

CATALYTIC PYROLYSIS OF IMPREGNATED BIOMASS

K. Bru, J. Blin, F. Broust, L. Van de Steene, G. Volle
CIRAD-Forêt

TA 10/16, 73, avenue J.-F. Breton, 34398 Montpellier, Cedex 5, France; Phone: +33 4 67 61 65 21; Fax: +33 4 67 61 65 15
Corresponding author : jblin@cirad.fr

ABSTRACT: An innovative way of catalysis was tested for its potential to reduce the amount of hydrocarbons produced during pyrolysis of oak wood. The experiments were carried out in a horizontal tubular reactor fed with a controlled flowrate of Nitrogen and equipped with accessories to collect char, liquid and gaseous products. Pyrolysis was done at 700°C with a Nickel or Iron based catalyst introduced inside the wood matrix by wet impregnation. In addition, a blank run was undertaken in which the biomass was acid-washed to determine the impact of demineralization. The influences of the catalyst nature and of the catalyst content in the wood on the reduction of condensable organic compounds were determined.

Depending on the experimental conditions, the liquid yield decreases from 7.3% to 31.9% when metals are inserted in the wood. Hydrocarbons are cracked into gaseous components and the concentration of H₂ has a significant increase. These results showed that biomass impregnated with Nickel and Iron is a promising way to reduce condensable organic compounds produced during pyrolysis.

Keywords: Pyrolysis, catalytic conversion, hydrogen.

1 INTRODUCTION

Biomass gasification is a promising alternative for heat and electricity production in small cogeneration units. The presence of condensable hydrocarbons makes the gas unsuitable for direct application in internal combustion motors, or for catalytic syngas shift conversion for the production of hydrogen or bio fuel (Fischer Tropsch). These tars are initially produced during pyrolysis, the first step of any thermochemical conversion processes.

The classical gas cleaning technology based on scrubbing is not acceptable because of wastewater production. Partial oxidation does not provide sufficient cleaning efficiency and moreover decreases gas heating value. Catalytic hot temperature cleaning provides sufficient efficiency of tar removal and does not decrease heating value of produced gas. Most of the studies in biomass gasification concern two ways of catalysis:

- mixing catalyst with biomass to reduce tar content in the gasification bed,
- using catalyst in a specific hot gas cleaning reactor (post treatment).

In both cases, catalyst efficiency is high at the beginning of their use, but their lifetime is limited because of carbon deposition, particle agglomeration and decrease of mechanical strength involving catalyst deactivation.

The purpose of the presented work is to evaluate a new catalytic way to limit the production of condensable hydrocarbons by wet impregnation of the biomass material with metal salts. Nickel and Iron were employed and tested as impregnated catalysts during pyrolysis of wood. These metals have been selected as Nickel [1-4] and materials containing Iron, as dolomite

(Ca(Mg_xFe_y)(CO₃)₂) or olivine((Mg_xFe_y)₂SiO₄), are classically used for tar cracking and reforming [5-8]

2 EXPERIMENTAL

2.1 Laboratory scale pyrolysis plant

The experimental set-up, shown in Figure 1, consists of a 50 mm diameter, 600 mm length cylindrical stainless steel reactor. It is equipped with a feeding chamber and adapted devices to quench liquid and collect gas samples. During experiment, the reactor is continuously flushed with pre-heated Nitrogen (18.3 10⁻³ Nm³/h at 400°C) to remove air from the reactor and all the gases produced during pyrolysis.

Feeding chamber is cooled with water in a double envelope to keep the sample at ambient temperature before introducing it in the hot zone. Approximately 10g of wood is loaded in a basket driven by a sliding handle. This basket is positioned in the cooled zone during the thermal stabilization of the reactor and is rapidly introduced in the hot zone reactor to start the pyrolysis.

At reactor outlet, a quench system is used to recover liquids. It consists of a cool water heat exchanger, a liquid nitrogen ethyl alcohol bath at around -50°C, and an electrostatic precipitator. To avoid hydrocarbon condensation before this system, the reactor exit is equipped with a resistive heater. The non condensable gas flow is then measured thanks to a precise volumetric flow-meter and is collected in a sampling bag.

The duration of a run is 20 min. The heating is then switched off and the basket moved back to the cooled zone. Once ambient temperature is reached, the remaining char in the basket is weighted. The total amount of oils produced is collected washing the coil cooler and the electrostatic precipitator with isopropyl alcohol : the total oil mass can then be weighted.

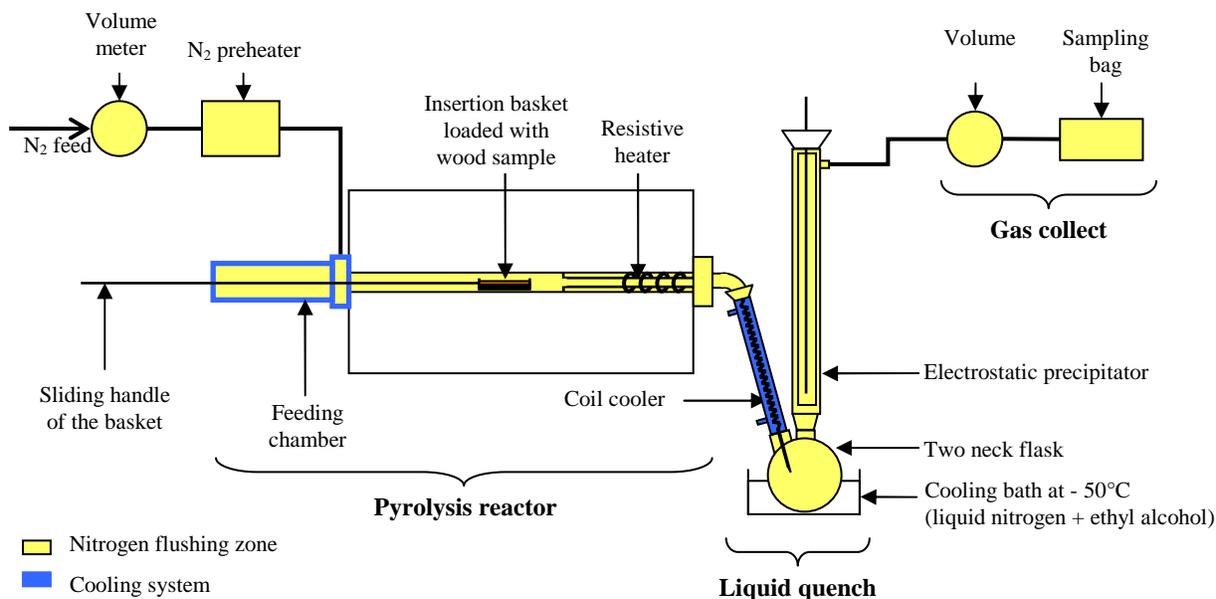


Figure 1: Schematic of the pyrolysis reactor

2.2 Wood preparation

The selected biomass was oak sawdust with a size range varying from 0.4 to 1.6 mm.

Metallic salts used for wood impregnation were nitrates as they do not contain carbon atoms, which could have altered the obtained results. The air-dried wood particles were impregnated by mixing 22 g of wood with 250 ml of a $\text{Ni}(\text{NO}_3)_2$ or $\text{Fe}(\text{NO}_3)_3$ aqueous solution at concentrations of 0.17 mol/l, 0.35 mol/l or 0.52 mol/l. The obtained mixture was stirred at ambient temperature during 3 days. The wood particles were then filtered and dried at 105°C for five days.

The wet impregnation of the wood leads to a washing of the samples, i.e a loss of some of its minerals [9]. Moreover, Nickel and Iron nitrate solutions are acid and this acidity intensifies this phenomenon. In order to evaluate the influence of the washing on the pyrolysis products and their composition, the wet impregnation method was also applied to wood particles in a sulfuric acid aqueous solution at pH = 2.8.

2.3 Characterization of gaseous products

The gaseous fraction, mainly composed of H_2 , CO , CO_2 and CH_4 , and some low molecular weight hydrocarbons such as ethane and ethylene, was analyzed after each experiment with a gas chromatograph provided with a Thermal Conductivity Detector (TCD) and a single injector connected to two columns: 5A Molecular Sieve and CP-Sil 5 CB. Helium and Argon were used as carrier gases respectively.

3 RESULTS AND DISCUSSIONS

3.1 Analysis of the impregnated wood

For each experiment, Nickel and Iron content in the impregnated wood have been determined by Inductively Coupled argon Plasma (ICP) emission spectroscopy after mineralization of the samples. The results are reported in Table I.

Table I: Metal content of the impregnated wood

Metal concentration in solution (mol/l)	Nickel content (mg/g of wood)	Iron content (mg/g of wood)
0.17	9.76	12.21
0.35	19.06	28.21
0.52	27.33	43.19

Results in Table I show that Fe is more easily impregnated in the wood than Ni.

As Domazetis and al. [10] showed in their study of catalytic gasification, complexes produced in solution by Ni and Fe and absorbed in the coal are $[\text{Ni}_4(\text{OH})_4]^{4+}$ and $\text{Fe}(\text{OH})^{2+}$. These complexes have not the same molecular dimensions and that could be an explanation to the above results : internal mass transfers inside the wood matrix are different for the two catalysts complexes. Some interactions between these complexes, the wood components and wood tannins in solution may also occur, enhancing more or less the impregnation. However this explanation has to be confirmed.

3.2 Results of the pyrolysis experiments

Pyrolysis experiments were carried out at 700°C and atmospheric pressure. The reaction bed was composed of oak impregnated wood. A thermocouple inside the bed allowed a continuous record of the sample temperature.

Figure 2 presents the temperature evolution in the wood during an experiment.

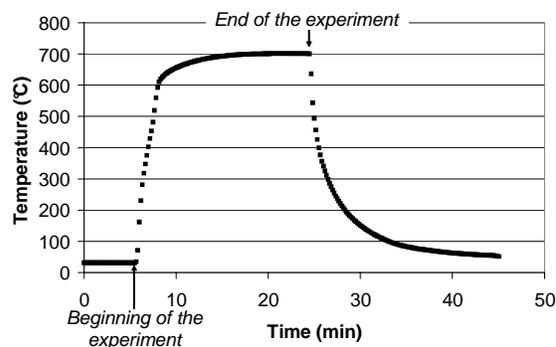


Figure 2: Bed temperature during an experiment

Bed heating rate is relatively high, namely nearly 190°C/min. Such heating is known to enhance liquid production [11], so the influence of the catalysis metal on liquid and gas yield will be easier to observe and to quantify.

Figure 3 and 4 present the product repartition of the pyrolysis at 700°C versus the catalyst content, each experiment being done twice. The yield of gas, liquid and solid are expressed as mass fraction with respect to the original biomass, i.e. on catalyst-free basis. The yields of different gases are expressed as “volume fraction” of the original biomass, which is calculated dividing the volume of each gaseous component by the same mass of wood than previously (cm³ of gaz/ g of initial wood).

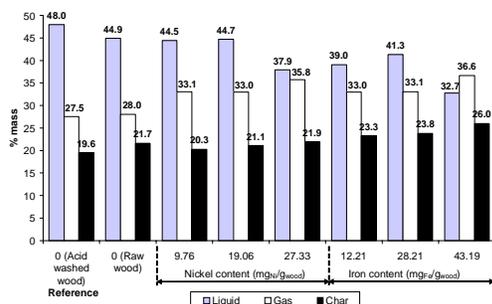


Figure 3: Influence of catalyst content on pyrolysis products

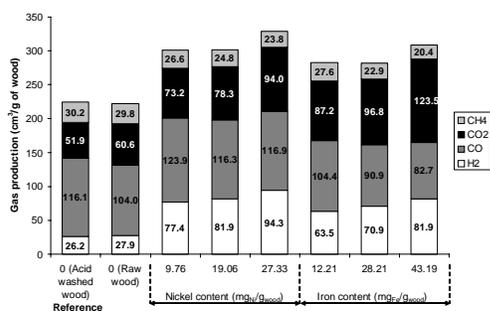


Figure 4: Influence of catalyst content on gas components

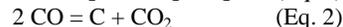
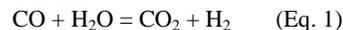
These figures show that liquid, gaseous and solid product collection is acceptable : mass balance is better than 94% for all the experiments despite condensable product recovery is difficult in such experiment [12-13]. Moreover, experiment reproducibility have shown a standard deviation of each product lower than 1.7.

Figure 3 shows the fraction of liquid produced during pyrolysis of raw wood is about 45%. Acid-washing shifts the chemical equilibriums with an increase of the liquid yield, from 44.9% to 48.0%, showing the catalytic role of mineral matter during pyrolysis. Part of the difference on the solid fraction can be due to the loss of minerals during the washing. It can also be observed in Figure 4 that CO increases and CO₂ decreases when the wood is acid washed. These results are in agreement with the works of Raveendran and al [14] that showed biomass demineralisation involves an increase in liquid yield and a decrease in gas yield during pyrolysis.

Since an acid washing is done when the wood is impregnated with catalyst, the results of the catalysed pyrolysis are compared with those obtained with the acid washed samples.

As expected, the presence of catalyst in pyrolysis experiments involves a decrease of liquid yield varying between 7.3% and 31.9% (% related to the liquid fraction of the reference sample) depending on catalyst concentration. In parallel the gas yield is increasing from 20.0% to 33.1% (% related to reference sample gas fraction). Figure 3 also underscores the influence of the catalyst amount in the wood on the obtained products. Indeed when catalyst content increases the liquid yield decreases whereas the gas yield increases. This shows the used catalyst enhances the gas formation to the detriment of the liquid. These results can be explained by the catalytic cracking of the liquid inside the wood. Indeed, since the catalyst is added to the wood matrix, liquids are certainly cracked as soon as they are produced. Cracking of liquid vapors, mainly heavy hydrocarbons, produces low molecular weight hydrocarbons and as a consequence is responsible for the gas yield increase.

Figure 4 shows the presence of the both catalysts decrease CO and CH₄ contents while they increase the production of H₂ and CO₂. The H₂ content increases with the catalyst load, reaching up to 3.4 times for the pyrolysis of wood containing 27.33g of Ni/g of wood compared to the reference sample. The raise in H₂ content is due to the hydrocarbon oxidation and dehydrogenation reactions. Indeed, Nickel catalysts are used in industrially important reactions for producing hydrogen and synthesis gas from hydrocarbon feedstock whereas Iron is used to dehydrogenate heavy hydrocarbons to produce CO and H₂. These two metals are also used for the metal reforming, which explains the reduction observed in CH₄ content [15-19]. Iron also promotes the water gas shift reaction (Eq. 1) and the Boudouard reaction (Eq. 2), leading to a reduction of the CO content.



So these reactions may occur during the pyrolysis, decreasing the CO content of the gas produced. The increase in CO₂ content and in char yield when Nickel or Iron is used seems to confirm the presence of others oxidations reactions, that has to be confirmed by further works.

Experiments performed with about 27-28mg_{metal}/g_{wood} allow comparing the efficiency of the two metals. With Nickel, the liquid production is reduced by 21.0% whereas this reduction is 14.0% with Iron and the gas yield rises by 30.2% and 20.4% respectively (% related to the reference sample). The composition of the gas produced shows the hydrogen production is 1.3 greater with Ni than with Fe. A decrease of Carbon Monoxide is also observed when Fe is used, this content being 82.7% for 43.19 mg of Fe/g of wood whereas it is 116.1% for the reference sample, while Ni has no influence on it. So, the comparison of the two catalytic pyrolysis points a greater effect of the Nickel out.

Finally, a slight raise in char production is observed when Iron is used. The same trend was obtained by Yu and al. [20] in a gasification study of coal impregnated with Iron. They explained this phenomenon by two mechanisms: firstly Iron stabilizes the functional groups (such as carboxyl groups) it is associated with and

secondly Iron generates solid carbon deposits on the char.

4 CONCLUSION

The experimental set-up used here allows studying the influence of two metals on the pyrolytic products since mass balances are better than 94%.

This preliminary study underscores Ni and Fe wood impregnation is efficient for decreasing the liquid yield and for increasing the gas yield produced during wood pyrolysis. So this is a promising way for the industrial application in biomass utilization for energetic purposes to produce clean gas for turbines and engines. Moreover, these catalysts are responsible for an increase in H₂ content and for a decrease in CH₄ content, leading the way for a possible use in Fisher Tropsch synthesis and fuel cell applications.

On going activities aim at evaluating temperature influence on catalytic pyrolysis. Liquid analysis will also allow determining the metals effect on organic compounds contents and so it will allow understanding the mechanisms implied in the catalytic pyrolysis.

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