Process-product studies on pyrolysis oil upgrading by hydrotreatment with Ru/C catalysts

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Pyrolysis oil, the product of the fast pyrolysis of lignocellulosic biomass, is an attractive renewable energy carrier. However, due to its high oxygen (up to 50 wt%) and water content (up to 30 wt%) and its relatively low storage stability, upgrading is required before it can be considered for (co-)feeding in existing refinery unit. An attractive way to upgrade pyrolysis oil is by hydrotreating in the presence of a metal catalyst. Catalytic hydrotreatment studies have been reported in the literature using a variety of catalysts, however, relations between process conditions and product properties are lacking.

We here report a hydrotreatment study on fast pyrolysis oil using a Ru/C catalyst to determine the effect of process severity (temperature, residence time) on relevant product properties (viscosity, residual TGA weight). The catalytic hydrotreatment of pyrolysis oil was performed in a bench scale continuous set-up with four packed bed reactors in series. Pelletized ruthenium (5 wt%) on carbon was used as the catalyst. After reaction, the viscosity, the TGA residual weight and the elemental composition of the product oils were determined. Statistical analysis reveals unique relations between the elemental composition of the oils and product properties (viscosity and TGA residue). These relations allow determination of relevant product properties with limited analysis (elemental composition) and may also be used to tailor the process conditions to obtain the desired product properties.

The experiments also provided insights in the molecular processes occurring during the hydrotreatment reaction. At low severity (temperature of 175^{o}C), the main process occurring was hydrogenation, as shown by a higher product H/C ratio. At higher severity (temperatures 225^{o}C and 275^{o}C), the H/C and O/C ratios decreased significantly and the M_w increased substantially (Figure 1), implying that repolymerization is occurring to a significant extent. At the highest process severity in the series (temperature from 175 – 375^{o}C), the H/C ratios increased while the O/C ratios and the molecular weight decreased, indicating that hydrocracking occurred at this stage.

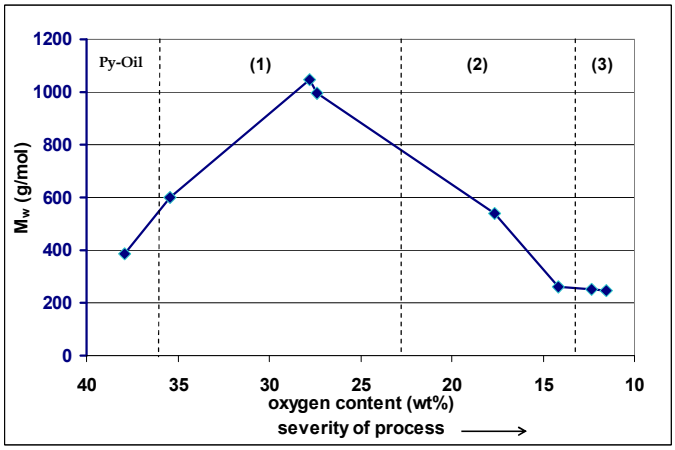

Figure 1 Mass average molecular weight of the products as a function of process severity

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