Eutectic solvents for the valorisation of the aqueous phase from hydrothermally liquefied black liquor

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ABSTRACT

The potential valorisation of the aqueous phase obtained after the hydrothermal liquefaction of Kraft black liquor by means of liquid-liquid extraction with new generation solvents was analysed for the first time ever. For this purpose, hydrophobic eutectic solvents (ES), based on combinations of menthol or thymol with octanoic, decanoic or dodecanoic acid, were tested to recover phenolic compounds from this wastewater. All of them showed high affinity for phenolic compounds and ethanol, but low affinity for the rest of the compounds, leaving a more biodegradable raffinate. Regarding phenolic compounds, the average extraction yields ranged from 66 % to 91 % with menthol-based ES and from 34 % to 98 % with thymol-based ES. The best solvent in terms of recovery and selectivity for phenolic compounds was 1:1 Menthol:Octanoic acid, with separation factors of 104.2 and 29.2 for phenolic compounds to volatile fatty acids and alcohols, respectively. In this regard, the results obtained open the simultaneous valorisation of the extract as a source of phenolic compounds, regenerating the ES, and the raffinate as a sustainable feedstock for further fermentation or catalytic processes.

1. Introduction

Kraft black liquor is an aqueous by-product obtained after the cooking stage in conventional pulp mills, containing compounds extracted from wood as well as the spent reagents used. This stream usually has a strong alkaline pH and contains relevant concentrations of sodium hydroxide and sodium sulphide, which are the inorganic salts used to separate the pulp from the rest of the compounds. In addition, it also contains a high organic load and toxic chemicals, so its proper management is mandatory [1]. For the Kraft process to be cost-effective, black liquor is simultaneously used in the own pulp mill as fuel and as a source of the spent inorganic salts by means of a recovery boiler. However, this strategy has some drawbacks, such as emissions of odours and gases, corrosion and fouling of equipment, significant energy requirements for the previous evaporation stage or the combustion of high value-added compounds with low heating value, such as carboxylic acids and hemicellulose. This last fact, together with increasingly stringent environmental regulations, is especially leading to the search for new methods of valorising black liquor [1–3].

In the context of energy and chemical production, and taking into account that around 85 % of Kraft black liquor is water, hydrothermal treatments are ideal for treating it, as they do not require previous evaporation or additional reagents and are more eco-friendly than incineration [4,5]. In this regard, hydrothermal liquefaction (HTL), which is carried out at subcritical water conditions (250–350 ºC and 100–200 bar), is gaining interest as a technique to produce biocrude from Kraft black liquor. This biocrude consists of most of the organic compounds from the Kraft black liquor and has a high heating value, so it is commonly used as biofuel, although its composition makes it also suitable as a source of high value-added chemicals, mainly aromatic compounds [5–7]. Nevertheless, the main drawback for its implementation at an industrial scale is the production of large volumes of a complex aqueous phase and hydrochar as by-products. Because of this, there has been little interest in applying this process to Kraft black liquor and only small-scale reactors have been used, as shown by Lappalainen et al. [8] in their review.

However, by using temperatures close to or slightly above the critical point of water and short residence times (a few minutes), the production of these by-products would be minimised [8] and, if a competitive and viable strategy for the management of these streams was proposed, the competitiveness of HTL would be greatly enhanced [6,7,9–13]. In this sense, hydrochar, which is the carbonaceous solid mainly formed by the

polymerisation and decomposition of aromatics and aliphatic hydrocarbons during the liquefaction process, has the potential to be used as an adsorbent for heavy metals [6,12]. Nevertheless, the aqueous phase is more difficult to be managed because the presence of phenolic compounds especially hinders the post-processing of this stream, being highly bio-toxic for the process or poisoning heterogeneous catalysts during subsequent biological or chemical treatments [13–15]. In this regard, some authors have proposed its supercritical water gasification to reduce the concentration of toxic compounds, produce syngas and recover the spent chemicals for the Kraft process [11]. Another proposal has been focused on its direct recirculation to the hydrothermal liquefaction stage to improve the biocrude yield [13]. Furthermore, taking into account that this residual liquid fraction contains compounds of industrial interest, several valorisation approaches by means of membrane filtration, biomass cultivation, anaerobic fermentation or hydrothermal gasification have been also proposed as well [13,14].

Among the available management approaches, liquid-liquid extraction shows a huge potential for both the recovery of valuable compounds and their removal to comply with statutory requirements about toxicity due to its advantages such as low energy consumption, large production capacity, fast-acting process, high selectivity of separation and ease of continuous operation and automation [16]. Nevertheless, the sustainability of this technique is challenged by the environmental and health impacts of conventional solvents, such as chlorinated hydrocarbons and ethers, which are usually characterised by high toxicity. For this reason, research in this field has addressed this issue by developing and using greener solvents [17–19]. Among these, deep eutectic solvents (DES) are promising green extractants formed by the mixture of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at mild temperatures (60–100 ºC). These hydrogen bonds enable the liquid solvents obtained to remain stable at temperatures below 100 ºC, and even at room temperature in most cases, due to the low melting point of the mixture. Owing to their properties (low or no toxicity, bioavailability and low price, among others), DES have the potential to replace the common extractants. In fact, these solvents have already been successfully employed for the extraction of several compounds, such as organic acids, phenolic compounds, biomolecules, pesticides, medicinal components and metals from different aqueous solutions [20].

Despite their proven potential, more research is needed as many different HBA-HBD combinations have been used for extracting compounds from solid biomasses [18,21], synthetic aqueous solutions or oils [15,22–25]. Nevertheless, either their utilisation with real wastewaters or the subsequent recovery and regeneration of the solvent have hardly been studied [15,18,20,22,26]. In fact, to the best of our knowledge, no studies dealing with the use of DES or any other green solvent for either the valorisation or detoxification of the aqueous phase from hydrothermal liquefaction of either black liquor or other biomass are currently available in the bibliography.

Therefore, the aim of this study was to assess, for the first time ever, the use of different hydrophobic eutectic solvents as extracting agents for the valorisation and/or detoxification of the aqueous phase from hydrothermal liquefaction of Kraft black liquor.

2. Materials and methods

2.1. Materials

The aqueous phase to be used in the different tests was obtained by hydrothermal liquefaction of Kraft black liquor provided by The Navigator Company (Portugal). Hydrothermal liquefaction was carried out in a continuous tubular reactor (see the setup in Fig. S.1 in the Supplementary material) and, on the basis of previous experiments, the operational conditions selected were 350 ºC, 240 bar and 17 min of residence time under an inert atmosphere.

After this treatment, the liquid fraction was withdrawn from the reactor and subjected to an initial liquid-liquid extraction to separate the biocrude from the aqueous phase, using a method adapted from Forchheim et al. [27]. For this purpose, the liquid fraction was initially acidified to pH = 4 with HCl and, subsequently, the biocrude was recovered using ethyl acetate as the solvent, at a ratio of 0.4 mL per 1 mL of sample. The resulting aqueous phase, whose main physicochemical properties are shown in Table 1, was finally stored at 4 °C until its use.

2.2. Preparation of eutectic solvents

Combinations of terpenes (menthol or thymol) with organic acids (octanoic, decanoic or dodecanoic acid) in molar ratios of 1:1 and 2:1 were chosen (Fig. 1) since these eutectic solvents (ES) proved to extract compounds, such as phenolic compounds, pharmaceutical products or lower alcohols, from aqueous solutions [15,28–30].

At this point, it is necessary to emphasise the difference between "eutectic solvents (ES)" and "deep eutectic solvents (DES)". Hansen et al. [31] stated that what characterises a DES is its marked deviation from the ideal behaviour of the solution, creating low-temperature melting solvents. In this regard, Martins et al. [32], who studied different eutectic mixtures based on terpenes and carboxylic acids, including the compounds used in this study, observed small deviations from the ideality. This fact implies that the interactions between the terpenes and the organic acids are slightly stronger than those observed in the pure terpenes. For this reason, although many authors referred to these mixtures as "deep eutectic solvents", it is preferable to call them "eutectic solvents", as suggested by Martins et al. [32] and Bergua et al. [29].

Regarding the molar ratios chosen, it is important to note that, although they do not correspond to the eutectic point, it is possible to obtain room temperature solvents over a wide range of compositions and is not constrained by any particular stoichiometric relationship between the components of the ES [32].

The procedure followed for the preparation of these solvents was that described by Sas et al. [15]: the corresponding amounts of each pure terpene and organic acid were mixed in a closed beaker at 70 °C using a hot plate magnetic stirrer until a homogeneous liquid was formed. During the formation of the ES, the primary driving forces for ES formation are hydrogen bonding, ionic and Van der Waals interactions between the HBA and the HBD [33,34]. In fact, ES are mixtures of HBD-HBA adducts as well as HBD-HBD and HBA-HBA adducts, as demonstrated by relevant literature about it [35]. Regarding menthol and thymol-based ES with carboxylic acids, Bergua et al. [29] concluded that menthol-based ES were less compact and structured mixtures, but more polar and showed stronger intermolecular interactions. In contrast, thymol-based ES were more compact due to the flatter structure of the aromatic ring. Furthermore, the hydroxyl group donates electronic density into the conjugated π-ring via a resonance effect, which is stronger than the inductive effect, so the capacity to form hydrogen bonds with carboxylic acids could be reduced.

After their preparation, ES solutions were stored in closed centrifuge tubes at room temperature and waited 48 h to check their stability. These solvents were liquid at room temperature, except for 1:1 Menthol:

Table 1
Characterisation of the aqueous phase.

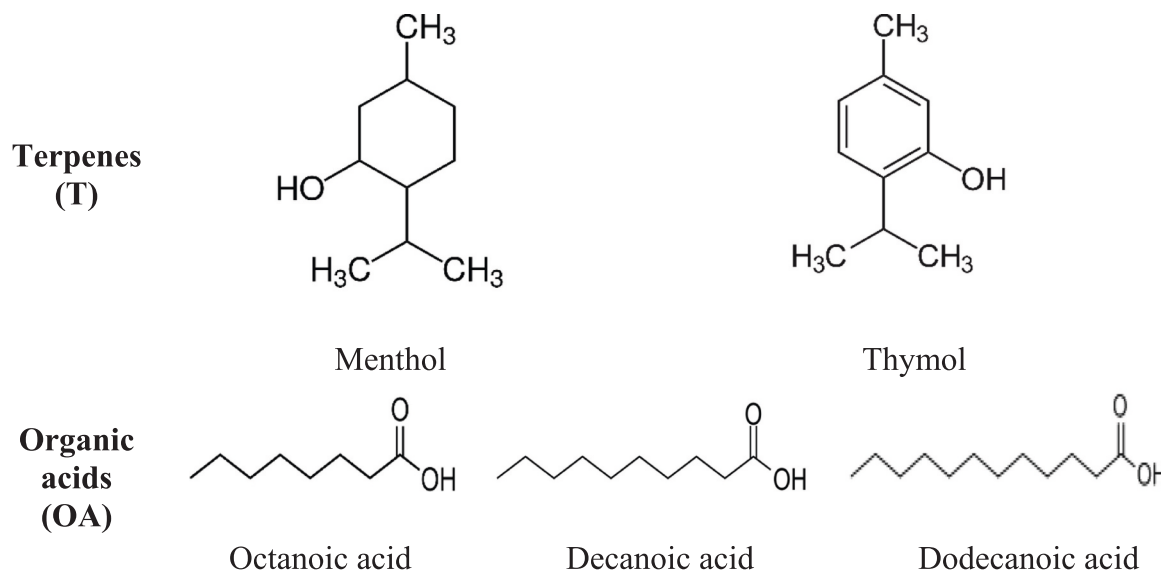| Parameters	Mean values
pH	4.1 ± 0.1
Total Organic Carbon (g/L)	29.7 ± 0.2
Total Inorganic Carbon (mg/L)	0.00 ± 0.01
Catechol (mg/L)	63 ± 5
Formic acid (g/L)	3.8 ± 0.5
Acetic acid (g/L)	5.0 ± 0.5
Glycolic acid (g/L)	1.3 ± 0.5
Lactic acid (g/L)	2.2 ± 0.5
Methanol (g/L)	2.6 ± 0.2
Ethanol (g/L)	1.0 ± 0.2
Fructose (mg/L)	72 ± 5

Fig. 1. Chemical structure of the terpenes and organic acids used.

Dodecanoic acid and 1:1 Thymol:Dodecanoic acid, which solidified when the temperature was lower than 40 ºC. Therefore, these two were discarded for subsequent extraction tests. For more information about the properties of these solvents, see the study conducted by Martins et al. [32].

2.3. Extraction assays

Firstly, ES solubilities in acidified water (pH = 4) were determined using a 50 % (v/v) water:ES ratio. All of them turned out to be highly immiscible in water, with very low solubility values for ES in water, and forming two well-differentiated phases, the upper one corresponding to ES. The hydrophobicity of these ES was also corroborated by the results reported by Martins et al. [32].

Extraction tests were performed at three different aqueous phase:ES ratios (50 %, 67 % and 75 % (v/v)), following a procedure adapted from Sas et al. [15]. The corresponding volumes of the aqueous phase and ES were added to 50 mL centrifuge tubes, which were afterwards shaken in a vortex for 60 s and then, centrifuged at 7000 rpm for 30 min. Finally, the heavier phase, corresponding to the aqueous phase, was taken and stored at 4 ºC for its further analysis.

After measuring the concentrations of the compounds in the aqueous phase before and after the extraction procedure, distribution coefficients (K_D) and extraction efficiencies (E) were defined according to Eqs. (1) and (2), respectively. For each pair of compounds, separation factors (S) were also calculated (Eq. 3) [3,15,17].

$$K_{D,i} = \frac{C_{i,org}}{C_{i,aq}} \tag{1}$$

Where $C_{i,org}$ and $C_{i,aq}$ are the concentrations of the compound "i" in the ES and the aqueous phase, respectively, after the extraction.

$$E \quad (\%) = \frac{C_{i,o} - C_{i,f}}{C_{i,o}} * 100 \tag{2}$$

Where $C_{i,o}$ and $C_{i,f}$ are the initial and final concentrations of the compound "i" in the aqueous phase, respectively.

$$S_{i,a} = \frac{K_{D,i}}{K_{D,a}} \tag{3}$$

Where $K_{D,i}$ and $K_{D,a}$ are the distribution coefficients of the compounds "i" and "a", respectively.

2.4. Analytical methods

Soluble carbon fractions (total, inorganic and organic carbon) were measured using a TOC analyser.

Phenolic compounds were measured using a High-Performance Liquid Chromatography (HPLC) equipped with a Kinetex® C18 PFP OOD-4462-EO (Phenomenex) column at a temperature of 30 ºC and a diode-array detector (DAD) set at 210 nm. An aqueous solution of H_3PO_4 and NaH_2PO_4 and methanol (80:20) was employed as the mobile phase, at a flow rate of 0.75 mL/min. Catechol was detected in relevant concentrations, as well as other two unidentified phenolic compounds, here called "Phenolic 1″" and "Phenolic 2″", with the retention time of the former being similar to catechol and the latter to phenol.

Concentrations of carboxylic acids, alcohols and reducing sugars were also chromatographically detected using an Aminex HPX 87H (Biorad) column, a refractive index detector (RID) and a diode-array detector (DAD) set at 210 nm. The temperature was set at 75 ºC for measuring glycolic and lactic acid concentrations and at 25 ºC for the rest of the compounds. The mobile phase was an H_2SO_4 4 mM solution at 0.65 mL/min. The compounds identified in relevant concentrations were formic and acetic acids (volatile fatty acids), glycolic and lactic acids (non-volatile hydroxy acids), methanol and ethanol (alcohols) and fructose (sugar).

Toxicity was assessed by a respirometric assay using a BM-EVO analyser (SURCIS S.L., Spain), with the air diffuser settled at 55 % and at a constant temperature of 20 ºC. The respirometer vessel was filled with 1 L of activated sludge (2.3 g of volatile suspended solids per litre) from the municipal wastewater treatment plant of Baiña (Asturias, Spain). The heterotrophic biomass yield coefficient (Y_H) for this sludge was 0.78 g/g, which was determined using sodium acetate [36]. In order to avoid nitrification interferences, a few drops of allyl thiourea (ATU) inhibitor were added. For each respirometric analysis, the SURCIS manufacturer's procedure was followed. 50 mL of a 4 g/L of sodium acetate solution was initially added to reach the maximum dynamic exogenous respiration rate and, afterwards, successive 10 mL sample doses were added every 7 min to assess the inhibition produced, expressed as the percentage reduction in respiration rates.

3. Results and discussion

Firstly, distribution coefficients and extraction efficiencies of the different ES for each compound, grouped by families, were analysed, as a previous stage to choose the most suitable ES for treating the aqueous

phase from the hydrothermal liquefaction of Kraft black liquor and to discuss possible valorisation methods according to the final composition.

3.1. Extraction of phenolic compounds

Starting with phenolic compounds, the distribution coefficients obtained for these with each ES are shown in Fig. 2 in function of the number of carbons of the organic acids.

In general, ES turned out to be quite effective for the extraction of phenolic compounds from the aqueous phase, especially for Phenolic 1 and Phenolic 2. Thus, even when distribution coefficients for catechol were the lowest, these varied from 1.9 to 2.6 using menthol-based ES and from 0.4 to 0.6 using thymol-based ones. At the same time, distribution coefficients for Phenolic 2 ranged from 5.8 to 8.2 with menthol and from 2.8 to 3.7 with thymol; whereas Phenolic 1, the most extracted compound, showed distribution coefficients with values that went from around 9–49 in presence of menthol or thymol, respectively.

As can be seen, menthol-based ES showed slightly higher affinities for either catechol or Phenolic 2 than those using thymol. On the contrary, it is interesting to note a significant increase in the removal of Phenolic 1 when menthol was replaced by thymol in the ES. Thus, for T:OA molar ratios of 1:1, K_D for thymol-based ES were around three times higher than using menthol. This behaviour was more evident when the proportion of thymol in the ES was increased to a T:OA molar ratio of 2:1, with K_D values that almost doubled those reported for thymol:OA molar ratios of 1:1. In fact, this was the only case where the T:OA molar ratio chosen had a significant effect on the removal of the corresponding phenolic compound.

Regarding the organic acids used, slightly lower extractions were observed when acids with longer chains were employed to prepare the ES, either using menthol or thymol. So, in terms of phenolic removal, using dodecanoic acid instead of octanoic acid can result in a 19 % lower distribution coefficient in the worst case (Phenolic 1 with 2:1 thymol-based ES).

If these results are explained in terms of extraction yields (see Fig. S.2, S.3 and S.4 in the Supplementary material), the maximum values for catechol and Phenolic 2 (70.2 % and 92.7 %, respectively) were obtained using 2:1 Menthol:Octanoic acid, whereas the maximum extraction for Phenolic 1 (98.2 %) corresponded to 2:1 Thymol:Octanoic acid. All these results were achieved using an aqueous phase:ES ratio of 50 % (v/v) during the extractions because, as expected, the lower the ES volume, the lower the extraction percentage. In fact, when ES proportion was decreased from 50 % to 25 %, 23.9 % less catechol, 7.2 % less Phenolic 1 % and 26.6 % less Phenolic 2 were extracted.

The high affinity of these ES for phenolic compounds is in agreement with the results obtained by Sas et al. [15], who reported extractions above 70 % for synthetic mixtures of 2-chlorophenol, o-cresol and phenol using Menthol:Octanoic acid (1:1) and Menthol:Decanoic acid (1:1).

3.2. Extraction of organic acids

Distribution coefficient values obtained for the main organic acids present in the aqueous phase from hydrothermal liquefaction of black liquor are shown in Fig. 3, in function of the ES tested.

It is clearly deduced that the affinity of the organic acids for hydrophobic ES was low, with distribution coefficients never exceeding
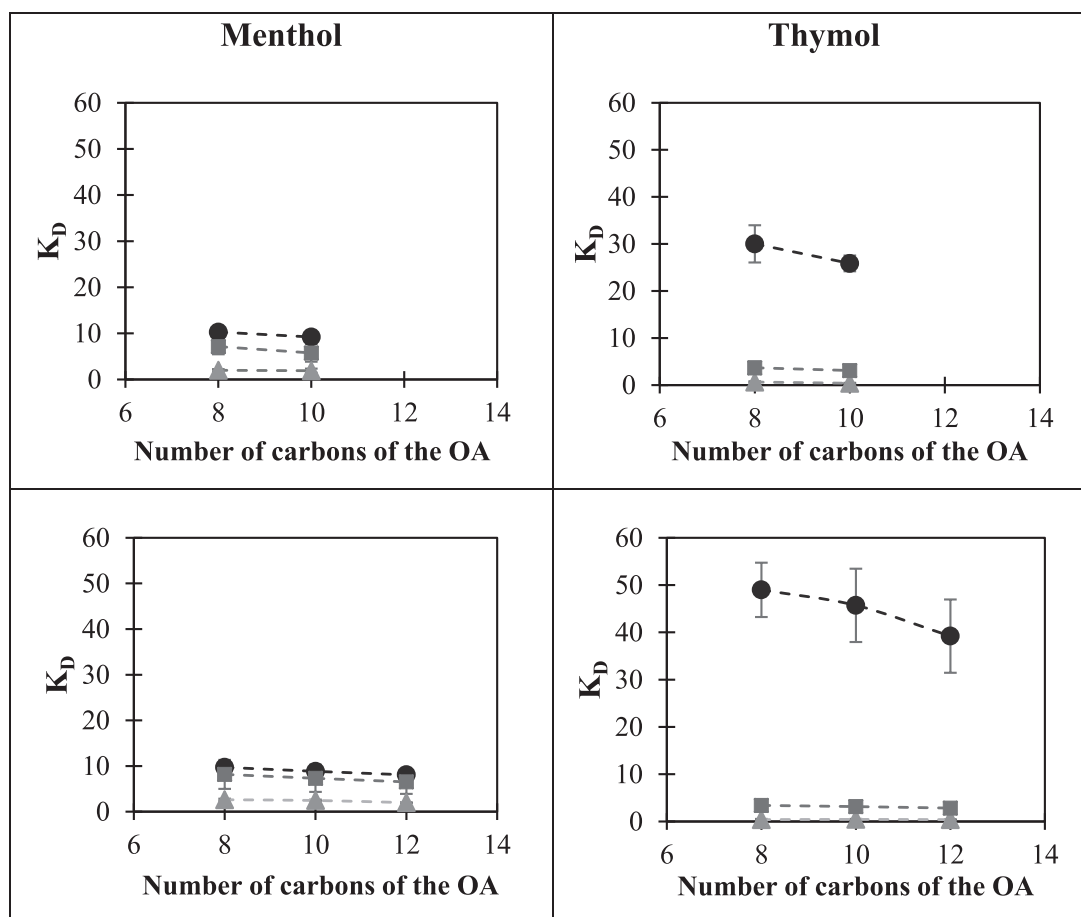

Fig. 2. Distribution coefficients for the main phenolic compounds (catechol (▲), Phenolic 1 (●) and Phenolic 2 (■)) present in the aqueous fraction from the hydrothermal liquefaction of Kraft black liquor using menthol-based or thymol-based ES as extracting agents.
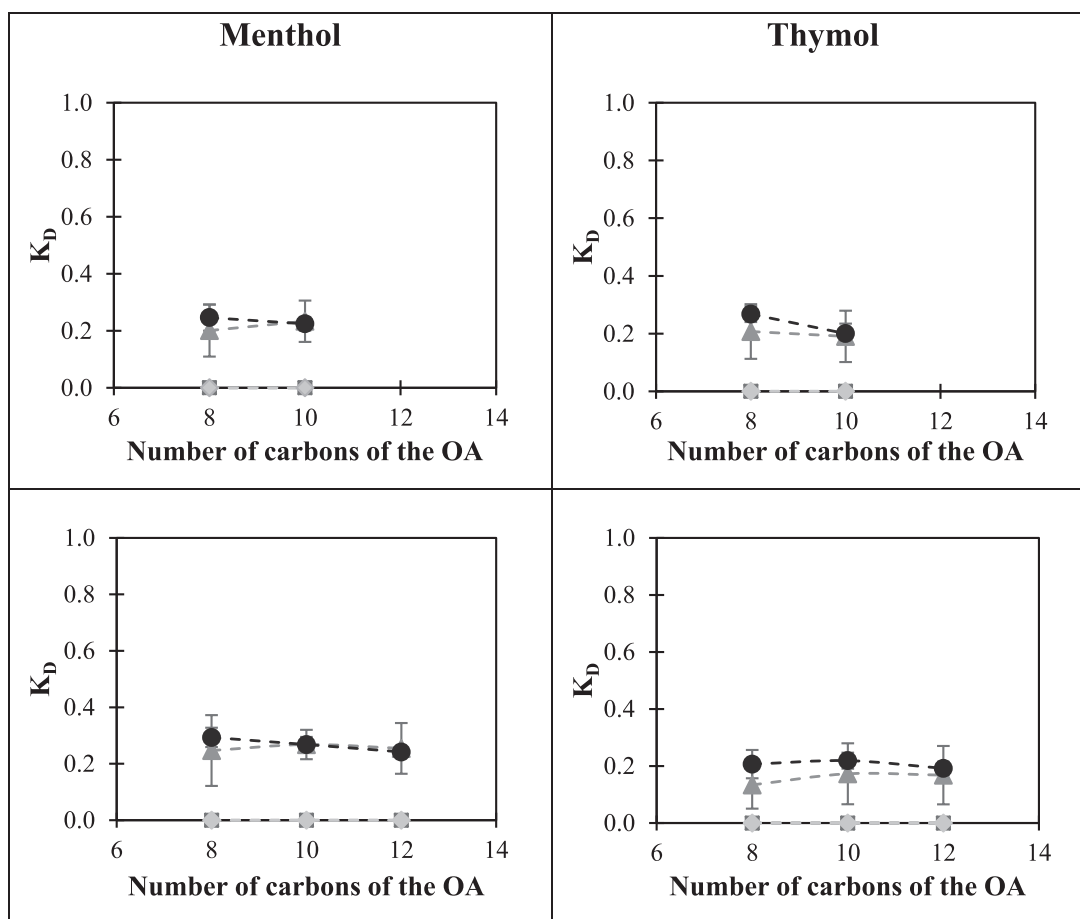
Fig. 3. Distribution coefficients for the main organic acids (formic (▲), acetic (●), glycolic (■) and lactic (◆) acids) present in the aqueous fraction from the hydrothermal liquefaction of Kraft black liquor using menthol-based or thymol-based ES as extracting agents.

0.3. These values, which are substantially lower than for phenolics even in the worst cases, confirm a selective separation of these families of compounds one from another during the process.

These results also revealed that the structure of the carboxylic acids affected the migration of these compounds to the organic phase (ES). Thus, a small percentage of the volatile acids was extracted, with less than one-quarter of the initial amounts of formic and acetic acids passing to the ES phase (see Fig. S.5 and S.6 in the Supplementary Material). Nevertheless, both non-volatile hydroxy acids (glycolic and lactic acids) remained entirely in the aqueous phase ($K_D = 0$). This behaviour was highly related to the hydrophobicity of these compounds, with those acids with a higher partition coefficient being more soluble in the ES. Thus, the acids arranged in increasing order of hydrophobicity (logP) are acetic (-0.2), formic (-0.5), lactic (-0.7) and glycolic (-1.1) acid, which also coincides with the decreasing order of distribution coefficients previously reported. In addition, this trend is in agreement with the results of Aşçı and Lalikoglu [37], who reported lower extraction results for non-volatile hydroxy acids than for volatile fatty acids using Trioctylphosphine oxide:Menthol (1:2) as the solvent and, in the case of the latter, higher extractions the higher the molecular weight of the acids.

Focusing now on the effect of the terpene and organic acid chosen on the solubilities, distribution coefficients for volatile fatty acids were very similar, they being negligible. In a similar way, the T:OA ratio used in ES preparation did not have a significant impact on the volatile fatty acid removal.

3.3. Extraction of alcohols and sugars

Finally, the distribution coefficients obtained for methanol, ethanol and fructose as a function of the ES used are shown in Fig. 4.

Regarding the extraction of alcohols with ES, ethanol showed higher distribution coefficients than methanol for all the solvents and conditions tested, which is consistent with the higher hydrophobicity of the former (log P of -0.3 versus -0.7) and with the trend reported by Verma and Banerjee [30] for the extraction of lower alcohols (ethanol, 1-propanol and 1-butanol) using Menthol:Dodecanoic acid (2:1), who found that the longer the chain of the alcohol, the higher the extraction efficiency. In all the cases, the affinities of the different ES for both alcohols were higher than for any volatile acids (see Fig. S.7 and S.8 in the Supplementary Material). In comparison to phenolic compounds, ethanol extraction yields were comparable to those reported for catechol when menthol-based ES were used and for Phenolic 2 in the case of thymol-based ones.

Concerning the ES composition, distribution coefficients for methanol were similar, regardless of the terpene or the organic acid chosen or their ratio. On the contrary, ethanol removals from the liquid phase were significantly influenced by the terpene used. Thus, this compound showed higher solubility in thymol-based than in menthol-based ES, with distribution coefficients around 50 % higher for the formers. It is interesting to note that the same behaviour, but more marked, was already observed for Phenolic 1. Similarly, when the number of carbons of the organic acid was increased, distribution coefficients for ethanol also slightly decreased either for menthol or thymol-based ES.

Finally, concerning sugars, only fructose was detected in the aqueous phase from hydrothermal liquefaction of Kraft black liquor. After ES
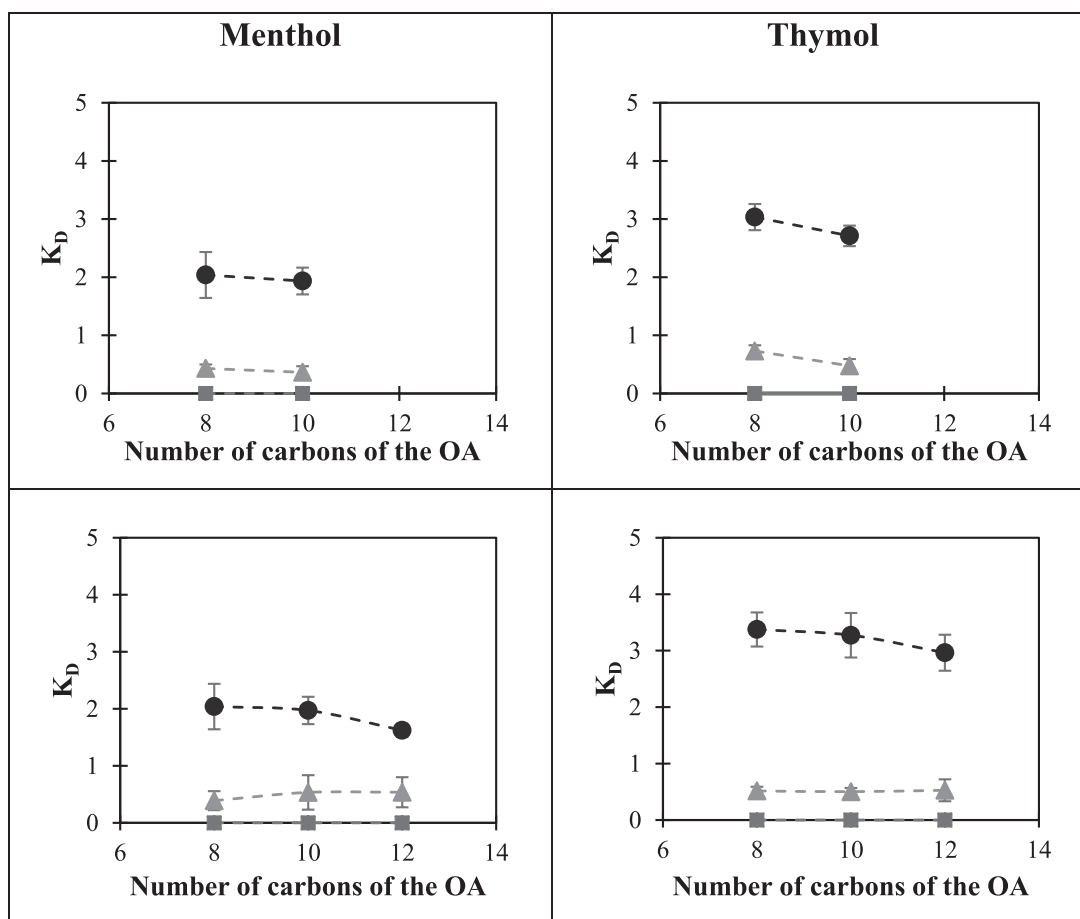
Fig. 4. Distribution coefficients for the main alcohols (methanol (▲) and ethanol (●)) and sugars (fructose (■)) present in the aqueous fraction from the hydrothermal liquefaction of Kraft black liquor using menthol-based or thymol-based ES as extracting agents.

extraction, results revealed that it remained entirely in the aqueous phase ($K_D = 0$) regardless of the ES tested, as it was predictable, given its high hydrophilic character (logP = −2.4).

3.4. Separation factors

Once the distribution coefficients have been obtained and discussed by families, it is necessary to compare them with each other in order to determine which would be the best solvent to achieve an efficient and selective separation of the compounds, especially those with higher toxicity, like the phenolic ones. For this purpose, "mean separation factors" were used. These were defined as the weighted averages of the distribution coefficients by families (phenolic compounds (PC), volatile fatty acids (VFA), non-volatile hydroxy acids (NVHA), alcohols (A) and sugars (S)) as a function of the initial concentration of each component

Table 2
Separation factors depending on the ES used.

T:OA	T	OA	PC/VFA	PC/A	Ethanol/Methanol
1:1	Menthol	Octanoic acid	104.2	29.2	4.7
		Decanoic acid	79.7	30.6	5.3
2:1	Menthol	Octanoic acid	82.3	31.3	5.2
		Decanoic acid	68.9	20.8	3.7
		Dodecanoic acid	65.9	18.7	3.0
1:1	Thymol	Octanoic acid	53.6	2.8	4.2
		Decanoic acid	61.2	2.7	5.7
2:1	Thymol	Octanoic acid	90.6	3.3	6.6
		Decanoic acid	79.7	3.2	6.5
		Dodecanoic acid	79.2	3.1	5.6

in the aqueous phase. Phenol equivalent concentration values were used for the unidentified phenolic compounds (Table 2).

Given that all the separation factors obtained were much higher than 1 due to the high weighted distribution coefficients of phenolic compounds with respect to the rest of the families, results from Table 2 corroborate that all the ES tested were very selective for the extraction of phenolic compounds. It is important to note that separation factors for phenolic compounds with respect to non-volatile hydroxy acids or sugars were not included in Table 2 because these compounds remained completely in the aqueous phase ($K_D = 0$). Therefore, the separation of these families was excellent. As for volatile fatty acids, separation factors were very high as only a small proportion of acetic and formic acids was extracted from the aqueous phase.

In the case of alcohols, the affinity of the ES tested for ethanol was comparable to that for catechol, showing even higher solubility in thymol-based ES, which implies low separation factors with respect to the phenolic compounds. On the contrary, the lower distribution coefficient values of the methanol in comparison to the ethanol ones involved that the former mainly remained in the aqueous phase. This fact proves a selective separation of these two compounds during the extraction process, this being coupled with the removal of phenolic compounds.

For all these reasons, 1:1 Menthol:Octanoic acid is proposed as the best solvent, as it had the highest value for PC/VFA ratio and one of the highest for PC/A. Thus, 62.5 % of catechol, 91.0 % of Phenolic 1, 90.2 % of Phenolic 2, 8.6 % of formic acid, 15.6 % of acetic acid, 24.8 % of methanol, 60.7 % of ethanol and 0 % of glycolic and lactic acids and fructose would be extracted for a ratio of 50 % (v/v) aqueous phase:ES.

This implies that the majority of the phenolic compounds present in

the aqueous phase from the hydrothermal liquefaction of Kraft black liquor, which are toxic in fermentation and poison catalysts, would be recovered in the extract along with part of the ethanol, which is also a fermentation inhibitor at high concentrations. This leaves a much more biodegradable raffinate, as corroborated by respirometry. In this respect, 10 mL of aqueous phase showed an inhibition percentage of 25 %, whereas after extraction with 1:1 Menthol:Octanoic acid in a ratio of 1:1 (v/v) aqueous phase:ES no inhibition occurred. Moreover, the addition of another 10 mL increased the inhibition percentages to 90 % and 43 %, respectively (see Fig. 5).

Therefore, this fraction would be suitable for use as a fermentation media, as a substrate for biogas production by anaerobic digestion, for added-value product recovery or for syngas production by catalytic aqueous phase reforming or supercritical water gasification. In addition, this residue also contains the salts spent in the Kraft process, so as a last step it could be used to recover and recirculate them to the cooking stage.

As for the extract, it could be used to recover the extracted compounds and regenerate the spent ES. In this sense, there are some reviews that discuss possible options that have been studied to recover extracted analytes and regenerate ES at laboratory scale, although the technique used depends on the solvent. In general, the methods studied are anti-solvent addition, crystallisation, membrane filtration, solid or liquid-liquid extraction and distillation [18,38–40]. Distillation could be proposed in this case as the boiling temperatures of phenolic compounds (245 ºC for catechol) are very different from those of alcohols (65 and 78 ºC for methanol and ethanol) and organic acids (101 and 118 ºC for formic and acetic acid). However, as far as we know, the boiling temperature for these ES are not available in the literature, only Dietz et al. [34] analysed the vapour pressure of some ES, including Thymol:Decanoic acid (1:1) and Menthol:Decanoic acid (1:1), reporting values of 466.3 and 540.9 Pa, respectively, at 100 ºC. Regarding the other alternatives, Della Posta et al. [38] stated that macroporous resins have been commonly used for ES regeneration, although this option is more expensive than the anti-solvent method, in which water is commonly used as the antisolvent. Nevertheless, since no studies have been found on the valorisation of the aqueous phase from hydrothermally liquefied Kraft black liquor, this is a first study to determine the separation efficiencies with these solvents. On this basis, further research is needed to find the most viable option to recover the extracted analytes and regenerate the ES.

4. Conclusions

Results showed that all the ES tested were highly effective as extractants for reducing the toxicity of the aqueous phase from the hydrothermal liquefaction of Kraft black liquor. These had high affinity for phenolic compounds and ethanol, low for volatile fatty acids and methanol and null for fructose and non-volatile hydroxy acids. Regarding the composition of the ES, the terpene used had a higher impact on the separation of phenolic compounds than the number of carbons of the organic acid, with the best solvent being 1:1 Menthol:Octanoic acid. After the extraction, the raffinate was much more biodegradable and would be suitable for being used as a fermentation medium, as a feedstock for gas production or as a source of organic acids and inorganic salts.

CRediT authorship contribution statement

Lucía Pola: Conceptualization, Investigation, Formal analysis, Data curation, Writing – original draft. **Sergio Collado:** Conceptualization, Methodology, Writing – review & editing. **Maximiliam Wörner:** Methodology, Investigation. **Ursel Hornung:** Funding acquisition, Supervision, Resources. **Mario Díaz:** Funding acquisition, Supervision.
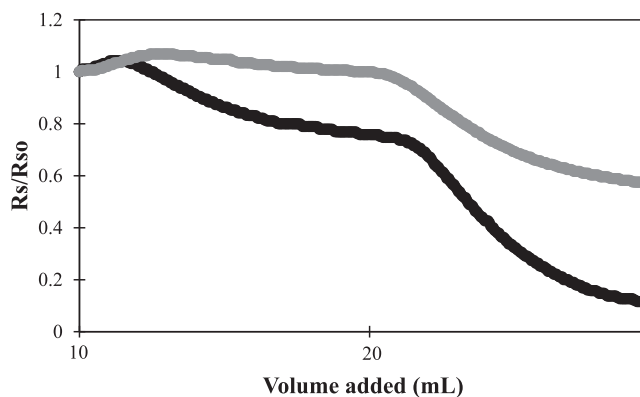
Fig. 5. Evolution of the dynamic exogenous respiration rate (Rs) with the addition of aqueous phase before (●) and after extraction with 1:1 Menthol:Octanoic acid in a ratio of 1:1 (v/v) aqueous phase:ES (⬤).

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.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.111040.

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