

Operating Parameters for the Circulating Fluidized Bed (CFB) Pyrolysis of Biomass

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Abstract

Fluidized bed fast pyrolysis of biomass is considered as having a high commercial potential for the thermal treatment of biomass and its transformation into mostly liquid hydrocarbons (bio-oil), together with char and gas. The number of pilot research rigs has risen exponentially during the last decade, with applications in circulating fluidized bed (CFB) prevailing over bubbling fluidized bed (BFB). Both BFB and CFB can meet most of the required operating conditions for fast pyrolysis (high heat transfer, small biomass particles...), although the operation of the CFB in plug flow mode is favoured since it can satisfy the extra condition of short and strictly controlled residence time.

Firstly, the kinetics and endothermicity of biomass pyrolysis are determined from extensive TGA and DSC experiments. For most biomass species, the reaction rate constant is $> 0.5 \text{ s}^{-1}$, corresponding with a fast reaction, so the requirement of a short reaction time for a high conversion can be met. Lab scale batch experiments and pilot scale CFB experiments show that an oil yield between 60 and 70 wt% can be achieved at an operating temperature of $510 \pm 10 \text{ }^\circ\text{C}$., thus confirming literature data. Using these kinetic results, a model is thereafter developed and applied to predict the yields of the different products in function of process operation variables (e.g. temperature, residence time). The predictions are in good agreement with the conversion experiments and literature data. Finally, all findings are used and illustrated in a design strategy of a CFB for the pyrolysis of biomass.

Keywords: biomass, pyrolysis, CFB, model, reaction kinetics, design

1. Introduction

Energy from biomass is recognized as the renewable energy source with the highest potential towards sustainable development in the near future (Maniatis *et al.*, 2003; Bridgewater, 2003; Faaij, 2006). Biomass provides already 14% of the world-wide primary energy production (IEA, 2006), but is largely squandered by inefficient use and unsustainable exploitation. To exploit the full potential of this energy source, new approaches and modern technologies are needed.

This paper targets pyrolysis as conversion technology because of its efficient energy production and the important advantage that mainly liquid fuels and solid char are formed, both easy to store and to transport. Pyrolysis oil moreover contains various chemicals with specific high-quality and added-value applications (Bridgewater, 2003). The expectations for pyrolysis in general, and for bio-oil in particular, are hence considerable (Bridgewater, 2003; Faaij, 2006). The alternative, albeit complementary thermochemical conversion technologies are combustion and gasification (Prins, 2005).

The production of bio-oil by pyrolysis is a technology on the edge between development and demonstration. The most important technological issues that remain to be solved, are related to the kinetics, the reaction modelling and the reactor hydrodynamics (Di Blasi, 2005). The study of the basic kinetics, the development of a model and design strategy for CFB biomass pyrolysis are the targets of the present paper, hence making an experimental and theoretical contribution to the development of pyrolysis.

2. Thermal conversion of biomass

Solid biofuels have a low energy density, which limits the commercial applications to locations close to the place of production. One way to solve this problem is the conversion of this feedstock into liquid fuel. These liquids have a higher energy density (Table 1) and are easy to store and transport.

Table 1: Bulk density, mean heating value and energy density of biomass and derived fuels

Energy carrier	Bulk density (kg m ⁻³)	Heating value (GJ t ⁻¹)	Energy density (GJ m ⁻³)
Straw	~ 100	20	2
Sawdust	~ 400	15	8
Pyrolysis oil	~ 1200	17	27
Char	~ 300	30	9

Source: Nan *et al.*, 1994

The two most important methods to convert biomass into liquid fuel are firstly the biochemical conversion by the enzymatic activity of micro-organisms (to e.g. ethanol) and secondly the thermochemical conversion by heat or oxidation. The biochemical conversion requires a feedstock that contains sugars or carbohydrates and a water content in excess of 40%. The thermochemical methods are best suited for dry biomass (moisture content < 10%) that is rich in lignin, since lignin better withstands enzymatic activity and is therefore less suited for biochemical conversion. Mainly wood and agricultural residues are thus appropriate for this thermochemical conversion. Three main routes exist to thermochemically convert biomass into energy: combustion, gasification and pyrolysis (Fig. 1).

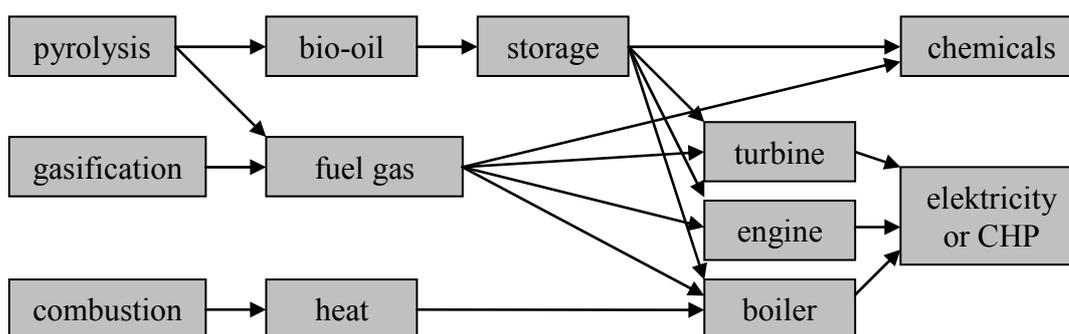


Figure 1: Alternative thermochemical conversions of biomass. Source: Bridgewater, 2003.

Combustion for the generation of heat and/or electricity (via steam) is widely used, but its efficiencies are rather low, and rated at 15% for small plants to 30% for larger and newer plants (Bridgewater, 2003), although combined heat and power (CHP) plants can have efficiencies up to 85%. Only the combustion of waste or residues is today economically feasible, although stack emissions and ash handling remain technical problems. Large scale gasification of biomass has been successfully demonstrated, but it is still relatively expensive in comparison to energy from fossil fuel. Various demonstration units were recently stopped, although gasification is capable of producing power from biomass at competitive price levels on a somewhat longer term. Biomass pre-treatment and tar/char-separation remain technological problems (Faaij, 2006). Biomass gasification will only be able to penetrate the market if it is completely integrated into a bio-energy system.

Pyrolysis is the thermal decomposition in the complete absence of an oxidizing agent (air or oxygen), or with such a limited supply that combustion or gasification do not occur to any appreciable extent. Pyrolytic cracking of biomass yields mainly liquids, together with a solid residue (char) and gas. In comparison to gasification, pyrolysis occurs at relatively low temperatures (673 to 873 K). High temperatures and long residence times promote the formation of gas, while low temperatures and long residence times promote the formation of char. Optimum to produce oils are medium

temperatures and short residence times, and thus high heating rates (Smolders et al., 2006).

This so called fast pyrolysis occurs in seconds only, thus reaction kinetics, phase transitions, heat and mass transfer play important roles. It is therefore critical to subject the biomass particles immediately to the optimum reaction temperature and to limit their exposure to lower temperatures, because this will promote the formation of char. One way to proceed, is to use small particles in a fluidized bed. Another possibility is to transfer the heat very quickly but only to the surface of the particle, as applied in ablative pyrolysis. Mainly vapours and char are produced. It is essential to separate the char from the vapours to prevent side reactions, since char acts as a cracking catalyst for the formed bio-oil. Char is recovered by a gas-solid separation technique (mostly cyclones). After cooling and condensation, a brown, low viscosity liquid is obtained with a heating value about half that of conventional fuels.

To achieve high oil yields the process parameters need to be accurately controlled. These essential parameters include (Bridgewater, 2003; PyNe, 2006):

- a very fast particle heating and heat transfer to the reaction surface;
- a reaction temperature around 773 K and temperatures of the vapour phase of 673 to 723 K;
- short residence times, for vapours less than 2 s;
- a fast char separation and cooling of the vapours, to avoid secondary cracking.

Within the common pyrolysis reactor designs, mostly fluidised beds are applied, operated in either bubbling or circulating mode: these systems can meet the basic requirements to achieve high oil yields i.e. fast heat transfer and fast separation of vapours and char. Only the CFB can meet the requirement of short, controllable residence time. The technological strength and the market attractiveness (Fig. 2) show that the CFB has therefore the highest commercial potential. The expected breakthrough of the CFB is conditioned by a better understanding of the hydrodynamics (flow regimes, residence time) and reaction kinetics of the biomass pyrolysis at different heating rates (Di Blasi, 2005).

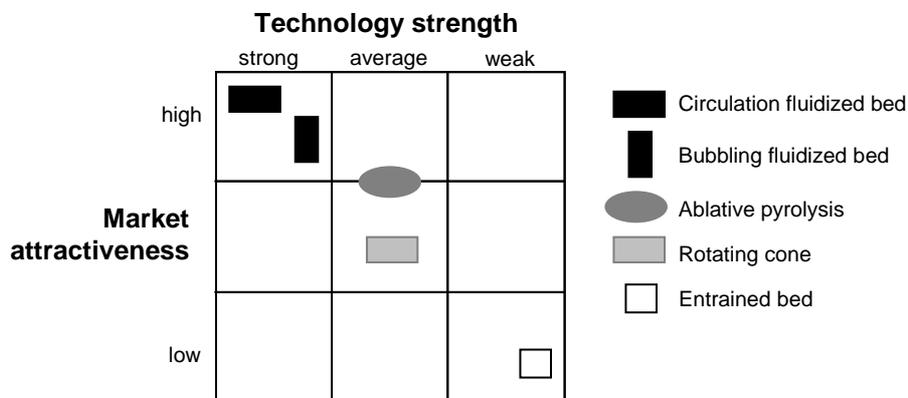


Figure 2: Status of the pyrolysis reactors. Source: PyNe, 2006.

3. Fundamentals of biomass pyrolysis reaction engineering

3.1. The kinetic constants of biomass pyrolysis

The kinetic constants of the pyrolysis of biomass are commonly determined by thermogravimetric analysis. A *Hi-res TGA 2950 Thermogravimetric Analyzer* was used at atmospheric pressure with a nitrogen flow of 50 ml min^{-1} . To meet the reaction heat requirements and to allow the reaction to be kinetically controlled, rather than by heat transfer, all experiments were performed at 100 K min^{-1} , previously determined as the minimal heating rate to accurately measure the kinetics (Van de Velden and Baeyens, 2007). All experiments were repeated at least three times and calculations use the average results, with a standard deviation of maximum 5%. The resulting TGA-profiles plot the weight loss in function of the temperature. They are similar for all the biomass species tested and the extensive theoretical and experimental review has been published by Van de Velden and Baeyens (2007). Essential results are hereafter summarized. The specific biomass species were selected because of previous literature references, or because of their potential in Europe: spruce, pine, poplar, eucalyptus, sawdust, sewage sludge, straw and the non-harvested stalks and leaves of sunflower and corn.

The reported results (Van de Velden and Baeyens, 2007) show that pyrolysis occurs in the temperature range between 473 and 673 K, depending on the type of biomass. This observed temperature range was also found in literature data (Di Blasi, 2005; Reina et al., 1998; Fang et al., 2005).

The pyrolysis reaction also produces a solid residue or char, noticed by a final limited loss of weight per unit of time. This char, consisting of minerals and the organic coking-residue of the biomass represents 25 to 35 wt%, with the exception of corn (only 10 wt%) and sunflower residue and sewage sludge, where the char fraction is significantly higher. The high ash content of sewage sludge is related to its well-known high content of minerals. The results correspond with previous literature data, i.e. 21% char for spruce (Fang et al., 2005), 30% for straw (Fang et al., 2005; Stenseng et al., 2001) and on average between 19 and 26% (Rath et al., 2003).

From the dynamic TGA experiments, it can be seen that the reaction is of the first order in biomass. The reaction rate constant k can hence be determined by Eq. (1) to (3), as used in e.g. Di Blasi (2005), Reina et al. (1998), Antal et al. (1980), Bilbao (1989).

$$dX(t)/dt = k (X_p - X(t)) \quad (1)$$

$$\text{with} \quad X(t) = (m_0 - m(t))/m_0 \quad (2)$$

$$X_p = (m_0 - m_\infty)/m_0 \quad (3)$$

with m_0 : initial weight of biomass (at $t = 0$) (mg)
 m_∞ : residual weight of biomass after the reaction (mg)
 $m(t)$: weight of biomass at time t during the experiment (mg)

As the weight of the sample is continuously registered, X en X_p are known parameters and the reaction rate constant can be derived from Eq. (1) at every moment. Because of the known temperature profiles of the TGA (known $\Delta T/\Delta t$), the reaction rate constant is also known in function of the temperature. The Arrhenius equation can be applied after transformation and plotting of the results as $\ln k$ versus T^{-1} . The activation energy and the pre-exponential factor can be derived from respectively the slope and the intersection of the obtained straight line with the $\ln k$ -axis. Results for e.g. spruce are illustrated in Figure 3.

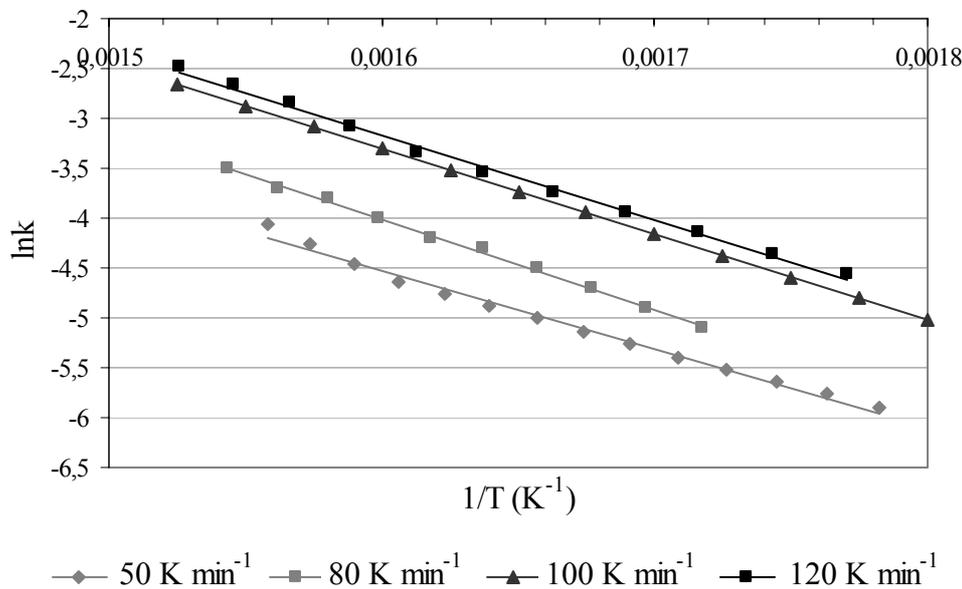


Figure 3: Temperature dependency of the reaction rate of the pyrolysis of spruce at different heating rates.

The activation energy of a specific biomass is nearly constant (and representative for the biomass type) at different heating rates, as can be seen from the parallel $\ln k$ versus T^{-1} lines of Fig. 3. This figure shows however that the pre-exponential factors, and thus the reaction rate constant depend on the heating rate. When the heating rate increases, the pre-exponential factor A (and thus k) increases first quickly to then reach a maximum value: at low heating rates insufficient reaction heat is supplied for the endothermic reaction. A heating rate of 100 K min^{-1} was proven to be sufficient to accurately study the kinetics of most biomass species (Van de Velden and Baeyens, 2007).

From these A and E_a values, the rate constant of the pyrolysis reaction can be calculated at any temperature, and values at 773 K (the optimum T in pyrolysis reactors) are included in Table 2 together with literature data. Literature data should be used with caution: although data for k , A and E_a are given, both the method and procedure used, and the heating rates are generally not included. It is however clear that the E_a values are in the range of those of the biomass components at their respective wt%: 195 to 213 kJ mol⁻¹ for cellulose, 105 to 111 kJ mol⁻¹ for hemicellulose and 34 to 65 kJ mol⁻¹ for lignin (Varhegyi et al., 1997), each present in biomass for around respectively 45, 30 and 25%. Moreover, it should be mentioned that the k values, with the exception of poplar and sludge, exceed 0.5 s⁻¹ corresponding to a fast reaction of the biomass. A high conversion can thus be achieved in short reaction times so that the possible occurrence of side reactions is limited.

Differential Scanning Calorimetry (DSC) experiments (Van de Velden and Baeyens, 2007) determined the endothermic heat requirements to between 280 and 400 kJ kg⁻¹, function of the biomass species.

Table 2: Kinetic constants from own experiments and literature

	Sample	E_a (kJ mol ⁻¹)	A (s ⁻¹) at 100 K min ⁻¹	k (s ⁻¹) at 773 K
Own experiments	Spruce	68.4	$3.47 \cdot 10^4$	0.824
	Eucalyptus	86.4	$1.06 \cdot 10^6$	1.52
	Poplar	54.1	$1.00 \cdot 10^3$	0.219
	Sawdust	75.8	$9.12 \cdot 10^4$	0.684
	Corn	77.0	$2.55 \cdot 10^5$	1.59
	Sun flower	63.9	$2.48 \cdot 10^4$	1.19
	Straw	76.3	$3.16 \cdot 10^5$	2.21
	Sewage sludge	45.3	$8.95 \cdot 10^1$	0.078
Thurner en Mann [11]	Oak	106.5	$2.47 \cdot 10^6$	0.156
Gorton en Knight [12]	Hard wood	89.52	$1.48 \cdot 10^6$	1.31
Nunn <i>et al.</i> [13]	Gumtree, hard wood	69.1	$3.64 \cdot 10^4$	0.775
Reina <i>et al.</i> [10]	Forest wood	95.4	$2.40 \cdot 10^5$	0.0852
Di Blasi and Branca [15]	Beech	95.4	$2.4 \cdot 10^5$	0.156

3.2. Experimental findings on conversion yields

Bio-oil, the main product, is obtained together with char and gas. These by-products can be burnt externally (to dry the biomass, in co-combustion etc.) or in the process, to supply the endothermic reaction heat. Char in itself has a heating value ($\approx 30 \text{ MJ kg}^{-1}$) comparable to petroleum cokes (“petcoke”), and can be valorised externally.

The yield of bio-oil, gas and char is measured by two sets of experiments, i.e. in a lab scale batch reactor, and in the pilot circulating fluidized bed of CRES (Centre for Renewable Energy Sources, Athens).

The pyrex batch reactor (Fig. 4) had a diameter of 25 mm, and a height of 250 mm. A thermocouple (diameter 300 μm , Philips Thermocoax) protruded into the biomass sample from the bottom of the reactor. An electrical heating (5 kW) surrounded the reactor and made it possible to quickly heat the reactor to temperatures of maximum 600°C. The whole set-up was thermally insulated.

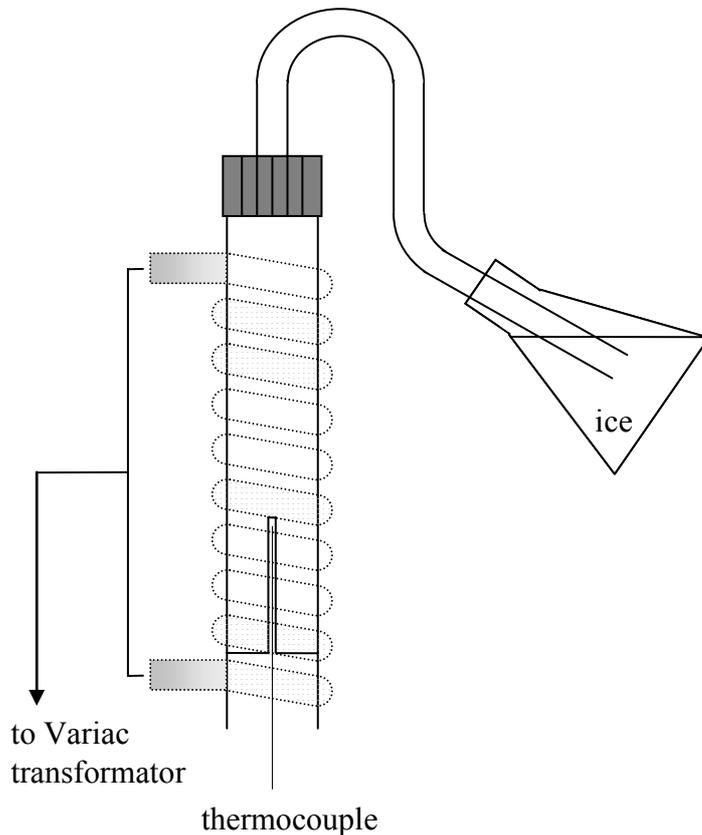


Figure 4: Batch reactor for measuring biomass conversions

The reactor is preheated to between 200 and 300°C, function of the tested biomass. A small amount of biomass ($\sim 2 \text{ g}$) was introduced and the reactor was then sealed and heated to the required temperature until the reaction was completed. The formed gasses and vapour escaped via the exhaust pipe and were lead in melting ice. The

formed vapour condense. The char remains in the reactor and the gasses are discharged to the atmosphere. The weight of the ice and of the reactor were measured before and after the reaction. Despite purging the reactor, a small amount of oxygen will be present: partial combustion can take place, which lowers the oil yield to a limited extent, as compared to the yield obtained in an oxygen free environment.

The oil yield can be calculated from the weight differences of each part of the set-up before and after the reaction. Every run at a certain temperature was repeated three times and mean results were processed.

The circulating fluidized bed of CRES is illustrated in Fig. 5. The riser (2) has an internal diameter of 80 mm and is 3,8 m high. At the bottom a bubbling fluidized bed (1) burns the formed and separated char. The char combustion gas is used as fluidization gas in the riser. Dry biomass ($< 300 \mu\text{m}$) is fed (up to 12 kg hr^{-1}) at a height of 1.4 m from the bottom. At start-up, the riser was electrically preheated. After the cyclone (3) the gas and vapors are further dedusted in an impingement separator (4) and the pyrolysis oil is condensed. The condenser (6), of shell-and-tube construction, is cooled with water (at 20°C). The residual gas flow is filtered (7) and emitted to the atmosphere. The by-pass (5) is only used in case of operational problems. The downcomer (8) recycles the bed material (sand) and the char via an L-valve to the char combustor.

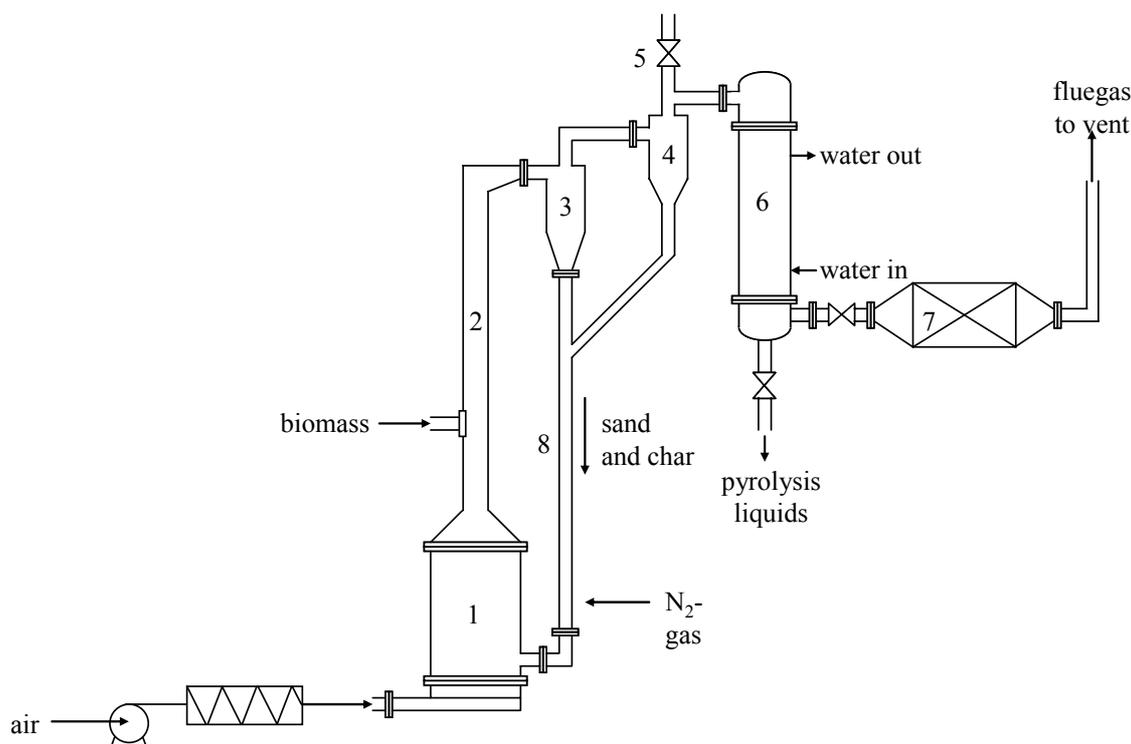


Figure 5: Construction of the CFB for the pyrolysis of biomass at CRES, with 1) BFB char combustor; 2) riser; 3) cyclone; 4) impingement chamber; 5) by-pass; 6) condenser; 7) filter; and 8) downcomer

The temperature profile of Figure 6 illustrates the nearly constant temperature obtained above the biomass injection point.

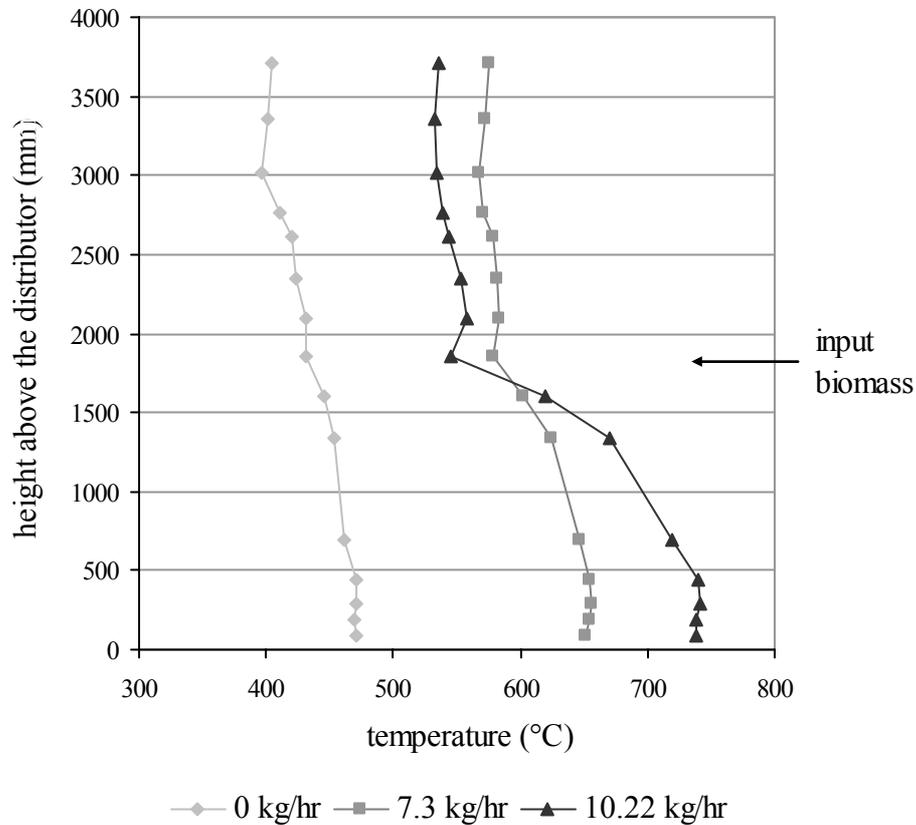
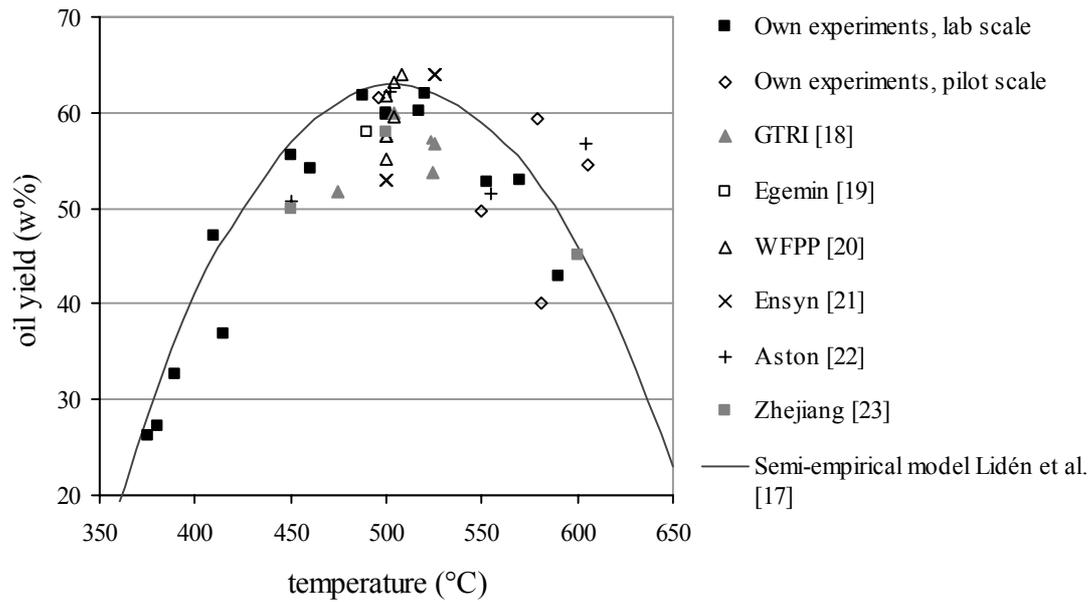


Figure 6: Temperature profile in the riser of the CFB at CRES

Both batch and CFB experiments were performed in the same temperature range. A maximum oil yield was obtained at approx. 510°C. Pilot scale experiments show a considerable scatter due to the residence time distribution of the biomass, measurement inaccuracies by the volumetric feeding of the biomass and others. Fig. 7 compares these yields to the semi-empirical model of Lidén *et al.* (1988) and to literature data, which show the same trend and the same yield of bio-oil with a maximum around 500°C and this despite the fundamental differences in reactor types, operational procedures and biomass feedstock.



researchers	Reference	pyrolysis reactor	biomass	Temperature range (°C)	Oil yields (wt%)
GTRI	Knight et al., 1984	Downdraft fixed bed	oak	475 - 525	51.8 - 60
Egemin	Maniatis et al., 1993	Entrained flow	saw dust	490	58
WFPP	Reina et al. 1998	BFB	spruce, maple, poplar	500 - 508	57.5 - 63.9
Ensyn	Graham et al., 1994	Downdraft fixed bed	cellulose, poplar, maple, lignin	500 - 525	54 - 62
		BFB	cellulose, poplar, maple, lignin	500 - 525	53 - 64
Aston University	Peacocke and Bridgewater, 1995	Ablative pyrolysis	unspecified wood	450 - 604	50.8 - 62.1
Zhejiang University	Luo et al., 2005	BFB	unspecified wood	450 - 600	45 - 58

Figure 7: Bio-oil yield, own experiments and literature data

4. Modelling approach

4.1. The fundamentals of the modelling approach

The literature widely adopts the Waterloo concept (Fig. 8), in its elementary (only primary reactions) or its more complex form (including secondary cracking of the produced bio-oil). Hydrodynamic parameters (fluidization regime, average residence time) link the conversion of an individual particle to a global conversion of all particles (Kunii and Levenspiel, 1991).

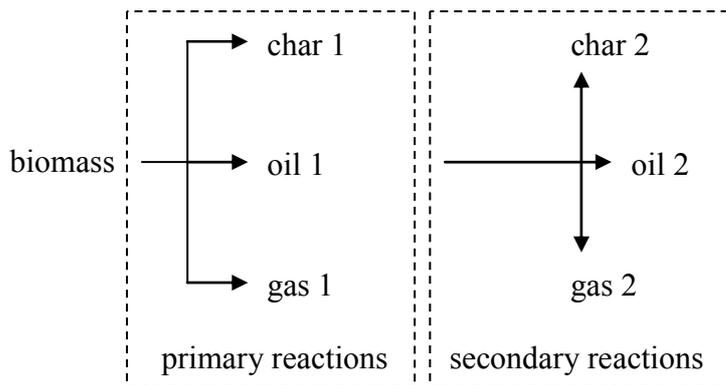


Figure 8: The biomass pyrolysis concept of the University of Waterloo. Source: Radlein *et al.*, 1991.

In a CFB small particles are used, where internal thermal effects are negligible. The reaction follows the continuous reaction model (Kunii and Levenspiel, 1991) and the reaction time can be controlled accurately by working in plug flow regime, which assures a uniform residence time of all particles. A comparison with fixed bed reactors (large biomass particles, thermally processed during a long time) or bubbling fluidized beds (medium size particles, in a perfectly mixed regime) is therefore out of question.

For the fixed bed reactors, which process large particles, the shrinking core mechanism (Kunii and Levenspiel, 1991) can be adopted. Most models represent the fixed bed as a continuous porous phase but they differ in complexity by their one or two dimensional approach, by including or omitting thermal gradients in the particles and turbulence in the reactor, by possibly including particle fracture, etc. (Yang *et al.*, 1995; Klose and Wiest, 1999; Peters *et al.*, 2003; Ravi *et al.*, 2004; Di Blasi *et al.*, 2004).

Bubbling fluidized beds are theoretically modelled by Gerhauser and Bridgwater (2003). Important conclusions are the interaction between the hydrodynamics and the occurring reactions, as well as the influence of the residence time and temperature on the secondary conversion of the vapour phase and thus on the bio-oil production.

The CFB reactor is only recently seen a topper in pyrolysis reactors and no references were found for their modelling. This paper is a first contribution.

The most important assumptions of this modelling approach were experimentally validated (Van de Velden and Baeyens, 2007; Van de Velden *et al.*, 2006; Van de Velden, 2006). These assumptions include:

- the use of the Waterloo concept, 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 implies a fast reaction without appreciable thermal resistances for heat transfer to and in the particle and with a reaction mechanism following the continuous reaction model;
- the kinetics of the individual particle follow a first order conversion and the Arrhenius expression;
- the temperature in the reaction zone is nearly constant and the high heat transfer coefficient provides an instantaneous heating of the biomass particles to bed temperature, even at the feeding point of the cold biomass

4.2. Model equations

The Waterloo concept (Radlein et al., 1991) for the pyrolysis of biomass represents the reaction as a two stage mechanism: the first (primary) reactions cause the formation of char, gas and bio-oil, the secondary reactions convert part of the bio-oil into an additional amount of gas and char. These secondary reactions are much slower than the primary reactions, which makes it possible to suppress these side reactions by the separation of the bio-oil and the char (char acts as a catalyst for the cracking of the bio-oil) and by limiting the residence time in the reaction zone to a few seconds only.

TGA experiments however demonstrate that the secondary formation of char does not occur, but that it on the contrary decomposes further albeit by a negligible amount. The secondary char formation was thus not considered. The secondary formation of gas from the bio-oil vapors however does occur and needs to be accounted for.

For the fast pyrolysis, two empirical equations have been presented: Eq. (4) by Lidén et al., 1988 and Eq. (5) by Samolada and Vasalos (1991).

$$CY = 0,542 + 0,215 CT - 0,956 CT^2 \quad (4)$$

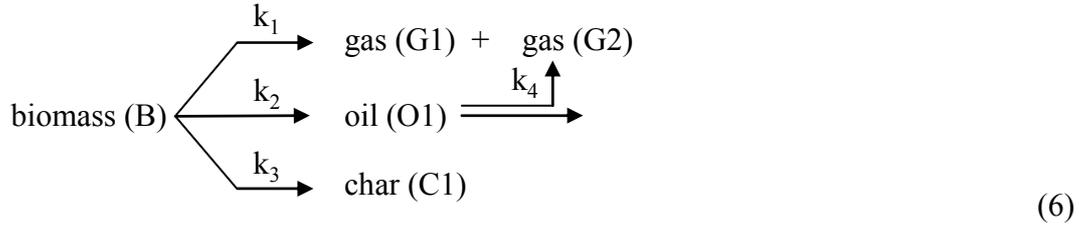
with CY: centered yield: $CY = 0,2$ (yield - 60)
 CT: centered temperature: $CT = 0,02$ (temperature - 500)

$$\text{Yield of bio-oil (in \% on dry weight)} = 55,19 - 11,5 P - 21,69 P^2 \quad (5)$$

with P: dimensionless pyrolysis temperature: $P = (T-560)/160$
 (T: pyrolysis temperature in °C)

These equations are a mere fitting of experimental results and thus coupled to specific working conditions, such as residence time, fluidization regime in the reactor etc., they do not have any theoretical background and do not account for the occurring mechanisms. The application of such equations for the design of reactors is therefore not recommended. The development of design equations with a fundamental basis is required and is discussed below.

The conversion equations used for modeling the biomass pyrolysis are represented in Eq. (6), where G1, O1 and C1 are primary and G2 and O2 secondary products. As already mentioned, the secondary formation of char is neglected.



The expression of these conversions in rate equations with the given rate constants is represented in mass fractions (equations 7a-d), being the mass of products ($m_i(t)$) at each moment divided by the initial amount of biomass ($m_B(0)$).

$$\frac{dm_B(t)}{dt} = -(k_1 + k_2 + k_3)m_B(t) = -k m_B(t) \quad (7.a)$$

$$\frac{dm_G(t)}{dt} = k_1 m_B(t) + k_4 m_O(t) \quad (7.b)$$

$$\frac{dm_O(t)}{dt} = k_2 m_B(t) - k_4 m_O(t) \quad (7.c)$$

$$\frac{dm_C(t)}{dt} = k_3 m_B(t) \quad (7.d)$$

At $t = 0$, $m_G(0) = 0$, $m_O(0) = 0$ en $m_C(0) = 0$, so the solutions of the above rate equations is given by equations 8a-d.

$$m_B(t) = \exp(-kt) \quad (8.a)$$

$$m_G(t) = -k(k-k_4)^{-1} (kk_1 \exp(-kt) - k_1 k_4 \exp(-kt) - k_2 k_4 \exp(-kt) - kk_2 \exp(-k_4 t) - kk_1 + k_1 k_4 - kk_2 + k_2 k_4) \quad (8.b)$$

$$m_O(t) = -k_2 (k - k_4)^{-1} \exp(-k_4 t) (\exp(-t(k - k_4)) - 1) \quad (8.c)$$

$$m_C(t) = k_3 k^{-1} (1 - \exp(-kt)) \quad (8.d)$$

The fractions of formed bio-oil, gas and char can be calculated with the above equations on the condition that the five kinetic constants (k , k_1 , k_2 , k_3 , k_4) are known. The global reaction constant k is known from the TGA experiments and is the sum of the three primary reaction rate constants (Eq. 9).

$$k = k_1 + k_2 + k_3 \quad (9)$$

In addition a relation exists between the three primary reaction constants (Eq. 10), because the amount of char after the completion of the pyrolysis reaction remains nearly constant ($m_{C,\infty}$).

$$k_3 = \frac{m_{C,\infty}}{1 - m_{C,\infty}} (k_1 + k_2) \quad (10)$$

Since equations (9) and (10) allow two kinetic constants to be determined, two unknown reaction rate constants (k_1 en k_4) need to be calculated. Extensive research in this primary and secondary pyrolysis gas formation was done by Di Blasi (2005), who represented these constants on average as:

$$k_1 = 14\,300 \exp\left(-106\,500/RT\right) \quad (11)$$

$$k_4 = 7\,900 \exp\left(-81\,000/RT\right) \quad (12)$$

with R: gas constant (8,31 J mol⁻¹K⁻¹)
 T: temperature (K)
 k_i: reaction rate constant (s⁻¹)

Having defined the kinetic constants, the remaining model parameter is the residence time, t . This residence time of the biomass particles in the riser of a CFB reactor depends on the operating fluidization regime. As already mentioned above, the residence time needs to be short and accurately controllable, so that plug flow is the most appropriate working mode. In a plug flow mode, all particles have a nearly constant residence time, which is therefore used in Eqns. (8).

The behavior of biomass particles in the riser of a CFB was extensively studied both by biomass tracer pulse injection method and analysis of the residence time distribution, and by positron emission particle tracking of a radioactively labeled biomass particle in the riser. Detailed results are presented elsewhere (Van de Velden et al., 2006; Van de Velden, 2006). Operation in plug flow mode is achieved only when gas velocity (U), and solid circulation rate (G) exceed minimum values, i.e.

$U \geq (U_{tr} + 1) \text{ m s}^{-1}$ and $G \geq 200 \text{ kg m}^{-2}\text{s}^{-1}$, with U_{tr} the onset velocity of the CFB-regime (best determined by Bi and Grace (Van de Velden et al., 2006; Van de Velden, 2006).

In plug flow, the overall conversion is equal to the conversion of the individual particle and depends on the residence time, and thus on the chosen gas velocity and particle circulation rate in the CFB. When a conversion of 90 to 95% is to be achieved with an average overall reaction rate constant of 1 s⁻¹, the required residence time is 2.5 s.

4.3. Model predictions

Equations 8a-d predict the amount of oil, gas and char formed, as well as the mass loss of the original biomass. The obtained result is illustrated as an example for spruce (with a residence time of 2.5 s) in Fig. 9. For other kinds of biomass, a similar trend is predicted. The relevant results for all types of biomass tested are represented in Table 3, and given as the oil yield at different temperatures and at the temperature of optimum yield.

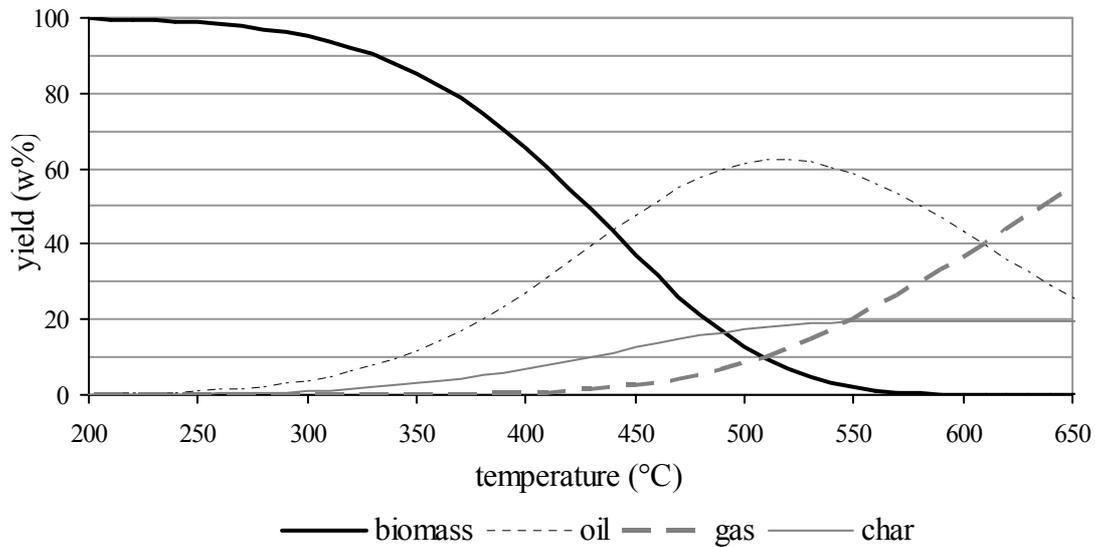


Figure 9: Model predictions of converted spruce and formed products

Table 3: Relevant model predictions for various types of biomass

	Optimum temperature (°C)	Oil yield (w%), at			
		optimum	400°C	500°C	600°C
spruce	520	62.5	27.1	61.6	43.4
eucalyptus	480	71.2	46.5	70.1	55.0
saw dust	490	74.7	47.7	74.5	59.2
corn	510	55.8	29.1	55.9	46.2
sun flower	420	59.2	58.8	56.3	45.4
straw	490	65.8	42.3	65.4	51.5

The predicted results show that the optimum temperature for fast pyrolysis lies between 420 to 520°C. At higher temperatures, more gas is produced by secondary reactions. To verify the model with experimental values, the predicted formation of oil is compared with the experimental conversion results (Fig. 10). The shape and the position of the curve, with optimum about 500°C is similar. The oil yields found in literature also lie around the model predictions (Fig. 10), despite the fact that often the essential parameters of particle size and residence time are not given. However, at lower temperatures, the experimental oil yield exceeds the predicted values, which is caused by the use of Equation (10), where the equilibrium char (at $t = \infty$) is an overestimation of the char at time t , so that the predicted yield of bio-oil is lower than the measured value. Practically, the reactor will be operated around the optimum temperature, which makes this deviation unimportant in reactor design.

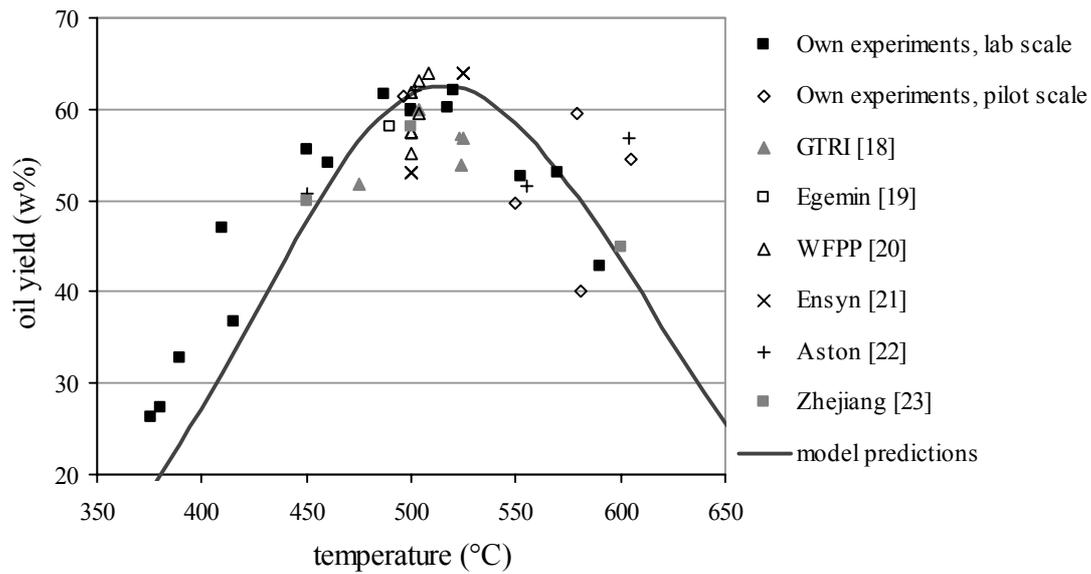


Figure 10: Comparison of experimental, predicted and literature oil yields

4.4. Sensitivity analysis

To evaluate the sensitivity of the model predictions to possible measurement errors, the influence of small variations in residence time, overall reaction rate constant (k) and particle size was investigated.

The influence of the residence time is limited, although the optimal temperature decreases when residence times increase (Fig. 11). This is expected since for a certain conversion X , with $1-X = \exp(-kt)$, the product kt is constant, so k and t vary inversely. The influence of the temperature then follows from the Arrhenius law.

When the reaction rate constant k is varied by $\pm 10\%$, the optimum temperature remains constant, but the oil yield increases for faster reactions with constant residence time (Fig. 12). The conversion indeed increases when k increases for a constant t .

When larger biomass particles are processed (e.g. $d_p = 5$ mm), the heat penetration has to be taken into account, and the overall reaction rate constant becomes a function of the combined resistance:

$$1/k_{hp} + 1/k_r = 1/k \quad (13)$$

with k_r the real reaction rate constant (s^{-1})
 k_{hp} the rate of heat penetration (s^{-1}) = $h a_m / c_p$ (with h : the heat transfer coefficient in the reactor ($W m^{-2}K^{-1}$), a_m : the specific surface of the particle (m^2kg^{-1}), and c_p : the specific heat of the particle ($J kg^{-1}K^{-1}$))

With $k_{hp} = 1,2 s^{-1}$, the global reaction rate constant k becomes 0,5 instead of 0,8 s^{-1} (Equation 13), and so the oil yield decreases considerably (Fig. 13). It is obvious that larger biomass particles do not meet the optimum conditions for fast CFB-pyrolysis, due to the additional resistance of heat transfer and penetration. Pyrolysis occurs more slowly and produces less bio-oil and more char.

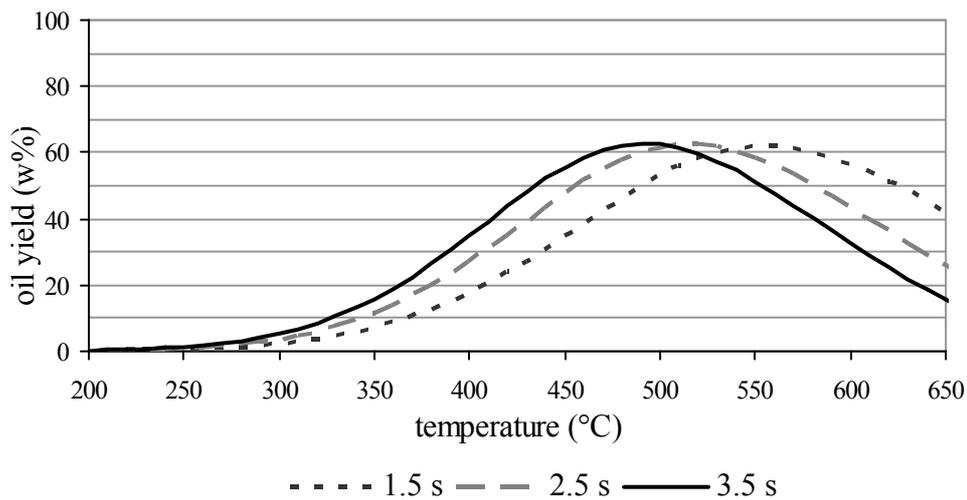


Figure 11: Influence of the residence time on oil yield

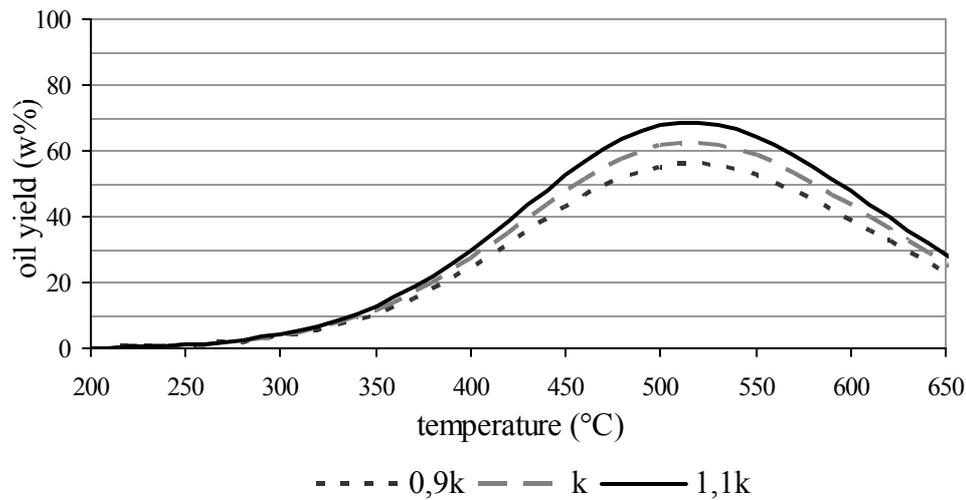


Figure 12: Influence of reaction rate constant on model predictions

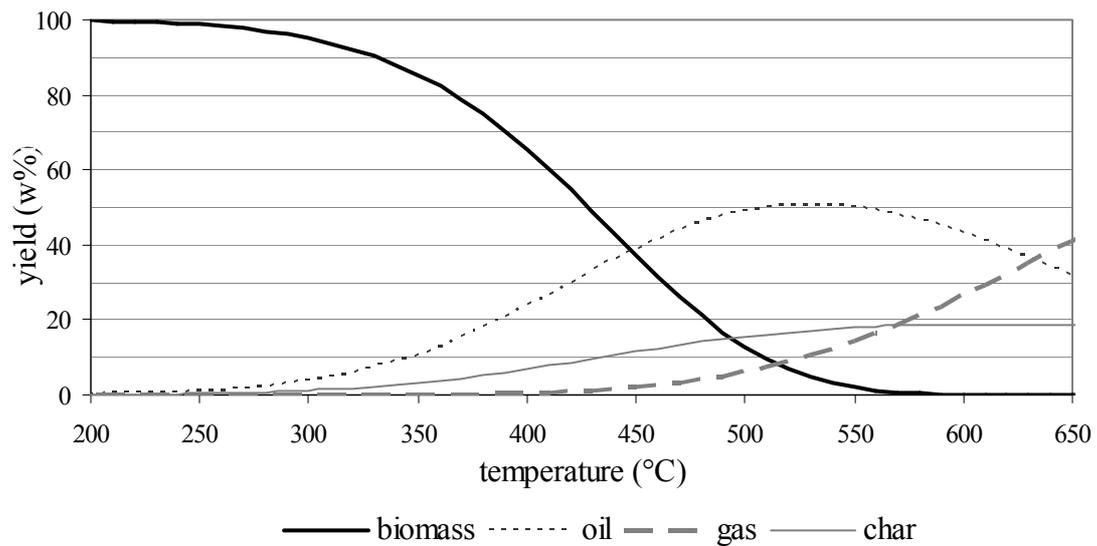


Figure 13: Influence of particle size: model predictions for $d_p = 5\text{mm}$

4.5. Final reactor design recommendations

The design of a biomass pyrolysis CFB is hereafter discussed. Since the components of the recycle loop (cyclone, downcomer, L-valve) use known techniques, the main purpose is the determination of the reactor (riser) dimensions required to ensure the desired conversion. Fig. 14 reviews the essential steps of this design.

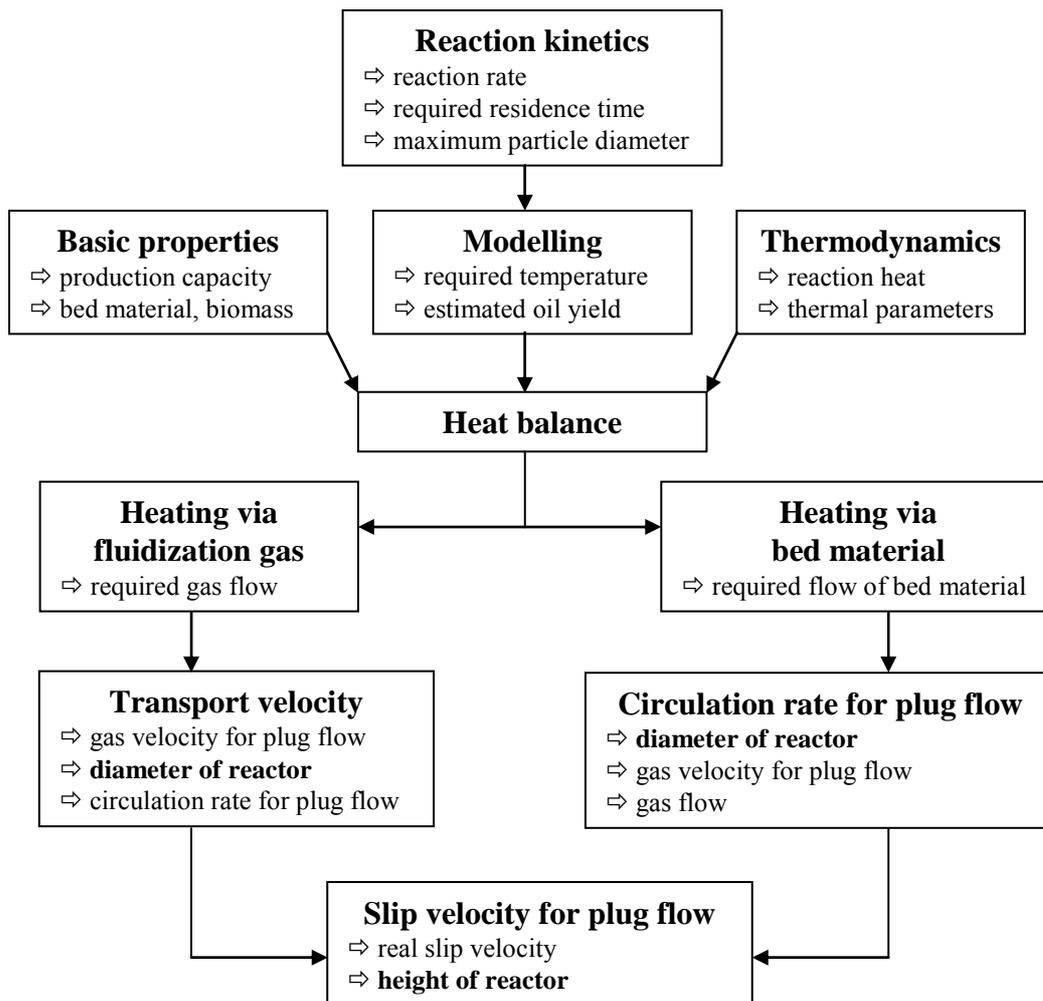


Figure 14: Proposed design strategy for pyrolysis in a CFB

The proposed model and reaction kinetics fix the required residence time for a required oil-production at a selected operating temperature (nomally close to 500 °C). The residence time needs to be very short (a few seconds only) to ensure fast pyrolysis, so the particles need to be small. This short residence time can be realized in one passage through the riser, so only recirculation of bed material is needed and the residence time will directly determine the height of the column. The operation of the riser is isothermal when fluidization velocity and circulation rate are sufficient. Physical and thermodynamic parameters define the heat balance (Van de Velden et al., 2006), which determines the required heat supply and transfer. This heat (heating of biomass and reaction heat) can be supplied by the combustion of the non-condensable pyrolysis gas, which can either preheat the circulating bed material, or the flue gas can deliver the heat directly. In both cases, the flue gas forms the oxygen free fluidization gas. The heating of the bed material has the advantage of separating the heat transfer and fluidization, which simplifies the process.

As was previously discussed, the pyrolysis of biomass in a CFB requires a plug flow regime to obtain a constant, controllable residence time. Plug flow can only be realised when the particle flux is high enough ($>200 \text{ kg m}^{-2}\text{s}^{-1}$) and when the gas velocity exceeds the transport velocity with minimum 1 m s^{-1} . Together with the heat balance, these requirements determine the diameter of the reactor. In the plug flow mode, the slip velocity, U_s , can be approximated by $U - U_t$ with U_t the terminal velocity of particles used as bulk bed material. 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^{-1} of biomass and produces 2 ton hr^{-1} of bio-oil. The riser of the CFB then 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^{-1} to ensure an operation in plug flow mode with a residence time of 2.5 s. The heat of the process can be supplied entirely by combustion of the pyrolysis gas and is done by preheating the circulating bed material so fluidization and heating are completely separated. The flue gas of the combustion forms the fluidization gas, together with the formed gas and vapors in the reactor. All the formed char can be valorized externally. This char has a heating value of $\pm 30 \text{ MJ kg}^{-1}$ (higher than coal) and can be used in the same way as petcoke, in e.g. co-combustion. A diagram of the complete process is given in Fig. 15, where three different oil recovery techniques are proposed: simple 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 condensation, leading to fouling of the heat exchanger surfaces.

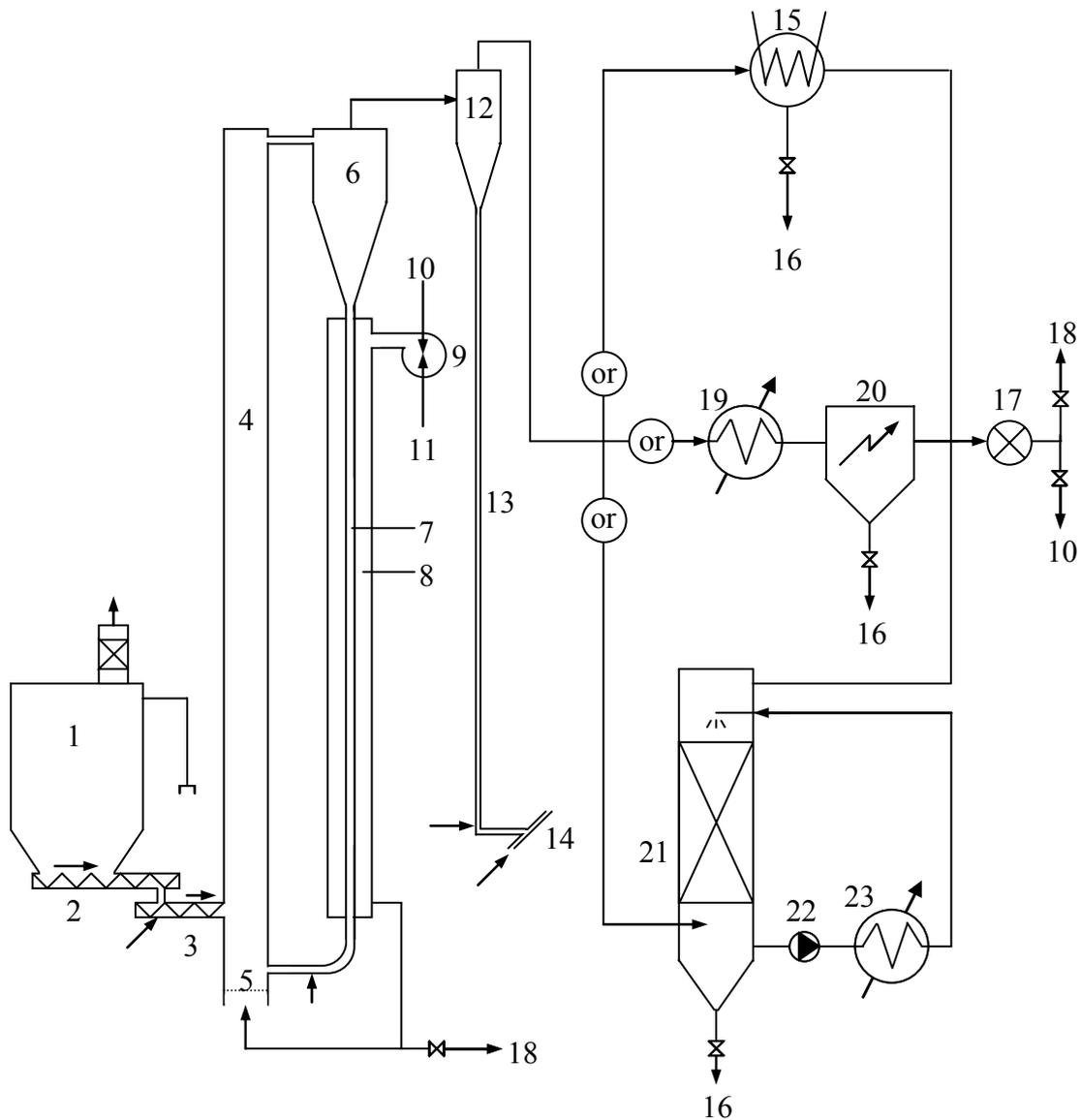


Figure 15: Schematic diagram of the global pyrolysis installation with 1) biomass hopper with pneumatic feeding and baghouse filter; 2) screw conveyor (variable rpm); 3) screw conveyor (high rpm); 4) riser; 5) tubular distributor for combustion gas; 6) low-efficiency (LE) cyclone for removing circulating bed material (sand), with cut-size 100 μm ; 7) downcomer and L-valve; 8) radiation heater; 9) burner; 10) non-condensable gas; 11) combustion air; 12) high-efficiency (HE) cyclone for char; 13) downcomer with L-valve; 14) pneumatic conveying of char to silo and densification; 15) condenser; 16) evacuation of bio-oil; 17) suction fan for non-condensable gas; 18) post-combustion chamber or flare; 19) cooler; 20) electrostatic precipitator; 21) scrubber - condenser; 22) circulation pump of bio-oil; and 23) cooler - heat exchanger.

An indicative economic evaluation of the pyrolysis process was made (Van de Velden et al., 2006), comparing the price per GJ (heating value of the product) of bio-oil and heavy fuel oil: the heating value of bio-oil is 16 to 19 MJ kg⁻¹, while that of fuel oil is ~ 41 MJ kg⁻¹. The required investment was estimated at 4.6 10⁶ € from Brammer et al. (2005). The annual operating costs vary from 2,5 to 2,7.10⁶ € yr⁻¹ for an annual production of 16 320 ton bio-oil, i.e. between 153 and 163 € ton⁻¹ bio-oil. For an average heating value of bio-oil, the costs are between 8,7 and 9,3 € GJ⁻¹. If the char is sold at 46 € ton⁻¹ (despite its calorific advantage over coal), a reduction of 1 € GJ⁻¹ is achieved. The current price of heavy fuel oil is 460 € ton⁻¹ or 11.2 € GJ⁻¹. The pyrolytic production of bio-oil is hence certainly economically viable, even allowing a profit margin of some 20 to 30 %.

5. Conclusions

TGA experiments on a wide variety of biomass particles determine the reaction kinetics and its Arrhenius dependency. For most of the biomass species, the reaction rate constant is > 0.5 s⁻¹, corresponding with a fast reaction. These results tie in with literature data, although the reader is cautioned in the use of literature data since experiments were often performed at non-representative testing conditions.

Lab scale batch experiments and pilot scale CFB experiments, show that fast pyrolysis can produce between 60 and 70 wt% of bio-oil at an operating temperature of 510 ± 10°C, confirming literature data obtained for different reactor types, operational procedures and biomass feedstock.

A model is proposed to predict the yield of oil, gas and char in function of operating parameters. Applying the model predicts oil yields that are in good agreement with own experimental and literature data. The model can be used in a CFB design strategy to predict the oil yield. The findings are finally applied to the design of a 10 MW (bio-oil) CFB which results in a riser of 0.4 m I.D. and 12.5 m height. Biomass pyrolysis in a CFB reactor is concluded to be technically and economically feasible.

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