MODELING OF PHYSICAL AND CHEMICAL PROCESSES DURING PYROLYSIS OF A LARGE BIOMASS PELLET WITH EXPERIMENTAL VERIFICATION

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INTRODUCTION

A desire for optimal energy recovery from biomass has led to furnace simulation (1) and interest in chemicals production has led to biomass gasifier modeling (2). However, global considerations employed in these models give little insight into fundamental physical and chemical processes occuring in individual biomass particles during devolatilization. In previous studies addressing these processes, the emphasis has been on burning times (3), heat transfer rates (4), and weight loss rates (5) rather than detailed prediction of volatiles composition during pyrolysis. Detailed intrinsic kinetics studies of small biomass particles to determine pyrolysis product distribution as a function of temperature and time have been conducted (6,7). However, the results were correlated with Arrhenius type equations using best-fit parameters rather than parameters related to chemical structure. The latter is a difficult task given the diverse physical nature of biomass (8) and the complex molecular structure of the natural polymers of which it is composed (9). Indeed, the effects of particle size and physical microstructure (anisotropy) on devolatilization have not been systematically investigated in experiments, nor modeled using fundamental principles. To what extent the internal geometry of the wood influences the rates of heat and mass transfer, and thus the reaction products' composition, is largely unknown. Of particular importance is the ability to predict the relative proportions of char, tar, and gas (and components therein) that result from a given biomass thermal conversion process and given feedstock.

The goal of this work is to use fundamental considerations to predict changes in biomass pyrolysis product composition. The approach taken is to model a single, well-characterized biomass pellet under varying conditions during pyrolysis. This model can then be used to refine the gasifier and combustor models when a suitable distribution function for the feedstock characteristics is determined. Independent variables are feedstock characteristics (particle size, density, moisture, composition) and thermal conversion process characteristics (heating rate, diluent gas composition). Dependent variables predicted are instantaneous particle temperature and density profiles, gas and tar release rates, and char yields as well as ultimate yields.

For verification of the model, experiments were conducted according to a Box-Behnken design(10). A 1-D model is presented here for comparison with the experiments, and a 2-D model is being developed. Understanding gained from this model will aid in process design for biomass gasification, wood combustor design, as well as aid in fire safety.

BRIEF EXPERIMENTAL DESCRIPTION

The experimental apparatus is described in detail elsewhere (11-13). Briefly, it is a single particle, 1-D reactor. One face of a well-characterized cylinder of wood, compressed sawdust, cellulose, or lignin is heated by a combustion- level radiant heat source (4-12 cal/cm^2-s). As the temperature front at which reaction occurs moves inward, volatile species flow toward the heated face under a slight pressure gradient. The escaping volatiles reduce the incident radiation and the time- dependent magnitude of this effect is

quantified (11). The progress of the temperature front is monitored by 3 thermocouples at 2, 4, and 6 mm from the surface and the surface temperature is measured with an infra red pyrometer. Density profiles along the length of the pellet (integrated over the diameter) are taken via an X-ray technique.

Outflowing volatiles are rapidly quenched by helium and swept to a cold trap where water and tars are collected and analyzed in detail (11) as a time-integrated sample . Uncondensed gases are sampled every 3-15 sec by an automatic gas chromatographic sampling valve which also triggers the X-ray device. Char and gases are also analyzed in detail.

Although the experimental results are intriguing, especially the effects of anisotropy, they are described elsewhere (11). The major emphasis in this preprint is on the formulation and validation of the mathematical model. Other modeling details and aspects such as sensitivity analysis are also presented elsewhere (11,13).

MATHEMATICAL MODEL

An analysis similar to that of Russel, et al (14) was done (11,13) to determine the characteristic times for physical and chemical rate processes in a devolatilizing wood particle. For a 1 cm particle, conduction heat transfer to the interior is two orders of magnitude slower than chemical reaction at high temperature. However, the devolatilization reaction rate is comparable to the heat transfer rate at low temperature. Because the net conduction rate is strongly influenced by reaction product outflow and therefore the reaction rate, a fully unsteady model with variable properties was developed.

Heat Transfer Model

A one dimensional energy balance on the devolatilizing particle is schematically shown in Fig. 1. A time-varying radiant heat flux (Q_1), uniform in the radial direction, heats the face of the particle. Conduction (Q_4) is offset by volatiles outflow (Q_6). The volatiles are assumed to be in thermal equilibrium with the solid behind the reaction front as they flow outward, and are assumed to flow in one direction only[1].

The heats of reaction for wood are not well-known and they have been observed to be functions of particle size (15). In this model, the latent heat of water is treated as a heat of reaction(Q_5), and the heat of the devolatilization reaction (lumped with Q_5) is treated as a parameter using published values as bounds (16).

In the radial direction, the cylinder is considered insulated and impermeable. The heated face boundary condition includes radiation heat loss (Q_3) and convection heat loss (Q_2) which is described using the carrier gas flowrate. The outflowing CO_2 and H_2O absorb the incident radiation. This phenomena is treated using an estimated absorption coefficient for water in the model, and the incident radiation is reduced by an amount corresponding to the instantaneous water outflow.[2] The unheated face is considered impermeable to volatiles owing to the imposed pressure. Radiative (Q_8) and convective heat loss (Q_7) at this surface are treated, however. The film heat transer coefficient at each face was calculated using Nusselt number correlations and the properties and flowrate of helium at conditions of the experiments.

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[1] It has been verified by Lee, et al, (17).

[2] Experimental verification of the net radiation arriving at the surface during a typical run was accomplished using a Medtherm heat flux gauge. These results were matched to the model using a value for the absorption coefficient which was a best-fit parameter.

For most previous modeling studies, the thermal conductivity and heat capacity of wood were modeled as linear functions of the initial and final (char) values (18) using either the porosity or density change (18-21). It should be observed, however, that these models require a final char density, heat capacity, and conductivity for every case considered, restricting their utility and predetermining the calculated char yield. Additionally, in this study experimental measurements of temperature profiles as a function of time indicated that the thermal conductivity was an order of magnitude higher than would be predicted if it were a function of density alone. Unfortunately, few measurements of wood thermal properties have been made at high temperature because of the attendant chemical reaction. Thermal conductivity was measured for our samples at low temperatures and a model analogous to Birkebak and Ozil (22) was developed to describe a radiation contribution to the temperature variation (11,13). The heat capacity and porosity of wood were described by linear functions of the density(11,13).

Chemical Reaction Model

A schematic of the chemical reactions considered and the lumping scheme for gas, tar, and secondary gases is given in Table 1. Rate coefficients for reactions 1,2 and 4 were taken from Ref. (6). Tar cracking reaction rates (k_5) were taken from Refs. (23) and (24) and alpha and beta are adjustable. The char production rate (k_3) is estimated from the work of Shafizadeh, who has measured the arithmetic sum of char production and gas production (25). In this work k_3 must be viewed as a parameter, and as discussed below, the model is extremely sensitive to its value. Water production by evaporation and dehydration reactions are lumped (k_4) and treated as an activated process. The generation term in the energy equation contains the heat of vaporization of water, since it is larger than the heats of reaction measured for wood (15,16).

Mass Transfer Model

In previous models, with a single reaction step (weight loss kinetics), the product distribution is unaltered by the presence or absence of a finite mass transfer rate (26) since only a lumped gas species is described. The only possible implication of a slow mass transfer step is a delayed appearance of the volatiles. The experimental studies (11) indicated that a mass transfer resistance was not significant for heating parallel to the grain direction. Since the model is one dimensional, anisotropy is not treated and inclusion of a mass transfer resistance at this stage is not warranted. The previous analysis of characteristic times for mass transfer is consistent with this observation and the rather open porous structure of wood. For comparison to experiment, the volatiles mass flux is computed as the instantaneous integral over the pellet length of the local total change in density (11,13).

Numerical Method and Equations

Limited space in the preprint prevents the presentation of the detailed equations. However, earlier versions of the model equations appear in Ref. (11) and the current model will be detailed in a forthcoming publication (13). The coupled partial differential equations for the pellet temperature, and species concentrations are solved in dimensionless form using a GEARB package (Finlayson,1980). For ease of comparison with experimental results, in this paper model predictions are given in dimensional form. The cases of thick pellets heated by high heat flux result in very sharp temperature and reaction fronts which lead to "stiff" systems of equations. Computation times and comments appear in Refs. 11 and 13.

RESULTS AND DISCUSSION

Comparison of the measurements to model predictions of the unsteady temperature profile as a function of time at 3 locations are shown in Fig. 2 for the case of an intermediate heat flux and the thinnest particle, 0.5 cm. The model overpredicts the temperature at short reaction times, but satisfactorily predicts the pseudo-steady temperatures at several depths after 200-300 secs. For other cases, similar overprediction occurs early in the pyrolysis, but the steady state temperatures are in agreement with experiment even for the highest heat flux and thickest particle. Previous studies (5,18) reported only predictions of steady state temperatures. It is felt that refinement of the absorption model for the net radiant heating of the wood surface will enhance agreement of temperature profiles in the early reaction period (11).

Fig. 3 presents the comparison of predicted gas release rate to experimental measurements for the same case as Fig. 2. Only uncondensed gas flux (not tar and water) is presented in the figure. As can be seen both the magnitude and shape of the volatiles release curve agree rather well with experiment. Correction of the temperature overprediction discussed earlier will delay the predicted gas release, in better agreement with experiment.

Extensive comparisons between model and experiment cannot be presented; however, similar agreement to that shown in Figs. 2 and 3 exists for most cases studied by experiment. Numerical difficulties are encountered for the cases with the sharpest fronts, i.e., steepest temperature gradients resulting from high heat flux and thick samples. Oscillations in the temperature and density profiles occur and a refinement of the numerical methods is indicated (27). However, these oscillations have little effect on the prediction of ultimate product distribution. As shown in Table 2, there is satisfactory agreement between predicted and measured gas, tar, and char yield for most cases. Agreement between these values was substantially improved when the experimental mass balance on water was very carefully analyzed and when the moisture release rate in the chemical reaction model and the energy balance was included.

A significant advance resulting from this modeling approach is that it is unnecessary to assume or measure a final value for char yield and thermal properties. Since char deposition is explicitly treated in the chemical reaction model, it is of interest to examine Fig. 4 in which the local density of char is presented as a function of reaction time for a case similar to those previously discussed. There is a slightly greater fraction of char produced when the reaction front is deeper in the sample, owing to the reduced heating rate experienced there. This is consistent with general observations in coal and wood pyrolysis that indicate char yield increases with slower heating. Since no char gasification reactions are currently incorporated into the reaction model, the char deposited near the surface of the sample retains its initial density throughout the reaction period. While it was foreseen that predictions of this nature could be confirmed with the X-ray density profiles, the resolution of this method is not sufficient to confirm this prediction.

The rate coefficient used for the char deposition reaction is estimated from the work of Shafizadeh (25). Behind the reaction front the deposited char insulates the unreacted wood and char thermal conductivity determines the subsequent temperature profile and rate of pyrolysis. Thus, the model is quite sensitive to both the value of the rate coefficient for char deposition as well as the model for the variation of wood and char thermal conductivity with density and temperature. If too little char is predicted, the char density is too low resulting in too slow a pyrolysis. If the char thermal properties are

incorrect as a function of temperature, the reaction can terminate prematurely or runaway can occur. A definite need exists for information on char deposition rates from carbonizing various fuel species (28), as well as on char thermal properties over a wide range of temperatures and porosities.

SUMMARY

A mathematical model of wood pyrolysis has been presented that is in satisfactory agreement with experimental reaction product distributions over a range of conditions of practical importance for gasification and combustion. Both chemical and physical processes are described using fundamental principles. Inclusion of water release and char deposition chemical reactions results in predictions of ultimate product distributions (gas, tar, and char yields) that are in good agreement with experiment and can aid in optimization of processes to maximize or minimize tar production. Predictions of products instantaneously released from a single wood pellet are in fair agreement with experiment. Computational difficulties are encountered for the cases with the steepest temperature gradients.

Previous studies (29) using a complex kinetic mechanism and heat transfer in a wood slab made no comparison to experimental results. Thus, this study provides both a data base (11) and a fundamental modeling approach that will enhance the understanding of the effects of physical properties and processes on the chemistry of devolatilizing biomass. Presentation of sensitivity analyses and further verification comparisons of the model are presented in a forthcoming article (13). Currently, pyrolysis product distribution as a function of particle size can be predicted only for the 1-D case. Extension of the model and experiments to realistic cases using 2-D samples is planned.

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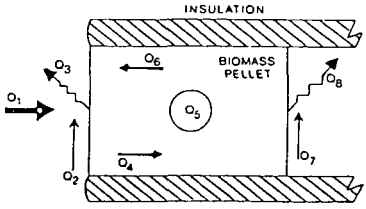

Fig. 1 - Schematic diagram of the heat transfer model.

TABLE 1

CHEMICAL REACTION MODEL

Reaction	Frequency Factor, s^{-1}	E_A, kcal/mol
$S \rightarrow G_1$	1.3×10^8	33.5
$S \rightarrow T_1$	2.0×10^8	31.79
$S \rightarrow C$	1.08×10^7	29.
$M \rightarrow W$	5.13×10^6	21.
$T_1 \rightarrow \alpha G_2 + \beta T_2$	1.48×10^6	27.29

Lumped Species Symbol	Identification
S	solid wood
C	char, high molecular weight tar (non-volatile)
M	moisture and chemically bound water in wood
W	vaporized water and released water
G_1	primary gases, e.g., CO_2, some CO, CH_4(?)
T_1	primary tar, e.g., phenols, levoglucosan
G_2	secondary gases, e.g., some CO, C_2H_4, C_2H_2, etc.
T_2	secondary tars, e.g., condensed aromatics (volatile)

α, β are adjustable parameters (stoichiometric coefficients).

TABLE 2
ULTIMATE PRODUCT DISTRIBUTION COMPARISON
EXPERIMENTAL RESULTS AND MODEL PREDICTIONS

1) For L = 0.5 cm, Heat Flux = 4 cal/cm^2-sec.

	Char	Tar*	Gas
Model	21.45	54.78	23.77
Expt.	18.05	62.33	19.63

2) For L = 1.0 cm, Heat Flux = 2 cal/cm^2-sec.

	Char	Tar*	Gas
Model	28.65	58.47	12.88
Expt.	25.12	62.37	12.52

3) For L = 1.5 cm, Heat Flux = 4 cal/cm^2-sec.

	Char	Tar*	Gas
Model	27.49	51.78	20.73
Expt.	22.82	53.98	23.20

* The tar yield includes water produced from the reactions but excludes water from the moisture evaporation.

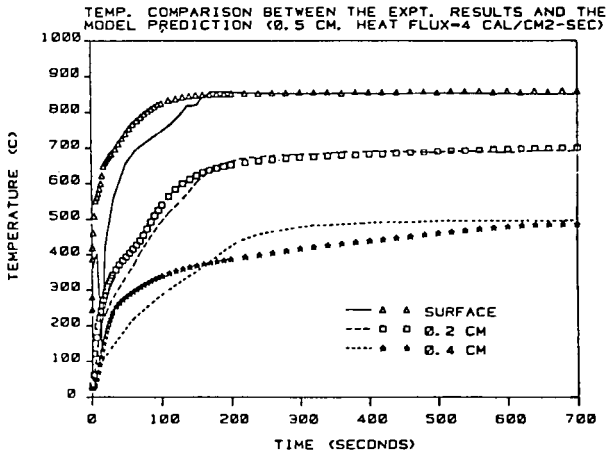

Fig. 2 - Temperature profile comparison - experiment (dashed lines) and model prediction (symbols) - 0.5 cm; ρ = .37 g/cc; initial thermal conductivity = 3.8 x 10^{-4} cal/cm-s-^{o}K

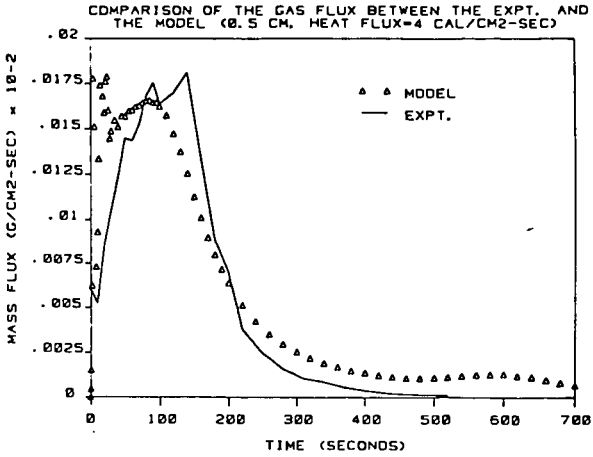

Fig. 3 - Total gas flux comparison - same conditions as Fig. 2

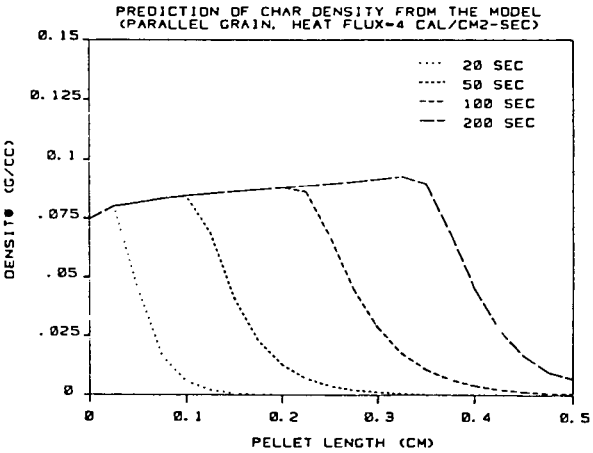

Fig. 4 - Predicted char deposition as a function of time - same conditions as Figs. 2 & 3.