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Characterization and utilization of aqueous products from hydrothermal conversion of biomass for bio-oil and hydro-char production: A Review

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Hydrothermal conversion (HTC) including hydrothermal liquefaction and hydrothermal carbonization, is a cost-effective and environmentally friendly thermochemical technology for the utilization of biomass. Bio-oil and hydro-char have been the subjects of intense research during the past decade, during which considerable amounts of aqueous products with high concentrations of organics and nutrients are produced, which were largely overlooked. Composition of hydrothermal conversion aqueous products (HTC-AP) strongly depends on the process conditions and biomass compositions, and also affects its further utilization. The present study systematically summarizes the main reactions occurring in HTC, characterization of HTC-AP, and factors affecting the compositions of HTC-AP. More importantly, recent advances of HTC-AP utilization techniques are summarized. Finally, the main challenges for future research on HTC-AP have been identified and possible solutions are given.

1. Introduction

Due to the increasing demand of energy, fossil fuel is diminishing rapidly. Researchers are considering adopting eco-friendly alternative energy to meet the demand. Biomass is one of the most important renewable energies, which can be converted into various products (bio-oil, bio-char, syngas, etc.) through thermochemical technologies, such as hydrothermal conversion (HTC) and pyrolysis 1, 2. HTC is a green technology since it does not require high energy input compared to pyrolysis, which can only use dry biomass. HTC is water-based thermochemical technology which handles biomass without the need for drying prior to use reducing overall energy consumption 3. It is also an environmentally friendly pre-treatment which does not require addition of other reagents. HTC in the present study refers to hydrothermal liquefaction and hydrothermal carbonization, which has been extensively investigated for bio-oil and hydro-char production for temperatures ranging from 170-350 oC 4-7. Hydro-char with higher heating values (HHVs) of around 23 MJ/kg can be used as solid fuel as it behaves like coal, while bio-oil with HHV at around 30 MJ/kg can be used as liquid fuel. There are a number of studies and reviews in the past few years focusing on the enhancement of bio-oil yields, upgrade of the bio-oil, and utilization of hydro-char from various biomass 8-10.

Around 20-50 % of the organics are transferred into the aqueous phase (HTC-AP) during the HTC process 1, 4, 11-18. The composition of HTC-AP is very complex due to the natural complexity of biomass, and it comprises both water-soluble and water-insoluble fractions. Currently the HTC-AP obtained from the HTC of various types of biomasses has not been well characterized. It is known that the HTC conditions significantly affect HTC-AP due to the changes of reaction pathways. Various reaction products, intermediates, as well as secondary polymeric compounds, including saccharides, volatile fatty acids, alcohols, cyclopentenones, phenols, amino acid, ammonia and melanoidins, can be found in HTC-AP depending on the feedstocks and reaction conditions 19, 20. Some of the HTC-AP products (*e.g.*, furans, pyridine and phenols) might be toxic and inhibitory to marine life, and have negative influences on fertility of land and water 20. Direct discharge of HTC-AP is likely to deteriorate the environment. Therefore, reducing the amount of dissolved organic carbon and nutrients in the HTC-AP and/or recapturing these compounds via a complementary process could be considered as an essential step in HTC future deployment 21.

To achieve the overall economic sustainability of the HTC process, it is important to utilize the HTC-AP to produce useful products 22-33. Previous studies tried to recover resources from HTC-AP before discharging into the environment through extracting valuable compounds, anaerobic digestion (AD), algae cultivation and recycling into HTC process or supercritical water gasification 34-40. However, there are many challenges for efficient utilization of HTC-AP. For example, HTC-AP obtained from HTC of algae had been attempted to be recycled for the cultivation of algae. However, it was found that toxic compounds in HTC-AP greatly inhibited the growth of algae even with a large dilution factor 20. The presence of toxic and refractory compounds in HTC-AP also resulted in low efficiency of AD for biogas production 34. To the best of our knowledge, there are no reviews available systematically describing the characteristics of HTC-AP and progress for the utilization of HTC-AP, which is very important for better utilization of HTC-AP in future studies to develop a sustainable process for the conversion of biomass.

The objectives of this review are to summarize the characteristics of HTC-AP as well as the production mechanisms under various HTC conditions, and to provide up to date knowledge on using HTC-AP to produce multiple products, and thereby to give perspectives on HTC-AP utilization.

2. Properties of HTC-AP

2.1 Components of biomass and their products in HTC-AP

2.1.1 General view of HTC-AP.The components of biomass are substantial factors in affecting reaction pathways and their aqueous products during HTC process. Many previous studies have conducted HTC on various types of lignocellulosic biomass including wood chip 41, 42, peanut shell and bamboo 43, digestate 44, bagasse 45, olive residues 46 and wheat straw 47. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin 48. Non-lignocellulosic biomass, including microalgae 49, sewage sludge 50, food wastes 21 and other biomass that mainly contain carbohydrates, protein and lipids, have also been well studied. Table 1 summarizes the main composition of HTC-AP obtained from HTC of various types of biomass. For the purposes of bio-oil component analysis from lignocellulosic biomass through HTC, the reaction mechanism and corresponding products of the main components (cellulose and lignin) have been thoroughly studied. It was found that complicated reactions including hydrolysis, decomposition, dehydration, deamination, Maillard reaction, decarboxylation, cyclization, and polymerization occurred during HTC process. Organics derived from different structures in HTC-AP have been categorized into major groups of volatile fatty acids (VFAs), alcohols, saccharides, amino acids, hydrocarbons, phenols derivatives, N-heterocyclic compounds, oxygenates (cyclic & straight), esters and ketones (Table 1).

2.1.2 Hemicellulose.Hemicellulose was firstly decomposed into its oligomers and then into monosaccharaides of xylose, galactose, glucose and fructose under mild (T<200 oC) HTC conditions 51. Nakasu et al. reported that total hemicellulose recovery was 65.0 % and most solubilized carbohydrates were present as oligomers when HTC was conducted at 190 oC for 10 min 52. Some carboxylic acids (e.g., lactic acid and acetic acid), furfural (5-hydroxymethyl-2-furaldehyde, 2- furaldehyde) and aldehydes could be generated subsequently 10, 53, 54. Figure 1 describes the degradation mechanism of hemicellulose hydrolysis in biomass. The hemicellulose polymers (HemPol) were first hydrolyzed to high molecular weight, soluble fragments (HemHDPOl)) of oligomeric portions, which kept the major structural features of original substrates at mild HTC condition (around 150 oC). They were then progressively depolymerized into low molecular weight (HemLDPOl) xylooligomers or glucose and mannose at a moderate temperature around 200 oC. The HemLDPOl reacts to give monomeric saccharides (denoted Mon, including xylose or mannose- glucose mixtures). Monomeric saccharides could be further converted into furanic products (denoted FurC, comprise furfural or HMF) at a harsh HTC condition. In further reaction stages, furfural and HMF were decomposed or repolymerized to other products 55. Typically, oligosaccharides account for 55-70 % of the dissolved fraction at moderate condition 55.

2.1.3 Cellulose.Cellulose is organized into micro fibrils surrounded by hemicellulose and encased inside a lignin matrix in biomass, and its degradation is more difficult than that of hemicellulose 19. The intensive hydrogen bonds within the cellulose structure together with its high crystallinity hinder the depolymerization of cellulose 51. It was reported that only the amorphous part (around 10 wt.%) could be dissolved in the HTC-AP under moderate conditions 51. The long chain polysaccharides were first decomposed into their oligomers and then transformed into monosaccharaides under more severe conditions. Glucose was the major monosaccharide and the monosaccharaides could be further transformed into furan derivatives (HMF), short chain organic acids and aldehydes 56-58. At the same time, some insoluble compounds could also be produced by polymerization reaction 59.

2.1.4 Other components. Lignin is also a major component in lignocellulosic biomass. The degradation rate is relatively low and phenolic compounds including phenol, methoxy-phenol, and catechol were the major products during HTC 48, 60, 61. Protein is also one of the major ingredients of non-lignocellulose biomass. The decomposition of biomass with proteins is more complex than that of other types of biomass. Amino acids, ammonia and nitrogenous compounds are major components produced from protein by deamination and cyclization 48, 61, 62. Amino acids such as glutamic acid, leucine, lysine and aspartate could undergo deamination to produce carboxylic acids, which would be further converted to pyrroles and amides at intense HTC conditions 21. Lipids in some algae and food waste can be decomposed into fatty acids and glycerol; degradation of glycerol leads to the production of formaldehyde, acetaldehydes and alcohols 48, 61, 63. It should be noted that the HTC-AP can be more complex since particles, colloidal and soluble substances are involved in the system 64.

It is worth noting that the weight loss during HTC-AP mainly results from the degradation of hemicelluloses at mild HTP conditions (200 oC). Oligosaccharides are the major primary hydrolysis products of hemicellulose at mild

**Table 1** Summary of main structures and major compounds of lignocellulosic and non-lignocellulosic biomass

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Biomass | Percentages of main structures | | | | |
| Lignocellulosic Biomass | Cellulose | Hemicellulose | Lignin | Major compounds into HTC-AP | Ref. |
| Woody biomass (*e.g.*, Aspen, Pine, Sawdust, poplar) | 38.6-63.6 | 7.7-20.2 | 17.6-32.7 | Phenols, furfurals, glycolic, acetic acid, alcohols and cyclopentenone | 65-68 |
| Switchgrass | 32.8 | 23.7 | 18.2 | VFAs, phenols, furfurals, sugars, alcohols and cyclopentenone | 69 |
| Crop Straw and Husk | 29.2-46.0 | 18.2-36.4 | 15.0-28.2 | VFAs, capronic acid, lactic Acid, furfural, sugars, alcohols and cyclopentenone | 70-76 |
| Orange Pomace | 14.3 | 6.3 | 3.3 | Acetic acid, HMF, furfurals, ethanol, acetone, butanone and alkyl derivatives | 77 |
| Sugar cane bagasse | 56.0 | 4.6 | 36.4 | VFAs, phenols, furfural, sugars, alcohols and cyclopentenone | 78 |
| Newspapers | 44.2 | 17.8 | 26.8 | VFAs, furfural, sugars, alcohols and phenols | 79 |
| Recycled paper | 60.8 | 14.2 | 8.4 | VFAs, furfural, sugars, alcohols and cyclopentenone | 80 |
| Spent grain | 18.5 | 26.5 | 19.1 | Cyclopentenones, carboxylic acids; pyrazines and ketones | 81 |
| Non-lignocellulosic Biomass | Protein | Carbohydrates | Lipids |  | Ref. |
| Food waste | 15.0-25.2 | 41.3-62.1 | 13.4-30.2 | VFAs, HMF, furfural, ethanol, ketones, alkyl derivatives of 2 cyclopenten-1-one | 82 |
| Sewage Sludge | 27.6-33.4 | 3.3-4.0 | 6.6-13.8 | VFAs, benzene, acetic acid, carbonic acid, alkenes, phenolic, aromatic compounds and pyrazines | 83 |
| Macro Algae | 12.2-30.9 | 54.3-83.6 | 0.9-6.2 | Nitrogenous compounds, long chain fatty acids, acetamide, alcohols, acetone and glycerol | 5 |
| Microalgae | 8.1-71.4 | 4.2-57.1 | 2.4-40.1 | VFAs, phenols, pyrazines, benzenes, alkanes and fatty acids | 84 |
| Mixed Cultural Algae | 27.2 | 17.9 | 5.7 | Short / long chain organic acids, amino acid, phenols, urea, N-heterocyclic compounds, acetamide and ketones. | 17, 85 |
| Dried Distillers Grains | 42.2 | 35.0 | 22.4 | Cyclopentenones, carboxylic acids, pyrazines, ketones, oxygenated aromatics | 18, 86 |
|  | | | | | |

conditions and any glucose observed in HTC-AP was less likely to derive from cellulose than from hemicelluloses. Under more severe conditions, the products are more complex, which may include furans, phenolic compounds and nitrogen derivatives.

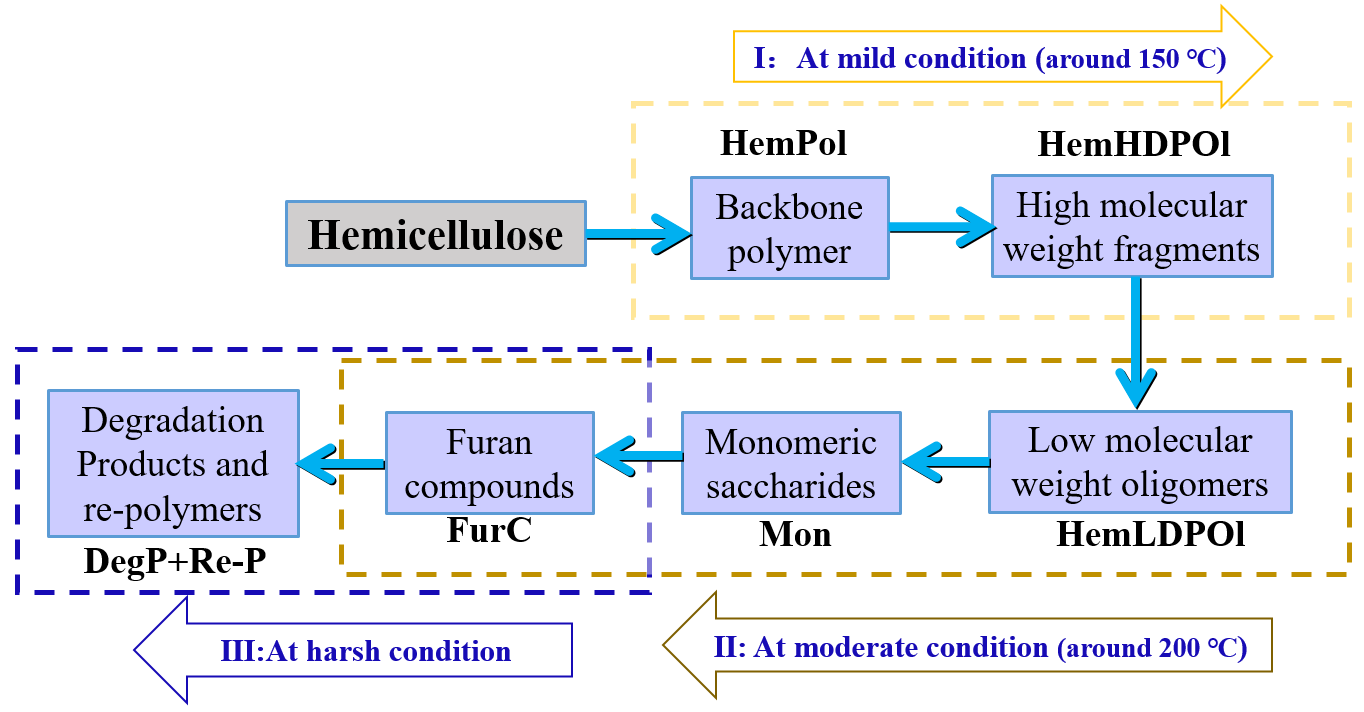
2.2 Interactions between different HTC-AP products

As Figure 2 shows, there are interactions (e.g., Reaction (e)) between degradation products of different components in the biomass during the HTC process. For example, the Maillard reaction between reducing sugars from carbohydrates hydrolysis and amino acids from proteins hydrolysis could occur at high temperatures (T>165 oC) and produce heavy nitrogenous polymers known as melanoidins 87, 88. The melanoidins formed by the Maillard reaction were largely responsible for the low biodegradation efficiency of HTC-AP 89. Posmanik et al. also concluded that more recalcitrant or inhibitive products were likely to derive from biomass containing protein because of the interactions between degradation products of proteins and carbohydrates or lipids 21. Additionally, for protein-rich biomass, the formation of ammonia from protein in HTC-AP increases the alkalinity, which may also influence the reaction of other components, including the formation of long-chain aliphatic compounds 90. For HTC of lignocellulosic biomass under severe conditions, initial degradation products (e.g., furans, ketones and phenolic compounds) from amorphous parts such as hemicellulose and lignin could undergo isomerization, dehydration, fragmentation and condensation reactions which could result in precipitation on the surface of cellulose, inhibiting water access to cellulose, preventing its degradation and forming char-like precipitates inside the hydrothermal liquefaction (HTL) reactor 19.

2.3 Commonly used parameters to characterize HTC-AP

The compositions of HTC-AP are complex and changeable, and there are some commonly used parameters including pH, COD/TOC, carbohydrates, ammonia nitrogen, total reaction medium nitrogen and phosphorus that provide general characteristics of HTC-AP. These parameters vary with the HTC conditions and types of biomass 16, 85, 91. Table 2 summarizes the parameters of HTC-AP from previous studies. The COD values varied in the range of 40-110 g/L for lignocellulosic biomass and 12-160 g/L COD for non-lignocellulosic biomass. The total organic carbon (TOC) values of HTC-AP usually ranges from 2 to 35 g/L 31, 32. The TOC value even reached 40 g/L when the HTC-AP was recirculated to an HTC process 27, 33.

The broad COD or TOC intervals of HTC-AP of different biomass types is a significant challenge for the overall sustainability of industrial processes if HTC-AP is considered as wastewater 92. HTC-AP has low pH (3.4-6.2) from



**Figure 1** Generalized kinetic mechanism for interpretation of hemicellulose hydrolysis.

lignocellulosic biomass due to production of large amount of volatile fatty acids 35. However, the HTC-AP of biomass with high protein content (up to 9.2) is generally alkaline, due to the production of ammonia 93.

Nitrogen and phosphorous compounds are the two main inorganics in HTC-AP, and these can be considered as potential nutrients and used for algae cultivation. The nitrogen content depends on the protein content of biomass 94. Generally, HTC-AP contains high concentration of ammonia (1.9-12.7 g/L) for the HTC of non-lignocellulosic biomass such as sludge, algae, et al. 36. The TP of HTC-AP was generally in the range of 0.5-1.0 g/L and the highest value was reported to be 18.9 g/L 20, 73. The transformation and bioavailability of P varied dependent on the type of biomass and operating conditions. Biomass with high metal contents (like Ca, Mg, Cu, Cd and Zn ) such as manure and sewage sludge can lead to insoluble phosphate precipitates while Fe and Al minerals have high affinities for P adsorption 95, 96. The HTC conditions such as low pH 97, 98, high reaction temperature 98, 99 and high reaction time 100 could promote the dissolution of these metals and the hydrolysis of phosphate. For example, 85 % of the P in microalgae *Nannochloropsis sp.* was transferred to HTC-AP 99. The highest P recovery in HTC-AP occurs when the algae slurry was processed at 400 oC 101 but for algae with high metal (e.g., Ca, Mg and Fe) contents, the rate of P transferring into AP could be lower than 30 % 36. Therefore, the biomass with low metal contents promote the transfer of P to HTC-AP 20, 36, 99.

2.4 I[nstrumental](javascript:;) [analysis](javascript:;) of HTC-AP

Due to the complexity of HTC-AP, a thorough understanding of the reactions occurring during HTC process is difficult, considering the interactions between different components in biomass. Quantitative and qualitative analysis can be conducted to investigate the chemical properties at molecular-level (Table 3). Gas chromatography-mass spectrometry (GC-MS) has been widely applied due to its versatility and the large library of mass spectra for compound identification 18. Many groups of products (e.g., aldehydes, phenols, ketones, esters organic acids and N&O-heterocyclic compounds) can be identified with a high degree of confidence. Furfural, carboxylic acids, and the trace amounts of phenolic compounds could also be determined by HPLC 51. For monosaccharide characterization, high-performance liquid chromatography (HPLC), which could be equipped with an HPX-87H (BIO-RAD) or Agilent Hi-Plex H columns and Refractive Index Detector, were usually used 51, 102. For xylooligomer determination, the HTC-AP could be subjected to quantitative post-hydrolysis (with 4 % sulphuric acid at 121 oC for 60 min), and then analyzed by HPLC. Monosaccharides and xylooligosaccharides (DP, 2-6) were also determined by high-performance anion exchange liquid chromatography (HPAEC) 102.

It should be noted that there were no sufficient quantitative analysis of both HTC-AP and bio-oil in literatures. Although some specific products were quantified as shown in Table 3, they may only account for very small fractions in the organics of HTC-AP, which was due to the limitations of each analytical technique. For example, GC-MS is the commonly used technique and NIST (National Institute of Standards and Technology) database was mostly used for identification of chemicals, but only part of organics (15-20 %) could be identified because the oven temperature of the GC was limited 103. In addition, due to limitations of peaks overlapping, the HPLC analysis also could not properly define the composition of complex mixture in the HTC-AP 51, 102.

Recently, more advanced techniques such as LC-MS, Two-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry (GC-GC-TOF-MS) and Direct Infusion Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) are recommended to better understand these aqueous products. However, GC-GC-TOF-MS could not measure organic compounds with molecular weight (MW)

**Table 2** Values of some important indexes of HTC-AP obtained under different parameters

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Feedstock | Operating Conditions c | HTC-AP yield (%) d | pH | COD (g/L) | TOC (g/L) | TN (g/L) | TP (g/L) | Ref. |
| Corn silage | T: 220 °C; RT: 6 h; SL: 4.3 % | - | 3.8 | 41.4 | 15.7 | 0.7 | 0.2 | 104 |
| Sugar beet waste | T: 338 °C; AF SL: 14.1 % | 55 | 4.7 | 110.4 | - | - | - | 92 |
| Pine; Corn stover | T: 350 °C; SL: 9.6-14.5 %; FR: 1.0-1.5 L/h; P: 20.7 MPa | 27.7-45 | 4.4 – 5.4 | 40.0-74.0 | - | - | - | 11 |
| Rice straw | T: 170-330 °C; SL: 9.6 - 14.5 %; RT: 30 min | 12.11-30.96 | 3.7 – 5.6 | 14.3-29.0 | 3.9 – 10.3 | - | - | 70 |
| Extracted grain waste | T: 331 °C; AF SL: 12.8 %; P: 20.1 MPa; FR: 4.0 L/h | 26 | 6.2 | 55.9 | - | - | - | 92 |
| Poplar wood chips | T: 220 °C; S/L: 20/100; RT: 4 h | 15 | 3.4 | 50 | 17.4 | - | - | 105 |
| Algal | T: 260-350 °C; RT: 30-90 min; SL: 10-20 % | 4-88 | 7.5-9.0 | 23.0-160.0 | 23.2-35.0 | 11.0-31.7 | 0.7-1.9 | 4, 37, 39, 106-108 |
| Grapes and pomace waste | T: 175-349 °C; RT:  30-120 min; P: 20.0 MPa | 29-42 | 7.5 | 57.0-84.7 | 21-26 | - | - | 77, 92 |
| Sewage sludge | T: 140-320 °C; RT: 15-240 min; SL: 2.4 % | 2-57 | - | 17.5-105.6 | 4.9-13.7 | - | - | 14, 109 |
| Municipal sludge | T: 225-275 °C; RT: 15-60 min | 27-67 | - | - | 2.487 | 0.514 | 0.048 | 100 |
| Digested sludge | T: 350 °C; AF SL: 11.5 %; P: 20.0 MPa; FR: 1.5 L/h | 26 | 8.0 | 48.2 | - | - | - | 92 |
| MSW pulp and digestate | T: 200-300 °C; RT: 30, 120 min; S/L: 40/100 | 1.3-6.9 g/100 g | 4.3-9.2 | 12.2-12.6 | 0.39-4.9 | 0.1-2.4 | 0.10 | 110, 111 |
| Oleaginous yeast | T: 345 °C; AF SL: 14.9 %; P: 20.0 MPa; FR: 1.5 L/h | 21 | 4.1 | 59 | - | - | - | 92 |
| c T: temperature; AF: ash-free; SL: solid load; P: pressure; FR: feed rate; S/L: solid/liquid mass ratio; RT: residence time; d base on carbon percentage | | | | | | | | |

higher than 1000 because of the limited maximum temperature 17, 49, 110, 112. More molecular information could be obtained through high resolution mass spectrometry techniques (FT-ICR-MS), with which only a small part of the structures can now be identified. New advanced techniques should be developed or introduced to give a better understanding of HTC-AP. Deciphering molecular structures of HTC-AP components is a key future direction which relies on the integrated use of complementary analytical techniques to further understand the formation and transformation of the aqueous products of biomass HTC.

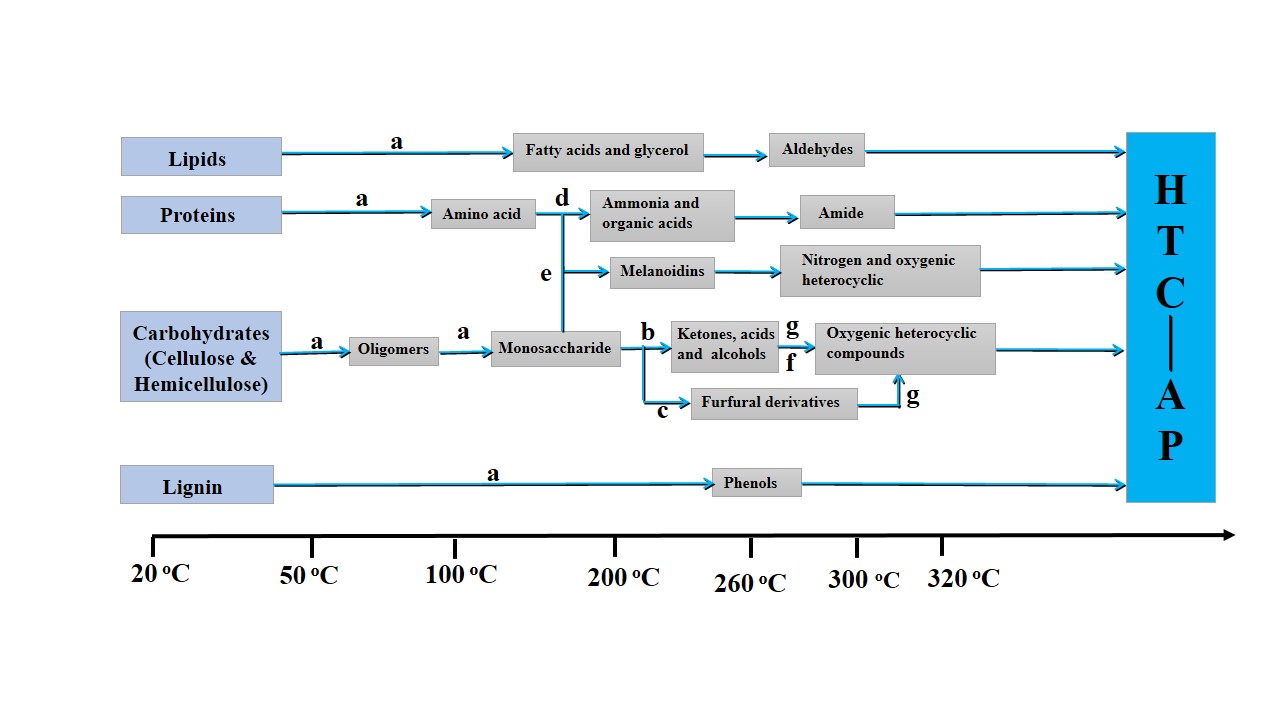
3. Influencing parameters of HTC-AP characteristics

The composition of HTC-AP is complex and variable. Reaction conditions, such as temperature, can shift reaction mechanism from one to another, and therefore changes in HTC conditions can substantially alter the composition of HTC-AP 21. Among the several parameters that may affect the HTC process and HTC-AP compositions, reaction temperature, reaction time, and solid/liquid (S/L) ratio have generally been considered as the key parameters. Although heating rate has been shown to be crucial for bio-oil production 19, 53, there is no study relating with the effects of heating rate on HTC-AP, which needs to be elucidated in the future studies.

3.1 The influence of governing factor-temperature on HTC-AP

Reaction temperature is the most important parameter influencing HTC products as well as the composition of HTC-AP. With the increase of temperature, the concentrations of organics in HTC-AP gradually increased because more organics were dissolved due to degradation of the biomass. However, sufficiently high temperatures would decrease the concentration of organics in HTC-AP because of polymerization reactions of intermediates 60, 73, 85, 113. It was reported that the TOC concentrations of HTC-AP obtained from Pontianak tropical peat increased when the temperature increased from 150 oC to 250 oC, while it decreased when temperatures rose from 250 oC to 270 oC due to repolymerization 114. The HTC-AP contained 78-90 % of the initial COD for HTC of synthetic food waste at 200 oC while HTC at 350 oC resulted in HTC-AP with lower organic content that was equal to 31-53 % of the initial COD. For HTC of algae, similar trends were also found when considering the effects of reaction temperature in the HTC process. For instance, COD values of HTC-AP decreased with an increase of temperature from 260 oC to 300 oC 17. It was concluded that the flexible COD values could result from the hydrolysis (decomposition) and repolymerization of different biomass components when the temperatures increased 35.

Reaction temperature also shows effects on the chemical compositions of HTC-AP. For lignocellulosic biomass, monosaccharides (e.g., glucose and xylose) in HTC-AP were detected when HTC temperature reached 120 oC, although the yields of which were very low 115. Higher temperatures can accelerate the hydrolysis of xylan-type hemicelluloses. Deng et al. reported that the concentration of xylose increased from 0.28 g/L at 170 oC to 6.86 g/L at 190 oC 116. In addition, a large number of oligosaccharides were also found, and among these



**Figure 2** Reaction pathways and corresponding product of different biological structures in biomass for HTC where (a) refers hydrolysis, (b) refers decomposition reaction, (c) refers dehydration, (d) refers deamination, (e) refers Maillard reaction, (f) refers decarboxylation, (g) refers cyclization reaction.

oligosaccharides, xylooligosaccharides and glucooligosaccharides were the major products 51. Monosaccharides and oligosaccharides had similar variation trends. For instance, the yield of xylooligosaccharides increased steadily from 2.49 to 61.69 g/kg when the HTC temperatures of wheat straw increased from 120 °C to 180 °C, and decreased dramatically to 1.24 g/kg at 200 °C due to its further degradation to xylose 115. It was found that the yield of

acetic acid, mainly coming from the acetyl groups on the hemicelluloses backbone, was much higher than that of other degradation products and increased with HTC temperature 35, 115.

Furfural and HMF were produced at high HTC temperatures (>200 oC) from dehydration of pentose and hexose, respectively, both of which could depress the enzymatic activity or biodegradability in the subsequent biological conversion process (e.g., ethanol production) 51. The HTC-AP from mixtures of polysaccharides, proteins, and lipids yielded the highest concentration of glucose at 200 oC. When the temperature increased to 250 oC, aldehyde, furan derivatives and small molecules acids such as acetic acid and levulinic acid were produced 21, 94, 117, 118. For the biomass containing protein, contents of amino acids derived from proteins decreased greatly from 7.1 % to 0.1 % (% RPA, relative pick area by GC-MS ) when the reaction temperature increased from 260 oC to 320 oC, and at the same time amide derivatives increased from 6.3 % to 16.3 % for HTC of mixed-culture algae 17. The RPA of acetic acid also decreased as the temperature increased from 260 oC to 320 oC, but the RPA of propanoic acid increased, which could be inferred that competitive reactions such as polymerization and decomposition might take place at the same time. Toor et al. also found that for HTC of *Spirulina* and *Nannochloropsis salina* at severe temperatures (250 to 330 oC), the major products were carboxylic acids, nitrogenous compounds and heterocyclic compounds due to deamination and decarboxylation reactions of amino acids and carboxylic acids 119. It was confirmed through 2D-HSQC NMR analysis that only a small amount of lignin products existed in the HTC-AP, and cleavage of the major linkages among lignin became severe at temperatures higher than 200 oC 115.

For the conversion of biomass, bio-oil or hydro-char was the target product and HTC-AP was usually the by-products. Therefore, optimal temperature was usually expected for the purposes of obtaining a higher bio-oil yield or a better hydro-char property 17. Higher HTC temperature and longer residence time might be favoured for bio-oil and bio-char quality improvement but might make the corresponding HTC-AP difficult for subsequent utilization, especially biological conversion. Therefore, to improve the HTC-AP utilization efficiency, a proper temperature should be reconsidered.

3.2 The influence of subordinate factors on HTC-AP

Residence time (RT) and other parameters also have effects on overall conversion rate and composition of HTC-AP products 23. However, they exert much less influence on biomass decomposition in comparison to temperature, and therefore they are considered as subordinate factors that influence HTC-AP 7, 10, 53, 120. It has been shown the effects of subordinate factors on the overall conversion depend on the HTC temperatures. For instance, an increase in either RT or S/L ratio does not influence the overall conversion at low temperature of 160 °C while an excessive increase of temperature from 190 °C to 210 °C leads to the decrease of carbohydrate (alginic acid) conversion in HTC-AP regardless of the RT or S/L ratio 51.

At moderate HTC temperatures (160-210 oC), it has been found that an increase of RT from 0 min to 5 min decreased the concentrations of oligosaccharides (degree of polymerization, DP<6) and increased the concentrations of mono- and disaccharides (e.g., cellobiose, xylose, glucose, fructose, mannose, arabinose, rhamnose and levoglucosan) in the HTC-AP 51. At higher HTC temperatures (such as 300 oC), a

**Table 3** Main chemical characterization technologies for analyze of HTC-AP

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Groups | Composition | Analytical method | Key notes | Ref. |
| Furans | 5-HMF and furfural | HPLC | 4u Hydro-RP column | 121 |
| Ketones | Levoglucosenone | HPLC | ACE C18 column | 51 |
|  |  | HPLC |  |  |
| Aldehydes, phenols, ketones, and esters | 2-methoxy- (C7H8O2), acetoin and dimethyl phthalate | GC-MS | Varian DB-5 column | 121 |
| Organic acids and N&O-heterocyclic compounds | Fatty acid, phenols and piperidine | GC-MS | ZB-WAX column | 6 |
| Organic acids, amides and N&O-heterocyclic compounds | Acetate, phenols and piperidine | GC-MS | HP-INNOWax quartz capillary column | 109 |
| Fatty acids | Fatty acids of C10−C18 | GC-FID | derivatized into their methyl esters | 18 |
| Fatty acids | Fatty acids of C14−C22 | HPLC-TOF-MS |  | 18 |
| Reducing sugars | 3,5-dinitrosa-licylic acid method |  |  |  |
| Di-saccharides | Cellobiose and xylose | HPLC  HPAEC | Agilent Hi-Plex H column | 51, 102 |
| Oligosaccharides | DP 2–6 saccharides of xyloo/glucoo ligosaccharides | HPLC, HPAEC and chemical hydrolysis | Agilent Hi-Plex H column  or 4% sulphuric acid at 121 oC for 60 min | 51, 102 |
| Acids | Lactic, formic, levulinic, acetic, guluronic and mannuronic acids | HPLC | Agilent Hi-Plex H column | 51 |
| Qualitative analysis | Unknow compound structure | 2D-HSQC NMR | Freeze-dried sample | 115 |
| Molecular weight and formula | GC-GC-TOF-MS, LC-MS and FT-ICR-MS | Molecular weight low than 1000, ratio of O/H, C/H and C/N, etc.; and higher molecular weight compounds | 17, 49, 110, 112 |
|  | | | | |

negative correlation was found between RT and the organic concentration (in COD value) with the increase of RT from 0 to 1 h for HTC of algae, which indicated that the organic matter in HTC-AP might be further converted to hydro-char. However, a further increase of RT to 1.5 h resulted in a sharp increase of COD values (from about 28 g/L at 1.0 h to about 69 g/L at 1.5 h) 17. Another study also showed that the COD values decreased from 27.7 g/L to 14.3 g/L when RT increased from 0.5 h to 2.0 h at 200 oC, while it was increased to 19.0 g/L when RT increased to 4.0 h for HTC of lignocellulosic biomass 35. The variation trends of organic concentrations in HTC-AP with the increase of RT could result from the hydrolyzation (decomposition) and repolymerization of different structures in biomass.

The heating method could also significantly influence the HTC-AP. It was reported that comparing to conventional heating, microwave was not only useful as alternative of heating method, but also could cause specific molecular activations. Higher glucose yield (up to 25%) and selectivity (75%) were obtained for cellulose hydrolysis with microwave-heating compared to conventional heating 122. Besides, microwave technology was an energy efficient method of heating and it has been widely accepted as a mild and controllable industrial scale processing tool in food and waste treatment 122-124.

To avoid microbial inhibitors production, both governing (temperature) and subordinative factors (RT, S/L ratio, etc.) should be considered. It was reported that the conversion of xylose towards degradation products, mainly furfural, reached similar concentration 2.73 mg/mL at 170oC for 180 min and 220oC for 15 min, indicating the reaction proceeded faster under higher temperature 125. It could be explained by Arrhenius equation 126, which was used to describe the correlation between reaction rate constant and temperature, assuming the activation energy is constant. The higher the HTC temperature was, the higher the reaction rate for the production of furfural from xylose was. The higher the HTC temperature was, the higher the reaction rate for the production of furfural from xylose was. Jeon et al. analyzed the effects of reaction time (0-40 min) and the temperature (160-220 °C) on HTC of alginic acid (main structure of algae), and found furfural was the major reaction product, which initially increased with RT but then decreased due to its conversion to humins and/or organic acids 127. Currently, it is not possible to estimate the energy input for different HTC conditions based on literatures. Furthermore, pilot-scale experiments are necessary to make such analysis.

3.3 The influence of combined hydrothermal severity on HTC-AP products

From the above analysis, it can be concluded that both HTC temperature and RT as well as other parameters influence the HTC processes and composition of HTC-AP. Sometimes a single HTC condition has not been proven to be enough to describe the influence or to compare the effects of HTC-AP. For instance, Zieminski et al. studied the HTC of sugar beet pulp at temperature between 120 oC to 200 oC with RT 20 min, and the highest recovery of reducing sugars (6.18 g/L) in HTC-AP was obtained at 160 oC for 20 min while the highest recovery of reducing sugars (12.25 g/L) was achieved at 200 oC for 10 min for HTC of sugarcane bagasse 128. The hydrothermal treatment severity (logRo) that can measure the HTC intensity by considering several parameters including HTC temperature and RT was therefore proposed in Eq. (1) 129.

The severity factors of HTC have been defined as a function of reaction temperature and RT according to Eq. (1), where “t” is the retention time (min), T is the reaction temperature (°C), Tref is the reference temperature (100 °C), and the fitted value (14.75) is based on activation energy, assuming pseudo-first-order kinetics. The equation is defined as follows:

logRo=log [t \* exp (T- Tref)/14.75] Eq. (1)

logRo was an integrated indicator to describe the influence of several parameters irrespective of the type of HTC conditions. It was reported that the production of acetic acid correlated well with logRo value as the concentration of acetic acid was 0.5 mg/mL at severity logRo of 3.3, and 3.41 mg/mL at severity logRo of 4.7. HTC-AP obtained at moderate severity was reported to yield more methane by anaerobic digestion as most of the sugars were transferred to the liquid fraction with minimum inhibitory compounds during HTC 35. The FTIR analysis also showed that at a wide range of severities (1.57-5.45) in HTC processes, water hydrolyzed and solubilized the amorphous part of hemicellulosic and cellulose (10 %), accompanied by partial breakdown of cell wall phenolics 64.

4. Utilization of HTC-AP

Resource recovery from HTC-AP is necessary because it contains large amounts of organics including carbohydrates, proteins, phenolic compounds, organic acids as well as some nutrients such as nitrogen and phosphorus. It would seriously pollute the environment if not properly treated as well as representing a wasted potential resource. In recent years, different methods have been applied to HTC-AP to recover energy and chemicals or to utilize the nutrients.

4.1 Valuable chemicals separation

As previously mentioned, the HTC-AP of biomass contains a large amount of organic compounds, many of which are valuable chemicals, including saccharides, lignin fragments, monosaccharides, phenol derivatives, fatty acids, cyclopentenones, long chain alkanes, esters, ketones and aldehydes 130, 131. Phenols and carboxylic acids are basic chemicals for the pharmaceutical and chemical industries 132. Monosaccharides can serve as platform chemicals for the production of ethanol and other products. Thus, direct separation of certain chemicals from HTC-AP could help to achieve efficient utilization of HTC-AP. Several methods for the separation of chemicals have been proposed.

Chromatographic separation is usually conducted with various resins, including adsorption resins, ion exchange resins, and cation exchange resins. Adsorption resin has been used to separate phenolic compounds, lignin fragments, furfural and 5-hydroxymethylfurfural from HTC-AP of lignocellulosic biomass 17, 133-135. With ion active groups on the skeleton, ion resins were widely applied to remove organic acids from HTC-AP, depending on the ion exchange or ion exclusive principles 136, 137. During this process, the saccharides in HTC-AP can be purified and some organic acids, such as acetic acid and lactic acid, can be recovered 138. Anion and cation exchange resin can separate the HTC-APs of lignocellulosic biomass into different fractions: monosaccharides, organic acids, and phenolic compounds 139. The cation resin can be used to further separate the mixture of glucose, xylose and arabinose, deriving xylose and arabinose with high purity 139. Since the composition of HTC-AP is very complex, the key of resin separation research is to improve the separation rate of different components. The regeneration of resin usually requires additional reagents, leading to high process costs and which needs further investigation.

Membrane separation is another potential method to separate target products from HTC-AP. The molecular weights of monosaccharides and acetic acid are quite different, making it possible for them to be separated by nanofiltration or reverse osmosis membranes 140. Aromatic compounds also have a higher retention ratio than acids on nanofiltration membranes with proper molecular weight cut-off, realizing the removal of organic acids into the permeate stream 141. Through two-stage nanofiltration or nanofiltration-reverse osmosis system, model HTC-AP can be separated into incomplete hydrolyzed biomass fragments, monophenols and cyclopentenones rich concentrate, and acetic acid permeate 142-143. Zhang et al. also used the nanofiltration technique to recover the carboxylic acid from HTC-AP and found that the membrane performance was strongly influenced by pH. Alkaline conditions led to much higher carboxylic acid rejection rate compared to acidic condition (from 17.3 % to 82.5 %) due to the charge exclusion effect 132. Nanofiltration can also be integrated with enzyme reaction to improve the separation rate of certain chemicals. With similar molecular sizes; glucose and xylose cannot be effectively separated by direct nanofiltration 144. Through enzymatically oxidization, glucose is converted into gluconic acid, which could be easily separated from xylose by nanofiltration 145. Similarly, the retention of phenolic acids on nanofiltration is significantly improved by polymerization of laccase, while the irreversible fouling and monosaccharide retention is reduced, facilitating the separation of phenolic acids and monosaccharides 145. However, the separation effect of actual HTC-AP is not as good as that of using model HTC-AP, which is affected by many factors including membrane fouling and the complexity of the actual HTC-AP.

The above separation methods of HTC-APs are still conducted in lab-scale experiments, and they will not be put into practice until the mechanisms are made clearer and costs made lower. The major obstacle for chemical separation from HTC-AP lies in the complicated composition of HTC-AP and the low concentration of valuable chemicals, which makes it difficult to extract pure single component from HTC-AP with high efficiency. In addition, the composition of HTC-AP is highly dependent on the feedstock and reaction conditions of the upstream HTL process. The existing separation techniques need to be further investigated and optimized in future studies to ascertain their performance, stability and cost effective against HTC-AP generated from a variety of biomass types. It is essential to develop more effective purification processes considering cost with combined separation techniques as a single method cannot handle the complexity of HTC-AP. For instance, other separation method such as single step or multiple step organic solvent extraction which can separate a group of chemicals from an HTC-AP based on different polarities of organic solvents 34, 146. The composition of the remaining HTC-AP was relatively simple and it was also tested for other utilization approaches. We found that a proper combination of chemical separation methods with other methods could efficiently separate high value-added chemicals as well as reduce the organic concentrations 34, 146.

One of the previous studies showed that the production of valuable chemicals (catechol, phenol, cresols, acetic acid, formic acid, furfural, and acetaldehyde) from lignin still face higher levels of price uncertainty 147. There are also some attempts for commercialization of HTC. Recently AVA Biochem established a 100% bio-based pilot scale plant for the production of 5-HMF via HTC, and it can also produce crystalline 5-HMF in various purities up to food grade. Now this process is ready for upgrade and enables the cost-effective production of 5-HMF on an industrial scale to become an economically competitive alternative to existing petroleum based chemicals 148. Another pilot scale plant was developed for extraction of chemicals through HTC of biomass at Aarhus University 149. The HTC process for the production of valuable chemicals is in the early stages of development (such as technical challenges) and therefore more lab and pilot-scale researches are needed to estimate its actual costs and environmental potential for different separation technologies.

4.2 Anaerobic digestion

AD constitutes a potentially complementary process that may allow further processing and concomitant resource recovery from HTC-AP. AD is a technologically simple and effectively biological process for the treatment of organic waste/wastewater, which can convert organics to biogas by anaerobic microorganisms 17, 34. It is known that biogas is a clean biofuel with many applications. Therefore, AD is a promising method to utilize HTC-AP especially considering its high organic contents. In fact, there are already some studies focusing on biogas production from HTC-AP via AD, and progresses have been achieved and the challenges for efficient biogas production have also been identified.

HTC-AP was directly used in AD in some previous studies. It was reported that only around 44 %-61 % of the COD was removed and converted to biogas after AD for the HTC-AP obtained from the HTC of mixed-culture wastewater algae in the temperature range of 260-320 oC, because part of the organics were not bio-degradable or even toxic to the microorganisms 17, 35. Our previous work showed that the methane yield of HTC-AP was strongly dependent on the temperature of HTC, e.g., the methane yield of HTC-AP achieved 314 mL CH4/g COD with HTC of straw at 200 oC, and it decreased to 217 mL CH4/g COD with HTC of straw at 320 oC. Further analysis showed that the amount of easily biodegradable organics, (e.g., saccharides) decreased while the hardly biodegradable organics (furans, phenols, etc.) increased with increase of HTC temperatures. Meanwhile, it has been shown that RT also had a negative correlation with methane production since the methane yield decreased from 314 mL CH4/g COD to around 250 mL CH4/g COD when the RT increased from 0.5h to 4 h. In addition, feedstock also affected the methane yield of HTC-AP 35. Under similar HTC conditions, the methane yield of HTC-AP of rice straw and sewage sludge were in the range of 217-314 mL CH4/g COD and 136-286 mL CH4/g COD, respectively. This could be due to the composition of sewage sludge (containing carbohydrate, protein, humus) being more complex compared to that of lignocellulosic rice straw, and some special reactions that make the HTC-AP more complicated such as the Maillard reaction (100-250 oC) that happened when the temperature reached a certain value 150. For the nitrogen-rich biomass (sewage sludge, algae, etc.), over 50 % of nitrogen in the feedstock was found to be retained in HTC-AP, and it resulted in the accumulation of ammonia and nitrogenous heterocyclic, which might inhibit AD process 20, 151.

Several methods have been proposed to remove the recalcitrant or toxic organics in HTC-AP to improve the biodegradability of the organics in HTC-AP. It was demonstrated that HTC-AP from cyanobacteria contained toxic compounds that could lead to low methane yield. Therefore, zeolite, granular activated carbon (GAC), and polyurethane matrices (PM), which had high capacity for pollutant adsorption, were added to the batch experiments for biogas production from HTC-AP of *cyanobacteria* 152. It was found that comparing with controls in the absence of such additives, the methane yields increased by 11 % (Zeolite), 37 % (GAC) and 36 % (PM), respectively. However, the adsorption of compounds has not been reported, and it was also not clear whether the addition of adsorbents in the anaerobic reactor can continuously enhance methane production considering the possible saturation after long-term operation. In another study, Shanmugam et al. utilized GAC in pre-treatment to remove recalcitrant or toxic organics in HTC-AP of algae, and found that 53 % of the COD in HTC-AP was removed by 30 % GAC, and that AD removed an additional 14.1% of the COD in HTC-AP, higher than that (12 %) using AD alone 153. GC-MS analysis was conducted and showed that GAC adsorption efficiently removed most of the organics, especially nitrogenous and phenolic compounds, which are potentially refractory organics. Nevertheless, the recovery of GAC was not tested in the above study, and this will be crucial for the economic pre-treatment of HTC-AP.

Organic solvents have been used to extract light oil from HTC-AP, and our previous work also examined whether the organic solvent extraction could affect methane yields of the HTC-AP. Four commonly used organic solvents (Petroleum ether (PE), cyclohexane (CH), dichloromethane (DM) and ethyl acetate (EA)) were chosen, and the methane yield of HTC-AP after PE extraction was improved by 21.7 %. DM was not suitable since there was no obvious methane production from HTC-AP presumably due to the residual presence of highly toxic DM after extraction. Although HTC-AP after EA extraction had a high methane yield, it was mainly due to the degradation of EA based on its high solubility 34. According to the above study, it is crucial to select the proper organic solvent for light oil extraction from HTC-AP in order to further improve the efficiency of AD.

Co-digestion was also tested in order to improve the methane yield of HTC-AP. [Fernandez](https://www.sciencedirect.com/science/article/pii/S096085241731578X" \l "!) et al. investigated the co-digestion of HTC-AP of algae and manure 4. Results showed that the highest methane yield was obtained at 20–30 % (S/L) HTC-AP, while there was a significant reduction (>80 %) in methane production at concentrations higher than 40 % (v/v) HTC-AP in the feed, This is probably due to the accumulation of chloride salts or inhibitory compounds such as pyridines, piperidines and pyrrolidines. Co-digestion can dilute the toxic compounds, and therefore promote methane production from HTC-AP.

Although there have been some progresses in improving methane yields of HTC-AP, more studies should be carried out to further improve the efficiency of AD. For example, Zero-valent iron (ZVI), which could be added to AD for HTC-AP treatment, is increasingly being applied in biological wastewater treatment to enhance the conversion of various contaminants such as nitro-aromatics and azo dyes 154, 155. In addition, ozone 156, electro-Fenton and Fenton reactions have been demonstrated to be used as pre-treatment to degrade some toxic or refractory organics in order to improve their anaerobic biodegradability 157, 158, and this could also be applied for AD of HTC-AP. It is also important to study the degradation mechanism of the major organic compounds (hydrocarbons, aromatic compounds, nitrogenous compounds, etc.) in HTC-AP obtained from HTC of various biomass to develop stable and optimized anaerobic treatment for effectively utilization of HTC-AP. Besides improving the efficiency of AD, the efficient treatment of AD effluents is also important since they often do not meet discharge standards and generally contain refractory organics. The combination of AD with aerobic treatment and advanced oxidation process (ozone-based processes, Fenton-based reactions, heterogeneous photocatalysis, sonolysis and combination of these technologies for generation of reactive free radicals) deserves investigation for the HTC-AP effluent. A combination of aerobic treatment and advanced oxidation has been successfully applied to the degradation of a wide spectrum of both organic and inorganic pollutants in effluents so as to meet the discharge standards 159-162.

4.3 Algae cultivation

Algae is one of the most potentially signiﬁcant sources for sustainable biofuels production in the future, and different algae species contain a wide variety of components (lipids, carbohydrates and proteins) and have different usages 163. However, mass production of algae needs a large amount of nutrient supply 164. It has been reported that algae can metabolize various waste streams including municipal wastewater and effluents from AD by using their nutrients and carbon sources. HTC-AP accumulates most of the feedstock essential nutrients (N, P, K et al.), and it could therefore support algae growth.

The use of HTC-AP in the algae culturing system could allow for multiple cycles of algae growth on each aliquot of incoming nutrients, which maximizes bioenergy production per unit of nutrient input. It has been shown in previous studies that the nutrients in HTC-AP could be used for algae cultivation 39, 40. Du et al. investigated the feasibility of using recovered nutrients from HTL-AP of algae for the cultivation of microalga *Chlorella vulgaris*, and it was shown that algae removed 45.5–59.9 % of total nitrogen, 85.8–94.6 % of total phosphorus and 50.0–60.9 % of COD on differently diluted HTL-AP (50-200 times) 40. Low-oil, mixed algal–bacterial biomass have been successfully cultured with the recycled HTC-AP in a previous study, and it was concluded that the ability to capture N and P from HTC co-products and to recycle them for algal cultivation would increase the potential of algal fuel production 165. HTC-AP of sewage sludge has been used for heterotrophic and mixotrophic microalgae cultivation 100, and algae had capability to grow after five consecutive cycles of growth in HTC-AP. It was also reported that increasing the ratio of NH3 to NH4+ could enhance the growth of algae 166, 167. HTC-AP was also demonstrated to provide macro and micro-nutrients to meet up the requirements of nutrients for algae growth. For example, Co is needed for vitamin B12 production and Mg is important for chlorophyll construction and photosynthesis which were present in HTC-AP 168-170. However, HTC-AP may lack certain nutrients other than N and P. For instance, Alba pointed out that Mg should be added to the HTC-AP of *Desmodesmus* sp. in order to provide enough nutrients for algae growth. The above study also claimed that algae production cost could be reduced by 50 % by replacing the nutrients with HTC-AP 166.

Although HTC-AP has been successfully used for the cultivation of algae, there are still serious challenges ahead. Many compounds present in HTC-AP can be inhibitory or toxic to algae, including ammonia and various organic compounds; e.g., HTC-AP of algae contained around 3000 mg L−1 NH4+-N in a previous study 39, and it was reported as highly toxic for several algae species 171. The organic compounds including phenol, toluene, propenal, allyl alcohol and benzene have been identified in HTC-AP and are known to be toxic to algal growth 172. Zhou et al. suggested that HTC-AP had inhibitory

**Table 4** Technologies for the utilization of HTC-AP

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Biomass | Parameters | Technology | Efficiency | Reference |
| Sludge | 300 °C for 20 min | Supercritical water gasification for H2 | Carbon efficiency 99.9 % | 38 |
| Dry poplar wood chips | 220 °C for 4 h | HTC-AP recirculation up to 4 times | COD from 50 to 101 g/L; TOC from 17.4 to 39.2 g/L; | 105 |
| Barley straw | 280-400 °C for 15 min | HTC-AP recirculation up to 3 time | oil yield increased from 34.9 to 38.4 wt. %; HHV from 27.29 to 28.4–29.4 MJ/kg | 76 |
| *C.vulgaris, S. dimorphous, C. fritschii, S. platensis* | 350 °C for 60 min; 300 °C for 60 min | Recycling for microalgae cultivation | *Chlorogloeopsis* at 400× and *Chlorella* at 200× achieved higher biomass yields | 37 |
| *Nannochloropsis oculata* | 350 °C for 60 min | HTC-AP used for heterotrophic micro-organisms growth | Best growth at 20 vol. % Aq Al | 173 |
| *Chlorella vulgaris* | 225-275 °C for 10-50 min | Recycling in presence of Na2CO3-HTC and HCOOH-HTC | Enhance bio oil yield, 32.6 wt. % & 16.1 wt. % respectively | 174 |
| *N. gaditana* | HTC at 350 °C for 15 min | SCWG at 450 °C for 30 min | 75 % of the nutrients replace nutrients recovered | 167 |
| Dried distillers grains | 350 °C for 20 min | HTC for recycling of HTC-AP up to 10 times with & without catalyst K2CO3 | Enhance the yield of bio oil 35 to 55 wt. % | 86 |
| Orange pomace | 175 & 260 °C for 30-120 min | Batch: 42 °C; AD for CH4 | 66.1 % for CH4 | 77 |
| *Nannochloropsis sp.* | 320 °C for 30 min | AD for CH4 or GAC + AD | 182 mL CH4/g COD | 153, 175 |
| Algal | 260-320 °C for 0-1.5 h | Batch; 37 °C; AD for CH4 | 44–61 % COD remove | 17 |
| Digestate of sewage sludge | 160 °C-250 °C for 30 min | Batch; 37 °C; AD for CH4 | 277 mL CH4/g COD at 220 °C; 260 mL of CH4 at 160 °C; 225.8 mL of CH4 at 250 °C | 111 |
| Cornstalk | 260 °C & 2.5 MPa for 0 h | Two-stage high-rate AD for H2 and CH4 | H2: 0–146 mL/g COD; CH4: 158–302 mL/g COD | 176 |
| Corn silage | 220 °C for 6 h | AD at 37 °C for CSTR & AF | COD (up to 75 %); TOC (up to 54 %) AF more stable as compare to CSTR | 104 |
| Swine manure | -- | Batch; 37 °C; AD for CH4 | 150–175 mL/g COD | 177 |
| Model biomass feedstocks | 200-350 °C for 20 min | Batch, 37 °C; AD for CH4 | 75–290 mL/g COD | 21 |
| Wheat straw | 180 °C for 15 min | Continuous (CSTR, UASB AF); 70 °C for H2 | 212 mL/g sugar | 178 |
| Sunﬂower stalks | 170 °C for 1 h | Batch; 35 °C for H2 | H2 yield decreased (2.04 – 0 mol H2) by increasing the dilute-acid hydrolyzate volume | 179 |
| Switchgrass | 190 °C for 10 min | UASB; 37 °C for H2 | 288 mL/g COD | 180 |
|  | | | | |

effects on algal growth because it contained high amount of ammonia and N heterocyclic compounds that disturbed the algae growth process, and significant dilution from 50 to 500 times was required 39, 181. *S. almeriensis* and *P. tricornutum* could not grow by direct use of HTC-AP obtained from *N. gaditana* and freshwater species *S. almeriensis* 117. Many nitrogenous toxic organic compounds were found inside the HTC-AP such as 3-dimethylamino-phenol, 2,2,6,6-tetramethyl-4-piperidone, 2,6-dimethyl-3-pyridinol, 2-picoline, pyridine, 1-methyl-2-pyrrolidinone and 2-pyrrolidinone from HTL of *Spirulina* algae 37, 182. Toxic compounds inside HTC-AP could be removed by using some adsorbents including activated carbon or zeolite 183. Activated carbon had been used in pre-treatment of HTC-AP before alga cultivation. In case of *Tetraselmis sp.*, the concentrations of phenolic and nickel were reduced from 1 to 0.1 (g/L) and 0.1 to 0. 067 (g/L) respectively, by being treated with activated carbon. The final dry weight of microalgae improved from 0.11 g/L to 0.41 g/L by keeping the dilution ratio of 1000 183.

It should be noted that most previous studies focused on the direct usage of HTC-AP for algae cultivation. However, many organics in HTC-AP are toxic to algae as previously mentioned, and the identification of such organics in various HTC-AP and the removal of them are necessary. The combination of AD and algae cultivation deserves further investigation since AD could remove certain amounts of organics that are toxic to algae and at the same time retain nutrients in the effluent 4, 184. In addition, different adsorbents could also be tested in order to remove such toxic organics for better utilization of HTC-AP as nutrients for algae growth. On a final note, the transformation of organics during algae cultivation have not been studied as far as we know, and this needs to be addressed.

4.4 Bioelectrochemical systems

Bioelectrochemical system (BES) is an emerging platform technology for wastewater treatment and for the production of energy and value-added chemicals, regarded as a sustainable and cost-effective method 185. Microbial fuel cell (MFC), the most normal BES, has been modified to microbial electrolysis cell (MEC), in which the electrons released by bacteria from the oxidation of organics in anode can combine with protons in the cathode to generate hydrogen, methane and other products instead of electricity by eliminating oxygen from the cathode compartment 186-188. BES has been successfully used for the production of energy and chemicals from various wastewater. Recently, it was also applied to HTC-AP and mainly focussed on hydrogen production 189, 190.

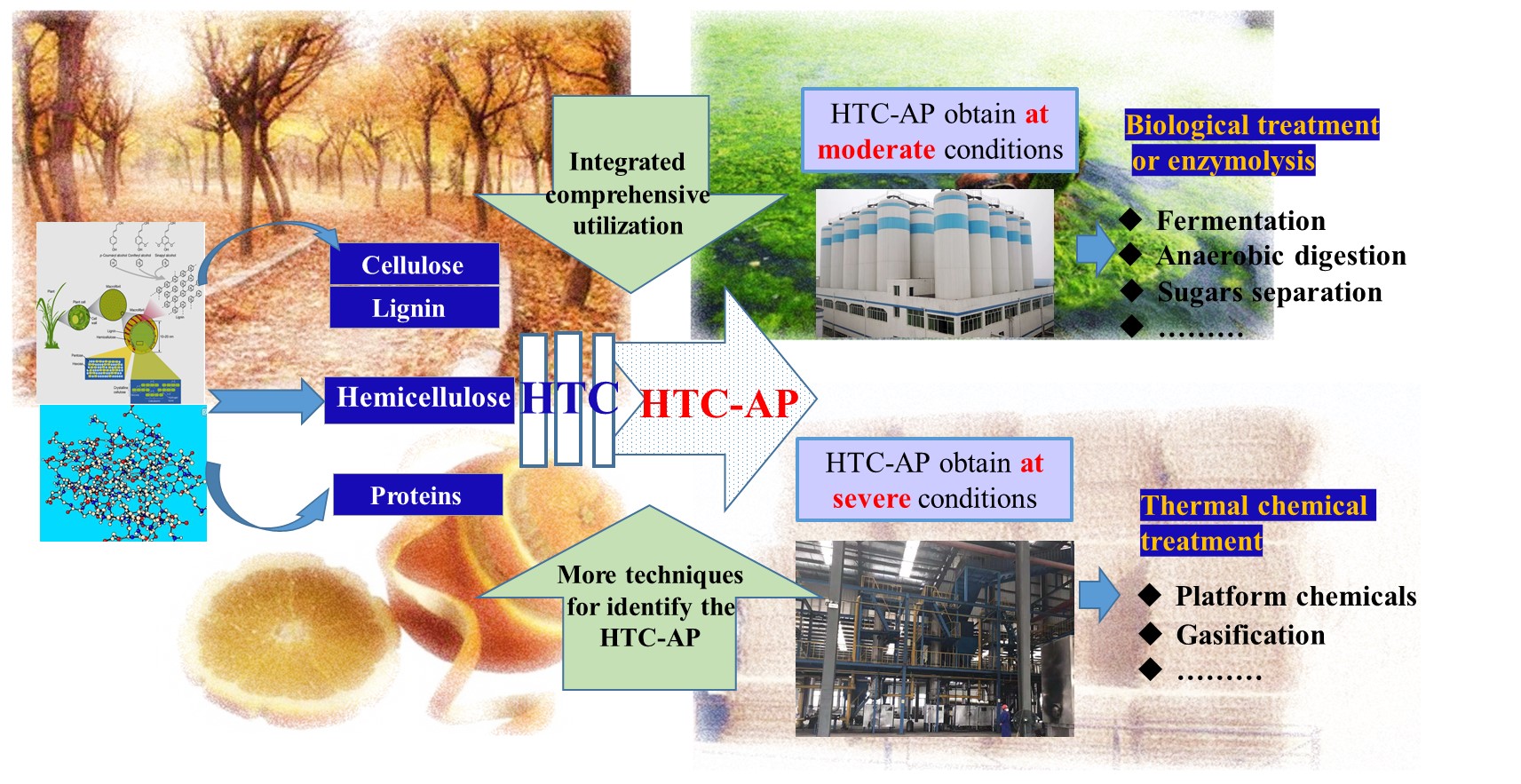
Furanic and phenolic compounds are commonly present in HTC-AP of lignocellulosic feedstocks, and these are highly inhibitory to certain microorganisms and can result in low efficiency of anaerobic digestion of HTC-AP 191. Efficient hydrogen production from a mixture of furanic and phenolic compounds at 400 mg/L by MEC has been demonstrated in a previous study 192. This article also identified the biotransformation of the compounds that took place via fermentation followed by exoelectrogenesis. However, a higher concentration (1200 mg/L) of the mixture seriously inhibited H2 production. Further study showed that the combination of the furanic and phenolic compounds gave a higher inhibitory effect to exoelectrogens than a single compound 193. The bio-transformation of three phenolic compounds (syringic acid (SA), vanillic acid (VA) and 4-hydroxybenzoic acid (HBA)) in MEC was also investigated and it was found that fermentative transformation occurred independently of exoelectrogenesis 190.

Fermentation products (acetate, catechol, and phenol for SA, VA and HBA respectively), which affect their further transformation by exoelectrogenesis, were also identified. Several recent studies also used real HTC-AP in MEC, which contains more complicated organics compared to synthetic wastewater. HTC-AP of cornstalk obtained at 312 oC was converted to H2 in a continuous up-flow fixed-bed MEC with different applied voltages, and the maximum hydrogen production rate was obtained at 1.0 V with 60 % COD removal efficiency 194. Although the increase of applied voltage to 1.2 V resulted in higher CO removal efficiency (80 %), the hydrogen production rate was significantly decreased, which could be due to the poor cathodic reaction without any catalyst and unstable electron transfer in the [anode](https://www.sciencedirect.com/topics/chemistry/anode). GC-MS analysis showed that furfural and HMF were fully removed, and most of the recalcitrant organics including [dimethyl phthalate](https://www.sciencedirect.com/topics/chemistry/dimethyl-phthalate) and [diethyl phthalate](https://www.sciencedirect.com/topics/chemistry/diethyl-phthalate) were well degraded. It was also shown that the organic loading rates (OLR) affected the performance of MEC, and maximum COD removal efficiency (around 83 %) was obtained at OLR 2 g COD/L/d with the maximum hydrogen production rate 3.92 mL/L/d 195. In addition, HTC-AP of swine manure was studied and it was found that the COD removal rate could reach 90-98 % in MEC, which was much higher than that of previous studies using AD process. However, the HTC conditions for swine manure was not mentioned in that study and the main organic composition in the HTC-AP was not reported. It should be noted that the coulombic efficiencies were very low (around 7 %-18 %) in the above studies. The acidogenesis and methanogenesis occurring in MEC might consume electrons to produce acids and CH4, and the internal recycling of electrons by electro-active bacteria may also contribute to efficiency reduction. Therefore, further studies should be conducted in order to improve the coulombic efficiencies of MEC to produce more H2.

More studies relating with BES for HTC-AP utilization should be conducted. Currently, most studies have utilized HTC-AP of lignocellulosic materials in BES, and the biotransformation of phenols and furans have been studied. HTC-AP of other biomass such as nitrogen-rich algae and sludge should also be tested in BES considering the presence of nitrogenous organics (Pyridine, diphenylamine, benzyl amine, etc.) with high toxicity in HTC-AP. In addition, the production of electricity and methane should also be investigated in BES for the utilization of HTC-AP. Considering methane production, the microorganisms in BES and AD are different, and therefore it might result in different degradation of organics in HTC-AP. However, there are no studies comparing organics degradation of HTC-AP in BES and AD systems. In addition, several studies have proposed to combine BES and AD to improve the overall conversion efficiency of organics to methane, and this could also be applied to HTC-AP 186. It should also be noted that BES itself still faces a lot of challenges including undesired electron sinks, high cost of materials for catalysts, electrodes and separators, and complex reactor configurations, all of which need to be solved for further scale-up 186.

4.5 Other technologies

Recent studies have also tried to develop other technologies for the utilization of HTC-AP (Table 4). It is known that *Rhodococci* strains can catabolize short and long chain alkanes, aromatics (nitro, hydroxyl, halogenated substituted), heterocyclic and polycyclic aromatic compounds and at the same time produce lipids, which could be further used for biofuels production 196-198. Therefore, the growth of *Rhodococci* strains on HTC-AP of wood and algae were studied, and it was found that more than 90 % COD could be removed and maximum accumulation of lipid could reach 0.46 g/g cell dry weight. This is very promising for lipid production by *Rhodococci* strains from HTC-AP. However, it should be noted that different types of HTC-AP and strains of *Rhodococci* significantly affected the lipid production, and this deserves further investigation 22, 199, 200. Previous studies showed that *Yarrowia lipolytica* is suitable for conversion of organics to lipid, and it also has ability to degrade organics such as hydrocarbons, aromatic compounds, and phenols 201-203, which might also be present in HTC-AP. Therefore, *Yarrowia lipolytica* could also be applied to the utilization of HTC-AP.



**Figure 3** Follow chart of HTC-AP and integrated utilization

Catalytic hydrothermal gasification (CHG) is a process in which organic compounds present in the HTC-AP are converted into gas consisting of H2, CH4, CO and CO2. It has been shown that the COD removal of HTC-AP of algae could reach 98 % with the addition of sodium hydroxide during CHG (600 oC and 35 MPa), indicating almost completed gasification of the organics in HTC-AP. Although CHG is very efficient for organic removal from HTC-AP, it is costly due to the use of noble catalysts (e.g., Ru/C and Pt/Al2O3) and is energy intensive due to the high operating temperature and pressure 204-206. This should be taken into consideration for the application of such process. The recycling of HTC-AP to HTC process has been applied, which could enhance the yield and quality of bio-crude oil. The yield was enhanced gradually from 34.9 wt. % to 38.4 wt. % after three cycles. And the HHVs of bio-crude oil from HTL with aqueous phase were slightly higher (28.4–29.4 MJ/kg) than those from HTL with fresh water. It is not known how many times the HTC-AP could be recycled, or whether the accumulation of certain organics in HTC-AP could have negative effects on bio-oil production after long-term recycling 76.

Currently, researchers are also trying to develop and adopt the combination of different technologies for utilization of HTC-AP. For example, anaerobic digestion and algae cultivation were combined for methane recovery and nutrients supply for the growth of *Chlorella vulgaris* from HTC-AP obtained from the HTC of swine manure, which was shown to be a feasible and advantageous process for energy recovery from HTC-AP 184.

5. Economic analysis and life cycle analysis (LCA) of HTC

Several previous studies made economic analysis and LCA of HTC. An economic analysis (EA) was made for HTC of woody biomass to produce the liquid fuel. The minimum selling price of woody biomass HTC fuel was US$ 4.44/gallon of gasoline equivalent (GGE) 207. In 2050, it was predicted that the cost of production would be around US$ 3.03–3.79/GGE (0.80–1.00 per litre), depending on the development of more cost-effective technologies and process improvements 208.

The integration of HTC of lignin to produce bio-chemicals within ethanol bio refinery was also evaluated. It was shown that a 2000 metric tonne per day (MTPD) corn stove bio refinery produced 61 MMgal/yr. of ethanol and different yields of lignin derived bio-chemicals. The minimum ethanol selling price (MESP) of $1.03 ± 0.19 per gallon was figured considering the production of lignin-derived catechol, phenol, cresols, acetic acid, formic acid, furfural, and acetaldehyde. The identified most inﬂuential factors on MESP were fixed capital investment, internal rate of return (IRR), feedstock price, cresols, catechol, and acetic acid prices. In terms of costs, the total purchased equipment cost was $114.5 MM, total installed cost (TIC) was $345.7 MM, and total capital investment was $624.5 MM. However, ethanol bio refinery adopting this lignin-to-chemicals strategy still faced higher levels of price uncertainty. The HTC process for the production of lignin-derived chemicals is in the early stages of development; thus more laboratory and pilot-scale research are needed to establish its potential for commercialization 147.

A LCA based on microalgae to green diesel via HTC was conducted using results from a continuous pilot-scale plant 209. The energy return on investment, as well as the greenhouse gas emissions, were calculated and compared to lipid extracted algal bio-diesel, petroleum fuels, corn-ethanol and soy biodiesel. It was shown that pilot scale facilities have life cycle burdens on equivalence with conventional biofuels. However, it was estimated that full scale facilities were more favourable since greenhouse gas emissions were lower compared to petroleum fuels and corn ethanol. The energy return on investment (EROI) was found to be between 1 and 3, and it was 2.7 for full scale production facilities. These EROI results were favourable compared to all conventional biofuels but not as high as petroleum-derived fuels. A sensitivity analysis revealed the yields of bio crude and efficient nutrient recycling had significant impacts to the EROI.

It should be noted that the utilization of HTC-AP was not included in the above analysis, which should further benefit to the HTC process. Nevertheless, HTC process is still in the early stages of development and more lab and pilot-scale researches are needed to establish its potential for commercialization.

6. Future directions

This review provides an up to date review on the progress of characterization and utilization of HTC-AP, and the challenges for future studies have been identified:

* The nature of composition of HTC-AP are both complicated and changeable, and the identification of the chemical compounds is still limited by today's analytical techniques, which affects the selection of methods.
* Part of the identified composition (dissolved sugar degradation products such as furans, production of nitrogenous organics like pyrazine and the uncontrollable precipitation of lignin-rich compounds) are recalcitrant or even toxic to microorganisms in biological treatment.
* There are still limitations for the technologies that investigated for the utilization of HTC-AP as previously mentioned.

HTC is mainly used for bio-oil and hydrochar production. HTC-AP is only a by-product and generally has complex nature, and therefore it might be difficult to produce HTC-AP with desired characteristics. In-stead, we can choose different methods for the utilization of HTC-AP based on their compositions. For example, if it is easier to be degraded by microorganisms, we can use biological process. If it contains a lot valuable compounds, we can choose separation technique. Currently, no one has suggested an optimum method for the utilization of HTC-AP, and a doable utilization of HTC-AP should be designed for comprehensive utilization of biomass. Sustainable strategies to develop alternative technologies for HTC-AP utilization will be critical.

Future studies could be conducted in the following aspects:

* Advanced techniques need to be adopted for identification of organic compounds, and the combination of different methods (such as FT-ICR-MS and LC-OCD-OND) to characterize in detail the HTC-AP is necessary to gain insight into HTC-AP composition.
* The residual organics in HTC-AP after various utilization methods need to be removed. This can be achieved by advanced oxidation, adsorption and other methods. In addition, pre-treatment of HTC-AP before utilization by advanced oxidation and adsorption could also be tested, which would reduce the toxicity and improve the utilization efficiency 184. Microbial pre-treatment could also be investigated. For example, *Cupriavidus basilensis* can mainly metabolize furfural and HMF, and therefore could be used to detoxify certain HTC-AP before biological utilization 210.
* Additionally, in order to strike a good compromise, it is of paramount importance to achieve an optimum control of the process between decomposition of macromolecules and production of inhibiters. Two different methods—the moderate and the severe HTC should be first chosen (Figure 3). If biological treatment is adopted to treat the HTC-AP, a moderate HTC condition is suggested to minimize the production of inhibitors. On the other hand, if thermal-chemical method such as gasification is used, a more severe HTC condition can be applied (Figure 3).
* Besides, more methods should be explored and designed. For example, using microwave instead of conventional heating for biomass HTC can achieve a higher conversion efficiency and sugar selectivity while inhibitors such as furan (higher sugar/inhibitors ratio) were mostly avoided 122. The HTC-AP containing low content of inhibitors will contribute to the higher efficiency for the subsequent biological utilization.

7. Conclusions

The composition of HTC-AP depends on both process conditions (e.g., temperature and reaction time) and substrate properties. There are also interactions between different organics (e.g., Maillard reaction). Therefore, the composition of HTC-AP is very complex and difficult to characterize. The combinations of different advanced techniques should be applied to identify the detailed compositions of HTC-AP. There have already been some progresses in the utilization of HTC-AP for production of various products. However, the efficient and complete utilization of HTC-AP is still a challenge due to the presence of toxic and refractory compounds. The development of new technologies for the full utilization of HTC-AP is urgent in order to make the HTC of biomass a sustainable processing technology.

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