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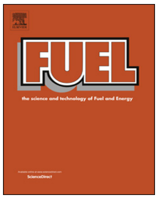

Full Length Article

The influence of volatiles to carrier gas ratio on gas and tar yields during fluidized bed pyrolysis tests

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ABSTRACT

The formation of tar and light hydrocarbons during pyrolysis of pruning waste pellets in a fluidized bed (FB) reactor was experimentally studied as a function of temperature (700–900 °C), gas residence time (0.8–2.0 s) and volatiles to carrier gas ratio (13/87–42/58 vol%). The latter is defined as the ratio between the volume flowrates of volatiles released from the fuel particle at a given instant and that of the carrier gas used for the experiment at the same instant, and it quantifies the concentration of volatiles in the bulk gas. Experiments were conducted to analyze separately the effect of each of these three parameters on the yield of the different pyrolysis products. Special attention was paid to study the influence of the concentration of volatiles in the gas (controlled by changing the carrier gas/fuel ratio), since this parameter has been usually neglected in lab-scale kinetics studies up to now. The yields of the main light gases CO, CO_2, H_2, C1-C3 hydrocarbons as well as 41 tar compounds, grouped in five families, are reported. The increase in the reactor temperature strongly influenced the composition of the gas, reducing the yield of light hydrocarbons, and aliphatic and heteroatomic tars, and increasing the yield of CO, H_2, benzene and polyaromatic hydrocarbons (PAH). The variation of the gas residence time between 0.8 and 2.0 s showed only slight influence on the yields of pyrolysis products. Remarkably, the increase in the concentration of volatiles from 13 to 27 (vol%) was seen to significantly affect the composition of the tar mixture, leading to higher yield of PAH while the yields of monoaromatic hydrocarbons decreased. This result highlights the significance of the concentration of volatiles during the study of the evolution of pyrolysis products.

1. Introduction

There is a global need for reducing the effects of global warming caused by the emission of greenhouse gasses. In this scenario, the main challenge is to reduce the dependency on fossil fuels for energy production. Waste derived fuels such as dried sewage sludge, municipal solid wastes or agricultural residues have the potential to replace conventional fossil fuels for power production. Several waste-to-energy processes, from conventional boilers to pyrolysis and gasification processes have been developed to improve the environmental performance of waste conversion [1]. Gasification technology has some advantages over direct combustion for the treatment of waste [2,3], but the presence of tar in the gas limits its direct use to applications where the gas is not cooled. Increasing tar conversion within the gasifier (primary tar conversion) reduces the need for intensive secondary treatment before burning the gas in an engine, improving the efficiency and economy of the process [4].

The influence of operational parameters on tar yield and composition needs to be considered during optimization of existing gasifiers as well as for the development of new systems. In recent years, several models have been published analyzing the homogeneous conversion of tar during biomass gasification/pyrolysis in different type of reactors, such as dual fluidized bed (FB) [5], conventional bubbling FB [6,7], tubular/drop-tube reactors [8] and circulating FB [9]. Different degrees of complexity have been applied to deal with the inherent complexity of the tar mixture containing hundreds of different compounds. Simplified reaction schemes using model compounds representing different tar families are usually assumed, while the kinetics and stoichiometry of the reactions are taken from literature data or obtained by dedicated experiments. In order to improve the prediction capability of existing models, tar and hydrocarbon reaction pathways have to be carefully studied in different conditions.

The composition of the gas produced during FB gasification and pyrolysis depends mainly on temperature and gas residence time in the reactor. Other variables influencing the gas composition are: the presence of catalysts in the reactor [10,11], the staging of the oxidant [12,13], the composition of the fluidization agent [14], the reactor throughput [15] and the fuel particle size [16].

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The influence of temperature on the composition of pyrolysis and gasification products has been widely studied during the last decades [17]. At temperatures below 700 °C, the tar and hydrocarbons in the gas mixture are the result of fragments from the parent fuel, having a high proportion of oxygen in their chemical structure. Between 700 °C and 900 °C, unsaturated hydrocarbons with 2–4 carbon atoms and aromatic compounds are the most abundant compounds, while above 900 °C soot is extensively formed from tars and hydrocarbons.

There are a few studies analyzing the influence of the gas residence time on tar composition [16,18–20]. Two approaches have been applied to study the influence of gas residence time on pyrolysis products. In the first approach, the location of the sampling point is changed along the reactor, keeping the operating conditions constant [16,20], whereas in the second approach, the flowrate of carrier gas is adjusted [18,19]. The latter is usually preferred because is simpler to implement and operate, but the concentration of pyrolysis products (volatiles) in the gas is changed together with the residence time, making it difficult to separate the individual effects of the two variables.

A common and simple experimental procedure to study pyrolysis/devolatilization products is to add a batch of fuel into the preheated reactor where a carrier gas is flowing continuously, and analyze the produced gas, tar and char fractions. In fluidized bed reactors operating at temperatures between 700 °C and 900 °C, the fuel devolatilization is almost complete after 40–80 s when coarse (mm-sized) particles are used [21]. However, since the release rate of volatiles changes with time during a batch test, so does the concentration of pyrolysis products in the gas. An alternative way to reproduce the conditions of the gas phase in industrial reactors (usually working under steady state flow, where the volatiles concentration is not time-dependent) is to feed both the fuel and the fluidizing gas continuously. However, even in this mode of operation, the conditions in the gas phase may not represent the situation in a large-scale reactor if the share of fuel to carrier gas is not the same in both devices: an excessive dilution of the gas phase with carrier gas or a slow fuel feeding rate (slower than the time necessary for the complete devolatilization of the fuel) could produce too diluted or time-dependent concentrations of volatiles.

During homogeneous tar conversion, various types of bimolecular reactions between light hydrocarbons and tar compounds occur [22,23]. The rate of bimolecular reactions, such as the Diels-Alder reactions or the HACA mechanism for PAH growth, are influenced by the concentration of the species involved in the reactions [24], so that the influence of this parameter should be known to model or reproduce the tar conversion in a FB gasifier (FBG). In spite of this, the effect of the concentration of gaseous species in the gas on tar and gas composition has often been neglected in experimental kinetic works.

Table 1 shows the gas composition in an air-blown FBG operating at temperatures between 750 and 950 °C with stoichiometric ratios (ratio of actual and stoichiometric oxygen flow) from 0.23 to 0.29 [25]. In these conditions the concentration of the measured hydrocarbons, including tars, is above 5 vol% while nitrogen is below 55 vol%. However, in different studies analyzing the conversion of tars and hydrocarbons at high temperature (with continuous fuel feeding), the amount of carrier gas exceeds the nitrogen concentration in conventional gasifiers. For instance, a nitrogen concentration in the gas higher than 85 vol% was used in [26] to study the homogeneous tar conversion during the pyrolysis of wood chips, and higher than 90 vol% in [27,28] to study the tar formation during wood pyrolysis and gasification.

Table 2
Ultimate and proximate analysis of the fuel (pruning waste pellets).

Proximate analysis		Analysis method
Moisture (wt% as received)	8.11	CEN/TS 14774-1
Ash (wt% dry basis)	4.95	CEN/TS 14775
Volatiles (wt% dry basis)	78.76	CEN/TS 15148
Fixed C (wt% dry basis)*	16.29	
Ultimate analysis		
C (wt% dry basis)	47.22	CEN/TS 11510
H (wt% dry basis)	6.36	CEN/TS 11510
N (wt% dry basis)	0.99	CEN/TS 11510
S (wt% dry basis)	0.06	ASTM D4239
O (wt% dry basis)*	40.42	

* By difference.

This paper aims at studying the influence of temperature, residence time and volatiles/carrier gas ratio, on tar and light hydrocarbon composition formed during the pyrolysis of pruning waste pellets in a FB reactor. Special attention is paid to determining the effect of the volatiles/carrier gas ratio (VCR). This parameter is usually neglected in the literature although its influence on the rate of tar and hydrocarbons reactions is recognized. The experimental conditions have been designed to modify each parameter independently. The parameters studied were adjusted to represent the experimental conditions in FBG [4]: the temperature was varied between 700 °C and 900 °C, the residence time of the gas between 0.8 and 2 s and the volatiles concentration in the gas between 13 and 42 vol%.

2. Experimental

2.1. Fuel

The fuel used was cylindrical pellets of biomass with a diameter of 6 mm and length between 5 mm and 15 mm. The fuel pellets were prepared with olive tree pruning using both branches and leaves. The resulting apparent density of the pellets was 1050 kg/m^3. Table 2 shows the ultimate and proximate analysis of the pellets used.

Table 1
Gas composition in a conventional FBG processing willow at different operation conditions [22].

Operating conditions					
ER	0.23	0.24	0.26	0.27	0.29
Bed temperature (°C)	759	807	854	906	955
Gas residence time (s)*	5.4	5.4	5.4	5.4	5.4
Gas composition					
CO (vol%)	16.5	16.3	15.2	16.0	17.0
H_2 (vol%)	6.9	8.0	10.4	11.4	12.3
CO_2 (vol%)	16.2	16.3	16.6	15.8	14.8
CH_4 (vol%)	4.9	4.8	4.5	4.1	3.8
C_2H_4 (vol%)	1.7	1.9	1.7	1.3	0.7
N_2 (vol%)	55	54	53	53	53
C_6H_6 (g/Nm^3) – (vol%**)	6.9 – 0.2	9.0 – 0.3	10.9 – 0.3	12.3 – 0.4	12.3 – 0.4
Total tar (g/Nm^3) – (vol%***)	54 – 0.9	26 – 0.4	20 – 0.3	14 – 0.2	12 – 0.2

* Aprox. Based on the position of the sampling port.

** Assuming ideal gas.

*** Assuming ideal gas and average molecular weight of 128.