Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase

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ABSTRACT

Upgrading of pyrolysis oil from biomass offers great potential economic and environmental benefits for the production of sustainable and renewable energy sources. Meanwhile, challenges remain in the development of technical- and cost-effective catalysts and operating processes. One promising approach is liquid phase upgrading, which exhibits numerous benefits. This paper reviews recent progress and future possibilities for obtaining fuels from biomass using this approach. Key upgrading reactions for different oxygenated compounds in pyrolysis oil, including ketonization, aldol condensation, alkylation, hydrodeoxygenation, and oxygenation are discussed. Development of effective catalysts and efficient integration of multiple consecutive reaction steps in one single reactor make liquid phase upgrading competitively advantageous.

1. Introduction

In recent years, utilization of biomass in the energy sector has attracted renewed interest across the world. While the output of other renewable sources is primarily electricity, biomass is able to produce liquid, gaseous, or solids of variable energy contents [1–5]. Among the different biomass conversion processes investigated in the last few decades, fast pyrolysis coupled with catalytic upgrading is one of the most attractive processes both economically and technologically [6–11]. Fast pyrolysis is a thermochemical conversion method in which the biomass feedstock is heated at high temperatures (500–800 °C) for a short period of time (<2 s) in the absence of air [11]. The vapors formed during pyrolysis condense into liquid products (so-called bio-oil). High yields of bio-oil are typically obtained, but the inherent characteristics of the product, including high viscosity, chemical instability, high corrosivity and incompatibility with conventional fuels, render it useless as a fuel. Stabilization can be accomplished by oxygen removal from the abundant oxygenated compounds present in the product, which include acids, aldehydes, esters, phenolics, furanics and oxygenated oligomers [12,13]. The production of stabilized bio-oils has received increasing attention in the pursuit of economically viable large-scale biomass conversion processes [14].

The various possibilities for stabilization of bio-oil proposed in the literature can be divided into four general strategies. The first one is to directly contact the vapor exiting the pyrolysis reactor with a catalyst before its condensation. This strategy, which has been under extensive study in recent years [15,16], has the advantage of preventing some of the polymerization and gum formation reactions that occur in liquid phase and greatly reduce viscosity and instability of bio-oil. The processes that have been investigated with this strategy include suitable catalysts that either deoxygenate the oxygenated compounds or utilize the oxygen functionalities to facilitate the formation of C—C bonds, for example, via ketonization of carboxylic acids or aldol condensation of aldehydes and ketones [17–22].

A second strategy that has been widely proposed since early 1980s is hydrotreating, which includes two options: (i) hydrotreating after condensation of bio-oil [23–27] and (ii) high-pressure post-pyrolysis hydrotreating integrated with a hydropyrolysis reactor [28].

In the former case, the pyrolysis vapors are first condensed and the liquid bio-oil is then transferred and treated in conventional hydrotreating units using commercial catalysts such as sulfided Co—Mo and Ni—Mo, similar to those employed in oil refineries. However, it was found that the low chemical and thermal stability of bio-oil make it unprocessable at high temperatures typically used in conventional hydrotreating units. In addition, the hydrogen consumption becomes exceedingly high. For example, when bio-oil from a poplar wood was hydrotreated over a sulfided Co—Mo catalyst at 355 °C and 13.8 MPa, the liquid product contained about 5% oxygen, but the yield was only 23% [25]. More importantly, coke formation and rapid catalyst deactivation is a common problem found in hydrotreating of bio-oils. Therefore, an additional pre-hydrogenation deoxygenation (HDO) step at moderate temperatures is required to stabilize the bio-oil, in which the most reactive groups are converted to less active ones to avoid severe

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coking in a subsequent step. The same catalysts such as sulfided Co—Mo or Ni—Mo have been used for both steps. It has been reported that this two-step process could produce yields up to 0.53 L refined-oil/L oil feed. However, almost half of this yield is composed of light alkanes, which probably arise from the small oxygenates (C1–C5) in the original bio-oil [24,25]. Over the last 25 years, much research has been carried out to develop more active and stable catalysts as well as to optimize reactor set-up for hydrotreating process and many progresses have been made. However, the large amount of hydrogen required and a substantial amount of carbon loss in light alkane products has impeded its commercialization.

The second option of this strategy is to conduct biomass pyrolysis under medium hydrogen pressure (20–35 bar) in a catalytic fluidized bed (so-called hydropyrolysis reactor) directly connected to a hydrotreating unit, which can further perform hydrodeoxygenation of liquid products and produce hydrogen by reforming some of the light gases obtained from hydropyrolysis [28]. This process has been shown to produce liquid oil with less than 2.2 wt% oxygen from a variety of biofeeds including bagasse, corn stover, algae and wood. However, the added complexity and risk of operating the pyrolysis unit under hydrogen does not result in improved liquid yield (>C5). Therefore, the loss of liquid yield remains as a major challenge for the hydrotreating approach.

A third strategy for biofuel production is co-processing pre-hydrogenated pyrolysis oil together with petroleum feedstocks in conventional petroleum refining units, such as fluidized catalytic cracking (FCC) and hydrotreating [29–33]. The obvious advantage of this approach is the reduced capital costs of utilizing existing refinery infrastructure and avoiding construction of new units exclusively dedicated to biomass processing. To elucidate the possibilities of co-processing approach, some studies have been conducted by co-feeding model oxygenated compounds and hydrocarbon feeds into FCC. For example, Lappas et al. [29] combined hydrodeoxygenation and co-processing in a FCC unit of a mixture of pyrolysis oil with vacuum gas oil (VGO). Before mixing it with VGO, the pyrolysis oil was hydrotreated. In comparison with VGO, the co-processing with pyrolysis oil resulted in higher coke production (0.5 wt%), lower liquid petroleum gas, and increased selectivity toward aromatics. In another study, Corma et al. [33] investigated the catalytic cracking of model bio-oil oxygenates such as glycerol and sorbitol mixed with VGO over different cracking catalysts to elucidate the main reaction pathways and the effect of cofeeding oxygenates. They pointed out that the catalytic cracking of oxygenates involves a complex reaction network. Gas phase products consisting of olefins, CO, CO_2, H_2, and paraffins are produced by dehydration, steam reforming, water gas shift, decarbonylation, and dehydrogenation/hydrogenation reactions. Aromatics are formed by condensation and Diels–Alder reactions of olefins and dehydrated species. Among those catalysts tested, ZSM-5 produced lower level of cokes and high amount of aromatics and olefins. The other catalysts investigated, i.e., a commercial FCC catalyst containing Y-zeolite and silica–alumina matrix, a commercial FCC catalyst with V and Ni impurities (ECAT), Al_2O_3, and pure HY produced high amounts of coke and low amounts of aromatics and olefins. Addition of oxygenated compounds to VGO did not significantly change the product distribution of the final products as compared with VGO alone. However, bio-oil compounds decreased the gasoline yield and overall conversion, increased the coke amount and the olefin to paraffin ratio of C2–C4 hydrocarbons. On the other hand, Bui et al. [31] studied the co-processing of bio-oil and petroleum model compounds under hydrodesulfurization conditions. Similar to the case of the catalytic cracking studies, decreased catalyst performance was observed at the relatively low temperature and high contact time used in the study. This decreased activity might be due to intermediate phenols competing with sulfur-containing molecules for hydrogenation sites. It is clear that while co-processing might be a promising route with great economical advantages, it presents serious challenges, including efficiency of the process and catalyst development, which require further investigation.

A fourth alternative for bio-oil upgrading that would avoid some of the problems associated with the above three strategies is to conduct catalytic conversion in liquid phase over pre-fractionated segments of bio-oil. This review will concentrate on this upgrading strategy. After condensation, the full bio-oil cannot be fractionated by conventional distillation since reheating this unstable liquid results in undesirable oligomerization reactions. However, there are different ways of accomplishing fractionation of the bio-oil during condensation, without the need to reheat it. One of them is to conduct the thermochemical conversion in stages. For example, one can conduct sequential heating treatments at increasing temperatures [34–38], which can thermally break down biomass components (hemicellulose, cellulose, lignin) at incremental temperature due to increased thermochemical stability. Initial heating at temperatures below 300 °C (first torrefaction) results in evolution of small oxygenates (primarily acetic acid and acetol) and water decomposed from hemicellulose. Subsequent heating to 400 °C leads to breaking down of cellulose producing mainly levoglucosan and hydroxymethyl furfural (HMF) [38]. In the final, fast-pyrolysis step (~550 °C), The more stable lignin fraction is decomposed, forming mostly phenolic compounds.

In this contribution, we will discuss current upgrading approaches and future possibilities for bio-oils involving this new strategy. Fig. 1 depicts the simplified approach for bio-oil upgrading in liquid phase. After a multi-stage pyrolysis of lignocellulosic biomass at different temperatures and reaction time the liquid product can be separated into light, medium and heavy oxygenate components. Therefore, the product mixtures from different stages can be selectively upgraded in liquid phase by different catalysts via different reaction approaches. Alternatively, the fractionation of bio-oil can be done during the condensation of the vapors [39]. Either of the two options enhances the upgrading process greatly since it reduces the complexity of the problem from dealing with a variety of different chemistries simultaneously to a series of simpler problems in tandem. While the hydrotreating approach treats the entire bio-oil as a common system, in this case, with a preceding fractionation, one can attack different fractions differently. Specifically, as illustrated in Fig. 1, from different bio-oil fractions one could: (i) partially remove unstable oxygen functional groups, (ii) couple C—C bonds to elongate the carbon chain and (iii) completely remove the remaining oxygen functionality. The light oxygenates, consisting of water-soluble compounds such as acetic acid, acetol, acetaldehyde, etc. can undergo condensation reactions to reduce acidity and partially remove oxygen. For example, ketonization of acetic acid (or even acetol) produces acetone, an attractive building block that can be further coupled with sugar derived compounds, such as furfurals [40]. Ketones can also be hydrogenated to alcohols, which in turn can be used as alkylating agents of phenolic compounds, via acid-catalyzed alkylation [41]. These products, with enlarged C-chain length, can undergo hydrodeoxygenation to produce long chain hydrocarbons, with minimum loss in liquid yield. The sugar derived compounds can either couple with acetone as mentioned above, or undergo oxidation to produce acids, which can also be ketonized and further upgraded as discussed above. The phenolics from lignin fraction of biomass (heavy products) can be alkylated with light alcohols or can undergo direct hydrodeoxygenation. The purpose of this review is to summarize the recent progress in liquid phase bio-oil upgrading and discuss some promising upgrading approaches.