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Biofuel from Fast Pyrolysis and Catalytic Hydrodeoxygenation.

Douglas C. Elliott

ABSTRACT

This review addresses recent developments in biomass fast pyrolysis bio-oil upgrading by catalytic hydrotreating. The research in the field has expanded dramatically in the past few years with numerous new research groups entering the field while existing efforts from others grow. The issues revolve around the catalyst formulation and operating conditions. Much work in batch reactor tests with precious metal catalysts needs further validation to verify long-term operability in continuous flow systems. The effect of the low level of sulfur in bio-oil needs more study to be better understood. Utilization of the upgraded bio-oil for feedstock to finished fuels is still in an early stage of understanding.

INTRODUCTION

Process research and development for biomass fast pyrolysis and catalytic hydrotreating (HT) of the bio-oil product has been ongoing for over 30 years. The level of effort has waxed and waned over the years essentially with the rise and fall of the price of petroleum. With the rise of the petroleum price since 2007, there has been another expansion in the research effort.ⁱ This review covers the past few years of R&D outcomes resulting from this higher level of activity. An important review of hydrodeoxygenation (HDO) processing includes a large portion describing developments in fast pyrolysis bio-oil upgrading.ⁱⁱ Another review written more specifically to bio-oil upgrading to fuels concludes that HT is the preferred route compared to non-hydrogenative catalytic cracking, which has also received extensive R&D.ⁱⁱⁱ Finally, the review from PNNL draws together the relevant publications from 2008 to 2013 to provide the basis for the multi-step-temperature HT required to upgrade fast pyrolysis bio-oil.^{iv} This review builds on that one and describes the most compelling research on the subject in the last 2-4 years.

Fast Pyrolysis

The specification of fast pyrolysis bio-oil is an important consideration. It has been well-defined in the CAS # 1207435-39-9.

“Liquid condensate recovered by thermal treatment of lignocellulosic biomass at short hot vapor residence time (typically less than about 5 seconds) typically at between 450-600 °C, at near atmospheric pressure or below, in the absence of oxygen, and using small (typically less than 5 mm) dry (typically less than 10% water) biomass particles.

A number of engineered systems have been used to effect high heat transfer into the biomass particle and quick quenching of the vapor product, usually after removal of solid byproduct “char”, to

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4 recover a single phase liquid product.

5 Bio-oil is a complex mixture of, for the most part, oxygenated hydrocarbon fragments derived
6 from the biopolymer structures. It typically contains 15-30% water. Common organic components
7 include acetic acid, methanol, aldehydes and ketones, cyclopentenones, furans, alkyl-phenols, alkyl-
8 methoxy-phenols, anhydrosugars, and oligomeric sugars and water-insoluble lignin-derived compounds.
9 Nitrogen- and sulfur-containing compounds are also sometimes found depending on the biomass
10 source.”
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15 Other types of biomass pyrolysis oil produced under less specified conditions, typically longer
16 residence time or lower temperature, will have a different chemical composition and will therefore have
17 different chemical and physical properties. The HT processing described in this review has been
18 developed to address the properties of fast pyrolysis bio-oil.
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23 24 Catalytic Hydrotreating of Bio-oil

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26 HT can be effective in removing heteroatoms, principally oxygen, and in producing useful
27 hydrocarbon liquids. Thermally staged treatment is required due to the thermally reactive nature of bio-
28 oil. This is a very important difference from HT of petroleum oils, which contain much lower heteroatom
29 contents and are inherently more thermally stable as a result. Bio-oil cannot be directly processed in a
30 petroleum refinery, but consideration has been given to how its blending into various petroleum streams
31 might be implemented.^v A recent comparison was made of the competitive chemical mechanisms
32 occurring in the hydrotreating environment, namely thermal polymerization versus catalytic
33 hydrogenation.^{vi} Two-stage HT has been the accepted practice for the last 25 years, but a new variation
34 involving the addition of solvent in the low-temperature first step to overcome coke formation has now
35 been reported.^{vii} However, the authors acknowledge the limited use of the data presented as the added
36 solvent was not separated, so the product was contaminated and recovery for reuse was not
37 demonstrated.
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44 3-stage HT has been demonstrated effectively for extended operation with bio-oil. The first goal
45 of 700 h of operation with a single catalyst load was achieved in 2012,^{viii} and during 2013 this effort was
46 extended to 1440 h of time on stream.^{ix} A recent patent application extends this concept to multi-port
47 injection of hydrogen at continually increasing temperature in order to control the exothermic reaction
48 through controlled addition of the hydrogen reactant.^x An alternative low-temperature pretreatment
49 step under development involves oxidation of the carbonyls in bio-oil to acids prior to more conventional
50 hydrotreatment.^{xi xii}
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54 Research continues to explore the HT of bio-oil produced from new biomass feedstocks.
55 Researchers at Pacific Northwest National Laboratory investigated the use of the phase separated heavy
56 (lignin-rich) fraction from bio-oil for production of liquid fuels and low-sulfur coke,^{xiii} bio-oil produced
57 from mountain pine beetle killed trees and hog fuel,^{xiv} and pine bio-oil and the extractant-rich top phase
58 from softwood pyrolysis.^{xv} Another effort by the Eastern Regional Research Center of the USDA
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Agricultural Research Service addressed the hydrotreatment of the low oxygen, high nitrogen bio-oil produced from pennycress seed presscake.^{xvi}

Effect of Sulfur

Bio-oil will contain more or less S depending on the initial biomass feedstock. The amount of S can vary from less than 50 ppm, as for clean white wood, to some tenths of percent for biomasses containing higher levels of protein. The use of precious metal catalysts is limited by the amount of S in the bio-oil as the metal catalysts would be readily poisoned. None the less, there is still significant interest in the use of precious metal catalysts for bio-oil HT.^{xvii} Most of the studies on precious metal catalysts have been done in short batch reactor tests or limited time on stream tests.

A group in China has evaluated the use of NiMo catalyst in the non-sulfided form. Building on their earlier effort, they identified optimum formulations and reduction conditions for catalysts that have very little activity (33% reduction of acetic acid at 200°C, 30 bar, but very little change in bio-oil).^{xviii} The group further examined a series of Ru and bimetallic catalysts at the same low severity conditions. CoRu was identified as the most active catalyst for acetic acid conversion (31%). When similarly applied on bio-oil there was little effect, but the step was proposed as a pretreatment to stabilize the bio-oil by reacting the acids to esters.^{xix} Surprisingly good HDO results with unsulfided CoMo/ γ -Al₂O₃ catalyst were reported in a comparative study wherein FeW/Si-Al, FeCr and mixed Ru/ γ -Al₂O₃ and Ni/SiAl catalysts were also tested.^{xx} While only moderate activity for reduction of acid and increase in HHV was found with the FeW and Fe-Cr catalysts, both the CoMo and the Ru-Ni were very active resulting in nearly complete HDO.

Precious Metal Catalysts

Much of the recent research has used precious metals on carbon supports. Pd has received wide-spread interest. Li's group at Curtin University in Australia, using a 5% Pd/C catalyst, has an important series of publications reporting the transformation of light species during hydrotreatment,^{xxi} the importance of holdup of heavy species in a packed-bed catalytic reactor,^{xxii} and the changes in aromatic structures.^{xxiii} However, there is no recognition or data provided relative to S poisoning of the catalyst and no indication of catalyst deactivation in these short tests, so the results may not be useful for an actual bio-oil HT process. A separate study from Korea reports only partial deoxygenation (55-60%) at 350°C and 60 min in a batch reactor using a 5% Pd/C catalyst.^{xxiv} A recent batch study shows that the reactive carbonyl components can be hydrogenated even at room temperature over a 10% Pd/C catalyst given sufficient time (16 h). (unpublished Rover MR, et al. 2015.), but again there is no consideration of S poisoning.

A modeling effort with Pt and Ni catalysts for phenol hydrogenation in liquid aqueous medium has been recently published.^{xxv} Applicable to bio-oil HT, the authors concluded that hydrogenation in the

liquid water phase would favor cyclohexanone formation, rather than the cyclohexanol favored in vapor phase reaction. This effort correlates well with Lercher's earlier study of Pd/C catalyzed hydrogenation of various phenolics in aqueous phase, which found that the saturated cyclic ketone was the important intermediate.^{xxvi}

Ru continues to be tested for bio-oil HT. A two-stage reactor with both beds filled with Ru/C catalysts was used as the source for analysis by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) of bio-oil and HT bio-oil.^{xxvii} The space velocity used was very high (3.3) so the extent of deoxygenation was not great (25 to 55%). There was limited evidence of saturation, but phenolics were stable. The time on stream was not given and there is no discussion of catalyst deactivation.

Recent attempts to improve the HT with precious metal catalysts have involved added polyethylene glycol as a solvent/dispersant. Switchgrass fast pyrolysis bio-oil was treated at low severity conditions (200-280 °C and 20-70 bar) using either Ru or Rh.^{xxviii} Although there is significant analysis of the products and mechanisms, showing mostly saturation and limited deoxygenation, there is no recognition of the sulfur poisoning issue. In these short batch tests poisoning of the catalyst by the sulfur in the bio-oil (reportedly in the range of 800 ppm for switchgrass^{xxix}) might not be an issue, but it would be deadly in long-term operation. Another study of Pt, Ru and Pd catalysts using bio-oil derived from switchgrass, eucalyptus, and equine manure at somewhat more severe conditions (320 °C, 140 bar) provides similar results, but again no analysis of S in the bio-oil was reported.^{xxx} The S level would be expected to be as high in these feedstocks or even higher in the manure derived bio-oil.

Innovative Use of Sulfided Catalysts

A semi-batch reactor was used over a range of temperature settings to evaluate sulfided NiMo versus precious metal catalysts.^{xxxi} In these short tests the S content was not considered, but catalyst analysis following the tests did show a significant effect of metal sintering for the precious metals on C supports, which would be expected to lead to catalyst deactivation. The authors concluded that the sulfided catalyst provided the desired reduction in acids, unlike the precious metals.

Hydrodenitrogenation of a sewage sludge fast pyrolysis oil was studied using a sulfided NiMo on phosphated alumina. When diluted at 10% in nonpolar solvent, N was reduced below the level of detection, while in polar solvent the activity was much more limited.^{xxxii}

Alternatives to Conventional Catalyst Supports

Most of the research on bio-oil HT has used conventional promoted Mo catalysts formulated on a high-surface area alumina support, typically γ -alumina. This form of alumina is not stable in hydrothermal conditions and earlier work has suggested it would not be stable for bio-oil HT. In addition, the alumina support has been reported to catalyze coke formation when processing phenolics. The

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4 mechanism for phenate binding to the catalyst has been studied recently and confirmed that the binding
5 occurred not on the Mo sites but directly on the alumina, thus indirectly poisoning the catalyst sites by
6 reducing the accessibility. This effect occurs for all but the most basic phenols tested, 2(4)-ethyl phenol
7 and guaiacol.^{xxxiii}
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10 An innovative bimetallic catalyst composed of Ni and Cu was based initially on alumina, but it was
11 found to be leached during the reaction and coke deposition was noted.^{xxxiv} Subsequent work compared
12 a range of support materials including zirconia, titania, silica, CeO₂-ZrO₂, C, and sibunitite. Titania (anatase)
13 was found to produce the most active catalyst, while the zirconia support appeared to be least affected
14 in the reaction environment, although it did change from amorphous to the monoclinic/cubic crystalline
15 form.^{xxxv} However, these metal catalysts remain subject to S poisoning and the short term nature of the
16 tests did not allow for steady state stability determinations.
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21 Ni metal catalysts were synthesized on mixed oxides and tested with guaiacol model compound
22 and a whole bio-oil feedstock. Of the oxides tested (Al-Si, Al-Ti, Ti-Si, Ti-Zr) the titania-zirconia support
23 was found to give the most active catalyst for guaiacol HDO. In tests with bio-oil, it was also found to be
24 active in a short batch test, but coking of the catalyst was visible to the eye.^{xxxvi}
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27 Further work with zirconia as the catalyst support for mixed precious metals was also reported.
28 The authors concluded that, of the metals tested (Rh, Pd, Pt, RhPt, RhPd, PdPt) Rh and Pd alone were the
29 most useful formulations. Tests for extended time showed deactivation of the catalyst. Concern for S
30 poisoning was suggested, but not investigated. Coke formation was found (2.7% C) but could be
31 removed by controlled oxidation below 400 °C. In a comparative test with sulfided CoMo on alumina it
32 was determined that the catalyst lost S during the reaction despite the 100 ppm of S in the feed. S
33 tolerance of the precious metals was not evaluated. Further, the activity of the CoMoS catalyst was
34 significantly lower than the precious metals based on metal weight, though twice as high based on
35 catalyst bed volume, due to the low metal loading (0.5%) for the precious metals.^{xxxvii}
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41 Specialty carbons have also been tested as catalyst supports. In addition to the sibunitite
42 mentioned earlier,^{xxxv} Ni or NiMo on carbon nanotubes has been evaluated in hydrotreating model
43 compounds and bio-oil at low temperature (<250 °C). A 10% Ni and 10% Mo formulation was
44 determined to be most effective. The activity of the catalyst was low at the low temperature, and the
45 short batch tests did not allow for stability determination.^{xxxviii} C nanofibers grown on an Inconel
46 monolith were also tested for supporting bimetallic Pt-Sn catalysts. The bimetallic form was found to be
47 more active and stable than either metal alone in model compound tests, but deactivation over the 3h
48 experiment was a concern.^{xxxix}
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52 A bi-phasic homogeneous catalyst has been tested for bio-oil HT. The report indicates that the
53 Ru-containing Shvo catalyst has activity even at low severity conditions (145 °C, 10 bar, 1h) in the
54 presence of acid for hydrogenation of double bonds without affecting aromatic rings resulting in the
55 almost complete conversion of ketones and aldehydes. However, recovery of the homogeneous catalyst,
56 which was soluble in bio-oil, remained a major problem.^{xl}
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Effect of Minerals

Recent investigations have addressed the presence of trace elements in the biomass feedstock and their fate through fast pyrolysis processing and HT of the bio-oil. Hot vapor filtration has been applied to reduce the mineral content in bio-oil, and the resulting effect in HT has been evaluated.^{xxix} The HT of the hot-vapor-filtered bio-oils, which were low in mineral content even unfiltered, showed minimal differences in catalyst activity over a 5 day test in a continuous-flow, fixed-bed catalytic reactor system. The elemental analysis of the used catalyst beds for filtered bio-oil showed evidence of less deposition compared to the catalysts used with non-filtered bio-oils from switchgrass, which was higher in mineral content. When biomasses with higher mineral content, like forest residues, were pyrolyzed and hydrotreated, it was confirmed that inorganic-laden biomass yields less bio-oil, but the resultant bio-oil can be upgraded to hydrocarbons at a higher yield than bio-oil from clean wood. Thus, the final hydrocarbon yield from clean or residue biomass pyrolysis/upgrading was unexpectedly similar.^{xiv}

Quality of Products

Analysis of the products of bio-oil HT has progressed beyond the more common elemental composition, component analysis by GCMS, and simple fuel properties such as density, viscosity and acid content. HT products with a range of residual oxygen content from 0.4 to 8% were distilled and the fractions analyzed by a suite of fuel and advanced chemical tests.^{xli} A separate study provided the important information on the properties that are relevant to bio-oil HT and utilization of the products.^{xlii}

Utilization of Hydrotreated Bio-oil

Mild hydrotreating has been applied to bio-oil in an attempt to sufficiently stabilize the bio-oil so that it can be processed in conventional petroleum processing systems. In one study, bio-oil was fractionated by water addition to force phase separation and then hydrotreated to residual oxygen levels varying from 14 to 27% (dry wt.). These products were produced using a precious metal catalyst and as a result were highly saturated and the carbonyls removed. The products produced could be successfully processed when diluted to 20% by Long Residue in a catalytic cracker. When coprocessed at 30% with straight run gas oil in a HDS unit, competition between HDS and HDO reactions was observed, but without permanent catalyst deactivation. The result of coprocessing was similar to processing only fossil oil and independent of the origin of the HDO bio-oil.^{xliii} In a separate study, the level of oxygen removal was higher yet the products were still often immiscible with hexane or toluene.^{xliv} The catalyst in this case was a sulfided NiMo, which resulted in a lower level of residual oxygen but also a lower H to C ratio, suggesting less saturation.

In an economic assessment of bio-oil HT, it was concluded that it is likely that some bio-oil components, upgraded to some degree, will be processed in existing refinery facilities and blended with petroleum-derived components to produce “drop-in” gasoline and diesel fuels. Large savings are

possible if more of the bio-oil upgrading can be done in existing refining facilities, but physical and economic feasibility is not known at this point, in part due to a lack of understanding of bio-oil composition at various stages of deoxygenation.^{xlv} The authors identified the most promising areas for economic improvement, which needed future research: 1) Identification of a stable upgrading catalyst, 2) Definition of the maximum level of oxygen that can be tolerated by the existing refining infrastructure, and 3) Improved oxygen removal during the pyrolysis step.^{xlvi}

CONCLUSION

The technology for producing infrastructure compatible fuels from biomass using fast pyrolysis and catalytic hydrotreating (HT) is in an early stage of development. The use of bio-oil produced at fast pyrolysis conditions needs to be confirmed when performing HT research. The question of the use of sulfided or unsulfided metal catalysts for bio-oil HT needs to be clarified in light of the variable amount of S in bio-oil products from various biomass feedstocks. New catalytic formulations and methods are under development and being tested. The use of batch reactor systems has limited utility for process development, except in the earliest stages, and R&D based on continuous-flow reactor systems needs to be expanded.

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