Biobased eutectic solvents– a natural catch 22

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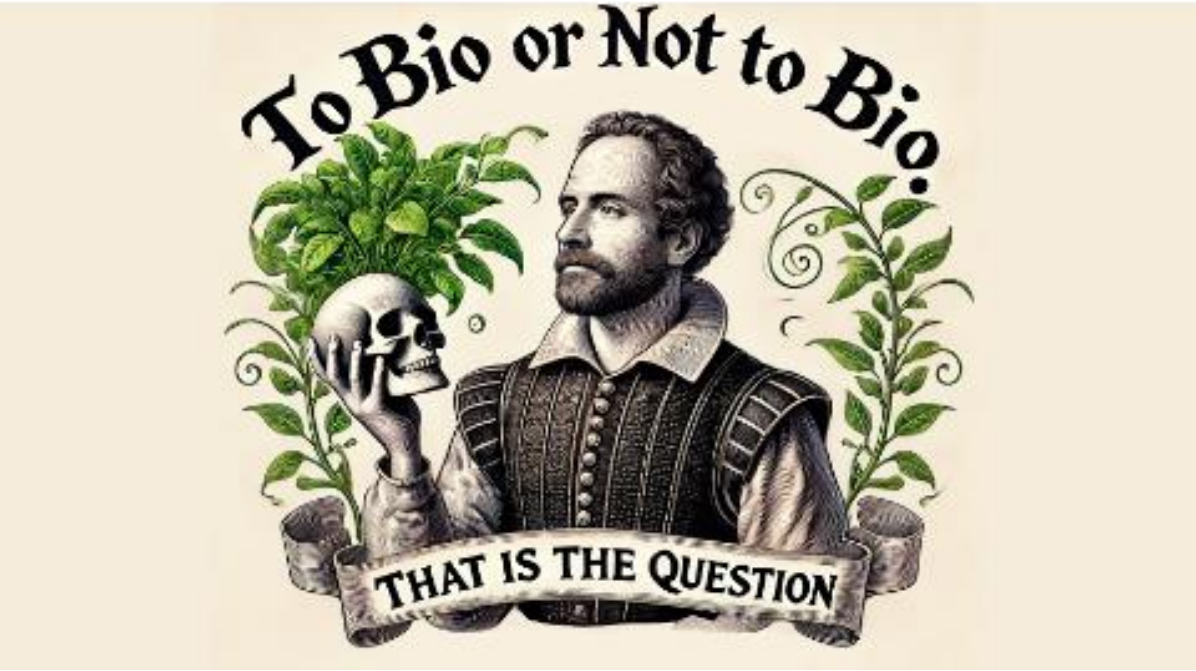

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As a consequence of mitigation measures to address fossil resources depletion and global warming impacts, the chemistry sector has witnessed a diversification of solvents driven by the shift from fossil-based to bio-based feedstocks.[1] Due to the possibility of obtaining chemical precursors from renewable sources, bio-based solvents are often labelled as green solvents whilst potentially neglecting the various complimentary factors that are required to grant this designation.[2] Chief amongst these is the rapidly growing field of neoteric solvents, particularly (deep) eutectic solvents (DES) and its subsets of bio-based natural deep eutectic solvents (NADES). DES are defined as "eutectic mixtures of Lewis or Brønsted acids and bases" and generated significant interest at the academic level in a wide range of areas from solvent extraction to catalysis.[3] Overlooking the issue of metastability and esterfication of certain NADES mixtures, it is by now well documented through various life cycle assessment (LCA) studies that the environmental sustainability of biochemicals is dependent on the bio-feedstock production and its land usage.[4–7] Whilst reductions in global warming impacts and fossil fuel dependence are possible particularly for biochemicals coming from biomass residues, managed forests, or fermentation, studies indicate this can comes at the expense of increased eutrophication and greater water scarcity. Such environmental trade-offs must not be overlooked when discussing sustainability, particularly given that the promotion of biomass for industry if enacted globally may result in a substantial increase in biomass demand.[8] Such is the catch-22 pitfall that NADES and other bio-based solvents must avoid, whereby a natural solvent is naturally detrimental when all factors are considered.

The ACS Green Chemistry Institute defines the ideal solvent not only in terms of "greeness", but one that must also meet the criteria of "scalability" and "wide utility" (https://reagents.acsgcipr.org/interpret-venn-diagrams/). These are two daunting criteria when considering that the global market for solvents is projected to reach 37.4 million metric tons by 2030, with alcohols accounting for 13.5 million metric tons.[9] To place these numbers in perspective, a simple calculation is shown in **Figure 1**. It estimates the land area required to substitute global solvent demand by two distinct hydrophobic NADES composed of thymol+menthol (orange) or palmitic acid+menthol (blue), assuming these components are exclusively obtained from thyme, mint, and palm oils respectively. Although **Figure 1** clearly represents an argument by *reductio ad absurdum* and should not be taken at face value, it serves to illustrate the issues facing NADES in scaling to industrially relevant volumes. Furthermore, scalability implies economy of scale – bar some small organic acids, alcohols, and sugars,[7] currently any large scale production of chemicals is based on fossil-fuels and the Haber–Bosch process (for nitrogen bearing compounds). To avoid being trapped in niche applications due to expensive manufacturing, DES research must be willing to accept the synthetic origin of solvent precursors.

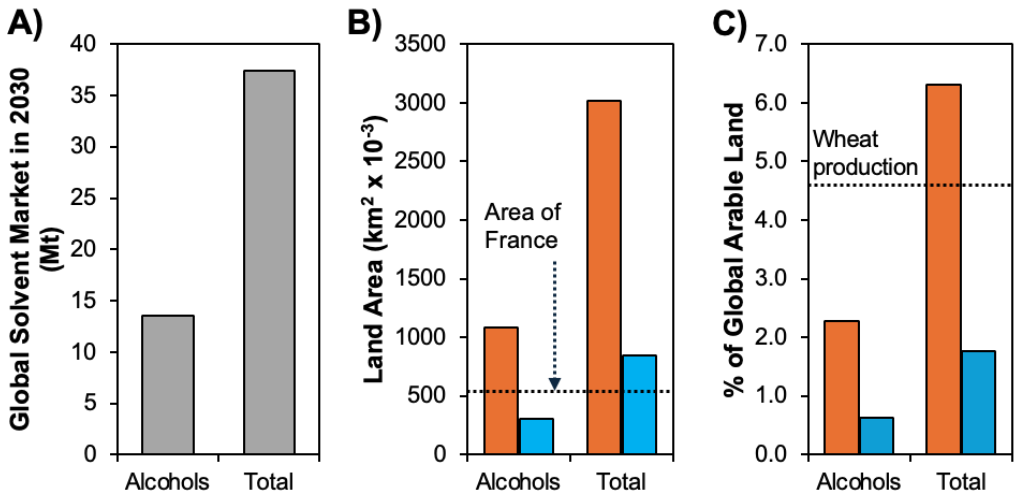

Figure 1. A) Projected alcohol and total global solvent market in 2030 in million metric tons (Mt).[9] B) Land area required and C) its relation to the global arable land (47.81×10^6 km^2 in 2022) to substitute the alcohol or total solvent demand in panel A) by fully bio-sourced thymol+menthol (orange) or palmitic acid+menthol (blue) eutectic solvents for $x_{menthol}$=0.5. Land area was estimated based on the production of 250 kg, 150 kg, and 3500 kg of oil per

hectare per annum for mint, thyme, and palm oil respectively along with a menthol, thymol, and palmitic acid content of 80%, 60%, and 44% in the respective oil extract.[10–12]

What does this mean for the future of green solvents and DES? The expressed opinion does not mean to suggest that these should be abandoned, all solutions are required to address climatic challenges ahead. Bio-refineries represent and integral part of the solution considering that chemical manufacturing is currently the third largest industrial subsector in terms of direct CO_2 emissions and the first in energy consumption.[13] Rather, this assessment serves to reinforce that natural does not automatically equate sustainable. The greenest solvent scenario is the absence of solvent. As this constitutes an impossibility for numerous applications, a solvent's greeness is therefore intrinsically linked to its application and the existing alternatives. LCA and toxicity studies are prerogatives for sustainability, as they often provide a more nuanced description given that net zero impact chemicals across all categories is unrealistic. This fallacy is perfectly exemplified in a recent work by Bhattacharyya et al., showing that a two order of magnitude reduction in carbon footprint and total variable costs was possible when substituting two "green" NADES by "dirty" H_2SO_4 with H_2O_2 for the leaching of lithium-ion battery black mass.[14]

Rather than justifying the use of DES due to their perceived, yet generally unjustified, green, non-toxic, and biodegradable nature, it is important to understand what differentiates DES from common solvents as to maximise their performance and minimize their impact. Most relevant of all is the capacity of DES to overcome solubility issues of target compounds through liquefaction, be it a metal extractants, catalyst, or pharmaceutical active ingredient, extending their liquid state applicability at a desired temperature. Only through recognising the advantages and limitations of DES can their usage be truly sustainable.

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REFERENCES

(1) Clark, J. H.; Farmer, T. J.; Hunt, A. J.; Sherwood, J. Opportunities for Bio-Based Solvents Created as Petrochemical and Fuel Products Transition towards Renewable Resources. *Int J Mol Sci* **2015**, *16* (8), 17101–17159. https://doi.org/10.3390/IJMS160817101.

(2) Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem Soc Rev* **2009**, *39* (1), 301–312. https://doi.org/10.1039/B918763B.

(3) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem Rev* **2014**, *114* (21), 11060–11082. https://doi.org/10.1021/cr300162p.

(4) Yang, Y.; Bae, J.; Kim, J.; Suh, S. Replacing Gasoline with Corn Ethanol Results in Significant Environmental Problem-Shifting. *Environ Sci Technol* **2012**, *46* (7), 3671–3678. https://doi.org/10.1021/ES203641P.

(5) Zuiderveen, E. A. R.; Kuipers, K. J. J.; Caldeira, C.; Hanssen, S. V.; van der Hulst, M. K.; de Jonge, M. M. J.; Vlysidis, A.; van Zelm, R.; Sala, S.; Huijbregts, M. A. J. The Potential of Emerging Bio-Based Products to Reduce Environmental Impacts. *Nat Commun* **2023**, *14* (1), 1–7. https://doi.org/10.1038/s41467-023-43797-9.

(6) Liao, Y.; Koelewijn, S. F.; van den Bossche, G.; van Aelst, J.; van den Bosch, S.; Renders, T.; Navare, K.; Nicolaï, T.; van Aelst, K.; Maesen, M.; Matsushima, H.; Thevelein, J. M.; van Acker, K.; Lagrain, B.; Verboekend, D.; Sels, B. F. A Sustainable Wood Biorefinery for Low-Carbon Footprint Chemicals Production. *Science* **2020**, *367* (6484), 1385–1390. https://doi.org/10.1126/SCIENCE.AAU1567.

(7) Ögmundarson, Ó.; Herrgård, M. J.; Forster, J.; Hauschild, M. Z.; Fantke, P. Addressing Environmental Sustainability of Biochemicals. *Nat Sustain* **2020**, *3* (3), 167–174. https://doi.org/10.1038/s41893-019-0442-8.

(8) Philippidis, G.; Álvarez, R. X.; Di Lucia, L.; Hermoso, H. G.; Martinez, A. G.; M'barek, R.; Moiseyev, A.; Panoutsou, C.; Itoiz, E. S.; Sturm, V.; van Leeuwen, M.; van Zeist, W. J.; Verkerk, P. J. The Development of Bio-Based Industry in the European Union: A Prospective Integrated Modelling Assessment. *Ecol Econ* **2024**, *219*, 108156. https://doi.org/10.1016/J.ECOLECON.2024.108156.

(9) Research and Markets. *Global Solvents Strategic Industry Report 2023-2030 - Green*. GlobalNewswire. https://www.globenewswire.com/news-release/2023/10/27/2768440/28124/en/Global-Solvents-Strategic-Industry-Report-2023-2030-Green-or-Eco-Friendly-Solvents-Poised-for-High-Gains.html (accessed 2025-02-27).

(10) Rajeswara Rao, B. R. Biomass and Essential Oil Yields of Cornmint (Mentha Arvensis L. f. Piperascens Malinvaud Ex Holmes) Planted in Different Months in Semi-Arid Tropical Climate. *Ind Crops Prod* **1999**, *10* (2), 107–113. https://doi.org/10.1016/S0926-6690(99)00012-6.

(11) Najar, B.; Pistelli, L.; Ferri, B.; Angelini, L. G.; Tavarini, S.; Stochmal, A.; Zuchowski, J. ˙; Kozachok, S.; Pérez, A. J.; Pecio, Ł. Crop Yield and Essential Oil Composition of Two Thymus Vulgaris Chemotypes along Three Years of Organic Cultivation in a Hilly Area of Central Italy. *Molecules* **2021**, *26* (16), 5109. https://doi.org/10.3390/MOLECULES26165109.

(12) Mancini, A.; Imperlini, E.; Nigro, E.; Montagnese, C.; Daniele, A.; Orrù, S.; Buono, P. Biological and Nutritional Properties of Palm Oil and Palmitic Acid: Effects on Health. *Molecules* **2015**, *20* (9), 17339–17361. https://doi.org/10.3390/MOLECULES200917339.

(13) IEA. *Tracking Clean Energy Progress 2023*; Paris, 2023. https://www.iea.org/reports/tracking-clean-energy-progress-2023 (accessed 2025-02-27).

(14) Bhattacharyya, S.; Vidal, R.; Alhashim, S. H.; Chen, X.; Ajayan, P. M. Comparative Assessment & Environmental Impacts of Lixiviants for Hydrometallurgical Lithium-Ion Battery Recycling. *Adv Energy Mater* **2025**, 2405348. https://doi.org/10.1002/AENM.202405348.

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In this viewpoint, the sustainability and green credential of bio-derived eutectic solvents are questioned and discussed.