Catalytic cracking of ligno-cellulosic biomass to fossil fuel additives

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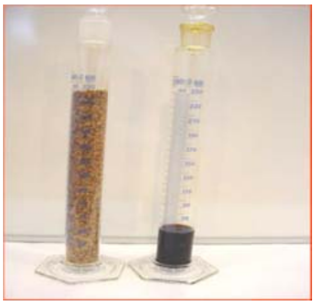
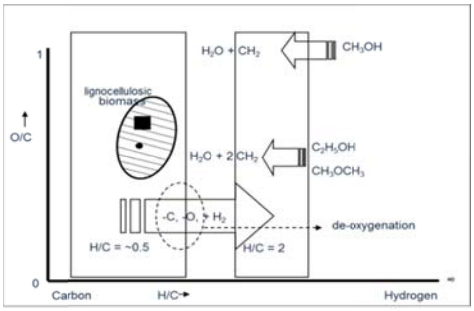


Lignocellulosic biomass from agricultural residues has the advantage for biofuels production as it does not compete with food chain industry. Its thermal conversion to liquid fuels *via* flash pyrolysis is a relatively well established and simple process. The resulting bio oil is a convenient feedstock for transport to a refinery and upgrading to make fuels/fuel additives. Unfortunately, pyrolysis process produces an oil of very poor quality (very viscous; highly acidic; high oxygen content and low heating value). It is a mixture of aromatic and aliphatic acids, aldehydes, ketones and alcohols. Fossil fuels have a H/C ratio of ~2.0 and compatible biofuels such as methanol, ethanol or dimethyl ether also have the same compositional requirements in addition to having water content present. Thermal pyrolysis oil has a H/C ratio of ~0.5. Similar to a Fluid Catalytic Cracking process, upgrading the bio-oil requires removal of not only coke, but also its oxygen content.



An *in situ* catalytic upgrading during the pyrolysis of biomass aimed at de-oxygenation of part of the carbon content in the biomass as CO_2, brings the properties of bio-oil closer to fossil fuels. Removal of oxygen, especially from carboxylic acids, *via* de-carboxylation lowers the acidity of the bio oil, a key requirement for its use.

Among the biomass components, the part that does not compete with food is lignin, thus it is the most appropriate, renewable feedstock for fuels. Lignin is a three dimensional polymer where all types of bonds between aliphatic and aromatic entities, e.g., C-C, C-H, C-O-C, are present. Design of a cracking catalyst should aim at rupturing these bonds. Two classes of bonds dominate the lignin structure, they are (i) C-O-C bonds involving an aliphatic and an aromatic carbon, α-O-4 and β-O-4, C-O-Me etc., and (ii) C-C bonds between two aromatic carbon atoms, 5-5, or between an aliphatic and aromatic carbon, β-1 and those in the alkyl substitutions on the aromatic ring. Selective cracking of the C-O-C bonds allows the required de-oxygenation, scission of C-C bonds lowers molecular weight and boiling point.

Enhanced de-oxygenation without carbon loss can also be achieved by hydrogenation. The aqueous phase of the bio-oil which contains dissolved oxygenates is a feedstock for hydrogen via aqueous phase reforming. Current challenges and issues involved in making the pyrolysis oil suitable for refinery applications will be discussed.

References

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