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Comprehensive Kinetic Modeling Study of Bio-oil Formation from Fast Pyrolysis of Biomass

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The aim of this work is to analyze the optimal operating conditions for fast biomass pyrolysis. The operating conditions required to maximize the yield of liquid products are investigated and discussed on the basis of a comprehensive mathematical model of wood/biomass devolatilization. Crucial issues are the fast and complete heating of biomass particles to reduce char formation and the rapid cooling of released products to reduce the role of secondary gas-phase pyrolysis reactions. Chemical kinetics as well as heat- and mass-transfer phenomena play an important role in this process; thus, a comprehensive kinetic model is applied. The proposed model, when compared to the majority of other devolatilization models, attempts to characterize pyrolysis reactions with a lumped stoichiometry using a limited number of equivalent components to describe not only gaseous products but also tar species. Model predictions are compared to experimental measurements not only with further validation in mind but also principally to verify the reliability of this comprehensive kinetic model of biomass devolatilization and combustion.

1. Introduction

The yearly world's current energy demands are in the region of 120 quadrillion kcal and are expected to grow by 50% over the next 2 decades.[1] Fossil fuels, which account for more than 95% of the overall consumption in the automotive field,[2] are the main source of energy being used. However, fossil fuels will not be able to cope with the predicted increases in demand, mainly in terms of their sustainability.[3] Greenhouse gas emissions and the presence of sulfur are two further major drawbacks in the exploitation of fossil fuels. The combination of supply depletion and environmental remediation costs are expected to increase the effective cost of oil, thus introducing the issue of new energy sources. Against this backdrop, biomass is at least partially acknowledged as an interesting and economical alternative to oil because of several of its characteristics. In the light of environmental concerns and legislation, biomass also emerges as a renewable and clean resource; the amount of CO_2 produced by biofuel combustion is, in theory, the same as that absorbed by plants as they grow. This evidence, together with low sulfur content, places biomass in the environmentally friendly product class in terms of pollutant emissions and greenhouse effect mitigation. Biomass is currently being underexploited because it has certain major drawbacks. The sheer variety of biomass sources results in different products whose properties require

characterization. The solid feedstock tends to agglomerate and, depending upon its composition, can corrode equipment, introducing further reactor design and configuration issues.[4] Nevertheless, increasing oil prices are expected to drive the wider use of biomass and the implementation of new technologies and processes. Thus, ongoing research into developing comprehensive biomass pyrolysis and combustion models is very useful.

2. Fast Biomass Pyrolysis

Biomass conversion processes involve direct combustion, pyrolysis, and gasification. Biomass pyrolysis is a thermal treatment occurring in the absence of oxygen and results in char, liquid, and gaseous products. Pyrolysis is also the first step in gasification and combustion processes. It is well-established that lower temperatures and longer residence times of gas and tar released by biomass favor char production, while short residence times and moderate temperatures optimize liquid or bio-oil yields. Higher temperatures and longer residence times increase the role of the successive decomposition of primary products favoring the conversion to gas products. Relatively small or thin particles in fluidized-bed reactors with short vapor residence times are examples of fast heating, while large, thick, or coarse particles (3−6 cm) or biomass briquettes in packed-bed reactors are involved in a slow heating process.[5,6] Fast pyrolysis would be typically used for maximizing liquid yields from small biomass particles. The pyrolysis temperature is about 700−850 K, with short vapor residence times. Bridgwater et al.[7] revised and discussed peculiar aspects of the design of fast pyrolysis processes with particular attention to reactor configurations and reaction temperature, heat-transfer and heating rates, particle size, vapor residence time, and secondary cracking reactions. They already

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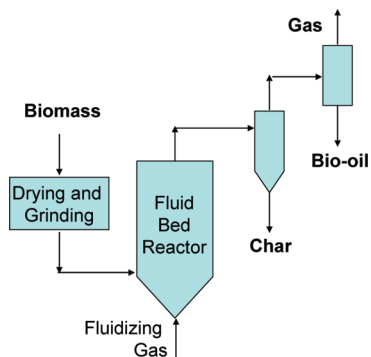
Figure 1. Schematic fluid-bed fast pyrolysis process (adapted with permission from Bridgwater et al.[7]).

Figure 2. Bio-oil yields in fast pyrolysis (adapted with permission from Di Blasi[6]).

concluded that the essential features of a fast pyrolysis process are (a) very high heating and heat-transfer rates, which usually require a finely ground biomass feed, (b) a carefully controlled pyrolysis reaction temperature of ∼770 K in the vapor phase, with short vapor residence times of typically less than 2 s, and (c) rapid cooling of the pyrolysis vapors to give the bio-oil product.

Figure 1 shows a very schematic view of a fluid-bed fast pyrolysis process. Biomass is dried to minimize the water in the bio-oil product and is properly grinded to obtain small particles and ensure fast heating and rapid reaction. Char and gas products can be suitably used to provide the required pyrolysis heat.

After condensation of the tar products released, up to 75 wt % bio-oil can be obtained. Bio-oil from wood is typically a dark red−brown liquid. It is highly polar, with a density of ∼1200 kg/m³, which is higher than that of the original biomass and fossil fuels.[8] Many pilot plants in Europe and U.S. have already been tested for oil production from pyrolysis. Biomass particles must be heated rapidly, and the residence time of the product gases must be short, while the endothermic pyrolysis reaction requires a high rate of heat transfer. To maintain the effective heat transfer during the pyrolysis process, it is crucial to progressively remove the char from the particle surface. This can be achieved with either small particles in fluidized beds or using ablative processes. Intensive experimental research is also underway in China and other developing countries into pyrolysis oil production from low-value biomass and agricultural residues.[9] Currently, bubbling and circulating fluidized-bed processes produce bio-oil on a commercial scale, using wood or wood waste.[10]

Bubbling beds work with vapor residence times that are typically between 3 and 10 s. The particle residence time can be quite high because cyclones recycle large entrained particles to the bed and only very small char particles can escape the cyclones. This makes it possible to use relatively large biomass particles, in the millimeter range. Although large particles give slightly lower liquid yields, they are not as costly to grind. The advantage of ablative processes is that they can treat larger biomass particles, thereby reducing the need for energy-intensive grinding.

Figure 2 summarizes some experimental data and clearly demonstrates the effect of the temperature on the bio-oil yields from fast pyrolysis.[6] Maximum yields, obtained at ∼750−800 K, span around 60 and 85 wt %. There are two reasons for the lowe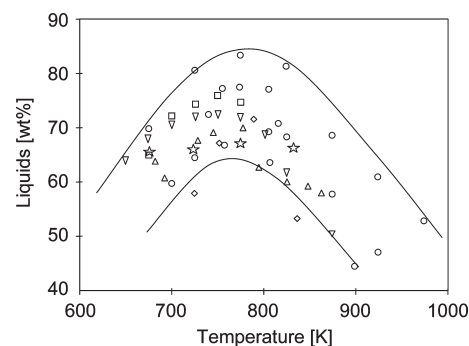r yields at low temperatures: incomplete devolatilization of the solid particles and favored char formation, because of cross-reticulation reactions of liquid and tar components. The lower bio-oil yields at high temperatures are due to the effect of the secondary bio-oil gas-phase reactions. It is thus clear that both chemistry and heat- and mass-transfer processes play a critical role in bio-oil yields from fast pyrolysis processes, in which rapid heating of the biomass particles and minimization of the secondary gas-phase reactions of released products are crucial.

Comprehensive models describe biomass degradation using chemical kinetic mechanisms coupled with conservation equations for heat and/or mass transport. Di Blasi[11] reviews and classifies the available kinetic models for biomass pyrolysis in terms of either one- or multi-component reaction mechanisms. The one-component models simplify the overall process in a single, global reaction, in which gases, tars, and char are formed from biomass. Despite their being easy to use, their applicability is very limited because of the high degree of simplification, which allows for a mainly qualitative prediction of the product yields and gives no information on the product distribution. In multi-component models, an effort is made toward the characterization of the initial biomass, which is generally represented in terms of three pseudo-components: cellulose, hemicellulose, and lignin. This type of model is able to predict with fair accuracy the decomposition rates and conversion time for most biomass samples, even though a detailed product distribution and composition is still lacking. These conclusions are similar to the ones reached by Moghtaderi in his critical review[12] on the state-of-the-art in pyrolysis modeling of lignocellulosic solid fuels; he found that special attention must be given to the development of more accurate and general chemical kinetic mechanisms. While the pyrolysis yields of gaseous products have been evaluated and are available for several biomasses, detailed chemical characterizations of bio-oil are often absent or largely incomplete. To right this situation in part at least, this paper analyzes the predictions of a kinetic mechanism of biomass/wood devolatilization in fast pyrolysis conditions. A similar kinetic analysis of fast pyrolysis of biomass in fluid-bed reactors using a simplified devolatilization mechanism with a very accurate model of intraparticle transport phenomena and highly simplified extra-particle tar cracking has already been investigated in the literature.[13] Di Blasi also provided particle heating rates, reaction temperatures, and conversion times and discussed the effects of several factors, such as external heat-transfer conditions, size, shape, and shrinkage of the wood particles.

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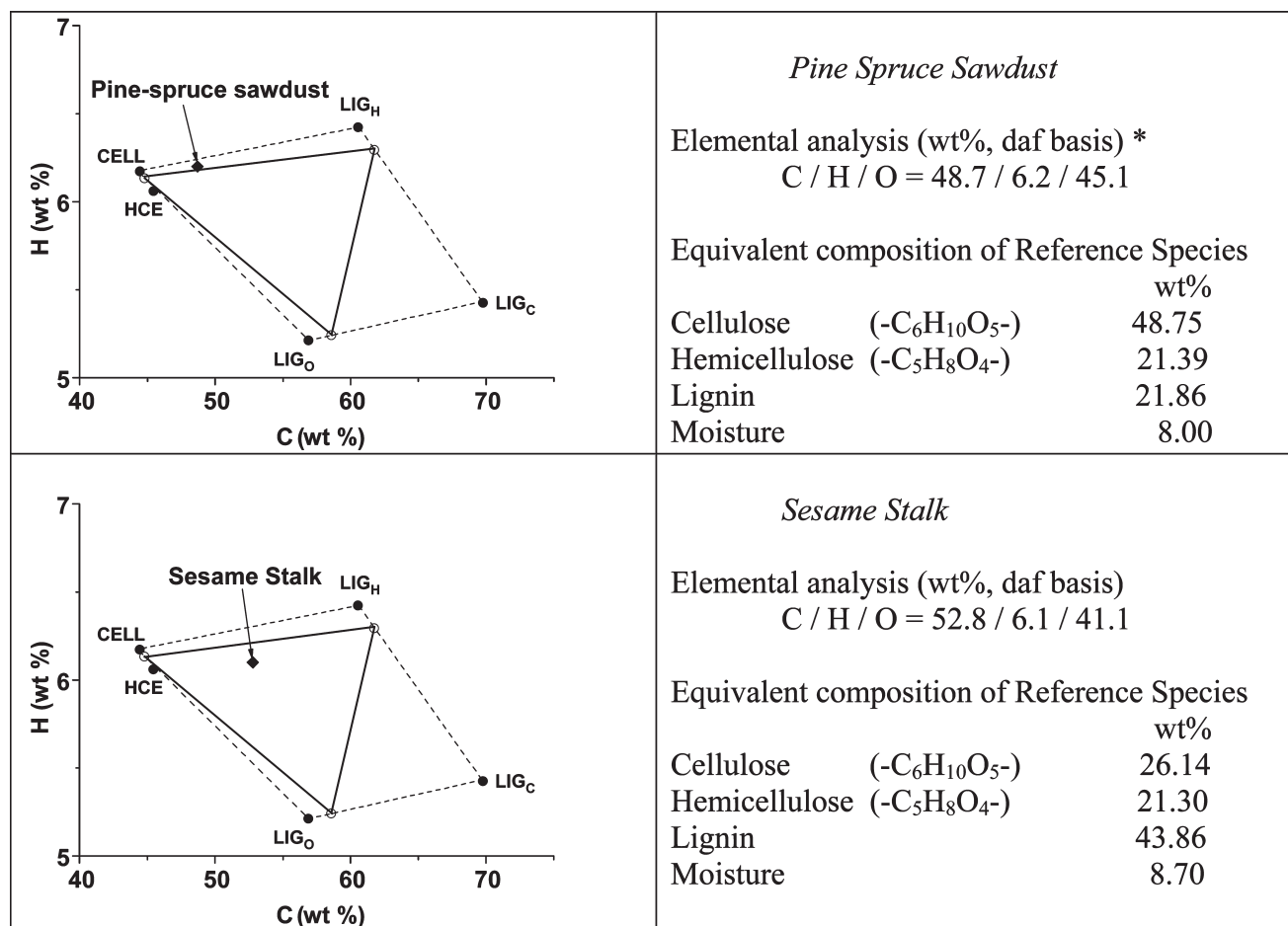
Pine Spruce Sawdust

Elemental analysis (wt%, daf basis) *
C / H / O = 48.7 / 6.2 / 45.1

Equivalent composition of Reference Species

		wt%
Cellulose	($-C_6H_{10}O_5-$)	48.75
Hemicellulose	($-C_5H_8O_4-$)	21.39
Lignin		21.86
Moisture		8.00

Sesame Stalk

Elemental analysis (wt%, daf basis)
C / H / O = 52.8 / 6.1 / 41.1

Equivalent composition of Reference Species

		wt%
Cellulose	($-C_6H_{10}O_5-$)	26.14
Hemicellulose	($-C_5H_8O_4-$)	21.30
Lignin		43.86
Moisture		8.70

Figure 3. Biomass characterization from elemental analysis to reference species[23,24] with the Phyllis biomass database (http://www.ecn.nl/phyllis/).

The multi-step kinetic model used in this work is based on the devolatilization reactions of reference components (cellulose, hemicellulose, and lignin) and was already discussed in a couple of previous papers. The former is mainly related to thermogravimetric experiments,[14] while the latter analyzes biomass devolatilization at high temperatures in an entrained flow reactor for syngas production.[15] A relevant feature of this kinetic model, when compared to the majority of other devolatilization models, is the attempt to characterize pyrolysis reactions with a lumped stoichiometry using a limited number of equivalent or pseudo-components to describe not only gaseous products but also tar species. Successive gas-phase reactions of released species are also described in a detailed kinetic model. Furthermore, this devolatilization model was also coupled to a model at the particle and reactor scale to describe the simultaneous mass- and heat-transfer resistances.[16] With reference to Figure 1, this comprehensive kinetic model, which is a first attempt to tackle a tough, multi-scale, multi-phase problem, includes and analyzes, at both the particle and reactor scale, the following steps of the fast pyrolysis process: (1) heating and drying of solid particles, including heat and mass resistances, (2) devolatilization of biomass, and (3) secondary gas-phase pyrolysis reactions.

The next two sections give a brief summary of the main characteristics of the kinetic model, for both the biomass devolatilization and the successive or secondary gas-phase reactions of released species.

3. Devolatilization Model of Biomass

The detailed composition of biomass is very complex and often goes beyond the chemical details required for practical use. A simplified, although representative, description of biomass composition can be given in terms of proximate analysis (moisture, ash, fixed carbon, and volatile matters), elemental analysis (C/H/S/N/O), and biochemical analysis (cellulose, hemicellulose, and lignin, together with extractives, in either water and ethanol or toluene). Biomass will be mainly characterized here in terms of the three major components: cellulose, hemicellulose, and lignin, together with inert ashes and moisture. Cellulose is a regular polymer, consisting of a linear chain of glucose units. Hemicellulose is a polysaccharide, derived mainly from glucose and xylose, consisting of shorter and branched chains. Lignin is a more complex polymer with branched and random structures, mainly derived from three monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols.[17]

3.1. Biomass Characterization. When biochemical analysis is available, it is possible to directly derive biomass composition in terms of cellulose, hemicellulose, lignin, moisture, and ash content. Alternatively, if only elemental analysis in terms of C/H/O content is accessible, then a suitable combination of the reference species

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can be properly derived from the three atomic balances. Biomass is thus characterized in terms of a proper combination of reference components. Thus, Figure 3 is a graphical representation of a couple of typical biomasses: pine spruce and sesame stalk. Starting from elemental analysis, biomass composition is obtained in terms of cellulose, hemicellulose, and different lignins. Details on this approach were already reported.[14]

3.2. Devolatilization Model of Reference Components of Biomass. Products from biomass pyrolysis are similar to the pyrolysis products from the three major components separately. Hemicellulose breaks down first at temperatures of 450−550 K. Cellulose follows in the temperature range of 500−620 K, while lignin components pyrolyze in a wider temperature range of 500−770 K. The high temperature required to complete the lignin devolatilization process explains why maximum oil yields from fast pyrolysis are reached at 750−800 K. Further confirmation of this came from the recent experiments[18] in a fixed-bed pyrolysis reactor. The decrease in char yield from 600 to 725 K is due to the completion of the lignin conversion of the pine wood biomass. From 770 K onward, the char yield reaches a constant value. The gas product has an average heating value of 15−22 MJ/Nm^3, depending upon feed and process parameters.

Typical water content in pyrolysis oil is 15−30 wt %, and phase separation usually occurs. Thus, the whole pyrolysis oil fraction consists of two phases: an aqueous phase containing a wide variety of low-molecular-weight organo−oxygen compounds and a more interesting non-aqueous, tarry phase containing insoluble heavy organic species. Typical organic compounds in complex bio-oil mixtures are methanol, formic, acetic, and propionic acids, acetone, alcohols, aldehydes, hydroxypropanone and hydroxybutanone, furfural, and methoxy- and dimethoxyphenols.[8]

Very recently, Azeez et al.[19] discussed in detail the chemistry of the devolatilization of cellulose, hemicellulose, and lignin components, on the basis of a reliable pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) analysis system, showing potential for further explanations of devolatilization mechanisms. They also did not observe any significant differences in the composition of pyrolysis bio-oils derived from African and European biomasses.

Moving on from this and similar experimental information, a multi-step kinetic model of biomass devolatilization was developed.[14] Cellulose, hemicellulose, and reference components of lignins decompose, release gases, and/or form intermediate components that are involved in substitutive additions and cross-linking reactions with a progressive charification of the solid residue. Levoglucosan (LVG) and hydroxylacetaldehyde (HAA) are typical cellulose decomposition products. Xylan is formed by hemicellulose. Phenol and phenoxy species are typical products of lignin decomposition. Table 1 reports the main volatile species involved in the lumped stoichiometries of the kinetic biomass devolatilization model. All of the heavy, lumped species represent a mixture of similar or analogous species with the given average chemical formula. The major features of this multi-step devolatilization model, including a detailed comparison to experimental measurements, are reported elsewhere,[14] while the Appendix summarizes the full detail of this kinetic model, including the reaction heat.

4. Secondary Gas-Phase Reactions

Volatile components released by biomasses are subject to successive gas-phase pyrolysis and/or oxidation reactions. Several of these species were already studied and involved in a detailed kinetic scheme of pyrolysis and oxidation of

Table 1. Main Volatile Species Released from Biomass Devolatilization

chemical name	formula	ΔH_f (kcal/mol)	ΔS_f (cal mol^{-1} K^{-1})
methanol	CH_4O	−48.1	57.3
ethanol	C_2H_6O	−56.3	67.4
glyoxal	$C_2H_2O_2$	−50.6	65.42
acetic acid	$C_2H_4O_2$	−103.9	67.4
hydroxylacetaldehyde	$C_2H_4O_2$	−73.5	73.6
ethylene glicol	$C_2H_6O_2$	−92.0	76.4
n-propanol	$1-C_3H_7OH$	−60.9	76.4
iso-propanol	$2-C_3H_7OH$	−65.1	74.3
hydroxyl-oxo-propanal	$C_3H_4O_3$	−102.8	88.4
propanal, 3-hydroxy-	$C_3H_6O_2$	−80.3	83.4
propane-1,3-diol	$C_3H_8O_2$	−96.9	87.2
propanedial	$C_3H_4O_2$	−65.8	79.7
n-butanol	$C_4H_{10}O$	−65.9	85.8
sec-butanol	$C_4H_{10}O$	−70.0	83.7
iso-butanol	$C_4H_{10}O$	−67.9	83.3
tert-butanol	$C_4H_{10}O$	−74.5	77.7
furan	C_4H_4O	−8.3	63.9
tetrahydrofuran	C_4H_8O	−44.2	72.3
butanedione	$C_4H_6O_2$	−78.4	84.3
xylofuranose	$C_5H_8O_4$	−151.5	104.9
furan-2-carboxaldehyde	$C_5H_4O_2$	−36.1	77.8
phenol	C_6H_6O	−25.0	76.9
levoglucosan (cellobiosan)	$C_6H_{10}O_5$	−200.9	113.7
5-(hydroxymethyl)furfural	$C_6H_6O_3$	−79.8	98.2
2,6-dimethoxyphenol	$C_8H_{10}O_3$	−113.5	134.4
4-(3-hydroxy-1-propenyl)-phenol	$C_9H_{10}O_2$	−49.8	110.2
3-(4-hydroxy-3,5-dimethoxy-phenyl)acrylaldehyde	$C_{11}H_{12}O_4$	−116.0	136.8

hydrocarbons.[20] The decomposition and combustion of alcohol fuels, such as propanol and butanol isomers, were also the subject of recent detailed kinetic studies.[21,22] The primary propagation reactions of other oxygenated species in Table 1 form intermediate products already considered in the whole kinetic scheme, and they were briefly discussed in a previous paper.[14] The complete kinetic model, in CHEMKIN format, together with thermodynamic properties of all involved species, is available on the website http://CRECKModeling.chem.polimi.it/.

It is clear from the above considerations that, on the basis of new, more accurate experimental information[19] and more accurate kinetic studies, the species involved in the multi-step kinetic model of biomass devolatilization and the successive gas-phase reactions can be easily modified and/or extended, thus improving the reliability of the model as a whole.

5. Oil and Gas Yields from Biomass Pyrolysis

The comprehensive kinetic model of biomass devolatilization is first applied to compare model predictions, with

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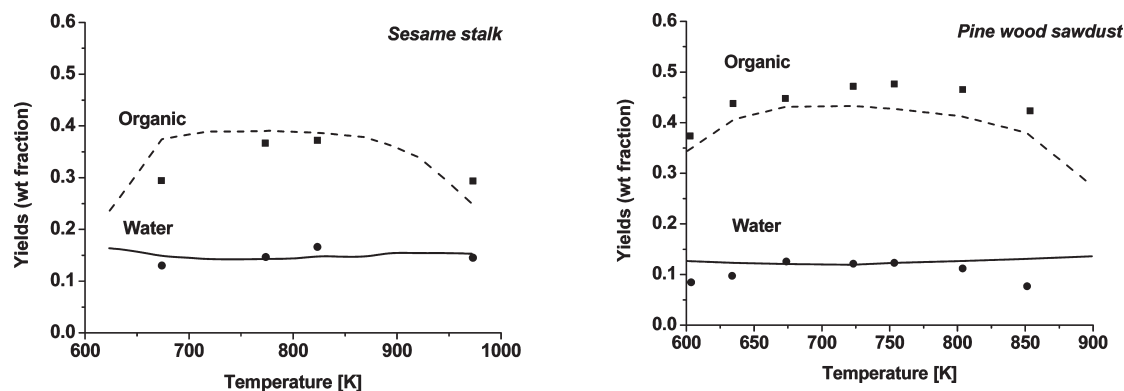
Figure 4. Yields of bio-oil and water from fast pyrolysis.[18,24]

Table 2. Experimental and Predicted Products from Fast Pyrolysis

biomass	Aguado et al.[23]		Ates et al.[24]		Westerhof et al.[18]	
	pine spruce sawdust		sesame stalk		pine wood	
	model	experiment	model	experiment	model	experiment
temperature (K)	720		770		750	
weight fractions						
solid residue	0.141	0.12	0.228	0.22	0.271	0.17
gases	0.172	0.17	0.231	0.26	0.179	0.23
total liquids	0.686	0.70	0.540	0.52	0.55	0.58
H_2O	0.116	0.09	0.142	0.16	0.126	0.12
organic liquids	0.570	0.61	0.398	0.36	0.424	0.46

experimental data obtained in different reactor configurations. Then, a parametric sensitivity study shows the effects of the reaction temperature, vapor residence time, secondary cracking reactions, and finally, heating rates and particle size.

5.1. Model Predictions and Comparisons to Experimental Measurements. The first example of comparisons refers to the fast pyrolysis of pine spruce sawdust, already characterized in terms of reference components in Figure 3. Aguado et al.[23] studied the pyrolysis of this biomass in a conical spouted bed, proving the stability and flexibility of this device across a wide range of conditions with low operating costs. Moreover, this reactor seems to fulfill the various requirements of flash pyrolysis: short gas residence time, rapid heating of the feed, and good gas−solid heat and mass transfer. A maximum yield of liquid of ∼70 wt % is experimentally obtained at 723 K. A quite flat maximum of ∼69 wt % is predicted by the devolatilization model in the temperature range of 690−740 K. Table 2 shows the comparisons between experimental measurements and predicted composition in terms of char, gas, and liquid (including water content). A similar comparison in the same table refers to the fast pyrolysis of sesame stalk in a fixed-bed reactor.[24] Once again, the biomass had previously been characterized in terms of reference species from the elemental C/H/O analysis by properly using the three atomic balances, as shown in Figure 3.

The model predicts a flat maximum liquid yield of ∼55 wt % in the temperature range of 700−850 K, while the experiments show the same maximum at 770−820 K. In line with the experimental data, the model predicts a water quantity at ∼14 wt %. Westerhof et al.[18] analyzed the fast pyrolysis of pine wood in a fluidized-bed reactor, observing a maximum oil yield of ∼55 wt % at 750 K. In line with the biochemical composition (cellulose, 35 wt %; hemicellulose, 29 wt %; lignin, 28 wt %), the model properly predicts the same maximum, always very flat in the temperature range of 650−800 K. This comparison is also reported in Table 2.

Figure 4 shows the influence of the temperature on bio-oil and water yields from sesame stalk and pine wood pyrolysis,[18,24] confirming a good agreement between the experimental data and model predictions both regarding the maximum yields and the effect of the temperature on those yields. Carbon oxides (CO_2 and CO) are the main gas species from primary devolatilization, while small quantities of CH_4 and C_2 hydrocarbons (C_2H_4 and C_2H_6) are also released. The primary H_2 yield is very limited and only occurs at high temperatures. For very small particles, the model predicts very flat bio-oil yields and gas formations at temperatures higher than 750−770 K, where the biomass devolatilization is completed. These facts agree quite well with the experiments.

At high temperatures, residual char becomes nearly constant, because further degradations are negligible. Chemical compositions of product liquids predicted by the model agree fairly well with the experimental data reported in the literature.[23,25] Bio-oil can consist of over 40% carbohydrates or sugars (mainly levoglucosan and cellobiosan), substituted phenol, guajacol, and syringol species derived from lignins spanning between 10 and 20%. Alcohols, aldehydes, furans, and small oxygenated species consitute up to 15−25%, while product water ranges between 10 and 20% of dry biomass.

5.2. Effect of the Biomass Composition and Pyrolysis Temperature. At 750−800 K, maximum oil content ranges between 55 and 80%, because of the different biomasses, as already shown in Table 2. A sensitivity analysis clearly indicates that the maximum oil yield is obtained from pure cellulose. As already observed, the bio-oil yield in Figure 2 shows a maximum, because of both the completion of primary biomass devolatilization and the secondary gas-phase reactions of tar vapors,

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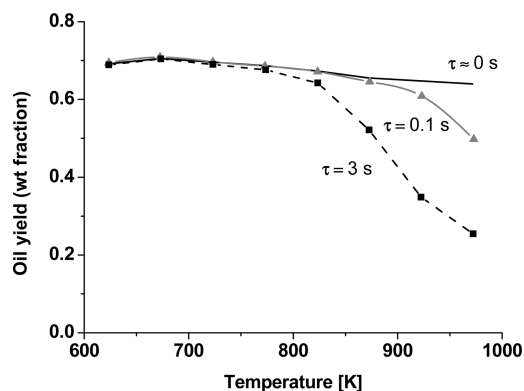
Figure 5. Effect of the secondary pyrolysis reactions. Predicted bio-oil yield versus the temperature at two vapor residence times.
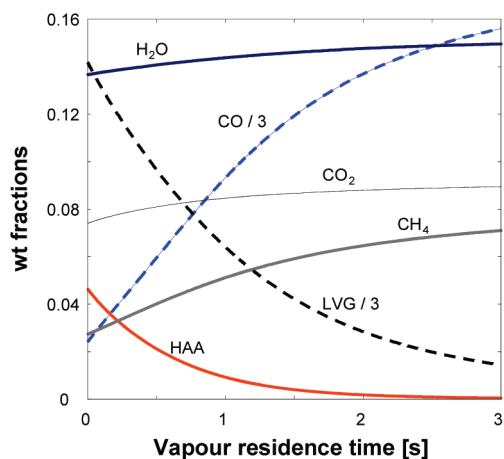

Figure 7. Pine spruce sawdust pyrolysis. Oil, gas, and char yields versus the temperature.[23]

Figure 6. Secondary pyrolysis reactions. Time evolution of major species at 923 K.

Figure 8. Effect of heat-transfer resistances. Predicted bio-oil yield versus the temperature at solid particle residence times of 1 and 10 min.

which are mainly active at high temperatures. Consequently, the gas yield increases continuously with the temperature.

A comprehensive mathematical model of biomass devolatilization, at both the reactor and particle scale, is required to properly describe the oil yield behavior. Heat diffusivity inside the solid particle and heat-transfer resistances help explain the partial volatilization of the biomass at low and intermediate temperatures. At high temperatures, detailed secondary pyrolysis reactions of tar species need to be accounted for with a proper vapor residence time.

5.3. Effect of the Secondary Gas-Phase Reactions. The pine spruce sawdust[23] considered previously was selected to show the effect of secondary gas-phase reactions of bio-oil components. To allow the secondary gas-phase reactions to occur, gas and tar species released by the biomass during the devolatilization process were maintained at the reactor temperature for 0.1 and 3 s, which are typical times for fast pyrolysis processes. Figure 5 shows the effect of these reactions and these different vapor residence times on the bio-oil yield. At temperatures higher than 900 K, significant decomposition of tar species is predicted even at very short residence times.

Figure 6 shows the conversion of LVG and HAA with the corresponding large increase in CO and other gas species. These data agree quite well with the experimental measurements, indicating a significant increase in CO/CO_2 ratios as the temperatures and effect of secondary pyrolysis increase.

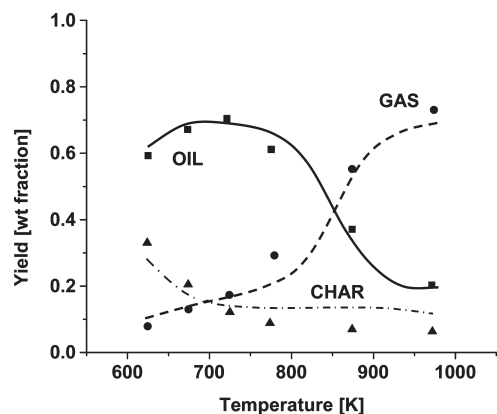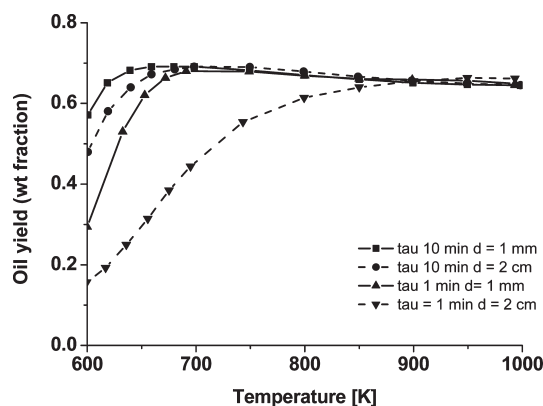Figure 7 shows the comparisons between experimental and predicted yields from fast pyrolysis in the spouted bed.[23]

Note that this good agreement for liquid and gas yields was obtained with an effective vapor contact time of ~5 s, significantly higher than the nominal one. This deviation could be due to the difficulty of measuring the effective gas residence times in the spouted bed reactor, in which gas recirculation is critical.

5.4. Effect of the Particle Size and/or Heating Conditions. At temperatures lower than 700 K, the devolatilization process is not completed. For large particles, the devolatilization times as well as the heat resistances become the critical parameters. At moderate temperatures, a relatively long residence time is necessary to complete the pyrolysis process of biomass to volatiles. Thermal diffusivity becomes a rate-determining factor for large particles. Figure 8 shows the effect of this partial devolatilization of biomass particles, as predicted by the model. Bio-oil yields against the pyrolysis temperature are reported at solid particle residence times of 1 and 10 min. As a result of the partial devolatilization, the oxygen content in the residual charcoal decreases when the pyrolysis temperature increases.

Simply combining the average conditions reported in Figures 5 and 8 makes it possible to explain and reproduce the experimental results reported in Figure 2 quite closely. Thus, Figure 9 shows the yields of oil, char, and gas from cellulosic and lignin biomasses. The two limit curves combine the effect of incomplete devolatilization and/or large particles at low temperatures, with the role of secondary pyrolysis reactions, at high temperatures.
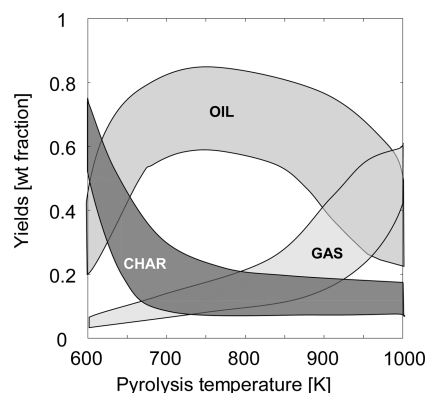
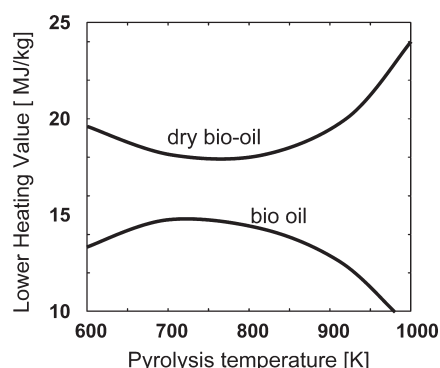**Figure 9.** Typical yields of oil, char, and gas from fast pyrolysis of biomass.

Figure 10. LHV of the pyrolysis bio-oil.

6. Heating Value of Bio-oil

Unlike fossil fuels, pyrolysis oils are polar with a large water content and a density higher than that of the biomass.[8] Figure 10 shows the behavior of the lower heating value (LHV) of the bio-oil versus the pyrolysis temperature. Again, these data refer to the fast pyrolysis of sawdust in the spouted bed[23] and are simply evaluated by considering all of the pseudo-species of the bio-oil with the enthalpy data reported in Table 1. The large differences between the LHVs of dry and wet oils at high temperatures are due to the effect of secondary pyrolysis. Because of the tar decomposition at high temperatures, the water fraction increases and the LHV of the oil decreases, while the hydrocarbon fraction in the dry oil increases with a clear effect on the LHV.

The LHV of pyrolysis oil is below 20 MJ/kg for pine spruce biomass compared to 42−45 MJ/kg for conventional petroleum fuel oils. The low energy density of bio-oil is due to both the water content and the presence of oxygenated species. Figure 10 also shows the LHV of completely dry bio-oil, even if water cannot be always and completely removed using conventional separation processes. The low heating value, low compatibility with fossil fuels, high viscosity, and chemical instability are properties that negatively affect bio-oil fuel quality.[26] Some of those deficiencies can be improved using relatively simple physical methods, while others require more complex chemical processing. The fresh and aged oils also had

different compositions, because of oil-aging reactions. However, the yields, quality, and stability of pyrolysis oil can also be modified by process variables, such as the heating rate, pyrolysis temperature, and residence times.[27]

7. Conclusions

A comprehensive kinetic model of biomass pyrolysis is presented and applied in this work. The examples reported clearly show and quantify the critical role of heat-transfer and secondary pyrolysis reactions in bio-oil yields from fast pyrolysis of biomass. The comprehensive kinetic model correctly predicts the relative amount of char, liquid, and gas fractions and also gives useful design- and optimization-related information. The lumped definition of oil components together with relating kinetics allows for a quantitative investigation of the effect of vapor residence times. In line with similar considerations made by Di Blasi,[13] further research is still necessary to improve bio-oil characterization and is crucial to a better understanding of the role played by tar components in the successive condensation or decomposition process.

In its present form, the kinetic model does not account for the catalytic activity of ashes. Nevertheless, the results obtained seem to confirm the reliability of this comprehensive kinetic model, not only at high temperatures in an entrained flow reactor for syngas production[15] but also for the analysis of bio-oil production from fast pyrolysis of biomass. This production could become more attractive within the context of biorefineries. Flexible pyrolysis processes, where biomass or biomass co-feeds with municipal wastes, plastics, and/or tires and petroleum residues, can be adapted to produce liquid fuels or gases to supply energy for transportation, heating, or electricity generation.[28]

Fonts et al.[29,30] pyrolyzed sewage sludge in a fluidized bed under different operating conditions, with the aim of producing high bio-oil yields. They also analyzed the influence of the operating conditions on the liquid properties (water content and heating value). The liquid yield was mainly influenced by the bed temperature. However, the nitrogen flow rate and solid feed rate, i.e., the gas and the solid residence time, also played a role. Elemental analysis (C/H/O = 58.8/9/32.2) clearly indicates that this feed is not a simple biomass but, because of its high C and H content, might be more correctly considered a plastic and biomass mixture. Once again, in this case, the oil yields, as well as the behavior of the water and heating value, are very similar to the ones already analyzed for the biomass pyrolysis. A similar study on the co-pyrolysis of biomass and synthetic polymers as an environmentally friendly way to transform biomass and plastic waste was recently reported.[31]

(26) Czernik, S.; Bridgwater, A. V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004,** *18,* 590–598.

(27) Fahmi, R.; Bridgwater, A. V.; Donnison, I.; Yates, N.; Jones, J. M. The effect of lignin and inorganic species in biomass on pyrolysis oil quality and stability. *Fuel* **2008,** *87,* 1230–1240.

(28) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A review. *Energy Fuels* **2006,** *20,* 848–889.

(29) Fonts, I.; Juan, A.; Gea, G.; Murillo, M. B.; Sanchez, J. L. Sewage sludge pyrolysis in fluidized bed, 1: Influence of operational conditions on the product distribution. *Ind. Eng. Chem. Res.* **2008,** *47,* 5376–5385.

(30) Fonts, I.; Juan, A.; Gea, G.; Murillo, M. B.; Arauzo, J. Sewage sludge pyrolysis in a fluidized bed, 2: Influence of operating conditions on some physicochemical properties of the liquid product. *Ind. Eng. Chem. Res.* **2009,** *48,* 2179–2187.

(31) Brebu, M; Ucar, S.; Vasile, C.; Yanik, J. Co-pyrolysis of pine cone with synthetic polymers. *Fuel* **2010,** *89,* 1911–1918.

Given the acknowledged complexity of biomass pyrolysis, it is clear that the modeling approach discussed in the paper may undergo revision, extension, and further validation in the future. The current biomass situation resembles the early days of the development of the carbochemistry and petrochemical industry. A large amount of research and process development is still required.

Appendix

Multi-step Kinetic Model of Biomass Pyrolysis

Table A1. Solid Devolatilization Kinetics[a]

reaction	kinetics (s^{-1})	heat of reaction (kcal/kg)
CELL $\rightarrow$ CELLA	$k = 8 \times 10^{13} \exp(-46000/RT)$	107
CELLA $\rightarrow$ 0.95HAA + 0.25GLYOX + 0.2CH$_3$CHO + 0.25HMFU + 0.2C$_3$H$_6$O + 0.16CO$_2$ + 0.23CO + 0.9H$_2$O + 0.1CH$_4$ + 0.61char	$k = 1 \times 10^{9} \exp(-30000/RT)$	215
CELLA $\rightarrow$ LVG	$k = 4T \exp(-10000/RT)$	175
CELL $\rightarrow$ 5H$_2$O + 6char	$k = 8 \times 10^{7} \exp(-32000/RT)$	−260
HCE $\rightarrow$ 0.4HCE1 + 0.6HCE2	$k = 1 \times 10^{10} \exp(-31000/RT)$	131
HCE1 $\rightarrow$ 0.75G\{H$_2$\} + 0.8CO$_2$ + 1.4CO + 0.5CH$_2$O + 0.25CH$_3$OH + 0.125H$_2$O + 0.625CH$_4$ + 0.25C$_2$H$_4$ + 0.675char	$k = 3 \times 10^{9} \exp(-27000/RT)$	107
HCE1 $\rightarrow$ XYLAN	$k = 3T \exp(-11000/RT)$	169
HCE2 $\rightarrow$ 0.2CO$_2$ + 0.5CH$_4$ + 0.25C$_2$H$_4$ + 0.8G\{CO$_2$\} + 0.8G\{COH$_2$\} + 0.7CH$_2$O + 0.25CH$_3$OH + 0.125EtOH + 0.125H$_2$O + char	$k = 1 \times 10^{10} \exp(-33000/RT)$	62
LIG-C $\rightarrow$ 0.35LIG$_{CC}$ + 0.1COUMARYL + 0.08FENOL + 0.41C$_2$H$_4$ + H$_2$O + 0.495CH$_4$ + 0.32CO + G\{COH$_2$\} + 5.735char	$k = 4 \times 10^{15} \exp(-48500/RT)$	144
LIG-H $\rightarrow$ LIG$_{OH}$ + C$_3$H$_6$O	$k = 2 \times 10^{13} \exp(-37500/RT)$	125
LIG-O $\rightarrow$ LIG$_{OH}$ + CO$_2$	$k = 1 \times 10^{9} \exp(-25500/RT)$	122
LIG$_{CC}$ $\rightarrow$ 0.3pCOUMARYL + 0.2FENOL + 0.35C$_3$H$_4$O$_2$ + 0.7H$_2$O + 0.65CH$_4$ + 0.6C$_2$H$_4$ + G\{COH$_2$\} + 0.8G\{CO\} + 6.4char	$k = 5 \times 10^{6} \exp(-31500/RT)$	69
LIG$_{OH}$ $\rightarrow$ LIG + H$_2$O + CH$_3$OH + 0.45CH$_4$ + 0.2C$_2$H$_4$ + 1.4G\{CO\} + 0.6G\{COH$_2$\} + 0.1G\{H$_2$\} + 4.15char	$k = 3 \times 10^{8} \exp(-30000/RT)$	24
LIG $\rightarrow$ FE2MACR	$k = 8T \exp(-12000/RT)$	138
LIG $\rightarrow$ H$_2$O + 0.5CO + 0.2CH$_2$O + 0.4CH$_3$OH + 0.2CH$_3$CHO + 0.2C$_3$H$_6$O + 0.6CH$_4$ + 0.65C$_2$H$_4$ + G\{CO\} + 0.5G\{COH$_2$\} + 5.5char	$k = 1.2 \times 10^{9} \exp(-30000/RT)$	−50

[a] Units are cal, mol, and s. G\{H$_2$\}, G\{CO\}, and G\{COH$_2$\} are species trapped in the metaplast and successively released to the gas phase.[14]