

# Catalytic Pyrolysis of Lignocellulosic Biomass to Bio-Oil - A Route to High Quality Bio-Fuels

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## Introduction

Role of biomass as an energy source is expected to increase in the coming years because of worldwide availability, zero net CO<sub>2</sub> emission, and low price. Liquefaction of biomass is very favorable for transport, storage and use of biomass. Thermal cracking of biomass (pyrolysis) is a relatively well established process to produce bio-oil under relative mild conditions (atmospheric pressure and 450 - 550 °C) [1], but the quality of the oil produced is far too poor for direct use as transportation fuel.

Pyrolysis oil consists of a complex mixture of aliphatic and aromatic oxygenates (e.g., acids, aldehydes, ketones) and particulates (solids). It is very viscous, acidic (pH<3) and unstable liquid with relatively low energy density (19 MJ/kg) compared to conventional fossil oil (30 MJ/kg). Such poor quality of the bio-oil requires costly post treatment and makes complete process economically less attractive. Removal of oxygen (deoxygenation), which allows overcoming the problems stated above, is possible, but the price is high.

Presence of proper catalysts during the pyrolysis process can affect the network of reactions (e.g. deoxygenation) and allows *in situ* upgrading of the bio-oil. A tremendous advantage might be that the expensive additional deoxygenation step can be avoided. Providing good contact between the solid catalyst and solid biomass is essential to improve the efficiency of pyrolysis process [2]. Further, lower pyrolysis temperature is crucial maximizing bio oil yield and quality.

In this presentation the results of catalytic pyrolysis of model biomass oxygenates and variety of biomass types (lignocellulose; switch grass; sugar cane) are reported. Different approaches for biomass pre-activation (mechano-chemical treatment, impregnation, precipitation) aimed at enhancing contact between solid catalyst/biomass and the subsequent influence on oil properties are discussed.

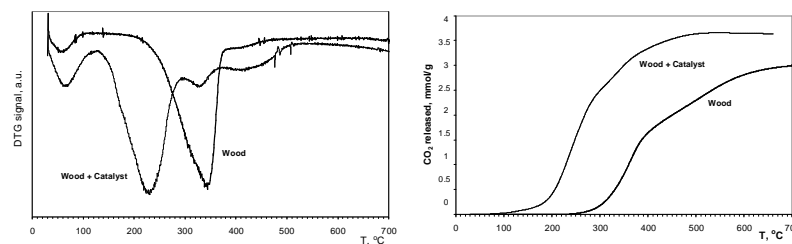
## Materials and Methods

Catalytic pyrolysis of model biomass components (cellulose, xylan and lignin) and different raw biomass were performed in a thermo gravimetric reactor combined with a mass-spectrometer. Effectiveness of a catalyst and a pre-activation procedure was estimated from (i) the temperature of decomposition and (ii) amount of CO<sub>2</sub> evolved (product of deoxygenation) during the temperature ramp (typically 10°C/min). Biomass catalytic cracking (BCC) experiments, resulting in bio-oil samples, were performed for different biomass/catalyst mixtures in a flash pyrolysis reactor [3]. Bio-oils obtained from non-catalytic and catalytic pyrolysis runs were characterized for acidity (pH), composition (CHNO-content) and energy content (heat of combustion).

## Results and Discussion

Using the appropriate combination of catalyst and pre-activation procedures, the decomposition temperature of biomass components can be strongly decreased. Thermal decomposition of biomass (wood) can be presented as superposition of decomposition of its main components: cellulose, hemicellulose and lignin. Slightly higher amount of solid residue was observed in the case of real biomass because of inorganic materials present. The decomposition of model biomass components tested is influenced by presence of catalysts in the following order: cellulose > lignin > xylan (hemicellulose). It will be shown that the preactivation step is critical.

Fig 1 gives a typical example of the pyrolysis of wood. The decomposition temperature of wood can be as much as 110 °C lower in the presence of a catalyst, without substantial increase in solid residue (Fig. 1a). Interestingly, the decrease in decomposition temperature was accompanied by increase in CO<sub>2</sub> production (Fig. 1b) especially at lower temperatures (350 – 400 °C). This shows that the deoxygenation of biomass occurred *via* decarboxylation. As suggested earlier, this is favorable to enhance the energy content of bio oil.



**Figure 1.** DTG (a) and CO<sub>2</sub> release (b) patterns for biomass as received and biomass pre-activated with a catalyst.

Properties of non catalytic pyrolytic bio-oil and bio-oil produced from catalytic pyrolysis (BCC technology) are compared. The latter contains less oxygen, is characterized by lower TAN number, higher heat combustion value. Catalytic pyrolysis is thus a very promising route for bio-oil production at a large scale.

## Significance

BCC technology opens new opportunities for large-scale bio-oil production from variety of biomass feedstocks at lower temperature (energy benefit) and with good product quality. In situ upgrading simplifies the process and reduces capital equipment costs.

## References

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