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Modeling Soot Formation from Solid Complex Fuels

Alexander J. Josephson^{1,2,*}, Emily Hopkins², Rodman R. Linn², and David O. Lignell¹

¹*Department of Chemical Engineering, Brigham Young University, Provo, UT*

²*Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM*

**Corresponding author: alexanderj@lanl.gov*

Abstract: While the phenomena of soot formation in gaseous flames is well studied and understood, extension of the fundamental mechanisms to systems containing complex solid fuels can introduce large uncertainties and inaccuracies. In this study, we have developed a detailed physics-based model for predicting the evolution of soot particles formed in systems containing complex-solid fuels such as wood or coal. This detailed physics-based model includes two particle-size distributions: that for soot particles and for soot precursor molecules. Sub-models for precursor creation, growth, and thermal cracking are included along with soot particle nucleation, coagulation, surface growth, aggregation, oxidation, and gasification. Validation work is presented comparing experimental results for a coal flame and biomass gasifier against model predicted values for soot concentrations and size distributions. The full detailed model can be computationally expensive when incorporated into CFD simulations; therefore, model simplifications are explored and presented in this work along with some preliminary work of applying particle formation physics to wildfire simulations.

Keywords: *soot formation, method of moments*

1. Introduction

The presence of soot particles in combustion processes has been observed for centuries, but only in the last several decades have the effects of these particles been studied, evaluated, and understood. Soot particles have significant effects on the thermal radiation emitted by a flame. This thermal radiation impacts both a flame's radiative heat transfer and heat loss: increasing radiative heat flux while at the same time decreasing local temperatures, which in turns affects flame chemistry. In addition, it is known that if soot particles break through the flame's oxidation layer they form air-bound aerosols which are both detrimental to human health and have negative environmental consequences.

Because of the aforementioned effects, it is important for researchers and modelers to understand mechanisms that govern the formation and behavior of soot particles in combusting systems. For gaseous-fuel flames, mechanisms of soot formation have been well-researched and detailed, but not as much for solid complex fuels such as wood or coal.

In general, it has been found that soot formation follows a series of well researched mechanisms described here. Soot precursors are polyaromatic hydrocarbons (PAHs) formed in fuel-rich areas, these precursors nucleate into soot particles. In gaseous fuels, the formation of PAHs is usually the rate-limiting step in soot formation; in solid fuels, however, PAHs are usually released during the initial pyrolysis of the fuel, bypassing this rate-limiting step [1]. After soot particle nucleation occurs, particles grows through kinetic interactions between particle surfaces and the surrounding

gas. At the same time, these particles combine together through coagulation. Once the particles reach a critical size, they begin to aggregate, forming chains of spherical particles. Concurrent to this formation process, there are periods of consumption, either through oxidation, or, in special circumstances, through gasification.

In this study, a detailed model has been developed for the formation of soot in solid fuel systems and that model is validated against two different experiments. This model is computationally expensive and thus is not appropriate for large-scale simulations. As a result, subsequent efforts have been made to simplify this model and some of these efforts will be presented here as well.

2. Detailed Model Development

The proposed detailed soot model describes two particle size distributions (PSD): that for soot precursors and that for soot particles. The precursor PSD is represented by a sectional approach and the soot PSD represented by the method of moments. This detailed model contains sub-models for precursor mechanisms (formation, growth, and thermal cracking) as well as soot particle mechanisms (nucleation, surface growth, agglomeration, and consumption).

2.1 Precursor Dynamics

Precursor formation is accomplished in two ways: the release of precursors during the primary pyrolysis of the parent fuel and through the build-up of PAHs from gas-phase mechanisms. In the following validation studies, the coal percolation devolatilization (CPD) [2] model and its biomass adaptation (CPD-bio) [3] were used to predict the release of tar during primary pyrolysis. These models were modified slightly to output a time-evolved sectional distribution of tar instead of an overall tar yield. Tar, which is defined as the volatiles that would condense if cooled to room temperature, are largely aromatic and act as a primary soot precursor in these systems.

The build-up of PAHs from gas-phase mechanisms is modeled using a temperature equilibrated ABF mechanism [4]. This mechanism contains 99 species and 544 reactions and reflects the building of aromatic rings up to pyrene from basic gas-phase components. The formation of pyrene adds to the section of the precursor distribution associated with its molecular weight.

Once precursors are formed, they may grow through the hydrogen-abstraction-carbon-addition (HACA) mechanism well established in the literature [4] or be consumed through oxidation or gasification. Either mechanism effectively moves molecules among different sections of the distribution as molecules either grow or shrink.

In addition, precursors may thermally crack, either shrinking in size or completely cracking to light gases. This process is modeled using a scheme developed by Marias, et al. [5] and adapted to this detailed model. In this submodel, precursors are classified into four different types, dependent on their chemical composition: phenol, toluene, naphthalene, or benzene. From these four types, the scheme depicted in Fig. 1 is applied. Each type cracks at a rate given by the model, when that type cracks it gives off some or all of its weight as light gases and the remaining converts into another type. As it is undesirable to resolve four types for each precursor section, the fraction of each type is kept constant throughout a simulation with the fraction amounts determined through a pre-simulation evaluation which estimates what the time-averaged fractions would be from inception to consumption of all precursors.

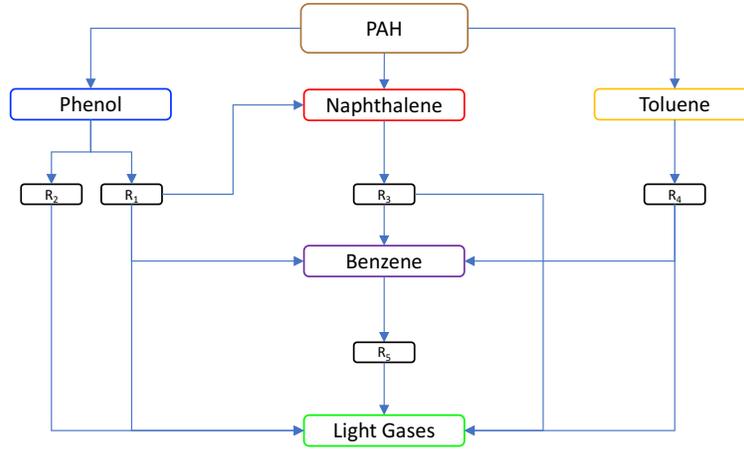


Figure 1: Thermal cracking scheme as applied to soot precursors. [5].

Precursors are also consumed through the nucleation process which converts precursors into primary soot particles.

2.2 Soot Particle Dynamics

Nucleation is accomplished by the coagulation of two precursor molecules. This nucleation is modeled by calculating a frequency of collision between precursors using the kinetic theory of gases. As they coagulate, the moments of the soot PSD are increased according to the PSD sections of the coagulating precursors.

Like the soot precursors, soot particles undergo interactions with the surrounding gases: surface growth via HACA, or consumption via oxidation/gasification. These surface interactions affect the soot PSD moments in the following way [6]:

$$\frac{dM_r}{dt} = \pi \left(\frac{6}{\pi\rho} \right)^{2/3} \frac{k_s m_0^{2/3-d}}{\Delta m} \sum_{k=0}^{r-1} \Delta m^{r-k} M_{k+d}, \quad (1)$$

Where k_s is the rate of reaction in $kg\ m^{-2}s^{-1}$, Δm represents the mass change due to a single reaction, m_0 is the mass of the primary soot particle (~ 400 kg/kmole), and d is a shape factor for the particle as introduced by Balthasar and Frenklach [7] to accommodate particle aggregation behavior. Fractal moments are resolved using interpolative closure between resolved whole moments.

Coagulation between particles is modeled according the coagulation scheme developed by Frenklach [8]; in which, coagulation is computed based on frequency of collision between particles in the continuum regime and free-molecular regime, then a weighted average is taken between the two based on a local particle Knudsen number.

Aggregate behavior is accounted for by introducing a 'surface moment,' M_d , as described by Balthasar and Frenklach [7]. This surface moment is used to compute the shape factor, d , mentioned above and is resolved using submodels present in Balthasar's paper.

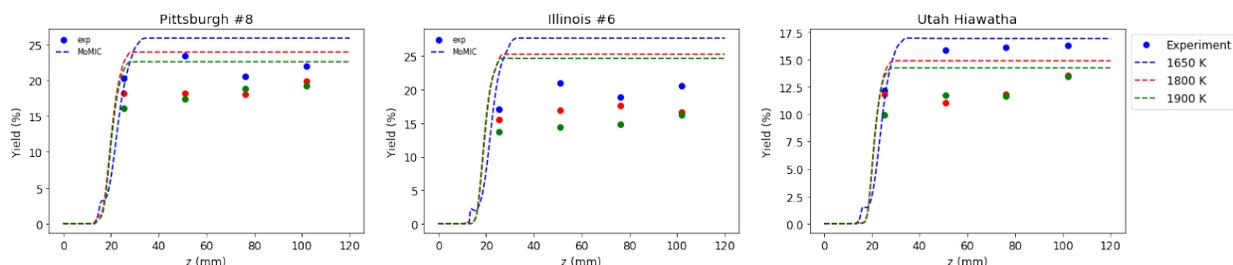


Figure 2: Comparison of model predicted total soot yields versus those measured soot yields for the Pittsburgh #8 coal at experimental temperature of 1650 K.

3. Validation

This model was validated against two different experiments: a coal-fired flat flame burner and a biomass gasifier.

3.1 Coal-System Validation

The coal-system experiment consists of data collected by Ma, et al. [9]. In the experiment, coal was fed into a flat-flame burner and particles were collected from the flame using a water-cooled nitrogen-quenched suction probe at four locations along the flame center-line. Collected particles were sent through a particle separation system which consists of a virtual impactor, a cyclone, and two soot filters. Large soot aggregates ($5+ \mu\text{m}$ in diameter) were separated from char particles using a sieve with $38 \mu\text{m}$ openings. Six different coal types were tested at three temperatures each.

Results produced by the proposed soot model are shown in Fig. 2 depicts the total soot yield as a percentage of the parent coal mass for three of the coal types. The dotted line represents the model predictions while the points represent the actual measured data. There is reasonable agreement between the model predictions and experimentally measured data as both experiment and model level out to similar concentrations after 30 mm. The model does tend to over-predict yields compared to experimental data, but trends remain consistent and within reasonable error between simulations and experiments.

Due to the configuration of the experiment, there are certain aspects of the proposed soot model that are validated very well by comparisons with this study; however, there are other aspects of the model which are not validated. In the experiment, soot concentrations are dominated by the nucleation of tar molecules to form soot particles, and because of this, the tar formation, PAH cracking, and PAH coagulation portions of the nucleation are well validated. The pyrene formation and surface growth of PAH molecules are not as well tested because the nature of the pre-mixed flame to which the coal particles were added discouraged the formation of pyrene and acetylene, meaning that the effect of these particular two mechanisms were minimal in this set-up.

Just as in the PAH phase, surface growth in the soot phase was also minimal for the same reason stated above. Also, since particles were collected in fuel-rich locations, the effects of soot oxidation/gasification were also minimal. This is consistent with the leveling of the curve shown in Figure 2. Soot coagulation, on the other hand, has been validated.

By measuring particles caught in the two different soot filters, the experimenters were able to

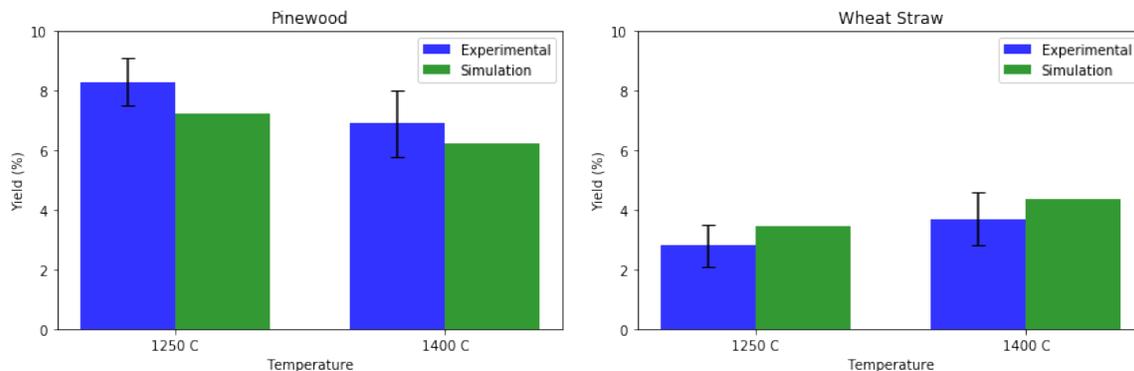


Figure 3: Comparison of model predicted total soot yields versus those measured soot yields for the three different biomass types at temperatures 1250 C and 1400 C.

separate soot particles that were $<5 \mu\text{m}$ in diameter. This allows the validation of the model's coagulation portion due to the shrinking concentration of smaller particles while the overall mass remains constant, indicating coagulation.

3.2 Biomass-System Validation

The wood-system experiment consists of data collected by Trubetskaya, et al. [10]. In this study, biomass was fed into a fast pyrolysis drop tube reactor. This reactor was held under gasification conditions, with no oxygen fed into the reactor. Soot particles were collected from the effluent gas of the reactor and a yield was determined for three different biomass types at two temperatures each.

Figure 3 compares simulations against experimental soot yield for two of the experiments. There is good agreement between yields measured and those predicted by the detailed soot model, with all predicted yields lying within or close to the experimental error bounds reported in the literature.

Like the coal-system, certain aspects of the model were better validated than others. The configuration of the gasifier reactor allowed for pyrene and acetylene to be produced thus validating mechanisms involving these species. However, residence time in the reactor was short, thus only 5-15% of the total soot yield was due to mechanisms involving pyrene or acetylene; whereas the rest was mostly due to nucleation of tars like in the coal experiment. Also like the coal experiment, effects of oxidation and gasification were minimal.

4. Simplified Model Development

As the detailed soot model is computationally expensive, recent research has centered on methods to simplify this detailed-model to more economical models for use in simulations.

Biomass Component	Total Tar Yield (%)	Average Tar Molecular Weight (kg/kmole)
Cellulose	47.9	460
Softwood Hemicellulose	30.5	400
Hardwood Hemicellulose	30.2	396
Softwood Lignin	62.4	528
Hardwood Lignin	53.5	546

Table 1: Total precursor yield along with average molecular weights for different biomass components after primary pyrolysis.

4.1 Sooting Potential

Work has been done to simplify the prediction of soot precursors released from biomass during primary pyrolysis. In the above validation cases, the CPD and CPD-bio models were modified to output a sectional distribution of tar released during devolatilization. This is computationally expensive for simulations, so a 'sooting potential' parameter was developed to reflect the total tar released by different components of biomass from primary pyrolysis.

It is known that biomass is made up of cellulose, hemicellulose, and lignin (extractives were excluded from this study as their contribution to biomass is minimal.) Fractional composition varies between species, but the components are the same, throughout all biomass. The exception to that rule being a distinction between hardwood and softwood for hemicellulose and lignin.

Using the CPD-bio model [3], the total tar released by the different components was modeled for a range heating rates (100-1000 K/s), pressures (0.6-1.2 atm), and maximum temperatures (800-3000 K). It was found that variations in these parameters had minimal impact on the total tar yield of the fuel and results for each component can be seen in Table 1. Finding the total tar yield of biomass is simply a matter of summing the total tar yield according to its fractional composition.

4.2 Mono-Dispersed Distributions

One option for model simplification is to assume that each PSD is mono-dispersed rather than a full distribution. This requires a reworking of submodels but is computationally inexpensive as only 3 parameters need to be resolved at each computational node rather than 14+.

The mono-dispersed distributions assume that the molecular weight of soot precursors is set and does not fluctuate enough to significantly affect results. In the case of biomass, that molecular weight is found by taking a weighted average of the components' molecular weights found in Table 1. This assumption means that only one parameter has to be resolved for the precursor PSD: the number density of the molecules.

The soot particle distribution, on the other hand, contains two terms to be resolved: the average weight of particles and the number density. The computational savings of transporting only three parameters as well the simplification of submodels allows considerable applicability of this simplified model, but accuracy decreases. The extent to which accuracy decreases is system dependent and a matter of ongoing research.

A cost-reducing strategy to be mentioned here but has to be done on a case-by-case basis involves a minor sensitivity analysis. Knowing the sensitivity of soot mechanisms to the combustion environment allows researchers to save on computational costs by omitting certain mechanisms

that could be considered negligible for their circumstances. For example: it is known that soot gasification can often be considered negligible [1], except in cases of high concentrations of H₂O or CO₂ (ie oxy-fuel combustion). It would be economical for researchers to remove this mechanism from simulations for air-fired combustion.

4.3 Surrogate Modeling

At times, the size of a computational node is too large to capture the physics of soot formation; such is the case for wild-fire simulations. Ongoing research is focused on creating surrogate models which can predict soot formation in such systems. These surrogate models are being created by first implementing the detailed-physics model described above to basic circumstances encountered in these systems (ie a forest floor, canopy, or grassland). By running fine-detailed simulations of these basic domains, we are able to obtain detailed data of soot yields.

Using these soot yields, we are able to tune simple surrogate models which contain environmental parameters as inputs (fuel density, temperature distribution, moisture content, etc.) Each of these surrogate models would need to be individually tuned to different basic domains, but in cases of repeatable domains, such as a forest, these surrogate models can be powerful in predicting soot yields without the computational cost of detailed physics resolution.

5. Conclusions

A physics-based detailed model for soot formation from solid complex fuels has been developed and validated against two separate experimental cases found in the literature. Simplifications to this model to reduce computational expenses are discussed here and are under further development.

6. Acknowledgements

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References

- [1] T. H. Fletcher, J. L. Ma, J. R. Rigby, A. L. Brown, and B. W. Webb, Soot in coal combustion systems, *Progress in Energy and Combustion Science* 23 (1997) 283–301.
- [2] T. H. Fletcher, A. R. Kerstein, R. J. Pugmire, M. S. Solum, and D. M. Grant, Chemical percolation model for devolatilization. 3. Direct use of carbon-13 NMR data to predict effects of coal type, *Energy & Fuels* 6 (1992) 414–431.
- [3] A. D. Lewis and T. H. Fletcher, Prediction of Sawdust Pyrolysis Yields from a Flat-Flame Burner Using the CPD Model, *Energy & Fuels* 27 (2013) 942–953.
- [4] J. Appel, H. Bockhorn, and M. Frenklach, Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C-2 hydrocarbons, *Combustion and Flame* 121 (2000) 122–136.
- [5] F. Marias, R. Demarthon, A. Bloas, and J. P. Robert-Arnouil, Modeling of tar thermal cracking in a plasma reactor, *Fuel Processing Technology* 149 (2016) 139–152.

- [6] M. Frenklach, Method of moments with interpolative closure, *Chemical Engineering Science* 57 (2002) 2229–2239.
- [7] M. Balthasar and M. Frenklach, Detailed kinetic modeling of soot aggregate formation in laminar premixed flames, *Combustion and Flame* 140 (2005) 130–145.
- [8] M. Frenklach, D. W. Clary, T. Yuan, W. C. Gardiner, and S. E. Stein, Mechanism of Soot Formation in Acetylene-Oxygen Mixtures, *Combustion Science and Technology* 50 (1986) 79–115.
- [9] J. Ma, T. H. Fletcher, and B. W. Webb, Conversion of coal tar to soot during coal pyrolysis in a post-flame environment, *Twenty-Sixth Symposium (International) on Combustion*, Vols 1 and 2 26 (1996) 3161–3167.
- [10] A. Trubetskaya, P. A. Jensen, A. D. Jensen, A. D. G. Llamas, K. Umeki, D. Gardini, J. Kling, R. B. Bates, and P. Glarborg, Effects of several types of biomass fuels on the yield, nanostructure and reactivity of soot from fast pyrolysis at high temperatures, *Applied Energy* 171 (2016) 468–482.