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Bio oil production from microalgae via hydrothermal liquefaction technology under subcritical water conditions

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ABSTRACT

The upsurge in the concerning issues like global warming, environmental pollution and depletion of fossil fuel resources led to the thrust on third generation biofuels. Algal research has gained a lot of importance in the recent years. Effective utilization of algal biomass in a single step is necessary as it can produce Bio-oil (BO), gases and in addition to a variety of valuable products, along with nutrient recovery. Hydrothermal liquefaction technology does not require the energy intensive drying steps and is an attractive approach for the conversion of algae to liquid fuels. This study investigates direct hydrothermal liquefaction (HTL) of microalgae (Algal biomass) to produce bio-oil using a high-pressure batch reactor under subcritical water conditions. Three different micro algae samples namely, *Chlorella vulgaris, Botryococcus braunii and Scenedesmus quadricauda* have been examined under hydrothermal liquefaction with different water concentrations (1:6, 1:7, 1:8, 1:9 & 1:10 ratio) at certain temperature range (200–320 °C), pressure (60 bars) and reaction time (30 min). Through liquefaction, the highest BO yield achieved with *S. quadricauda* was 18 wt% at 1:9 ratio. The chemical components of the obtained bio-oil were analyzed via gas chromatography and the results indicated that the algal BO was composed of furan, phenol, acid, and ester derivatives. Moreover, it was found that by increasing the temperatures, the BO yields increased. This was due to the polymerization reactions that converted the small biomass components into heavier molecules. FTIR spectra showed high percentage of Aliphatic, Phenolic, alcoholic, Carboxylic and Hydroxyl groups for solid residues.

1. Introduction

With the increasing global issues, researchers all over the world have been making efforts to mitigate the growing issues which paved a way towards clean development and green innovations. One such innovation was production of biofuels. This involved partial or complete replacement of fossil resources by carbon-neutral renewable ones. Biomass utilization as an alternative feedstock to fossil fuels has been a major breakthrough. Biomass is a promising feedstock since it is abundant and cheap and can be transformed into fuels and chemical products (Biller and Ross, 2012). Microalgae biofuels are also likely to have a much lower impact on the environment and on the world's food supply than conventional biofuel-producing crops. When compared with plant biofuel, micro algal biomass has a high caloric value, low viscosity and low density, properties that make microalgae more suitable for biofuel than lignocelluloses materials (Miao et al., 2004). There are several methods of biomass conversion to liquid fuels which can be in either biochemical or thermo-chemical routes. Thermo chemical conversions are processed at several higher degrees of temperature in the presence of appropriate catalysts and without catalyst to obtain liquid products from different sources. In general, thermo chemical conversions are much rapid than the biochemical conversions. Thermo-chemical conversions are generally implied to upgrade biomass by heating under pressurized and oxygen deprived enclosure. It can be further classified into combustion, gasification, Pyrolysis, and hydrothermal processing (Gollakotaa et al., 2018). Gasification is a process of partial oxidation at high temperatures to produce gaseous fuel products. Pyrolysis involves the production of bio-oil, gases and charcoal in the absence of air at medium to high temperatures among which, hydrothermal processing (HTP) is one of the promising routes that has

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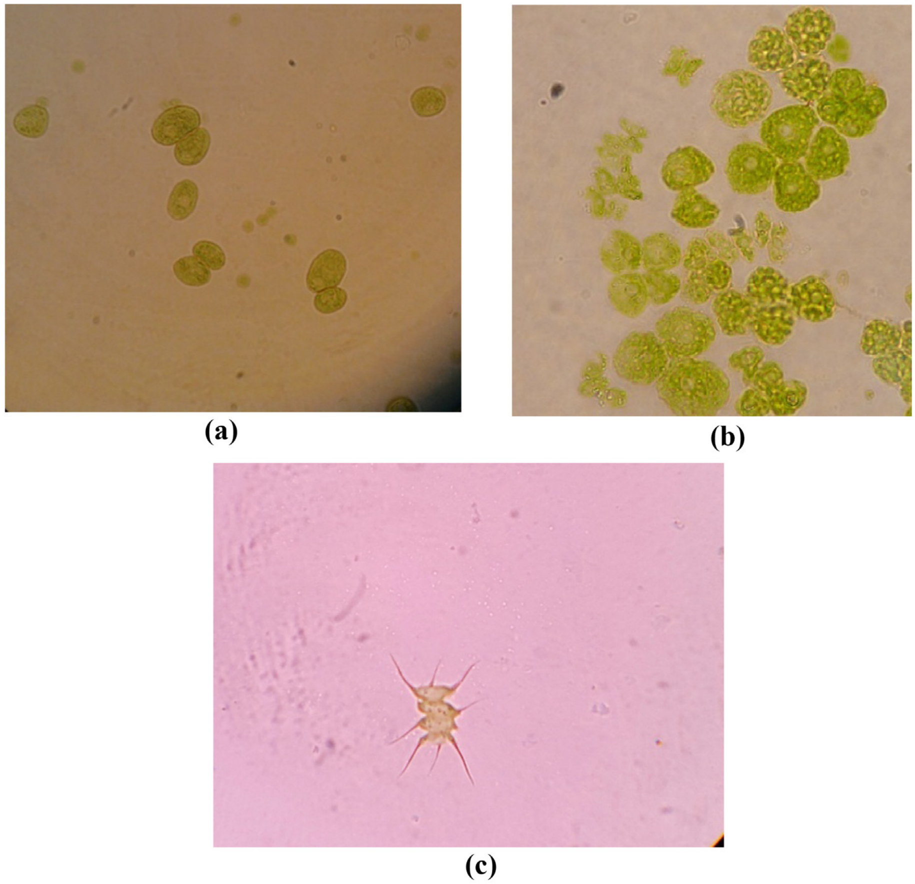

Fig. 1. microscopic observation of the three algal strains (a) *C. vulgaris*, (b) *B. braunii*, (c) *S. quadricauda*.

drawn attention in the recent years. In HTP operation, the conditions depend upon various temperatures. At low temperatures, less than 200 °C, the process is referred to as HT carbonization (HTC). HTC is a type of HTP in which biomass is heated in water at mild temperature of below 200 °C and a mild pressure of below 2 MPa to create a char product or bio char. The main goal of this process is to increase the carbon-to-oxygen ratio in the product. The product thus formed will have the potential to be used for synthesis of gas and conversion as a carbon neutral supplement to natural coal. The end product can also be converted to industrial chemicals and soil nutrient amendment. (Heilmann et al., 2010; Titirici and Antonietti, 2010).

Hydrothermal liquefaction (HTL) is a type of HTP in which the biomass is converted into bio-crude/bio-oil using water at sub- or super-critical temperatures and pressures. Generally the temperature and pressure range for a typical HTL are 280–380 °C and 7–30 MPa, respectively and are sufficient to keep water in a liquid state. The primary product of HTL is a black organic liquid called bio-crude or BO and the main by-products are solid residue, aqueous products or water soluble product and gases. The solid residue is also known as biochar. BOs produced by this process have high oxygen content and higher nitrogen content (in case of algae as feedstock) although this makes the BOs generally un process able with petroleum feed stocks but it can serve as a starting material for valuable petroleum based fuels and products such as polymers, aromatics, lubricants etc. (Abdel Kader et al., 2015). The advantage of hydrothermal liquefaction is that it can process both dry and wet biomass, so biomass feedstock drying is no longer needed. Since microalgae biomass usually has high moisture content, the drying process requires a large amount of thermal energy due to the high heat of vaporization of water (Saqib Sohail et al., 2011). Moreover, in comparison with other methods, BOs production by HTL has near zero SOx emissions (Douglas et al., 2015). In HTL, many studies were carried out using chemical solvents instead of water as a reaction medium but water has several advantages over chemicals as it is ecologically safe, Non toxic, cheap, readily available and environmentally benign solvent. At normal conditions water will not react with any organic compounds. In HTL process the properties of water will change with increase in temperature. Moreover, water itself has a catalytic role in various processes due to its higher degree of ionization at the increased temperature. In HTL conditions water is a powerful ecological polar organic solvent due to the strong decrease of its dielectric constant with temperature. Water molecules isolate the reaction intermediates and serve as a physical fencing between them. In fact, water is the driving force in HTL, as it acts both as a catalyst and a reactant. (Savage, 2009; Demirbas, 2011).Temperature, reaction time and biomass to water ration are the most effective parameters in HTL Process as they play the key roles in determining the amount and the quality of products (Anastasakis and Ross, 2011; Yin et al., 2010; Xu and Lad, 2007; Liu et al., 2012). Therefore, the objective of the present work is to evaluate and experimentally explore the effect of hydrothermal liquefaction on the microalgae (*C. vulgaris*, *B. braunii* and *S. quadricauda*) biomass under subcritical water conditions for BO production at different water concentrations and at varying temperature range to (200–320 °C). The chemical composition of BO was analyzed by GC/MS analysis.

2. Materials and methods

2.1. Isolation and identification of microalgae

The microalgae samples were collected from the algal blooms of local contaminated Lakes in Hyderabad, Telangana, India. Microscopic examinations were conducted to check for the availability of lipid