

Biomass Pyrolysis in a Fluidized Bed Reactor. Part 1: Literature Review and Model Simulations

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The literature on biomass pyrolysis regarding kinetics, models (single particle and reactor), and experimental results is reviewed from an engineering point of view. Predictions of existing single particle models derived from a detailed description of the transport phenomena and literature data on measured intrinsic chemical kinetics are presented. The main conclusions from the literature and modeling studies can be summarized as follows: (1) the available knowledge on kinetics and transport phenomena has not been integrated properly for reactor design, (2) complex two-dimensional single particle models do not provide more accurate, or otherwise better, information for engineering calculations than do the simple one-dimensional models, and (3) single particle models predict (for all available kinetics) that the influence of the particle size on the liquid yield is limited. This effect can be explained with the effective pyrolysis temperature, a parameter that represents the particle's average temperature at which the conversion is essentially taking place.

1. Introduction

Biomass is becoming increasingly important as a renewable source. Fast pyrolysis is one of the possible technologies facilitating the fuelling of biomass into a wide variety of energy production installations. It is a high temperature (ca. 500 °C) process in which biomass is rapidly converted, in the absence of oxygen, to vapors, gases, and charcoal. After cooling and condensation, a dark brown liquid is formed that is often called bio-oil. The process is optimized toward maximal bio-oil production. Apart from direct combustion in boilers or prime movers for the production of heat, shaft power, or electricity, bio-oil is also considered for upgrading to blending components for transportation fuel through either hydrogenation^{1,2} or gasification followed by Fischer–Tropsch or methanol synthesis.^{3–7}

From pyrolysis handbooks and overview papers,^{8–15} it is learned that for optimal fast pyrolysis in terms of liquid yield, the temperature required is approximately 500 °C, the biomass particle size should be small (≤ 2 mm), and the produced vapors should be separated from the char and condensed immediately to prevent secondary cracking to gaseous products.

The last two statements are insufficiently supported by theoretical or experimental evidence. In some cases, even contradictory experimental findings have been reported in the literature. These statements are, however, crucial for reactor and process design. For instance, a reevaluation of the most suitable reactor configuration would be required if larger biomass particles could be used. Moreover, it is insufficiently recognized that the process temperature for a maximum liquid yield may differ from the one for a specific bio-oil quality.

This research includes two separate parts. Part I is concerned with a literature review and modeling stud-

ies, while part II¹⁶ contains the experimental validation of model results. It is meant to study fast pyrolysis in fluid beds and to clarify the reference points for reactor design. Although the research is dealing mainly with pyrolysis in a fluidized bed, application of the results presented is not restricted to it. The fluid bed experiments reported in part II are representative for pyrolysis carried out under known and spatially isotherm external conditions, and high heat transfer rates to the particle. Apart from fluidized beds, those conditions prevail in many other reactor types such as a circulating fluid bed, a transported bed reactor, a rotating cone, or a cyclonic reactor. Fixed bed type reactors, screw reactors, and ablative reactors are, however, of a different nature.¹⁷

The behavior of the individual biomass particles inside the reactor is important for the design of a pyrolysis reactor. Parameters such as the conversion time (reaction rate), the time-averaged bio-oil yield and quality, and the particles' residence time and spatial distribution are essential. They are determined by the feedstock type and dimensions, as well as by the prevailing reactor conditions (e.g., the external heat transfer coefficient). The conversion time and the time-averaged yields can be predicted with single particle pyrolysis models. Once the particles' devolatilization rate is known, the required hold-up of reacting particles (ranging from fresh biomass to charcoal) in the reactor can be calculated for a certain biomass throughput. The required hold-up of reacting particles determines, among others, the volume of the reactor. Knowledge of the product selectivity observed for single particles, data on secondary cracking of the vapor products, the overall mixing state of the gas phase, and the char hold-up (tar cracking) are all required to determine the optimal process temperature for a maximum bio-oil yield and/or a desired bio-oil quality.

In part I (this paper), the literature on biomass pyrolysis concerned with experimental results, in particular the effect of the operating conditions, kinetics,

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Table 1. Experimental Details of Reported Kinetic Measurements

	Wagenaar et al.	Chan et al.	Thurner and Mann	Di Blasi and Branca ^a
feedstock	pine 100–125 μm	undefined sawdust (compressed)	oak sawdust 650 μm	beech <80 μm (TGA) 100–500 mm (TF)
reactor	TGA/drop tube (DT)	single particle Pyrex reactor	tube furnace (TF)	TGA/tube furnace (TF)
temperature/ $^{\circ}\text{C}$	280–400 (TGA) 500–600 (DT)	not indicated	300–400	300–435 (TGA) 300–435 (TF)

^a To determine their kinetic expressions, Di Blasi and Branca used experimental data of various origins, besides the results of their own measurements with beech wood.

and models, is reviewed from an engineering point of view. Predictions of existing single particle models derived from a detailed description of the transport phenomena and literature data on measured intrinsic chemical kinetics are presented. In part II¹⁶ (subsequent paper), experimental results of fluid bed pyrolysis are presented and compared with predictions of these models.

2. Literature Review

The literature on biomass fast pyrolysis is quite extensive, and excellent technology reviews^{8–15} are available. In the following subsections, the available literature with respect to the parameters important for reactor design will be briefly discussed. Four types of investigations are especially relevant in this respect. Quite a number of publications are dedicated to the intrinsic kinetics of primary and secondary decomposition reactions and product distribution. A second type of published papers is concerned with the development of single particle models in which the reaction kinetics are combined with intraparticle transport phenomena and heat transfer from the bulk to the particle. The third series of investigations deals with laboratory and pilot-plant measurements of product distributions as a function of the reactor temperature, the type/size of feedstock, and (occasionally) the vapor residence time. We will focus here on results obtained for fluid beds, because the experimental part of this work (part II¹⁶) also deals with fluid bed pyrolysis. Finally, a few publications on reactor design that appeared recently in the literature will be discussed.

2.1. State of the Art of Fast Pyrolysis Technology. Although laboratory studies regarding the thermal decomposition of various organic substances have been carried out for a much longer period, the technology development of “fast” and “flash” pyrolysis started only some 20 years ago when the advantages of liquefying biomass in such a simple way were gradually recognized. During the 1980s and the early 1990s, research was focused on the development of special reactors such as the vortex reactor,^{18,19} rotating blades reactor,^{20,21} rotating cone reactor,^{22,23} cyclone reactor,^{24,25} transported bed reactor,²⁶ vacuum reactor,^{27,28} and the fluid bed reactor.^{26,29,30}

Since the late 1990s the process realization emerged, resulting in the construction of pilot plants in Spain (Union Fenosa),^{31,32} Italy (Enel),²⁶ UK (Wellman),³³ Canada (Pyrovac, Dynamotive),^{34,35} Finland (Fortum),³⁶ and The Netherlands (BTG).²³ In the U.S. and Canada, Ensyn's entrained flow bed process³⁷ is applied at a scale of around 1 ton/h for commercial production of a food flavor called “liquid smoke”. Dynamotive and BTG announced demonstration installations of 2–4 tons biomass throughput per hour to be under construction. These companies aim at the utilization of bio-oil for

energy production and, in a later stage, chemicals. Many pilot-plant projects have stopped, soon or late after the initial testing. At the time of writing (March 2005), the plants of Union Fenosa, Enel, Wellman, Fortum, and Pyrovac's large-scale installation in Jonquiere, Canada, were not in operation any more. This may be caused by a lack of confidence in economic prospects and markets, or by legislative limitations.

A successful co-firing test with 15 tons of bio-oil has been conducted in a 350 MWe power station in The Netherlands.³⁸ Entrained flow gasification (high pressure, oxygen blown) of bio-oil and bio-oil/char slurries has been demonstrated also on a substantial scale.⁴

2.2. Kinetics and Rate Expressions. A general concern in the measurement of pyrolysis kinetics is the exclusion of heat transport limitations. Wagenaar et al.^{39,40} concluded that the application of a thermogravimetric analysis (TGA) is therefore limited to ca. 450 $^{\circ}\text{C}$. At higher temperatures, he used small particles in a drop tube furnace. TGA is the most frequently used tool for kinetic analysis of biomass conversion. Grønli et al.⁴¹ report on a Round-Robin study in which eight laboratories with access to five different types of thermogravimetric analyzers performed pyrolysis experiments at heating rates of 5 and 40 $^{\circ}\text{C}/\text{min}$ while using Avicel PH-105 cellulose as feedstock. The eight laboratories measured char yields in the range of 2.9–10.5 wt % (at 40 $^{\circ}\text{C}/\text{min}$). For a certain fixed value of the weight loss, the scatter in the temperature measurement was about 17 $^{\circ}\text{C}$. Grønli et al. ascribed the differences in results primarily to variations in the thermal lag of the instruments used, and to the different heating rates applied. The thermal lag is defined as the difference between the temperature of the direct environment of the sample, which is controlled by the TGA, and the actual temperature of the sample.⁴² This Round-Robin concludes that (i) biomass pyrolysis kinetics are inherently difficult to measure by any technique, but that TGA gives the most reliable data, and (ii) differences between studies using the same feedstock are still significant and caused by systematic errors in the applied methods. Similar discussions on the impact of systematic errors during the determination of pyrolysis kinetics are reported by Antal and Várhegyi.^{43–45} Kinetic expressions describing merely the weight loss of biomass have been published frequently in the literature.^{43,46–51} For woody biomass, however, kinetics including the selectivity to the products are determined only by Wagenaar et al.,⁴⁰ Chan et al.,⁵² Thurner and Mann,⁵³ and Di Blasi and Branca.⁵⁴ In Table 1, the details of the experimental apparatuses and conditions used by these researchers are summarized.

The experimental data on which these kinetic expressions are based vary a lot with respect to both the product distribution and the reaction rate, possibly due to the fact that different types of wood were used. In

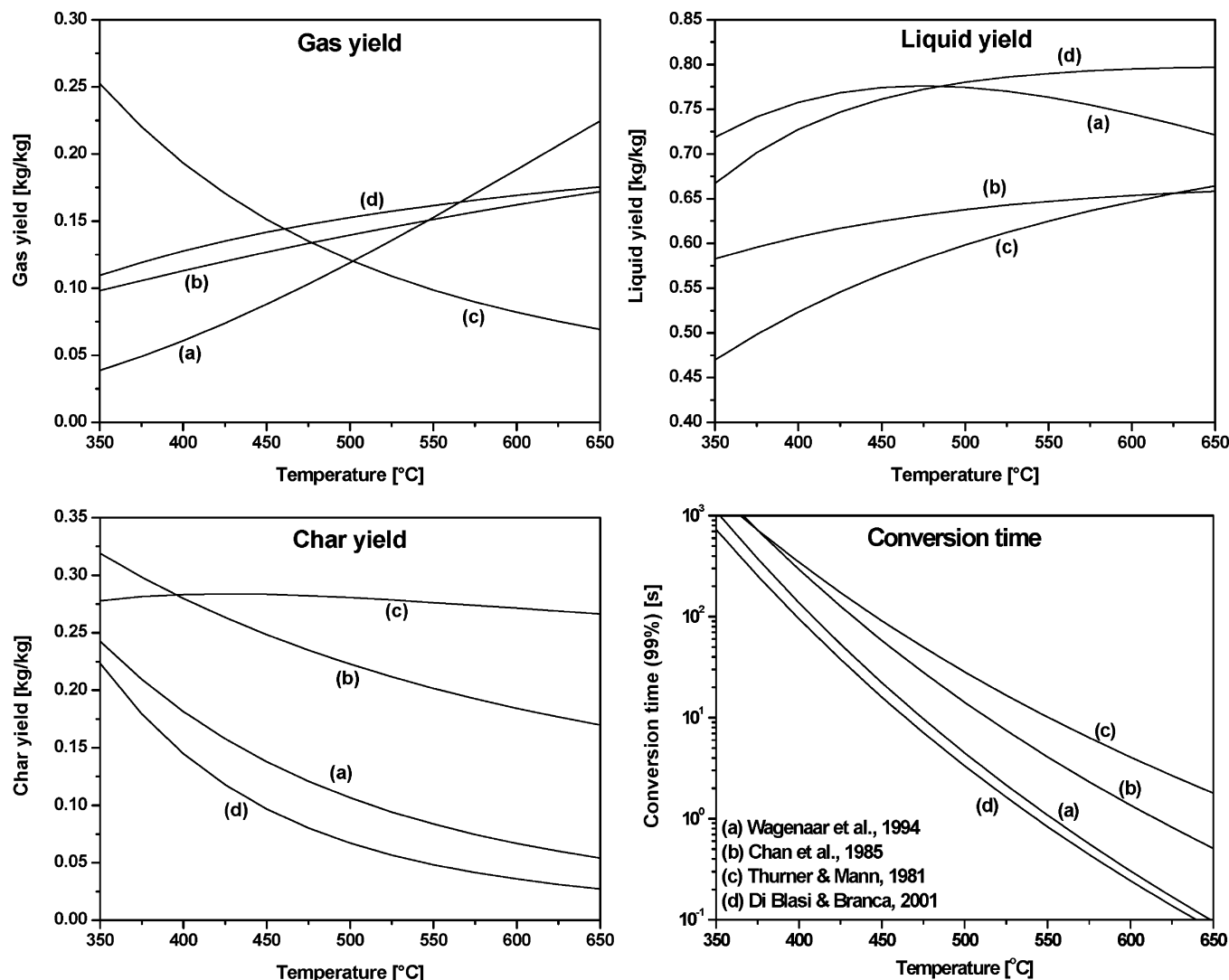


Figure 1. Product yields and conversion time (99% conversion) as predicted by the intrinsic kinetics of (a) Wagenaar et al.,⁴⁰ (b) Chan et al.,⁵² (c) Thurner and Mann,⁵³ and (d) Di Blasi and Branca.⁵⁴

Figure 1, the yields and conversion time as predicted by these intrinsic kinetics are plotted. Intrinsic kinetics can be used to predict pyrolysis experiments when heat transfer to and within the particle is much faster than the chemical kinetics. Provided that the enthalpy of reaction is zero or negligible relative to the heat required to heat the biomass, the chemical reactions inside the particle take place at the reactor temperature. In case of a significant endothermic reaction enthalpy, the reaction temperature is always (somewhat) lower than the reactor temperature.

Clearly there is a lot of difference between the predictions of the various kinetic data sets, and trends are sometimes even not uniform (see Figure 1).

The kinetic parameters of Wagenaar et al.,⁴⁰ Chan et al.,⁵² Thurner and Mann,⁵³ and Di Blasi and Branca⁵⁴ were derived while assuming a single process for the decomposition of wood, including three parallel first-order decay reactions for the formation of the product classes. This is the so-called "Shafizadeh" scheme.⁵⁵ The three lumped product classes are permanent gas, liquids (bio-oil, tar), and char, a classification that has become standard over the years. Dried wood was used as feedstock in all four kinetic studies mentioned. All of the condensable organic products, including the formed water, were indicated as liquids. However, the amount

of water in the produced liquid phase was never reported. Hence, the available kinetics cannot predict the moisture content of the produced liquid. In a practical pyrolysis process with a feed stream of 10–15 wt % moisture content, the water in the liquid phase has two origins, moisture from the feedstock and water produced by chemical reactions. Char does not only represent a carbonaceous solid, but can also include high-molecular-weight tar components^{56–61} and minerals. It should be noticed that the kinetic selectivity expressions are obtained by regression of yield versus temperature data. In the absence of any underlying mechanistic model, extrapolation outside the experimentally validated regime is basically impossible. Stenseng et al.⁶² validated several reaction rate expressions against experimental data of wheat straw pyrolysis, for conditions outside the range they were derived from. They concluded that none of the rate expressions could be extrapolated outside the range of applied conditions and that a widely applicable kinetic model for pyrolysis is still missing. In their analysis, they included: a first-order decay reaction, a three parameter nucleation model, a distributed activation energy model, and a superposition model based on first-order reactions. Of these reaction rate equations, the distributed activation energy model showed the best performance. The

others failed completely when applied outside the validated regime, while the distributed activation energy model could still predict trends. Distributed activation energy models have also been discussed by Varhegyi et al.,⁶³ Wojtowicz et al.,⁶⁴ and Rostami et al.⁶⁵ They found again a good agreement between model predictions and experimental results. Unfortunately, the reported kinetics using the distributed activation energy approach only considered the total conversion of biomass and not the selectivity toward the products.

The kinetic constants of tar conversion are determined by Antal,⁶⁶ Diebold,⁶⁷ Liden et al.,⁶⁸ and Boroson et al.^{69,70} Diebold, Liden et al., and Boroson et al. interpreted their experimental results with a single first-order rate equation for the cracking of tar to permanent gases. Antal, however, proposed a scheme of two parallel (competing) first-order reactions to permanent gases and refractory condensable materials. Antal,⁶⁶ Diebold,⁶⁷ and Liden et al.⁶⁸ did measurements for different limited temperature ranges. On the basis of these measurements Wagenaar et al.^{39,40} derived a rate expression for a much wider temperature range, from 450 to 800 °C. As explained further in section 2.4 "Vapor Residence Time", char catalyzes the decomposition of tar.

To conclude, there is wide variation in data published for combined values of the preexponential factor and activation energy. Published rate and selectivity expressions may be valuable in describing trends, but they can hardly ever be used for reliable quantitative prediction of anything else than the corresponding original data. The scatter in the reported results is caused by systematic errors in the measurement technique, the type of biomass, and by the employed interpretation models. In view of the complex reaction network including even catalytic effects of minerals, it is indeed unrealistic to expect that the thermal degradation of biomass can be described accurately with a simple set of rate/selectivity equations.

2.3. Single Particle Models. During the last 60 years, many models have been published concerning the thermal degradation of a single biomass particle. In 1946, Bamford⁷¹ formulated the first model for the weight loss of wooden sheets being exposed to gas flames. Many researchers subsequently used this basic model. Roberts et al.,⁷² for instance, modified the model by incorporating the effect of internal convection. Publications concerned with detailed modeling of biomass pyrolysis on particle level are those by, for example, Di Blasi^{73–75} and Bellan and co-workers.⁷⁶ These detailed models include chemical kinetics, moisture evaporation, particle shrinkage, heat transfer to and through the particle (conduction, convection, and radiation), and convective mass transfer inside the particle. It has been concluded by several researchers that the contribution of the diffusion flux of the produced vapors, as compared to convective flow, can be neglected.^{77–79} In the single particle models, moisture evaporation is described with an Arrhenius-type equation.^{77,80,81}

Pyle and Zaror⁸² showed that it is relatively easy to identify the controlling steps of wood pyrolysis. They gave guidelines for the simplification of a one-dimensional pyrolysis model to models for (1) "kinetically controlled", (2) "external heat transfer controlled" (uniform particle temperature), and (3) "internal heat transfer controlled" (shrinking core) pyrolysis. Py and Py' numbers were proposed, which can be used to

determine whether heat transfer or reaction is the faster mechanism. The model results were validated successfully against experimental pyrolysis data of large cylindrical pine wood particles with a high l_p/d_p ratio. The cooling effect of the outward flowing vapors has been studied and quantified by Di Blasi,^{73,74} Janse,⁸¹ and Kersten.⁷⁷

Most model results reported in the literature are difficult to apply directly with respect to reactor design because they are focused on the description of intra-particle phenomena rather than on the prediction of reaction rates and product distributions as a function of the operating conditions prevailing in practical pyrolysis reactors.

2.4. Continuous Laboratory Experiments in Fluid Beds. The first results of fluidized bed pyrolysis were those by Scott and co-workers. In a series of publications,^{12,29,83–86} they presented data obtained in their Waterloo bench-scale plant (~20 g/h) and pilot-plant (max 3 kg/h). The experimental program involved variation of the feedstock, reactor temperature, vapor residence time, and particle size. In the Waterloo plants, liquid yields (organics plus water) ranging from 60 to 85 wt % on moisture free feedstock basis were reported, depending on the biomass type and the operating conditions. A selection of later publications concerned with fluidized bed pyrolysis are those by Agblevor et al.,⁸⁷ Horne and Williams,⁸⁸ Peacocke et al.,^{20,89,90} Hague,⁹¹ Bilbao et al.,⁹² Luo et al.,⁹³ and Olazar et al.⁹⁴ Regarding the trends, the results obtained are in good agreement with those reported in the original work of Scott et al. However, in later investigations, the highest liquid yields of Scott and co-workers (>80 wt %) could never be reproduced anymore. In the following subsections, the reported effects of the operating conditions are discussed. While analyzing the effect of the operating conditions, it must be realized that the reported mass balance closure is typically around 90–95%. Hence, a rather small difference (say 3%) in results (e.g., yields) cannot be interpreted as a distinct trend.

Reactor Temperature. Quite some experimental results can be found in the literature^{12,20,29,83–94} regarding the influence of the fluid bed temperature on the product distribution, particularly the bio-oil yield. As a function of temperature, the liquid yield goes through a maximum. For a variety of feedstock types, it has been observed that the maximum yield of bio-oil is obtained at temperatures of around 400–550 °C. However, taking into account the experimental errors, it can be argued that many researchers actually observed a plateau in the liquid yield over several decades of degrees centigrade within the range of 400–550 °C. Over the whole temperature range, generally, a monotonic decrease in char yield and corresponding increase in gas yield was found.

According to Scott et al.,⁸⁵ the best bio-oil quality in terms of caloric value and hydrogen over carbon ration is also achieved at the maximum yield temperature. Over the past decade, a number of authors, including Scholze et al.^{95,96} and Oasmaa et al.,^{97,98} discussed the quality of bio-oil in some more detail.^{99–101}

Biomass Particle Size. Surprisingly, the biomass particle size has hardly been a systematically varied parameter in fluidized bed fast pyrolysis research. The attention was focused mainly on "flash" pyrolysis requiring heating rates over 1000 °C/s and, consequently, very small particles ($d_p < 1$ mm). The published work

regarding the influence of the particle size on the yield and quality of bio-oil was limited to the size range from 44 μm to 2 mm.^{29,83,102} In this range, no significant influence of the particle size on the product yields has been reported.

In fixed beds, the particle size has been varied over a wider range.^{61,103} Figueiredo et al.⁶¹ observed that oil yields of holm oak wood chips did not vary as a function of the particle size in the range from 0.4 to 2 mm. Roy et al.¹⁰³ reported that a yield of almost 74 wt % of bio-oil (total liquids including water) was obtained from air-dried aspen saw dust at 450 °C, while a yield of 67 wt % was achieved for 1 cm aspen wood chips. Kelbon et al.¹⁰⁴ did experiments with single particles heated by an arc lamp at constant flux (W/m^2). At a flux of $8.4 \times 10^4 \text{ W}/\text{m}^2$, they found that the liquid yield of 1.5, 1, and 0.5 cm (length) wood cylinders was 65, 48, and 38 wt %, respectively. For fluxes of 16.8 and 25.2 W/m^2 , they observed nearly identical liquid yields for all particle sizes.

Unfortunately, literature results regarding the effect of the particle size over a wide range in a single reactor are not available. One could try to derive a relation on the basis of data from different reactor types. However, this relation would be very difficult to interpret because of the fundamental differences between the reactors used, particularly concerning the intra-reactor temperature gradients, the external heat transfer coefficient, extra-particle vapor residence time, and the hold-up of char being a cracking catalyst.

For this paper (part I), the particle size has been varied therefore over a wide range ($d_p = 0.01\text{--}20 \text{ mm}$) in simulations with single particle models. In part II,¹⁶ these model predictions are compared with results of real pyrolysis experiments in a fluid bed ($d_p = 0.7\text{--}17 \text{ mm}$).

In some publications, the effect of the particle size on the conversion time^{81,105–107} is discussed on the basis of both measurements and modeling. Particle sizes up to a few centimeters were used in the experiments. It was found that the observed conversion times and intraparticle temperature gradients, as a function of the particle size, could be well understood from simple one-dimensional single particle models (Bamford's model⁶³).

Heating Rate and Heat Flux. The effect of the heating rate has only been studied: (i) in (semi-)batch fixed bed reactors installed in a laboratory oven,^{108,109} (ii) by heating single particles in an oven,^{105,110,111} and (iii) by heating single particles with a lamp.^{104,112} In all experiments, the heating rate ($^\circ\text{C}/\text{s}$) or the heat flux (W/m^2) of the biomass sample is controlled and monitored accurately. The general conclusion from the batch tests is that the applied heating rate has a significant effect on the pyrolysis process, particularly on the oil yield, which is reported to drop in case of lower heating rates at otherwise constant conditions. Theoretical analysis on the effects of the heating rate is also available in the literature, for example in the work by Lede.^{113–115}

In practical pyrolysis reactors such as fluid beds, neither the heating rate nor the heat flux are independent variables. They are in fact nonstationary and dependent on local conditions. It is not clear how experiments under “controlled” heating conditions can be translated to continuous reactors.

Vapor Residence Time. Scott et al.¹² and Liden et al.⁶⁸ measured the effect of the vapor residence time in

a fluid bed reactor in the range of 0.2–0.9 s. At 525 °C, they found that in this range the liquid yield dropped from 75 to 60 wt %. Lower oil yields at prolonged vapor residence time are ascribed to cracking and polymerization reactions of vapors to gases and solids, respectively. On the basis of their measurements, Liden et al.¹¹⁶ derived the kinetic constants for tar cracking while assuming a first-order decay reaction. Besides by Liden et al., cracking reactions of pyrolysis vapors have been studied and quantified also by Boroson et al.,⁶⁹ Antal,⁶⁶ and Diebold.⁶⁷ However, they measured homogeneous tar cracking, whereas Liden et al.¹¹⁶ used a fluid bed with a considerable char hold-up. The first-order kinetic constants (k) vary between ~ 0.04 and $0.20 \text{ (s}^{-1}\text{)}$ at 500 °C. This range is rather large; the lowest value allows a vapor residence time of 5 s to keep the loss of primary tar limited to 10%, the highest value only 1 s.

Vapor cracking rates cannot be compared on residence time and temperature basis only, because also the amount of char in the reactor is reported to have a significant effect on the extent of cracking. Boroson et al.¹¹⁷ performed controlled experiments in which they led pyrolysis vapors over a char bed. They found that already at 400 °C a fraction of wood tar is very reactive in the presence of wood char. No “catalytic” rate equations, containing specific information on the char used, are available in the literature.

An interesting observation was reported by Freil et al.,¹¹⁸ who showed that, at 650 and 850 °C, the liquid yield decreased due to homogeneous gas-phase cracking for vapor residence times increasing from 0.1 to 1 s. It remained, however, constant for any longer residence times. This behavior cannot be explained with a single first-order decay reaction for tar cracking. However, with the scheme of Antal⁶⁶ that includes parallel reactions of primary tar to gases and refractory (less reactive) tar, it can be explained indeed. According to this mechanism, primary tar can be converted rapidly to gases and less reactive refractory tar that does not, or very slowly, decompose. The explanation further assumes that primary tar and refractory tar form a single liquid upon condensation.

Both the single reaction and the competing reactions scheme plea for a reactor design in which the produced vapors are quenched rapidly as this maximizes the liquid yield. In addition, the competing reactions scheme predicts that at increased vapor residence time the composition of the liquid is changing from primary tar to refractory tar. This adds an oil quality aspect to the discussion of the vapor residence time. If primary tar would be a better bio-liquid constituent than refractory tar, short residence times would be preferred even though the total liquid yield remains unaffected. Unfortunately, there are no studies available that analyze the composition of the recovered liquid as a function of the vapor residence time.

2.5. Reactor Design and Modeling. The number of publications concerning fluid bed design and modeling is limited. Di Blasi^{74,107} presented a fluid bed model in which the emphasis is completely on the single particle behavior. A reactor model is introduced via the external heat transfer coefficient and an extra-particle residence time of the gas phase to account for vapor cracking in the bulk. On the other hand, Lathouwers and Bellan¹¹⁹ developed a fluid bed reactor model based on a multi-fluid approach including the kinetic theory of granular flow. In this model, a computational fluid dynamics

Table 2. Properties Used for the (Base-Case) Model Simulations

property	unit	value
moisture content biomass	wt %	7.5
particle density biomass	kg/m ³	660
skeletal density biomass	kg/m ³	1500
enthalpy of reaction	J/kg	0
molar mass gas	g/mol	20
molar mass vapors	g/mol	224
specific heat biomass	J/(kg·K)	$10^3 \times (1.5 + 10^{-3}T)^a$
specific heat char	J/(kg·K)	$10^3 \times (0.42 + 2.09 \times 10^{-3}T - 6.85 \times 10^{-7} \times T^2)^a$
specific heat gas and tar	J/(kg·K)	$1560 + 0.567(T - 298)^b$
viscosity gas and tar	Pa s	3×10^{-5}
heat conductivity gas and vapors	W/(m ² ·K)	$0.0688 + 1.61 \times 10^{-4}(T - 298)^b$
heat conductivity biomass (axial)	W/(m·K)	0.25
heat conductivity biomass (radial)	W/(m·K)	0.15
heat conductivity char (axial)	W/(m·K)	0.20
heat conductivity char (radial)	W/(m·K)	0.10
permeability biomass (axial)	m ²	10^{-16} (10^{-14}) ^c
permeability biomass (radial)	m ²	10^{-12} (10^{-14})
permeability char (axial)	m ²	10^{-12} (10^{-12})
permeability char (radial)	m ²	10^{-14} (10^{-12})
pyrolysis kinetics	Wagenaar et al., ⁴⁰ Chan et al., ⁵² Thurner and Mann, ⁵³ and Di Blasi and Branca ⁵⁴	
vapor cracking kinetics	Liden et al., ¹¹⁶ Diebold, ⁶⁷ Boroson et al., ⁶⁹ and Wagenaar et al. ^{39,40}	
fluid bed heat transfer coefficient	W/(m ² ·K)	Prins et al. ¹²²
initial temperature	°C	25

^a From Grønli;¹²³ T in kelvin. ^b Derived for pyrolysis gas on the basis of the polynomials in Reid et al.;¹²⁴ T in kelvin. ^c Values between brackets are for isotropic particles.

description of a fluid bed is coupled with the devolatilization characteristics of discrete particle classes. The results of this comprehensive model are, however, not straightforward to interpret and to use for reactor design. It is not clear how the energy required is brought into the reactor and how, in practice, a preheated biomass feed (up to 225 °C) could be created. Gerhauser^{120,121} employed CFD modeling to study fluidized bed reactor scale-up. He concluded that the heat input into the fluidized bed is a major concern for pyrolysis reactors with a size of 100 tons per day or larger.

3. Single Particle Model Calculations

Two models, adopted from the literature, are used in this work. Results of simulations will be presented and compared with experimental results (part II¹⁶), to evaluate the descriptive and predictive power of such single particle models.

(1) The first is a two-dimensional (2D) model as described by Di Blasi.⁷⁵ In this model, both conductive and convective heat transport are taken into account and the physical properties (e.g., permeability, conductivity) can be anisotropic. The convective fluxes of vapors and gases are modeled with Darcy's law. For more information regarding the model, the reader is referred to the original publications.^{75, 77}

(2) The second is a one-dimensional (1D) model as proposed by Bamford⁷¹ that assumes the heat transfer within the particle to occur by conduction only.

The major assumptions of both models are that (i) cylindrical particles are considered, (ii) the volume of the particle does not change during devolatilization, (iii) there is thermal equilibrium between the vapors and the solid matrix, and (iv) the enthalpy of the pyrolysis reaction is zero (the effects of an endothermic reaction will be discussed to a certain extent). The pyrolysis reaction is described by the scheme proposed by Shafizadeh.⁵⁵ As mentioned before, the liquid phase predicted by the used pyrolysis kinetics includes, next to organics, all of the water produced. The applied kinetics were derived for dry wood, while wood with a moisture

content of ca. 7.5 wt % was used in the experimental part of this work (part II¹⁶). Therefore, evaporation of this moisture has been incorporated in the single particle models. Moisture evaporation is described by an Arrhenius rate equation as proposed by Bryden and Hagge.⁸⁰ The liquid yield resulting from the single particle models is thus made up out of liquid predicted by the primary kinetics, plus the moisture evaporated from the feed. The actual moisture content of this liquid cannot be predicted because the formed water was not separately taken into account in the kinetic studies (see section 2.2). Cracking of vapors to gas is modeled as a first-order reaction. In the model, the conversion time (τ) was defined as the time at which 99% (wt) of the initial biomass is decomposed. The conversion is calculated using the equation below:

$$X = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

The coupled system of partial differential equations describing the model is solved by applying the method of lines in a DAE solver environment in MATLAB[®]. Tests were performed to ensure that the obtained results were grid independent and convergent. For the 2D model, usually a grid of 40 × 40 spatial grid cells showed sufficient accuracy. Table 2 gives the physical properties of the particles used in the calculations. Dimensionless numbers used in this paper (e.g., Bi , κ) are always based on initial values of the involved parameters (e.g., λ , ρ , C_p).

4. Simulation Results and Discussion

In the first subsection, 4.1, the results of the 1D and 2D model will be compared. The effects of the external heat transfer coefficient and the particle size will then be discussed in subsections 4.2 and 4.3, respectively. In part II,¹⁶ more simulation results will be presented to allow a proper comparison with experimental results of fluid bed pyrolysis. In this work, we focus on the conversion time (reaction rate) and the product yield.

Table 3. Model Predictions of the 1D and 2D Model for Pyrolysis of a Wood Particle with $d_p = 5$ mm at 527 °C (800 K)^a

l_p/d_p permeability	intrinsic kinetics	2D model			1D model ∞
		1 isotropic	1 anisotropic	3 anisotropic	
τ , s	2	22	20	34	35
gas yield, kg/kg	0.14	0.1	0.1	0.09	0.09
liquid yield	0.77	0.77	0.78	0.76	0.76
char yield	0.09	0.13	0.12	0.15	0.15

^a Conditions are listed in Table 2. Primary decomposition kinetics and tar cracking (intraparticle) kinetics are adapted from Wagenaar.^{39,40} Deviations from Table 1: biomass density = 600 kg/m³, heat conductivity biomass in radial direction = 0.1 W/(m·K), moisture content = 0 wt %, external heat transfer coefficient = 400 W/(m²·K).

These particle-related parameters are important for reactor design. The importance of a good estimate of the conversion time for reactor design becomes clear when realizing that at a given feed rate the required hold-up of reacting particles (from fresh biomass to char) is approximately proportional to the conversion time. The hold-up of reacting particles determines, among others, the total reactor volume and is important from an operational point of view. The amount of char in a fluid bed in case of 3 mm particles, for instance, is limited to ca. 5 wt % of the total bed,^{125,126} higher fractions cause fluidization problems (e.g., heavy segregation). The product yield, in particular the oil yield, is important because the pyrolysis process aims at a maximum oil production.

4.1. Comparison between 2D or 1D Models. Table 2 shows the predicted conversion time and product yields for a dry wood particle with a diameter of 5 mm that was supposed to be converted at a reactor temperature of 527 °C (800 K). Simulation results of the 2D- and 1D-model are compared. The corresponding conversion time and yields of kinetically controlled pyrolysis are also included in Table 3. With the 2D-model, the effects of isotropic versus anisotropic permeability and the l_p/d_p have been analyzed. The 1D-model, obviously, represents a particle with infinite l_p/d_p . The typical anisotropic structure of wood causes all of the produced vapors to flow out of the particle in axial direction near the reaction front, parallel to the fibers. In case of particles with an isotropic structure, the produced vapors flow out over the whole surface of the particle (see Di Blasi et al.⁷⁵ and Kersten⁷⁷). As a consequence of this difference in outflow pattern of produced vapors, heating of anisotropic particles will not be counteracted so much by the cooling effects of these vapors. Hence, when comparing identical particles with different permeability orientation, the isotropic particle will have a longer conversion time. For gasification conditions ($T > 800$ °C), the difference in conversion time between particles with isotropic and anisotropic permeability can be up to 50% (see Kersten⁷⁷). At pyrolysis conditions (say $T < 550$ °C), however, this effect is limited to 10% (see Table 3 and Kersten⁷⁷), which is small in comparison with the uncertainties in the chemical kinetics. The simulations indicate that, for typical pyrolysis temperatures, the cooling effect of the out flowing produced vapors does not have an important influence on the pyrolysis time. With respect to the product yields, the influence of the permeability orientation is marginal (see Table 3). Kersten⁷⁷ concluded on the basis of simulations with a full 2D model, including vapor cracking kinetics,³⁹ that under pyrolysis conditions (~ 500 °C) intraparticle tar cracking does not proceed to a significant extent.

Simulations with the 2D and 1D model give nearly identical conversion times in case of particles with a

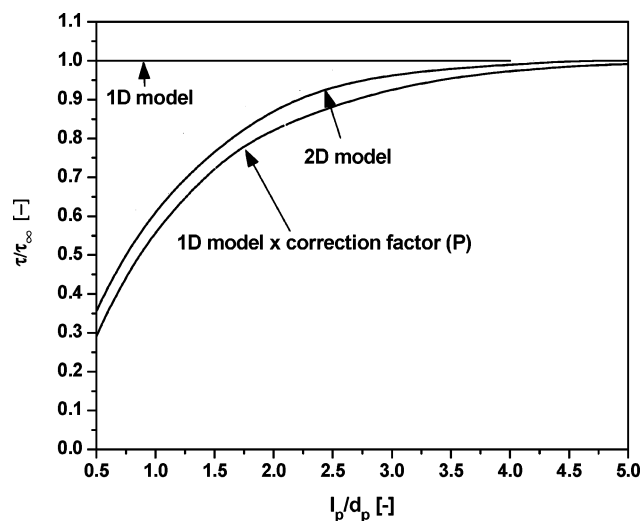


Figure 2. Effect of l_p/d_p on the conversion time, τ . τ_∞ stands for the conversion time at infinite l_p/d_p . Reactor temperature is 527 °C (800 K). Other conditions/properties are listed in Table 2.

large aspect ratio ($l_p/d_p \geq 3$) (see Table 3 and Figure 2). The effect on the product distribution is marginal, and the conversion time is overpredicted slightly by the 1D model. This conclusion has been put forward also by Miller and Bellan.¹²⁷ Particles with $l_p/d_p < 3$ require two-dimensional models for accurate prediction of the conversion time because below this value a significant amount of heat penetrates into the particle through the flat surface (see Figure 2). However, analysis of the data in Figure 2 shows that for engineering purposes also a one-dimensional model combined with a correction factor to account for the effect of l_p/d_p gives good results. In this case, the one-dimensional model is used to calculate the conversion time at $l_p/d_p = \infty$, where after Fourier's linear conductive heat equation is used to scale the results to finite length over diameter ratios. With the Fourier equation, the heating time (τ_H) of a particle with given l_p/d_p can be compared with the heating time of a particle with the same diameter for $l_p/d_p = \infty$ at otherwise identical conditions. The ratio of these heating times is used as a correction factor (P) to scale the conversion time calculated with the 1D model to finite l_p/d_p ratios. Analytical solutions of the Fourier equation are available (see, e.g., Carslaw and Jaeger¹²⁸) to enable quick calculation of P .

$$\tau(l_p/d_p) = \tau_{l_p/d_p=\infty}(\text{1D model}) \cdot P(l_p/d_p) \quad (2)$$

$$P(l_p/d_p) = \frac{\tau_H(l_p/d_p, d_p, \kappa, Bi)}{\tau_H(l_p/d_p = \infty, d_p, \kappa, Bi)} \quad (3)$$

As mentioned before, the thermal diffusivity κ and the dimensionless number Bi are based on initial conditions

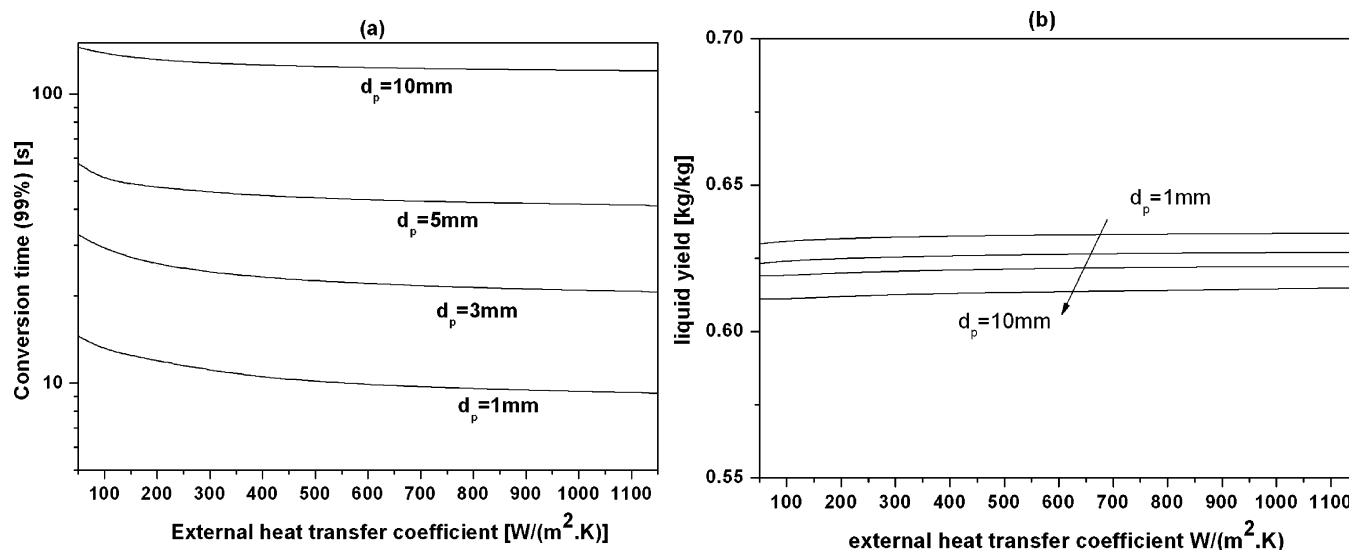


Figure 3. Effect of the external heat transfer coefficient on the conversion time (a) and the liquid yield (b). Simulations were performed with the 1D model. Primary decomposition kinetics of Chan⁵² were used. Reactor temperature is 500 °C; other conditions/properties are as in Table 1.

and can have different values for the radial and axial direction. The scaling procedure described above includes only the effect of the l_p/d_p ratio. The influence of the cooling outflow of the vapors is not included in the one-dimensional model. However, as stated before, for typical pyrolysis temperatures the effect of convective heat transport is limited.

Concluding, for engineering calculations that should provide estimates on the conversion time and the product yields a 1D model provides sufficient accuracy for particles with $l_p/d_p > 3$, and for particles with $l_p/d_p < 3$ the results of a 1D model can be scaled with a correction factor (P).

The analysis above has been presented while using the intrinsic kinetics of Wagenaar.^{39,40} For the other kinetic data sets, similar qualitative results have been obtained.

4.2. External Heat Transfer Coefficient, α . For a given particle, α is determined by the reactor type and by the operating conditions. In fluid beds, high external heating rates can be reached ($\alpha \approx 1000$ W/(m²·K)), whereas for instance in fixed beds and rotary kilns external heating is much slower ($\alpha \approx 100$ W/(m²·K)). Figure 3 shows results of simulations (1D model) of pyrolysis at 500 °C in which the external heat transfer coefficient has been varied over the range of 50–1200 W/(m²·K). Conversion times and product yields are plotted against α for four different particle sizes. For small particles of 1–3 mm, the external heat transfer coefficient has a clearly noticeable effect on the conversion time. In a fluid bed, the conversion is about 1.5 times faster as compared to slow heating conditions (see Figure 3a). In fact, in a fluid bed such small particles approach the kinetically controlled regime. A factor 1.5 difference in the estimate of the conversion time (reaction rate) is important for reactor design, as it corresponds to a factor of 1.5 in the hold-up of reacting particles.

For larger particles of 5–10 mm, the influence of the external heat transfer coefficient on the conversion time is small. Because of the relatively low thermal conductivity of wood, heat conduction in the particle is the limiting step in the heating process of large particles. Model simulations indicate that for particles larger than

5 mm the effect of α on the conversion time is never more than 20% in the practical range of $\alpha = 100$ –1200 W/(m²·K). The impact of the external heating on the product yield is small. Figure 3b shows the influence of α on the liquid yield. The influence of α on the gas and char yield is just as low as for the liquid yield.

4.3. Particle Size Effect. In Figure 4a, the predicted liquid yield (1D model) is plotted versus the particle size for a reactor temperature of 500 °C. Such a curve is of importance for fast pyrolysis because it predicts at which particle size the liquid yield starts to decrease. The calculations show a constant or nearly constant liquid yield at 500 °C as a function of the particle size up to 20 mm (see Figure 4a), irrespective of the kinetics applied. This can be explained by combining the measured intrinsic kinetics with the knowledge about the heat transport to and inside a pyrolyzing particle. To clarify this, an effective pyrolysis temperature (Π) is defined that can explain the product distribution for heat transfer limiting conditions on the basis of the intrinsic kinetics (measured for small particles). In analogy with the Thiele modulus concept,¹²⁹ the effective pyrolysis temperature Π allows using intrinsic kinetics, after a correction for transport limitations, for predicting the product yields at the temperature of the bulk. Hence, Π is the temperature at which the decomposition reactions are actually taking place with respect to the product distribution. It turns out that the volume-averaged value of the local temperature at which the reaction rate is maximal (T^*) is a good estimator for Π .

$$T^*(x,y,z) = \max \left(-\frac{\partial \rho_{\text{bio}}}{\partial t}, T \right) \quad (4)$$

$$\Pi = \frac{\int_V T^*(x,y,z) \, dV}{V} \quad (5)$$

The analysis on the effective pyrolysis temperature is similar to an earlier analysis by Lede¹¹⁴ regarding the reaction temperature of solid particles undergoing volatilization. Lede did simulations for ablative and chemically controlled conditions. In the first case, the

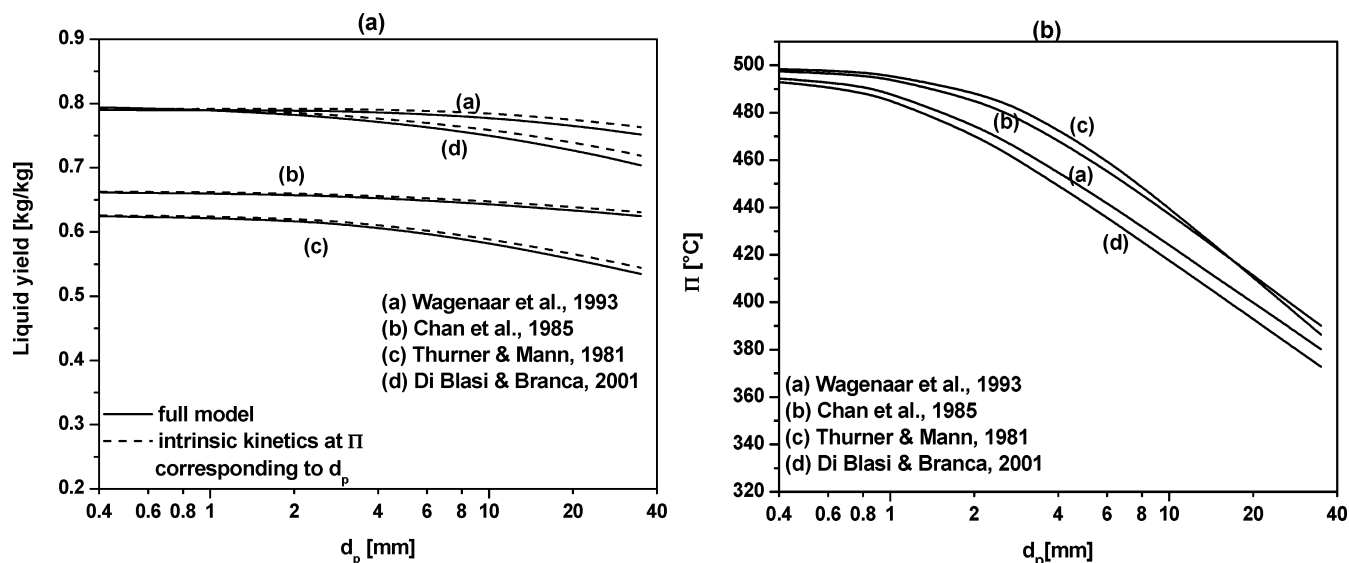


Figure 4. (a) Predicted oil and char yield versus the particle size for the kinetic data sets (a–d). Next to the results of the full 1D-model (—), also the intrinsic oil yields evaluated at Π corresponding to its value at d_p are presented (---). (b) Effective pyrolysis temperature versus the particle size for the kinetic data sets (a–d). Reactor temperature = 500 °C; other conditions/properties are as in Table 1.

reaction is taking place in a very thin layer close the surface of a big particle, while in the second case the particle temperature is uniform. He concluded that the temperature at which the reaction starts varies within narrow limits, while the temperature at which the reaction proceeds stabilizes as a function of the conversion degree. This was ascribed to both the endothermicity of the reaction and the fact that the reaction is fast as compared to heat penetration. Apparently, the latter effect must be dominant because simulations with $\Delta H = 0$ also yielded a nearly constant temperature during the conversion. The observed stabilized reaction temperature, with a range of ca. 100 °C between the beginning and end of the conversion, was compared with a phase change. Several authors saw “phase-change”-like behavior in pyrolysis experiments.^{113,115} On the basis of model calculations, Narayan and Antal⁴² have shown that, in a TGA experiment, the temperature at which the conversion actually takes place remains nearly constant (like in a phase-change), irrespective of the values of model parameters such as the heating rate of the environment, the enthalpy of reaction, and the heat transfer coefficient. In the present work, the temperature at which the reaction actually takes place has been analyzed in the presence of intraparticle temperature gradients instead of at a spatial uniform particle temperatures or ablative conditions. For this, a particle average reaction temperature has been defined.

Figure 4b shows this effective pyrolysis temperature versus d_p , calculated with the 1D single particle model for the kinetic data sets (a–d). In Figure 4a, the intrinsic liquid yields evaluated at Π corresponding to its value at d_p (hence at $\Pi(d_p)$) are presented, next to results of the full model. Clearly, there is good quantitative agreement between these two yields. Only the liquid yield is plotted. For char and permanent gas, the agreement was found to be just as good. Obviously, for small particles Π equals nearly the reactor temperature. Π then decreases when the particle size increases due to transport limitations. Model simulations show that for a typical pyrolysis temperature of 500 °C, the drop in Π is restricted to ca. 100 °C for particles up to 20 mm (see Figure 4b). This observation is in line with

simulation results of Narayan and Antal⁴² and Lede,¹¹⁴ which showed that the actual reaction temperature did not vary as a function of the degree of conversion for TGA and ablative conditions.

Such a small difference between the reactor temperature and the effective reaction temperature (Π) explains why the cooling effect of out flowing vapors (see section 4.1 and Kersten⁷⁷) is not that important for a typical pyrolysis temperature of 500 °C. If Π is close to the bulk temperature, the additional energy required to heat the produced gases and vapors to bulk conditions is small. The effect of the used kinetic data set on the curves of Π versus d_p is limited, because the activation energy does not vary much for these data sets. According to Wagenaar's⁴⁰ and Chan's⁵² intrinsic decomposition kinetics (see Figure 1), the oil yield is hardly dependent on the temperature in the range between 500 and 400 °C. Therefore, the oil yield predicted by the particle model including these kinetic data remains practically constant up to $d_p = 20$ mm at a reactor temperature of 500 °C, despite the fact that the characteristic reaction temperature decreases due to heat transport limitations. The intrinsic kinetics of Di Blasi and Branca⁵⁴ and Thurner and Mann⁵³ show a more profound effect on the oil yield in this temperature range, resulting in a slightly decreased bio-oil yield for larger particles pyrolyzed at 500 °C.

As mentioned before, single particle models predict that at 500 °C the influence of intraparticle cracking of tars can be neglected for all of the available tar decomposition kinetics. These tar decomposition kinetics were determined in gas-phase reactors or in a fluid bed with a relatively low char hold-up. Inside a reacting particle, however, the produced vapors flow outward via a char matrix with a high specific area, which is known to have catalytic activity toward tar cracking. If this char layer is extremely active (much more reactive than in the gas-phase cracking of tars), then three effects could occur upon increasing the particle size and, accordingly, the vapor residence time inside the particle: (1) the liquid yield decreases because primary tar is converted to gases only (e.g., Liden⁶⁸), (2) the composition of the liquid changes because primary tar decomposes to other liquid compounds,⁶⁶ and (3) a

combination of (1) and (2) occurs. Experimentally it has been found now that the liquid yield remains more or less constant in the range of $d_p = 0.7\text{--}17$ mm in a fluid bed reactor. However, the water content of the recovered liquid appeared to increase with increasing particle size (see part II¹⁶).

To conclude, up to particles of 20 mm the effective pyrolysis temperature drops maximally 100 °C, which, according to the intrinsic kinetics, results in a just marginal decrease in the liquid yield, a decrease in gas yield of about 5 wt %, and a corresponding increase in char yield.

5. Conclusions

The main conclusions can be summarized as follows:

(1) The literature on biomass pyrolysis has been reviewed. Many excellent studies have been reported with a high level of detail. However, it appears to be rather difficult to extract reliable quantitative information on conversion rates and product yields required for process design.

(2) For kinetic studies, the pyrolysis products have been lumped into the classes gas, liquid, and char. Yet the quality/composition of these classes (e.g., the water content of the liquid) depends strongly on the operating conditions. For practical application and optimization, kinetics should also be able to predict the product quality. Such kinetic schemes are not available yet.

(3) There is a lot of scatter in the reported biomass kinetics and selectivity data.

For exactly the same feedstock, significant differences already occur because of systematic errors in the experimental methods. Intrinsic reaction rates published for different biomass types vary up to a decade, and even trends are sometimes not uniform. This is probably related to differences in composition and structure.

(4) For a given set of kinetics, one-dimensional single particle pyrolysis models provide sufficient accuracy for engineering calculations. For particles with $l_p/d_p > 3$, the one-dimensional will do, and for particles with $l_p/d_p < 3$ the results of a 1D model can be scaled with a correction factor, P . P is the ratio of the heating time of a particle with finite l_p/d_p over a particle with infinite l_p/d_p at otherwise identical conditions. Also, the cooling effects of out flowing vapors, the influence of anisotropy, and intraparticle tar cracking can be neglected at fast pyrolysis conditions.

(5) Model calculations show that the external heat transfer coefficient (related to the reactor type) has little influence on the product yields at typical fast pyrolysis temperatures. Only for small particles (say ≤ 3 mm), and low values of α , the influence of α on the conversion time is clearly notable.

(6) Contrary to the common belief, single particle models predict (for all available kinetics) that the influence of the particle size on the liquid yield is very limited. This phenomenon can be explained with an effective pyrolysis temperature, a parameter that represents the temperature at which the conversion is essentially taking place averaged over the particle's volume.

(7) While the influence of the biomass particle size, its effective pyrolysis temperature, and the vapor residence time, on the liquids yield is limited, the liquid composition may change substantially.

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Nomenclature

T = temperature, K
 C_p = specific heat capacity, J/kg·K
 P = correction factor
 d_p = particle diameter, m
 Bi = Biot number, $Bi = \alpha \cdot L_c / \lambda$, L_c is the characteristic length of the particle
 Py = pyrolysis number, $Py = \lambda / (\kappa \cdot \rho \cdot C_p \cdot L_c^2)$
 Py' = pyrolysis number (external), $Py' = \alpha / (\kappa \cdot \rho \cdot C_p \cdot L_c)$, $Py' = Bi \cdot p_y$
1D = one-dimensional
2D = two-dimensional
DAE = differential algebraic equation
MWe = million Watts equivalent
 l_p = particle length, m
 t = time, s
 V = volume, m³
 X = conversion, defined as $X = (W_0 - W) / (W_0 - W_\infty)$
 W = mass of the biomass particle, kg

Greek Symbols

Π = effective pyrolysis temperature, °C
 λ = heat conductivity, J/(m·s·K)
 ρ = density, kg/m³
 κ = thermal diffusivity, $\kappa = \lambda / (\rho \cdot C_p)$
 τ = conversion time, s
 τ_H = heating-up time, s
 α = external heat transfer coefficient, J/(m²·s·K)

Subscripts

H = heating up
p = particle
 x, y, z = coordinates
 ∞ = infinite or final state
bio = biomass
0 = initial state

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