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Bio-oil valorization: A review

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ABSTRACT

Fuels from biomass (biofuels) are used to mitigate the greenhouse gases produced through the utilization of fossil fuels. Non-edible or waste biomass can be pyrolyzed to produce bio-oil. The oil, an unstable and low energy product, can be further upgraded through hydrodeoxygenation to produce gas and/or diesel range hydrocarbons and value added chemicals. The objective of this review is to explore upgrading techniques that are currently being researched and utilized. This review reveals several aspects that in turn will serve as an aid for bio oil valorization, such as, evaluating characterization techniques involved in understanding salient features of bio-oil, insight of bio-oil pretreatment methods for water removal to increase heating values and decrease risk of catalyst poisoning in subsequent hydroprocessing, studies regarding model compound upgrading, reaction mechanism and finally, provides brief review of common catalysts for hydrotreatment of bio-oil in order to yield value added chemicals and fuels.

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1. Introduction

Hydrocarbons, especially liquid and gaseous fuels, are vital to the transportation industry. Traditionally, the desirable hydrocarbons are produced from fossil fuel sources. However, the continuous use of fossil fuels for hydrocarbon and energy sources has caused severe global problems through increasing the concentration of carbon dioxide (CO_2) in the atmosphere.

Of primary concern, is the current availability of such sources; fossil fuels are being consumed without replacement, creating a volatile market with ever increasing prices. The consumption of fossil fuels caused gradual depletion of world's accessible oil reservoirs. Companies are failing to find new reserves of oil sufficient to meet the future need. Most oil producers are investing in more capital-intensive projects, needing to drill in remote places and deeper to obtain oil. The extensive use of fossil fuels and related chemicals introduces greenhouse gases, such as, CO_2, chlorofluorocarbons (CFCs) and methane into the atmosphere causing the "greenhouse gas effect". This second problem of global warming effect of CO_2 and other greenhouse gases on the environment has generated a lot of public and political concern. Renewable energy resources can be one of the potential alternative solutions to fossil fuels and their derivatives. They have become a large focus of research, as energy sources due to their reduced environmental risks and pollution. In addition to their sustainable favorability, renewable energy resources are, in general, more evenly distributed over earth's surface than fossil fuels and may be exploited using less capital-intensive technologies. Hence, they increase the scope for diversification and decentralization of energy supplies and the achievement of energy self-sufficiency at a local, regional, and national level [1].

Biomass is one such promising alternative and has a worldwide abundance. Despite the complexity associated with biomass as a feed for bio-oils, the use of biomass is rapidly expanding. Several industries have commercialized the production of so-called first generation bio-fuels, bio-ethanol from sugar-like products (sugar, starch, etc.) and bio-diesel (from rapeseed, sunflowers, etc.). However, the scale of production of these first generation biofuels in bio refineries appears to be several times lower than typical unit operations in refineries (few barrels a day compared to thousands of barrels per day in conventional refineries) [2]. Besides, these feeds are in competition with the food industry, which may raise ethical questions as well.

Thus, there is a demand for a second generation of biofuels. Lignocellulosic feed stocks (wheat straw, rice straw, corn, sugarcane bagasse etc.), non-food crops and wood are energy crops, which are converted into second generation bio-refineries. Possible biofuel conversion technologies of said biomass are: fermentation processes (conversion of the cellulosic materials to low molecular weight sugars through chemical and/or physical processes; then, subsequent conversion to ethanol via fermentation), gasification to produce bio-syngas for further upgrading to methanol or gas/diesel, or liquefaction with further upgrading either through gasification or deoxygenation, hydrogenation etc. to produce gas and/or diesel range hydrocarbons and value added chemicals. Bio-oil obtained through fast biomass pyrolysis technique is also considered as one of such second generation bio-fuel. Though, it exhibits higher energy content than biomass and is considered to be easy transportable source of fuels and chemicals, it needs to be upgraded for further use as engine fuel, owing to its high instability, viscosity, polarity and corrosiveness [3]. Low heating values than petrofuels and immiscibility with petrofuels prevents use of crude bio-oil as a fuel additive for some boilers and engines [3–5].

Nevertheless, biomass is still not widely used for biofuel production. The main reasons are the presence of contaminants (including ash, water, and oxygen), the variation in chemical composition, and its low energy density. To overcome these issues, an indirect approach seems advantageous. A possible indirect approach would be the conversion of biomass into a more uniform and stable structure, after which secondary conversion processes, would transform the intermediates into transportation fuels and value added chemicals. The primary conversion process referred to, in this introduction, is the pyrolysis (fast) of biomass. Here, the biomass is subjected to rapid heating to temperatures in the range of 450–650 °C with a residence time of <2 s in an oxygen free atmosphere [6]. Incomplete degradations occur, which yield three major products: char (mostly carbon which can be employed to enrich soil, as a source for activated carbon, or as a solid fuel additive), fuel gas (usable in any combustor or syngas feed), and liquid oil to be further upgraded to a bio-fuel.

In recent years, the liquid products obtained from pyrolysis of biomass have received considerable attention. However, the important aspect is that, these liquids from biomass are not useful as fuels except as direct boiler applications and possibly for some types of turbine and large diesel applications after being modified [7]. In order to make bio-oil to be useful as transportation fuel, it requires chemical transformation to increase thermal stability and reduce volatility, viscosity through oxygen removal and molecular weight reduction. Further, bio-oil does not naturally blend with conventional petroleum fuel. It may be possible to add a solvent or to emulsify mixtures of bio-oil and fuel oil in order to get homogeneous blends. Apart from catalytic cracking and hydrotreating, organic solvents addition and emulsification are also reported as one of the way to improve the quality of the bio-oil [8,9]. However, organic solvent utilization is associated with handling and disposal problems and emulsification of bio-oil with diesel provides a short-term approach to the use of bio-oil in diesel engines. Moreover, fuel properties such as heating value, cetane value and corrosivity are not satisfied. This leaves two feasible avenues for bio-oil upgrading: atmospheric pressure upgrading (catalytic cracking) and high pressure upgrading (hydrotreating) [10,11].

Catalytic cracking is a conventional petroleum reforming process, capable of decomposing heavy fractions into medium and light distillates. The process occurs in the presence of an acidic and preferably hydrophobic catalyst, typically ZSM-5, to produce H_2O, CO_2 or CO under atmospheric pressure. The same technology can be applied to the reforming of highly oxygenated and bulky bio-oil. The high temperatures associated with this process, are able to cleave bonds in the larger molecules as well as deoxygenate compounds present in the pyrolysis oil, and produce desirable (generally aromatic) fuel-range hydrocarbons. Atutxa et al. [12] have successfully applied HZSM-5 in the deoxygenation of the bio-oil in their investigation on catalytic pyrolysis of biomass (Pinus insignis) over H-ZSM-5 zeolite, in a spouted bed reactor.

Hydrotreating (HDT) is another conventional form of petroleum hydroprocessing technology. It is generally used to saturate olefins and aromatics and remove contaminants (sulfur, nitrogen, metals),

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