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Fast Pyrolysis of Biomass in a
Circulating Fluidised Bed

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Van de Velden et al.: Fast Pyrolysis of Biomass in a Circulating Fluidised Bed (CFB)

FAST PYROLYSIS OF BIOMASS IN A CIRCULATING FLUIDISED BED

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ABSTRACT

CFB biomass pyrolysis produces mostly bio-oil. Reaction rates are fast ($k > 0.5 \text{ s}^{-1}$). Yields exceed 60 wt% of bio-oil at 500 °C and at a residence time for oil and char $\tau < 2.5 \text{ s}$. as achieved in plug flow CFB-mode, shown by PEPT to occur at $U > (U_{tr} + 1) \text{ m/s}$ and $G > 200 \text{ kg/m}^2 \text{ s}$.

INTRODUCTION

Biomass is a renewable energy source with high potential (1,2). Its pyrolysis mainly forms storable bio-oil and solid char; bio-oil also contains value-added chemicals (1). Important design issues are kinetics, modelling and reactor hydrodynamics (3,4). Pyrolysis proceeds in the absence of O_2 and takes seconds only at moderate temperatures ($\sim 500 \text{ }^\circ\text{C}$). Char is a cracking catalyst for bio-oil and must be removed from the vapour. After condensation, a brown, low viscosity liquid is obtained. High oil yields (1,5) are achieved at: (i) very fast particle heating; (ii) temperature of $\pm 500 \text{ }^\circ\text{C}$; (iii) short τ and (iv) fast char separation and vapour condensation.

Fluidised beds achieve the fast heat transfer. Both bubbling fluidised beds (BFB) and circulating fluidised beds (CFB) can therefore be used for fast pyrolysis, each with its known advantages and drawbacks. Whereas a BFB will operate at a gas velocity to mix biomass and sand, albeit with a controlled carry-over of light char particles, the CFB will rely on the controlled co-existence of char and sand in the riser, followed by a selective separation of sand (return loop) and char (product). At present, both BFB (e.g. Wellman, University of Hamburg) and CFB (e.g. ENEL, VTT/Ensyn, CRES) are being investigated. The present research also focuses on CFB. Only further comparative studies between both fluidised beds will confirm or contest the tentative status of pyrolysis reactors as presented in Fig. 1. The main advantage of the CFB is the possibility to achieve a short and controllable τ for char. Both its success in coal combustion and minerals' processing, and its general advantages over bubbling fluidised beds have moreover confirmed its technological strength and market potential (Fig. 1).

The paper (i) reviews the kinetics, conversion and modeling; (ii) studies the particle movement and τ in a CFB by PEPT; and (iii) proposes a process design and tentative economics

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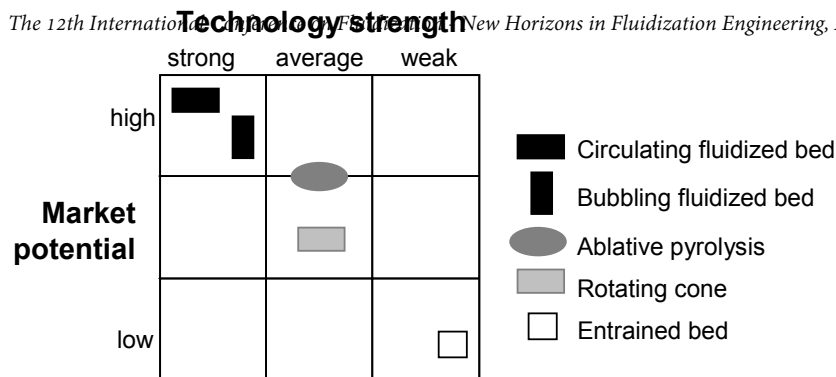


Figure 1. Status of the pyrolysis reactors (5)

KINETICS AND ENDOTHERMICITY

Theory and experiments have been published (6). Differential Scanning Calorimetry (DSC) determines the endothermic heat at 210 (eucalyptus) to 430 kJ kg⁻¹ (sawdust). The kinetics of the pyrolysis are commonly determined by thermogravimetric analysis (TGA). Pyrolysis produces a solid residue or char, i.e. minerals and the organic coking-residue of the biomass, representing 25 to 35 wt%, with the exception of corn (only 10 wt%) and sunflower residue and sludge (40 to 50 wt%). The reaction is of the first order in biomass, with an Arrhenius-dependent reaction rate constant, k . The activation energy (E_a) is function of the biomass type. The pre-exponential factors (A), and thus k , depend on the heating rate, and achieve a maximum value at a heating rate of 100 K/min, where the reaction is kinetically controlled rather than by heat transfer. Such heating rates are easily achieved in a CFB. Values of k at 500 °C (the optimum temperature for pyrolysis) exceed 0.5 s⁻¹ (except poplar and sludge): a high conversion can thus be achieved in short reaction times, limiting side reactions.

CONVERSIONS, BIO-OIL YIELD AND MODELLING

The yield of bio-oil, gas and char is measured in a lab scale batch reactor and in a pilot CFB (Centre for Renewable Energy Sources, CRES), illustrated in Fig. 2. The riser has an I.D. of 80 mm and is 3,8 m high. The bottom bubbling fluidized bed burns the separated char. The char combustion gas is used as fluidization gas in the riser. Dry biomass (< 300 μm) is fed (up to 12 kg/hr) at a height of 1.4 m from the bottom. At start-up, the riser is electrically preheated. A nearly constant temperature is obtained above the biomass injection point.

Both batch and CFB experiments were performed in the same temperature range. Fig. 3 depicts the experimental oil-yields, literature data and model predictions. Despite differences in reactor types, procedures and biomass used, all results show the same yield of bio-oil with a maximum (60 – 65 wt%) around 500°C.

CFB hydrodynamics link the conversion of an individual particle to the overall conversion of all particles (13). The basis of the model (14,15) includes:

- the use of the Waterloo concept (16), with primary and secondary reactions;
- the possibility of suppressing (but never completely avoiding) the secondary reactions by a short and nearly constant residence time for the biomass particles and the vapours;

- the use of small biomass particles in a fast reaction without thermal resistance to/in the particle and progressing according to the continuous reaction model (13);
- the reaction of the individual particle is of 1st order with Arrhenius dependence of k;
- the temperature in the reaction zone is nearly constant and the high heat transfer provides an instantaneous heating of the biomass particles to bed temperature.

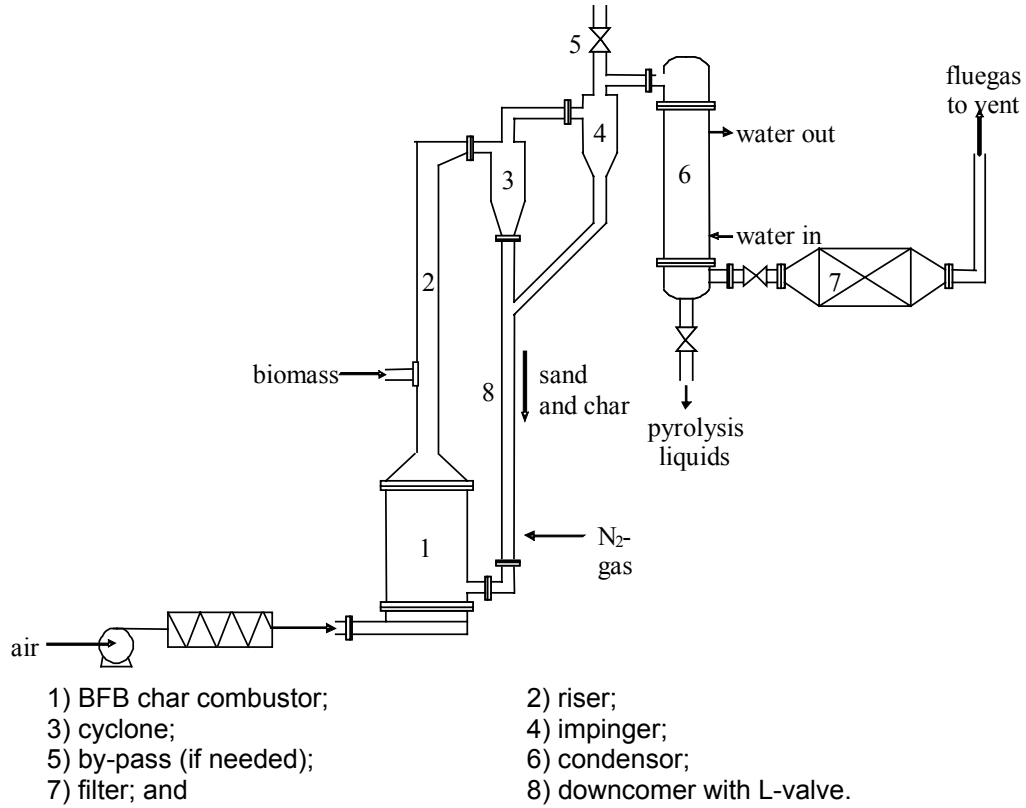


Figure 2. CFB at CRES, Athens

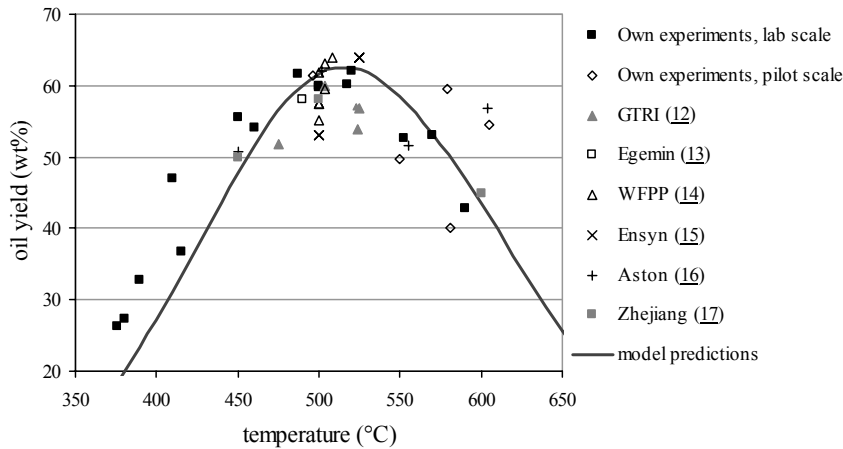


Figure 3. Bio-oil yield, own experiments, literature data and model predictions

A detailed model description, with kinetic rate constants for primary and secondary reactions, has been given in Van de Velden and Baeyens (14,15). As can be seen in Fig. 3, model predictions and experimental data are seen in fair agreement. The critical model parameter is the residence time, τ .

PARTICLE MOVEMENT IN THE RISER OF A CFB

The residence time of the biomass particles in the riser of a CFB reactor depends on the operating fluidization regime. As mentioned before, τ needs to be short and accurately controllable, thus plug flow is the most appropriate working mode: all particles have a nearly constant residence time. In the core/annulus mode on the contrary, extensive (back-) mixing occurs and particles are subject to a wide residence time distribution. Previous studies (17,18) mostly assess operations at moderate values of the solids circulation fluxes ($\leq 100 \text{ kg/m}^2\text{s}$). The present study extends this to $> 600 \text{ kg/m}^2\text{s}$, using Positron Emission Particle Tracking (PEPT, 19) to study the movement and population density of particles in the CFB-riser. The particles used for labeling were sand (90 to 120 μm) and radish seed ($\sim 500 \mu\text{m}$), chosen to represent respectively the behavior of the bed material and a biomass or char particle in the riser. The single particles were labeled using ^{18}F (to 600 to 900 μCi) through surface adsorption and activation (20,21).

A small scale CFB was used of I.D. 46 mm and height of 2 m. The bed material used was rounded sand with a mean diameter of 120 μm and a particle density of 2260 kg/m^3 . Operating conditions varied between 1 and 10 m/s for the superficial gas velocity and between 25 and 622 $\text{kg/m}^2\text{s}$ for the solids circulation flux.

The emitted γ -rays are detected by a positron-camera built by two detectors, each with an active surface area of 0.3 by 0.6 m. The obtained data determine the instantaneous velocity as well as the probability of the tracer being located in specific parts of the equipment domain. Both types of particle show similar results. It is clear that the global hydrodynamics of the system are being determined by the bed material, also due to the very low concentration of biomass tracer.

RESULTS AND DISCUSSIONS

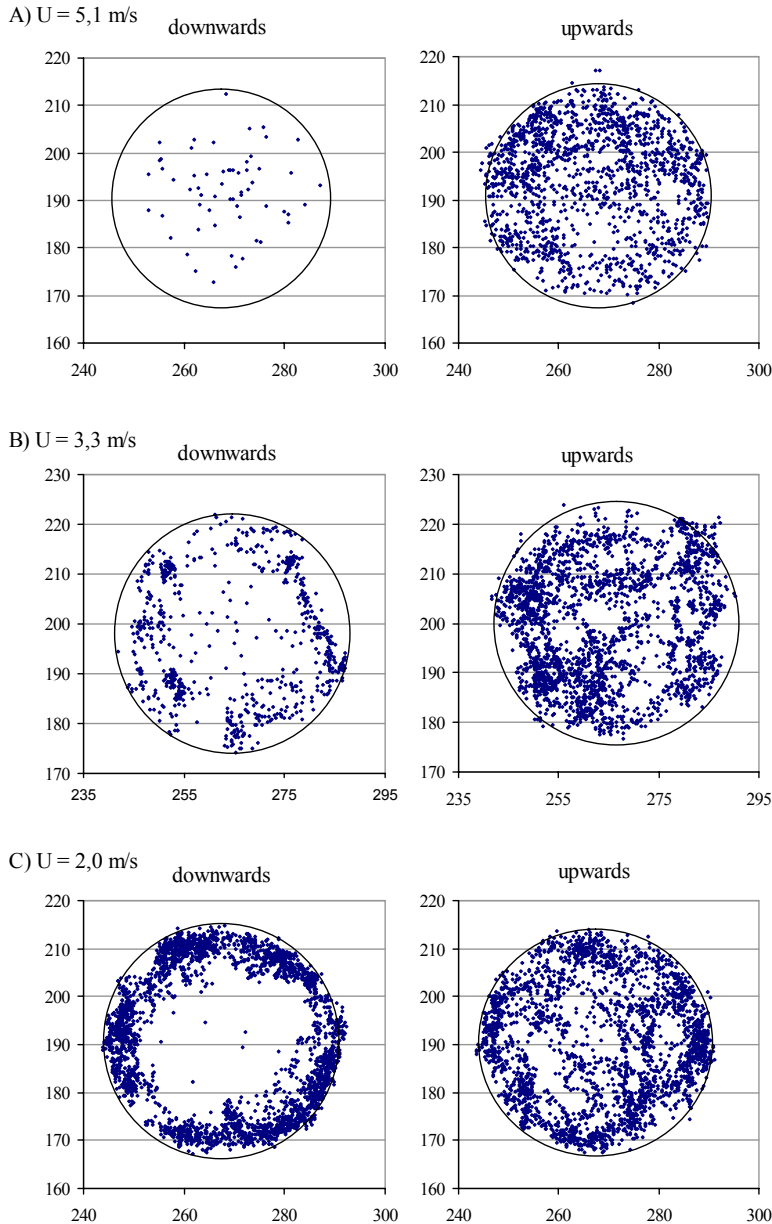
The result of each experiment is a long list in the X-, Y- and Z-locations as function of time. Between successive points, the distance traveled within a given time interval can be calculated. The occurrence of both mixed (up and down) and dominant core flow (up only) is strongly dependent upon combined values of gas superficial velocity and solids circulation rate (Fig. 4). The contour of the riser is also indicated. Data outside this contour are due to the accuracy of 1 to 2 mm of the tracer location through PEPT.

At lower (U,G)-values, no stable circulation in the riser could be obtained and the bed was still behaving in a bubbling or turbulent mode. A minimum superficial gas velocity (the transport velocity, U_{tr}) is needed to operate in the CFB-mode. This was experimentally verified for sand (92 and 120 μm , 2260 kg/m^3) and FCC catalyst (73 μm , 1670 kg/m^3) (22). The equation of Bi and Grace (23) fits the experimental findings. For practical design the predicted velocity is preferably increased by 20% as safety measure (24).

All experimental and literature data of overall particle movement mode are

represented in Fig. 5, which illustrates that it is indicated to:

- operate at gas velocities $U > (U_{tr} + 1)$ m/s and this to guarantee a stable CFB-regime, even at high values of G ;
- operate at a solids circulation flux $G > 200$ kg/m²s for core flow and < 150 kg/m²s if operation in the mixed mode (core/annulus) is required (irrespective of U).



Reactions requiring core flow operation, such as biomass pyrolysis, should be carried out in a riser at $U > (U_{tr} + 1)$ m/s and $G \geq 200$ kg/m²s, while common gas/solid reactions (combustion, calcination...) can advantageously be operated at $U > (U_{tr} + 1)$ m/s and $G \leq 150$ kg/m²s. These limits are related to the small CFB of the research. Reactors of different dimensions and/or using different materials could see these limits altered, although literature values from various scales confirm the proposed values. To study this scaling effect, research in CFB-risers 0.1 to 0.3 m I.D. is ongoing.

Figure 4. Cross-sectional view of the riser with left: downwards moving particles and right: upwards moving particles; at solids circulation flux of 260 kg/m²s. The plots show all the particle locations over the height of the viewed section, integrated over the time of the run.

The particle slip velocity, U_s , is commonly defined as $U_s = U/\epsilon - U_t$ with ϵ the voidage in the riser (≥ 0.98) and U_t the terminal velocity of the particle. Experimental results

have demonstrated that this equation only holds when the core flow mode is fully reached (Fig. 6).

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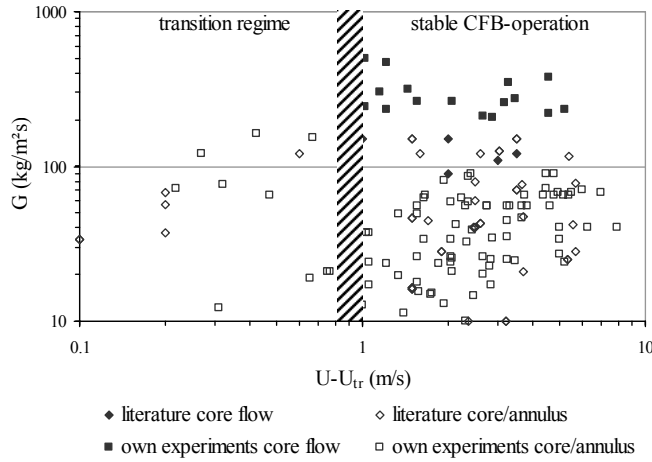


Figure 5. Core flow and core/annulus flow regime in function of G and U-U_{tr}.

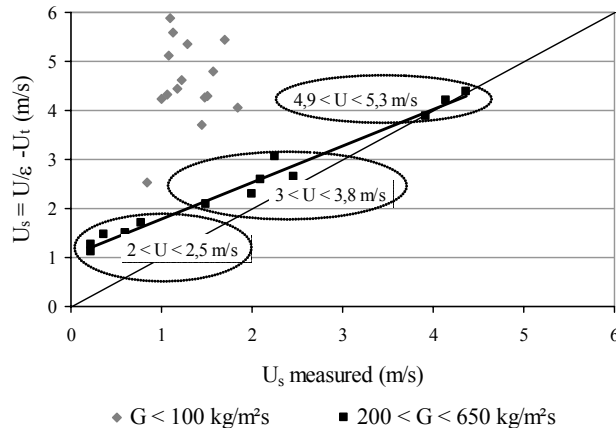


Figure 6. Comparison of theoretical and experimentally measured slip velocity.

For low values of G, U_s is normally a fraction only of the theoretical value. In plug flow, the same conclusion holds at low values of U, but at high superficial gas velocities, as used in commercial risers, the slip velocity can be calculated as U_s ≈ U - U_t, since ε is close to 1.

FINAL REACTOR DESIGN

The main purpose is the determination of the reactor (riser) dimensions required to ensure the desired conversion. The model and reaction kinetics define the required residence time for a required oil-production at a selected operating temperature (normally close to 500 °C). The short residence time (a few seconds only) implies the use of small particles, practically in the range of 100-300 μm, and the conversion to be completed in a single pass through the riser. The operation of the riser is isothermal when fluidization velocity and circulation rate are sufficient. The heat balance (14,15) determines the required heat supply. This heat (heating of biomass and reaction heat) can be supplied by the combustion of the non-condensable pyrolysis gas, which can either indirectly preheat the circulating bed material, or can deliver the heat directly. In both cases, the combustion gas forms the nearly O₂-free

fluidization gas. The indirect heating of the bed material separates the heat transfer and fluidization, which simplifies the process.

The pyrolysis of biomass in a CFB requires a core flow regime to obtain a constant, controllable residence time, achieved for $U > U_{tr} + 1$ (m/s) and $G > 200$ (kg/m²s). Together with the heat balance, these values determine the diameter of the reactor. In the core flow mode, the slip velocity, U_s , can be approximated by $U - U_t$. The required bed height (H) is hence: $H = U_s t$. This design strategy is applied to a 10 MW (bio-oil) reactor, which consumes 3.4 ton/hr of biomass and produces 2 ton/hr of bio-oil. The riser has a diameter of 0.4 m and is 12.5 m high. The circulation rate of bed material (sand) should be 115 ton hr⁻¹ and the gas velocity 5.6 m/s for operation in plug flow with a residence time of 2.5 s. The heat of the process is totally supplied by combustion of the pyrolysis gas, that indirectly preheats the circulating bed material. The combustion gas forms the fluidization gas, together with the pyrolysis gas and vapour. The char (30 MJ/kg) can be recovered. A diagram of the complete process is given in Fig. 7, where three different oil recovery techniques are proposed: indirect condensation, electrostatic precipitation, or combined scrubbing-condensation. The latter is recommended because of the high cost of electrostatic precipitation and the problem of preferential deposition of lignin during indirect condensation, leading to fouling of the heat exchanger surfaces.

An indicative economic evaluation of the process was made (14,15), comparing the price per GJ (heating value of the product) of bio-oil and heavy fuel oil, resp. 16 to 19 MJ/kg and ~ 41 MJ/kg. The required investment was estimated at 4.6 10⁶ €. The annual operating costs vary from 2,5 to 2,7.10⁶ €/yr for an annual production of 16,320 ton bio-oil, i.e. between 153 and 163 €/ton bio-oil, corresponding with an average 8,7 to 9,3 €/GJ. If the char is sold at 46 €/ton (despite its calorific advantage over coal), a reduction of 1 €/GJ is achieved. The current price of heavy fuel oil is 460 €/ton or 11.2 €/GJ. The pyrolytic production of bio-oil is hence economically viable, even with a profit margin of some 20 to 30 %.

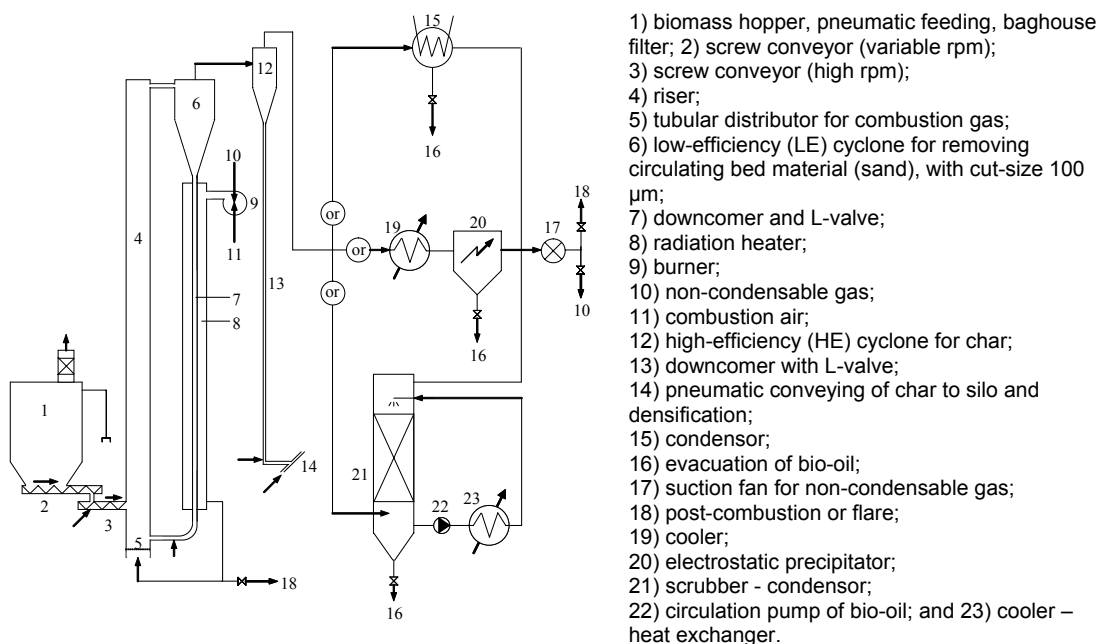


Figure 7. Schematic diagram of the global pyrolysis installation

CONCLUSIONS

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TGA experiments determine the reaction rate (mostly $> 0.5 \text{ s}^{-1}$) and its Arrhenius dependency. Batch and CFB experiments yield between 60 and 65 wt% of bio-oil at $\sim 500 \text{ }^\circ\text{C}$ and very short residence times of the biomass particles. A model predicts the yield of oil, gas and char in function of operating parameters. The residence time of the biomass particles in the riser depends on the fluidization regime. In a plug flow mode, all particles have the required nearly constant residence time. Plug flow is achieved only when $U \geq (U_{tr} + 1) \text{ m/s}$ and $G \geq 200 \text{ kg/m}^2\text{s}$. All findings are used in designing a plug flow CFB for 10 MW (bio-oil) in a riser of 0.4 m I.D. and 12.5 m height. The CFB biomass pyrolysis appears technically and economically viable.

NOMENCLATURE

k	reaction rate constant (s^{-1})		velocity resp. (m/s)
U, U_{tr} , U_s , U_t	superficial gas velocity, transport velocity, particle slip velocity and particle terminal	τ	residence time (s)
		ε	voidage (-)
		G	solids circulation flux ($\text{kg/m}^2\text{s}$)

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