

Omnisoot: an object-oriented computational package for the simulation of the gas phase synthesis of carbonaceous nanoparticles

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1 Introduction

The formation of carbonaceous nanoparticles such as soot and Carbon Black (CB) is a complex and multi-scale process that involves chemical reactions, heat transfer, and fluid and particle dynamics and spans over wide length ($\sim 10^{-12}$ to 1 m) and time ($\sim 10^{-15}$ to 1 s) scales. Understanding the effect of process parameters on particle concentration, morphology, and composition is not trivial, but crucial in health and environmental impacts soot and functional properties of CB. Soot particles are broad-band light absorbers [1], and emitted in large scales (≈ 9.5 megatons of soot) acting as the third strongest contributor to climate change after methane and carbon dioxide [2]. Because of their small size (classified as $\text{PM}_{2.5}$), soot particles can deposit on lung tissues and penetrate other organs through the bloodstream [3] and cause asthma [4] and heart disease [5]. On the other hand, CB is the largest flame-made nanomaterial by production value and volume (~ 15 megatons per year with a worth of \$17B) extensively used as a reinforcing agent in rubber and tire industries [6], and conductive additive in lithium-ion batteries [7]. CB is primarily manufactured by the furnace process which suffers from low mass yield and excessive emission, generating 4 tons of CO_2 per each ton of product on average [8]. Alternative technologies such as plasma-powered reactors for co-generation of hydrogen and CB from methane decomposition has drawn considerable interest [9, 10, 11] thanks to advantages over conventional methods in terms of yield and reduction of CO_2 emission or other pollutants [12]. Controlling CB yield, structure, morphology and composition is crucial to produce specific grades of CB tailored for various applications in both conventional and new production methods. However, the effect of process parameters such as feedstock composition, pressure, and temperature-time-history on CB properties has not been completely understood yet due to complexities of gas chemistry and CB inception and surface growth. Therefore, there is a clear need for robust computational models to predict yield, particle structure and composition under different process conditions [13] and to reduce soot emission in combustion devices.

"soot" and "Carbon Black" are distinct materials in terms of chemical properties and synthesis process [14]. While soot usually refers to the unwanted particulate matter formed during incomplete combustion of any carbon-containing material with variable organic content and a large variation in C/H ratio [14], CB is commercially produced under highly controlled partial combustion or thermal decomposition of hydrocarbons. This work focuses on soot particles generated under controlled laboratory conditions from fuels with known compositions. The mature soot formed in methane and ethylene premixed flame can reach 95% elemental C/H ratio [15], which is close to CB composition. The comparison of transmission electron microscopy (TEM) images of industrially produced CB [16] with soot sampled from diesel fuel [17, 18] indicates similarity of their morphology and structure. Hereafter, soot will be used to collectively refer to carbonaceous nanoparticles produced in flame/reactor during combustion/pyrolysis processes.

The TEM analysis of soot sampled from flames [18], reactors [19], and engines [20] with different fuels and process conditions revealed a common fractal-like morphology, often characterized as agglomerates of primary particles. High resolution transmission electron microscopy (HRTEM) of soot primary particles showed clusters of precondensed Polycyclic Aromatic Hydrocarbons (PAHs) [21] pointing to PAH as main soot precursors. This hypothesis was also supported by thermodynamic stability of PAHs enabling them to resist dissociation at high flame temperatures [22].

However, the transition PAHs (soot precursors) to incipient soot, known as *soot inception* has not been well understood at the level of pathways and elementary reactions [23] primarily due to uncertainties in PAH (precursor) chemistry, and the kinetics of PAH growth into soot particles, which is highly reversible hence sensitive to local temperature, pressure and intermediate species concentration [23].

It is not clear how PAH clusters form and what forces allow the binding occur and resist dissociation at flames temperatures (≥ 1600 T). Frenklach [24] characterized the clustering as a physical process where the sticking of PAHs upon collision forms dimers held together by Van der Waals (vdW) forces without involving chemical reactions. In fact, Herdman and Miller [25] found that the binding energy of PAHs dimers due to dispersive and electrostatic forces increases linearly with molecular mass and reaches the limit of exfoliation energy for graphite. However, the entropy barrier of dimerization increases with PAH size making them unfavorable under equilibrium conditions. So,

PAHs as large as circumcoronene ($C_{54}H_{18}$) can only form dimer to survive flame temperatures [23]. However, the concentration of large PAHs are too low to account for the observed number density of soot particles in flames [26].

Despite the gaps in fundamental understanding of soot formation and limitations of diagnostics methods, models have been developed describe the soot inception and growth. These models have been formulated as a set of clear pathways that explain soot inception based on collisions of PAH molecules. They have to be consistent with current knowledge of soot physics, feasible to be coupled with chemistry and particle dynamics models, and able to predict soot mass, PSD and morphology observed in flames and reactors.

The classic description of soot inception relies on PAH dimerization where collision of two PAH molecules (monomers in this context) forms a dimer held together by Van der Waals forces [27]. The dimerization is a irreversible process with an efficiency that accounts for the reversibility or dissociation of dimers. The theory postulates that PAH growth continues by sequential addition of a monomer (PAH molecule) forming stacks of dimers, trimers, tetramers and so on to reach a certain mass threshold that marks the emergence of incipient soot [27], but for practical purposes, a dimer is usually considered as incipient soot. Here, we call this model *Irreversible Dimerization*. Irreversible Dimerization has been used to predict soot formation in burner-stabilized premixed [28, 29], counterflow diffusion flames [30, 31], coflow diffusion flames [32, 33]. A collision efficiency factor ranging between 10^{-6} to 1 is also employed to adjust the inception flux and PAH adsorption rates to achieve desired soot mass and size distribution. PAHs of moderate sizes such as pyrene (4 rings) to coronene (7 rings) have been considered as the starting point of inception due to their thermodynamic instability that justifies the irreversibility at high temperatures [27]. However, the theoretical calculations [34] and experiments [35] indicated that PAH dimerization is highly reversible in flame conditions.

The inception flux of irreversible dimerization is mainly controlled by PAH concentration due to weak temperature dependence, so it produces new particles at low temperatures (even less than 500 K) [36] despite experimental evidence for termination of inception below 1200 K [37, 38]. Also, the arbitrary selection of efficiency factors alters the distribution of mass between inception of surface growth the could significantly change soot mass, PSD, and morphology [39]. Miller [40] used equilibrium constant for PAH dimerization to calculate the net dimerization rate and demonstrated that the collision of PAHs larger than circumovalene (~ 800 amu) could last long enough grow into incipient soot. However, the concentration of PAHs drops rapidly with size [23]. The entropy barrier of dimerization is significant for larger PAHs [41].

Eaves et al. [42] relaxed the irreversibility assumption, and developed a reversible clustering model to simulate inception using an array of PAHs from naphthalene to benzo-pyrene. Building on that work, Kholghy et al. [43] emphasized on the necessity of chemical bond formation after physical PAH clustering for accurate prediction of volume fraction, primary particle diameter and PSD in ethylene coflow diffusion flames. Later, Kholghy et al. [44] proposed the *"Reactive Dimerization"* model which starts with reversible collision of PAHs leading to physical dimers held with vdW forces that are graphitized and form chemically-bonded dimers that serve as soot nuclei grow via surface reactions. They also performed a systematic analysis on the contribution of different PAHs, and concluded that one- and two-ring aromatics account for almost all of inception flux in the so-called *"sooting flame"* [29]. However, Frenklach and Mebel [45] pointed out that an inception model that initiated with a highly reversible step similar to Reactive Dimerization [44] cannot produce sufficient flux of particles to match measurements of the benchmark burner-stabilized stagnation flame [46]. Instead, they proposed a HACA-driven mechanism where addition of monomer molecule to its radical activated by hydrogen abstraction for a stable dimer via an E-Bridge bond formation, and this sequential process continues to form trimers, tetramers, and larger PAH clusters.

The gas-phase chemistry of aromatics can be extended to account for chemical growth of incipient soot via surface reactions [24]. This hypothesis, known as "chemical similarity" postulates that the reactions occurring on the soot surface are similar to those involving large molecules of PAHs in the gas phase. It also provides means to describe the rates of surface growth and particle oxidation in terms of elementary chemical reactions. In other words, it is assumed that the surface of soot particles is made up of lateral faces of larges PAHs covered with C-H bonds. This is the basis

for HACA mechanism [27, 47] that assumes the soot surface to consist of hydrogenated sites with a predefined density. Mass growth on soot surface requires H-abstraction to form a radical site, followed by acetylene attack similar to growth of PAH molecules in the gas-phase. The reactivity of these sites changes with time and temperature [48, 49], described as soot aging. For modelling purposes, a temperature-dependent multiplier, usually represented by α , was introduced to account for these effects. Appel et al. [47] showed α changes with temperature and particle size.

Adsorption of PAHs on the surface of soot particles is also a viable growth mechanism [27], more specifically called physisorption or chemisorption depending on the mechanisms driving the adsorption process [50]. There is still debate over the stability of adsorbed PAH molecules on soot surface [51]. Following the hypothesis that PAHs are building blocks of soot particles, a mechanism similar to inception is often used to describe PAH-soot growth.

In typical soot formation processes such as flames and reactor, soot particles are formed at high concentrations (10^{12} 1/cm³), and inception and surface growth are relatively short compared to the total residence of soot particles. As a result, coagulation becomes dominant rapidly attaining both [52] self-preserving size distribution (SPSD) [53] and asymptotic fractal-like structure [54]. The evolving fractal-like structure of agglomerates quantified by their mobility diameter normalized by primary particle, d_m/d_p , and gyration, d_m/d_g , diameters can be described with power laws derived from mesoscale simulations [55]. The collision frequency of agglomerates depends on their evolving fractal-like morphology. Also, polydisperse agglomerates collide more frequently than monodisperse ones. The enhancement in their collision frequency reaches an asymptotic value of 35% [52] or 82% [56] in the free molecular or transition regimes, respectively at SPSPD regardless of the polydispersity in their constituent primary particles. Particle morphology formed by inception, surface growth and agglomeration can be tracked precisely by mesoscale simulations, such as Discrete Element Modeling (DEM) [57]. However, they are computationally expensive and interfacing them with chemical kinetics in computational fluid dynamics (CFD) simulations is not trivial [58]. This limits their application. So, sectional population balance models (SPBM) are often used to track agglomerate and primary particle size distribution [59], morphology [60], and composition [32] in complex laminar [32] and turbulent flows [61]. Using the SPBMs coupled with relations for agglomerate fractal-like structure [62] and collision frequency [63], particle size distribution, morphology and composition can be tracked accurately. However, the computational cost of SPBMs increases exponentially with the number of sections [64] and particle properties [32] tracked. Thus, one property (e.g. agglomerate mass) is typically tracked with SPBMs to reduce computational cost. This does not allow to account for agglomerate fractal-like structure [65, 66] which limits SPBM accuracy in predicting surface growth and coagulation rate of agglomerates and their size distribution.

Alternatively, particle dynamics can be tracked by the method of moments (MOM) [67] or monodisperse population balance models (MPBM) [68]. Such models only track average particle properties (e.g. moment ratios) and their accuracy could be limited if unrealistic assumptions (e.g. approximating agglomerates as monodisperse and perfect spheres) are used. However, when inception and surface growth are short [69] and high particle (number) concentrations are formed [55], they lead to rapid attainment of self-preserving size distributions (SPSD) and agglomerates having asymptotic structure [52]. In this case a MPBM or MOM can be assembled on a firm scientific basis with accuracy on par with DEM [57], SPBM [70] and experimental data [71, 72, 73]. Such models can be readily interfaced with CFD simulations [74] without significant computational cost, making them ideal for three-dimensional and even turbulent flame simulations.

The MOM tracks moments of the PSD and estimates average particle properties such as mass [75], surface area [76], the number of constituent primary particles per agglomerate, n_p [67], or even particle composition [77] using the ratio of the moments. The MOM with four equations was used to describe synthesis of optical fibers by simultaneous reaction, diffusion, coagulation and thermophoresis of SiO₂ in laminar flow reactors assuming a lognormal PSD [78]. The MOM with interpolative closure (MOMIC) was developed to predict simultaneous nucleation, surface growth and coagulation of soot agglomerates and estimate its PSD with six equations [67]. To calculate source terms of the transported moments, additional moments that are not tracked are needed preventing the closure of the system of differential equations with the MOM [75, 79]. Thus, often the PSD shape is assumed a priori [75] or extra equations are solved to estimate it [68].

The MPBMs do not have the closure problem and calculate average particle properties by tracking their total concentration, mass [68] and area [80, 81]. Kruis et al. [68] used a 2-equation MPBM (known as the semi-empirical model) to track soot concentration and mass in (non-premixed) flames assuming spherical particles. Good agreement was achieved for measured soot mass. However, the specific surface area [81] and coagulation frequency of spheres are significantly smaller compared to that of agglomerates with the same mass underestimating their oxidation rate [70] and overestimating their concentration [40]. Kruis et al. [68] proposed a 3-equation MPBM to account for the fractal-like structure of nanoparticle agglomerates during coagulation and sintering. Agglomerate volume and area were used to obtain their equivalent primary particle diameter, d_p , and n_p . Then, agglomerate collision diameter, i.e. d_g , was calculated by D_f , d_p and n_p to account for their fractal-like structure that affects their collision frequency. Tsantilis and Pratsinis [80] extended the MPBM to predict hard-(chemically-bonded) and soft- (physically-bonded) agglomerates during synthesis of SiO_2 and TiO_2 [82] nanoparticles with simultaneous reaction, surface growth, coagulation and sintering. Such a MPBM applies best at high concentrations when inception and surface growth are short [69] resulting in the dominance of coagulation where particles rapidly reach their SPSP and asymptotic fractal-like structure. This is often the case for soot emitted from a variety of combustion devices or CB reactors where inception and surface growth are limited to only a few milliseconds when temperature is very high (i.e. $T \geq 1500\text{K}$) [44].

Here, we develop a computational package, called *omnisoot*, that integrates functionalities of Cantera [83] in a set of zero-dimensional reactors combined with different soot inception and surface growth models and particle dynamics models. This allows *omnisoot* to track the formation and evolution of soot coupled with gas chemistry to predict its yield, morphology, composition and size distribution. Therefore, the package can be used for fundamental understanding of soot formation including pathway analysis, reaction mechanism assessment, and the estimation of inception flux, and more importantly for process design and optimization of CB production in typical industrial reactors under different fuel compositions, temperatures, pressures and residence times. The theoretical background and governing equations for different sub-models of *omnisoot* are explained in detail. Then, the code is validated by comparing its results with benchmark DEM simulations and by ensuring elemental mass and energy balance for all models. Finally, three use cases of *omnisoot* are presented to highlight its capability in predicting gas chemistry, and soot yield, structure, and size distribution in shock-tubes, flow reactors and well-stirred reactors.

2 Theoretical Foundation & Governing Equations

The mathematical basis for *omnisoot* is explained in the top-to-bottom hierarchical order. The highest level is the reactors that include the transport equations of gas mixture and "soot variables". Soot formation source terms are handled by the particle dynamics model that mainly addresses particle size distribution (PSD), morphology and coagulation rate. The "*PAH growth model*" computes the contribution of inception and adsorption to source terms based on PAHs designated as precursors. Similarly, the "*surface reactions*" model obtains the surface growth and oxidation rate by HACA mechanism and passes them to the particle dynamics model.

2.1 Assumptions and conventions

Here, the main conventions and assumptions used in the derivation of the mathematical model are listed below.

1. The ideal gas law is used to calculate physical, transport, and chemical properties of gas mixture.
2. \dot{s}_k denotes the rate production/consumption of k_{th} gaseous species due to soot inception, surface growth and oxidation. It is positive when the species is released to gas mixture.
3. Each soot agglomerate consists of spherical monodisperse primary particles in point contact.

4. The word “*particle*” refers to soot both in spherical and agglomerate shape.
5. The density of soot is assumed constant at the value of 1800 kg/m³. Soot density changes with its maturity level, which is often linked to the elemental C/H ratio of soot particles [84]. The considered value represents an average between density of mature soot with high C/H ratio ($\rho = 2000\text{kg/m}^3$) and that of nascent soot with small C/H ratios ($\rho = 1600\text{kg/m}^3$) [85, 84].
6. The incipient soot particles are 2 nm in diameter, so no particles could exist with a primary particle diameter smaller than 2 nm. The number of carbon atoms in the incipient soot particle is calculated from the mass of a sphere with the diameter of 2 nm assuming pure carbon content.

$$\begin{aligned} d_{p,min} &= 2 \text{ nm} \\ n_{c,min} &= \frac{\pi}{6} \rho_{soot} d_{p,min}^3 \frac{1}{MW_c} \approx 378. \end{aligned} \quad (1)$$

7. The calculation of PAH adsorption and soot oxidation requires “*soot concentration*” which is defined as the number of soot agglomerates per unit volume of gas. The number density of agglomerates, N_{agg} , are tracked per unit mass of gas mixture i.e. *mol/kg_{gas}*. So, soot concentration can be calculated by multiplying agglomerate number density by gas density as:

$$[\text{soot}] = \rho \cdot N_{agg}. \quad (2)$$

8. The specific heat, internal energy and enthalpy of soot are approximated by those of pure graphite, and employed to close the energy balance in the system [86].
9. Soot particles and gas are in thermal equilibrium during soot formation processes.
10. There is no temperature gradient within each agglomerate.
11. *Soot variable* refers to the features/properties of soot particles tracked by the particle dynamics model and used in the soot transport equations.
12. *PAH growth* is a unit of the soot model with a set of pathways that determine the rate of inception and adsorption from PAHs in the gas mixture.
13. *Surface reactions* is a unit of the soot model that describes the addition of acetylene to soot surface, and removal of carbon via oxidation by OH and O₂ in the HACA scheme. The model does not consider soot oxidation with CO₂, H₂O and NO_x.
14. The single superscript, i denotes the section number of a soot variable or a derived property. For example, d_p^i is the primary particle diameter of section i . The double superscript, ij represents a property related to two sections. For example, β^{ij} is the collision frequency of the sections i and j . In the case of the monodisperse model, the section number can be ignored because it is equivalent to the sectional model with one section.
15. The computation of morphological parameters (d_p , d_m , d_g , and n_p) and diffusion coefficient are done similarly by both particle dynamics models, so they are explained separately in standalone sections.
16. *precursors* refers to the PAHs larger than naphthalene used for inception and surface growth (PAH adsorption). The list of precursors with their chemical formula and molecular weight is provided in Table 1. It should be noted that the precursors can be dynamically changed by omnisoort’s user interface.

Table 1: The names, symbols, chemical formula and molecular weight of the soot precursors used by omnisoot

| Species name | Symbol | Chemical formula | W [kg/mol] |
|-------------------|--------|---------------------------------|------------|
| Naphthalene | A2 | C ₁₀ H ₈ | 0.128 |
| Phenanthrene | A3 | C ₁₄ H ₁₀ | 0.178 |
| Pyrene | A4 | C ₁₆ H ₁₀ | 0.202 |
| Acenaphthylene | A2R5 | C ₁₂ H ₈ | 0.152 |
| Acephenanthrylene | A3R5 | C ₁₆ H ₁₀ | 0.202 |
| Cyclopentapyrene | A4R5 | C ₁₈ H ₁₀ | 0.226 |

2.2 Constant Volume Reactor

This reactor assumes that the volume of system does not change during the process. In the absence of soot, this leads to gas with constant density. However, soot formation converts part of gaseous species to solid particles thereby affecting its volume and density. Note that, continuity, species and energy transport equations only track gas mixture properties. Figure 1 illustrates the control volume over the gas mixture targeted by mass and energy balance equations. Any mass converted to solid soot particles leaves the control volume. Mass and energy passes through the control surface around solid particles by soot formation processes. Reactor volume is the sum of volume of gas mixture and solid particles.

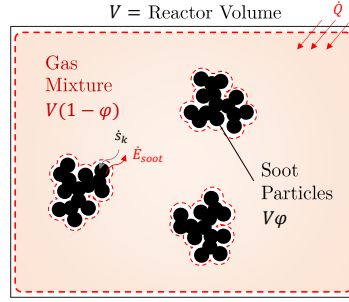


Figure 1: The schematics of control volume considered for the constant volume reactor that encompasses the gas mixture and excludes the soot particles. Mass and energy are transferred between gas and soot particles.

The continuity equation for this reactor can be written as:

$$\frac{d}{dt}(\rho(1-\varphi)) = (1-\varphi) \sum_i \dot{s}_i W_i. \quad (3)$$

Similarly, the species equation for species k is expressed as:

$$\frac{dY_k}{dt} = \frac{1}{\rho} (\dot{\omega}_k + \dot{s}_k) W_k - \frac{1}{\rho} Y_k \sum_i \dot{s}_i W_i. \quad (4)$$

The transport equation for a generic soot variable, ψ can be written as:

$$\frac{d\psi}{dt} = S_\psi - \frac{\psi}{\rho} \sum_i \dot{s}_i W_i. \quad (5)$$

The energy balance for the gas mixture can be simplified to the rate change of temperature. An

external heat source of \dot{Q} is considered to account for possible heat loss/gain of the reactor.

$$\frac{dT}{dt} = \frac{1}{\rho(1-\varphi)c_v + \rho_{soot}\varphi c_{v,soot}} \left[-(1-\varphi) \sum_k e_k (\dot{\omega}_k + \dot{s}_k) W_k + u_{soot}(1-\varphi) \sum_k \dot{s}_k W_k + \frac{\dot{Q}}{V} \right]. \quad (6)$$

2.3 Constant Pressure Reactor

This reactor is a closed system similar to CVR, but the pressure stays constant throughout the process and the boundaries of the system can move changing its volume. Fig.2 shows an illustration of constant pressure reactor (CPR). The heat transfer can occur through reactor walls and soot particles, which changes the internal energy of gas mixture.

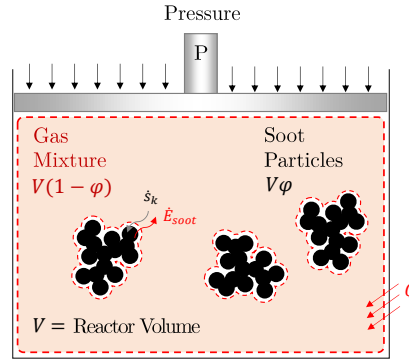


Figure 2: The schematics of control volume in the pressure reactor around the gas mixture excluding the soot particles. Mass and energy pass through the boundaries of gas and soot.

The rate change of mass, species, and soot variables for the constant pressure reactor (CPR) are the same as CVR given in Eqs. 3, 4, and 5, respectively. The energy equation is written as:

$$\frac{dT}{dt} = \frac{1}{\rho(1-\varphi)c_p + \rho_{soot}\varphi c_{p,soot}} \left[-(1-\varphi) \sum_k h_k (\dot{\omega}_k + \dot{s}_k) W_k + h_{soot}(1-\varphi) \sum_k \dot{s}_k W_k + \frac{\dot{Q}}{V} \right]. \quad (7)$$

2.4 Perfectly Stirred Reactor

In this reactor, gas enters with a mass flow rate \dot{m}_{in} , composition of Y^* and temperature of T^* , instantaneously mixes and homogeneously reacts with the mixture resident inside the reactor. The reacting gas reaches a spatially uniform temperature and composition described by T , and Y . It is assumed that temperature, composition and soot properties of the outflow are the same as reactor. Figure 3 illustrates the schematics of PSR. \dot{m}_{in} and \dot{m}_{out} refer to inflow and outflow gas mass flow rates, respectively. Under no-soot conditions, the inlet and outlet mass flow rates are equal, but the gas mixture loses mass by soot formation, so \dot{m}_{out} is slightly less than \dot{m}_{in} . The pressure of reactor is assumed to stay constant during the process [87]. The nominal residence time of gas mixture in the reactor is defined as:

$$\tau = \frac{\rho V}{\dot{m}_{in}}. \quad (8)$$

The conservation of mass can be written for PSR by considering the mass flux of in- and outflow, and the removal of mass due to soot generation as:

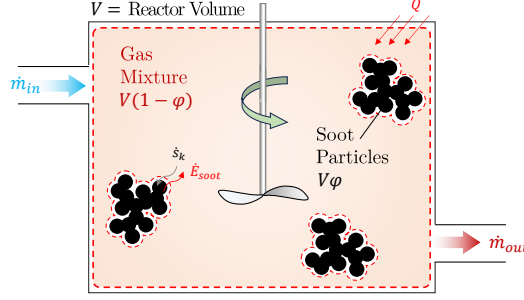


Figure 3: The schematics of control volume considered for the perfectly stirred reactor that encompasses the gas mixture and excludes the soot particles. Mass and energy are transferred between gas and soot particles. The inlet flow brings species and enthalpy into the control volume and the outflow discharges them. The gas mass flow at the outlet is less inlet due to partial conversion of gaseous species to soot.

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + (1 - \varphi) \sum_i \dot{s}_i W_i. \quad (9)$$

The density is not determined by solving the continuity equation, but rather from ideal gas law and assuming a constant pressure and the composition from solving the species transport equations as:

$$\frac{dY_k}{dt} = \frac{1}{\tau} (Y_k^* - Y_k) + \frac{1}{\rho} \left[(\dot{\omega}_k + \dot{s}_k) W_k - Y_k \sum_i \dot{s}_i W_i \right]. \quad (10)$$

The soot transport equations can also be expressed as:

$$\frac{d\psi}{dt} = \frac{\dot{m}_{in}}{\rho V (1 - \varphi)} (\psi^* - \psi) + S_\psi - \frac{1}{\rho} \psi \sum_i \dot{s}_i W_i. \quad (11)$$

The energy equation for this reactor is written as:

$$\begin{aligned} \frac{dT}{dt} = \frac{1}{\rho (1 - \varphi) c_p + \rho_{soot} c_{p,soot} \varphi} & \left[\frac{\dot{m}_{in}}{V} (h^* - h) - \frac{\dot{m}_{in}}{V} \sum_k (Y_k^* - Y_k) h_k \right. \\ & \left. - (1 - \varphi) \sum_k (\dot{\omega}_k + \dot{s}_k) W_k h_k + (1 - \varphi) \sum_i \dot{s}_i W_i h_{soot} + \frac{\dot{Q}}{V} \right]. \end{aligned} \quad (12)$$

2.5 Plug Flow Reactor

The plug flow reactor (PFR) is an ideal representation of a channel or duct with a constant cross-sectional area where a steady-state one-dimensional flow changes temperature, composition, and soot properties along the channel. There is no spatial gradient over the cross-section due to strong mixing. Diffusion along the channel is negligible. The pressure is assumed constant along the reactor.

The continuity equation for PFR is written as:

$$\frac{d}{dz} (\rho u (1 - \varphi)) = (1 - \varphi) \sum_i \dot{s}_i W_i. \quad (13)$$

The momentum equation can also be established as:

$$u(1 - \varphi) \sum_i \dot{s}_i W_i + \rho u (1 - \varphi) \frac{du}{dz} = - \frac{d}{dz} (p(1 - \varphi)) - \frac{\tau_w}{R_H}. \quad (14)$$

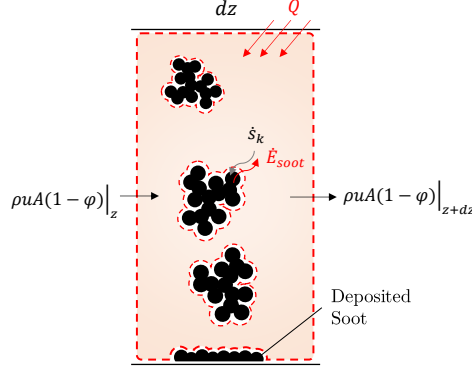


Figure 4: The schematics of control volume for a differential element along PFR that includes the gas mixture and excludes the soot particles considering wall heat transfer. The model considers mass and energy are transfer between gas and soot as well as wall deposition along the reactor.

where τ_w is the wall shear the can be determined from fraction factor, f as:

$$\tau_w = \frac{1}{2} \rho u^2 f. \quad (15)$$

The friction factor, f can be calculated with a good accuracy for the entire range of Reynolds number, Re , from laminar to turbulent flow using the explicit formula given by Haaland [88]:

$$\frac{1}{f^{1/2}} = -1.8 \log \left(\frac{6.9}{Re} + \left[\frac{\epsilon/D_H}{3.7} \right]^{1.11} \right), \quad (16)$$

where ϵ is the roughness of reactor wall. R_H and D_H are hydraulic radius and diameter, respectively that can be determined from cross-section geometry of reactor as:

$$D_H = 4R_H = \frac{4A_c}{P_c}, \quad (17)$$

A_c and P_c are cross-sectional area and wetted perimeter of the reactor. The species equation can be expressed as:

$$\frac{dY_k}{dz} = \frac{1}{\rho u} \left[(\dot{\omega}_k + \dot{s}_k) W_k - Y_k \sum_i \dot{s}_i W_i \right]. \quad (18)$$

The soot transport equations can also be written as:

$$\frac{d\psi}{dz} = \frac{S_\psi}{u} - \frac{\psi}{\rho u} \sum_i \dot{s}_i W_i - \frac{4}{D_H} \frac{k_{dep}^i \psi}{u}. \quad (19)$$

where k_{dep}^i is the deposition velocity of soot particles of section i calculated as:

$$k_{dep} = \frac{Sh \cdot D^i}{D_H}. \quad (20)$$

where Sh is the Sherwood number, which is 3.66 for a laminar flow and calculated using the Berger and Hau correlation [89] for the turbulent flow in terms of Re and Sc , Schmidt number as:

$$Sh = 0.0165 Re^{0.86} Sc^{1/3}. \quad (21)$$

The energy equation can be expressed as:

$$\frac{dT}{dz} = \frac{1}{\rho u(1-\varphi)c_p + \rho_{soot}u\varphi c_{p,soot}} \left[-(1-\varphi) \sum_k h_k (\dot{\omega}_k + \dot{s}_k) W_k + h_{soot}(1-\varphi) \sum_k \dot{s}_k W_k + q'' \frac{P_c}{A_c} \right] \quad (22)$$

where q'' is the wall heat flux provided as a function of reactor length or flow residence time that represents external heating or heat loss in the reactor.

3 Particle Dynamics

Population balance models rely on the Eulerian description of particles where bulk properties of particle population such as number density, mass or surface area are treated as continuous quantities and tracked by solving scalar transport equations. These methods are computationally cheaper compared with mesoscale models such as DEM, and can be easily interfaced with chemical kinetics in CFD solvers to simulate soot formation in turbulent configurations. Here, we use two particle dynamics models: a monodisperse population balance model (MPBM) based on four variables leading to 4 transport equations in total, and a fixed sectional population balance model (SPBM) tracking three variables per section. The total number of transport equations in the sectional model is determined by the number of sections and number of equations solved per section. The first two/three variables in the MPBM/SPBM enables description of number, mass, and evolving fractal-like morphology of soot agglomerates that are necessary to accurately predict collision frequency of agglomerates [90] as well as oxidation and surface growth rates [70]. The last variable tracks the number of hydrogen atoms in agglomerates that allows the model to capture the soot composition, thereby its maturity [32], and surface reactivity [77]. The tracked variables are used to address particle dynamics that includes (i) reconstructing particles morphology by determining characteristic diameters from tracked soot variables, (ii) calculating collision frequency and coagulation source term, (iii) combining the contribution of inception, PAH adsorption, surface growth and oxidation into source terms. First, common features of both particle dynamics models are reviewed. As mentioned before, any parameter with superscript i denotes the section number, which can be ignored/dropped for the MPBM that only has one section. For example, d_m^i can be replaced with d_m .

3.1 Soot Morphology

The evolving fractal-like structure of agglomerates is quantified by their mobility diameter normalized by primary particle, d_m/d_p , and gyration, d_m/d_g , diameters that can be described with power-laws derived from mesoscale simulations. Incipient soot is initially a sphere formed of PAHs with constant density that grows in size by surface reactions and forms agglomerates by coagulation. The collision frequency of particles depends on their evolving fractal-like structure [90]. Some simplifying assumptions are made to reconstruct the particle morphology from tracked variables. The primary particles of each agglomerate are similar enough that can be described by mean size and composition. They also stay in point contact during surface growth and agglomeration i.e. the necking is ignored. ~~A universal fractal dimension, $D_f = 1.9$ is used for agglomerates larger than sphere [91].~~ Mobility and gyration diameters are the diameter of a sphere with the same translational and rotational properties of the agglomerate, respectively. The employed power-laws have been shown to describe the morphology of soot from premixed [71], diffusion [92] flames, and diesel engines [93]. Figure 5 illustrates the schematics of a soot agglomerates with 12 primary particles and depicted d_p , d_m , and d_g .

n_p^i is the number of primary particles per agglomerate for i^{th} section that can be obtained by dividing the number density of primary particles by the the number density of agglomerates of that section as:

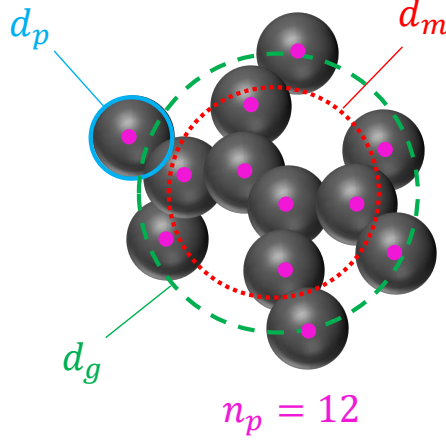


Figure 5: The schematics of a soot agglomerates with 12 primary particles ($n_p = 12$). Primary particle (d_p), mobility (d_m), and gyration (d_g) are shown.

$$n_p^i = \frac{N_{pri}^i}{N_{agg}^i}. \quad (23)$$

Primary particle diameter, d_p^i , can be obtained from total carbon content and number density of primary particles using

$$d_p^i = \left(\frac{6}{\pi} \frac{C_{tot}^i \cdot W_{carbon}}{\rho_{soot}} \frac{1}{N_{pri}^i \cdot Av} \right)^{1/3}. \quad (24)$$

The DEM-derived power-laws [55] relate d_m^i and d_g^i to d_p^i and n_p^i as

$$d_m^i = d_p^i \cdot n_p^{i 0.45}, \quad (25)$$

$$d_g^i = \begin{cases} d_m^i / (n_p^{i -0.2} + 0.4), & \text{if } n_p^i > 1.5 \\ d_m^i / 1.29, & \text{if } n_p^i \leq 1.5 \end{cases} \quad (26)$$

The collision diameter, d_c^i is the maximum of d_m^i , d_g^i :

$$d_c^i = \max(d_m^i, d_g^i) \quad (27)$$

d_m^i , d_g^i , d_c^i are used to calculate the source terms due to the surface growth, oxidation, PAH adsorption and coagulation. The volume equivalent diameter, d_v^i , is the diameter of the sphere with the same mass as agglomerate, and it is obtained as:

$$d_v^i = d_p^i \cdot n_p^{i 1/3} \quad (28)$$

The primary particle surface area is calculated from d_p^i assuming spherical primary particles.

$$A_p^i = \pi d_p^{i 2}, \quad (29)$$

A_{tot}^i (for each section) is defined as the total surface area of soot particles per unit mass of gas mixture obtained as

$$A_{tot}^i = N_{pri}^i \cdot Av \cdot A_p^i. \quad (30)$$

3.2 Diffusion of soot particles

The diffusion coefficient of soot particle, D^i , is calculated as

$$D^i = \frac{k_B T}{f^i}, \quad (31)$$

where f^i is the friction factor of particles in gas,

$$f^i = \frac{3\pi\mu d_m^i}{C^i(d_m^i)}, \quad (32)$$

where C^i is the Cunningham function that corrects the friction factor given a diameter in the continuum regime for transition and free molecular regimes as:

$$C^i(d) = 1 + \frac{2\lambda}{d} \left(1.21 + 0.4 \cdot \exp\left(\frac{-0.78d}{\lambda}\right) \right), \quad (33)$$

where λ is the mean free path of gas given as:

$$\lambda = \frac{\mu}{\rho} \sqrt{\frac{\pi W_{gas}}{2k_B A v T}}. \quad (34)$$

Note that, λ is a property of the gas mixture that does not depend on particle morphology and size section. The mean velocity, c^i and mean stop distance of particles, λ_a^i can be calculated as:

$$c^i = \sqrt{\frac{8k_B T}{\pi m_{agg}^i}}. \quad (35)$$

$$\lambda_a = \frac{8D^i}{\pi c^i}. \quad (36)$$

The mean distance of particles are also calculated as:

$$\delta_a^i = \frac{1}{d_c^i \lambda_a^i} \left[(d_c^i + \lambda_a^i)^3 - (d_c^{i2} + \lambda_a^{i2})^{3/2} \right] - d_{c,j}. \quad (37)$$

3.3 Coagulation efficiency of soot particles

The coagulation efficiency of soot particles is commonly assumed as unity meaning that every collision between two soot particles successfully results in formation of a new agglomerate. However, numerical models [94] and experimental evidence [95] showed that the coagulation efficiency can significantly change with particle size and temperature drastically decreasing for particles smaller than 10 nm in the free molecular regime ($Kn \gg 10$) due to their high kinetic energy that excess the attractive forces [96]. The coagulation efficiency of two colliding particles can be described as Narsimhan and Ruckenstein [94]:

$$\zeta^{ij} = 1 - \left(1 + \frac{\Phi_0^{ij}}{k_B T} \right) \exp \left(-\frac{\Phi_0^{ij}}{k_B T} \right), \quad (38)$$

where Φ_0 is the potential well depth i.e. the minimum interaction energy between two colliding particles. Hou et al. [97] calculated Φ_0 for soot particles 1-15 nm by considering the attraction and repulsion between constituent carbon and hydrogen atoms, and proposed a equation based on the reduced diameter, d_r^{jk} of colliding particles as:

$$\Phi_0^{ij} = -6.6891 \times 10^{-23} (d_r^{jk})^3 + 1.244 \times 10^{-21} (d_r^{jk})^2 + 1.1394 \times 10^{-20} d_r^{jk} - 5.5373 \times 10^{-21} \quad (39)$$

$$d_r^{jk} = \frac{d_c^i + d_c^j}{d_c^i + d_c^j} \quad (40)$$

Eq. (39) is valid for d_r^{jk} between 1 and 7 nm, and ζ^{ij} is assumed as 1 for particles with reduced diameter larger than 7 nm.

3.4 Soot Composition

The composition of soot is characterized by their elemental carbon to hydrogen ratio (C/H) is a measure of soot maturity and increases from $C/H < 2$ for incipient soot [98] to $2 < C/H < 10$ for nascent soot [99] and $C/H > 20$ for mature soot [100]. The soot agglomerates are assumed to have pure carbon graphitic core [32] with all hydrogen atoms on the surface [77]. C/H ratio can be obtained from total carbon and hydrogen content as:

$$\left(\frac{C}{H}\right)^i = \frac{C_{tot}^i}{H_{tot}^i}. \quad (41)$$

The carbon content of each agglomerate is a predefined parameter in the SPBM (depending on the section the agglomerate is placed), but it can be calculated from dividing C_{tot} by N_{agg} for the MPBM. The hydrogen content of each agglomerate is calculated for both particle dynamics models as:

$$H_{agg}^i = \frac{H_{tot}^i}{N_{agg}^i}. \quad (42)$$

3.5 Monodisperse Population Balance Model

The MPBM used in this research tracks the number density of primary particles (N_{pri}) and agglomerates (N_{agg}), total carbon (C_{tot}) and hydrogen (H_{tot}) content of soot particles per unit mass of gas mixture. The morphological parameters such as primary particle, mobility and gyration diameters obtained from these soot variables are the average values for the population.

3.5.1 Coagulation

Coagulation is the process during which solid and hard soot particles collide and attach at point of contact leading to larger agglomerates. This process conserves the soot mass and composition and number density of primary particles, so coagulation only affects N_{agg} . I_{coag}^N accounts for the decay rate of N_{agg} by the binary collision of soot particles by

$$I_{coag} = -\frac{1}{2}\zeta\beta N_{agg}^2, \quad (43)$$

where β is the collision frequency of agglomerates for the free molecular ($Kn > 10$) to continuum regime ($Kn < 0.1$), and ζ is the coagulation efficiency explained in Sec.3.3. The value of β in the transition regime ($0.1 < Kn < 10$) can be calculated from the harmonic mean of the continuum (β_{cont}) and free molecular (β_{fm}) regime values. Additionally, an enhancement factor of 1.82 is applied to take into account the effect of polydispersity [56] as:

$$\beta = 1.82 \frac{\beta_{fm}\beta_{cont}}{\beta_{fm} + \beta_{cont}}, \quad (44)$$

$$\beta_{fm} = 4\sqrt{\frac{\pi k_b T}{m_{agg}}} d_c^2, \quad (45)$$

$$\beta_{cont} = 8\pi d_c D. \quad (46)$$

Alternatively, β can be obtained using Fuchs interpolation [101] as:

$$\beta = \beta_{cont} \left(\frac{d_c}{d_c + 2\sqrt{2}\delta} + \frac{8D}{\sqrt{2}c_r d_c} \right)^{-1}. \quad (47)$$

3.5.2 Source terms

The source terms of tracked variables combines the effect of the inception, PAH adsorption, surface growth and oxidation and coagulation.

$$S_{N_{agg}} = \frac{I_{N,inc}}{n_{c,min}} + I_{coag}. \quad (48)$$

$$S_{N_{pri}} = \frac{I_{N,inc}}{n_{c,min}}. \quad (49)$$

$$S_{C_{tot}} = I_{C_{tot},inc} + I_{C_{tot},gr} + I_{C_{tot},ads} + I_{C_{tot},ox}. \quad (50)$$

$$S_{H_{tot}} = I_{H_{tot},inc} + I_{H_{tot},gr} + I_{H_{tot},ads} + I_{H_{tot},ox}. \quad (51)$$

The partial source terms in Equations 48-51 denoted by I are determined by PAH growth and surface reaction model explained in Sections 5 and 4, respectively.

3.6 Sectional Population Balance Model

A SPBM with the fixed pivot is used to describe particle dynamics [102]. The mass range of particles are divided into discrete sections each of which includes agglomerates of the same mass. Inception introduces new particles to the first section with the mass corresponding to the incipient particle. The particles of first section can migrate to upper sections by gaining mass via surface growth and coagulation, and return to lower sections when they lose mass through oxidation. The mass of sections is determined by a geometric progression with a scale factor equal to the mass of incipient soot particle, and a common ratio of SF, known as sectional spacing factor. The mass of each section is approximated by the carbon content of agglomerates in moles as:

$$C_{agg}^i = \frac{n_{c,min}}{Av} \cdot SF^{(i-1)}. \quad (52)$$

where (i-1) represents the exponent of SF. The mass of hydrogen is ignored in the placement of agglomerates in the sections. The total number density of agglomerates, N_{agg}^i [mol/kg], and primary particles, N_{pri}^i [mol/kg] are tracked for each section. Morphological parameters are determined for each section according to the equations in Section 3.1.

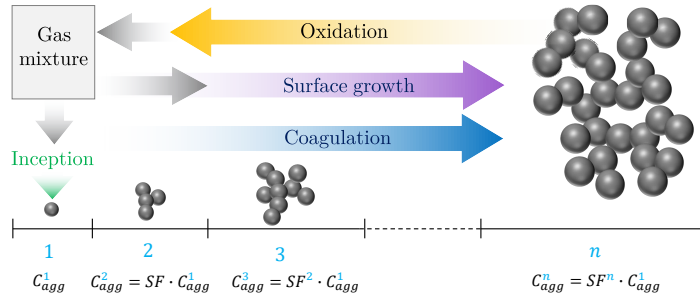


Figure 6: The illustration of sections of SPBM. The mass of sections grows progressively by the scale factor of SF. Inception introduces new particles to the first section that propagate to the upper section via coagulation and surface growth and return to lower sections by oxidation

3.6.1 Coagulation

In SPBM approach, collisions between particles from every two sections are considered. The new particles formed by coagulation are placed in ~~a upper~~ section with the mass equal to sum of mass of particles involved in the collision. When the mass of yielded particle lies between two consecutive sections, the particles are divided among these sections proportional to their mass. One possible scenario is that the mass of the newly formed particle is greater than the last section, thus leaving tracked mass range. Losing mass is a potential problem with the fixed pivot sectional model, which can be avoided by selecting proper number of sections and spacing factor to ensure the last sections stay empty during the simulation.

The collision frequency between sections j and k can be obtained from the harmonic mean of the values in the continuum and free molecular regimes as:

$$\beta^{jk} = \frac{\beta_{fm}^{jk} \beta_{cont}^{jk}}{\beta_{fm}^{jk} + \beta_{cont}^{jk}}, \quad (53)$$

$$\beta_{fm}^{jk} = \sqrt{\frac{\pi k_b T}{2} \left(\frac{1}{m_{agg}^j} + \frac{1}{m_{agg}^k} \right) (d_c^j + d_c^k)^2}, \quad (54)$$

$$\beta_{cont}^{ij} = \frac{2k_B T}{3\mu} \left(\frac{C^j}{d_m^j} + \frac{C^k}{d_m^k} \right) (d_c^j + d_c^k)^2. \quad (55)$$

The collision frequency can also be determined from the Fuchs interpolation similar to the MPBM as:

$$\beta^{jk} = \beta_{cont}^{ij} \left[\frac{d_c^j + d_c^k}{d_c^j + d_c^k + 2 + \delta_r^{jk}} + \frac{8(D^j + D^k)}{\bar{c}_r^{jk} (d_c^j + d_c^k)} \right]^{-1}, \quad (56)$$

where δ_r^{jk} and \bar{c}_r^{jk} are the mean square root of mean distance and velocity of particles, respectively.

$$\delta_r^{jk} = \sqrt{\delta_a^{j2} + \delta_a^{k2}}, \quad (57)$$

$$\bar{c}_r^{jk} = \sqrt{c^{j2} + c^{k2}}. \quad (58)$$

Coagulation redistributes the total number of agglomerates and primary particles as well as hydrogen atoms among the sections. The partial coagulation source terms for N_{agg}^i , N_{pri}^i and H_{tot}^i can be calculated as:

$$I_{N_{agg}}^i = \sum_{k=1}^{n_{sec}} \sum_{j=k}^{n_{sec}} \left(1 - \frac{\delta_{jk}}{2} \right) \eta_{ijk} \zeta^{jk} \beta^{jk} N_{agg}^j N_{agg}^k - N_{agg}^i \sum_{k=1}^{n_{sec}} \zeta^{im} \beta^{im} N_{agg}^m. \quad (59)$$

$$I_{N_{pri}}^i = \sum_{k=1}^{n_{sec}} \sum_{j=k}^{n_{sec}} \left(1 - \frac{\delta_{jk}}{2} \right) \eta_{p,ijk} \eta_{ijk} \zeta^{jk} \beta^{jk} N_{agg}^j N_{agg}^k - N_{pri}^i \sum_{k=1}^{n_{sec}} \zeta^{im} \beta^{im} N_{agg}^m. \quad (60)$$

$$I_{H_{tot}}^i = \sum_{k=1}^{n_{sec}} \sum_{j=k}^{n_{sec}} \left(1 - \frac{\delta_{jk}}{2} \right) \eta_{h,ijk} \eta_{ijk} \zeta^{jk} \beta^{jk} N_{agg}^j N_{agg}^k - H_{tot}^i \sum_{k=1}^{n_{sec}} \zeta^{im} \beta^{im} N_{agg}^m. \quad (61)$$

where δ_{jk} is the Kronecker delta defined as:

$$\delta_{jk} = \begin{cases} 1, & \text{if } j = k \\ 0, & \text{if } j \neq k \end{cases} \quad (62)$$

In Equation (59), η_{ijk} assigns newly formed agglomerates to the two consecutive section in order to conserve mass during coagulation [60].

$$\eta_{ijk} = \begin{cases} \frac{C_{agg}^{i+1} - C_{agg}^{jk}}{C_{agg}^{i+1} + C_{agg}^i}, & \text{if } C_{agg}^i \leq C_{agg}^{jk} < C_{agg}^{i+1} \\ \frac{C_{agg}^i - C_{agg}^{jk}}{C_{agg}^i + C_{agg}^{i-1}}, & \text{if } C_{agg}^{i-1} \leq C_{agg}^{jk} < C_{agg}^i \\ 0 & \text{else} \end{cases} \quad (63)$$

where $C_{agg}^{jk} = C_{agg}^j + C_{agg}^k$. Similarly, $\eta_{p,ijk}$ in Equation (60) and $\eta_{h,ijk}$ in Equation (61) adjust the number primary particles and hydrogen atoms added to consecutive sections based on their mass, respectively.

$$\eta_{p,ijk} = \frac{C_{agg}^i}{C_{agg}^{jk}} (n_p^j + n_p^k), \quad (64)$$

$$\eta_{h,ijk} = \frac{C_{agg}^i}{C_{agg}^{jk}} (H_{agg}^j + H_{agg}^k), \quad (65)$$

3.6.2 Source terms

The source terms are split into four parts showing the contribution of different soot formation and evolution factors. The effect of surface growth and PAH adsorption are combined (denoted by the subscript gr,ads) because they are similar mass-gaining mechanisms.

$$S_{N_{agg}} = (S_{N_{agg}})_{inc} + (S_{N_{agg}})_{gr,ads} + (S_{N_{agg}})_{ox} + (S_{N_{agg}})_{coag}, \quad (66)$$

$$S_{N_{pri}} = (S_{N_{pri}})_{inc} + (S_{N_{pri}})_{gr,ads} + (S_{N_{pri}})_{ox} + (S_{N_{pri}})_{coag}, \quad (67)$$

$$S_{H_{tot}} = (S_{H_{tot}})_{inc} + (S_{H_{tot}})_{gr,ads} + (S_{H_{tot}})_{ox} + (S_{H_{tot}})_{coag}. \quad (68)$$

Inception introduces equal number of agglomerates and primary particles to the first section.

$$(S_{N_{agg}})_{inc} = \frac{1}{Av} \frac{I_{N,inc}}{C_{agg}^i}, \quad i = 1. \quad (69)$$

$$(S_{N_{pri}})_{inc} = \frac{1}{Av} \frac{I_{N,inc}}{C_{agg}^i}, \quad i = 1. \quad (70)$$

$$(S_{H_{tot}})_{inc} = I_{H,inc}, \quad i = 1. \quad (71)$$

Surface growth and PAH adsorption increase the (carbon) mass and hydrogen content of agglomerates, and transfer them to upper sections. The removal rate of agglomerates (N_{agg}^i) from the original section due to surface growth and PAH adsorption must be equal to the addition rate of agglomerates to the target section to conserve the mass, and it is calculated by dividing the mass growth rate by the difference of the mass of the adjacent sections.

$$(S_{N_{agg}})_{gr,ads} = \frac{1}{Av} \begin{cases} -\frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} & \text{if } i = 1 \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} - \frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} & \text{if } 1 < i < n_{sec} \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} & \text{if } i = n_{sec} \end{cases} \quad (72)$$

As agglomerates move up/down through sections, they carry the number of primary particles as well as hydrogen atoms, so the transfer rate of agglomerates is multiplied by n_p^i and H_{agg}^i , respectively.

$$(S_{N_{pri}})_{gr,ads} = \frac{1}{Av} \begin{cases} -\frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} & \text{if } i = 1 \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} n_p^{i-1} - \frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} n_p^i & \text{if } 1 < i < n_{sec} \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} n_p^{i-1} & \text{if } i = n_{sec} \end{cases} \quad (73)$$

$$(S_{H_{tot}})_{gr,ads} = \frac{1}{Av} \begin{cases} -\frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} H_{agg}^i + I_{H_{tot},gr}^i + I_{H_{tot},ads}^i & \text{if } i = 1 \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} H_{agg}^{i-1} - \frac{I_{C_{tot},gr}^i + I_{C_{tot},ads}^i}{C_{agg}^{i+1} - C_{agg}^i} H_{agg}^i + I_{H_{tot},gr}^i + I_{H_{tot},ads}^i & \text{if } 1 < i < n_{sec} \\ \frac{I_{C_{tot},gr}^{i-1} + I_{C_{tot},ads}^{i-1}}{C_{agg}^i - C_{agg}^{i-1}} H_{agg}^{i-1} + I_{H_{tot},gr}^i + I_{H_{tot},ads}^i & \text{if } i = n_{sec} \end{cases} \quad (74)$$

Similarly, the agglomerates lose (carbon) mass by oxidation, and descend to the lower sections carrying primary particle and hydrogen.

$$(S_{N_{agg}})_{ox} = \frac{1}{Av} \begin{cases} \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i} & \text{if } i = 1 \\ \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} & \text{if } 1 < i < n_{sec} \\ -\frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} & \text{if } i = n_{sec} \end{cases} \quad (75)$$

$$(S_{N_{pri}})_{ox} = \frac{1}{Av} \begin{cases} \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} n_p^{i+1} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i} & \text{if } i = 1 \\ \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} n_p^{i+1} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} n_p^i & \text{if } 1 < i < n_{sec} \\ -\frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} n_p^i & \text{if } i = n_{sec} \end{cases} \quad (76)$$

$$(S_{H_{tot}})_{ox} = \frac{1}{Av} \begin{cases} \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} H_{agg}^{i+1} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i} H_{agg}^i + I_{H_{tot},ox}^i & \text{if } i = 1 \\ \frac{I_{C_{tot},ox}^{i+1}}{C_{agg}^{i+1} - C_{agg}^i} H_{agg}^{i+1} - \frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} H_{agg}^i + I_{H_{tot},ox}^i & \text{if } 1 < i < n_{sec} \\ -\frac{I_{C_{tot},ox}^i}{C_{agg}^i - C_{agg}^{i-1}} H_{agg}^i + I_{H_{tot},ox}^i & \text{if } i = n_{sec} \end{cases} \quad (77)$$

4 Surface reactions model

The heterogeneous surface reactions are described by hydrogen-abstraction-acetylene-addition (HACA) mechanism [27, 47]. The soot growth in HACA scheme is based on a sequential process similar to

PAH growth. The hydrogenated arm-chair sites ($C_{\text{soot}} - H$) on the edge of aromatic rings are dehydrogenated by H abstraction forming C_{soot}° that bonds with C_2H_2 resulting in an additional aromatic ring with hydrogenated site. These sites can also be attacked by O_2 or OH . The elementary reactions that describe this sequential process are listed in Table 2. The rate of mass growth by HACA is obtained from the reaction of C_2H_2 with dehydrogenated sites as:

$$\omega_{gr}^i = \alpha^i k_{f4} [C_2H_2] [C_{\text{soot}}^\circ]. \quad (78)$$

where k_{f4} denotes the forward rate of Reaction 2 in Table 2, and $[C_{\text{soot}}^\circ]$ is obtained by multiplying the surface density of dehydrogenated sites, χ_{soot}° with total surface area of soot (per unit of mass of gas mixture) as:

$$[C_{\text{soot}}^\circ] = \frac{\rho}{A_v} A_{\text{tot}}^i \cdot \chi_{\text{soot}}^\circ. \quad (79)$$

χ_{soot}° is calculated by assuming the steady-state for $[C_{\text{soot}}^\circ]$ in the system of reactions in Table 2:

$$\chi_{\text{soot}}^\circ = \frac{k_{f1} [H] + k_{f2} [OH]}{k_{r1} [H_2] + k_{r2} [H_2O] + k_{f3} [H] + k_{f4} [C_2H_2] + k_{f5} [O_2] + k_{f1} [H] + k_{f2} [OH]} \chi_{\text{soot}_{CH}}, \quad (80)$$

where $\chi_{\text{soot}_{CH}}$ is the surface density of hydrogenated sites estimated based on the assumption that soot surface is covered with stacks of benzene rings [47]. Considering the stack spacing of 3.15 Å and 2 C-H bonds per benzene ring length, the surface density of hydrogenated sites, $\chi_{\text{soot}-H}$, is calculated to be $0.23 \text{ site}/\text{\AA}^2 = 2.3 \times 10^{19} \text{ site}/\text{m}^2$, which gives the maximum theoretical limit of the reaction sites.

In Equation (78), α is the surface reactivity factor between 0 and 1 that represents the decline of reaction sites from the theoretical limit due to particle aging, growth and maturity [103, 104], and it has been observed to depend on temperature time history [105, 49]. The value of α has been described using constant target-specific values as well as empirical equations based on particle size and flame temperature. A detailed review of these can be found in the chapter 4 of [106]. Here, the empirical equations proposed by Appel et al. [47] is used to calculate α :

$$\alpha^i = \tanh \left(\frac{12.56 - 0.00563 \cdot T}{\log_{10} \left(\frac{\rho_{\text{soot}} \cdot A_v}{W_{\text{carbon}}} \frac{\pi}{6} d_p^3 \right)} - 1.38 + 0.00068 \cdot T \right). \quad (81)$$

Alternatively, Blanquart and Pitsch [76] related α to the number of surface hydrogen atoms on the soot particles.

$$\alpha^i = \frac{H_{\text{tot}}^i}{C_{\text{tot}}^i}. \quad (82)$$

The contribution of HACA to growth source terms can be computed from HACA rates considering the number of carbon atoms in C_2H_2 and number of arm-chair and zig-zag hydrogenated sites on soot particle [77] using

$$I_{C_{\text{tot}},gr}^i = 2\omega_{gr}^i / \rho, \quad (83)$$

$$I_{H_{\text{tot}},gr}^i = 0.25\omega_{gr}^i / \rho. \quad (84)$$

The rate change of C_2H_2 concentration due to mass growth is written as:

$$\left(\frac{d[C_2H_2]}{dt} \right)_{gr} = - \sum_{i=1}^{n_{sec}} \omega_{gr}^i. \quad (85)$$

The rate of release of H radicals into the gas mixture due to surface growth is:

$$\left(\frac{d[H]}{dt} \right)_{gr} = 1.75 \sum_{i=1}^{n_{sec}} \omega_{gr}^i. \quad (86)$$

Table 2: Rate coefficients for the various surface reactions in Arrhenius form $k = AT^n \cdot e^{-E/RT}$

| No. | Reaction | | A $\left[\frac{\text{m}^3}{\text{mol}\cdot\text{s}}\right]$ | n | $\frac{E}{R}$ [K] |
|-------|---|---|---|-------|-------------------|
| (R 1) | $\text{C}_{\text{soot-H}} + \text{H} \rightleftharpoons \text{C}_{\text{soot}^\circ} + \text{H}_2$ | f | 4.17×10^7 | 0 | 6542.52 |
| | | r | 3.9×10^6 | 0 | 5535.98 |
| (R 2) | $\text{C}_{\text{soot-H}} + \text{OH} \rightleftharpoons \text{C}_{\text{soot}^\circ} + \text{H}_2\text{O}$ | f | 10^4 | 0.734 | 719.68 |
| | | r | 3.68×10^2 | 1.139 | 8605.94 |
| (R 3) | $\text{C}_{\text{soot}^\circ} + \text{H} \longrightarrow \text{C}_{\text{soot}} + \text{H}_2\text{O}$ | f | 10^4 | 0.734 | 719.68 |
| (R 4) | $\text{C}_{\text{soot}^\circ} + \text{C}_2\text{H}_2 \longrightarrow \text{C}_{\text{soot-H}}$ | f | 80 | 1.56 | 1912.43 |
| (R 5) | $\text{C}_{\text{soot}^\circ} + \text{O}_2 \longrightarrow 2 \text{CO}$ | f | 2.2×10^6 | 0 | 3774.53 |
| (R 6) | $\text{C}_{\text{soot-H}} + \text{OH} \longrightarrow \text{CO} + \frac{1}{2} \text{H}_2$ | f | 1.3×10^7 | 0 | 0 |

The carbons on the surface of soot are oxidized via reaction with O_2 and OH which decreases total carbon of soot and releases CO and H_2 to gas mixture. The oxidation process is described by HACA mechanism. O_2 and OH oxidation rates are calculated as

$$\omega_{ox,O_2}^i = \alpha^i k_{f5} [\text{O}_2] [C_{soot^\circ}^i], \quad (87)$$

$$\omega_{ox,OH}^i = \alpha^i k_{f6} [\text{OH}] [soot^i]. \quad (88)$$

The oxidation source term is calculated considering the number of carbon atoms removed from soot through each oxidation pathway by

$$I_{C_{tot},ox}^i = -(2\omega_{ox,O_2}^i + \omega_{ox,OH}^i) / \rho, \quad (89)$$

We assume that oxidation does not change the number of surface hydrogen atoms. The rate change of concentration of CO , H and OH by oxidation is calculates as:

$$\left(\frac{d[\text{CO}]}{dt}\right)_{ox} = \sum_{i=1}^{n_{sec}} \omega_{ox,O_2}^i. \quad (90)$$

$$\left(\frac{d[\text{O}_2]}{dt}\right)_{ox} = - \sum_{i=1}^{n_{sec}} \omega_{ox,O_2}^i. \quad (91)$$

$$\left(\frac{d[\text{OH}]}{dt}\right)_{ox} = - \sum_{i=1}^{n_{sec}} \omega_{ox,OH}^i. \quad (92)$$

$$\left(\frac{d[\text{H}_2]}{dt}\right)_{ox} = \frac{1}{2} \sum_{i=1}^{n_{sec}} \omega_{ox,OH}^i. \quad (93)$$

5 PAH growth models

Here, four different PAH growth models are used to describe the conversion of PAHs to incipient particles and their adsorption on existing agglomerates. As mentioned before, the soot inception and surface growth is not fully understood yet, but there is substantial evidence to support the collision

of PAHs as a key step in inception and surface growth [107, 46, 108]. So, global inception models have been developed based PAH collision consisting of different pathways with single- or multi-step reactions. The collision frequency of gaseous species including PAH molecules and polymers depend on their mass and diameter, and it is obtained as:

$$\beta_{dim_{jk}} = 2.2 \cdot d_r^2 \sqrt{\frac{8\pi k_B T}{m_r}} \quad (94)$$

where d_r and m_r are reduced diameter and mass for two PAH molecules, respectively.

$$d_r = 2 \frac{d_{PAH_k} \cdot d_{PAH_j}}{d_{PAH_k} + d_{PAH_j}} \quad (95)$$

$$m_r = \frac{m_{PAH_k} \cdot m_{PAH_j}}{m_{PAH_k} + m_{PAH_j}} \quad (96)$$

The mass of each PAH molecule is obtained from its molecular weight as:

$$m_{PAH_j} = \frac{W_{PAH_j}}{Av} \quad (97)$$

The diameter of PAH is calculated from its mass and density.

$$d_{PAH_j} = \left(\frac{6 \cdot m_{PAH_j}}{\pi \cdot \rho_{PAH_j}} \right)^{1/3} \quad (98)$$

The density of a PAH molecule is estimated using the relation proposed by Johansson et al. [109].

$$\rho_{PAH_j} = 171943.5197 \frac{W_{carbon} \cdot n_{C,PAH_j} + W_{hydrogen} \cdot n_{H,PAH_j}}{n_{C,PAH_j} + n_{H,PAH_j}} \quad (99)$$

The collision frequency of PAH_j and soot agglomerates in each section can be determined for the entire regime by harmonic mean of the collision frequency in the free molecular and continuum regimes as:

$$\beta_{ads_j}^i = \frac{\beta_{fm,ads}^i \cdot \beta_{cont,ads}^i}{\beta_{fm,ads}^i + \beta_{cont,ads}^i} \quad (100)$$

$$\beta_{fm,ads_j}^i = 2.2 \sqrt{\frac{\pi k_B T}{2} \left(\frac{1}{m_{agg}^i} + \frac{1}{m_{PAH_j}} \right)} (d_g^i + d_{PAH_j})^2 \quad (101)$$

$$\beta_{cont,ads_j}^i = \frac{2k_B T}{3\mu} \left[\frac{C^i(d_m)}{d_g^i} + \frac{C^i(d_{PAH_j})}{d_{PAH_j}} \right] (d_g + d_{PAH_j}) \quad (102)$$

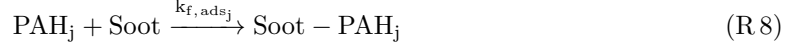
where C^i is the Cunningham function calculated as Equation 33.

5.1 Irreversible Dimerization

The irreversible dimerization is based on the irreversible collision of PAHs leading to their clustering/polymerization that forms dimers, trimers, and tetramers until the polymer mass reaches a threshold that can be considered a solid particle. For practical purposes, dimer is usually considered as a incipient particle that grows by surface growth and coagulation. A single-step irreversible collision of two similar PAHs forms a new dimer as:



Similarly, the adsorption of each PAH molecule on soot particles is described by the irreversible collision of soot and PAH_j as:



The forward rate of dimerization, k_{f,dim_j} and adsorption, k_{f,ads_j} in Reactions (R 7) and (R 8) are calculated from Equations (94) and (100), respectively.

$$k_{f,dim_j} = \gamma_{inc} \cdot \beta_{jk,PAH} \cdot Av, \quad (103)$$

$$k_{f,ads_j}^i = \gamma_{ads_j} \cdot \beta_{j,ads}^i \cdot Av, \quad (104)$$

where γ_{inc} and γ_{ads} are the collision efficiencies for dimerization and adsorption, respectively. Their value vary in $[10^{-7}, 1]$ range, and usually chosen to match the predicted soot mass with the experimental data. Here, $\gamma_{inc} = 10^{-4}$ and $\gamma_{ads} = 10^{-3}$. The rate of dimerization and adsorption from PAH_j are calculated accordingly as:

$$w_{dim_j} = \eta_{inc} k_{f,dim_j} [\text{PAH}_j] [\text{PAH}_j], \quad (105)$$

where η_{inc} is the inception adjustment factor to globally modify the inception flux without changing the internal rate constants of the inception model. The partial source terms for inception are calculated as:

$$I_{N,inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} w_{dim_j} 2n_{PAH_j,C} \quad (106)$$

$$I_{C_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} w_{dim_j} 2n_{PAH_j,C} \quad (107)$$

$$I_{H_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} w_{dim_j} 2n_{PAH_j,H} \quad (108)$$

The rate of PAH adsorption for each section is obtained as:

$$w_{ads_j}^i = \eta_{ads} k_{f,ads_j}^i [\text{soot}] [\text{PAH}_j] \quad (109)$$

where η_{ads} is the adsorption adjustment factor to globally modify the PAH adsorption rate. The contribution of PAH adsorption to the source terms are expressed as:

$$I_{C_{tot},ads}^i = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} w_{ads_j}^i n_{PAH,C} \quad (110)$$

$$I_{H_{tot},ads}^i = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} w_{dim_j}^i (n_{PAH,H} - 2) \quad (111)$$

Each PAH molecule loses one H atom becoming a radical that forms bonds with a dehydrogenated site on soot surface, so two H atoms are released during the process that is taken into account in Equation (111).

The formation of a dimer consumes two PAH molecules, and during adsorption one PAH molecule is removed from the gas mixture, so the total rate of PAH_i removal by the irreversible dimerization is obtained as:

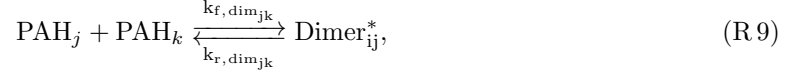
$$\left(\frac{d[\text{PAH}_j]}{dt} \right)_{inc} = -2w_{dim_j} - \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (112)$$

During the adsorption process one H₂ is released to the gas mixture.

$$\left(\frac{d[\text{H}_2]}{dt} \right)_{inc} = \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (113)$$

5.2 Reactive Dimerization

This model is built on Irreversible Dimerization with two main differences: The first step of dimerization and adsorption is reversible forming physically bonded dimers followed by a irreversible carbonization that leads to chemical bond formation in dimers [44]. This approach allows formation of homo- and heterodimers. The dimerization of PAH_j and PAH_k is described as:



where Dimer_{jk}^* and Dimer_{jk} physically and chemically bonded dimers, respectively, from PAH_j and PAH_k. The forward rate of physical dimerization, $k_{f, \text{dim}_{jk}}$ is calculated from Equation (94) as:

$$k_{f, \text{dim}_{jk}} = p'' \cdot \beta_{jk, \text{PAH}} \cdot Av, \quad (114)$$

where $p'' = 0.1$ accounts for the probability of PAH-PAH collisions in “FACE” configuration that results in successful vdW bond formation [110]. The reverse rate of physical dimerization, $k_{r, \text{dim}_{jk}}$ is obtained from the dimerization equilibrium constant [40] as:

$$\log_{10} K_{eq} = a \frac{\epsilon_{jk}}{RT} + b, \quad (115)$$

$$k_{r, \text{dim}_{jk}} = k_{f, \text{dim}_{jk}} 10^{-b} e^{-a\epsilon_{jk} \ln(10)/(RT)}, \quad (116)$$

$$\epsilon_{jk} = cW_{jk} - d, \quad (117)$$

$$W_{jk} = \frac{W_j \cdot W_k}{W_j + W_k}, \quad (118)$$

where $a = 0.115$ (obtained from pyrere dimerization data [35]) and $b=1.8$ [44], $c=933420$ j/kg, and $d=34053$ j/mol [44].

The rate of chemical bond formation, k_{reac} is defined in the Arrhenius form [36] as

$$k_{\text{reac}} = 5 \times 10^6 \cdot e^{(-96232/RT)}. \quad (119)$$

Assuming a steady state condition for the physical dimers, $\partial[\text{Dimer}_{jk}^*]/\partial t = 0$, the rate of formation of chemically-bonded dimers can be obtained as

$$\omega_{\text{dim}_{jk}} = \eta_{\text{inc}} k_{\text{reac}} \frac{k_{f, \text{dim}_{jk}} [\text{PAH}_j] [\text{PAH}_k]}{k_{r, \text{dim}_{jk}} + k_{c, \text{dim}}}. \quad (120)$$

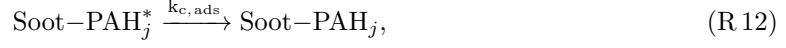
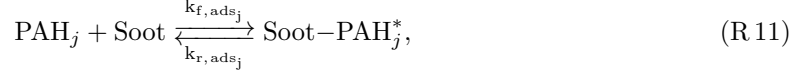
The contribution of dimer formation to partial source terms is expressed by looping over all combinations of PAHs as:

$$I_{N, \text{inc}} = \frac{1}{\rho} \sum_{j=1}^{n_{\text{PAH}}} \sum_{k=j}^{n_{\text{PAH}}} \omega_{\text{dim}_{kj}} (n_{\text{PAH}_j, C} + n_{\text{PAH}_k, C}), \quad (121)$$

$$I_{C_{\text{tot}}, \text{inc}} = \frac{1}{\rho} \sum_{j=1}^{n_{\text{PAH}}} \sum_{k=j}^{n_{\text{PAH}}} \omega_{\text{dim}_{kj}} (n_{\text{PAH}_j, C} + n_{\text{PAH}_k, C}), \quad (122)$$

$$I_{H_{\text{tot}}, \text{inc}} = \frac{1}{\rho} \sum_{j=1}^{n_{\text{PAH}}} \sum_{k=j}^{n_{\text{PAH}}} \omega_{\text{dim}_{kj}} (n_{\text{PAH}_j, H} + n_{\text{PAH}_k, H}), \quad (123)$$

Similarly, PAH adsorption is described by a two-step process where the collision of PAH_j with soot agglomerates leads to physically bonded Soot – PAH* that is carbonized and forms chemically-bonded Soot – PAH added to soot surface.



The forward rate of PAH-soot collision is calculated from Equation (100), and the reverse rate is determined same as inception (Equation(116)).

$$k_{f,ads}^i = \beta_{jk,ads}^i \cdot Av, \quad (124)$$

$$k_{r,ads}^i = k_{f,ads}^i \cdot 10^{-b} e^{-a\epsilon_{soot,j} \ln(10)/(RT)}, \quad (125)$$

$$\epsilon_{soot,j} = cW_{soot,j} - d, \quad (126)$$

a, b, c, d values are the same as those used in inception. Computing $\epsilon_{soot,j}$ also requires "equivalent soot molecular weight", W_{soot} for section i, which is estimated from carbon mass of each agglomerate as:

$$W_{soot}^i = \frac{C_{tot}^i W_{carbon}}{N_{agg}^i} \quad (127)$$

The rate constant of carbonization of Soot – PAH_j* is defined as in the Arrhenius form similar to inception (Equation (119)). The prefactor is adjusted based on matching the numerical PSD [36] with measurements in the ethylene pyrolysis in a flow reactor [111].

$$k_{c,dim} = 2 \times 10^{10} \cdot e^{(-96232/RT)}. \quad (128)$$

The total adsorption rate can be calculated assuming a steady-state concentration for physically adsorbed PAH on soot, $\partial[\text{Soot-PAH}^*]/\partial t = 0$ calculated in a similar way to inception flux (Equation (120)) as

$$\omega_{ads_j}^i = \eta_{ads} k_{c,ads} \frac{k_{f,ads_j} [\text{Soot}] [\text{PAH}_j]}{k_{r,ads_j} + k_{c,ads_j}}, \quad (129)$$

The contribution of PAH adsorption rate to partial source terms can be expressed as:

$$I_{C_{tot,ads}}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} \omega_{ads_j}^i n_{C,PAH_j}, \quad (130)$$

$$I_{C_{tot,ads}}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} \omega_{ads_j}^i (n_{H,PAH_j} - 2). \quad (131)$$

The rate of removal of PAH from gas mixture due to adsorption is given as

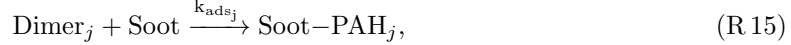
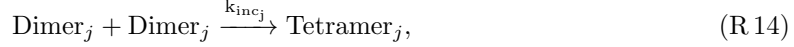
$$\left(\frac{d[\text{PAH}_j]}{dt} \right)_{inc} = - \sum_{k=1}^{n_{PAH}} w_{dim_{jk}} - \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (132)$$

During the adsorption process one H₂ is released to the gas mixture.

$$\left(\frac{d[\text{H}_2]}{dt} \right)_{inc} = \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (133)$$

5.3 Dimer Coalescence

Dimer coalescence model is a multi-step irreversible model proposed by Blanquart and Pitsch [76] where self-collision of PAH molecules form dimers that are intermediate state between gaseous PAH molecules and solid soot particles. The self-coalescence of dimers forms incipient soot particles. Alternatively, dimers can adsorb on the surface of existing soot particles and contribute to their surface growth. The equations are based on implementation of Dimer Coalescence by Sun et al. [112] for a sectional model.



where the rate constant of dimerization, k_{dim_j} and inception k_{inc_j} are calculated from collision rate of PAHs in Equation (100).

$$k_{\text{dim}_j} = \gamma_{\text{dim}_j} \cdot \beta_{jj, \text{PAH}} \cdot Av, \quad (134)$$

$$k_{\text{inc}_j} = \beta_{jj, \text{dimer}} \cdot Av, \quad (135)$$

where γ_{dim_j} is the dimerization efficiency that is assumed to scale with fourth power of PAH molecular weight [77] as:

$$\gamma_{\text{dim}_j} = C_{N,j} \cdot W_{\text{PAH}_j}^4, \quad (136)$$

Blanquart and Pitsch [76] estimated the constant $C_{N,j}$ by comparing the profiles of several PAH species with experimental measurements in a single premixed benzene flame [113], and provided a efficiency values for various PAHs that are listed in Table 1 in [77]. The rate of dimer collision is expressed as:

$$w_{\text{dim}_j} = \eta_{\text{inc}} k_{\text{inc}_j} [\text{Dimer}_j] [\text{Dimer}_j] \quad (137)$$

Similarly, the rate of adsorption of dimers on soot particles is obtained as:

$$w_{\text{ads}_j}^i = \eta_{\text{ads}} k_{\text{ads}_j}^i [\text{soot}]^i [\text{Dimer}_j] \quad (138)$$

Assuming fast dimer consumption leads to the steady-state concentration of dimers that can be determined by solving a quadratic equation as:

$$a_{\text{inc}_j} [\text{dimer}]^2 + b_{\text{ads}_j} [\text{dimer}] = \omega_{\text{dim}_j} \quad (139)$$

$$[\text{Dimer}_j] = \begin{cases} \frac{-b_{\text{ads}_j} + \sqrt{\Delta_j}}{2a_{\text{inc}_j}}, & \text{if } \Delta_j \geq 0 \\ 0 & \text{if } \Delta_j < 0 \end{cases} \quad (140)$$

$$\Delta_j = b_{\text{ads}_j}^2 - 4a_{\text{inc}_j} \omega_{\text{dim}_j} \quad (141)$$

where $a_{\text{inc}_j} = k_{\text{inc}_j}$ and b_{ads_j} is calculated by summing the adsorption rate of dimer for all sections and dividing it by the dimer concentration.

$$b_{\text{ads}_j} = \sum_{i=1}^{n_{\text{sec}}} k_{\text{ads}_j}^i [\text{soot}]^i \quad (142)$$

After determining the concentration of each dimer, the contribution of inception and PAH adsorption to source terms of tracked soot variables can be calculated similar to previous inception models considering the number of carbon and hydrogen atoms involved in the process.

$$I_{N,inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 4\omega_{inc_j} n_{PAH_j,C}, \quad (143)$$

$$I_{C_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 4\omega_{inc_j} n_{PAH_j,C}, \quad (144)$$

$$I_{H_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 4\omega_{inc_j} (n_{PAH_j,H} - 2), \quad (145)$$

$$I_{C_{tot},ads}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} 2\omega_{ads_j}^i n_{C,PAH_j}, \quad (146)$$

$$I_{C_{tot},ads}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} 2\omega_{ads_j}^i (n_{H,PAH_j} - 2). \quad (147)$$

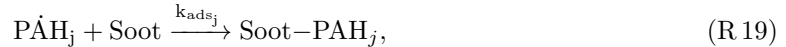
The rate of removal of PAHs and release of H₂ due to inception and PAH adsorption is calculated as:

$$\left(\frac{d[PAH_j]}{dt} \right)_{inc} = -4 \sum_{k=1}^{n_{PAH}} w_{inc_j} - 2 \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (148)$$

$$\left(\frac{d[H_2]}{dt} \right)_{inc} = 2 \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (149)$$

5.4 E-Bridge Formation

The E-Bridge Formation was originally proposed by Frenklach and Mebel [45] to describe soot inception using a HACA-like scheme that starts with dehydrogenation of PAH monomers, often pyrene, which forms the monomer radicals and continues with of sequential addition of the radicals to PAHs that form dimers, trimers and larger polymers until the PAH structure reaches the mass threshold and the clustering process becomes irreversible. Here, a modified version of EBridge Formation model is used where dimers are considered as incipient soot, and monomer radical are adsorbed on soot agglomerates. This PAH growth model is described using the following set of pathways:



The rate constants of Reactions (R 16)&(R 17) are listed in Table 3 while those of dimer production and adsorption are calculated based on Equations (94)&(100), respectively. For both steps, it is assumed the all collisions are successful i.e. 100% collision efficiency for radical-monomer and radical-soot.

$$k_{inc_j} = \beta_{jj,PAH} \cdot Av, \quad (150)$$

$$k_{ads_j}^i = \beta_{ads_j}^i \cdot Av, \quad (151)$$

Table 3: Rate coefficients for the monomer de-/hydrogenation reaction of E-bridge formation in Arrhenius form $k = AT^n \cdot e^{-E/RT}$ [45]

| Reaction | A | $\left[\frac{\text{m}^3}{\text{mol}\cdot\text{s}}\right]$ | n | $\frac{E}{R}$ [K] |
|----------|---|---|------|-------------------|
| (R 16) | f | $98 \times n_{C,PAH_j}$ | 1.8 | 7,563.519 |
| | r | 1.6×10^{-2} | 2.63 | 2145.346 |
| (R 17) | f | 4.8658×10^7 | 0.13 | 0.0 |

The rate of dimer formation and adsorption is calculated as:

$$w_{dim_j} = \eta_{inc} k_{inc_j} [PAH_j] [P\dot{A}H_j] \quad (152)$$

$$w_{ads_j}^i = \eta_{ads} k_{ads_j}^i [Soot]^i [P\dot{A}H_j] \quad (153)$$

The calculations of rate of inception and PAH adsorption from PAH_j requires the concentration of corresponding monomer radical that can be determined by applying the steady-state assumption for $P\dot{A}H_j$.

$$\begin{aligned} \frac{d[P\dot{A}H_j]}{dt} = 0 \\ k_{f,d_j} [PAH_j] [H] - k_{r,d_j} [P\dot{A}H_j] [H_2] - k_{f,h_j} [P\dot{A}H_j] [H] - k_{inc_j} [P\dot{A}H_j]^2 \\ - \sum_{i=1}^{n_{sec}} k_{ads_j}^i [P\dot{A}H_j] [Soot]^i = 0 \end{aligned}$$

The above equations can be rearranged as a quadratic equation similar to the dimer coalescence.

$$a_{inc_j} [P\dot{A}H_j]^2 + b_{ads_j} [P\dot{A}H_j] + c_j = 0, \quad (154)$$

$$a_{inc_j} = k_{f,d_j} \quad (155)$$

$$b_{ads_j} = k_{r,d_j} [H_2] + k_{f,h_j} [H] + \sum_{i=1}^{n_{sec}} k_{ads_j}^i [Soot]^i \quad (156)$$

$$c_{inc_j} = k_{f,d_j} [PAH_j] [H] \quad (157)$$

Finally, solving the quadratic equation for each PAH results in concentration of the radical using the following equation as:

$$[P\dot{A}H_j] = \begin{cases} \frac{-b_{ads_j} + \sqrt{\Delta_j}}{2a_{inc_j}}, & \text{if } \Delta_j \geq 0 \\ 0 & \text{if } \Delta_j < 0 \end{cases} \quad (158)$$

$$\Delta_j = b_{ads_j}^2 - 4a_{inc_j} c_j \quad (159)$$

The contribution of inception and adsorption to the partial source terms for E-Bridge formation can be written as:

$$I_{N,inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 2\omega_{inc_j} n_{PAH_j,C}, \quad (160)$$

$$I_{C_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 2\omega_{inc_j} n_{PAH_j,C}, \quad (161)$$

$$I_{H_{tot},inc} = \frac{1}{\rho} \sum_{j=1}^{n_{PAH}} 2\omega_{inc_j} (n_{PAH_j,H} - 2), \quad (162)$$

$$I_{C_{tot},ads}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} \omega_{ads_j}^i n_{C,PAH_j}, \quad (163)$$

$$I_{C_{tot},ads}^i = \frac{1}{\rho} \sum_{i=1}^{n_{PAH}} \omega_{ads_j}^i (n_{H,PAH_j} - 2). \quad (164)$$

The rate of removal of each PAH involved in soot inception and PAH adsorption and release of H_2 to the gas mixture can be expressed as:

$$\left(\frac{d[PAH_j]}{dt} \right)_{inc} = -2 \sum_{k=1}^{n_{PAH}} w_{inc_k} - \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (165)$$

$$\left(\frac{d[H_2]}{dt} \right)_{inc} = \sum_{i=1}^{n_{sec}} w_{ads_j}^i. \quad (166)$$

6 Gas scrubbing rates

The rate of production/destruction of species involved in soot formation must be taken into account to preserve the mass and energy balance in reactive systems. In order to do that, the production rate of gaseous species calculated by Cantera must be corrected for the rate of release/consumption due to PAH growth and surface reaction models.

$$\left(\frac{d[PAH_j]}{dt} \right)_{tot} = \left(\frac{d[PAH_j]}{dt} \right)_{gas} + \left(\frac{d[PAH_j]}{dt} \right)_{inc} + \left(\frac{d[PAH_j]}{dt} \right)_{ads}. \quad (167)$$

H_2 is released to the gas mixture due to inception, PAH adsorption as well as oxidation.

$$\left(\frac{d[H_2]}{dt} \right)_{tot} = \left(\frac{d[H_2]}{dt} \right)_{gas} + \left(\frac{d[H_2]}{dt} \right)_{inc} + \left(\frac{d[H_2]}{dt} \right)_{ads} + \left(\frac{d[H_2]}{dt} \right)_{ox}. \quad (168)$$

Surface growth consumes C_2H_2 and adds H_2 to the gas mixture.

$$\left(\frac{d[C_2H_2]}{dt} \right)_{tot} = \left(\frac{d[C_2H_2]}{dt} \right)_{gas} + \left(\frac{d[C_2H_2]}{dt} \right)_{gr}. \quad (169)$$

$$\left(\frac{d[H]}{dt} \right)_{tot} = \left(\frac{d[H]}{dt} \right)_{gas} + \left(\frac{d[H]}{dt} \right)_{gr}. \quad (170)$$

Oxidation uses O_2 and OH to remove carbon from soot particles and generates H_2 and CO .

$$\left(\frac{d[CO]}{dt} \right)_{tot} = \left(\frac{d[CO]}{dt} \right)_{gas} + \left(\frac{d[CO]}{dt} \right)_{ox}. \quad (171)$$

$$\left(\frac{d[O_2]}{dt} \right)_{tot} = \left(\frac{d[O_2]}{dt} \right)_{gas} + \left(\frac{d[O_2]}{dt} \right)_{ox}. \quad (172)$$

$$\left(\frac{d[OH]}{dt} \right)_{tot} = \left(\frac{d[OH]}{dt} \right)_{gas} + \left(\frac{d[OH]}{dt} \right)_{ox}. \quad (173)$$

7 Code Validation

A set of simulations was performed to ensure the accuracy and reliability of omnisooot for prediction of soot formation. Aerosol dynamics is validated by comparing the results of population balance models implemented in omnisooot with those of DEM simulations from literature. Carbon and hydrogen mass and energy balance is also rigorously evaluated to ensure that residuals fall within the bounds of acceptable numerical error.

7.0.1 Collision Frequency

The collision frequency function determines the rate at which two particles collide, which results in the reduction of total number of agglomerates and increase in size. In the absence of strong flow shear or external forces, Brownian motion is the main driving force for particle coagulation. As explained in Sections 3.5.1 & 3.6.1, omnisooot employs harmonic mean and Fuchs interpolations to calculate collision frequency of agglomerates from free-molecular to continuum regimes based on gas mean free path, and particle morphology.

The test case for validation of collision frequency is based on the DEM simulation of 2000 monodisperse spherical particles with the density of 2200 kg/m^3 in a cubic cell with the constant temperature of 298 K and pressure of 1 atm [114]. Figure 7 depicts the collision frequency plotted against Knudsen number ($\text{Kn} = 2\lambda/d_m$) obtained by omnisooot using harmonic mean (red solid line) and Fuchs interpolation (green dashed line) and DEM results of Goudeli et al. [114]. The Fuchs interpretation perfectly matches DEM data over the free-molecular ($\text{Kn} < 10$) to the continuum ($\text{Kn} > 10$) range. Harmonic mean is also in good agreement with the DEM results in the free-molecular and continuum regime, but slightly underpredicts the collision frequency in the transition regime ($0.1 \leq \text{Kn} \leq 10$) with relative errors less than 16%.

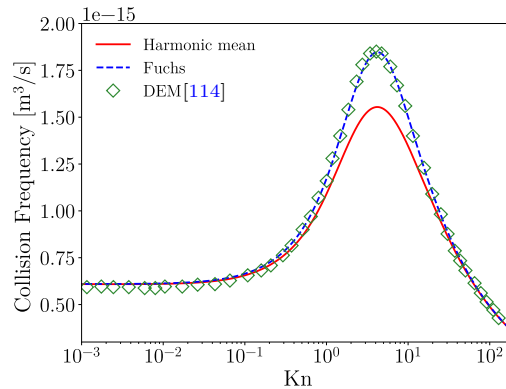


Figure 7: The comparison of collision frequency, β , obtained by omnisooot using harmonic mean (red solid line) and Fuchs interpolation (green dashed line) with DEM results (symbols) [114]

7.1 Coagulation

This test case was designed and conducted to validate the coagulation sub-unit of both particle dynamics models, MPBM and SPBM, by comparing the results of omnisooot with those of DEM [115]. The constant volume reactor was used for this test case, but it will be applicable to other reactors and flame models as long as the particle residence time matches with the values obtained by DEM. An adiabatic reactor with the volume of 1 m^3 is initialized with 2.6261×10^{18} spherical particles 2 nm in diameter. The initial conditions are indicated in Table 4. The particles are allowed to coagulate in the free molecular regime and grow in size while no inception, PAH adsorption and surface growth occur. Figure 9 demonstrates the number density of agglomerates (N_{agg}) and primary particles (N_{pri}), and mobility (d_m) and gyration (d_m) diameters of particle obtained by omnisooot that are

Table 4: The simulations conditions of the coagulation test case [115]

| Property | Value |
|-------------|---|
| Composition | CH ₄ :0.425, O ₂ :0.435, N ₂ :0.14 |
| T | 1830 K |
| P | 1 atm |
| N_{agg}^1 | 3.514×10^{-5} mol/kg |
| N_{pri}^1 | 3.514×10^{-5} mol/kg |
| d_p^1 | 2 nm |

in good agreement with DEM results. N_{pri} is conserved during coagulation resulting in identical flat lines for both particle dynamics models, but N_{agg} declines over time with the higher decay rate for SPBM because it accounts for the polydispersity of agglomerates that results in larger collision frequency compared to MPBM. Therefore, mean mobility and gyration diameter of SPBM (red lines in Fig. 9-b) are slightly larger than those of MPBM (blue line of the same figure).

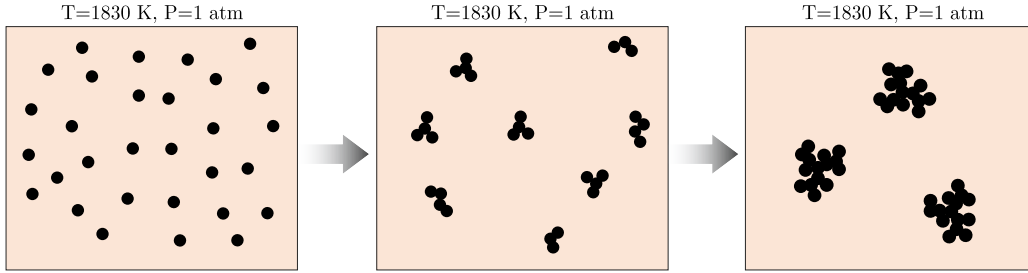


Figure 8: The schematic of agglomeration process in the coagulation test cases where initially spherical particle collide and form agglomerate

MPBM model cannot resolve PSD because of the monodispersity assumption. In contrast, SPBM tracks the number concentration of particles in separate sections that can be used to construct evolving PSD and calculate mean properties and determine the spread of size distribution of particles during coagulation. Figure 10-a shows the standard deviation of mobility diameter, σ_g predicted by SPBM in close agreement with DEM results. σ_g starts from unity indicating a monodisperse population at the beginning of simulation, and it finally reaches 2.03 that is the signature standard deviation of the free molecular regime [116]. Fig. 10 demonstrates the evolution of non-dimensional PSD from $t=1$ ms to 677 ms. The PSD is plotted for the normalized concentration, $\Psi = \bar{v}n_{agg}(v, t)/N_{agg,inf}$ and dimensionless volume, $\eta = v/\bar{v}$, where $n_{agg}(v, t)$ is the size distribution function of agglomerate, v particle volume, \bar{v} mean particle volume, $N_{agg,inf}$ total number concentration of agglomerates. For short residence times, $t \approx 4$ ms, the PSD resembles a half bell curve because the majority of particles has sizes close to $d_0 = 2$ nm with the average volume close to the minimum volume, so the particles with $\eta \approx 1$ has the largest concentration. As particles grow by coagulation, the PSD rapidly transitions to a full bell-curve ($t \geq 22$ ms) and does not change for longer residence times, $t \geq 447$ ms marking the attainment of SPSD in a good agreement with DEM results. This confirms the capability of SPBM implemented in omnisoot to capture SPSD for soot agglomerates as a signature of Brownian-driven particle coagulation.

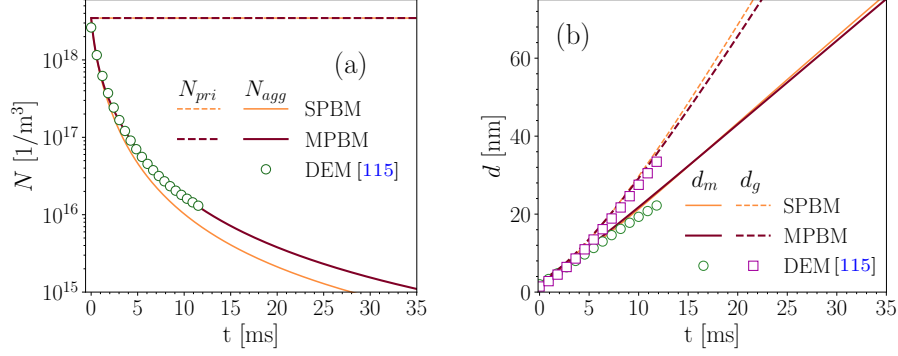


Figure 9: The total number concentration of agglomerates and primary particles (a), and mobility and gyration diameter (b) obtained with omnisoot using MPBM and SPBM that are in close agreement with the DEM results [115] indicating the validation of coagulation sub-model

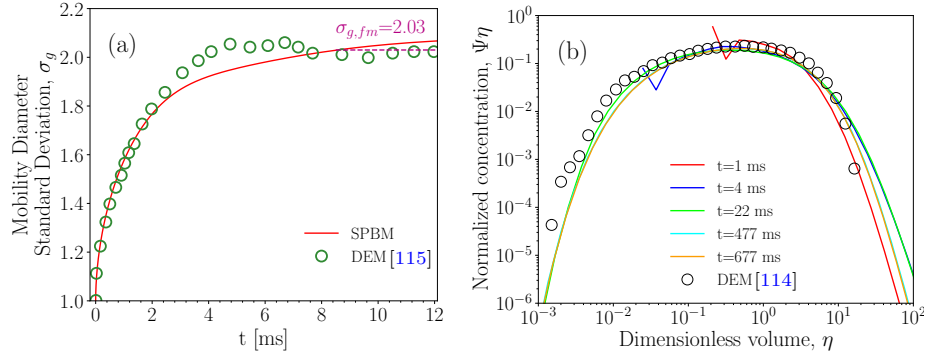


Figure 10: The standard deviation (residual) of mobility diameter, σ_g obtained with SPBM in close agreement with DEM results [115] (left pane) that reaches $\sigma_{g, fm} = 2.03$ characteristic of the free molecular regime [116]; the particle size distribution (normalized number concentration of agglomerates) is plotted against non-dimensional volume in the right pane) at different residence times that overlaps after initial transient phase marking the attainment of self-preserving size distribution in good agreement with DEM results [114]

7.2 Constant Volume Reactor

The pyrolysis of 30% CH_4 diluted in N_2 with the initial temperature and pressure of 2455 K and 3.47 atm, respectively, was simulated using the constant volume reactor model in the residence time of 40 ms. The combination of available PAH growth and particle dynamics models leads to eight different cases that were simulated to ensure the conservation of mass and energy. Here, we focus on the total elemental balance of carbon and hydrogen because they are involved in soot processes. Figure 11 demonstrates the relative error of total carbon, hydrogen and energy of system for different PAH growth and particle dynamics models in the constant volume that falls below 10^{-10} for all parameters confirming the validity of model in satisfying the mass and energy balance in the constant volume reactor using all models.

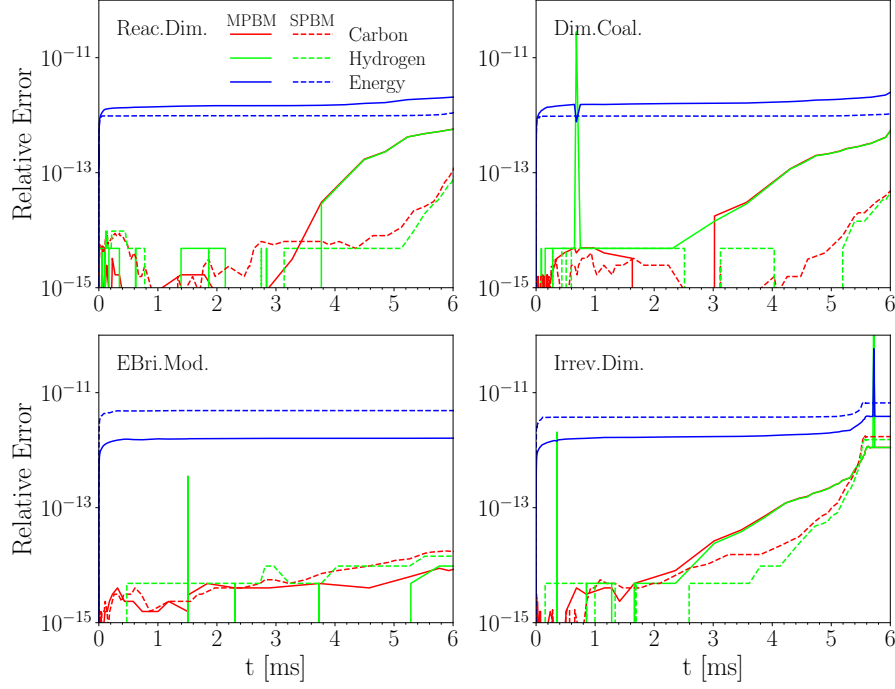


Figure 11: The relative error (residual) of total carbon (red line) and hydrogen (green line) mass, and total internal energy residual of gas and soot (blue line) plotted against residence time during pyrolysis of 30% $\text{CH}_4\text{-N}_2$ at 2455 K and 3.47 atm in the constant volume reactor simulated using different PAH growth models along with MPBM (solid line) and SPBM (dashed line)

7.3 Constant Pressure Reactor

The pyrolysis of 5% $\text{CH}_4\text{-Ar}$ in a shock-tube with post-reflected-shock temperature and pressure of $T_5=2355$ K and $P_5=4.64$ atm, respectively, was simulated using CPR model. Figure 12 shows the relative error of total carbon, hydrogen and energy of system for different PAH growth and particle dynamics models in the constant volume that falls below 10^{-10} for all parameters confirming the validity of model in satisfying the mass and energy balance in the constant pressure reactor using all models.

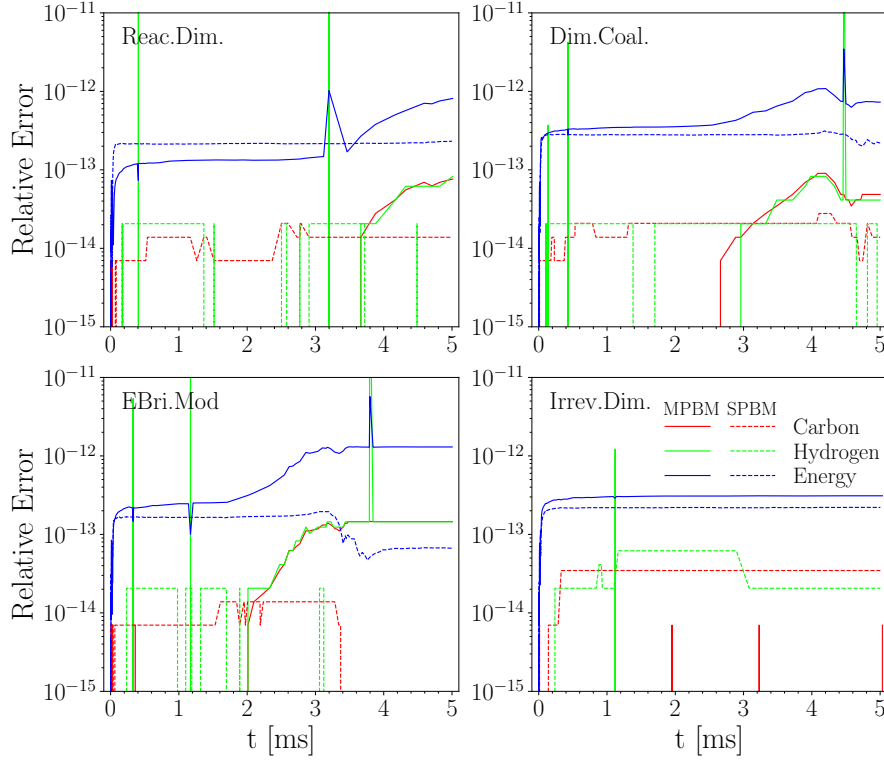


Figure 12: The relative error (residual) of total carbon (red line) and hydrogen (green line) mass, and total internal energy residual of gas and soot (blue line) plotted against residence time during pyrolysis of 5% CH_4 -Ar at 2355 K and 4.64 atm simulated using the constant pressure reactor with different PAH growth model, MPBM (solid line) and SPBM (dashed line)

7.4 Plug Flow Reactor

Methane pyrolysis in an adiabatic flow reactor is used to check elemental carbon and hydrogen, and energy balance in the PFR model. The inlet flow enters the reactor at the composition of 30% CH_4 diluted in N_2 , and $T=2100$ K and $P=1$ atm. Figure 13 shows the residual of total elemental carbon and hydrogen, and energy up to 40 cm of the reactor length using all PAH growth and particle dynamics model. The residuals are in the order of 10^{-11} and start to grow at the beginning of the reactor by pyrolysis of CH_4 and the formation of intermediate species such as C_2H_2 and PAHs. This initiates soot inception of surface growth affecting the gas chemistry and energy that ends near $x=10$ cm, and then the coagulation of particles is dominant with no affect on mass and energy of particles. As a result, PFR model of omnisoot satisfied the conservation of the mass and energy.

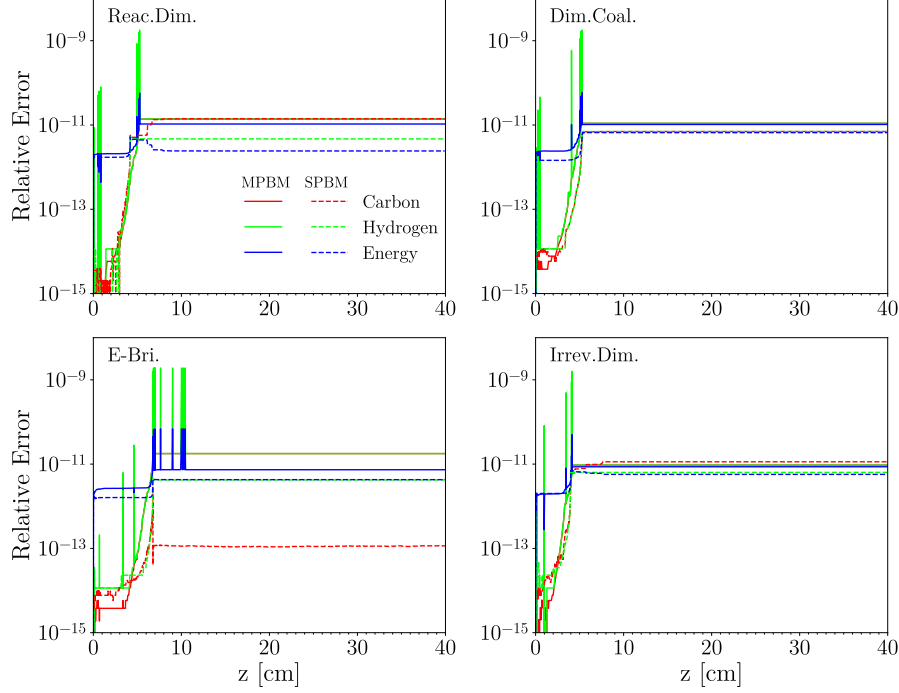


Figure 13: The relative error (residual) of total carbon (red line) and hydrogen (green line) mass, and total internal energy residual of gas and soot (blue line) plotted against reactor length (cm) in the adiabatic flow reactor during pyrolysis of 30% $\text{CH}_4\text{-N}_2$ at 2100 K and 1 atm simulated using different PAH growth models and MPBM (solid line) and SPBM (dashed line)

7.5 Perfectly Stirred Reactor

The mass and energy balance are investigated for soot formation during ethylene-air oxidation at $\phi = 2$ in a perfectly stirred reactor. The simulation conditions were chosen based on the combustor implemented and utilized by Stouffer et al. [117]. The reactants initially at 300 K enter a reactor of 250 ml that works under atmospheric pressure. The simulation is initialized from a high temperature (2000 K) to avoid trivial solution (cold reactant leaving the reactor with no chemical reactions) and to ensure the model captures a sustained combustion. The residence time of products in the reactor is 8.5 ms. Figure 14 shows the relative error of total elemental carbon and hydrogen mass and total enthalpy of gas and soot, which is less than 10^{-6} for all combinations of particle dynamics and PAH growth models.

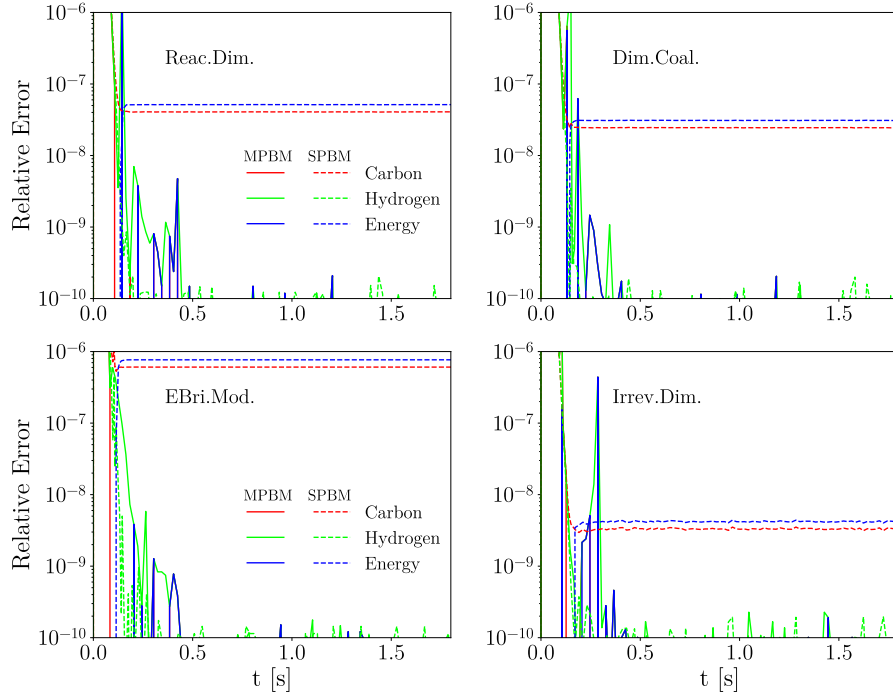


Figure 14: The relative error (residual) of total carbon (red line) and hydrogen (green line) mass, and total internal energy residual of gas and soot (blue line) plotted in simulation time during adiabatic combustion of C_2H_4 -air with $\phi = 2.1$ atm simulated using different PAH growth models and MPBM (solid line) and SPBM (dashed line)

8 Results and Discussion

8.1 Methane pyrolysis in shock-tube using constant pressure reactor

The pyrolysis of 5% CH_4 -Ar was investigated using a constant pressure reactor model (CPR) for the post-shock temperature, T_5 range of 1800-3000 K, and pressure, P_5 range of 4.7-7.1 bar. P_5 was not specified for each experiment (characterized with T_5), so we assume that P_5 linearly increases with T_5 in the specified pressure range. Caltech mechanism was used to describe gas chemistry. The inception and PAH adsorption rates were adjusted using η_{inc} and η_{ads} , respectively to match the predicted carbon yield at $t=1.5$ ms over the studied T_5 and P_5 with the extinction measurements at $\lambda=632$ nm [118]. The measured carbon yield was retrieved from the reported yield $\times E(m)$ considering the maximum variability in the absorption function of soot from 0.174 [119] to 0.37 [120] in the literature. A parametric study was performed on the inception and adsorption adjustment factors using a grid search approach. Each factor was varied across 11 logarithmically spaced values ranging from 10^{-4} to 1, resulting in 99 simulation cases for each data point (792 simulations in total). The combinations of η_{inc} and η_{ads} were sorted using the average relative error all data points to find the combinations(s) of adjustment factors resulting in the minimum prediction error for carbon yield. Fig.15 shows a heat map of the mean relative error normalized by the maximum value for Reactive Dimerization. The largest error occurs for the combination of the maximum inception and minimum PAH adsorption corresponding to $\eta_{inc} = 1$ ($\log_{10}(\eta_{inc}) = 0$) and $\eta_{ads} = -4$ ($\log_{10}(\eta_{ads}) = -4$). The area with the lowest normalized error (less than 5%) was outlined in blue, and it covers a larger number of adjustment factor pairs that lead to the accurate prediction of carbon yield, but might change the predicted morphology. To better understand these effect, we took a multi-step approach: i) the model was run without soot to focus on the chemistry of precursors and C_2H_2 ,

ii) the inception models were optimized using equal adjustment factors $\eta_{inc}=\eta_{ads}$ iii) the inception models were optimized with the minimum adsorption rate, $\eta_{ads} = 10^{-4}$ (labeled as *Min Ads*) and the minimum inception flux, $\eta_{inc} = 10^{-4}$ (labeled as *Min Ads*).

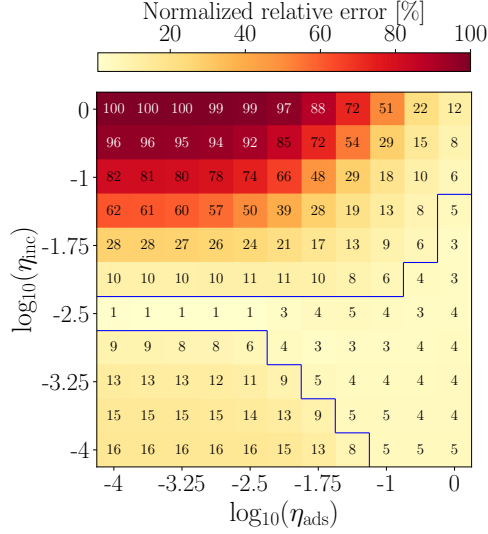


Figure 15: The relative error of carbon yield normalized by the maximum value at $t=1.5$ ms for 5% CH_4 obtained using Caltech mechanism and Reactive Dimerization

Fig. 16-a shows the carbon mass fraction (CMF) of soot precursors (individual PAHs and total) and C_2H_2 at 1.5 ms over the studied temperature range when no soot model is deactivated. While the precursors exhibit a bell-shape behavior, the CMF of C_2H_2 linearly increases with temperature and level off after reaching 85% $T_5 \approx 2400\text{K}$. Among the considered PAHs, A2, A2R5, and A4R5 contain the majority of carbon and are expected to be major contributors to soot inception and surface growth via adsorption.

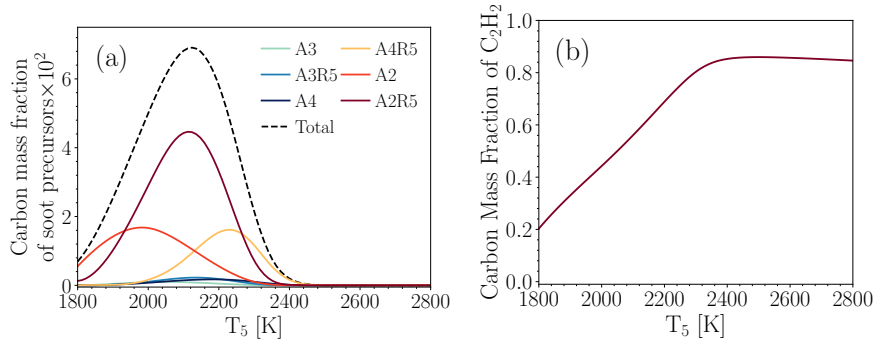


Figure 16: The bell-shape temperature profile of carbon mass fraction of soot precursors (A2 and larger) combined (a) and C_2H_2 (b) at $t=1.5$ ms during pyrolysis of 5% (red line) and 10% CH_4 -Ar (green line) obtained using CPR model with Caltech mechanism without considering soot

Next set of simulations were conducted by using equal adjustment factor ($\eta_{inc} = \eta_{ads}$) to minimize prediction error of mean soot carbon yield. Fig. 17 compares soot carbon yield and d_p predicted using the different inception models and the sectional population balance model with the data from extinction measurements [118]. A skew exponential curve (represented by the black dotted line) was

fitted to the data to highlight the trend in carbon yield, and its likely peak at 12%. Soot carbon yield has a bell-shape profile similar to the one shown for soot precursor because soot inception flux and mass growth are directly tied to the concentration of precursors used by the inception models. The yield and predicted by Reactive Dimerization in the low temperature range (less than the temperature of the peak yield). EBridge Modified seems to be shifted to higher temperatures compared to other inception models indicating different temperature dependence of this model (PAH dehydrogenation) is described with an Arrhenius rate as opposed to the other model where inception is initiated with physical collision of PAHs. The predicted d_p uniformly increases with T_5 to the peak value of 12.5 nm at 2700 K where yield is very low ($\approx 10^{-7}$), and then rapidly falls to the minimum possible diameter in the model, 2 nm.

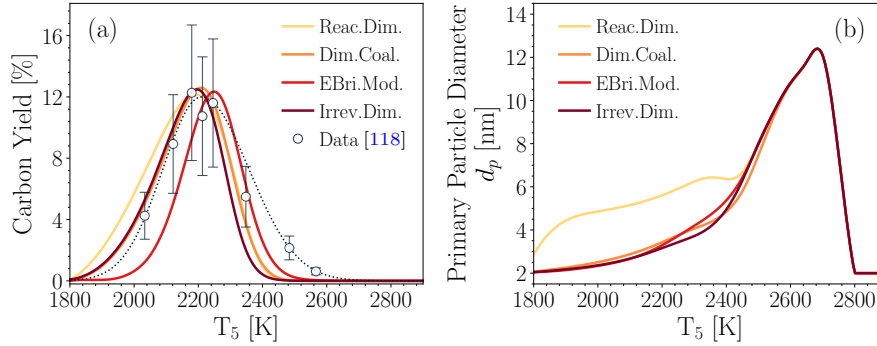


Figure 17: The bell-shape temperature profile of soot carbon yield at $t=1.5$ ms (a) and increasing primary particle diameter, d_p obtained using Caltech mechanism and different inception models optimized using equal adjustment factors to minimize the prediction with extinction measurements [118]. The dashed line was added to show the trend in the measurements.

The differences in d_p by the inception models is overall negligible except for Reactive Dimerization, which predicts a larger d_p in $T_5 < 2500$. The d_p trends can be better understood by examining Eq.(24) indicating that d_p is proportional of the third-root of C_{tot}/N_{pri} . C_{tot} describes total carbon mass converted to soot through inception and surface growth while N_{pri} is only determined by inception flux. As a result, d_p is controlled by the ratio of surface growth (HACA and PAH adsorption) rate to inception flux. The ratio of carbon mass gained up to 1.5 ms by each pathway to the total soot carbon mass is calculated and shown in Fig.18. In the low temperature range, $T_5 < 2000$ K, Reactive Dimerization (Fig.18-a) directs the majority of the converted carbon to HACA and PAH adsorption resulting in larger C_{tot}/N_{pri} and d_p values. The carbon mass fraction of inception decreases with temperature for all inception models leading to higher d_p values up to 2700 K and it increases afterwards that changes d_p trends.

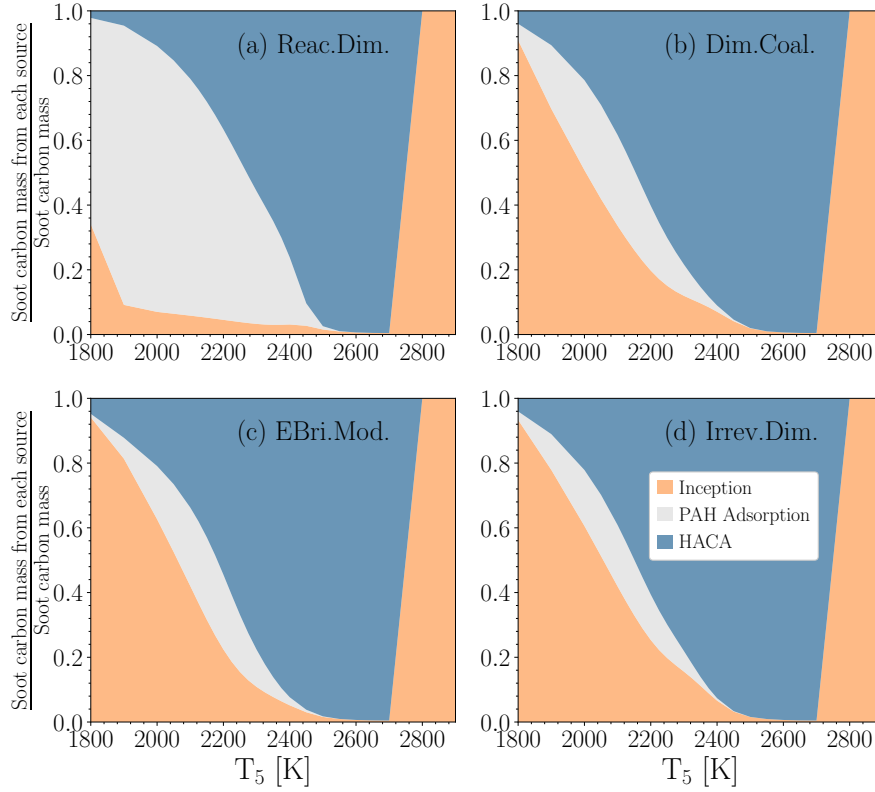


Figure 18: The soot carbon mass from inception, PAH adsorption and HACA normalized by total soot carbon mass at $t=1.5$ ms for 5% in Ar obtained using Caltech mechanism and different inception models calibrated to minimize the prediction with extinction measurements [118].

As shown in Fig.19, the inception models optimized using the minimum inception (η_{inc}) and PAH adsorption (η_{ads}) adjustment factors result in the carbon yield values indistinguishably close except for EBridge Modified model that is slightly shifted to higher temperatures in both cases. The minimum adsorption case has a higher peak and a narrower profile compared the minimum inception. Fig.19 demonstrates the variation in d_p among the inception models with the minimum inception (solid line) mode compared to the minimum adsorption (dashed line) that show negligible sensitivity to the inception model. In the minimum inception mode, the majority of soot mass comes from PAHs, so d_p shows a bell-shape profile with a peak close to the temperature of CMF of precursors (dashed line in Fig.16). Reactive Dimerization has the largest variation at the peak from 2 to 21 nm for the minimum inception and adsorption, respectively. The global adjustment factors were used to alter the contribution of precursors to inception and surface growth without changing the internal rate constants of inception models. A close agreement was achieved between the predicted and measured carbon yield in different modes of inception and PAH adsorption that can result in different soot morphology. Characterizing primary particle size in the experiment can reduce the uncertainty in the model and restrict the range of expected inception and surface growth rate and highlight the need to account for missing pathways and phenomena involved in soot yield and morphology.

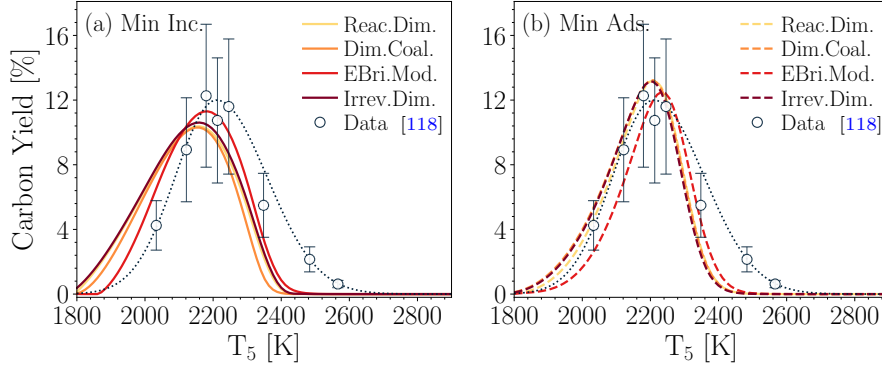


Figure 19: The comparison of soot carbon yield at $t=1.5$ ms when the minimum inception (a) and the minimum PAH adsorption (b) adjustment factors were applied to minimized the prediction error compared to measurements [118] for 5% CH_4 -Ar obtained using Caltech mechanism and different inception models.

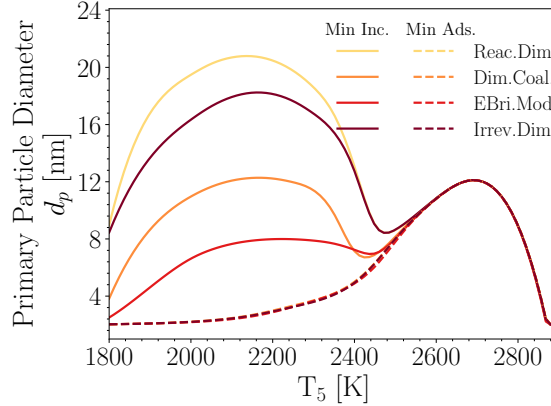


Figure 20: The comparison of mean primary particle, d_p at $t=1.5$ ms when the minimum inception (solid lines) and adsorption (dashed lines) were applied to minimized the prediction error compared to measurements [118] for 5%-Ar obtained using Caltech mechanism and different inception models.

8.2 Ethylene pyrolysis in a flow reactor

The PFR model was used to simulate the pyrolysis of %0.6 $\text{C}_2\text{H}_4 - \text{N}_2$ in a flow reactor 1.4 m long and 16 mm in diameter. Fig.21 shows the axial temperature profile with $T_{\text{max}}=1673$ K imposed on the model, which was calculated based on the thermocouple measurements by Mei et al. [121] for various flow rates along the reactor centerline. The temperature starts from 300 K at the entrance and increases to reach the hot zone with the temperature within 10% of T_{max} . The length of hot zone changes from 0.71 m for $Q=8$ L/min to 0.76 m for $Q=12$ L/min due to the advection effect. The temperature drop to 650 K near the end of the reactor.

The inception and PAH adsorption adjustment factors were varied to match the predicted PSD with measurements at the end of reactor for various volumetric flow rates, Q of 8.5, 11 and 12 L/min shown in Fig. 22. The parametric analysis showed that only a single set of adjustment factors exist for each inception model that minimizes the prediction error of PSD across the flow rates. The KAUST mechanism [122] was used to describe gas chemistry as it results in better agreement with PSD measurements compared to Caltech. A bimodal size distribution can be observed for $Q=8$ L/min (Fig. 22-a) that was attributed to the continuous inception alongside the coagulation [107]. The comparison of simulations with measurements reveals different temperature dependence of inception

models. Irreversible Dimerization and Dimer Coalescence capture the bimodality of PSD in good agreement with the measurements, but the other two models predict a nearly unimodal PSD. The number concentration of the first section is lower by more than three orders of magnitude for Reactive Dimerization and EBridge Modified indicating the lack of active inception at the sampling location due the temperature drop near the end of reactor that suppress soot inception.

All inception models captured the disappearance of shoulder in the PSD at 11 and 12 L/min because the particle residence time is shorter compared to 8 L/min and the sampling was done before coagulation becomes dominant and forms the second peak. However, a one order of magnitude underprediction of the number concentration of incipient particles can be observed when Reactive Dimerization and EBridge Modified are compared with irreversible inception models.

Fig.22 shows the evolution of total number concentration of agglomerates, N_{agg} along the reactor. The predictions of the inception models are relatively close until $z \approx 1.1$ m the corresponds to end of hot zone in the reactor, but N_{agg} is larger for Irreversible Dimerization and Dimer Coalescence beyond that point because the inception continues in the low temperature region. The irreversible models are in better agreement with measurements for 8 and 11 L/min, but overestimate the final number concentration at 12 L/min.

As shown in Fig.24, soot inception flux exhibits a sharp increase as the flow enters the hot zone of the reactor. The axial distance at which inception flux exceeds 10^7 is the same for all inception models because it is mostly determined by the PAH chemistry, but the location is shifted downstream with flow rate because of shorter residence times. The difference between inception models is not significant in the hot zone. While the inception flux continues to grow for Irreversible Dimerization and Dimer Coalescence beyond the hot zone, Reactive Dimerization and EBridge predict a rapid decrease in inception flux by more than 3 orders of magnitude due to temperature drop.

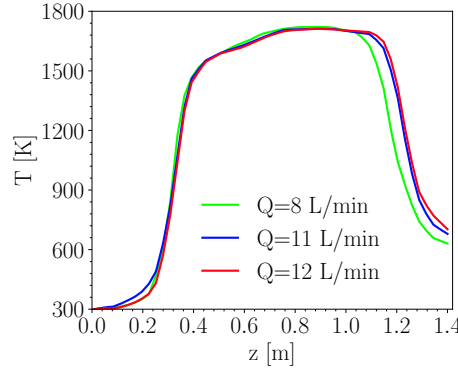


Figure 21: The centerline temperature along the reactor for $Q=8$, 11, and 12 L/min interpolated from the thermocouple measurements [121]. The yellow area represent the region with temperature larger than 1200 K.

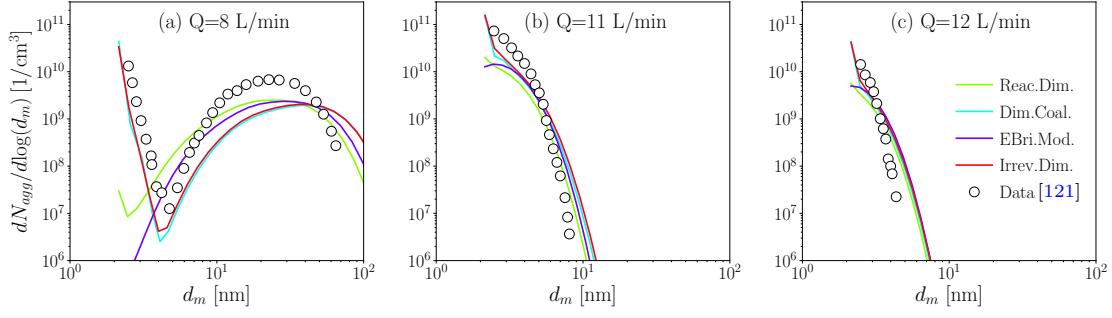


Figure 22: The particle size distribution at the end of PFR for Q=8.5 (a), 11 (b), and 12 L/min (c) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [121].

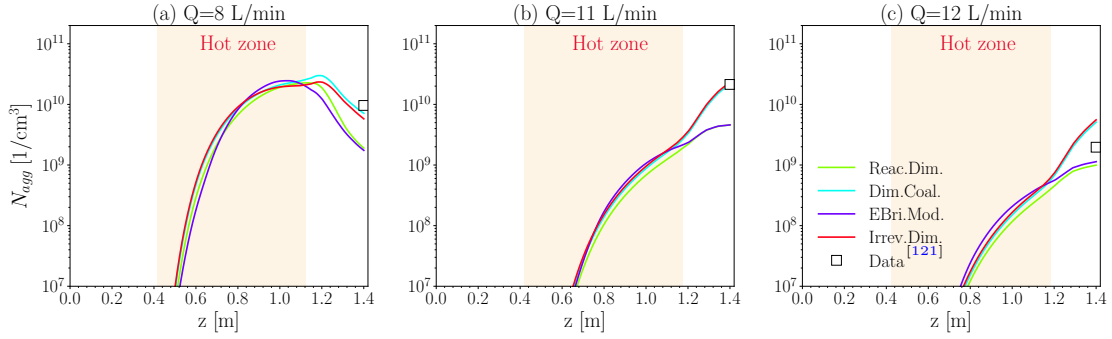


Figure 23: The total number of agglomerates along the PFR for Q=8.5 (a), 11 (b), and 12 L/min (c) obtained using KAUST mechanism and different inception models compared with data [121].

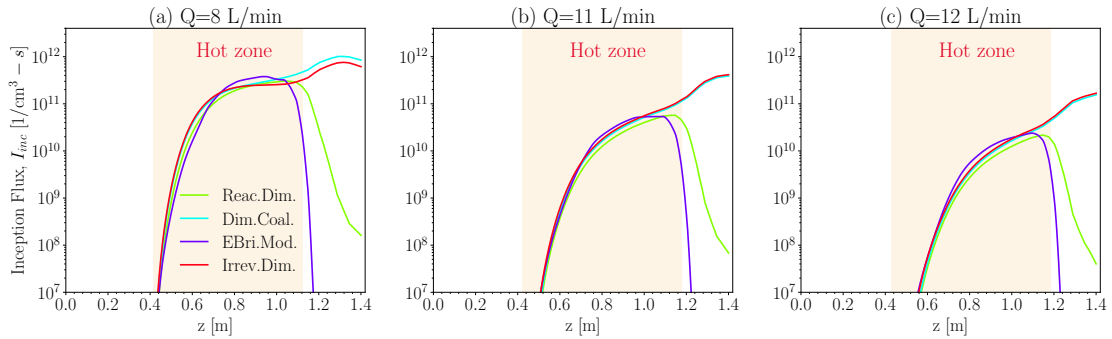


Figure 24: The soot inception flux along the PFR for Q=8.5 (a), 11 (b), and 12 L/min (c) obtained using KAUST mechanism and different inception models.

8.3 Ethylene oxidation in a partially-stirred reactor

Manzello et al. [123] utilized NIST well-stirred reactor (WSR) connected to a flow reactor to study soot formation during ethylene oxidation at equivalence ratios, $\phi = 1.9, 2.0$, and 2.1 , and provided

PSD measurements at the end of flow reactor using nano-differential mobility analyzer (Nano-DMA). The WSR had the same size of the reactor used by Manzello et al. [123] and explained in Sec.7.5. The flow reactor is 70 cm long with an inner diameter of 5.1 cm. A coupled PSR-PFR reactor model of omnisooot was used to simulate soot formation during the combustion and flow evolution in the device. The nominal residence time, τ of flow in the PSR is 11 ms Manzello et al. [123]. The reactants are assumed to enter PSR at 300 K with an inlet mass flow rate, $\dot{m}_{in} = \rho V / \tau$ where ρ was calculated at reactor temperature of 1723 K suggested by Lenhert and Manzello [124]. The PFR is assumed to be adiabatic. The calculated average axial velocity in the PFR is 14.5 m/s close to the values suggested by Manzello et al. [123]. KAUST mechanism was used to describe gas chemistry.

The inception and PAH adsorption adjustment factors were varied for each PAH growth model to match the predicted PSD with the measurements as closely as possible for all three ϕ s. As shown in Fig. 25, all inception model capture the peak number concentration and the unimodal shape of the PSD, which indicates that particle inception has ceased, and coagulation is the dominant growth mechanism. As reported in Table 5, the geometric mean mobility diameter, $d_{m,g}$ and the geometric mobility standard deviation, $\sigma_{m,g}$ obtained using all inception models are in good agreement with the values calculated from the measured PSD [123]. As it can be seen in Fig.25-(a) & (b), the spread of predicted PSD is narrower than that of measurements for $\phi=1.9$ and 2.1, which corresponds to under-prediction of $\sigma_{m,g}$ for these equivalence ratios.

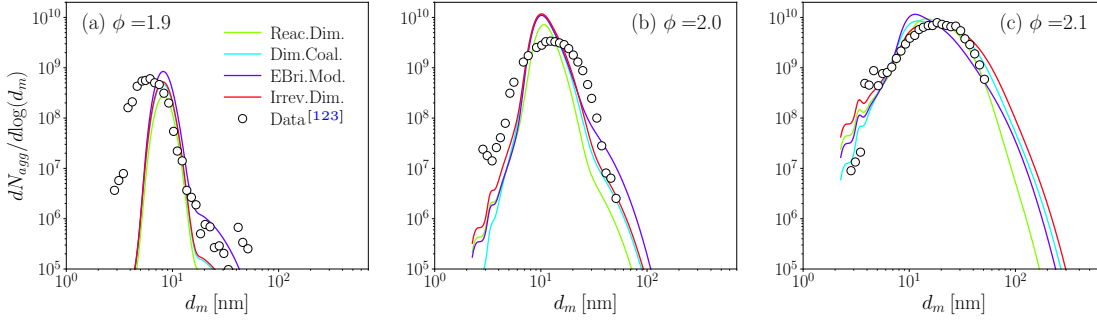


Figure 25: The particle size distribution at the end of PFR for $\phi=1.9$ (a), 2.0 (b), and 2.1 (c) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [123].

Table 5: The geometric mean mobility diameter, $d_{m,g}$, and the geometric mobility standard deviation, $\sigma_{m,g}$ obtained using different inception models compared with the value calculated from the measured PSD [123]

| | $\phi = 1.9$ | | $\phi = 2.0$ | | $\phi = 2.1$ | |
|---------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | $d_{m,g}$ [nm] | $\sigma_{m,g}$ | $d_{m,g}$ [nm] | $\sigma_{m,g}$ | $d_{m,g}$ [nm] | $\sigma_{m,g}$ |
| Data [123] | 6.04 | 1.25 | 12.40 | 1.49 | 17.66 | 1.64 |
| Reactive Dimerization | 8.27 | 1.14 | 11.10 | 1.21 | 16.88 | 1.58 |
| Dimer Coalescence | 8.18 | 1.14 | 10.76 | 1.24 | 16.99 | 1.68 |
| EBridge Modified | 8.27 | 1.15 | 11.02 | 1.27 | 14.56 | 1.58 |
| Irreversible Dimerization | 8.19 | 1.14 | 10.96 | 1.25 | 18.44 | 1.78 |

All inception models underpredict the number concentration of small particles ($d_m < 6$ nm) at $\phi=1.9$. The discrepancy decreases for $\phi=2$ and the model predictions align well with the measurements. The number concentration of the smallest measured particle (≈ 2 nm) is less affected by equivalence ratio compared to the numerical results. This suggests a stronger sensitivity of the PAH production rate to variation of ϕ from 1.9 to 2.1, which directly impacts soot inception flux. The strong similarity of profiles of A2R5 mole fraction and soot inception along the reactor shown in Fig. 26 highlights the dominant role of PAH chemistry on soot inception. Another important observation is that A2R5 mole fraction is not affected by the inception model. One order of magnitude increase in peak A2R5 mole fraction due to the change of ϕ from 1.9 to 2.1 is amplified leading to two orders of magnitude increase in inception flux.

As shown in Fig. 27, primary particle diameter, d_p along the flow reactor is nearly the same for all inception models at $\phi=1.9$, and the difference becomes noticeable. Reactive Dimerization predicts the largest final d_p because it directs more PAH mass to surface growth rather than inception, which is consistent with lower peak number concentration observed in Fig. 25. d_p rapidly drops at the beginning of the reactor flow due to the rise in the production of incipient particles (spherical particle 2 nm in diameter) that lowers the mean d_p of particles, and then it increases by surface growth. The final d_p slightly increases with ϕ , but its range is similar for ϕ values. As shown in Fig. 28, soot volume fraction is very sensitive to equivalence ratio, which can be explained by the strong effect of equivalence ratio on PAH production, inception flux, and number of particles. The analysis of surface growth rates of PFR model revealed that more than 95% of soot mass is gained through HACA. Fig. 29 illustrates the coupling between number concentration of agglomerates, N_{agg} and HACA growth rate and their change due to equivalence ratio.

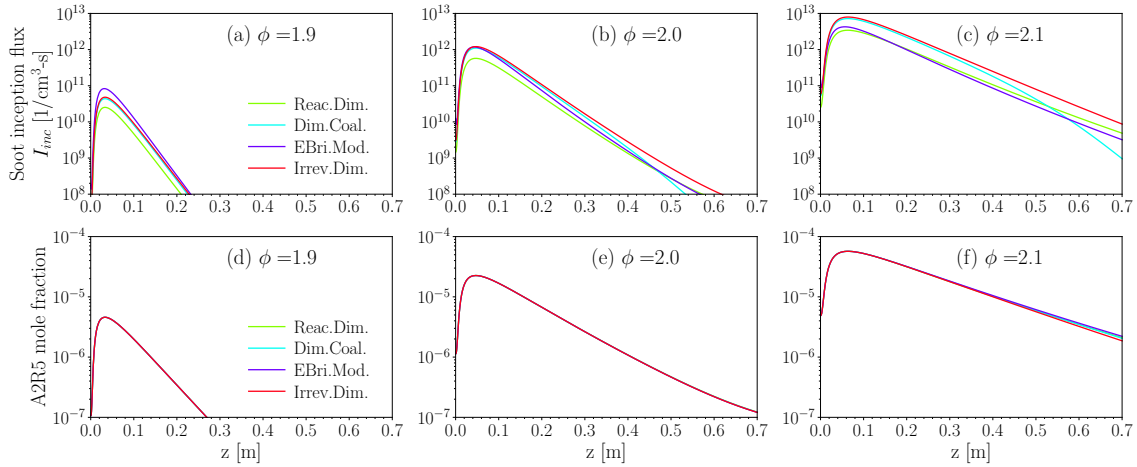


Figure 26: The soot inception flux, I_{inc} and acenaphthylene, A2R5 mole fraction along the PFR for $\phi=1.9$ (a,d), 2.0 (b,e), and 2.1 (c,f) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [123].

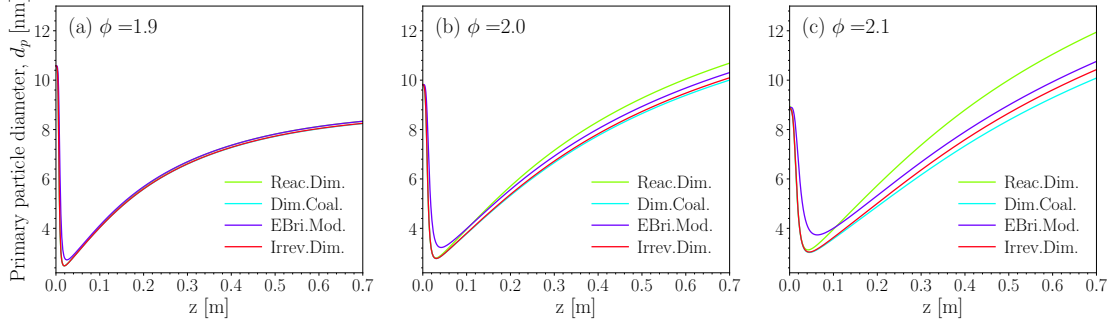


Figure 27: The primary particle diameter, d_p along the PFR for $\phi=1.9$ (a), 2.0 (b), and 2.1 (c) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [123].

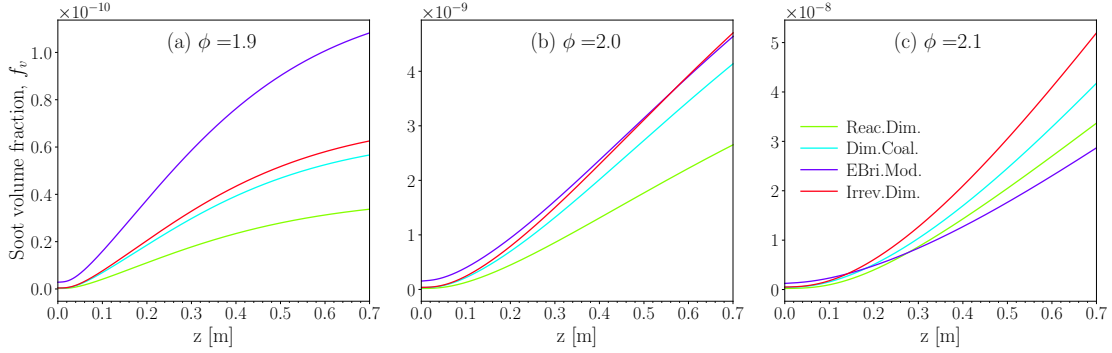


Figure 28: The soot volume fraction along the PFR for $\phi=1.9$ (a), 2.0 (b), and 2.1 (c) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [123].

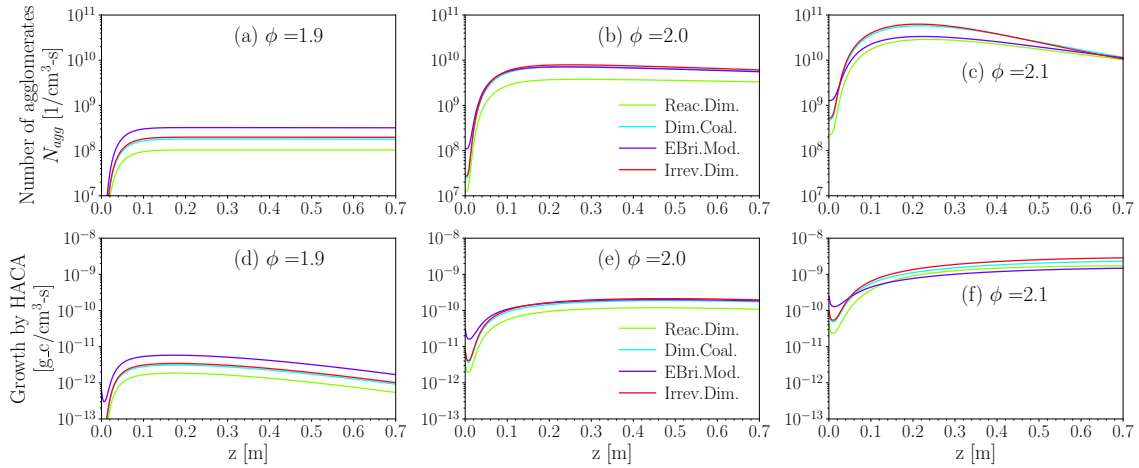


Figure 29: The number of agglomerates, N_{agg} and the rate of carbon addition by HACA along the PFR for $\phi=1.9$ (a,d), 2.0 (b,e), and 2.1 (c,f) obtained using KAUST mechanism and different inception models calibrated to match the predictions with measurement [123].

9 Conclusion

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