Catalytically assisted gasification of biomass

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1. The INECSE Project

The necessity to find large scale new energetic vectors is becoming more and more urgent. The end of petrol era combined to the alarming emission level of pollutants drive the research to find cleaner fuels, from production to consumption. Obviously, the overall process is strongly conditioned by economical considerations, linked to production, transport and end-use of the fuel. The INtegrated Energy Conversion for a Sustainable Environment (INECSE) related activities cover four critical areas of future energetic technologies: integration of renewable in high efficiency systems, development of low-to-zero emission processes, production and utilization of H_2 and other sustainable fuels as well as capture and sequestration of CO_2. INECSE is a research training project funded by the European Commission under the Sixth Framework Program. INECSE is part of the Early Stage Research Training of Marie Curie Actions. It unites eight European research centers both from academic and industrial fields and is coordinated by Enel Italia. Participants are: Enel Italia, Abo Akademi (FL), University of Cardiff (UK), Delft University of Technology (NL), Instytut Energetyki (PL), C.N.R., Istituto di Ricerche sulla Combustione (IT), Technical University of Munich (D), Universität Stuttgart (D). The INECSE Training Programme has been launched with the mission of training a new European class of researchers in the field of energy technology. The new scientists will contribute to the development of the new energy conversion systems in international, multi-partner projects. Moreover, the INECSE programme will provide future researchers with a multidisciplinary technical and scientific background, making easier their interactions with other international research groups.

2. Introduction

Changing present energetic system from fount to end use implies a comparable efficiency to fossil hydrocarbons system (since related infrastructure already exists) and few pollutants releasing.

Among all possible clean and economically feasible energy carriers production, biomass conversion to a hydrogen-rich gas is a very seductive idea [1]. On the first hand, hydrogen burns producing only water, on the second hand, biomass is a practically non exhaustive energy fount and has a CO2 neutral effect on environment. All the matter produced by biological organisms can be considered biomass, but for energetic applications, wastes from human activity like paper and plastics also enter the definition. Biomass from wood is accepted as one of the best feedstock for energetic production, for reasons of availability, costs and relative homogeneity. Wood can be seen as an arrangement of organic polymers containing in some extent mineral matter. Biomass (mainly wood) combustion is still largely used all over the world, specially in developing countries, but even if cheaper, its thermal efficiency is very low. In the optic of energy production, biomass can be converted preferentially to gas, liquid or solid before further use. Conversion to solid has been used for centuries to make coal through the pyrolysis process, but the reaction is too slow to be of interest in fuel production at large industrial scale. Biomass liquefaction is commonly used today. The main liquefaction process is pyrolysis, but direct liquefaction with supercritical water is quite promising. Biomass gasification is accepted as one of the best solutions for

biomass conversion, since the process can be easily down scaled and allow a good control of the products distribution. The present project focus on catalytically assisted biomass gasification applied to syngas production.

2.1. Catalytic biomass gasification

When an oxidant gas (air, steam, CO2, O2) is flowed on a biomass particle at a sufficient temperature (>500°C) with an oxidant/fuel Equivalent Ratio in the range 0.25<ER<0.5, most of the products are gaseous and liquid. The process is called gasification and can be oriented towards liquid or gas production. If gas is the expected phase, liquid becomes undesired and is called tar. Tar, defined as all organic compounds with higher molecular mass than benzene are highly undesired in a conversion processes since they condense in the cold parts of the plants, plugging the tubes and provoking agglomeration. In practice, under the above-described conditions, the gasification of the particle occurs through a pyrolytic step which leads to particle devolatilisation. The produced species are permanent gases, but also very reactive radicals formed by small polymeric chains. In gasification conditions, secondary reactions involving primary tars (acetol, acetic acid, guaiacol formed during pyrolysis step) initiates at 700-850°C, producing secondary compounds (phenolics and other monoaromatics). At higher temperatures, tertiary conversion to polyaromatic hydrocarbons (PAHs) starts and the soot formation is observed simultaneously[2]. All these reactions take place in the gas phase between permanent gases and tar vaporized species. The surface of the char formed by devolatilisation of the original particle catalyze those reactions. Resultant coked-char and condensable species are then exposed to the oxidizing agent for further decomposition. If the heating rate is high enough (hundreds of °C per second) to provoke immediate devolatilisation of the solid fuel, and if the temperature is high enough (>750°C) to avoid condensation reactions, gas phase is mainly produced. It is constituted of CH_4, CO_2, H_2O(vap), H_2, CO and light hydrocarbons like C_2H_4. It can be further processed towards hydrogen-rich gas by methane and ethylene reforming, as well as by water gas shift reaction. In order to solve the problem of tar formation in biomass gasification, two approaches exist both based on the use of a catalyst to reduce tar formation: primary methods (catalyst is the bed material) and secondary methods (the catalyst acts down stream). Both of these techniques shown good tar reduction capability, but for reasons of costs, the use of a simple process is generally preferred. This is the reason why biomass gasification and tar reduction is preferentially developed in a single fluidized bed.

The use of a catalyst has different goals: enhance gas formation, enhance reforming reactions of hydrocarbons contained in the gas and avoid soot-induced deactivation (soot oxidation capability). Such a catalyst is commonly called tar reduction or tar conversion catalyst.

Three groups of catalyst materials have been applied in biomass gasification systems – non-metallic oxides, alkali metals and supported metallic oxides[3]. The most widely studied non-metallic primary catalysts for biomass gasifier tar conversion are dolomites-calcium magnesium carbonates. Dolomites are a cheap, natural mineral, but are not attrition resistant and very sensitive to CO_2 concentration, then not very suitable for applications in fluidized beds. Alkali salts are mixed directly with the biomass as it is fed into the gasifier. It is well known from several fundamental studies of cellulose and biomass pyrolysis that alkali metals enhance char formation reactions during thermochemical conversion[4]. Lower carbon conversion, increased ash content, and difficult recover of alkali metals make those metals unattractive gasification catalysts for commercial use. The success of reforming biomass gasification tars with supported Ni-based catalysts has also been extensively proved, but these catalysts deactivates due to soot poisoning and are very sensitive to chlorine and sulfur[1]. Other transition metals like iron, copper and chrome were also tested in biomass gasification (both inside and outside the bed). Copper have the same behavior as nickel, and of all the iron

oxides, only Fe_2O_3 shows significant activity (comparable to dolomite). Chrome activity enhances hydrogen production from biomass. Mixed metallic oxides has been less studied in biomass gasification applications, but their activity in hydrocarbons reforming as well as in soot oxidation is well known. They provide a very good dispersion of their constitutive metals, and the structure is thermally and chemically very stable. Soot removal catalysts used in diesel engine applications could be successfully applied to biomass decomposition, since tertiary tars are known to polymerize, coking the char particles as well as the bed material. Some recent studies highlight the activity of mixed oxides (CoCr2O4) or noble metal supported catalysts in soot and more specifically aromatics oxidation [5,6].

Woody biomass fuels have very low heat conduction properties, mainly due to the water content (10 to 50% in mass), which makes difficult the heat transfer to the solid fuel and the conversion efficiency. A number of different techniques has been set up to insure the fast heating of the biomass. Among them, fluidized bed technology is one of the most promising since once heated, the system provides a bed of hot solids with a liquid-like behaviour. The heat is consequently transferred very quickly (more than 100°C·s-1) to the introduced biomass fuel. Fluidized bed technologies are very sensitive to tar formation as it causes agglomeration of the bed material. The material of a fluidized bed has a much higher density than the fed biomass fuel. Once fluidized, a lower density and the production of volatile endogenous bubbles[7] is likely to result into biomass segregation on the top of the bed, reducing in turn considerably the conversion rate[8]. To increase the contact time between catalyst surface and solid fuel, mixing has to be improved. This can be achieved using some ad hoc configuration of the reactor with the goal of improving particles circulation into the reactor. Possible techniques are: to fluidized bed material under condition of a relatively high fluidizing gas velocity; to increase the density ratio biomass/catalyst. A similar approach was made by Rasul in 1998 for bagasse gasification in spent ZMS-5 catalyst and pumice stone beds[9]. A very light material, once fluidized would retain the biomass inside the bed for a longer time, thus increasing the contact time until total devolatilisation. According to this theory, a preliminary studies have been carried out to find a suitable support for this specific application.

3. Proposed catalyst

Cenospheres or so-called flying ash, produced in coal combustion industrial plants are a very light material. They can be described as hollow silico-aluminate spheres at the micronic and are generally used as fillers for paints or plastics to increase mechanical properties without altering the density. These features make this material a possible candidate as support for the active phase. Furthermore, being a by-product, they are very cheap, having negligible effects on the cost of the overall process.

Concerning the active phase, a lanthanum-cobalt mixed oxide with the addition of small amounts of Rhodium will be possibly deposited on the cenospheres. Such a material is expected to provide an hydrocarbon reforming activity, as well as oxidation activity, thus limiting coke deposition and consequent catalyst deactivation.

3.1. Support characterization

Hollow ceramic micro spheres called Fillite 300A were provided by Trelleborg Italia. Their properties are summarised in Tab.1. In order to avoid cohesive comportment, we first sieved the former material to obtain a range of 125-212 microns. The morphology of the material was investigated with a Philips XL30 SEM equipped with a EDAX instrument.

The particles are quite spherical with bubbles inclusions in the shell. They are mainly constituted of Si and Al oxides with some traces elements as Fe, Na, Ti, Ca and K (Tab.2). The particle size distribution of Fillite in the size range 125-212 μm, the Sauter diameter is found to be 146.5 μm (Fig.1c).

Particles size distribution	5-355 microns
Average wall thickness	5-10 % of sphere diameter
Average particle density	700-900 kg·m^{-3}
Average bulk density	400-480 kg·m^{-3}
Packing factor	60-65 %
Melting temperature	1400°C
Shell hardness	Mohs scale 6
Crush strength	140-280 kg·cm^{-2}
Filling gas	70% CO_2, 30 % N_2

Tab.1 properties of Fillite 300A

a)   b)   c)

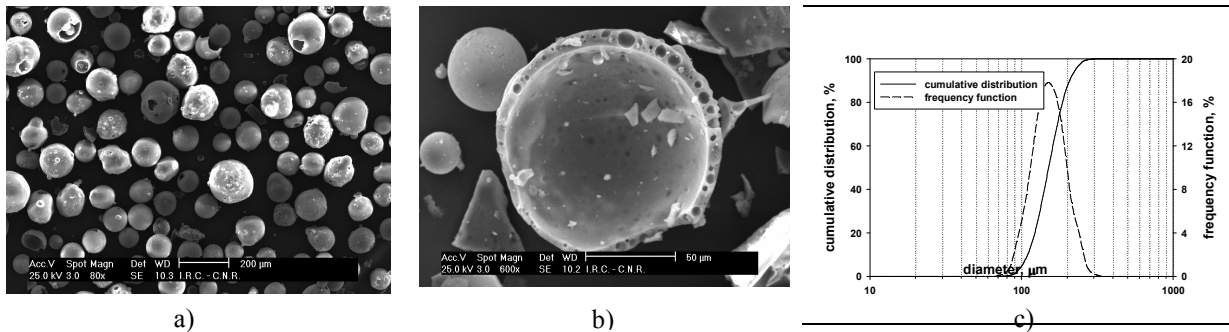*Fig.1 a) SEM image of cenospheres particle size 125-212 μm, b)SEM image of inner surface and shell of one sphere, c)size distribution.*

The X-Ray diffraction pattern (Fig.2) of grinded cenospheres was obtained with a PW 1100 Philips diffractometer (CuKa). It clearly shows the amorphous quartz and crystalline mullite parts of the material.
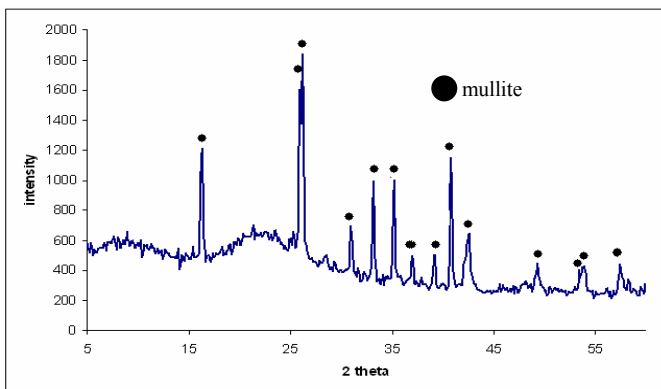

Fig.2 X-Ray pattern of the cenospheres.

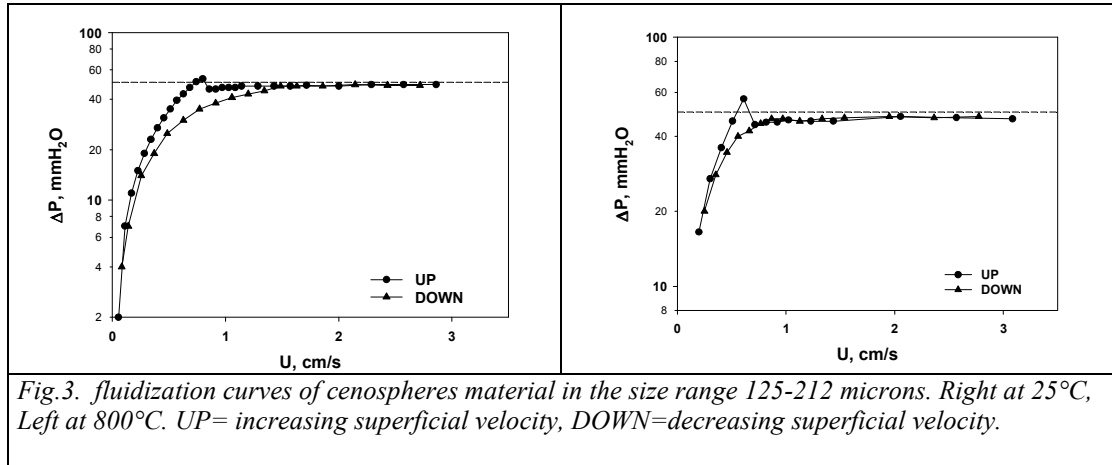| Elements	Na	Al	Si	K	Ca	Ti	Fe
weight percent	1,04	33,25	59,51	0,98	0,39	3,25	1,58

Tab.2 EDX analysis of Fillite on the external surface of a sphere.

As the use in fluidized bed for biomass gasification was the aim of the present research, a critical point was to determine the fluidization properties of the cenospheres. The material in the selected range is a "class A" material according to Geldart classification.
Fluidization tests were performed in a stainless steel cylindrical reactor (diameter =1" and 400 mm high), heated by a Tersid furnace. Pressure drop was measured by difference before and after bed with two ABB HART series 600T EN transductors. A ceramic filter was placed downstream the reactor to collect elutriated fines (>300 nm).

A fluidization test at ambient temperature followed by another at 800°C confirmed the ability to fluidize of the micro spheres. Pressure drops versus superficial gas velocity have been measured in experiments carried out at 25°C and 800°C (Fig.3). Experimental data have been worked out to obtain the experimental values of the minimum fluidization velocities (Umf) found to be 0.6 cm·s^{-1} at 800°C and 0.8 cm·s^{-1} at 25 °C

Fig.3. *fluidization curves of cenospheres material in the size range 125-212 microns. Right at 25°C, Left at 800°C. UP= increasing superficial velocity, DOWN=decreasing superficial velocity.*

To verify the resistance of cenospheres to attrition in operating conditions, we performed an ad-hoc test at 800°C and U=10 cm·s^{-1} (more than ten times the Umf at this temperature but far below the velocity at which the bed is carried away).
Such a measurement was carried in a similar reactor as the one used for fluidization, but coupled with two copper filters to allow continuous fines removal during the experiment.
Fig.4 shows the curve of attrited fines of fillite 125-212 μm under non reactive conditions. It is possible to note that after the initial peeling off of the particle asperities, a steady state condition is approached with a relatively low value of E=2 to 3 mg per minute. Granulometric analysis have also been performed on samples after fluidization tests at 25 °C or 800°C and after attrition test.

Fig.4 *Abrasion curve of cenospheres (125-212 microns),800°C, U=10 cm·s^{-1}*
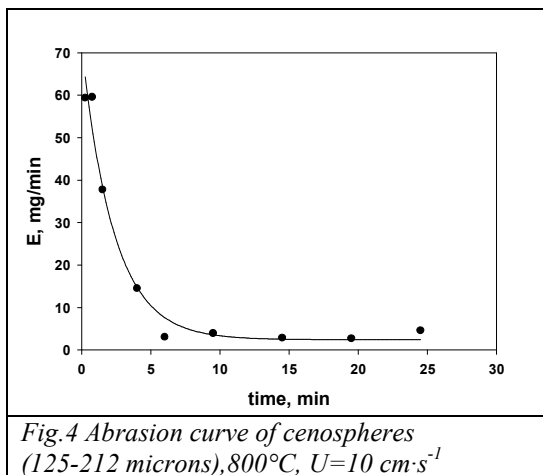
	d_{Sauter} (μm)
Fresh fillite	146.5
fillite after fluidization at 25°C	146.5
fillite after fluidization at 800°C	147.2
fillite after abrasion test at 800°C and 10cm.s^{-1}	151.6

Tab.3 *particles size distribution evolution after exposure to different conditions*

Under the experimental conditions tested, Sauter diameter of three distributions are practically the same (Tab.3). However, according to a shrinking particle model with no collapses of the particle during its life-time inside the bed, assuming a reduction of the external size of the particle due to attrition a relatively short life time is expected. This is of course a critical aspect for an industrial applications (costs linked to bed replacement) of the support

considered. In fact the mass loss due to attrition can drive both to material transport out of the bed as elutriable fines or collapse of the particles into elutriable or relatively high dense not elutriable fragments.

3.2. Support activation

Deposition of the active mixed oxide on the cenospheres is not a trivial task for two main reasons: i) cenospheres have a very low surface area and a small concentration of hydroxyl groups to graft the metal oxide, ii) cenospheres floats on water (generally used as solvent) leading to a poor contact between support and precursors salts. Different techniques have been used to deposit metals on this material, by surface modification (activation) [10] or electroless process [11]. On the basis of preliminary investigations, ethanol is the most suitable solvent since it allows both a good cenospheres immersion and a complete precursors salts dissolution. Coating of cenospheres with a thin alumina layer prior to the active phase will provide both a higher surface area and a mechanical strengthening will be carried out in the near future.

4. Conclusion

Hydrogen-rich gas can be produced by biomass gasification provided that tar formation is limited by using a catalyst. The fluidized bed technology is the most suitable since it favors a fast heating of the biomass fuel. The use in a catalyst bed requires special catalytic properties: i) a density close to that of the biomass particle, ii) a good mechanical resistance, iii) a good activity in reforming and oxidation reactions.
Preliminary studies of the present research work have been devoted to determine the catalyst support meeting these requirements and the composition of the active phase.

5. References

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