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Catalytic Hydrodeoxygenation of Biomass Pyrolysis Vapor Model Compounds over Molybdenum Sulfide Catalysts: Influence of Support, H₂S and Water

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Introduction

Conventional fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies [1]. The produced bio-oil must be further processed in order to decrease the content of oxygen (from 15-30 wt% down to <1 wt%) and thereby enhance important fuel properties such as heating value, acidity and stability [1,2]. Upgrading of condensed pyrolysis oil is challenged by severe polymerization and coking upon heating. Instead, it is proposed to perform pyrolysis in the presence of hydrogen and an HDO catalyst for immediate stabilization and upgrading of reactive pyrolysis products. Downstream deep HDO potentially ensures removal of oxygen down to <1 wt%. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup is being constructed at DTU Chemical Engineering with a planned commissioning in Spring 2016. With a capacity of 100 g/h solid biomass, the aim is to provide a proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.

In this contribution, a combined experimental, characterization and theoretical study of catalytic hydro-deoxygenation of biomass pyrolysis vapor model compounds over molybdenum sulfide catalysts is presented. The influence of support, H₂S and water on activity, selectivity and deactivation is investigated.

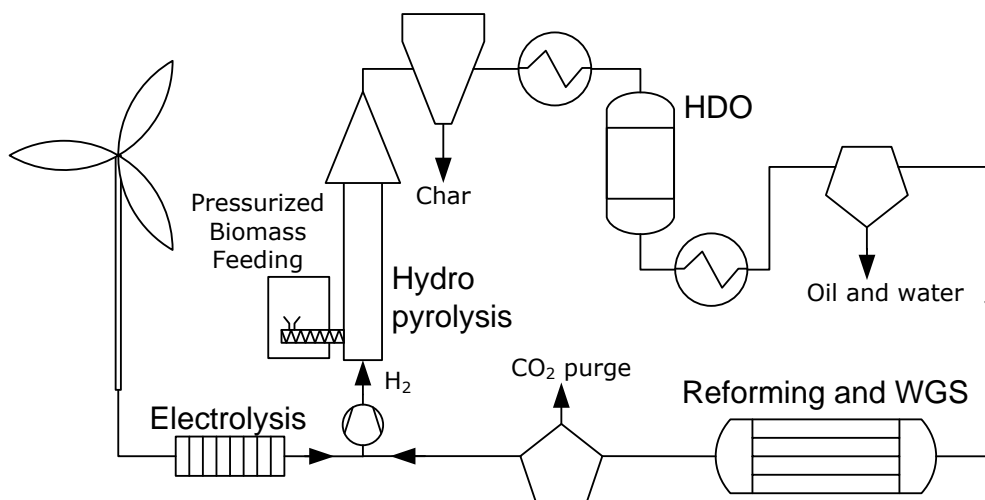


Figure 1 Simplified process diagram including catalytic hydro-pyrolysis (25-40 bar H₂ and 400-500°C), char separation, temperature adjustment, deep HDO (25-40 bar H₂ and 300-400°C), liquid separation, steam reforming and water gas shift (WGS). Additional H₂ is potentially provided from wind powered electrolysis of water. Produced char is gasified for H₂, burned for energy or used as fertilizer.

Experimental

Catalytic HDO is investigated in a separate vertical fixed bed reactor, typically operated in trickle bed mode with a load of 1-5 g catalyst. This reactor setup can be operated up to 550°C and 120 bar and it is possible to feed 5 gasses and 2 liquids. The reactor effluent is separated into gas (analysed online by GC-TCD) and liquid (analysed offline by GCMS-

FID). Pyrolysis vapor model compounds are applied individually and in mixtures in order to investigate reaction mechanisms of individual compounds and interactions such as competitive inhibition. Especially cellulose fragments are of interest as these are very reactive and contribute to undesired polymerization and coke formation reactions. To aid the understanding of the reaction and deactivation mechanisms, Density Functional Theory (DFT) and advanced characterization such as X-ray Absorption Fine Structure (XAFS) are employed.

Results and discussion

Ethylene glycol (EG) is a simple model poly alcohol for catalytic HDO activity tests in which ethane is the desired product. In initial experiments, the conversion of EG has been investigated at 50 bar (40 bar H₂, 500 ppm H₂S, balance N₂) and 275-400°C over supported NiMoS catalysts. The catalysts have been pre-sulfided in a flow of 12% H₂S in H₂ at 360-380°C and approximately 1 barg for 7 h. For steady state operation, carbon balances are closed within 90-100%. Full conversion of EG and 90-100% yield of ethane has been obtained with a commercial NiMoS/ γ -Al₂O₃ catalyst (supplied by Haldor Topsøe A/S) at an EG weight hourly space velocity (WHSV) of 2.3 h⁻¹ and 3 mol% EG in the feed. The activity remained stable with no deactivation for 47 h on stream. Increasing the WHSV, however, showed that this catalyst is in fact subject to significant deactivation. In an experiment with a higher WHSV of 8.4 h⁻¹, deactivation was observed over 40 h on stream and it was seen that resulfidation could not fully regenerate the spent catalyst. This indicates that the catalyst was not only deactivated by surface S-O exchanges, but also by other mechanisms. Analysis of the spent catalyst revealed a deposition of 11.8 wt% carbon. Support materials with lower acidity than γ -Al₂O₃ are of interest in HDO where coke formation should be limited [2]. A MgAl₂O₄ supported NiMoS catalyst (3.2 wt% Mo and 0.6 wt% Ni in oxide form, Ni/Mo = 0.3) has therefore been synthesized and tested. Initial experiments indicate limited activity below 310°C. Above 310°C both hydrogenation activity and especially cracking is observed to increase with temperature. While the ethane yield reached a maximum of \approx 60% above 350°C, the yield of CO, CO₂ and CH₄ continued to increase to a total C₁ yield of \geq 20% at higher temperatures. The coke deposition on the spent catalyst (60 h on stream) was 5.1 wt% carbon indicating that non-acidic supports are promising for HDO catalysts.

Work in progress and planned work cover the development of active, selective and stable HDO catalysts. This work is based on an investigation of catalyst formulation, reaction and deactivation mechanisms as well as operating conditions and includes:

- Preparation, characterization and test of NiMoS and CoMoS catalysts on supports with varying acidity (e.g. MgAl₂O₄, Al₂O₃, ZrO₂ and more).
- Activity tests using EG and other model compounds such as furfural or glycerol.
- Investigation of the influence of feed H₂S/H₂O ratio on catalyst activity and deactivation.
- Theoretical investigation (DFT) of EG reaction pathways and stability of sulfide catalyst surfaces at different H₂S/H₂O ratios.
- Advanced characterization (in-situ and ex-situ) of fresh and spent catalysts.

Special attention is paid to operating conditions (e.g. temperature, residence time and partial pressure of H₂, H₂O and H₂S) and to tolerance against water and sulfur.

Conclusions

Supported molybdenum sulfide catalysts show promise in HDO of model compounds. A combined experimental, characterization and theoretical study of catalytic HDO gives a good basis for investigating the influence of support, H₂S and water. This allows for an understanding of reaction and deactivation mechanisms which facilitates development active and durable catalysts for the proposed coupled hydrolysis and hydrodeoxygenation process.

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