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Review of recent reports on process technology for thermochemical conversion of whole algae to liquid fuels

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This review considers the recent developments in which there has been a tremendous expansion of the research and development focused on process development for the thermochemical processing of whole algae for the production of fuels. There are several key elements to this expanded interest in thermochemical processing: 1) the processing is applied to whole algae, not just lipid extracts, and as a result higher product yields have been demonstrated; 2) the feedstock composition is not so critical to the process, so that a wider range of algae growth scenarios has been considered; and 3) the envisioned products are actual hydrocarbon fuels, which are infrastructure compatible. Based on these three elements one can envision a more widely expanded utilization with more flexible growth options and more direct market applications of products. Algae can be processed by dry pyrolysis or in water slurry by hydrothermal liquefaction. In either case, the liquid oil product can be hydroprocessed to liquid hydrocarbon fuels. Recovery and recycle of nutrients is possible through treatment of the aqueous byproduct to promote sustainable production of the algae feedstock. In all cases the cost of the algae feedstock is the primary uncertainty in the economic analysis of such processing.

Contents

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1. Introduction

In the last five years there has been a tremendous expansion of the research and development focused on the thermochemical processing of whole algae for the production of fuels [1]. There are several key elements to this expanded interest in thermochemical processing:

1) Processing is applied to whole algae, not just lipid extracts, and as a result higher product yields have been demonstrated;
2) Feedstock composition is not so critical to the process, so that a wider range of algae growth scenarios have been considered; and
3) Envisioned products are actual hydrocarbon fuels, which are infrastructure compatible.

Based on these three elements one can envision a more widely expanded utilization with more flexible growth options and more direct market applications of products.

This review surveys the most recent developments in whole algae thermochemical conversion to liquid fuels, which address the issues of process development and commercialization. Other recent reviews deal with more fundamental chemical conversion issues and provide a more detailed background [2,3]. This review is more focused on continuous-flow hydrothermal liquefaction (HTL) and process results which show how it can be brought into a commercial application, such as water recycle and biocrude upgrading to hydrocarbon fuels. This review is meant as an update for those already cognizant of the issues of thermochemical processing of biomass and relates to HTL algae processing, specifically.

Thermochemical conversion of algae can be divided into the direct pyrolysis of dry algae and the high-pressure processing of algae in water slurries. In fact, the wet (hydrothermal) processing seems to have the better fit for algae utilization because the algae are grown in very dilute water systems. The partial dewatering of the algae-containing media to the level of 10–20% dry solids, usually accomplished by mechanical means for HTL, is a less energy intensive processing option compared to the thermal drying to >90% dry solids as is required for pyrolysis. The difference in the required moisture content for the two processing options relates to the value of liquid water in the pressurized system used in HTL, wherein it serves as a heat transfer medium and moderator, while in fast pyrolysis the requirement for boiling off the water in the reactor would result in a large heat sink, which would slow the heating process and interfere with the fast pyrolysis mechanisms. The vast majority of the R&D in thermochemical conversion of algae to fuels is based on hydrothermal processing, and, specifically, HTL to produce a biocrude product. Pyrolysis is relegated to laboratory investigations with little hope for commercial application due to the negative energy balance resulting from the prerequisite feedstock drying.

Thermochemical conversion of algae, in the form of hydrothermal liquefaction, is just moving out of the laboratory to scaled-up pilot plant operations [4]. There is no commercial application of algae thermochemical processing to fuels. There are several small algae processing companies basing their business on thermochemical conversion (HTL) of whole algae. For the most part the research and development work is found in universities and national laboratories around the world.

2. Thermochemical conversion of whole algae

2.1. Feedstock effects

A key element of thermochemical conversion of whole algae is that the thermochemical process is inherently feedstock agnostic. All forms of biopolymers breakdown under thermochemical processing conditions [5]. Therefore, whole algae are processed, not just lipid extracts. The chemistry involves a complex of reactions from hydrolysis to dehydration, depolymerization to condensation, and various forms of heteroatom removal to reduce the heteroatom “contaminants” and other trace elements and to concentrate the energy in the algae biopolymers into more hydrocarbon-like structures, which are near fuel quality. A comparative study of algae and other lignocellulosic biomass (pine wood and grape residue) showed that the biocrude yield was higher from algae [6]. As a result, the algae feedstock does not need to be grown under strictly controlled conditions with the intent to maximize the lipid content. In fact, carbohydrate and protein structures, as well as lipids, can be converted directly into fuels by the thermochemical process [7]. Of course, lipids produce the highest yield of biocrude, >90 wt.%, but proteins and carbohydrates also produce significant yields of biocrude, particularly at higher temperature, 350 °C. Further, it was reported that these two components produced higher biocrude yields when mixed than when tested individually, suggesting interaction which leads to higher biocrude production from whole biomass [7]. In addition, the algae species do not need to be carefully controlled, as any algae species, as well as cyanobacteria and other species, can be converted by thermochemical means. The differences in these species appears to have only minimal impact on the HTL process with differences in yield indistinguishable from the experimental variation due to the different batch reactor methods used. Mixed algae culture grown in open wastewater treatment systems has shown even better HTL biocrude yield and quality than that from laboratory grown monocultures [8]. Other wastewater treatment studies suggest mixed cultures of *Chlorella sp.*, *Scenedesmus obliquus* and cyanobacteria (blue green algae) with several other algal species bio-augmented into the culture including *Chlorella protothecoides*, *Chlorella vulgaris*, *Botryococcus braunii*, *Nannochloropsis oculata*, *Spirulina platensis*, *Scenedesmus dimorphus*, and *Chlamydomonas reinhardtii* produced useful results and provides the basis for the University of Illinois' HTL-based E^2-Energy concept [9]. The team also reported using mixed-culture algae directly from wastewater as HTL feedstock with reasonable results [10]. These advantages for whole algae processing contrast with other thermochemical methods being developed for direct recovery of the lipids as a biodiesel product through transesterification under supercritical conditions [11] with and without hydrothermal carbonization pretreatment [12].

HTL of macroalgae has also been studied to a limited extent in the laboratory. University of Leeds performed batch reactor studies with feedstock slurries at 21 wt.% dry solids and concluded that the highest yields of biocrude (10–18 wt.%) were derived from *L. saccharina* and *A. esculenta*, while biochar yields were higher (11–19 wt.%). By claiming both as energy products, the authors concluded that both species produced energy yields equivalent to anaerobic digestion but greater than fermentation [13]. Higher biocrude yields were reported by the research team at Henan Polytechnic University in China using small batch reactors. They reported up to 32 wt.% of solvent-extracted biocrude produced at 370 °C when the algae slurry concentration of 23 wt.% was used [14]. Other similar limited batch surveys have been reported with both green and brown macroalgae [15]. PNNL reported HTL of macroalgae in a continuous-flow reactor. *L. saccharina* was processed over a range of slurry concentrations up to 22 wt.% and biocrude yields as high as 28 wt.% (58 wt.% on carbon basis) were reported, without using a solvent extraction recovery step [16]. Using the PNNL system the biochar yield was reported as part of the mineral precipitate, which was very low (up to 4 wt.%). In addition, the PNNL system