

Biomass Gasification Between 800 and 1,400 °C in the Presence of O₂: Drop Tube Reactor Experiments and Simulation

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Beech sawdust particle conversion in a drop tube furnace was studied between 800 and 1,400 °C. Particular attention was paid to the influence of temperature and to the presence of oxygen on the gasification process. As temperature increases, light hydrocarbon production decreases and the CO + H₂ production (gas of interest for biofuel production) increases. Presence of oxygen in the gasification atmosphere allows consuming a high part of light hydrocarbons and enhancing carbon conversion into gas. However, high yields of CO₂ and H₂O were observed and the total yield of CO + H₂ was lower than in pyrolysis conditions.

1. Introduction

Biomass gasification is generally considered as one of the most promising alternative way of energy production for electricity, heat and transport. To produce biofuels from syngas, Entrained Flow Reactor (EFR) is known as one of the most suitable reactor. The main advantage of this technology is the high conversion of biomass into syngas with very low tar contents. Currently, only coal gasification is available at commercial scale and biomass gasification using this technology is not achieved.

EFR is characterized by high operating temperature (~1,500 °C), high pressure (>30 bar), short particle residence time (~5 s) and high heat flux at particle surface (>1 GW.m⁻²). It is generally operated as an autothermal reactor which means that a part of biomass is burnt to supply enough energy for gasification reactions. Biomass particles have to be small (~300 μm) to avoid transfer limitations in the particle and therefore to maximize the gasification rate.

The phenomenology linked to biomass conversion in conditions similar to those of an EFR has rarely been studied until now. The experimental device usually used to reproduce some conditions of an EFR is the Drop Tube Reactor (DTR). Some works deal with experimental biomass gasification studies in a DTR at temperature above 1,000 °C. Fast pyrolysis of biomass in inert atmosphere has been studied by Zhang et al. (2006) and Septien et al. (2012). Other studies deal with gasification with the addition of H₂O (Septien et al. (2013), Zhang et al. (2010)), of O₂ (Zhang et al. (2010), Zhou et al. (2009)) or a mixture of O₂ and H₂O (Qin et al. (2012)).

The present study aims to investigate the influence of the presence of O₂ in the atmosphere on biomass gasification in an EFR. Preliminary calculations were made to estimate an appropriate range of experimental conditions. The experiments were conducted in a DTR with beech wood particles of 315 to 450 μm.

2. Preliminary calculations

As said before, biomass gasification process using EFR need to be developed. Indeed some pilot scale EFR using biomass as feedstock already exist (Weiland et al. (2013)) but no industrial plant based on this

technology is working yet. It implies a lack of knowledge of actual operating conditions in this type of reactor.

To choose relevant experimental conditions for our experimental study, an EFR was modelled (Figure 1) with some design choices and assumptions.

In the pressurized biomass feeding line, the biomass volume concentration was considered to be 20 v%. Heat losses were estimated at $100 \text{ kW}\cdot\text{m}^{-2}$ of intern surface. Thermodynamic equilibrium at the output of the reactor (Gibbs Energy minimization) was assumed.

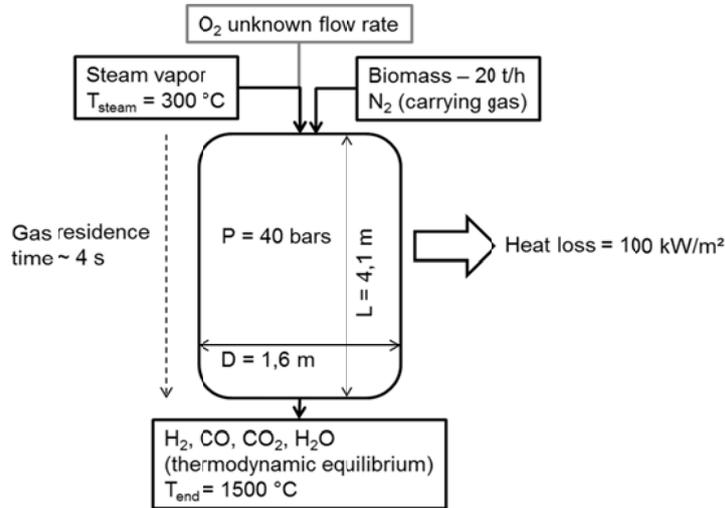


Figure 1: Scheme of the modelled EFR

From these data and assumptions, an energy balance was calculated on the reactor to evaluate the needed oxygen flow rate for different steam inlet flow rates. Results are given in Table 1. The $\text{H}_2\text{O}/\text{C}$ ratio is defined as the whole mass of water injected (steam and moisture) on the mass of carbon contained in the injected biomass.

The cold gas efficiency is defined by Eq (1).

$$\eta = \frac{Q_{\text{products}} \text{LHV}_{\text{products}}}{Q_{\text{biomass}} \text{LHV}_{\text{biomass}}} \quad (1)$$

Where Q_i is the mass flow rate and LHV_i is the Lower Heating Value.

Table 1: Results of preliminary calculations

	H₂O/C	0.14	0.5	1
Input data	O ₂ /Biomass (g/g)	0.57	0.62	0.68
	P _{N₂} (bar)	14.4	9.1	6.0
	P _{steam} (bar)	0	13.4	21.2
	P _{O₂} (bar)	25.6	17.5	12.8
Output data	Product Gas LHV (MJ/kg db)	12.7	11.9	10.7
	H ₂ /CO (mol/mol)	0.50	0.62	0.76
	Cold gas efficiency	0.71	0.66	0.59

These calculations show that the cold gas efficiency increases as $\text{H}_2\text{O}/\text{C}$ ratio decreases. Experimental conditions were then chosen as the ones corresponding to the lower $\text{H}_2\text{O}/\text{C}$ ratio.

3. Experimental

3.1 Biomass characteristics

Biomass used as feedstock in this study is beech sawdust. Particles were sieved in a size range of 315 to 450 μm . The proximate analysis and the ultimate analysis of this biomass are shown in Table 2.

Table 2: Proximate and ultimate analysis of beech sawdust

Proximate analysis		Ultimate analysis (wt% dry ash free basis)	
Moisture (wt%)	9.8	C	50
Volatile matter (wt% dry basis)	85	H	5.8
Fixed carbon ^b (wt% dry basis)	14.2	N	<0.3
Ash (wt% dry basis)	0.8	S	0.014
		O ^b	44

^b by difference

3.2 Description of the drop tube reactor

The drop tube reactor (DTR) is represented in Figure 2. It consists of an alumina tube inserted in a vertical electrical heater with three independent heating zones. The dimensions of the tube are 2.3 m in length and 0.075 m in internal diameter. The heated zone is 1.2 m long. The DTR works at atmospheric pressure and can reach a maximum temperature of 1,400 °C.

The wood particles are continuously fed into the reactor using a gravimetric feeding system. The main gas stream, which can be N₂ or a mixture of N₂, air and/or H₂O, is electrically pre-heated before entering the reactor.

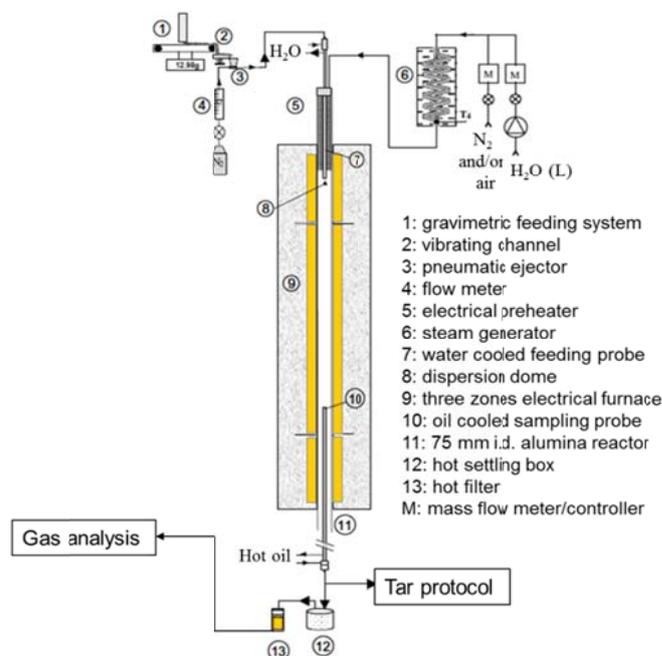


Figure 2: Scheme of the drop tube reactor

An oil-cooled (110 °C) sampling probe can be inserted at different heights in the bottom half of the reactor to collect gas and the remaining solid. A fraction of the exhaust gas is sucked in the sampling probe. One part passes through a settling box and a filter and flows to gas analyzers and another part passes through the tar protocol. This part of the experimental facility is heated (150 °C) to avoid steam and tar condensation.

3.3 Gas analysis

A micro-gas chromatograph (μ -GC) allows analyzing main gaseous products (CO₂, CO, CH₄, N₂, H₂, C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₆H₆). A Flame Ionization Detector (FID) gives the total hydrocarbons content of the gas. H₂O content in the gas was measured by a psychrometer.

3.4 Conditions of the experiments

In this study, experiments were performed in a nitrogen inert atmosphere and an oxygen containing atmosphere at several temperatures, 800 °C, 1,000 °C, 1,200 °C and 1,400 °C. Conditions of experiments with oxygen were deduced from preliminary calculations for an EFR (Table 1). The O₂/biomass ratio was kept constant and equal to 0.42 (g/g, db). Gas sampling was performed at the bottom of the heated zone

and the gas residence time was kept constant for each test run (4.3 s). Experimental conditions are given in Table 3. Experiments with oxygen and pyrolysis tests at 800 °C were performed twice.

Table 3: Operating conditions of experiments

Pyrolysis experiments				
Temperature (°C)	Biomass feedstock rate (g.min ⁻¹)	Air flow rate (NL.min ⁻¹)	N ₂ flow rate (NL.min ⁻¹)	O ₂ partial pressure (bar)
800	1.3	0	18.8	0
1,000	1.3	0	15.9	0
1,200	0.65	0	13.7	0
1,400	0.65	0	12.1	0
Partial oxidation experiments				
Temperature (°C)	Biomass feedstock rate (g.min ⁻¹)	Air flow rate (NL.min ⁻¹)	N ₂ flow rate (NL.min ⁻¹)	O ₂ partial pressure (bar)
800	1.3	1.8	17.1	0.020
1,000	1.3	1.8	14.1	0.023
1,200	1.3	1.8	12.0	0.027
1,400	1.3	1.8	10.3	0.030

This DTR is designed for small biomass feeding rates and for working in diluted conditions. Although the O₂ partial pressure is much lower (0.02-0.03 bar) than in an EFR (Table 1), the O₂/biomass mass ratio was chosen to be representative of an EFR in order to have similar behaviour for gas phase reactions.

4. Results and discussion

4.1 Gas yields

Individual gas yields are given in Figure 3 (H₂, CO, H₂O, CO₂) and Figure 4 (CH₄, C₂H₂, C₂H₄, C₆H₆).

In pyrolysis experiments, H₂, CO, H₂O, CO₂ and CH₄ are the major gas species, followed by C₂H₂, C₂H₄, C₂H₆, C₃H₈ and C₆H₆. H₂ and CO yields increase with temperature, while H₂O, CH₄ and C₂H₄ yields decrease. CO₂ yield slightly increases with temperature until 1200 °C and then decreases. C₂H₂ and C₆H₆ yields reach a maximum at about 1,000 °C. C₂H₆ and C₃H₈ yields can only be quantified at 800 °C in pyrolysis conditions – 12.10⁻⁵ and 9.10⁻⁵ (mol.g⁻¹, db) respectively.

The water gas shift equilibrium can partly explain evolutions of CO, CO₂, H₂ and H₂O yields (from 800 °C to 1,400 °C, K_{shift}/ K_{shift-eq} passes from 0.06 to 1.2 in pyrolysis conditions and from 0.08 to 1.3 in presence of oxygen). The tendencies observed for C₂H₄, C₂H₆, C₃H₈ and CH₄ yields can be explained by cracking and reforming reactions which are enhanced by high temperature. C₂H₂ and C₆H₆ yields show a different evolution with temperature. The presence of a maximum can be explained by two different and competitive phenomena (Roth, 2006). First, C₂H₂ is mostly produced by thermal degradation of light hydrocarbons and C₆H₆ can be produced by polymerization of C₂H₂. On the opposite, C₂H₂ and C₆H₆ are two important precursors of soot production which occurs from 900 °C and reach a maximum at about 1,400 °C.

In the presence of O₂, gas species yields evolutions versus temperature are approximately the same as in the pyrolysis tests. Three major differences are noticed. First, H₂, C₂H₂, C₂H₄, C₂H₆, C₃H₈ and C₆H₆ are lower in presence of O₂ than in pyrolysis conditions. It can be explained by combustion reactions which compete with the other reactions of production or consumption of these products. Secondly, CO₂ and H₂O yields are higher in presence of O₂ than in pyrolysis conditions. Combustion reactions are also responsible for this result. The third difference concerns the evolution of CO and CO₂ yields versus temperature. CO yield reaches a minimum and CO₂ yield reaches a maximum at about 1,000 °C. This behaviour is not easy to understand and no explanation can be given for the moment.

4.2 Carbon conversion

Other products of pyrolysis and partial oxidation of biomass are char, tars (condensable species) and soot. In order to estimate these products, balances on carbon detected in gas phase are given in Table 5. During experiments char and soot were sampled. Char could be sampled in all experimental conditions although soot production was detected only from 1,000 °C with few soot particles. Above 1,000 °C soot was produced in higher amount in pyrolysis case and also in presence of oxygen. Carbon conversion into gas is shown in Figure 5 as a function of temperature. It is higher in presence of oxygen than in an inert atmosphere. Char and/or tar combustion could explain this observation. Production of soot could explain the decrease of carbon conversion in gas phase as temperature increases in the presence of O₂.

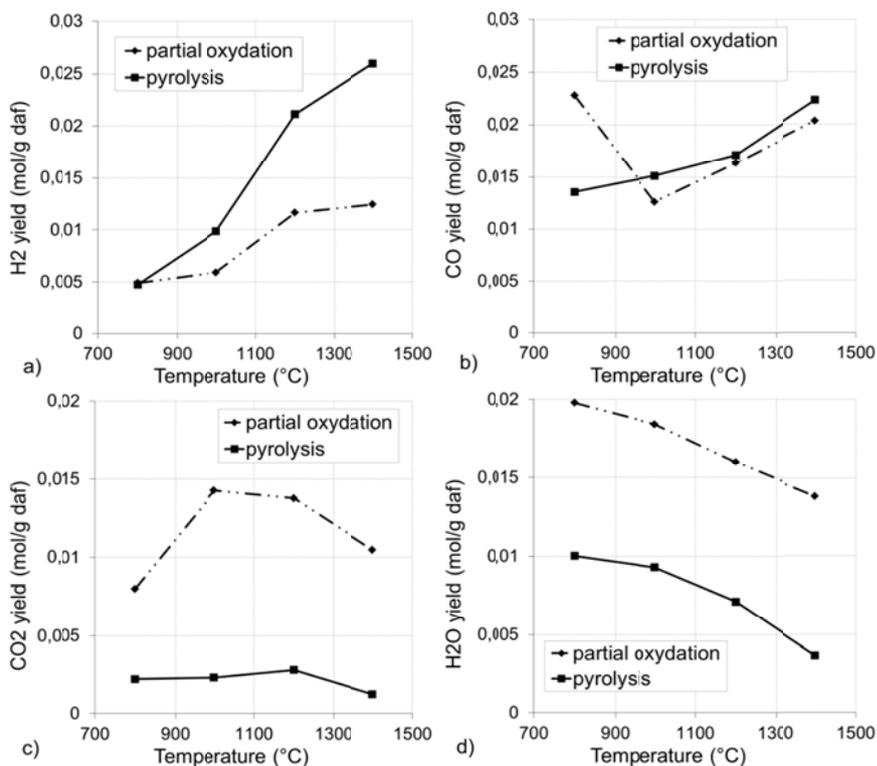


Figure 3: Experimental yields of H₂ (a), CO (b), CO₂ (c) and H₂O (d) in pyrolysis conditions and in presence of oxygen

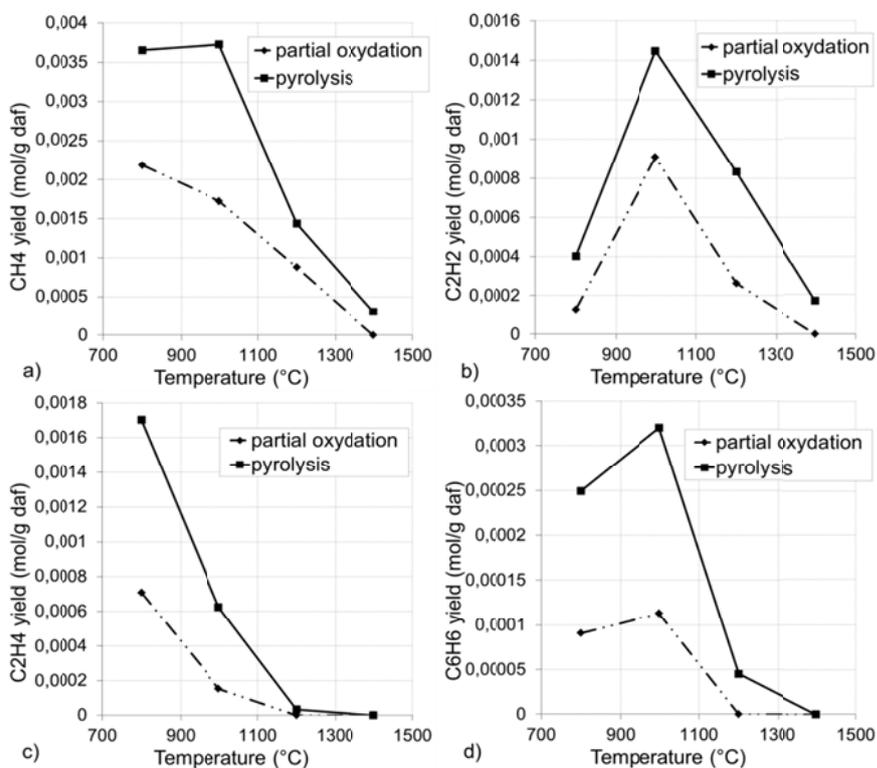


Figure 4: Experimental yields of CH₄ (a), C₂H₂ (b), C₂H₄ (c) and C₆H₆ (d) in pyrolysis conditions and in presence of oxygen

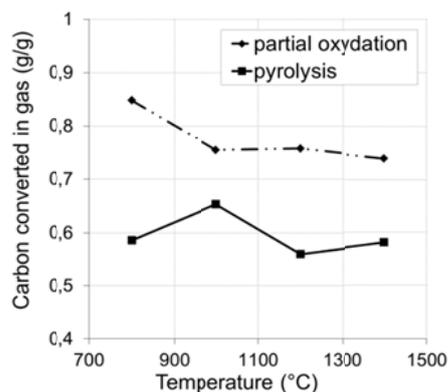


Figure 5: Part of carbon initially in biomass converted in gas (incondensable species)

5. Conclusion and prospects

Fast pyrolysis and partial oxidation of beech sawdust were experimentally investigated in a DTR focusing on the effect of temperature on biomass conversion and gas production. Temperature has an important influence on the carbon conversion and the gas phase composition. As temperature increases, light hydrocarbon production decreases and the CO + H₂ production (gas of interest for biofuel production) increases. Presence of oxygen in the gasification atmosphere allows consuming a high part of light hydrocarbons and enhancing gas carbon conversion into gas. However, high yields of CO₂ and H₂O were observed and the total yield of CO + H₂ was lower than in pyrolysis conditions.

This study will be completed by tar and char analyses and quantification which will allow specifying elemental balances. Other experiments will be conducted in presence of oxygen and steam to investigate the influence of steam on biomass conversion and gas phase reactions. The experiments will be simulated with the GASPARD modelling tool (Septien et al., 2013), which includes models for biomass pyrolysis, char gasification, gas phase reactions and soot production in our DTR. The model will be improved to predict accurately biomass gasification in presence of O₂. This will allow better understanding of phenomena involved in biomass gasification.

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