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Molecular characterization and atomistic model of biocrude oils from hydrothermal liquefaction of microalgae

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ABSTRACT

Hydrothermal liquefaction (HTL) converts wet biomass into biocrude oils that can serve as a green substitute to fossil crude oil for several applications, i.e., biofuel or additive for asphalt. However, the use of biocrude oils in such applications has been limited by a lack of detailed characterization of its molecular components. This hinders the establishment of molecular models for biocrude oil that can be used to establish computationally the links between HTL parameters, chemical composition of biocrude, and its macroscopic properties and applications. Understanding such links would significantly reduce the need of expensive and time-consuming trial-and-error HTL experimentation. Here, we present the first molecular model of biocrude oil from microalgae derived from a detailed analytical characterization by pyrolysis gas chromatography mass spectrometry (Py-GC–MS) with non-negative matrix factorization (NNMF), supported by an extensive literature research. The selected molecules are then characterized by conceptual density functional theory (DFT) calculations. These are then used to evaluate the reactivity and intermolecular interactions of biocrude oil in upgrading and oxidative ageing processes, which are the most relevant for its aforementioned application as biofuel or as additive for asphalt. The results show that the properties of the light fraction of biocrude oil favor its use for biofuel. In the case of additive for asphalt pavement, the light fraction is less prone to oxidative ageing, while the heavy fraction might still be useful to provide the rheological properties required for asphalt concrete.

1. Introduction

Hydrothermal liquefaction (HTL) has gained momentum in the last decade as a thermochemical process for converting wet bioresources (water content > 50 wt%), e.g., algae, manure, and sewage sludge, into a sort of bitumen called biocrude oil. HTL avoids the need of drying the biomass feedstock before processing it [1] and benefits from the special properties of hot compressed liquid water at near-critical conditions (280–350 °C, 10.0–22.1 MPa), also called subcritical water. These properties include, among others, high availability of hydronium and hydroxyl ions, lower density and lower conductivity than those at standard conditions [2]. In HTL, water acts not only as a solvent, but also as a reactant, favoring hydrolysis reactions to degrade the biomass structure into biocrude oil. This substance has been suggested as a green material for several applications like biofuel [3] or asphalt replacement [4].

Microalgae have received a great deal of attention as feedstock for HTL, because of their higher photosynthetic efficiency compared to terrestrial plants [5]. Extensive experimentation has been carried out in the last years in batch [6,7] and continuous reactors [8,9], leading to biocrude oil yields above 50 wt% (dry, ash free) [10]. The high potential of HTL to recover the nutrients from algal slurries in solid [11] and liquid forms [12,13] has been reported as well, which has the potential of significantly reducing the nutrient needs for microalgae cultivation by internally recycling nutrients from the HTL step to the cultivation step.

Extensive experimental research on HTL has shown that process parameters, such as temperature, reaction time or type of feedstock, have a direct effect on the classes of compounds present in biocrude oil and their relative concentration [14]. This impacts the physical, chemical and mechanical properties of biocrude oil and therefore its intended application. Defining the links between HTL process parameters,

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chemical composition of biocrude oil, and its performance in different applications, demands a deep level of understanding that it is hard to acquire only by experimentation. The establishment of such links can be greatly accelerated by the development of computational molecular models of biocrude oil that use detailed analytical characterization as input. Such models enable a bottom-up study of the structure-property relationships of biocrude oil, in order to understand how individual classes of molecules affect macroscopic properties like viscosity, resistance to oxidation or upgrading potential, which are critical for the aforementioned applications as biofuel or as additive for asphalt. By establishing such links, the development of biocrude oils with tailor-made compositions depending on the intended application becomes feasible. The composition of biocrude oil is known to be affected by parameters such as HTL reaction parameters (temperature, reaction time, biomass:water ratio) and feedstock [15]. These can be adjusted to tune the molecular composition of biocrude oil bringing it closer to the optimal compositions predicted computationally, severely reducing the need of expensive and time-consuming trail-and-error-based HTL experimentation.

The difficulty in characterizing the molecules present in biocrude oil has been forestalling the development of such models to the present. Traditional techniques like gas chromatography – mass spectrometry (GC–MS) provide a limited degree of characterization of the complex and heavy matrix of biocrude oil [16]. Fortunately, new tools have been used over the last years (e.g., FT-ICR-MS [17–19] or Py-GC–MS [16]), enabling a much larger degree of characterization, making available sufficient experimental data for the development of molecular models. Applying non-negative matrix factorization (NNMF) to Py-GC–MS has proven to be useful for fast analysis of large sets of samples [20]. This approach does not provide data about individual molecules in the biocrude oil, but rather about classes of compounds. This is particularly advantageous when analyzing complex mixtures of organic compounds like biocrude oils, as grouping the data into classes of compounds helps to simplify the system. This is a common practice in petrochemical analyses as well, i.e., with the traditional SARA analysis that classifies asphalt chemical components according to its solubility in specific organic solvents.

Here, biocrude oils produced in an HTL continuous reactor at 350 °C are analyzed by stepwise Py-GC–MS, applying the NNMF method. Based on this experimental characterization and extensive literature research, we propose a set of molecules representative of each class of compounds to create the first molecular model of biocrude oil. The selected molecules are then subjected to DFT calculations to optimize their geometry and calculate their electronic structure. Conceptual DFT descriptors [21] like the Fukui function and the global chemical hardness are then applied in combination with molecular electrostatic potential (MEP) maps to provide a qualitative and quantitative analysis of the reactivity of the different model molecules. This information allows evaluating the response of the different classes of compounds upon upgrading or oxidative process, which are especially relevant for the use of biocrude oil as biofuel or asphalt replacement, respectively.

2. Materials and methods

2.1. Biocrude oil production

Biocrude oil was produced in a continuous stirred tank reactor at 350 °C and a residence time of 15 min, using two different concentrations of microalgae (9.1 wt% and 18.2 wt%) in the feed slurry. From now onwards, these samples of biocrude oil will be referred to as SA9.1 and SA18.2, respectively. Details about the experimental procedure, together with the handling of the HTL products and their separation, can be found elsewhere [22].

2.2. Biocrude oil analyses

The biocrude oil was subjected to several analyses to ascertain its molecular composition. The ash content of biocrude was calculated under inert conditions at 800 °C. Thermogravimetric analyses (TGA) were performed on a NETSZCH STA 449 F1 Jupiter thermal gravimetric analyzer, under N_2 flow (100 mL·min^{-1}) from 25 to 700 °C with a ramp of 10 °C·min^{-1}, in order to obtain information of the weight loss with increasing temperatures of the biocrude oil. For the Py-GC–MS analyses, four consecutive steps at different temperatures (200, 280, 350 and 500 °C) were applied to the biocrude oil samples for 10 min, using a temperature ramp of 600 °C·min^{-1} with a CDS 1000 pyroprobe. Each biocrude oil was analyzed two times for reproducibility purposes. Small samples (< 0.1 mg) were placed in a quartz tube and kept under 100 mL·min^{-1} of N_2 during the experiment, and the evolved vapors were collected for every temperature step on a solid-phase microextraction (SPME) fiber that was subsequently desorbed in the injector port of the GC–MS system. Decoupling pyrolysis and analysis by using a SPME fiber has proved as a successful approach to analyze materials such as bio-oils from flash pyrolysis of biomass [23] or micropollutants from biomass pyrolysis [24]. More details of the sampling method can be found in a previous paper [16].

The mass loss caused by the thermal desorption/pyrolysis at each temperature step (measured by TGA) was correlated to the area detected by Py-GC–MS at each step. This allowed calculating the concentration of each class of compounds identified, resulting in a pseudo-quantitative characterization of the molecular composition of the biocrude oils. A non-negative matrix factorization method was used to resolve overlapping substances and interpret the Py-GC–MS data. The molecules detected during the low temperature steps of Py-GC–MS (200 and 280 °C) were attributed to the thermal desorption of GC detectable compounds present in biocrude oil, constituting the light fraction of biocrude oil. The heavy fraction of biocrude oil is constituted by the chemical compounds detected during the high-temperature steps of Py-GC–MS. These are fragments that evolve from the thermal degradation of larger biocrude oil molecules during the analysis. Hence, they are interpreted as markers of larger precursors, in order to obtain the actual chemical components of biocrude.

The non-volatile part of biocrude oil (above 500 °C, after subtracting the ash) was taken as the asphaltene fraction. This fraction was characterized by scaling up the stepwise pyrolysis procedure. In this procedure, 1 g of sample was placed in the middle of a quartz tube (10 mm diameter and 100 mm length) that was pyrolyzed in 800 mL quartz pyrolysis chamber, fluxed with 1000 mL·min^{-1} of N_2 and inserted coaxially to an electrically heated furnace. The sample was subjected to the same thermal desorption/pyrolysis steps used in analytical stepwise Py-GC–MS, yielding at the end of the 500 °C step a solid residue in the quartz tube (defined as asphaltenes in the procedure). These conditions are supposed to cause the volatilization of the non-asphaltene fraction of biocrude oil and cleave the alkyl side chains from the aromatic cores of asphaltenes. The solid residue was scratched from the quartz tube and subjected to elemental analysis. Elemental analysis was conducted using a Thermo Fisher organic elemental analyzer (Flash 2000) configured for solid samples using a copper/copper oxide column and calibrated with 2,5-Bis-(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT).

An important issue of stepwise pyrolysis is that the thermal reactivity of the sample should be negligible in comparison to its volatilization during the first two steps, whereas in later steps, thermal reactivity (pyrolysis) is used to identify high molecular weight compounds (by means of pyrolysis product identification). The use of a slow pyrolysis ramp and good heat transfer, in combination with the minimal amount of sample used and a relatively high nitrogen flow to purge the quartz tube, favors the volatilization, minimizing the thermal reactivity of the evolved vapors.

Selecting which macromolecules originate the smaller markers