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Hydrothermal liquefaction of biomass for jet fuel precursors: A review

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ABSTRACT

Climate change is an important issue facing the world today and carbon reduction has become the focus of attention for all countries. Alternative bio-fuels are an important means to achieve carbon emission reduction. The production of jet fuel precursors from biomass by hydrothermal liquefaction (HTL) has received a lot of attention due to its mild conditions and environmental friendliness. Lignocellulosic biomass and algal biomass are considered as the second and the third generation biomasses as promising raw materials for alternative fuel preparation. Among them, lignocellulosic biomass has been extensively studied due to its wide range of sources and can be divided into one-step HTL and stepwise HTL according to the process method. Algal biomass has been extensively studied experimentally due to its short growth cycle and the fact that it can sequester large amounts of carbon without taking up arable land. In this paper, the feedstock composition of different biomasses is reviewed for the HTL of biomass. A detailed review of the process characteristics, reaction pathways and influencing factors for the HTL production of jet fuel precursors from lignocellulosic biomass and algal biomass is also presented. Theoretical references are provided for further process optimization and bio-crude quality upgrading.

1. Introduction

With the increasingly severe global climate change, greenhouse gas emissions have become a focus of attention for all countries. The use of clean energy to replace traditional fossil fuels has been vigorously developed in various industries. In air transportation, due to the complex working environment of aircraft, high flight speed, and high requirements for energy supply equipment, jet engines are still the mainstream form of aviation engines in the medium to long term. Liquid fuel, as the “blood” of the engine, is also irreplaceable. Therefore, the aviation industry believes that biofuel is the most viable alternative to jet fuel in the near future [1]. The International Civil Aviation Organization (ICAO) reports that global fuel consumption is approximately 160 million tons. In addition, ICAO expects fuel consumption to increase by 2.2%–3.1% over the next 30 years, starting in 2015 [2]. The world commercial aviation industry has committed to becoming carbon neutral from 2020 and to halving the carbon emissions of the aviation industry by 2050 compared to 2005. This is a daunting challenge as commercial aviation is expected to continue growing by 4%–5% per year during this period.

Although the refining process of biomass requires the same thermal and chemical energy input as petroleum to prepare hydrocarbon fuels, the production of hydrocarbon fuels from biomass as a feedstock can effectively reduce CO_2 emissions in terms of the whole life cycle because biomass absorbs a large amount of greenhouse gasses during the growth process [3]. The current process of preparing hydrocarbon liquid fuels from biomass can be divided into two parts in terms of steps: biomass treatment and hydrogenation of bio-crude (intermediates), and there are usually four biomass treatment methods: oil and grease extraction (for oil-bearing plants), HTL, pyrolysis, and gasification. HTL has advantages in terms of environmental protection because it is carried out in water and does not require the use of large amounts of organic solvents. The process is carried out in subcritical water at 240–380 °C [4], which is lower than pyrolysis and gasification temperatures and has advantages in terms of energy consumption. HTL can also make full use of the components in biomass. Therefore, HTL is an advantageous treatment method for biomass. The pathway of HTL of biomass consists of three main steps, depolymerization followed by decomposition and recombination [5]. Changes in key process parameters such as reaction temperature and re-

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tention time can lead to changes in the repolymerization, condensation, and decomposition of components of different phases. Due to the chemical reaction mechanism of HTL of biomass is complex because biomass is a complex mixture of carbohydrates, lignin, proteins, and lipids [6].

Biomass fuels have been developed in three generations depending on the source. The first generation is mainly oil-bearing food crops, and there is a problem of “competition with people for food”. The second generation is lignocellulosic biomass represented by straw, and the third generation is algal biomass. Among them, the second generation biomass has been widely used in the production of bioethanol and biodiesel due to its wide source, but because of its low energy density it requires a high input of negative entropy flow in the production process. Moreover, the third generation biomass, on the other hand, is regarded as a source of energy material with important development prospects because of its short growth cycle, the ability to absorb large amounts of CO_2 during growth, the ability to be cultivated in seawater, and the fact that it does not occupy arable land [7].

Currently, a large number of research results exist on the hydrolysis of lignocellulosic biomass and the HTL of algal biomass. Hydrolysis of carbohydrates produces monosaccharides, furfural, 5-hydroxymethyl furfural (5-HMF), levulinic acid (LA), *etc*., while the HTL of algal biomass produces bio-crude with oil as the main product. However, algal biomass fractions also contain carbohydrates (mainly cell wall components). If it can be applied rationally, it will positively affect the efficiency of biomass utilization. Therefore linking the hydrolysis processes of the two generations of biomass is of great importance for the HTL of biomass. There are few studies and reviews on this part. In this paper, we will review the HTL of two generations of biomass based on their differences and connections in the application process.

2. Raw material for biomass

Both lignocellulosic biomass (derived from plant materials like agricultural residues, forestry waste, and energy crops) and algal biomass (derived from microorganisms such as algae) offer a wide range of feedstock options. This diversity allows for flexibility in selecting the most suitable feedstock based on factors like geographical location, climate conditions, and available resources. The use of cellulosic and algal biomasses promotes sustainable resource management. Lignocellulosic biomass can be sourced from agricultural residues and other waste materials, reducing the dependence on traditional fossil fuels. Algal biomass can be cultivated in non-arable land, including wastewater ponds, reducing competition with food crops for arable land. This section provides an overview of the feedstock characteristics of both types of biomass.

2.1. Lignocellulosic biomass

A large amount of woody fiber resources such as wood processing waste, corn cobs, corn straw, wheat straw, cotton seed husk, rice husk and sugarcane bagasse are produced annually in the world, which are rich in woody fiber. The annual production of lignocellulosic biomass is about 170 billion tons [8], and it has not been efficiently utilized and properly treated, which has caused serious environmental pollution and waste of resources. Therefore, the resource utilization of lignocellulosic biomass has been one of the research topics in biomass energy. In 2006, Chheda *et al.* [9] proposed a complete process flow for the production of liquid alkanes from carbohydrates in biomass through a combined process of dehydration → aldol condensation → hydrogenation and dehydration → hydrogenation, and demonstrated the feasibility of the process.

The main components in lignocellulosic biomass are cellulose, hemicellulose and lignin. The differences in their sources lead to differences in the content of their components [10]. Cellulose, as the main component of plant cell walls, is stable in nature and is usually combined with hemicellulose and lignin. Rice straw, corn straw, wheat straw, hardwood, softwood, and other lignocellulosic biomass feedstocks can be used as raw materials for liquid-phase decomposition of biomass, and their prices are relatively cheap and abundant in China. Lignocellulosic biomass has a complex cellulose-hemicellulose-lignin structure, and they can be converted into fuels and high value-added chemicals such as renewable gas, bio-oil and ethanol through thermochemical and biochemical conversion technologies. A summary of the content of various components in a typical biomass is shown in Table S1 (Supporting information) [10–14]. The molecular structure of the main components of lignocellulosic biomass is shown in Fig. 1.

From Table S1, it can be concluded that lignocellulosic biomass generally has high cellulose and hemicellulose content. Meanwhile, cellulose and hemicellulose are important raw materials for the preparation of liquid alkanes by hydroxyaldehyde condensation [15]. The products of lignin depolymerization and hydrogenation are aromatic, and pyrolysis of lignin has become a more common mode of depolymerization due to its high depolymerization requirements [16]. Therefore, this paper focuses on the hydrolysis of cellulose and hemicellulose in lignocellulosic biomass.

2.2. Algae biomass

Compared to traditional terrestrial biomass, microalgae have obvious advantages: first, they reproduce quickly and have a short growth cycle. If calculated on an area basis, its yield is 15–300 times that of other traditional oil crops, which makes it possible

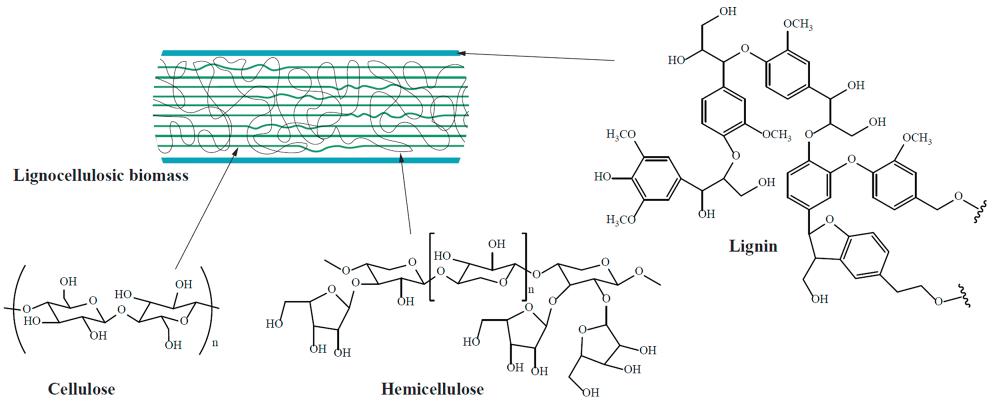

Fig. 1. Molecular structure of the components of lignocellulosic biomass.

to meet large demand. Second, it can be harvested all year round and does not require arable land. Third, microalgae farming consumes less fresh water than terrestrial crops, and the salts and organic matter in its own water can also be used as fertilizer [7]. Fourth, carbon dioxide can be used as a carbon source for microalgae growth, thus the algae culture process can absorb the greenhouse gasses in the atmosphere [17]. Fifth, the carbohydrate polymerization in algal biomass is lower than that of lignocellulosic biomass, which is more easily degraded [18]. Therefore, the development of hydrocarbon fuel production using microalgae has a broad application prospect.

The main components in algal biomass are proteins, lipids and carbohydrates. The content of the components varies among different species of microalgae, with some of them containing up to 30%−50% lipids [19]. Microalgae with high lipid content are more suitable as feedstock for biofuel preparation. A summary of the chemical composition content of typical microalgae species is shown in Table S2 (Supporting information) [18,20–26].

In summary, lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, of which cellulose and hemicellulose are the main carbohydrate components, rich in glucose and xylose units. In contrast, algal biomass consists mainly of proteins, fats, carbohydrates, and a variety of biologically active substances, which are particularly characterized by fatty acid-rich fats.

3. Reaction mechanism of HTL

In order to make the rationale for the effect of process conditions on the target and by-products of HTL of biomass clearer, the hydrolysis mechanisms of the major components in biomass are reviewed in this section.

3.1. Hemicellulose HTL

Cellulose and hemicellulose have different hydrolysis processes and products due to their different structures and degrees of polymerization. Hemicellulose produces five-carbon sugars (including xylose and arabinose) and six-carbon sugars (including glucose, galactose, mannose, *etc.*) by hydrolysis, while xylose, which is usually the most abundant of the hydrolyzed monosaccharides, is used as a model compound instead of hemicellulose in most studies [27]. The hydrolysis reaction of hemicellulose is relatively mild and has a high conversion rate, which can reach more than 90% under certain conditions [28–30]. Five-carbon sugars can generate furfural, an important platform compound, through dehydration reactions. Xylose dehydration to produce furfural from biomass is a major commercial process to add value to biomass [31]. Furfural is a versatile key derivative that can be used as an excellent solvent for organic materials and for the synthesis of desired compounds such as furfuryl alcohol, 2-methylfuran [32], succinic acid [33] and maleic acid [34]. It can also be converted to alkanes by condensation hydrogenation [15]. Therefore, furfural has been identified as a valuable platform chemical for biofuel production.

Furfural is chemically unstable and is prone to resinization losses and acid polymers [35], and will also polymerize with xylose or itself under certain conditions to produce substances such as humins. This affects the furfural yield and negatively affects equipment maintenance. The possible reactions and side reactions of hemicellulose during hydrolysis are shown in Fig. 2a.

3.2. Cellulose HTL

The hydrolysis temperature of cellulose is usually higher than that of hemicellulose. In the hydrolysis of lignocellulose, the hydrolysis of cellulose generally occurs after hemicellulose [14]. In the hydrolysis reaction of cellulose, it is first hydrolyzed to glucose. Glucose is isomerized to fructose during the catalytic conversion, while it can also form water-insoluble oligosaccharides of low polymerization by its own condensation. Further dehydration of fructose can be converted to 5-HMF, which is an important platform compound for cellulose degradation and an important raw material for industry. 5-HMF and its derivatives are widely used in fine chemicals, pharmaceuticals, degradable plastics, energy and other fields [36]. Jiang *et al.* [37] summarized in detail the chemical processes involved in the conversion of 5-HMF to a variety of fuels and chemicals.

Through hydration reaction, 5-HMF can be converted to LA and formic acid. LA, an important platform compound, has been ranked as one of the top 10 biomass-derived chemicals [38]. A portion of glucose undergoes condensation with 5-HMF to produce some by-products, which are sources of humins substances and some soluble polymers. Glucose also produces small amounts of furfural during the conversion process [39]. The possible reactions and side reactions of cellulose during hydrolysis are shown in Fig. 2b.

3.3. Lipid HTL

As the main component of lipid-based biomass, lipids contribute the most long-chain fatty acids and fatty acid esters through HTL, which are important precursors of carbon alkanes. Lipids generally present in the form of triglycerides in algae, which are hydrolyzed to produce fatty acids and glycerol. If alcohols are added during HTL, part of the fatty acids will be converted to fatty acid esters [40]. A few fatty acids also undergo amination reactions with amines to form fatty acid amides, decarboxylation to alkanes and alkenes, and reactions with amino acids to form nitrogen-oxygen (N&O) heterocyclic compounds, *etc.* [24,41]. The mechanism reaction of lipids hydrolysis is shown in Fig. 2c.

3.4. Protein HTL

Protein, as a highly abundant component of algal biomass, is important for the influence of HTL products. Protein increases the nitrogen content in bio-crude, which is detrimental to the preparation of bio-aviation fuel. Therefore studying the hydrothermal properties of proteins has become a concern for many researchers. According to the study of Hanna *et al.* [42] on HTL of soy protein, protein hydrolysis will start at 140 °C, and as the temperature increases, the protein hydrolysis products first rise and then fall, reaching an extreme value at 260 °C. The hydrolysis temperature usually lasts until about 400 °C [43]. In addition to deamidation to form amines and self-condensation to form cyclic amides, the hydrolysis products of proteins and amino acids also undergo a Maillard reaction with reducing sugars to form *N*-heterocyclic compounds [44]. Meanwhile, amino acids generate hydrocarbons and some oxygenated compounds through diamino-decarboxylation, which go to the oil phase and can increase the yield of bio-crude. The reaction mechanism of protein hydrolysis is shown in Fig. 2d.

3.5. Interaction

During HTL of microalgal biomass, the hydrolysis product of carbohydrates, reducing sugars, and the hydrolysis product of proteins, amino acids, undergo an interaction called Maillard reaction (Fig. 2e) [44]. N&O heterocyclic compounds (including Indoles, Quinolines, *etc.*) will be generated, and a small part of them will enter the bio-crude, negatively affecting the oil quality. N&O heterocyclic compounds can refined by hydrogenation to form cycloalkanes and aromatic hydrocarbons, but this requires more stringent conditions [45]. Zhang *et al.* [44] used soya protein

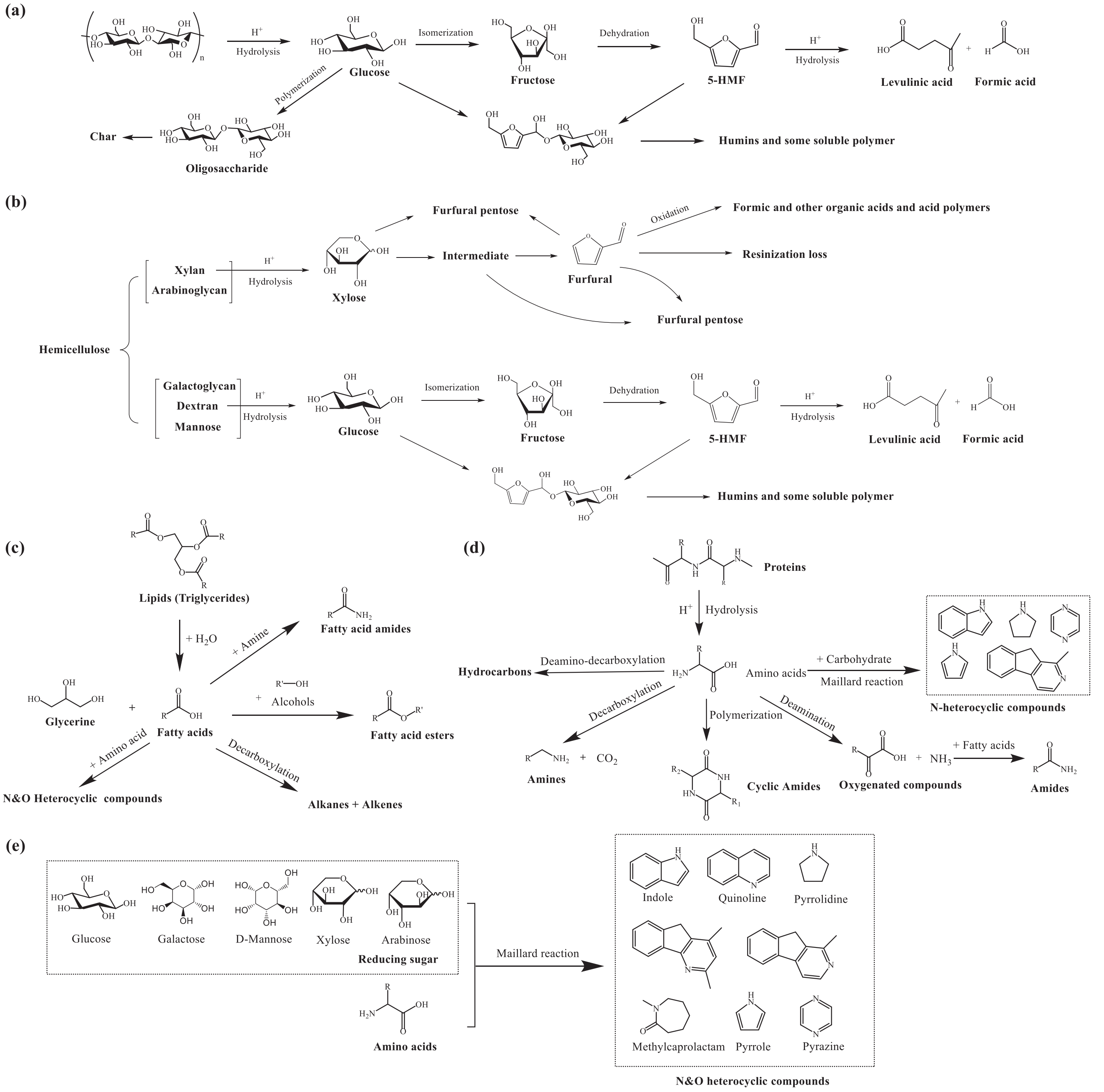

Fig. 2. Possible reactions pathways of (a) hemicellulose conversion platform compounds, (b) cellulose conversion platform compounds, (c) HTL of lipids, (d) HTL of protein, and (e) Maillard reaction to form N&O heterocyclic compounds.

and glucose as model compounds to study the effect of temperature on the Maillard reaction and found that the product increased with increasing temperature from 160 °C to 280 °C. Sheng *et al.* [46] found that the interaction could be maximized when the ratio of soya protein to glucose was 3.

4. Process conditions of HTL

4.1. HTL of lignocellulosic biomass

4.1.1. Effect of process methods

HTL of lignocellulosic biomass is divided into one-step HTL and stepwise HTL according to whether the hydrolysis reaction and dehydration reaction are carried out in the same reactor [47], as shown in Fig. 3. At present, the one step hydrolysis method is used more often in industry, because its process is relatively simple and the investment in reaction equipment is relatively small. However, the disadvantage is also very obvious, because of the instability of furfural, it is easy to react with xylose or itself in the aqueous phase to generate by-products such as humins, thus having a negative impact on the yield of furfural. The main reasons affecting the efficiency of hydrolysis are temperature, catalyst type, liquid phase environment and other factors.

4.1.1.1. One-step HTL. The one-step method is divided into single-phase system and two-phase system according to the liquid phase environment system. The current industrial application of furfural is basically single-phase system. Because of the instability of

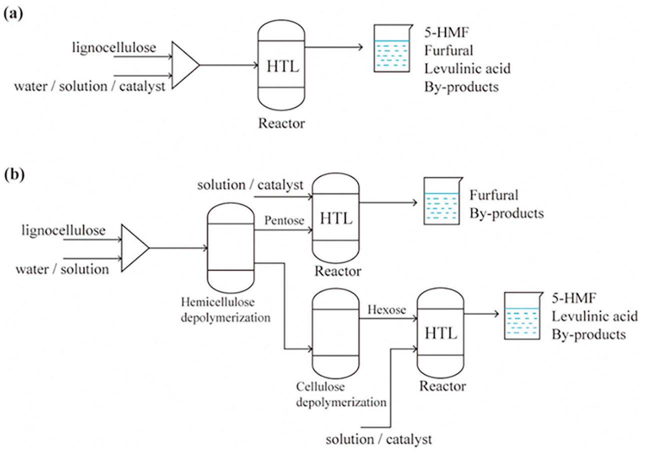

Fig. 3. Process flow diagram of (a) one-step HTL and (b) stepwise HTL.

furfural, it is easy to transform into other substances in the process of hydrolysis, so the yield of producing furfural in single-phase system is relatively low. The two-phase system is to extract the furfural generated in the aqueous phase into the organic phase rapidly by adding the organic solvent insoluble in water, so as to reduce the side reaction in the catalytic reaction and improve the yield of furfural. The study by Avci *et al.* [48] showed that dilute H_3PO_4 is a better catalyst than sulfuric acid for the production of furfural from corn stover, at a solid-liquid ratio of 1:20, H_3PO_4 vol concentration of 0.75% and a temperature of 200 °C for 20 min of holding, a maximum furfural yield of 10.8 ± 0.3 g/100 g of straw was obtained, corresponding to a theoretical yield of 61.6%. Girisuta *et al.* [49] studied the detailed kinetics of cellulosic acid-catalyzed hydrolysis to LA using microcrystalline cellulose as raw material, and the maximum yield of LA was 60 mol% at 150 °C, 1.7 wt% initial cellulose intake, and 1 mol/L sulfuric acid. Xu *et al.* [27] studied the preparation of furfural from corn stover by HTL, using water/γ-pantolactone (GVL) = 1:9 (v:v) as solvent and *p*-toluenesulfonic acid (PSTA-POM) as catalyst, and the yield of furfural was 80.4 mol% when held at 170 °C for 10 min. Also the catalyst could be cycled at least 5 times without significant loss of activity, and the furfural yield was increased to 83.5 mol% by holding at 190 °C for 100 min. Li *et al.* [30] studied a one-step HTL process for the conversion of corn stover to furfural and LA catalyzed by SAPO-18 zeolite, using water/GVL (1:4) as the reaction solvent. The ratio of Brønsted and Lewis acid sites affected the selectivity and yield of the products. When B/L = 0.11, the yield of furfural could reach 95.1 mol% with 40 min retention time at 205 °C. The yield of LA could reach 70.2 mol% with B/L = 0.17 at 180 °C with 80 min retention time.

Regarding two-phase systems, Chheda *et al.* [50] studied the dehydration of monosaccharides and polysaccharides in a two-phase system to produce furfural and 5-HMF. The results showed that the use of an organic extraction phase consisting of a two-phase system methyl isobutyl ketone (MIBK)–2-butanol mixture or dichloromethane (DCM) can handle high concentrations of feedstock (10 wt% to 30 wt%) with higher solvent recovery, which can lead to higher economic benefits. Shi *et al.* [39] used a two-phase system consisting of THF and concentrated $NaHSO_4$-$ZnSO_4$ as a catalyst to convert cellulose to aqueous 5-HMF after hydrolysis. The yield of 5-HMF was 53% and cellulose conversion was 96% when held for 60 min. Kaur *et al.* [51] studied the yield of hemicellulose converted to furfural using pre-hydrolysate as a raw material, and the yield of furfural was 65% in a two-phase system consisting of methyl isobutyl ketone and acidic hydrolysate held at 170 °C for 100 min. Xing *et al.* [29] studied the hemicellulose extracted from coniferous wood by acid-catalyzed study, the furfural yield was up to 87 mol% in a two-phase system of dilute hydrochloric acid-tetrahydrofuran, held at 160 °C for 60 min.

4.1.1.2. Stepwise HTL. Stepwise HTL, which is now widely studied in the laboratory, involves the hydrolysis of biomass to monosaccharides and the dehydration of monosaccharides to platform compounds in separate reactors. Since hemicellulose depolymerization temperature is lower than that of cellulose and lignin, hemicellulose can be hydrolyzed first by low temperature pretreatment. The reaction process for the production of furfural, 5-HMF and LA from lignocellulosic biomass by a stepwise process broadly consists of (1) hydrolysis of hemicellulose and cellulose to monosaccharides (hemicellulose completes hydrolysis before cellulose), (2) catalytic conversion of five-carbon sugars to furfural, and (3) catalytic conversion of six-carbon sugars to 5-HMF or LA [52].

4.1.1.3. Hydrolysis of cellulose and hemicellulose to monosaccharides. During the HTL of biomass, hemicellulose undergoes hydrolysis first, while its hydrolysis yield is relatively high. Zhang *et al.* [53] studied and analyzed the conditions of hemicellulose hydrolysis in rice straw, and the hemicellulose hydrolysis rate was 77.0%–94.2% in 3% sulfuric acid solution, biomass dry substrate/solution = 1/10, and holding at 120 °C for 90 min. Liu *et al.* [54] found that in the study of hemicellulose hydrolysis in corn straw with 0.1 mol/L $FeCl_3$ as catalyst and holding at 140 °C for 20 min yielded 87.7% xylose. Zu *et al.* [55] treated corn stover with dilute hydrochloric acid to improve xylose yield, and then treated the residue with lime to change the lignin structure and dissolve the cellulose surface. Dilute hydrochloric acid pretreatment at 120 °C for 40 min followed by lime pretreatment at 60 °C for 12 h (lime loading of 0.1 g/g) with a cellulase dosage of 5 FPU/g resulted in 78.0% and 97.0% glucose and xylose yields, respectively.

Cellulose is hydrolyzed under higher conditions, and high yields are usually obtained with the combined action of catalysts and bioenzymes. Hou *et al.* [56], by pretreating rice straw with a two-stage combination of choline chloride/oxalic acid-choline chloride/urea, found that holding at 100 °C for 3 h in a solution containing 5% water was the optimal process, and the yield of glucose during enzymatic digestion was 90.2%, and the xylose yield was 12.8%. In a study on catalytic hydrolysis of bagasse, Chen *et al.* [57] found that pretreatment with 0.1 mol/L $FeCl_3$ (solid-liquid ratio of 1/10) for 30 min at 170 °C in a liquid phase environment, followed by enzymatic digestion using cellulase and β-glucosidase, 81.9% of cellulose could be converted to glucose.

4.1.1.4. Catalytic conversion of pentose to furfural. Furfural can be produced by dehydration of xylose, so researchers usually use xylose as a model compound when studying the yield of furfural from HTL of substances. Zhang *et al.* [58] found high activity through the dehydration reaction of xylose catalyzed by Bronsted acid, with a high furfural yield of 78.5 mol% at water/GVL (1:19) as the solvent and holding at 170 °C for 30 min. Zhang *et al.* [59] studied the reaction of $AlCl_3$-catalyzed dehydration of xylose to furfural, with ionic liquid [BMIM]Cl as the liquid phase environment, and a furfural yield of 82.2 mol% could be obtained at 160 °C for 1.5 min of holding, which was higher than the furfural yields of 19.1%, 31.4%, and 33.6% produced by direct hydrothermal treatment of untreated corn cob, grass, and pine wood. Meanwhile, after extraction of furfural, [BMIM] Cl and $AlCl_3$ could be recovered after four consecutive runs and without activity loss. There are additional yield summaries for furfural detailed in Table 1 [27,30,51,29,60].

Table 1
Summary of the yield of HTL of cellulose-based biomass.

Liquid phase medium	Catalyst	Reaction conditions	Mass yield (%)	Refs.
Hydrolysis of hemicellulose (pentosan) to pentose: $(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5$				
3% H_2SO_4, Solid/solvent ratio = 1:10		120 °C, 90 min	77–94.2	[53]
0.1 mol/L $FeCl_3$	$FeCl_3$	140 °C, 20 min	87.7	[54]
1 wt% HCl	cellobiase dosage of 20 CBU/g substrate	120 °C, 40 min	97.0	[55]
Hydrolysis of cellulose (dextran) to glucose: $(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$				
	Choline chloride/oxalic acid-choline chloride/urea	100 °C, 3 h	90.2	[56]
BMIMCl, Solid/solvent ratio = 1:10	Cellulase and β-glucosidase, 0.1 mol/L $FeCl_3$	130 °C, 30 min	81.9	[57]
lime loading: 0.1 g/g, pH 12.4	Cellulases dosage of 5 FPU/g substrate	60 °C, 12 h	78.0	[55]
Conversion of xylose to furfural: $C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O$				
Water/GVL = 1:9	PSTA-POM	170 °C, 10 min	51.5	[27]
Water/GVL = 1:19	Bronsted acid	170 °C, 30 min	50.2	[58]
[BMIM]Cl	$AlCl_3$	160 °C, 1.5 min	52.6	[59]
Water/GVL = 1:4	SAPO-18 (B/L = 0.11)	205 °C, 40 min	60.9	[30]
MIBK, pH = 1.25	H^+	170 °C, 100 min	41.6	[51]
Tetrahydrofuran (THF)	HCl	160 °C, 60 min, 220 psig	55.7	[60]
Water/THF = 1:2	0.48 mol/L HCl	164 °C	57.6	[29]
Conversion of arabinose to furfural: $C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O$				
Butane/water = 4:1	Lewis acidic ionic liquid	140 °C, 30 min	38.4	[62]
98 wt% Formic acid		170 °C, 60 min	39.7	[61]
Oxalic acid		200 °C, 50 min	33.9	[64]
Water-cyclopentyl methyl ether	Nafion NR50, NaCl	170 °C, 40 min	26.9	[63]
Conversion of glucose to 5-HMF: $C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3H_2O$				
Water/diglyme = 1:3	ZrP	180 °C, 2 h	42.7	[67]
Water/diglyme = 1:3	ZrP	180 °C, 3 h	44.1	[67]
Lewis+Bronsted	m-ZrP	155 °C, 6 h	32.3	[68]
[EMIM]Cl	$CrCl_3$	100 °C, 3 h	47.6	[66]
[EMIM]Br	Al_2O_3-b-0.05	140 °C, 3 h	34.8	[69]
DMSO	SnPCP@MnO_2−PDA	150 °C, 5 h	39.1	[70]
Conversion of glucose to LA: $C_6H_{12}O_6 \rightarrow C_5H_8O_9 + CH_2O_2 + H_2O$				
Water/GVL = 1:4	0.3 mol/L H_2SO_4	160 °C, 90 min	41.3	[71]
Water/GVL = 1:4	SAPO-18 (B/L = 0.17)	180 °C, 80 min	45.2	[30]
Solid/water ratio = 1:15	$S_2O_8^{2-}$/ZrO_2-SiO_2-Sm_2O_3: 13.3%	200 °C, 10 min	45.	[72]

Arabinose, as one of the monosaccharide components of hemicellulose hydrolysis, is usually less abundant than xylose, and the yield of corn stover hydrolysis is about 2% [55]. Its dehydration reaction has also been studied by some researchers [61–64]. Zhao *et al.* [62] used a butane-water mixture as a green solvent system for the production of furfural from arabinose and obtained 60% furfural yield and 100% conversion of arabinose by holding at 140 °C for 30 min using Lewis acidic ionic liquid as a catalyst. According to the kinetic analysis, the decrease in furfural yield was mainly due to the condensation reaction between furfural and intermediates, and the self-degradation of furfural had less effect on the decrease in yield when the reaction time was extended. Dussan *et al.* [61] focused on the dehydration kinetics of several monosaccharides and found that the formic acid concentration was more selective for the dehydration of L-arabinose to furfural than for D-xylose. The predicted maximum furfural yield of L-arabinose (62.1%–63.6%) was lower than the predicted maximum furfural yield of D-xylose (65.0%–67.7%). Le *et al.* [63] investigated the dehydration of pentose to furfural in a water-cyclopentyl methyl ether (CPME) two-phase system under microwave radiation. Furfural was generated from D-xylose, L-arabinose, and xylan in the presence of Nafion NR50 and NaCl heated between 170 °C and 190 °C with maximum yields of 80%, 42%, and 55%, respectively.

4.1.1.5. Catalytic conversion of hexose to 5-HMF or LA. The current types of catalysts for the preparation of 5-HMF include homogeneous catalysts (including inorganic acids, ionic liquids, and metal chlorides), and non-homogeneous catalysts (including molecular sieves, ion exchange resins, metal oxides and their complexes, heteropolyacids, and carbon-based solid acids) [65].

Zhao *et al.* [66] investigated the catalytic effect of the metal chloride $CrCl_3$ in ionic liquid solvent [EMIM]Cl on the conversion of glucose to 5-HMF, and the yield of 5-HMF was close to 70 mol% when held at 100 °C for 3 h. Various metal halides were also found to catalyze the conversion of fructose to 5-HMF, and only trace amounts of LA were formed in these reactions, indicating that metal halides can enhance the selectivity of 5-HMF. Jain *et al.* [67] in their study of the catalytic conversion of glucose and fructose to 5-HMF found that zirconium phosphate could act as an effective catalyst for the generation of 5-HMF using water/diethylene glycol dimethyl ether(diglyme) = 1:3 (v/v) as a biphasic system, with a 5-HMF yield of 61 mol% at 180 °C for 2 h and 63 mol% at 180 °C for 3 h. Saravanan *et al.* [68] investigated the effect of solid acid catalysts on the conversion of glucose and 5-HMF yield in HTL. The strong Lewis acid and strong base sites in zirconium m-phosphate (ZrP) effectively promoted the isomerization of glucose to fructose, which was dehydrated only at the weak Brønsted acid site, with a maximum conversion of glucose up to 83.8% and a maximum yield of 5-HMF up to 46.6 mol% at the reaction conditions of holding at 155 °C for 6 h. Hou *et al.* [69] were able to achieve yields of up to 49.7% for the conversion of high concentrations of glucose (up to 10 wt%) to 5-HMF by using Al_2O_3-b-0.05 as a catalyst in [EMIM]Br media. The conversion was higher than that of

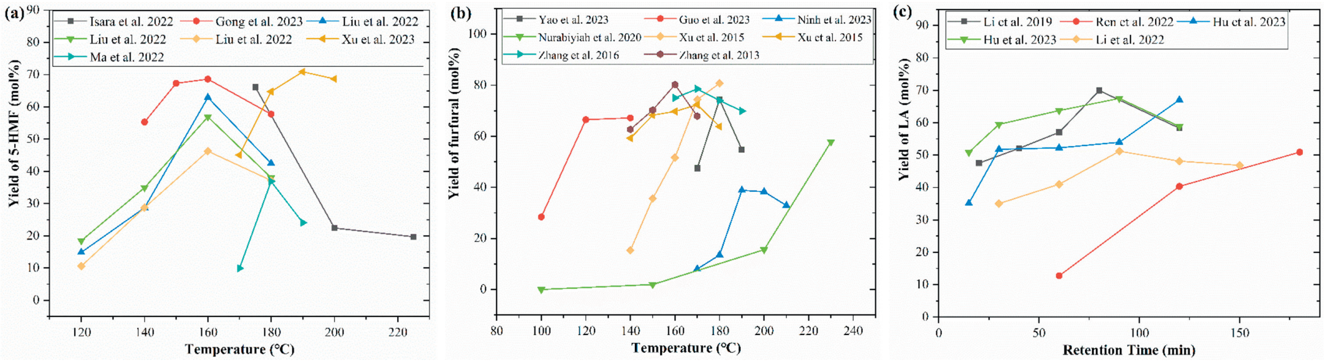

Fig. 4. Effect of temperature on yield of (a) 5-HMF [73,75–78], (b) furfural [27,58,59,79–81,83], and (c) LA [30,82,84,85].

the non-homogeneous [EMIM]Cl/Al_2O_3-b-0.05 and homogeneous EMIMBr/$AlCl_3$ ionic liquid systems. Li *et al.* [70] found that MnO_2-PDA was able to catalyze the conversion of glucose to 5-HMF, and the yield of 5-HMF was 55.8% in dimethyl sulfoxide (DMSO) and 41.2% in water/THF under the synergistic effect of SnPCP and MnO_2-PDA, with little loss of activity after 5 repetitions of SnPCP@MnO_2-PDA.

LA was first obtained from the catalytic preparation of glucose and fructose with high yields, but the high cost of monosaccharides has prevented LA from being used in large-scale applications. However, biomass is abundantly rich in cellulose, and the cost of LA can be significantly reduced by using cellulose-based biomass as feedstock. Li *et al.* [71] catalyzed the two-step hydrolysis of corn stover to furfural and LA in water/GVL by 0.2 mol/L sulfuric acid. The low temperature hydrolysis at 140 °C and high temperature hydrolysis process at 190 °C resulted in 70.65 mol% yield of furfural and 57.7 mol% yield of LA. Chen *et al.* [72] found that the theoretical yield of LA could reach 70% by hydrolysis of rice straw under the optimal conditions of holding at 200 °C for 10 min, 13.3% solid super acid, and 1:15 solid-liquid ratio.

The yields for different reaction conditions are summarized in Table 1.

4.1.2. Effect of reaction conditions

Drawing insights from the compilation of diverse process methods outlined in Table 1, it becomes evident that the pivotal reaction conditions shaping the conversion of biomass into platform compounds encompass reaction temperature, retention time, catalyst composition and loading, as well as liquid phase medium. In the previous section, the effects of different process methods and solvent systems on the yield of target products were mainly described. In this subsection, we will distill and summarize the main trends of the effects of reaction temperature, retention time, and catalyst.

4.1.2.1. Reaction temperature. Reaction temperature is an important factor affecting the yield and selectivity of furfural, 5-HMF and LA. In general, there exists an optimal reaction temperature for the preparation of platform compounds. Researchers have carried out a series of experimental studies on the effect of temperature on the yield of platform compounds (Fig. 4) [27,30,58,59,73–85].

The trend of 5-HMF yield with temperature is summarized in Fig. 4a. It can be concluded that 5-HMF shows a trend of increasing and then decreasing with increasing temperature. The optimum temperature is usually between 150 °C and 200 °C. Among them, Xu *et al.* [78] obtained an optimum yield of 70.95 mol% at 190 °C using microcrystalline cellulose as raw material and (5)Hf/ZSM-5 as catalyst with the addition of $AlCl_3$, NaCl, a liquid phase environment of H_2O/THF = 1/4 (v/v) and a retention time of 120 min. Gong *et al.* [75] also obtained a high 5-HMF yield of 67.3 mol% by catalytic conversion of Ball milled cellulose formate with H_2O/DMSO = 1/4 (v/v) and HCl with $AlCl_3$ at 150 °C for 20 min. Liu *et al.* [76] compared the effect of temperature on the conversion of 5-HMF from cellulose, glucose, and fructose. All three feedstocks were maximized at 160 °C.

As shown in Fig. 4b, the trend of furfural yield with temperature has a similar conclusion, with the optimum temperature usually occurring at 120–190 °C. Zhang *et al.* [58] experimentally investigated the conversion of xylose to furfural in GVL, with the catalyst sulfonated carbon catalyst and retention time of 30 min, reaching a maximum yield of 78.5 mol% at 170 °C. Xu *et al.* [27] used corn cob-derived xylan as raw material and PTSA-POM

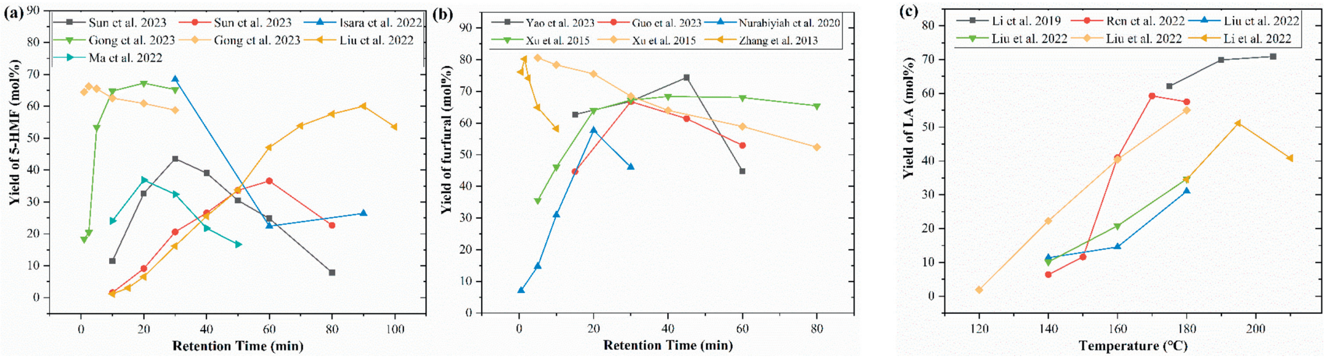

Fig. 5. Effect of retention time on yield of (a) 5-HMF [73–77], (b) furfural [27,59,79–81], and (c) LA [30,76,82,84].

Table 2
Effect of catalysts on the preparation of platform compounds.

Ref.	Raw Material	Reaction condition	Catalyst	Yield	Brief summary
5-HMF					
Sun *et al.* [74]	Cellulose	H_2O/MIBK = 1/4 (v/v), 180 °C, 60 min	$FeCl_3$-NaCl	40.0 mol%	The yield reached a maximum of 40.0% at a catalyst concentration of 0.02 mol/L, followed by a gradual decrease with increasing catalyst concentration.
			$FeCl_3$-LiCl	36.5 mol%	The yield first rises and then decreases, reaching a maximum of 36.5% at a catalyst concentration of 0.06 mol/L.
Isara *et al.* [73]	Glucose	H_2O, 200 °C, 60 min	No cataylst	6.5 wt%	Al-MCM-41 catalyzed the conversion of glucose to 5-HMF much better, with the yield of 5-HMF being 7.6 times higher than that without the catalyst, as well as much higher than that with other catalysts.
			ZSM-5	21.1 wt%	
			MCM-22	25.8 wt%	
			Al-MCM-41	49.8 wt%	
			Cr/MCM-22	15.7 wt%	
Ma *et al.* [77]	Glucose	180 °C, 20 min, LiBr hydrate/acetone	No cataylst	41.7 mol%	$AlCl_3$ significantly increased the yield of cellulose conversion to 5-HMF. Continued increase in the concentration of $AlCl_3$ led to a decrease in the yield of 5-HMF. Excess Lewis acid may lead to the degradation of 5-HMF to humins.
	Fructose		No cataylst	93.4 mol%	
	Cellulose		No cataylst	37.1 mol%	
	Cellulose		$AlCl_3$	75.1 mol%	
LA					
Isara *et al.* [73]	Glucose	H_2O, 200 °C, 60 min	No cataylst	4.1 wt%	MCM-22 catalyzed the conversion of LA from glucose much better, with the yield of LA being 14.2 times higher than that without the catalyst, as well as much higher than that with other catalysts.
			ZSM-5	47.1 wt%	
			MCM-22	58.3 wt%	
			Al-MCM-41	35.6 wt%	
Ren *et al.* [82]	Cellulose	H_2O, [MIMPS]Cl, 170 °C, 2 h	5 mol% $ErCl_3$	20.6 mol%	The LA yield peaked at an $ErCl_3$ concentration of 50 mol% and continued to increase the catalyst concentration with a slight decrease in LA yield.
			10 mol% $ErCl_3$	27.5 mol%	
			50 mol% $ErCl_3$	33.0 mol%	
			100 mol% $ErCl_3$	30.1 mol%	
Li *et al.* [84]	Corncob	H_2O/GVL = 1/4, 195 °C,90 min	No cataylst	1.8 wt%	The conversion of Corncob to LA was 18 times higher than without catalyst using MoCMP as catalyst.
			MoCMP	33 wt%	
Furfural					
Ninh *et al.* [81]	Hemi-cellulose	H_2O/GVL = 1/4, 190 °C, 150 min	Cel-MSGO	55.1 mol%	Cel-MSGO was effective in increasing the yield of hemicellulose to furfural.
Yao *et al.* [79]	Corncob	180 °C, 45 min	acetic acid/$FeCl_3$	47.6 wt%	The combination of $AlCl_3$ with acetic acid and citric acid accelerated cellulose degradation, and NaCl inhibited furfural yield.
			citric acid/$FeCl_3$	42.9 wt%	
			acetic acid/ $FeCl_3$/ NaCl	11.5 wt%	
Guo *et al.* [80]	Bamboo with DES	TMAB/LA (1:9), 140 °C, 30 min	$FeCl_3 \cdot 6H_2O$	63.4 mol%	The electronic configuration of the cations in the catalyst results in a different order of cation generation, which affects the catalytic effect.
			$AlCl_3 \cdot 6H_2O$	67.1 mol%	
			$CuCl_2 \cdot 2H_2O$	86.9 mol%	
Xu *et al.* [27]	Xylose	H_2O/GVL = 1/10, 170 °C, 10 min	PTSA-POM: 0.5 wt%	67.8 mol%	The loading of PTSA-POM was increased to a certain value and the catalytic effect no longer continued to increase with loading.
			PTSA-POM: 1.0 wt%	80.5 mol%	
			PTSA-POM: 2.1 wt%	76.7 mol%	

as catalyst in GVL with 40 min retention time to obtain the highest yield of 72.3 mol% at 170 °C.

It seems to be due to 5-HMF and furfural are unstable at higher temperatures and tend to be decomposed and transformed. Below 200 °C, higher temperatures make it easier to convert 5-HMF to LA. Therefore, LA usually shows an increasing trend with increasing temperature in the range of 120–200 °C (Fig. 4c).

4.1.2.2. Retention time.

Retention time is an important factor that affects the yield of platform compounds. Researchers have conducted numerous experiments to explore the optimal retention time of the process [27,30,59,73–85]. The related summary is shown in Fig. 5.

The yield of 5-HMF usually showed a tendency to increase and then decrease with the increase of retention time. The optimal reaction time is usually within 0–100 min depending on the conditions of raw material, catalyst, reaction temperature, *etc.* (Fig. 5a). Gong *et al.* [75] investigated the effect of retention time on the catalytic conversion of ball milled cellulose and glucose to 5-HMF. Under the same catalyst and liquid-phase environment, the optimum retention time was 2.5 min for glucose and 20 min for cellulose, which means that cellulose needs more retention time than glucose in the catalytic hydrolysis to 5-HMF due to the need for depolymerization. Sun *et al.* [74] demonstrated experimentally that the optimum retention time changes in the presence of different catalysts. In H_2O/MIBK, the optimum yield of 43.5 mol% was achieved at 30 min with $FeCl_{3}$-NaCl catalyst and 36.5 mol% was achieved at 60 min with $FeCl_3$-LiCl catalyst at a reaction temperature of 180 °C.

The yield of furfural has a similar trend with retention time, which decreases when the retention time exceeds a certain critical value (Fig. 5b). The optimum retention time for the conversion of pentose to furfural seems to be shorter than that of 5-HMF, which is usually below 50 min. Meanwhile, the reaction temperature has an effect on the optimal retention time. Xu *et al.* [27] found that the highest furfural yield of 80.4 mol% was achieved with xylose in GVL catalyzed by PTSA-POM at 180 °C for 5 min. If the reaction temperature was 150 °C, the maximum yield at 40 min was only 68.4 mol%.

The yield of LA usually shows a gradual increase with time within a certain retention time range (Fig. 5c). Since LA is converted from 5-HMF by hydration [39], the increase in reaction time produces more LA and less 5-HMF, while no decomposition of LA occurs within a certain time range.

4.1.2.3. Catalyst.

In the field of lignocellulosic biomass hydrolysis, the catalyst plays a critical role. It has an important impact on shaping the limits of platform compound yield, reducing the optimal reaction temperature conditions and minimizing the optimal retention time. Therefore, it is necessary to summarize and analyze the experimental data on the hydrolysis of biomass to platform compounds with different catalysts and their loadings, which is significant for an in-depth understanding of catalysis.

The effect of catalysts on the preparation of platform compounds is summarized in Table 2. Catalysts accelerate the decomposition and conversion of lignocellulosic biomass into platform compounds by providing an appropriate reaction environment and reducing the reaction activation energy. The presence of a catalyst can significantly increase the reaction rate and achieve higher product yields. Sun *et al.* [74] and Ren *et al.* [82] noted that the loading/concentration of the catalyst has an effect on the yield of the platform compounds. There is usually an optimal loading for each catalyst for different target products. In addition, different additives can change the optimal loading of the catalyst [74].

Isara *et al.* [73] investigated the catalytic effect of several different catalysts on the conversion of glucose to 5-HMF and LA under the same reaction conditions. It can be concluded that the catalyst has a great influence on the product and selectivity of the target products. The type and nature of the catalyst can adjust the product distribution of the reaction. Different catalysts may lead to different by-product generation pathways, which may affect the yield and composition of the platform compounds. Liu *et al.* [76] found that $ZnCl_2$ had different effects on the catalytic conversion of glucose and fructose to 5-HMF and LA. In addition, reusability testing of catalysts is also a concern for researchers as it greatly affects the economics of biomass industrial applications. Most of the studies concluded that the catalyst activity was able to be above 70% after three reuses [27,73,76,82,84,85].

Therefore, it is especially important to select the appropriate catalyst according to the target product in the hydrolysis process of lignocellulosic biomass. It plays a crucial role in increasing the target products, reducing the by-products, improving the production efficiency and reducing the energy consumption.

4.2. HTL of algal biomass

The main form of lipids present in algae are triglycerides, containing both saturated and unsaturated fatty acids. The lipid content directly affects the yield of HTL bio-crude. The yield of bio-crude was higher in high lipid algae compared to low lipid algae [23]. In terms of the contribution to the yield of bio-crude, the order is lipid > protein > carbohydrate [86]. Current research on HTL of microalgae focuses on the oil phase material, including yield and composition in bio-crude, while the control of hydrothermal process conditions is the key to improve bio-crude yield and optimize chemical composition. The influencing factors include but are not limited to reaction temperature, retention time, organic solvent addition, process method, biomass-to-solvent ratio, *etc.*, while the effects of these reaction conditions have been described in detail in a large number of articles.

4.2.1. Temperature

The effect of HTL reaction temperature is a key condition of interest for relevant researchers in recent years, and the reaction temperature has a significant effect on the yield and quality of bio-crude from HTL of microalgae. According to the summary in Table S2, the composition content of different species of algal biomass varied, mainly in the content of protein, carbohydrates and lipids, and a large number of studies based on HTL of different species of algae achieved important conclusions. Based on the results of a large number of studies, it has been generally concluded that there is no optimal HTL temperature, because the yield and component content of the products need to be determined by a combination of feedstock selection, catalyst, solvent, and other reaction factors [87]. Fig. 6 shows the variation of bio-crude yield with temperature for HTL of typical microalgae [20,41,21,23,88,89]. The effect of key components of the bio-crude with temperature is shown in Fig. 7.

Tang *et al.* [21] studied HTL of *Nannochloropsis* (high oil content) and *Spirulina* (high protein content) by obtaining the highest bio-crude yield of 41.0% and 33.3% at 280 °C and 260 °C for *Nannochloropsis* and *Spirulina*, respectively. The gas yield increased with increasing temperature, and the solid residue had an opposite trend. For the components in bio-crude, more fatty acids were transferred to fatty acid amides as the temperature increased. Gai *et al.* [41] conducted an experimental study on the HTL of *Chlorella* and *Spirulina* and showed that the highest bio-crude yield was 42.8% at 280 °C for *Chlorella* and 41.9% at 300 °C for *Spirulina*. The reaction temperature had a significant effect on the chemical composition of the aqueous fraction of bio-crude. The bio-crude obtained at higher reaction temperatures (280–320 °C) had a higher percentage of aliphatic functional groups. Toor *et al.* [22] studied the HTL of saline *Nannochloropsis* and *Spirulina* and found that the optimal HTL temperature for *Spirulina* was 310 °C, while the optimal HTL temperature for *Nannochloropsis* was 350 °C with a maximum bio-crude yield of 46%. The extraction of bio-crude from biomass in supercritical water is not as effective as subcritical water. Meanwhile, the HTL process produces solid residues containing high levels of protein. Zhang *et al.* [44] found that glucose or carbohydrates contributed little to the yield of bio-crude, but it could neutralize the negative effect of protein and improve the HTL performance of the Maillard reaction in an optimal ratio. In the HTL tests with glucose and soy protein as model compounds, the highest oil phase yield was obtained at 280 °C, while the yield of solid residue gradually decreased with increasing temperature.

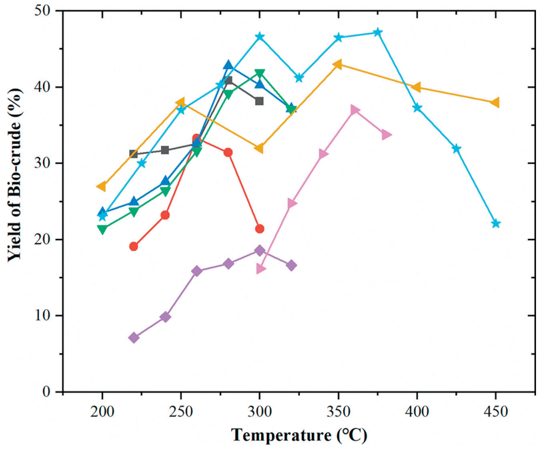

Fig. 6. Effect of temperature on bio-crude yield of HTL of microalgae. —■—: *Nannochloropsis* for 30 min by Tang *et al.* [21]; —●—: *Spirulina* for 30 min by Tang *et al.* [21]; —▲—: *C. pyrenoidosa* for 60 min by Gai *et al.* [41]; —▼—: *S. platensis* for 60 min by Gai *et al.* [41]; —◆—: *E. prolifera* for 30 min by Zhou *et al.* [23]; —◀—: *Nannochloropsis* sp. for 60 min by Brown *et al.* [88]; —▶—: *Dunaliella tertiolecta* for 30 min by Zou *et al.* [20]; —★—: *Desmodesmus* sp. for 60 min by Garcia *et al.* [89].

According to the results of the above study, the yield of bio-crude usually increases and then decreases with the increase of temperature. This can be understood as the biomass undergoes decomposition, condensation and repolymerization reactions during HTL. Elevated temperatures lead to a predominance of decomposition reactions, and thus elevated temperatures promote hydrolysis. When the temperature exceeds a certain temperature, the yield of bio-crude decreases significantly, which may be due to further decomposition of bio-crude to form small molecules of gasses or water-soluble substances [90]. Meanwhile, the variation of solid residues with temperature decreased gradually with increasing temperature. This may be due to the fact that the solid residues include unhydrolyzed inorganic salts and ash as well as polymeric substances. The increase in temperature increases the rate of hydrolysis of carbohydrates. The reducing sugars generated can react to form platform compounds that enter the aqueous phase (*e.g.*, furfural, 5-HMF) and also react with the hydroly-

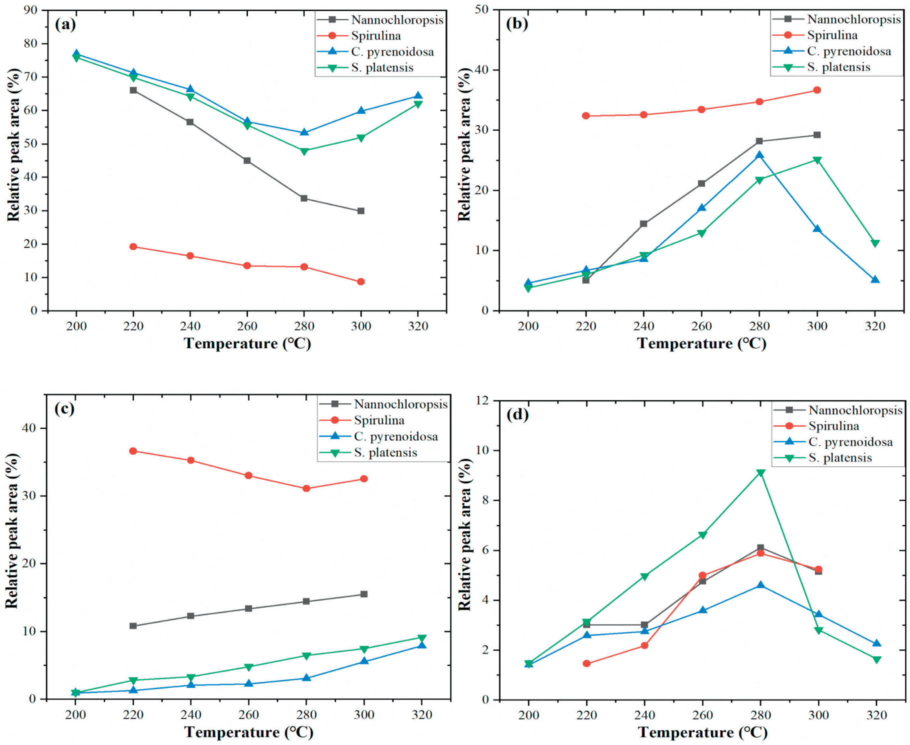

Fig. 7. Effect of temperature on key components of bio-crude. (a) Fatty acids and O-containing compounds; (b) Amide; (c) N&O-heterocyclic compounds; (d) Hydrocarbons. *Nannochloropsis* and *Spirulina* by Tang *et al.* [21], and *C. pyrenoidosa* and *S. platensis* by Gai *et al.* [41].

sis products of proteins to form N-heterocycles that enter the oil phase [44]. This leads to a reduction in the products of water-insoluble substances.

According to the changes in the relative peak area of the key components in the bio-crude in Fig. 7, the fatty acids and O-containing compounds content of *Nannochloropsis* and *Spirulina* decreased with increasing temperature, and that of *C.pyrenoidosa* and *S.platensis* first decreased and then increased with increasing temperature. In contrast, the content of amides showed the opposite trend. This suggests that higher temperatures lead to more compounds from protein and carbohydrate conversions reacting with fatty acids, resulting in a decrease in fatty acids selectivity, which is again inhibited when the temperature reaches a certain critical value. The increased N&O-heterocyclic components content in bio-crude other than *Spirulina* implies that higher temperatures cause more protein hydrolysis to amino acids and more Maillard reaction to occur.

4.2.2. Retention time

Retention time has an important effect on the yield and quality of bio-crude, and the product yield and composition content varied for different retention time under the same temperature conditions. Zou *et al.* [91] found that the maximum yield of bio-crude was 25.8% at a reaction temperature of 360 °C and a retention time of 50 min using *Dunaliella tertiolecta cake* as feedstock. The conversion of biomass and bio-crude yield increased with increasing retention time at retention time less than 60 min, while remaining essentially constant after 60 min. Zhou *et al.* [92] studied algal HTL at 300 °C for 5-60 min and found that the yield of bio-crude was highest at 30 min and decreased slightly with continued increase in retention time, and the aqueous phase product continued to decrease with increasing retention time. The reason for this may be that the prolongation of the retention time results in the loss of some small organic molecules in the evaporation of the product from the aqueous phase. The solid residue, on the contrary, showed a decrease followed by a slight increase in the range of 5-60 min. This variation pattern can be explained by the fact that too short reaction time is detrimental to the oil formation process, but too long reaction time promotes the tendency of gas and coke formation, leading to a decrease in bio-crude yield. Jena *et al.* [93] conducted HTL experiments on *Spirulina* with retention time from 0 to 120 min at 350 °C. The maximum bio-crude yield was achieved at 60 min. With increasing retention time, the light oil content increased and the heavy oil content decreased, stabilizing after 90 min. The aqueous phase products and solid residue yield then gradually decreased with the increase of retention time. The increased time causes the carbon content in bio-crude to increase, and the nitrogen content rises and then decreases, with the highest at 90 min. Fig. 8 visualizes the trend of the effect of retention time on the bio-crude yield of HTL.

In addition, the flash heating HTL method is more in line with industrial models and is able to reduce the heating time substantially. When studying short time HTL, which is strongly influenced by the heating rate, flash heating HTL can more accurately determine the effect of residence time on HTL. Garcia *et al.* [94] studied the kinetics of protein hydrolysis in microalgae using fast hydrolysis through a continuous flow reactor. Tang *et al.* [95] found no significant difference in the quality of bio-crude by comparing flash heating HTL with conventional HTL at a retention time of 30 min. Dong *et al.* [90] used the flash-heated HTL method to study the HTL of microalgae and found that the bio-crude yield with a retention time of 3 min at a temperature of 300 °C was higher than that with a retention time of 30 min, and the quality of bio-crude also had better performance.

4.2.3. Solution effect

The reaction solvent is crucial for the yield and chemical composition of the bio-crude. Water is the most commonly used reaction solvent because it is one of the advantages of HTL processes, such as the treatment of wet-based biomass (without drying) to

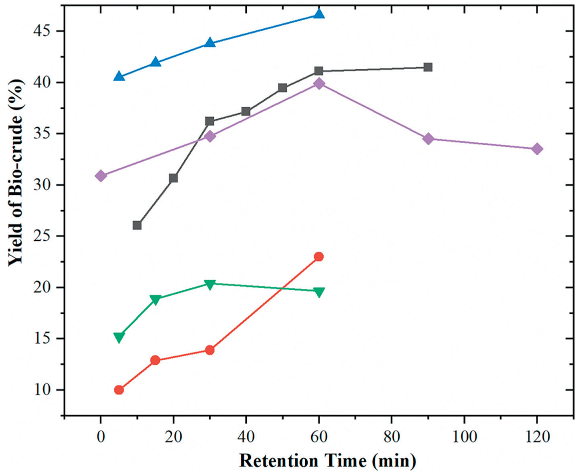

Fig. 8. Effect of retention time on bio-crude yield of HTL of microalgae. —■—: *Dunaliella tertiolecta* with 360 °C by Zou *et al.* [20]; —●—: *Desmodesmus* sp. with 200 °C by Garcia Alba *et al.* [89]; —▲—: *Desmodesmus* sp. with 300 °C by Garcia Alba *et al.* [89]; —▼—: *E. prolifera* with 300 °C by Zhou *et al.* [92]; —◆—: *S. platensis* with 350 °C by Jena *et al.* [93].

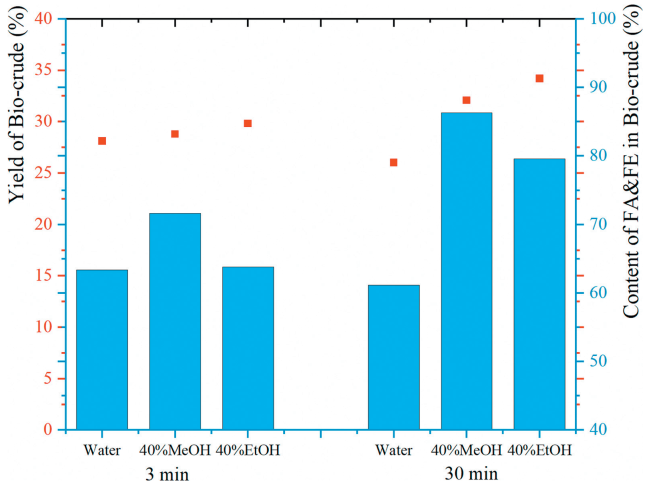

Fig. 9. Effect of different liquid phase medium on HTL [90].

facilitate the recovery of inorganic substances in water. However, organic solvents or organic-water mixtures are increasingly being used to increase yield of bio-crude and improve the component content of bio-crude. For example, by adding alcohols to the reaction medium, fatty acid esters become the main chemical component in the bio-crude [96,97]. In addition, since the critical point of organic solvents is lower than that of water, this means that the addition of organic solvents leads to milder reaction conditions [98]. However, organic solvents face the problem of high solvent cost in the application of HTL of biomass, which affects its industrial application.

Another negative effect of using organic solvents is that organic solvents may increase the nitrogen content in the bio-crude [4]. Hu *et al.* [99] found that the use of organic solvents as liquid phase media increased the nitrogen content in the bio-crude while increasing the yield of the bio-crude. The nitrogen content in the bio-crude obtained in HTL using methanol as the medium was 8.39 wt%, which was higher than that of 6.17 wt% in the bio-crude obtained using water as the medium. Zhang *et al.* [100] found that the nitrogen content of bio-crude obtained by HTL with Chlorella as feedstock and ethanol as medium was up to 10 wt%.

If an organic solvent-water co-solvent is used instead of water or organic solvent as a medium for HTL, it seems to be effective in increasing the yield and reducing the nitrogen content in the bio-crude, which also reduces the energy consumption due to dehydration. Due to synergistic effects [100–102], nitrogen-containing compounds such as heterocycles, amides, urea and oximes in bio-crude can be significantly reduced in organic solvent-water mixtures (*e.g.*, methanol-water mixtures). Several studies have shown that the use of organic solvents or organic-water co-solvents as liquid media can increase the yield of bio-crude [99]. Li *et al.* [102] investigated the effect of methanol-water co-solvents on HTL of municipal wet wastewater, and the yield of bio-crude was up to 46.5 wt% with 38.1% of esters and 37.4% of methyl esters using methanol-water as the medium. In a study by Dong *et al.* [90] on the effect of methanol-water co-solvent on the HTL of microalgae, it was found that the yield of bio-crude could reach 32.1% with 40% methanol-water (v/v) as medium and 34.2% with 40% ethanol-water (v/v) as medium under 260 °C retention time for 30 min, which was higher than the same conditions with water as medium (26.03%). Meanwhile, the addition of methanol or ethanol further enhanced the content of fatty acids and fatty acid esters (FA&FE) in bio-crude (Fig. 9).

Meng *et al.* [103] found that ethanol-water co-solvent had a synergistic effect on HTL of algae, and the highest bio-crude yield of 42.5% was achieved when held at 320 °C for 30 min, with an ethanol-water volume ratio of 4/6 and a biomass solid-liquid ratio of 1 g/15 mL, using *Cyanobacteria* as feedstock. Zhang *et al.* [100] studied the highest bio-crude yield of 57.3% and the lowest solid residue yield of 9.4% when using ethanol-water co-solvent as the reaction medium with *Chlorella vulgaris* as the feedstock when the ethanol content was 40% (v/v). Peng *et al.* [101] investigated the effect of different ethanol concentrations on the HTL of *Chlorella vulgaris*, where the addition of ethanol contributed to the deoxygenation and hydrogen supply of bio-crude due to dehydration and decarboxylation reactions, while the addition of ethanol could also enhance the ester exchange reaction to form more esters.

The addition of methanol/ethanol not only significantly increased the percentage of oil phase in the product, but also significantly increased the selectivity of fatty acids to fatty acid esters. This may be due to the fact that the addition of methanol/ethanol increased the conversion of triglycerides, increased the average molecular weight of bio-crude (fatty acid esters of the same carbon chain length have a higher molecular weight than fatty acids), and alcohols have a higher priority to react with fatty acids compared to amino acids.

In addition to the influence of the solvent on the HTL product, the solid-liquid ratio of the reactants has some influence on the HTL process. In general, the optimal biomass-to-water ratio varies for each experiment (depending on feedstock type, operating parameters, reaction unit capacity, *etc.*). The ratio of algae to water has a certain threshold, beyond which further increase in water content leads to a decrease in the yield of bio-crude and an increase in the yield of solid residues. It should also be noted that the amount of water content directly affects the thermal energy input per unit of biomass during warming, which will affect the energy efficiency of the process [87]. Jin *et al.* [104] studied HTL of spirulina and marshmallow and found that a low solid/liquid ratio of the feedstock (*i.e.*, high water content) was not effective in improving the energy efficiency of the HTL process. As the water increases, more heat input is required per unit of biomass warming. As the water content increases, the bio-crude yield increases. The maximum is reached at a solid/liquid ratio of 1/5.8, and further increase in water content leads to a decrease in yield. The variation of solid residue yield is opposite to that of the bio-crude.

Table 3
Effect of catalysts on bio-crude from microalgae HTL.

Ref.	Raw material	Catalyst	Reaction condition	Yield ofbio-crude (%)	Yield of solid residue (%)	Effect of bio-crude quality
Zhou *et al.* [92]	*D. tertiolecta cake*	No cataylst	300 °C, 30 min	20.4	16.2	HTL with 5 wt% Na_2CO_3 as catalyst contained more carbon and lower oxygen elements
		5 wt% Na_2CO_3		23.0	14.4	
Yang *et al.* [105]	*E. prolifera*	no cataylst	270 °C, 20 min	28.5	10.6	Prepared with the acid catalyst had better flowability compared to the catalyst-free condition
		0.02 mol/L sulfuric acid		15.0	16.5	
		0.2 mol/L acetic acid		15.9	13.6	
Duan *et al.* [106]	*Nannochloropsis sp.*	No cataylst	350 °C, 60 min	35.0		Pd/C, Pt/C, Ru/C and CoMo/γ-Al_2O_3 significantly decreased the viscosity of bio- crude. The noble metals (Pt, Pd, Ru) increased the H/C ratio of the bio-crude. Pt, Ni and CoMo significantly decreased the O/C ratio in the bio-crude.
		Pd/C		56.9		
		Pt/C		48.1		
		Ru/C		50.1		
		Ni/SiO_2-Al_2O_3		50.6		
		CoMo/Al_2O_3		54.0		
		Zeolite		46.0		
Xu *et al.* [107]	*C. pyrenoidosa*	No cataylst	300 °C, 20 min	33.1	24.4	Ce/HZSM-5 can significantly increase the content of C and H element and decrease the content of N element in bio-crude.
		HZSM-5		34.1	23.9	
		Ce/HZSM-5		50.0	17.1	

4.2.4. *Catalysts*

In HTL studies of algal biomass, the majority of studies are based on zero catalyst for environmental protection and low cost, but some studies have found some improvements in product yield and quality with the addition of certain catalysts. For the effect of homogeneous catalysts, Zhou *et al.* [92] studied HTL of Macroalgae *Enteromorpha prolifera* and found that the yield of bio-crude could reach 23% with 5 wt% aqueous Na_2CO_3 solution as solvent and held at 300 °C for 30 min, while the yield of bio-crude was only 20.4% when deionized water was used as solvent. The results of elemental analysis showed that the bio-crude obtained with the use of catalyst contained more carbon and lower oxygen elements. Zou *et al.* [91] studied the effect of using Na_2CO_3 as a catalyst on the HTL of *Dunaliella tertiolecta cake*. The catalyst addition had a relatively significant effect on the conversion rate of biomass, but not significant enough on the yield of bio-crude. The addition of a small amount of catalyst (5 wt%) had a positive effect on the liquefaction, but a negative effect was observed when the amount of Na_2CO_3 continued to increase. The highest bio-crude yield of 25.8% was obtained with 5 wt% Na_2CO_3 as catalyst at 360 °C for 50 min of retention time. Yang *et al.* [105] investigated the effect of acid catalysts on HTL of algal sharks, and the addition of sulfuric acid or acetic acid as catalysts had a negative effect on the production of bio-crude, with a decrease in yield, along with lower hydrocarbon and higher oxygen content in the bio-crude. However, the bio-crude prepared with the acid catalyst had better flowability compared to the catalyst-free condition.

For the effect of non-homogeneous catalysts, Duan *et al.* [106] investigated the catalytic HTL of *Nannochloropsis* sp. In the absence of H_2, there was no significant trend in bio-crude yield with increasing loading of catalysts Pd/C, Pt/C, Ru/C and CoMo/γ-Al_2O_3, but the viscosity of bio-crude decreased significantly. The noble metals (Pt, Pd, Ru) increased the H/C ratio of the bio-crude. Pt, Ni and CoMo also significantly decreased the O/C ratio in the bio-crude. Xu *et al.* [107] showed that Ce/HZSM-5 significantly enhanced the acidity of Lewis acid and resulted in smaller particle size and larger specific surface area. Ce_4O_7 was highly dispersed with trivalent and tetravalent cerium in the zeolite skeletal channel, which accelerated the catalytic liquefaction of *Chlorella*. The catalyst resulted in a higher content of elemental C and H and a lower content of N in the bio-crude, which had a positive effect on the bio-crude quality. From the present study, the use of catalysts in the HTL stage did not bring significant improvements and the use of catalysts in the subsequent hydrorefining stage could bring more significant gains [45]. The effects of catalysts on microalgae HTL bio-crude are summarized in Table 3.

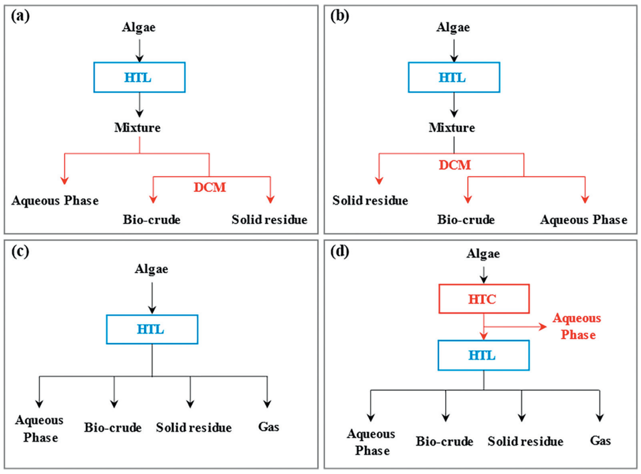

Fig. 10. Schematic diagram of (a) separation-extraction method, (b) extraction-separation method, (c) one-step HTL, and (d) two-step HTL.

4.2.5. *Experimental process*

The process of HTL can be classified according to the phase separation method into two types: Separation-extraction method and extraction-separation method [108], as shown in Figs. 10a and b. The current experiments have been studied for both phase separation methods, and the difference is mainly reflected in whether the DCM extract from the aqueous solution (defined as the aqueous phase extract) is collected into the bio-crude. Tang *et al.* [95] specifically analyzed the composition of the aqueous phase extract by GC–MS, and found that the aqueous phase extract yielded about 2.6%–4.3% and contained about 18% of *N*-heterocyclic compounds, about 67.7% of DKP derivatives of about 67%, and oxygenated compounds of about 20%. Diego *et al.* [108] studied the products of different phase separation methods, and the yield of the products was highly dependent on the chosen separation method, and direct extraction of the oil phase from the mixture resulted in an increased yield of bio-crude, but also increased the nitrogen and oxygen content of the bio-crude. Therefore, as a biofuel, extracting the oil phase directly from the mixture will reduce the quality of the bio-crude.

The process can also be divided into one-step HTL method and two-step HTL method depending on the experimental method. The schematic diagrams of one-step and two-step HTL are shown in Figs. 10c and d. The difference between the two processes is whether or not a hydrothermal carbonization (HTC) step is added before the HTL. Most of the current studies are based on the one-

Table 4
Effect of gas medium on HTL of biomass.

Ref.	Raw material	Reaction condition	Gas medium	Yield of bio-crude (%)	Yield of solid residue (%)	Effect of bio-crude quality
Duan *et al.* [106]	*Nannochloropsis sp.*	350 °C, 60 min	He	35.0		Less influence on the elemental content of bio-crude
			3.5 MPa H_2	46.2		
Yin *et al.* [115]	Cattle manure	0.5 mol NaOH, 310 °C, 15 min	CO	48.7	8.0	
			H_2	44.7		
			N_2	38.5	10.1	
			Air	27.8		
Dong *et al.* [90]	Nannochloropsis	280 °C, 30 min	N_2	27.2	4.19	Slight decrease in N heterocyclic compounds and increase in bioactive substances (Cholesterol) using air as the medium
			Air	24.7	5.63	

step method. In contrast to the one-step method, the two-step method has a positive impact on the improvement of bio-crude quality. Miao *et al.* [109] investigated that yeast first separated sugars and proteins at a lower temperature. The remaining biomass (biochar) was then converted to bio-crude at a higher temperature. The resulting aqueous product was recycled as a carbon and nitrogen source for the yeast culture. In the first step of the low temperature reaction, the effect of temperature on the yields of sugars, proteins and inhibitory compounds (acetic acid and 5-HMF) was investigated and it was concluded that the highest yields of sugars and proteins and the lowest yields of inhibitory compounds were obtained at 180 °C. In the second step of the high-temperature reaction, the highest bio-crude yield was achieved at 240 °C. The two-step HTL produced higher quality bio-crude with higher fatty acids content and lower nitrogen content compared to the one-step HTL. Wang *et al.* [110] compared the two-step HTL with the one-step HTL of *Enteromorpha clathrata*. It was concluded that there was little difference in the yield of bio-crude produced by the two-step HTL, but the solid residue rate was lower than that of the one-step HTL.

Some other researchers have performed protein extraction or lipid extraction from microalgae and subjected the remaining microalgae to HTL experiments. Barreiro *et al.* [111] performed a technical evaluation of a novel biorefining process using enzymatic protein extraction. The effect of this process on the composition and yield of the bio-crude obtained by HTL of two strains of algae (*N. gaditana* and *S. almeriensis*) was analyzed. In this study, the algae were subjected to lipid extraction and protein extraction, respectively, and the residual algae were subsequently liquefied in subcritical water to produce bio-crude. The results indicate that protein extraction from microalgae prior to HTL may help to improve the process economy and reduce the nitrogen content in the bio-crude. Also, the extracted proteins could be converted into valuable amino acids. Tang *et al.* [112] conducted an experimental study of HTL of defatted *Nannochloropsis* using an organic solvent (methanol or methanol/DCM) to extract most of the lipids from the microalgae. The remaining algal residue was hydrothermally liquefied to obtain a significantly lower yield of bio-crude compared to non-degreased microalgae. At the same time the carbon and nitrogen content of the bio-crude increased, the oxygen content decreased, the fatty acid content decreased significantly, and the nitrogenous substances (amides, N-heterocycles) increased significantly.

4.2.6. Gas phase medium

Reducing gasses as gas phase medium can facilitate bio-crude production to some extent [113]. Reducing gasses facilitate the intermediates to undergo bond breaking to obtain small molecule intermediates and thus come to enhance the oil production by inhibiting the intermediates' reactions such as condensation, cyclization, and repolymerization to produce tar and coke [114]. As shown in Table 4, Duan *et al.* [106] used *Nannochloropsis* sp. as feedstock and held at 350 °C for 60 min. The bio-crude yield with hydrogen as gas medium was about 32% higher than that of helium. Yin *et al.* [115] investigated the effect of CO, H_2, and air on HTL using cattle manure as feedstock. Based on the yield results, it was shown that reducing gas can effectively increase the yield of bio-crude while decreasing the yield of solid residue. Air, on the other hand, decreases the yield of bio-crude. Dong *et al.* [90] obtained similar results using *Nannochloropsis* as feedstock and also found that air as a gaseous medium was able to increase the content of bioactive substances in bio-crude. Akhtar *et al.* [113] discussed that the reducing gasses CO and H_2 make more fragment radicals more stable during HTL, probably due to the higher affinity exhibited by biomass radicals for CO or H_2. Using N_2 as the gas phase medium leads to lower yield of bio-crude, mainly due to the little involvement of N_2 in the liquefaction reaction, and the results suggest that reactive gasses have a positive effect on HTL than inert gasses. However, the use of CO as the gas phase medium poses a challenge because it is dangerous and harmful to health. The use of H_2 can also increase the cost and hydrogen consumption of the process.

5. Conclusion

This paper compiles the main advances in the preparation of bio-crude and jet fuel precursors from HTL of biomass using second and third generation biomass represented by lignocellulosic biomass and algal biomass as feedstock. Two generations of biomass have a wide range of applications as precursors for the production of alternative fuels for aviation. Their HTL mechanisms and reaction conditions are quite different.

In the application of lignocellulosic biomass for the preparation of platform compounds *via* HTL, the process method, reaction temperature, residence time, and catalyst selection play a crucial role in the production of platform compounds. By summarizing and analyzing the results of a large number of studies, it can be concluded that the two-phase system method and the stepwise HTL method have advantages in terms of hydrolysis efficiency and liquid phase recovery. Choosing the appropriate reaction temperature, retention time, and catalyst loading according to the feedstock can effectively increase the yield of the target products and reduce the side reactions during the biomass HTL reaction.

For the study of algal biomass hydrolysis, most of the current studies are based on the targeted regulation of reaction conditions to improve the yield and quality of bio-crude. There are many factors affecting the reaction conditions, such as reaction temperature, retention time, reaction solvent, catalyst, solid-liquid ratio of raw materials, gas-phase medium, and process methods. By summarizing the laws of different influencing factors, it is important to control the process conditions to reduce the side reactions and the formation of by-products during the HTL reaction of biomass. Improving the yield and quality of bio-crude through the control of reaction conditions is a key element of industrial applications of HTL of algal biomass.

There are both differences and links between the two types of biomass. The most suitable feedstock can be flexibly selected according to factors such as geographical location, climatic conditions and available resources. Meanwhile, the process method of preparing jet fuel precursors from lignocellulosic biomass can also provide a theoretical reference for the industrial utilization of carbohydrates from algal biomass.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109142.

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