Catalytic hydropyrolysis – Effect of CoMo loading and support acidity


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1. Intro
Recent research has shown that catalytic hydropyrolysis of biomass is an efficient process for the production of renewable liquid fuels [1,2]. In this process fast pyrolysis and hydrodeoxygenation (HDO) is combined, ensuring that the reactive oxygenates formed during the pyrolysis, which may participate in polymerization reactions [3], are hydrogenated immediately, thus leading to a stable product with a low oxygen content compared to pyrolysis oil [4]. However, despite being a very promising process, there is very limited information in the open literature regarding the effect of the catalyst in the fluid bed reactor.

In this work we have investigated the effect of the CoMo loading and the support acidity on the product distribution and composition. The catalysts were tested in their sulfided form. The oxide catalyst precursors were characterized with BET, ICP-OES, NH₃-TPD, and Raman spectroscopy, and the spent catalysts were studied with SEM and STEM. The organic phase was analyzed with GC×GC-MS/FID, GC-AED, and the S, H, and O concentrations were measured.

2. Results and discussion
Catalytic hydropyrolysis of beech wood was conducted in a fluid bed reactor at 450 °C and 26 bar pressure. Using MgAl₂O₄ (MgAl) as support the CoMo loading was varied between 4 and 12 wt.% with a Co/Mo atomic ratio of 0.3. The effect of the support acidity was tested by maintaining a CoMo loading of 4 wt.% and testing two supports consisting of zeolite (H-ZSM-5) mixed with alumina, denoted at CoMoZA#1 and CoMoZA#2. CoMoZA#2 contained 44 % more zeolite than CoMoZA#1.

Increasing the CoMo loading from 4 to 12 wt.% decreased the condensable organic yield from 25.2 to 22.7 wt.% dry ash free basis (daf) while increasing the C₁-C₃ yield from 10.3 to 14.0 wt.% daf, as shown in Figure 1. Using CoMoZA#1 and CoMoZA#2 decreased the condensable organic yield to 24.4 and 23.9 wt.% daf, respectively.
The C₁-C₃ gas yield also increased to 13.0 wt.% daf for CoMoZA#1 and 13.9 wt.% daf for CoMoZA#2 mainly due to an increase in the C₂-C₃ yield.

Figure 1 Effect of the CoMo loading and support acidity on the condensable organic yield (A), and gas yield (B).

Analysis of the condensed organic phase showed that the concentration of monoaromatics and napthenes increased with increasing CoMo loading, while the concentration oxygenates decreased, see Figure 2. Using CoMoZA#1 and CoMoZA#2 efficiently removed the oxygenated aliphatics, and increased the concentration of aromatics.

Figure 2 Effect of the CoMo loading and support acidity on the concentration of napthenes, mono and diaromatics (A), and oxygenates (B).

References