



Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel



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ABSTRACT

Thermal conversion of biomass via pyrolysis, torrefaction, or liquefaction is an attractive process with significant economic potential. The main challenge of this technology is the upgrading of the intermediate liquid product (bio-oil) due to its complex composition. The components of bio-oil can be divided into light aqueous soluble oxygenates, furanics, phenolics, sugars and anhydrosugars, and larger oligomers. Since any single upgrading approach can only target the conversion of one or two families of compounds a combination of separation and conversion is necessary.

A number of fundamental studies with model compounds have been done in the last few years and important concepts about reaction mechanisms and nature of active catalysts have been developed. Unfortunately, the complexity of bio-oil has hampered the impact of these fundamental studies on the practical applications. It is an important challenge to predict how each compound or family of compounds will behave over a catalyst in the presence of other families, when the entire mixture is fed. It is important to take into account that catalysts may quickly deactivate if the entire bio-oil is present, even when they were effective in the presence of a more pure stream. This knowledge should help guide the separation to evaluate the most effective catalytic upgrading strategies. The present review highlights recent advancements made with the conversion of model compounds present in bio-oil, as well as strategies to combine this knowledge with separation advancements in an effort to increase the amount of carbon in the biomass that can be economically converted to fuels and chemicals.

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1. Introduction

The conversion of biomass to liquid fuels and chemicals through fast pyrolysis, torrefaction, or liquefaction carries great economic potential over alternative methods such as fermentation or gasification [1–3]. These techniques utilize heating in the absence of air to produce solid, liquid, and gas streams. A significant fraction of energy goes into the growth, harvesting, and transportation, but the final liquid product can be converted into fungible fuel if properly upgraded. The challenge lies in the complexity of this liquid stream, which may lead to low liquid yields after upgrading. Biomass fast pyrolysis oil, or bio-oil, contains over 400 different oxygenated compounds with a variety of functional groups [4–6]. These compounds can be divided into several families, including light aqueous soluble oxygenates, furanics, phenolics, sugars and anhydrosugars, and larger oligomers. Unfortunately, any single catalytic approach

could only target the conversion of one or two families of compounds to valuable products, while sacrificing the rest to coke or light gases.

The most common upgrading approach is to add hydrogen to the biomass via hydrotreating in an attempt to remove the oxygen while preserving the C–C bonds. Unfortunately, a backbone of six carbons is the lower limit of what can be incorporated into liquid transportation fuels due to the high vapor pressures of short carbon chain hydrocarbons. 40–60% of the carbon in the bio-oil consists of light oxygenates containing 5 carbons or less.⁸ e.g. formic acid (1 carbon); acetic acid, glycolaldehyde (2 carbons); propionic acid, acetol (3 carbons); furan, butanoic acid (4 carbons), furfural, furfuryl alcohol (5 carbons) are among the most abundant compounds in this range.

This means that the most commonly proposed approach of pyrolysis followed by hydrotreating [7] can only convert a fraction of the carbon in the bio-oil to gasoline range compounds, while wasting the rest as light gases. An alternative approach of promoting condensation reactions to build C–C chains would be effective for the conversion of the light molecules containing 5 or fewer

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carbons to build the carbon chain length up to the gasoline/diesel range. However, the conditions necessary for this condensation also typically favor polymerization of the larger oxygenates to produce a resin that is difficult to upgrade catalytically and ultimately yields low-value coke. Any single catalytic upgrading strategy with the entire bio-oil sacrifices a significant portion of the biomass in an effort to upgrade the rest, which is why single catalytic approaches typically result in a small portion of the carbon in the biomass ending up as liquid hydrocarbon fuel [8].

In order to improve the amount of carbon in the biomass that is converted to valuable liquid products, the various compounds and functional groups present in bio-oil need to be separated, at least to some degree to make them controllable. This would allow catalysts and conditions that favor the production of valuable fuel range compounds and chemicals, rather than undesirable losses to polymerization products, coke, and light gases.

Obviously, the introduction of additional separation steps would lead to higher costs. However, the benefits in the net volume of transportation fuel produced from a given amount of biomass resulting from an additional separation step could outweigh the additional processing costs. Since the fraction of carbon lost with current technologies is exceedingly high, there is significant room for process improvement.

The separation of compounds present in bio-oil is not an easy task. Due to the variety of chemical functional groups present, bio-oils are reactive and chemically unstable. Even at room temperature, compounds present in the mixture of bio-oils slowly polymerize and produce resins that cannot be easily upgraded [8,9]. Distillation is not an effective route for the separation of components since increased temperatures accelerate polymerization rapidly leading to tar formation. One very simple approach that has been utilized is the addition of a solvent. If a hydrocarbon-based solvent like tetralin or water/organic solvent mixture is added to the bio-oil, a phase separation results. The more polar compounds partition preferentially in the aqueous phase, while the less polar ones are enriched in the organic phase. Unfortunately, this simple separation does not solve all of the problems since only a small fraction of compounds remain in the organic phase and, more importantly, there is a variety of bio-oil components that are immiscible in both water and organic solvent. For example, starting with a raw bio-oil stream and diluting it in water at high dilution produces a low-viscosity mixture. Upon introducing this dilute stream into a biphasic mixture of a hydrocarbon-based solvent like tetralin and water, the compounds in the bio-oil phase separate into hydrocarbon-soluble, water-soluble, and insoluble fractions. More troublesome, upon heating this dilute stream, a tar with much higher viscosity than the original bio-oil is obtained, despite the high dilution in water and oil. This experiment demonstrates the complexity of the problem of dealing with these compounds in a single mixture.

Additional separation strategies exist, including the sequential condensation of pyrolysis oil vapors [10], more complex solvent extraction [11–14], and staged thermal degradation of the biomass [15]. However, one of the important challenges associated with the effectiveness of separation techniques lies in deciding what the targets for separation should be. Should the separation be aimed at creating streams that are more amenable for storage and transportation? or, should they maximize the potential liquid product after catalytic upgrading? Separation is only effective if one knows how to take advantage of the compounds that are present and missing from the streams resulting from the separation.

This uncertainty has hampered the impact of fundamental studies with model compounds on the practical applications. Due to the complexity of bio-oils, it is a challenge to predict how each compound or family of compounds will behave over a catalyst in

the presence of other families, when the entire mixture is fed. This complexity obscures not only the analysis, but the effect of crucial phenomena such as catalyst deactivation and competitive adsorption on catalyst performance. It may have prompted some applied researchers working with real mixtures to discount the value of model compound studies and lean to more empirical approaches.

The addition of a catalyst *in situ* during the pyrolysis, so-called “catalytic pyrolysis,” generates partially upgraded bio-oils with modified characteristics that are easier to separate due to the creation of more hydrophobic product molecules. It is important to note that catalytic pyrolysis is generally viewed as the upgrading of primary pyrolysis vapors, rather than a modification of the pyrolysis process itself, which is responsible for the generation of initial pyrolysis vapors [16]. Therefore, the catalyst essentially is in contact with the entire mixture of primary pyrolysis vapors generated during such processes. Because of this, the location of a catalyst with respect to the primary pyrolysis vapors is an important consideration for reactor design, but will not be the focus of this review.

In order to improve the overall process, one should learn from the results from model compounds, but taking into account that catalysts may quickly deactivate if the entire bio-oil is present, even when they were effective in the presence of a more pure stream. This knowledge should help guide the separation to evaluate the most effective catalytic upgrading strategies. The present review highlights recent advances made with the conversion of model compounds present in bio-oil, as well as strategies to combine this knowledge with separation advances in an effort to increase the amount of carbon in the biomass that can be economically converted to fuels and chemicals.

2. Staged and thermal fractionation

In fast pyrolysis, biomass is very rapidly heated to $\sim 500^\circ\text{C}$ in the absence of air, which converts solid biomass to a liquid bio-oil with liquid yields as high as 70%, with the remaining part of the biomass converted to noncondensable gases, solid char, and ash. Biomass residence time in a fast pyrolysis reactor is typically 1–2 s. By contrast, torrefaction is carried out at lower temperatures ($200\text{--}320^\circ\text{C}$) for longer periods of time (i.e., residence time of minutes). Torrefaction is generally carried out in order to produce a higher energy density solid, and the water and light gases, which are generated during torrefaction are generally not captured, although they may be used as fuel to heat the biomass.

Fractionation via staged condensation of the bio-oil to obtain multiple, less complex liquid product streams has been proposed by Pollard et al. [17]. In this method, the pyrolysis vapors are sequentially condensed, so the heavier products are condensed first and the lighter ones, later. This approach consists of three traps, maintained at temperatures of 102, 77, and 18°C , respectively coupled with electrostatic precipitators between each step. By using this approach, some separation of the chemical groups is obtained. For example, the heaviest fraction obtained in the first high temperature trap consists of mainly levoglucosan as well as larger phenolic and sugar oligomers. The final low temperature trap is enriched in acetic acid present in the bio-oil along with several other lighter boiling oxygenates [17].

A limitation of this approach is that the vapor product starts with the entire composition and one could not accomplish a differentiated catalytic upgrading of the different families of compounds. While separation by sequential condensation may minimize some of the complex interactions mentioned above, oligomerization and polymerization in the liquid phase before stabilization may still be a problem.

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