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Green recovery of platform chemicals from hydrothermal carbonization process water

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ABSTRACT

This study explores the side-recovery of platform chemicals in the hydrothermal carbonization waste-to-energy chain. Up to 90 % of target chemicals, furfural and 5-hydroxymethylfurfural, were green extracted from the process waters using the hydrophobic deep eutectic solvent decanoic acid/thymol. Wheat straw and rice husk reacted (1/4 solid/water ratio) for up to 120 min and at 180 and 230 °C. The dissolved chemicals built up to 5.9 g/L, accounting for 12 % of the total carbon. Extractions from the process waters and those from reference solutions behaved similarly. The solvent affinity toward furfural is 3.5 times higher than that of 5-hydroxymethylfurfural. The aqueous raffinates chromatographic outline demonstrated the recyclability for prosecuting the HTC. Focused experiments mimicked the functioning of an industrial cascade of two crosscurrent mixer settlers. Extraction yields were 90.7 and 65.8 % for furfural and 5-hydroxymethylfurfural. The counterflow arrangement, simulated by the Kremser method, gave corresponding higher yields, 96.9 and 73.4 %, respectively.

1. Introduction

Contemporary chemical engineering sustains development by designing intensified productions while preserving environmental safety. Despite the pretentious proclamations of worldwide supranational authorities, the complete green transition is not a matter of a few years (Smil, 2019). A too-rapid global change would imply insufferable restrictions in the advanced countries and abrupt halts of the emerging nations' progress. The scenario analyses show that a realistic policy is to inject progressively increasing alternative green processes into the existing productive cycles (Hainsch et al., 2022; Bazilian et al., 2020). Waste-to-value chains fit the agenda (Darmawan et al., 2022; Arneil et al., 2013). The search for alternative pathways for producing chemicals that the contemporary lifestyle cannot do without relies on biomass as the primary resource (Antar et al., 2021). Lignocellulosic biomass could undergo deconstruction to value-added platform chemicals *via* a broad spectrum of biological, chemical, and thermochemical treatments (Okolie et al., 2021). The literature sifts through candidate processes considering affordability, sustainability, and bulk-scale practicability (Choe et al., 2020; Liang et al., 2023; Singh et al., 2022). Hydrothermal carbonization (HTC), a process in which biomass and subcritical hot compressed water slurries undergo valorizing transformations, is recognized for its versatility and mildness. In the early years, researchers focused on HTC as a convenient process for densifying the energy content of wet residuals by transforming them into a coal-like material, the hydrochar (HC). A perusal of the more recent literature shows the evolution toward more specialized, integrated applications. HTC is now direct to tuning the structure of hydrochar finely (Wang et al., 2018) to produce super-performing materials (Xu et al., 2022) and to incorporate the process into biorefineries (Cavali et al., 2023; Zhang et al., 2023).

Hydrochar is not the only HTC product worth studying: a complete analysis should consider the liquid phase. The hydrothermal carbonization proceeds along two parallel pathways; the first is a complex reaction network that refines the biomass reducing the hydrogen and oxygen content of the solid phase. The products of the deconstruction accumulate in the process water (PW). The long-time fate of these chemicals is condensation and polymerization to give the so-called secondary hydrochar and, ultimately, increase the yield of the carbonaceous material (Ischia and Fiori, 2021). Consequently, research on the HTC process water is appropriate for enlarging the knowledge on hydrochar formation and for the dissolved chemicals in themselves (Borrero-López et al., 2020; Atallah et al., 2019).

The detection of platform chemicals in HTC liquids, their time course, and the possibility of monitoring their evolution by simple,

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lumped measurements were treated in a previous paper (Gallifuoco et al., 2022). This contribution treats the recovery of selected chemicals from the HTC process water under mild conditions. To produce green chemical building blocks is not devoid of environmental concerns *per se*. Comprehensive reviews highlight the bottlenecks to overcome for achieving full sustainability, the perspective of competitiveness with the petro-based routes, and the market forecasts (Sheldon, 2014; Takkellapati et al., 2018; Brun et al., 2017; Gunukula et al., 2018). The selection of candidate pathways among the many laboratory studies must be accurate and exhaustive. A key discriminant factor should be the concreteness of scaling up to industrial productions. In the authors' opinion, there is room for HTC in the bulk production of green platform chemicals. The easiness of reactor design, the mildness of operational conditions, and the process versatility make HTC appealing to chemical industries tackling the switch from traditional productions to the green paradigm.

Hydrothermal processes that use pure carbohydrates as raw material are well assessed and could ensure quantitative conversions (Modugno and Titirici, 2021). However, exploiting low-cost lignocellulosic residues would be preferable to boost sustainability, according to the precepts of the economy of scale and waste minimizations. Enlightening papers and reviews conceptualize biomass-derived production of essential chemicals *via* hydrothermal treatments (Zhang et al., 2023; Burguete et al., 2016). Biomass recalcitrance could limit production rate, selectivity, and yield. Tailored pretreatments and using catalysts are the usual recipes to overcome the obstacles avoiding exacerbating the process severity (Yang et al., 2019; Hou et al., 2021; Zhao et al., 2021). The approach of this study is to adopt essential HTC conditions (no pretreatment, no additives) with the cognizance of losing efficiency in return for the process's cheapness. The selected biomass are wheat straw and rice husk, multi-purpose residues ranging from hundreds of millions of tons per year.

The withdrawal of liquid-phase substances should alter the autocatalytic HC formation rate. At the micro-scale, solid matrix active loci's local reaction time distribution (Gallifuoco, 2019) will turn out warped. The expected macroscopic outcome is the lowering of solid phase energy densification and yield because of the reduction of the driving force for sustaining long-time HC formation. Under these constraints, one could envisage two possible industrial applications. A single-step, short reaction time HTC designated for the sole production of chemicals. A two-step combined short and long reaction time HTC: the first stage for producing chemicals, an intermediate stage for removing selected molecules, and a final reaction stage for building an hydrochar of acceptable, albeit reduced, energetic properties. Whatever the choice, the green recovery of platform chemicals needs accurate investigation. PW contains a broad spectrum of strategic bioderived chemicals, scoring top in all the lists crowding the literature, and their recovery is worth investigating to address the passage from laboratory to industry (Gallifuoco et al., 2022; Wüst et al., 2020). This explicative study focuses on 5-hydroxymethylfurfural (HMF) and furfural (FF), universally recognized as cardinal biomolecules (Alves Silva et al., 2021; Jaswal et al., 2022). Selective extraction with a green solvent should be the proper sustainable separation process (Winterton, 2021; van Osch et al., 2015). It comes naturally to resorting to hydrophobic deep eutectic solvents (DES) that recently have pervaded the literature in general, particularly on biomass processing (De Oliveira Vigier et al., 2015; Elgharbawy et al., 2020; Devi et al., 2023). Mixtures of decanoic acid (DEC) with terpenoids give rise to DESs thoroughly studied for the thermodynamics of HMF and FF extraction from aqueous solutions with favorable partitions (Dietz et al., 2019; Dietz et al., 2018). This contribution focuses on the DES obtained using thymol (THY) as the hydrogen bond acceptor. Most of the available papers deal with the extraction from model water solutions, which are much simpler than HTC liquid phases. To the authors' knowledge, the only application to multi-component feedstocks concerns the detoxification of lignocellulosic hydrolysates for boosting the subsequent bioconversion step (Makoś et al., 2020). The need for more information imposes severe limitations on industrial developments. This study has two purposes: exploring the DES-PW interactions and proposing an investigation methodology to select the biomass and HTC conditions appropriate for recovering a target chemical.

2. Materials and methods

2.1. Materials

All the chemicals were laboratory, reagent-grade, commonly available on the market. The waste biomasses come from local groves. All analyses and experiments used ultrapure demineralized water.

2.2. Methods

2.2.1. HTC reactions

A previous paper (Gallifuoco et al., 2017) details the stainless-steel 200 cm^3 batch reactor, controls, and service equipment. All HTC reactions occurred at a water/biomass ratio of 4/1 on a dry basis. Ten grams of solid and water were loaded into the reactor, and the vessel was sealed and evacuated of air with a vacuum pump (ABM model 3EKF56). The reactor warmup required about 20 min (9 °C/min ramp). The study explored two temperatures (180 and 230 °C) and six residence times (0, 10, 15, 30, 60, and 120 min). The residence time of 0 implies that the reactor was quenched as it reached the setpoint temperature. The cooling down to room temperature occurred by immersing the vessel in a large cold-water bath. The procedure lasted 6 min, after which the products were recovered immediately. The gas phase (2 % *w*/w of the dry biomass, on average, prevalently CO_2) was discharged. A standard filtration separated PW (stored at 4 °C for subsequent experiments) from wet HC (oven-dried at 105 °C up to constant weight and stored at room temperature). All kinetic runs were conducted once, given the 4 % relative error recorded in hundreds of previous experiments.

2.2.2. DES preparation

The two constituent solids (DEC and THY) were weighted to obtain a 1:1 M ratio and added to a rounded bottom Pyrex® glass flask. A swing incubator (EDISON, New Brunswick Scientific), thermostated at 40 °C ensured the gentle mixing of the powders. Although the eutectic liquid appeared within the first 15 min, the incubation lasted up to 120 min to guarantee the complete dissolution of micro-crystals invisible to the naked eye. The preparation stays liquid at room temperature indefinitely.

2.2.3. Solvent extractions

Standard FF and HMF extractions from PW went according to the following procedure. In a glass tube were added 2 g of water phase and different amounts of DES (from 1 to 4 g) to give 0.5, 1, and 2 DES/PW weight ratios. The mixture was shacked gently for 60 min in a water bath (Haake, GH) thermostated at 30 °C to allow equilibrating of the two liquids then centrifuged (Chermle, ZK380) at 8000 rpm for 30 min. The heavy aqueous phase (raffinate) was carefully recovered with a syringe and stored at 4 °C for subsequent determinations.

The indicators of extraction quality are the partition coefficient (K) and the extraction yield (EY).

$$K = w_S / w_A \tag{1}$$

$$EY = \frac{m_S}{m_{i,A}} = \frac{m_{i,A} - m_{f,A}}{m_{i,A}} \tag{2}$$

In Eqs. (1) and (2), w stays for the extractant mass fraction in the DES (subscript S) and aqueous phase (subscript A), respectively, EY for the extraction yield, m for the extractant mass, measured in the aqueous phase before (i) and after (f) the extraction.

A manipulation of Eqs. (1) and (2) by simple mass balances, omitted for brevity, furnishes the relationship between EY and K expected for simple solutions, *i.e.*, when no additional masked effects superimpose to the extraction.

$$EY = \frac{K}{\frac{M_A}{M_S} + K} \tag{3}$$

In the above equation, M_A and M_S are the mass of the aqueous and solvent phases.

2.2.4. *Analytical*

Hydrochars ultimate compositions went according to ASTM D3176-89, 2002 using a Perkin-Elmer 2400 Series II elemental analyzer. Solid yields and dry weight determinations followed UNI EN ISO 18134-2, 2015. HPLC analyses (Waters–Alliance e2695 separation module) detected FF, HMF and sugars with a Supelcogel-Ca column (30 cm × 7.8 mm, 80 °C, mobile phase 0.1 % phosphoric acid/water, 0.5 ml/min) and a refractive index detector (Waters 2414, 30 °C). Organic acids were separated with a C 18 reverse phase Phenomenex - Kinetex column (5 μm 100 A° 250 × 4,6, 35 °C) and detected with the UV–Vis detector (Waters 2489, 200 nm). HPLC analyses referenced to calibration with standard pure chemicals solutions for computing the concentrations. Each of the previously described analyses was in triplicate. Total dissolved carbon was detected spectrophotometrically (Hach Lange GMBH, LCK381).

3. Results and discussion

3.1. *Background description of liquid phase development*

This study envisages a specialized process for the simultaneous production of target chemicals and hydrochar. The correct development requires the preliminary assessment of the interactions between solid and liquid phases during the proceeding of HTC. One needs to consider to what extent the intermediate recovery of dissolved building blocks would subtract carbon otherwise destined to increase the energy content of the final product. The literature delineates the relevant reaction network to the most extreme detail (Wüst et al., 2020) For the present paper, the following simplified description will suffice. FF and HMF originate from hemicellulose and cellulose, respectively. The two hydrolysis products of the polymers (xylose and glucose) undergo dehydration, eliminating three water molecules to give FF and HMF. The long-term fate of these target chemicals is to disappear from the PW *via* two parallel pathways: degrading to waste CO_2 and undergoing further transformation, particularly polycondensation, entering the solid-phase hydrochar-enriching reaction chains. The degradation is likely negligible within the temperature range adopted, as confirmed by the small amount of gas recovered from the reactor. Therefore, the chemical reaction engineering lumps to straightforward, consecutive reaction steps. Being FF and HMF the intermediates, their concentration should peak at a specific reaction time. The kind of biomass, reaction temperature, and process duration are the available interventions for steering the optimal recovery.

Figs. 1 and 2 and Table 1 show the interrelationship between these critical parameters, providing sufficiently exhaustive information for undertaking the subsequent investigation of the solvent extraction procedures.

3.2. *HTC experiments*

3.2.1. *Liquid phase investigation*

Fig. 1 is about the liquid phase and reports the progress of the dissolved carbon associated with FF and HMF (CL) as a fraction of the instantaneous liquid-phase total organic carbon (TOC) for the straw (a) and the husk (b). Lines connecting points help highlight the trends. The two biomasses display a similar behavior, with only minor quantitative differences. At 180 °C (open symbols, dashed lines), the fraction of the organic carbon confined in FF peaks within 90 min (straw) and 120 min (husk), while that associated with HMF does not appear for up to 30 min of HTC reaction; after that, it increases slowly. The trends at 230 °C (full symbols, solid lines) are somewhat different: FF decreases continuously from zero to 120 min, while HMF peaks within 30 min of reaction. The formation and depletion processes are activated, *i.e.*, their rate increases with temperature. One can speculate that the evolution of HMF is generally slower than that of FF, the latter likely attaining the maximum during the warmup to 230 °C. Further experiments at intermediate temperatures could test the hypothesis but are out of the scope of this contribution. Conversely, Fig. 1 furnishes two essential hints: the relative abundance of the target chemicals depends strongly on HTC reaction temperature and duration; the two extractables account for a maximum of 16 ÷ 18 % of the total organic carbon dissolved in the PW.

3.2.2. *Solid phase investigation*

Fig. 2 considers the solid phase coexisting with the evolving PW and displays the ratio of the higher heating value of the two chemicals (HHV_L) to that of the corresponding hydrochar (HHV_S) as a function of time. This parameter estimates how much the hydrochar energy reduction would be following the complete removal of FF and HMF from the liquid phase. The qualitative trends are like that of Fig. 1 but now the husk produces values generally lower than the straw. This evidence should indicate that the husk furnishes a hydrochar of better energy density. Fig. 2 shows that the HHV associated with the two chemicals is at most 6 ÷ 8 % of that of the hydrochar. Finally, Table 1 allows completing the discussion. Data concern yields and other quantities that help assess HTC performances. The ratio of FF and HMF masses to that of the dry biomass initially loaded to the reactor FF/B and HMF/B, respectively, quantifies the extent of conversion to target chemicals. At 180 °C and with both biomasses, the maximum conversion to FF ranges

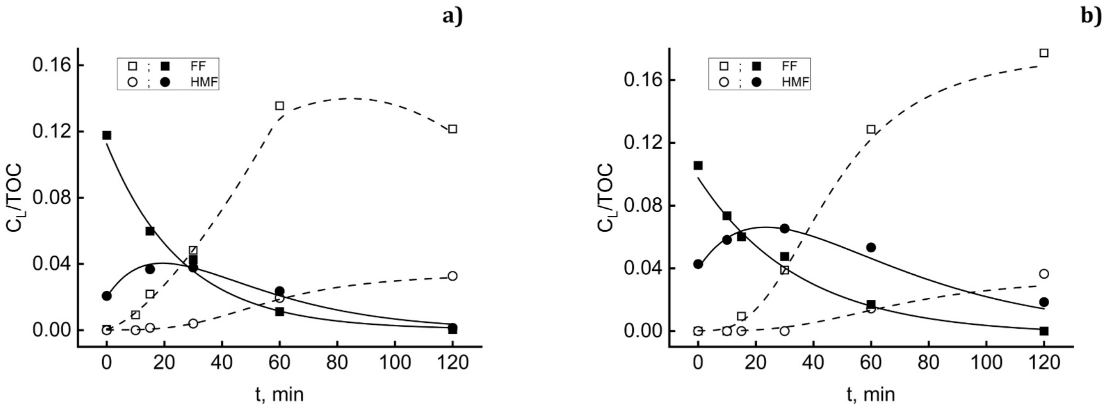

Fig. 1. Dynamics of the dissolved carbon associated to FF and HMF as a fraction of the total carbon for the straw (a) and the husk (b).

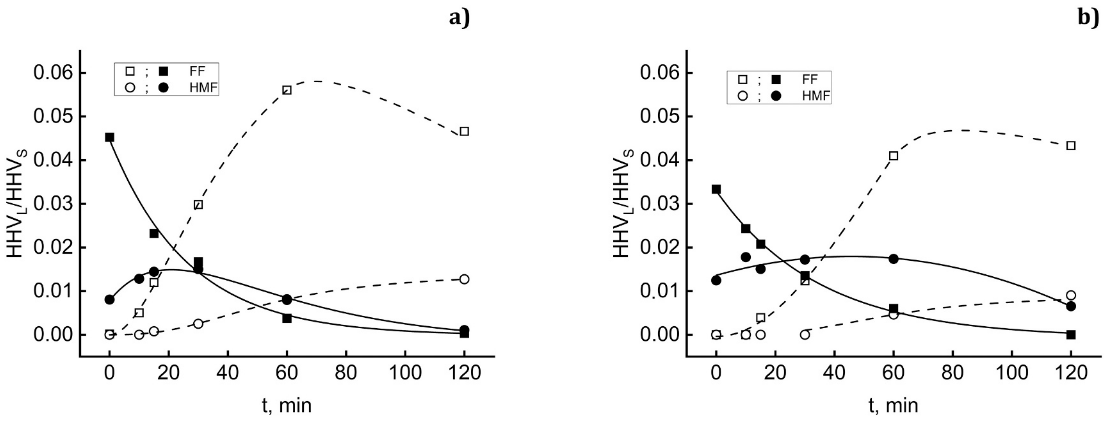

Fig. 2. Dynamics of the ratio of the higher heating value of the two chemicals (HHV_L) to that of the corresponding hydrochar (HHV_S) for the straw (a) and the husk (b).

Table 1
List of solid and liquid phase properties for assessing HTC performances.

Biomass	T [°C]	t [min]	FF/B [%]	HMF/B [%]	FF/HEM [%]	HMF/CEL [%]	FF/HMF	CL/Ctot [%]
Straw	180	0	0.0098	–	0.0418	–	–	22.4460
		10	0.2720	–	1.1590	–	–	35.4940
		15	0.6650	0.0475	2.8310	0.1420	14.0000	36.2900
		30	1.5830	0.1430	6.7370	0.4280	11.0370	39.1700
		60	2.9930	0.4700	12.7350	1.4030	6.3696	30.6120
		120	2.5770	0.7600	10.9670	2.2700	3.3889	26.8230
	230	0	2.4080	0.4630	10.2460	1.3830	5.1978	28.4640
		10	0.9290	0.7180	3.9530	2.1430	1.2937	44.4030
		15	1.1880	0.7990	5.0560	2.3850	1.4872	29.3380
		30	0.8550	0.8290	3.6360	2.4750	1.0307	29.2360
		60	0.1970	0.4510	0.8390	1.3470	0.4368	26.0920
		120	0.0152	0.0556	0.0645	0.1660	0.2727	31.4450
Husk	180	0	–	–	–	–	–	12.5130
		10	–	–	–	–	–	18.6030
		15	0.2240	–	1.2780	–	–	29.5400
		30	0.6710	–	3.8370	–	–	24.0070
		60	2.1530	0.2630	12.3050	0.7020	8.1746	24.2470
		120	2.3690	0.5330	13.5370	1.4220	4.4428	19.7800
	230	0	1.8070	0.7300	10.3240	1.9460	2.4751	24.2930
		10	1.2970	1.0260	7.4130	2.7350	1.2648	25.0000
		15	1.0520	0.8250	6.0110	2.2010	1.2745	24.8950
		30	0.6700	0.9200	3.8260	2.4530	0.7281	21.4680
		60	0.2690	0.8400	1.5360	2.2410	0.3198	24.0780
		120	–	0.3500	–	0.9340	–	27.2760

between 2 and 3 %, while the yield to HMF remains very low. At 230 °C, the increase in FF depletion rate makes it unrealistic to recover the chemical from PW unless planning to extract the chemical at time zero (FF/B = 2.4 % and 1.8 % with straw and husk, respectively). The conversion to HMF remains negligible. A more specific kind of yield refers to the mass of the origin polymers, cellulose (CEL), and hemicellulose (HEM) contained in the raw biomasses. Taking an average from data available in the literature, one can assume that the CEL content is 33.5 % and 37.5 % for straw and husk, respectively, and that the corresponding datum for HEM is 23.5 % and 17.5 %. Excluding significant cross-reactions, one can consider FF coming exclusively from HEM. Table 1 shows that, at the explored HTC conditions, the conversion of FF to HEM goes up to 13 % with both biomasses. The analogous quantity for HMF refers to CEL and gives a maximum yield of around 2 %, which indicates CEL is more recalcitrant than HEM, at least for the biomasses of this study. Finally, Table 1 reports the carbon partition as the ratio between the liquid (C_L) and the total one (solid plus liquid, C_{TOT}). The straw gives rise to liquid phases containing up to 44 % of the carbon available in the original biomasses and the husk up to 30 %. The above discussion sums up encouraging findings. Notwithstanding the limited yields to the target chemicals, their recovery is worth considering as a side-production in a primary biomass-to- energy process. Possible industrial processes could benefit from the available degrees of freedom (type of biomass, target chemicals, HTC reaction conditions) for boosting conversions.

3.3. *Green solvent extractions*

3.3.1. *Comparison between PW and model solutions*

The remaining part of this study is on FF and HMF extraction. The discussion deals with a selection of data, the synopsis of all the extracted liquids being available in the supplementary material as Table S1.

Despite the prominent literature on furans partition between water and green solvents, the treatment of the HTC liquid phase is a novelty. PW contains plenty of chemicals that could interfere with a selective DES extraction.

In step with the exploratory ends of this study, the primary focus is comparing target chemicals extraction from demineralized water and PW. Fig. 3 shows the results. To assess the inherent capability of DEC-THY, ten equimolar aqueous solutions of both FF and HMF, ranging from 0.5 to 100 mM and created on purpose (group A 1–10, Table S1), were extracted with the solvent at a mass ratio of 1:1 and assayed before

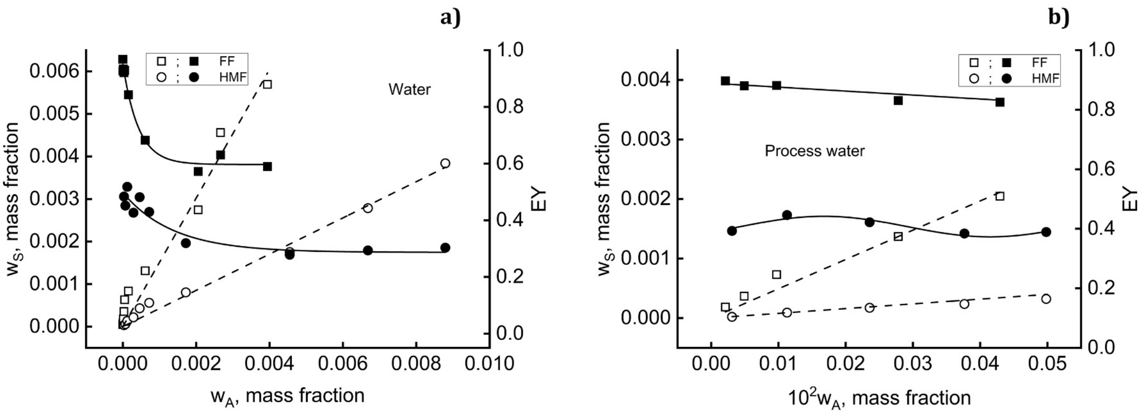

Fig. 3. DES extraction behavior as a function of liquid phase concentrations in pure water (a) and in PW (b). Left Y-axes, extractants mass fraction in DES. Right Y-axes, extraction yields.

and after the treatment. Fig. 3a shows data as a function of the analyte mass fraction in the raffinates. The left Y-axis (open symbols) reports the equilibrium concentration in the organic phase calculated by the difference mass balance in the aqueous solution. The slope of the segments connecting each point to the origin gives the Ks. Although these values depend on the water phase concentration, one can take the slopes of dashed lines (linear correlations, $R^2 > 0.93$) as the unique partition coefficient, which results in 1.512 for FF and 0.426 for HMF, respectively. This finding establishes the average relative affinity of DEC-THY toward FF and HMF. Taking the ratio of the two partition coefficients, one obtains that solvent selectivity toward FF is 3.5 times higher than that of HMF. This datum indicates the appropriateness of seeking a compromise between completeness of extraction and efficiency of separation. Besides, further selectivity improvements could result from variating extraction parameters, most likely the pH. In the frame of this discussion, one could conclude that using DEC-THY solvent for the separation is conceivable. The extraction yields refer to the right Y-axis (full symbols; lines connecting data points highlight the trends). As expected, the EY decreases as the water phase concentration increases for both chemicals, and FF displays larger values in all the explored ranges. Interestingly, the EY of FF is close to the unity in the low concentration range, foreshadowing an almost total removal from dilute solutions. Fig. 3b is about PW. The aqueous solutions originated from the same HTC liquid (C21 in Table S1) diluted with demineralized water to give an array of different concentrations, necessarily less concentrated than those of part a). Also, the linear correlations (dashed lines through open symbols) hold with PW. Notably, the partition coefficients are higher than those in water solutions. The affinity for the FF contained in PW increases to 4.92, more than threefold those for water solutions. For HMF, there is an amplification, too, albeit more contained (from 0.43 to 0.93). In the presence of PW, the solvent selectivity increases from 3.5 to 5.29. This interesting effect is worth future investigations to clarify if the enhancement is general or due to the combination of DES, extractants, and biomass this study deals with. Some basic controls should exclude masked effects superimposed on the extraction, which could drive the separation. The pH of all PWs assayed remained unchanged after the contact with DES. The peaks in the HPLC chromatograms of the extracted PWs (see Fig. S1 in the Supplementary material) are similar and appear at the same retention time as those of untreated PWs. Control tests performed with the internal standard technique, *i.e.*, adding known quantities of FF and HMF to samples of PW (data not shown for brevity), ruled out ghost detections. Within the frame of the present contribution, it suffices to grant the enhancement of extraction performances in PW as a beneficial effect. A detailed analysis of the organic phase would clarify the phenomenon better. This step ahead, which will furnish also significant information on separated products' purity, is presently under investigation for a subsequent paper on the optimization of the extraction process. Finally, Fig. 3b shows that also for PWs, the extraction yield for FF is higher than that of HMF (right Y-axis, full symbols, and lines connecting points help follow the trends).

3.3.2. *Assessment of PW extractions*

Further investigation originating from the outcomes of Fig. 3. In designing an industrial extraction process, relying on a predictable equilibrium behavior is paramount. That could only sometimes be true when treating complex mixtures such as PWs, where the variability of the raw biomass and HTC reaction conditions produce out-of-standard aqueous phases.

Relying on literature findings (Dietz et al., 2019), the assumption of total immiscibility between the aqueous and solvent phases holds so that in Eq. (3) M_A and M_S do not change during the extraction. Deviation from the ideality could appear if the solvent chemically interacts with some aqueous phase component. Fig. 4 reports EY as a function of K for both FF and HMF coming from pure water solutions and PWs of disparate HTC conditions. Eq. (3), at a fixed ratio M_A/M_S, represents a rectangular hyperbola with a horizontal asymptote of one. The experimental results arrange perfectly to these trends, whatever the parent feedstock, the M_A/M_S, the kind of extractant, and the original reaction condition. Full lines connecting points show the nonlinear fittings to hyperbolae, while the dashed lines trace the curves extrapolated out of the experimental ranges. In conclusion, Fig. 4 confirms the reliability of Eq. (3) as a design tool for developing an industrial process of solvent extraction combined with HTC.

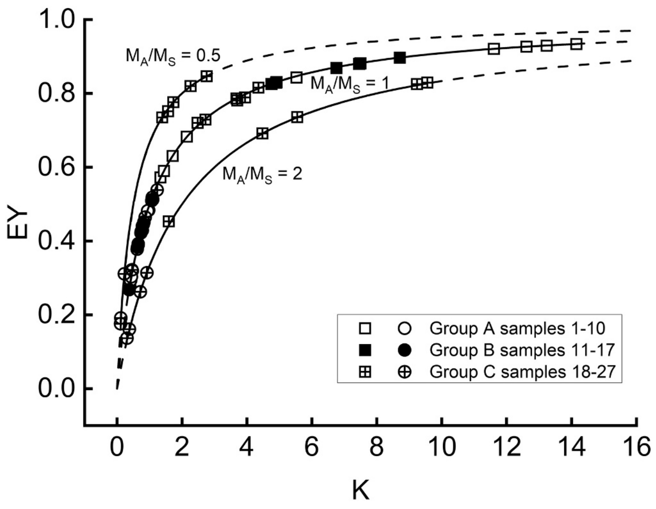

Fig. 4. Extraction yields as a function of the partition coefficients.

Although relatively diluted in the PWs, furans migrate efficiently in the organic phase, and the aqueous raffinate maintains the outline of a liquid recyclable in further HTC processes. The experiments so far described encourage prosecuting the research on industrial implementations.

3.3.3. Basic findings preparatory to industrial process optimization

Given the full-scale extraction process development, several alternative DESs are worth considering. The optimal choice relies on environmental, economic, and safety ponderings. In the confines of the present work, it is advisable to test the selected solvent against its ability to push to the completeness of the recovery of FF and HMF in a multistage, continuous extraction. The first possibility would be to arrange the industrial mixer settlers in a crosscurrent cascade, in which the aqueous stream encounters consecutive aliquots of fresh solvent. The setup of a laboratory experiment that mimics the scheme is easy. To the scope, 4 g of PW (C23) underwent extraction with 4 g of solvent according to the procedure already defined. The raffinate was carefully recovered, a small aliquot was stored for analyses, and the remaining was weighed and contacted with the same amount of fresh solvent. Further analyses gave the residual FF and HMF. The procedure is tantamount to operating a two-stage, continuous process with a 2:1 overall feed ratio. Table 2 shows the process performances. The first stage removes from the entering aqueous phase 74.0 % of FF and 45.3 % of the HMF. The mass ratio of FF to HMF lowers from 1.10 to 0.53. The second stage receives the raffinate from the first one and pushes the EY up to 90.7 % for FF and 65.8 % for HMF. The final mass ratio is 0.30. These quantities suggest that adding a third stage would be unprofitable because the separation enhancement is not warrantable due to the higher process cost.

Remarkably, the high affinity for the solvent displayed by FF would suggest that DEC-THY is suitable for separating it from aqueous solutions containing HMF and coming from other processes. Operating the multistage separation according to a counterflow arrangement would save the solvent. The laboratory simulation of this latter configuration is not straightforward and would require specific equipment for obtaining significant results; however, it is not necessary in the framework of the present contribution. The approximative linear equilibrium (see discussion of Fig. 3) and the almost complete phase insolubility allows one to predict process performances with simplified calculation, *e.g.*, by the Kremser equation or modifications thereof (Fraser and Shenoy, 2004). Table 2 also summarizes the main results of a continuous process treating the same feed of the cross-current experiment. At a feed ratio of 2:1, with two stages, the system achieves a separation efficiency of 96.9 % for furfural and 73.4 % for hydroxymethylfurfural, with a final concentration of 0.048 and 0.386 g/kg, respectively. The Kremser method furnishes only approximate outputs, although helpful for steering the full-scale development and future, more in-depth investigations oriented to process optimization.

This contribution's last set of experiments is preparatory to comparing different phase contacting modalities in the extraction step. The wet HC recovered from the reactor by filtration contains, on average, 70.5 % humidity, most likely of the same composition as the filtered PW. For maximizing the platform chemicals production at the industrial scale, one could consider two alternatives: dehydrate as much as the wet HC by filter pressing it and send to the extraction stage the total PW; perform a slurry extraction contacting with the DES the whole suspension coming from the reactor and then dehydrating the exhaust HC. The latter procedure deserves investigation since the extractive performance could be affected by the presence of the suspended solid (Zhao et al., 2023). A further HTC reaction (time zero, 230 °C) furnished new materials to the scope. After the filtration, some aliquots of PW underwent the usual DES extraction procedure as a reference. Other aliquots of PW were mixed with the proper weight of wet HC to give the same total liquid volume of the corresponding reference, and the suspension underwent extraction under identical conditions. Fig. 5 shows the results as a function of M_A/M_S. Part a) reports the FF and HMF extraction yields, and part b) the FF to HMF selectivity. The presence of the solid suspension worsens the extraction performance. The unfavorable effect is maximum when the amounts of aqueous and organic phases are comparable ($M_A/M_S = 1$) and diminishes when one of the two phases is preponderant. The superimposition of mass transfer resistances and interfacial phenomena could explain the results of Fig. 5. These last findings could address further research oriented to the process development, including the extraction kinetics and the mixing fluid dynamics.

Finally, assessing the proper procedure for limiting the cost of solvent regeneration is an undeniable goal. Shortcut estimates, commonly adopted with more traditional solvents, could be insufficient due to the relative scarcity of knowledge on DES properties. Future laboratory experiments could furnish the information required to get reliability. The recent literature on hydrophobic DES industrial applications directs to the proper experiments (van Osch et al., 2020; Isci and Kaltschmitt, 2022; Naga Sai et al., 2021). Generally, papers dealing with furans production from waste biomass portray process layouts in which DES regeneration occurs by vacuum (around 6 kPa) distillation, exploiting the solvent low volatility. Given the similarity with the HTC-mediated process depicted here, a similar downstream processing is conceivable. A broader spectrum of future, specific experiments will help clarify the matter. This contribution intended to demonstrate the process feasibility by selecting specific target chemicals, feedstocks, reaction conditions, and a solvent. The many degrees of freedom available to the industrial designer inspire confidence for the transfer of technology to industrial production. Research on the lab scale is in progress along several lines: characterizing the extracts for the organic phase product distribution, evaluating possible procedures for product recovery and solvent regeneration, and assessing how the raffinate process waters would interact with biomass in a subsequent HTC step aimed at hydrochar production.

Table 2
Synopsis of results for a 2-stages cross- and counter-current extraction.

Configuration		Concentration of the feed [g/kg]		Exit concentration of the raffinate [g/kg]		Extraction yield [%]	
		FF	HMF	FF	HMF	FF	HMF
Cross-current[a]	Stage 1	1.599	1.452	0.415	0.794	74.0	45.3
	Stage 2	0.415	0.794	0.148	0.496	90.7	65.8
Counter-current[b]		1.599	1.452	0.048	0.386	96.9	73.4

[a] Experimental.
[b] Kremser simulation.

4. Conclusions

Process waters from biomass hydrothermal carbonization are a sustainable source of valuable platform chemicals. Target molecules are recoverable through extraction with green solvents. The study shows the favorable migration of furfural and 5-hydroxymethylfurfural from the aqueous phase to the deep eutectic solvent decanoic acid/thymol. The proposed process, uncatalyzed and applied to waste feedstocks, is cheaper than the traditional hydrothermal treatments of pure carbohydrates. The better affordability stimulates the scale-up to an industrial side-production in the waste-to-energy chain based on hydrothermal carbonization. The raffinate process water is re-usable as the liquid phase in the hydrothermal reactor for prosecuting the conversion of biomass to hydrochar. The results address further investigation oriented to the full-scale process development on chemicals recovery by DES extraction.

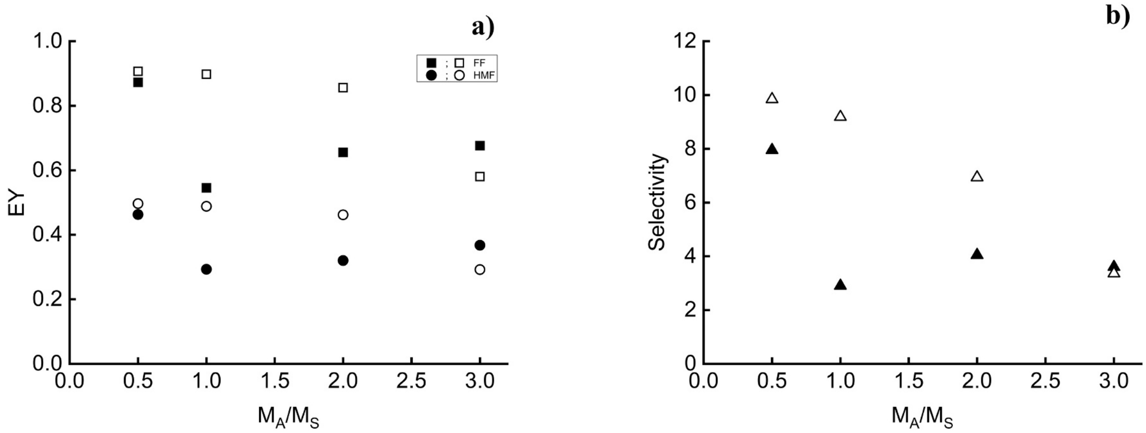

Fig. 5. Comparison of extraction modalities: conventional (open symbols) and slurry (full symbols). Extraction yield (a) and selectivity (b) as a function of water/solvent ratio.

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CRediT authorship contribution statement

Luca Taglieri: Writing – original draft, Validation, Conceptualization. **Agata Spera:** Investigation, Data curation. **Alberto Gallifuoco:** Writing – original draft, Validation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biteb.2024.101815.

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