

# Biocarbonates Derived from CO<sub>2</sub> and Terpenes: Molecular Design for Aqueous Mixture Treatment Driven by COSMO-RS

Alejandro Belinchón, Elisa Hernández, Javier Vázquez, Rubén Santiago, Cristian Moya, Marcos Larriba, Pablo Navarro,\* and José Palomar



Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 9635–9643



Read Online

ACCESS |



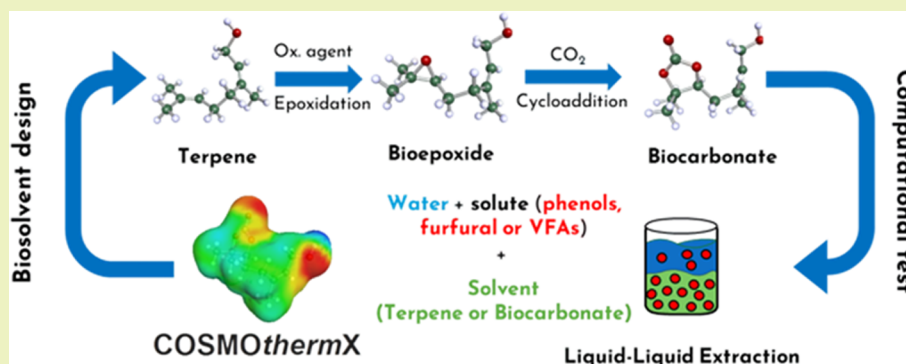
Metrics & More



Article Recommendations



Supporting Information



**ABSTRACT:** In this work, the use of plant-derived raw materials, such as terpenes, gives great strength from a sustainability perspective and enables dealing with the biocarbonate concept. Biocarbonates are produced only from CO<sub>2</sub> and residues or bio-derived compounds, describing cycloaddition reactions that couple CO<sub>2</sub> and a terpene, the latter after epoxidation, avoiding environmental charges from petroleum-derived epoxides. In this work, a comprehensive database (derived from 30 terpenes) accounting bioepoxides and corresponding biocarbonates was developed, by means of molecular simulation. Optimized structures realized by the DFT method allow using a priori tools to scan the possible applications of this new class of sustainable solvents. Using a COnductor-like Screening Model for Realistic Solvents, different biocarbonates were evaluated for their physical properties and capacity to remove value-added or contaminant solutes from aqueous mixtures, namely, furfural, phenolic compounds, and volatile fatty acids. It was found that biocarbonates derived from terpenes generally present a higher affinity for solutes in comparison with neat terpenes. Indeed, biocarbonates allowed achieving the recovery of 99% of phenol, 98% of furfural, and 87% of acetic acid, also pointing to an advantageous scenario of higher boiling points and densities and comparable solvent losses in the aqueous phase to terpenes.

**KEYWORDS:** biocarbonate, terpene, COSMO-RS, CO<sub>2</sub> conversion, liquid–liquid extraction

## INTRODUCTION

Anthropogenic carbon dioxide is one of the fundamental problems of climate change.<sup>1</sup> Carbon capture and utilization is a valid strategy to reduce emissions and promote the valorization of CO<sub>2</sub> to produce chemicals, fuels, and materials of interest,<sup>2</sup> as well as improving the sustainability of many chemical processes and industries.<sup>3</sup> Among other CO<sub>2</sub>-derived products, cyclic carbonates stand out for their potential applications (extractive agents<sup>4,5</sup> or in synthesis and catalysis<sup>6,7</sup>) as more sustainable solvents than those used in industry. The most frequent cyclic carbonate synthesis route is by the reaction of CO<sub>2</sub> with epoxides.<sup>6</sup> However, there are some drawbacks to this synthesis route in sustainability parameters because a recent life cycle assessment showed that the use of petroleum-derived raw materials, like propylene

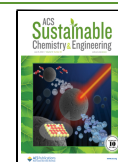
oxide,<sup>8</sup> implies high CO<sub>2</sub> emissions related to its synthesis and should be replaced by lower impact compounds.

On the other hand, industries, agriculture, and the general population use and release many compounds into wastewater. All the practice generates various pollutants that must be eliminated, such as phenolic compounds<sup>9</sup> or specifically bisphenol A.<sup>10</sup> In this sense, terpenes have been tested and proved as efficient extracting agents in the separation of other compounds of interest from aqueous mixtures, such as

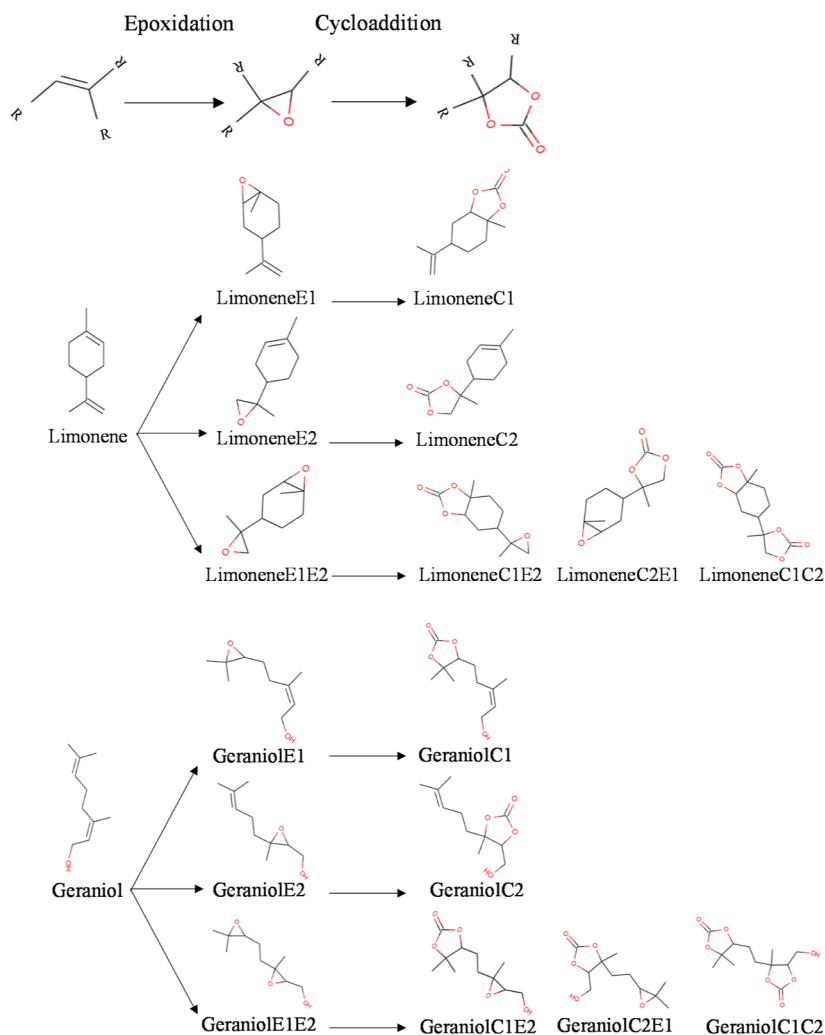
Received: May 20, 2022

Revised: June 30, 2022

Published: July 12, 2022



Scheme 1. Possible Biocarbonates That Can Be Formed from Limonene and Geraniol



furfural<sup>11</sup> or volatile fatty acids (VFAs).<sup>12</sup> Terpenes are natural solvents of plant origin with outstanding technical and chemical properties. Therefore, terpenes can be considered a renewable, ecological, and economical raw material.<sup>13</sup> Therefore, terpenes could be successful substitutes for petroleum solvents, such as dichloromethane, toluene, or hexane, for the extraction of several solutes, even emerging applications in the extraction of natural products.<sup>14</sup> These green natural products can be transformed into novel and valuable compounds used to produce fragrances, perfumes, or pharmaceuticals, as well as into useful synthetic intermediates.<sup>15</sup> More recently, terpenes have been presented as a sustainable alternative to fix CO<sub>2</sub> and produce cyclic carbonates, enabling the biocarbonate concept.<sup>16</sup> It requires a prior intermediate step where terpene in the presence of an oxidizing agent generates a terpene oxide (epoxide).<sup>17</sup> This epoxide is capable, in the presence of a suitable catalyst, to react with CO<sub>2</sub> in a cycloaddition reaction to produce biocarbonates in a similar way to other petroleum-derived epoxides.<sup>18</sup>

Biosolvents are emerging compounds of different nature that aim at addressing green and sustainable principles in the solvent formulation. There are different options in the literature such as biomass-derived compounds (i.e., furfural, lactic acid, and their derivatives, glycerol, and its derivatives),<sup>19</sup> carbohydrates,<sup>20</sup> terpenes,<sup>21</sup> ionic liquids,<sup>22</sup> and natural

eutectic solvents,<sup>23</sup> among others. Hydrophobic biosolvents stand as relevant to water treatments, replacing VOCs,<sup>19</sup> methyl isobutyl ketone,<sup>24</sup> or ethyl acetate.<sup>10</sup> The role of this new class of hydrophobic biosolvents emerges interestingly and synergistically by contributing to the CO<sub>2</sub> circular economy.

The objective of this work is to enable the development of biocarbonates through a COnductor-like Screening Model (COSMO) and guide the terpene selection from both physical properties and extractive property points of view. First, the design of a database of bioepoxides (30) and biocarbonates (30) derived from terpenes and CO<sub>2</sub> is done by DFT molecular simulations. This is found to be essential in the literature due to the lack of synthesized and characterized species, namely, limonene carbonate,<sup>25</sup> pinene carbonate,<sup>26</sup> myrcene carbonate,<sup>27</sup> terpinen-4-ol carbonate,<sup>16</sup> menthane carbonate,<sup>27</sup> or carvone carbonate.<sup>16</sup> Second, the physical properties of the biocarbonates and the corresponding terpenes were cross-evaluated by using predictions of a COSMO for Realistic Solvents (COSMO-RS), as well as by determining how they are influenced by adding one or more CO<sub>2</sub> groups in the chemical structure, in looking for solvents that provide a more efficient CO<sub>2</sub> consumption. Third, these biocarbonates have been tested in applications in which terpenes have been proven to be effective extractors of common solutes from water to phenolic compounds, furfural,

and VFAs, which is accomplished by means of activity coefficients at infinite dilution and liquid–liquid extraction calculations driven also by the COSMO-RS. The COSMO-RS is a trustable and valid method to predict the use of potential biocarbonates because it was massively validated for the same terpene–solute systems, providing an adequate qualitative and quantitative image that helps select the most appropriate terpene for each application.<sup>24,28</sup> Because the carbonate group is equivalent to other functional groups that massively covered screening terpenes, it is reasonable to find acceptable COSMO-RS predictions for these new biosolvents.

## COMPUTATIONAL DETAILS

**Molecular Geometry Optimization.** Turbomole 7.4<sup>29</sup> software with the COSMO continuous solvation method was used to optimize the structure of all the compounds (terpenes: 30, bioepoxides: 32, and biocarbonates: 41) to its minimum energy state with BP86/TZVP computational levels using the solvent effect.<sup>30</sup> The structures of all the bioepoxides and biocarbonates employed are shown in Tables S1 and S2, based on the terpene structure. As shown in Scheme 1, the oxidation of the terpene takes place at the double bond of the molecule in the corresponding terpene, where an oxygen atom is attached to each of the carbons. In the presence of a catalyst, this bond is opened for the cycloaddition of CO<sub>2</sub> and forms a cyclic carbonate. Although the most typical structures of the terpenes in Scheme 1 resulting from the epoxidation process are limonene oxide (LimoneneE1)<sup>16</sup> and geraniol oxide (GeraniolE1),<sup>31</sup> the fact that they have two different double bonds makes the formation of different carbonates and opens up the option to study how the site of cycloaddition or the presence of two cyclic carbonate groups in the same molecule would influence their properties. Only double-bonded terpenes were chosen for this study.

**Properties of Biocarbonates Derived from Terpenes.** The \*.cosmo file obtained from Turbomole software was used to predict the different thermodynamic properties of the pure compounds in COSMOtherm v. 19<sup>32</sup> software. This software employs COSMO-RS for thermodynamic calculations. The properties computed were the octanol–water partition coefficients in wet octanol, normal boiling point, density, and molecular weight of the terpenes and their respective biocarbonates.

**Activity Coefficient Calculation with COSMO-RS.** Using COSMOtherm v. 19 software, the activity coefficients at infinite dilution at 298 K of solutes, phenols (phenol, 2-chlorophenol, 2-nitrophenol), bisphenol A, furfural, and VFAs (acetic acid, propionic acid, butyric acid, and valeric acid), in the different terpenes and their respective biocarbonates were calculated to compare the efficiency between the different compounds as solvents. It has been previously shown that the predictions of COSMO-RS for the calculations of activity coefficients with terpenes reasonably agreed with the experimental data.<sup>24</sup> The \*.cosmo files for the solutes not found in the COSMOtherm database were created following the same methodology as the biocarbonates.

**Liquid–Liquid Extraction Calculation with COSMO-RS.** A “liquid extraction” calculation for phenol, furfural, and acetic acid was performed using COSMOtherm software. The first phase (S) containing pure solvent (terpene or derived carbonate) was specified, while the second phase (F; 1 kg) consisted of the desired solute in water at a concentration based on the literature (0.5 mg/mL for phenol,<sup>28</sup> 10 mg/mL

for furfural,<sup>24</sup> and 2 mg/mL for acetic acid<sup>12</sup>). Two S/F (0.5 and 2) mass ratios were studied by changing the total mass of the S phase. The extraction yield ( $Yld_i$ ) of the solutes was calculated as described in eq 1.

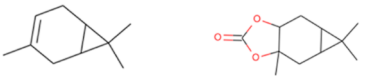


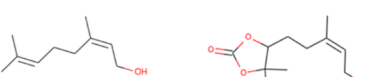
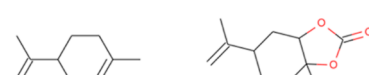




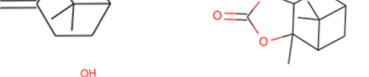
$$Yld_i(\%) = \frac{C_{i,0}^{aq} - C_i^{aq}}{C_{i,0}^{aq}} \cdot 100 \quad (1)$$

where  $C_{i,0}^{aq}$  is the initial concentration of solute i in the aqueous phase and  $C_i^{aq}$  is the concentration of solute i in the aqueous phase after the extraction.

## RESULTS AND DISCUSSION

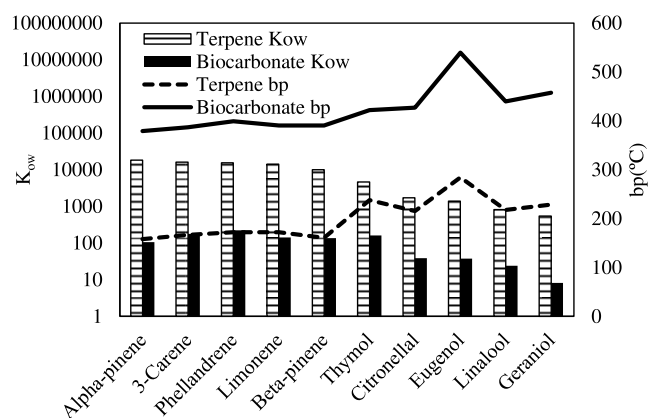
**Database of Carbonates and Epoxides and Their Physical Properties.** After modeling the optimized structure of several conventional terpenes (selecting 10 representatives of the whole behavior as a reference shown in Table 1, while the remaining 20 are shown in Table S1), the structures of bioepoxides and biocarbonates derived from these terpenes were modeled (listed in Tables 1 and S1, S2). As explained above, for the terpenes with various double bonds, there are numerous biocarbonate/bioepoxide possible structures; thus, geraniol and limonene are selected as a reference to observe

**Table 1. Structure of the Main Terpenes and Their Corresponding Biocarbonate**

Terpene	Biocarbonate
3-Carene	
Citronellal	
Eugenol	
Geraniol	
Limonene	
Linalool	
Phellandrene	
Alpha-pinene	
Beta-pinene	
Thymol	

how the position and number of the carbonate substituents influence on the properties of the compounds. Once these structures have been optimized, octanol–water coefficient ( $K_{ow}$ ), boiling point, and density of terpenes and corresponding biocarbinates are predicted by means of COSMO-RS calculations.

As seen in Figure 1, terpenes exhibit a higher  $K_{ow}$  value than biocarbinates (500–18,000 for terpenes against 8–100 for



**Figure 1.** Octanol–water partition coefficient at infinite dilution of selected terpenes (striped bars) and their corresponding biocarbinates (solid bars) calculated by COSMO-RS at 298 K and boiling point (bp) of selected terpenes (striped line) and their corresponding biocarbinates (solid line) calculated by COSMO-RS at 1 atm.

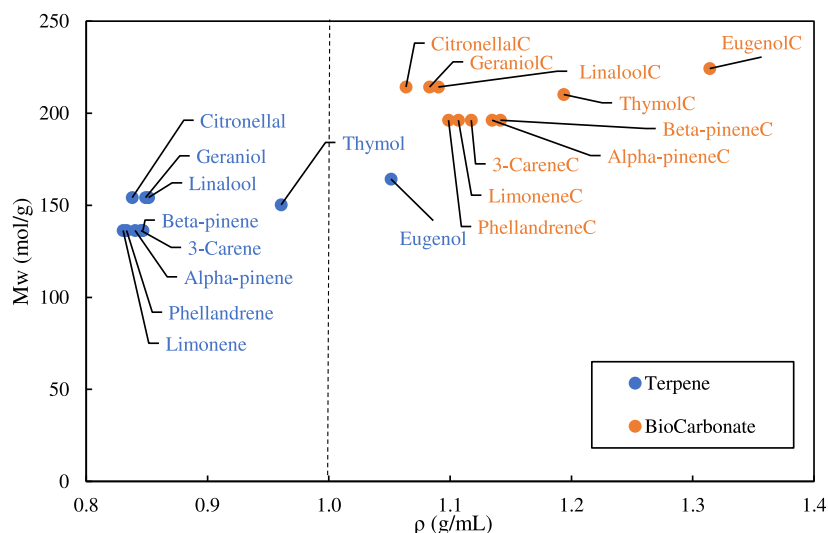
carbonates). This indicates that, even though both types of compounds present a hydrophobic behavior, biocarbinates present higher polarity than terpenes, implying lower hydrophobicity despite the increase in the molecular size. Moving to boiling points (Figure 1), the addition of carbonate groups to terpenes implies remarkably lower volatility because boiling points of terpenes range between 160 and 290 °C while those of biocarbinates range between 380 and 540 °C. Finally, biocarbinates show higher densities and molecular weights than terpenes, as seen in Figure 2. In general, carbonate's

density is higher than water and approximately 25–35% higher than that of terpenes.

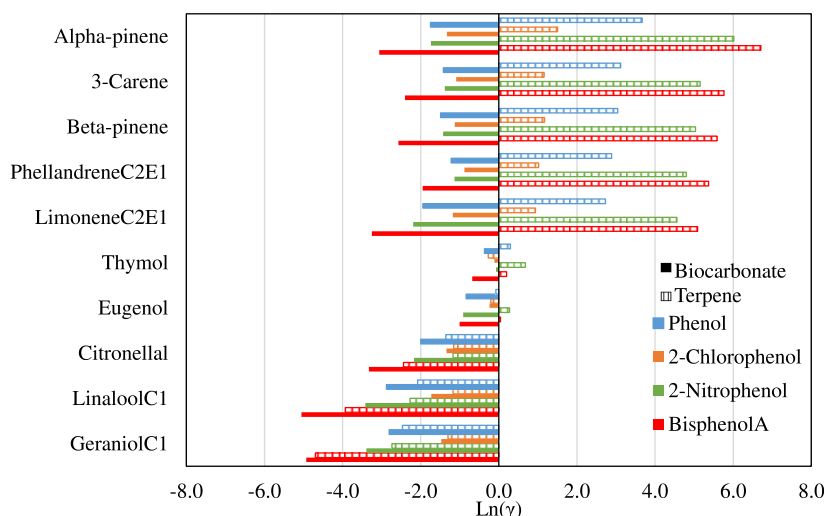
The implications of these changes in the properties of carbonates with respect to terpenes are clear when employed in a liquid–liquid extraction to remove solutes from aqueous solution: (i) the higher affinity for water of the biocarbinates implies greater solvent losses in the water-rich phase than using terpenes; (ii) the increase in the boiling point helps biocarbinates to enhance the regeneration step in comparison with terpenes, allowing to design more sustainable systems; and (iii) the higher density of biocarbinates than water's suggests that in a LLE the biocarbinates-rich phase would settle as the bottom layer, while when using terpenes, the solvent-rich phase would be the upper layer. To this respect, biocarbinates are the most beneficial in these operations as they are enhanced by working with more dense solvents due to mixing, mass transfer, and phase splitting processes.

Regarding the influence of adding more carbonate groups and their positioning, Figure S4 shows the  $K_{ow}$ , boiling point, densities, and molecular weights for limonene, geraniol, and their possible derivatives. As seen in Figure S1A, the hydrophobicity decreases with the addition of functional groups: using limonene as a reference, the terpene is the most hydrophobic compound (limonene), followed by the carbonates with one carbonate group (limoneneC1 and limoneneC2), then the ones with one carbonate group and one epoxide group (limoneneC1E2 and limoneneC2E1), and finally the one with two carbonate groups (limoneneC1C2). As seen in Figure S1B,C, the boiling points, molecular weights, and densities follow the opposite trend: adding more carbonate (or epoxide) groups increases the value of the three variables as: limoneneC1C2 > limoneneC1E2  $\approx$  limoneneC2E1 > limoneneC1  $\approx$  limoneneC2 > limonene. This behavior is the same in the four studied properties for geraniol as for limonene.

Regarding melting points, they cannot be easily estimated by COSMO-RS but the addition of polar groups, from the terpene structure to the biocarbinates one, can be quickly linked to an increase in the melting and boiling points, the latter predicted and discussed above. Available biocarbinates



**Figure 2.** Density against molar weight of the main terpenes (blue) and their corresponding biocarbinates (orange) calculated by COSMO-RS at 298 K.



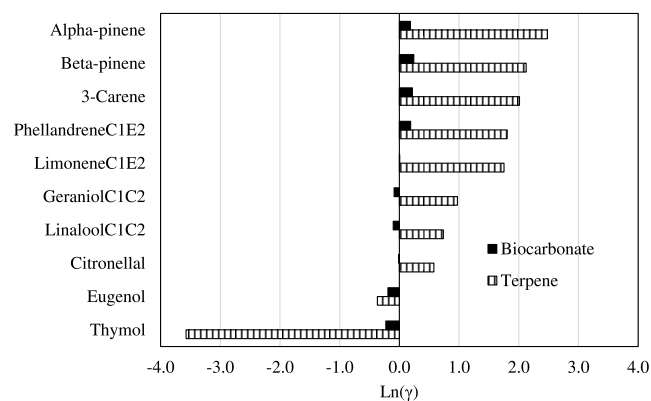
**Figure 3.** Predicted activity coefficients at infinite dilution of phenol, 2-nitrophenol, 2-chlorophenol, and bisphenol A in terpenes and their corresponding biocarbonate at 298.15 K using COSMO-RS.

are liquids, namely, limonene carbonate and pinene carbonate, but carbonates derived from terpenes with higher melting points could be solids at room temperature, depending on the self-interaction promotion or not by adding new polar groups. The uncertainty in this issue; however, opens three different routes to use biocarbons in water treatment: (i) liquid–liquid extraction from room temperature to optimal temperatures considering conditioning of regenerated solvent (above room temperature due to the solvent boiling point); (ii) liquid–liquid extraction from the melting point of the terpene to optimal temperature considering conditioning of the regenerated solvent (greater because the solvent boiling point will be above the melting point); and (iii) enabling lower temperatures in the extraction step by creating biocarbonate-based eutectic solvents to increase the liquid range of use.

**Activity Coefficient Screening.** After having evaluated the properties of terpene-derived carbonates, their suitability as solvents for the extraction of compounds of interest from water is analyzed using the activity coefficient at infinite dilution of the solute in these solvents, a reference thermodynamic parameter. Figure 3 reports the activity coefficient for phenol, 2-chlorophenol, 2-nitrophenol, and bisphenol A in the 10 selected terpenes and their corresponding biocarbons. As seen, terpenes exhibit diverse values for the activity coefficient for all solutes, ranging from low ( $\ln \gamma \approx -5$ ) to great values ( $\ln \gamma \approx +7$ ). However, the derived carbonates always present a favorable interaction with these solutes, that is, the logarithm of the activity coefficient is negative in all cases, which suggests high extraction yields. Moreover, for both carbonates and terpenes, the solvent–solute interaction is not strongly influenced by the different phenolic compounds: when the interaction is favorable, it is generally favorable for the four solutes and vice versa. It can be observed that there are certain terpenes for which the solute–solvent interaction is unfavorable, such as alpha-pinene, 3-carene, or beta-pinene, while their corresponding carbonates present a favorable interaction, which consequently establishes these carbonates as good candidates for the substitution of these terpenes. On the other hand, there are terpenes, such as geraniol or linalool, for which both the terpene and corresponding carbonate show a favorable interaction with the solutes, so that although

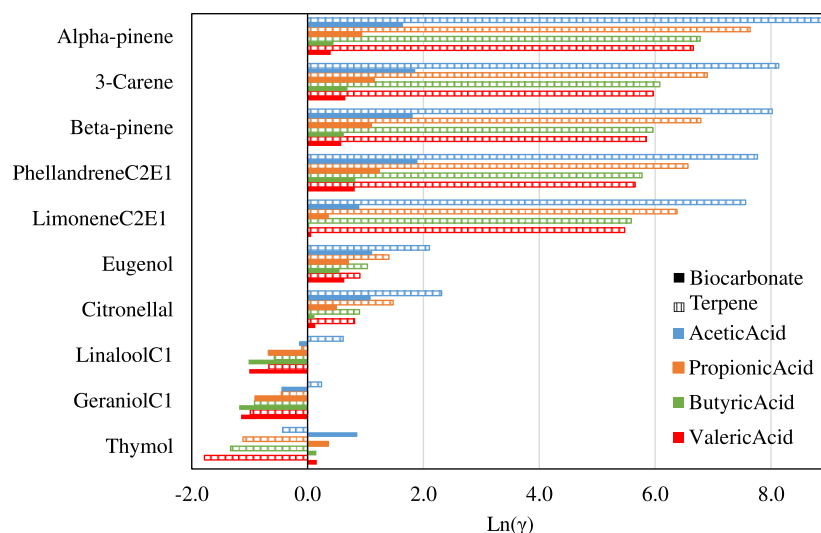
carbonates appear more favorable than terpenes, it is not a significant improvement. Therefore, it is concluded that there are certain terpenes whose performance in the extraction of these solutes could be greatly improved by the addition of carbonate groups, but the extent of this improvement depends on the terpene, as can be seen in Figure S2 in Supporting Information for a more extended terpene database. In addition, generally, bisphenol A and 2-nitrophenol show greater improvements of the activity coefficients in biocarbons with respect to terpenes, while 2-chlorophenol's activity coefficients in terpenes or biocarbons are the most similar.

Next, the activity coefficients of furfural in the selected terpenes and their derived biocarbons are shown in Figure 4. It is observed that except for eugenol and thymol, the



**Figure 4.** Predicted activity coefficients at infinite dilution of furfural in the main terpenes and their corresponding biocarbonate at 298.15 K using COSMO-RS.

remaining terpenes show an unfavorable interaction with furfural (positive values of  $\ln \gamma$ ). In the case of biocarbons, generally, they present remarkably more favorable solute–solvent interaction than terpenes, except for eugenol and thymol. It follows that, except in cases where the interaction of terpene with furfural is favorable ( $\ln \gamma < 0$ ), biocarbons are expected to perform better as extracting solvents than the corresponding terpenes. However, it is worth noting that biocarbons show less affinity for furfural ( $\ln \gamma \approx -0.3$  to



**Figure 5.** Predicted activity coefficients at infinite dilution of acetic acid, propionic acid, butyric acid, and valeric acid in the main terpenes and their corresponding biocarbonate at 298.15 K using COSMO-RS.

0.3) than for phenolic solutes ( $\ln \gamma \approx -5$  to  $-0.5$ ; Figure 3). Activity coefficients of furfural in other terpenes and derived carbonates can be found in Figure S3 of Supporting Information, showing that the derived biocarbons present a higher chemical affinity with furfural than terpenes, except, as mentioned above, when the activity coefficient of furfural in terpene is negative (thymol, carvacrol, eugenol, and verbenone).

Afterward, the interaction between VFA solutes and terpenes and biocarbons is evaluated by means of the activity coefficients at infinite dilution, depicted in Figure 4. As seen, there are terpenes, such as citronellal, phellandrene, or alpha-pinene, portraying unfavorable VFA activity coefficients ( $\ln \gamma \approx 0.9$  to  $8.9$ ), while their corresponding carbonates present lower activity coefficients ( $\ln \gamma \approx 0.1$  to  $1.6$ ), implying that the extraction of VFAs with said terpenes could be improved by selecting their derived carbonates instead. On the other hand, linalool and geraniol terpenes and their derived carbonates exhibit similar VFA activity coefficients ( $\ln \gamma$  moves between  $-0.5$  and  $-1.3$  both for terpenes and carbonates), meaning that VFA extraction with both compounds would render similar yields. Finally, thymol exhibits very favorable VFA activity coefficients ( $\ln \gamma < -0.5$ ), while its corresponding biocarbonate ( $\ln \gamma \approx 0.5$ ) presents a less favorable affinity with VFAs. Activity coefficients of these VFAs in other terpenes and derived carbonates can be found in Figure S4 of Supporting Information, portraying that usually when the terpene interaction with VFAs is favorable, adding carbonate groups worsens the affinity, while adding carbonate groups could be beneficial for the terpenes with unfavorable activity coefficients ( $\ln \gamma > 0.1$ ) of VFAs in the solvent.

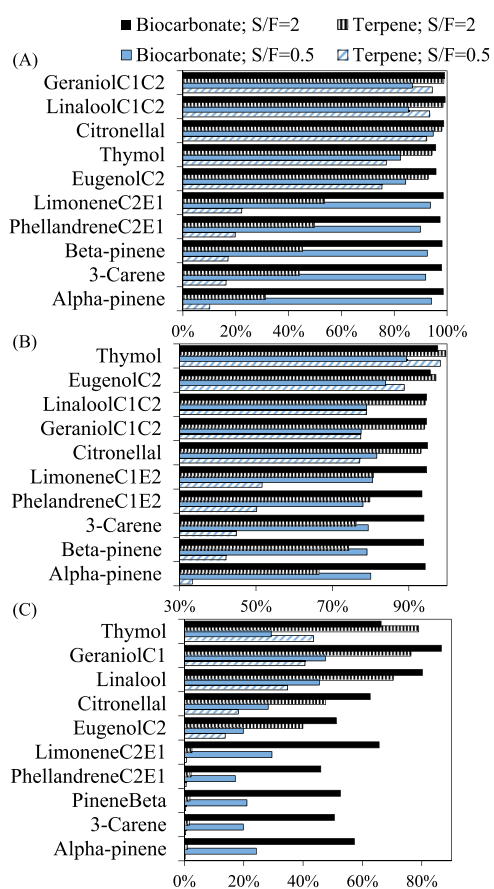
Besides, the activity coefficients of phenol, furfural, and acetic acid in limonene, geraniol, and their possible carbonate derivatives, depending on the quantity or positioning of carbonate or epoxide functional groups, are studied and collected in Figures S5–S7 in Supporting Information, respectively. As seen, in the case of limonene, the addition of carbonate or epoxide groups always improves the interaction with the solutes ( $\sigma$ -profiles collected in Figure S8A in Supporting Information). The trend is different for each solute, but in general the addition of an epoxide group and a

carbonate group is the most favorable option (limoneneC2E1 or limoneneC1E2), due to the increased hydrogen bond acceptor (HBA) character of the molecules, as can be seen in the  $\sigma$ -profiles collected in Figure S8B in Supporting Information. In the case of geraniol, for phenol and acetic acid, the picture is the same: the higher HBA character of geraniolC1 (Figure S8C in Supporting Information) improves the affinity for the solutes with respect to the terpene, while the other alternative biocarbons present lower affinity with the solutes. In the case of furfural, compared to terpene, all possible carbonates improve the affinity, with geraniolC1C2 showing the most affinity to furfural, due to its both acceptor and donor characters.

**Liquid–Liquid Extraction Analysis.** Once the solute–solvent interactions have been preliminary analyzed, a study of the solute extraction from water using terpenes and biocarbons is carried out by COSMO-RS. Figure 6 collects phenol, furfural, and acetic acid extraction yields, in selected terpenes and their derived biocarbons. As expected, a higher  $S/F$  mass ratio benefits the extraction of solutes in every case. Attending to terpene performance, alpha-pinene, 3-carene, beta-pinene, phellandrene, and limonene exhibit a low extraction yield for both  $S/F$  ratios and with the three solutes, while the corresponding biocarbons, eugenol, citronellal, linalool, geraniol, and thymol, exhibit high extraction yields with both  $S/F$ . As observed, solute extraction with terpenes of this first group is always improved by the addition of carbonate groups. Thus, the addition of a carbonate group is highly recommended in the extraction of these solutes for this group of terpenes, while it is not too relevant for the rest.

In the case of phenol (Figure 6A), biocarbons show a homogeneous behavior independently of the  $S/F$  ratio, ranging from 82 to 96% for a  $S/F = 0.5$  and almost a complete recovery of phenol (>95%) for a  $S/F = 2$  when using any carbonate. The differences in the extraction yield between different terpenes and different carbonates are anticipated in Figure 3, given that the terpenes and carbonates presenting the best extraction yields are those with the lowest activity coefficients and vice versa.

Moving to furfural (Figure 6B), the behavior is not as homogeneous as with phenol and the extraction yields are



**Figure 6.** Calculated solute extraction yield with selected terpenes (striped bars) and corresponding derived biocarboxates (solid bars), for  $S/F$  mass ratios of 0.5 (blue) and 2 (black) for (A) phenol, (B) furfural, and (C) acetic acid.

lower but generally indicating that the extraction of furfural with terpenes is less advantageous than with their derived carbonates, except for thymol and eugenol, because furfural extraction yields with terpenes range from 33 to 99%, while with derived carbonates they range from 80 to 98%. In addition, to achieve a furfural recovery higher than 90%, it is necessary to select a 2  $S/F$  ratio (except for thymol), while in phenol it was achievable with a 0.5  $S/F$  ratio, due to the higher furfural initial concentration (10 g/L) than phenol (0.5 g/L).

Regarding acetic acid extraction yields, as reported in Figure 6C, it can be observed that acetic acid extraction is significantly more favored in the derived carbonates (24–84% yield) than in their corresponding terpenes (0.3–79% yield), except for thymol. It should be noted that using 0.5 and 2.0  $S/F$  ratios, achieving an acetic acid yield higher than 90% was not possible neither using terpenes nor carbonates. As presented in Figure 5, acetic acid would be the most difficult solute to extract among the studied VFAs, concluding that higher extraction yields would be obtained for the rest of the VFAs. In addition, differing from the other solutes, for which the achieved yields were more homogeneous; geraniol- and linalool-derived carbonates, as well as thymol terpene, stand out above the other solvents with the highest yields. Thus, for the extraction of acetic acid, the use of carbonate groups is encouraged because they allow achieving the highest extraction yields (80–87%).

Regarding solvent losses in the water-rich phase, Table 2 lists the solvent losses for thymol- and geraniol-derived

**Table 2.** Thymol, Geraniol, Thymol-Derived Biocarboxate, and Geraniol-Derived Biocarboxate Losses in the Water-Rich Phase for an  $S/F$  Mass Ratio of 2 with Different Solutes

	solvent losses			
	thymol		geraniol	
	terpene (%)	biocarboxate (%)	terpene (%)	biocarboxate (%)
phenol	0.1	0.2	0.1	2.2
furfural	0.1	1.0	0.1	10.2
acetic acid	0.1	0.2	0.1	1.7

carbonates, as representatives because they present the highest and lowest  $K_{ow}$  values (Figure 1), and their corresponding terpenes. The solvent losses for the rest of terpenes and biocarboxates can be found in Tables S2 and S3 in the Supporting Information. As anticipated in Figure 1, biocarboxates are more soluble in water than terpenes that is why they present higher, but comparable, solvent losses. In the case of terpenes, solute and  $S/F$  present minimal influence on solvent losses. However, in the case of biocarboxates, furfural extraction implies the lowest biocarboxate losses for a  $S/F = 0.5$  and the highest solvent losses for a  $S/F = 2$ , while acetic acid and phenol follow the opposite trend. Nevertheless, there are cases, such as thymol-derived biocarboxate, for which biocarboxate losses are only slightly higher than those of thymol, especially for phenol and acetic acid extraction. In the said case, the higher boiling point of the biocarboxate would be an advantage for separating the solvent from water by distillation.

## CONCLUSIONS

In this work, a database of terpene-derived biocarboxates with optimized molecular structures has been successfully created. It has been evidenced, by COSMO-RS computational analysis, that the addition of carbonate groups to terpenes causes an increase in polarity, density (obtaining higher values than water), and boiling temperature. These biocarboxates have also been tested in the separation of compounds of different natures from water: such as phenolic compounds, VFAs, or furfural, which are relevant in the removal of pollutants or recovery of value-added compounds' current studies. Their performance in these separations has been compared with that of the original terpenes from which they are derived, by means of activity coefficients at infinite dilution and extraction yields. Biocarboxates have demonstrated great potential as solvents, being a competitive alternative to terpenes in the extraction of these solutes from water, reaching high extraction yields (87–99%). Therefore, the use of terpene-derived biocarboxates is a sustainable way of employing captured  $CO_2$  with useful applications, even improving the performance of terpenes in some cases. It has been found that biocarboxate losses in water can be slightly higher than terpenes' ones, related to lower  $K_{ow}$  values; however, environmental compatibility of terpenes and biocarboxates derived from terpenes smoothens this negative drawback, comparable or even better solvent performance, and an easier regeneration due to higher boiling points of biocarboxates in comparison with terpenes.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02993>.

Structure of terpenes, bioepoxides, and biocarbonates; terpene and biocarbonate losses in water in the extraction of phenol, acetic acid, and furfural; octanol–water partition coefficient, boiling point, density, and molecular weight of biocarbonates derived from limonene and geraniol; predicted activity coefficients of furfural, phenols, and VFAs in terpenes and biocarbonates; and sigma profiles of biocarbonates derived from limonene and geraniol (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Pablo Navarro – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain; [orcid.org/0000-0002-0017-3898](https://orcid.org/0000-0002-0017-3898); Email: [pablonavarro@uam.es](mailto:pablonavarro@uam.es)

### Authors

Alejandro Belinchón – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain

Elisa Hernández – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain

Javier Vázquez – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain

Rubén Santiago – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain; [orcid.org/0000-0002-6877-9001](https://orcid.org/0000-0002-6877-9001)

Cristian Moya – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain; [orcid.org/0000-0001-5107-7751](https://orcid.org/0000-0001-5107-7751)

Marcos Larriba – Chemical Engineering and Materials Department, Complutense University of Madrid, Madrid 28040, Spain; [orcid.org/0000-0003-0058-6841](https://orcid.org/0000-0003-0058-6841)

José Palomar – Chemical Engineering Department, Autonomous University of Madrid, Madrid 28049, Spain; [orcid.org/0000-0003-4304-0515](https://orcid.org/0000-0003-4304-0515)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acssuschemeng.2c02993>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors are grateful to Ministerio de Ciencia e Innovación of Spain (projects PID2020-118259RB-I00 and PDC2021-120881-I00) and Comunidad de Madrid (project P2018/EMT4348) for financial support and Centro de Computación Científica de la Universidad Autónoma de Madrid for computational facilities. E.H. thanks Spanish Ministerio de Universidades for awarding an FPU grant FPU20/03198. R.S. thanks Ministerio Universidades for his Margarita Salas contract (CA1/RSUE/2021-00585).

## REFERENCES

(1) IEA. Global Energy Review 2021, IEA: Paris. <https://www.iea.org/reports/global-energy-review-2021> (accessed on April 1, 2022).

(2) Marocco Stuardi, F.; MacPherson, F.; Leclaire, J. Integrated CO<sub>2</sub> capture and utilization: A priority research direction. *Curr. Opin. Green Sustainable Chem.* **2019**, *16*, 71–76.

(3) Rafiee, A.; Rajab Khalilpour, K.; Milani, D.; Panahi, M. Trends in CO<sub>2</sub> conversion and utilization: A review from process systems perspective. *J. Environ. Chem. Eng.* **2018**, *6*, S771–S794.

(4) Navarro, P.; Hernández, E.; Rodríguez-Llorente, D.; Maldonado-López, I.; Santiago, R.; Moya, C.; Belinchón, A.; Larriba, M.; Palomar, J. Fine-tune simultaneous dearomatization, desulfurization and denitrogenation of liquid fuels with CO<sub>2</sub>-derived cyclic carbonates. *Fuel* **2022**, *321*, 124005.

(5) Santiago, R.; Moya, C.; Hernández, E.; Cojocar, A.-V.; Navarro, P.; Palomar, J. Extending the ability of cyclic carbonates for extracting BTEX to challenging low aromatic content naphtha: the designer solvent role at process scale. *Comput. Chem. Eng.* **2021**, *154*, 107468.

(6) Pescarmona, P. P. Cyclic carbonates synthesised from CO<sub>2</sub>: Applications, challenges and recent research trends. *Curr. Opin. Green Sustainable Chem.* **2021**, *29*, 100457.

(7) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110*, 4554–4581.

(8) von der Assen, N.; Bardow, A. Life cycle assessment of polyols for polyurethane production using CO<sub>2</sub> as feedstock: insights from an industrial case study. *Green Chem.* **2014**, *16*, 3272–3280.

(9) Tor, A.; Cengeloglu, Y.; Aydin, M. E.; Ersoz, M. Removal of phenol from aqueous phase by using neutralized red mud. *J. Colloid Interface Sci.* **2006**, *300*, 498–503.

(10) Rodríguez-Llorente, D.; Navarro, P.; Santiago, R.; Águeda, V. I.; Álvarez-Torrellas, S.; García, J.; Larriba, M. Extractive removal and recovery of bisphenol A from aqueous solutions using terpenoids and hydrophobic eutectic solvents. *J. Environ. Chem. Eng.* **2021**, *9*, 106128.

(11) Xin, K.; Song, Y.; Dai, F.; Yu, Y.; Li, Q. Liquid–liquid equilibria for the extraction of furfural from aqueous solution using different solvents. *Fluid Phase Equilib.* **2016**, *425*, 393–401.

(12) Rodríguez-Llorente, D.; Bengoa, A.; Pascual-Muñoz, G.; Navarro, P.; Águeda, V. I.; Delgado, J. A.; Álvarez-Torrellas, S.; García, J.; Larriba, M. Sustainable Recovery of Volatile Fatty Acids from Aqueous Solutions Using Terpenoids and Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2019**, *7*, 16786–16794.

(13) Dejoye Tanzi, C.; Abert Vian, M.; Ginies, C.; Elmaataoui, M.; Chemat, F. Terpenes as Green Solvents for Extraction of Oil from Microalgae. *Molecules* **2012**, *17*, 8196.

(14) Boutekedjiret, C.; Vian, M. A.; Chemat, F. Terpenes as Green Solvents for Natural Products Extraction. In *Alternative Solvents for Natural Products Extraction*; Chemat, F., Vian, M. A., Eds.; Springer Berlin Heidelberg, 2014; pp 205–219.

(15) Monteiro, J. L. F.; Veloso, C. O. Catalytic Conversion of Terpenes into Fine Chemicals. *Top. Catal.* **2004**, *27*, 169–180.

(16) de la Cruz-Martínez, F.; Martínez de Sarasa Buchaca, M.; Martínez, J.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Rodríguez-Diéguez, A.; Castro-Osma, J. A.; Lara-Sánchez, A. Synthesis of Bio-Derived Cyclic Carbonates from Renewable Resources. *ACS Sustainable Chem. Eng.* **2019**, *7*, 20126–20138.

(17) Mahamat Ahmat, Y.; Madadi, S.; Charbonneau, L.; Kaliaguine, S. Epoxidation of Terpenes. *Catalysts* **2021**, *11*, 847.

(18) Harman-Ware, A. E. Conversion of Terpenes to Chemicals and Related Products. *Chemical Catalysts for Biomass Upgrading*; Wiley, 2020; pp 529–568.ch13 DOI: 10.1002/9783527814794.ch13 (accessed 2022/04/07).

(19) Li, Z.; Smith, K. H.; Stevens, G. W. The use of environmentally sustainable bio-derived solvents in solvent extraction applications—A review. *Chin. J. Chem. Eng.* **2016**, *24*, 215–220.

(20) Gu, Y.; Jérôme, F. Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. *Chem. Soc. Rev.* **2013**, *42*, 9550–9570.

(21) Tobiszewski, M. Analytical chemistry with biosolvents. *Anal. Bioanal. Chem.* **2019**, *411*, 4359–4364.



(22) Hulsbosch, J.; De Vos, D. E.; Binnemans, K.; Ameloot, R. Biobased Ionic Liquids: Solvents for a Green Processing Industry? *ACS Sustainable Chem. Eng.* **2016**, *4*, 2917–2931.

(23) He, Y.; Huang, Q.; Wang, P. Design and evaluation of novel bio-based deep eutectic solvents for highly efficient bioproduction of chiral aryl alcohol. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 1980–1988.

(24) Cañada-Barcala, A.; Rodríguez-Llorente, D.; López, L.; Navarro, P.; Hernández, E.; Águeda, V. I.; Álvarez-Torrellas, S.; Parajó, J. C.; Rivas, S.; Larriba, M. Sustainable Production of Furfural in Biphasic Reactors Using Terpenoids and Hydrophobic Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2021**, *9*, 10266–10275.

(25) Maltby, K. A.; Hutchby, M.; Plucinski, P.; Davidson, M. G.; Hintermair, U. Selective Catalytic Synthesis of 1,2- and 8,9-Cyclic Limonene Carbonates as Versatile Building Blocks for Novel Hydroxyurethanes. *Chem.—Eur. J.* **2020**, *26*, 7405–7415.

(26) Eze, V. C.; Rehman, A.; Patel, M.; Ahmad, S.; Harvey, A. P. Synthesis of cyclic  $\alpha$ -pinane carbonate – a potential monomer for bio-based polymers. *RSC Adv.* **2022**, *12*, 17454–17465.

(27) Fiorani, G.; Stuck, M.; Martín, C.; Belmonte, M. M.; Martín, E.; Escudero-Adán, E. C.; Kleij, A. W. Catalytic Coupling of Carbon Dioxide with Terpene Scaffolds: Access to Challenging Bio-Based Organic Carbonates. *ChemSusChem* **2016**, *9*, 1304–1311.

(28) Rodríguez-Llorente, D.; Cañada-Barcala, A.; Muñoz, C.; Pascual-Muñoz, G.; Navarro, P.; Santiago, R.; Águeda, V. I.; Álvarez-Torrellas, S.; García, J.; Larriba, M. Separation of phenols from aqueous streams using terpenoids and hydrophobic eutectic solvents. *Sep. Purif. Technol.* **2020**, *251*, 117379.

(29) TURBOMOLE V7.3 2018, Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 2007 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.

(30) Klamt, A.; Schuurmann, G. COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799–805.

(31) Cubillos Lobo, J. A.; Martínez, J. J.; Rojas, H.; Marín-Astorga, N. Oxidation of geraniol using niobia modified with hydrogen peroxide. *Rev. Fac. Ing., Univ. Antioquia* **2019**, *0*, 106–112.

(32) COSMOlogic University of Karlsruhe and Forschungszentrum Karlsruhe GmbH. *COSMOtherm*, 2019, Release 19.

## Recommended by ACS

### Greening the Synthesis of Biorenewable Fuels and Chemicals by Stoichiometric Reagentless Organic Transformations

Saikat Dutta.

AUGUST 26, 2022  
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

READ 

### From Biomass to Green Aromatics: Direct Upgrading of Furfural–Ethanol Mixtures

Juan Gancedo, Salvador Ordóñez, *et al.*

MAY 26, 2022  
ACS SUSTAINABLE CHEMISTRY & ENGINEERING

READ 

### Tandem Reactions for the Synthesis of High-Density Polycyclic Biofuels with a Double/Triple Hexane Ring

Yizhuo Wang, Hong Wang, *et al.*

MAY 30, 2022  
ACS OMEGA

READ 

### Waste-to-Fuel Approach: Valorization of Lignin from Coconut Coir Pith

Daria Lebedeva, Joseph S. M. Samec, *et al.*

MARCH 01, 2022  
ACS AGRICULTURAL SCIENCE & TECHNOLOGY

READ 

Get More Suggestions >