

Molecular footprint of co-solvents in hydrothermal liquefaction (HTL) of *Fallopia Japonica*



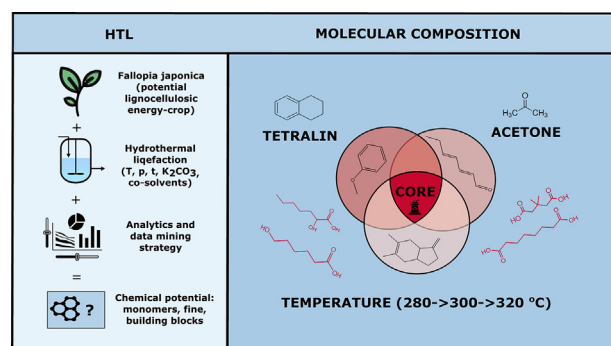
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GRAPHICAL ABSTRACT



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ABSTRACT

The influence of co-solvents on hydrothermal liquefaction (HTL) of *Fallopia Japonica* was studied as a function of temperature. Combination of low and high-resolution mass spectrometry with multi-layered data mining strategy resulted in a comprehensive characterization of the reaction products, mostly water-soluble organics (WSO) with a broad spectrum of chemical functionalities. The non-targeted analysis revealed the presence of a core composition in the samples independent of the process conditions and consisting of hydroxycarboxylic acids, imids, lactones, lactams, phenolics, various short-chain oxygenated aliphatics, and cyclohexane derivatives. Changes in process conditions did not affect those species showing that a part of the HTL product is not susceptible to process tailoring by addition of co-solvents. The findings indicated that the effect of tetralin is a combination of solubilization and scavenging resulting in an increased abundance of monomeric aromatics. For acetone, the results pointed to the promotion of retro-aldol splitting yielding low molecular weight oxygenates.

1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical technique for the depolymerization of biomass feedstocks into fuels and chemicals by

means of near- or supercritical water ($T_{cr} = 374\text{ °C}$, $p_{cr} = 22.1\text{ MPa}$) [1]. The method is versatile in terms of feedstocks, does not require biomass drying, and it takes place in a benign and environmentally friendly solvent with easily adjustable properties [2]. Currently, HTL is on the

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technology readiness level 5 (TRL5) with the method tested on a pilot scale [3,4] and an upcoming demonstration plant (TRL 6–7) [5]. The focus of HTL and most modern commercial biorefinery concepts lies on the production of low-carbon footprint alternatives for transportation fuels, mainly road diesel, marine, and jet biofuels. Liquid energy carriers produced from biomass are an attractive biorefinery goal because their expansion would curb the use of petroleum and thus mitigate the overall CO₂ emissions from the transportation sector, by far the worst environmental polluter. In a recent study by Pedersen et al. [6], it was shown that renewable transportation drop-in fuels from lignocellulosic biomass can be produced through hydrothermal liquefaction and upgrading for approx. 0.82–1.14\$/GLE. It has been argued that the economic viability of all biomass conversion processes in general, and HTL in particular, could be increased further by a co-production of high-value chemicals. This concept originated from the petroleum industry, where the petrochemicals represent a significant portion of the industry's overall value chain despite their relatively low volume output [7,8]. Researchers have studied conversion of biomass into monomeric building blocks, key platform intermediates, and fine chemicals by a plethora of biological and thermochemical conversion techniques with varying degree of success. The focus today is on high-value aromatics from lignin and sugars, furfural, and 5-hydroxymethylfurfural from lignocellulose, but numerous other pathways have been proposed [9], including thermochemical routes. Chemicals of interest from HTL include small aliphatic oxygenates and aromatic monomers.

The two most elementary challenges associated with the concept of hydrothermal biomass-fueled chemical factory are poor selectivity and low yields, typically varying from 5 to 25% [10]. While significant progress in process optimization has been achieved by tailoring with catalysts and co-solvents [9], another fundamental aspect of the problem, namely the poor understanding of liquefaction due to the lack of proper characterization of the complex products, remains to be overcome. The heterogeneity of HTL products originates from the randomness of conversion ruled by series of competing reactions including depolymerization by hydrolysis of ester and ether bonds in the biopolymers, secondary transformations of the produced monomers into intermediates, and repolymerization by condensation and cyclization resulting in a complex product pool [11,12]. Analysis and characterization of HTL products is therefore an area of on-going research and the most common techniques are able to describe certain fractions, e.g. gas chromatography mass spectrometry (GC–MS) covers only the volatiles. The results obtained by Bridgwater et al. [13] for products from pyrolysis specified that the content could be divided into 5–10 wt.% hydrocarbons, 10–25 wt.% oxygenated compounds (phenols, aldehydes, ketones and moderately polar alcohols), and 30–45 wt.% highly polar compounds with low, moderate, and high molecular weights. According to a similar study by Valdez et al. [14] on the composition of liquefaction products, only 10–35 wt.% of the compounds could be identified with GC–MS, with the fraction going as high as 30–50%, in the case of co-liquefaction (HTL in water/organic solvent reaction media) as described by Biller et al. [15]. Villadsen et al. [16] concluded that the standard GC–MS is inadequate for determining highly polar compounds such as sugars and fatty acids [17]. More advanced techniques including coupling of high performance liquid chromatography with mass spectrometry (HPLC–MS) and Fourier transform ion cyclotron resonance (FT-ICR) are under development around the world, e.g. up to 6000 individual peaks were identified by FT-ICR [18], but currently suffer from not being quantitative or only analyzing certain fractions of the HTL products. It was previously shown that a combination of novel analytical and statistical tools, such as high resolution mass spectrometry (HRMS) [19] and multivariate data analysis (MDA) [20], provides the tools needed for handling the high level of complexity of HTL products.

The focus of the current work was the development of strategies for effective and comprehensive characterization of the complex products from hydrothermal liquefaction and similar processes through the combination of standard (electron impact gas chromatography mass spectrometry, EI-GC–MS) and state-of-the-art analytical instrumentation (ultra

high performance liquid chromatography coupled to high resolution mass spectrometry, UHPLC–HRMS) with customized data processing and mining techniques. The aim was to apply those tools to understand the mechanistic behavior of co-solvents in catalytic hydrothermal near-critical liquefaction of *Fallopia Japonica*, an invasive plant native to East Asia, Japan, China, and Korea. Its high resilience and low requirements (fast-growing, low water input, high tolerance to a wide range of soil types, pH values, salinity, and temperature regions: above –35 °C [21]), would qualify *Fallopia* as an attractive lignocellulosic energy crop candidate, thus turning an environmental burden into a sustainable source of fuels/chemicals [22]. Different processes [23,24] have already been considered for exploiting the potential of *Fallopia*, including pyrolysis [25]. Despite the fact that lignocellulosic biomass feedstocks such as *Fallopia* are generally considered too complex for modeling of an already complicated and poorly understood conversion process [26], it is important to study set-ups mimicking the real life applications of HTL for a more realistic evaluation of its potential. As shown by Carrier et al. [27] in a study comparing the conversion of biopolymers and lignocellulose, a chemical interaction between the intermediates from hemicellulose and cellulose leads to shifts in reaction pathways and thus significantly diverging final products.

The potential of *Fallopia Japonica* as a biorefinery feedstock for HTL in the presence of a homogeneous catalyst (K₂CO₃) and co-solvents (acetone and tetralin) was studied as a function of conversion temperature. Both have been reported as effective tools for process optimization and product tailoring, increasing the conversion as well as selectivity [26]. Potassium carbonate was applied as a typical alkali salt catalyst promoting base-catalyzed aldol splitting of the lignocellulosic monomers [28]. K₂CO₃ was preferred over alternatives, e.g. alkali hydroxides such as NaOH, due to its low price and higher activity towards depolymerization of lignocellulosic biomass [29]. The co-solvents were selected based on their differing properties. Acetone is an aprotic polar compound, i.e. it has a lone electron pair that can accept hydrogen bonds, but it has no acidic hydrogen centers [9]. Tetralin, on the other hand, is a non-polar solvent unable of creating hydrogen bonds nor accepting an acidic proton, but effective as a hydrogen donor [30]. Co-solvents in general are reported to increase fuel yields from HTL and to improve their properties [31] by solubilization of reaction products and scavenging of reactive intermediates [32]. A summary expanding the co-solvent effects with physical changes to the reaction system, e.g. medium viscosity, compound solubility, and ion solvation, as well as the thermodynamics of the chemical transformations, including lowering the activation energy of transient reactions, was recently provided by Shuai and Luterbacher [9]. Previous studies of acetone as a solvent and co-solvent reported reaction mechanism shifts [33] and promotion of products such as dehydroabietic acid, furans and phenolics [34] with abundant ketonic groups [35]. Part of the effect is attributed to the incorporation of the co-solvent molecule into the products by its reaction with intermediates, e.g. 3-furanmethanol to form trans-furfurylidene acetone. Tetralin as a co-solvent, on the other hand, is expected to act as proton donor promoting reduction of the reactive intermediates, an effect shown for both the liquefaction of coal [36] as well as biomass [37]. He et al. [33] demonstrated that while non-polar co-solvents such as tetralin have little effect on the conversion itself, they offer a simple and effective polarity-based measure for fractionation of HTL products resulting in a purely liquid fraction more suitable for hydro-treating than the mixed aqueous/semi-solid product obtained without co-solvent. Both acetone and tetralin are interesting, yet relatively unexplored co-solvent candidates for product tailoring in HTL.

2. Materials and methods

2.1. Materials

The biomass used in this study was a freshly harvested *Fallopia Japonica*, both leaves and branches. The plants were cut into smaller pieces, dried in an oven at 105 °C for 24 h, ground down to a particle

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