

Set up of a pilot scale catalytic fluidized bed reactor for Biomass gasification

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The paper deals with the setup of a fluidized bed reactor and its utilization for preliminary experimental tests of biomass gasification. Two different bed materials have been adopted: inert quartzite as reference case, and Ni-alumina catalyst. The gasification tests have been carried out at steady state, under operating conditions typical for gasification as reported in the paper. The gas analyses have been performed with dedicated instrumentation, like continuous analyzers and gas-chromatograph, and adopting a standard protocol for tar sampling and characterization. The influence of the equivalence ratio (Φ) and the steam-fuel ratio (Ψ) on the concentration of stable gases (e.g. H_2 , CO_2 , CO , CH_4 and light hydrocarbons) as well as on the efficiency of tar conversion has been studied. In particular the catalyst enhances the H_2 yield as well as reduces the tar production, whatever Φ and Ψ are.

Keywords: gasification, biomass, fluidized bed, catalysis, hydrogen, tar

1. Introduction

Biomass fuels can easily undergo gasification (Bridgwater, 2003) for producing a syngas to be utilised for power generation or chemicals synthesis thank to their large volatiles content and high char reactivity. Nevertheless, the gasification process still requires research and optimisation in order to limit the presence of undesired species, namely condensable organic compounds (tar) and fine particulate, with a size lower than 1 μm . They are co-produced during the gasification process and exert a detrimental effect on the process efficiency (Ni et al., 2006). In fact, too much tar in the syngas reduces the yield in valuable species, like H_2 , CO and CH_4 . Therefore, the reduction or decomposition of tar is a large obstacle for achieving a reliable biomass gasification process. In this framework, the fluidized bed technology assisted by catalysis is very promising, since it favors a fast heating rate of the biomass particles and provides a good mixing between gas, biomass and catalyst (Kunii and Levenspiel, 1991), both critical factors for increasing the gas yield and cleanness .

A high efficiency in tar removal and hydrocarbon reforming is reported for nickel base artificial catalysts (Han and Kim, 2008). Commercial available catalysts are not suitable for fluidized beds, where the attrition phenomena are relevant (Magrini-Bair et al.,

2007). The development of a suitable artificial catalyst for fluidized bed application has been reported by Miccio et al. (2008). That catalyst was proven to be enough resistant with respect to fragmentation and abrasion phenomena inside the bed as well as effective in both steam reforming of light hydrocarbons and tar reduction. Furthermore, a stable activity of the catalyst was noted over several hours of operation.

The present paper reports on the setup and the experimental procedure of a fluidized bed reactor that can accomplish gasification and pyrolysis tests of various solid fuels at different operating conditions. A comparison of experimental results in terms of stable gas concentrations, tar yield and tar composition is proposed for beds of inert quartzite sand and Ni-catalyst at different equivalence ratios (Φ) and steam-fuel ratios (Ψ).

2. Experimental

2.1 Experimental facility

The scheme of the gasification facility is drawn in figure 1.

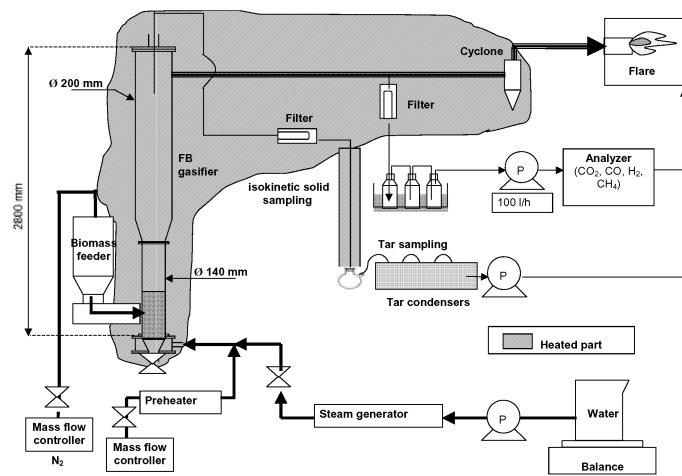


Figure 1: experimental apparatus used for gasification tests

The fluidized bed reactor is formed by two vertical stainless steel tubes having different size and connected by means of a conical adapter. The lower tube has an internal diameter of 140 mm and a height of 1010 mm whereas the upper tube is 200 mm ID and 1800 mm high. The gas distributor at the bottom of the fluidizing column has a conical shape and a total volume of around one liter. The gas passes through 72 holes, 1.5 mm ID that are arranged in 6 regular rows along the conical surface. The fuel is under-bed fed into the reactor by means of a screw conveyor, 130 mm above the conical distributor. The fuel flow rate is regulated by means of an additional screw feeder, rotating at changeable rate and directly connected to a sealed fuel hopper. A flare equipped with a LPG pilot flame burns the syngas coming from the gasifier upstream the chimney. Distilled water is fed by means of a peristaltic pump with adjustable rate (0-1.8 L/h) to an electric tubular steam generator in order to produce steam at moderate gauge pressure (10 kPa) and temperature up to 400 °C. The steam directly enters the wind box

of the gas distributor where it is mixed with the air flow, preheated up to 600°C. An auxiliary nitrogen stream is used for inertising the fuel feeding devices and enters into the gasifier together with the fuel.

The gasification products are isokinetically sampled from the reactor at an elevation of 1800 mm from the gas distributor by means of a coaxial vertical tube 15mm ID. They are passed through a hot ceramic filter with a 200 nm nominal capture efficiency, to remove solid particles and in sequence through a condenser system to trap tars and water. The tube and the filter are kept at 450°C by means of heating tapes from the sampling point to the condenser. A high precision pump (Zambelli mod. Digit-ISO) is used for the suction of the sampled gas, aerosol and solid.

The concentration of permanent gases is measured on-line by means of continuous analyzers for H₂, CO, CO₂, CH₄. Gaseous samples are also taken in 3L bags and off-line subjected to a gas chromatograph FID analysis for determination of major hydrocarbon species.

2.2 Materials.

Spruce wood pellets have been used as fuel, whose properties are reported in Table 1. Quartzite sand and the nickel based catalyst prepared and characterized as reported in Miccio et al (2008) have been employed as bed materials. Their properties are also reported in Table 1.

Table 1: properties of bed materials and biomass fuel.

Fuel	Spruce-wood pellet	Bed Material	quartzite	catalyst
Dimension of biomass particles, mm	6x20	Density, kg/m ³	2600	1800
Moisture, % by mass	8.4	Average size, μm	250	150
Volatiles, % by mass	74.2	Minimum fluidization velocity, cm/s	2.2	0.6
Fixed carbon, % by mass	17.1	Terminal velocity, m/s	2.3	1.1
Ash, % by mass	0.3	Geldart's group	B	A-B
Carbon, % by mass dry	49.3	Active phase	-	Nickel
Hydrogen, % by mass dry	5.9	Ni content, % by mass	-	5.5
Nitrogen, % by mass dry	<0.1	Surface area, m ² /g	-	156
Oxygen, % by mass dry	44.4	Attrition rate constant	< 10 ⁻⁸	2.5·10 ⁻⁷
Stoichiometric air, kg/kg	5.4			
Low heating value, MJ/kg	18.5			

2.3 Operating conditions and test procedure.

The operating conditions of the gasification tests are reported in Table 2.

The bed temperature T and the fluidization velocity U have been kept constant while the equivalence ratio ϕ , and the steam/fuel ratio Ψ have been changed.

Steady state tests of gasification have been carried out following a standard experimental procedure. The reactor is heated up to the desired temperature (700-800°C) thanks to the air pre-heater and the electrical resistances in presence of an air stream of around 8 kg/h through the distributor and the bed. Generally, the plant is ready for gasification in 2-3 hours. Then the fluidization air flow is set at the assigned value, the steam generator is turned on and the water is pumped to produce the desired steam flow rate at around 400 °C. Afterwards, the biomass feeding is started, together with an inertizing nitrogen flow of 0.75kg/h.

Table 2: operating conditions of the experiments

Operating conditions	
Pressure, kPa	101
Bed height, m	0.18
Bed temperature, °C	780
Fluidization velocity, m/s	0.3
Equivalence ratio, -	0.17-0.29
Steam/Fuel ratio, -	0.6-0.9

Under steady conditions of the monitored variables, namely temperatures and gas molar fractions, the measurements are taken and recorded. A 20 min. sampling with the isokinetic probe is done. The solid particles in the hot filter and the sample at the cyclone are weighed after the experiments; their size distribution is determined off-line by means of a laser granulometer. The liquid phase products are weighed, separately with respect to their Dew point. Then, the condensate is dissolved in dichloromethane, to separate water from tar. The speciation of the condensed heavy tars (Dew point higher than 20°C) is performed by a HP 9600 series gas chromatograph equipped with a HP 35 Phenyl-Ethyl-Methyl-Siloxane column, linked to an Agilent Technologies Chemstation Rev.A.10.01-1635. The analysis is only restricted to the family of

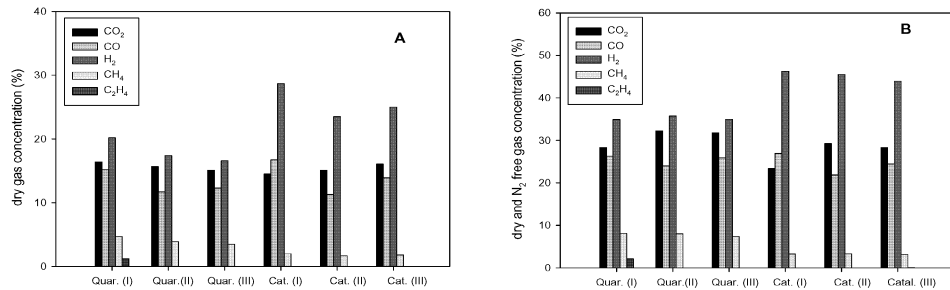


Figure 2: dry gas composition at the exit of gasifier- panel A= dry basis, panel B dry and nitrogen free basis

$T = 780^{\circ}\text{C}$; $U = 0.3\text{m/s}$; (I) $\Phi = 0.17$ and $\Psi = 0.65$; (II) $\Phi = 0.29$ and $\Psi = 0.91$; (III) $\Phi = 0.29$ and $\Psi = 0.65$

chemical species that are prescribed by the tar protocol of the CEN/TS 15439 normative (Technical Specification, 2006)

A sample of the syngas is also analyzed off-line by a micro gas chromatograph Agilent equipped with TCD detectors in order to determine the presence of light hydrocarbons. At the end of the gasification runs the total amount of char contained in the gasifier, i.e. the carbon load (W), is determined by integrating the CO and CO₂ profiles obtained by sending an assigned air flow rate to burnt-off the residual carbon. W is defined as the total mass of the carbon in the bed.

3. Results

Table 3 and Fig. 2 report the results of preliminary tests. Figure 2 shows the average molar fraction on dry (A) and dry/nitrogen-free (B) basis for CO₂, CO, H₂, CH₄ and C₂H₄ in the syngas for gasification tests carried out at different Φ and Ψ for both bed materials. Keeping constant the steam/biomass ratio (test I and III), the lower equivalence ratio, the smaller the CO₂ molar fraction, the higher are CO and H₂ molar fractions as clearly appears in Fig 2B. In contrast, a negligible effect of Ψ is noted (tests II and III), indicating that the water is well in excess as reactant. The increased oxygen availability enhances the total combustion path and depresses the bed carbon load, as indicated in Table 3.

As expected, the catalyst improves the gasification performance of the reactor whatever Φ and Ψ are adopted for the test. In particular, the H₂ molar fraction attains an higher value, while those of methane and ethylene decrease, since the hydrocarbon steam reforming reactions (CH₄ and C₂H₄) are accelerated by the presence of the catalyst.

The tar concentration on dry basis in the syngas is reported in Table 3. Lower tar content is observed in presence of the catalyst, whatever Φ and Ψ are used in the test. The measured values, even high, are in agreement with the data reported in literature (Gil et al. 1999).

Table 3. TAR concentration during the biomass gasification tests. $T=780^{\circ}\text{C}$; $U=0.3\text{m/s}$; (I) $\Phi=0.17$ and $\Psi=0.65$; (II) $\Phi=0.29$ and $\Psi=0.91$; (III) $\Phi=0.29$ and $\Psi=0.65$

	Quar. (I)	Quar. (II)	Quar. (III)	Cat. (I)	Cat. (II)	Cat. (III)
TAR (g/m ³ _n)	14.6	26.1	26.1	8.4	17.6	16.9
Carbon load (kg/kg)	0.21		-	0.63		0.39

The gas-chromatographic analysis of the collected samples confirm that the tar is a complex mixture of hydrocarbons, where a large number of different species can be detected. More abundant products are naphthalene, acenaphthylene, fluorene, phenanthrene, fluranthene, indene, and pyrene. This findings are in agreement with data reported by Pfeifer et al. (2004), under similar experimental conditions. Moreover, the catalyst significantly simplifies the family of detected species in the tar.

Surprisingly, the increase of the equivalence ratio enhances the tar yield. Higher tar contents and lower bed carbon loads are obtained at $\Phi=0.29$ and $\Psi=0.65$. Therefore, the

tar concentration seems to be correlated with W , suggesting an activity in tar removal of the carbon present in the reactor under steam rich atmosphere. Probably, the porous carbonaceous particles adsorb the tar and, in turn, the increased residence time in the reactor enhances the tar conversion, mainly by steam reforming.

The elutriation is very low for the quartzite bed, only entrained char particles being retrieved in the filter and cyclone. Higher elutriation rates have been obtained for the catalyst. It is worth to note that the U/U_{mf} ratio adopted in the gasification tests for the catalyst is around 5 times higher than for the quartzite, leading to a larger elutriation. Congruently, the samples collected at the filter and cyclone for the catalyst have a lower carbon content, less than 10% by weight.

4. Conclusions

The preliminary gasification tests of a biomass carried out in a pilot scale fluidized bed with inert or catalytic bed material confirm that the composition of the syngas as well as the tar concentration are appreciably modified in presence of the catalyst.

The tar concentration is reduced of around 50% by the Ni-alumina catalyst with respect to the reference test carried out in quartzite. The tar nature is also affected by the presence of the catalyst.

The catalyst exhibits a rather good mechanical resistance as well as a stable activity. Therefore it can be considered as a suitable material for fluidized bed catalytic gasification.

The fate of the char particles deserves further research for the implication with tar adsorption and, consequently, improved conversion in the bed.

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