What Should We Demand from the Catalysts Responsible for Upgrading Biomass Pyrolysis Oil?

The sustainability, feasibility, and overall commercial readiness of biofuels are still a matter of intense debate. While the potential benefits of replacing a sizable fraction of fossil fuels by liquids from renewable sources are obvious, substantial barriers for implementation must still be overcome. For example, it is widely recognized that biofuel development can only be sustainable if it does not interfere with production of human food and animal feed. So, significant efforts have been directed toward utilization of cellulosic wastes in the production of ethanol. However, cellulose is only a part of biomass, which leaves an important fraction unconverted in the form of waste or low-quality fuel. The Perspective contributed by Hicks to this issue of *The Journal of Physical Chemistry Letters*[1] points out the importance of fully utilizing the whole biomass, including the more recalcitrant parts, such as lignin, to minimize the impact on the supply and the cost of food. He emphasizes that lignin is an attractive raw material for biofuels due to its relatively low O:C ratio compared to cellulose and hemicellulose and its high energy content.

Thermochemical methods are effective for converting whole lignocellulosic biomass from a variety of sources, including low-moisture grasses, wood, and standing vegetation not suitable for lumber. Hicks[1] compares the advantages and disadvantages of fast pyrolysis and indirect liquefaction as the two most popular thermochemical methods for producing liquids from solid biomass, with the former being preferred due to its potential to readily produce liquids without the initial utilization of hydrogen or high pressures. Unfortunately, the pyrolysis liquid products contain a wide variety of oxygenated products that include three main families of compounds: (i) small acids, aldehydes, and ketones (such as acetic acid, acetol, acetone, etc.); (ii) furfural, levoglucosan, and other sugar-derived compounds; and (iii) lignin-derived phenolics.

Therefore, the main challenges faced by future refiners of the liquids obtained from whole biomass will not only include the elimination of oxygen, but also the retention of carbon in the product, with minimum hydrogen consumption. At the same time, the resulting liquid needs to have specific properties, either as a final fuel component or as a stabilized intermediate to be further processed in conventional oil refineries. For example, direct conversion of the as-produced pyrolysis oil in a conventional hydrotreating (HDT) process could accomplish the O removal, but it would fail in maximizing C retention. HDT of the small oxygenates would result in undesirable production of C_2–C_3 gases products rather than liquids in the target fuel range (C_6–C_{14}).

As a result, it is important to evaluate these challenges and the role that different catalysts could play in the conversion of each of these families of oxygenates in the light of potential reaction paths. In his Perspective,[1] Hicks emphasizes that the development of highly selective and durable catalysts will be key to the success of biofuel upgrading technologies.

What Must We Expect from These Catalysts? In the first place, with the appropriate catalysts, we can utilize the relatively high reactivity of the oxygen functionalities (carboxylic, carbonyl, hydroxyl, and ketonic groups) to conduct C–C bond forming reactions, such as ketonization and aldol condensation. That is, instead of eliminating the oxygen functionalities too early, a catalytic cascade approach may allow us to take advantage of their reactivity before attempting the deoxygenation. Oxide catalysts are generally effective in catalyzing ketonization of carboxylic acids, but reducible oxides such as ceria and ceria-based double oxides (e.g., $CeZrO_2$[2]) can even catalyze the ketonization of small aldehydes. Reducibility of these oxides is thought to be responsible for this high reactivity toward aldehydes, as shown in a recent study by Chen and Mullins.[3] They have pointed out that while acetaldehyde only shows a weak interaction on fully oxidized $CeO_2(111)$, desorbing intact at 210 K, it chemisorbs strongly on reduced $CeO_{2-x}(111)$ desorbing at much higher temperatures, with formation of more reactive species. Aldol condensation can be used to build C–C chains not only with the aldehydes arising directly from the pyrolysis oil, but to utilize furfurals from the dehydration of sugars via cross aldol condensation. For example, while furfural cannot undergo the self-aldol reaction due to the absence of alpha H in the molecule, it can certainly undergo cross condensation with acetone, which can be directly produced from abundant acetic acid via ketonization. Acidic and basic zeolites are also effective in catalyzing C–C bond forming reactions, but with a higher selectivity to aromatics than those obtained on metal oxides. For example, ZSM5 can convert propanal selectively to C7–C9 aromatics via a reaction path that involves consecutive aldol reactions, followed by cyclization.

In a subsequent step, one can attempt to deoxygenate the resulting products, which may now have C numbers around the target range, but still contain a significant amount of oxygen. Ketones and alcohols are relatively easily deoxygenated via hydrogenation/dehydration, under mild conditions.[4] By contrast, the hydrodeoxygenation of phenol and methyl-substituted phenols is a more demanding reaction. Researchers have debated whether hydrodeoxygenation of phenolics must proceed via hydrogenation of the phenyl ring followed by elimination of H_2O or it can also proceed by direct hydrogenolysis of the $C(sp^2)$–O bond without breaking the aromaticity. The latter route, appears energetically unfavorable since the $C(sp^2)$–O bond is stabilized by delocalization of the out-of-plane O lone-pair orbital. Yet, some authors have supported the role of this path based on the observed low concentration of saturated or partially saturated rings in the products. However, as proposed by Massoth et al.,[5] a likely reaction path is one that starts with a fast, non-rate-limiting, hydrogenation step of a double bond in the aromatic ring, producing a surface intermediate that converts the $C(sp^2)$–O bond into a $C(sp^3)$–O aliphatic bond that is easier to cleave either on a metal or via dehydration on an acid

site. Therefore, bifunctional catalysts (e.g., Pt/H-Beta[6]) are particularly effective since hydrogenation/dehydrogenation occurs on the metal function while dehydration can occur on the acid sites. When the operating temperatures are high, dehydrogenation of the ring is favored, and the products are mostly aromatics. By contrast, at lower temperatures the products contain saturated rings and consume more hydrogen.[7]

While many studies have reported the use of catalysts that are reasonably effective in catalyzing the different types of desirable reactions with individual model compounds, the situation becomes much more complicated when the entire mixture of pyrolysis oil compounds is fed on a given catalyst. The presence of impurities such as alkalis, as well as S- and N-containing compounds makes the task even more difficult, and severe catalyst deactivation is one of the greatest challenges of the upgrading of lignin. Among the lignin-derived phenolics, those with multiple oxygen functionalities are the most highly deactivating. As described by Popov at al.[8] guaiacol, a common component of pyrolysis oil chemisorbs strongly on alumina by formation of doubly anchored phenates while phenol and anisole form monoanchored species. In addition to this strong adsorption of phenolics, catalyst deactivation may be greatly accelerated by the presence of oligomers, char particles, and inorganics typically found in pyrolysis oil. It is not entirely clear whether the heavy oligomers are entirely due to recondensation of phenolics and other components as the vapors condense or they are even present in the original vapor phase. If their presence is not significant in the latter case, methods such as catalytic pyrolysis and upgrading of vapors might greatly stabilize the most reactive components and extend catalyst life.

Novel ideas are being explored to minimize the complications and catalyst deactivation associated with handling the whole mixture. This is an exciting area that will open new research opportunities. For example, Lercher et al.[9] have utilized a method of catalytic depolymerization of lignin in the liquid-phase and proposed that phenolic monomers are the only primary products of base-catalyzed hydrolysis while oligomers are formed in secondary recondensation steps. The critical aspect in this method is then the inhibition of oligomerization, for which they use boric acid to suppress condensation reactions. In another recent example, Huber et al.[10] studied the combination of hydrolysis with catalytic pyrolysis to separate the products into different streams that are more or less enriched in any of the families mentioned above. Multistage methods like this will allow the subsequent catalytic refining steps to focus on the required specific chemistry (C–C bond formation, C–O bond cleavage, etc.). Another alternative mentioned by Hicks in his Perspective[1] is the use of ionic liquids (ILs) to enhance the access to specific sites accelerating the rate of bond cleavage at moderate temperatures. For example, he describes studies in which IL were combined with metal chlorides to depolymerize lignin model compounds by facilitating the cleavage of β-O-4 linkages, yielding guaiacols as primary products. While use and recycle of IL would involve additional process complications and additional cost, these liquids offer the possibility of tailoring them with specific properties by an appropriate functionalization or a specific combination of ions. This unique tunability of IL makes them very attractive for biomass processing and other applications.[11] Combination of IL with some of the catalytic functions described above will open an interesting number of possibilities for further research.

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