

PREDICTING VAPOR PRESSURES OF TAR AND METAPLAST DURING COAL PYROLYSIS*

Thomas H. Fletcher
Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551-0969

David M. Grant and Ronald J. Pugmire
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

INTRODUCTION

Models of coal pyrolysis have progressed from simple one or two step empirical Arrhenius expressions that correlate total mass release during devolatilization,^{1,2} as reviewed by Anthony and Howard,³ to detailed descriptions of hydrocarbon chemistry and mass transport.⁴⁻⁸ These models describe the yields and compositions of pyrolysis products from coal under a wide range of heating conditions and ambient pressures. During pyrolysis of softening coals, a liquid phase appears that is referred to as metaplast. Release of pyrolysis gases and tar vapors inside the particle cause bubble formation in the softened coal particle, followed by swelling (increase in the particle diameter) with large internal voids (cenosphere formation). The softened state is followed by crosslinking or repolymerization which solidify the char matrix. As the coal particle is heated to sufficiently high temperatures, the light species in the metaplast are released as hydrocarbon vapors, along with light gases. Coal tar is generally defined to consist of those species which are released from the coal during pyrolysis which condense at room temperature and pressure. Low rank coals and lignites generally give low tar yields, and do not exhibit much softening or swelling behavior; this non-softening behavior may be caused by early crosslinking reactions.⁹ High rank coals (i.e., anthracites and low volatile bituminous coals) contain low amounts of volatile matter, and hence coal particles remain relatively intact during pyrolysis unless fragmentation occurs.

Mass transport affects coal pyrolysis in two ways: (1) as the ambient pressure increases, the tar yield decreases, and (2) as particle size increases, the tar yield decreases. However, there seem to be regions where the two mass transport effects are not controlling. For instance, in vacuum, the small pressure generated inside the pyrolyzing coal particle from the release of light gases and tar vapors may control the process. Also, total volatiles yields from a lignite were observed to remain constant with increasing ambient pressure,¹⁰ although this is probably due to the low tar yield of the lignite. Changes in coal pyrolysis yields as a function of particle size for diameters less than 200 μm are small.¹¹

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Different theoretical treatments of mass transfer effects on coal tar evolution are reviewed by Suuberg¹². Bubble transport models have recently been developed to describe intraparticle transport of tar and gases, along with the resultant characteristics of the char particle.^{8,13} The radial transport of bubbles from the particle interior to the particle surface is calculated in these models using a momentum equation and an effective diffusivity. Other models⁵⁻⁷ assume that the particle is small, and do not treat radial transport of material from the interior of the particle. These models are generally applicable for particles less than 200 μm in diameter, where product yields are nearly independent of particle size. In all of these models, however, the effects of pressure are treated assuming some relationship between vapor pressure, molecular weight, and temperature. As the ambient pressure increases, only the species with high vapor pressures (i.e., low molecular weight) are released from the metaplast as tar. In vacuum, even relatively high molecular weight species may have vapor pressures higher than the ambient pressure and are released as tar.

VAPOR PRESSURES OF COAL PYROLYSIS PRODUCTS

Vapor pressure data on coal tar are unavailable, so vapor pressure correlations based on compounds found in coal tar are generally used to develop vapor pressure correlations based on molecular weight. Unger and Suuberg¹⁴ proposed a vapor pressure correlation based on fitting the boiling points of six aromatic hydrocarbons at a total pressure of 6.6×10^{-4} atm (0.5 mm Hg). These compounds were selected because of their high molecular weight (198 to 342) and their lack of heteroatoms. The resulting correlation is:

$$P_i^v = \alpha \exp\left(\frac{-\beta MW_i^\gamma}{T}\right) \quad (1)$$

where $\alpha = 5756$, $\beta = 255$, and $\gamma = 0.586$, and units are in atmospheres and Kelvin. The form of Eq. 1 is related to the Clausius-Clapeyron equation, assuming that the heat of vaporization is proportional to molecular weight.

Several investigators have attempted to use the Unger-Suuberg correlation to describe tar release from the metaplast. Many investigators use the form of the Unger-Suuberg correlation, but not the constants proposed by Unger and Suuberg. Solomon and coworkers⁵ used the Unger-Suuberg correlation multiplied by an arbitrary factor of 100 in order to fit tar and total coal volatiles yields as a function of pressure. Niksa⁶ used a similar form that was easy to integrate analytically, with $\gamma = 1$, and used α and β as adjustable parameters in a comprehensive devolatilization model in order to fit tar molecular weight data from Unger and Suuberg.¹⁵ Oh and coworkers⁸ and Hsu¹³ found that by using the Unger-Suuberg correlation, good agreement could be achieved with high temperature pyrolysis data ($T > 873$ K) but not with low temperature data ($T < 873$ K). The current work suggests why the Unger-Suuberg correlation does not apply to coal pyrolysis conditions, and suggests an alternate correlation.

The vapor pressure correlation of Unger and Suuberg¹⁴ was based only on low vapor pressures (0.5 mm Hg), and has been extrapolated to much higher pressures and molecular weights in coal devolatilization models. Reid, et al.¹⁶ recommend using the Antoine equation to calculate vapor pressures (if constants are available) when the vapor pressure is in the range 10 to 1500 mm Hg

(.01 to 2 atm). However, Reid and coworkers conclude that no correlation produces good agreement with data for $P_i^v < 10$ mm Hg (.01 atm). The approach used here is to develop new constants for Eq. 1 based on additional data at both low and high vapor pressures in order to apply to a wide range of coal pyrolysis conditions..

Gray, et al.^{17,18} measured vapor pressures as a function of temperature for twelve narrow boiling fractions distilled from coal liquids produced from SRC-II processing of Pittsburgh seam bituminous coal. In their study, temperatures ranged from 267 K to 788 K, and the coal liquids exhibited molecular weights as high as 315 with vapor pressures as high as 35 atm. It is assumed that these are representative of low molecular weight tars released during primary pyrolysis. Gray and coworkers discuss equations of state that fit the vapor pressure data using critical properties of the liquid (i.e., the critical temperature and pressure). However, for the purposes of coal pyrolysis, critical properties are not well known, and simpler correlations are preferable.

The constants derived from a curve fit of the data of Gray, et al.^{17,18} using Eq. 1 are shown in Table 1, along with the expressions used by Unger and Suuberg and by Niksa. This correlation, referred to hereafter as the Fletcher-Grant correlation, agrees very well with the measured vapor pressures of the different molecular weight fractions, as shown in Fig. 1. It is interesting that the coefficient on the molecular weight (γ) from the Fletcher-Grant curve fit to the data of Gray and coworkers is 0.590, which is very close to the value of 0.586 found by Unger and Suuberg. The value of β from the Unger-Suuberg correlation is 255, which also compares reasonably well with the value of 299 in the Fletcher-Grant correlation. The major difference between the two correlations is the value for α ; the value of α in the Fletcher-Grant correlation is fifteen times greater than in the Unger-Suuberg correlation. This trend is consistent with recent modeling efforts⁵, where the vapor pressure from Unger-Suuberg correlation was multiplied by a factor of 100 in order to achieve agreement with a wide range of experimental data.

The Fletcher-Grant vapor pressure correlation presented in Table 1 was compared with boiling point data for 111 compounds at pressures of 5, 60, 760, and 7600 mm Hg (0.0066, 0.079, 1.0, and 10 atm). Boiling point data were obtained from Perry and Chilton;¹⁹ a list of the selected compounds is available.²⁰ Molecular weights as high as 244 are considered in this set of compounds. Long chain alkanes (hydrogen to carbon ratios greater than 1.5) and heteroatoms with more than two oxygen atoms were not considered in this data set, since they do not occur in coal tars to a significant extent. Boiling point data at 10 atmospheres were only available for five compounds (benzene, phenol, toluene, aniline, and ethylbenzene). The Fletcher-Grant correlation was found to agree surprisingly well with the boiling points of these compounds at all four pressures, as shown in Fig. 2a. This is a simplistic vapor pressure expression, and the variations in the chemical structures of the various compounds are not considered. The correlation proposed by Unger and Suuberg¹⁴ agrees with this set of data at the lowest pressure, but predicts higher boiling points than the average of the data at pressures of 1 and 10 atm (see Fig. 2a).

Coal pyrolysis experiments have been conducted at pressures as high as 69 atm,²¹ with reported tar molecular weight distributions extending into several thousand amu. Figure 2b shows an extrapolation of three vapor correlations to higher temperatures, pressures, and

molecular weights than shown in the left panel, representing a wide range of pyrolysis conditions. The difference between the Fletcher-Grant correlation and the Unger-Suuberg correlation becomes more pronounced at higher pressures. For example, the predicted boiling point of a species with a molecular weight of 400 amu by the Fletcher-Grant correlation is nearly 500 K lower than that predicted by the Unger-Suuberg correlation. In contrast, the parameters in the vapor pressure correlation used by Niksa⁶ were used as fitting parameters to achieve agreement with measured molecular weight distributions. As shown in Fig. 2b, the Niksa correlation gives boiling points that are 800 K lower than predicted by the Fletcher-Grant correlation at atmospheric pressure for a molecular weight of 400 amu. The Fletcher-Grant vapor correlation agrees with measured vapor pressures of coal liquids and boiling points of pure compounds over a wide range of pressures; the constants α , β , and γ used in the correlation are fixed, thereby reducing the number of unknown parameters in coal pyrolysis models.

APPLICATION TO PRESSURE-DEPENDENT COAL PYROLYSIS CALCULATIONS

The chemical percolation devolatilization (CPD) model was developed by Grant, et al.⁷ to describe coal pyrolysis based on the chemical structure of the parent coal. The CPD model treats coal as an array of aromatic clusters, connected by aliphatic labile bridges. As the coal is heated, labile bridge scission creates finite fragments consisting of several aromatic clusters which are no longer attached to the infinitely large coal matrix. Percolation lattice statistics are used to describe the relationship between labile bridge scission and the generation of aromatic clusters of finite size (forming tar and metaplast). This model was extended to treat the effects of heating rate and temperature,²² and recently extended to treat vapor-liquid equilibrium between tar and metaplast as well as crosslinking of the metaplast.²³ In the CPD model, the assumption is made that all gaseous species (light gases and tar vapors) are convected away from the particle due to the increase in volume between the gas and solid. The convection step is assumed to be instantaneous compared with the chemical reactions of bond scission and char formation. This approach is similar to those of Niksa⁶ and Solomon, et al.,⁵ who treat the internal mass transfer in an approximate manner, based on the convection of tars by light gases. The low molecular weight clusters are released as tar vapor, while the high molecular weight clusters are not vaporized, and remain in a liquid or solid state within the char matrix as metaplast.

The Fletcher-Grant correlation is combined with Raoult's law and a flash distillation calculation²⁴ at each time step to determine the partitioning between vapor and liquid for each aromatic cluster size. A detailed description of the equations used is provided by Fletcher and Hardesty.^{20,24} The treatments of mass transfer determine where vapor-liquid equilibrium between tar and metaplast may occur. Bubble transport models assume vapor-liquid equilibrium within the small bubbles and at the vapor-liquid interface in the large bubbles. In the CPD model, the tar vapor and light gases leave the vicinity of the particle as they are formed, and only the tar and light gas formed in the last time step are considered to be in vapor-liquid equilibrium with the metaplast. In a different approach used by Solomon, et al.⁵ and by Niksa,⁶ the tar vapor is convected only by the light gas, and it is assumed that the volume of vaporized tar is insignificant compared to the volume of evolved light gas. If tar vapor is formed, but no light gases are formed at the same time, the tar vapor is trapped within the particle. Other approaches allow for the possibility that some liquid from the metaplast may be entrained in the light gas in an attempt to explain reported molecular weights greater than 1000 amu,¹² where

the molecular weight is too high to allow vaporization. However, there is a large disagreement on the methods for measurement of tar molecular weight distributions, and recent data do not exhibit such large molecular weights.^{5,25}

The vapor pressures predicted by the Fletcher-Grant correlation drop steeply with molecular weight, implying that there is little vaporization of high molecular weight compounds. In other words, most of the tar vapor at a given temperature consists of compounds with vapor pressures higher than the ambient pressure. It is assumed that the volume of tar vapor alone is sufficient to cause rapid evolution from the vicinity of the particle, without the necessity of transport by lighter gases. This is consistent with experimental results of Suuberg, et al.¹² which indicate that tar evaporation is more important than transport of liquid tar by light gas.

Comparisons between predictions made with the CPD model and experimental tar and total volatiles yields measured as a function of pressure are presented in Fig. 3. Data for a Pittsburgh #8 bituminous coal are from heated grid experiments by Anthony¹⁰ and by Suuberg and coworkers.²¹ Particle heating rates in these experiments were approximately 1000 K/s for the Suuberg data and 700 K/s for the Anthony data, with a final temperature of 1273 K and hold times ranging from 2 to 10 s. Model predictions were made with a heating rate of 1000 K/s and a 5 s hold time at 1273 K using the chemical structure coefficients from Solum, et al.²⁶ for a Pittsburgh No. 8 coal, with slight adjustments made to two parameters to match the tar and total volatiles yield data at 1 atm.²³

The dashed line in Fig. 3a represents the predicted yield if there is no pressure drop inside the particle, whereas the solid line represents a minimum internal particle pressure P_{min} of 0.01 atm. A minimum internal particle pressure of 0.2 atm was used by Solomon and coworkers.⁵ The pressure buildup inside the particle is due to volume expansion of light gases and tars during coal devolatilization. The predictions made using $P_{min} = 0.01$ agree quite well with the reported total volatiles and tar yields for the bituminous coal.

Model predictions of the pressure-dependent devolatilization behavior of a lignite are shown in Fig. 3b, along with data from Anthony¹⁰ and Suuberg.²⁷ The tar yield for this lignite is very low, and hence the small effect of pressure on total yield compared to the bituminous coal. Total volatiles yields for the lignite decrease only slightly with increasing pressure in both the experimental data and the model predictions. The predicted tar yield decreases slightly with increasing pressure, but the gas yield increases to compensate, and hence the slight decrease in total volatiles yield with increased pressure.

The lignite contains a large amount of mass in the side chains and bridges; the number of aliphatic carbons per cluster determined by NMR analyses for lignites is twice that determined for bituminous coals.^{23,28} At atmospheric pressure, the gas precursors (side chains) attached to the tar are released as tar, and can detach from the tar as light gas if the ambient gas temperature is high enough. In heated grid experiments, the gas is immediately quenched, and the gas precursors remain in the tar. At elevated pressures, more tar remains in the lignite, and the associated side chains are released as light gas. Due to the large mass in the side chains, the increased gas yield largely compensates for the decrease in tar yield, and the total volatiles yields is almost independent of pressure.

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Table 1
Vapor Pressure Correlations for Coal Pyrolysis Tar and Metaplast

	$P_i^y = \alpha \exp\left(\frac{-\beta MW_i^y}{T}\right)$		
	α	β	γ
Unger-Suuberg ¹⁴	5756	255	0.586
Niksa ⁶	70.3	1.6	1.0
Fletcher-Grant (this work)	87,060	299	0.590

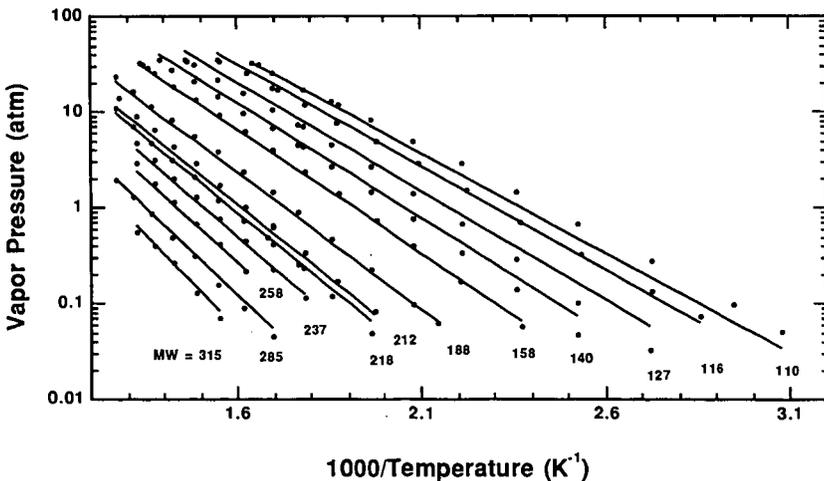


Figure 1. Comparison of the Fletcher-Grant vapor pressure correlation with vapor pressure data from Gray, et al.^{17,18} for twelve narrow boiling fractions of coal liquids from a Pittsburgh seam coal.

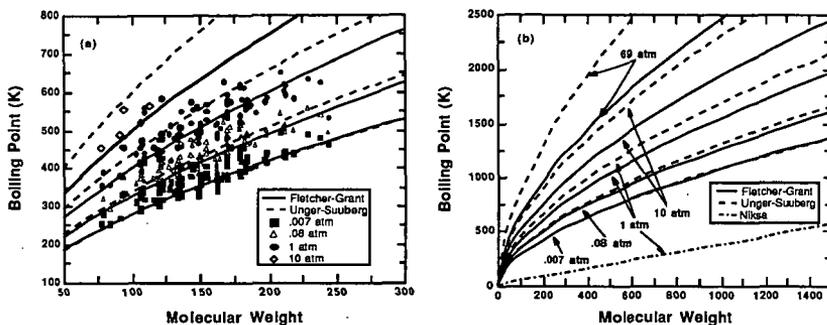


Figure 2. Comparison of the Fletcher-Grant, Unger-Suuberg,¹⁴ and Niksa⁶ vapor pressure correlations (a) with boiling point data for 111 organic compounds at pressures of .007, .08, 1, and 10 atm (5, 60, 760, and 7600 mm Hg) and (b) at pyrolysis conditions.

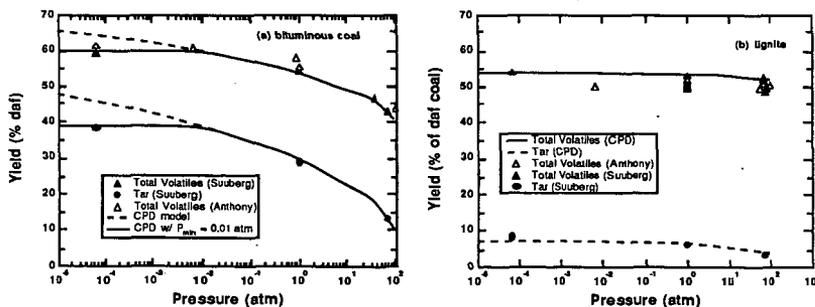


Figure 3. Comparison of CPD model predictions with pressure-dependent tar and total volatiles yield data from Anthony¹⁰ and Suuberg, et al.^{21,27} for (a) bituminous coal and (b) lignite. Dashed lines represent predictions with no minimum internal particle pressure; solid lines represent predictions with a minimum internal pressure of 0.01 atm.