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## Catalytic conversion of beech wood pyrolytic vapors

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## ABSTRACT

Catalytic fast pyrolysis (CFP) of beech wood chips was undertaken in a laboratory-scale fixed bed reactor equipped with a biomass semi-continuous dispenser. During pyrolysis, chars are retained on a quartz frit and the pyrolytic vapors are entrained through a fixed-bed catalyst to be converted. Several acidic catalysts such as zeolites H-Beta, zeolite HMF1 and 5% Ni supported on HMF1 were screened in this equipment. The Ni/HMF1 catalyst was also tested in the presence of 1 vol.% of hydrogen in the feed stream. Mass and carbon balances were carefully checked and the gas, liquids and solids fractions were analyzed in-depth to evaluate the impact of the catalyst compared to thermal conversion. In the presence of a catalyst, with a low catalyst-to-biomass ratio of 0.1, a lower amount of bio-oil was formed but it contained less oxygen. The bio-oils were characterized by bi-dimensional GC (GCxGC) coupled with MS and FID detectors. The amount of gaseous products also increased in the presence of all catalysts. In addition of the deoxygenation, gel-permeation chromatography (GPC) showed a decrease of the highest molecular masses in the bio-oil after catalytic treatment, which confirms the conversion of some oligomers. The presence of Ni enhanced the deoxygenation reactions while the addition of H<sub>2</sub> is also beneficial to the bio-oil composition.

## 1. Introduction

Rising energy demand requires new available energy sources that can be efficiently converted into fuels [1,2]. Biomass and bio-residues can be converted to more valuable and renewable energy forms via different thermochemical processes including pyrolysis [3]. For many years, conventional pyrolysis, using high temperatures (500–800 °C), has been applied to charcoal production [4] but it is only during the last 30 years that fast pyrolysis was developed. The concept is the rapid heating of biomass at a temperature around 500 °C with short reaction times of up to 2 s in an oxygen-free environment to optimize the yield of liquids [3,5–9]. However, pyrolytic bio-oils contain a significant amount of reactive oxygenated species and they need to be stabilized and subsequently deeply deoxygenated to be compatible with traditional fossil fuels [10–13]. A mild hydrogenation step was first proposed to stabilize the bio-oil, in which the most reactive components such as small carboxylic acids are converted [14,15]. However high pressure catalytic treatment can also be used [16]. This first stage constitutes an expensive part of the process due to hydrogen consumption and it can also give rise to new heavy molecular weight compounds originating mostly from glucose and its conversion products [17]. Therefore, alternative pathways, allowing a partial deoxygenation before vapor condensation, have been explored such as catalytic fast

pyrolysis (CFP) [18–21]. For instance, biomass fluidized catalytic cracking (BFCC) process was proposed with mesoporous or zeolitic catalysts [22–25] and later on industrialized by KiOR but tumbled into bankruptcy. Another strategy consists on the impregnation of a catalyst precursors on the biomass [26,27], and a wide variety of catalytic precursors has been investigated [28–31], but it has to face the problem of catalyst consumption and its regeneration. A third route is using a catalytic bed located after the pyrolysis stage to convert the vapors before condensation [32–34]. In the first strategies, the catalyst is in direct contact with the biomass at the required pyrolysis temperature (often higher than the classical catalytic temperature used) and usually high catalyst-to-biomass ratios are required [35–38]. In the second case, the catalytic reactor can be heated at a different temperature than the pyrolysis reactor and only the pyrolytic vapors are in contact with the catalyst which allow to decrease the catalyst-to-biomass ratio. It has also the advantage of preventing the interactions with ashes since filters can be introduced to separate these solids. Therefore, this second configuration seemed to us very attractive since it allows to screen catalytic solids independently of the pyrolysis step, whereas the catalyst is never in contact with ashes, which can impair the catalyst activity.

Since 2007, the number of publications concerning pyrolysis combined with a catalytic conversion of the vapors has increased drastically and various catalysts were tested. Interesting results were obtained with

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nickel phosphides which enhanced deoxygenation compared to Ni/SiO<sub>2</sub>, Pd/C and acidic materials [39] in the presence of H<sub>2</sub>. Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [40], supported MgO [41], TiO<sub>2</sub> nanorods, CeOx–TiO<sub>2</sub> mixed oxides, pure CeO<sub>2</sub>, ZrO<sub>2</sub>, and MgO [42] were also reported to enhance the conversion of pyrolytic vapors. However, zeolites are often considered as the most efficient catalysts and the numerous screening led to identify ZSM-5 zeolite as one of the most active catalysts for deoxygenation, taking into account the yield of liquid [24,32,43–45]. Further, the addition of metal on various zeolites was reported to improve the conversion of pyrolytic vapors. For instance, comparison between ZSM-5 zeolites and ZSM-5-supported metal catalysts (Ga [46], Mo-Cu [47], Fe, Zr, Co [48], Co [49]) always showed an increase in the liquid yield or, interestingly, the enhancement of the selectivity to aromatic, hydrocarbon and naphthalene derivatives. As regards to the oxidation state of the supported metal, the comparison between Ni in metallic and oxide forms supported on ZSM-5 showed a convergence of activity during experiments, which was explained by the reduction of NiOx/ZSM-5 catalyst under the biomass pyrolytic vapors containing H<sub>2</sub> and CO [50]. However, most of the time in all those previous works, the catalyst-to-biomass ratio is still quite high (0.5–20 in wt.) and should be reduced to get a viable catalytic process.

In this work, we carried out the catalytic conversion of beech chips pyrolytic vapors using H-Beta and HMFI (Mobil five equivalent to ZSM-5) zeolite catalysts and a Ni/HMFI supported catalyst in a laboratory-scale continuous fixed bed reactor with a cumulated catalyst-to-biomass ratio of 0.1. The effect of catalyst was investigated by in depth characterization methods of the different obtained fractions comparing with thermal conversion without catalyst. The effect of gas vector atmosphere was also investigated by addition of 1%vol. H<sub>2</sub> to the inert atmosphere in the presence of a 5% Ni catalyst on HMFI-90.

## 2. Materials and methods

The starting biomass material consists in beech tree chips with a size of 2–3 mm purchased from J. Rettenmaier & Söhne (JRS). It has been characterized by elemental analysis (Table 1) and thermogravimetric analysis (TGA) under O<sub>2</sub> which indicated 2.8 wt% of mineral components (Fig. S1 in Supplementary material). TGA measurement also performed under N<sub>2</sub>, showed that 17 wt% of non-volatile residues were formed after heating the beech wood up to 1000 °C. The solvents (CH<sub>2</sub>Cl<sub>2</sub>, Acetone) were purchased from Carlo Erba Reagents (≥ 99.8%) and used without any further purification. The zeolites H-Beta and HMFI-90 were provided by Grace and CTI, respectively. HMFI-90 stands for the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, i.e. it corresponds to an atomic Si/Al ratio of 45. The zeolite powders were crushed and sieved to reach particle diameter in the range 100–300 μm. The BET surface area was 707 ± 2 for H-Beta and 422 ± 2 for HMFI-90 with Si/Al ratio of 16.5 and 40, respectively.

The higher heating value (HHV) in MJ kg<sup>-1</sup> was estimated for the starting biomass and the bio-oils according to Dulong's formula [51]:

$$\text{HHV} = 0.3383C + 1.422(\text{H-O}/8)$$

**Table 1**  
CHONS elemental analysis and ashes for beech biomass.

Chemical element		Mass composition (%)
Carbon	C	46.3 ± 2
Hydrogen	H	6.3 ± 0.1
Oxygen	O	36.1 ± 2
Nitrogen	N	0.1 ± 0.1
HHV (MJ kg <sup>-1</sup> ) according Dulong Formula		18.2
Ashes (at 1000 °C) from TGA under O <sub>2</sub>		2.8 ± 0.2
Water		8 ± 1

Where C, H, O are the mass percentage of carbon, hydrogen and oxygen, respectively, obtained by elemental analysis (Table 1).

### 2.1. Preparation of catalysts

H-Beta and HMFI zeolites were used directly after in situ calcination at 500 °C for 60 min under N<sub>2</sub> in the pyrolysis set up. This step removes the adsorbed water present in the micropores of the zeolites, and hence, allows a better estimation of the mass balance in the experiments.

A 5%Ni/HMFI-90 catalyst was prepared by incipient wetness impregnation. The nickel precursor was Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and after maturation and drying, the catalyst was calcined at 550 °C before an in situ reduction at 500 °C during 1 h under 10% H<sub>2</sub>/N<sub>2</sub> (500 mL/min). The experimental loading of Ni measured by ICP analysis was 4.9 wt%. After the experiment, the catalysts were recovered and the amount of deposited organic compounds was determined by elemental analyses.

The specific surface areas and pore volume and distribution were measured by nitrogen physisorption using a 3-Flex surface characterization analyzer (Micromeritics) allowing low P/P<sub>0</sub> adsorption measurements (10<sup>-9</sup> relative pressure range for N<sub>2</sub>) and the characterization of micro- and meso-porosity.

### 2.2. Pyrolysis-Catalysis reactor system (Fig. 1)

The woody biomass, previously dried in oven at 110 °C, is stored in a hopper kept under a nitrogen flow of 6 Lh<sup>-1</sup>. Beech tree chips were introduced with a good accuracy at the top part of a 30 cm long reactor tube by mean of a solid powder dispensing system (*Parimix*). Inside the reactor, a stainless steel inlay with staggered blades allows to slow down and distribute the wood in the pyrolysis volume (Fig. 1). Wood chips fall in a pit machined in a rotating cylinder and by choosing the frequency of the rotation, the charge injected is known accurately and controlled, after calibration of the device. Every 18 s, 100 mg of wood chips were dropped into the reactor maintained at 500 °C. In a typical 1 h experiment, the total amount of wood reacted was approximately 19 g ± 1 g. The main reactor consists of a quartz tube containing two porous quartz frits, the first frit allows retains the char and unconverted wood in order to protect the catalyst supported on the second frit (Fig. 1). 2 g of catalyst are used in each experiment. A nitrogen flow of 24 Lh<sup>-1</sup> is fed at the reactor inlet, resulting in a total nitrogen flow of 30 Lh<sup>-1</sup> through the catalyst bed, which is placed directly under the pyrolysis reactor and maintained between 458 °C and 468 °C depending of the exothermicity/endothermicity of the occurring reactions. In some experiments, 1 vol.% of hydrogen was added in the N<sub>2</sub> flow. A catalyst-to-biomass ratio of 1:10 was used. At the reactor outlet, the vapors are condensed in a trap at 4 °C where the main part of the bio-oil is collected. This condenser is followed by an electrostatic trap to capture the finest oil droplets. A final trap of silica gel protects the micro-GC used for on-line gas analysis. The liquid effluents were characterized by CHONS analysis, Gel-permeation chromatography (GPC), and GCxGC with MS or –FID detectors.

The reproducibility of the mass balance (bio-oil + gases + solid residues) was evaluated by performing at least three similar runs with beech wood in the absence of catalyst. The catalytic experiments were repeated at least two times. The accuracy of the measurements/data mass balance were evaluated at 0.05 wt% for the char, 1.5 wt% for gas analysis, 5 wt% for the bio-oil and aqueous phase.

### 2.3. Products recovery procedure

The bio-oils formed by pyrolysis of beech wood are viscous and tend to stick to the glassware. A protocol was developed to recover the bio-oils while minimizing the losses. After pyrolysis, all glassware parts were washed with dichloromethane in order to recover all the fractions. Then, the organic and aqueous phases were separated in a separating funnel. After decantation, the organic phase was evaporated under

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