Optimizing catalytic deoxygenation of biomass derived fast pyrolysis vapors

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1 Introduction and scope

The concept of de-centralized smaller scale pyrolysis plants that locally valorize available biomass by densifying its energy content into a bio-crude is of increasing interest world-wide. Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies at optimized temperature, pressure, and residence time of the liberated pyrolysis vapors[1]. Reducing the oil`s oxygen content and acid number to stabilize the oil deserve prioritized attention[2] and allow further processing in oil refineries. We propose a biomass based polygeneration plant (Fig. 1) that is able to co-produce heat, power, bio-oil and fertilizer (ashes) with high overall efficiency and flexibility. The concept is suitable for medium-scale decentralized plants when including gas combustion engines and also for large-scale power plants if the engine is replaced by a boiler and steam cycle. Deoxygenation can be obtained by catalytic upgrading over zeolites. To date, the medium pore size ZSM-5 zeolite has been found to provide a high aromatic yield and the least amount of coke[3] in upgrading of pyrolysis vapors. However, coke formation in the reaction of pyrolysis vapors over the zeolites and steam induced dealumination leads to rapid deactivation[4]. Maintaining the catalyst`s activity during multiple regeneration steps is needed to prove the economic attractiveness of bio-oil plants. Optimization of the catalyst system and testing of the catalyst under real conditions is thus the main focus of this PhD study.
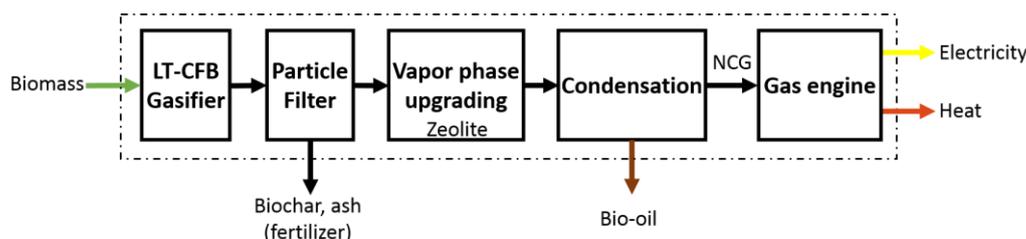

Figure 1: Process scheme of polygeneration plant comprised of various technologies.

2 Experimental approach and results

A bench scale fast pyrolysis unit is used to screen the performance of parent and modified catalysts. The oils are analyzed for water and elemental composition and subjected to GC-MS and SEC analysis. Mass and energy balances are conducted to corroborate the results. Catalytic vapor deoxygenation increases the heating value (Table 1).

Repeated upgrading and regeneration cycles have been conducted for straw and wood derived pyrolysis vapors with the parent ZSM-5 zeolites. The temperature during oxidative regeneration has to be carefully controlled in order avoid a loss of acid sites by steam. Through introduction of mesopores by NaOH leaching we aim to improve both the zeolite`s active time on stream and the long-term stability throughout multiple regeneration cycles. The modified catalysts are analyzed by nitrogen and argon physisorption, NH_3-TPD, XRD, XRF and TEM analysis to correlate the catalyst activity with its structure and acidity. Both acidity and ratio of micro to mesopores (Fig. 2) are steered towards limited coke formation at maximum valuable product yield. Further modifications of the zeolite for enhanced hydrothermal stability are considered in order to speed up the regeneration.

As a next step we will test the catalytic performance of the prepared hierarchical zeolites.

Table 1: Oxygen content and higher heating values of feedstock and bio-oils

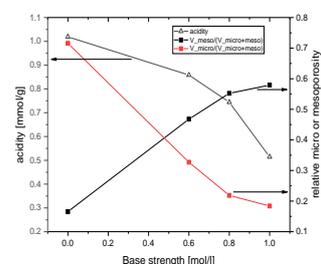| source	oxygen [wt-%]$_{daf}$	HHV$_{db}$ [MJ/kg]
wood feedstock	40.8	22
heavy fraction of pyrolysis oil	30.8	25.4
heavy fraction of upgraded pyrolysis oil	22.6	29.9

Figure 2: Change in acidity and relative micro/mesopore volume of ZSM-5 with increasing NaOH leaching severity

References

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