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## Article

# Biocrude Production from Wheat Straw at Sub and Supercritical Hydrothermal Liquefaction

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**Abstract:** In this study, hydrothermal liquefaction (HTL) of wheat straw (WS) in sub (350 °C) and supercritical (400 °C) water with and without alkali catalyst was performed to investigate the potential of WS for the production of biocrude. The influences of temperature and catalyst were studied for the HTL products. Results showed that maximum biocrude yield (32.34 wt. %) with least solid residue (4.34 wt. %) was obtained at subcritical catalytic condition, whereas the carbon content was slightly higher in biocrude at supercritical. The higher heating value (HHV) for biocrude is around 35 MJ/kg for all four conditions. The major compounds in biocrude were observed as ketones, alcohols, acids, and hydrocarbons. At 350 °C, 44–55% of the carbon recovered into biocrude. The products were characterized in terms of elemental composition, higher heating values, organics, and inorganic compounds in different phases. To keep in consideration the scale-up of HTL process for continuous plant, aqueous phase from HTL was also recirculated which showed the fruitful outcomes by increasing the biocrude yield at each cycle.

**Keywords:** wheat straw; sub-supercritical HTL; catalyst ( $K_2CO_3$ ); biocrude; inorganics; and aqueous phase recirculation

## 1. Introduction

The consumption and demand for energy are continuously increasing due to rapid growth in population and the global economy. However, depletion of fossil fuel reservoirs and increasing greenhouse gasses (GHG) emissions are harmful to the environment. As an alternative to fossil fuels, biomass has become a more attractive resource for years as a renewable source of energy. The utilization of biomass for the production of energy reduces GHG emission as well as dependency on fossil fuels [1].

Lignocellulosic biomass is non-edible and potentially available in the world in the form of forest, wood, and agricultural residue that can be adopted for the fuel production [2]. Wheat straw (WS) is a by-product of wheat crop and reported as second-largest potential lignocellulosic biomass in the world [3], with the estimated energy potential of  $47 \times 10^{18}$  J [4]. It was reported that annual production of WS was approximately around 887 million tons in 2012 globally. However, due to lack of efficient machinery system for collection of WS from field crops etc., most of the amount of WS remains unutilized [5]. Traditionally, WS has been used for soil chopping, field burning, or sold to market for different uses. In the Europe Union (EU), especially Denmark has much experience with straw-fired power plants [6]. The open burning of straw has faced challenges like emissions of particulate matter, which can cause several environmental issues and especially deteriorate the air quality and it results in several health diseases [7]. In contrast, utilization of the WS for biofuel production reduces the

air pollution and improves the circular economy. Wheat crops at the same time produce grain and generate straw as a residue that can be used for biocrude production, which results in profit at both ends. Recently Palmieri et al. investigated the straw management methods at farm-gate. For the first option, they analyzed the straw by incorporating it into the crop soil or burning it, and the second option was baled and the straw was sold for biofuel production. By comparing both scenarios, they concluded that the second option is more economic and environmentally friendly and it contains more benefits [4].

For decades, the thermochemical conversion route has been famous for the proper heating and biomass oxidation for the production of the biofuel. Hydrothermal liquefaction (HTL) is a well-known thermochemical process, which can deal with wet as well as a dry feedstock under different process conditions, i.e., temperature 250–450 °C and 100–350 bar [8]. In HTL, water plays a key role at sub and supercritical conditions in converting the organic matter into energy valuable products via decomposition, hydrolysis, and depolymerization [9,10].

The utilization of the catalyst for the hydrothermal processing is favorable to enhance the process efficiency. Homogeneous catalysts contain alkali salts that enhance the biocrude yield by accelerating the water-gas shift reaction [11]. Among alkali catalysts, potassium carbonate ( $K_2CO_3$ ) is considered more catalytically active and economical [12].

In the available literature, several studies have been published on the different types of straw. For example, Harry et al. performed the liquefaction experiments for the conversion of Flax straw into valuable chemicals, i.e., furfural (mainly used in lubricating oil) at 175–325 °C under the pressure of 0.1–8 MPa for 0–120 min in an autoclave and achieved maximum yield of 0.75 mass fraction % at 250 °C [13]. Patil et al. reported that maximum HHV of 28 MJ/kg for bio-oil can be obtained by utilizing WS through liquefaction with water-alcohol mixture as a reactive medium at subcritical condition and obtained >30 wt. % oil yield [14]. Similarly, Zhu et al. studied the HTL of the barley straw by using slow heating in autoclave and reported an increase biocrude yield from 17.88 to 34.85 wt. % by the addition of  $K_2CO_3$  catalyst [15]. Straw has also been used for the production of bioethanol in which pretreatment was required to reduce the lignin concentration [16–18].

The production of biocrude from WS, investigation of influence of temperature and alkali catalyst on HTL products, and carbon/nitrogen recoveries are reported in this study. Furthermore, aqueous phase recirculation was applied to explore the impact of aqueous phase on the overall energy recovery. The aqueous phase from HTL needs proper attention to recover the energy in the form of organic carbon. The potassium (K) concentration in aqueous phase may reduce the catalyst dosage by recirculation of the aqueous phase within the HTL system. It seems to be a sustainable method to reduce the cost of wastewater treatment and consumption of fresh water for HTL process at large scale. The impact of aqueous phase recirculation on HTL products is discussed in Section 3.7.

The aim of this study is to provide the comparative information about the production and properties of the biocrude through hydrothermal liquefaction at sub- and supercritical conditions. The influence of alkali catalyst ( $K_2CO_3$ ) on HTL products is also discussed. Additionally, the impact of aqueous phase recirculation was explored on the properties of the biocrude. This article also highlights the distribution of inorganic elements among the HTL products. This study can be considered as a parametric study to obtain the fundamental knowledge about the conversion of WS biomass before launching at a continuous plant scale for the production of biocrude.

## 2. Materials and Methods

### 2.1. Feedstock Characterization

WS was used as received from wheat crop field located in Aalborg, Denmark. WS was crushed through a grinder machine (Cyclone mill, Foss, Cyclotec 1093, Hillerød, Denmark) and screened with the help of the sieves in the range between 0.5 and 1.0 mm size. After that, moisture content, ash

content, fiber analysis, and elemental composition (Table 1) were performed. Potassium carbonate ( $K_2CO_3$ ) was used as a catalyst during the experimental process.

**Table 1.** Characterization of wheat straw used for the hydrothermal liquefaction (HTL) experiments.

| Elemental Analysis <sup>a</sup> (% , daf) and Fibre Mass Composition (% , db) <sup>b</sup> |       |
|--|-------|
| Carbon   | 42.15 |
| Hydrogen   | 6.21  |
| Nitrogen   | 0.82  |
| Oxygen (by difference)   | 50.82 |
| Cellulose  | 37.92 |
| Hemicellulose  | 30.24 |
| Lignin   | 4.69  |
| Ash <sup>c</sup>   | 6.92  |
| Moisture content (% , as received) <sup>d</sup>  | 5.39  |
| Higher heating value (MJ/kg) <sup>e</sup>  | 16.53 |
| H/C  | 1.76  |
| O/C  | 0.91  |

<sup>a</sup> Ultimate analysis was carried out in a Perkin Elmer 2400 Series II CHN/O system; <sup>b</sup> Fibre composition was determined by FOSS Cyclotec 1093; <sup>c</sup> Ash content measured by heating a sample to 850 °C and held isothermally for 2 h; <sup>d</sup> Moisture content measured through moisture analyzer (Kern, MLS, Buch-Holm, Denmark) at 120 °C; <sup>e</sup> Higher heating value (HHV) measured through Bomb Calorimeter.

## 2.2. HTL Experimental Setup and Product Analysis

Initially, feedstock slurry was loaded corresponding to 20% dry matter of WS with distilled water for a total slurry of 21 g in a stainless steel batch reactor of 41 mL for HTL experiments. The experiments were carried out in triplicates at sub and supercritical conditions, with and without a catalyst and the mean values were reported. After the loading of slurry into the reactor, the reactors were closely tightened, purged with nitrogen at 10 MPa to make the proper settlement of slurry in a reactor. The reactors were then inserted into the preheated sand bath at 350 and 400 °C for the reaction time of 15 min at which pressures were achieved 18 and 35 MPa respectively. Thermocouples were connected to the reactors during the HTL experiments so that the temperature was monitored throughout the reaction time. The methodology of the overall experimental setup was adopted from Shah et al. [19]. For the aqueous phase recirculation experiments, the reactors were loaded by adjusting the dilution ratio of aqueous phase and demineralized water by 50:50 to make the slurry of total 21 g with biomass loading 4.43 g. However, the concentration of  $K_2CO_3$  adjusted as 2% of total slurry. Two cycles (R1 and R2) of experiments were conducted at reference condition, i.e., 350 °C catalytic by recirculation of aqueous phase back to the reactor. The formulae for products yield, higher heating values of biocrude and solid residue, and energy recovery are mentioned below. In this study, product's yield are reported on dry ash-free (daf) basis.

$$\text{Biocrude yield (\%)} = (\text{Weight of the biocrude} / \text{Weight of the biomass used}) \times 100 \quad (1)$$

$$\text{Solid yield (\%)} = (\text{Weight of the solid residue} / \text{Weight of the biomass used}) \times 100 \quad (2)$$

$$\text{HHV (MJ/kg)} = (0.3419)\text{C} + (1.11783)\text{H} + (0.1005)\text{O} - (0.1034)\text{N} \quad (3)$$

$$\text{Energy Recovery, ER (\%)} = (\text{HHV of product} / \text{HHV of biomass used}) \times \text{product yield} \quad (4)$$

After the completion of liquefaction process, reactors were placed in the water bucket for cooling for 30 min. The gas phase was not collected and allowed to be vented off from the reactor valve. The aqueous phase was collected for further analysis. Subsequently, the reactor was washed with acetone to collect the other products. For the extraction of solids, the mixture was filtered through pre-weighed filter paper (particle retention: 5–13 µm) with vacuum filtration technique, after that the solid sample was dried in the oven at 105 °C for 24 h to obtain the solid yield. Acetone was evaporated

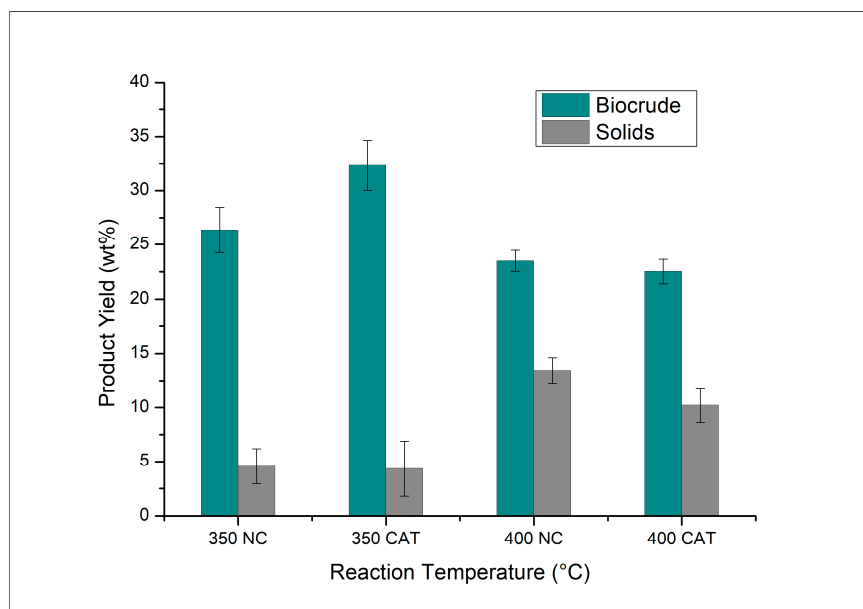
through the rotary evaporator at 60 °C, 56 Mbar and a water-immiscible reagent Diethyl Ether (DEE, Sigma Aldrich, ACS reagent, anhydrous, >99.0%, Søborg, Denmark) was added to recover the biocrude. Pedersen et al. experienced the combined utilization of acetone and diethyl ether for the recovery of HTL products (oil) from lignocellulosic model compounds [20].

After performing the HTL experiments, biocrude, solid residue, and aqueous phase were characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to investigate the inorganics. The detailed procedure of ICP-AES was followed as described by Shah et al. [19]. Additionally, for detection of CHNO, biocrude, and solids sample were measured through the elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O, Shelton, WA, USA). Whereas oxygen was calculated by difference. HHVs of biocrude and solid residue were calculated through Channiwala and Parikh correlation [21]. The thermal behavior of the biocrude was assessed by the Thermogravimetric Analysis (TGA) by using instrument (TA instrument Discovery, ELTRA Elemental Analyzers, Haan, Germany) under the nitrogen atmosphere at 800 °C. Organic compounds in biocrude samples were analyzed through gas chromatography–mass spectrometry (GCMS). For Total Organic Carbon (TOC) and Total Nitrogen (TN) in the aqueous phase, reagent vials and a spectrophotometer unit were used. Additionally, pH of the aqueous phase was measured with WTW pH meter.

### 3. Results and Discussion

#### 3.1. Influence of Temperature and Catalyst on Product Yield

The temperature played an important role and was considered as one of the main factors in the HTL process. The process conditions are reported as 350/400 °C NC/CAT for the non-catalyst and catalyst respectively. The effect of process temperature on product yields is illustrated in Figure 1. It can be observed that temperature has a significant effect on product yield. The maximum biocrude yield was 32.34 wt. % obtained at 350 °C CAT condition and comparatively decreased (23.50 wt. %) with the increasing of temperature at 400 °C. The decreasing of biocrude yield at a higher temperature may be due to thermal cracking of biocrude compounds into gas phase or water-soluble products.



**Figure 1.** Product yields at the sub and supercritical temperature with and without alkali catalyst.

Generally, the biocrude yield is also affected by the concentration of carbohydrates available in biomass used; however, for the thermal stability of liquid fuel; cellulose and hemicellulose primarily contribute their part. Whereas process temperature and pressure are the main responsible factors for

changing the assembly of the long-chain polymers by altering carbon, hydrogen, and oxygen into small chain hydrocarbons [22]. As compared to lignin, cellulose demonstrated higher biocrude conversion due to the molecular chain of lignin is difficult to liquefy while the cellulose and hemicellulose have weak bonding force [23–25]. The decreasing of biocrude yield at supercritical condition might be due to water critical point (373.74 °C) because the increasing temperature could be responsible for the polymerization of macromolecules of biocrude into gaseous formation or production of solid residue [26]. Additionally, another reason for decreasing of biocrude yield is occurrence of the condensation reaction to the solid residue.

Accompanied by biocrude, the observed trend is different for solid residue. The solid yield was increased as the temperature increased. It indicates a higher degree of repolymerization. The maximum solid residue was obtained at the supercritical as 10.22–13.46 wt. % while 4.34–4.57 wt. % at the subcritical condition. Wang et al. also reported the maximum solid formation for the deoxy-liquefaction of WS at 400 °C [27]. It was reported that the utilization of the catalyst reduces the tar formation for the thermochemical process [28]. The previous studies of lignocellulosic biomass through HTL route have also reported the increasing of solid yield with respect to temperature [29–31].

In HTL process, the addition of catalyst plays a vital role as literature supports that alkali catalysts ( $K_2CO_3$  and KOH) performed well as compared to other catalysts to improve the biocrude yield and reduces the char formation [32–36]. According to findings of this study, it was observed that the addition of alkali catalyst ( $K_2CO_3$ ) enhances the biocrude yield at subcritical temperature as shown in Figure 1. The biocrude yield improved approximately 5.99% from 26.35 to 32.34 wt. % in catalyst run, while solid yield remains almost the same at 350 °C.

However, catalyst did not increase biocrude yield at supercritical temperature. It can be hypothesized that at supercritical conditions, catalyst might accelerate the cracking reactions, which results in higher formation of the gaseous, or aqueous phase as maximum value for TOC was observed at 400 CAT (33.52 g/L).

By the addition of the catalyst, hydroxide and bicarbonate were formed due to the reaction of catalyst with warm water which results in increasing the liquefaction process in the form of increasing biocrude yield [37]. Furthermore, the employment of the catalyst may reduce the condensation and repolymerization of the intermediate products made by the decomposition of lignin content, which leads to enhance the biocrude yield. Zhu et al. conducted a detailed study on the influence of alkali catalysts on the product yield of barley straw through HTL route at subcritical condition and concluded that  $K_2CO_3$  can efficiently enhance the biocrude yield as well as the quality of biocrude [15].

In conclusion, with the addition of the catalyst, no major effect was observed on solid yield at subcritical condition. However, at supercritical, catalyst reduced the formation of solid residue in this study. Additionally, the biocrude yield was increased at the subcritical condition with catalyst run, whereas no significant increase of biocrude yield was observed at supercritical.

### 3.2. Analysis of Biocrude

Generally, biomass contains 30–50% oxygen and HTL aims to produce the biocrude with less oxygen content. This can happen by the two pathway reactions, i.e., dehydration (removal of oxygen in the form of  $H_2O$ ) and decarboxylation (removal of oxygen in the form of  $CO_2$ ). Mostly in HTL, high temperature and pressure are responsible for the removal of oxygen through dehydration of biomass, while decarboxylation and breaking of long-chain carboxylic acids through which oxygen content decreases in the form of  $CO_2$  [38]. Table 2 represents the elemental analysis of biocrude produced at the sub and supercritical along with higher heating value (HHV), energy recovery (ER), hydrogen-carbon (H/C), and oxygen-carbon (O/C) ratios. Additionally, the values of WS are also listed to get an idea for the conversion of biomass to biofuel.



**Table 2.** Elemental composition, HHVs, atomic ratios, and energy recovery of biomass and HTL biocrude obtained at different process conditions.

| Samples | C <sup>a</sup> | H <sup>a</sup> | N <sup>a</sup> | O <sup>b</sup> | H/C  | O/C  | HHV <sup>c</sup> (MJ/kg) | ER (%) |
|---------|----------------|----------------|----------------|----------------|------|------|--------------------------|--------|
| WS      | 42.15          | 6.21           | 0.82           | 50.82          | 1.76 | 0.91 | 16.53                    | -      |
| 350NC   | 70.77          | 8.25           | 1.33           | 19.65          | 1.39 | 0.21 | 35.25                    | 56.18  |
| 350CAT  | 72.61          | 8.06           | 1.14           | 18.19          | 1.33 | 0.18 | 35.54                    | 69.53  |
| 400NC   | 74.21          | 8.15           | 1.37           | 16.27          | 1.31 | 0.16 | 35.97                    | 51.14  |
| 400CAT  | 73.07          | 8.01           | 1.64           | 17.28          | 1.32 | 0.17 | 35.50                    | 48.38  |

<sup>a</sup> Dry ash free; <sup>b</sup> Oxygen calculated by difference; <sup>c</sup> HHV calculated by using Channiwala and Parikh correlation.

The carbon content of biocrude was slightly increased (from 70.77 to 74.21%) with increase of temperature. As temperature increased, oxygen concentration declined from 19.65 to 16.27%. Oxygen content was reported by Cheng et al. [39] for the HTL of pine sawdust as  $33.99 \pm 0.14$  and  $29.32 \pm 0.07$  for non-catalyst and with  $K_2CO_3$  respectively. By the HTL of oak wood at subcritical condition, Caprariis et al. [40] also found the oxygen content of 24.2 wt. %, which is significantly more than we experienced in this study for dealing with lignocellulosic biomass.

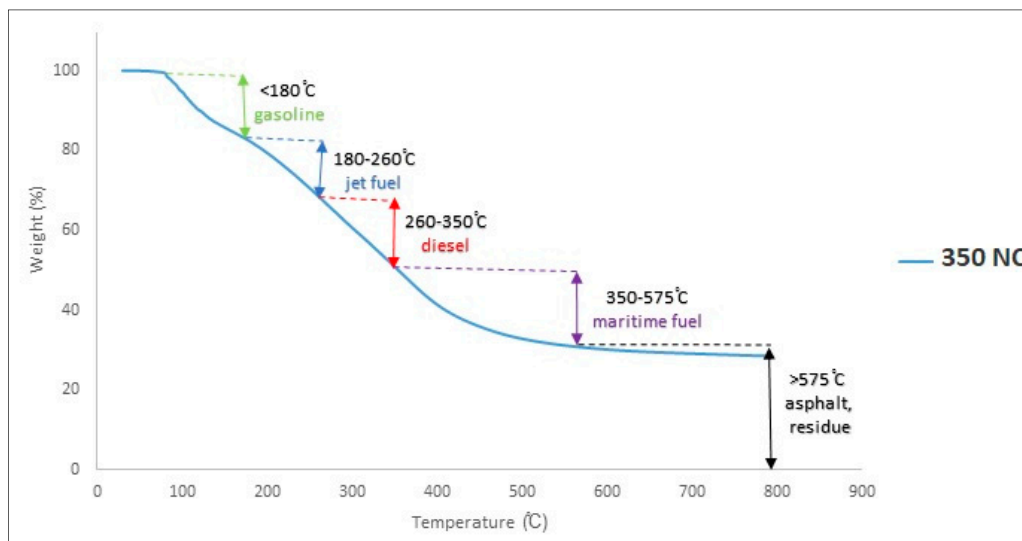
The range for hydrogen and nitrogen was found almost the same for all experimental runs. Additionally, HHV of all biocrude was also found with a minor difference in range between 35.25 and 35.97 (MJ/kg). A greater heating value of the biocrude indicates that a major part of the oxygen has been shifted into other products, i.e., gases or aqueous phase. Even though the addition of catalyst contributed to enhancing the biocrude yield, it did not have so much of an impact on the quality of the biocrude. Along with maximum biocrude yield, maximum energy recovery of 69.53% was also observed at catalytic 350 °C and minimum 48.38% at supercritical condition. In conclusion, it was observed that catalyst did not significantly affect the overall biocrude quality or HHV.

It was also experienced that the nitrogen content remained in the range of 1.14–1.64% irrespective of the process conditions. The mass of carbon in biocrude was observed in the range between 44.24 and 55.72% of the carbon available in the biomass. The lower concentration of oxygen in the biocrude was detected with respect to the original biomass. The reduction in oxygen content takes place due to dehydration and decarboxylation reactions. Furthermore, this is also the case in the form of water phase and carbon dioxide. The increase of carbon content and oxygen reduction results in the higher HHV in the biocrude as compared to the biomass. The details of carbon and nitrogen recovery in HTL products during sub and supercritical conditions are presented in Section 3.5. The H/C and O/C atomic ratios for biocrude were also calculated in range between 1.31 and 1.39 and 0.16–0.21 respectively. The range of O/C ratios in biocrudes was lower as compared to feedstock, which could improve the viscosity of biocrude. Furthermore, it will result in reduction of hydrogen requirement for upgrading of biocrude. However, HTL biocrude required the upgrading process to make higher H/C ratio to compare with the petroleum fuel.

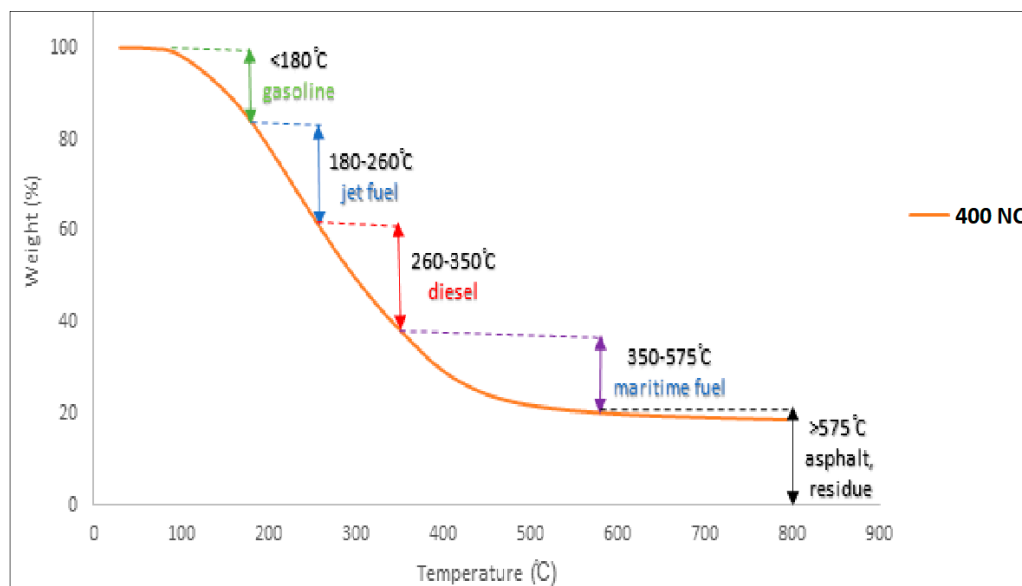
### 3.2.1. Thermal Behavior of Biocrude

The thermogravimetric (TG) technique was used to evaluate the weight loss during the thermal decomposition of the biocrude. Here only non-catalytic biocrudes 350NC and 400NC were taken for the analysis as demonstrated in Figures 2 and 3, respectively, reflecting the biocrude fractions.





**Figure 2.** Thermogravimetric curves of the biocrudes obtained at 350 °C.



**Figure 3.** Thermogravimetric curves of the biocrudes obtained at 400 °C.

The volatility curves of both biocrude samples show that almost 55 to 60% of the weight of the biocrude contained volatile components, which denotes the segments of gasoline, diesel, and jet fuel. The temperature has some influence on the overall thermal behavior of biocrude obtained at different temperature conditions. It was verified from the volatilities curve that under nitrogen atmosphere, 30 and 20% of heavy residue were left for 350NC and 400NC respectively after heating the biocrudes at 800 °C.

### 3.2.2. Organic Compounds Composition of Biocrude

The organic compounds present in biocrude were recognized by using Gas Chromatography-Mass Spectrometry (GCMS) technique with a boiling point under 300 °C. The detailed information about the obtained compounds name, retention time (RT), and peak area contribution is provided in Table 3.

**Table 3.** Main chemical compounds detected in the biocrude at all four conditions.

| No.                           | RT (min) | Compounds                               | Peak Area (%) |         |        |         |
|-------------------------------|----------|---|---------------|---------|--------|---------|
|                               |          |   | 350 NC        | 350 CAT | 400 NC | 400 CAT |
| Ketones                       |          |   |               |         |        |         |
| 1                             | 2.71     | 2-Butanone                              | ND            | 4.06    | 1.28   | 2.08    |
| 2                             | 7.78     | 2-Pentanone, 4-hydroxy-4-methyl-        | 3.37          | 6.93    | 8.25   | 10.17   |
| 3                             | 9.22     | 2-Cyclopenten-1-one, 2-methyl-          | 1.93          | 2.71    | 2.35   | 1.51    |
| 4                             | 10.22    | 3-Ethylcyclopentanone                   | ND            | 0.57    | 0.38   | 0.43    |
| 5                             | 10.44    | 2-Cyclopenten-1-one, 3-methyl-          | 1.01          | 1.98    | 3.79   | 1.51    |
| 6                             | 11.46    | 4,4-Dimethyl-2-cyclopenten-1-one        | 0.62          | 0.75    | 1.25   | 1.19    |
| 7                             | 11.78    | 2-Cyclopenten-1-one, 2,3-dimethyl-      | 2.74          | 4.65    | 5.10   | 4.93    |
| 8                             | 12.87    | 2-Cyclopenten-1-one, 3-(1-methylethyl)- | 0.86          | 1.83    | 1.86   | 1.97    |
| 9                             | 22.32    | 2-Pentadecanone, 6,10,14-trimethyl-     | 1.25          | 1.34    | 0.72   | 1.11    |
| 10                            | 22.89    | 2-Nonadecanone                          | 1.92          | 2.51    | 1.69   | 2.04    |
| Acids                         |          |   |               |         |        |         |
| 11                            | 2.77     | Acetic acid                             | 2.21          | 1.59    | 2.31   | 2.04    |
| 12                            | 16.01    | 2,5-Octadecadiynoic acid, methyl ester  | 0.51          | 0.68    | 0.55   | 0.88    |
| 13                            | 19.51    | 5-Benzofuranacetic acid, 6-ethenyl      | 0.57          | 0.43    | 0.36   | ND      |
| 14                            | 23.44    | n-Hexadecanoic acid                     | 4.42          | 5.66    | 4.88   | 2.51    |
| 15                            | 25.33    | Octadecanoic acid                       | 0.75          | 0.44    | 0.55   | ND      |
| 16                            | 29.65    | Oleic acid, eicosyl ester               | 0.53          | ND      | 0.32   | 0.94    |
| Oxygen Aromatics              |          |   |               |         |        |         |
| 17                            | 10.77    | Phenol                                  | 1.75          | 5.06    | 3.79   | 3.08    |
| 18                            | 12.05    | Phenol, 2-methyl-                       | 2.08          | 2.06    | 2.41   | 2.36    |
| 19                            | 13.87    | Phenol, 3-ethyl-                        | 3.23          | 4.81    | 6.23   | 4.48    |
| 20                            | 14.29    | Creosol                                 | 3.33          | 3.89    | 3.22   | ND      |
| 21                            | 15.57    | Phenol, 4-ethyl-2-methoxy-              | 5.62          | 5.36    | 2.94   | 1.62    |
| 22                            | 16.57    | Phenol, 2,6-dimethoxy-                  | 3.64          | 1.43    | 0.74   | ND      |
| Hydrocarbons                  |          |   |               |         |        |         |
| 23                            | 8.94     | 2-Octene                                | 1.56          | ND      | 0.43   | ND      |
| 24                            | 11.64    | 1-Methylcyclooctene                     | 0.75          | 0.36    | ND     | 0.39    |
| 25                            | 14.77    | 1,5,5-Trimethyl-6-methylene-cyclohexene | 0.81          | 1.06    | 1.56   | 1.16    |
| 26                            | 17.12    | Hexadecane                              | 1.39          | 0.85    | 1.20   | ND      |
| 27                            | 25.16    | Octadecane, 3-ethyl-5-(2-ethylbutyl)-   | 1.49          | 0.34    | ND     | 0.45    |
| Alcohols and Aldehydes        |          |   |               |         |        |         |
| 28                            | 12.81    | Cyclohexanol, 3,3,5-trimethyl-          | 0.41          | ND      | ND     | ND      |
| 29                            | 18.29    | 1,1-Diphenyl-4-phenylthiobut-3-en-1-ol  | 0.55          | ND      | ND     | ND      |
| 30                            | 9.86     | cis-4-Decenal                           | 2.01          | 0.79    | 1.21   | 0.45    |
| Nitrogen containing compounds |          |   |               |         |        |         |
| 31                            | 25.38    | 9-Octadecenamide                        | 0.63          | 0.53    | ND     | ND      |
| Total area                    |          |   | 51.94         | 62.67   | 59.37  | 47.30   |

ND: Not detected.

From the GCMS outcomes, the biocrude compounds were categorized into six main classes named as ketones, acids, oxygen aromatics, hydrocarbons, alcohols, and nitrogen-containing compounds. From the elemental analysis, it was observed that WS contains 50.82% oxygen, which may result in a higher number of ketones and alcohols as also observed by Patil et al. for the HTL of WS [14]. It was also observed that the addition of catalyst slightly enhances the peak area of ketones at 350 °C. Among ketones, [2-Pentanone, 4-hydroxy-4-methyl-] and [2-Cyclopenten-1-one, 2,3-dimethyl-] covered the greater area.

From the carbohydrates available in WS, the hemicellulose is the first element that starts to decompose due to its greatly oxygenated branches, which are easier to break down. The destruction of hemicellulose produces acetic acid and other organic acids [41]. Acids were found at all reaction conditions including short-chain acids and long-chain fatty acids. [n-Hexadecanoic acid] has major contribution in all four conditions. Acetic acid and Octadecanoic acid slightly reduced at catalytic run. The presence of high acid content is not favorable for the biocrude quality.

The thermal decomposition of lignin produces phenolic compounds and their derivatives, which then convert into gaseous form. However, lignin also plays an important role to produce low and high molecular weight molecules known as tar or char [42]. Oxygen aromatics were also detected in all biocrude samples, among them [Phenol, 3-ethyl-], [Phenol, 4-ethyl-2-methoxy-], and [Phenol, 2,6 dimethoxy-] were major contributors. The increasing peak of Phenol compound was observed from 1.75 to 5.06% at subcritical catalytic condition.

Biocrude obtained at 350 °C has higher hydrocarbons as compared to 400 °C mainly [Hexadecane], [Octadecane, 3-ethyl-5-(2-ethylbutyl)-], and [1-Methylcyclooctene]. This might be due to the cracking of long-chain aliphatic compounds into short ones or the formation of other cyclic compounds at the higher temperature [43]. Alcohols were only detected at 350 °C NC while the [cis-4-Decenal] was identified at all four conditions. The result showed that the fact that the biocrude had a much lower concentration of nitrogen compounds may be due to a much smaller percentage of N in WS. The nitrogenous compounds [9-Octadecenamide] were only found at subcritical condition. The lower concentration of nitrogenous compounds shows one of the quality parameters of HTL biocrude. The high nitrogen-containing compounds at one end contaminate the atmosphere by the emissions of NO<sub>x</sub> during combustion, and on the other end, it leads to high viscosity and instability of biocrude. Therefore, biocrude needs to be upgraded by hydrotreating for the removal of heteroatoms to convert the biocrude into drop-in fuel.

### 3.3. Analysis of Solid Residue

Solid residue, also known as biochar, is one of the byproducts of the HTL process. The char is rich in inorganics formed by the HTL process that can be refined for effective utilization as a fertilizer in agricultural sector [44–46] or as a raw material for gasification process [47]. The elemental analysis (dry-ash free basis), HHV, and atomic ratios of biochar samples are summarized in Table 4. It was experienced that, with increasing temperature from 350 to 400 °C, the carbon content was increased in solids from 54.56 to 58.66%. Additionally, the oxygen concentration was decreased from lower temperature to higher temperature. It was observed that by the addition of the catalyst, the carbon content decreased in solid residue. The carbon reduced due to lower solid product yields as shown in Figure 1 and a greater amount of carbon was also experienced in biocrudes at catalytic conditions. Shah et al. also reported the declining trend of carbon content in solid residue by the addition of catalyst at sub-supercritical HTL for sewage sludge [19]. While nitrogen almost remains the same in all conditions. The temperature does not have as much influence on heating values of solids. The lower H/C ratios in solid residue show the consumption of hydrogen that might be responsible for the formation of unsaturated and aromatic compounds in solids residue [15]. However, O/C was high in the range between 0.47 and 0.71; this may be due to a high degree of deoxygenation.

**Table 4.** Elemental composition (daf), HHVs, and atomic ratios of solid residue.

| Samples | C     | H    | N    | O     | H/C  | O/C  | HHV (MJ/kg) <sup>a</sup> |
|---------|-------|------|------|-------|------|------|--------------------------|
| 350 NC  | 54.56 | 3.19 | 1.29 | 40.96 | 0.70 | 0.56 | 26.20                    |
| 350 CAT | 48.93 | 3.18 | 1.01 | 46.88 | 0.77 | 0.71 | 24.89                    |
| 400 NC  | 58.66 | 2.71 | 1.34 | 37.29 | 0.55 | 0.47 | 26.69                    |
| 400 CAT | 54.53 | 2.76 | 1.12 | 41.59 | 0.61 | 0.57 | 25.79                    |

<sup>a</sup> HHV calculated by using Channiwala and Parikh correlation.

In continuous scale-up HTL plant, coke and char formation is common. The increase of char and coke formation is undesirable for the HTL plant because they result in the decrease of biocrude yield and may cause blockage of the plug-flow reactor. However, the catalyst can be used to reduce the char formation in general, but the recovery of catalyst is a challenging task in HTL process which can also be tackled by increasing the biocrude yield via fast heating system as discussed by researchers [38,48].

It can be concluded from the results that temperature has less impact on the quality of solid residue during the HTL process. Whereas the catalyst prevented the transference of carbon to solid residue.

### 3.4. Aqueous Phase Analysis

HTL is famous for the utilization of water as a reaction medium, which is obtained at the outlet end of the HTL process and can be termed as the aqueous phase. Table 5 reflects the different parameters of the aqueous phase generated by the HTL of WS at the sub and supercritical conditions. It was observed that the pH of aqueous phase is affected by both temperature and catalyst. The acidic nature of aqueous phase was experienced at all conditions. From 350 to 400 °C, the pH increased from 3.87 to 4.19 while with the addition of catalyst it increases from 5.43 to 6.82. The acidic range of resulted aqueous phase may be due to the formation of monomeric sugars by the hydrolysis of available sugar compounds, which degraded and converted into organic acids. The variation in pH mainly depends upon the process operating conditions and feedstock composition [49,50]. Total organic carbon (TOC) was also affected by temperature and catalyst. At both subcritical conditions, the high concentration of TOC was observed by addition of catalyst from 25.94 to 30.67 g/L, while it slightly increased at both supercritical conditions from 28.62 to 33.52 g/L. The increase of TOC by the addition of alkali catalyst was also experienced by Shah et al. and other researchers [19,51,52]. Pedersen et al. also experienced higher concentration of organic carbon in the water phase by the co-liquefaction of lignocellulosic biomass with glycerol for continuous HTL plant [53].

**Table 5.** pH, TOC, and TN in the aqueous phase.

| Parameter | 350NC | 350CAT | 400NC | 400CAT |
|-----------|-------|--------|-------|--------|
| pH        | 3.87  | 5.43   | 4.19  | 6.82   |
| TOC (g/L) | 25.94 | 30.67  | 28.62 | 33.52  |
| TN (g/L)  | 0.26  | 0.37   | 0.45  | 0.58   |

Total nitrogen (TN) was found in small concentration in aqueous phase in the range between 0.26 and 0.58 g/L; it was discussed earlier that WS has lower nitrogen content. It was experienced that both temperature and catalyst impact the nitrogen recovery in aqueous phase. TN increased from 0.26 g/L to 0.37 g/L by the addition of the catalyst at subcritical and from 0.45 g/L to 0.58 g/L at supercritical conditions. At catalytic conditions, TN increased as 0.1 g/L.

For the HTL plant at large scale, it is a kind of essential and economical aspect to recover the energy from water phase. The aqueous phase is identified as an energy source due to the energy contained in the form of organic carbon, phosphorus, nitrogen, and other nutrients that need to be addressed in an efficient way. Pacific Northwest National Laboratory (PNNL) has suggested the effective application of aqueous phase by recirculation for HTL that improves the carbon efficiency, biocrude yield, and quality. At the other end, aqueous phase recirculation may reduce the process cost due to the saving of freshwater consumption and wastewater treatment from the HTL process [54]. Owing to this perspective, the recirculation of the aqueous phase has been applied in this study (Section 3.7) to explore the impact of aqueous phase on the overall energy recovery of biocrude.

### 3.5. Carbon and Nitrogen Recoveries in HTL Products

The Carbon Recovery (CR) and Nitrogen recovery (NR) of all product phases from the HTL process were calculated on a dry ash-free basis as shown in Figures 4 and 5 respectively. Based upon the equations mentioned by Shah et al. [19], recoveries in products were calculated. The CR and NR for the aqueous phase were determined by the measurement of TOC and TN respectively.

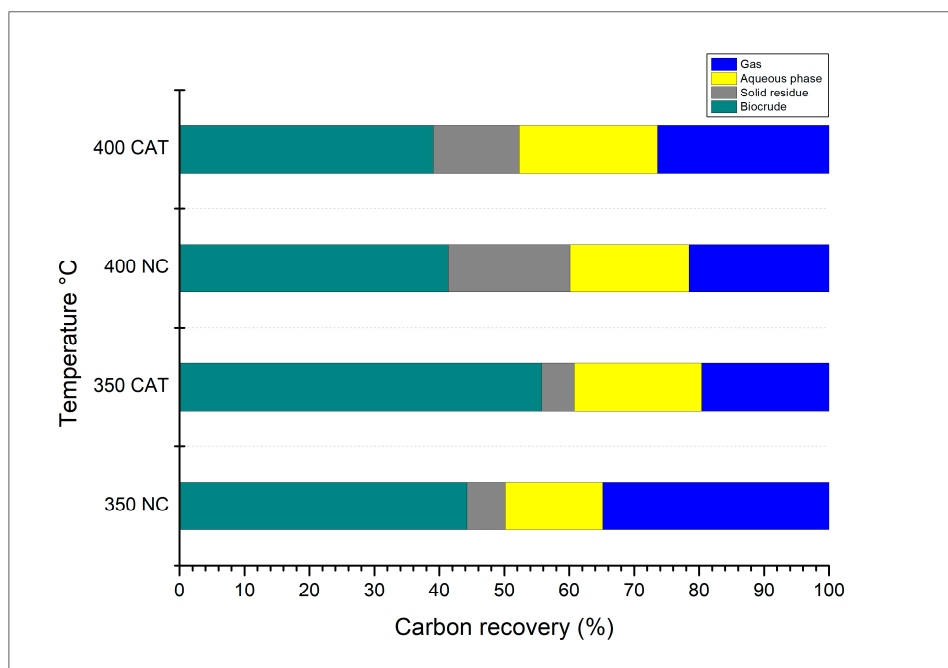


Figure 4. Carbon recovery in HTL products.

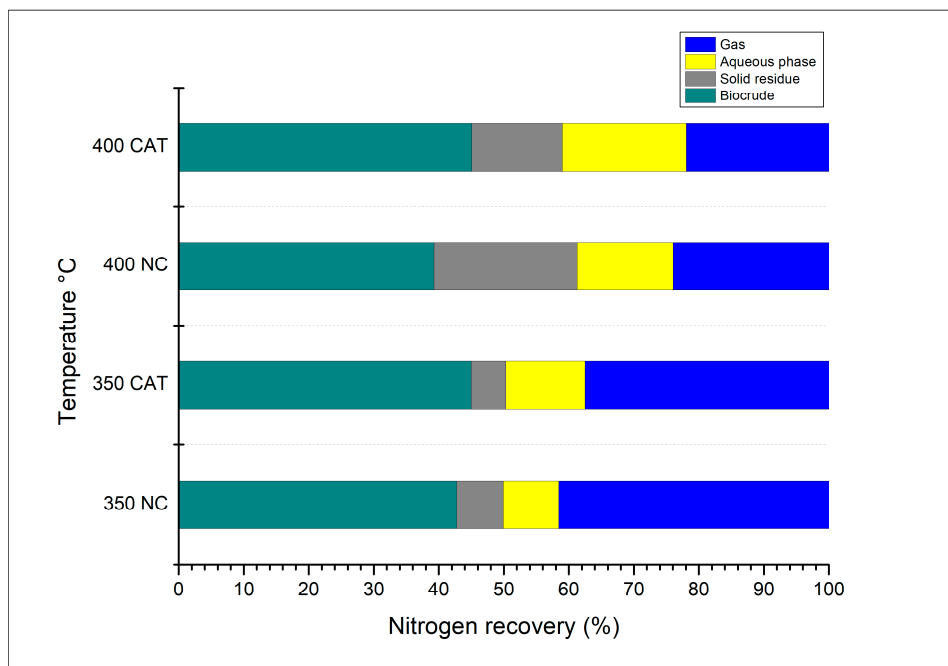


Figure 5. Nitrogen recovery in HTL products.

From the experimental results of this study, it was observed that in non-catalyst conditions, the variation in temperature did not affect more CR in biocrude. The approximately same trend was observed at 350 NC and 400 NC for CR in biocrude. While by the addition of the catalyst, CR was highly increased in biocrude from 44.24 to 55.72% at the subcritical condition. The catalyst decreased the CR in solid residue while remaining approximately the same in biocrude at supercritical condition.

Interestingly, it was noted that temperature has a high impact on CR in the case of solid residue and increased from 5.92 to 18.73% and maximum at supercritical non-catalytic due to higher solid yield. Lower carbon concentration in solids was observed at a lower temperature. Due to slightly higher TOC of aqueous phase at catalyst run, it was noticed that catalyst has more influence on CR in aqueous

phase. The carbon and nitrogen recoveries for the gaseous product were calculated by difference on the basis of mass balance. For all four conditions, maximum CR in biocrude was obtained at 350 °C catalytic run, which was also observed by Zhu et al. for the liquefaction of barley straw [29].

The temperature did not influence on the NR of biocrude and almost the same trend was found at sub/supercritical condition, while addition of catalyst slightly increases the transformation of nitrogen to biocrude. Additionally, in the case of solids, maximum nitrogen recovery was obtained at the non-catalytic supercritical condition, which was about 21.99%. A very small amount of nitrogen was shifted to the aqueous phase in range 5.35–7.19% at subcritical temperature.

### 3.6. Inorganic Elements in HTL Products

During the HTL of WS at the desired temperature, the inorganic elements present in the feedstock were transferred to different phases of products. The available concentration of inorganic elements in biocrude, solid, and aqueous phase were explored. It was observed that the concentration of inorganic elements mainly transferred to a solid residue. The distribution of each inorganic element is given on the basis of its concentration and the weight of the product phase obtained during the HTL. Whereas the relative percentage of each inorganic element was calculated by dividing the sum of the total concentrations of the all detected inorganic elements.

The mass distribution of inorganic elements at the sub and the supercritical temperature are shown in Figures 6 and 7, respectively. The trend of the shifting of inorganic compounds was quite different at both temperature conditions. Only catalytic samples were tested for the ICP-AES.

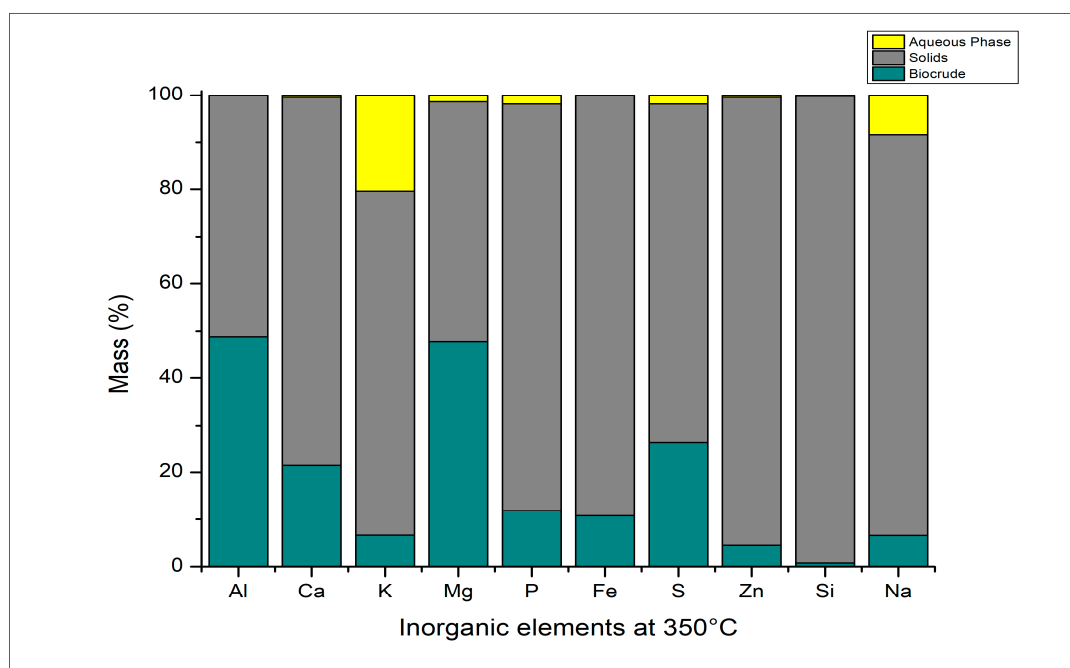
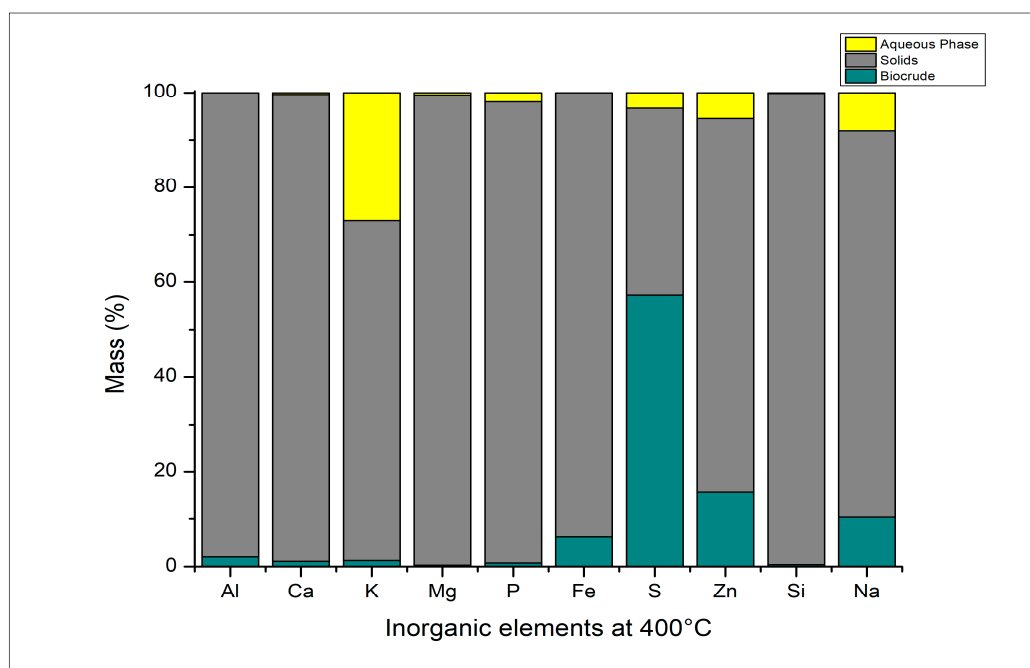


Figure 6. Mass distribution of inorganic elements at 350 °C.



**Figure 7.** Mass distribution of inorganic elements at 400 °C.

At 350 °C catalytic condition, aluminum (Al) and Magnesium (Mg) had approximately the same distribution in biocrude and solids, while a small amount of Mg was also observed in aqueous phase. A different behavior was observed for potassium (K) and sodium (Na), those were getting more occupied in aqueous phase as compared to other detected inorganic elements. This trend of shifting of K and Na to water phase was also observed by Conti et al. [55] for the HTL of wastewater-irrigated willow at supercritical condition.

The presence of K in the aqueous phase could be beneficial for recirculation of aqueous phase at continuous HTL plant. It may reduce the catalyst  $K_2CO_3$  dosage quantity. Except Al and Mg, for most inorganics, the mass recovery in the solids was more than 70%. Silicon was almost recovered in the solid residue. Furthermore, the high concentration of phosphorus (P), approximately 86%, was found in solids residue, which may be available in the form of phosphates with their associated alkali elements like sodium, calcium, etc. Due to the existence of these treasured nutrients, HTL solid residue can be employed as a fertilizer for soil improvement and as farming fertilizer.

At 400 °C catalytic condition, the trend was different as compared to subcritical condition. Aluminum, calcium, magnesium, phosphorus, and silicon were mostly transferred to a solid residue while the considerable amount of potassium and some amount of sodium and sulfur were transferred into the aqueous phase. One of the possible reasons behind this trend may be a high degree of solubilization of these compounds at the higher temperature (400 °C) and pressure (350 bar) which increase the ionic product of the water, which results in the high concentration of these inorganic compounds into HTL water phase [56]. Furthermore, it was noted that at higher reaction temperature, the total content of heavy metals was accumulated in solid residue, which was also indicated by Huang et al. [57].

Sulfur was the only compound found maximum around 60% in biocrude at supercritical temperature. The heavy metals like Zn and Fe were detected at both temperature conditions in the biocrude with some variation.

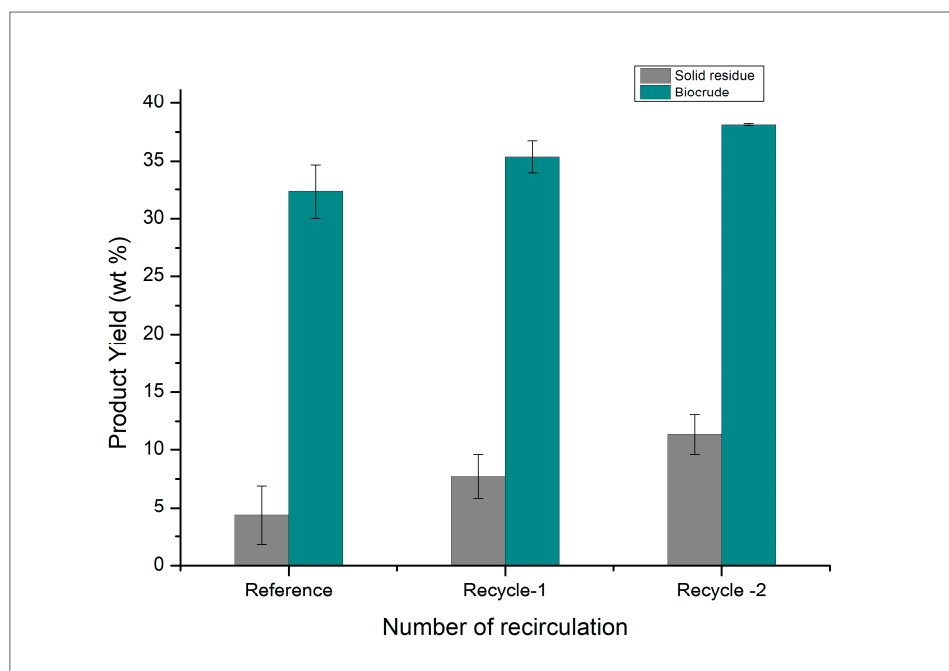
Based on these outcomes, it can be concluded that the presence of nutrients like macronutrients (P), secondary macronutrients (Ca, Mg), and micronutrients (Fe, Zn) are mainly observed in the solid residue. At the downstream of HTL, nutrient enrich solids can be fruitfully implemented as soil fertilizer. For the scale-up continuous HTL plant, the presence of high concentration solid residue,



inorganic waste at down streams may result in the reactor blockage in the system due to solid deposition. The issue can be rectified by adopting the hot filter system next to the process reactor, as also suggested by the PNNL for continuous HTL plant [58].

### 3.7. Aqueous Phase Recirculation

To keep in consideration the continuous HTL plant, aqueous phase was recirculated to analyze the effect of aqueous phase recirculation on product yield, as shown in Figure 8. Additionally, it will also reduce the consumption of fresh water for large-scale continuous plant.



**Figure 8.** Variation in product yield with aqueous phase recirculation.

The product yield is compared with the reference case (350 °C CAT), which was the optimum case of this study. It was observed that by the recycling of aqueous phase into the system, the biocrude yield was increased from 32.34 to 38.12% after two rounds of recycling. The organic compounds, particularly acids, present in aqueous phase may be responsible for enhancing the biocrude yield via rapid degradation of organic matter. Additionally, a significant increase of solid residue yield was observed from 4.34 to 11.33% after two cycles, which is almost more than double as compared to fresh run. This may be due to the reactive substances present in the aqueous phase that polymerize to form solid residue. Recently, Shah et al. conducted the detailed study on aqueous phase recirculation by using sewage sludge for HTL and got successive increment in biocrude yield [59]. Table 6 shows the elemental analysis (daf basis) of the biocrude and solid residue, along with their HHVs obtained after aqueous phase recirculation.

**Table 6.** Elemental composition, HHVs, and energy recoveries of biocrude and solid residue after aqueous phase recirculation.

| Parameter           | Biocrude<br>Ref-Run | Biocrude<br>Recycle-1 | Biocrude<br>Recycle-2 | Solids<br>Ref-Run | Solids<br>Recycle-1 | Solids<br>Recycle-2 |
|---------------------|---------------------|-----------------------|-----------------------|-------------------|---------------------|---------------------|
| C (%)               | 72.61               | 73.61                 | 72.86                 | 48.93             | 48.95               | 41.82               |
| H (%)               | 8.06                | 8.15                  | 7.76                  | 3.18              | 3.52                | 3.53                |
| N (%)               | 1.14                | 1.33                  | 1.32                  | 1.01              | 1.39                | 1.21                |
| O (%)               | 18.19               | 16.91                 | 18.06                 | 46.88             | 50.72               | 52.10               |
| HHV (MJ/kg)         | 35.54               | 35.83                 | 35.26                 | 24.89             | 25.62               | 23.35               |
| Energy recovery (%) | 69.53               | 76.66                 | 81.31                 | 6.67              | 11.94               | 16.01               |

The HHV of biocrude obtained by recirculation of aqueous phase was almost stable as 35 MJ/kg due to the almost same number of carbon and other elements in biocrude. While the heating value of solid residue slightly decreased from 25.62 to 23.35 MJ/kg after two cycles. Furthermore, energy recovery was increased after each cycle from reference condition (69.53%) to recycle-2 (81.31%) in biocrude, which may enhance after increasing the number of cycles. The detailed investigation of aqueous phase recirculation for HTL process for the betterment of quality and quantity of biocrude may be a case for future work.

From this study, it can be concluded that the recirculation of the aqueous phase from HTL process of WS does not improve the biocrude quality but certainly increases the biocrude quantity. Furthermore, hydrotreating or upgrading can play a vital role in the betterment of biocrude quality. In summary, this study recommends that the aqueous phase generated from HTL process can be recycled and reprocessed as an active reaction medium for the process to enhance the biocrude yield while reducing the overall waste generation and make the HTL an economical process.

#### 4. Challenges for Continuous HTL Processing

This study is based upon the experimental results at the batch scale; however, it can play a vital role as a screening test to implement the WS for continuous HTL plant. Biocrude yield along with solid residue and quality of obtained biocrude are the main parameters to analyze the process efficiency. From the lab experimental experience, higher biocrude yields good quality of obtained biocrude associated with HHVs supporting the utilization of WS for continuous HTL plant. As observed, aqueous phase recirculation also becomes beneficial to enhance the biocrude yield with a reduction of freshwater consumption. Additionally, instead of treatment of wastewater phase before dispose-off at downstream, aqueous phase recirculation approach may reduce the overall cost of HTL continuous plant, which makes the process more efficient and economical. However, there are some parameters which need proper attention too. For utilization of WS, as a dry lignocellulosic feedstock, pumpability is one of the challenges for continuous HTL plant and the fate of chlorine [6] to reduce the inside slagging of reactor are the additional gaps for the future studies. Our research group recently reviewed the detailed investigation on continuous HTL process, which highlights the different aspects of continuous HTL process [8].

#### 5. Conclusions

In this study, wheat straw was used as a feedstock along with distilled water and thermally liquefied at the sub and supercritical temperature with and without the alkali catalyst  $K_2CO_3$ . The outcome of the experimental analysis shows that maximum biocrude yield (32.34 wt. %) with least solid residue (4.34 wt. %) was obtained at subcritical catalytic condition. Whereas the carbon content was slightly higher in biocrude at supercritical. The maximum energy recovery in biocrude was observed 69.53% and 51.14% at the sub and supercritical temperature respectively. Additionally, the greater concentration of phosphorus, calcium, and magnesium was observed in biochar, which shows the capability of using solid residue as a soil conditioner or fertilizer.

Due to the significant volume of organic carbon in HTL aqueous phase, the organic-rich water was recycled. The aqueous phase recirculation shows the fruitful outcomes by increasing the biocrude yield and energy recovery at each cycle, which indicates the possibility of the aqueous phase recirculation for continuous HTL plant at commercial scale, which will definitely make the process economic and environmental friendly.

**Author Contributions:** T.H.S. (Experiments, products analysis, result interpretation, and main contribution in overall writing and designing of the manuscript). S.S.T. (Conceptualization, methodology and supervision). A.A.S. (Experiments, products characterization, and results interpretation). T.H.P. (Paper review and data interpretation), and L.A.R. (Main supervision and overall conceptualization). All authors have read and agreed to the published version of the manuscript.

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