

Platinum Group Metal Catalysed Hydrodeoxygenation Of Model Bio-oil Compounds

Investigating catalysts for upgrading bio-oils to fuels and chemicals

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Introduction

The use of biomass as a starting point for the manufacture of chemicals and fuels has been the subject of increasing research effort in recent years. A wide range of biomass sources are being investigated and reported in the literature, but with a particular focus on second generation biorenewables, which use non-food sources of biomass. Examples of such biomass sources include algae-derived products, agricultural residues, wood and residues from forestry plantations and municipal solid wastes. Waste products are of particular interest due to their low cost and availability in large volumes. Analyses carried out by the United States Department of Energy suggest that future potential resources of sustainable biomass in excess of 1 billion tonnes will exist in the USA alone, in the form of agriculture residues, forestry biomass and energy crops. Such resources could be made accessible with only modest changes in land use and agricultural practises (1).

A range of technologies are currently under investigation to convert these feedstocks through to useful chemicals and fuels. Examples of such technologies include gasification to syngas, followed by conventional conversion to higher molecular weight compounds (for example, *via* Fischer-Tropsch synthesis, or methanol synthesis followed by methanol conversion technology),

fermentation and hydroprocessing. Two process routes that have attracted increased interest in recent years are fast pyrolysis and advanced biotechnology combined with thermochemical conversion. These offer very different approaches to the conversion of waste biomass sources to useful chemicals and fuels. However, realisation of the potential of either option as a route to bio-derived products will require developments in both catalyst and process technology.

Fast Pyrolysis

Fast pyrolysis involves rapidly heating biomass in the absence of oxygen to generate so-called 'bio-oil', essentially a depolymerised and partially deoxygenated product. This may be carried out either in the presence of a catalyst (catalytic fast pyrolysis) or using a non-catalytic medium (for example sand). For biomass containing high levels of complex organic polymers, such as lignin and cellulose, pyrolysis is a convenient method of converting a solid material, often with a high water content, into a liquid suitable for further processing. It is also cited as a versatile technology option, in principal suitable for use with a range of feed materials.

Economic analyses indicate that pyrolysis is a potentially attractive route to drop-in hydrocarbon fuels from biomass. Data published by the United States Department of Energy predicts that pyrolysis has the potential to offer a low capital and low operating cost route to hydrocarbon fuels when compared with other biomass-based technologies (2). The advent of low cost hydrogen from shale gas has also been predicted to advantage pyrolysis-based routes to fuels (3). However, as noted above, developments in catalyst technology are required to economically upgrade pyrolysis oils through to conventional hydrocarbon fuels.

Pyrolysis Oil Upgrading: Model Compound Studies

Pyrolysis oil is a complex mixture of many smaller organic compounds, a small selection of which is shown in **Figure 1** (4). In addition to these organic species, pyrolysis oil is also characterised by high levels of water (very variable, but water levels of 20% and above are quite usual), a high organic acid content (usually measured by total acid number, which would typically be in excess of 100) as well as a variety of inorganic impurities that can act as catalyst poisons. Given the complexity of pyrolysis oil and the challenges involved in accurately analysing the composition of the oil, many catalyst development studies have used model compounds to develop the catalysis needed to successfully upgrade pyrolysis oil to fuels and chemicals.

The transformation of pyrolysis oil to the molecules found in drop-in hydrocarbon fuels (see **Figure 2** for some examples of such molecules) requires a number of catalytic transformations, for example deoxygenation, carbon-carbon bond formation, isomerisation and aromatisation. Hydrodeoxygenation is a convenient route to use hydrogen to eliminate oxygen from the molecules present in pyrolysis oil and a range of catalysts have been shown to be effective for this conversion (5, 6). Some of our work

in Johnson Matthey has investigated the potential of metal-supported systems for pyrolysis oil upgrading *via* hydrodeoxygenation and some representative results are shown in **Figure 3**. This shows data for the hydrodeoxygenation of the model compound *m*-cresol, carried out in a batch autoclave reactor using a selection of supported nickel, palladium and platinum catalysts. Tests were carried out over a period of 2 hours at a hydrogen pressure of 20 barg and using a fixed metal to *m*-cresol mass ratio of approximately 1:2500, the latter being used to account for differences in the metal loading in each of the catalysts. The products identified by gas chromatography (GC) were a combination of hydrocarbons, predominantly methylcyclohexane and toluene, and the oxygenates 3-methylcyclohexanol and 3-methylcyclohexanone. As can be seen from these data, high conversion of *m*-cresol is readily achieved using all three catalysts at 275°C under these test conditions. Selectivity towards hydrocarbons varies over the three catalysts, with the supported platinum catalyst demonstrating the highest selectivity to hydrocarbons at 275°C. Repeating the experiment with the 0.3% platinum on alumina catalyst at 300°C results in a significant increase in the degree of deoxygenation and yield of hydrocarbon products.

Other catalysts are reported in the literature as also being effective for deoxygenation of such model

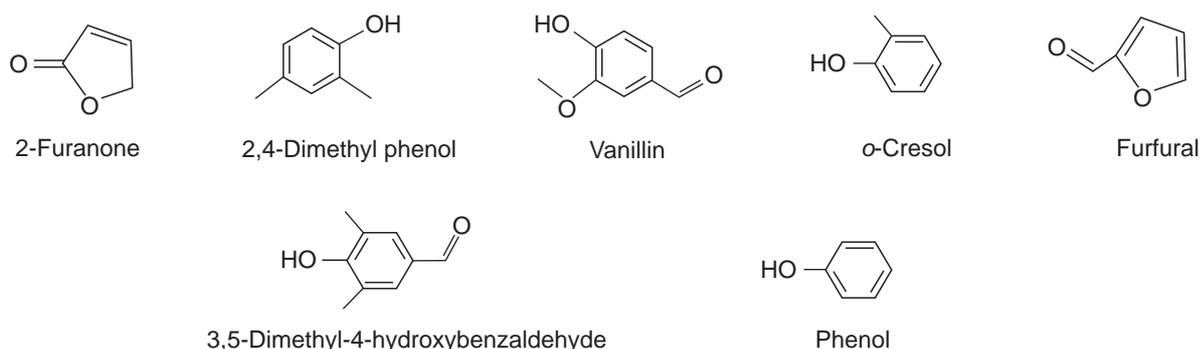


Fig. 1. Examples of molecular species found in pyrolysis oil. Data taken from (4)

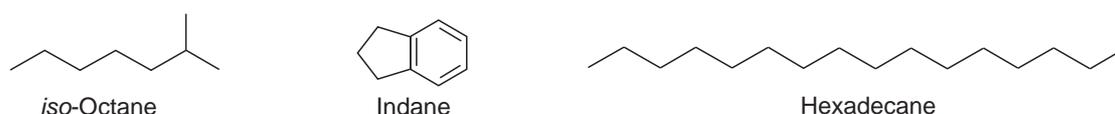


Fig. 2. Examples of molecular species present in hydrocarbon fuels

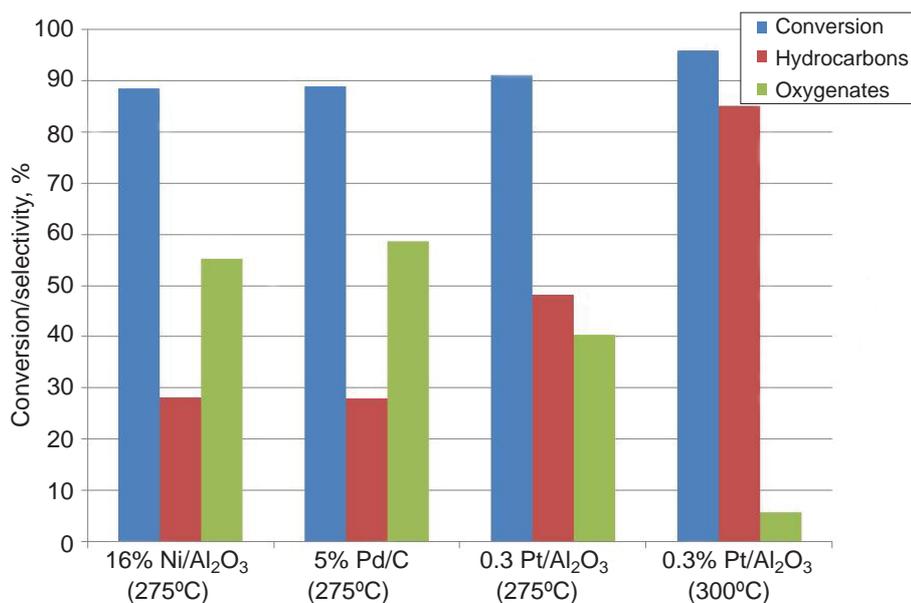


Fig. 3. Hydrodeoxygenation of *m*-cresol over supported nickel, palladium and platinum catalysts

compounds, including hydroprocessing catalysts such as supported cobalt-molybdenum (CoMo) and nickel-molybdenum (NiMo) catalysts (7, 8). Such materials undergo a pre-sulfiding step to yield the active form of the catalyst, a sulfided CoMo or NiMo site. Compared to the sulfur-based active sites found in CoMo and NiMo catalysts, the supported metal systems described above offer the advantage of a sulfur-free active site, particularly suited to conversion of feeds low in sulfur and for the production of low-sulfur fuels.

Bifunctional Catalysis

The development of more complex, bifunctional catalysts has opened up alternative reaction pathways for deoxygenation. Figure 4 shows some more model compound data, again for the hydrodeoxygenation of *m*-cresol over a selection of platinum-based catalysts (9). At 150°C and a hydrogen pressure of 20 barg, a 1% platinum on alumina catalyst was shown to give 100% conversion of *m*-cresol, but with a high selectivity to methylcyclohexanol and only 2% yield of hydrocarbons (methylcyclohexane). In contrast, a 1% platinum on a beta zeolite catalyst, also operating at 150°C, gave 100% *m*-cresol conversion, but with 99% yield of methylcyclohexane. Use of the beta zeolite by itself in the presence of hydrogen gave no measurable *m*-cresol conversion in these studies at

temperatures up to 200°C. These data are consistent with hydrogenation of the aromatic ring occurring over platinum sites on the catalyst, with deoxygenation being driven by acid sites on the zeolite component of the active surface, for example *via* dehydration, followed by subsequent hydrogenation of the C–C double bond generated by water elimination. A simplified reaction scheme is given in Figure 5. Supporting evidence for this reaction pathway comes from studies carried out on 3-methylcyclohexanol, the product from the ring hydrogenation of *m*-cresol. If this substrate is reacted with the beta zeolite at 150°C and at a hydrogen pressure of 20 barg, 100% conversion of the alcohol is achieved. The product distribution is more complex than that determined for the 1% platinum on beta zeolite catalyst, due to the presence of a number of unidentified products, but is dominated by methylcyclohexene (57% selectivity). The use of bifunctional catalysts offers lower temperature routes for deoxygenation when compared to the temperatures required to achieve hydrodeoxygenation using conventional metal-supported catalysts.

Fatty Acid Conversion

Metal-supported zeolite catalysts such as those described above have also been shown to be effective for the conversion of other compounds to hydrocarbon

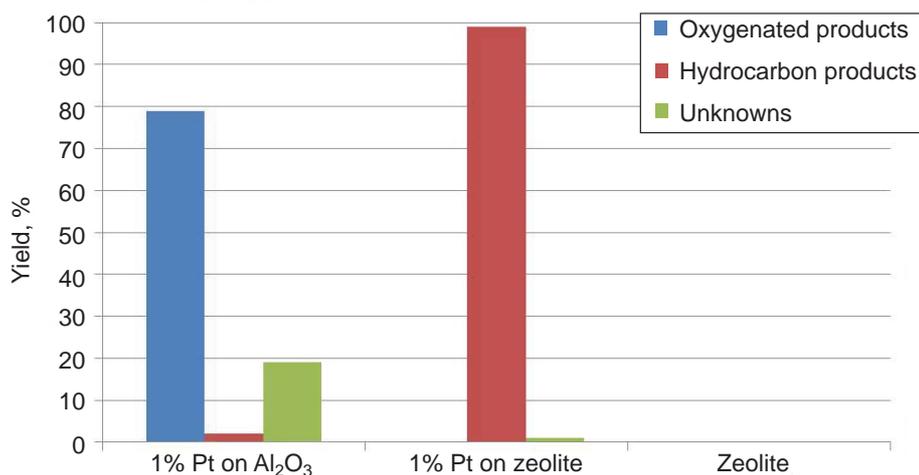


Fig. 4. Hydrodeoxygenation of *m*-cresol over supported platinum and zeolite catalysts. Data taken from (9)

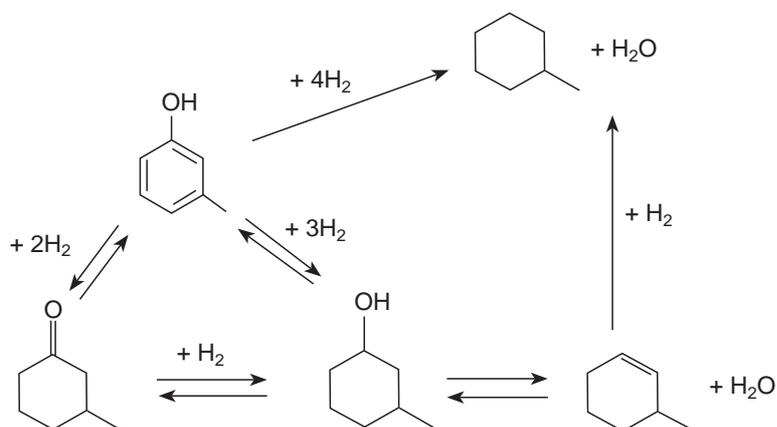


Fig. 5. Simplified reaction scheme for *m*-cresol hydrodeoxygenation

molecules suitable for use in fuels. Long chain fatty acids and methyl esters have been recognised as interesting starting points for the synthesis of linear hydrocarbons such as those found in diesel fuels. Current commercial sources of these molecules, for example palm oil, are not economically attractive starting points for fuel production. However, the development of advanced biotechnology offers the potential for the generation of these molecules from waste streams such as carbon oxides and methane.

The development of catalysts for the conversion of fatty acids and methyl esters to hydrocarbon molecules has also been examined in our labs, initially using model compound studies. In a typical study, a feed of palmitic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$) in a hydrocarbon solvent

(dodecane) underwent reaction under a hydrogen atmosphere over a range of catalysts. **Figure 6** shows the product distribution achievable for a selection of supported palladium and platinum catalysts (10). A 5% palladium on carbon catalyst, operating at 298°C and 10 barg, was shown to give 54% conversion of the palmitic acid feed, with high selectivity to the linear C15 hydrocarbon *n*-pentadecane under these conditions. No other products were detected in this study. The use of a 5% platinum on zeolite catalyst (mordenite, with a silica to alumina ratio of 20) under the same process conditions resulted in 95% conversion of the acid feed and a markedly different product distribution, determined by GC analysis as comprising 41% linear C15 hydrocarbon, 2% branched C15 hydrocarbons,

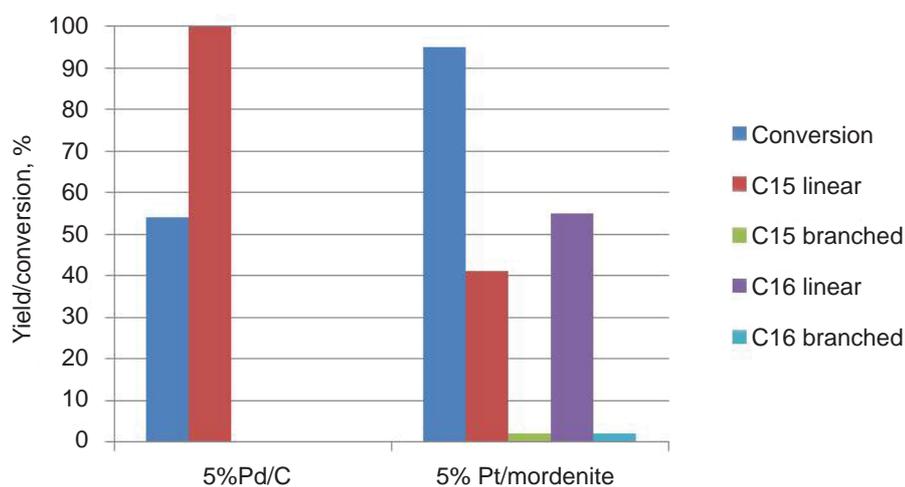


Fig. 6. Hydrodeoxygenation of palmitic acid over palladium on carbon and platinum on mordenite catalysts. Data taken from (10)

55% linear C16 hydrocarbon and 2% branched C16 hydrocarbons. The degree of fatty acid conversion and the distribution of hydrocarbon molecules in the product have been shown to be influenced by both process conditions (for example, hydrogen partial pressure) and catalyst details (metal loading, zeolite type, silica to alumina ratio) (10). This allows different hydrocarbon molecules to be obtained from the fatty acid feed, including linear and branched alkanes and aromatic hydrocarbons, the latter of particular interest for aviation fuel applications.

In contrast to the supported metal systems described above, the use of bifunctional catalysts in biomass conversion offers the potential for lower temperature operation, with resultant advantages in catalyst deactivation rates. Control of the acid functionality in the catalyst also allows a different range of hydrocarbon products to be produced, in particular more branched and aromatic hydrocarbons, which positively influences the fuel properties of the resultant hydrocarbon mix.

Beyond Model Compound Studies

As noted above, many biomass feeds, and in particular pyrolysis oil, are a complex mixture of organic compounds, acids, water and inorganic species. The presence of these additional components has a significant effect on the catalysis. For example, the water and acid components of bio-oil are of great significance in the choice of an upgrading catalyst, causing significant restructuring and potentially physical destruction of the catalyst.

Model compound studies such as those described above can play an important role in the development of catalysts suitable for biomass upgrading and an understanding of reactivity patterns. However, they do not adequately address all of the key technical challenges associated with biomass upgrading, in particular catalyst deactivation and longevity. In order to progress these aspects of catalyst development, studies using real bio-derived feedstocks are essential.

Conclusions

The model compound studies presented here have demonstrated the feasibility of using catalysis in combination with fast pyrolysis and biotechnological routes to upgrade a variety of biomaterials to fuels. Both technologies open up the potential to use low cost feeds as precursors to drop-in hydrocarbon fuels. Fast pyrolysis is particularly well suited to deal with a wide range of bio-feeds and to break down the complex organic polymers to smaller oxygenated molecules suitable for catalytic upgrading. In the catalytic conversion of fatty acids and methyl esters to hydrocarbons, modification of the catalyst and process conditions has also been shown to give the ability to produce a variety of molecules and hence to tailor the final composition of the fuel. Further work remains to be done, in particular to optimise the catalysts to deal with the combination of high water content, organic acids and inorganic poisons and overcome the challenges inherent in this promising area.

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