Research paper

Hydrogen assisted catalytic biomass pyrolysis. Effect of temperature and pressure

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ABSTRACT

Beech wood has been converted into a mixture of oxygen-free naphtha and diesel boiling point range hydrocarbons by using catalytic hydropyrolysis in a fluid bed reactor with a $CoMoS/MgAl_2O_4$ catalyst, followed by deep hydrodeoxygenation (HDO) in a fixed bed reactor loaded with a $NiMoS/Al_2O_3$ catalyst. The effect of varying the temperature (365–511 °C) and hydrogen pressure (1.6–3.6 MPa) on the product yield and organic composition was studied. The mass balance closed by a mass fraction between 90 and 101% dry ash free basis (daf). The yield of the combined condensed organics and C_{4+} varied between a mass fraction of 17 and 22% daf, corresponding to an energy recovery of between 40 and 53% in the organic product. The yield of the non-condensable gases varied between a mass fraction of 24 and 32% daf and the char yield varied between 9.6 and 18% daf. The condensed organics contained a mass fraction of 42–75% aromatics, based on GC × GC-FID chromatographic peak area, and the remainder was primarily naphthenes with minor amounts of paraffins. The condensed organics were essentially oxygen free (mass fraction below 0.001%) when both reactors were used. Bypassing the HDO reactor increased the oxygen concentration in the condensed liquid to a mass fraction of 1.8%. The results show that catalytic hydropyrolysis may be a viable way to process solid biomass into liquid and gaseous fuels.

1. Introduction

Recent research has shown that catalytic hydropyrolysis is an efficient process for producing diesel and gasoline hydrocarbons from biomass [1,2]. The reactive molecules formed by fast pyrolysis are immediately hydrogenated, thus inhibiting polymerization and other undesired properties of conventional fast pyrolysis bio-oil. In this process, the pyrolysis takes place at an elevated hydrogen pressure and in the presence of a HDO catalyst. The basic concept of hydropyrolysis share similarities with the Bergius process (high temperature and high hydrogen pressure) [3–5], however in the Bergius process coal and heavy oil is mixed into a slurry, while hydropyrolysis is a gas phase process. Steinberg et al. [6] showed in 1985 that using fast hydropyrolysis of wood at high temperatures (600–1000 °C) over 90% of the carbon can be converted into hydrocarbons, mainly methane and other gases. It has also been shown that catalytic hydropyrolysis of lignin can give oil mass yields up to 80% [7]. Despite that hydropyrolysis is not a new concept it has first in the recent years become a popular method for producing liquid fuels from biomass. Using a pyroprobe reactor,

Melligan et al. [8] showed that conducting the pyrolysis of Miscanthus in an atmosphere of H_2 instead of He decreased the concentration of ethanoic acids in bio-oil. It has also been shown that zeolites impregnated with reduced transition metals increase the hydrocarbon yield and decrease the molecular size of the phenols [8–10]. Other groups have been pursuing the high pressure, non-catalytic hydropyrolysis of biomass in an inverted cyclone or fluid bed reactors followed by downstream catalytic HDO of the product vapors prior to oil and water condensation [11–13]. Marker et al. [1,2] have proposed a process called Integrated Hydropyrolysis and Hydroconversion (IH²®). Their process consists of a fluid bed reactor, where the catalytic hydropyrolysis takes place, and a fixed bed hydroconversion reactor, where the deep HDO takes place. Different types of biomass were tested, and the yield of condensed organic liquid and C_{4+} hydrocarbons in the product gas phase varied between a mass fraction of 20.6 and 46.3%. The IH²® process has been able to run continuously for 750 h in a pilot plant with a biomass feeding rate of 50 kg per day. The composition of the catalyst used in the IH²® process has not been reported. Carbon footprint analysis of the IH²® process showed that producing

Abbreviations

AED	Atomic emission detector
conc	Concentration
daf	Dry ash free basis
diAro	Diaromatics
DMDS	Dimethyl disulfide
FID	Flame ionization detector
GC	Gas chromatograph
HDO	Hydrodexoygenation
HHV	Higher heating value
mAro	Monoaromatics
MS	Mass spectrometry
Naph	Naphthenes
O-Ali	Oxygenated aliphatics
Par	Paraffins
PhO-	Oxygenated aromatics
SIMDIS	Simulated distillation by GC
Temp.	Temperature
tetAro+	Tetraaromatics
triAro	Triaromatics

liquid fuels from this process, when compared to conventional production from fossil fuels, decreases the emission of greenhouse gases with 67–86% [14]. Dayton et al. [15–17] also conducted several studies on catalytic hydropyrolysis using loblolly pine with a setup that did not include an additional HDO reactor after the fluid bed catalytic hydropyrolysis reactor. Using a commercially available hydrotreating catalyst gave an initial low oil yield (mass fraction below 5%), but the oil yield increased over time to a mass fraction of 12.5% as the catalyst deactivated [15]. Several experiments at different temperatures and hydrogen pressures with a commercially available NiMo hydrotreating catalyst have also been conducted with the same setup [16]. The catalyst was reduced in hydrogen and not sulfided prior to the experiments. Liquid organic yields between a mass fraction of 12.6 and 25.6% with an oxygen mass fraction between 2.4 and 11.9% and a char yield between 7.4 and 26% were obtained depending on temperature, total pressure and hydrogen partial pressure. The carbon recovery in the organic liquid and C_{4+} gases varied between 34.8 and 42.0%, thus being significantly higher than for zeolite based catalytic pyrolysis [16]. These results indicate that catalytic hydropyrolysis is a potential technology for converting solid biomass to liquid transportation fuels. The knowledge base on this type of process in the open literature is however still scarce. Often the catalyst composition is not reported and the liquid oil produced is not characterized in depth. Furthermore the combination of catalytic hydropyrolysis followed by HDO is not fully understood.

In this study, catalytic hydropyrolysis of beech wood has been performed in a fluid bed reactor with a sulfided commercial CoMo/MgAl$_2$O$_4$ catalyst followed by a HDO reactor loaded with a sulfided commercial NiMo/Al$_2$O$_3$ catalyst. The concept is thus similar to the IH$^{2\circledR}$ process [1]. With this reactor combination it is expected that the biomass can be converted into a mixture of naphtha and diesel. It is well-known that the temperature is an important parameter in pyrolysis [18], thus the effect of the temperature is investigated in the range relevant for catalytic hydropyrolysis (365–511 °C). There is also a lack of knowledge of the effect of hydrogen pressure on catalytic hydropyrolysis of wood, and the effect of pressure is therefore investigated in the range 1.6–3.6 MPa. Furthermore equilibrium calculations indicate that the liquid product composition changes in the tested temperature and pressure range. This is to our knowledge the first study in the open literature of hydropyrolysis of wood using a sulfided hydrotreating catalyst. In order to get a comprehensive understanding of the effect of the temperature and pressure the produced oil is extensively characterized.

2. Material and methods

2.1. Biomass feedstock

Bark free beech wood supplied by Dansk Træmel (Product number: 10000251250390) was used as biomass. The particle size was approximately 200–700 μm. The moisture mass fraction was 6.72% (dried at 105 °C) and the ash mass fraction was 0.59% dry basis. The composition and the higher heating value (HHV) of the beech wood are shown in Table 1.

2.2. Catalysts

The catalyst used in the fluid bed reactor was a CoMo/MgAl$_2$O$_4$ catalyst supplied by Haldor Topsøe A/S. The active CoMo phase was chosen because it is an efficient hydrodeoxygenation catalyst [20–27], and MgAl$_2$O$_4$ was chosen as support due to its mechanical strength and moderate acidity, anticipating it would lead to less attrition and char formation in the fluidized bed. The catalyst was received as extrudates and was crushed and sieved to obtain a particle size between 180 and 355 μm. This particle size distribution was chosen to obtain a good fluidization of the bed. A fresh load of 50 g catalyst was used in each experiment. The fixed bed reactor was loaded with 173 g NiMo/Al$_2$O$_3$ catalyst supplied by Haldor Topsøe A/S. The catalyst was shaped as extrudates and was used as received. To ensure a high degree of deoxygenation in all experiments the catalyst in the fixed bed reactor was replaced between experiment 5 and 6. The catalysts in both reactors were sulfided prior to each experiment to obtain the most active phase.

2.3. Experimental setup

A bench scale setup was constructed and a simplified piping and instruction (PI) diagram is shown in Fig. 1. The feeding system consists of a gas mixing system (H$_2$, H$_2$S, N$_2$), where the gas flows are controlled by Brooks mass flow controllers (Model: SLA5850). A liquid feeding system supplying dimethyl disulfide (DMDS; Sigma-Aldrich ≥99%) with a pump and evaporator (operating temperature: 200 °C) was used for sulfidation of the catalysts. Because of the relatively high cost of bottled H$_2$S, DMDS was used during the sulfidation. A pressurized

Table 1
Composition of bark free beech wood.

C	499	g kg^{-1} dry
H	60	g kg^{-1} dry
N	1.3	g kg^{-1} dry
O	430	g kg^{-1} dry
K	1.2	g kg^{-1} dry
Ca	1.3	g kg^{-1} dry
S	48	mg kg^{-1} dry
Na	9.9	mg kg^{-1} dry
Mg	350	mg kg^{-1} dry
Si	140	mg kg^{-1} dry
P	75	mg kg^{-1} dry
Cl	2.0	mg kg^{-1} dry
Mn	170	mg kg^{-1} dry
Fe	24	mg kg^{-1} dry
Cu	2.1	mg kg^{-1} dry
Zn	4.9	mg kg^{-1} dry
Sr	4.6	mg kg^{-1} dry
HHV[a]	19.7	MJ kg^{-1}

^{a} Calculated from Milne formula: 0.341 × C + 1.322 × H - 0.12*O - 0.12 × N + 0.0686*S - 0.0153 × ash [19].