Hydrothermal Liquefaction of Breadfruit Pulp under Subcritical Water Condition for the Production of Bio-oil

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Abstract

The waste generated from agro-activities are enormous, due to high demand for food to meet the ever growing human population. These waste can be converted into useful product for various applications. This work converted agro-waste from breadfruit processing (breadfruit pulp) to bio oil through hydrothermal liquefaction (HTL). Central composite design (C-CD) of response surface method (RSM) was applied using Design Expert software to design the experiment for the bio oil production. The produced bio oil and hydrochar as well as the feedstock was characterized by carrying out ultimate, proximate, and thermogravimetric analysis. The chemical composition of the bio oil was also determined through GCMS and FTIR analysis. The experimental result gave maximum oil yield of 48.9% at the parameter combination of 300 $^\circ$C reaction temperature, and water-biomass ratio of 10, at reaction time of 50 minutes and heating rate of 5 $^\circ$C/min. The ultimate analysis showed that the bio-oil contains 45.09% carbon, 2.49% hydrogen, 0.67% nitrogen, 0.58% sulphur, and 51.27% oxygen. The proximate analysis gave moisture, ash, volatile matter, and fixed carbon content of 12.7%, 2.6%, 42.6%, and 41.8%, respectively for the bio-oil. The GCMS analysis showed that the oil is composed majorly of organic acid, and hydrocarbon of alkenes and alkynes family, which is confirmed by the FTIR analysis. The energy recovery analysis showed that the HTL process recovered 48.5% of the energy in the breadfruit pulp in the bio-oil, while 39.7% was recovered in the hydro-char. This shows that the HTL is suitable for bio-oil production from breadfruit pulp. The produced bio-oil can be upgraded to bio-diesel for diesel engine application, while the hydrochar can be used as solid fuel or as a filler for fertilizer production.

Keywords: Hydrothermal liquefaction; Breadfruit Pulp; Bio-oil; Hydrochar; Water-Biomass Ratio

Introduction

The surge in economic activities as a result of significant rise in global population has accelerated the demand for energy, globally. This is because, energy is very essential for economic activities, and this growing demand is predominantly met through fossil fuels, thereby resulting in excessive reliance on these sources for power generation [1]. This leads to excessive consumption of fossil fuels, thereby emitting harmful gases such as carbon dioxide (CO_2), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2). These emissions contribute to environmental issues like global warming, acid rain, and the formation of hazardous particulate matter. Additionally, they play a major role in the formation of ground-level ozone (smog), which can damage lung tissue and increase the risk of respiratory conditions such as asthma, bronchitis, and other chronic diseases [1,2,3]. More so, fossil fuels are non-renewable sources of energy as they are derived from pre-historic fossils and will not be able to replenish at the rate at which it is been consumed [4]. Therefore to meet the ever growing demand for energy with less impact on the environment, there is need to source for other alternative clean energy sources, to reduce or replace the consumption of fossil fuels.

The quest for alternative source of energy in order to reduce fossil fuels consumption and still meet up with the global energy demand has led researchers to point towards biomass due to its availability and ease of handling [1]. Biomass was once the global major energy source before the advent of fossil fuels. Fossil energy being the cheapest and easily accessible, dominated all other energy resources over the recent past. However, fossil oil depletion and its uneconomical extraction have once again highlighted biomass as a source of energy in transportation and power generation related applications. More so, huge potential lies in the use of biomass for the production of various chemical products [5]. Biomass conversion into fuels and chemicals can share demand loads of fossil fuels to avail cheaper means of transportation, electricity, and chemicals. This will help to save foreign reserves and boost economic activities in regions of the world, which lack in fossil fuel resources but have abundant biomass [6]. Moreover, biomass conversion would rid our environment of waste and reduce dumping costs such as in incineration of municipal wastes [7].

The methods for biomass conversion into biofuels, which are capable of substituting petroleum-derived fuels, are complex and ranges from biochemical conversion processes to severe catalytic thermochemical processes. However, the conversion of biomass into bio-oil are only possible through pyrolysis or hydrothermal liquefaction processes [8]. Pyrolysis is the thermochemical process of decomposing organic materials in the absence of oxygen at elevated temperature [9]. While hydrothermal liquefaction (HTL), is a thermochemical technique that transforms diverse biomass feedstocks into bio-oil through a treatment with pressurized hot water at subcritical temperatures and pressures [8].

HTL requires operating temperature of 300 °C to 350 °C at a pressure of 5 MPa to 20 MPa for 5mins to 60 mins, wherein water is in the liquid form [8]. While Sahu et al [10] and Gollakota *et al* [11], with some other researchers, reported operating conditions within the temperature range of 250 °C to 380 °C and pressure range of 5 MPa to 28 MPa. HTL process begins with solvolysis of biomass in micellar forms, followed by the disintegration of biomass fractions (cellulose, hemicellulose, and lignin), and then the thermal depolymerization into smaller fragments [12]. HTL, which mimics the processing of fossil fuels buried deep inside the earth, occurs in minutes or hours. It produces oil with low oxygen content as opposed to other processes like fast pyrolysis, and proves to be very energy efficient as it entails temperatures lower than those reached during pyrolysis [8]. HTL possess several advantages that makes it an attractive and efficient biomass conversion option over other thermochemical conversion techniques, because it does not require prior thermal drying and thus suitable for the production of bio oil from biomass with varying moisture contents. Secondly, it uses hot pressurized water as a reaction medium, hence, other chemicals may not be necessary. Thirdly, HTL is less corrosive to equipment than other conversion alternatives, and the whole process is versatile and environmentally friendly [13].

Several biomass has been employed for bio oil production through HTL by various researchers. These biomasses ranges from

first generation to third generation feedstock. The first generation feedstock includes the edible seeds and plants such as maize, wheat, sugarcane, sugar beet, cassava, and corn. However, the competitiveness of the of the first generation feedstock with food led to development of second generation feedstock, which include lignocellulosic resources, woody biomass and inedible seeds such as jatropha curcas, as well as waste oil feedstocks, all of which are available at low prices. Presently, third generation feedstock which include microalgae and some other microorganisms such as cyanobacteria, bacteria, fungi, and yeast, has been developed to eliminate concerns of the first and second generation feedstock, and other resources over land [14]. The type of biomass used for HTL plays an important role in biocrude production. This is because different biomass has different constituents such as lignin, hemicelluloses, and cellulose, which behave differently to hydrothermal temperature variations [15]. Among the three major components, lignin is most stable in nature and its molecular chain is relatively difficult to fracture, but it can be easily coked during liquefaction process. On the other hand, the physical structure of cellulose and hemicellulose is relatively simple with relatively weak hydrogen bonding and stacking interactions, showing poor thermal stability and thus higher degradability in HTL [16]. In general, high cellulose and hemicelluloses content in biomass yields more bio-oil in HTL process. For example, hardwood samples (cherry) produced more oils than softwood (cypress) due to the high lignin contents in later biomass [16].

Different researchers has reported different biomass conversion through HTL, ranging from second, third (algae) and even the combination of second and third generation feed stock [14]. Briman *et al* [17], studied the effect of possible interaction between three different feeds (protein-rich microalgae, lignocellulosic wood, and carbohydrate-rich sugar beet pulp), at the temperature of 250 °C and 350 °C, and residence time of 10 mins, using 10 wt% (in water) binary mixtures (1:1 wt basis) and a (1:1:1 wt basis) ternary mixture. The results showed that the mixture of the feedstock plays a role in the HTL, reducing the amount of biocrude produced against the estimated values for binary and ternary mixtures, on the basis of linear averaging of the results for the single feeds. Also Kiran *et al.* [19] investigated the effect of different algal biomass namely, Chlorella vulgaris, Botryococcus braunii and Scenedesmus quadricauda on bio oil yield, under hydrothermal liquefaction with different water concentrations (1:6, 1:7, 1:8, 1:9 & 1:10 ratio) at temperature range of 200–320 °C, pressure (60 bars) and reaction time (30 min) and reported highest bio-oil yield with S. quadricauda at 1:9 ratio. Feng *et al.* [16], also investigated the liquefaction of three feedstocks; white spruce bark, birch bark, and white pine bark under the same processing conditions. It was observed that the bio-oil yields were 58%, 67%, and 36%, respectively. The high oil yield recorded with white spruce bark and birch bark is as a result of high cellulose and hemicellulose in the biomasses.

The use of other biomasses for bio oil production through hydrothermal liquefaction has been reviewed. These include the use of different species of algae [20 - 25] for bio oil production via HTL. Other reviewed works, combined algae and other second generation feedstock such as micro algae, wood and sugar beet pulp [18], and microalgae (chlorella pyrenoidosa, CP) and lignocellulosic biomass (rice husk, RH) [26]. While some other researchers used only the second generation feedstock such as fruit processing wastes (cornelian cherry stones) [27], barley straw [28], dairy manure [29], Litsea Cubeba Seed [30], oil palm biomass; empty fruit bunch(EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) [31], and real biomass: (water hyacinth, and rice straw), microcrystalline cellulose, and xylan [32], for bio oil production through HTL. However, the use of breadfruit pulp for bio oil production through HTL has not been reported, and this frms the knowledge gap for this work.

Breadfruit, also known as Treculia Africana is a species in the genus Treculia and belongs to the taxonomic family of Mureccae. It is used as a food plant in Nigeria and some other countries of West Africa. The edible seeds are rich in high quality vegetable protein, oil and carbohydrate, and contains some essential vitamins and minerals [33]. It comes in nature as fruit head with the seed embedded inside the pulp as seen in figure 1. The pulp are allowed to decay before the extraction of the seed for easy extraction. The ruminant pulps after seed extraction are discarded as waste. Hence the need to convert it into a useful product, in order to eliminate the waste.

Figure 1: Breadfruit head

Materials and Method

Material's Collection and Preparation

The feedstock used for the bio-oil production was decayed breadfruit pulp. The decayed breadfruit pulp was collected from a farm refuse dump located at Ogboji, in Orumba South Local Government Area of Anambra State, Nigeria, where the breadfruit seed extraction is been carried out. The collected feedstock was sun dried for seven days to reduce the moisture, in order to determine the actual weight of feedstock used for the experiment. The dried feedstock was then grinded using manual grinder to increase the surface area and allow for easy interaction with water during reaction

Experimental Design and Procedures

The production of bio oil via hydrothermal liquefaction (HTL) of breadfruit pulp was carried out with HTL batch reactor with a reaction chamber volume of 1.6 liter. The reaction chamber is embedded inside the reactor housing for safety. The reactor was designed for a maximum working pressure of 10 bar. Before the bio production, an experimental design was carried out in order to provide a guide for the bio oil production experiment. This was done using Central Composite Design (CCD) of Response Surface Method (RSM) with the aid of Design Expert software, version 10. The four major factors that affects hydrothermal liquefaction reaction such as water-biomass ratio, reaction temperature, reaction time and heating rate were chosen as the dependent variables, while the bio oil and hydrochar yield was chosen as the responses. The selected high and low values of these factors are presented in table 1. This design of experiment gave a total of thirty runs with different process parameter combination.

The process parameter combinations from the experimental design was used to carry out the liquefaction experiment. The experiment was carried out under subcritical condition using HTL autoclave reactor. The reactor was loaded with the sample at a biomass-water ratio of 1:5, 1:7.5, and 1:10 according to the experimental design. For each of the biomass-water ratio, 100 grams of the prepared sample and the corresponding mass of water that gives the ratio was loaded in the reactor, and sealed using the provided clamps. The voltage regulator and the thermocouple of the reactor was adjusted to a setpoint that will give the required heating rate and temperature respectively. The reactor is then powered and the stirrer turned on, to allow for the HTL of the biomass. The reactor was monitored until the required temperature is reached, and the residence timing starts. The reaction was allowed to proceed until the required residence time is reached, then the reactor was turned off and allowed to cool before the product collection and separation. This experimental processes was repeated for all the experimental runs produced by the experimental design.

Table 1: DOE factors for bio oil production

Factor	Name	Unit	Low Level	High Level
A	Reaction Temperature	$^\circ$C	200	300
B	W-B Ratio		5	10
C	Reaction Time	min	20	50
D	Heating Rate	$^\circ$C/min	5	10

Product Separation and Yield

The mixture of liquid and solid products collected from the reactor after the reaction was first separated by filtering. The solid residue was rinsed with ethyl acetate to extract the oil trapped within the solid product. The mixture of the residue with the solvent was also filtered. The solid residue was then pressed to drain the oil and solvent within the solid product. The solid product termed hydrochar was sun dried, while the filtrate which was the mixture of oil, water and ethyl acetate was then taken to lab for separation. The ethyl acetate within the filtrate was first recovered by distillation, while the water and the oil solution was separated by centrifugation.

The recovered products after separation which were bio oil and hydrochar were weighed and recorded. The recorded weights of each of the products were used to determine the product yield of each of the products using the equations;

$$\%Y_{BO} = \frac{m_{BO}}{m_B} \times 100 \quad (1)$$
$$\%Y_{HC} = \frac{m_{HC}}{m_B} \times 100 \quad (2)$$

Where %YBO and %YHC, are the percentage bio oil, and hydrochar yield by mass, respectively. mBO, and mHC, are the masses of the recovered bio oil and hydrochar respectivey. While mB is the mass of the biomass used as feedstock for the reaction. This was repeated for each of the runs to determine the product yields for each of the parameter combination.

Sample Testing

The bio oil and the corresponding hydrochar produced from the experimental run that gave the highest oil yield was characterized alongside with the feedstock. The characterization carried out on the samples include; ultimate, proximate, thermogravimetric, gas chromatography-mas spectrometery (GC-MS), and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

Ultimate Analysis

The ultimate analysis was done using Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer, to determine the carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) content of the samples, as described by Harissanker et al [34]. The oxygen (O) content was obtained by mass difference. The obtained elemental constituents of the samples were used to determine high heating values (HHV) of the samples using equations (3), as described by Ezenwa et al [1]

$$HHV = 0.349C + 1.1783H + 0.1005S - 0.1034O - 0.0151N \quad (3)$$

The high heating values of the samples was used to determine the energy recovered (ER) from the feedstock into the bio oil and hydrochar using equation (4) as described by Ezenwa et al [1].

ER = \frac{\text{HHV of Product} \times \text{mass of product}}{\text{HHV of Feedstock} \times \text{mass of feedstock}}\:\:\: (4)

Proximate Analysis

The proximate analysis was conducted to determine their moisture, ash, volatile mater and fixed carbon contents of all the samples. The moisture, ash and volatile matter contents were obtained according standards; ASTM E872-82, ASTM E1755- II, and ASTM E 872, respectively as described by Ezenwa et al [1]. The obtained data was employed in equations (5), (6), and (7) to obtain the moisture, ash, and volatile matter contents of the samples respectively. While the fixed carbon content was obtained by subtracting the sum of moisture, ash, and volatile matter content from 100% as seen in equation (8).

$$\%MC = \frac{(W_i - W_d)}{W_i} \times 100 \quad (5)$$

$$\%AC = \frac{W_a}{W_d} \times 100 \quad (6)$$

$$\%VM = \frac{W_d - W_h}{W_d} \quad (7)$$

$$\%FC = 100\% - (\%AC + \%VM + \%MC) \quad (8)$$

Where %MC, %AC, %VM and %FC are the percentage moisture, ash, volatile matter and fixed carbon contents of the samples respectively. Wi and Wd is the weight of the sample before and after drying, while Wa is the weight of ash obtained after burning the samples in the furnace at 550 $^{\circ}$C for 8 hours. Wh is the weight of the sample after heating the dried sample in a furnace at 900 $\circ$C for 7 min to drive off the volatiles.

Thermogravimetric (TGA) Analysis

Thermogravimetric Analysis was conducted using thermogravimetric analyzer (Perkin Elmer TGA 4000). This was done to determine the thermos-physical properties of the samples. To carry out the analysis, a measured sample was loaded in the furnace of the analyzer and the start icon was clicked to run the analysis. The furnace was allowed for the measurement to complete before returning it back into the cool position, and the crucible removed. The result of the analysis is then displayed on the screen.

Gas Chromatograph Mass Spectrometry (GC-MS) Analysis

The GC-MS analysis was carried out by injecting the sample into the spectrometer through a port that is heated to 300° C, where the material is volatilized. The gaseous component is separated as they flow through the column based on size and/or polarity. The sample components that are more volatile and smaller in size will then travel through the column more quickly than others into the MS region where the separated components are blasted with electrons, causing them to break up and turn into positively charged ions. The detector within the MS region then detects and records the filtered ions and the mass spectrum. The mass spectrum is used to identify the components by comparing each to reference libraries of over 275,000 unique spectra.

FTIR Analysis

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out using FTIR spectrometer (Agilent Technology Cary 630), to identify the functional group within the sample. The spectrometer was interphase with a computer that is controlled by a window called MicroLab PC window. To carry out the analysis, the instrument was turned on and allow to warm-up for 15 minutes before launching the MicroLab PC window. 15 mg of the sample was loaded and sample alignment was checked before sampling. After sampling the peaks were picked and labelled by dragging, to acquire the wavenumbers as well as Transmittance or Absorbance.

Results and Discussion

Experimental Result

The result of the hydrothermal liquefaction experiment for each of the parameter combination obtained from the experimental design is presented in table 2. Form the table, it can be seen that the parameter combination that gave the highest oil yield of 48.9% was obtained from the parameter combination of 300 ^{o}C reaction temperature, and water-biomass ratio of 10, at 50 minutes reaction time and heating rate of 5 ^{o}C/min. The obtained bio oil and hydrochar is shown in figure 2(a) and (b) respectively. The bio oil is a viscous fluid that is darkish brown in colour with a decayed pungent smell. The produced bio-oil can be upgraded and used for diesel engine application, or can be used as coolant in cutting applications. While the bio char is a black solid residue that are left after the separation of the liquefaction products. The solid residue can be used for several purposes such as in the production of briquettes, fertilizer and for carbon capture.

Table 2: Hydrothermal liquefaction experimental result

Std	A: Reaction Temperature (^{o}C)	B: W-B Ratio	C: Reaction Time (min)	D: Heating Rate (^{o}C/min)	Oil Yield (%)	Hydrochar (%)
1	200	5	20	5	34.8	35.9
2	300	5	20	5	44.7	30.6
3	200	10	20	5	37	34.6
4	300	10	20	5	46.2	29.8
5	200	5	50	5	29.8	38.9
6	300	5	50	5	36.6	35.1
7	200	10	50	5	40.5	32.5
8	300	10	50	5	48.9	27.5
9	200	5	20	10	32.1	36.9
10	300	5	20	10	43.8	39.8
11	200	10	20	10	35.4	35.5
12	300	10	20	10	45	30.8
13	200	5	50	10	26.3	37.7
14	300	5	50	10	34.1	36.2
15	200	10	50	10	38.7	33.7
16	300	10	50	10	46.6	30.2
17	150	7.5	35	7.5	29.9	38.9
18	350	7.5	35	7.5	42.1	30.3
19	250	2.5	35	7.5	24.3	40.4
20	250	12.5	35	7.5	41.8	32.5
21	250	7.5	5	7.5	37.5	34.9
22	250	7.5	65	7.5	39.9	33.1

23	250	7.5	35	2.5	45.3	31
24	250	7.5	35	12.5	42.2	31.4
25	250	7.5	35	7.5	47	29.9
26	250	7.5	35	7.5	42	31.5
27	250	7.5	35	7.5	45	30.1
28	250	7.5	35	7.5	46.8	29.8
29	250	7.5	35	7.5	47.9	28.6
30	250	7.5	35	7.5	44.7	31.6
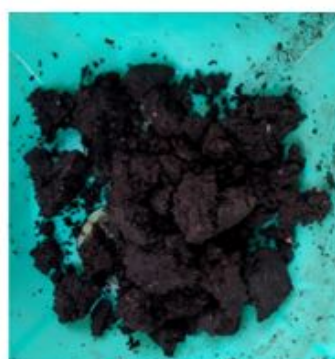
Figure 2: (a) Bio oil and (b) hydrochar obtained from hydrothermal liquefaction of breadfruit pulp

Effect of the Process Parameter on Oil Yield

The effects of the process parameters (A: reaction temperature, B: water-biomass ratio, C: reaction time, and D: heating rate) are shown in figure 3. The figure shows that temperature is one of the major factors that affects hydrothermal liquefaction because it controls the extent depolymerization and secondary cracking. In figure 3(A) it can be seen that maximum oil yield occurs at moderate temperature of about 300°C. This is because the temperature is sufficient enough to enhance depolymerization, followed by decarboxylation and dehydration. However at low temperature, there is limited depolymerization of biopolymers due to insufficient temperature. Hence there will be incomplete conversion of the biomass components. Similarly the oil yield also tend to decrease at higher temperature above 300°C because secondary cracking dominates at higher temperature, thereby leading to increase in gas formation and production of lighter oil. This can be seen to agree with some reported literatures such as in Elliott [35] and Coronado et al, [36].

In figure 3(B), it can be seen that increase in water-biomass (W-B) ratio increases the oil yield, until at higher W-B ratio when the yield begins to drop. Though low W-B ratio favours oil yield due to increase in collision frequency of reactive intermediates, but hindrances such as poor mixing and mass transfer tends to lower the yield compered to moderate W-B ratio. However, maximum yield is seen at moderate W-B ratio of 7-8. This is because the water is sufficient for proper mixing and good heater transfer, thereby enhancing hydrolysis and depolymerization. But at higher W-B ratio, oil yield decreases because dilution reduces the concentration of relative intermediates, thereby limiting repolymerization of the feedstock into oil. This is in agreement with the reports of Gollakota et al [11] and Elliot [35].

In figure 3(C), it is seen from the figure that oil yield slightly increases and the reaction time increases from 20 mins to 32mins. Beyond 32 mins of reaction time, the oil yield begins to decrease. This is because at long time, secondary reactions such as repolymerization, condensation, cracking and formation of gas and char occurs.
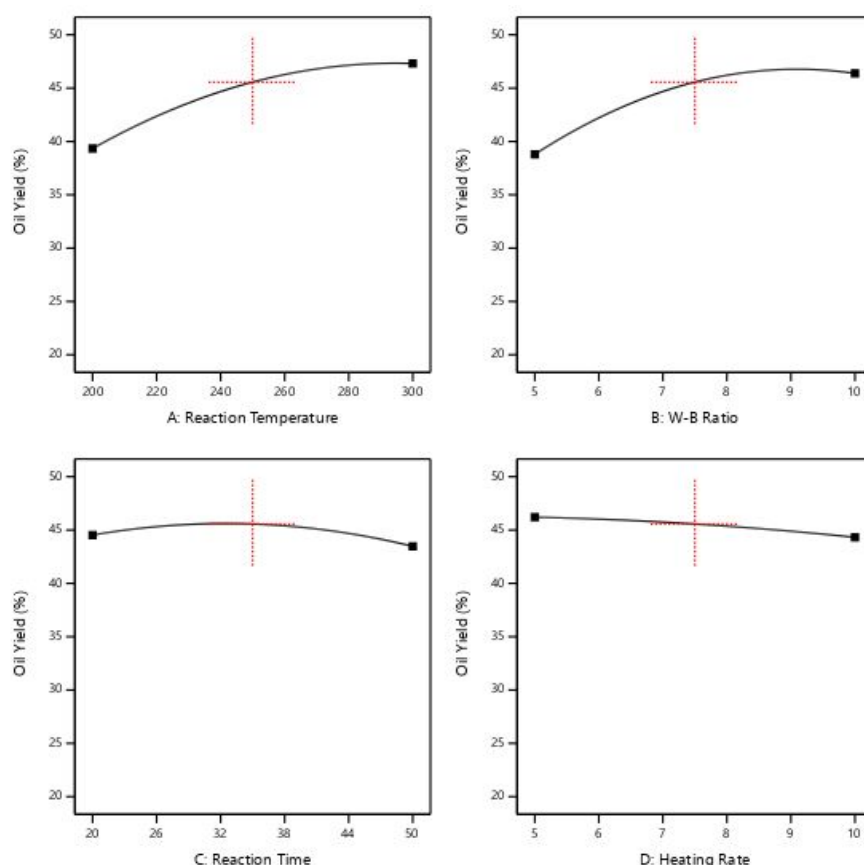
Figure 3: graph of oil yield against (A) reaction temperature, (B) W-B ratio, (C) reaction time and (D) heating rate

Test Result

Ultimate Analysis Result

The result of the ultimate analysis conducted on the samples (breadfruit pulp, bio-oil, and hydrochar), are presented in table 3. This gave the carbon, hydrogen, nitrogen, sulphur, and the oxygen content of the samples, as well as their high heating values, hydrogen-carbon and oxygen-carbon ratios. This values are compared with bar chart as shown in figure 3.

Table 3: Ultimate analysis result of the samples

Samples	Elemental Composition					HHV (MJ/kg)	Energy
	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen		Recovery (%)
BF pulp	38.53	3.6	1.64	0.67	55.56	11.99	
Bio-oil	45.09	2.49	0.67	0.58	51.27	13.43	48.5
Hydro char	40.79	3.95	0.31	0.31	54.64	13.23	39.7

Figure 4 compares the ultimate analysis result of all the samples. The colour codes represents the each of the samples as labelled in the chart. It can be seen that the bio-oil has higher carbon content compared to the biomass feedstock and its hydro char after HTL. This could be as a result of the HTL process which the feedstock undergone before the production of the oil. The hydro char has a higher carbon content compared to the feedstock. This makes it suitable briquette and fertilizer application. Consequently, the higher heating value seen at the products (bio-oil and hydro char) as compared to feedstock material (breadfruit), showed that the HTL processes improved on the energy content of the products. It can also be seen from the energy recovery bar, that 48.5% of the feedstock energy was recovered in the bio-oil via HTL, while 39.7% is recovered in solid residue.

This shows that 11.8% of the feedstock energy was lost during the process. This shows that HTL is suitable for bio oil production from breadfruit pulp.
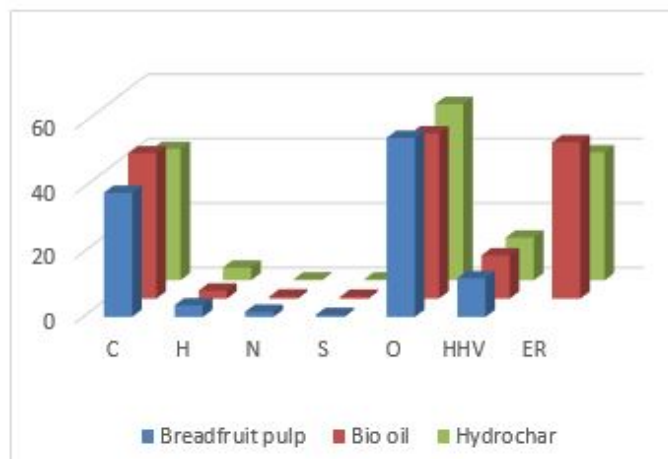

Figure 4: Comparative presentation of the samples elemental composition, high heating value and the energy recovery result

Proximate Analysis Result

The proximate analysis was conducted on the samples (breadfruit pulp, bio-oil, solid residue and the briquettes), to determine the moisture, ash, volatile and fixed carbon content of the samples. The result of the proximate analysis is presented in table 4.

Table 4: Proximate analysis of the samples

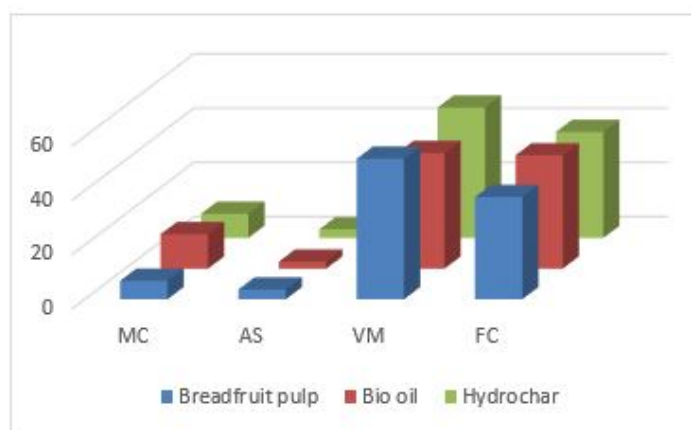| Samples	Moisture	Ash	Volatile	Fixed carbon
BF pulp	6.8	3.6	51.8	37.7
Bio Oil	12.7	2.6	42.6	41.8
Bio Char	8.9	3.2	48.1	39.1

Figure 5: Comparative presentation of the proximate analysis of the samples

The result of the proximate analysis of table 4, was analyzed and presented in figure 4. The colour code of the chart indicate the results of the different samples. While the bars represents the moisture, ash, volatile matter (VM), fixed carbon (FC), and the energy recovery (ER) of the samples as seen in the figure. It was observed that moisture content of 12.7% was seen in the oil which is slightly lower than that, reported by Mussatto et al. [37], but within the range reported by Khanh-Quang *et al.* [38]. The bio-oil sample exhibited higher moisture content compared to the other samples, which can be attributed to the nature of

the hydrothermal liquefaction (HTL) process. The figure also showed that the ash content in the bio-oil was significantly lower than in the other samples, indicating that HTL effectively reduces the ash content of the biomass feedstock. Additionally, the bio-oil had the lowest volatile matter content, as shown by the shorter bars in the figure. This may be due to its relatively low carbon content, which likely burns off more completely during the test, resulting in lower measured volatile matter. The fixed carbon of the bio oil was seen to be lesser than the carbon content obtained from the ultimate analysis. This is expected because some of the organic carbon will escape as volatile matter emissions during combustion.

TGA/DTA Result

The result of thermogravimetric and differential thermal analysis of the samples are shown in figure 6(a) to 6(c) for the produced bio-oil, breadfruit pulp and the hydrochar, respectively. Thermogravimetric analysis determines the decomposition by mass loss over a temperature range, while differential thermal analysis determines the endothermic and exothermic event temperatures, and shows phase transitions [39].
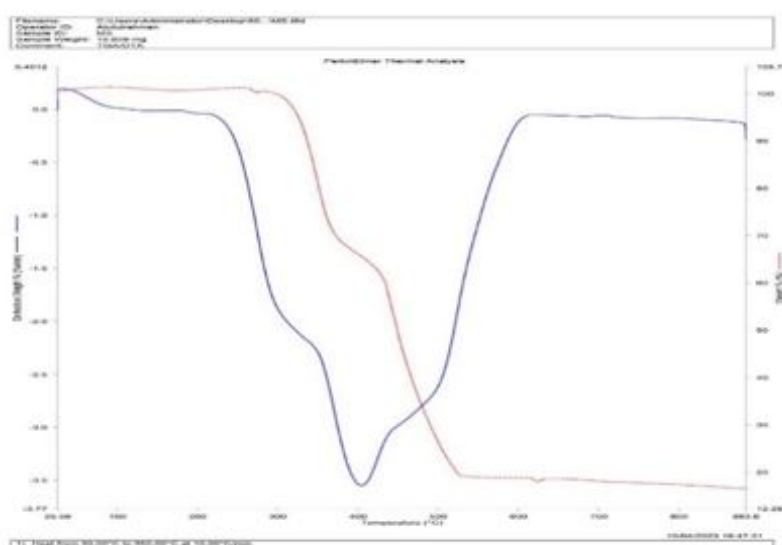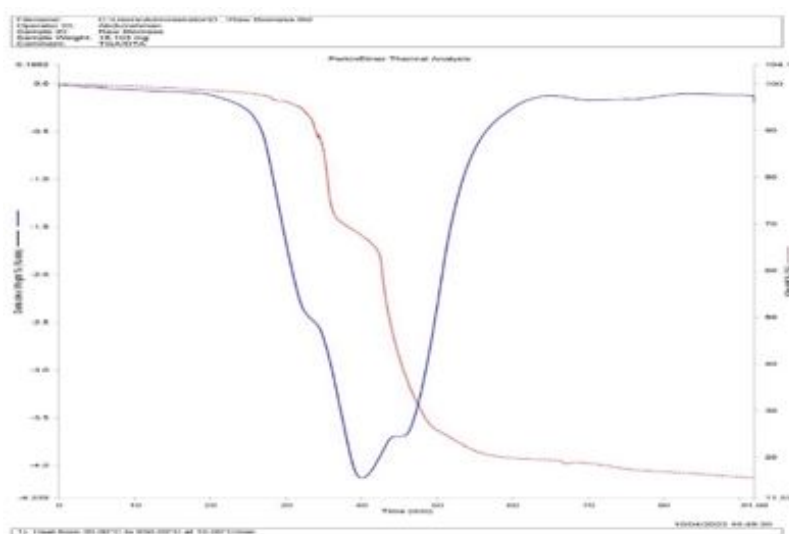

Figure 6(a): TGA/DTA curve for the bio oil

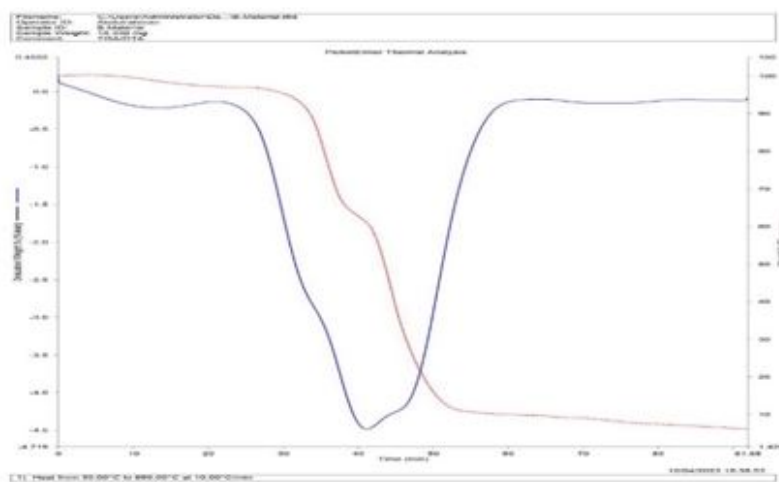**Figure 6(b):** TGA/DTA curve for the breadfruit pulp

Figure 6(c): TGA/DTA curve for the hydrochar

The graph in red colour represent the TGA result while the graph in blue represent the DTA result. In figure 6(a), the TGA result showed an initial mass loss of 6% within the temperatures of 100 – 120°C which indicates drying process. The second mass loss of about 36% occurred between the temperatures of 350 – 450°C, which indicates decomposition with removal of CO and other volatile matter. This can also be referred to as the volatile content of the bio-oil [40]. The difference in the earlier reported volatile matter content could be due to the temperature used for the test, which may have resulted to loss of some fixed carbon due to high heating. The third mass loss of 44% occurred between the temperatures of 450 -550 °C. This mass loss can be termed fixed carbon content of the bio-oil, while the remaining mass can be termed ash content, according to Khairuddin *et al.* [40]. It can be seen that the bio-oil was stable up to the temperature of 350 °C before decomposition. The changes in masses seen in the DTA curve of figure 6(a), is due to dehydration, decomposition and combustion, and the curve is seen to be endothermic. The sample showed no reaction until the onset temperature of 350 °C, at which the endothermic reaction starts. This heat absorption occurred between 350 – 600 °C, and then returned to baseline. At this point of stability the material left could be ash as interpreted by the TGA curve.

The TGA/DTA curve of the breadfruit pulp as seen in figure 6(b) showed an initial mass loss of 3% within the temperature 100 – 120°C which indicates the drying process. The second loss of mass occurred between the temperatures from 270 – 420°C, which indicates decomposition with removal of CO, and the percentage mass loss of 40% which is assumed to be the volatile matter within the feedstock. The third mass loss of 34% occurred between the temperatures 420 - 600 °C. This mass loss can be termed the fixed carbon content, while the remaining mass can be termed the ash content. It can also be seen that the breadfruit pulp was thermally stable up to the temperature of 250 °C before decomposition and the curve is endothermic. The sample showed no reaction until the onset temperature of 200 °C, at which the endothermic reaction starts. This heat absorption occurred between 350 – 650 °C, and then returned to baseline. At this point of stability the material left could be ash as interpreted by the TGA curve. Figures 6(a) and (b) showed that the bio-oil was more thermally stable than its parent feedstock. Also the heat absorption is seen to be higher in the feedstock compared to the bio-oil.

Also the TGA curve of the obtained hydrochar from HTL of breadfruit pulp as seen in figure 6(c) showed an initial gradual mass loss of 5.5% between the temperature 100 – 300 °C which indicates the dehydration region. The second loss of mass occurred between the temperatures from 300 – 400 °C, which indicates decomposition with removal of CO, and the percentage mass loss of 31.2% seen within that region is assumed to be the volatile matter content of the solid residue. The third mass loss of 49.8% occurred between the temperatures 400 - 550 °C as seen in figure 6(c). This indicates combustion with air accompanied with removal of CO_2. This mass loss can be termed fixed carbon content, while the remaining mass can be termed the

ash content. This high content of fixed carbon within the hydrochar validates the need to employ the solid residue for fuels purposes such as briquetting purposes. It can also be seen that the hydrochar was thermally stable up to the temperature of 300 $^{\circ}$C before decomposition. These changes in masses due to dehydration, decomposition and combustion is seen the DTA curve to be endothermic. The sample showed no reaction until the onset temperature of 300 $^{\circ}$C, before the decomposition starts. This heat absorption occurred between 300 – 550 $^{\circ}$C, and then returned to baseline. At this point of stability the material left could be ash as interpreted by the TGA curve.

GCMS Analysis Result

The main chemical components of the produced bio oil are presented in table 5. They were extracted from the GCMS analysis raw result, by removing the components with quality factor less than 50%. It was observed that the components of the bio-oil are majorly oxygenated hydrocarbons and alkenes as seen in table 5. The oxygenated hydrocarbons are majorly organic acid and esters, which are normally found in bio-oils obtained from the hydrothermal liquefaction of biomasses [41]. The organic acids include hexadecanoic acid (palmitic acid), 9,12-octadecadienoic acid (linoleic acid), and 2-methylpentyl formate. While n-Propyl 11-octadecenoate is grouped under esters. These oxygenated hydrocarbons comes hydrolysis and decomposition of lignin content of the biomass during HTL. The 2-methylpentyl formate can be traced to the ethyl acetate used in rinsing the reactor container and solid residue after the HTL process.

Table 5: Chemical composition of the bio-oil

Chemical Compound	Chemical Formula	CAS	Quality Factor	Molar weight(g/mol)
2-methylpentyl formate	$C_7H_{14}O_2$	381670-34-4	53	130.1
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	000112-39-0	89	270.4
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{18}H_{32}O_2$	000112-63-0	93	280.4
6-Octadecenoic acid, methyl ester, (Z)-	$C_{19}H_{36}O_2$	002777-58-4	97	296.5
1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-	$C_{14}H_{24}$	062951-96-6	58	192.3
n-Propyl 11-octadecenoate	$C_{21}H_{40}O_2$	1000336-71-7	53	324.5

FTIR Result

The result of Fourier Transform Infrared (FTIR) spectrum carried out on the produced bio-oil is presented in figure 7. The FTIR analysis was done to identify the molecular compounds within the bio-oil. The nature and wavenumber of the peaks as appeared in figure 7, was used to identify the functional groups within the sample. This was done with the infrared spectroscopy correlation table. The first peak is broad and strong, and appeared at the wave number of 3338 cm^{-1}, which is an indication of carboxylic acid from the FTIR correlation table. This correlates with the result of the GCMS analysis that indicated the chemical content of some organic acid such as palmitic and linoleic acid. The second peak is broad and weak, and appeared at a wave number of 2113.4, which is an indication of alkyenes. The third peak is sharp with medium intensity and falls under the wave number of 1650 - 1566 cm^{-1}, which is an indication of alkenes. This correlates with the GCMS result that presented the content of 1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-, that belongs to the alkene family. Also the forth peak is sharp and weak and falls under the wavenumber of 1440 – 1395 cm^{-1}, which is an indication of carboxylic acid. From the spectrum interpretation, it can be conclude that the bio-oil produced from the HTL of breadfruit pulp is majorly composed of organic acid, and hydrocarbons of alkene and alkyne family.
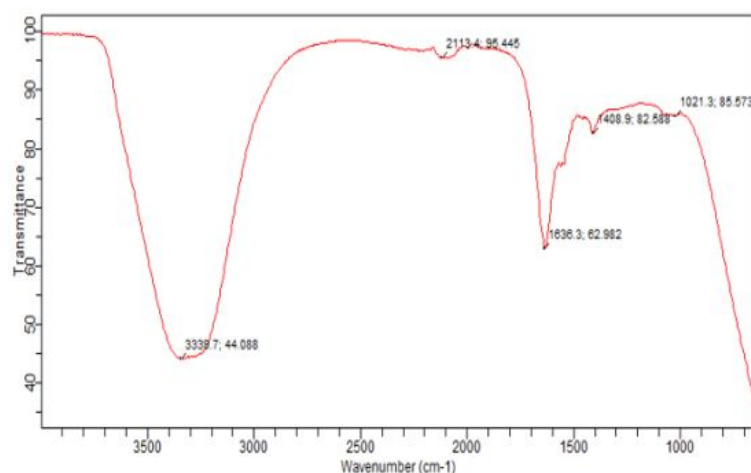
Figure 7: FTIR spectrum of the bio-oil

Conclusion

This work successfully demonstrated the technical feasibility and promising potential of producing bio-oil from breadfruit pulp through hydrothermal liquefaction process. The 48.9% oil yield obtained from this work shows that breadfruit pulp which is an abundant underutilized tropical biomass from breadfruit processing, can give a substantial fraction of bio oil under optimized condition, which can be further upgraded to transport fuels. The process also generated char fraction that maybe leveraged for agricultural or material applications, thereby enhancing the overall resources efficiency.

The results obtained from the characterization of the produced oil highlight breadfruit pulp as a viable feedstock for decentralization of biofuel production, particularly in regions where breadfruit is abundant. This will help to boost the contribution of biomass in meeting the global energy demand, thereby reducing the demand load on fossil fuels. Also the HTL's ability to process wet biomass without extensive drying further strengthens its suitability for tropical agro-industries.

Finally, this research advances the understanding of breadfruit pulp biomass valorization and contributes to the development of renewable circular bioenergy pathways. However, further work is required to investigate the effect of pressure on the oil yield from HTL of breadfruit pulp, and the catalytic upgrading of the bio oil. Also, future work should focus on the techno-economic analysis and system-level sustainability assessment to fully evaluate the commercial viability.

References

1. Ezenwa Obiora Nnaemeka, Mgbemena Chinedum Ogonna, Emagbetere Eyere, (2024). Utilization of solid residue from hydrothermal liquefaction of breadfruit pulp for the production of bio-briquette using cassava starch as binder. Heliyon 10: e24081.

2. Månberger A (2021) Reduced Use of Fossil Fuels can Reduce Supply of Critical Resources. Biophysical Economics and Sustainability, 6.

3. Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnology Resources Int. 1: 1-13.

4. Osueke CO, Uzendu P, Ogbonna ID, (2013) Study and Evaluation of Solar Energy Variation in Nigeria. International Journal of Emerging Technology and Advanced Engineering, ISSN 2250-2459, ISO 9001:200. 3.

5. Nada Kh MA Alrikabi (2014) "Renewable Energy Types," Journal of Clean Energy Technologies. 2: 61-4.

6. Güney Taner (2019) Renewable energy, non-renewable energy and sustainable development, International Journal of Sustainable Development & World Ecology, 26:5, ISSN: 1350-4509. 389-97.

7. Abdeshahian P, Lim JS, Ho WS, Hashim H, Lee CT (2016) Potential of biogas production from farm animal waste in Malaysia. Renew Sustainable Energy Revolution; 60: 714–23.

8. Matayeva Aisha, Francesco Basile, Fabrizio Cavani, Daniele Bianchi, Stefano Chiaberge (2019). Development of Upgraded Bio-Oil Via Liquefaction and Pyrolysis. Horizons in Sustainable Industrial Chemistry and Catalysis. 231–56.

9. Fahmy TYA, Fahmy Y, Mobarak F, El-Sakhawy M, Abou-Zeid RE (2018) Biomass pyrolysis: past, present, and future. Environment, Development and Sustainability.

10. Sahu SN, Sahoo NK, Naik SN, Mahapatra DM (2020) Advancements in hydrothermal liquefaction reactors: overview and prospects. Bioreactors. 195–213.

11. Gollakota ARK, Kishore N, Gu S (2018) A review on hydrothermal liquefaction of biomass. Renewable and Sustainable Energy Reviews, 81: 1378–92.

12. Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB (2015) Hydrothermal liquefaction of biomass: Developments from batch to continuous process. Bioresource Technology. 178: 147–56.

13. Castello Daniele, Thomas Helmer Pedersen, Lasse Aistrup Rosendahl (2018) Continuous Hydrothermal Liquefaction of Biomass: A Critical Review. Energies. 11.

14. Najafpour D Ghasem (2015) Biofuel Production. Biochemical Engineering and Biotechnology, 689 second edition. 20: 597–630.

15. Cheng F, Le Doux T, Treftz B, Woolf S, Yu J et al. (2019) Modification of a pilot-scale continuous flow reactor for hydrothermal liquefaction of wet biomass. MethodsX, 6: 2793–806.

16. Zhang J, Chen WT, Zhang P, Luo Z, Zhang Y (2013) Hydrothermal liquefaction of Chlorella pyrenoidosa in sub- and super-

critical ethanol with heterogeneous catalysts. Bioresource Technology. 133: 389–97.

17. Goswami G, Makut BB, Das D (2019) Sustainable production of bio-crude oil via hydrothermal liquefaction of symbiotically grown biomass of microalgae-bacteria coupled with effective wastewater treatment. Scientific Reports, 9.

18. Brilman DWF, Drabik N, Wądrzyk M (2017) Hydrothermal co-liquefaction of microalgae, wood, and sugar beet pulp. Biomass Conversion and Biorefinery, 7: 445–54.

19. Kiran Kumar P, Vijaya Krishna S, Verma K, Pooja K, Bhagawan D, et al. (2018) Bio oil production from microalgae via hydrothermal liquefaction technology under subcritical water conditions. Journal of Microbiological Methods.

20. Shakya R, Whelen J, Adhikari S, Mahadevan R, Neupane S (2015) Effect of temperature and Na 2 CO 3 catalyst on hydrothermal liquefaction of algae. Algal Research, 12: 80–90.

21. Diego López Barreiro, Wolter Prins, Frederik Ronsse, Wim Brilman, (2013) Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects. Biomass and Bioenergy. 53: 113-127.

22. Reddy HK, Muppaneni T, Ponnusamy S, Sudasinghe, N, Pegallapati A, et al. (2016) Temperature effect on hydrothermal liquefaction of Nannochloropsis gaditana and Chlorella sp. Applied Energy, 165: 943–51.

23. Huang Zhaodan, Wufuer Anaerguli, Wang Yuanyuan, Dai Liyi (2018). Hydrothermal liquefaction of pretreated low-lipid microalgae for the production of bio-oil with low heteroatom content. Process Biochemistry, 69: 136–43.

24. The Ky Vo, Seung-Soo Kim, Hoang Vu Ly, Eun Yeol Lee, Choul-Gyun Lee, et al. (2017) A general reaction network and kinetic model of the hydrothermal liquefaction of microalgae Tetraselmis sp., Bioresource Technology. 241: 610-9.

25. Gai C, Zhang Y, Chen WT, Zhang P, Dong Y (2015) An investigation of reaction pathways of hydrothermal liquefaction using Chlorella pyrenoidosa and Spirulina platensis. Energy Conversion and Management, 96: 330–9.

26. Gai C, Li Y, Peng N, Fan A, Liu Z (2015) Co-liquefaction of microalgae and lignocellulosic biomass in subcritical water. Bioresource Technology, 185: 240–5.

27. Akalın MK, Tekin K, Karagöz S (2012) Hydrothermal liquefaction of cornelian cherry stones for bio-oil production. Bioresource Technology, 110: 682–7.

28. Zhu Z, Rosendahl L, Toor SS, Yu D, Chen G (2015) Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation. Applied Energy, 137: 183–92.

29. Theegala CS, Midgett JS (2012) Hydrothermal liquefaction of separated dairy manure for production of bio-oils with simultaneous waste treatment. Bioresource Technology, 107: 456–63.

30. Wang F, Chang Z, Duan P, Yan W, Xu Y, et al (2013) Hydrothermal liquefaction of Litsea cubeba seed to produce bio-oils. Bioresource Technology, 149: 509–15.

31. Chan YH, Yusup S, Quitain AT, Uemura Y, Sasaki M (2014) Bio-oil production from oil palm biomass via subcritical and supercritical hydrothermal liquefaction. The Journal of Supercritical Fluids, 95: 407–12.

32. Gao Ying, Chen Han-ping, Wang Jun, Shi Tao, Yang Hai-Ping, et al. (2011). Characterization of products from hydrother-

mal liquefaction and carbonation of biomass model compounds and real biomass. Journal of Fuel Chemistry and Technology. 39.

33. Enibe SO, Asiegbu CP, Njoku HO (2011) Continuous-Flow Depulping Machine for Treculia Africana. Global Journal of Engineering Research. 10: 77-103.

34. Harisankar S, Vishnu Mohan R, Choudhary Vaishali, Vinu R, (2022) Effect of water quality on the yield and quality of the products from hydrothermal liquefaction and carbonization of rice straw. Bioresource Technology. 351: 127031.

35. Elliot DC (2016) Review of recent reports on biomass liquefaction by hydrothermal processing. Renewable Energy, 87: 971-6

36. Coronado I, M Stekrova, M Reinikainen, P Simell, L Lefferts, et al. (2016) A review of catalytic aqueous-phase reforming of oxygenated hydrocarbons derived from biorefinery water fractions. International Journal of Hydrogen Energy. 41: 11003-32.

37. Mussatto SI, Motta IL, Filho RM, Luuk van der Wielen L, Capaz R, et al. (2022) Sustainable Aviation Fuels: Production, Use and Impact on Decarbonization. Comprehensive Renewable Energy (Second Edition). 5: 348-71.

38. Khanh-Quang Trana, Aksel Junge Klemsdala , Wennan Zhangb , Judit Sandquistc , Liang Wangc et al. (2017) Fast hydrothermal liquefaction of native and torrefied wood. Energy Procedia. 218 – 23

39. Ordonez-Loza J, Chejne F, Jameel AGA, Telalovic S, Arrieta AA, et al. (2021) An investigation into the pyrolysis and oxidation of bio-oil from sugarcane bagasse: Kinetics and evolved gases using TGA-FTIR. Journal of Environmental Chemical Engineering, 9: 106144.

40. Khairuddin Md Isa, Suhardy Daud, Nasrul Hamidin, Khudzir Ismail, Saiful Azhar Saad, et al. (2011) Thermogravimetric analysis and the optimisation of bio-oil yield from fixed-bed pyrolysis of rice husk using response surface methodology (RSM). 33: 481–7.

41. Tekin Kubilay, Karago¨z Selhan (2013) Non-catalytic and catalytic hydrothermal liquefaction of biomass. Res Chem Intermed 39: 485–98