

CONTINUOUS FAST PYROLYSIS OF BIOMASS AT HIGH TEMPERATURE IN A FLUIDIZED BED REACTOR

S. Rapagna', E. Tempesti, P. U. Foscolo and E. Parodi***

DEPARTMENT OF CHEMISTRY, CHEMICAL ENGINEERING AND MATERIALS,
UNIVERSITY OF L'AQUILA, 67100 L'AQUILA, ITALY

*DEPARTMENT OF MECHANICAL ENGINEERING, UNIVERSITY OF BRESCIA, 25060
BRESCIA, ITALY

**FUEL EXPERIMENTAL STATION, 20097 MILANO, ITALY

In order to perform biomass pyrolysis a continuous fluidized bed reactor (bench scale unit) has been assembled. The influence of experimental conditions such as heating-up time and optimum particle diameter is presented. By feeding the biomass (almond shells) directly into the bubbling bed, pyrolysis has been performed at temperatures ranging from 730° to 930°C at constant feed rate (44 g/h). Remarkable increase of H₂ in the product gas is observed when steam rather than an inert carrier such as nitrogen is used thus confirming the potential of this approach.

Keywords: fast pyrolysis of biomass, fluidized bed reactor

Introduction

A good deal of attention has been focused on the thermal conversion of biomass to gas and liquids, particularly on the products obtainable from short-time, high temperature pyrolysis of wood and other lignocellulosic materials. By definition, pyrolysis implies decomposition by heating in the absence of oxygen. Traditionally the heating was done slowly, over long periods of time to give maximum yields of charcoal. Only in recent years has some attention been paid to the effects associated with short time rapid heating of wood particles. In general two approaches to fast pyrolysis of biomass have been used. The primary objective of one approach is the determination of conditions for maximum yield of liquids from biomass, particularly forest materials [1]. In order to obtain high liquid yields, the processes reported operate over a range of 400°–650°C. The qualitative and quantitative yield of liquid (oil) product is extremely dependent on the biomass used. Resinous and tar product formation is unavoidable.

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A second approach of fast pyrolysis is currently under investigation. Its main objective is to produce a maximum yield of gas which under non catalytic conditions is normally ethylene or higher olefins. Processes such as 'ultra pyrolysis' [2, 3], 'ablative pyrolysis' [4], flash pyrolysis described by Antal *et al.* [5] and the fluidized bed processes of Kuester [6], have been reported in recent years for the production of olefins. These processes are characterized by high temperatures (>650°C) and residence time of 1 s or less.

The highest yield of gas has been obtained very recently [7] from flash pyrolysis of almond shells by using a sand fluidized bed reactor at 890°C and at a residence time of volatiles of 2.3 s.

The scope of this study is to investigate the continuous flash pyrolysis of biomass in a fluidized bed, in order to maximize gas yield, particularly hydrogen.

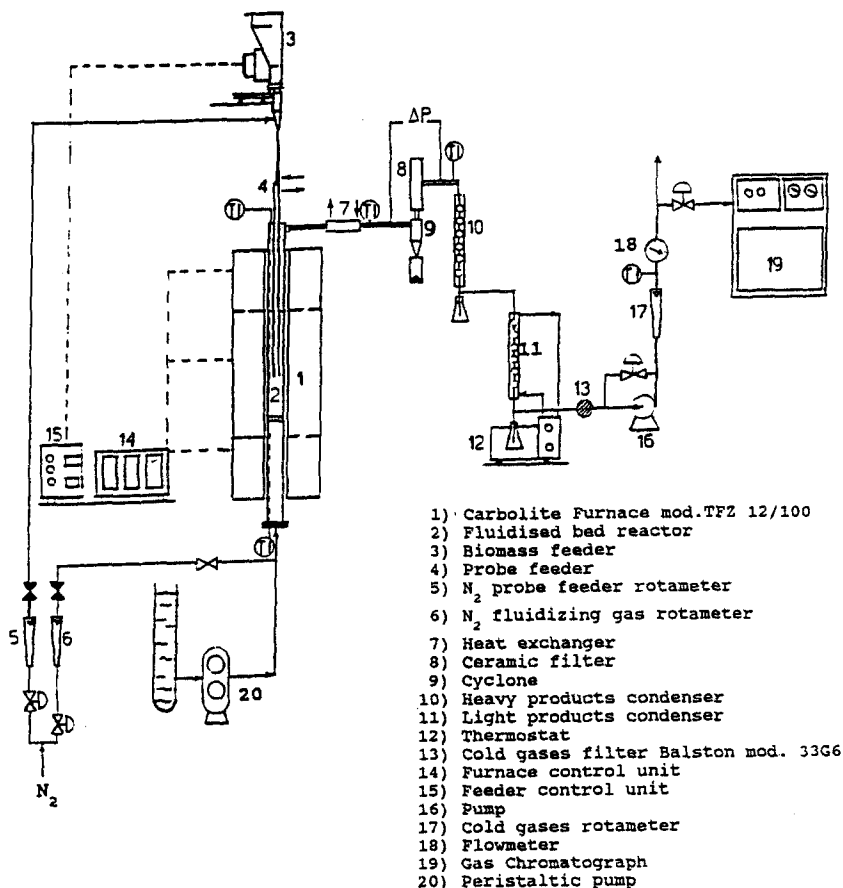


Fig. 1 The major parts of the pyrolysis unit

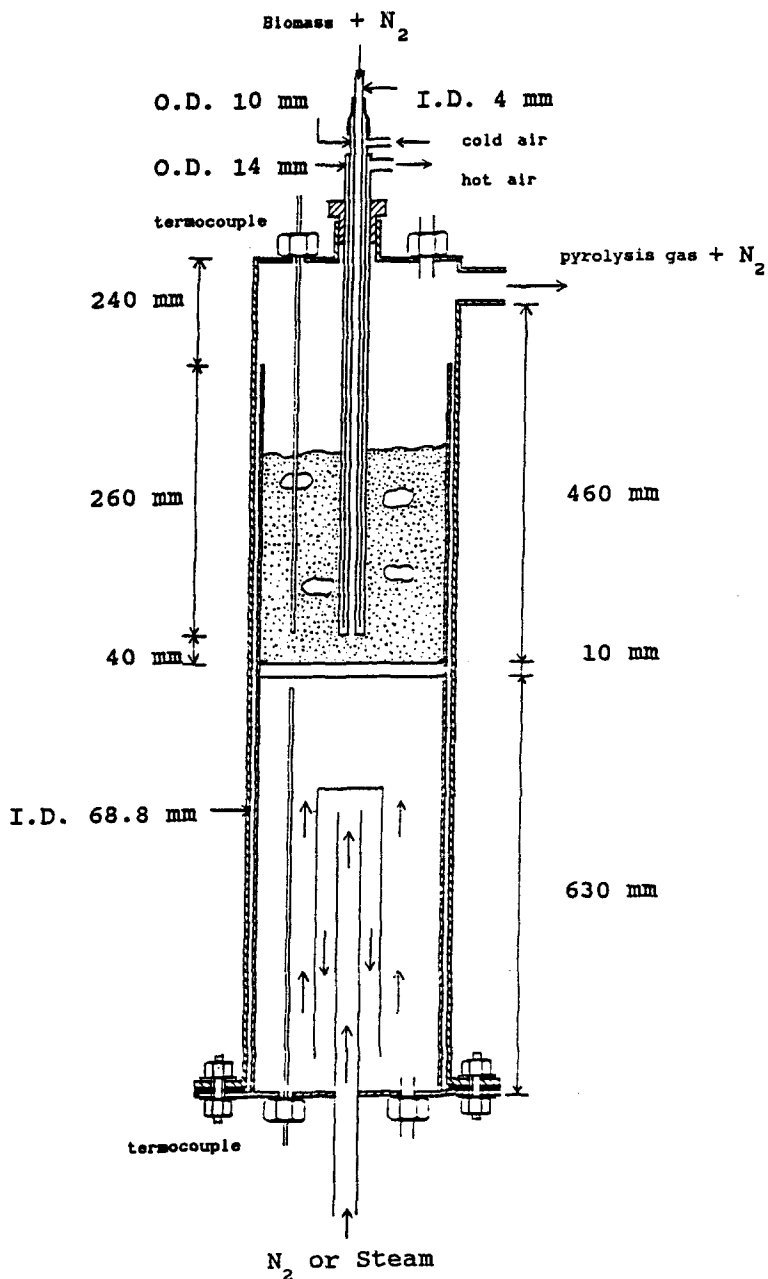


Fig. 2 Reactor scheme

Experimental

Bench-scale gasification plant

A flow scheme of the system designed to operate at temperatures up to 1000°C is reported in Fig. 1. A small flow of N₂ (ca. 24 lt/h) is used to feed the biomass in the entrainment tube, the feeder being hermetically closed. To prevent biomass degradation the tube is cooled with air (Fig. 2).

To maximize hydrogen production specific runs were carried out using steam (90 gr/h) rather than nitrogen.

The fluidized bed reactor is a I.D. 60 mm austenitic stainless steel ASTM A 312, with a porous disc (SCHUMALITH, pore size: 10 μm) designed to operate up to 1200°C (Fig. 2). The temperatures in the reactor are measured with two thermocouples, one immersed in the bubbling bed and another located under the porous disc.

The fluidized bed is made of Alumina fine particles ($\rho_p = 1650 \text{ kg/m}^3$, $d_p = 107 \mu\text{m}$).

The hot pyrolysis gas, after separation of solid particles, is cooled with two condensers. The first condenser uses water as cooling agent while the second uses a mixture of water and diethylene glycol (-10°C).

Gas products (H₂, CO and CH₄) were analyzed by gas chromatography. A Molecular Sieve 5A (1 m, 4 mm I.D.) column was used with Ar as carrier gas at 60°C (flow rate 65 ml/min) for H₂. For CO and CH₄ He was used as carrier gas.

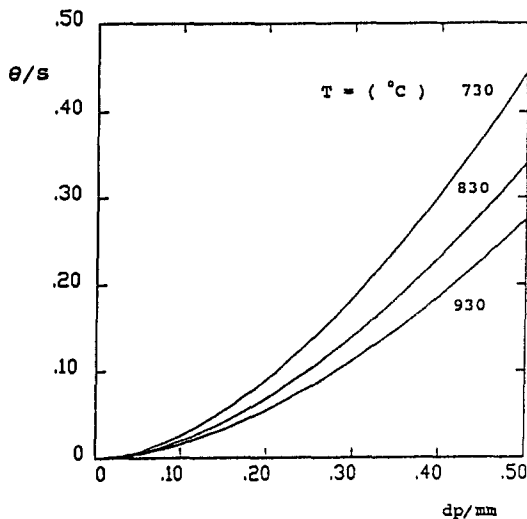


Fig. 3 Particle heating-up time as function of particle size and bed temperature

Choice of physical parameters

To predict the heating up time, Θ , of the biomass particles fed to the reactor, we have used the procedure suggested in the literature [8] to evaluate the unsteady state conduction of heat in a solid sphere, with the consideration of the additional heat transfer resistance at the outer surface of the particle immersed in the bed. This has been estimated according to the recent suggestions made by Turton and Levenspiel [9], adding also the radiative contribution. Figure 3 shows the time calculated in this way for different particle sizes and bed temperatures, needed to heat the center of a particle up to 500°C. This is commonly considered the required temperature level to assure the extend of the pyrolysis process at a significant rate.

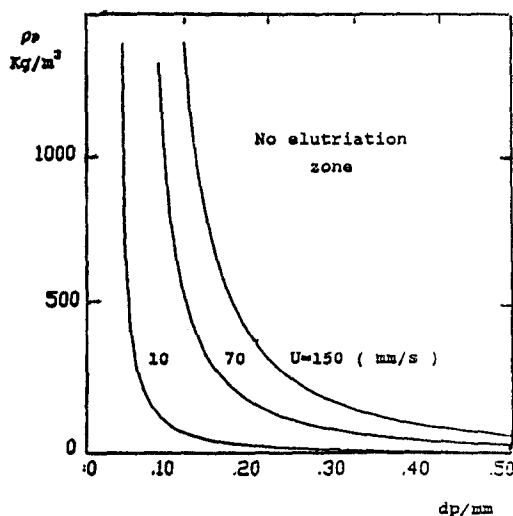


Fig. 4 Boundary line delimiting the particle elutriation zone as function of superficial velocity; $T = 930^{\circ}\text{C}$

Figure 4 shows the boundary lines (at 930°C) delimiting the elutriation region for biomass particles of different sizes (d_p) and densities (ρ_p), when the superficial velocity of the fluidizing gas (U) is fixed. Additional data have already been reported [10].

In Fig. 5, the minimum fluidizing velocity, (U_{mf}) and the minimum bubbling velocity (U_{mb}), of alumina are reported as function of temperature.

The Ergun equation [11] has been used to predict the minimum fluidizing velocity while keeping the minimum fluidization voidage constant with temperature and equal to the value measured at ambient conditions ($\epsilon_{mf} = 0.4$). According with the Foscolo and Gibilaro model [12] minimum bubbling voidages of the bed were calculated changing density and viscosity of the fluidizing gas as function

of the temperature, and successively minimum bubbling velocities were calculated with the correlation of Richardson and Zaki [13]. From Fig. 5 it may be seen that at high temperatures in order to have a bubbling regime in the bed it is necessary to operate with gas velocities sensible higher (3 times) than the minimum fluidizing velocity.

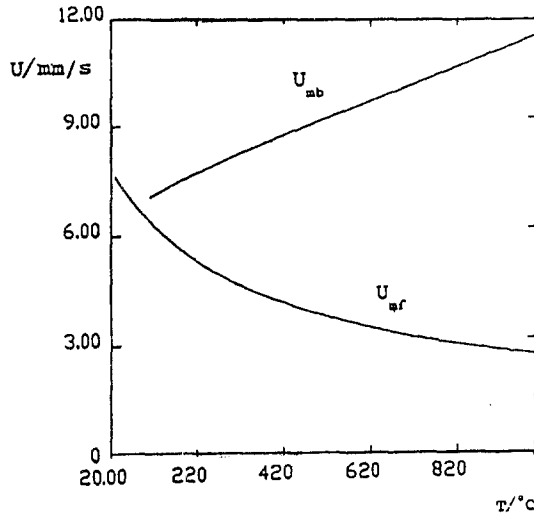


Fig. 5 Effect of temperature on U_{mf} and on U_{mb} of alumina ($d_p = 107 \mu\text{m}$, $\rho_p = 1650 \text{ kg/m}^3$), fluidized by N_2

Table 1 Properties of biomass used

	raw	Almond shells	
		dry	daf
Moisture / %wt	8.84	0.00	0.00
Ash / %wt	1.16	1.17	0.00
Vol. matter / %wt	72.45	79.48	80.42
C / %wt	45.31	49.70	50.29
H / %wt	5.48	6.01	6.08
O / %wt	38.53	42.49	42.99
HHV/kcal·kg ⁻¹		4730	
Mean diameter / μm		372	
Cellulose / %wt	29		
Hemicellulose / %wt	28		
Lignin / %wt	35		

Table 2 Gas and liquid yields at different temperatures

	Fluidizing gas	Reactor temperature / °C		
		730	830	930
Yield of gas	Nitrogen	0.82	1.05	1.20
Nm ³ /kg of biomass	Steam	1.32	1.43	1.48
Yield of liquid	Nitrogen	0.023	–	–
kg/kg of biomass	Steam	–	–	–
Estimated residence	Nitrogen	8.0	6.8	6.0
time/s	Steam	5.8	5.2	4.7

Results and conclusions

In Table 1 we report some typical analysis of the feedstock used.

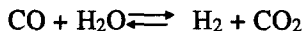
Table 2 reports the gas and liquid yields obtained at different temperatures using N₂ and steam as carrier gas. With regard to previous data [7] we thus confirm that by using a fluidized bed reactor on increasing the temperature at ca. 900°C the liquid yield is negligible. Relative to the same cited reference however, under inert atmosphere we obtain higher volume fractions of hydrogen (Table 3).

Table 3 Typical results with no catalysts under inert atmosphere or steam

	Fluidizing gas	Reactor temperature, °C		
		730	830	930
% of H ₂	Nitrogen	27.0	39.0	50.0
	Steam	51.5	52.5	53.5
CO	Nitrogen	43.0	48.0	49.0
	Steam	18.1	19.0	19.1
CH ₄	Nitrogen	9.8	3.0	0.5
	Steam	8.6	8.5	8.8

Due to the great number of possible reactions involved in the pyrolysis of biomass (depolymerization, disproportionation, dehydration, decarboxylation, random scission, cracking and reforming of the volatiles), this result cannot be easily rationalized. In any case the influence of the support cannot be disregarded since it is known that less acidic supports reduce carbon buildup [14].

In order to maximize the hydrogen content in the gaseous product steam rather than an inert carrier such as nitrogen has been used since it is known that under these conditions the water gas shift reaction:



is driven to equilibrium and tar formation is reduced.

Indeed under comparable experimental conditions (Table 3) a marked increase of hydrogen production is observed particularly at lower temperatures while methane formation seems to be unaffected by the temperature.

To further enhance H₂ production we are now considering the opportunity to specifically oxidize the methane obtained by noncatalytic pyrolysis either by duly coating the support or alternatively by placing a mono- or multifunctional catalyst in a secondary reactor immediately after the fluidized bed reactor. Further work is in progress.

By using a continuous fluidized bed pyrolysis plant (bench-scale unit) it has been shown that:

- under the reported experimental conditions it is possible to minimize the liquid fractions and maximize the gas yield (>90%);
- the overall yield of gaseous products is thoroughly affected by using steam instead of an inert carrier, specifically as far as hydrogen production is concerned.

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Zusammenfassung — Zur Durchführung der Pyrolyse von Biomasse wurde ein kontinuierlicher Wirbelschichtreaktor gebaut. Es wird der Einfluß der Versuchsbedingungen wie z.B. Aufheizzeit und optimaler Partikeldurchmesser beschrieben. Wird die Biomasse (Mandelschalen) direkt in die Wirbelschicht eingeleitet, wurde die Pyrolyse bei Temperaturen zwischen 730° und 930°C bei einer konstanten Einspeisegeschwindigkeit von 44 gr/h durchgeführt. Wird anstelle eines inerten Trägergases (z.B. Stickstoff) Wasserdampf verwendet, kann im Produktgas ein bemerkenswerter Anstieg von H₂ verzeichnet werden, was die Leistungsfähigkeit dieser Näherung bestätigt.