Tar cracking and reforming in fluidized-bed biomass gasification conditions

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Abstract :

In this work realized by CIRAD, a specially designed crossed fixed-bed reactor was used to characterize thermal and catalytic tar reduction due to cracking and reforming reactions in fluidized-bed gasification conditions. Coriolis and mass flow meters are used respectively to control water and gas (N_2, H2, CO, CO_2) contents in the feeding atmosphere. A partial pressure of tar in the atmosphere is obtained by saturating gases at a precisely controlled temperature. The solid bed is deposited on a filtering sheet and can be inert (by using sand) or catalytic. Condensable species were quantified semi-continuously with a gas chromatograph (GC), and then recovered thanks to a cooling device placed after it. Then, a GC coupled with a mass spectrometer is used to quantify species in low concentrations. Gaseous species were continuously quantified by µGC. In this work, the tar retained is naphthalene, as it is usually considered as a reference of tars present in fluidized-bed gasifiers. Thermal tar destruction is studied by introducing naphthalene in our reactor containing an inert sand bed; catalytic tar destruction is realized using two kinds of well-known catalytic beds: olivine and nickel on olivine. The influence of hydrogen and water contents on tar destruction and on the catalyst lifetime is also considered.

1. Introduction

Biomass gasification is considered as one of the best alternative to fossil energy, but there are still some critical issues that prevent its full development. Eleven partners (academic and industrial) are gathered in GAYA, a project supported by ADEME. This project aims at producing synthetic natural gas from biomass gasification in a dual fluidized-bed. One of the main issues of gasification is the high tar content of the syngas [1], especially when this syngas is used on catalysts for methanation reactions: it is considered that the amount of tars in syngas should not exceed 5mg/Nm^3 in order to prevent early catalyst deactivation [2, 3]. To reduce tar content, gas treatments like filtering, gas-washing, thermal cracking or catalytic beds are studied, but one of the most

interesting option is to reduce tars at its source by using a catalyst inside the fluidized-bed. This catalyst replaces the fluidizing media, and should therefore be temperature and attrition-resistant, while remaining catalytically active to improve tar cracking. Several studies have been conducted to select, synthesize and experiment catalysts in fluidized-bed conditions, and the results show important decline of the tar amount, depending on the different catalysts [4 - 15]. The most studied and promising catalysts are olivine and impregnation of metals on olivine, for their low cost, high efficiency and mechanical resistance.

In this study, we will present a new fixed-bed reactor ALIGATOR that was developed in CIRAD and used for these experiments. We chose to investigate the efficiency of olivine and nickel on olivine catalysts at a laboratory scale and

compare it to the thermal conversion of our tar model on an inert sand bed. Naphthalene was chosen as tar model, since it is one of the main constituent of gasification tars, and its polyaromaticity makes it tough to convert even at high temperatures.

2. Experimental

The difficulty in designing a fixed-bed reactor for catalytic tar cracking lies in the need to guarantee:

- Tar content in the atmosphere around all grains inside the bed is similar and controlled
- Gas flows are sufficient to avoid external mass transfer limitations

The crossed fixed bed reactor that was specially developed is called Aligator (Figure 1). The bed is crossed by all of the atmosphere gases. The flow rate of these gases is high enough (232mL/min at STP) to ensure that contact time remains low.

The apparatus consists in an external 36mm i.d. and 435mm long, electrically heated quartz tube, and an internal 26mm i.d. and 410mm long quartz tube, equipped with a filtering sheet at 40mm from the top of the tube. The gas which passes through the catalytic bed is previously preheated in the annular space between the external and the internal tube. The pressure on the top of the bed is measured; this pressure remains close to atmospheric, proving that the gases are well evacuated.

The gas preparation system (figure 2) consists in three Brooks mass flow controllers that control the gas flow of all species except for water and tar. Tar is introduced into the gas by a bubbling system. The temperature of the tar is precisely controlled by a heating/cooling device: a PT100 probe measures the temperature inside and a high flow rate
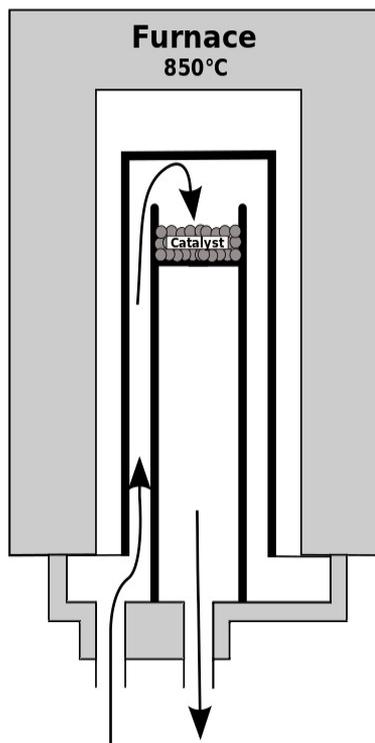

Figure 1: Aligator scheme

fluid regulates the whole system. The theoretical amount of tar into the gas is calculated with Antoine's law. To check if the experimental and theoretical partial pressure of tar are in accordance, the bubbling system is weighted before and after each test, and this amount is compared to the measures of the analytical system. Afterwards, liquid water is introduced in the gas line by a coriolis flowmeter at a temperature of 240°C. To prevent tar or water condensation, all lines are heated from the tar bubbling to the end of the analytical system at a temperature of 150°C.

Downward the catalytic bed, gases are analyzed by different devices. The first one is a Perkin-Elmer GC-TCD. The amount of gas injected is controlled by the loop of a 6-ways valve. The column is a Varian CP-Borabond Q, heated from 150°C to 300°C during 18 minutes to measure essentially benzene, toluene and naphthalene. The gas is then cooled to -10°C to condense water and heavy tars. Results obtained with GC-TCD are validated using a GC-MS. In this case, a valve samples the gas to another cooler full of acetone. Species are recovered for identification and quantification on Agilent GC 6890 fitted with 5975 mass spectrometer system. Samples are diluted in acetone and two injections mode are used to analyze light and heavy tars. The column is a J&W DB1701, heated from 40 to 270°C. Detection uses electron impact at 70eV.

After this cooling system, the incondensable species are carried to a Varian µGC4900. Three columns are calibrated for the analysis and quantification of H_2, CO, CO_2, O_2, CH_4, C_2H_2, C_2H_4, C_2H_6, Benzene and Toluene.

3. Methodology

3.1 Catalyst preparation

Olivine comes from Magnolithe GmbH in Austria. It was calcined at 1600°C during 3 hours before crushing and grinding down to a granularity of 300-800µm by Magnolithe. Catalysts
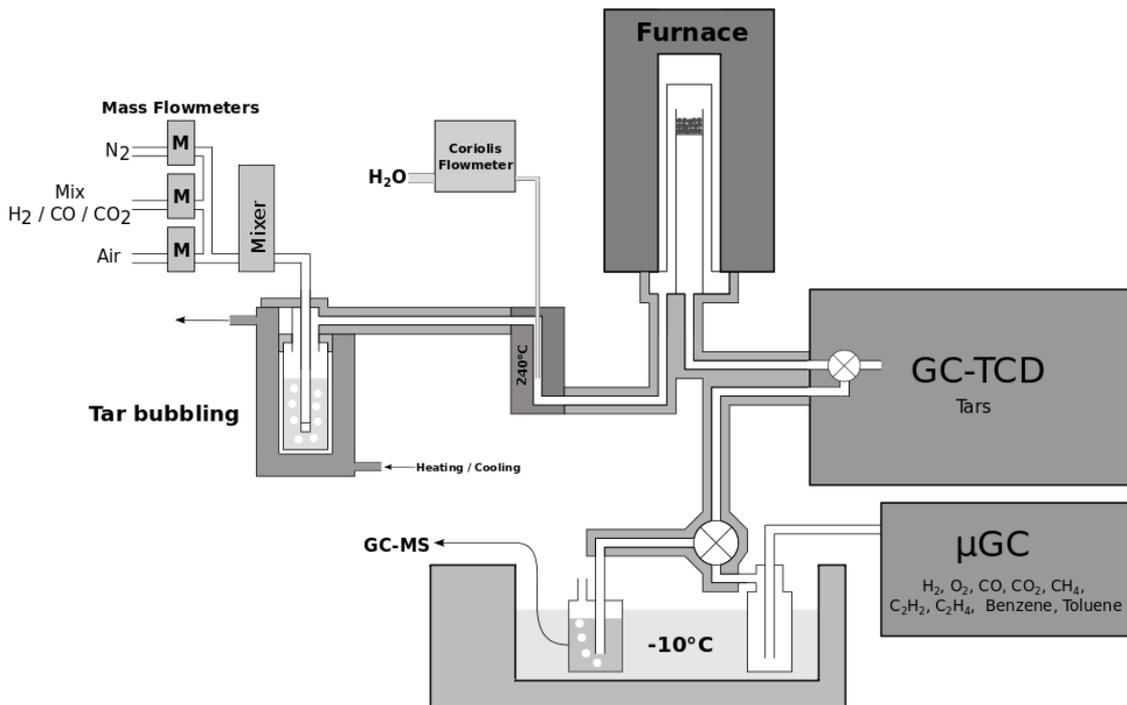

Figure 2: Experimental apparatus

were prepared according to the literature [6, 7].

	$H_2/H_2O=1.5$	$H_2/H_2O=0.75$
H_2	30%	15%
CO	23%	11%
CO_2	13%	6%
H_2O	20%	20%
N_2	13,75%	47,75%
Naphthalene	0,25%	0,25%

Table 1: Initial gas molar fraction

Olivine was recalcined in our laboratory before use, at 1100°C under air during 4 hours, with a heating rate of 3°C/min.

Ni/olivine catalyst was prepared by wet impregnation of $Ni(NO_3)_2$,6H_2O over Magnolithe olivine. Water was removed in a rotary evaporator, and the preparation was dried overnight at 105°C. Then, it was crushed back to its initial granularity, and calcined at 1100°C during 4 hours.

Catalysts were characterized by ICP and gave the following mass fractions: Olivine contains 6% of Fe, 40% of Mg, 38% of Si and 0.2% of Ca. Ni/olivine contains 4% of Ni, 5% of Fe, 38% of Mg, 36% of Si and 0.1% of Ca.

3.2 Experimental conditions

Each test is operated as follows: 2.468g of catalyst is deposited on the filtering sheet; the bed heights is around 3mm. Gas concentrations were chosen to represent the atmosphere of a dual-fluidized bed (table 1, first column), and temperature was set to 850°C if unspecified.

Total gas flow was set to 232 mL/min at STP for each experiment, and naphthalene concentration to 14 g/m^3 at STP. Space velocity for the whole reactor was 256.h^{-1} and weight hourly space velocity (WHSV) for the catalyst was 0.33.h^{-1}. When oxidation cycles were conducted, air flow was set to 150 mL/min at STP during 15 minutes at 950°C. Then, tar cracking was achieved during 40 minutes at 850°C with both H_2/H_2O ratios using gas concentrations indicated in table 1.

4. Results and discussion

The first experiments were conducted in order to quantify the amount of non-catalytic cracking of naphthalene. The amount of hydrogen over water is a critical aspect for catalyst functioning [16, 17], and the experiments were carried on for $H_2/H_2O=1.5$ and $H_2/H_2O=0.75$.
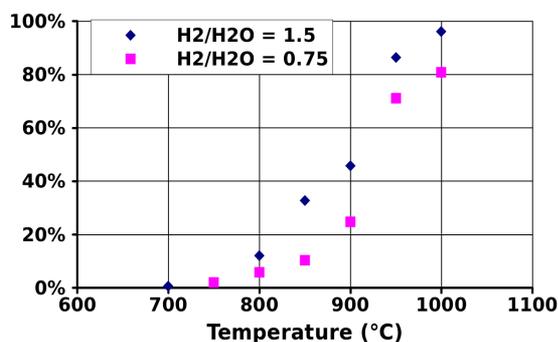

Figure 3: Naphthalene conversion on inert sand bed

Figure 3 shows the amount of naphthalene converted on an inert sand bed depending on the temperature. Naphthalene is difficult to convert with temperature alone, and results at 850°C are especially low: 30% conversion for

$H_2/H_2O=1.5$ and 9.5% for $H_2/H_2O=0.75$. The difference between the two experiments is about 50°C for the same conversion rate; we can see that the amount of hydrogen in gas is very important for tar destruction, at every temperature from 800 to 1000°C. However, even with a high amount of hydrogen at 1000°C naphthalene does not reach 100% conversion, and tars can still be detected. GC-MS shows consistent results at 900°C with GC-TCD analysis (Table 2).

Experiments have then been realized with the two catalysts: olivine and Ni/olivine. They gave very different activity compared to sand (figure 4). Ni/olivine showed a great performance at naphthalene conversion, even at low hydrogen ratio: the conversion reaches 100% for each experiment. Olivine showed clearly a better efficiency than sand for $H_2/H_2O=1.5$, but for $H_2/H_2O=0.75$ the difference is very low: this is in agreement with the literature [17], which states that Fe-based catalysts

	$H_2/H_2O=1.5$	$H_2/H_2O=0.75$
Naphthalene	1470 ppm	1885 ppm
Benzene	58 ppm	35 ppm
Toluene	3 ppm	Traces
Styrene	Traces	Traces
Indene	2 ppm	3 ppm
Phenanthrene & Anthracene	Traces	Traces

Table 2: GC-MS analysis on condensable species at 900°C

like olivine need a minimal amount of hydrogen to be active in tar destruction.

As can be seen in figure 4, Ni/olivine catalyst showed very good activity toward naphthalene conversion at 850°C. Results in literature [8] show that Ni/olivine catalyst can deactivate in presence of air. The purpose of this catalyst is to be used in a dual fluidized-bed, and it will therefore be in contact with air when passing through its oxidizing reactor.
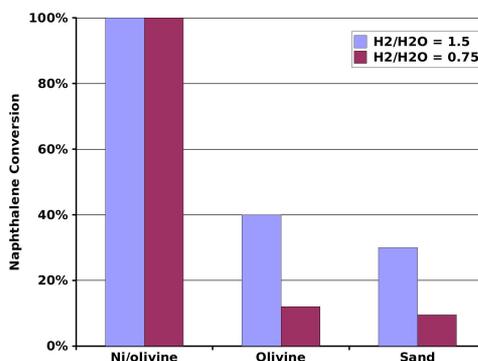

Figure 4 : Naphthalene conversion rate for sand, olivine and Ni/olivine bed at 850°C

In order to determine if deactivation by air could be a problem, we tested Ni/olivine through oxidations / reduction cycles, and tar conversion was measured between each cycle. Figure 5 shows very good results for this catalyst, with almost 100% conversion after each oxidation, and for each H_2/H_2O ratios. It didn't deactivate over 7 cycles, but we detected a very small amount of benzene in the gas that increased after each oxidation cycle. Although this amount is very small (a few ppm), we can see that there is a significant difference between the two hydrogen over water ratios, with higher concentration of benzene when $H_2/H_2O=0.75$.

These results on benzene might suggest that even if Ni/olivine is very efficient, it is sensitive to hydrogen concentration, and it may deactivate earlier under low hydrogen pressure. However, no formal conclusion can be obtained on this since no other sign of deactivation were detected.
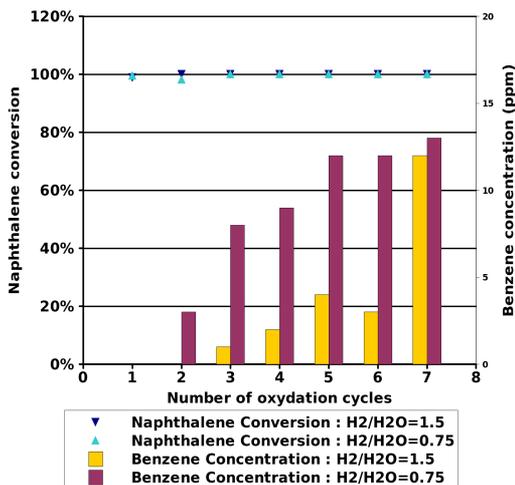

Figure 5 : Naphthalene conversion at 850°C over oxidation cycles

5. Conclusion

Naphthalene destruction in gasification conditions has been studied with and without catalyst, and the influence of the ratio H_2/H_2O has been considered. Deactivation of the nickel over olivine catalyst was particularly tested with oxidation cycles. Naphthalene is very resistant to conversion in gasification condition, and even at a temperature of 1000°C and a hydrogen over steam ratio of 1.5 it was never completely converted without a catalyst. Olivine alone shows some activity toward naphthalene conversion with $H_2/H_2O=1.5$, but with a ratio of 0.75 its activity is much lower and there is small differences with a sand bed. However, Ni/olivine catalyst showed complete conversion of naphthalene at 850°C whatever the hydrogen partial pressure. Oxidation cycles had little influence on this catalyst, except for the apparition of a small amount of benzene in the gas. This may be a sign of aging of the catalyst, but more studies are needed to reach further conclusions.

Acknowledgements

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