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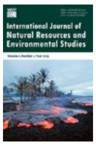

Research on Hydrogenation Treatment of Plant-based Biomass

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ABSTRACT

Biofuels have emerged as a potential substitute for fossil fuels, with production occurring through a range of methods, including physico-chemical processes and other techniques involving biomass. Plant-based biomass has significant potential for biofuel production and holds considerable promise for future applications in the petrochemical industry. Plant-based biomass is composed primarily of two types: lignocellulosic and microalgal. During processing, pyrolysis enhances the efficiency of upgrading; however, the resulting bio-oil contains numerous oxygenated compounds, the presence of which impairs the bio-oil's performance, rendering it unsuitable for direct use as a fuel. Accordingly, the selective utilisation of catalysts for hydrotreating is imperative, as this reduces the oxygen content and enhances the quality of the bio-oil.

KEYWORDS

Biofuels; Pyrolysis; Lignocellulosic Biomass; Microalgae; Hydrogenation.

1. INTRODUCTION

With the continuous development of modern society and the growth of population base, the human demand for energy use is increasing. Energy sources mainly include oil, coal, natural gas and electricity. Among the reasons why the petroleum industry is struggling to develop, there are mainly the following aspects:

1. Environmental aspects: burning oil emits many hazardous gases that pollute the atmosphere. Oil is one of the major fossil fuels, and its combustion products contain components such as CO2, CO, CS and VOCs, which are one of the main sources of greenhouse gases and particulate pollutants. 2. Economic aspect: the turbulent international situation and the rise in oil prices have led to a gradual decrease in the national consumption of petroleum energy, and this, coupled with the influence of the domestic environment itself, has led to signs of a collapse of the market for petrochemicals industries. 3. Social aspect: The development of new energy sources has made the traditional petrochemical industry gradually lose its advantages, which makes it even more necessary to find high-quality energy sources that can replace oil. 4. Political level: In response to the national dual-carbon goals, so that the petroleum industry to the ‘green’ forward, the human race for the replacement of fossil fuels research, will gradually be put on the agenda.

Advanced biofuels with physicochemical properties similar to petroleum fuels and high calorific value are one of the most popular alternatives, so the use of biological feedstocks for the preparation of engine fuels and chemical add-ons has emerged. Compared to the first generation of organic matter biofuels, the second generation of lignocellulosic biomass and the third generation of microalgae biomaterials have received focused attention from scholars at home and abroad. In modern biorefineries, there are many problems in the preparation of biofuels from lignocellulose, such as the separation of lignocellulosic components, the structural modification of lignin, and the selection of catalysts in hydrotreating. Microalgae plant materials, similar to lignocellulose, also have difficulties in their pretreatment processes such as drying, alkalisation and acidification, as well as in hydrogenation. Also, there are hindrances to increase the yield by altering the algal genes to affect the metabolism from a microscopic point of view. These issues are great challenges that are under research or unknown.

2. PYROLYSIS

Pyrolysis is a promising technological tool. Pyrolysis is a process that takes advantage of the thermal instability of a substance and thermally decomposes it under anaerobic conditions to produce a liquid phase, a gas phase and a solid phase, where the liquid phase is the biofuel oil produced from the conversion of biomass. General conventional pyrolysis is divided into slow pyrolysis, medium pyrolysis, fast pyrolysis and flash pyrolysis. By adding different process conditions, they can also be classified as catalytic fast pyrolysis, catalytic co-pyrolysis and microwave assisted pyrolysis [1].

2.1. Catalytic Fast Pyrolysis (CFP)

The use of different catalysts improves the quality of biofuels by increasing the selectivity and yield when converting biomass into fuels and other industrial products. Ropoo et al [2] used different proportions of wood, seeds, leaves and their mixtures for CFP and experiments were carried out using conventional zeolites as well as the addition of a nickel based catalyst, Ni-HZSM-5, and the results showed that the loading of Ni-HZSM-5 showed better selectivity for better selectivity and the aromatic yield can be increased up to 60.3 %.

2.2. Catalytic Co-Pyrolysis (CCP)

CCP is a new method derived from conventional pyrolysis. Mixing and co-feeding biomass with hydrogen-containing substances for a synergistic effect increases the yield and improves the properties of pyrolysis products. Okopi et al [3] used domestic food waste for CCP to enhance aromatic and aliphatic hydrocarbons through the addition of treated eggshells and activated biochar as catalysts, which were utilised to enhance aromatic and aliphatic hydrocarbons by their high selectivity for hydrocarbons.

2.3. Microwave Assisted Pyrolysis (MAP)

Make microwave into the interior of the biomass feedstock, dielectric heating from the inside out, so that the feedstock molecules to accelerate the vibration and rotation, and then heat the feedstock. MAP has the advantages of fast heating rate, short reaction time, good selectivity, etc. Yue et al [4] used microwave-assisted and doped catalysts (HZSM-5, γ-Al2O3, etc.) and urea to pyrolyse soybean straw, and to increase the pyrolysis product bio-oil in the indole, which provides a green route for the production of prepared indole.

3. BIOFUELS

3.1. Bio-diesel

Biofuels are fuels prepared from organic matter and plants (wood, crops, etc.). The most common biofuels are biohydrogen, biodiesel, bioethanol, fuelwood and biogas. According to the development and utilisation of different feedstocks, biofuels can be divided into three generations: the first generation of biofuels is mainly made from edible crops (containing rapeseed oil, cane sugar, starch, etc.), from which biodiesel and ethanol are produced; the second generation of biofuels is made from lignocellulosic feedstocks, which are pre-treated and converted into biofuels by physical, biological and chemical methods; and the third generation of biofuels is made from non-food sources, such as a variety of algal organisms. [5]

The properties of biofuels are overwhelmingly determined by the properties of fatty acids, which vary from plant to plant. A comparison of the properties of plant-based biofuels (arborvitae, linseed, olive, etc.) with those of fossil fuels is shown in Table 1.

Table 1 Biodiesel and petrodiesel[6]

Physico-chemical properties	Biodiesel	petrodiesel
kinematic viscosity/(40 °C)	3.8-4.62	3.64
density/(kg/m3)	862.5-874	846.3
Acidity Grade/ (mg KOH/gm)	0.03-0.17	0.35
Cloud point(°C)	-2.6-17	-14
Pour point(°C)	-13-13.4	-15
flash point(°C)	157-168	55
calorific value(MJ/Kg)	40.10-46.39	42.72
Cetane number	49-64	48.3
Ash(%, w/w)	0.002-0.0012	0.01
C/H/S(%, w/w)	62.1-86.98/13.02-37.9/0-0.0042	81.33/12.78/0.2

3.2. Plant-based biofuels

3.2.1. Lignocellulose

Lignocellulosic biomass is the main component of wooden materials and crops, consisting of 35 % to 40 % cellulose, 25 % to 35 % hemicellulose and 20 % to 30 % lignin, and the structural molecules are shown schematically in Fig 1.

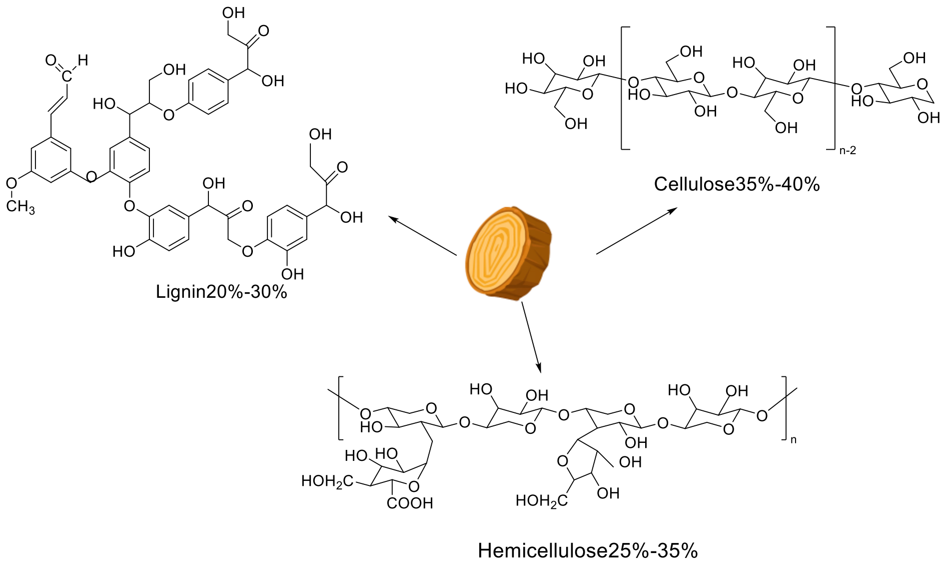

Fig.1 Lignocellulose: molecular structure of cellulose, lignin, hemicellulose

Bio-oil obtained from lignocellulosic pyrolysis cannot be directly used as fuel due to its high acidity, very poor stability and low calorific value, and requires further hydrodeoxygenation (HDO) treatment to detach the oxygen-rich elements in the bio-oil in the form of H2O and CO2, and thus improve the physical and chemical properties of the product. In addition, HDO is easily blended with crude oil for synergistic treatment. The type of catalyst used in this process is determined by the complex structure of its carrier and the acidity of the feedstock, however, high acidity can rupture the intermediates, leading to a reduction in product targeting and a decrease in lignocellulosic conversion.

Yan et al [7] hydrotreated lignocellulose using catalysts (H-BEA, Ni/BEA, Ni/Fe-BEA and Fe/BEA) in an intermittent reactor and showed the highest selectivity for monoaromatic hydrocarbons (85.1 %) and benzene (BTEX) selectivity of 62 % for Ni-Fe-BEA at 400 °C and an initial H2 pressure of 3.0 MPa. Caprariis [8] improved the hydrocarbon ratio and calorific value of the resulting biocrude oil by hydrocatalysing lignocellulose after hydrothermal liquefaction using Ni, Fe and Zn catalysts.

For the three main components of lignocellulose, they can also be obtained through novel biorefinery methods of fractional distillation and hydrotreating to obtain chemicals and fuels, thus facilitating the development of production in downstream industries and contributing to the energy sector.

3.2.1.1. Lignin hydrotreating

Lignin is an abundant natural polymeric material that is a major component of plant cell walls and the reinforcing structure of lignocellulose. Its chemical nature is a versatile cross-linked polyphenol. [9] Zhang et al [10] used etched Ni/ZSM-5 as a catalyst to react at 140 °C for 4 h under H2 pressure of 2 Mpa, and lignin was completely converted to a cycloalkane liquid. This method provides a new option for the efficient use of lignin hydrotreating. Lin et al [11] used nickel-based catalysts with different carriers (SiO2, Al2O3, SZM-5) for hydrotreating under different acidity conditions, and the results showed that the product selectivity could be improved by varying the carriers and acidity.

Pouya et al [12] used HY (molecular sieve) catalyst for in-situ catalytic pyrolysis of lignin, which can reduce coke and increase the conversion of monomeric phenols; also used FeReOx/ZrO2 as a non-in-situ catalyst under mild reaction conditions, and the former HDO had a significant enhancement of aromatics in comparison to some conventional catalysts. Wei et al [13] hydro-liquefaction reaction of lignin under tetrahydronaphthalene (THN)/ lignin ratio of 4:1, 400 °C, initial hydrogen pressure of 3.0 Mpa, and the use of MoS2 for 4 h. The lignin liquid conversion and oil yield were 95.3 % and 83.5 %. Zhou et al [14] selectively hydrodeoxygenated the β-O-4 ether bond in lignin into fuels such as naphthenes using NiLa/CNT. Charles et al [15] carried out hydrogenation reactions with lignin-like model compounds (anisole, guaiacol, 1,2-dimethoxybenzene, etc.) and explored the influencing factors such as temperature, pressure and reaction time, and concluded that the cleavage and hydrogenation of the C-O bond do not interfere with each other under appropriate temperature conditions.

3.2.1.2. Cellulose hydrotreating

Cellulose, which consists of multiple glucose units covalently linked by acetal functional groups, is a major component of plant cell walls and a widely distributed renewable and biodegradable natural polymer [16]. Cellulose is converted to glucose during pyrolysis and by some chemical methods it is eventually changed to chemical industrial products such as acetic acid, acetone, etc. Cong et al [17] dissolved cellulose in NaCl-toluene-aqueous solution for cascade treatment to obtain 5-methylfurfural (MFA), then hydrodechlorination with Pb/C to obtain 2-methylfuran (2-MF), and the two in acidic resin for alkylation reaction, and finally, the two in acidic resin. Alkylation was carried out, and finally fuel was obtained by hydrodeoxygenation under the co-catalysis of Ni/HAP and HZSM-5. Cellulose can also be directly hydrotreated by different catalysts. Frecha et al [18] used carbon nanofibre supported nickel-based catalyst (Ni/NCF) to hydrotreat cellulose to obtain sorbitol. Zhang et al [19]used a nickel-based bimetallic carbon catalyst with embedded structure to hydrotreat cellulose to obtain sorbitol with good catalytic activity. Its yield could reach 67.8 %.

3.2.1.3. Hemicelluloses hydrotreating

Hemicellulose is a polymer consisting of different types of monosaccharides (galactose, xylose, arabinose, etc.) through chemical bonding. Therefore the molecular structure of hemicellulose from different sources is different. Jaffar et al [20] used pyrolysis hydrotreating catalytic treatment of agricultural biomass wastes (rice straw, willow, etc.) to obtain methane yield hemicellulose>cellulose>lignin. Wang et al [21] proposed a tandem hydrothermal pyrolysis and gas-phase hydrogenation deoxygenation process and used Pb/Al2O3 catalysts for hemicellulose This process was carried out to produce 171.1 mg/g of oxygenated biofuel with 89.2 % conversion. Yati et al[22]used 2-methylfuran further derived from xylose, a hemicellulose derivative, with butyraldehyde for catalytic hydrotreating to obtain high carbon diesel fuel.

3.2.2. Microalgae

The main components of microalgae include carbohydrates, proteins and fats. Of these, triglycerides are the main feedstock for the production of biofuels. Microalgae can consume less land and be produced in large quantities under controlled conditions. In addition, studies have shown that microalgae is a renewable and promising feedstock for biofuels that can meet the world's demand for fuel. [23]

Algal biomass can be converted to bio-oil through pyrolysis and hydrothermal liquefaction. Biochar, bio-oil and syngas can be obtained through pyrolysis, while hydrothermal liquefaction is the conversion of biomass into bio-oil by physicochemical and other methods in a high temperature and high pressure water environment. Algae bio-oil is then enhanced by HDO reaction.

The degree and type of wet and dry algae, as well as the structural modification of the algae have an effect on the final bio-oil yield obtained. Shi et al [24] hydrotreated dry and wet algae. The modification of crude esters of dry and wet algae at a temperature of 350 °C and a catalyst loading of 30% resulted in higher quality biofuels.

Ajay K et al [25] used new NiMo carbide catalysts for HDO on algal bio-oils to improve the quality. NiMo carbides were synthesised using co-impregnation method for oxidative phase and carbothermal reduction method with high activity for the reduction of oxygen content in the synthesis of oxygenated compounds. The maximum deoxygenation rate of NiMo-C catalyst was 94 % at temperature 400 °C, time 2.75 h and catalytic loading at 10 %.Steven M et al [26] pretreated algal biomass by dilute acid to improve the potential of microalgae oil yield quality and yield, and also effectively reduced the hazardous impurities in it, reduced the risk of catalyst hazards in the process of hydrodeoxygenation, and increased the algal It also reduces the risk of catalyst hazards during hydrodeoxygenation, increasing the feasibility of algae hydrotreating. Wet algae require further drying and pyrolysis to complete the bio-oil conversion, but this process is complicated. Hydrothermal liquefaction is the direct physicochemical conversion of wet algal material to bio-oil and other liquid phases in an aqueous environment and is suitable for the conversion of aqueous plants and wet biomass. Marinic et al [27] utilised hydrothermal liquefaction to treat Chlorella vulgaris with HDO for 4h at 350 °C and H2 pressure of 50 bar using catalysts NiMo/γ-Al2O3 to improve the rate of deoxygenation to obtain 21.6 % C18, 10.4 % C17, 10.7 % C16 and 5.1 % C15. Moazezi et al. [28] also used Chlorella vulgaris, and the thermochemical conversion followed by hydrogenation resulted in an increase of bio-oil yield up to 52%, a reduction of heteroatoms O, N, and S by 13, 7, and 100%, respectively, and an increase of calorific value by 7%. In addition, the hydrotreating of microalgae to obtain higher yields of aviation biofuels is being studied in depth both at home and abroad. [29-31]

4. SUMMARY

For plant-based biomass: lignocellulosic biomass and algal biomass, such research is of great economic and environmental importance. The use of organic feedstocks in the production of the process enables a rich variety of fuels and other high value-added chemicals to be obtained. The main challenges in the HDO process of lignocellulosic bio-bio-oils are pyrolysis, catalyst activity, and leaching of acid phase components from the bio-oil. The three major components of lignocellulosic composition, cellulose, hemicellulose, and lignin, need to be separated and then subjected to HDO treatment or other processing to make them suitable for fuel and chemical applications due to the large differences in their hydrogen and oxygen contents. Obviously, different process conditions, such as pretreatment, temperature, hydrogen pressure, ratio of feedstocks, and choice of catalyst type, affect the processing results. In process studies of algal bio-oils, wet algae are not suitable for sintering, which would add a lot of tedious processes, and bio-oils can be produced by hydrothermal liquefaction. Most of the algal bio-oil is still obtained by pyrolysis, and this process can use catalytic pyrolysis to improve the quality of bio-oil, and then HDO treatment to obtain higher quality bio-oil. Algal bio-oils and lignocellulosic bio-oils have similar problems during process studies, such as the choice of catalyst type, sintering, and various production conditions. Therefore, the development of high-performance catalysts for plant-based biomass processing and production is one of the most important issues at present. So far, such research has not been further developed, however, in the face of the low-carbon, energy-saving and environmentally friendly environment, modern refining needs to develop new catalysts. These catalysts must maintain good stability and activity during the processing and conversion of plant-based biomass.

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