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Mild Hydrothermal Liquefaction of High Water Content Agricultural Residue for Bio-Crude Oil Production: A Parametric Study

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Abstract: Depleting petroleum reserves together with the associated environmental concerns have intensified the exploration of alternatives to petroleum. Wet food processing wastes present promising bioresources for liquid fuel production via hydrothermal liquefaction (HTL) followed by additional upgrading. In this study, tomato plant waste (TPW) was utilized as a feedstock for the production of bio-crude oils via HTL at medium-temperature (220–280 °C) in water or a water–ethanol (17/3, *v*/*v*) medium in a 600 mL autoclave reactor. Effects of various operating parameters, such as catalysts (H_2SO_4 or KOH), reaction time (15–60 min) and reaction temperature (220–280 °C) on product yields were investigated. This study showed that a high yield (45.1 wt%) of bio-crude oil was achieved from HTL of TPW in water–ethanol medium at 250 °C in the presence of acid catalyst H_2SO_4. The oil, gas and solid residue (SR) products were analyzed for their chemical and structural properties.

Keywords: hydrothermal liquefaction; agricultural wastes; tomato plant wastes; bio-crude oil

1. Introduction

Since its discovery, petroleum has been the dominating source of liquid transportation fuels and chemicals [1]. However, the fast depletion of petroleum reserves, the environmental challenges such as greenhouse gas emission, and the concerns over energy security, have intensified the efforts in searching for alternatives [2]. Due to their immense supply, cost-effectiveness and cleanliness, bio-renewable resources (i.e., bioresources) are believed to be promising candidates to replace petroleum. The use of organic residues for bioresource production present the additional benefit of eliminating a waste stream, while at the same time producing a valuable product [3]. These organic residues include agricultural residues and food-processing wastes (e.g., crop residues, energy plants, wet greenhouse wastes, etc.), forestry residues (e.g., sawdust, bark, lignin, etc.), and municipal wastes (e.g., municipal solid wastes, wastewater sludge, etc.). In the past decades, many research efforts have been made in the conversion of bioresources to liquid fuels and chemicals via biological, thermal, thermochemical or catalytic technologies. The conversion of biomass into energy and chemicals can be achieved in two broad pathways: Biological (fermentation and anaerobic digestion) and thermo-chemical processes (combustion, gasification, and liquefaction/pyrolysis) [4]. Among all different biomass conversion technologies, hydrothermal liquefaction (HTL) has attracted a considerable amount of attention since the process can efficiently convert inedible biomass into bio-oils (or bio-crude oils) [5]. At temperature

ranges between 250 and 370 °C, the hydrothermal process is defined as hydrothermal liquefaction, resulting in the production of a liquid fuel known as biocrude oil [6]. The bio-oil products can be utilized directly as a source for chemicals (such as bio-phenols and bio-polyols) or can be upgraded into drop-in bio-fuels (such as green gasoline and biodiesel) through catalytic cracking and hydro-treatment. Agricultural and forestry residues are immense, inexpensive and clean. For Canada alone, the amount of potential agricultural residues has been estimated at 29.3 Mt oven dried (OD) biomass per year, among which 17.8 Mt OD biomass/year may be available for energy and chemical production [7].

Besides its high yield, HTL is particularly suitable for biomass with high moisture content since HTL uses hot-compressed water as the medium, and the wet feedstock has received a lot of attention in the research field [8,9]. One example is wet greenhouse wastes such as tomato residues, as HTL eliminates the need of costly de-watering process that is otherwise required in other thermal/thermo-chemical processes. Approximately 9310 tons tomato plant wastes (TPW) per year are generated from 921 acres of tomato greenhouses within Ontario, Canada, based on personal estimation by the Ontario Ministry of Agriculture and Food (OMAFRA). Currently the harvested tomato plants are disposed of as waste, which has negative impacts on the environment. Meanwhile very little attention has been directed towards biofuel production from TPW.

Direct hydrothermal liquefaction can effectively convert wet biomass into bio-crude oils in sub-critical water conditions. The bio-crude oil produced from an organic solvent-water mixture proved to be advantageous with respect to oil yield and quality [10]. However, not much work has been reported on hydrothermal liquefaction of TPW, particularly under mild conditions saving energy input. Thus, the main objectives of this work are to produce bio-crude oil from agricultural residues with an emphasis on TPW through hydrothermal liquefaction. Moreover, most of the data in HTL literature was obtained at either alkaline or neutral conditions while limited data was available for acidic conditions. Furthermore, it has been demonstrated that pH plays an important role in HTL formation [11,12]. The reaction pathways of HTL change with acidic, neutral and alkaline conditions [13]. These reaction pathways were dependent on each other. Under weak alkaline conditions, the reaction pathway can change gradually from an alkaline pathway to an acidic one [14]. Since HTL bio-oils are extracted from the corresponding aqueous products, the influence of acidic, neutral and alkaline conditions on HTL reaction pathways and liquid products are expected to change HTL bio-oil yields and compositions.

The present work aims to develop innovative technologies (hydrothermal liquefaction) for valorization of agricultural residues into bio-fuels and bio-chemicals; and to optimize the conditions via investigating the effects of temperatures, catalysts, and residence time on oil yield and solid residue yield. The characteristics of bio-crude oil will be analyzed in terms of chemical structure, elemental composition, and structural composition. This work would provide an approach to convert wet agricultural wastes into bio-crude oil under mild conditions, without creating waste to threaten human health and the environmental balance.

2. Materials and Methods

2.1. Materials

Tomato plant wastes (TPW) were collected in a timely manner from a local greenhouse in Guelph, Ontario, cut into pieces and slurry, and stored in fridge for 2 weeks. Reagent grade sulfuric acid (95–98 wt%) were obtained from ACROS, New Jersey, USA. Potassium hydroxide, denatured alcohol and acetone were all purchased from Fisher Scientific. All reagents were used without further purification.

2.2. Hydrothermal Liquefaction of Tomato Plant Wastes

Pre-screening of the agricultural residues for the liquid fuels was conducted to determine tomato plant wastes (TPW) as the feedstock for this work. All HTL tests were carried out in a 600 mL autoclave

reactor (Parr Instruments Co. Moline, PA, USA), which was made of stainless steel. The typical experiment was performed as per the following procedure: 10 g of TPW on dry basis with 200 mL solvents (mixture of water–ethanol either 17/3 v/v, or water only, including the moisture content within the TPW feedstock) and 1 g of catalyst (i.e., 10 wt% with respect to dry feedstock) were adequately premixed in a beaker. Then the feed was transferred into a glass liner to fit in the 600 mL autoclave reactor, equipped with a mechanical agitation system (Figure 1). After loading the feed and sealing the reactor, the air in the reactor was removed by purging the reactor with N_2, followed by pressurizing the reactor with N_2 at 1 MPa. The reactor was then heated (for about 0.5 h) to a preset temperature of 220–280 °C, under the maximum pressure of 6.5 MPa, and remained at the temperature for a certain period. After the specified time elapsed, the reactor was quenched to room temperature using an ice-water bath. The slurry collected and rinsed from the autoclave was filtered followed by filter paper rinsed with acetone. The solid residues (SR) on the filter paper were dried at 105 °C for 12 h. The filtrate was evaporated in a rotary evaporator under reduced pressure at up to 70 °C to remove the water (including the pyrolytic water produced from the feedstock in the HTL process) and ethanol solvents (if any). The remaining oily liquid is the bio-crude oil product, or simply bio-oil. The yield of SR and bio-oil was defined as their weight percentage in relation to TPW loaded in the test on dry basis. For simplicity, the yield of gas products mainly consisting of CO_2 (confirmed by GC analysis) was not quantified separately, as the yield is normally lower than 5 wt% under such low temperature applied in this study. Instead, the lumped yield of gaseous products plus the pyrolytic water produced in the HTL process, designated as yield of Water + Gas, was obtained by mass balance. Each run was repeated for three times and average value was taken.

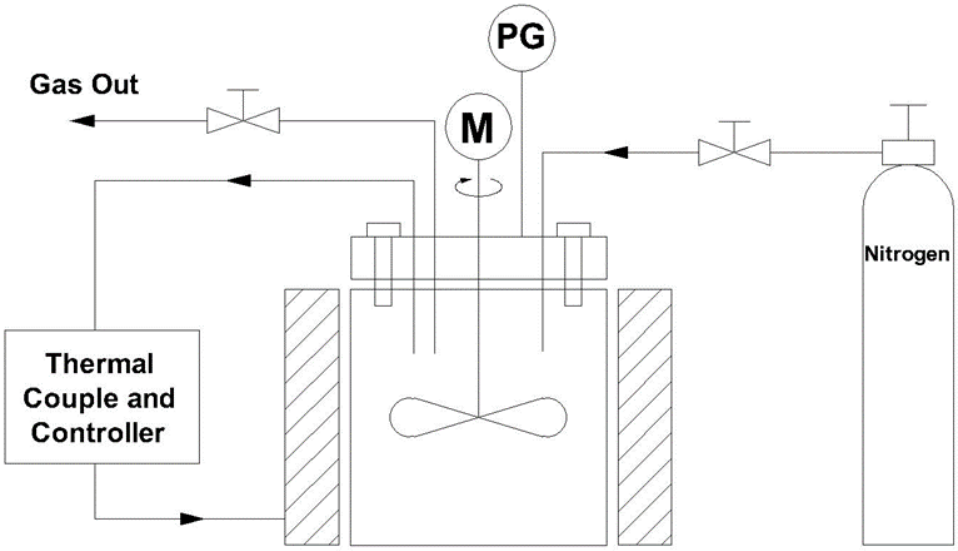

Figure 1. Schematic diagram of the batch reactor.

The co-solvents (200 g, including moisture within TPW) and catalyst (1 g) were selected as the medium and the acidic mediums were prepared using sulfuric acid, when pH value was around 2.6. The basic mixtures were prepared using potassium hydroxide and pHi (initial pH value) appeared to be around 8–9.

The separation procedure of liquefied products is shown in Figure 2. Upon desiccation, the liquid products were fractionated into a water-soluble fraction and an acetone-soluble fraction. The other main streams were gaseous products and solid residue.

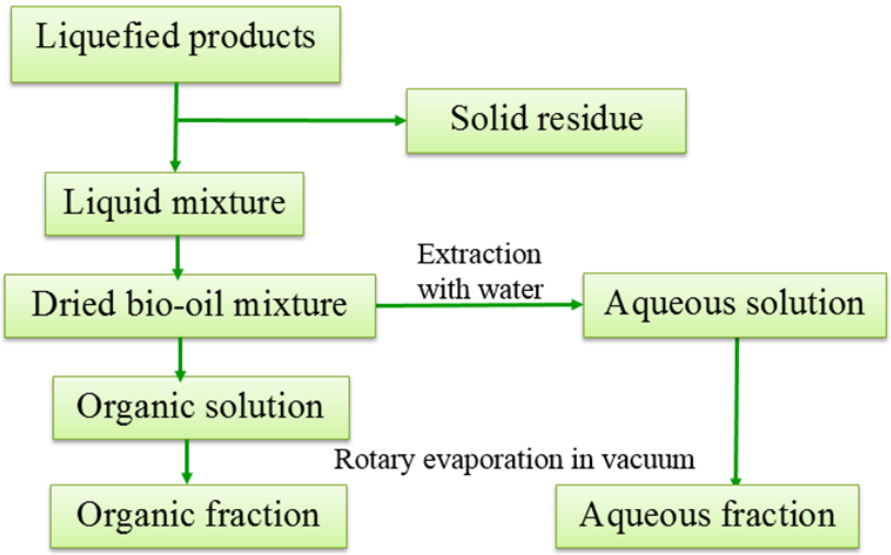

Figure 2. Separation of bio-crude, including aqueous fraction and organic fraction, and solid residues from hydrothermal liquefaction (HTL) product mixture.

2.3. Characterization

The proximate analysis (ash, volatile matter and fixed carbon) of the TPW was carried out as per ASTM standards. The sample was placed in the muffle furnace (Thermo Scientific F48055-60, Waltham, MA, USA) at 105 °C for at least 16 h before being moved to desiccator for cooling. The TPW was then re-weighed and the change between initial and final weight was expressed as moisture content by percentage (ASTM-E871). The dried solid samples were then ignited at 575 °C for 5 h in a muffle furnace to determine the ash content (ASTM-E1755). The volatile matter (VM) was measured by firing the sample at 950 °C for 7 min (ASTM-E872). The remaining weight after subtracting the contents of volatile matter, moisture, and ash was reported as the fixed carbon (FC) content.

The pH values of liquid samples were acquired using a digital pH meter (Thermo Orion, Nanjing, China, model 210A). The C, H, N, S contents of dry TPW and bio-oil samples were determined by an elemental analyzer (Thermo Fisher Flash EA 1112, Waltham, MA, USA). Oxygen content was estimated based on an assumption that the samples only contain the elements of C, H, N, O and ash. The higher heating value (HHV) of each product/fraction was determined based on the ultimate analysis using the Dulong formula:

$$\text{HHV (MJ/kg)} = 0.3383Z_C + 1.422\,(Z_H - Z_O/8) \quad (1)$$

where Z_C, Z_H and Z_O are the weight percentages of carbon, hydrogen and oxygen, respectively.

The chemical compositions and properties of the HTL products were analyzed using a Fourier transfer infrared spectra (FTIR), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), and thermogravimetric analysis (TGA). IR spectra of bio-crude oils were directly collected by a Perkin-Elmer FTIR spectrometer (Waltham, MA, USA). The liquefied products were qualitatively analyzed using GC-MS. The bio-oils soluble in mixture of water and acetone were diluted in ethanol. The structures of bio-oil fractions were probed by an Agilent 7890B GC coupled with a 5977A MSD, using a 30 m × 0.5 mm × 0.25 μm DB-5 column with temperature programing as follows: 1 min hold at an initial temperature of 50 °C, followed by a 15 °C/min ramp to a final temperature of 280 °C with a 5 min hold. An MSD capillary column (apolar) was also used with a temperature program from 60 to 300 °C at a rate of 15 °C/min. The gaseous products were analyzed by a gas chromatograph (SRI 8610C-GC) to determine the concentration of individual gas. Columns on the GC included a silica gel packed column. Compounds were detected and quantified with thermal conductivity detectors that were calibrated using a refinery gas calibration mix (Agilent, Santa Clara, CA, USA, part #5184-3543) after column separation. Helium at 0.55 ± 0.01 MPa pressure was used as

the carrier gas for the analysis. The thermal stability and decomposition of bio-oil were investigated by thermogravimetric analysis (TGA) using an SDT Q600 thermal analysis system (TA Instrument, New Castle, DE, USA). The bio-oil samples (5–10 mg) were measured in nitrogen or air atmosphere at a flow rate of 50 mL/min, ramping from 50 to 900 °C at 10 °C/min.

3. Results and Discussion

3.1. Feedstock Characterization and Experimental Design

The TPW was first subjected to proximate and ultimate analysis as shown in Table 1. The design parameters and corresponding yield of the experiments are displayed in Table 2. Three duplicates were conducted for each reaction condition to ensure acceptable reproducibility of the experimental results.

Table 1. Proximate and ultimate analysis of tomato plant wastes (TPW) (wt% on Dry Basis).

Moisture Content	**92.2 ± 0.03**
Volatile matter	62 ± 0.52
Ash	32 ± 0.08
Fixed carbon	6 ± 0.06
Elemental composition (%)	
C	34.8 ± 0.22
H	5.0 ± 0.11
O [a]	23.4 ± 0.16
N	4.0 ± 0.08
S	0.3 ± 0.02
HHV (MJ/kg)	12.4 [b]

[a] Calculated by difference (100%-C%-H%-N%-S%-Ash%). [b] Higher Heating Value (HHV) calculated by Dulong formula, i.e., HHV (MJ/kg) = 0.3383C + 1.422(H − O/8).

Table 2. Experimental design *.

Entry	**Name**	**Temperature (°C)**	**Holding Time (min)**	**Solvent**	**Catalyst**	**Oil Yield (%)**	**Solid Residue (%)**
1	250-30-N-H_2O	250	30	H_2O	N/A	30.46	42.79
2	250-30-A-H_2O	250	30	H_2O	H_2SO_4	40.42	47.37
3	250-30-A	250	30	H_2O and EtOH	H_2SO_4	44.95	45.08
4	250-30-B	250	30	H_2O and EtOH	KOH	45.60	48.54
5	220-30-A	220	30	H_2O and EtOH	H_2SO_4	42.35	55.16
6	250-30-A	250	30	H_2O and EtOH	H_2SO_4	44.95	45.08
7	280-30-A	280	30	H_2O and EtOH	H_2SO_4	40.70	41.03
8	250-15-A	250	15	H_2O and EtOH	H_2SO_4	39.71	50.58
9	250-30-A	250	30	H_2O and EtOH	H_2SO_4	44.95	45.08
10	250-45-A	250	45	H_2O and EtOH	H_2SO_4	41.19	41.58
11	250-60-A	250	60	H_2O and EtOH	H_2SO_4	45.88	39.86

* Each run was repeated for three times and average value was obtained, with the maximum deviation of ±3%.

3.2. Effect of Operating Conditions on HTL and Process Optimization

3.2.1. Effect of Reaction Medium and Catalyst

The effects of catalyst and solvent were firstly investigated. The H_2SO_4 as acid catalyst enhanced the oil yield from 30.5 wt% to 40.4 wt%, at 250 °C in water for 30 min (Figure 3). If the mixture of water–ethanol (16/3, *v*/*v*) was used as the reaction medium in the presence of H_2SO_4 under the same other conditions, the oil yield (OL) increased further to 45 wt%. This indicated that the presence of an acid catalyst and ethanol as a co-solvent in the reaction medium favored the HTL of TPW into bio-oil product. In the same co-solvent under the same conditions, the addition of KOH as base catalyst brought a similarly yield of bio-oil (~46 wt%) as that of the test with the acid catalyst. However, a higher SR yield (~49 wt%) with KOH catalyst, compared with approximate 45 wt% SR with the acid

catalyst. This is reasonable because base catalysts are more effective in converting biomass with high lignin content while acid catalysts are effective for feedstocks with high cellulose and hemicellulose content such as TPW. Therefore, more water soluble and low-boiling point components are generated among biocrude using acidic catalyst. These low-boiling point components could easily vaporize and lose during desiccation, appearing lower yield. Therefore, H_2SO_4 is believed to be more effective than KOH as a catalyst for the low-temperature HTL of TPW for bio-crude oil production under the present conditions [13].

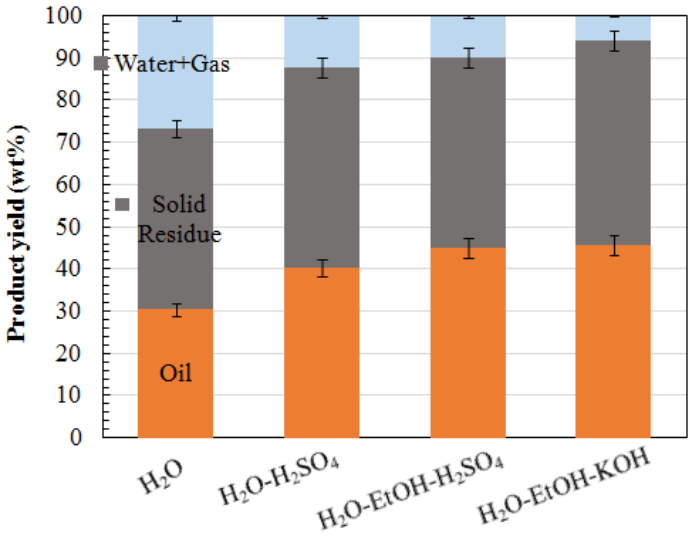

Figure 3. Effects of reaction mediums and catalysts on product yields (250 °C, 30 min).

3.2.2. Effects of Reaction Temperature

We then performed the tests at various temperatures: 220, 250, and 280 °C, respectively, while keeping the other conditions the same (i.e., H_2O-EtOH medium, 30 min, H_2SO_4 as catalyst). The dependence of product yields on temperatures are illustrated in Figure 4. As the temperature increased from 220 to 250 °C, the bio-oil yield increased by approx. 3%, accompanied by a decrease in SR yield by 10 wt%. Thus, a higher temperature facilitated an increase in bio-crude oil generation and biomass conversion (lowering the SR yield). A further increase in the operating temperature to 280 °C resulted in a continued decrease in SR yield, suggesting further enhanced biomass conversion, as expected. However, bio-oil yield dropped from ~45 wt% at 250 °C to ~38 wt% at 280 °C. Thus, 250 °C seems to be the optimal temperature under the present conditions for bio-oil production, mainly because of the lignocellulosic content of TPW. Another clear trend observed from Figure 4 is that a higher temperature leads to a higher yield of Water + Gas due to enhanced pyrolysis and liquefaction reactions, which is consistent with the published results in other literature [15].

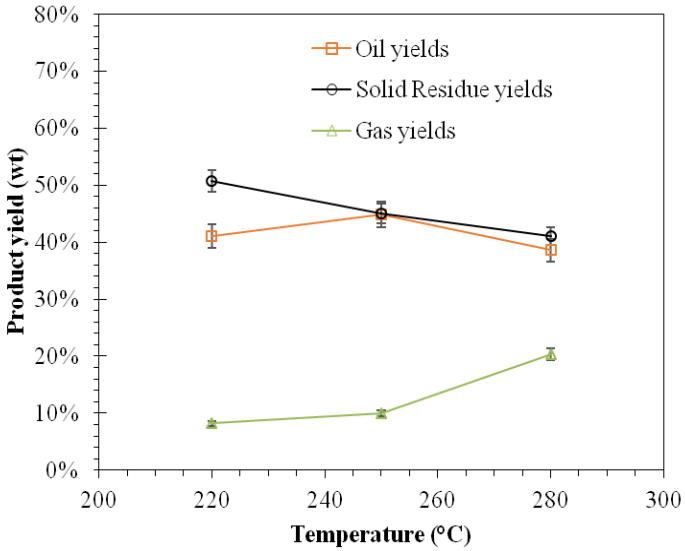

Figure 4. Effects of reaction temperature on product yields (H_2O-EtOH medium, 30 min, H_2SO_4 catalyst).

3.2.3. Effects of Holding Time

Effects of holding time were examined by performing the HTL tests for various lengths of time (15, 30, 45 and 60 min) under the same other conditions (i.e., H_2O-EtOH medium, 250 °C, H_2SO_4 catalyst). The obtained product yields vs. reaction time are presented in Figure 5. Generally, a longer reaction time or temperature leads to an incensement of biomass conversion (reducing SR yield) and larger formation of water and gases compounds. However, bio-oil yield appeared to peak at approx. 45 wt% for 30–45 min. 45 min also seems to be a proper time for biomass conversion, resulting in the lowest SR yield. A holding time longer than 45 min slightly increased the SR yield, likely due to the formation of char or solid residues by condensation/repolymerization reactions of the liquid products, as reported often in the literature [16].

Based on the above preliminary studies on reaction parameter screening for bio-crude oil production from TPW via low-temperature HTL, the optimal conditions appear to be: H_2O-EtOH medium, 250 °C reaction temperature, H_2SO_4 catalyst, and 30 min reaction time. As a continued work of this study, the optimal reaction conditions will be investigated further by experimental design via response surface methodology.

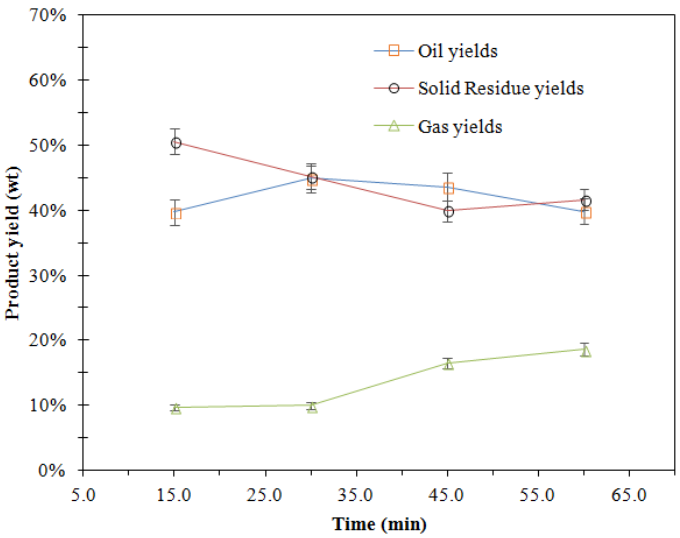

Figure 5. Effects of holding time on products yield (H_2O-EtOH medium, 250 °C, H_2SO_4 catalyst, heating time for 0.5 h).

3.3. Structural Analyses of Bio-Crude Oils

To examine the chemical compositions/structures of bio-crude oils, some representative bio-crude oil samples were analyzed by GC-MS, FTIR, and TGA. Table 3 presents GC-MS results of the bio-crude oil obtained from HTL of TPW in water–ethanol medium at 250 °C for 30 min catalyzed by H_2SO_4. The main compounds identified in the TPW-derived bio-oil are nitrogen-containing compounds such as N,N-Dimethylacetamide (~37 area%) and 4-Pyridinal (~10 area%), which are believed to be derived from the protein component of the feedstock, as evidenced by the high N content (4 wt%) of TPW (Table 1). The oil is also rich in acetic acid (19 area%), likely derived from degradation of carbohydrates/holocellulose in the feedstock. Other compounds such as ketones, esters and aromatics were also detected, as commonly reported in the literature [17–19]. However, it shall be noted that limited by the GC-MS technique, only volatile fractions (with boiling points <280 °C) of the bio-crude oils (normally less than 20 wt% of the total oils, determined by TGA of the oils) were identified.

Table 3. Gas chromatography–mass spectrometry (GC-MS) results of the bio-crude oil obtained from HTL of TPW in water–ethanol medium at 250 °C, 30 min with H_2SO_4 catalyst.

PK	RT [a]	Area Pct [b]	Library/ID	CAS	Qual [c]
1	2.68	19.35	Acetic acid	000064-19-7	90
2	3.2	2.22	Thiophene	000110-02-1	38
3	3.67	2.77	2-Hexanol, 3-methyl-	002313-65-7	59
4	3.89	3.75	1H-Imidazole, 2-ethenyl-	043129-93-7	35
5	4.27	2.51	2-Pentanone, 4-hydroxy-4-methyl-	000123-42-2	38
6	4.89	1.69	Pyrimidine, 4,6-dimethyl-	001558-17-4	52
7	5.01	36.75	N,N-Dimethylacetamide	000127-19-5	94
8	8.5	9.87	4-Pyridinol	000626-64-2	83
9	10.25	0.47	3-Oxabicyclo[3.3.0]oct-7-en-2-one, 7-methoxy-	1000155-61-4	49
10	12.63	0.56	6-Isopropenyl-4,8a-dimethyl-4a,5,6,7,8,8a-hexahydro-1H-naphthalen-2-one	086917-79-5	91
11	13.33	0.47	D-Ribitol, 1-deoxy-1-heptylamino-	1000158-66-6	43
12	13.73	1.27	Hexadecanoic acid, ethyl ester	000628-97-7	60
13	13.97	3.01	Benzene, 1-chloro-4-ethoxy-	000622-61-7	38
14	14.34	2.05	Isonipecotic acid, N-(3-cyclopentylpropionyl)-, ethyl ester	1000361-08-3	38
15	14.58	2.49	Benzyl alcohol, 4-methoxy-6-fluoro-	000405-09-4	35
16	14.94	4.77	2,5-Piperazinedione, 3,6-bis(2-methylpropyl)-	001436-27-7	49
17	15.26	1.43	Benzene, 1-methoxy-3-(methylthio)-	002388-74-1	60
18	15.46	2.66	Phenol, 3,5-dimethoxy-	000500-99-2	46
19	15.73	0.63	Pyrrolidine, 1-(7-nitrodibenzofuran-2-sulfonyl)-	1000302-59-9	46
20	16.69	0.77	Carbamate, N-(2-naphthyl)-, 3-pentynyl ester	1000197-96-0	41
21	18.1	0.52	Benzoic acid, 3-methoxy-, 2-(2-nitrophenyl-2-oxo)ethyl ester	331277-43-1	38
Total		100			

[a] Room temperature, [b] Area percentage, [c] Quality.

The GC-MS results indicated the presence of a significant number of N-containing compounds and carboxylic acid (acetic acid). Figure 6 allows for a comprehensive understanding of the functional group characteristics with spectral band assignments and interpretation based on previous publications [20]. The holding time or catalyst didn't distinct the oily products and we further assigned the major absorbance [21].

The GC-MS chromatograms of an aqueous fraction of liquefied products with lower boiling points and lower molecular weights are summarized in Table 4. The major components in the AF are fatty acids, pyridinol compounds and thiosemicarbazides. According to Biller et al. [22], the AF from HTL processes contained several orders of magnitude higher of all nutrients required for algae growth. Further works are expected to investigate the suitability of this aqueous phase for algae cultivation [23]. GC-MS results of the bio-crude oil obtained from HTL of TPW with KOH catalyst are presented in Table 5. About 41% of the acidic compounds, suggesting that the TPW decomposed under the alkaline condition. As the carboxylic acids produced from TPW under alkaline conditions, the initial alkaline hydrothermal condition can gradually become acidic [14]. The carboxylic acids produced under initial

alkaline conditions could neutralize the input alkalis and the aqueous reaction media could then become acidic, thus activating the acidic pathway.

Table 4. GC-MS results of the aqueous fraction of bio-crude oil obtained from HTL of TPW in water–ethanol medium at 250 °C, 30 min with H_2SO_4 catalyst.

PK	RT	Area Pct	Library/ID	CAS	Qual
1	3.69	19.93	Acetic acid	000064-19-7	91
2	3.99	0.96	Propanoic acid	000079-09-4	37
3	5.29	50.57	Propanoic acid	000127-19-5	91
4	7.19	0.67	2-Pyrrolidinone, 1-methyl-	000872-50-4	81
5	7.58	2.40	2-Propanone, dimethylhydrazone	013483-31-3	40
6	7.9	7.20	Pentanoic acid, 4-oxo-	000123-76-2	80
7	8.18	3.64	2-Furancarboxylic acid, 4-pentadecyl ester	1000280-64-0	38
8	8.58	4.60	4-Pyridinol	000626-64-2	91
9	8.75	1.61	3-Pyridinol	000109-00-2	83
10	15.92	0.67	2-Methyl aminomethyl-1,3-dioxolane	057366-77-5	30
11	16.29	1.31	Pyrimidine-2,4,6(1H,3H,5H)-trione, 1,3-diethyl-5-[(1,3-diethyl-2,4,6-trioxoperhydro-5-pyrimidinyl)methylene]-	128644-14-4	25
12	16.81	2.90	Thiosemicarbazide, 4-(1-adamantylcarbonyl)-	300799-69-3	35
13	17.03	1.09	Thiosemicarbazide, 4-(1-adamantylcarbonyl)-	300799-69-3	30
14	17.30	1.86	1H-Pyrrole-2,4-dicarboxylic acid, 5-formyl-3-methyl-, diethyl ester	002199-60-2	38
15	17.61	0.59	N-(5-Chloro-2-methoxy-phenyl)-2-(5-methoxy-1H-benzoimidazol-2-ylsulfanyl)-acetamide	1000295-83-8	15
Total		100			

Table 5. GC-MS results of the bio-crude oil obtained from HTL of TPW in water–ethanol medium at 250 °C, 30 min with KOH catalyst.

PK	RT	Area Pct	Library/ID	CAS	Qual
1	2.8985	0.8511	Cyclopropane, ethenylmethylene-	019995-92-7	37
2	3.1593	34.6287	Acetic acid	000064-19-7	90
3	3.4265	6.442	Acetic acid, hydrazide	001068-57-1	9
4	3.9546	9.6236	Propylene Glycol	000057-55-6	72
5	4.1009	3.359	2-hydroxy-2-methyl-4-heptanone	054862-91-8	43
6	4.3427	5.6599	Acetamide, N-(aminoiminomethyl)-	005699-40-1	50
7	4.4699	4.6055	2-Pentanone, 4-hydroxy-	004161-60-8	64
8	4.6289	1.6247	*n*-Capric acid isopropyl ester	002311-59-3	27
9	4.9025	2.1625	Pyrazine, 2,5-dimethyl-	000123-32-0	53
10	5.0743	1.5347	2-Cyclopenten-1-one, 2-methyl-	001120-73-6	30
11	5.1443	17.7941	N,N-Dimethylacetamide	000127-19-5	91
12	6.6712	0.9744	Pyrazine, 2-ethyl-3,5-dimethyl-	013925-07-0	38
13	7.2438	0.5655	Ethanone, 1-(1-cyclohexen-1-yl)-	000932-66-1	43
14	7.6191	0.4386	6-Methyl-2,3-dihydropyran-2,4-dione	000541-98-0	49
15	14.0193	2.155	3-(Ethyl-hydrazono)-butan-2-one	1000194-94-0	35
16	14.3947	0.9634	2-Methylcyclohexylamine	007003-32-9	27
17	14.9355	1.9235	Cyclohexane, 1,2,3-trimethyl-	001678-97-3	25
18	15.2981	1.7533	Cyclohexa-2,4-dienecarboxylic acid, 4-hydroxy-1-methyl-6-oxo-, ethyl ester	1000304-34-0	45
19	15.4763	2.9403	L-Proline, N-valeryl-, hexyl ester	1000345-48-3	53
Total		100			

The bands between 3505 and 3065 cm^{-1} could be assigned to either N-H or O-H stretching bonds representing amine or hydroxyl groups. The absorption bands of asymmetrical/symmetrical C-H stretching (3000–2850 cm^{-1}) and CH_3 bending (1390 cm^{-1}) vibrations are related to aliphatic methylene groups, indicating the presence of alkane groups. Significant heteroatom functionality (1700–1050 cm^{-1}) was also observed as expected from the GC-MS characterization (Tables 3 and 4). The GC-MS results were found to be consistent with FTIR characterization, indicating the presence of a significant number of N-containing compounds and carboxylic acid (acetic acid). The stretching bands of C=O groups (1730−1630 cm^{-1}) correspond to the fatty acids and ester groups in the crude bio-oil.

Consistent with nitrogenous compounds identified by GC-MS, small peaks representing amine groups were reflected by the weak N–H bending vibrations (1650–1530 cm^{-1}). Bands at 1445 are assigned to C=C stretching vibrations in aromatic groups. The strong absorbance near 1400 cm^{-1} is assigned to mononuclear aromatic compounds or the scissoring band in methylene groups. Bio-crudes obtained at different temperatures have FTIR of quite similarity (data not shown).

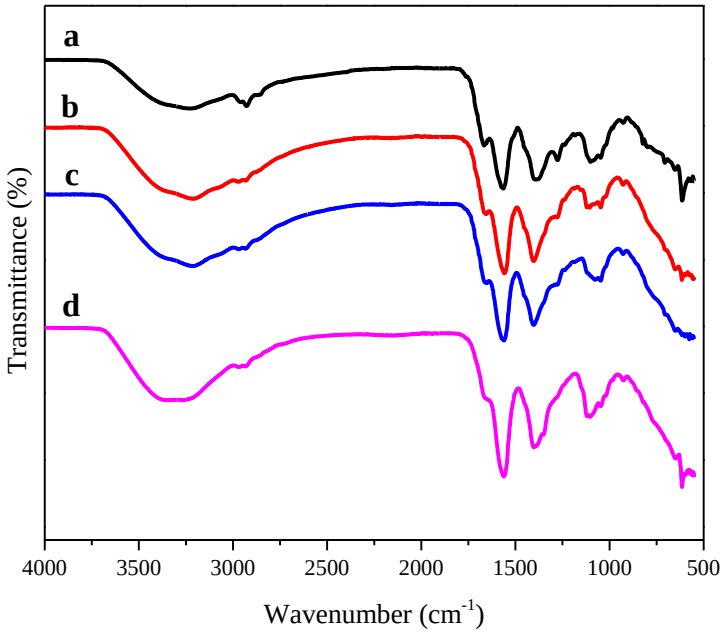

Figure 6. FTIR spectrum of the bio-crude oils derived from TPW, representing 250-30-A (**a**), 250-45-A (**b**), 250-60-A (**c**), and 250-30-B (**d**).

3.4. Elemental Distribution of Oily Products

TPW, the bio-oil, the organic fraction (OF), aqueous fraction (AF) and solid residue from optimal conditions were subjected to an element analyzer for their C, H, N, S, and O contents (Table 6). The C and O contents of the bio-oil are close to those of TPW, showing negligible difference. The HHV of the residue was higher than that of TPW, but close to that of OF, because the undissolved lignin and ash were the main components in the residue. Moreover, the C content and HHV of the OF increased considerably, while the O content was much lower than that of TPW and solid residue because of the deoxygenation resulting from dehydration and condensation reactions catalyzed by sulfuric acid. As-produced bio-oil revealed about 35% improvement in HHV has taken place with the HTL. Due to the mild liquefaction conditions, the HHV of OF (18.5 MJ/kg) was lower than that of heavy oil (~27 MJ/kg) [24] and the upgraded oil (~36 MJ/kg) [25] produced by the liquefaction under high pressures and high temperatures. It shall be noted that the obvious increment of the HHV and decrement of the ash content in the OF implies its potential upon biofuel upgrading.

Table 6. Elemental composition, ash and HHV of HTL feedstock and products.

Sample	N/%	C/%	H/%	S/%	O/%	Ash/%	HHV/MJ/kg
TPW	4.0	34.8	5.0	0.3	23.4	32.5	12.4
250-30-A	5.5	31.8	4.1	1.9	30.9	25.8	12.3
Residue	1.3	30.9	4.1	3.7	0.1	59.9	16.3
250-30-A-OF	4.6	48.6	5.4	0.8	31.5	9.1	18.5
250-30-A-AF	7.7	20.2	3.4	0.0	39.8	28.9	4.6

3.5. Thermal Stability, Volatile Matter upon Decomposition and Proximate Analysis of Bio-Crude Oil

Thermal gravimetric analysis (TGA) measures the weight losses of the sample as the temperature increases. Figure 7 shows the weight percentage (TG) and weight loss derivative curves (DTG) of TPW and bio-crude oil (250-30-A) in air. The decomposition of the oils started at 227 °C, peaked at 333 °C, and ended at 730 °C. According to Figure 7, about 20% of the bio-crude oils had a boiling point less than 300 °C, indicating that only a small fraction of bio-crude oil with lower molecular weights was detectable by GC-MS. The obtained bio-crude oils need upgrading for application as biofuel, comparing to the petroleum crude oil of which 45 wt% can be vaporized at 250 °C [26]. The TPW lose weight easily under 400 °C but slowly after 500 °C, mainly because of the high ash content within TPW feedstock.

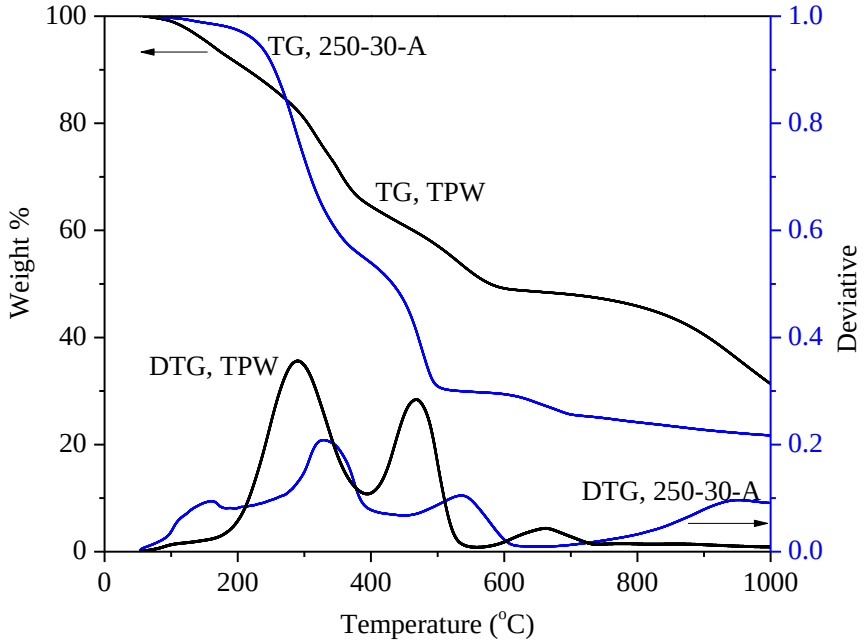

Figure 7. Thermal gravimetric analysis (TGA) and weight loss derivative curves (DTG) profiles of the bio-crude oils and TPW.

3.6. Analysis of Gaseous Products

GC analysis of gaseous products showed the presence of N_2, CH_4, CO and CO_2. The resulting gases contain 79–89% of N_2 as the HTL runs were conducted under the protection of N_2. The relative concentration of gases to N_2 is presented in Table 7. Being the major product, CO_2 constitutes 6–15% among all gases. The CO_2 and CO can be formed by hydrothermal reactions such as decarboxylation, water gas shift reaction, and gasification of solid residues (char), as well as being favored by reactive hot compressed water while H_2 might be consumed by the reverse-water gas shift reaction.

$$\text{Decarboxylation: } R \leftrightarrow R_1 + CO_2 \quad (2)$$

$$\text{Gasification: } C + H_2O \leftrightarrow H_2 + CO \quad (3)$$

$$\text{Water gas shift reaction: } H_2O + CO \leftrightarrow H_2 + CO_2 \quad (4)$$

Under basic conditions, the contents of CO and CO_2 were less than those under acidic conditions. Higher concentration of CO_2 was observed at 250 °C under acidic conditions as a result of enhanced decarboxylation and water gas shift reactions. The holding time enhances the concentrations of CO and CO_2 accordingly up to 45 min, while the holding time of 60 min resulted in lower concentration, suggesting that a longer holding time favored reverse decarboxylation and gasification.

Table 7. Concentration of gaseous products (relative to N_2 upon GC analysis) under various conditions.

Entry	Name	CH_4	CO	CO_2	N_2
1	250-30-A	0	1.17	12.93	81.80
2	250-30-B	0.01	0.37	6.86	88.99
3	220-30-A	0.01	0.73	10.88	86.43
4	250-30-A	0	1.17	12.93	81.80
5	280-30-A	0.02	2.45	8.20	79.96
6	250-15-A	0.00	1.19	6.68	83.02
7	250-30-A	0	1.17	12.93	81.80
8	250-45-A	0.01	2.11	13.96	82.66
9	250-60-A	0.01	1.27	10.40	85.72

4. Conclusions

Hydrothermal liquefaction (HTL) presents a viable route for converting agricultural waste with high moisture content into liquid fuel, with low energy input comparing to other thermo chemical technologies. We extracted HTL bio-oils from the TPW under mild conditions, focusing on the influence of acidic and alkaline conditions on HTL liquid products. This study primarily investigates the effects of hydrothermal reaction parameters on the yield and structure of bio-crude oil products from tomato plant wastes. It has shown that up to 45.08% yield of bio-crude oil could be produced from TPW, ranging between 30% and 45% under different conditions. Acid catalyst, alcohol co-solvent, and appropriate temperature favored bio-crude oil yield. The holding time did not affect the oil yield significantly. The optimal HTL condition appears to be at 250 °C, acidic water–ethanol co-solvent medium, for 30 min with the initial N_2 pressure of 1 MPa. The bio-crude oils are rich in fatty acids, aromatic compounds, fatty esters and carbohydrate derivatives, which are consistent with the identification by GC-MS and FTIR. The produced bio-oil has potential energy applications for biodiesel production and as a feedstock of fermentation.

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