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Algal remnant transformation to 5-HMF under biphasic solvent conditions: The solvent selection supported by predictive computational methods

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PURPOSE OF THE ABSTRACT

Algal biomass is a promising alternative for renewable lignocellulosic sources because of its efficient photosynthesis, high growth rate, and its ability to grow under aquatic conditions. Furthermore, the recalcitrance of the algal cell wall is not as challenging as that of lignocellulosic walls due to the absence of a lignin sheet. Several valuable compounds (e.g. PUFAs, pigments, lutein, astaxanthin or ß-carotene) can be extracted from the lipophilic fraction within the microalgal biomass, leaving a residual biomass containing primarily proteins and carbohydrates.

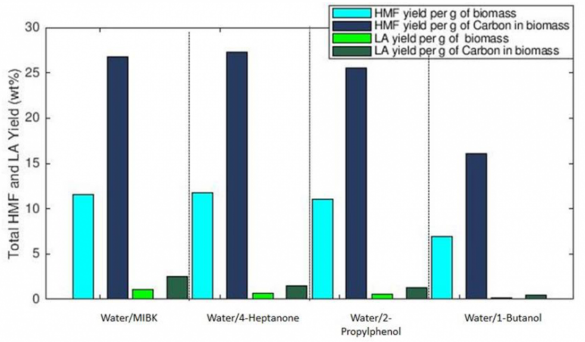
In this study we aim to valorize this lower valued, defatted remnant from the ß-carotene producer Dunaliella salina, which is able to adapt to varying saline conditions. This exceptional ability is due to its weak, fragile cell wall, making this biomass source also a promising candidate for direct transformations. Our aim is to exploit this potential to transform the remnant algal biomass to 5-hydroxy methyl furfural (5-HMF). Due to the commercial importance of 5-HMF, we aim to maximize the yield of the intermediate 5-HMF and suppress the forward reaction toward the lower valued levulinic acid (LA). It is known experimentally that the transformation of purified cellulose and sugars is favored under biphasic reaction conditions [1]. To identify potential solvents for the biphasic transformation of algal defatted biomass we implement results from two independent, computational methods. Using the quantum chemical based conductor-like screening model for real solvents, COSMO-RS, a highly favorable partition of 5-HMF into the organic phase in an aqueous/propyl phenol mixture was predicted [2]. On the other hand, the universal continuum solvation method (SMD) identified aqueous-C7-ketones mixtures for 5-HMF removal [3].

We experimentally investigated the direct transformation of the algal defatted remnant to 5-HMF in the computationally predicted solvent/H2O mixtures using the zeolite HZSM-5 as an acidic heterogeneous catalyst to facilitate the transformation. The influence of the solvent system on the biomass conversion to 5-HMF and LA is presented in Figure 1. The C-yield to 5-HMF with the 4-heptanone/H2O system was slightly higher (27.3 %) compared to that of propyl phenol/H2O solvent system (25.6 %). Additionally, the formation of LA was suppressed and a high selectivity (94.9 %) of 5-HMF was achieved in the 4-heptanone/H2O solvent system. The reaction time of 120 min at 180 °C was found to be optimal in terms of C-yield to 5-HMF for the 4-heptanone/H2O system. The experimentally measured partition of the 5-HMF between the liquid phases, both in the biomass transformation investigations as well as with pure model compounds, agreed very well with the COSMO-RS predictions, and

expectedly, 5-HMF was highly concentrated in the propyl phenol phase (see Figure 2).

In our study we could demonstrate high conversion of defatted algal biomass to the valuable and renewable 5-HMF in a one-step process. The selected solvent system strongly influences the reactivity of biomass-derived compounds by either extracting the desired intermediate into a separate phase or by controlling the reaction kinetics. The computational predictions were shown to deliver valuable suggestions for solvent selection, showing that the design of complex biomass transformations can be supported by such methods.

FIGURES



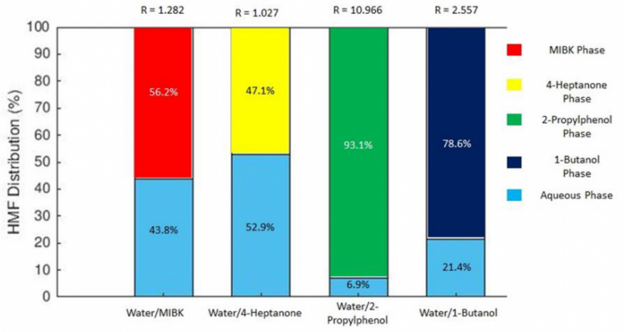


FIGURE 1

The overall HMF and LA yield in different biphasic solvent systems.

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FIGURE 2

The measured HMF distribution and partition coefficient R in the biphasic systems

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KEYWORDS

algal biomass | computational chemistry | hydroxy methyl furfural | biphasic solvent

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