Two-stage gasification: fine characterisation of wood chips pyrolysis step in a continuous fixed bed reactor

Milhé M., Dufourny A., Van de Steene L., Commandré J.M., Martin E.

CIRAD-PERSYST, TA B42/16, 73 rue JF Breton, 34398 MONTPELLIER Cedex 5, France, phone: +33 4 67 61 53 52 (fax: 65 15), e-mail: mathieu.milhe@cirad.fr

Abstract:

Two-stage gasification is a proven technology for combined heat and power generation, particularly as it enables the production of a high quality, virtually tar-free gas.

In this work, we focused on the pyrolysis step of the process and carried out a parametric study on the effect of temperature and bed height on the yields and quality of the char/gases/tars produced.

We used the Continuous Fixed Bed reactor (CFiB) at CIRAD that replicates the pyrolysis zone separately from the rest of the process.

At the reactor outlet, char, gases and oils were sampled and analyzed; this enabled mass balance calculations over the whole process and provided relevant information on evolution and composition of pyrolysis products.

When the temperature varied from 350 to 600°C, char yield decreased from 40 to 25% wt. while gases yield increased from 9 to 38% wt. Regarding condensates, pyrolytic water remained constant while secondary tars (phenol) increased when increasing pyrolysis temperature. Moreover, a larger bed height seems to favor secondary reactions on pyrolysis condensates, leading to the formation of additional char and gases.

I.   Introduction

Gasification processes have recently regained interest as a possible source of renewable energy for hydrogen production, liquid fuel synthesis (Fischer-Tropsch) or decentralized energy production. Of the different processes available, the fixed-bed offers the advantage of technical simplicity; however a major drawback is the high tar content of the producer gas.

A special staged gasification unit has been developed in recent years by XyloWatt, the NoTar™ process. In this process, the pyrolysis and gasification steps occur in two fixed beds that are physically separated. This configuration gives very low tar contents at the outlet of the reactor thanks to a homogeneous oxidation zone, where nearly all the organic compounds arising from pyrolysis are burned. Such oxidation also produces the required energy and reactant gases for the subsequent gasification step. It is therefore very important to characterize the pyrolysis step in order to optimize the process as a whole; however, very few studies have focused on pyrolysis in continuous fixed beds. The main difference with other processes is that the gas phase flows through the hot char bed, leading to a greater extent of heterogeneous secondary pyrolysis reactions. This paper aims at investigating the role of operating conditions on this process with a pilot scale reactor.

II: Apparatus and analyses

II.1 Pilot description

The Continuous Fixed Bed Reactor (CFiBR) is a vertical tubular reactor originally developed to study char gasification in fixed beds. It is described below (fig. 1).

Wood chips are fed by means of a conveyor belt (1) and introduced into the reactor via two pneumatic valves (2) acting as an airlock. The valves are water-cooled because of their proximity to the burner zone.

Energy is provided by two propane burners (3) in order to create an inert atmosphere of exhaust gases (CO_2 and H_2O in N_2 at high temperature). Propane and air flowrates are controlled by two Brooks mass flow meters.

The reacting zone itself is a 20cm in diameter and 160cm high vertical tube, made of refractory stainless steel. It is provided with tapping pipes every 10 cm up to 80 cm high to measure pressure and temperatures and to sample gases ((1) to (11)). They are placed helicoidally in order not to disrupt downward bed flow. The reactor is surrounded by refractory wool insulation. The bottom of the reactor takes the form of a circular grid with 1 cm holes, fitted with a scraper. The scraper is moved by a crank (4) below the reactor to force the char through the grid. It can also be moved downwards in order to purge the reactor quickly. The char is collected in a closed vessel beneath (5).

In an initial version, two 2-metre long stainless steel tubes were used as gas condensers, at the bottom of which two flasks were used as oil/tar collectors. The remaining vapours and gases were then driven to the post-combustion chamber. After several plugging issues, this solution will be finally replaced by a 400°C electrically heated-line to post-combustion.
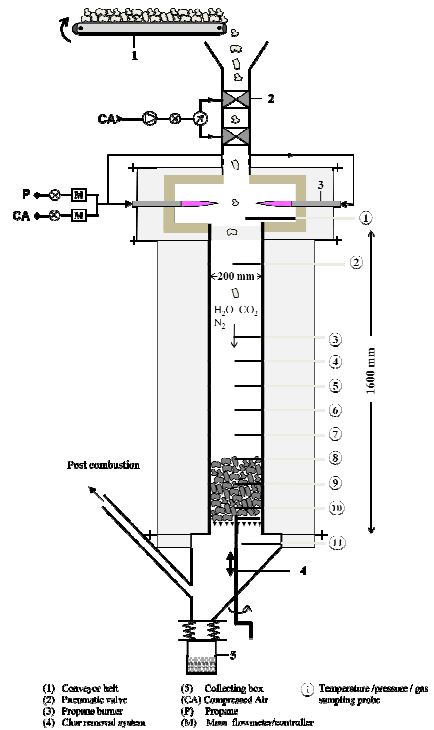

Figure 1: Diagram of the CFiBR for pyrolysis experiments

II.2 Monitoring and stationary regimes

In this study, we operated with bed heights of 15 or 25 cm. Thermocouples placed at these heights are used to control the bed height.

- Bed monitoring
Bed height control is based on the temperature difference between the exhaust gases from the burners and the cold wood chips falling on the top of the bed. When the bed height reaches the monitoring thermocouple, its temperature falls quickly below the bed temperature. Some char is then removed using the scraper, involving a slight decrease in bed height: the thermocouple returns to its former temperature once out of the bed.
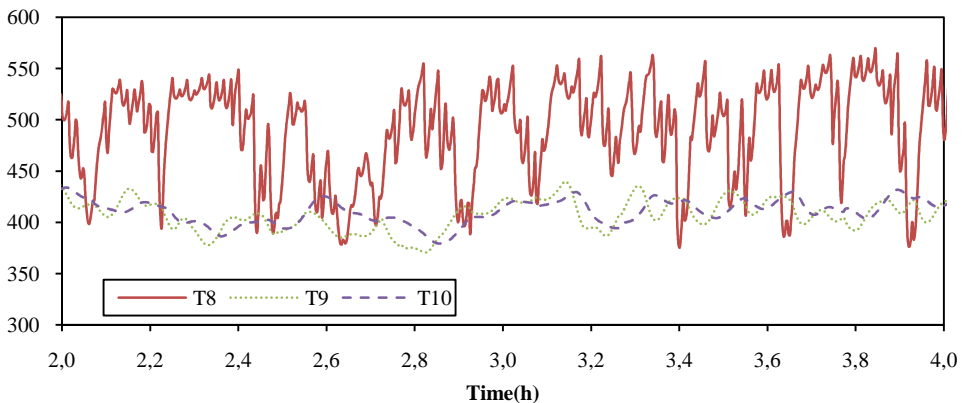
Char removal is limited to around 80 grams, corresponding to a maximum decrease of about 2 cm of the bed: this value was chosen not too high, to keep as constant as possible a bed height, and not too low, to enable easy control of the bed height.

Bed temperature is the mean temperature measured at the bottom of the fixed-bed, 5 cm above the grid.

- Obtaining a stationary regime

When starting an experiment, the reactor is first loaded with previously pyrolysed char for the heating up period. When the exhaust gases temperature reaches about 500°C at the bed surface, wood chips feeding begins. Burner power is then adjusted to reach the desired temperatures in the fixed bed.Generally, the stationary regimes obtained did not allow a better accuracy than +/-25°, as the bed temperature fluctuated regularly. An example of a stationary regime at 400-425°C and a 25 cm bed height is illustrated in fig. 2. As can be seen, the control thermocouple T8 fluctuates from the inlet gases temperatures (about 550°C) down to the bed temperature (about 400°C) when covered with wood chips.

The smaller fluctuations of T8 are due to cold wood chips entering the reactor every minute provoking a slight temperature decrease.

II.3 Sampling and analyses

In this study, all the yields are expressed as % wt. on a dry basis in $g_{product}/g_{biomass}$.

- *Chars*

Char is defined as the solid residue of pyrolysis, a carbonaceous porous material containing a certain amount of volatile matter (VM).

Char yield Y_{char} is calculated as follows, according to the ash tracer method:

$$Y_{Char} = 1 - \frac{1 - \frac{A_{wc}}{A_{Char}}}{1 - A_{wc}}$$

A_{wc} and A_{Char} are the ash contents of wood chips and char (resp.). They are obtained by combustion of the samples in a muffle furnace according to standard AFNOR NF EN 1860-2 and AFNOR XP CENT/TS 14775 (resp.).

T(°C)

Figure 2: Example of a stationary regime in the CFiBR with a 25 cm bed height (T8 is above the surface, T9 in the middle and T10 at the bottom of the bed)

We assumed two things here: (i) that ashes are homogeneously distributed between the wood chips char collected and the fines lost in the process; (ii) that most of it stays in the solid phase during pyrolysis [1].

Due to wood chips heterogeneity, char was sampled 4 or 5 times during a stationary regime; all the samples were then mixed and ground in one batch before analyses.

A first approach was to directly weigh the char sampled at the bottom of the reactor. This technique did not allow a precise quantification, as the calculated flowrates were too sensitive to the bed height control operation.

VM contents were measured according to standard AFNOR XP CENT/TS 14775.

- Condensates

Gases are sampled under the char bed (1) through a sampling train consisting of five impingers in a row as shown in fig. 3. The first impinger (2) is empty and at ambient temperature in order to condensate most of the water generated without freezing it; the next two impingers (3) are filled with 200 ml of isopropyl alcohol and placed in a -20°C cold bath (6); they lead to an empty impinger with a quartz frit (4) in the cold bath and finally to an impinger filled with silicagel at ambient temperature (5). The gases then pass through the pump (7) and a gas meter (9) prior to the sampling for micro-GC analysis (10). A rotameter (8) is used to control gas flow rates in the train.

The sampling method requires that at least 0.1 Nm3 of gases are sampled in order to have sufficient accuracy for condensate yields estimation. However, the high fines content of the gases prevents us from working at too high a sampling flow rate; as a consequence, each sampling has to last for at least 25 minutes. The impingers are then weighed and their contents gathered for Karl-

Fischer and GC-MS analyses to measure water and organic compounds contents in the condensates. When calculating pyrolytic water content, caution is necessary, as water in the condensates also comes from wood chips drying.
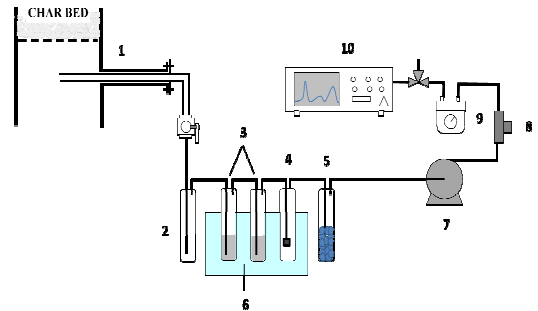
Figure 3: Diagram of the sampling train used in the experiments

- Permanent gases

After oil condensation in the sampling train, permanent gases are measured online in a Varian micro-gas chromatograph CP4900 equipped with two columns (poraplot Q for CO_2, C_2H_4 and C_2H_6 and molsieve 5Å for H_2, O_2, N_2, CH_4 and CO quantification).

Raw measurements include exhaust gases from the burners; blank tests were necessary to characterize the composition of the exhaust gases for each set of operating conditions. The resulting N_2, CO_2 and CO flows are then deducted from the measured values, giving the pyrolysis gases composition.

This method gives accurate results for char and permanent gas yield estimation; however the large sources of error in the condensate yield estimation prevented us from obtaining accurate mass balances (generally between 90 and 110% wt. d.b.). For that reason, the results presented here were calculated by deducting total condensate yields from char and gas yields.

III: Pyrolysis experiments, results and interpretation

- Parametric study

In this study, we firstly focused on the effect of pyrolysis temperature on products distribution (char, oils, pyrolytic water and permanent gases) and on their properties.

We then studied the influence of the char bed height on products distribution with a view to characterizing the effect of a char bed on secondary pyrolysis reactions.

- Biomass feedstock

The biomass used in this study is maritime pine wood chips; proximate and ultimate analyses are shown in table 1. The size distribution of the wood chips shows that more than 90%wt. is between 2 and 14 mm wide.

Table 1: Proximate and ultimate analyses of the wood chips used

Moisture (%wt. w.b.)	7-13
Proximate analysis (%wt. d.b.)	
Ashes	0.39
Volatile matter	83.3
Fixed carbon	16.3
Ultimate analysis (%wt. d.b.)	
C	53.0
H	5.8
N	0.1
O *(by difference)*	40.7

III.1 Influence of bed temperature on mass balance and products

For this set of experiments, the operating conditions were a wood chips flowrate of 4 kg/h and a bed height of 15 cm (i.e. char residence time was about 30 min). Pyrolysis products distributions and compositions have been studied over a range of temperatures comprised between 350 and 600°C: products distribution is shown in fig.4.
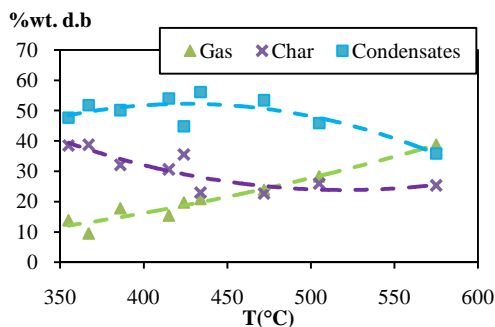
Figure 4: Evolution of products yields vs. bed temperature

III.1.1 Mass balance

The profiles obtained are similar to those observed in other studies on "slow" pyrolysis [2]:

- Char yield decreases with increasing temperatures, from 40 to 25% wt. (d.b.), and seems to stabilize at 25% above 500°C.

- Condensates yield (pyrolysis water included) shows a slight peak at about 450°C (55% wt. d.b.), and decreases sharply above that temperature.

- Gases yield increases linearly with pyrolysis temperature, from 10 to 40% wt. (d.b.) between 350 and 600°C.

Products properties are discussed in more details below.
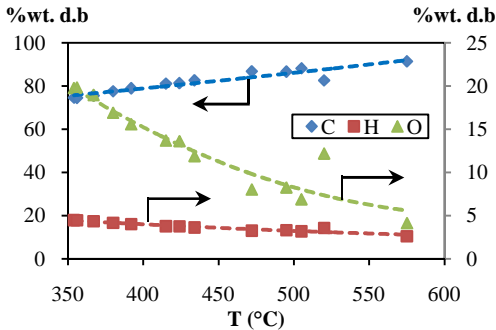
III.1.2 Char quality

Volatile matter (VM) content in the chars versus pyrolysis temperature is plotted in fig.5.

VM content in char decreases from 36 to 7 % wt. between 350 and 580°C. Increasing the pyrolysis temperature above 600°C would probably not have a significant effect on char yield since the VM content is already low.
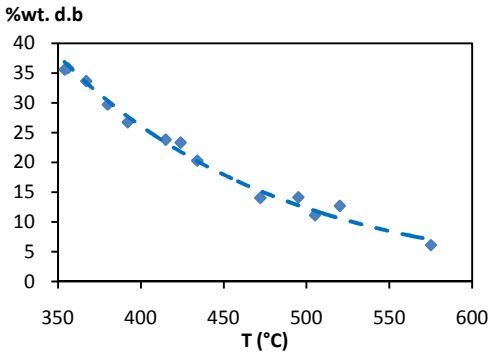
Figure 5: Char MV content vs. pyrolysis temperature

Figure 7: Pyrolytic water and oil yields vs. pyrolysis temperature
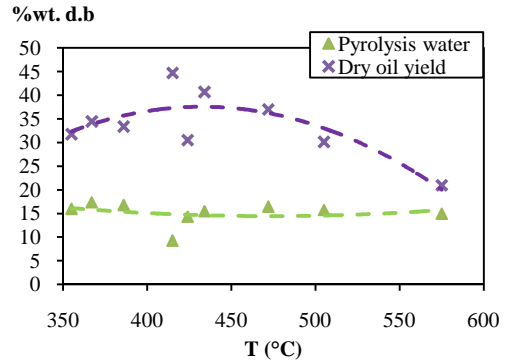
C, H and O contents in char are plotted in fig. 6.

Figure 6: C, H and O contents in chars vs. pyrolysis temperature

III.1.3 Condensable phase composition

Condensates can be separated into two phases, organic compounds (pyrolysis oil and/or tars) and water (coming from pyrolysis reactions, wood chips drying).
Evolutions of pyrolysis water and dry oil yields versus pyrolysis temperature are plotted in fig. 7.
The evolution of dry oils is analogous to that of total condensates, while pyrolytic water yields remain constant in the temperature range studied.

Peak oil production is about 40% wt. (d.b.) between 400 and 450°C. This value is lower than that observed in flash processes (peak production of 60% wt. at 500-550°C): this may be explained by a lower heating rate of the wood chips compared to the smaller particles used in flash pyrolysis. The char bed may also have a catalytic effect on oil cracking reactions [3].
The fact that pyrolytic water production does not vary with temperature, may indicate two things:
- Heating up of the wood chips is slow enough over the temperature range studied to allow dehydration reactions that are promoted at low pyrolysis temperatures and would have been less important at a higher heating rate. [4]
- Under these operating conditions, the water-gas shift reaction does not seem to play an important role in product distribution.
The evolution of three main components of pyrolytic oil is represented in fig. 8. Levoglucosan, phenol and naphthalene were chosen as they are considered representative compounds for the three main tar groups (as classified by Evans and Milne [5]). Levoglucosan is a typical primary pyrolysis compound, while phenol mainly comes from secondary

reactions; naphthalene is an important component of PAHs, products of the thermal evolution of oils.
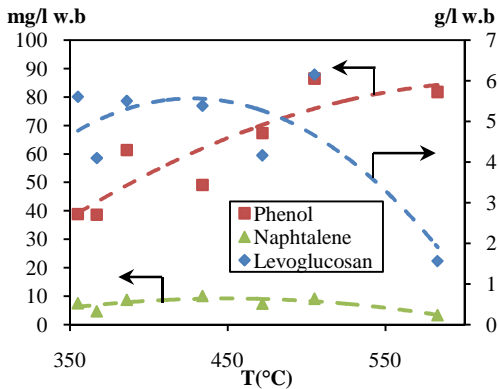
Figure 8: Evolution of three tarry compounds vs. pyrolysis temperature

In the temperature range investigated, levoglucosan concentration decreases sharply above 500°C (around 5 g/l to less than 2 g/l in condensates) while phenol content increases regularly (from 40 to 80 mg/l). Naphthalene content remains low at these temperatures as PAHs formation requires higher temperature levels [5].

III.2.1.4 Gas composition
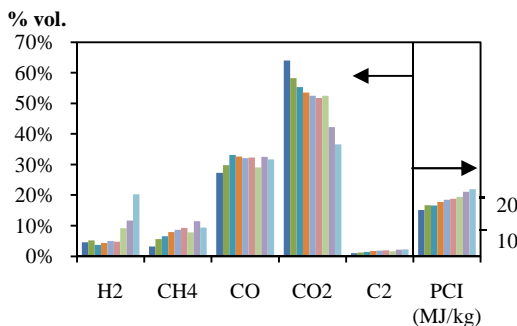
Figure 9: Gas composition with increasing pyrolysis temperatures (356-387-424-440-472-487-505-529-583°C) and corresponding LHV. C2 is the sum of C_2H_4 and C_2H_6.

The increase in gas yields with temperature can be explained by two phenomena: wood chips release more VM when increasing bed temperature and the cracking of pyrolysis oils produces additional permanent gases above 450°C. The combination of these two effects leads to an evolution of pyrolysis gases composition, illustrated in fig.9 between 356 and 583°C.

We can distinguish several effects here:
- CO and CO_2 are the main pyrolysis gaseous products. The decrease in CO_2 content with temperature can be explained by the fact that it mainly comes from primary pyrolysis reactions [6] and not from secondary reactions that gain importance with temperature. CO content remains stable above 400°C.
- The proportion of H_2 mainly increases above 500°C, which may be due to oil cracking [7]. Above this temperature, its content increases rapidly to 20% vol.
- CH_4 content also increases with temperature, but it remains below 10% vol. in the temperature range studied. C_2H_4 and C_2H_6 production follows the same trend, but their content remains low (about 2% vol.) even close to 600°C.
Overall, non condensable combustible gases content increase with temperature: this implies an increase in the LHV of non condensable pyrolysis gases from 16 to 22 MJ/kg (i.e. 5.7 to 10.9 MJ/Nm3) over the temperature range studied.

III.2.2 Influence of char bed height on mass balances

In this section, we studied the effect of a higher char bed (25 cm instead of 15 cm) on pyrolysis products distribution. As all the other parameters are kept identical (wood chips feed stock and flow rate,

temperature range and pyrolysis atmosphere composition) the only changes in the process are:
- Char residence time increases to 60 min.
- Vapors contact time in the bed is multiplied by about 1.7 at equivalent pyrolysis temperatures.

In fig. 10 to 13, evolution of product yields are illustrated for the two bed heights over the temperature range studied.

%wt. d.b
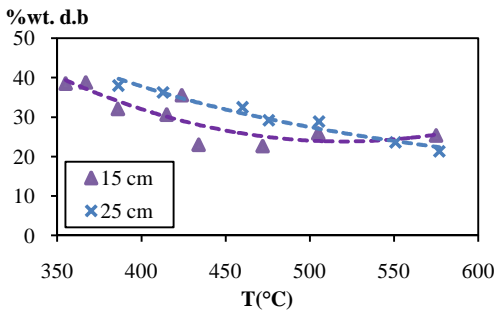
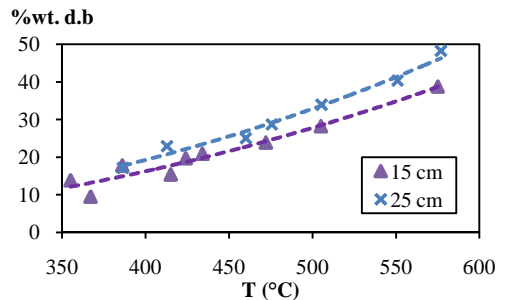**Figure 10: Comparison of char yields for two bed heights**

Char yields (fig. 10) are slightly higher with a higher bed; this may be due to a greater extent of condensation and polymerization reactions between oils and the char bed under these operating conditions. These differences are more marked at lower pyrolysis temperatures (5% wt. d.b. at around 400°C).
It is interesting to note that these chars show very little difference in terms of VM content (see fig. 11) in spite of their different yields. This means that the differences in yields in a higher bed are due to additional deposition of carbonaceous material and not to incomplete pyrolysis.

%wt. d.b
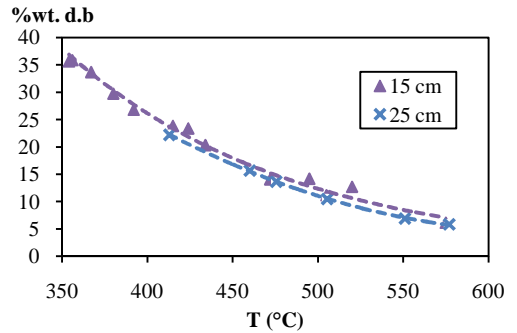
**Figure 11: Char VM content vs. bed temperature for two bed heights**

Pyrolysis gases production (see fig. 12) seems enhanced by the increase in bed height. This increase appears to be more pronounced at higher temperatures. As the corresponding chars had the same heating rates and temperature history between the two bed heights, this additional production of gases probably comes from secondary reactions of pyrolytic oils.

%wt. d.b

Figure 12: Comparison of permanent gases yields for two bed heights

As a consequence of the previous effects, condensate yields (see fig. 13) decrease when bed height is increased; this effect is particularly marked in the 400-500°C temperature range.

%wt. d.b
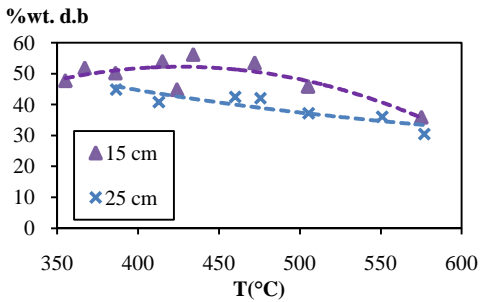
Figure 13: Comparison of condensates yields for two bed heights

These differences seem to fade above 550°C, temperatures at which thermal cracking of oil is sufficient to hide the catalytic activity of the char bed.

All these results regarding the influence of a higher char bed need to be confirmed by further experiments on larger bed heights.

IV: Conclusion

Wood chips pyrolysis was characterized at pilot scale in a continuous fixed bed reactor in operating conditions similar to industrial ones. A methodology was developed to operate in a stationary regime and to sample all products at the outlet of the fixed bed.

A parametric study was then conducted, and the influence of bed temperature and char bed height on the evolution of products distribution and composition were investigated.

When the temperature varied from 350 to 600°C, char yield decreased from 40 to 25% wt. while gases yield increased from 9 to 38% wt. Regarding condensates, pyrolytic water remained constant while secondary tars (phenol) increased when increasing pyrolysis temperature. Moreover, a larger bed height seems to favor secondary reactions on pyrolysis condensates, leading to the formation of additional char and gases.

This parametric study is going on with further work focusing particularly on the role of catalytic cracking of oils in the char bed. The role of a higher steam concentration in pyrolysis atmosphere on products and compositions will also be investigated. These experimental results will be of great help in understanding and predicting behavior of the pyrolysis step in two-stage gasifiers.

V: Acknowledgements

VI: References

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