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The solvent miscibility table updated: miscibility and potential applications of green solvents

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Green solvents play a central role in the design of more sustainable chemical processes. Among the properties influencing solvent selection, miscibility is important, especially during the work-up and analysis steps. However, traditional miscibility tables are limited in scope as they have not been updated with emerging green solvents. In this study, the miscibility of 28 green solvents was evaluated visually and the results were presented in an updated miscibility table. The choice of solvents was based on the CHEM21 solvent selection guide and included four additional solvents that were not initially included based on their potential synthetic route from biomass. Nine traditional hazardous solvents were included for comparison and to facilitate potential substitution strategies, but in general, solvents that are known to be toxic and/or facing restrictions were not included to disincentivise their use. The selection criteria for the solvents were outlined, and illustrative application examples for both miscible and immiscible solvent pairs were provided to support the practical application of green solvents.

Green foundation

1. It is well established that solvent substitution can help reduce the environmental impact of the chemical industry, but data that can inform and direct this shift are lacking. This work delivers an actionable solvent selection tool that supports the direct replacement of hazardous solvents with greener alternatives, accelerating the transition to safer, more sustainable chemical processes.
2. We mapped the miscibility of 406 binary solvent pairs involving 28 green solvents and nine conventional benchmarks. This experimentally validated dataset enables informed solvent substitution, avoiding trial-and-error and reducing toxic solvent use at scale in an easy-to-use format.
3. The work is the first part of a body of work that can be expanded to include temperature-dependent behaviour and incorporate as-of-yet-undiscovered green solvents as they are developed. Integration of this tool with LCA data and digital solvent selection tools would maximise industrial impact.

Introduction

Solvents are widely used throughout the chemical industry, often accounting for at least 50% of the total mass of chemicals used.[1–4] They can be implemented as reaction media to solubilise reactants and influence the reaction kinetics, thermodynamics, yields, and product distribution.[5] They also play a major role in purification processes such as recrystallization, chromatography, and extractions (liquid–liquid and liquid–solid).[5] Solvents are selected for an application based on their different physicochemical properties (boiling point, viscosity, polarity, miscibility with water, *etc.*).[2,4]

The handling of common solvents often leads to health, safety and/or environmental hazards.[1,2,4,6] For example, toluene, *N*-methylpyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) are classified as toxic for reproduction and are suspected of causing harm to unborn children.[7] They also cause eye and skin irritation.[7] They are used as solvents for the production of other chemicals, notably for consumer products such as paints, coatings and textiles. Since 2018, the use of NMP and DMF has been restricted by REACH in consumer products to <0.3 wt%.[7] Toluene is under review by ECHA for its use in adhesives, spray paints and tattoo inks due to toxicity issues. The Danish and Finnish governments had already restricted its use in 2017.[7]

As such, there has been growing interest in recent years in finding alternatives to traditional solvents, commonly called "green solvents".[1,5] The "greenness" is a new parameter that must be considered in the selection of solvents, but scientists often struggle to agree on a simple definition. They can be generally characterised as solvents that reduce the environmental impact of a chemical reaction or a process that requires a reac-

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tion medium to proceed forward. More specifically, they should possess at least one green property, namely, being bio-based, environmentally benign, non-toxic and/or energy efficient.[1,5]

To help with the selection of greener solvents, different stakeholders proposed solvent selection guides, in particular GSK, Sanofi, and Pfizer.[8–10] While these guides were a significant step forward towards greener chemistry, they were specific to each company's processes and products.[1,8–10] In 2015, a European consortium called CHEM21, aiming to harmonise and broaden the scope to more general applications and users, released the "CHEM21 Solvent Selection Guide".[2] This guide provided a scoring system based on the health hazard statements (H3xx), the physical properties (*e.g.*, boiling point, flash point, and autoignition temperature) and the acute environmental toxicity (H4xx).[2] Importantly, classic as well as less-common solvents were included in this guide, divided into four categories (recommended, problematic, hazardous and highly hazardous chemicals).[2] Anticipating that new green solvents will be developed in the future, CHEM21 also developed a spreadsheet into which solvent properties could be inputted, allowing future solvents to be assigned a comparable score with existing solvents.[2]

However, the selection of a solvent also involves its physical properties, such as boiling point, viscosity, polarity and miscibility. The last parameter is particularly important, notably for the selection of suitable solvents for a work-up or as a reaction medium. Miscibility is defined as the ability of two or more substances to mix together in all proportions, forming a homogeneous solution without separating into distinct phases.[11,12]

While certain tools/software can predict the miscibility of two solvents, many subtle parameters must be considered, and ultimately, it must be tested experimentally.[13] Miscibility tables, which appeared in the 1950s, indicate the miscibility (total or partial) and the immiscibility of common solvents with each other.[13] However, to the best of our knowledge, they have not been updated since then, despite the many solvents that have since been developed, both green and non-green.

Due to this remaining gap in solvent data, chemists are still likely to choose more hazardous common solvents.[13] As such, this work aims to encourage the selection of greener solvents for liquid/liquid extractions or co-solvent precipitation by updating the miscibility table to include some of the more recently available green solvents.

Materials and methods

Acetonitrile (≥99.9%), *t*-butanol (≥99%), chloroform (99.0–99.4%), ethanol (≥99.8%), ethyl acetate (≥99.5), methanol (≥99.9%), NMP (≥99%) and toluene (≥99.7%) were supplied by Honeywell. Acetone (≥99.8%), anisole (99%), *n*-butanol (99%), *n*-butyl acetate (≥95%), cyclohexanone (≥99%), *p*-cymene (≥99%), dichloromethane (DCM) (≥99.8%), diethyl ether (≥95%), dimethyl carbonate (DMC) (99%), 2,5-dimethylfuran (99%), 1,4-dioxane (≥99%), ethyl-L-lactate (97%), gamma-valerolactone (GVL) (98%), glycerol (99%), formic acid (≥98%), isopropanol (99.5%), methyl ethyl ketone (MEK) (>99%), methyl isobutyl ketone (MIBK) (≥95%), 2-methyltetrahydrofuran (2-MeTHF) (≥99%) and tetrahydrofuran (THF) (≥99.5%) were supplied by Thermo Fisher Scientific. Acetic acid (≥99.5%) was supplied by Scientific Laboratory Supplies (SLS) Ltd. Dimethyl sulfoxide (DMSO) (≥99.9%), diethyl succinate (99%), hexane (≥97%) and Cyrene (99%) were supplied by Sigma Aldrich. 2,2,5,5-Tetramethyloxolane (TMO) (99.5%) was supplied by Addible Ltd. Propylene carbonate (99%) was supplied by Fluorochem Ltd. Isooctane (99%) was supplied by TCI EU Ltd.

All miscibility tests were carried out at room temperature. 1.0 mL of a solvent was added to a 5.0 mL glass vial using a Pasteur pipette. 1.0 mL of a second solvent was added dropwise using a Pasteur pipette and shaken. Their miscibility was visually assessed: if the two solvents formed two layers, they were classified as immiscible; if there was only one layer, they were miscible; and if the mixture formed a two-phase system only in different proportions of the solvents, the miscibility was partial, and more precise tests were conducted. Precision tests were carried out on blends that were found to be partially miscible in the screening tests. 1.0 mL of a solvent was added to a 5.0 mL glass vial using a micropipette. A micropipette was used to add 1.0 mL of a second solvent in 20.0 μL increments.

Results and discussion

The solvents included in this study are shown in Table 1. The choice of solvents was guided by published solvent selection guides and availability. In particular, the CHEM21 guide was referred to as it provides a harmonised assessment of solvent greenness based on three factors: "Safety", "Health", and "Environment", with a final "Recommendation" being assigned based on the scores of the three criteria. Recommendation categories were "Recommended", "Problematic", "Hazardous", and "Highly Hazardous".

Importantly, as the authors of the CHEM21 guide have already acknowledged, the guide does not consider certain important factors. For example, it assigns a relatively poor environmental score (7/10) to high-boiling-point solvents like propylene carbonate or gamma-valerolactone (GVL), as these are considered difficult to recycle or work up.[2] However, in some applications, solvent evaporation is not an issue, making high-boiling-point solvents more suitable. Notably, solvents like NMP and dichloromethane (DCM) receive the same score of 7/10 due to their classification as "toxic to aquatic life with long-lasting effects" (H411). These issues cannot be considered equal, as renewable energy could be used to remove high-boiling-point solvents such as propylene carbonate, negating this issue, whereas NMP is inherently damaging to the environment. Therefore, while the guide is an excellent resource and its use is recommended, the assessment result should be considered along with other factors, particularly the application and system in which the solvent is used. For this

Table 1 CHEM21 greenness assessment of new solvents

Solvent	BP (°C)	Safety score	Health score	Env. score	Ranking by default	Bio-based potential[ref.]
Acetic acid	118	3	7	3	Problematic	Yes[24–28]
Acetone	56	5	3	5	Recommended	Yes[29–32]
Acetonitrile	82	4	3	3	Problematic	Yes[33,34]
Anisole	154	4	1	5	Recommended	Yes[35]
Chloroform	61	2	7	5	Highly hazardous	No
Cyclohexanone	156	3	2	5	Problematic	Yes[36,36,37]
Cyrene	203	1	2	7	Problematic	Yes[38–41]
DCM	40	1	7	7	Hazardous	No
Diethyl ether	34	10	3	7	Highly hazardous	No
Diethyl succinate	218	1	5	7	Problematic	Yes[42–44]
2,5-Dimethylfuran	92	4	5	5	Problematic	Yes[16,45,46]
1,4-Dioxane	101	7	6	3	Hazardous	No
DMC	90	4	1	3	Recommended	Yes[47–51]
DMSO	189	1	1	5	Problematic	No
Ethanol	78	4	3	3	Recommended	Yes[38,52–55]
Ethyl acetate	77	5	3	3	Recommended	Yes[38,56–58]
Ethyl lactate	155	3	4	5	Problematic	Yes[38,59–64]
Formic acid	101	3	7	3	Problematic	Yes[24,65–68]
Glycerol	290	1	1	7	Problematic	Yes[38,69–73]
GVL	207	1	5	7	Problematic	Yes[38,74–79]
Hexane	69	8	7	7	Hazardous	No
Isooctane	99	5	2	7	Problematic	Yes[18]
Isopropanol	82	4	3	3	Recommended	Yes[80,81]
MEK	80	5	3	3	Recommended	Yes[51,82–84]
Methanol	65	4	7	5	Recommended	Yes[85–89]
2-MeTHF	80	6	5	3	Problematic	Yes[38,90,91]
MIBK	117	4	2	3	Recommended	Yes[92–94]
n-Butanol	118	3	4	3	Recommended	Yes[38,95–99]
n-Butyl acetate	126	4	2	3	Recommended	Yes[100–104]
NMP	202	1	9	7	Hazardous	Yes[105]
p-Cymene	177	4	5	5	Problematic	Yes[38,106–108]
Propylene carbonate	242	1	2	7	Problematic	Yes[109–111]
t-Butanol	82	4	3	3	Recommended	Yes[112,113]
THF	66	6	7	5	Problematic	Yes[114–116]
TMO	112	4	5	5	Problematic	Yes[117]
Toluene	111	5	6	3	Problematic	No
Water	100	1	1	1	Recommended	n/a

Table adapted from the CHEM21 solvent guide.[2] The "Bio-based potential" column shows reported synthetic routes from biomass but is not exhaustive. DMSO – dimethyl sulfoxide; DMC – dimethyl carbonate; NMP – *N*-methylpyrrolidone; GVL – gamma-valerolactone; THF – tetrahydrofuran; DCM – dichloromethane; MEK – methyl ethyl ketone; MIBK – methyl isobutyl ketone; 2-MeTHF – 2-methyltetrahydrofuran; and TMO – 2,2,5,5-tetramethyloxolane.

reason, the present study includes not only "Recommended" solvents but also some considered "Problematic" that nonetheless possess green attributes.

The bio-based origin (or potential thereof) of a solvent was an important factor, as transitioning away from petroleum-derived chemicals is more urgent than ever. As such, some solvents with established synthetic routes from biomass or atmospheric CO_2 were included despite being categorized as problematic. These were glycerol, GVL, Cyrene, diethyl succinate and propylene carbonate, all due to their high boiling points. Similarly, acetic and formic acid are corrosive, which results in a high health hazard score, but when handled appropriately, their use is manageable and so they were included. A column titled "bio-based potential" was included in Table 1, and references are provided for the proposed synthetic routes from biomass. The commercial validity of these routes was not considered, as it is beyond the scope of this work.

In addition, three solvents that were not classified at the time the guide was released were also chosen: 2,2,5,5-tetramethyloxolane (TMO), 2,5-dimethylfuran and isooctane. TMO is a new, safer alternative to toluene due to its superior predicted toxicity profile and resistance to autoxidation.[14] Although it is part of the ether family, it has similar solvation properties to hydrocarbon and aromatic solvents like heptane and toluene.[15] 2,5-Dimethylfuran is easily produced from biomass *via* 5-hydroxymethylfurfural (HMF).[16] It can have interesting solvent properties even though it is reactive under acidic conditions and has a yellow colour, making it unsuitable for certain applications.[17] Isooctane can also be produced from biomass. Global Bioenergy notably established a fermentation process of bio-based sugars to obtain isobutene.[18] In 2016, they developed a partnership with Lantmännen Aspen to convert this molecule into isooctane, for biofuel applications.[18] If hydrocarbons need to be used in a process, isooctane could thus be a better option.

These three solvents could be retrospectively assigned scores using the CHEM21 calculation spreadsheet, which is included in the SI of the solvent guide article.[2] By inputting known data into the spreadsheet for each solvent, isooctane was described as "Problematic" due to scores of 5/10, 2/10, and 7/10 in the "Safety", "Health" and "Environment" categories, respectively. As TMO and 2,5-dimethylfuran have not yet received full REACH approval, they were automatically assigned "Health" and "Environment" scores of 5 by default (this also applied to GVL, diethyl succinate and *p*-cymene). This resulted in a default ranking of "Problematic" for each of these solvents, although this classification can be significantly improved in the future once REACH registration has been achieved. Notably, TMO and 2,5-dimethylfuran would receive a "Recommended" score upon successful REACH registration (Table S1, SI).

Finally, a selection of common solvents (hexane, diethyl ether, toluene, chloroform, DCM, THF, 1,4-dioxane, NMP and methanol) was also included for comparative purposes. They were selected to represent a wide range of chemical groups and to have a broad distribution of physical properties and Hansen Solubility Parameters (HSPs) (Fig. S1, SI). Hexane is a particularly low polarity, aprotic hydrocarbon solvent; diethyl ether is a highly hazardous, volatile, low polarity ether solvent; toluene is a 'workhorse' low polarity but polarisable aromatic solvent with moderate volatility; chloroform is a low-polarity halogenated solvent that is denser than water; DCM is a volatile halogenated solvent of moderate polarity and high polarizability; 1,4-dioxane is a water miscible, volatile ether of moderate polarity aprotic solvent commonly used in organosolv biorefining; THF is a water miscible, volatile, mid polarity aprotic solvent; NMP is a dipolar aprotic amide solvent with a high boiling point; and methanol is a volatile polar protic alcohol that, while potentially bio-based, is toxic.

Table 2 shows the updated miscibility table, which includes more recently proposed greener solvents as introduced above. The IUPAC definition of miscibility is the "capability of a mixture to form a single phase over certain ranges of temperature, pressure, and composition".[11] From the point of view of a researcher in the lab, this is not particularly helpful, as most mixtures of solvents will form a single phase if the percentage of the second solvent in the total volume is sufficiently low. As such, in this work, miscibility is defined from a practical perspective to quickly aid a lab-based chemist in solvent choice for applications such as liquid–liquid extraction or co-solvent precipitation. In the updated miscibility table shown in Table 2, two solvents are:

- **Miscible** when they fully mix in any proportion at room temperature (18–20 °C).
- **Partially miscible** when they form a homogeneous solution only at certain concentrations at room temperature (18–20 °C).
- **Immiscible** when they do not mix and form a heterogeneous solution with two layers that can be observed visually at room temperature (18–20 °C).

Demixing upon nucleation is not considered in this work due to the unlimited possibilities of solutes in a dual solvent system. Similarly, mixing upon nucleation is not considered for the same reason. Furthermore, solvents that were found to be partially miscible/immiscible at room temperature in this work could potentially mix to a higher degree with increasing temperatures or pressures.[6,19] However, the table cannot be extrapolated to account for such conditions.

Experiments were carried out at room temperature (18–20 °C) and atmospheric pressure to assess the miscibility of the selected solvents. For the immiscible solvent pairs (even when refractive indices are similar), temporary turbidity, small droplets, or emulsion-like behaviour appeared while stirring but disappeared after settling, resulting usually in two distinct layers. These visual clues provided sufficient indication of phase separation under our experimental conditions. For the miscible solvent pairs, a phenomenon that could be associated with the thin-film interference effect (light reflection resulting in different colours while swirling) was often observed which gradually disappeared as the solvents interacted and fully mixed.[20,21]

The solvents were organised in Table 2 according to increasing relative energy distance (R_a) from water using HSP theory (see Table S2, SI). This roughly corresponds to a decreasing trend in polarity/hydrogen-bonding ability down the table and explains why immiscible solvent pairs tend to cluster at the edge of the table. It also means that likely replacements for a target traditional solvent should be located near the target solvent in the table.

The miscibility table was colour coded to illustrate the interaction between solvent pairs. The solvents found to be miscible were highlighted in off-white, the partially miscible in light grey and the immiscible in dark grey. The letters in the light grey correspond to a legend at the bottom that describes the concentrations at which the solvents are miscible/immiscible. The letter R indicates that the solvents reacted or interacted exothermically, as heat was released while mixing. In addition, the solvent names were colour coded according to the CHEM21 guide as described above, so greener alternatives can be quickly identified for different applications.

For example, in liquid–liquid extraction, it is necessary to use immiscible solvents to separate compounds based on their solubility in each phase. Water is typically used as one phase, so identifying an immiscible solvent to extract organic molecules is required. Table 2 highlights many green solvents which could be effective, such as TMO, dimethyl carbonate (DMC), ethyl acetate, or 2,5-dimethylfuran. They have relatively low boiling points, making them suitable as they are easy to remove in the subsequent steps.

Liquid–liquid extraction could also be applied to overcome the high boiling points of some green solvents (Cyrene, propylene carbonate, GVL, and diethyl succinate). A work-up could be facilitated by using liquid–liquid extractions. For instance, propylene carbonate is immiscible with TMO at specific ratios and is fully immiscible with methanol or isooctane. Similarly, GVL and Cyrene are immiscible with isooctane. These more volatile solvents could be used to extract target compounds, allowing easier subsequent solvent removal.

Selective precipitation is another strategy, which involves using miscible solvents in which the substrate has limited solubility. For example, water can be used in combination with Cyrene or GVL to induce precipitation. Similarly, polar, hydro-

Table 2 Updated miscibility table of green and classic solvents

	Water	Glycerol	Methanol	Ethanol	Isopropanol	*n*-Butanol	Formic acid	*t*-Butanol	Acetic Acid	Ethyl Lactate	DMSO	DMC	NMP	GVL	Acetone	1,4-Dioxane	THF	Cyrene	Acetonitrile	DCM	Diethyl Succinate	Ethyl Acetate	Anisole	MEK	n-Butyl Acetate	Cyclohexanone	Chloroform	Propylene Carbonate	2,5-Dimethylfuran	MIBK	2-MeTHF	Diethyl Ether	TMO	*p*-Cymene	Toluene	Hexane	Isooctane
🟩 Water	■	□	□	□	□	A	□	□	□	□	□	B	□	□	□	□	□	□	□	■	■	C	■	D	■	E	■	F	■	■	■	■	■	■	■	■	■
🟨 Glycerol	□	■	□	□	□	■	□	□	□	□	□	■	□	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
🟩 Methanol	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	■	G
🟩 Ethanol	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 Isopropanol	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 *n*-Butanol	A	■	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 Formic acid	□	□	□	□	□	□	■	□	□	□	R	□	□	□	□	□	R	□	□	□	□	□	□	□	□	□	□	□	R	□	R	□	□	■	■	■	■
🟩 *t*-Butanol	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 Acetic Acid	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□
🟨 Ethyl Lactate	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 DMSO	□	□	□	□	□	□	R	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	■	H	□	■	■
🟩 DMC	B	■	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟥 NMP	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	I
🟨 GVL	□	■	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■
🟩 Acetone	□	■	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟥 1,4-Dioxane	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 THF	□	■	□	□	□	□	R	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 Cyrene	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	■
🟨 Acetonitrile	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	■
🟥 DCM	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟨 Diethyl Succinate	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 Ethyl Acetate	C	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 Anisole	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 MEK	D	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□
🟩 *n*-Butyl Acetate	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□
🟨 Cyclohexanone	E	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□
🟫 Chloroform	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□
🟨 Propylene Carbonate	F	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	J	K	□	■	■
🟨 2,5-Dimethylfuran	■	■	□	□	□	□	R	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□
🟩 MIBK	■	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□
🟨 2-MeTHF	■	■	□	□	□	□	R	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□
🟫 Diethyl Ether	■	■	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□	□	□	□
🟨 TMO	■	■	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	J	□	□	□	□	■	□	□	□	□
🟨 *p*-Cymene	■	■	□	□	□	□	■	□	□	□	H	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	K	□	□	□	□	□	■	□	□	□
🟨 Toluene	■	■	□	□	□	□	■	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	■	□	□
🟥 Hexane	■	■	■	□	□	□	■	□	■	□	■	□	■	□	□	□	□	■	■	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	■	□
🟨 Isooctane	■	■	G	□	□	□	■	□	□	□	■	□	I	■	□	□	□	■	■	□	□	□	□	□	□	□	□	■	□	□	□	□	□	□	□	□	■

🟩 Recommended
🟨 Problematic
🟥 Hazardous
🟫 Highly Harzardous

■	Immiscible
X	Miscible at certain concentrations
□	Miscible
R	Reaction observed upon contact

	Immiscible if:
A	85% > n-Butanol > 4%
B	98% > DMC > 14%
C	98% > Ethyl acetate > 9%
D	91% > MEK > 29%
E	94% > Cyclohexanone > 9%
F	93% > Propylene Carbonate > 14%
G	100% > Isooctane > 32%
H	85% > n-Butanol > 4%
I	96% > Isooctane > 20%
J	86% > TMO > 39%

DMSO = Dimethyl sulfoxide
DMC = Dimethyl carbonate
NMP = *N*-Methylpyrrolidone
GVL = *gamma*-Valerolactone
THF = Tetrahydrofuran

DCM = Dichloromethane
MEK = Methyl ethyl ketone
MIBK = Methyl isobutyl ketone
2-MeTHF = 2-Methyltetrahydrofuran
TMO = 2,2,5,5-Tetramethyloxolane

gen-bonding ethanol could be used in combination with low-polarity TMO.

A particularly interesting insight obtained during this study was the partial miscibility of certain solvent pairs, which can potentially open new possibilities in purification. For example, TMO and propylene carbonate are immiscible at concentrations of 86% > TMO > 39%. This means that TMO could be used as a precipitation solvent at low or high percentages of composition or as an extraction solvent at more equal percentage compositions. The usefulness of this observation would depend on temperature, pressure and solute nucleation effects, but it can potentially be harnessed to optimise a purification system.

The updated solvent miscibility table can also be useful in suggesting solvent blends as alternatives to traditional hazardous solvents. Cyrene and glycerol are promising bio-based compounds. However, their high viscosities can limit their applicability in some processes.[22] Even small amounts of co-solvents can significantly reduce viscosity. Indeed, glycerol has a viscosity of 1500 cP at 20 °C, and the addition of 9% of water decreases it to 220 cP – a sevenfold decrease.[23] Other co-solvents may be preferable to water, as water can be difficult to remove from the reaction medium or may interfere with the reaction itself. Therefore, understanding the miscibility of these viscous solvents with less viscous alternatives becomes essential.

Conclusion

Solvent miscibility is an important criterion in the selection of solvents for a process. While miscibility tables have been developed to guide researchers, they have not been expanded to include many of the newer green solvents. This study thus aimed to address this gap by updating the solvent miscibility table to include green solvents. The green solvents were largely selected from the list of "Recommended" solvents in the Chem21 guide but include some solvents with at least a proposed synthetic route from biomass. Some classic solvents were also chosen for comparison based on their HSPs, but in general, hazardous solvents were eliminated in an effort to incentivise the use of greener solvents.

The updated table was colour coded, and solvents were ordered according to their distance from water based on Hansen Solubility Parameters. The determination of miscibility/immiscibility was carried out visually, as it aimed to aid lab-based chemists who require a quick reference for solvent miscibility. Partial miscibility required precision tests to determine solubility limits and these are provided in the legend. Finally, some potential applications of this guide for the lab researchers in the chemical industry are suggested.

While this work contributes to filling an important knowledge gap, the study is ongoing—new solvents with different and interesting properties continue to emerge, and simple experimental tests can be used to extend and update the miscibility data over time.

Author contributions

Olga Clavilier contributed to conceptualisation, formal analysis, investigation, methodology, supervision, validation, visualisation, and writing – original draft. Darragh Foy contributed to investigation. Fergal Byrne contributed to conceptualisation, formal analysis, funding acquisition, methodology, project administration, resources, supervision, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting the findings of this study are available in the SI. Supplementary information: CHEM-21 scores for new solvents, and supplementary figures showing Hansen Solubility Parameters of solvents. See DOI: **https://doi.org/10.1039/d5gc02901e**.

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References

1 F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. R. McElroy and J. Sherwood, *Sustainable Chem. Processes*, 2016, **4**, 7.
2 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2015, **18**, 288–296.
3 D. J. C. Constable, C. Jimenez-Gonzalez and R. K. Henderson, *Org. Process Res. Dev.*, 2007, **11**, 133–137.
4 J. Sherwood, H. L. Parker, K. Moonen, T. J. Farmer and A. J. Hunt, *Green Chem.*, 2016, **18**, 3990–3996.
5 P. G. Jessop, *Green Chem.*, 2011, **13**, 1391.
6 *Handbook of solvents*, ed. G. Wypych, ChemTec, Toronto, New York, 2001.
7 Search for Chemicals - ECHA, **https://echa.europa.eu/search-for-chemicals**, (accessed 31 March 2025).
8 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.
9 D. Prat, O. Pardigon, H.-W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. Ruisseau, P. Cruciani and P. Hosek, *Org. Process Res. Dev.*, 2013, **17**, 1517–1525.

10 K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, *Green Chem.*, 2008, **10**, 31–36.
11 T. I. U. of P. and A. Chemistry (IUPAC), IUPAC - miscibility (MT07230), https://goldbook.iupac.org/terms/view/MT07230, (accessed 31 March 2025).
12 W. J. Work, K. Horie, M. Hess and R. F. T. Stepto, *Pure Appl. Chem.*, 2004, **76**, 1985–2007.
13 W. M. Jackson and J. S. Drury, *Ind. Eng. Chem.*, 1959, **51**, 1491–1493.
14 Addible, https://www.addible.eu/, (accessed 1 April 2025).
15 F. P. Byrne, W. M. Hodds, S. Shimizu, T. J. Farmer and A. J. Hunt, *J. Cleaner Prod.*, 2019, **240**, 118175.
16 N. A. Endot, R. Junid and M. S. S. Jamil, *Molecules*, 2021, **26**, 6848.
17 E. J. Stamhuis, W. Drenth and H. Van Den Berg, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 167–176.
18 Global Bioenergies – Acteur de la transition environnementale, https://www.global-bioenergies.com/, (accessed 31 March 2025).
19 C. M. Hansen, in *Hansen solubility parameters: a user's handbook*, CRC Press, Boca Raton, 2nd edn, 2007.
20 Thin Film Interference | Harvard Natural Sciences Lecture Demonstrations, https://sciencedemonstrations.fas.harvard.edu/presentations/thin-film-interference, (accessed 20 August 2025).
21 3.5, https://phys.libretexts.org/Bookshelves/University_Physics/University_Physics_(OpenStax)/University_Physics_III_-_Optics_and_Modern_Physics_(OpenStax)/03%3A_Interference/3.05%3A_Interference_in_Thin_Films, (accessed 20 August 2025).
22 C. Sullivan, Y. Zhang, G. Xu, L. Christianson, F. Luengo, T. Halkoski and P. Gao, *Green Chem.*, 2022, **24**, 7184–7193.
23 K. Takamura, H. Fischer and N. R. Morrow, *J. Pet. Sci. Eng.*, 2012, **98–99**, 50–60.
24 Y. Chen, Y. Yang, X. Liu, X. Shi, C. Wang, H. Zhong and F. Jin, *Mol. Catal.*, 2023, **545**, 113199.
25 J. L. Martín-Espejo, J. Gandara-Loe, J. A. Odriozola, T. R. Reina and L. Pastor-Pérez, *Sci. Total Environ.*, 2022, **840**, 156663.
26 D. Kiefer, M. Merkel, L. Lilge, M. Henkel and R. Hausmann, *Trends Biotechnol.*, 2021, **39**, 397–411.
27 E. Budsberg, R. Morales-Vera, J. T. Crawford, R. Bura and R. Gustafson, *Biotechnol. Biofuels*, 2020, **13**, 154.
28 Q. Qian, J. Zhang, M. Cui and B. Han, *Nat. Commun.*, 2016, **7**, 11481.
29 B. O. Armijo-Galdames and J. C. Sadler, *ACS Sustainable Chem. Eng.*, 2024, **12**, 7748–7756.
30 F. E. Liew, R. Nogle, T. Abdalla, B. J. Rasor, C. Canter, R. O. Jensen, L. Wang, J. Strutz, P. Chirania, S. De Tissera, A. P. Mueller, Z. Ruan, A. Gao, L. Tran, N. L. Engle, J. C. Bromley, J. Daniell, R. Conrado, T. J. Tschaplinski, R. J. Giannone, R. L. Hettich, A. S. Karim, S. D. Simpson, S. D. Brown, C. Leang, M. C. Jewett and M. Köpke, *Nat. Biotechnol.*, 2022, **40**, 335–344.
31 H. Yang, B. Huang, N. Lai, Y. Gu, Z. Li, Q. Ye and H. Wu, *Microb. Cell Fact.*, 2019, **18**, 6.
32 C. P. Rodrigues, P. D. C. Zonetti and L. G. Appel, *Chem. Cent. J.*, 2017, **11**, 30.
33 A. Tripodi, E. Bahadori, D. Cespi, F. Passarini, F. Cavani, T. Tabanelli and I. Rossetti, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5441–5451.
34 L. Mei, C. Feng, Y. Wang, Q. Yu, W. Xin, W. Chu, Y. Wang, X. Zhu, S. Liu, H. Wang and L. Xu, *Ind. Eng. Chem. Res.*, 2023, **62**, 14234–14243.
35 Y. Ma, S. Conroy, A. Shaw, I. M. Alliati, B. F. Sels, X. Zhang and X. Tu, *JACS Au*, 2023, **3**, 3101–3110.
36 Q. Meng, M. Hou, H. Liu, J. Song and B. Han, *Nat. Commun.*, 2017, **8**, 14190.
37 S. Gundekari, B. Biswas, M. Varkolu, K. Srinivasan and T. Bhaskar, in *Biomass, Biofuels, Biochemicals*, ed. T. Bhaskar and A. Pandey, Elsevier, 2021, pp. 301–327.
38 F. G. Calvo-Flores, M. J. Monteagudo-Arrebola, J. A. Dobado and J. Isac-García, *Top. Curr. Chem.*, 2018, **376**, 18.
39 Y. Wang, M. Dai, G. Luo, J. Fan, J. H. Clark and S. Zhang, *Chemistry*, 2023, **5**, 2322–2346.
40 X. Meng, Y. Pu, M. Li and A. J. Ragauskas, *Green Chem.*, 2020, **22**, 2862–2872.
41 J. E. Camp, *ChemSusChem*, 2018, **11**, 3048–3055.
42 A. Orjuela, A. Kolah, X. Hong, C. T. Lira and D. J. Miller, *Sep. Purif. Technol.*, 2012, **88**, 151–162.
43 C. S. López-Garzón, M. Ottens, L. A. M. van der Wielen and A. J. J. Straathof, *Chem. Eng. J.*, 2012, **200–202**, 637–644.
44 L. Daviot, T. Len, C. S. K. Lin and C. Len, *Catalysts*, 2019, **9**, 272.
45 X. P. Nguyen, A. T. Hoang, A. I. Ölçer, D. Engel, V. V. Pham and S. K. Nayak, *Fuel Process. Technol.*, 2021, **214**, 106687.
46 A. S. Nagpure, N. Lucas and S. V. Chilukuri, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2909–2916.
47 K. Kohli, B. K. Sharma and C. B. Panchal, *Energies*, 2022, **15**, 5133.
48 S.-H. Pyo, J. H. Park, T.-S. Chang and R. Hatti-Kaul, *Curr. Opin. Green Sustainable Chem.*, 2017, **5**, 61–66.
49 C. Choomwattana, A. Chaianong, W. Kiatkittipong, P. Kongpanna, A. T. Quitain and S. Assabumrungrat, *Chem. Eng. Process.*, 2016, **107**, 80–93.
50 H. Ohno, M. Ikhlayel, M. Tamura, K. Nakao, K. Suzuki, K. Morita, Y. Kato, K. Tomishige and Y. Fukushima, *Green Chem.*, 2021, **23**, 457–469.
51 A. R. Varma, B. S. Shrirame, S. Gadkari, K. R. Vanapalli, V. Kumar and S. K. Maity, *Chem. Eng. J.*, 2024, **489**, 151297.
52 Y. Li, H. Sun, Y. Zhang, X. Wang, M. Gao, X. Sun and Q. Wang, *Ind. Crops Prod.*, 2024, **212**, 118351.
53 J. R. Melendez, B. Mátyás, S. Hena, D. A. Lowy and A. El Salous, *Renewable Sustainable Energy Rev.*, 2022, **160**, 112260.
54 S. Sharma, S. M. Arumugam, S. Kumar, S. Mahala, B. Devi and S. Elumalai, in *Biomass, Biofuels, Biochemicals*, ed. H. Li, S. Saravanamurugan, A. Pandey and S. Elumalai, Elsevier, 2022, pp. 95–116.

55 N. Yan and S. Ding, *Trends Chem.*, 2019, **1**, 457–458.
56 S. Zhang, F. Guo, W. Yan, W. Dong, J. Zhou, W. Zhang, F. Xin and M. Jiang, *Appl. Microbiol. Biotechnol.*, 2020, **104**, 7239–7245.
57 J. Xiao, P. An, H. Liu, M. Ji, Y. Wang, J. Fu, J. Rizkiana, Y. Li, G. Xu and L. Shi, *Chem. Eng. Process.*, 2025, **209**, 110199.
58 C. Löser, C. Kupsch, T. Walther and A. Hoffmann, *Eng. Life Sci.*, 2021, **21**, 137–153.
59 C. S. M. Pereira, V. M. T. M. Silva and A. E. Rodrigues, *Green Chem.*, 2011, **13**, 2658–2671.
60 R. A. Tusso-Pinzón, A. Castillo-Landero, L. G. Matallana-Pérez and A. Jiménez-Gutiérrez, *Chem. Eng. Process.*, 2020, **154**, 108041.
61 N. Asthana, A. Kolah, D. T. Vu, C. T. Lira and D. J. Miller, *Org. Process Res. Dev.*, 2005, **9**, 599–607.
62 P. Stipsitz, M. Mandl and M. Harasek, *Open Res. Eur.*, 2021, **1**, 82.
63 P. Stipsitz, M. Mandl and M. Harasek, *Open Res. Eur.*, 2021, **1**, 82.
64 X. Li, X. Zhang, H. Jian, X. Xu and Y. Xi, *ACS Omega*, 2019, **4**, 16009–16015.
65 X. Chen, Y. Liu and J. Wu, *Mol. Catal.*, 2020, **483**, 110716.
66 D. A. Bulushev and J. R. H. Ross, *ChemSusChem*, 2018, **11**, 821–836.
67 F. Valentini, V. Kozell, C. Petrucci, A. Marrocchi, Y. Gu, D. Gelman and L. Vaccaro, *Energy Environ. Sci.*, 2019, **12**, 2646–2664.
68 D. Voß, M. Kahl and J. Albert, *ACS Sustainable Chem. Eng.*, 2020, **8**, 10444–10453.
69 M. Pagliaro and M. Rossi, *The Future of Glycerol: New Uses of a Versatile Raw Material*, The Royal Society of Chemistry, 2008, pp. 1–17.
70 Z. Y. Ben, H. Samsudin and M. F. Yhaya, *Eur. Polym. J.*, 2022, **175**, 111377.
71 H. W. Tan, A. R. Abdul Aziz and M. K. Aroua, *Renewable Sustainable Energy Rev.*, 2013, **27**, 118–127.
72 C. A. G. Quispe, C. J. R. Coronado and J. A. Carvalho Jr, *Renewable Sustainable Energy Rev.*, 2013, **27**, 475–493.
73 A. I. Eghbili, B. A. Bader, B. Y. Bulgasem, S. G. Fnaish, I. S. Ibrahem and F. F. Mohamed, *J. Chem. Chem. Sci.*, 2020, **10**, 277–286.
74 S. Dutta, I. K. M. Yu, D. C. W. Tsang, Y. H. Ng, Y. S. Ok, J. Sherwood and J. H. Clark, *Chem. Eng. J.*, 2019, **372**, 992–1006.
75 T. Raj, K. Chandrasekhar, R. Banu, J.-J. Yoon, G. Kumar and S.-H. Kim, *Fuel*, 2021, **303**, 121333.
76 Z. Zhang, *ChemSusChem*, 2016, **9**, 156–171.
77 X. Kong, S. Wu, Y. Jin, L. Liu and J. Liu, *Energy Fuels*, 2017, **31**, 12232–12237.
78 A. Chauhan, R. Bal and R. Srivastava, *Energy Fuels*, 2024, **38**, 5998–6011.
79 M. Khalid, M. Granollers Mesa, D. Scapens and A. Osatiashtiani, *ACS Sustainable Chem. Eng.*, 2024, **12**, 16494–16517.
80 J. Kato, T. Matsuo, K. Takemura, S. Kato, T. Fujii, K. Wada, Y. Nakamichi, M. Watanabe, Y. Aoi, T. Morita, K. Murakami and Y. Nakashimada, *Biotechnol. Biofuels Bioprod.*, 2024, **17**, 13.
81 X. Shi, J. Chang, M. Kim, M.-E. Lee, H.-Y. Shin and S.-O. Han, *Bioresour. Technol.*, 2024, **396**, 130416.
82 D. Penner, C. Redepenning, A. Mitsos and J. Viell, *Ind. Eng. Chem. Res.*, 2017, **56**, 3947–3957.
83 M.-X. Shen, C.-Q. Deng, J. Yang and J. Deng, *Green Chem.*, 2024, **26**, 10290–10298.
84 Z. Parhizi, M. Nayebi, E. Mohammadzadeh and R. Torfi, *J. Chem.*, 2022, **2022**, 8448260.
85 P. Gautam, Neha, S. N. Upadhyay and S. K. Dubey, *Fuel*, 2020, **273**, 117783.
86 M. Thakare, S. Pandit, C. Pandit, S. Ray, A. M. Alkahtani, K. F. Alabbosh, N. Ranjan, S. J. Geetha and S. J. Joshi, *Biocatal. Agric. Biotechnol.*, 2024, **57**, 103061.
87 J. Lu, W. Zhang, C. S. K. Lin, Y. Jiang and F. Xin, in *Handbook of Biofuels Production (Third Edition)*, ed. R. Luque, C. S. K. Lin, K. Wilson and C. Du, Woodhead Publishing, 2023, pp. 231–252.
88 S. Khan, G. Jain, A. Srivastava, P. C. Verma, V. Pande, R. S. Dubey, M. Khan, S. Haque and S. Ahmad, *Sustainable Mater. Technol.*, 2023, **38**, e00729.
89 S. Subudhi, K. Saha, D. Mudgil, P. K. Sarangi, R. K. Srivastava and M. K. Sarma, *Environ. Sci. Pollut. Res.*, 2025, **32**, 7432–7448.
90 V. Pace, P. Hoyos, L. Castoldi, P. Domínguez de María and A. R. Alcántara, *ChemSusChem*, 2012, **5**, 1369–1379.
91 H. H. Khoo, L. L. Wong, J. Tan, V. Isoni and P. Sharratt, *Resour., Conserv. Recycl.*, 2015, **95**, 174–182.
92 F. Wang, L. Xu, J. Huang, S. Wu, L. Yu, Q. Xu and Y. Fan, *Mol. Catal.*, 2017, **432**, 99–103.
93 A. A. Al-Rabiah, R. R. Alkathiri and A. A. Bagabas, *Processes*, 2022, **10**, 1992.
94 G. Torres, C. R. Apesteguía and J. I. Di Cosimo, *Appl. Catal., A*, 2007, **317**, 161–170.
95 J. Zhang, S. Wang and Y. Wang, in *Advances in Bioenergy*, ed. Y. Li and X. Ge, Elsevier, 2016, vol. 1, pp. 1–68.
96 Y. Jiang, J. Liu, W. Jiang, Y. Yang and S. Yang, *Biotechnol. Adv.*, 2015, **33**, 1493–1501.
97 Y. Liu, Y. Yuan, G. Ramya, S. M. Singh, N. T. L. Chi, A. Pugazhendhi, C. Xia and T. Mathimani, *Fuel*, 2022, **327**, 125166.
98 Z. Lin, W. Cong and J. Zhang, *Fermentation*, 2023, **9**, 847.
99 S. Abel, J. Tesfaye, L. Gudata, N. Nagaprasad, K. Subramanian, M. Mani, R. Shanmugam, L. P. Dwarampudi, A. Roy, B. Stalin and R. Krishnaraj, *Biomass Convers. Biorefin.*, 2022, DOI: **10.1007/s13399-022-02749-x**.
100 A. Arpornwichanop, K. Koomsup, W. Kiatkittipong, P. Praserthdam and S. Assabumrungrat, *J. Taiwan Inst. Chem. Eng.*, 2009, **40**, 21–28.
101 S. H. Ali, O. Al-Rashed, F. A. Azeez and S. Q. Merchant, *Bioresour. Technol.*, 2011, **102**, 10094–10103.
102 G. Li, C. Wang, C. Guang and Z. Zhang, *Sep. Purif. Technol.*, 2020, **235**, 116163.

103 Y. Lv, Y. Jiang, J. Lu, H. Gao, W. Dong, J. Zhou, W. Zhang, F. Xin and M. Jiang, *Biotechnol. Biofuels*, 2021, **14**, 203.

104 H. Wang, W. Liu, L. Gao, Y. Lu, E. Chen, Y. Xu and H. Liu, *Bioprocess Biosyst. Eng.*, 2020, **43**, 593–604.

105 T. M. Lammens, M. C. R. Franssen, E. L. Scott and J. P. M. Sanders, *Green Chem.*, 2010, **12**, 1430–1436.

106 M. A. Martín-Luengo, M. Yates, M. J. Martínez Domingo, B. Casal, M. Iglesias, M. Esteban and E. Ruiz-Hitzky, *Appl. Catal., B*, 2008, **81**, 218–224.

107 M. Salgado-Ramos, S. Tabasso, E. C. Gaudino and G. Cravotto, *Ind. Eng. Chem. Res.*, 2024, **63**, 7507–7518.

108 H.-H. Lin, D. Mendez-Perez, J. Park, X. Wang, Y. Cheng, J. Huo, A. Mukhopadhyay, T. S. Lee and B. H. Shanks, *Biotechnol. Biofuels Bioprod.*, 2022, **15**, 126.

109 S. Ghorai, D. Nanda, A. Ghosh and P. S. Dash, *Mol. Catal.*, 2024, **553**, 113720.

110 A. I. Adeleye, D. Patel, D. Niyogi and B. Saha, *Ind. Eng. Chem. Res.*, 2014, **53**, 18647–18657.

111 G. Zhang, N. Xu, B. Sun, F. Sun, X. Liu, W. Xu and Z. Yang, *Ind. Eng. Chem. Res.*, 2024, **63**, 17148–17157.

112 J. Brzeski and P. Skurski, *Heliyon*, 2019, **5**, e02133.

113 J. Cheng, N. Yan, J. Li, M. Ye, W. Zhou and Q. Liang, *CN Pat.*, CN1108283C, 2003.

114 Y. Zhu, J. Yang, F. Mei, X. Li and C. Zhao, *Green Chem.*, 2022, **24**, 6450–6466.

115 J.-P. Lange and S. H. Wadman, *ChemSusChem*, 2020, **13**, 5329–5337.

116 V. M. Shinde, G. N. Patil, A. Katariya and Y. S. Mahajan, *Chem. Eng. Process.*, 2015, **95**, 241–248.

117 F. P. Byrne, J. H. Clark, C. Angelici, E. de Jong and T. J. Farmer, *Sustainable Chem.*, 2021, **2**, 392–406.