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Research Article

Assessment of Product Yield and Characteristics of Biocrude from Hydrothermal Liquefaction

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Abstract

Biomass is a promising renewable energy source for fuel conversion. Hydrothermal liquefaction technology converts biomass into an energy-rich biofuel called biocrude which can potentially substitute fossil fuels. In this study, wet biomass namely water hyacinth, banana pseudostem, banana peduncle, wine waste and beer waste were investigated for biocrude production. The biomass macro molecules underwent anaerobic thermochemical disintegration to yield biocrude in the range of 7.3 to 16% at the hydrothermal liquefaction temperature and pressure of 275 °C and 15 MPa respectively. Wine waste showed higher biocrude yield (16%) among the selected biomass materials with aqueous phase (63%) and char (3%) as by products. The recovered biocrude showed good quality fuel properties similar to diesel and bio-diesel with heating value of about 30 MJ kg^{-1}. GCMS and FTIR analyses proved the biocrude to be rich in aliphatic and aromatic fuel and chemical derivatives of alkenes, alcohols, ketones and amines which necessitate its potential to drop in advanced fuels and chemicals for supplementing conventional resources.

Keywords: Biocrude, FTIR, GC-MS, Hydrothermal liquefaction, Wet biomass, Wine waste

Introduction

Biomass is a significant carbon-neutral energy source for the production of fuels and chemicals with very low GHG emissions compared to conventional fuels. It offers a great potential for energy production and replacement for fossil fuels. Biomass can be utilized for various energy generation processes by either biochemical or thermochemical conversion routes. India being an agricultural country is bestowed with abundant biomass resource with its estimated availability of 500 million metric tons per annum (MNRE, 2022). Out of the total availability, 40% of bio-wastes are wet with moisture content above 50%. Generally, the bio-derived thermochemical treatment converts only dry biomass to fuels whereas the wet biomass can also be thermally converted to an energy rich fuel through hydrothermal (HT) processing. Thus, the biomass pretreatment by drying is omitted in HT process, saving energy and costs.

Hydrothermal liquefaction (HTL) is one of the hydro processing techniques, carried out at 200-350 °C with high pressures up to 20 MPa to convert wet biomass into liquid fuel called biocrude (Li *et al.*, 2014). In hot, compressed and wet environment, water medium undergoes physical and chemical transformations reforming the complex bio-polymers *viz.*, cellulose, hemicellulose and lignin of biomass to biocrude. HTL biocrude has higher energy content compared to the bio-oil produced from pyrolysis, a conventional thermochemical technique (Huber *et al.*, 2006) and is also a source of various chemical compounds. It can be directly used as a marine fuel (Ramirez *et al.*, 2015) or can be upgraded to approach transportation fuels (Minowa *et al.*, 1998). Various studies have been experimented to distinguish and quantify biocrude from other related constituents in HTL but standards are not yet available

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to prescribe the conditions, composition and derivation of products. Hence a detailed investigation is required to further understand the mechanisms and properties of biocrude for fuel applications.

Keeping in view, this work was taken up to study the potential of the wet biomass namely water hyacinth, banana pseudo stem, banana peduncle, wine waste and beer waste for biocrude production by hydrothermal liquefaction process. The characteristics of the biocrude were analyzed for the fuel properties and hydrocarbon composition with respect to feedstock in order to access the possibility of derivation of fuel or chemical components.

Materials and Methods

Biomass selection was done by characterization as per ASTM and NREL methods (ASTM, 1989; NREL, 2012). The biomass was selected based on the availability, high moisture content, volatile matter and cellulose composition. HTL experiments were conducted in a laboratory scale high pressure reactor of 5 liters capacity. The reactor was equipped with an insulated electric heater, magnetic driven agitator to stir up the components for uniform processing and condenser to condense the reaction vapors yielding biocrude. The reactor line diagram is shown in Figure 1.

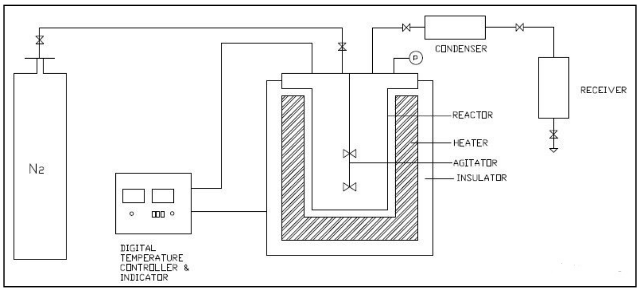

Figure 1: Schematic representation of HTL reactor setup

HTL Experiments

Selected biomass was mixed with deionized water in the ratio of 1:3 and fed up to a working volume of 3 litres. HTL experiments were carried out at 275 °C temperature, 15 MPa pressure and 40 min retention time in an air-tight anaerobic environment. Nitrogen gas was used to purge the residual air in the reactor. Then the reactor was heated up to 275 °C, after which the retention time was maintained. Reaction vapors were released to the condenser and the condensate was collected in the receiver. The reactor was then cooled down to room temperature by circulating water from the cooling tank. At the end of the experiment, condensate and the left-over reaction mixture were collected and processed downstream for the separation of HTL products. The biocrude and aqueous phase were separated by solvent extraction using Dichloromethane (DCM). The reaction mixture was filtered to separate the solid residue from the aqueous phase. The solid residue was oven dried at 105 °C to obtain char. The yield of biocrude was calculated by the following equation (Xiu *et al*., 2010; Shah *et al*., 2020).

Biocrude Characterization

The fuel properties like heating value, flash point, fire point, cloud point, pour point, density and viscosity were determined as per the ASTM methods (ASTM, 2016; ASTM, 2017) and compared with fuel oil standards (NREL, 2016). GC-MS (Model ITQ 900, Thermo Scientific) was used to analyze the chemical composition of biocrude. FTIR analysis of biocrude provided the functional group characteristics of biocrude which was performed using Fourier Transform Infrared Spectrophotometer (IR affinity-1S model, Shimadzu).

Results and Discussion

Biomass Characteristics

The selected biomass showed higher moisture content ranging from 73.5 to 93.8% which finds its suitability for HTL process. They had higher volatile matter (61 to 85.6%) and higher cellulose content (21-38%), which favors in increased liquid fuel yield (Divyabharathi and Subramanian, 2022). The characteristics of the selected biomass are given in Table 1.

Yield of Biocrude

HTL experimental results of the selected biomass showed a higher biocrude yield of 16% for wine waste at the set conditions of temperature and pressure. Minimum yields of biocrude (7-9%) were obtained for samples of water hyacinth and banana peduncle. This is due to the fact that wine waste exhibited higher cellulose (37.8%) and volatile content (85.6%) in the biomass which favored higher biocrude production (Li *et al*., 2020). Cellulose, being a natural polymer starts degradation at (240 °C) to levoglucossan and then to oil (major product) and char (Isa *et al*., 2011). Since the operating HTL temperature favors the

Table 1: Characteristics of the selected biomass

Properties	Water hyacinth	Banana peduncle	Banana pseudo stem	Wine waste	Beer waste
Moisture, %	89.00	92.00	93.80	81.17	74.50
Volatile content, %	61.69	76.70	82.50	85.61	71.24
Fixed carbon, %	30.57	22.18	4.77	31.22	23.02
Ash content, %	7.74	1.12	12.73	1.17	5.74
Heating value, MJ kg^{-1}	13.62	15.50	19.12	25.74	16.40
Cellulose, %	21.00	26.00	22.73	37.80	27.00
Hemicellulose, %	10.00	15.00	20.60	28.20	24.00
Lignin, %	5.65	8.20	9.70	4.34	5.04

decomposition of cellulose, it was easier for the fragments to readily solubilize and react to form hydrocarbons. However, the volatiles (61-76%) and cellulose (21-26%) contents of water hyacinth and banana peduncle were comparatively lower, which resulted in lower yields. Previous studies also reported similar yields of 25% for microalgae and 21% for Indonesian bio-residues (Biller and Ross, 2011). The yield of biocrude obtained from the HTL of selected biomass are given in Table 2. Other significant byproducts of HTL process were the aqueous phase and char, whose yield ranged from 63-86.5% and 1.2-3%, respectively for the selected biomass. Figure 2 shows the overall yield distribution of HTL products. With biocrude as the major product, energy recovery was found to be maximum for wine waste of about 18%.

Table 2: Biocrude yield of selected biomass

Properties	Yield of HTL products (%)		
	Biocrude	Aqueous co-product	Char
Water hyacinth	7.33	86.55	2.98
Banana peduncle	9.33	69.82	2.18
Banana pseudo stem	12.00	80.73	1.45
Wine waste	16.00	63.27	2.76
Beer waste	10.67	85.45	1.27

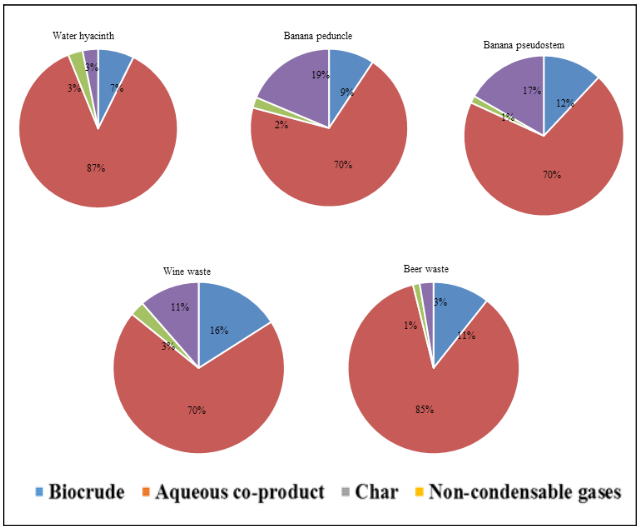

Figure 2: Yield distribution of HTL products

HTL Biocrude Characterization

The fuel properties of biocrude produced from HTL of biomass are summarized in Table 3. The heating value of the biocrude ranged between 18 and 30 MJ kg^{-1} which was comparable to the biodiesel and diesel values of 40 MJ kg^{-1} and 45 MJ kg^{-1}, respectively (NREL, 2016). The flash and cloud points of the biocrude ranged from 98 to 118 °C and -3 to 8 °C, respectively which was comparatively low to biodiesel (100 to 170 °C and -3 to 15 °C, respectively). This improves the cold flow property and ignition quality of the fuel. This shows the potential of biocrude in replacing or blending with existing fuels.

GC-MS analysis identified the major composition of the biocrude by comparison with the NIST mass spectral library values. The chromatogram showing the major peaks of components in wine waste biocrude obtained at 275 °C, 40 min and 15 MPa is shown in Figure 3. The major peaks shown in Figure 3 at corresponding retention time represent 4-methyl-3-Penten-2-one at 2.643; 4-hydroxy-4-methyl-2-Pentanone at 2.932; 2-Carene at 4.976; D-Limonene at 5.203; 1,2,3,4-tetramethyl-Benzene at 5.120; γ-Terpinene at 5.792; 1-methyl-Cyclohexene at 6.535; Propanamide at 18.879; and 1,3-Cyclohexanediol at 22.07. Hence the major

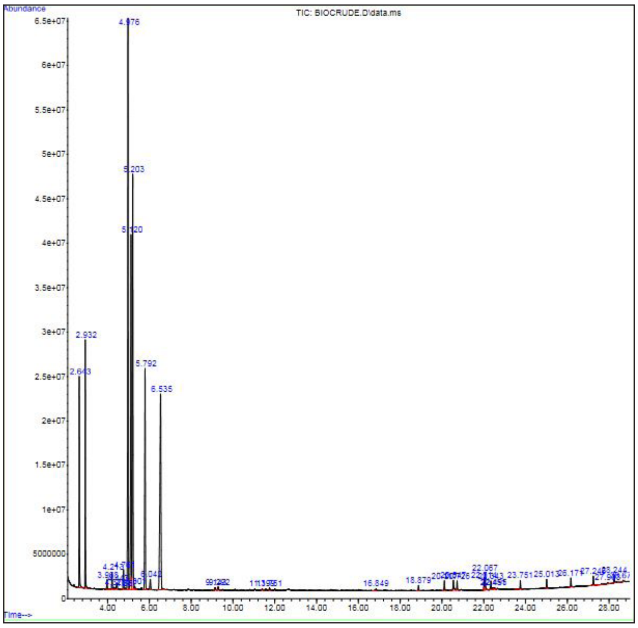

Figure 3: GC-MS chromatogram of wine waste biocrude

Table 3: Fuel properties of HTL biocrude of selected biomass

Fuel properties	Water hyacinth	Banana peduncle	Banana pseudo stem	Wine waste	Beer waste
Heating value, MJ kg^{-1}	18	20	28	30	24
Flash point, °C	118	112	106	98	108
Fire point, °C	126	120	116	106	112
Cloud point, °C	8	3	2	-3	4
Pour point, °C	13	8	7	6	9
Viscosity, cst	204	212	188	162	168
Density, kgm^{-3}	970	990	940	880	900

compounds detected were aromatic alcohols, aliphatic and aromatic hydrocarbons with few amounts of esters, ketones, cyclic hydrocarbons and oxygenates. The major portion of hydrocarbons was derived by the degradation reactions of cellulose and hemi-cellulose. The presence of cyclic hydrocarbons and cyclic oxygenates are due to the reploymerization reactions which affects the biocrude quality on storage (Sharma *et al*., 2020). This problem can be addressed by means of further down-streaming with suitable up gradation techniques.

Figure 4 shows the FTIR spectrum of biocrude obtained from wine waste. It confirmed the major spectra detected by GC-MS that the biocrude is a complex mixture of aromatic and aliphatic derivatives showing strong bands at 3700-3900 cm^{-1}. The C-H stretching groups and C=O groups can be identified with the bands at 1500-1800 cm^{-1} which was reliable with the hydrocarbon peaks detected by GC-MS. Lower peaks at 9700-900 cm^{-1} depicts C=O bands which indicates lesser amounts of ketones and oxygenates. Similar results were reported by Koochaki *et al*. (2020). From the analyses, it is evident that biocrude is a source of various chemical compounds like phenolics, aromatics, carboxylic acids, alkanes, ketones, esters, aldehydes, nitrogenates *etc*.

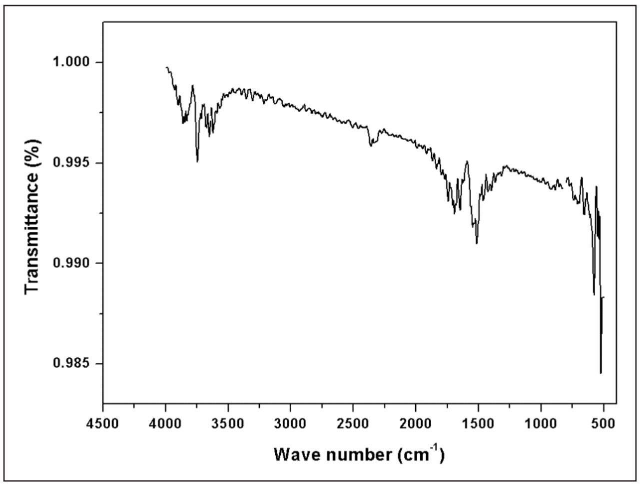

Figure 4: FTIR spectrum of wine waste biocrude

Conclusion

In this study, the hydrothermal conversion of various wet biomass to biocrude for higher yield and its fuel quality by GCMS and FTIR analysis were investigated. Among the selected biomass materials for hydrothermal liquefaction, wine waste resulted in higher yield of biocrude (16%) due to its higher volatile (85.6%) and cellulose composition (37.8%). HTL of wine waste resulted in biocrude of higher energy content (30 MJ kg^{-1}) which is greater than the heating value of pyrolytic bio-oil and had comparable fuel properties with existing transportation fuels like diesel and biodiesel. The GC-MS and FTIR analysis also results proved that biocrude is promising source of fuels and chemicals like alkenes, alcohols, ketones, acids and amines. Thus HTL provides a sustainable pathway to drop-in fuels and chemicals offering a potential replacement for fossil fuels in near future.

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