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Qualitative improvement of bio-oil derived from hydrothermal liquefaction of liquid fertiliser drained *Kappaphycus alvarezii*

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Abstract

The purpose of this investigation was to explore the possibility of utilising post-sap residues for bio-oil production, that are produced after liquid fertiliser extraction from *Kappaphucus alverizii,* red macroalgae. The sap — a liquid fertiliser — was expelled by crushing the *K. alverizii*. The residual macroalgae were hydrothermally liquified at varying operating conditions (temperature, biomass to solvent ratio, residence time, catalyst dose), in order to understand its influence over the product-distribution and composition from thehydrothermal liquefaction (HTL) process. The maximal yield for crude bio-oil was 28.4 ± 0.6 wt.%, which was possible only when the HTL reactor was operated in presence of a ZSM-5 catalyst at 300 °C using 20 g of biomass for 30 min duration. Still, the bio-oil derived from the HTL process seems to possess higher oxygen content. Hence, the hydro-deoxygenation (HDO) process was carried out to upgrade the crude bio-oil into oxygenates less oil. The bio-char along with ZSM-5 derived from the previous HTL process was utilised as a catalyst in the HDO process. Catalysed HDO processes were able to improve the HHV of upgraded oil to 36.7 MJ/kg. Overall, this study implies that the crude bio-oil can be effectively produced from the post-sap residue, which can be further upgraded to calorific-rich fuel.

Keywords Liquid fertiliser · Hydrothermal liquefaction · Bio-oil · ZSM-5 catalyst · Hydro-deoxygenation · Upgraded oil

1 Introduction

Algae was found to be a promising source in the production of renewable energy source as it can fix carbon dioxide by means of photosynthesis. The algae are found abundant as it is not considered a food source so far except for some species. Algae are classified into two categories and they are microalgae and macroalgae. Both algae are utilised for the production of biofuel but when compared to microalgae, macroalgae is found to be economically viable and has many advantages to industries as well as to academic research [1]. Macroalgae is found everywhere and can be cultivated easily in coastal regions. In India, at present actual harvest of macroalgae annually is 22,000 tonnes which are 2.5% of the total potential harvest which is 870,000 tonnes [2]. In Tamil Nadu, the available area for seaweed cultivation is 20,000 ha, out of which 9891.35 ha (coastline) is only cultivated. From that cultivated area, 22,044 tonnes of fresh weight is harvested every year, which includes the Tamil Nadu coastline as well as Pondicherry as of the 2006 report [3].

Red seaweed has more advantages over other seaweeds as it can grow in coastal areas without any of the below-listed components such as freshwater, CO_2, fertiliser and land. Compared to other macroalgae, red macroalgae has faster CO_2 sequestration and growth rates. The red macroalgae have different carbohydrate constituents (galactan, glucan and cellulose) when compared to brown macroalgae (laminarin, cellulose and alginate) and green macroalgae (pectin, cellulose and starch). The coagulative property of red macroalgae was found to be very good when compared with green and brown macroalgae [4]. Hence, recently, the chemical products such as carrageenan, agar, alginate etc. were produced using red macroalgae for instance *Gracilaria* sp, *Kappaphycus* sp. etc [5]. These macroalgae were generally regarded as rejects after their utilisation by industries worldwide. The consumption of algal rejects from various streams is a challenging process. Some industries convert algal rejects to fertilisers

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via bioprocessing methods [6]. Apart from the conversion of algal rejects to manure, the high demand for the replacement of fossil fuels creates the urge to focus on algal rejects in the production of biofuel [7].

The increase in the usage of fossil fuels leads to the depletion of the non-renewable resource and in turn, increases the demand for crude-based products. This leads to a hike in the price of crude-based products, biomass as a source in the production of biofuel replaces the dependency on non-renewable energy and it attracts many researchers to focus on biofuel production [8, 9]. The abundance, cost-effectiveness and availability of biomass make it comfortable in the production of biofuels [10]. Many kinds of macroalgae are utilised by many researchers in recent times for biofuel production. The species such as *Ulva prolifera* [11, 12], *Enteromorpha prolifera* [13], *Gracilaria corticate* [14], *Spirogyra* sp. [15], *Cladophora socialis* [16], and *Oedogonium* [17, 18] are utilised as a whole in the production of biofuels. However, only a few researchers were exploring the possibility of producing biofuel from the rejects of macroalgae, especially in the bio-ethanol production sector [19].

The biomass obtained from different sources is converted into biofuel by two technologies which are thermochemical and biological/biochemical techniques. In thermochemical technologies, the treatment process available is gasification, pyrolysis, and liquefaction. The biochemical conversion technique includes fermentation and digestion [20]. From the thermochemical treatments, hydrothermal liquefaction (HTL) is found to be a promising technique for the conversion of moisture-rich complex feedstock into biofuels. Because, water is the main ingredient in the HTL process, thus the extra energy needed for the dewatering and drying process can be saved, which was usually demanded by the pyrolysis process. Additionally, the HTL process can be operated at low temperatures compared to the gasification and pyrolysis processes. Moreover, the product derived through pyrolysis usually possesses higher oxygen content compared to the HTL process [21]. This could be a huge drawback to the recovery of energy from bio-oil. Hence, the HTL process was preferred for recovering the energy from the feedstock. For the conversion of feedstock to biofuels, water (wastewater) is transferred to its critical condition (280–370 °C, 100–250 bar), where the water properties are altered and water behaves like a medium for the organic matter decomposition [22]. Many studies for the various feedstock with different parameters such as feedstock composition, pH, temperature, co-solvents and catalyst have been performed[23]. Moreover, the recent exploration suggested that the HTL process could become economically viable on a commercial scale. Some of the significant changes in the HTL process during past decades are co-liquefaction [24], nutrient recovery from HTL aqueous phase (HTLaq) for algal growth [25] and the machine learning prediction for desirable bio-oil in terms of quality as well as quantity [26].

The study was intended to extract liquid fertiliser from *Kappaphucus alverizii*. Later, the rejects accumulated after the extraction process were utilised as feedstock for bio-oil production using the hydrothermal liquefaction process. In order to improve the quality and quantity of bio-oil, a heterogeneous catalyst such as ZSM-5 was used. Because, ZSM-5 is commercially utilised in the petroleum refining process due to its selective cracking, alkylation, isomerization and aromatization. In addition, it can improve the stability of bio-oil by enriching the proportion of alkanes, olefins and ketones while decreasing the organic acids[12, 27]. Following, the upgradation of crude bio-oil using biochar containing ZSM-5 obtained from the previous HTL process was performed to minimize the oxygenated compounds in upgraded oil. The composition variation in crude bio-oil and upgraded oil were discussed in detail. This research provides insight into the usage of post-sap aquatic biomass and improves the production and functional compounds of bio-oil.

2 Materials and methods

2.1 Collection of seaweed

Kappaphucus alverizii, a seaweed sample, was collected from the Kanniyakumari district seashore, located in Tamil Nadu, India. In order to eradicate the impurities, symbiotic organisms and solid particles from the collected seaweed, the collected seaweed was washed continuously using freshwater [28]. After washing, the seaweed was sun-dried and collected in a sealable bag and transported to the lab for research purposes.

2.2 Extraction of liquid fertiliser from red seaweed

The raw macroalgae (*K.alverizii*) was rinsed thoroughly with freshwater after collecting it physically. In order to expel the sap, the macroalgae were initially chopped and blended with distilled water in a ratio of 1:1. The mixture was milled mechanically under ambient conditions. The result obtained was in the form of slurry, which was further filtered using filter paper. After filtration, the liquid sap was collected as filtrate, while the solid residues were separated as retentate. The collected sap was regarded as a liquid fertiliser and stored at 4 °C because the sap is generally prone to contamination due to the presence of

nutrients [28, 29]. The presence of organic carbon, nitrogen, phosphorus and potassium was estimated using the standard protocol provided in CPCB [30].

2.3 Hydrothermal liquefaction

2.3.1 Operating conditions

The biomass residue from the post-sap of *K. alvarezii* was utilised for the hydrothermal liquefaction (HTL). In a highly pressurised stainless-steel reactor of 500 mL capacity with a maximum temperature of 350 °C, a hydrothermal liquefaction process was performed with a 10 °C /min heating rate. At 5 MPa pressure in the nitrogen environment, with a working water volume of 200 ml varying load of the biomass (10, 20 and 30 g) was added in the HTL medium (i.e. water) and liquefication was performed at 280–320 °C temperature range with a temperature variation of 20 °C for every successive run. For the attainment of a homogenous reaction, agitation was performed at 720 rpm using a variable speed controller for the different holding times, ranging from 15 to 45 min duration. In order to enrich the quality and quantity of bio-oil, a heterogeneous catalyst such as ZSM-5 was utilised for the entire experiment. At each run, the product yield of different phases was measured to obtain the optimum temperature, biomass load, residence time and catalyst load for the liquefaction process. The gas which is generated at the time of the reaction is collected and analysed in gas chromatography aided with a thermal conductivity detector.

$$\text{Catalyst Dose(wt.\%)} = 100 \times \frac{\text{Weight of catalyst (g)}}{\text{Weight of feedstock(g)}} \quad (1)$$

2.3.2 HTL product stream separation

By combining an equal amount of liquified mixture with the separating solvent, bio-oil extraction can be performed. Here, hexane is utilised as a separating solvent for the separation of an oil phase and solid phase from the mixture and this separation was performed using a separating funnel (250 mL). The separating funnel bottom layer which is called as organic phase was transferred to the round bottom flask of known volume and vacuum refined for removing the traces of hexane (separating solvent) from the oil. The final weighing of the round bottom flask has to be performed to know the weight of the oil phase acquired. The product of oil phase or solid residue or aqueous phase yield can be estimated in terms of weight using the below expression.

$$\text{Product yield(\%)} = 100 \times \frac{\text{Mass of product(g)}}{\text{Mass of feedstock (g)}} \quad (2)$$

2.3.3 Hydro-deoxygenation of bio-oil

In the same pressurised stainless-steel reactor, hydro-deoxygenation (HDO) was performed, prior to the HDO process, the reactor was washed thoroughly. In addition to bio-oil, the reactor was filled with acetone of equal portions and bio-char along with ZSM-5 derived from previous HTL runs was utilised as a catalyst in the HDO process. The hydrogen gas was purged with 50 bar pressure inside the reactor. The experiments were conducted at 300 °C temperature for the duration of 90 min with homogenous 450 rpm mixing at a heating rate of 15 °C/min [31]. The final bio-oil obtained is seen in the form of yellowish brown and this is referred to as upgraded bio-oil. The composition of upgraded bio-oil was compared with liquified bio-oil.

2.4 Characterisation of feedstock and products

2.4.1 Biochemical analysis

Protein content estimation By using the Lowry method, the protein content of the biomass was estimated. As an initial step, the feedstock was hydrolysed at the temperature of 100 °C for 10 min duration using NaOH (0.1 mL) [32]. The resultant from the hydrolyzation of feedstock was combined with the mixtures of 1 (2% of $C_4H_4KO_6$): 1 (1 % of $CuSO_4.5H_2O$): 100 (2% of $NaHCO_3$) and the mixture was undisturbed for 10 min. The resultant after 10 min was reacted with Folin reagent (0.1 mL) for the time duration of 30–60 min without any agitation. Using a UV-visible spectrophotometer, the final results were analysed at 750 nm. The protein content estimation can be analysed using the expression provided below.

$$\text{Protein(\%)} = 100 \times \frac{\text{weight of protein(g)}}{\text{weight of feedstock(g)}} \quad (3)$$

Lipid content estimation The biomass lipid content can be estimated by dissolving 1 g of feedstock with chloroform and methanol in the ratio of 1:2 which is suggested in Bligh, Dyer [33]. Centrifugation of the resultant was performed at the rpm of 3×10^3 for the time duration of 10 min and finally, the supernatant was removed. Again, the above-prescribed steps were repeated with the addition of chloroform (2 mL) to the pellets and centrifuged for 3×10^3 rpm. By using the supernatant, the phase separation was performed by KCl

(1%). The bottom layer is collected as lipids and separated and finally weighed. The lipid content estimation can be analysed using the expression provided below

$$\text{Lipid}(\%) = 100 \times \frac{\text{weight of lipid(g)}}{\text{weight of feedstock(g)}} \quad (4)$$

Carbohydrate content estimation The carbohydrate content was estimated by the protocol given by Dubois et al. [34]. The hydrolysate (2 mL) from the feedstock is mixed with concentrated H_2SO_4 (5 mL) and 80% of phenol (0.05 mL). The addition of concentrated H_2SO_4 was by direct means to the mixture surface to attain proper mixing. The mixture tube was undisturbed for a time duration of 10 min and using a water bath, the mixture is heated to the temperature of 25–30 °C for around 10 to 20 min. Using a UV-visible spectrophotometer, the mixture absorbance was noted at 490 nm. The carbohydrate content estimation can be analysed using the expression provided below

$$\text{Carbohydrate}\ (\%) = 100 \times \frac{\text{weight of carbohydrate(g)}}{\text{weight of feedstock(g)}} \quad (5)$$

2.4.2 Proximate analysis

The ash, moisture, volatile matter and fixed carbon content were estimated for raw *Kappaphycus alvarezii* and post-sap residues of *K. alvarezii*. The ash content was estimated by the process of decomposing the dry feedstock in the muffle furnace at the temperature of 575 °C for the time duration of 180 min. The feedstock was dried until the weight becomes constant which was prescribed in ASTM E1755-01 [35]. The moisture content in the feedstock was determined by drying the feedstock at 103 °C in the oven for the time duration of 960 min, which was prescribed in ASTM E0871-82 [36]. The volatile matter was obtained by heating the sample in an inert atmosphere at 950 °C and fixed carbon was obtained from the difference (100 – ash – volatile matter) [36].

2.4.3 Ultimate analysis

By means of the CHNS elemental analyser, the content of carbon, hydrogen, nitrogen, and sulphur in feedstock and fuel can be estimated. The bio-oil elemental oxygen can be calculated by the difference (O% = 100% -C%-H%-N%-S%). From the estimated CHNSO content, the HHV (Higher Heating Value) can be calculated by the expression provided below [37].

$$\text{HHV}\left(\frac{MJ}{kg}\right) = 1.443 \times \left(H - \left(\frac{O}{8}\right)\right) + 0.0942 \times S + 0.3383 \times C \quad (6)$$

2.4.4 GC-MS analysis

Using gas chromatography-mass spectroscopy (GC-MS), the crude bio-oil and upgraded oil which is obtained from HTL and HDO process were analysed. The utilised model is Agilent 7890 GC with Agilent auto-injector 7683B with flame ionization detector (FID). Helium was used as a carrier gas with a 1 ml min^{-1} flow rate. The temperature of the column was initially set to 50 °C and finally increased to 250 °Cwith a 10 °C/min heating rate [38].

3 Results and discussion

3.1 Extraction of sap from macroalgae

3.1.1 Compositional analysis of feedstock

Prior to the sapping process, the compositional analysis was performed for *K. alvarezii* macroalgae. The physicochemical properties such as proximate and ultimate analysis were carried out on a dry basis as per ASTM standards to understand the basic properties of raw materials. As of proximate analysis, the *K. alvarezii* comprised 16.2 ± 0.6 wt.% of ash, 53.9 ± 1.4 wt.% of volatile matter, 15.3 ± 0.1 wt.% of moisture and fixed carbon of 14.5 ± 0.3 wt.%. It has been reported that the presence of ash content in *K. alvarezii* was attributed to the presence of several major minerals, such as calcium, magnesium, potassium and sodium [19].

The ultimate analysis revealed that the biomass possessed a nitrogen content of 2.4 ± 0.3 wt.%), which is considered a potential nutrient for plant growth. On the other hand, the other elements such as carbon, hydrogen, sulphur and oxygen contributed 31.2 ± 1.1*wt.* %, 6.1 ± 0.2 wt.%, 2.7 ± 0.1 wt.%and 41.3 ± 0.9 wt.%, respectively. The presence of higher sulphur contributed to the existence of sulphate groups in *K. alvarezii*. The existence of elemental nitrogen in marine algae is generally accounted for by ammonium (NH_4^+), nitrites (NO_2^-) and nitrates (NO_3^-) [39].

In addition to that, the biochemical composition of *K. alvarezii* was also performed, which reveals that carbohydrates contributed majorly to 62.5 ± 1.7 wt.%, followed by the protein of 7.5 ± 0.3 wt.% and lipid of 1.9 ± 0.2 wt.%. In addition to inorganic nitrogen, organic nitrogen was also available in the form of protein. The presence of this nitrogen was due to amino acids, phycobilins (pigments) and N-containing plant tissues. The existence of higher carbohydrates in *K. alvarezii* was due to k-carrageenan, which is a popularly commercialised product [29]. The record of lower lipid content in *K. alvarezii* has coincided with previous investigations [39].

3.1.2 Quantification of bio-simulants from macroalgae

The raw material utilised in this study was red macroalgae *Kappaphycus alvarezii*. The collected raw material was conditioned as per the instruction provided in the methodology. The amount of sap that was able to extract from the biomass through the crushing process was around 58 ± 1.1 wt.% with a loss of 2 wt.%. The primary chemical components of fertiliser such as organic carbon, nitrogen (N), phosphorus (P) and potassium (K) were determined for the sap extracted from *K. alvarezii*. The result revealed that *K. alvarezii*-sap (K-sap) comprised 0.73 ± 0.03 wt.% of organic carbon, 0.18 ± 0.06 wt.% of nitrogen, 0.02± 0.01 wt.% of phosphorus and 3.76 ± 0.07 wt.% of potassium. The leftover solid residue was around 40 ± 0.6 wt.%, which was regarded as *K. alvarezii*-reject (K-reject) and utilised as feedstock for the hydrothermal liquefaction process (HTL) process.

3.2 Hydrothermal liquefaction of K-reject

3.2.1 Fuel properties of HTL feedstock

The *K. alvarezii* leftover derived from the post-sap extraction process was used as feedstock for the hydrothermal liquefaction process. Prior to the HTL process, the compositional analysis was performed for *K. alvarezii* rejects (K-reject). The physicochemical properties such as proximate and ultimate analysis were carried out on a dry basis as per ASTM standards to understand the basic properties of raw materials. The volatile and ash contents have a great influence on the thermochemical conversion of biomass and impede the yield and quality of bio-oil [40]. The presence of higher volatile matter (36.1 ± 1.2 wt.%) and lower ash contents (18.4 wt.%) implies that the biomass can be combusted and subsequently utilised as an energy source. In addition, the proximate results reported that the feedstock possessed a moisture content of 22.2 ± 0.4 wt.% and fixed carbon of 23.3 ± 0.5 wt.%. The presence of low moisture is beneficial in terms of energy utilisation for the reaction to occur [41].

The ultimate analysis revealed that the biomass possessed higher content of carbon (29.2±0.8 wt.%) and oxygen (36.4±1.3 wt.%). On contrary, the other elements such as nitrogen, hydrogen and sulphur were recorded lower. Specifically, the presence of nitrogen (1.8±0.1 wt.%) was significantly lower compared to typical microalgae biomass utilised as HTL feedstock. Nitrogen is a crucial parameter that influences the quality of bio-oil as it results in the generation of higher N-containing compounds in the liquefaction process. These N-containing compounds will result in corrosion on storage or atmospheric pollution on combustion. Additionally, the presence of lower sulphur content will result in a higher quality of bio-oil with a lesser concentration of sulphur liquid fuel, i.e. the formation of lesser by-products emission (SO_x) on combustion. The existence of higher oxygen will influence the bio-oil quality by the generation of undesirable oxygenated liquid products [40]. Overall, these elemental compositions will significantly influence the calorific value of the energy-dense feedstock. The equation used to estimate the higher heating value (HHV) was provided in section 2. HHV of feedstock was found to be lower (11.4 MJ/kg), which might be attributed to higher O, which countered the content of carbon. Fuel with lower O/C and H/C was usually regarded as better fuel due to less water vapour, low energy loss and smoke on combustion [42]. The O/C and H/C were found to be 1.0 and 2.3 for K-reject.

In addition to that, the biochemical composition of *K. alvarezii* was also performed, which reveals that carbohydrates contributed majorly to 53.4 ± 1.5 wt.%, followed by the protein of 4.3 ± 0.1 wt.% and lipid of 1.6 ± 0.4 wt.%. The reduction in protein content after extraction was evident that some of the nitrogen content was transferred to K-sap, which will reflect on the formation of low N-containing compound on bio-oil production and thereby improves the quality of bio-oil.

3.2.2 Influential parameter on HTL product yield

In this research study, post-sap residues from *K. alvarezii* were utilised as feedstock for the hydrothermal liquefaction process in order to create extra revenue from de-sapped biomass. The investigations were performed on four crucial parameters, such as biomass to the solvent ratio (10 g, 20 g and 30 g of biomass in each 200 mL solvent), thermal conditions (280 °C, 300 °C and 320 °C), residence time (15 min, 30 min and 60 min) and catalyst dose (10 wt.%, 15 wt.% and 20 wt.%) that influence the distribution of product during HTL process.

Effect of biomass to solvent ratio During the investigation of biomass to solvent ratio in the reaction medium, the water (i.e. solvent) was maintained as a constant and the dose of feedstock was varied from 10 to 30 g with an increment of 10 units interval. All these experiments were performed under an optimised reaction temperature of 300 °C, a residence time of 30 min, catalyst dose of 15 wt.%. The result from Fig. 1 depicts that the bio-oil yield raised to the peak of 28.4 ± 0.6 wt.% from 23.7 ± 0.9 wt.% while increasing the biomass from 10 to 20 g and concurrently, a decline in the formation of solid residue from 41.6 ± 1.1 wt.% to 34.5 ± 0.8 wt.% were observed. These ascend in bio-oil might be corresponded to the role of active hydrogen residing in the water, which was utilised as a reaction medium in this case. The role of active hydrogen was to stabilise the intermediates and thereby inhibit the accumulation of solid residues (Fig. 1). However, exceeding 20 g per 200 mL led to a descend in the peak of bio-oil yield, which might

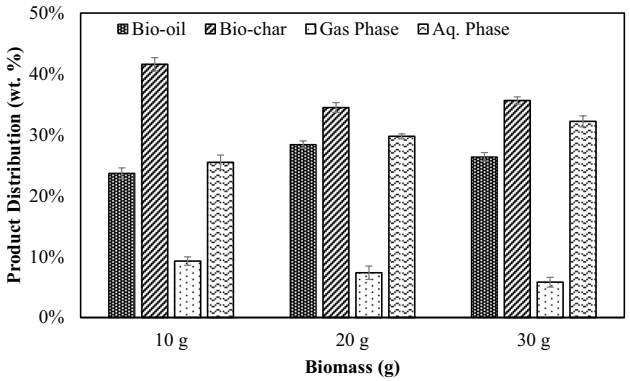

Fig. 1 Influence of water to K-reject ratio on HTL product distributions (conditions: 300 °C, 200 mL H_2O, 30 min, 15 wt.% ZSM-5)

be attributed to either deficit of solvent that is required for depolymerisation of biomass or as a consequence of a non-homogeneous mixture between solvent and biomass, which might result in low efficacy of HTL process.

Occasionally, the reduction in the yield of biomass might also be contributed to an increase in the formation of solid residues [43]. Based on the results depicted in Fig. 1, it can be perceived that the formation of solid residue tends to ascend with descend in the yield of bio-oil. At the same moment, the rise in the peak of HTL aqueous phase (HTL_{aq}) was also noticed during the decline in the yield of bio-oil, which could be the consequence of hydration, solvolysis and hydrolysis of raw biomass [44].

Effect of thermal conditions The influence of thermal conditions on the distribution of HTL products such as bio-oil, bio-char, gaseous phase and HTL_{aq} was explored by varying the temperature from 280 °C with an increment of 20 units interval until the decline in the yield of bio-oil was noted in Fig. 2. In order to optimise the favourable reaction temperature, the HTL process was performed with a biomass to solvent ratio of 10% with a catalyst dose of 15 wt.% for 30 min. The exponential increase in the yield of liquefied fuel from 24.7 ± 0.5 wt.% to 28.4 ± 1.2 wt.% was achieved while increasing the reaction temperature of HTL from 280 to 300 °C and in parallel, the declining trend in the formation of bio-char from 39.4 ± 0.8 wt.% to 34.5 ± 0.7 wt.% were observed. At 300 °C, the products apart from bio-oil and bio-char are HTL_{aq} (29.8 ± 0.8 wt.%) and gaseous phase (7.4 ± 0.5 wt.%). The composition of gaseous compounds was not determined in this study.

The increasing trend in the yield of liquified oil was found until the temperature was 300 °C beyond that the fall in the yield of biomass was recorded. Initially, the increase in the yield of liquified oil with raise in temperature from 280 °C was favoured by the cracking of macromolecules residing in the feedstock [45]. However, the raise in the reaction temperature beyond the critical point at which the highest peak of bio-oil was recorded, the ascend in the yield of the gaseous phase from 7.4 ± 0.5 wt.% to 10.6 ± 0.8 wt.% were seen. This phenomenon could be attributed to the trigger in the secondary decomposition beyond 300 °C, where the gasification reaction tends to begin. At the same moment, beyond 300 °C, the repolymerisation reaction tends to happen, which devours the bio-oil compounds to form solid residues such as bio-char [46]. The optimum thermal conditions for processing post-sap residues were concluded based on the maximal yield of bio-oil.

Effect of residence time The post-sap residue was hydrothermally liquefied with varying reaction residence time from 15 min with an increment of 15 units interval under an optimised reaction temperature of 300 °C, biomass to solvent ratio of 10%, and catalyst dose of 15 wt.%. From Fig. 3, it can be inferred that the maximal yield of liquified oil (28.4 ± 1.2 wt.%) was seen at 30 min of residence time. This could be the result of breakage in C–C bonds of post-sap residue, dehydration, decomposition and repolymerisation of intermediates.

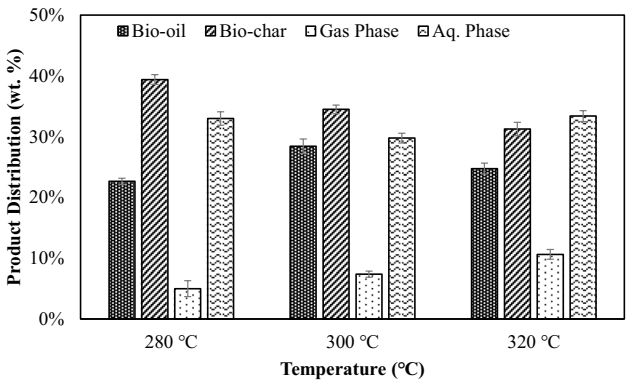

Fig. 2 Influence of thermal conditions on HTL product distributions (conditions: 20 g K-reject, 200 mL H_2O, 30 min, 15 wt.% ZSM-5)

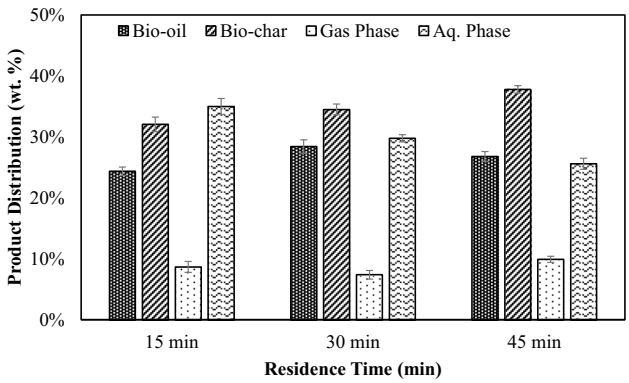

Fig. 3 Influence of residence time on HTL product distributions (conditions: 300 °C, 20 g K- reject, 200 mL H_2O, 15 wt.% ZSM-5)

When the residence time was increased beyond 30 min, the fall in the yield of bio-oil (26.8 ± 0.9 wt.%) was observed. Concurrently, an increase in the formation of bio-char and gaseous phase was found while a decline in the bio-oil yield. This phenomenon could be attributed to the cracking of liquified oil into low molecular compounds such as gaseous products and the repolymerisation of monomers into solid residue, which was bio-char [12]. The optimum residence time for processing post-sap residues were concluded based on the maximal yield of bio-oil.

Effect of catalyst dose The hydrothermal liquefaction of post-sap residue was performed with varying catalyst doses from 10 wt.% with an increment of 5 units interval under an optimised reaction temperature of 300 °C, biomass to solvent ratio of 10%, and residence time of 30 min. This optimisation study was intended to enhance the bio-oil yield in terms of quality and quantity using a catalyst. Generally, during the liquefaction of feedstock, the macromolecules residing in biomass tend to decompose to form solid (bio-char), liquid (bio-oil + aqueous phase) and gaseous products, whereas in the catalytic HTL process, the catalyst alters the reaction environment based on varying acid site, pore size and volume, which favours the liquefaction reaction by reducing polycondensation, repolymerisation etc [47]. The result of the influence of varying catalyst doses on different HTL products was illustrated in Fig. 4.

Under optimised conditions, the non-catalytic HTL process was able to achieve maximum bio-oil and bio-char yield of 18.3 ± 0.7 and 40.3 ± 0.8 wt.%. In contrast, the usage of ZSM-5 catalyst (15 wt.%) in the hydrothermal liquefaction process led to the increase in bio-oil yield of 28.4 ± 0.8 wt.% and a decrease in bio-char yield to 34.5 ± 0.8 wt.%. The possible explanation could be that the ZSM-5 catalyst has higher acidic-base sites, which facilitated the breakdown of the macromolecule into the desired product with ease [48]. Compared to the non-catalytic process, the catalytic hydrothermal liquefaction improved the production of bio-oil yield by 55%. This increase in the bio-oil yield may be attributed to higher catalyst diffusivity in the sub-critical water. Similar improvements in the yield by the catalytic process were reported in the literature by Ma et al. [12].

When the catalyst dose was increased beyond 15 wt.%, the fall in the yield of bio-oil was noted, whereas gaseous products tend to ascend. Because, a higher dose of catalyst facilitates the higher active surface area for the reactant, which in turn promoted the higher fraction of cracking that led to the production of more gases. In addition, it has also been reported that a lower-than-required catalyst dose will result in a deficit of catalyst for breaking the macromolecules residing in biomass [12].

3.2.3 Hydro-deoxygenation of bio-oil

Effect of catalyst on HDO process The bio-oil derived from post-sap residues of *K. alvarezii* was subjected to an upgradation process, such as the hydro-deoxygenation process. On hydro-deoxygenation, the bio-oil was transformed into four product streams such as upgraded oil, water-soluble materials, coke and gas. In this study, the upgrading process was carried out using a different dose of bio-char containing ZSM-5, which was obtained as a solid residue from the previous HTL process. This investigation was intended to explore the effect of bio-char containing ZSM-5 on the yield of upgraded oil. The hydro-deoxygenation of bio-oil was performed with varying catalyst doses from 5 wt.% with an increment of 5 units interval under a reaction temperature of 300 °C, the residence time of 90 min. The results of all four product streams on the influence of bio-char containing ZSM-5 were illustrated in Fig. 5.

From Fig. 5, it can be seen that the upgraded oil yield was increased from 22.4 ± 0.7 wt.% to 24.2 ± 0.4 wt.%. This minimal increase in the upgraded oil could be attributed to

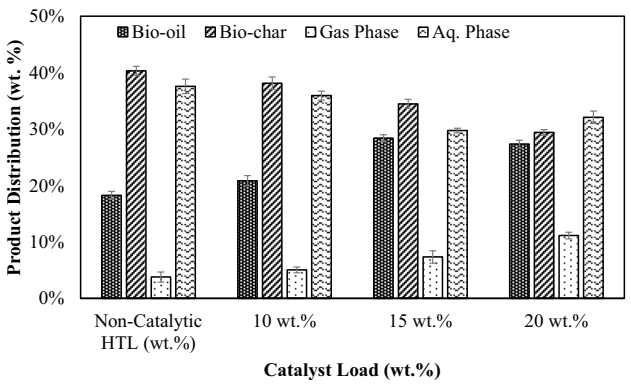

Fig. 4 Influence of catalyst load on HTL product distributions (conditions: 300 °C, 20 g K- reject, 200 mL H_2O, 30 min)

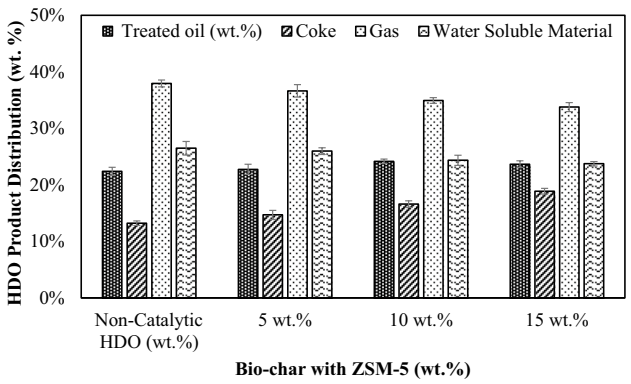

Fig. 5 Influence of bio-char containing ZSM-5 on HDO product distributions (conditions: 300 °C, 90 min)

the H_2 reaction atmosphere, where the presence of a stable H–H bond led to lower reactivity. The higher gas and water solubles were found to be higher in the non-catalytic HDO process compared to the catalytic process.

On treating the bio-oil using the HDO process, the coke formation was increased from a non-catalytic process to a catalytic process. The higher coke yield was recorded for 10 wt.% bio-char containing ZSM-5 (16.6 ± 0.6 wt.%). This increase in the formation of coke was consistent with the literature on catalytic upgrading of bio-oil [49]. The possible explanation could be for two reasons, firstly the formation of solid precipitates while the catalyst is dispersed in the bio-oil and secondly more catalysts aid the hydrogenation of oil and lowered the asphaltenes stability, which in turn promoted the coke formation. On contrary, the lower gas yield was recorded for the catalytic HDO process under H_2 atmosphere. This implies that the catalyst was able to control the evolution of radicals and thereby inhibiting the formation of gas. Besides, the yield and the physical properties such as viscosity were found to be lower and the odour was similar to diesel.

3.2.4 Influence of operating conditions on bio-oil and upgraded oil composition

CHNS elemental analysis Ultimate analysis and higher heating value (HHV) of crude bio-oil derived from post-sap residues of *K. alvarezii* and upgraded oil from HDO of crude bio-oil were exhibited in Table 1, respectively. The crude bio-oil from K-reject exhibited lower C and H content because of its higher ash content. On the other hand, the presence of nitrogen content was due to protein in K-reject, however, in this case, the lower nitrogen content was recorded because of the de-sapping process prior to the hydrothermal liquefaction process. During de-sapping, the reduction in N-content was recorded, which subsequently resulted in lower N-content (3.5 wt.%) in crude HTL bio-oil. On the usage of a catalyst, further reduction in N-content was observed, which was desirable because the upgrading process involving the denitrogenation concept is usually regarded difficult step. Similarly, a significant decrease in the oxygen content was observed, this could be attributed to the reaction of oxygen and carbon to produce CO, CO_2 and water [50]. The increase in hydrogen element compared to non-catalytic HTL bio-oil could indicate the existence of higher aliphatic compounds in catalytically derived HTL bio-oil. The ultimate analysis of this crude bio-oil is in agreement with the early article published by Nallasivam et al. [51]. The HHV of crude bio-oil derived from post-sap residues of *K. alvarezii* was assessed to be 33.9 MJ kg^{-1}, which was found to be higher than crude bio-oil derived from pyrolysis of the same feedstock [29]. No significant differences were found between C and H content as well as HHV of catalysed crude bio-oil and uncatalysed upgraded oil. However, the reduction in N was observed, the possible explanation could be the denitrogenation reaction offered by subcritical water. Likewise, the reduction in sulphur content was also observed.

Upgradation of the oil strategy resulted in a significant reduction of nitrogen, sulphur and oxygen, as a consequence HHVof upgraded oil was improved to 36.7 MJ kg^{-1} from 33.9 MJ kg^{-1}. This indicates that deoxygenation and decarboxylation reactions enhanced with the usage of a ZSM-5 catalyst. In terms of nitrogen removal, the catalysed crude bio-oil (1.2 wt.%) and upgraded oil (0.5 wt.%) displayed higher removal compared to their uncatalysed counterpart. The considerable decrease in oxygen content was facilitated by the ZSM-5 catalyst for both crude bio-oil and upgraded oil. The fuel possessing a lower ratio of H/C and O/C was anticipated to be better fuel. Because fuel with lower H/C and O/C will result in lower smoke on combustion, low energy loss and less water vapour [52]. In this study, the H/C and O/C were observed to be lower for upgraded oil compared to crude bio-oil Table 1. This could be a result of

Table 1 Comparison of crude bio-oil, upgraded oil and benchmarked crude oil

Composition	Uncatalysed crude bio-oil	Catalysed crude bio-oil	Uncatalysed upgraded oil	Catalysed upgraded oil	Crude oil[c]
Carbon (wt.%)	50.6	69.8	69.9	74.4	83–86
Hydrogen (wt.%)	6.8	9.4	9.5	9.9	11–14
Nitrogen (wt.%)	3.5	1.2	0.8	0.5	<1
Sulphur (wt.%)	0.8	0.6	0.2	-	<4
Oxygen (wt.%)[a]	38.3	18.9	19.6	15.2	<1
HHV[b] (MJ kg^{-1})	20.1	33.9	33.9	36.7	44
H/C (mol mol^{-1})	1.62	1.62	1.62	1.59	1.5–2.0
O/C (mol mol^{-1})	0.57	0.20	0.21	0.15	~ 0

[a]Determined by difference [O]=100%-[C]-[H]-[N]-[S]; [b]HHV, higher heating value; [c] Referred from Asadieraghi et al. [53]

the deoxygenation reaction that happened during the upgradation of crude bio-oil.

As per commercial crude oil composition (CHNS) reported by Asadieraghi et al. [53], the carbon and hydrogen content of bio-oil should be in the range of 83–86 wt.% and 11–14 wt.%. But, the carbon and hydrogen content of catalysed upgraded oil was found to be slightly lower compared to the benchmarked crude oil, this could be attributed to the presence of higher ash content. This resulted in lower HHV when compared with benchmarked crude oil. In addition, it has been reported that the oil must possess nitrogen and oxygen content below 1 as well as O/C and H/C must be in the range of 0 and 1.5–2.0, respectively. From Table 1, it can be inferred that the composition of nitrogen, sulphur, O/C and H/C is similar to that of benchmarked crude oil; however, the oxygen content was still in the range higher than expected, which requires further treatment.

GC-MS characterisation The derived bio-oil from post-sap residues of *K. alvarezii* was dark-brown in colour with viscous nature and smoky odour. On contrary, the upgraded oil was light-brown in colour with low viscosity and smelled like diesel, particularly those produced at 300 °C with biochar with a ZSM-5 load of 10 wt.%. In this study, gas chromatography and mass spectrometry (GC-MS) were utilised to distinguish some of the molecular components of bio-oil and upgraded oil.

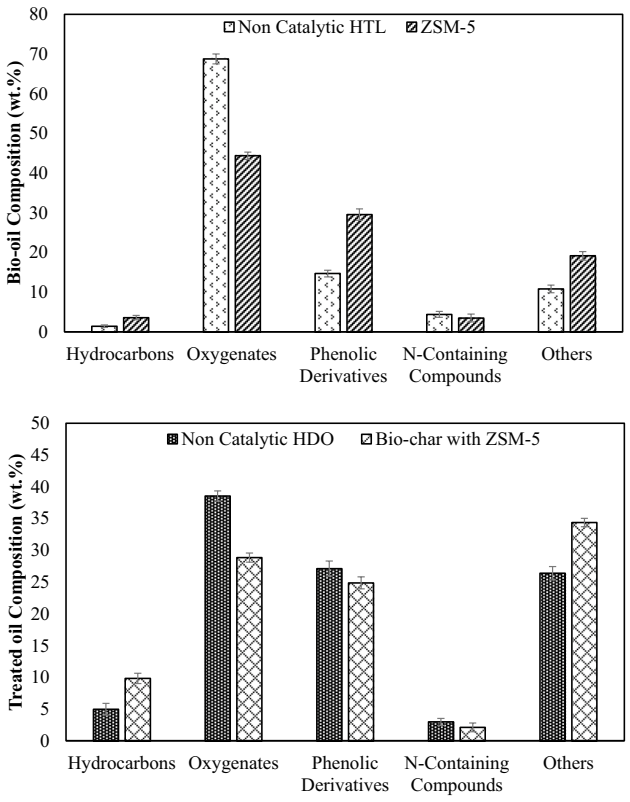

Fig. 6 Analysis of GC-MS for crude bio-oil (top) and upgraded oil (bottom)

A comparison of crude bio-oil and upgraded oil using GC-MS was illustrated in Fig. 6. From Fig. 6, it can be seen that, the composition of crude bio-oil was completely different from the upgraded oil. The GC-MS results showing higher mass yield were discussed for both crude bio-oil and upgraded oil. The HTL bio-oil exhibited the presence of hydrocarbons, phenolic compounds, oxygenates, amide, pyrrole, acids, alcohols, aldehydes, esters etc., whereas the upgraded oil possessed similar kind of functional groups that existed in crude oil but in different concentrations. The compositions of crude bio-oil and upgraded oil were categorised under the following groups: hydrocarbons, oxygenates, phenolic derivatives, N-containing compounds and others.

The bio-oil derived from catalytic liquefaction displayed higher hydrocarbon yield compared to the non-catalytic liquefaction process as shown in Fig. 6 (top). The amount of hydrocarbon usually relies on the hydrolysis and decarboxylation of fatty acids derived from lipids. The existence of low hydrocarbons was mainly attributed to the presence of low lipids in the feedstock. The phenolic compound was found to be higher in catalytic liquefaction (29.5 ± 1.4 wt.%) compared to non-catalytic liquefaction (14.7 ± 0.8 wt.%). This phenomenon could be due to the deconstruction and cyclisation reaction of many polymeric sugars. The presence of some sulphated constituents was due to the sulphonated polysaccharides in red macroalgae commonly known as k-carrageenan. The role of k-carrageenan was to provide structural integrity to the cell wall from external forces.

On catalytic liquefaction of post-sap residues, the decrease in the N-containing compounds from 4.4 ± 0.7 wt.% to 2.7 ± 0.4 was seen in crude bio-oil. The presence of higher nitrogen content in non-catalytic bio-oil was due to the existence of amide, pyrrole and nitrile, which are usually regarded as N-containing compounds. The presence of these compounds was mostly due to the protein that is undergoing hydrolysis, cyclization and decarboxylation. In addition, the presence of N-heterocyclic compounds is due to the Maillard reaction between carbohydrates and proteins. The bio-oil derived from non-catalytic liquefaction showed higher possession of O-containing compounds (68.8 ± 1.3 wt.%), which later on reduced during the catalytic liquefaction process. These results suggest that the ZSM-5 catalyst has the potential to de-nitrogenate and de-oxygenate the crude bio-oil, which was in agreement with the result acquired from the elemental analysis of crude bio-oil. Even though the presence of O-containing compounds was predominant in crude bio-oil, hence it has been suggested to perform hydrodeoxygenation of crude bio-oil.

On upgradation, several compositions exist in upgraded oil were varied significantly. During the upgradation of crude oil under H_2 atmosphere, the reduction in phenolic

compounds from 29.5 ± 1.4 wt.% to 24.9 ± 1 wt.% for optimised catalytic HDO was observed. The decrease could be due to the hydrogenation of phenolic compounds to benzene and its derivatives. Under optimised conditions, the increase in hydrocarbon was found in upgraded oil (9.8 ± 0.8 wt.%), compared to crude bio-oil (3.6 wt.%). The hydrocarbon composition was majorly populated with long-chain alkanes. The N-containing compounds were drastically reduced during the HDO process. Oxygenated compounds were found higher in the non-catalytic HDO process, whereas in the catalytic HDO process, the oxygenated compounds were limited to 28.9 ± 0.7 wt.%. Overall, the ZSM-5 catalyst was able to deoxygenate around 58% of oxygenated compounds during crude bio-oil production as well as upgraded oil production. Still, the upgraded oil requires additional treatment for possessing higher-than-required oxygenated compounds.

4 Conclusions

This study revealed that the catalytic hydrothermal liquefaction and catalytic hydro-deoxygenation were promising in the production of a higher yield of bio-oil and minimising the oxygenates and nitrogenates in the product. The optimum reaction temperature, biomass to solvent ratio, residence time and catalyst dose for processing post-sap residues were found to be 300 °C, 10%, 30 min and 15 wt.%,which was concluded based on the maximal yield of bio-oil (28.4 ± 0.6 wt.%). Upgradation of catalytically produced crude bio-oil resulted in a reduction of oxygenated compounds by 35% as well as an increment in HHV by 7.58% in the upgraded oil. When compared to the uncatalysed HDO process, the usage of bio-char containing ZSM-5 derived from the previous HTL process, as a catalyst in the HDO process was found to improve the quality of upgraded oil rather than the quantity. Overall, this study concludes that most of the CHNS properties in upgraded oil are comparable with the benchmarked crude oil. Therefore, it can be concluded that bio-oil with higher quality can be derived from the reject of *Kappaphucus alverizii* after its application as a fertiliser.

Author contributions This declaration is not applicable.

Data availability This declaration is not applicable.

Declarations

Ethical approval This declaration is not applicable.

Competing interests The authors declare no competing interests.

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