ISGC 2022

N°261 / OC
TOPIC(s) : Biomass conversion / Chemical engineering

Computational solvent screening for the organosolv fractionation of lignocellulosic biomass

AUTHORS

Laura KÖNIG-MATTERN / MAX PLANCK INSTITUTE FOR DYNAMICS OF COMPLEX TECHNICAL SYSTEMS, PROCESS SYSTEMS ENGINEERING, SANDTORSTRASSE 1, MAGDEBURG
Anastasiia KOMAROVA / ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, LABORATORY OF SUSTAINABLE AND CATALYTIC PROCESSING, STATION 6, LAUSANNE
Steffen LINKE / OTTO VON GUERICKE UNIVERSITY MAGDEBURG, CHAIR FOR PROCESS SYSTEMS ENGINEERING, UNIVERSITÄTSPLATZ 2, MAGDEBURG
Liisa RIHKO-STRUCKMANN / MAX PLANCK INSTITUTE FOR DYNAMICS OF COMPLEX TECHNICAL SYSTEMS, PROCESS SYSTEMS ENGINEERING, SANDTORSTRASSE 1, MAGDEBURG
Jeremy LUTERBACHER / ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, LABORATORY OF SUSTAINABLE AND CATALYTIC PROCESSING, STATION 6, LAUSANNE
Kai SUNDMACHER / MAX PLANCK INSTITUTE FOR DYNAMICS OF COMPLEX TECHNICAL SYSTEMS, PROCESS SYSTEMS ENGINEERING/OTTO VON GUERICKE UNIVERSITY MAGDEBURG, CHAIR FOR PROCESS SYSTEMS ENGINEERING, SANDTORSTRASSE 1/UNIVERSITÄTSPLATZ 2, MAGDEBURG

PURPOSE OF THE ABSTRACT

Motivation

Climate change and the dependence on depleting fossil resources require the development of new sustainable routes in the chemical industry. Lignocellulosic biomass is the most abundant terrestrial source of renewable carbon and its main constituents lignin, cellulose and hemicellulose can be converted into fine and platform chemicals. Therefore, biomass fractionation is the key step in lignocellulose biorefineries aiming at the separation of the macromolecular fractions while minimizing structural alterations. In this study, we present a computational screening of more than 8000 solvent candidates for their ability to effectively solubilize lignocellulosic biomass, also considering environmental, health and safety (EHS) criteria. The computational approach is experimentally evaluated using the aldehyde-assisted fractionation technique which protects the beta-O-4 linkages of lignin, preventing lignin condensation and therefore facilitating further depolymerization and biomass upgrading [1, 2].

Methods

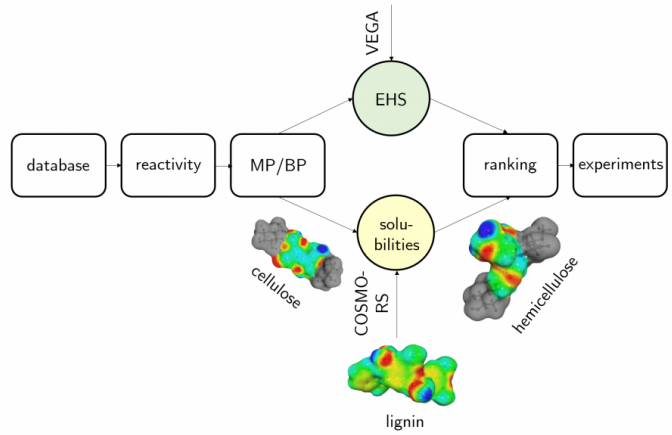
We computationally screened a database of more than 8000 solvent candidates, also including ionic liquids (ILs) and deep eutectic solvents (DESs), and subsequently eliminated unsuitable molecules (see Fig. 1). In a first screening step, we excluded molecules that potentially react with the biomass or with the pretreatment liquor. We restricted the choice of solvents to molecules being liquid at typical pretreatment temperatures of 70-200°C as given by their melting points (MPs) and boiling points (BPs). In order to predict environmental, health and safety (EHS) criteria, we applied quantitative structure-activity relationship (QSAR) models implemented in VEGA. Based on the QSAR predictions, we derived the overall greenness score (OGS) as a metric to quantify benign EHS properties [3, 4].
Subsequently, we predicted the solubilities of each biomass fraction in the solvent candidates using COSMO-RS (COSMOthermX19, COSMOlogic). For the cellulose fraction, we used a cellotetraose molecule with capped end-groups to capture intramolecular hydrogen-bonding. The lignin fraction was modeled by monolignols, as well

as dimers and trimers composed of guaiacyl and sinapyl units connected via beta-O-4 bonds. Hemicellulose was modeled as a fragment of a glucuronoxylan chain with capped end-groups. All molecules were modeled quantum mechanically using TURBOMOLE 7.3. The molar solubilities of each fraction in the pure solvents are denoted as x_fraction, where x_fraction is element [0, 1] and the subscript fraction refers to the set {lignin, hemicellulose, cellulose}. In the case of lignin, we averaged the solubilities of all lignin representatives. Finally, we ranked the solvents according to their Euclidian distance from the optimal point (x_lignin, x_hemicellulose, x_cellulose, OGS) = (1, 1, 1, 1). Finally, we experimentally investigated the performance of the identified solvents in the aldehyde-assisted fractionation procedure using Birch wood [2].

Results and discussion

Of the initial 8011 solvent candidates, 3525 were identified as being non-reactive with the biomass and pretreatment liquor, and also having suitable MPs and BPs for biomass processing. Therefore, these were excellent candidates to further investigate their EHS properties and the solubilities of the biomass fractions. There is good qualitative performance of COSMO-RS solubility predictions for lignin in various solvents compared to experimental data. As visible in Fig. 2, several solvents with beneficial EHS properties are predicted to have high solubilities for all biomass fractions and therefore ranked highly. Among the highly ranked solvent classes were ethers, pyridines, sulfoxides, and pyrrolines, as well as several commercially available ionic liquids and deep eutectic solvents. Preliminary experimental results revealed that several solvent candidates ensure effective solubilization and isolation of the biomass fractions.

FIGURES



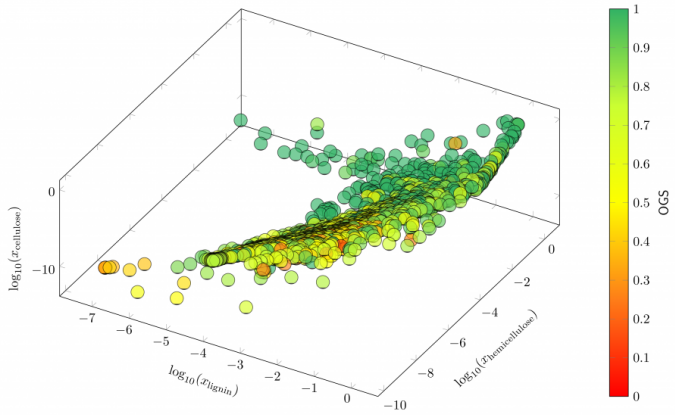


FIGURE 1

Screening approach

More than 8000 solvent candidates were screened for their suitability in the organosolv fractionation of lignocellulosic biomass. The most promising solvents identified in the screening were evaluated in experiments.

FIGURE 2

Solubilities of cellulose, hemicellulose and lignin, and OGS

Solubilities of the lignocellulose fractions in the identified solvents were predicted using COSMO-RS. The color refers to the overall greenness score OGS, a metric measuring beneficial EHS properties.

KEYWORDS

lignocellulose | biorefinery | solvent selection | biomass fractionation

BIBLIOGRAPHY

[1] Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Héroguel, F.; Li, Y.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde Stabilization Facilitates Lignin Monomer Production during Biomass Depolymerization. Science 2016, 354 (6310), 329–333. https://doi.org/10.1126/science.aaf7810.

[2] Talebi Amiri, M.; Dick, G. R.; Questell-Santiago, Y. M.; Luterbacher, J. S. Fractionation of Lignocellulosic Biomass to Produce Uncondensed Aldehyde-Stabilized Lignin. Nat Protoc 2019, 14 (3), 921–954. https://doi.org/10.1038/s41596-018-0121-7.

[3] Linke, S.; McBride, K.; Sundmacher, K. Systematic Green Solvent Selection for the Hydroformylation of Long-Chain Alkenes. ACS Sustainable Chem. Eng. 2020, 10795–10811. https://doi.org/10.1021/acssuschemeng.0c02611.

[4] König-Mattern, L.; Linke, S.; Rihko-Struckmann, L.; Sundmacher, K. Computer-Aided Solvent Screening for the Fractionation of Wet Microalgae Biomass. Green Chem. 2021, 10.1039.D1GC03471E. https://doi.org/10.1039/D1GC03471E.