# INFLUENCE OF THE STOICHIOMETRIC RATIO ON TAR COMPOSITION DURING FLUIDIZED BED GASIFICATION

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ABSTRACT: Fluidized bed gasification is a promising technology for the energetic valorization of biomass and wastes. However the presence of heavy tars limits the use of the gas to applications where the gas is not cooled. Several parameters such as the temperature profile inside the gasifier and the gas residence time influence the concentration and composition of the tar mixture and thus the gas dew point. In autothermal air-blown fluidized bed gasifiers the stoichiometric ratio (fed air/stoichiometric air) determines the reactor temperature but the influence over the tar composition depends on the competition of the different fractions (light gas, char and tar) for the oxygen available. This paper analyzes the tar composition in the gas produced during the conversion of biomass pellets in a fluidized bed reactor when the stoichiometric ratio is raised from 0 (pyrolysis) to 0.21 (standard autothermal gasification with air). The tests were conducted at 800°C and 900°C and constant gas residence time and volatiles/carrier gas ratio. The results are discussed and compare with previous literature works, explaining some aspects of existing tar conversion models for biomass gasification.
Keywords: fluidized bed, gasification, tar.

## 1 INTRODUCTION

The availability of different lignocellulosic resources such as agricultural wastes, forest residues, or waste wood is an interesting alternative to fossil fuels for energy production. Gasification technology has several advantages over conventional boilers for biomass and waste conversion in medium-scale plants (1,2). The use of fluidized bed gasifiers (FBG) has several advantages over that in fixed/moving bed or entrained-flow, such as the accommodation to fuel quality (3). These alternative fuels usually contain higher amounts of inorganic contaminants (K, Cl, S, etc…) that are released to the gas phase during fuel conversion. The syngas produced in FBG, containing most of the energy of the original fuel in chemical form, can be cleaned before its combustion in gas turbines, engines or boilers. Gaseous contaminants can be divided in two groups: inorganics and heavy tars (hydrocarbons condensing at temperatures 300-400°C). The presence of heavy tars requires the use of expensive secondary tar cleaning devices before the gas is cooled. The use of models predicting the evolution of tar composition and condensation behavior under different conditions is helpful for designing new gas cleanup strategies.

The conversion of a fuel particle during gasification can be divided in two different processes: drying-devolatilization and secondary conversion. During devolatilization, the particle is heated to the reactor temperature and decomposed into three main fractions: char, tar, and light gas. The yield and composition of these fractions depend on different variables, such as the particle heating rate and reactor temperature (4), whereas they are rather insensitive to the gas composition surrounding the fuel particles (5). The secondary reactions, either homogeneous or heterogeneous, modify the composition of the gas generated in the devolatilization step. The extent of these reactions depends on the reactor conditions, such as temperature, residence time, composition of the surrounding atmosphere, presence of catalysts, and so forth.

In autothermic FBG the increase in stoichiometric ratio (ER) produces an increase in the reactor temperature which, in turn, modifies the composition of the tar/hydrocarbon mixture. Direct interaction between oxygen and tar is known to strongly influence the tar composition (6). However in FBG the oxygen concentration decays to zero rapidly by reactions with volatiles and char. Therefore the direct interaction between oxygen and tar (and hydrocarbons) is limited by the competition of the different fractions (char, tar and gas) for the available oxygen.

The present work aims at studying the extent of the direct interaction of oxygen with tars and hydrocarbons during FBG of biomass pellets decoupling the influence of the stoichiometric ratio over the reactor temperature. Detailed characterization of tars and hydrocarbons produced during the semi-continuous operation of a laboratory-scale FB reactor is reported. During the experiments the ER is raised from 0 (pyrolysis conditions) up to 0.21 maintaining constant the gas residence time, fluidization velocity and the volatiles/carrier gas ratio. The tests were conducted at two different temperatures, 800°C and 900°C, in order to analyze the tar oxidation at operation temperatures relevant in FBG.

## 2 EXPERIMENTAL

### 2.1 Fuel

The fuel used was biomass (pruning waste) pellets with 6mm of diameter and length ranging from 5mm up to 15mm. Table 1 shows the ultimate and proximate analysis of the pellets used.

### 2.2 Reactor

The FB reactor is made of refractory steel and it is heated by an electrical furnace of 10 kW. It is divided in two zones, a bottom part with an internal diameter of 53 mm and 192 mm of height, and a freeboard with internal diameter of 81 mm and 240 mm of height. A conical transition zone with height of 50 mm connects the bottom and freeboard parts. The inert bed material used was 500g of bauxite (aluminosilicate) with particle size between 250 and 500 μm, having a minimum fluidization

velocity of 0.20 m/s. The fuel is fed from the top of the freeboard, falling down to the dense bed.

The concentration of $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$ and $C_3H_8 + C_3H_6$ (both in one peak) were analyzed using a micro-GC model 3000A. The tar fraction was collected using a sampling train with the configuration described in (7) using isopropanol as solvent. Tar samples were analyzed by GC-FID giving the concentration of 41 different compounds from benzene to perylene. The different tar compounds have been lumped according with the classification described in (8).

**Table I:** Ultimate and proximate analysis of the fuel

| Proximate analysis | |
|---|---|
| Moisture (wt.% as received) | 8.11 |
| Ash (wt.% dry basis) | 4.95 |
| Volatiles (wt.% dry basis) | 78.76 |
| Fixed C (wt.% dry basis) | 16.29 |
| **Ultimate analysis** | |
| C (wt.% dry basis) | 47.22 |
| H (wt.% dry basis) | 6.36 |
| N (wt.% dry basis) | 0.99 |
| S (wt.% dry basis) | 0.06 |
| O (wt.% dry basis)* | 40.42 |

2.3 Experimental procedure

An experimental procedure was applied to vary independently the experimental parameters (temperature, gas residence time and volatiles concentration in the fuel gas) being the rest constant. The fuel was fed in several pre-weighted batches from the top of the reactor while nitrogen or nitrogen/air mixtures were used as fluidizing agent. The fuel batches are added every 10s to the fluidized bed reactor. Since the complete devolatilization of the fuel lasts more than 60s the interval of 10s between additions produces a constant concentration of the different compounds in the gas phase. The amount of air in the nitrogen/air mixtures was adjusted for the different ERs maintaining the fluidization velocity constant. The aim of this procedure was to vary the volatiles/carrier gas ratio from the gas residence time by adjusting both the weight of the fuel batches and the flowrate of the fluidizing agent.

Table 2 presents the experimental conditions tested. Every test condition was carried out two/three times to assess the repeatability. The results presented show the average yields and the error bars for the different conditions tested.

**Table II:** Experimental conditions tested

| Temperature (°C) | 800 | 900 |
|---|---|---|
| ERs | 0, 0.07, 0.14, 0.21 | 0, 0.07, 0.14, 0.21 |
| Volatiles/fluidizing agent ratio (vol.%) | 32 | 38 |
| Gas residence time (s) | 1.5 | 1.5 |
| Fluidization velocity (m/s) | 0.45 | 0.45 |

3   RESULTS AND DISCUSSION

Fig. 1 presents the yields of light hydrocarbons at 800°C and 900°C for stoichiometric ratios between 0 and 0.21. The increase in the temperature from 800°C up to

900°C significantly influences the composition of the hydrocarbon mixture, which is explained by dehydrogenation, polymerization and C-C bond scission reactions, in agreement with previous works on gasification and pyrolysis. However, the yields of the different hydrocarbons analyzed present only slight variations (within the standard deviation of the tests) when the stoichiometric ratio is increased from 0 to 0.21. In a conventional autothermic FB gasifier the increase in the stoichiometric ratio results in a temperature increase. The results presented here highlight the actual significance of the oxygen-light hydrocarbons interaction decoupling the effect of the temperature. According with the results the rise of the oxygen concentration does not increase the oxygen availability for light hydrocarbons conversion. Therefore, in the conditions studied, the oxygen fed is mainly reacting with other compounds produced during devolatilization such as light gas or char.

The yields of methane, ethane and ethylene at both temperatures are similar to those found for higher stoichiometric ratios using olive tree pruning pellets (9). It can be concluded that, even with an ER as high as 0.35 (not analyzed here but in (9)), the oxidation of hydrocarbons during FBG is not enhanced.
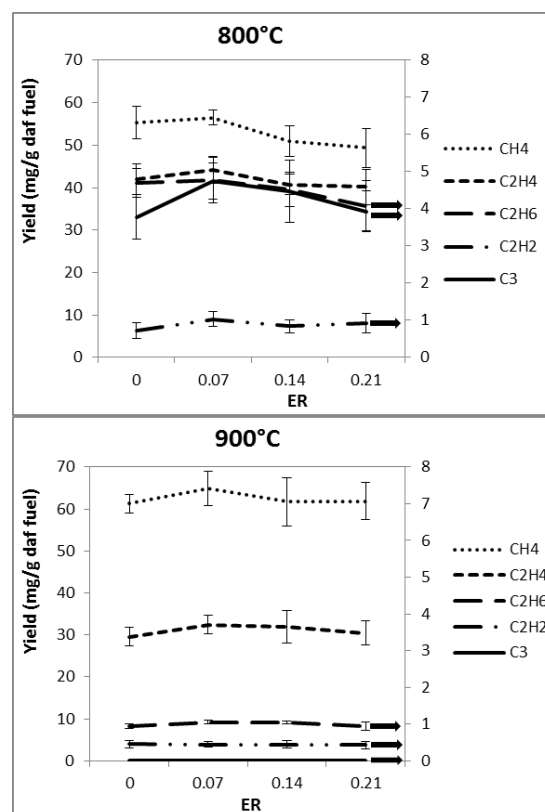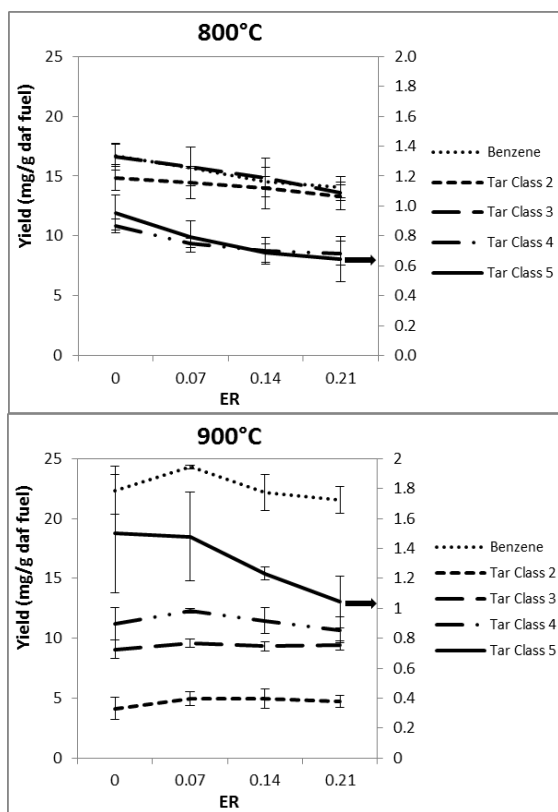


**Figure 1:** yields of light hydrocarbons at 800°C and 900°C for stoichiometric ratios between 0 and 0.21

Fig. 2 presents the yields of benzene and the different tar compounds at 800°C and 900°C for stoichiometric ratios between 0 and 0.21. At 800°C the increase in the ER produces a slight reduction in the yields of the different tar compounds. This reduction is higher for the heaviest tars (tar class 5) whose yield drops from 0.95 mg/gdaf fuel in pyrolysis conditions to 0.64 mg/gdaf fuel at ER=0.21. The different tars analyzed (aromatic and polyaromatic compounds) are produced by thermal

conversion of primary tars (10). During FBG this maturation of the tar occurs on the way of the gas along the freeboard where the oxygen concentration is zero. Therefore, only a limited interaction between oxygen and aromatic compounds occurs (except for when operation with secondary air injection). The reduction observed in the yields of the different tar classes with ER is probably caused by the partial combustion of primary tar (precursor of the aromatic tar) in the bottom part or the reactor where the concentration of oxygen is noticeable.

When the temperature is raised to 900°C the influence of the ER on the yield of the different tar compounds is lower and, in most cases, within the standard deviation of the tests carried out. This is probably related to the reduction of the interaction between oxygen and primary tar compounds in the reactor. Therefore as the temperature is increased, the oxygen fed to the reactor combines preferentially with other primary compounds such as char, hydrogen or carbon monoxide.



**Figure 2:** yields of benzene and the tar compounds at 800°C and 900°C for stoichiometric ratios between 0 and 0.21

In FBG units the oxygen concentration decays rapidly along the dense bed. During devolatilization the fuel particles tend to float on the dense bed, where the oxygen concentration is lower, due to the fast release of volatiles. Hence the interaction of volatiles with oxygen is limited to particular zones of the gasifier. This makes the tar and light hydrocarbon conversion process to be mainly driven by the temperature profile of the gasifier. The results presented here highlight the scarce interaction between oxygen and hydrocarbons during the gasification tests carried out in top-fed FB. The low interaction between oxygen and hydrocarbons can be partly explained by the low

fluidization velocity used in these tests (2.5 times the minimum fluidization velocity) limiting the rate of mixing of fuel particles in the axial direction. This circumstance reduces the presence of devolatilizing particles in the bottom part of the dense bed where the oxygen concentration is higher. However the negligible interaction of light hydrocarbons (and primary tars) with oxygen is not only justified by the segregation on the fuel particles during devolatilization to the top of the dense bed. The oxygen bypassing the dense bed in bubbles is neither converting the hydrocarbons in the top of the dense bed. Hence the lower reactivity of hydrocarbons as compared with other fuel gases (such as CO and $H_2$) (3) is behind the lack of its direct interaction with oxygen.

## 4 CONCLUSIONS

The paper analyzes the influence of temperature (800-900°C) and the stoichiometric ratio (0-0.21) on the composition of light hydrocarbon and tar mixtures during bubbling fluidized-bed gasification of wood pellets. The increase in the reactor temperature affects significantly the light hydrocarbon mixture and, to a lesser extent, the tar composition. However the variation of the stoichiometric ratio has very slight influence over the composition of light hydrocarbons and tars for a given temperature. These results are consequence of the negligible interaction between oxygen and the hydrocarbons formed during devolatilization. The origin of this limited interaction is the natural tendency of devolatilizing particles to float on the bed surface, where the oxygen concentration is very limited, together with the lower reactivity of hydrocarbons as compared with CO and $H_2$.

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## 6 ACKNOWLEDGEMENTS