



Thermochemical liquefaction of algae for bio-oil production in supercritical acetone/ethanol/isopropanol



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ABSTRACT

Thermochemical conversion processes such as supercritical fluid extraction are used for producing bio-fuels from biomass. Supercritical fluid extraction process is decomposition process of lignocellulose or other organic materials thermally under supercritical conditions at 250–400 °C temperature range under high pressure (4–5 MPa). In this study, the supercritical fluid extraction was used to produce bio-oils from algae. Supercritical fluid extraction trials were performed in a cylindrical reactor (75 mL) in organic solvents (acetone, ethanol and isopropanol) under supercritical conditions with (ferric chloride, potassium hydroxide) and without catalyst at the temperatures of 255, 275 and 295 °C. The effects of process variables including temperature and catalyst on product yields were investigated. The produced liquids at 295 °C in supercritical liquefaction were analyzed and characterized by elemental, GC–MS and FT-IR. 160, 122 and 108 different types of compounds were identified by GC–MS obtained in acetone, ethanol and isopropanol respectively. Bio-oils from supercritical liquefaction were composed of various organics including aromatics, nitrogenated and oxygenated compounds. Bio-oils obtained from supercritical liquefaction were found to have higher calorific values and superior fuel properties compared to feedstock.

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1. Introduction

A very big increase is being observed at the environmental problems because of the fast increase of the population of the world, industrialization and excess use of fossil based fuels. Because of the close relationships of the countries with each other, these environmental problems have been a global problem by getting out of country dimension. This circumstance has changed the point of view of all countries on renewable energy sources and has increased the interest on alternative energy sources [1].

Solar, wind, hydroelectric, biomass and geothermal energy can be considered as the renewable energy sources [2]. Among these sources, forest wastes, energy plants, water plants, waste vegetable oils and biomass that consist of organic oriented wastes have taken great attention as a potential to be used for production of the bio-fuels and have no greenhouse effect compared to the fossil fuels [3–6].

Biomass based feedstocks can be transformed into the more valuable energy forms with thermal, biological and physical

methods. Most of the biomass based feedstocks have been used with the traditional method named as direct burning from back to today. Besides, solid, liquid and gas fuels can be obtained from biomass sources by using thermochemical processes and have the potential to be used more efficiently. Besides, it is possible to reduce the negative environmental effects resulting from direct burning process by using the thermochemical transforming processes [7]. The bio-oil that is obtained from the biomass has more advantages than the traditional use. The most important advantage is that it has high energy volume, easy storage capacity and easy transport features.

Bio-oil can be used as fuel in the engines, turbines and burning units directly, besides, it can be converted into products with higher quality and volume using catalytic cracking, hydrodeoxygenation, emulsification, and steam reforming [7]. For producing biofuel from the biomass, thermochemical methods such as gasification, pyrolysis and liquefaction are the most common used [8]. Gasification of the biomass is the conversion of the solid fuels into a gas mixture that can be burned directly. In this process, the solid fuels such as biomass that contain carbon are being decomposed at high temperature and a high energy density gas mixture is obtained [1]. Pyrolysis method is the process of decomposition of the organic materials with heat in the inert atmosphere or in

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vacuum at temperature range between 350 and 800 °C. In the pyrolysis process, biomass is heated in the absence of oxygen, producing solid (biochar), liquid (bio-oil) and gas products.

The other method that is used for biomass liquefaction is the supercritical liquid extraction. Supercritical liquid extraction is considered to be more effective than the liquid solvent extractions at the industrial field of purification, recrystallization and fractionation processes [9]. Supercritical liquid extraction is used to produce biodiesel, bio-oil and biohydrogen [10]. The liquefaction process with supercritical liquid extraction is the process of thermal decomposition of lignocellulosic or other organic materials in the solvent media at the 250–400 °C temperature range, under high pressure (4–5 MPa). In the supercritical liquid extraction, water also can be used besides the organic solvent such as acetone, ethanol, methanol, isopropanol. Recently, there are studies in which water is being mixed with the organic solvents such as ethanol–water or isopropanol–water used as solvent [11].

It has been determined that the product variability of the bio-oil obtained with the supercritical liquid extraction processes using organic solvents has been compared with the other thermochemical processes.

The alga that is one of the eukaryotic organisms can be in single-celled or multi-celled structure and contains various valued organic compounds such as lipids, sulfated cell-wall polysaccharides and some functional compounds [9]. Algae are found abundantly in nature and they grow spontaneously. Next generation algal biofuels are taking the attention of the researchers that are interested with the alternative energy sources. The most taking attention and making it an attractive raw material is that algae are able to produce more oil compared with the other raw materials [12].

Out of its oil content, algal biomass is being evaluated as an alternative source for the valued compounds such as protein, amino acid and carbohydrates [13,14].

Besides, because algae are using CO₂ more effective at the photosynthesis process compared with the other biomass sources [15], algal biofuels have more advantages together with their CO₂ sequestration feature compared with the other biofuels [16]. Algae can be used at the production of the commercial products such as bio methane [17], bio ethanol [18] and bio hydrogen [19,20], besides it is being thought that this raw material source can be used for obtaining bio-oil together with the supercritical liquid extraction method. There are many studies in which new materials have been obtained from different types of algae together with liquefaction and gasifying by using supercritical ethanol, methanol and water as solvent [21–23].

In a study [22], it has been tried to obtain raw biodiesel with the direct conversion of algae in the supercritical ethanol medium. In the supercritical ethanol conditions, fatty acid ethyl esters have been obtained with the extraction and transesterification of the oils at the algae simultaneously. In the study, the dry algae/ethanol rate 1/6 and 1/15, reaction temperature range between 245 and 270 °C and reaction time period has been determined as 2–30 min. In the supercritical ethanol conditions, at the transesterification reaction, it has been seen that extra use of ethanol has positive effect on the formation of fatty acid ethyl ester [23] and extra quantity algae has fastened the formation rate of ethyl ester [24]. It is known that the heat has positive effects on the product obtained [25]. Together with increasing the temperature, a fast increase has been observed at the quantity of the products obtained up to 265 °C, when reached to 270 °C, decrease has been observed at the products obtained. Maximum fatty acid ethyl esters have been obtained at 265 °C, at the 20 min of reaction period, at 1/9 dry algae/ethanol rate and about 67%. The maximum calorific value has been determined as 43 MJ/kg for the biodiesel obtained.

Table 1

Main characteristics of the algae.

Components	
Ultimate analysis ^a (%)	
Carbon	36.53
Hydrogen	4.01
Nitrogen	2.92
Oxygen ^b	56.54
H/C molar ratio	1.30
O/C molar ratio	1.16
Empirical formula	CH _{1.30} N _{0.068} O _{1.16}
Higher heating value (MJ/kg)	
Dulong's formula	7.94

^a Weight percentage on dry and ash free basis.

^b By difference.

In another study, it has been tried to produce biodiesel from algae at the supercritical methanol media. In the first step of the study, extraction and transesterification of algae has been done at the same time. At the end of the trials, the optimum conditions for the study have been determined as follows; wet algae/methanol rate is 1/5, reaction temperature is 255 °C, and reaction period is 25 min [23]. Besides, there are studies at the literature in which lipids have been obtained from algae with supercritical CO₂ and supercritical dimethyl ether extraction and algae has been gasified with supercritical liquid extraction [9,21].

On the other hand, recently, supercritical alcohols are considered as an alternative solvent at the liquefaction process of the biomass because of their features. Because of the features of the alcohols such as being better solvent, having fewer corrosion effects, to be able to be separated from the products easily and high product efficiency, they are preferred more [26]. Supercritical fluids provide unique mass and heat transfer properties such as gas-like diffusivity and liquid-like density and completely miscible with liquid/vapor products, which facilitate and promote the reactions [27].

In most of the studies carried out, it has been tried to obtain biodiesel with the simultaneous extraction and transesterification of the lipids and other organic compounds that are present at the structure of algae.

In this study, green fresh water algae have been used as biomass source. To utilize the all components present in the structure of algae, supercritical liquefaction of the algae with acetone, ethanol and isopropanol and transformation into new products was carried out in this study.

2. Material

Algae samples have been collected from a stream bed located at Sakarya region of Turkey. Collected samples have been cleaned from the non-pure items and have been dried at 50 °C in driven oven for 1 week of time period.

It has been grinded in the 0.425 mm dimension at the laboratory and pulverized. Before the supercritical liquefaction processes, it has been grinded and elemental analysis of the samples have been done. Elemental analyzer (LECO CHNS-932) was used to perform the ultimate analysis of the sample. Higher heating value (HHV) was calculated by Dulong's formula using the results of ultimate analysis. The main characteristics of feedstock (algae) obtained from the ultimate analysis are given in Table 1.

2.1. Experimental procedure

The liquefaction experiments were conducted in a 75 mL capacity cylindrical autoclave made of stainless steel with dimensions of 30 mm inner diameter, 60 mm outer diameter and 145 mm height.

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