



Process improvements for the supercritical in situ transesterification of carbonized algal biomass



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HIGHLIGHTS

- Biodiesel made from algal hydrochar with supercritical in situ transesterification.
- High biodiesel yields achieved with low ethanol loadings at 275 °C.
- Supercritical reaction medium is water tolerant, permitting use of rectified ethanol.
- Preventing the thermal loss of unsaturated fatty acids is critical to high biodiesel yields.

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ABSTRACT

This work focuses on the production of biodiesel from wet, lipid-rich algal biomass using a two-step process involving hydrothermal carbonization (HTC) and supercritical in situ transesterification (SC-IST). Algal hydrochars produced by HTC were reacted in supercritical ethanol to determine the effects of reaction temperature, time, ethanol loading, water content, and pressure on the yield of fatty acid ethyl esters (FAEE). Reaction temperatures above 275 °C resulted in substantial thermal decomposition of unsaturated FAEE, thereby reducing yields. At 275 °C, time and ethanol loading had a positive impact on FAEE yield while increasing reaction water content and pressure reduced yields. FAEE yields as high as 79% with a 5:1 ethanol:fatty acid (EtOH:FA) molar ratio (150 min) and 89% with a 20:1 EtOH:FA molar ratio (180 min) were achieved. This work demonstrates that nearly all lipids within algal hydrochars can be converted into biodiesel through SC-IST with only a small excess of alcohol.

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1. Introduction

To date, the commercialization of algal biofuels at prices competitive with petroleum has been stymied by the lack of technologies capable of processing wet biomass into fuels. Likewise, producing an advanced biofuel or biomass-based diesel from algae that meets the carbon reduction requirements of the second US Renewable Fuel Standard (i.e., a 50% lifecycle greenhouse gas emissions reduction relative to petroleum) is difficult if the biomass must be dried using non-solar means prior to fuel conversion. We addressed the challenge of processing wet biomass in our previous work, which described a two-step method to convert algal biomass into biodiesel through hydrothermal carbonization (HTC) and uncatalyzed, supercritical in situ (trans)esterification (SC-IST) with ethanol (Levine et al., 2010). In this process, algae are grown and then harvested to produce a 10–20% total solids slurry that is reacted in and with hot liquid water (190–250 °C) at autogenic pressures to conglomerate cells into an easily

filterable solid (i.e., carbonized solids or hydrochar) that retains the lipids and produce a sterile, nutrient-rich aqueous phase. In the second step, lipids within the hydrochar are converted into biodiesel (i.e., fatty acid ethyl esters, FAEE) without prior solvent extraction by use of supercritical ethanol ($T_c = 240.9$ °C, $P_c = 6.1$ MPa). This work focuses on the optimization of SC-IST to achieve high FAEE yields with low alcohol loadings.

In situ transesterification has traditionally been limited to base-catalyzed reactions of common biodiesel feedstocks like soybeans. Although high yields are achievable at moderate temperatures, subcritical catalytic in situ transesterification typically requires a large excess of alcohol, is highly sensitive to water, and requires long reaction times. For example, flaked soybeans containing 7.4 wt.% moisture were reacted at 23 °C for 8 h with alkaline methanol (~180:1 methanol:fatty acid (MeOH:FA) molar ratio) to achieve 93% conversion of lipids to biodiesel (Haas et al., 2003). Subsequent work demonstrated that by reducing the moisture content (Haas and Scott, 2007) and physically pre-treating the biomass (Haas and Wagner, 2011b), high yields could be obtained in shorter times (~1.5–5 h) and with less methanol (~9–25:1 MeOH:FA). While improved, methanol use was still much higher

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than commercial transesterification of oils, which is typically carried out at a 2:1 MeOH:FA molar ratio. Excess alcohol is required in most cases just to submerge the biomass (e.g., 7.5 mL MeOH was required to cover 5 g of flaked soybeans, equivalent to ~45:1 MeOH:FA molar ratio), with a secondary effect being the dilution of any water present to below inhibitory concentrations (Haas et al., 2003).

Recently, microalgae have been investigated as a feedstock for subcritical in situ transesterification. Since algal biomass typically contains a higher proportion of FA than traditional oilseeds, acid-catalyzed reactions, which do not form soaps, are more commonly performed. Similar to previous work done with soybeans, high conversions have only been observed at high alcohol loadings (>100–200:1 MeOH:FA) and with dry biomass (Ehimen et al., 2010; Haas and Wagner, 2011a; Johnson and Wen, 2009; Wahlen et al., 2011). For example, Ehimen et al. (2010) found that when *Chlorella* containing just 0.7 wt.% moisture (dry weight basis; equivalent to ~0.16 wt.% water in the total reaction mixture) was reacted at 60 °C for 6 h with ~105 MeOH:FA molar ratio and 100 wt.% H₂SO₄ (oil basis), equilibrium conversion to fatty acid methyl esters (FAMES) was reduced by ~20% compared to reactions with dry biomass. When biomass moisture content exceeded 31.7% (dry basis) or water constituted more than ~9.5 wt.% of the reaction mixture, transesterification was totally inhibited.

Considering the costs and energy inputs associated with drying and processing the biomass prior to subcritical in situ transesterification as well recovering the excess alcohol following the reaction, we have chosen to explore supercritical alcohols as a reaction medium for in situ transesterification. SC-IST may benefit from reduced costs since it does not require catalysts or their recovery and generally has a higher tolerance for feedstocks containing water and FAs. Although supercritical methanol and ethanol have been well studied as a medium for catalyst-free biodiesel production from pure vegetable oils (Pinnarat and Savage, 2008), relatively little work has explored SC-IST. Patil et al. (2011a,b) demonstrated the conversion of lipids within wet *Nannochloropsis* to biodiesel using supercritical methanol, but MeOH:FA molar ratios above 1600 were employed. In another work, dry rice bran was reacted with ~90:1 MeOH:FA molar ratio and CO₂ as a co-solvent at 300 °C, but ester yields were unsatisfactorily low (~50%) (Kasim et al., 2009). Finally, there have been reports on the thermochemical liquefaction of dry algal biomass, as well as other feedstocks, in supercritical alcohols (Huang et al., 2011; Zhou et al., 2012). From our perspective, liquefaction in alcohol to produce bio-oil and in situ transesterification to produce biodiesel describe the same process. Both bio-oil and biodiesel yields are determined after removing solids from the reaction mixture and evaporating excess alcohol, and in both cases some form of upgrading or cleanup will be required before the fuel is engine-ready. From the literature available, liquefaction work tends to focus mostly on pre-dried, low-lipid feedstocks, favoring the presentation of total bio-oil yields over ester yields, while qualitatively identifying reaction products by GC–MS and ignoring the excessive use of alcohol (estimated >1500:1 EtOH:FA molar ratio). On the other hand, in situ transesterification work typically employs GC–FID to quantitatively determine ester yields while neglecting other components in the crude biodiesel (e.g., nitrogen-rich compounds derived from the biomass) and what measures must be taken to remove them.

This work builds upon our earlier exploratory experiments to better understand how SC-IST can be accomplished with low alcohol loadings. Levine et al. (2010) demonstrated that the lipids within a wet hydrochar (~46% moisture) could be converted into FAEE when reacted with ethanol. The highest ester yield (60%) at 275 °C was achieved after a 120 min reaction with 50:1 EtOH:FA

molar ratio. In the present work, significantly lower EtOH:FA ratios were employed and biodiesel was generated from both wet and dry hydrochars under a variety of process conditions. Regression analysis was used to understand the effects of reaction temperature, time, ethanol loading, water content, and pressure. Finally, a kinetics model is presented to describe the conversion of algal lipids to FAEE under supercritical conditions, and the utility of the lipid-extracted hydrochar is discussed.

2. Methods

2.1. Feedstock cultivation and hydrothermal carbonization

Lipid-rich *Chlorella protothecoides* (UTEX #255) was grown as a biodiesel feedstock using sequential photo- and heterotrophic growth stages as previously described (Levine et al., 2012). Freshly harvested biomass (~20% total solids) was loaded by mass into 316 stainless steel (SS) reactors (4 or 28 mL total volume) fashioned from Swagelok parts (two caps and one port connector). Once loaded, reactors were immersed in a preheated, isothermal fluidized sand bath at 200–250 °C for 15–120 min and then promptly removed and cooled in water. Upon cooling, the hydrochar was recovered by filtering under light vacuum (P2 Glass microfiber filter, Whatman). The wet hydrochar was then either reacted directly, stored at 4 °C prior to reaction, or dried (65 °C for 1 or 24 h) and then reacted. A complete description of the HTC conditions used and the hydrochar lipid content can be found in Table 1. Each hydrochar is designated with a letter in Table 1 that is referenced throughout this work. For one experiment, multiple 28 mL reactions (215 °C for 30 min) were pooled and the reaction mixture was sent to Pall Corporation's Scientific and Laboratory Services for filtration tests on commercial equipment (hydrochar A).

2.2. Supercritical in situ transesterification

SC-IST was carried out in 1.6 mL SS Swagelok reactors with wet or dry hydrochars. Factorial experiments were carried out to

Table 1
Characterization of algal hydrochars.

Parameter	Hydrochar		
	A	B	C
Carbonization temp. (°C)	215	220	235
Carbonization time (min)	30	60	60
Total FAEEs (wt.%) ^a	75	58	51
<i>Fatty acid (% of FAEEs)^b</i>			
C16:0	13	13	13
C18:0	3	2	2
C18:1	65	57	57
C18:2	16	24	24
C18:3	2	2	2
<i>Lipid composition (wt.% of total)^c</i>			
FA	4	9	28
MG	Trace	2	8
DG	7	19	28
TG	89	71	37

^a Total fatty acid ethyl esters (FAEEs) were determined by acid-catalyzed in situ transesterification and quantified by GC–FID considering only the amount of each FAEE listed in the table; other FAEEs were detected but typically comprised <5% of the hydrochar mass. FAEE yields from supercritical in situ transesterification were computed only on the basis of these five esters.

^b Sum of percentages does not total to 100 due to rounding.

^c The proportion of fatty acids (FA), monoglycerides (MGs), diglycerides (DGs), and triglycerides (TGs) in the total lipid extract was determined by hexane–isopropanol extraction and quantification by high temperature GC–FID.

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