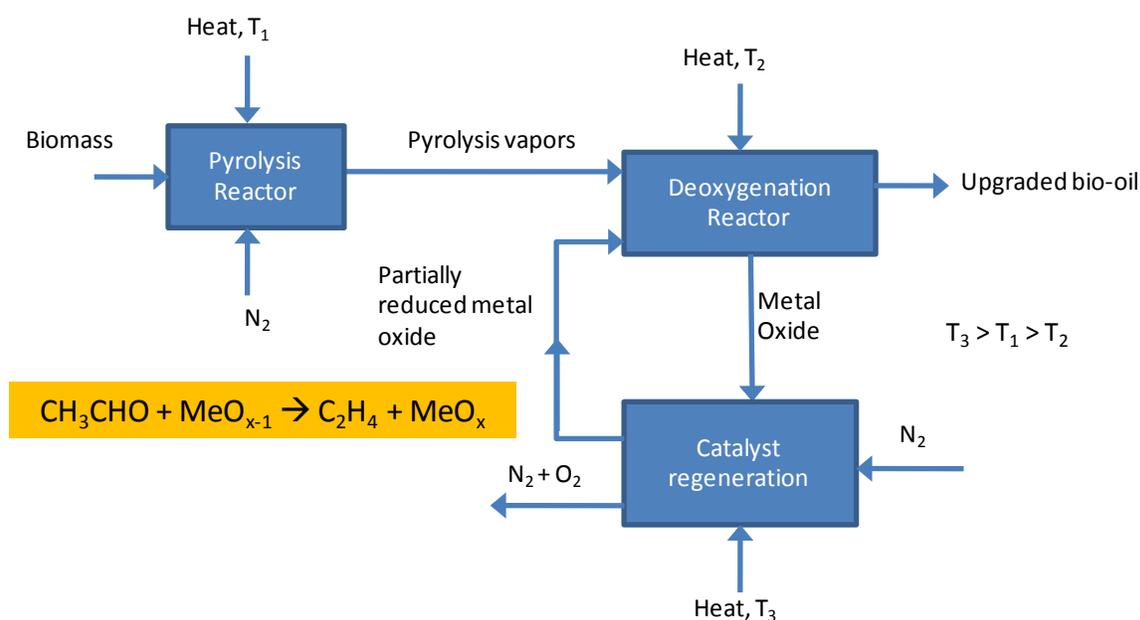


August 17, 2011

## Catalytic Fast Pyrolysis: Pyrolysis Vapors Upgrading

PNNL is working in the NABC catalytic fast pyrolysis team with the objective of minimizing H<sub>2</sub> consumption and maximizing carbon efficiency. The approaches are based on incorporating catalytic conversion steps during the cooling/condensation step of pyrolysis in an attempt to better control secondary reactions. The approaches and catalysts developed at PNNL have been shared among the other partners of the catalytic fast pyrolysis team. The sharing of fundamental knowledge generated allows the team to gain a more thorough understanding of the testing results to effectively select the best approach(s) and conditions.

One of the concepts being explored is based on chemical looping using reducible metal oxides to selectively remove oxygen from the pyrolysis vapors without H<sub>2</sub> input. The concept is shown in Figure 1 below.

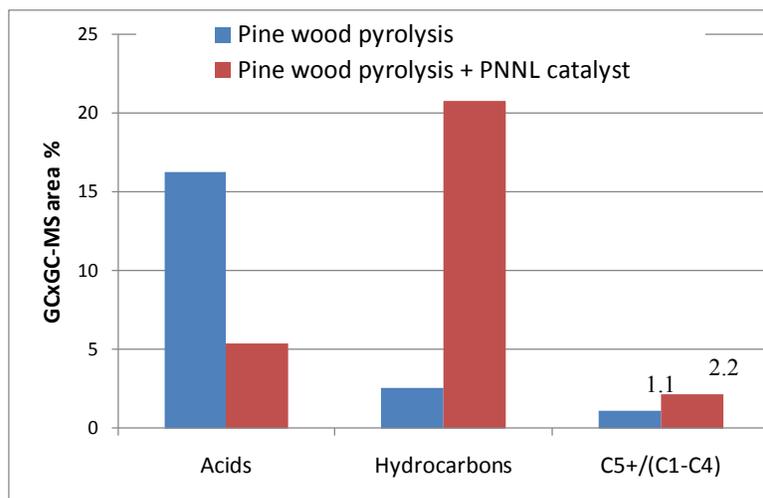


**Figure 1. Schematic of the chemical looping deoxygenation concept.**

The pyrolysis vapors pass over the deoxygenation catalyst where they react with the partially reduced metal oxide (MeO<sub>x-1</sub>). The pyrolysis vapors are reduced (deoxygenated) while the metal oxide is oxidized (MeO<sub>x</sub>), as shown in a model reaction of acetaldehyde to ethylene in Figure 1. The metal oxide is then heated in N<sub>2</sub> at a higher temperature where it is reduced to MeO<sub>x-1</sub> and recycled back to the reactor. A few promising metal oxide catalysts were identified through first principles theoretical calculations and experiments with model compounds.

However, due to the high reactivity of deoxygenated products such as ethylene on these metal oxides, which results in undesired C-C cleavage and/or polymerization events, this concept proved to be more challenging than anticipated. Therefore, we concluded that while the deoxygenation concept based on chemical looping seems to be feasible, the challenges that need to be overcome are too great for the time line of the NABC. The results generated under this task have recently been published (Mei, D.; Karim, A.M.; Wang, Y. 2011. "Density functional theory study of acetaldehyde hydrodeoxygenation on MoO<sub>3</sub>." *Journal of Physical Chemistry C*, 115(16), 8155-8164. doi:10.1021/jp200011j) and the knowledge gained from this effort has been leveraged in the identification of better hydrolysis catalysts, another research area in the NABC.

Another approach under development is upgrading of pyrolysis oil vapors via hydrodeoxygenation of longer chain molecules using H<sub>2</sub> generated in-situ from the reforming of light oxygenates. This approach is based on the multi-functional and hierarchically structured catalysts that have been developed at PNNL. Using pine forest product residual as a feedstock and a pyrolysis probe coupled to a GCxGC-TOF-MS, we have recently demonstrated that addition of such a novel catalyst results in significantly improved quality of pyrolysis products. Specifically, as shown in Figure 2, analysis of experimental results shows *the relative reduction in total acids by a factor of >3 while the hydrocarbons are increased by a factor of >6*. As a result, the ratio of C<sub>5+</sub> molecules to the smaller molecules is doubled in the presence of PNNL's catalyst. It should be noted that these experimental results were obtained without any external H<sub>2</sub> supply. The results are very promising and show the feasibility of pyrolysis vapors upgrading without external H<sub>2</sub> supply. Larger scale testing is currently being performed to better quantify carbon yield to oil and the oil oxygen content. Techno-economic analysis based on this approach will be conducted. This work has resulted in two invention disclosure reports and four peer-reviewed publications that are currently in preparation.



**Figure 2. Pine wood pyrolysis with and without PNNL's hierarchically structured multi-functional catalyst. Pyrolysis was performed in the pyrolysis probe at 600°C and 20 psig in He.**