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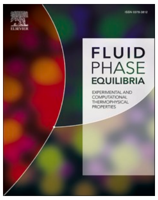

Terpenoids as solvents for the separation of 2,3-butanediol from water: Phase equilibria and process evaluation

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ABSTRACT

2,3-butanediol (2,3-BDO) is a versatile platform chemical that can be produced via fermentation in aqueous solution. The energy intensive recovery of the high boiling 2,3-BDO from water via distillation hinders the economic viability of biotechnological produced 2,3-BDO. Hence, extraction-distillation processes using novel solvents from the class of terpenoids, namely menthol, thymol, and carvacrol, are proposed. To this end, binary and ternary liquid-liquid equilibrium (LLE) data for H_2O, 2,3-BDO, and each terpenoid, as well as boiling point data for 2,3-BDO and the respective terpenoid, are measured. The thermodynamic phase equilibria are correlated with the non-random two liquid (NRTL) model and consecutive process design of the extraction-distillation processes is conducted using Aspen Plus. Conventional solvents (isobutanol, 1-butanol, and oleylalcohol), thymol, and carvacrol are assessed in terms of specific exergy demand for the production of 2,3-BDO. The lowest specific exergy demands were found for oleyl alcohol (5.38 kJ g^{-1}) and thymol (5.14 kJ g^{-1}), carvacrol (5.49 kJ g^{-1}). Hence, terpenoids are a competitive class of solvents and should be included in solvent screening approaches.

1. Introduction

2,3-butanediol (2,3-BDO) is a short chain diol that has several applications, e.g. as precursor for flavoring agents (diacetyl) or biofuels (methyl-ethyl-ketone), and as an ingredient for the pharmaceutical and cosmetic branch [1]. The bio-based production of 2,3-BDO from glucose via fermentation is widely studied with high titers of up to 178 g/L in the fermentation broth [2,3].

However, the efficient separation of the diluted 2,3-BDO remains the most expensive step in the overall process and is a major challenge for the scientific community [4]. The industrial separation of bio-based 2,3-BDO is currently conducted via costly filtration, centrifugation, and ion exchange steps followed by energy intensive distillation of the aqueous medium [5,6]. Multiple studies for the separation of 2,3-BDO have been conducted to identify concepts for the separation of the high boiling, hydrophilic diol from water [7]. Concepts like pervaporation [8,9], salting out extraction [10], and solvent extraction have been investigated [11–13]. In particular, solvent extraction is expected to be a promising purification strategy due to simple scalability and broad experience in industrial applications. To this end, the scientific community mainly focused on low boiling alcohols as solvents such as 1-butanol, isobutyl alcohol, or 2-heptanol [11,14]. Due to low distribution coefficients and selectivity, large amounts of solvent are required to recover 2,3-BDO via extraction from its aqueous environment. For subsequent purification and solvent recovery, the loaded solvent is distilled yielding 2,3-BDO as the bottom product with non-volatile carbon impurities. Further, evaporating large amounts of solvents consumes large amounts of energy and reduces the energy efficiency of the process. Therefore, the quest for novel solvents for the separation of 2,3-BDO from water arises [15].

High boiling solvents benefit from 2,3-BDO being the low boiling compound that can be obtained as the head fraction of the distillation column without non-volatile carbon impurities (see Fig. 1). Further, the reboiler duty is reduced, since less solvent is evaporated. The high boiling long chain compound oleyl alcohol was studied previously for extraction of 2,3-BDO from water [16]. It has superb extraction properties, such as good distribution coefficient and very high selectivity resulting from low cross-solubility. However, high viscosity and expensive distillation under vacuum (to even achieve a temperature level that can be served by high pressure steam) make it an unviable solvent [14].

A novel class of solvents is the family of terpenoids. Terpenoids are a

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group of natural products that are structurally derived from isoprene as a subunit [17]. These molecules can be obtained from plants [18], but can also be chemically synthesized from platform chemicals like benzene, m-cresol and propene [19]. In the context of solvent extraction terpenoids are mainly used as constituents of deep eutectic solvents (DES) [20–23]. DES are mixtures usually composed of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) resulting in strong hydrogen bonding and large deviations from ideal melting points [24]. Terpenoids can form strong hydrogen bonds due to their molecular structure, leading to their extensive use in the preparation of DES. Especially, phenolic terpenoids like thymol and carvacrol are so-called asymmetric HBD and therefore induce extraordinary strong molecular interactions suiting them for extraction [25,26]. But also HBA that origin from the class of terpenoids like menthol are frequently used [27, 28]. To make use of terpenoids in extraction they are usually liquified via DES formation by addition of an HBA or HBD that binds to the corresponding free hydrogen association side. Recently, a study from Choe *et al.* focused on the use of terpenoid based DES for the extraction of 2,3-BDO from water [29]. When mixing thymol with undecenoic acid superior distribution coefficients and selectivity in comparison to conventional solvents were achieved [29]. However, the unsaturated carboxylic acid undecenoic acid is unsuited for typical solvent regeneration via distillation due to possible esterification with the present hydroxy groups (2,3-BDO or thymol). As an alternative to DES formation, liquification can also be achieved by increasing the temperature to a moderate level (e.g. 313.15 K). The benefit is that no additional HBA or HBD is necessary for liquification, resulting in a free association side which can be targetted by a hydrogen bond forming solute in extraction [30, 23]. Even though there is a variety of studies using terpenoids as solvents, only Rodriguez-Llorente *et al.* used pure thymol or carvacrol as solvents, for the separation of pharmaceuticals and antibiotics from hospital wastewater [31,32]. Interestingly, compounds with similar molecular structure to phenolic terpenoids such as 2-sec-butylphenol have been found to be suitable solvents for the extraction of 2,3-BDO from water in previous studies, indicating that also terpenoids might be promising solvents in extraction [33]. To assess the potential of terpenoids as hydrophobic, high boiling solvents in extraction-distillation processes, the separation of 2,3-BDO from water is investigated within this work. To this end, three readily available terpenoids are selected (menthol, thymol, and carvacrol) and the relevant thermodynamic phase equilibria data is collected. We present ternary liquid-liquid equilibrium (LLE) data of H_2O, 2,3-BDO, and a terpenoid. Binary vapor-liquid equilibrium (VLE) data of 2,3-BDO and the respective terpenoid is displayed. Based on the LLE and VLE data, the non-random two-liquid (NRTL) model is used to correlate the non-ideal behavior of the liquid phase in the mixtures. The validity of the resulting parameterizations is verified using the isoactivity and Gibbs stability criteria as suggested in the literature [34]. To quantify the conceptual advantage of the separation of 2,3-BDO via extraction using terpenoids, an assessment via AspenPlus 11® is conducted. The processes are compared in terms of their exergy requirements with a purely distillative process and extraction-distillation processes from literature using conventional solvents [16,14,35].

2. Materials and methods

2.1. Chemicals

In Table 1 the used chemicals, supplier and purities are given. No additional purification steps were applied; all chemicals were used as received.

2.2. Experimental determination of liquid-liquid equilibrium data

All liquid-liquid equilibrium (LLE) experiments were conducted in 20 mL screw cap glass vials in a HLC Heating-ThermoMixer MHR 23 from DITABIS. All measurements were conducted as triplicates. Compositions of distilled water, 2,3-BDO, and terpenoid were prepared, whereby the mass ratio of distilled water to terpenoid was 1:1. The vials were shaken for at least 16 h at 500 rpm. Before sampling, the vials were hold at temperature for at least 2 h with no shaking to allow for settling. The organic phase was analyzed via Karl-Fischer Titration (KF) to determine the water content and samples were prepared by diluting 1 g of the organic phase with 1 g of acetonitrile. High performance liquid chromatography (HPLC) was used to determine the mass fraction of 2,3-

Table 1
Compounds, abbreviation, supplier (origin), reported purity of used chemicals.

Compound (IUPAC name)	Abbreviation	Supplier (Origin)	Reported Purity
Deionized water	H_2O	In-house produced	Conductivity < 0.7 µS cm−1
2,3-Butanediol (D-, l-, *meso* isomers)	2,3-BDO	VWR Chemicals (Germany)	$\geq$ 98 % (mass), isomer ratio: (DL : *meso*) = (6.7 : 93.3)
(1R,2S,5R)-Menthol	Menthol	VWR Chemicals (Germany)	$\geq$ 99 % (mass)
5-Methyl-2-(propan-2-yl) phenol	Thymol	VWR Chemicals (Germany)	$\geq$ 98 % (mass)
5-Isopropyl-2-methylphenol	Carvacrol	VWR Chemicals (Germany)	$\geq$ 98 % (mass)
Acetonitrile	ACN	VWR Chemicals (Germany)	$\geq$ 99.9 % (volume)
Ethanol	EtOH	VWR Chemicals (Germany)	$\geq$ 99.8 % (volume)
Methanol	MeOH	VWR Chemicals (Germany)	$\geq$ 99.8 % (volume)
Trifluoroacetic acid	TFA	Carl Roth GmbH + Co. KG (Germany)	$\geq$ 99.9 % (mass)

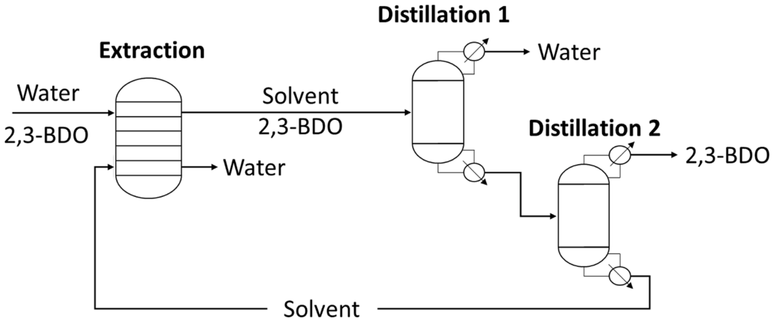

Fig. 1. Extraction-distillation process for the separation of 2,3-BDO from water via extraction by high boiling solvents and consecutive distillation. In an extraction column 2,3-BDO is extracted from water into an organic phase. The extract is purified in two distillation steps. In the first distillation column co-extracted water is separated. In the second distilation column 2,3-BDO is obtained in the head fraction and the solvent stream in the bottom is recycled.

BDO in the organic phase (samples were diluted with methanol in volumetric ratio of 1:1). The aqueous phase was analyzed via HPLC to determine the mass fractions of 2,3-BDO, thymol, and carvacrol in the aqueous phase. GC was performed to measure the mass fraction of menthol in the aqueous phase (since menthol was not detectable via HPLC). GC samples were prepared by taking 100 µl from the organic phase and adding them to 900 µl ethanol for dilution. The remaining mass fractions (water in aqueous phase and terpenoid in organic phase) were calculated via closing condition.

HPLC analysis was conducted with an Agilent 1200 HPLC equipped with a Nucleodur C18ec column. For detection of 2,3-BDO a Refractive Index Detector (RID) was used. The detection of the aromatic terpenoids thymol and carvacrol was performed via Diode Array Detector (DAD) at 254 nm. Two eluents were used to create a gradient throughout the measurement. Eluent A is a mixture of 995 mL water, 50 mL methanol and 5 mL trifluoracetic acid. Eluent B is pure methanol. At a constant flow of 0.5 mL/min eluent A is applied for 4 min. A gradient to a composition 25 % A and 75 % B is applied for 1 min. The ratio of 25A/75B is hold for 7.5 min and is then changed back to pure solvent A. To achieve optimal results, the RID is purged for 4 min before every injection. For GC analysis an Agilent 7890 GC was used with a column obtained from CS-Chromatography of the type FS-CW 20 M-CB-1 (PEG 20,000, i.d. 530 µm; 25 m x 1 µm). The oven was heated in a gradient (353.15 K hold 3.5 min, to 453.15 K with 50 K/min, hold 2.5 min, to 473.15 K with 50 K/min, hold 3 min). A sample volume of 2 µL, a flow rate of 8 mL/min helium and a split ratio of 5:1 is applied.

The distribution coefficient D_i of component i and selectivity S are used to describe the thermodynamic equilibrium. The distribution coefficient is defined as

$$D_i = \frac{w_{i,\mathrm{E}}}{w_{i,\mathrm{R}}}$$

where $w_{i,\mathrm{E}}$ denotes the mass fraction of the solute in the extract and $w_{i,\mathrm{R}}$ the mass fraction of the solute in the raffinate. The selectivity is derived from the quotient of the distribution coefficients of the solute (i) and water (j):

$$S_i = \frac{D_i}{D_j}$$

For uncertainty determination gaussian error propagation was applied to the measured mass fractions, as presented in Section 1 in the Supplementary Information. The uncertainty of the measuring device, the slope of calibration, and the error resulting from replicates were included.

2.3. *Experimental determination of boiling point data*

Differential scanning calorimetry (DSC) measurements were conducted to determine the boiling points of the binary systems 2,3-BDO - menthol, 2,3-BDO - thymol, and 2,3-BDO - carvacrol. Indium samples with a defined melting point of 429.75 K were used for calibration. The DSC1 STARe System from Mettler Toledo was used. Samples of the pure compounds and different molar ratios of 2,3-BDO with menthol, thymol, or carvacrol were prepared by inserting 40 µL of the mixture into an aluminium crucible (filling size 100 µL). The crucible was then hermetically sealed to prevent evaporation and equipped with a pinhole. A nitrogen flow of 80 mL/min was applied to avoid condensation in the furnace. All measurements were performed in triplicates. The samples were initially hold at 298.15 K for 2 min and consecutively heated to 523.15 K with a heating rate of 25 K/min. The obtained DSC thermograms were analysed via the STARe Software (V9.20). Analysis of the onset of the evaporation peak was conducted to derive the isobaric boiling point line at atmospheric pressure as presented in literature [36, 37].

2.4. *Thermodynamic modeling of phase equilibrium data*

We use the well-known non-random two-liquid (NRTL) activity coefficient model to correlate experimental LLE data [38]. The following model equations are used to express the activity coefficient γ_i:

$$\ln\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{kj}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}; (\tau_{ii} = 0)$$

$$\alpha_{ij} = 0.3; (\alpha_{ij} = \alpha_{ji}); (\alpha_{ii} = 1)$$

To model the temperature dependent binary LLE data, binary interaction parameters were regressed by adjusting a_{ij} and b_{ij} using an objective function (OF) based on molar fractions in equilibrium to fulfill the isoactivity condition. To expand from binary to ternary LLEs, the remaining binary pairs were regressed by only adjusting b_{ij} and fixing a_{ij} to zero. To correlate boiling temperatures for pTx vapor-liquid equilibrium (VLE) data, an individual set of NRTL parameters was regressed.

$$OF_{\mathrm{LLE}}(x) = RMSD(x)_{\mathrm{aq}} + RMSD(x)_{\mathrm{org}}$$

$$RMSD(x)_{\mathrm{aq/org}} = \sqrt{\frac{1}{I \cdot N} \sum_{i=1}^{I} \sum_{j=1}^{N} \left(\frac{x_{i,n}^{\mathrm{exp}} - x_{i,n}^{\mathrm{NRTL}}}{u_{i,n}(x)} \right)^2}$$

$$OF_{\mathrm{VLE}}(T) = \sqrt{\frac{1}{N} \sum_{j=1}^{N} \left(\frac{T_n^{\mathrm{exp}} - T_n^{\mathrm{NRTL}}}{u_n(T)} \right)^2}$$

The resulting correlation was checked for validity by plotting the tangent plane to the gibbs energy of mixing surface and the miscibility boundaries according to parameterization in Section 2 in Supplementary Information.

2.5. *Process modeling*

Aspen Plus V11 was used to assess the extraction distillation-processes using terpenoids in terms of specific exergy demand. The NRTL-model was chosen to cover non-idealities in the liquid phase. Two parametersets were used to model the different phase equilibria (LLE and VLE) individually. The parameters regressed in this work were used for the description of the LLE (parameterset 1) and the VLE (parameterset 2). The remaining binary parameter to describe the VLE were taken from Aspen data bank (2,3-BDO—H_2O). The extraction-distillation process is entered by the feed stream consisting of 10 w % of 2,3-BDO in water at 298.15 K. The extraction was realized in all processes using the multistage extraction column model with 10 theoretical separation stages in isothermal operation mode at 313.15 K and atmospheric pressure. The amount of solvent (terpenoid) was determined using a design specification to achieve a fixed recovery of 2,3-BDO. The recovery of 2,3-BDO is specified to be 90 % and a final purity of 99 w % is constraint to be comparable to processes assessments from literature [16,35].

To purify the extract two distillation columns are necessary. In a first distillation column the co-extracted water is removed whereas in a second distillation column 2,3-BDO and the solvent are separated. The first distillation column is modelled at atmospheric pressure with 12 theoretical separation stages and a distillate to feed ratio corresponding to the mutual solubility of water in the solvent. The reflux ratio is minimized via sensitivity analysis while maintaining a recovery of 2,3-BDO of more than 99 % in the bottom stream. The second distillation column is modelled at atmospheric pressure with 18 theoretical separation stages and distillate to feed ratio corresponding to the mass fraction of 2,3-BDO in the solvent. The reflux ratio is minimized via sensitivity analysis while maintaining a purity of 2,3-BDO of more than 99 w % in the distillate. The distillations columns are modelled using the radfrac model. No pressure loss along the distillation columns was considered. The condensers were modeled as total condenser. All processes (including processes from literature) are evaluated based on their product specific exergy demand to not only account for the energy demand in the reboilers, but also for the temperature level. The specific exergy demand is defined as:

$$\text{specific exergy demand (SXD)} \; = \sum \frac{\dot{Q}_{\text{reboiler}} \cdot \left(1 - \frac{298.15\ \text{K}}{T_{\text{reboiler}}}\right)}{\dot{m}_{\text{product}}}$$

where $\dot{Q}_{\text{reboiler}}$ is the heat duty for the distillation columns, T_{reboiler} is the temperature level in the reboiler, and $\dot{m}_{\text{Product}}$ is the mass flow of gained 2,3-BDO product stream.

3. Results and discussion

LLE data of binary systems consisting of water and a terpenoid (menthol, thymol, carvacrol) was measured experimentally in a range between 298.15 K and 363.15 K. Further, ternary LLE data by addition of 2,3-BDO was measured experimentally at 363.15 K at atmospheric pressure. The mass fractions were determined as described in Section 2.2. The experimentally derived mass fractions in organic (org) and aqueous (aq) phase of binary systems are summarized in Table 2, while the ternary systems are given in Table 3. Error propagation for uncertainty determination of the measured mass fractions as well as the determined uncertainties was conducted as described in Supplementary Information in Section 1.

Since menthol and thymol are solids at 298.15 K as well as thymol at 313.15 K, no binary LLE data is documented.

The cross-solubility of the water in the organic phase and of the terpenoids in the aqueous phase is comparable to conventional solvents like 1-octanol [39,40]. Especially, menthol shows very low cross-solubility, which is important for possible reuse of the raffinate stream after extraction. However, the distribution coefficient of menthol is low, ranging between 0.1 and 0.155. Hence, large amounts of solvent are necessary in counter-current extraction to achieve high recovery of 2,3-BDO, making menthol rather unfeasible as a possible solvent. The distribution coefficients of thymol and carvacrol are very similar to each other and in a range between 0.55 and 0.66, whereby thymol has slightly higher distribution coefficient. Further, the cross solubility of water in the organic phase is lower for thymol in comparison to carvacrol, leading to a high selectivity of thymol. The distribution coefficient (*D*) and selectivity (*S*) are presented in Fig. 2 and documented in Table 4.

The distribution coefficients achieved with the tested terpenoids within this work are slightly lower than the distribution coefficients achieved with conventional solvents like 1-butanol (0.73 –0.88) or isobutanol (0.65 –0.84) and in the same range like oleyl alcohol (0.51 –0.67). Nevertheless, the selectivity is significantly increased compared to 1-butanol (1.51 –2.94) or isobutanol (2.27 –2.92). Oleyl alcohol has superb selectivity (4.73 –184.97) resulting from the low co-extraction of water, but major drawbacks in terms of applicability as stated before [41–43].

The obtained LLE data was successfully correlated and validated as described in Section 2.4 using the NRTL model. The corresponding NRTL parameters used for process design can be found in Table 5.

The derived ternary diagrams are presented in Fig. 3. All three extraction systems are characterized by a type I miscibility gap and all tie-lines cross the mixing point, indicating good agreement with the mass balance. The correlation using the NRTL model sufficiently describes the slope of the tie-lines and the cross-solubilities.

To evaluate the proposed process in Fig. 1, boiling point data of binary mixtures consisting of 2,3-BDO and a terpenoid (menthol, thymol, carvacrol) and corresponding standard deviations representing the 95 % confidence intervall were measured. The measurements were conducted as described in Section 2.3 using DSC and are presented in Table 6. The boiling points of the pure substances are in agreement with boiling points found in literature as presented in Table 7.

The boiling point data was used to correlate NRTL parameters as described in Section 2.4. To calculate the pure component vapor pressures, antoine parameters taken from literature are used (see Table 8). The used antoine equation is given as

$$\log\,(p) = A - \frac{B}{(T + C)}$$

where the temperature *T* is given in K and the resulting pressure *p* is given in kPa.

The correlated NRTL parameters of the binary pairs are documented in Table 9. Further, the NRTL parameters for the binary pair 2,3-BDO –H_2O were taken from the AspenPlus internal APV110 VLE-IG database. To model the H_2O – terpenoid interactions, the NRTL parameters from the temperature dependent binary LLEs are used. The experimental boiling points as well as the calculated correlation of boiling point and

Table 2
The experimental binary LLE data of the binary systems consisting of water and a terpenoid (menthol, thymol, carvacrol) between 298.15 K and 363.15 K at atmospheric pressure (99.07 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure in $u(p) = 0.9$ kPa.

System	Temperature	$w^{\text{org}}_{H_2O}$ /kg kg^{-1}	$u_{w^{\text{org}}_{H_2O}}$ /kg kg^{-1}	$w^{\text{org}}_{\text{Terpenoid}}$ /kg kg^{-1}	$u_{w^{\text{org}}_{\text{Terpenoid}}}$ /kg kg^{-1}	$w^{\text{aq}}_{H_2O}$ /kg kg^{-1}	$u_{w^{\text{aq}}_{H_2O}}$ /kg kg^{-1}	$w^{\text{aq}}_{\text{Terpenoid}}$ /kg kg^{-1}	$u_{w^{\text{aq}}_{\text{Terpenoid}}}$ /kg kg^{-1}
Menthol	298.15 K	–	–	–	–	–	–	–	–
	313.15 K	0.01320	0.00060	0.98680	0.00060	0.99970	0.00003	0.00030	0.00003
	323.15 K	0.01600	0.00120	0.98400	0.00120	0.99970	0.00005	0.00030	0.00005
	333.15 K	0.01800	0.00080	0.98200	0.00080	0.99970	0.00011	0.00030	0.00011
	343.15 K	0.01970	0.00350	0.98030	0.00350	0.99960	0.00005	0.00040	0.00005
	363.15 K	0.02490	0.00060	0.97510	0.00060	0.99960	0.00005	0.00040	0.00005
Thymol	298.15 K	–	–	–	–	–	–	–	–
	313.15 K	–	–	–	–	–	–	–	–
	323.15 K	0.03690	0.00220	0.96310	0.00220	0.99840	0.00008	0.00160	0.00008
	333.15 K	0.03840	0.00080	0.96160	0.00080	0.99830	0.00005	0.00170	0.00005
	343.15 K	0.03880	0.00130	0.96120	0.00130	0.99810	0.00007	0.00190	0.00007
	363.15 K	0.03900	0.00060	0.96100	0.00060	0.99800	0.00008	0.00200	0.00008
Carvacrol	298.15 K	0.03540	0.00090	0.96460	0.00090	0.99870	0.00003	0.00130	0.00003
	313.15 K	0.03900	0.00060	0.96100	0.00060	0.99840	0.00005	0.00160	0.00005
	323.15 K	0.04030	0.00070	0.95970	0.00070	0.99820	0.00007	0.00180	0.00007
	333.15 K	0.04110	0.00180	0.95890	0.00180	0.99800	0.00009	0.00200	0.00009
	343.15 K	0.04170	0.00070	0.95830	0.00070	0.99780	0.00004	0.00220	0.00004
	363.15 K	0.04220	0.00070	0.95780	0.00070	0.99740	0.00016	0.00260	0.00016

Table 3

The experimental ternary LLE data for the ternary systems consisting of water, 2,3-BDO, and a terpenoid (menthol, thymol, carvacrol) at 313.15 K and atmospheric pressure (99.07 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure in $u(p) = 0.9$ kPa.

System	$w^{org}_{H_2O}$ /kg kg^{-1}	$u_{w^{org}_{H_2O}}$ /kg kg^{-1}	$w^{org}_{2,3-BDO}$ /kg kg^{-1}	$u_{w^{org}_{2,3-BDO}}$ /kg kg^{-1}	$w^{org}_{Terpenoid}$ /kg kg^{-1}	$u_{w^{org}_{Terpenoid}}$ /kg kg^{-1}	$w^{aq}_{H_2O}$ /kg kg^{-1}	$u_{w^{aq}_{H_2O}}$ /kg kg^{-1}	$w^{aq}_{2,3-BDO}$ /kg kg^{-1}	$u_{w^{aq}_{2,3-BDO}}$ /kg kg^{-1}	$w^{aq}_{Terpenoid}$ /kg kg^{-1}	$u_{w^{aq}_{Terpenoid}}$ /kg kg^{-1}
Menthol	0.0180	0.0006	0.0046	0.0003	0.9774	0.0007	0.9537	0.0004	0.0459	0.0005	0.0004	0.0000
	0.0203	0.0006	0.0099	0.0005	0.9698	0.0008	0.9096	0.0021	0.0898	0.0021	0.0006	0.0000
	0.0217	0.0006	0.0155	0.0011	0.9628	0.0013	0.8677	0.0005	0.1316	0.0007	0.0007	0.0001
	0.0222	0.0006	0.0211	0.0012	0.9567	0.0013	0.8278	0.0059	0.1713	0.0059	0.0008	0.0000
	0.0238	0.0006	0.0290	0.0023	0.9472	0.0024	0.7904	0.0018	0.2087	0.0020	0.0009	0.0000
	0.0240	0.0006	0.0384	0.0020	0.9376	0.0021	0.7521	0.0014	0.2468	0.0018	0.0011	0.0000
Thymol	0.0384	0.0007	0.0178	0.0005	0.9438	0.0008	0.9657	0.0004	0.0326	0.0004	0.0017	0.0001
	0.0412	0.0007	0.0375	0.0011	0.9213	0.0013	0.9311	0.0022	0.0666	0.0023	0.0023	0.0000
	0.0437	0.0006	0.0549	0.0020	0.9014	0.0020	0.9027	0.0004	0.0950	0.0006	0.0022	0.0001
	0.0472	0.0006	0.0768	0.0023	0.8760	0.0024	0.8697	0.0013	0.1273	0.0014	0.0029	0.0008
	0.0509	0.0006	0.0981	0.0028	0.8511	0.0029	0.8404	0.0013	0.1566	0.0014	0.0030	0.0001
	0.0550	0.0006	0.1223	0.0039	0.8227	0.0039	0.8105	0.0021	0.1855	0.0017	0.0040	0.0019
Carvacrol	0.0405	0.0008	0.0200	0.0011	0.9395	0.0014	0.9652	0.0004	0.0331	0.0016	0.0017	0.0001
	0.0442	0.0007	0.0366	0.0019	0.9192	0.0020	0.9351	0.0001	0.0630	0.0029	0.0019	0.0001
	0.0477	0.0009	0.0527	0.0030	0.8996	0.0031	0.9070	0.0004	0.0907	0.0042	0.0023	0.0002
	0.0500	0.0006	0.0685	0.0035	0.8815	0.0035	0.8805	0.0011	0.1170	0.0055	0.0025	0.0001
	0.0547	0.0007	0.0876	0.0046	0.8577	0.0047	0.8522	0.0006	0.1448	0.0066	0.0030	0.0001
	0.0584	0.0006	0.1049	0.0057	0.8367	0.0057	0.8285	0.0023	0.1681	0.0080	0.0034	0.0002

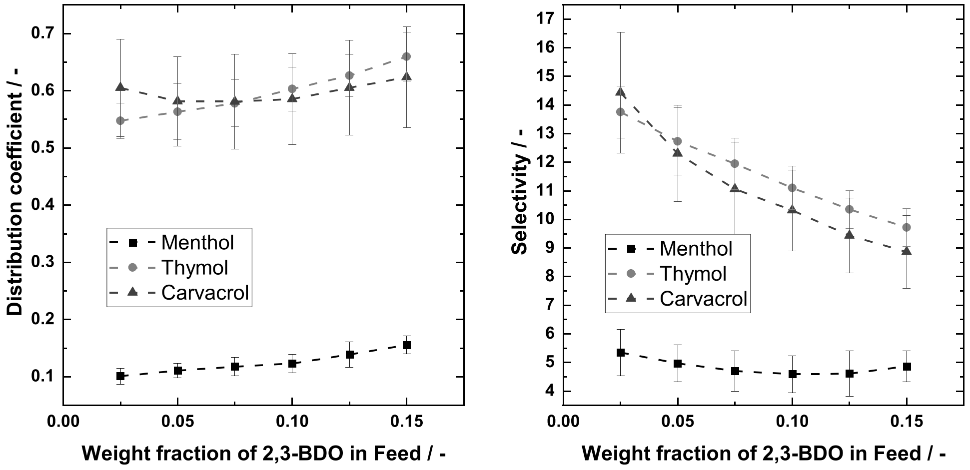

Fig. 2. Distribution coefficients (a) and selectivity (b) in the ternary system water, 2,3-BDO, and terpenoid (menthol, thymol, carvacrol) as a function of the weight fraction of 2,3-BDO in the feed composition.

Table 4

The experimental distribution coefficients and selectiviy for the extraction of 2,3-BDO at 313.15 K and atmospheric pressure is presented. Further the standard deviation corresponding to a 95 % confidence intervall is documented.

System	$D_{2,3-BDO}$	$\sigma_{K,\ 2,3-BDO}$	$S_{2,3-BDO}$	$\sigma_{S,\ 2,3-BDO}$
Menthol	0.10083	0.01397	5.34847	0.81525
	0.11072	0.01284	4.96729	0.64111
	0.11761	0.01604	4.69715	0.69642
	0.12311	0.01618	4.58802	0.65068
	0.13895	0.02221	4.60833	0.78405
	0.15549	0.0159	4.86532	0.54894
Thymol	0.54724	0.0308	13.75492	0.90512
	0.56322	0.0488	12.72631	1.18576
	0.57785	0.04085	11.94386	0.90133
	0.60302	0.03852	11.10229	0.76152
	0.62618	0.03673	10.34707	0.65959
	0.6595	0.04261	9.72132	0.66651
Carvacrol	0.60497	0.08493	14.43383	2.10653
	0.58115	0.07784	12.30192	1.68646
	0.58085	0.08308	11.06347	1.63638
	0.58517	0.07917	10.31700	1.41663
	0.60511	0.08316	9.43554	1.31698
	0.62359	0.08822	8.86192	1.26704

dew point line is given in Fig. 4.

Menthol is the terpenoid with the lowest boiling point (489.15 K) which is still approximately 36 K higher than the boiling point of 2,3-BDO. Despite the large difference in boiling points, separation of 2,3-BDO from menthol via distillation is not feasible due to low relative volatility at high contents of 2,3-BDO. Further, the bubble point line of menthol could not be correlated satisfactory by the NRTL-model, due to its very unusual form (measurement errors are possible, but in fractional distillation experiments no purity higher than 96 % was achieved). Hence, menthol was not considered as solvent in process evaluation.

The boiling point lines of thymol and carvacrol were correlated successfully and the corresponding VLEs indicate that separation of the binary systems can be achieved via rectification. Based on the regressed NRTL parameters, the extraction-distillation processes for the separation of 2,3-BDO from water using different solvents were assessed as described in Section 2.5. In Fig. 5 the SXD for the purification of 2,3-BDO resulting from processes taken from literature (distillation and extraction-distillation) are presented. The benchmark process is based exclusively on distillation leading to a SXD of 9.39 kJ g^{-1} (grey bar), corresponding to the benchmark process from previous work [35]. Further, the SXD of three solvents assessed in literature (isobutanol, 1-butanol, and oleyl alcohol) are presented as blue bars. In comparison

Table 5
NRTL paramters for correlation of ternary LLE data.

LLE	Component *i*	Component *j*	a_{ij}	a_{ji}	b_{ij} / K	b_{ji} / K	α_{ij}
Menthol	H2O	2,3-BDO	0	0	−2272.4864	−139.6155	0.3
	H2O	Menthol	6.6757	0.0155	749.728	814.657	0.3
	2,3-BDO	Menthol	0	0	1525.5668	−2499.8804	0.3
Thymol	H2O	2,3-BDO	0	0	−1576.2451	−171.8844	0.3
	H2O	Thymol	5.6492	0.4639	582.256	338.552	0.3
	2,3-BDO	Thymol	0	0	888.1685	−2418.3827	0.3
Carvacrol	H2O	2,3-BDO	0	0	−1841.1975	−133.3636	0.3
	H2O	Carvacrol	5.94033	0.12388	561.158	462.864	0.3
	2,3-BDO	Carvacrol	0	0	362.1483	−2497.2367	0.3

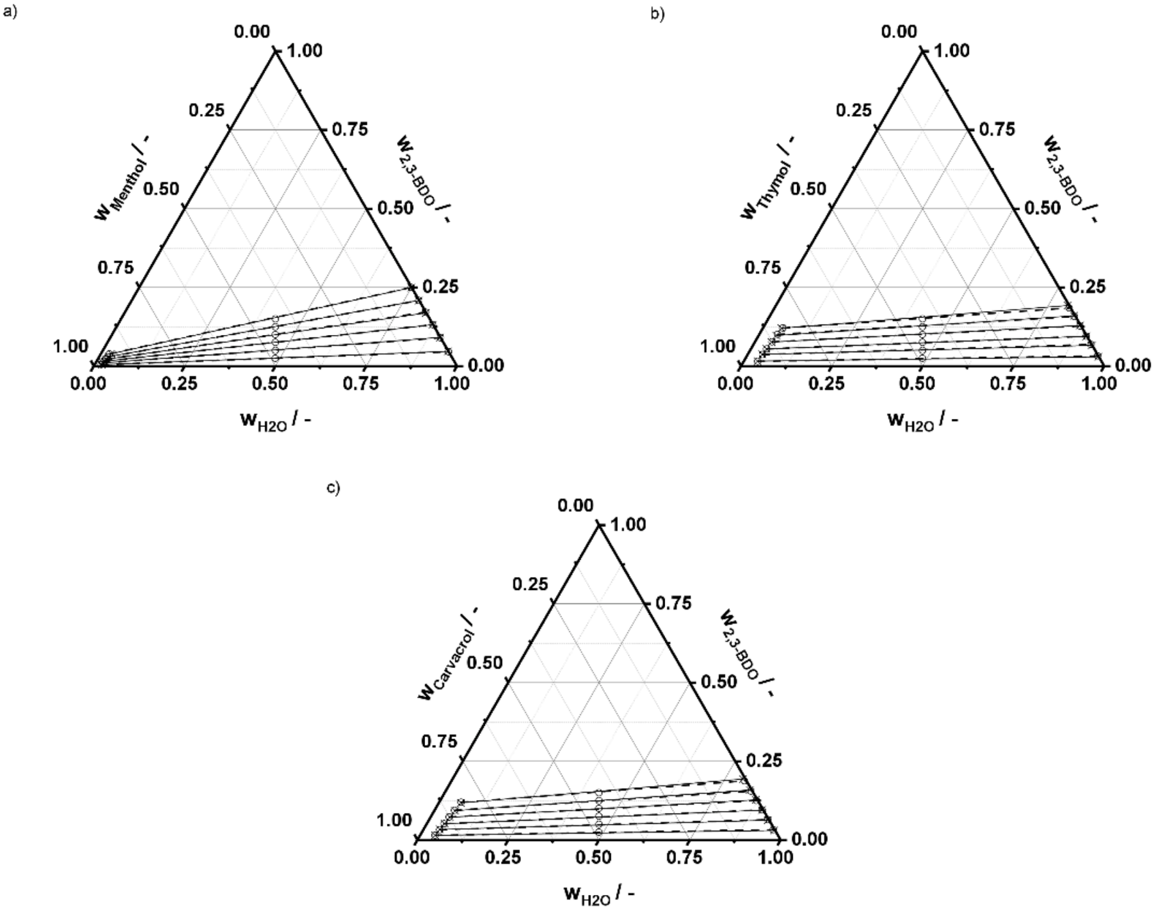

Fig. 3. Ternary diagrams of the mass fraction of the extraction systems consisting of water, 2,3-BDO, and menthol (a), thymol (b), or carvacrol (c) at 313.15 K. Open circles with dashed line indicate experimental tie-line data and black cross with straight line correspond to the correlation using the NRTL model.

to the benchmark process, the SXD resulting from extraction-distillation processes using short-chain alcohols as solvents is reduced. The short-chain alcohols isobutanol and 1-butanol both show similarly high distribution coefficients and low selectivity as described previously, which lead to similar SXD (isobutanol: 7.48 kJ g^{-1}, 1-butanol: 6.95 kJ g^{-1}). Since both, isobutanol and 1-butanol, are low-boiling solvents compared to 2,3-BDO, large amounts of solvent as well as co-extracted water are evaporated in distillation. Further, the high cross-solubility of the short-chain alcohols in water makes the recovery of the alcohols from the raffinate stream a necessity. These drawbacks in extraction-distillation processes using short-chain alcohols as solvents lead to only minor reduction of the SXD compared to the benchmark process. In the extraction-distillation process using oleyl alcohol as the solvent 2,3-BDO is the low boiling component. This leads to a significantly reduced SXD (5.38 kJ g^{-1}), since only the small product fraction instead of the large solvent excess has to be evaporated. Further, the extraction-distillation process using oleyl alcohol as solvent benefits from acceptable distribution coefficients and high selectivity of the solvent for 2,3-BDO. Very little amounts of water are co-extracted, leading to simplification of the downstream process. The novel solvents evaluated within this study (thymol and carvacrol) are presented in green bars. The SXD of thymol and carvacrol are similar (5.14 kJ g^{-1} and 5.49 kJ g^{-1} respectively) and in the same order of magnitude of the SXD in the oleyl alcohol process and in the case of thymol, the SXD is even smaller than for oleyl alcohol. Considering that the distribution coefficients of the terpenoids are higher than the ones from oleyl alcohol but the selectivity is lower and the resulting SXD is in the same range as oleyl alcohol, terpenoids represent a trade-off of the performance indicators for solvents in extraction.

Overall, the benefits of high-boiling solvents concerning the SXD are

Table 6
Experimental boiling point data for the binary systems consisting of 2,3-BDO and a terpenoid (menthol, thymol, carvacrol) at atmospheric pressure (99.07 kPa, the uncertainty in pressure is $u(p) = 0.9$ kPa. Standard deviations are representing the 95 % confidence intervall.

$x_{2,3-\mathrm{BDO}}$/mol mol^{-1}[a]	T_b^{Menthol} / K	σ / K	T_b^{Thymol} / K	σ / K	$T_b^{\mathrm{Carvacrol}}$ / K	σ / K
0	489.13	0.26	505.65	0.07	512.02	1.74
0.1	482.37	2.17	495.34	0.32	502.16	1.73
0.2	475.06	0.73	485.42	0.94	492.24	2.23
0.3	466.81	0.77	476.86	0.68	485.18	2.04
0.4	462.52	1.01	471.27	0.29	478.53	0.64
0.5	460.63	0.43	467.77	0.91	473.60	1.31
0.6	458.98	0.33	464.14	0.81	468.12	1.25
0.7	457.35	0.78	460.95	1.01	464.68	0.63
0.8	455.63	0.42	457.84	0.82	461.26	1.20
0.9	454.72	0.44	455.80	0.73	456.93	1.66
1	453.56	0.33	453.45	0.35	454.23	2.10

[a] The uncertainty of the mole fractions of 2,3-BDO results from the weighing error and triplicates and is given as $u(x_{2,3-\mathbf{BDO}}) \leq 0.001$.

Table 7
Comparison of experimental boiling points from this work and literature.

Component	T_b / K in this work	T_b / K in literature	Source	Deviation from this work / K
2,3-BDO	453.75	453.13	[44]	0.62
Menthol	489.13	489.6	[45]	0.47
Thymol	505.65	505.03	[46]	0.62
Carvacrol	512.02	510.45	[47]	1.57

demonstrated via process assessment, while the trade-off between distribution coefficient and selectivity is discussed. The terpenoids investigated in this work represent solvents with moderate selectivity as well as distribution coefficient, making them competitive solvents in process design that were advantageous over the polar short chain alcohols with high distribution coeffcients and comparable to the highly selective solvent oleyl alcohol. The trade-off between higher distribution coefficients and lower selectivity has to be evaluated for the specific case study of interest. Hence, we conclude that terpenoids are promising solvents for process design, which need to be investigated in depth in future and should be included in traditional solvent screening approaches.

Table 8
Antoine parameters to calculate the pure component vapor pressure of 2,3-BDO, menthol, thymol, and carvacrol are taken from literature.

Component	A	B	C	Source
2,3-BDO	7.9516	2445.3	−42.55	[44]
Menthol	6.30127	1690.923	−94.49	[44]
Thymol	5.29	2522.33	−28.58	[46]
Carvacrol	5.34179	2549.857	−32.705	[46]

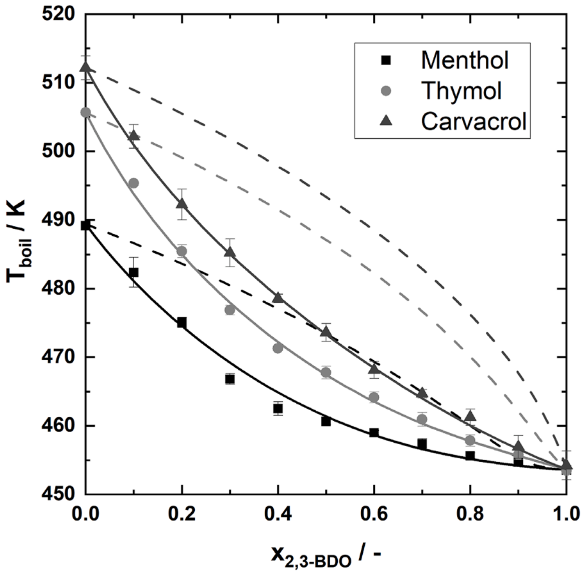

Fig. 4. Binary boiling point data of 2,3-BDO and terpenoids (menthol, thymol, carvacrol). The experimental boiling points (menthol: black squares, thymol: light grey circles, carvacrol: dark grey triangles) and standadrd deviations are presented. The experimental boiling points are correlated using the NRTL model. The corresponding bubble point lines are presented as full lines and the calculated dew point lines are presented as dashed lines.

4. Conclusion

Three terpenoids (menthol, thymol, and carvacrol) were investigated as solvents for the extraction of 2,3-butanediol from water. Liquid-liquid equilibrium data was derived and the relevant performance parameters distribution coefficient and selectivity were presented and discussed in the light of previously published solvents for the separation of 2,3-butanediol from water. While menthol has low distribution coefficients (0.1 –0.16), the aromatic terpenoids thymol and caravcrol have similar distribution coefficients in the range between 0.55 to 0.66 and selectivities from 8.47 to 12. In comparison to published solvents the terpenoids can be classified as solvents with moderate distribution coefficents and selectivies for the separation of 2,3-butanediol from water. To model and evaluate the proposed extraction-distillation process for the separation of 2,3-butanediol from water, the gathered liquid-liquid equilibrium data was correlated using the NRTL model and the NRTL parameters were documented. Further, boiling point data for the binary systems consisting of 2,3-butanediol and the three terpenoids was measured using differential scanning calorimetry. The boiling point data was correlated using the NRTL model and the vapor-liquid equilibrium data was derived to design and assess the destillation sequence in the proposed extraction-distillation process. While thymol and carvacrol can be easily separated from 2,3-butanediol via distillation, menthol shows a tangent-pinch-azeotrop with 2,3-butanediol prohibiting easy and energy efficient separation of the mixture. Hence, only the

Table 9
NRTL paramters for correlation of binary VLE data.

VLE	Component *i*	Component *j*	a_{ij}	a_{ji}	b_{ij} / K	b_{ji} / K	α_{ij}
Menthol	H2O	2,3-BDO	−0.0755	−0.0533	938.639	−325.453	0.3
	H2O	Menthol	6.6757	0.0155	749.728	814.657	0.3
	2,3-BDO	Menthol	0	0	1145.52	−492.95	0.3
Thymol	H2O	2,3-BDO	−0.0755	−0.0533	938.639	−325.453	0.3
	H2O	Thymol	5.6492	0.4639	582.256	338.552	0.3
	2,3-BDO	Thymol	0	0	1002.22	−561.37	0.3
Carvacrol	H2O	2,3-BDO	−0.0755	−0.0533	938.639	−325.453	0.3
	H2O	Carvacrol	5.94033	0.12388	561.158	462.864	0.3
	2,3-BDO	Carvacrol	0	0	457.69	−494.93	0.3

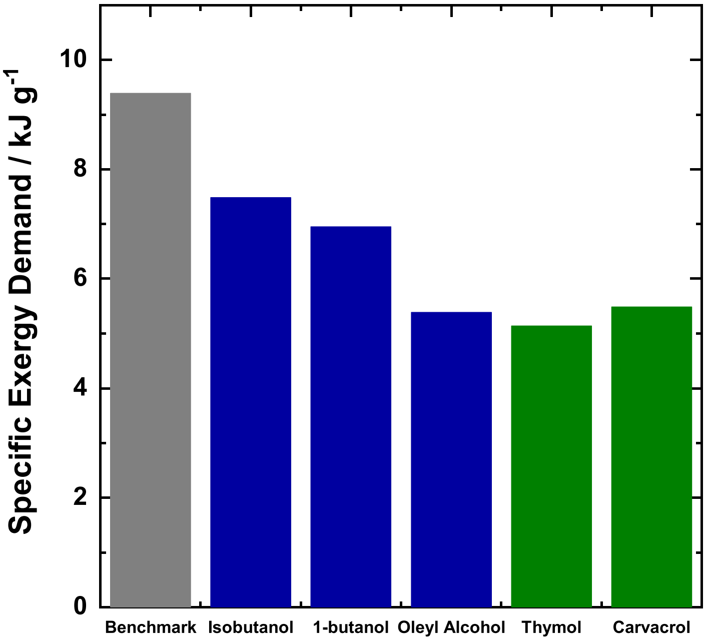

Fig. 5. Specific exergy demands for the sepration of 2,3-BDO from water in a benchmark distillation process (grey bar), several extraction-distillation processes using different solvents from literature (blue bars), and extraction-distillation processes using terpenoids (green bars).

extraction-distillation processes for the separation of 2,3-butanediol from water using thymol and carvacrol as solvents were assessed in terms of specific exergy demand. To compare the investigated terpenoids, the specific exergy demands of a distillation-based benchmark process and published extraction-distillation processes using three different solvents (1-butanol, isobutanol, and oleyl alcohol) are documented and discussed. The presented terpenoids benefit from a trade-off of high distribution coefficients and selectivity and were found to be comparable to oleyl alcohol. It can be concluded that terpenoids have the potential to make extraction-distillation processes more efficient and that they should be included into solvent screening approaches as promising green new solvents.

CRediT authorship contribution statement

William Graf von Westarp: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Janik Hense:** Writing – review & editing, Methodology, Conceptualization. **Moritz Haas:** Methodology, Writing – review & editing. **Andreas Jupke:** Writing – review & editing, Project administration, Funding acquisition.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2025.114572.

Data availability

Data will be made available on request.

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