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Research article

Heterogeneous catalytic upgrading of biocrude oil produced by hydrothermal liquefaction of microalgae: State of the art and own experiments

Diego López Barreiro [a,*], Blanca Ríos Gómez [b], Frederik Ronsse [a], Ursel Hornung [b], Andrea Kruse [b,c], Wolter Prins [a]

[a] Department of Biosystems Engineering, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium
[b] Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmoltz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Conversion Technology and Life Cycle Assessment of Renewable Resources (440f), Institute of Agricultural Engineering, University Hohenheim, Garbenstrasse 9, 70599 Stuttgart, Germany

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ABSTRACT

This paper reviews the literature on upgrading of biocrude oil obtained by hydrothermal liquefaction of microalgae. It analyses the influence of several parameters (e.g., temperature, operation mode, reaction time, catalyst) on the yields and properties of the upgraded product. Some own experiments are performed based on the review outcomes, comparing for the first time the application of heterogeneous catalysis to biocrude oil obtained from two different algae species: *Scenedesmus almeriensis* (freshwater) and *Nannochloropsis gaditana* (marine). The conditions applied were 4 to 8 MPa hydrogen atmosphere in 10 mL microautoclaves at 400 °C and 4 h. The influence of two catalysts (Pt/Al_2O_3 and HZSM-5) and the effect of water addition to the reaction medium were investigated. Many of the effects were found to be caused by the temperature applied, rather than by the catalyst. The conditions applied improved the quality of the algal biocrude oil, viz. by reducing its amount of heteroatoms, saturating and cracking its molecules, and increasing its volatility. The degree of upgrading to a transportation biofuel in the experiments herewith reported, as well as in the literature studies, is however still insufficient and demands further developments of the upgrading techniques.

1. Introduction

The high photosynthetic efficiency of microalgae [1] has raised many expectations in the last years regarding the opportunity of substituting large amounts of fossil fuels by algae-based biofuels, especially by means of biodiesel production from the lipid fraction [2] or, more recently, by means of hydrothermal liquefaction (HTL) [3]. HTL produces biofuels from microalgae without the need of drying the feedstock, turning the whole microalgal biomass into biocrude oil, an aqueous phase with organic matter dissolved in it, a solid residue and a gaseous product. Typical conditions applied for HTL of microalgae are 280 to 375 °C, 5 to 25 MPa [4] and reaction times of 5 to 60 min.

However, researchers have not yet succeeded to produce a biofuel directly applicable for transportation, and it is commonly reported that microalgal HTL biocrude oil requires further upgrading to improve its properties. A main problem here is its high content of heteroatoms which, in case of N or S, causes harmful emissions upon combustion [3]. Its high viscosity (caused by the abundance of long and complex molecules in the biocrude oil) and high acidity make it also difficult to store and transport [5].

Research in the field of algal biocrude oil upgrading is limited so far and has been carried out mainly in Savage's group [6,7] from the University of Michigan (USA). The PNNL (USA) [8], the Henan Polytechnic University in China [9], and other groups from Europe (Twente, Leeds) [3, 10] have been active as well. The low number of publications on this field can be attributed to the limited production capacity of microalgae HTL biocrude oil, as batch microautoclaves were used in most of the experiments reported in literature for this conversion technique. However, recent research has demonstrated the possibility of producing larger amounts of biocrude oil in continuous set-ups, managing to successfully run the process at various conditions for several hours [8,11]. This opens the door for further developments to improve the properties of microalgal biocrude oil.

Upgrading steps are needed to obtain a final product with a better quality and to make it suitable for e.g., blending in already-existing petrochemical refineries. The objective is to turn the biocrude oil into an upgraded oil by increasing the H/C ratio and reducing the amount of oxygen, nitrogen and sulphur. Various studies are available regarding biocrude oil upgrading, and they will be discussed in more detail in the following sections. Different catalysts (e.g., zeolite, platinum, ruthenium) in several supports (e.g., carbon, alumina) have been considered in these studies.

Indeed, this paper aims at providing a review of the literature currently available on microalgal HTL oil upgrading, combined with some

* Corresponding author.
E-mail address: Diego.LopezBarreiro@UGent.be (D. López Barreiro).

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own experiments. Two catalysts commonly used in the literature (HZSM-5 and Pt/Al_2O_3) were used to upgrade the oil from continuous HTL of two algae species (*Scenedesmus almeriensis* and *Nannochloropsis gaditana*). The experiments were carried out in batch microautoclaves at a temperature of 400 °C, for a residence time of 4 h and with a catalyst loading of 20 wt%. Two processing routes were followed: a dry one just under high-pressure H_2, and a wet one where also a certain quantity of distilled water was added to the reaction medium.

1.1. Heterogeneous catalysis for oil upgrading: reasons and methods

Microalgal HTL produces a biocrude oil with a typical carbon content above 70 wt% [12]. This biofuel is characterized also by a relatively high higher heating value (HHV) of typically 36–38 $MJ \cdot kg^{-1}$. However, it is not ready for use as a transportation fuel because of its high content in heteroatoms and its high viscosity, among other issues. For instance, the presence of nitrogen (related to the presence of proteins in the microalgal feedstock) or sulphur is undesired due to the expected NO_x and SO_x emissions upon combustion of the biofuel. The oxygen content (typically ca. 10 wt%) is less troublesome, as it is low enough to allow co-processing with fossil petroleum in current biorefineries [13]. However, oxygen in the biocrude oil is present, among other molecules, in fatty acids, increasing the total acidic number (TAN) of the biofuel [14]. The high TAN of microalgal biocrude oil (though lower than in biocrude oils from HTL of lignocellulosic biomass) [8] leads to corrosion problems. Besides, a high concentration of oxygenated compounds can cause stability problems [15]. Therefore the reduction of the oxygen content or the modification of its chemical functionality is still desired.

Taking this into account, it is clear that a catalytic upgrading step is required. This step should promote those reactions (i.e., cracking, hydrocracking, hydrogenation, decarboxylation, decarbonylation, hydrodeoxygenation, hydrodenitrogenation, hydrodesulphuration) that remove the chemical functionalities causing the undesired properties of the biocrude oil, reducing the content of heteroatoms while improving the fluidity and stability of the oil. As an outcome of the extensive research on upgrading of pyrolysis oil from lignocellulosic biomass, two main processes have been typically proposed by applying heterogeneous catalysis [15]: hydrodeoxygenation and zeolite cracking.

Hydrodeoxygenation, and its related processes of hydrodenitrogenation and hydrodesulphuration, require high pressures of H_2 and the use of sulphide/oxide catalysts (e.g., $Co\text{-}MoS_2/Al_2O_3$) or transition metal catalysts like Pt/Al_2O_3 [15]. The use of sulphide forms is said to enhance the deoxygenation and desulphurization activity compared to the metal in its oxide state, though the risk of contaminating the upgraded oil with sulphur is higher. However, not sufficient data is currently available in the literature regarding microalgae HTL oil upgrading to confirm this issue. The high pressures of H_2 are needed to reduce the limitations in transferring hydrogen to the biocrude oil. The temperature should remain relatively low (between 250 and 450 °C) to prevent polymerization and polycondensation reactions that reduce the oil yields and enhance the production of coke. One problem typically associated with the use of HDO catalysts is their poisoning by nitrogen species, which could be challenging when applying them to microalgae biocrude oil (characterized by a relatively high nitrogen content, typically 5–7 wt%).

The second technique is zeolite cracking, which is related to fluid catalytic cracking (FCC) processes [16]. Zeolites are three-dimensional porous materials with very high surface areas and adsorption capacities. Although their catalytic role is still not yet fully understood, it is known that their catalytic activity is based on acid-site catalysis. The advantage of zeolite cracking over HDO is that it is applied at atmospheric pressures, without the addition of any H_2. However, the temperature range for this technique is between 300 and 600 °C [15], which is clearly higher than for HDO. Reactions similar to those occurring in HDO take place, although cracking is the main one [15,16].

The upgrading of pyrolysis oil is mainly done in two steps [17]. The first one involves mild conditions (ca. 275 °C) that reduce the oxygen content while stabilizing the oil to prevent secondary reactions that could deactivate the catalyst. The second step uses harsher conditions (450 °C) and lower residence times to further decrease the content of heteroatoms. Each step requires a different catalyst. However, this approach has been used only in one literature study involving microalgal HTL biocrude oil [8]. Its impact is expected to be lower in HTL biocrude oil than in pyrolysis oil, as biocrude oil is stabilized by water during the HTL reaction and is considered as a final product, whereas pyrolysis oil is an unstable intermediate product that is prone to react further, reducing the oil yield [18]. However, some kind of pretreatment prior to the catalytic step might still be useful here too, according to the results provided by some researches [5,9]. Pretreating the HTL biocrude oil could lower its content of heteroatoms, thus reducing the risk of catalysts poisoning during the oil upgrading step.

In the rest of the available studies about microalgae HTL oil upgrading the approach has been somewhat different, applying techniques typically used for heavy fuel processing: a single step at high temperature, assisted in many cases by the use of supercritical water to dissolve the biocrude oil and overcome the typical mass transfer limitations between the hydrogen and the biocrude oil by bringing them to a single phase [6,19]. Supercritical water would provide the system with an environment of gas-like transport properties while keeping liquid-like densities.

1.2. Conditions for heterogeneous catalytic upgrading of algal biocrude oil

Several investigations have dealt with the application of heterogeneous catalysis for obtaining algae biofuels by HTL. Two main strategies have been typically used: in-situ simultaneous HTL plus catalytic upgrading by introducing the catalyst in the HTL reaction medium; or applying catalysts to upgrade the biocrude oil in a subsequent step after the separation of the HTL products. Most of the work has focused on the last pathway, to avoid any problems of catalyst deactivation by water and inorganic material present in the algal feed slurries for HTL. Also the recycling of nutrients through the aqueous phase produced in HTL, viz. to cultivate new microalgae, can be seriously hindered if catalysts are mixed with the reaction medium. Leaching of the catalyst to the water is quite likely to occur then [20].

Several studies are available in the literature considering simultaneous production and upgrading of HTL biocrude oil from algae (in-situ catalytic upgrading) [21,22]. However, the focus of this paper will be on heterogeneous catalytic upgrading as a subsequent step after HTL, where biocrude oil acts as feed and an upgraded oil is the targeted product. The data provided in the next sub-sections refer to this type of configuration and analyses the work published so far. Parameters to be considered are the reduction of the nitrogen content and the O/C ratio of the biocrude oil, as well as the increase of the HHV and the H/C ratio. In most of the investigations, small quantities of water or organic acids (i.e., formic acid) were applied together with the heterogeneous catalyst.

Table 1 gathers a summary of the conditions presently reported in the literature. It shows the pressure of H_2 applied, the temperature range investigated, the catalysts tested, the catalyst loading (expressed in wt% as the ratio between the mass of catalyst and the mass of biocrude oil) and the holding time (in h for batch experiments) or liquid hourly space velocity (LHSV, in h^{-1} for continuous operation).

1.2.1. Gas environment and pressure

The pressure in upgrading studies is provided by H_2, which acts as the hydrogen donor for saturation and cracking reactions [15]. The values reported for the initial H_2 pressure vary between 3.4 and 15 MPa. The mixtures H_2-biocrude oil-catalyst exhibit severe mass transfer limitations that can be reduced by intense mixing of all the phases and/or by applying high H_2 pressures. The only way of providing