that a higher fraction (as compared to the water solvent) relative to the ORC would be required to optimally extract LG. The divergent trends is corroborated to the substantial amounts of carboxylic acids, particularly acetic acid in the AC, which increases the relative

polarity of the AC. This in turn increases the affinity of the AC for polar compounds such as LG and thus explains the increased performance of the AC solvent over water.

3.1.1.2 *Model predictions*

Both qualitative and quantitative trends of model predictions of LG extraction were very comparable with experimental data, most especially for the case of *miscanthus*, which recorded comparatively lower RMSE in comparison to wheat straw. RMSE recorded for *miscanthus* (22.6 for water and 23.5 for AC) was about 10 times less than corresponding figures recorded for wheat straw (35.0 for water and 32.3 for AC). Also, for most instances, the model under-predicted the fractions of extracted LG at all conditions of STOR, which could be ascribable to the limitations of the UNIFAC-DMD model in accurately predicting the low concentrations of organic compounds in aqueous media as well as the unavailability and/or the high uncertainties associated with pure component vapour pressure data of LG. Besides, the UNIFAC-DMD model is primarily designed using vapour-liquid equilibrium (VLE) data and might be less precise for modelling Liquid-liquid equilibrium (LLE) systems, typical for the case of LG extraction. Interestingly, the remarkable trends of the AC performing generally better than water in extracting LG were equally well represented by the model predictions, further ascertaining the increased performance of AC in extracting LG as compared with water.

3.1.2 Extraction during quenching condensation

3.1.2.1 *Experimental investigations*

LG extraction during direct contact condensation of hot pyrolysis volatiles followed similar procedure employed for studies that tested the hypothesis of quench media, particularly the water quench on yield and composition of fast pyrolysis vapours [28]. Except that in this instance, condensation temperature on first staged condenser was adjusted to a

lower temperature of 40 °C to facilitate the recovery of nearly all condensates on the first condensation stage, thereby instituting a single-step condensation process. An immiscible product of the spent water quench (which served as solvent) and the condensed ORC were collected on the first condensation stage. This product was then separated by means of a separating funnel after which both products were further characterised for LG and other anhydrosugars such as xylosan. Distribution of LG in recovered products are presented in **Fehler! Verweisquelle konnte nicht gefunden werden.** (*miscanthus*) and Table 2 (wheat straw). As per the available resources, only the water-quench was practically investigated for this process. Regardless, model predictions of both the water and the AC quench were investigated and compared, which has subsequently been discussed in section 3.1.2.2.

For *miscanthus*, a 100% extraction of LG into the spent water quench phase was achieved. In addition, all other anhydrosugars ended up in this fraction. No LG ended up in the other recovered condensate fractions (ORC and AC). Similar observations were made for the case of wheat straw, except that no LG was detected in the recovered spent water quench phase or in any of the other recovered product fractions. With the comparatively high ash content of wheat straw, it has a greater tendency of generating minimised concentrations of LG due to catalysed secondary cracking reactions aided by the alkali and alkaline earth metals present in ash as have been previously demonstrated elsewhere [39,84,93,94]. Degradation of LG in a filter cake that proceeds the hot pyrolysis segment used for coke separation could also be very much liable for the absence of LG in the recovered liquid products. This is evident in the presence of other much more stable anhydrosugars (Dianhydro-α-D-glucopyranose, 1,4:3,6-) that were still recovered in the water extract phase.

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Table 1. Distribution of Levoglucosan (LG) and other anhydrosugars in the recovered condensate fractions following quenching of hot pyrolysis volatiles with water (miscanthus case).

Condensate fraction	percent fraction of sugar extracted	
	LG	Other anhydrosugars
ORC (Raffinate)	0.00	0.00
Spent water quench (Extract)	100.00	100.00
AC	0.00	0.00

Table 2. Distribution of Levoglucosan (LG) and other anhydrosugars in the recovered condensate fractions following quenching of hot pyrolysis volatiles with water (wheat straw case).

Condensate fraction	Percent fraction of sugar extracted	
	LG	Other anhydrosugars
ORC (Raffinate)	0.00	0.00
Spent water quench (Extract)	0.00	100.00
AC	0.00	0.00

3.1.2.2 Model predictions

The effects of the respective solvent quench (water and AC) to pyrolysis vapours ratio (m_q/m_v) on the fraction of LG extracted into the resulting solvent-quench extract phase was also probed for both biomass feedstocks. For the water quench scenario, LG extracted into the water quench phase sharply rose with the increase of m_q/m_v for both biomass feedstocks. However, peak LG extraction was attained at ratios of about 5.0 for wheat straw and a little over 6.0 for *miscanthus* (Fig. 4). As per the only available experimental data, an m_q/m_v ratio of 2.0 was just enough to optimally extract all LG into the water quench phase. For the AC quench scenario, LG extraction for both biomass feedstocks were seen to increase steadily with the increase of m_q/m_v. Peak extraction was attained at an m_q/m_v of

8.0 for both biomass feedstock. A further increase in this parameter did not result in any further increments. Compared to the case of the water quench, extraction using AC performed better than water for most of the m_q/m_v ratios. The divergent figures recorded for model prediction as against the experimental data again hints at complex association and hydrogen bonding interactions that occur between water and hot pyrolysis vapours, most of which the modified UNIFAC Dortmund (UNIFAC-DMD) model can hardly handle as have been previously elucidated [28].

Comparing solvent extraction to extraction during quenching condensation, the latter comes with some promising advantages. These include the efficiency of employing significantly lower amounts of solvent to optimally extract LG. Quenching of the hot pyrolysis volatiles rapidly cools down these volatiles, thereby minimising the incidence of further decomposition of LG into much stable products such as cellobiosan and xylose. For solvent extraction, LG is only extracted after the ORC has been recovered. With the ORC highly susceptible to aging reactions right from its production, generated LG in the ORC also gradually diminishes with time. This would mean decreased LG concentration in ORC, implying higher possibilities of lower concentration gradient during solvent extraction. This in effect would require much higher STOR to maximally exploit LG as observed. Furthermore, extraction during quenching also eliminates the need for downstream liquid-liquid extraction processes or setups. This is an important contribution towards saving additional costs and energy in the extraction of LG from FPBOs.
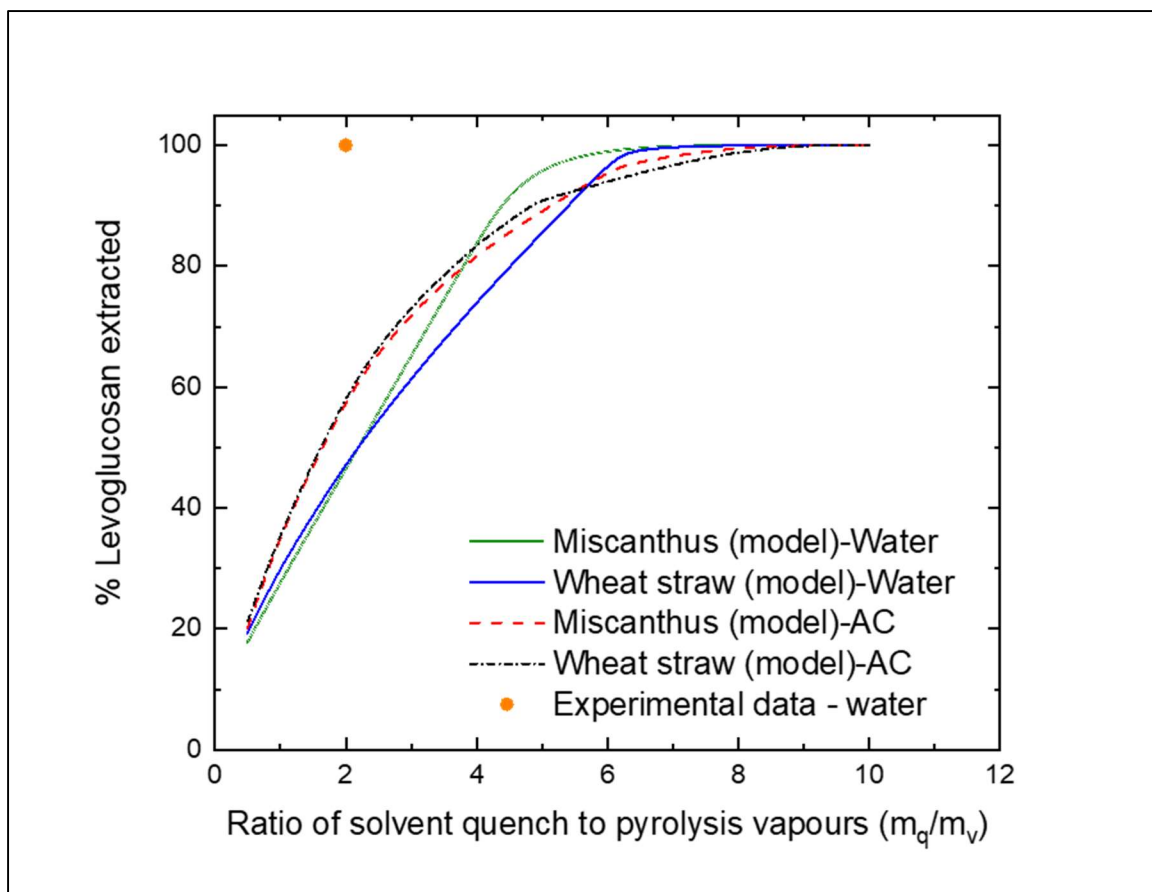
Fig. 4. Model predicted effects of the ratio of solvent quench to pyrolysis vapours (m_q/m_v) on the fraction of Levoglucosan extracted. Experimental data point (for water) is same for wheat straw and *miscanthus*.

4 Conclusion

The use of direct contact condensation of hot pyrolysis vapours with water as quench has proved to be very efficient in optimally recovering Levoglucosan (LG) produced from the fast pyrolysis of biomass. A 100% LG together with other anhydrosugars were retained in the recovered water quench phase following condensation. Compared to solvent extraction, the technique proved to be highly efficient for sugar extraction from fast pyrolysis bio-oils (FPBOs), as it requires significantly lower solvent to feed ratio for optimum LG recovery and eliminates the need for downstream liquid-liquid extraction setups. The use of the aqueous pyrolysis condensate fraction in recovering LG from FPBOs, has also proved to perform

better than using fresh water, particularly for the case of bench-scale solvent extraction. This is a favourable addition towards attaining a sustainable pyrolysis biorefinery as it eliminates the need and additional costs that will have to be incurred in cases where fresh water solvent ought to be supplied from external sources. In addition to its prospects in predicting vapour-liquid equilibrium behaviour of fast pyrolysis vapours, the modified UNIFAC Dortmund (UNIFAC-DMD) model also demonstrated huge prospects in accurately predicting the liquid-liquid equilibrium behaviour between water and FPBOs.

Supporting Information

GC-MS Analyses of raffinate, extract and corresponding ACs obtained from quenching condensation of pyrolysis vapours with water as quench, Surrogate mixtures of ORCs and ACs derived from wheat straw and *miscanthus* used as input for solvent extraction modelling in ASPEN Plus (PDF).

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