Biomass Pyrolysis Liquefaction Technique: State of Research and Development Trends

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Abstract. Biomass as the only renewable carbon sources in nature are considered to be huge amount, environmentally friendly and carbon neutral resources. Exploiting biomass as an energy utilization not only maximizes deal with the agricultural and forestry waste, but also refining high value-added bio-based chemicals products. As one of the important means of bio-refinery conversion processes, biomass pyrolysis liquefaction technique (BPLT) has been popular in producing fuel product since the late 1970s due to its advantages in its short process, strong adaptability, rapid response, high conversion rate and easy commercialization, etc. This paper provides an overview of current research progresses in the BPLT. Summarizes the latest research results of the combined processes for BPLT in feedstock pretreatment, pyrolysis liquefaction process and bio-oil upgrading. In the section of feedstock pretreatment, three methods of microwave drying, baking and pickling are introduced. In the section of pyrolysis process, two new processes of catalytic pyrolysis and mixed pyrolysis are discussed. The final part of the paper deals with recent technologies from five aspects in the bio-oil upgrading: catalytic hydrogenation, catalytic cracking, catalytic esterification, emulsified fuel and separation and purification. Afterward, the paper analyzes the industrialization development trends of BPLT. The paper suggests that the production and upgrading of pyrolysis oil to hydrocarbon fuels is an economically attractive path. By critically evaluating their potential and challenges, we finally conclude, with the continuous maturity of various technical links such as feed prep, fast pyrolysis and upgrading, BPLT is expected to form a relatively complete technology industrial chain within 5 to 8 years, and gradually realized the industrialization in the true sense.

1. Introduction
Biomass as the only renewable carbon sources in nature are considered to be huge amount, environmentally friendly and carbon neutral resources [1, 2]. The existing comprehensive utilization
methods of biomass resources are quite numerous. Many ways have high resource utilization and economic benefits, but limited consumption, and the utilization of agricultural and forestry waste resources cannot be fundamentally solved [3]. Therefore, all countries in the world placed efficient use of biomass resources in an important position [4-6]. Exploiting biomass as an energy source not only maximizes deal with the agricultural and forestry waste, but also refining high value-added products [7, 8]. Moreover, biomass is the only renewable energy source that can be liquefied [9]. Simultaneously, biomass energy is also a carrier for the balance of CO2 and O2 in the atmosphere through photosynthesis, and will play a vital role in energy security and carbon emission reduction [10]. Establishing and enhancing the economic system of low carbon cycle to exploit biomass resources by developing the bioenergy industry into a ‘Green Economy’ is one of the seven National Strategic Goals of the Government of China [11].

However, Biomass have the characteristics of low energy density, high moisture contents, high dispersion, difficulty in collection and transportation, difficulty in large-scale centralized treatment, and rich potassium in bio-ash [12, 13]. If the technical ideas of petroleum refining, coal chemical industry and natural gas utilization are completely copied used in the biomass energy conversion, the vast majority of biomass energy enterprises will have small scale and poor efficiency, and even have to rely on policy subsidies to survive. How to efficiently and rationally utilize and transform biomass energy to compete with other energy sources has become a challenge for domestic and foreign biomass energy researchers and producers.

The bio-refinery was first proposed on Science by Bungay in 1982, defines bio-refinery as a facility that integrates the biomass conversion processes and equipment together to produce fuels, power, and chemicals from biological materials [14]. In 2006, a review by Ragauskas and coworkers in the journal Science further emphasis that the integration of agroenergy crops and bio-refinery manufacturing technologies offers the potential for the development of sustainable bio-power and biomaterials that will lead to a new manufacturing paradigm [15].

As one of the important means of bio-refinery conversion processes, biomass pyrolysis liquefaction technique (BPLT) has been popular in producing fuel product since the late 1970s due to its advantages in its short process, strong adaptability, rapid response, high conversion rate and easy commercialization, etc. [16-18]. Much research effort has been made in the last three decades with many technological breakthroughs [19, 20]. Groupe PyroVac Inc., from Canada and Ecosun bv, from The Netherlands, have built the first PyrocyclingTM industrial scale plant in Jonquie`re, Province of Que`bec, Canada, based on vacuum pyrolysis technology in the mid-1990s [21]. Globally, a number of pilot plants have been operating at up to 200 kg h-1 feedstock processing capacity to convert woody biomass into bio-oil. These plants include DynaMotive, Canada; ENEL, Italy; Ensyn, USA; Bioware Tecnologia, Brazil; PYTEC, PKA, Chemviron Carbon, Germany; DynaMotive, Compact Power, UK; Lambiotte, Belgium; Novasen, Senegal; and BEST Energies, Australia [22]. The University of Petroleum of China also built the industrial demonstration device in 2007 through the cooperation with industry and research institutes in Guangrao, Shandong province. The industrial demonstration device and obtained products from BPLT were shown in Fig.1. But spoken objectively, the realization of the biorefinery concept remains a challenge. Economic performance has been a primary barrier to commercial deployment [23]. From the view point of technical, there are two major deficiencies: technical imperfection and incomplete technology.
Figure 1. Industrial demonstration device and obtained products from biomass pyrolysis liquefaction technique in China (a: heavy oil, b: light oil, c: wood vinegar, d: biochars, e: net gas, f: silicon potassium fertilizer).

The deep utilization of low-grade biomass energy by pyrolysis liquefaction technology is of great significance for reducing fossil fuel consumption and improving the ecological environment [24]. Based on a brief introduction to BPLT, this article summarizes the latest research results of BPLT from three aspects: raw material pretreatment, BPLT process and bio-oil upgrade. Finally, points out that the future prospects of BPLT. Specifically, are: In Section 2, a brief introduction on BPLT that are being used for bio-oil production are discussed; followed by overview of the state of research and development trend of BPLT from the feedstock pretreatment, process chain and end products upgrading. Section 3 which describes the three processing methods of feedstock pretreatment. Afterward, catalytic pyrolysis and mixed pyrolysis processes are reviewed in 4 pyrolysis liquefaction process, 5 bio-oil upgrading; and Section 6 provides conclusions and recommendations for future work.

2. Biomass pyrolysis liquefaction process overviews

2.1. Biomass pyrolysis liquefaction technology
BPLT is a thermochemical conversion process that producing liquid fuels occurs at moderate temperature (about 500 °C) and anoxic conditions from thermal cracking of biomass [25]. The pyrolysis gas is then rapidly condensed to achieve the products of liquid (bio-oil), a part of gaseous (combustible gas) and solid (carbon powder) [26]. Bio-oil is the main product, and the dry yield is around 70% [27]. Bio-oil is easy to store and transport, and it is a large consumable product for industrial and agricultural industries [28]. Moreover, there is no geographical limitation of product scale and consumption.

The factors affecting the BPLT are mainly the heating rate, reaction temperature, the gas phase residence time and the quenching of the pyrolysis gas. The yield and calorific value of pyrolysis products of agricultural and forestry waste biomass under the optimal reaction conditions are listed in Table 1. It can be seen that the sum of the energy yields of the three products of BPLT is greater than 100% regardless of whatever raw materials used. The reason is that the pyrolysis reaction is an endothermic reaction, and the absorbed heat is converted into chemical energy stored in the pyrolysis products.
Table 1. Yields and caloric values of pyrolysis products of agricultural and forestry waste biomass.

| Pyrolysis products | Bio-oil | Combustible gas | Carbon powder | Total |
|--------------------|---------|-----------------|---------------|-------|
| Agricultural waste (water content ≤ 10%, calorific value ≈ 15 MJ/kg) | | | | |
| Higher heating value (HHV) | 15 ~ 16 MJ/kg | 12 ~ 13 MJ/m³ | 18 ~ 20 MJ/kg | / |
| Mass yield (%) | 45 ~ 55 | 18 ~ 23 | 25 ~ 35 | 100 |
| Energy yield (%) | 50 ~ 55 | 15 ~ 20 | 35 ~ 40 | > 100 |
| Forestry waste (water content ≤ 10%, calorific value ≈ 17 MJ/kg) | | | | |
| Higher heating value (HHV) | 17 ~ 18 MJ/kg | 13 ~ 14 MJ/m³ | 24 ~ 25 MJ/kg | / |
| Mass yield (%) | 60 ~ 70 | 15 ~ 20 | 15 ~ 20 | 100 |
| Energy yield (%) | 63 ~ 67 | 12 ~ 16 | 25 ~ 30 | > 100 |

2.2. Chemical composition of bio-oil

The chemical composition of bio-oil is very complicated. In addition to containing 20% ~ 30% moisture and a small amount of solid particles such as carbon powder, it also contains hundreds of organic compounds such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, and furans. More than 400 compounds have been detected [29], among which only a few organic compounds contents such as acetic acid is more than 1.0 wt.%, and other single components are generally less than 1.0 wt.%.

However, many compounds in the components of these less than 1.0 wt.% contents were high value-added chemicals, such as o-methylphenol, m-methylphenol, etc. Moreover, many of these substances were found in most bio-oils that prepared from most biomass raw materials. But some substances are only present in bio-oil prepared from certain raw materials.

Elemental and mineral analysis of rice husk and its bio-oil are shown in Table 2. From Table 2, we can see that the content of three organic elements of carbon, hydrogen and oxygen in the bio-oil is greater than the raw material. However, the content of inorganic elements is greatly reduced, except for iron. The higher Fe element in bio-oil may be due to bio-oil being precipitated in the pyrolysis reactor, condenser or stainless-steel storage vessel during the preparation and storage process.

Table 2. Elemental and mineral analysis of rice husk and its bio-oil.

| Pyrolysis products | C       | H       | O       | N       | S       | Si      | K       | Ca      | Mg      | Mn      | Fe      |
|--------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Rice husk          | 38.6954646.530.670.216.8200.3600.1600.0510.0330.006 | | | | | | | | | | |
| Bio-oil            | 40.6281549.790.610.030.0960.0090.0060.0020.0010.060 | | | | | | | | | | |

2.3. Physicochemical properties of bio-oil

Bio-oil is a colored liquid with micro-phase heterogeneity, and its heterogeneity is determined by the type of raw materials, pyrolysis reaction conditions, condensation process, storage conditions and storage time. In addition, its color is related to the type of raw materials, chemical compositions and the amount of fine carbon powder particles, from dark reddish brown to brown, with a unique odor.

The properties of bio-oil are complex due to the presence of solid particles, waxy substances, aqueous phase particles and heavy micelles. The water- and water-soluble components of the bio-oil formed a continuous phase, and the water-insoluble lignin lysate is suspended in the continuous phase as a type of micro-emulsion. Additionally, the components of water-oil two-parent maintains the two-phase stability of the bio-oil as an emulsifier. The main physicochemical properties of bio-oil are listed in Table 3.
2.4. Applications of biomass pyrolysis products

The schematic process description and products formation from pyrolysis were shown in Fig.2. Fast pyrolysis is considered in this review. The biomass was heated to approximately 500 °C in less than 1 second, and then rapidly cooled termination reaction [30]. Moderate temperatures and short vapour residence time are optimum for producing liquids [31]. The liquid product, known as bio-oil, is obtained in yields up to 75% by weight on a dry feed basis [32]. The main product bio-oil upon BPLT can be directly used as fuel oil for thermal equipment such as boilers and kiln, and it can be used as fuel for power equipment such as internal combustion engines after upgrading. In addition to being transported and stored at a lower cost than solid biomass, bio-oil and upgraded oil can be used in applications ranging from value-added chemicals to transportation fuels. The bio-oil product was presented as an environmentally friendly green biofuel candidate [33].

The bio-chars (12% yields) as a by-product can be directly mixed with coal to make honeycomb briquettes for combustion, and it can be further processed into activated carbon and other products. Biochars can be used for various industrial applications, such as solid fuel [11], soil improver [34], carrier for slow release of fertilizers [35], and raw material for high-performance activated carbon [33]. The combustible gas (13% yields) can be supplied to the surrounding residents as a domestic gas through gas storage cabinet and pipe network. Furthermore, it can be used for generate electricity. The calorific value of the gas was up to 5000 kcal/m3 (1kcal = 4.184kJ). In addition to be used for cooking by direct combustion, it can also be used for power generation and combined cooling, heating and power (CCHP) [36].

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![Figure 2. Schematic process description and products formation from pyrolysis.](image-url)
2.5. Pyrolysis reactor configurations

As the core of the whole pyrolysis process, the choice of reactor largely determines the final distribution of the product, so the choice of reactor type is the key to various technical routes.

2.5.1. Circulating fluidized bed reactor. Process overview: The hot carrier sand was blown out of the reactor together with the by-product solid biochars, then enters the biochars combustion chamber. Biochars were burned in the combustion chamber to release heat transfer to sand, and the heated sand was returned to the reactor to provide the heat required for biomass pyrolysis. These constitutes a complete cycle [37].

Advantages: Excellent heat transfer. High degree of mixture. Can handle large quantity. Low quality feedstock. High reaction rates. Low residence time. Particle recycling [38].

Disadvantages: Complex operation due to inclusion of fluidity. High dust content in biooil. Formation of eutectics at high temperature. Require high gas flow velocities than fixed bed. Operation more difficult than fixed bed reactor.

Demonstration plant: 100 tpd (200 tpd green wood) plant in Ensyn in Ottawa, Canada [39]. Velden et al. [40] found that the bio-oil yield as high as 60% to 70% when the reaction temperature was 500-510 °C by simulating the pyrolysis process of a circulating fluidized bed reactor.

2.5.2. Entrained flow reactor. Process overview: Feed material is typically fed into the top of the reactor, co-current with a gas stream [41].

Advantages: High degree of feedstock flexibility. Short residence time. Ash easily removed as slag [42].

Disadvantages: High amount of oxidizing agent required. High capital cost due to high reaction parameter [42].

Demonstration plant: There are currently no large-scale commercial plants.

2.5.3. Ablative pyrolysis reactor. Process overview: Biomass particles are carried into the reactor by using superheated flow of steam or nitrogen gas, and enter into the reaction tube of the vortex reactor along the tangential direction. Biomass granules undergo intense cracking reaction on the wall of the reactor (temperature of 625 °C) under high-speed centrifugal force. The product bio-oil film remaining on the wall of the reactor will evaporate rapidly, while the incompletely reacted biomass particles are re-synthesized continuously through the circulation loop [32, 43].

Advantages: Low cost and simple equipment. Feeding without particle size requirements [31, 32].

Disadvantages: Mechanically driven. Biomass particles are easily separated from high temperature walls. [44].

Demonstration plant: Typical ablative pyrolysis reactors are the vortex reactor developed by the National Renewable Energy National Laboratory (NREL) in the 1990s and the ablation reactor studied by ASTON University, UK. [45-47].

2.5.4. Moving bed or auger pyrolysis. Process overview: A granular or bulk solid reactant or catalyst is continuously added to the top of the reactor. As the reaction progresses, the solid material gradually moves downward and is finally discharged continuously from the bottom. The fluid passes through the solid bed from bottom to top (or top down) to carry out the reaction [48].

Advantages: Robust. Do not require large volumes of carrier gases. Provides good control of residence times.

Disadvantages: It is difficult to control the uniform downward movement of solid particles.

Demonstration plant: max size 2083kg/h in Anhui Yineng Bio-energy Ltd., China; max size 500kg/h in Abritech, Canada; max size 200kg/h in Lurgi LR, Germany, Renewable Oil Intl, USA [30].

2.5.5. Rotating cone reactor. Process overview: The rotary cone reactor is a new type of biomass flash pyrolysis reactor that maximizes bio-oil production. The biomass rises spirally along the high
temperature cone wall along with the preheated inert heat carrier. During the ascent, the hot sand transfers its heat to the biomass, causing the biomass to crack at high temperatures [49].

Advantages: Fast heating speed. Short retention time of solid phase and gas phase. The reaction process does not require a carrier gas and does not require a large device volume [50].

Disadvantages: Some structures of the reactor are not perfect enough [51].

Demonstration plant: BTG, University of Twente, Netherlands; BioEcon, Netherlands; Kior USA [30]. Lédé et al. [52] found that the biomass material was pyrolyzed by a rotating cone reactor at 627-710 °C, and a maximum yield of 74% bio-oil was obtained.

The reactors described above each have their own advantages and disadvantages. For example, a circulating fluidized bed reactor combines a combustion chamber with a fluidized bed reactor for performing pyrolysis reaction. Although the reactor manufacturing cost is lowered, while the complexity of the operation is greatly improved. The vortex device in the ablative reactor has a serious wear on the inner wall when the material moves at a high speed on the reactor wall, and it is also difficult to maintain the material rate during the enlargement design. In the rotary cone reactor, the material and sand are fed into the reactor and spiral upward as the rotating cone rotates until it is discharged from the cone. Therefore, the rotating cone reactor also has a problem of inner surface wear of the cone.

3. Feedstock pretreatments
Biomass resources have the disadvantages of strong hydrophilicity, high oxygen content and low energy density. Excessive moisture in the biomass feedstock tends to delay the pyrolysis reaction, increase the cost of heating, and destabilize the pyrolysis liquefaction product. Therefore, pretreatment of feedstock is particularly important. As the simplest pretreatment method for crushing and drying, although it can improve the heat transfer performance of biomass feedstock, reduce its moisture contents and improve its pyrolysis characteristics, the biomass feedstock with simple pretreatment still has high moisture contents and bulk density. Moreover, excessive moisture in the raw material will cause the moisture content of the bio-oil to be high, which not only reduces its calorific value, but also affects the stability of the bio-oil. Therefore, in order to further improve the quality of pyrolysis materials, this paper will review the pretreatment methods such as drying, roasting, compression molding and pickling.

3.1. Dry
The drying procedure of biomass feedstock plays a very important role in its liquefaction process, especially for marine biomass. One of the bottlenecks in the conversion of algae into biofuels is the drying process. A moisture content of at most 10 % is desired for algal biomass prior to oil extraction to maximise biofuel yield [53]. Dry pretreatment mainly has two methods: hot air drying and microwave drying. These two drying methods were all changed the surface structure of biomass feedstocks, promoting the transfer of heat and the evolution of volatiles during pyrolysis. However, microwave drying has the advantages of high efficiency and uniformity compared to hot air drying. The rate of microwave drying is more than 5 times the rate of hot air drying [54]. The bio-oil yield pretreated by microwave drying is higher during the pyrolysis process, mainly because microwave drying can promote the cracking of the two main oil-producing components of cellulose and hemicellulose, and at the same time effectively inhibit the secondary cracking of biomass pyrolysis gas. Villagracia [53] et.al. considered three microwave intensity levels (300, 600, and 900 W) to dry 10, 20, and 30 of microalgae (Chlorella vulgaris) mass, and found that the 20 W/g microwave drying setting gave a lower specific energy requirement with the original structure of the raw materials qualitatively.

3.2. Roast
Roast is a low-temperature slow pyrolysis process with a reaction temperature between 200 and 300 °C under atmospheric pressure and inert gas atmosphere. This pretreatment method could change the fiber structure of the feedstocks, improving the crushing performance of the biomass. Furthermore, it partially removes the oxygen existed in the biomass and increase the energy density of the biomass. However,
due to the high temperature through the roast process, the cracking of hemicellulose causes decrease in biomass mass yield and energy yield. What is more, roast increased the energy consumption.

3.3. Acid-eluting ash
In addition to non-metallic elements such as C, H, O, N, and S, the biomass components also contain small amounts of metal elements such as Ca, K, Na, Cl, and Mg. They are generally present in the ash in forms of oxides or salts, which catalyzed in the pyrolysis process, resulting influences the distribution of pyrolysis products, bio-oil components and pyrolysis mechanisms. In order to understand the mechanism of the metal elements, the general method is to carry out the acid-eluting ash pretreatment for biomass.

The pretreatment of acid-eluting ash can improve the yield of bio-oil [55];
The removal of K+ and Ca2+ is beneficial to the production of single bonds and high molecular substances [56, 57];
The reduction in metal elements increases the temperature and maximum pyrolysis rate in the main pyrolysis zone [58].
Yoo et.al [59] found that bio-crude oil produced by fast pyrolysis from the empty fruit bunches with nitric acid washing was 98%, while the biomass treated with tap water merely of 48%. Zhang et.al [56] further confirmed that potassium promoted the conversion of large molecular compounds (such as levogluconosan) to furans. The existence of potassium reduced the yield of aldehydes and enhanced that of furfural. Wang et.al [60] was systematically investigated the potential influence of demineralization for the kinetics and pyrolysis behaviors of Chlorella vulgaris using thermogravimetric analysis coupled by fourier transform infrared spectrometer, and shows the physiochemical structure changes in carbohydrate and protein components of microalgae compared with the non-removal of inorganics. For evolved gas, acid washing suppressed the formation of CO2 and increased the generation of C-H [60].

4. Process design
Although the bio-oil prepared by conventional pyrolysis technology has higher yield, but there are challenges associated with the properties of most bio-oils that make it unsuitable for use as fuel. The processes entailed in biomass pyrolysis liquefaction technique was shown in Fig.3. Bio-oil produced from lignocellulosic biomass is acidic, unstable, viscous and can contain high amounts of oxygen, dissolved water, and solids [61]. At present, scholars at home and abroad mainly improve the quality of bio-oil, such as catalytic pyrolysis and mixed pyrolysis.

![Figure 3. Processes entailed in biomass pyrolysis liquefaction technique.](image-url)
4.1. Catalytic pyrolysis

Catalytic pyrolysis refers to a pyrolysis reaction process for obtaining high yield and high-quality bio-oil by changing the biomass pyrolysis gas component with the participation of a catalyst. According to the requirements of bio-oil fuel quality upgrade and the demands of catalytic pyrolysis for industrial applications, the catalytic pyrolysis process needs to meet the following six criteria:

- It can promote secondary cracking of oligomers to form volatile products, thereby reducing the average relative molecular mass and viscosity of bio-oil, and improving the thermal stability of bio-oil;
- It can reduce the content of aldehyde products, thereby improving the chemical stability of bio-oil;
- It can reduce the content of the acid-containing product, thereby reducing the acidity and corrosivity of the bio-oil;
- It can deoxidize as much as possible to promote the formation of hydrocarbon products or other low-oxygen products, thereby increasing the calorific value of bio-oil, but avoiding the formation of carcinogenic products such as polycyclic aromatic hydrocarbons.

The oxygen element was removed in the form of CO or CO$_2$. If it is removed in the form of H$_2$O, it must be ensured that the water and the organic liquid product after catalytic pyrolysis can be separated by itself;

- The catalyst must have a long service life.

Aiming at different catalysts, researchers have carried out a lot of research work on biomass catalytic pyrolysis around the above six criteria. At present, most of the catalysts studied are solid super acids, strong bases and alkali salts, metal oxides and chlorides, zeolite molecular sieves (such as HZSM-5, HY), mesoporous molecular sieves (such as MCM-41, MFI, SBA-15, MSU) and catalytic cracking catalyst. However, from the perspective of catalytic effects, they have their own advantages and disadvantages. For example, catalytic cracking catalysts can reduce the content of phenolic substances in bio-oil, improve the chemical stability of bio-oil, and increase the content of hydrocarbons in bio-oil, but on the other hand, it promotes the formation of moisture, biochars and non-condensable gases, and reduces the yield of bio-oil. Zeolite-based molecular sieves have good deoxidation performance, and they can obtain liquid hydrocarbon products mainly composed of aromatic hydrocarbons after catalysis, but they are easily deactivated in the process of catalytic pyrolysis, and regeneration is difficult. Mesoporous molecular sieve catalysts have high deoxidation activity, but their hydrothermal stability is poor and expensive. However, bifunctional and multifunctional catalysts are now a research hotspot. Cheng et al [62] integrated the bifunctional Co/HZSM-5, Zn/HZSM-5 and Co-Zn/HZSM-5 catalysts with zinc hydrolysis, found that Co or Zn modified HZSM-5 catalysts improved the yields of bio-crude and gas compared to no catalyst treatment, and it decreased the contents of oxygenated compounds including ketones, acids, alcohols and phenols. Feng et al [63] investigated the upgraded method of phenolic compounds in situ hydrodeoxygenation with the aqueous phase reforming of methanol with bifunctional catalysts combined Raney Ni with HZSM-5. They demonstrated that in situ hydrodeoxygenation using bifunctional catalysts is a promising and efficient route for converting biomass-derived phenolic compounds into fuel additives and liquid hydrocarbon biofuels.

So far, no catalyst has been found to take into account the above six principles in the biomass pyrolysis process. Therefore, the main research work of catalytic pyrolysis at this stage remains in the screening and development of catalysts.

4.2. Mixed pyrolysis

The co-pyrolysis liquefaction of biomass with other materials is referred to as mixed pyrolysis. At present, scholars have studied most on the co-pyrolysis of coal and biomass. Due to the coal pyrolysis liquefaction process consumes a large amount of hydrogen, the reaction temperature is high, and needs to be carried out with the participation of catalysts and other solvents, the cost of coal liquefaction is too high; on the other hand, the quality of bio-oil obtained by BPLT is low. These disadvantages limit their application. However, the mixed pyrolysis of coal and biomass can reduce the reaction temperature under their synergistic effect and significantly increase the quality and yield of the liquefied product. At present, it is generally believed that the co-pyrolysis liquefaction reaction of biomass and coal belongs
to the free radical reaction process [64], that is, the coal and the biomass each undergo a pyrolysis reaction to generate free radical "fragments". Due to the "fragments" not stable enough, they either combined with hydrogen to form primary hydrogenation products with a much lower molecular weight than coal and biomass, or combined with each other to undergo a polycondensation reaction to form a polymer biochars product. In this process, part of the hydrogen can be supplied by the biomass, thereby reducing the amount of hydrogen supplied by the outside. At this stage, there are few reports on the research of products formed by co-pyrolysis of biomass and coal. Altieri et al. [65] studied the characteristics of co-liquefaction products of lignin and bituminous coal at 400 °C, in which benzene solubles in liquid products are 30%, and benzene solubles obtained by liquefaction of coal and lignin alone are about 10%. Zhou Hua et al. [66] studied the co-pyrolysis liquefaction of rice straw and coal, and obtained that the liquefied product has a n-hexane soluble matter of 42.5% when the amount of rice straw added is 50% (w), the reaction temperature is 400 °C, and the reaction time is 60 min, which was 9.7% higher than the corresponding weighted average calculation.

5. Bio-oil upgrading
Owing to the original bio-oil has a series of disadvantages, such as poor stability, acidity and corrosivity, high moisture contents, low calorific value, and no compatibility with fossil fuels, so it needs to be upgraded when expanded the application of bio-oil and enhance its use valuation [67, 68]. Currently, bio-oil upgrade methods mainly included catalytic hydrogenation, catalytic cracking, catalytic esterification, emulsified fuel oil, separation and purification.

5.1. Catalytic hydrogenation
Biomass crude oil is a brownish black liquid obtained by rapidly thermal cracking of biomass resources at a medium temperature (500-600 °C), extremely short residence time (within 2 s), and isolating oxygen conditions [69]. The composition and physicochemical properties of bio-oil were affected by many factors such as the type of raw materials, water content, reactor type, reaction parameters, and product collection methods, etc. Moreover, Bio-oil contains various oxygen-containing organic compounds containing oxygen, aldehydes, ketones, alcohols, phenols, furans. Therefore, it has the characteristics of high moisture and oxygen content, particulate impurities, high viscosity, poor stability, low volatility and strong corrosiveness, which are incompatible with conventional fossil fuels (diesel, gasoline) and therefore cannot be used directly in vehicle fuel [70, 71]. Catalytic hydrogenation is the hydrotreatment of bio-oil under high pressure (7 MPa ~ 20 MPa) and with hydrogen or in the presence of a hydrogen supply solvent, in which oxygen is removed as H2O or CO2 [72, 73]. Thereby significantly reducing the oxygen content in the bio-oil, increasing the calorific value of the bio-oil and improving the stability of the bio-oil. At present, the most studied catalysts are CoMo and NiMo, which have the advantages of high hydrogenation activity, disadvantages of easy deactivation and contamination of products [62]. In addition, some scholars have studied metal catalysts such as Ni and Cu, and noble metal catalysts such as Ru/C, Ru/TiO2, Ru/Al2O3, Pt/C, and Pd/C [73-75]. The experimental result shows that the noble metal catalyst has higher activity than the ordinary metal catalyst. Due to the significant polymerization of bio-oil above 80 °C, in order to avoid catalyst deactivation caused by bio-oil coking during hydrogenation, two-stage catalytic hydrotreating of bio-oil can be carried out in the process [76, 77]. That is, the bio-oil is first subjected to mild catalytic hydrotreating at a lower reaction temperature, and then the product obtained after mild hydrogenation is subjected to deep deoxidation using conventional hydrogenation conditions [78]. Fig. 4 shows the two-stage catalytic hydrogenation diagram. Dabros et al [79] reviewed the presents and discusses the progress in combining fast pyrolysis and catalytic hydrodeoxygenation (HDO) to produce liquid fuel from solid, lignocellulosic biomass, and conclude that single stage HDO of condensed bio-oil is unsuited for commercial scale bio-oil upgrading, as the coking and polymerization, which occurs upon re-heating of the bio-oil, rapidly deactivates the catalyst and plugs the reactor. Dual or multiple stage HDO has shown more promising results, as the most reactive oxygenates can be stabilized at low temperature prior to deep HDO for full deoxygenation. Compared with the traditional catalytic hydrogenation technology, the two-stage catalytic
hydrogenation process has better performance, but there are still have problems in the actual operation, such as low product yield, high operating cost and discontinuous process [80, 81]. Based on this, some scholars have proposed an idea of mild hydrogenation, that is, at a lower temperature and a shorter residence time, only a small amount of hydrogen are used to saturate those active unsaturated aliphatic hydrocarbons, so that the stability of obtained bio-oil will be improved [82-84]. However, the initial viscosity is greatly increased, which is the same as the problem encountered in the traditional catalytic hydrogenation process. A design case on “Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking” issued by the U.S. Department of Energy Office of Scientific and Technical Information proved that the pyrolysis oil is almost completely deoxygenated by a combination of hydrodeoxygenation and decarboxylation [71]. Therefore, how to exploit a highly active catalyst at mild reaction conditions is the key to the development of bio-oil catalytic hydrogenation technology.

Figure. 4. Block Diagram of Bio-Oil Upgrading [85].

5.2. Catalytic cracking
Catalytic cracking is a technique for cracking macromolecules in bio-oil into small-molecule hydrocarbons under the action of a catalyst, in which oxygen is removed in the form of H₂O, CO, CO₂ [86]. It is generally not necessary to add H₂ during the catalytic hydrogenation cracking of bio-oil, and the reaction conditions are atmospheric pressure or low pressure. Unlike the catalytic pyrolysis process, it must start reacting after the bio-oil heats up again. Therefore, compared with the former technology of catalytic hydrogenation, the catalytic pyrolysis can avoid the energy loss in the process of pyrolysis gas condensation and bio-oil heating, and also avoid the catalyst coking problem caused by the thermal effect in the bio-oil heating process. Moreover, the average relative molecular mass of pyrolysis gas is small, which is more suitable for the catalytic reaction process, so that direct catalytic pyrolysis of biomass is more advantageous. But the core of both catalytic hydrogenation and catalytic cracking technology is the choice of catalyst [74, 75]. To date, various zeolites have been tried to upgrade bio-oils as HZSM-5 zeolite can selectively convert oxygenates species in the bio-oil to aromatics compounds due to its small pore opening and strong acidity [87-89]. However, extensive carbon deposition results in very short catalyst lifetimes [90]. To enhance the catalytic activity of zeolite for various reactions, metal is usually loaded on zeolite [91-93]. Widayatno et. al [94] investigated in details the upgrading of bio-oil from biomass pyrolysis over Cu-modified β-zeolite catalyst in a down-draft fixed-bed reactor. It is found that high silica β-zeolite has high selectivity to the hydrocarbon during the upgrading process.

Catalytic cracking and catalytic hydrogenation technologies are the two most important methods for refining bio-oil at present, but there are still many problems to be solved in order to achieve industrial applications. Mainly include:

- Improve the yields of the target products by studying the catalytic reaction mechanism to find suitable reaction conditions.
- Looking for new catalysts, and studying its deactivation characteristics, then slowing down its rate of deactivation by suitable methods.

...
Establish a circulating fluidized bed catalytic cracking reaction system and a two-stage fluidized bed catalytic hydrogenation system to achieve continuous regeneration of the catalyst.

In the mild catalytic process, it is avoided that by-product (water) cannot be separated from the organic product by controlling the appropriate degree of deoxidation.

5.3. Catalytic esterification
Catalytic esterification is the esterification reaction between a carboxyl group in a bio-oil and a hydroxyl group of an alcohol solvent under the action of a solid acid or a solid base to achieve the purpose of reducing the acidity of the bio-oil and improving the stability of the bio-oil [95]. On the one hand, the catalytic esterification process reduces the acidity of the bio-oil and reduces its corrosivity, on the other hand, the reaction of the carboxyl group with the hydroxyl group produces a large amount of water [46, 96]. Therefore, the difficulties in catalyzing esterification technology are developing a suitable catalyst, and selecting suitable reaction conditions to accelerate the esterification reaction rate. Simultaneously, achieving self-separation of excess water and organic phase. At present, researchers have developed a multifunctional catalyst to make the hydrogenation process and the esterification reaction simultaneously, and achieved good performance [97, 98]. Xu et al. [99] carried out one step hydrogenation–esterification over Raney Ni catalyst (RN) and Mo, Sn, Fe, Cu modified Raney Ni catalysts (RNs) in the presence of methanol to converted bio-oil into stable and combustible oxygenated organics (alcohols and esters), there was no ketone & aldehyde detected and the contents of acids and phenols decreased from 49.04% and 7.35% to 8.21% and 3.84%. The conversion of acids could reach to 85.01% which was nearly to the conversion of acetic acid in MCB. The contents of alcohols and esters increased from 5.79% and 4.74% to 53.61% and 33.66%. The content of stable and combustible oxygenated organics reached to 87.27% after OHE of light fraction of raw bio-oil.

5.4. Emulsified fuel
At present, there are still many difficulties in using bio-oil as a fuel for internal combustion engines. Bio-oil produced by fast pyrolysis is very viscous, highly acidic and does not ignite easily as it contains a substantial amount of structural water [87]. It is not only necessary to improve the properties of bio-oil, but also to redesign the structure of the internal combustion engine [100]. However, the bio-oil can be directly used by being miscible with other liquid fuels by the emulsification of the surfactant [101]. Researchers have successfully formulated stable emulsifiers containing different proportions of bio-oil by using various cationic [102], anionic [103], zwitterionic [104] and nonionic surfactants [105]. The applications of bio-oil emulsifiers to replace part of diesel fuel in internal combustion engines is an effective means to expand the application of bio-oil at this stage. However, the cost of the emulsifiers is too high, mainly due to the cost of the surfactant and the energy input during the emulsification process. The emulsifiers cannot be placed for a long time, and the viscosity of the emulsion is too much to meet the requirements of some internal combustion engines [106, 107].

5.5. Separation and purification
The existing research result shows that the potential separation components of bio-oil are: phenol, MCP, o-cresol, p-cresol, guaiacol, 4-methylguaiacol, acetyl alcohol, p-vinyl phenol, 4-vinyl guaiacol, etc [108]. If the catalyst is selectively introduced into the pyrolysis reaction system and changing the gas phase atmosphere on the basis of the existing pyrolysis liquefaction technology, the content of high-value components such as pyrazine heterocyclic compounds in the pyrolysis product will be multiplied [20, 109, 110]. Then, the bio-oil is divided into two parts: rich and low-valued by means of grading and condensing, the former accounts for about a quarter of all bio-oil, and can be used as a raw material for separating and extracting high value-added chemical and chemical products, so it can be called chemical bio-oil. The latter accounts for about three-quarters of all bio-oil and can be used directly as a fuel for thermal equipment such as boilers and kilns, so it can be called fuel bio-oil [110, 111]. Del Pozo et.al [112] studied two liquid-liquid extraction methods, an extraction at original pH and an acid-base extraction to separate compounds of an aqueous phase (AP) containing acetic acid, monosaccharides
and phenolic derivatives, and a non-aqueous phase (NAP) composed of phenolic derivatives and fatty acids and their methyl esters, found that phenolic derivatives, potentially useful in food, pharmaceutical and/or cosmetic industry, were found in both AP hexane and NAP ethyl acetate phases. Finally, methyl esters of fatty acids which could be directed to produce biodiesel were found in NAP hexane phase. Saber et al. [113] reviewed the production and upgrading of algal (marine biomass) bio-oil, extract triacylglycerides (TAGs) and fatty acids from algae to produce biodiesel via esterification/transesterification reactions. The development of microalgae biodiesel has become a research hotspot, called the third generation biodiesel feedstocks, it have emerged as one of the most promising alternative sources of lipid for use in biodiesel production because of their high photosynthetic efficiency to produce biomass and their higher growth rates and productivity compared to conventional crops [114, 115]. Moreover, according to the analysis of the existing market conditions, it is estimated that the value of chemical products separated and extracted of chemical bio-oil can reach more than 20,000 yuan per ton. In other words, the bio-oil prepared by selective pyrolysis can have a value of more than 5,000 yuan per ton of chemical oil, which is much higher than the value of the same quality conventional bio-oil. It can sufficient to offset the added cost of introducing process measures such as selective pyrolysis and fractional condensation.

6. Future prospects
BPLT has the characteristics of short process flow, strong adaptability of raw materials, rapid reaction, high conversion rate, large transformation intensity and easy industrialization. Based on these, countries and regions in the world have formulated strategic plans for biomass energy development, increased investment in biomass energy studies, strengthened the cultivation of high-end biomass industries, and seized the commanding heights of biomass energy economic development.

Although the fuel grade of bio-oil is not high, but it is a liquid fuel, which is a higher grade than the same low-grade straw solid fuel. The volumetric energy density of bio-oil is 8 to 10 times than that of straw. Therefore, if the straw is subjected to dispersive pyrolysis liquefaction directly in the raw material production place, and the bio-oil is collected, applied or re-processed subsequently. Bottlenecks such as collection, transportation and storage of large-scale direct conversion of straw can be effectively avoided.

On the basis of the prior art, the catalyst is selectively introduced into the pyrolysis reaction system and changing the gas phase atmosphere, the content of high-value components such as pyrazine heterocyclic compounds in the pyrolysis product is multiplied.

The bio-oil is then divided into chemical bio-oil and fuel bio-oil by fractional condensation process. The chemical bio-oil is used to separate and purify high value-added chemicals, which can significantly improve the economics of BPLT.

At present, BPLT has entered the stage of industrialization demonstration. With the continuous maturity of various technical links such as raw material collection and pretreatment, selective pyrolysis and fractional condensation, bio-oil upgrades, BPLT is expected to form a relatively complete technology chain and industrial chain within 5 to 8 years, and gradually realized the industrialization in the true sense.

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