

## Effects of Extra-particle Secondary Reactions of Fresh Tars on Liquids Yields in Hardwood Pyrolysis

Michael L. Boroson, Jack B. Howard, John P. Longwell,  
and William A. Peters

Department of Chemical Engineering and Energy Laboratory  
Massachusetts Institute of Technology  
Cambridge, MA 02139

### Introduction

Wood pyrolysis involves a complex system of chemical and physical processes. It is not yet possible to identify and model the individual reactions occurring during pyrolysis; however, a simplified model using lumped product groups such as tar, char, and gases can provide insight into the overall process.

Upon heating wood decomposes by an unknown series of bond-breaking reactions. The species formed by this initial step may be sufficiently immobile to preclude rapid escape from the particle. Consequently they may undergo additional bond-breaking reactions to form volatiles or may experience condensation/polymerization reactions to form higher molecular weight products including char. During transport within the particle volatile species may undergo further reactions homogeneously in the gas phase or heterogeneously by reaction with the solid biomass or char. The rate of volatiles mass transport within and away from the particle will influence the extent of these intraparticle secondary reactions. After escaping the particle, the tars and other volatiles may still undergo secondary reactions homogeneously in the vapor phase or heterogeneously on the surface of other biomass or char particles. Depending on reaction conditions intra- and/or extra-particle secondary reactions can exert modest, to virtually controlling influence on product yields and distributions from wood pyrolysis.

There exists a substantial amount of literature on the primary pyrolysis of wood. The literature on homogeneous secondary reaction kinetics of wood pyrolysis tars, however, is limited to only two studies (1,2) and no literature exists on the heterogeneous secondary reactions of tar over fresh wood char. The objective of the present study, therefore, was to obtain improved quantitative understanding of the homogeneous and heterogeneous extra-particle secondary reactions of sweet gum hardwood pyrolysis tar under conditions pertinent to gasification, combustion, and waste incineration. Sweet gum hardwood was chosen for two reasons: (a) this type of wood has commanded interest as an energy crop in the southern United States, and (b) secondary reaction results can be compared to sweet gum hardwood primary pyrolysis results already reported in the literature (3).

Results on homogeneous tar cracking are presented below. Studies of heterogeneous cracking of tar vapors over freshly generated wood char are in progress. Results will be presented.

### 1. Experimental

Yields of individual primary and secondary pyrolysis products as affected by reaction conditions and physical and chemical characteristics of "primary" (newly formed) and "secondary" (surviving thermal treatment) tar samples, were needed to fulfill the study objectives.

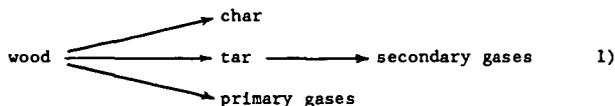
A two-chamber tubular reactor (Fig. 1) developed by Serio (4) for systematic studies of secondary reactions in coal pyrolysis, was adapted for the present measurements. In this apparatus "primary" tar, *i.e.*, tar that has undergone minimal extra-particle secondary reactions, is generated in an upstream reactor (No. 1) by heating a shallow packed bed of biomass, usually at a constant heating rate (typically 12°C/min). This tar and other volatiles are rapidly swept into a second reactor (No. 2) by a continuous flow of carrier gas (helium with an argon tracer). Here the volatiles are subjected to controlled extents of post-pyrolysis thermal treatment at temperatures between 400 to 800°C, pressures from 120 to 250 kPa, homogeneous residence times (V/F) between 0.9 and 2.2 sec, and heterogeneous space times ( $V_b/F$ ) between 5 and 200 msec.

Four reactor configurations have been employed in the present investigation. In Mode I runs, only the first-stage reactor is used, and freshly evolved wood pyrolysis products spend little time at high reaction severities. Thus they reflect minimal contributions from secondary reactions and are taken as well representative of the tars evolved near the wood surface. In the present work tars so evolved will be defined as "primary" tars. In Mode II runs, only the second-stage reactor is used, and yields and surface characteristics of fresh char as a function of initial wood bed depth are determined. In Mode III runs, the empty second reactor is connected downstream of Reactor 1, preheated, and then maintained isothermal. Homogeneous secondary reactions of wood tar vapors are studied quantitatively by controlling their extent of thermal treatment in this reactor and measuring its effect on product yields, tar loss and tar composition. In Mode IV runs, the second reactor is packed with a mixture of wood and quartz and again connected downstream of Reactor 1. Reactor 2 is first heated to 800°C to generate the fresh char then cooled to the desired reaction temperature prior to heating Reactor 1. Heterogeneous secondary reactions of wood tar vapors are studied by varying the temperature and heterogeneous residence time over the bed of char and quartz.

Product characterization includes quantifying tar and light volatiles yields, and global analysis of tars. A Perkin-Elmer Sigma 2B Gas Chromatograph was used to determine the yields of carbon monoxide, carbon dioxide, methane, acetylene, ethylene, ethane, and C<sub>3</sub> hydrocarbon gases. Size exclusion chromatography (SEC) was used to determine the weight averaged molecular weights of the primary and secondary tars. The equipment is a Waters Associates ALC/GPC 201 SEC system with two  $\mu$ styragel columns, 500 and 100 Å, in series, and a 405 nm UV detector.

## 2. Mathematical Modeling

Wood pyrolysis involves a complex set of parallel and series chemical reactions frequently influenced by heat and mass transfer, and tractable models generally must be built upon simplifying assumptions. Our model assumes the following reaction sequence:



and describes each of the above pathways with a single-reaction, first-order rate constant, the parameters for which are determined by curve-fitting product yield data. The kinetic parameters for the formation of char, tar, and primary gases from pyrolysis of the same sweet gum hardwood used in this study have been reported (3). The present modeling focuses on homogeneous cracking of the tar vapor and on the secondary gas formation reactions.

Net cumulative yields of unreacted tar and of individual gaseous products from tar vapor cracking were calculated as the difference between the cumulative amount of each entering (from Mode I runs) and leaving (from Mode III runs) Reactor 2. The data were then fit to the kinetic equation

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i) \quad 2)$$

where  $V_i$  is the yield of material  $i$  at time  $t$ ,  $V_i^*$  is the ultimate value of  $V_i$  at long residence times and high temperatures, and  $k_i$  is the global rate coefficient. Thus the rate of tar cracking at any time is modeled as first order in the difference between the ultimate (minimum) yield of tar (wt% of nonreactive tar) and the total amount of tar unconverted at that time. The rate of formation of an individual gaseous product is first order in the difference between the ultimate (maximum) yield of that gas and the amount of that gas generated up to that time. The kinetic parameters for homogeneous tar cracking and individual gaseous product

formation were found by a least squares parameter fitting technique.

### 3. Results and Discussion

Approximately fifty runs were performed to generate a broad data base on product yields as a function of primary and secondary reactor operating parameters. Good overall material balances and reproducibility were obtained. Selected tars collected from these runs were further characterized by SEC.

#### 3.1 Homogeneous Cracking Product Yields

Product yields were determined for each experiment as described in Section

1.2. Representative yields for primary pyrolysis of wood and for homogeneous secondary tar cracking at 600, 700, and 800°C are shown in Table 1.

Primary pyrolysis products from the first reactor were tar, char, water, carbon dioxide, carbon monoxide, and a trace of methane. More reactive primary products, such as tar, become reactants for secondary reactions, when the thermal treatment reactor (Mode-III) is in place. These secondary reactants, and products arising from their secondary reactions can in turn be identified by observing whether their yield increases, decreases, or remains constant when changing from Mode I to Mode III, or when increasing the Mode III temperature. Tar, for example, is a primary product and a secondary reactant as demonstrated by its high yield from Mode I experiments and its decreasing yield with increasing reaction severity in Mode III experiments. For residence times of about 1 sec. homogeneous tar conversion ranged from 9wt% at 500°C to 30wt% at 600°C and up to 88wt% at 800°C.

Carbon dioxide is both a primary and secondary product, since the yield in Mode I is about half the total CO<sub>2</sub> yield from high severity Mode III runs (800°C, Table 1). Carbon dioxide accounted for about 14% of the tar lost during secondary tar cracking.

Carbon monoxide and methane are evolved in modest quantities from Reactor 1. However, most of the production of these compounds along with acetylene, ethylene, ethane, and hydrogen arises from secondary reactions as evidenced by their substantial yield increases in the Mode-III experiments.

Carbon monoxide was the major product of secondary tar cracking at all temperatures, accounting for about 60-70wt% of the tar cracked. Methane and ethylene accounted for about 10 and 11wt% of the tar cracked, respectively, and the remaining 2-4wt% of the tar was cracked to form acetylene, ethane, and hydrogen. At high tar cracking severities (> 85%) the dry gas composition by volume was 48% CO, 19% H<sub>2</sub>, 13% CH<sub>4</sub>, 11% CO<sub>2</sub>, and 7% C<sub>2</sub>H<sub>4</sub>, with traces of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>.

Negligible amounts of char were observed in the second stage of the tubular reactor upon completion of experiments on homogeneous cracking of tar vapor. This implies that when char formation is observed in wood pyrolysis other pathways such as liquid phase tar condensation reactions, possibly surface assisted, are responsible. This picture is consistent with the ablative pyrolysis studies of Lede et al. (5) who found that char formation in wood devolatilization can be prevented by rapidly removing prompt pyrolysis tar liquids from wood surfaces at elevated temperature.

#### 3.2 Tar characterization

The tar samples collected after different extents of homogeneous secondary thermal treatment were characterized by size exclusion chromatography (SEC). The weight average molecular weight behavior of tars as a function of conversion is shown in Figure 1. As shown, the average molecular weight of tar surviving secondary cracking is lower than the molecular weight of primary tar (640 gm/mole) entering the cracking reactor. Average molecular weights tend to decrease with increasing conversion; however, the change in average molecular weight over the range of conversion 20-80% is small after a sharp drop in average molecular weight from zero to ten percent conversion. This behavior is consistent with tar cracking occurring by a random scission mechanism.

#### 3.3 Homogeneous Kinetics

Yield data from the tubular packed bed reactor were used to calculate kinetic

parameters as described in Section 2. Resulting best fit kinetic parameters for formation of secondary gases and for the homogeneous cracking of tar are given in Table 2.

The extent of secondary reaction is a function of both temperature and time. The separate effects of temperature and time can be described by a single parameter called "reactor severity," equal to the product of the rate constant at the reactor temperature and the isothermal residence time. Plots of the experimental yield of tar and individual gaseous products as a function of the dimensionless reactor severity ( $kt$ ) are shown in Figures 2 - 5 together with smooth curves denoting the corresponding model predictions. The model predicts the experimental yields with an error generally less than ten percent.

Homogeneous kinetic results of this study were compared to results found in the literature. Vapor phase cracking of wood pyrolysis tars from an unspecified softwood was studied by Diebold (1) and cracking of tars from both cherry and yellow pine was studied by Mattocks (2). Due to differences in product group definitions as well as modeling techniques and assumptions, our results could not be directly compared to the results of Mattocks.

Diebold's kinetic parameters for the cracking of volatiles to gases ( $A = 10^{5.19} \text{ sec}^{-1}$ ,  $E = 87.5 \text{ kJ/mole}$ ) are comparable to the tar cracking parameters from this study ( $A = 10^{4.98} \text{ sec}^{-1}$ ,  $E = 93.3 \text{ kJ/mole}$ ). Over the common temperature range of experimentation (650 - 800°C) the rate constant of Diebold is only 3 - 3.5 times higher than that found in this work despite the differences in the reactor type and wood producing the primary volatiles. The small discrepancy could be due to effects of wood type, to slight differences in the models, or to Diebold's need to calculate the gas composition entering the isothermal section of his volatiles cracking reactor. In the present work the entering gas composition is measured directly in the Mode I runs.

#### 4. Conclusions and Significance

The experimental results of this study identified and quantified those products generated by primary pyrolysis of wood and those formed by extra-particle secondary cracking of newly-formed wood pyrolysis tar. Tar, char, water, and carbon dioxide are primary products of wood pyrolysis. Additional carbon dioxide, however, is also formed by vapor phase cracking of tar. Carbon monoxide, hydrogen, methane, ethylene, acetylene, and ethane are products of homogeneous secondary cracking of wood tars, although modest amounts of CO, and trace quantities of methane are also observed under conditions chosen to arrest vapor phase tar cracking (Mode I). Carbon monoxide accounts for about 65 wt% of the products when fresh wood tar undergoes vapor phase cracking.

Tars surviving various extents of post pyrolysis secondary thermal cracking were characterized by size exclusion chromatography (SEC). SEC indicates that tars surviving vapor phase cracking are lower in weight-average molecular weight than the uncracked tars. In addition, there was no evidence for tar molecular weight growth among these surviving tars. This result is consistent with the experimental observation of negligible coke production during vapor phase tar cracking.

The experimental yields of the individual gaseous products from homogeneous cracking of wood pyrolysis tar can generally be predicted by global single-reaction first-order kinetic models to within better than ten percent. These first-order kinetic parameters are sufficiently intrinsic to be used in reactor design calculations including predictions of the contributions of extra-particle homogeneous vapor phase tar reactions. These parameters can also be used to estimate the kinetics of intra-particle homogeneous reactions of tar vapor, but further work will be needed to define the validity of this application.

#### Notation

- $A_1$  - Arrhenius pre-exponential factor for species 1
- $E_1$  - apparent Arrhenius activation energy for species 1
- $k_1 = A_1 \exp(-E_1/RT)$  - Arrhenius rate constant
- R - gas constant
- T - absolute temperature

$V_1^*$  - ultimate yield in weight percent of wood of species 1  
 $V_1$  - yield in weight percent of wood of species 1  
 $V$  - volume of reactor 2  
 $V_b$  - volume of char bed in reactor 2  
 $F$  - volumetric gas flow rate at reactor 2 temperature

#### Acknowledgements

Most of the above work was supported by the National Science Foundation, Division of Chemical and Process Engineering, Renewable Materials Engineering Program, under Grant Nos. CPE-8212308 and CBT-8503664. We also gratefully acknowledge an NSF Fellowship for M. Boroson and financial support by the Edith C. Blum Foundation of New York, NY and the Robert C. Wheeler Foundation of Palo Alto, CA. Drs. M. K. Burka, J. Hsu, L. Mayfield, and O. R. Zaborsky (NSF) have served as technical project officers. Christine Clement and Anne Reeves have made valuable contributions to this work.

#### Literature Cited

1. Diebold, J. P., "The Cracking Kinetics of Depolymerized Biomass Vapors in a Continuous, Tubular Reactor," M.S. Thesis, Dept. of Chemical and Petroleum-Refining Engineering, Colorado School of Mines, Golden, Colorado (1985).
2. Mattocks, T. W., "Solid and Gas Phase Phenomena in the Pyrolytic Gssification of Wood," M.S. Thesis, Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey (1981).
3. Nunn, T. R., J. B. Howard, J. P. Longwell, and W. A. Peters, "Product Compositions and Kinetics in the Rapid Pyrolysis of Sweet Gum Hardwood," Ind. Eng. Chem. Process Design Develop., 24, 836-844, (1985).
4. Serio, M. A., "Secondary Reactions of Tar in Coal Pyrolysis," Ph.D. Thesis, Dept. of Chemical Engineering, MIT, Cambridge, Massachusetts (1984).
5. Lede, J., J. Panagopoulos, and J. Villermaux, "Experimental Measurement of Ablation Rate of Wood Pieces, Undergoing Fast Pyrolysis by Contact With a Heated Wall," Am. Chem. Soc. Div. of Fuel Chem. Preprints, 28 (5), 383 (1983).

Table 1. Product Yields (weight % of wood)  
 as a Function of Thermal Treatment

	Primary Yields	Secondary Reaction Yields		
		600°C 1.2 s	700°C 1.0 s	800°C 1.0 s
Tar	52.8	36.6	16.6	6.1
Char	18.3	18.1	18.4	17.8
CH <sub>4</sub>	0.4	1.7	3.8	5.5
CO	3.2	14.7	25.7	35.7
CO <sub>2</sub>	6.8	9.7	11.4	13.2
C <sub>2</sub> H <sub>2</sub>	0.0	0.1	0.5	0.6
C <sub>2</sub> H <sub>4</sub>	0.0	1.2	3.6	5.4
C <sub>2</sub> H <sub>6</sub>	0.0	0.1	0.3	0.4
H <sub>2</sub> O	16.3	17.3	17.0	15.2
H <sub>2</sub>	0.0	0.1	0.6	1.0

Table 2: Kinetics Parameters for Gas Formation and Tar Cracking

	log A (sec <sup>-1</sup> )	E (kJ/mole)	v* (wt% of wood)
CH <sub>4</sub>	4.89	94.1	5.83
C <sub>2</sub> H <sub>4</sub>	5.76	109.3	5.17
C <sub>2</sub> H <sub>6</sub>	7.52	138.8	0.38
CO <sub>2</sub>	2.55	48.8	13.20
CO	4.66	87.8	36.33
H <sub>2</sub>	6.64	128.4	1.09
TAR	4.98	93.3	5.79

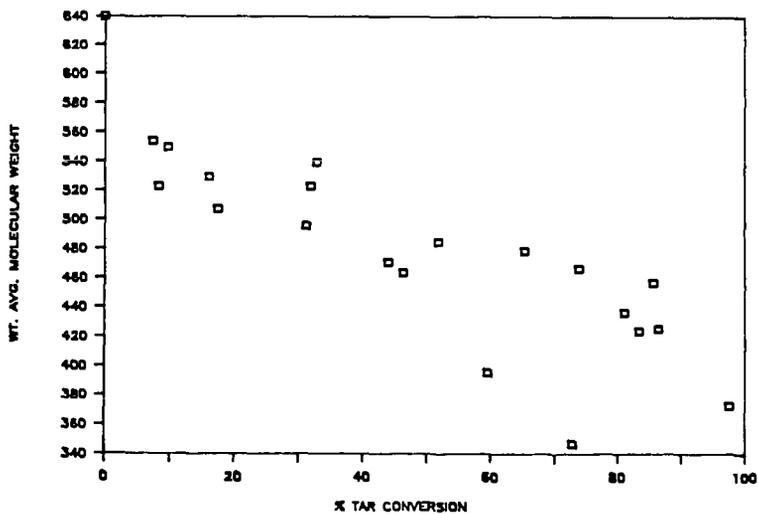


Figure 1: Effect of Vapor Phase Thermal Treatment on Weight Average Molecular Weight of Surviving Tar

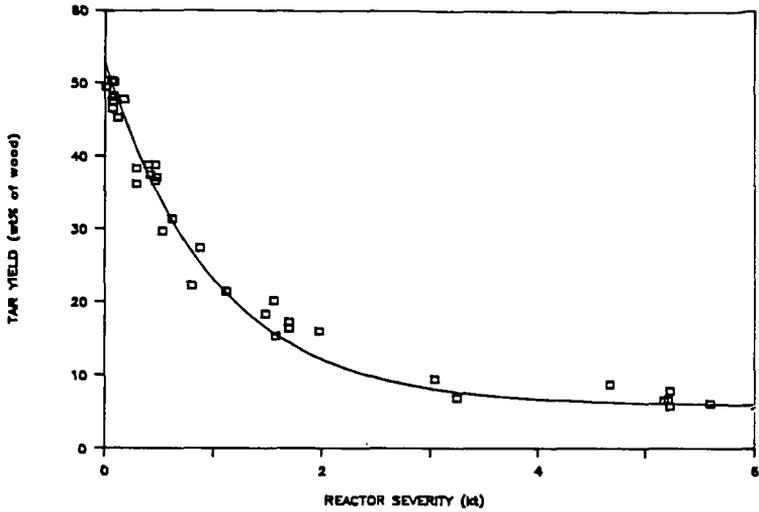


Figure 2: Effect of Reactor Severity on Tar Yield (— model prediction)

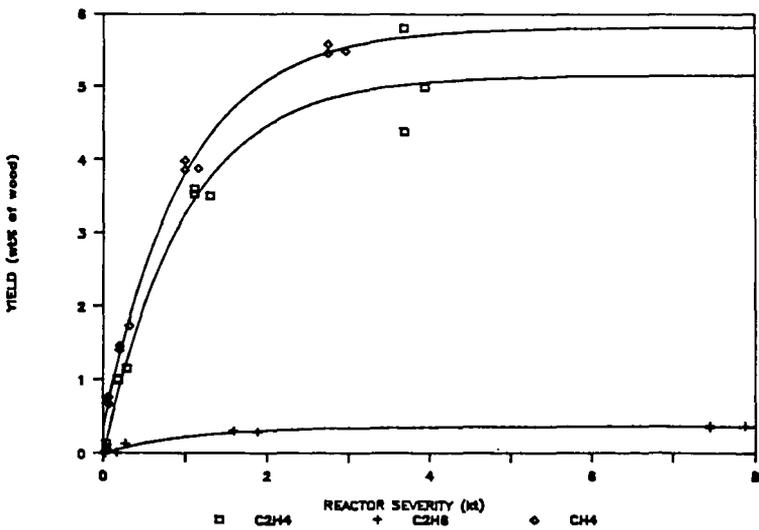


Figure 3: Effect of Reactor Severity on Ethylene, Ethane, and Methane Yields (— model prediction)

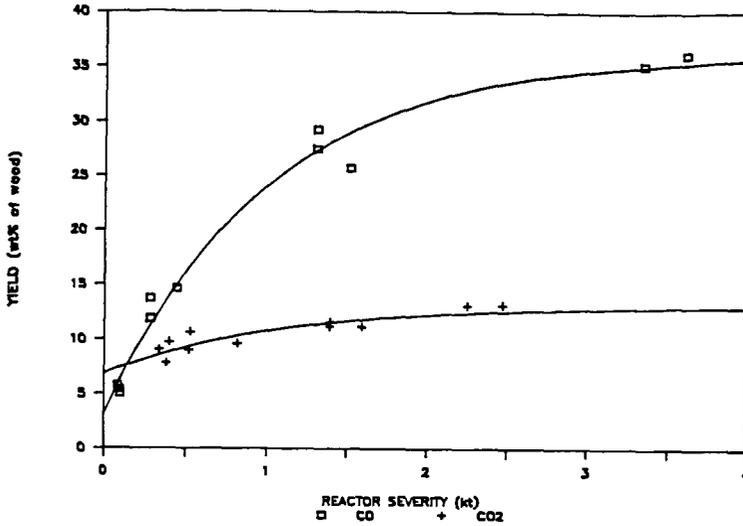


Figure 4: Effect of Reactor Severity on Carbon Monoxide and Carbon Dioxide Yields ( — model prediction)

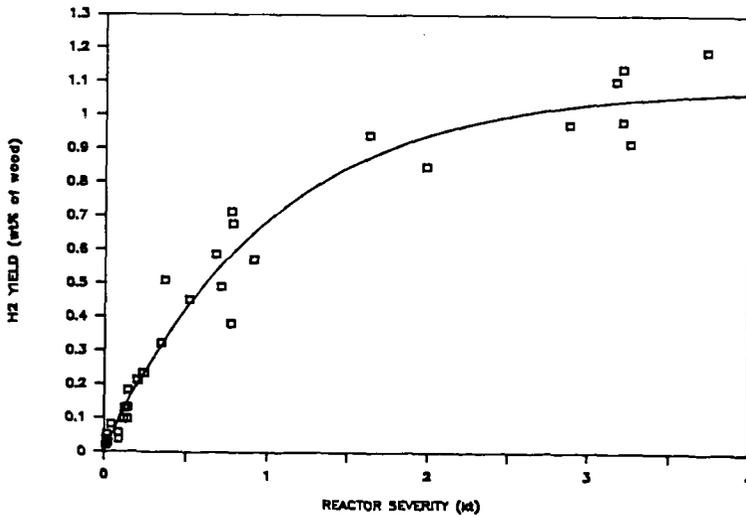


Figure 5: Effect of Reactor Severity on Hydrogen Yield ( — model prediction)