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Impact of torrefaction on syngas production from wood

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A B S T R A C T

Torrefaction is a way to treat biomass before transportation or thermochemical conversion. It can be used to increase the energy content of wood or to facilitate grinding. The purpose of this paper was to quantify the impact of such a treatment on the behaviour of wood during gasification by steam at high temperature to produce syngas. The aspects of both gas yields and reaction kinetics were considered.

Beechwood was submitted both to light torrefaction and severe torrefaction, using a specially designed crossed fixed bed reactor. The initial wood and the torrefied woods were first characterised, then gasified in a new laboratory high-temperature entrained flow reactor (HT-EFR) at 1400 °C for 2 s in an atmosphere containing 20 vol% steam in N₂. The syngas produced was then analysed. The experiments were modelled using a thermo-dynamical equilibrium approach.

It was confirmed that torrefaction decreased the O/C ratio. The quantity of syngas produced increased with the severity of the torrefaction. The equilibrium approach describes the results satisfactorily.

Gasification experiments carried out at a lower temperature – 1200 °C – indicated that the chars from torrefied woods are less reactive towards steam than the char from wood.

Keywords:

Torrefaction

Gasification

Wood

Gas yields

Reaction kinetics

1. Introduction

Thermo-chemical conversion of biomass is a means to produce energy and to reduce greenhouse gases. Rapid gasification of biomass at high temperature is one of the most promising technologies for the production of syngas. It can be achieved in several seconds in an entrained flow reactor. At high temperature (1400 °C), it is possible to obtain a syngas (CO, H₂ and CO₂) containing very small amounts of residual hydrocarbons and solid carbon (char). Heat and mass transfers are very effective in this kind of reactor, but the biomass must be dried and ground to particles measuring several hundreds of micrometers prior to injection. These preliminary steps, especially grinding, consume large amounts of energy and represent obstacles that need to be overcome in order to expand the use of biomass in thermochemical processes.

Torrefaction is a technology which allows moisture and low weight organic volatile components of biomass to be removed, producing a hydrophobic solid product with an increased energy density (on a mass basis) and greatly increased grindability [1–5]. Electricity requirements for size reduction of torrefied wood are 50–85% smaller in comparison with fresh wood [6,7].

To reduce solid mechanical properties, torrefaction is generally achieved in the temperature range of 220–300 °C, under an inert atmosphere. It forms three phases: a solid product of a dark colour,

an acidic aqueous phase and permanent gases such as CO and CO₂ [2,8], typically 20% of CO and 80% of CO₂ [9].

The kinetics of torrefaction reactions in the temperature range of 230–300 °C can be described accurately by a two-step mechanism. The first step is representative of hemicellulose decomposition, while the second step represents cellulose decomposition [10]. At temperatures above 300–320 °C, fast thermal cracking of cellulose may cause tar formation, so operation below 300 °C is recommended.

Despite torrefaction is an energy consuming treatment, several works can be found on the advantages – in terms of the energy efficiency of a process – of torrefaction as a pre-treatment prior to gasification [9]. The concept of torrefaction – aided gasification is similar to two-stage pyrolysis-gasification but the advantage is that the heat requirements for torrefaction are smaller than those for pyrolysis at higher temperatures [9].

Some studies on torrefied wood reactivity have been realised under air in TGA or thanks to a burner [2,3]. However, studies carried out on gasification concern only raw biomass [11,12]. To our knowledge, no works can be found on the impact of torrefaction on the behaviour of wood during gasification by steam at high temperature in an entrained flow reactor, neither in terms of syngas quantities and composition, nor in terms of solid gasification kinetics.

In this paper, gas yields and reaction kinetics obtained during gasification of torrefied woods were studied. Beechwood was submitted to light torrefaction (240 °C) and severe torrefaction

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(260 °C), using a specially designed crossed fixed bed reactor. After characterisation, initial wood and torrefied woods were gasified in a new high-temperature entrained flow reactor at 1400 °C and 1200 °C for 2 s in an atmosphere containing 20 vol% steam in N₂. The syngas produced was analysed. The experiments conducted at 1400 °C were modelled using a thermodynamical approach. Experiments carried out at 1200 °C gave information on chemical reaction kinetics.

2. Experimental

2.1. Characterisation of beechwood

Beechwood was supplied by Lignex, France, as 50–500 µm particles. They were stored in plastic bags in a dark place at the temperature of the laboratory. The 80–200 µm fraction was selected by sieving prior to any analysis or experiment. The ultimate analysis of the selected particles was compared to that of the supplied sample and did not deviate by more than 0.5%, attesting to a non-selective sampling.

The wood contained 10% moisture. As indicated by ultimate analysis performed on the dry wood, and reported in Table 1, the wood contained 50.3% of C, 5.3% of H and 44.4% of O on a dry ash free basis (daf). Proximate analysis performed on dry wood indicated a quantity of volatile matter of 84.2% and 0.3% of ash, resulting in a fixed carbon amount of 15.5%.

2.2. Torrefaction reactor and operating conditions

Wood particle torrefaction was carried out in a specially designed reactor enabling accurate control of the temperature inside the sample body and rapid removal of the product gas. As illustrated in Fig. 1, the reactor consisted of a 60 mm i.d. quartz tube in which 25 g of wood particles were deposited on a ceramic wood layer. The reactor was surrounded by a 2 kW electrical furnace. The inert atmosphere gas, N₂, was fed from the bottom at a flowrate of 0.3 l min⁻¹ at STP, heated along the lower part of the reactor and crossing the sample bed. It was expected that this method would ensure a good thermal contact between gas and all particles, while taking the gas products of torrefaction away from the bed (at a Darcy velocity of 0.0034 m s⁻¹ at 250 °C). At the top of the reactor, a ceramic wool swab prevented air from entering the reactor by natural convection effects. The gas temperature upstream of the sample was recorded.

Particles were deposited in the cold reactor. The inert gas flow was started and maintained. The reactor was then heated to the stage temperature, following a ramp at 10 K min⁻¹. The temperature was maintained for 1 h alternatively at 240 °C and 260 °C; natural cooling was then allowed to occur.

When collecting the torrefied samples from the reactor, a uniform colour was observed inside the sample body – which was darker than the initial wood – attesting to a uniform torrefaction progression. Indeed, other tests performed even on much smaller samples but without inert gas circulation resulted in clearly non-uniform conversion inside the sample body.

1: reactor; 2: furnace; 3: thermocouple; 4: ceramic wool; 5: wood

Fig. 1. Torrefaction reactor.

2.3. Gasification reactor and operating conditions

The gasification of wood and torrefied woods was carried out in a High Temperature Entrained Flow Reactor (HT-EFR) specifically set up to achieve high heating-rate wood gasification. This HT-EFR is electrically heated by a 18 kW three-zone electrical furnace, and is able to reach 1600 °C in a 1 m long isothermal reaction zone. As illustrated in Fig. 2, wood particles were fed at a very constant mass flowrate of 0.5 g min⁻¹ thanks to a new in-house-designed gravimetric feeding system, and continuously injected in the reactor through a hot-oil cooled feeding probe. They were uniformly dispersed on the section of a 75 mm i.d. alumina reactor swept by 22.4 l min⁻¹ at STP of an atmosphere gas containing 20 vol% of steam in N₂. With such solid and gas flow rates, steam is present in largely stoichiometric conditions. Atmosphere gas was generated by feeding the controlled flows of water and nitrogen in a 2 kW electrical steam generator. This atmosphere gas was then preheated using a 2.5 kW electrical battery of heating elements before reaching the 1 m long isothermal reaction zone, itself heated by the electrical furnace. Gasification took place in the reactor during a controlled residence time (typically several seconds). At 1760 mm downstream of the injection point, gases and particles were sampled by a hot-oil cooled probe, and separated using a settling box and a filter, both heated to avoid water condensation. The water was first condensed in a heat exchanger, and non-condensable gases were forwarded to:

- a non dispersive IR analyser and FTIR analyser to quantify CO, CO₂, CH₄, C₂H₂ and C₂H₄,
- a TCD to quantify H₂.

Table 1
Ultimate analysis and proximate analysis of wood and torrefied woods.

	Ultimate analysis (daf mass %)					Proximate analysis (dry mass %)		
	C	H	N	S	O	Ash	Volatile matters	Fixed carbon
Beechwood	50.3	5.3	0	0	44.4	0.3	84.2	15.5
Torrefied beechwood 240 °C	51.7	5.4	0	0	42.9	0.35	80.6	19.2
Torrefied beechwood 260 °C	54.4	5.2	0	0	40.4	0.4	75.7	24.2

Fig. 2. Gasification reactor.

During experiments, the atmosphere gas and the reactor walls were heated to 1200 °C or 1400 °C. Measurements of the gas phase temperature inside the reactor indicated temperatures close to those of the reactor walls, with a difference always lower than 30 °C.

3. Results

3.1. Characterization of torrefied woods

Wood was dried overnight at 105 °C, and then torrefied. After torrefaction at 240 °C and 260 °C, the observed mass losses were 11.5% and 21.0%, respectively of the mass of dry wood. The experiments were repeated and the results deviated by less than 1%. These results are in agreement with the literature [2,8–10]. But it is interesting to note that the composition of biomass fuels has a significant impact on the amount of solid residue after torrefaction [2].

As illustrated in Fig. 3, the torrefied wood showed darker brown colours than the initial wood, tending towards black after severe

Fig. 3. Photography of particles of beechwood (a), torrefied beechwood at 240 °C (b) and torrefied beechwood at 260 °C (c).

torrefaction. After the two treatments, the wood particles – observed with an optical microscope – preserved their external shape aspect.

The volatile matter content decreased from 84.2% for wood down to 80.6% and 75.7% for the torrefied woods (Table 1). This is in agreement with the results of Bridgeman et al. who showed that the trend is towards a reduction in volatile matter and an increase in fixed carbon and ash content [2]. From the ultimate analysis also reported in Table 1, it can be seen that the O content decreased from 44.4% for wood down to 42.9% and 40.4% for the torrefied woods, which represents a decrease of 3.4% and 9.0% after torrefaction at 240 °C and 260 °C respectively. In terms of the O/C ratio, the value decreased from 0.88 for wood down to 0.83 and 0.74 for the torrefied woods; which is in agreement with the literature [2,8,9].

These results attest that torrefaction is a way to increase the energy density of the wood by removing oxygen. This is confirmed by the LCV of the products that were measured in a IKA C5000 bomb calorimeter: 19532 kJ kg⁻¹ and 20742 kJ kg⁻¹ for the torrefied wood at 240 °C and the torrefied wood at 260 °C, respectively, to be compared with 17782 kJ kg⁻¹ for the initial wood, i.e. an increase of 17% (in the case of torrefied wood at 260 °C). Prins et al. showed that the energy density increases with torrefaction temperature and found an increase of 20% at a torrefaction temperature of 280 °C [8].

3.2. Gasification experiments and results

3.2.1. Gasification experiments and modelling at 1400 °C

The two torrefied woods – and the initial wood as a reference – were gasified at a temperature enabling a nearly complete conversion to H₂, CO and CO₂: 1400 °C. This value was retained from previous experiments. The gas volume fractions in the flue gas were converted into yields, on a dry ash free (daf) basis, and reported in Fig. 4. Each experiment was repeated two or three times enabling repeatability error bars to be drawn on the graph. The analysis indicates that the gasification was actually complete: the concentration of CH₄ and other hydrocarbons like C₂H₂ and C₂H₄ were inferior to 30 ppm, the detection limit of the analysers. This corresponds to quantities of less than 0.2% of the dry wood. The two torrefied woods produced more H₂ and CO than the parent wood, respectively 7% and 20% more, which was an expected result since their O content was lower than that of wood. CO₂ yields were quite similar for the wood and the torrefied woods.

Fig. 4. Gas yields obtained during gasification of beechwood and torrefied beechwoods at 1400 °C under 20% of steam.

As far as the solid residue is concerned, only grey coloured ash was recovered after gasification, in such small quantities that collecting and weighing them would not have been accurate.

Given the small size of the particles and the high operation temperature, a thermo-dynamical equilibrium type model was selected to describe the previous experiments. The FactSage® software with the “FACT 5.3” data base (4429 species) was used to this purpose. The inputs of the model were:

- the quantities of C, H and O contained in the dried wood as determined from ultimate analysis;
- the quantities of H and O contained by steam and of N in the atmosphere;
- the temperature of gasification;
- the pressure of the reactor (atmospheric).

The results are reported in Fig. 5 together with experimental results. They show that model and experiments are in agreement concerning H₂ and CO₂ yields. The CO yields obtained with the model are higher than those obtained during experiments. This model shows that carbon mass balance is not closed – with an error of 8% – during experiments. This error can be attributed to the sum of uncertainties resulting from ultimate analysis of the woods and of gas sampling and analysis.

As regards CH₄ and hydrocarbon amounts produced, the model predicts no CH₄ no C₂H₄ and no C₂H₂. This is in agreement with the results obtained experimentally.

It can be concluded that the thermo-dynamical equilibrium approach can be retained in such conditions to describe the gas yields from woody and torrefied wood biomass.

Fig. 5. Experimental gas yields and “model” gas yields for gasification at 1400 °C of beechwood and torrefied beechwoods.

Fig. 6. Gas yields obtained during gasification of beechwood and torrefied beechwoods at 1200 °C under 20% of steam.

3.2.2. Gasification experiments at 1200 °C – kinetic aspects

The following section aims at answering a question: does torrefied wood require more severe conditions for gasification to operate? Indeed, the previous experiments of complete gasification did not provide information on this point. The gasification was therefore also operated at a lower temperature, 1200 °C, to compare the gasification progress in the cases of wood and of torrefied woods.

The results reported in Fig. 6 show that gas yields of wood and torrefied woods are quite similar. However, CO and H₂ yields of torrefied woods are slightly higher than those of wood, as was the case with experiments at 1400 °C where equilibrium was reached. It can be noted that CO₂, CO and H₂ yields are lower at 1200 °C than at 1400 °C, showing that gasification is not finished at 1200 °C.

During rapid high temperature pyrolysis of thin wood particles, CH₄ is produced in quantities of about 6% of the dry wood [13–15]. CH₄ is then cracked and reformed by steam and converted to CO and H₂, but this species is the most thermally stable hydrocarbon species and takes the longest time to reform by steam. However, it can be observed in Fig. 6 that the residual amounts of CH₄ are similar after gasification of wood and torrefied woods, which confirms that chemical reaction kinetics in gas phase are quite similar.

As regards the amounts of residual carbon, i.e. carbon that was not gasified into CO and H₂ by steam, the quantities collected were approximately 1.1% of the initial mass of wood and 4.8% of the initial mass of torrefied wood. Sampling of solid residue in the entrained flow reactor was not isokinetic. Therefore, these results are not very accurate but clearly show that more char is collected after gasification of torrefied woods. Moreover, proximate analysis performed on all solid residues showed that the char from wood contained 66% of ash, whereas the chars from torrefied woods contained 26% of ash. Chars from torrefied woods contained more residual carbon, which confirms that they are less reactive than the char from wood. One could think of using the ash tracer method to calculate the conversion progress of char gasification in the two cases of wood and torrefied wood. Nevertheless, the calculation would not be accurate enough, regarding the very low ash content of the parent wood.

4. Conclusions

The gasification for 2 s at 1400 °C of a wood and of its product after torrefaction with two levels of severity indicated that the torrefied woods produce approximately the same quantities of CO₂, 7% more H₂ and 20% more CO than the parent wood. In these conditions where thermo-dynamical equilibrium is reached, this

result is consistent with the increase in the C and H content induced by torrefaction.

From gasification experiments performed at a lower temperature, 1200 °C, it can be stated that the kinetics of gasification in gas phase of torrefied wood is comparable to that of the parent wood. However, the chars from torrefied woods are less reactive towards steam than the char from wood.

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