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Overview of upgrading of pyrolysis oil of biomass

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Abstract: Pyrolysis oil, obtained from fast pyrolysis of biomass, is a promising renewable energy source which has received widespread interests for its characteristics as combustion fuels used in boiler, engines or gas turbines and resources in chemical industries. However, the pyrolysis oil as a fuel has many unfavourable properties due to its chemical composition, making it corrosive, viscose and thermally instability. Therefore, bio-oil must be properly upgraded to produce high quality biofuel for using as transportation fuels. In this review article, various types of upgrading processes have been discussed in detail including physical refining routes, chemical refining and total pyrolysis refined routes. Finally, a new upgrading route, Physical-Chemical Refining (PCR) is proposed, which will be a very promising refining route of bio-oil.

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Keywords: Biomass; Pyrolysis oil; Upgrading bio-oil; Physical-Chemical Refining (PCR)

Introduction:

The use of renewable sources is increasing because of global warming, negative environmental impact due to the use of fossil fuels and the increase of energy demand and availability of waste materials [1]. Biomass, as a renewable source of energy which contains low nitrogen and few sulphur, maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels [2].

Nowadays, several sustainable technologies are available with the aims of the energy conversion of biomass, such as thermochemical conversion, biological conversion [1]. Thermochemical conversion is considered to be a promising technology for production of chemicals and energy from biomass [3]. The thermochemical conversion process contains, mainly, pyrolysis, gasification, liquefaction and supercritical fluid extraction [4]. Among these conversion processes, pyrolysis is regarded as an emerging technology for liquid oil production, by which biomass can be converted to valuable bio-oil, char and gaseous products. Bio-oil can be used as an intermediate pretreatment step to convert solid biomass into a higher energy content transportable liquid for subsequent processing for heat, power, biofuels, and

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chemicals. However, bio-oils are complex mixtures of water and various organic compounds, mainly including acids, alcohols, ketones, aldehydes, phenols, esters, sugars, furans, hydrocarbons, multifunctional compounds, as well as large molecular oligomers. The water, acids, aldehydes and large molecular oligomers are mainly responsible for the poor fuel properties of bio-oil. Due to the unique composition, bio-oil is highly oxygenated, acid and corrosive to common materials, thermally and chemically instability, as well as non-miscible with petroleum fuels. These poor fuel properties make bio-oil only possible to be used in boilers and furnaces, but hard to be directly used in diesel engines and gas turbines [5]. To overcome these disadvantages, various physical or chemical methods have been proposed to upgrade bio-oil before it can be accepted commercially.

In this article, we reviewed a great amount of literature and broadly divided these bio-oil upgrading technologies into four groups: physical methods such as emulsion, filtration, solvent addition, distillation; chemical refining route such as catalytic hydrogenation, fluidized catalysed cracking, catalytic esterification, steam reforming; co-pyrolysis refining and physical-chemical refining route.

1. Physical methods

1.1 Emulsion

The presence of the polarity compounds, such as phenol, substituted phenols, and aromatic carboxylic acids etc in the bio-oil, make it impossible to blend with the diesel [6]. But with the help of proper surfactants, homogenous emulsions can be obtained. Physical properties of the emulsification of bio-diesel oil would be more similar to that of diesel than that of bio-oil itself, and the negative effects of ash and char in bio-oil would be less because of dilution by diesel. Some preliminary studies indicated that the emulsions could be successfully utilized in internal combustion engines. The problems we face are, the cost of the surfactants is too high.

1.2 Filtration

Bio-oil contains alkali metals, solid particles and bio-char, which decrease storage stability and cause problems in applications. Filters such as granular filter [7] and glass wool hot vapour filter were used to upgrade the quality of the bio-oil including the viscosity, solids content and ash content and the acidity. However, the water content of the bio-oil higher than the unfiltered bio-oil, the heating value is still lower compared to the fossil fuel, which is the most important bottleneck in application.

1.3 Solvent addition

Adding an organic solvent to the bio-oil can reduce its viscosities and improve its stability, what's more, this method is simple and easy to implement. Researchers often use ethanol and other alcohols methanol as an additive. Bidtasang P et al.[8] found that methanol was the most effective additive from a cost perspective.

1.4 Distillation

The most common route of bio-oil physical refining is distillation as well as the petroleum refining. Based on the different boiling point of each component, the bio-oil can be divided into quasi gasoline, quasi diesel and quasi aviation kerosene. Majhi A et al. [9] found that 10wt% of component whose initial boiling point (IBP) was lower than 140℃ had a very high quality. After distillation, bio-oil can be made further refined.

2. Chemical methods

2.1 Catalytic hydrogenation

The bio-oil has a high oxygen content, which affects the homogeneity, polarity, heating value (HV), viscosity, and acidity of the oil. Therefore, bio-oil must be properly upgraded to remove the oxygen and in this way make it resemble crude oil. Catalytic hydrogenation is a high pressure operation where hydrogen is used to remove oxygen in the form of H_2O or CO_2 from the bio-oil, receiving a high quality oil product [10]. The biggest problems are the catalyst deactivation and the cost of H_2 is too high.

2.2 Fluidized catalyzed cracking

Fluidized catalyzed cracking (FCC) is a process in which bio-oil macromolecules were cracked into smaller molecules by zeolite catalysts in a catalyzed reactor. The most common catalysts used in FCC process are ZSM-5 (MFI) and Y (FAU) zeolites which have a good activity in 340 ~500℃ and can be easily regenerated by burned in oxygen [11].

2.3 Catalytic esterification

Catalytic esterification is an operation where alcohols are used to react with carboxylic acids in bio-oil with the help of catalysts, and generates esters. The esterification can remove most of the acids, which reduces the corrosiveness of bio-oil and increases its stability. The esterification reaction is normally catalyzed by solid acid, solid alkali, and an ionic liquid ion exchange resins [12]. However, catalytic esterification process generates large amount of carbon residue which can lead to the rapid inactivation of catalysts.

2.4 Steam reforming

Steam reforming is an efficient process for hydrogen production through the steam heat and under the action of catalyst, which can make the organic matter decompose completely and restructure, removing the carbon and oxygen in the form of CO_2 and CO [13].

3. Co-pyrolysis method

The co-pyrolysis of biomass with industrial waste substantially increases the value of the gas produced and the thermal efficiency of the process and could potentially be a good solution to improve the bio-oil quality. In addition, the use of a mixture of biomass with fossil fuels reduces the total CO_2 emissions and the environmental impact. Zhang H Y et al. added hydrogen-donor solvents such as alcohols in the pyrolysis of sawdust. The results showed that the yield of hydrocarbons was significantly increased while the condition was as mild as biomass pyrolyzed alone [14].

4. Physical-Chemical Refining

Based on the shortcomings of the mentioned refining routes and the considerations of economic feasibility, this article proposed a refining route of bio-oil, which was referred as physical-chemical refining route. From the economic point of view, the step of extraction of high-value chemicals like phenols (phenol and guaiacol) and aldehydes (furfural and butanedial) from biomass before hydrodeoxygenation is desirable. The oil fractions can be separated by the way of water extraction and obtain water-insoluble and water-soluble fractions, which can be separated further. Oxygen free organics (hydrocarbons) generally are water insoluble while oxygenated components (phenols, aldehydes, ketones, alcohols, acids and so on) almost are water soluble. High-value chemicals can be separated from the water phase by distillation or extraction. Oil phase is divided into different fractions through atmospheric and vacuum distillation unit, and then decide whether or not they need further hydrotreating refining according to the properties of the fractions.

5. Conclusion

This article firstly analyzed the advantages of producing liquid oils from biomass pyrolysis, followed by the detailed evaluation of present refining routes of bio-oil, and at last proposed a unique bio-oil refining route. The result reveals that physical-chemical refining route can maximize the value of bio-oil and is a promising way of bio-oil refining in the future.

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Biography

Huijun Yang, master student from Tianjin University, China, focuses on fast pyrolysis of biomass research.