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## Catalytic hydropyrolysis using sulfided Mo, CoMo and NiMo catalysts in a fluid bed reactor

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### Introduction

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. Therefore, in this work we have tested the effect of using a sulfided CoMo, NiMo, and Mo catalyst in catalytic hydropyrolysis.

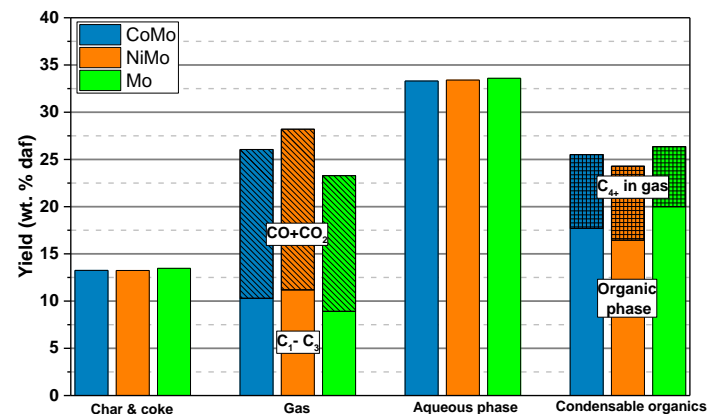
### Materials and Methods

Catalytic hydropyrolysis has been conducted in a fluid bed reactor at 450 °C and 26 bar pressure using beech wood as biomass. In each experiment 50 g of catalyst was loaded into the fluid bed reactor, the biomass feeding rate was between 271 and 275 g/h, and the feed time was 3.5 hours. The catalysts were prepared by incipient wetness impregnation of MgAl<sub>2</sub>O<sub>4</sub>, with a surface area of 54-58 m<sup>2</sup>/g. The produced organic phase was analyzed with GC×GC-FID/MS, GC-AED and the density, oxygen, sulfur, and hydrogen content were measured. Furthermore, the fresh catalysts were characterized with BET, ICP-OES, NH<sub>3</sub>-TPD, and Raman spectroscopy, and the spent catalysts were studied with SEM and STEM.

### Results and Discussion

Catalytic hydropyrolysis of beech wood formed four main products: liquid organic and aqueous phases, solid char and gasses, see Figure 1. The solid and aqueous phases were not affected by the type of catalyst. The yield of condensed organics and C<sub>4+</sub> in the gas varied between 24.3 and 26.4 wt.% on dry ash free basis (daf) and was lowest for the NiMo and highest for the Mo. The oxygen content in the organic phases are shown in Table 1 and was between 9.0 and 11.7 wt.% dry basis (db), and was highest for the Mo and lowest for the NiMo. The carbon recovery in the condensed organics and C<sub>4+</sub> in the gas was 39% for both the CoMo and Mo catalyst, but 37% for the NiMo catalyst. The reason for the lower carbon recovery with the NiMo catalyst was that it had a higher cracking and de-carbonylation activity. Furthermore, GC×GC-MS/FID showed that the organic phase from the experiment with the NiMo catalyst contained more phenols than the organic phase from the experiment with the CoMo, but the same amount of oxygenated aliphatics. The results suggest that the reason for the lower HDO activity of the NiMo is that it first hydrogenates the aromatic ring prior to removing the oxygen, but the formation of naphthenes are not favored by the

thermodynamics at the applied test conditions [1]. Our results therefore indicate that the CoMo catalyst is the most suitable to use in catalytic hydropyrolysis due to the higher carbon recovery and the low oxygen content in the organic phase.



**Figure 1.** Product distribution for catalytic hydropyrolysis of beech wood using sulfided CoMo, NiMo and Mo catalyst.

Studying the spent catalysts with STEM showed that both calcium and potassium are transported from the biomass to the catalysts. Potassium was well-distributed on the catalysts, while calcium was found as larger particles (40-200 nm). This could potentially lead to catalyst deactivation and requires further study.

**Table 1. Oxygen content in the organic phase and carbon recovery**

Catalyst	CoMo	NiMo	Mo
O (wt.% db)	9.0	10.2	11.7
Carbon recovery in organic phase and C <sub>4+</sub> (%)	39	37	39

### Significance

This is the first catalytic hydropyrolysis study using a fluid bed reactor that correlate the catalyst composition and structure to the product distribution and composition. These results provide direction for future research in this process.

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