

Solar driven pyrolysis in a novel autothermal fluidized bed reactor

R. Solimene*, **C. Bevilacqua***, **A. Cammarota***, **A. Cante***,
G. Coppola**, **M. Galbusieri*****, **E. Marinò***, **F. Montagnaro****,
S. Padula***, **C. Tregambi*****, **M. Troiano*****, **P. Salatino*****

solimene@irc.cnr.it

* Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche,
Piazzale V. Tecchio 80, 80125 Napoli (Italia).

** Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II,
Complesso Universitario di Monte Sant'Angelo, 80126 Napoli (Italia).

*** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli (Italia).

Abstract

A novel concept of autothermal fluidized bed reactor is proposed in a dual interconnected fluidized bed configuration for solar driven pyrolysis finalized to bio-oil and biochar production. The proper process conditions were established on the basis of fluidized bed characterization of devolatilization rate of a woody biomass. Preliminary results of solar driven pyrolysis are also reported.

Introduction

Energy production by use of renewable sources is currently a hot research topic to both reduce the greenhouses gas emissions and decrease the dependence of Countries from fossil fuels. Solar energy will surely play a key role in the forthcoming energy scenario due to its wide diffusion and availability. A possible way to take advantage of solar energy is the use of Concentrated Solar Power (CSP) systems. In this technology, optical sun tracking mirrors are used to concentrate the solar energy onto a receiver to eventually drive a power cycle or sustain a chemical process. Integration of CSP with ThermoChemical Energy Storage (TCES) enables virtually unlimited time scale of energy storage and highly increases the technology dispatchability [1]. Since TCES often involves gas/solid chemical processes, use of multiphase reactors such as Fluidized Beds (FBs) is frequently considered in the current literature. An interesting pathway for TCES is the production of solar fuels by means of solar driven coal/biomass torrefaction, pyrolysis and gasification [2–3]. Synthesis of solar fuels allows the production of high value energy carriers which can be conveniently transported and processed in already existing distant plants. In this study, solar driven pyrolysis of a woody biomass was performed in a novel concept of solar autothermal FB reactor. Devolatilization rate of the considered biomass was investigated in a conventional FB reactor as a function of the bed temperature and particle size to properly select the optimal process conditions for solar tests. Preliminary solar driven pyrolysis tests were performed in the newly designed autothermal FB reactor.

Conceptual outline of the process

Figure 1 reports a conceptual scheme of the solar driven autothermal FB reactor in a dual interconnected FB (DIFB) configuration.

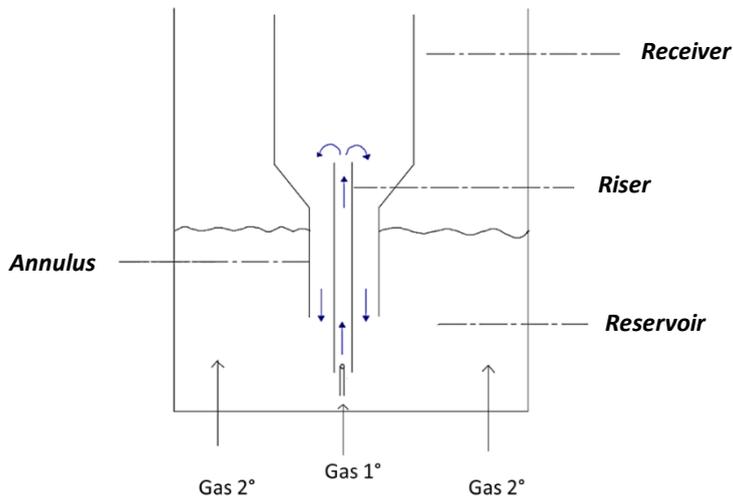


Figure 1. Conceptual scheme of the proposed reactor.

The DIFB system consists of: i) a conventional main FB unit (reservoir), which acts as residual char/solid separator and sensible heat storage (bulk zone); ii) the solar autothermal FB reactor, dipped inside the main FB reactor, made of a volumetric receiver/reactor (collection zone), where the concentrated solar energy is focused, and of two concentric tubes behaving as heat exchanger. Bed solids rise in the internal tube (riser) and descend along the gap between the two tubes (annulus). The volumetric receiver has a conical-cylindrical geometry, is connected to upper part of the annulus and behaves as particle disengagement section. During the system operation, the bulk zone is kept close to minimum fluidization conditions to ensure the required solid mobility, char/bed solids separation and minimization of heat losses. An inert gas stream is fed to the riser through a nozzle, inducing the solids circulation from the bulk to the collection zone. Biomass particles are fed into the collection zone, where their temperature is increased by direct interaction with the concentrated solar radiation and eventually reactions occur. Hot pyrolysis gases are recovered at the exit of the collection zone. Solid char particles fall down along the walls of the conical section and eventually are conveyed into the annulus. Here, the particles move by gravity towards the bottom where they finally re-enter the bulk zone and can be discharged. During their descending path along the annulus, particles transfer their heat to the solid suspension in the riser. This feature allows autothermal operation of the reactor with the recovery of the sensible heat of the reaction products, highly increasing the efficiency of the process and the maturity of the technology.

Fluidized bed pyrolysis kinetics

A stainless steel bubbling fluidized bed reactor 17 mm ID and about 1 m high was used for lab-scale devolatilization experiments (Fig. 2A). The reactor consists of a lower section, an upper section and an inter-flange of connection between the two logs. The upper section contains part of the bed material and the freeboard zone. It is equipped with a double valve system at the top to enable the loading of the bed and the batch-wise injection of fuel particles. Furthermore, two tubes are welded laterally to the column for fluidization gas outlet and for the measurement of freeboard pressure, respectively. The inter-flange length contains most of the bed material and hosts a tube, welded laterally, bearing a thermocouple (K-type) to measure the temperature in the fluidized bed about 0.01 m above the distributor plate. Another tube is laterally welded to the column and serves as system of rapid discharge of bed particles. The lower section is used as wind box. The fluidizing gas is metered through a wind box and a gas distributor made of a set of stainless steel nets. Technical nitrogen from cylinders was used as fluidizing gas. The fluidizing gas-flow rate was established by setting the upstream pressure of a critical orifice located along the gas feeding line. The reactor was operated at a pressure slightly larger than atmospheric pressure by means of a calibrated flow restriction at the exhaust consisting of an orifice with an adjustable cross section. This restriction was periodically cleaned to remove tar deposits generated during fuel pyrolysis. The reactor could be steadily operated at temperatures up to 900°C by means of a 1 kW cylindrical oven 0.8 m high equipped with a PID temperature control system. A high-precision (accuracy better than 0.06 mbar) piezo-resistive electronic pressure transducer with rapid time response (less than 1 ms) and 100 mbar full-scale was connected to the pressure tap to measure the time-resolved gas pressure in the reactor. Experiments were carried out using wood chips. Table 1 reports the main fuel properties in terms of lower heating value, proximate and ultimate analyses. For devolatilization experiments, fuel particles with a diameter from 0.2 mm to 1 mm were used after sieving in the ranges 0.2-0.3 mm, 0.3-0.42 mm, 0.42-0.59 mm, 0.59-0.84 mm, 0.84-1 mm. Pressure was continuously monitored in the fluidized-bed reactor during the experiments. Gas pressure inside the reactor increases during devolatilization as the incremental flow rate due to volatile matter emission flows across the calibrated flow restriction at the exhaust. The selection of the steady-state overpressure in the reactor, dictated by the flow rate of fluidizing gas through the calibrated flow restriction at the exhaust, determines the time evolution of the phenomena. After careful optimization, the best trade-off was found as an overpressure of about 20 mbar for all the tests, carried out at three temperatures, 400°C, 500°C and 600°C. The bed of sand (300-400 μm , 13 g) was fluidized with nitrogen to rule out the influence of volatile matter and char combustion on the recorded pressure profiles. The upstream pressure at the critical orifice was kept at a constant value of about 2.4, 3.0 and 3.6 bar at 600, 500 and 400°C, respectively. The fluidizing gas velocity was in each case about 5 times the incipient fluidization velocity.

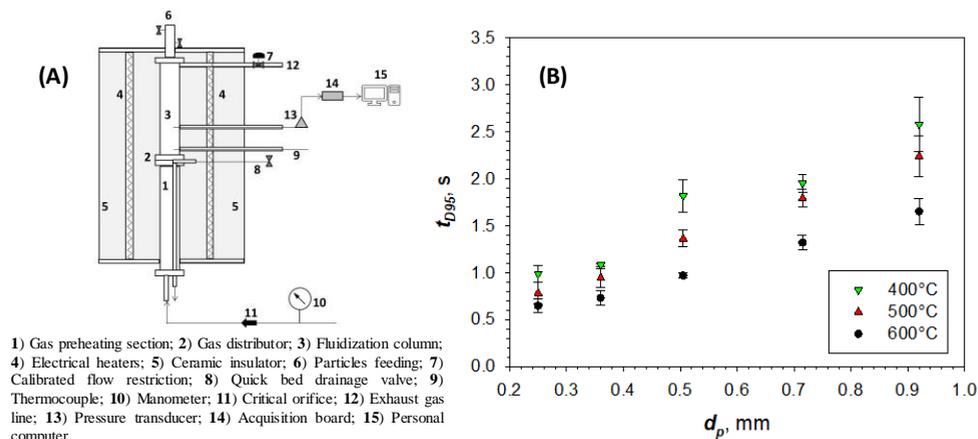


Figure 2. (A) Schematic of the apparatus used for the devolatilization tests; (B) Devolatilization time as a function of the particle size at three temperatures.

The tests consisted of the injection of a batch of fuel particles (about 20 mg) in the fluidized bed followed by complete devolatilization. The pressure signal was continuously logged during the experiments at a sampling rate of 1,000 Hz by means of a purposely developed LabVIEW program. Pressure time-series were analyzed in the light of a model of the experiment described elsewhere [4] in order to determine the time for 95% devolatilization degree, t_{D95} . The devolatilization time is reported in Fig. 2B as a function of the fuel particle size for the three selected temperatures. t_{D95} increases with increasing fuel particle size and with decreasing devolatilization temperature. Furthermore, if fast pyrolysis process is targeted, devolatilization times lower than 1 s are preferred. This means that, as evident in Fig. 2B, fuel particles in the size ranges 0.2-0.3 and 0.3-0.4 mm are suitable for such a process, while if 0.42-0.59 mm particles are used, only a devolatilization temperature equal or higher than 600°C can be chosen as pyrolysis temperature. Furthermore, particles larger than 0.59 mm are not suitable from a kinetic point of view for the fast pyrolysis process at the investigated temperatures.

Table 1. Fuel properties.

Proximate Analysis (as received, % _w)		Ultimate Analysis (dry basis, % _w)		LHV (as received), kJ/kg
Moisture	37.22	Carbon	49.16	
Volatile matter	39.21	Hydrogen	5.02	
Fixed carbon	15.85	Nitrogen	0.63	
Ash	7.73	Sulfur	0.10	
		Chlorine	0.10	
		Ash	12.31	
		Oxygen (by difference)	32.68	

Solar assisted pyrolysis in autothermal reactor

The batch FB reactor used for the solar driven pyrolysis tests, designed on the concept described in the previous section, is depicted in Fig. 3A. It consists of an unconventional FB reactor made of two concentric circular columns: the internal one represents the riser, the external one the annulus. As the system is not coupled with a biomass reservoir, #4 equispaced holes are drilled at the bottom of the riser to allow an internal material circulation. The active length of the riser and annulus is of 80 and 70 mm, respectively. The total inventory of the reactor ranges between 15–20 g. An electronic mass flow controller is used to ensure and control solid circulation in the reactor. A single K-type thermocouple is located at the bottom of the riser column, at the same height of the holes drilled for the solid circulation. The concentrated solar radiation is focused at the top of the riser column and simulated by a short arc Xe lamp of 7 kW_{el} coupled with an elliptical reflector.

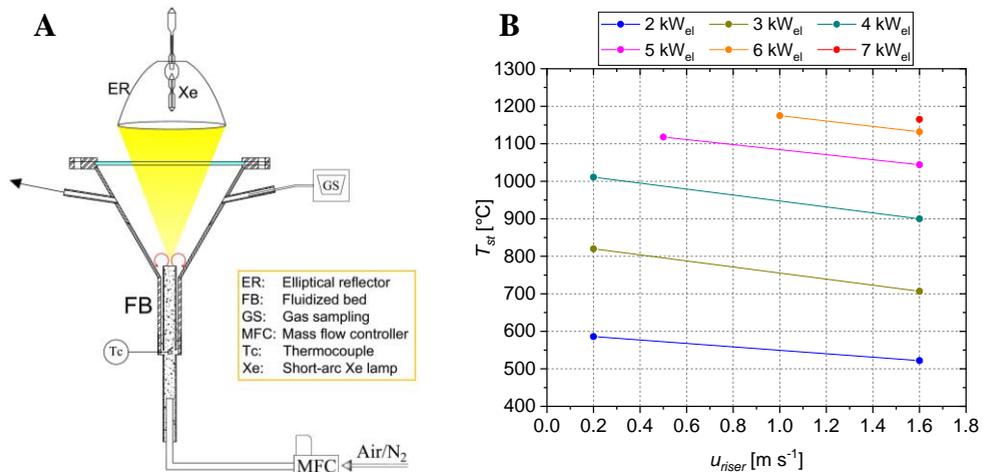


Figure 3. (A) Outline of the solar FB reactor; (B) Map of operability with mullite.

At full power, a peak flux of 2.1 MW m⁻² is obtained in the focal point, while the total thermal power supplied to the system is of about 2 kW_{th}. Gas sampling is performed with a refrigerated conical flask to collect the condensable bio-oil, and with gas sampling bags for the incondensable gas species. For the pyrolysis tests, a mullite powder ($d_{Sauter}=210 \mu\text{m}$, $\rho_{bulk}=1555 \text{ kg m}^{-3}$) was used as inert material in the FB. The inherent operability map, reporting the steady-state temperature (T_{st}) vs. the gas velocity inside the riser (u_{riser}) for different input power of the solar simulator, is reported in Fig. 3B. Concerning the woody biomass, a particle size of 0.2-0.3 mm and a process temperature of 500°C were selected according to the pyrolysis kinetics results. In this way, t_{D95} values about 0.8 s, and a fast-pyrolysis process can be performed. During a typical test, the FB is charged with 15 g of mullite. Solid circulation is started at $u_{riser}=1.6 \text{ m s}^{-1}$ using N₂ as fluidizing gas, and the solar simulator is powered on at 2 kW_{el}. Once the desired temperature is achieved and the system is at steady-state conditions, a sample of 2 g of woody

biomass is fed to the reactor through one of the gas discharge port by means of a pneumatically controlled cylinder-piston device. Liquid and gas are collected for the whole duration of the test. Liquid fraction is weighed with a 0.01 g precision analytical scale, while gas sampling bags are analyzed by gas chromatography. From first experimental results, a bio-oil yield of 14%_w was obtained. This result is quite low if compared with literature data [5] where bio-oil yields higher than 50%_w are reported. A possible explanation is that gas recirculation inside the conical freeboard of the FB reactor leads to longer gas residence times and promotes thermal cracking reactions. Results of gas analysis are shown in Fig. 4. N₂ concentration is very high and close to 98.5%_v mainly because gas sampling was prolonged until the complete collection of the pyrolysis gas. Main gas species are carbon dioxide, methane, hydrogen, butane, and ethylene. Traces of 3-methyl-1-butene, pentane, isopentane, isohexane were also detected.

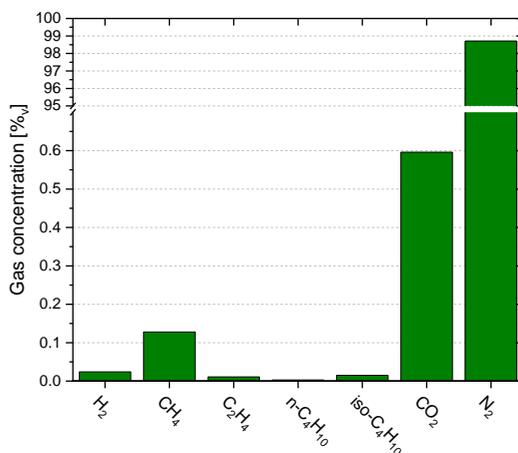


Figure 4. Results of gas analysis on sampling bags.

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