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Mechanism of soot formation: an experimental and modeling study

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Mécanismes de formation de suies : étude expérimentale et numérique

Résumé : La formation de nanoparticules de carbone en environnement de combustion résulte d'un réseau de processus chimiques remarquablement complexe, dont beaucoup restent encore partiellement compris. Au fil des années, la modélisation cinétique chimique a évolué, passant de formulations empiriques simples à des mécanismes détaillés capables de décrire à la fois l'évolution des précurseurs en phase gazeuse et la dynamique des particules. Malgré ces progrès, d'importants défis subsistent, notamment dans la description de la nucléation de la suie et l'identification des facteurs régissant la croissance des particules. Ces limitations restreignent la capacité prédictive des modèles actuels pour des technologies de combustion plus propres et la synthèse de matériaux carbonés par flamme. Dans ce travail, la modélisation cinétique chimique est utilisée pour mieux comprendre les processus fondamentaux contrôlant la formation de la suie à partir de la pyrolyse de combustibles aliphatiques et aromatiques. Un outil informatique dédié, le Soot Mechanism Automated Generator (SMAuG), a été développé. SMAuG est un framework basé sur Python, conçu pour construire automatiquement des sous-mécanismes de particules selon des classes de réactions et des règles prédéfinies. La dynamique des particules est représentée à l'aide d'un modèle sectionnel discret avec des espèces BIN pseudo-lumpées, couplé à un mécanisme en phase gazeuse défini par l'utilisateur. Dans cette étude, le mécanisme ICARE HAP a été choisi pour décrire la formation des précurseurs en phase gazeuse. Le modèle développé dans cette thèse introduit plusieurs avancées clés : (i) mise à jour de la chimie en phase gazeuse pour la pyrolyse du C_2H_2 et la formation de polyynes ; (ii) nouvelles voies réactionnelles pour la croissance des hydrocarbures aromatiques polycycliques (HAP) via des interactions radical-polyynes ; (iii) voies synergétiques couplant la chimie des HAP et des polyynes ; (iv) mise en œuvre d'une nouvelle classe d'intermédiaires BIN activés ; et (v) optimisation des paramètres cinétiques régissant la nucléation et la croissance en surface. La validation du modèle a été réalisée à partir d'expériences en tube à choc menées à ICARE avec divers combustibles, allant de l'acétylène — choisi pour étudier la chimie des polyynes — aux composés aromatiques comme le benzène et le toluène, qui testent les voies liées aux HAP. Les simulations montrent une très bonne concordance avec les profils expérimentaux de la fraction volumique de suie dans le temps, ce qui constitue une réussite notable compte tenu de la complexité inhérente au système. Des validations supplémentaires contre des données bibliographiques, incluant des profils de suie dépendant de la température, des temps d'induction et des taux de croissance, ont confirmé la fiabilité du modèle. Des évaluations complémentaires ont étendu l'analyse à d'autres combustibles, notamment des espèces aliphatiques (éthylène, propylène, propyne, cyclopentène) et aromatiques (éthylbenzène, styrène), ainsi qu'à des mélanges contenant du toluène, du benzène, du cyclopentène et des intermédiaires C_2/C_3 . Des analyses cinétiques détaillées ont permis d'identifier les voies principales menant à la formation des noyaux initiaux de suie dans différentes conditions thermodynamiques, soulignant le rôle clé des voies polyynes et leur interaction avec les intermédiaires PAH. En résumé, le modèle proposé offre un cadre complet et flexible pour la simulation de la formation de nanoparticules de carbone dans les systèmes pyrolytiques et la production de noir de carbone. Son développement futur soutiendra des applications pratiques en combustion, notamment la propagation de la flamme et la conversion d'énergie.

Mots clés : modélisation cinétique chimique, formation de suie, nanoparticule de carbone, hydrocarbures aromatiques polycycliques, polyynes, tube à choc, modèle sectionnel discret.

Mechanism of soot formation: an experimental and modeling study

Summary: The formation of carbon nanoparticles in combustion environments arises from a remarkably intricate network of chemical processes, many of which remain only partially understood. Over the years, chemical kinetic modeling has progressed from simple empirical formulations to detailed mechanisms capable of describing both the evolution of gas-phase precursors and particle dynamics. Despite this progress, significant challenges persist, particularly in the description of soot nucleation and the identification of factors governing particle growth. These limitations restrict the predictive capability of current models for cleaner combustion technologies and flame-based synthesis of functional carbon materials. In this work, chemical kinetic modeling is used to improve the understanding of the fundamental processes controlling soot formation from the pyrolysis of aliphatic and aromatic fuels. A dedicated computational tool, the Soot Mechanism Automated Generator (SMAuG), has been developed. SMAuG is a Python-based framework designed to automatically construct particle sub-mechanisms according to predefined reaction classes and rules. Particle dynamics are represented using a discrete sectional model with pseudo-lumped BIN species, which is coupled to a user-defined gas-phase mechanism. In this study, the ICARE PAH mechanism was selected to describe the formation of gas-phase precursors. The model developed within this thesis introduces several key advancements: (i) updated gas-phase chemistry for C_2H_2 pyrolysis and polyynes formation; (ii) new reaction pathways for the growth of polycyclic aromatic hydrocarbons (PAHs) via radical-polyynes interactions; (iii) synergistic routes coupling PAH and polyynes chemistries; (iv) implementation of a new class of activated BIN intermediates; and (v) optimization of the kinetic parameters governing nucleation and surface growth. Model validation was carried out using shock-tube experiments performed at ICARE with a range of fuels, from acetylene—chosen to probe polyynes chemistry—to aromatic compounds such as benzene and toluene, which test the PAH-related pathways. The simulations show very good agreement with experimental soot volume fraction time-histories, a significant achievement considering the inherent complexity of the system. Additional validation against literature data, including temperature-dependent soot profiles, induction times, and growth rates, confirmed the reliability of the model. Further assessments extended the analysis to additional fuels, including aliphatic species (ethylene, propylene, propyne, cyclopentene) and aromatic molecules (ethylbenzene, styrene), as well as mixtures containing toluene, benzene, cyclopentene, and C_2/C_3 intermediates. Detailed kinetic analyses identified the dominant routes leading to the formation of initial soot nuclei under different thermodynamic conditions, highlighting the key role of polyynes pathways and their interplay with PAH intermediates. Overall, the proposed model provides a comprehensive and flexible framework for the simulation of carbon nanoparticle formation in pyrolytic systems and carbon black production. Its further development will support future applications to practical combustion configurations, including flame propagation and energy conversion systems.

Keywords: chemical kinetic modeling, soot formation, carbon nanoparticle, polycyclic aromatic hydrocarbons, polyynes, shock tube, discrete sectional model



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Do not go gentle into that good night,
Old age should burn and rave at close of day;
Rage, rage against the dying of the light.

Though wise men at their end know dark is right,
Because their words had forked no lightning they
Do not go gentle into that good night.

Good men, the last wave by, crying how bright
Their frail deeds might have danced in a green bay,
Rage, rage against the dying of the light.

Wild men who caught and sang the sun in flight,
And learn, too late, they grieved it on its way,
Do not go gentle into that good night.

Grave men, near death, who see with blinding sight
Blind eyes could blaze like meteors and be gay,
Rage, rage against the dying of the light.

And you, my father, there on the sad height,
Curse, bless, me now with your fierce tears, I pray.
Do not go gentle into that good night.
Rage, rage against the dying of the light.

Dylan Thomas

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***“A wizard is never late, nor is he early, he arrives precisely when
he means to.” — Gandalf the Gray***

Abstract

The chemistry involved in the formation of carbon nanoparticles in combustion devices is a complex and complicated subject, involving many steps that are often poorly characterized. The development of the related chemical kinetic models has evolved over time, from simple empirically-derived mechanisms of a few reactions for the simulation of global parameters to detailed models capable of reproducing the evolution of the gas-phase precursors and the particle kinetics. Still, the current models face many challenges related to the description of the nucleation process and the definition of the factors affecting the particle growth. This hinders their utilization as predictive tools for the design of cleaner combustion devices and flame-based synthesis of carbon functional materials. The present work employs chemical kinetic modeling to further advance our fundamental understanding of key elements in the soot formation chemistry from the pyrolysis of aliphatic and aromatic fuels.

First, the Soot Mechanism Automated Generator (SMAuG) was designed and constructed. SMAuG is a user-friendly Python framework capable of automatically generating particle chemical kinetic sub-models based on the reaction classes and rules, with the discrete sectional model with pseudo-lumped BIN species chosen as a method to describe the particle distribution. The particle chemistry is coupled to a gas-phase sub-mechanism defined by the user; in this case, the ICARE PAH chemical kinetic model was selected for the simulation of the gas-phase particle precursors.

The model, subsequently developed as part of this thesis, contains various new implementations compared to similar models in the literature: i) a new gas-phase chemistry for C_2H_2 pyrolysis and polyynes formation; ii) new pathways for the formation of polycyclic aromatic hydrocarbons starting from reactions between polyynes molecules and radicals; iii) new synergistic reactions combining PAH and polyynes chemistry; iv) implementation of a new class of activate BIN intermediates; v) optimized reaction rate parameters for nucleation and growth processes with respect to the gas-phase used in this work. The model was validated against experiments in a shock tube performed at ICARE on a variety of fuel

molecules, ranging from acetylene, which was selected to probe the polyynes chemistry applied to soot formation, to aromatic fuels such as benzene and toluene, for the validation of the reactions involving PAH compounds. The simulation results show excellent agreement with the experimental profiles in terms of soot volume fraction time-histories, an outstanding achievement considering the complexity of the task. Other validation targets were soot volume fraction profiles as a function of the temperature, soot induction times, and soot growth rates, also from literature investigations. The model performances were also tested for different fuel molecules, from aliphatics (ethylene, propylene, propyne, cyclopentene) to aromatics (ethylbenzene, styrene), as well as mixtures containing toluene/benzene/cyclopentene and C2/C3 intermediates. Chemical kinetic analyses were performed to identify the main pathways leading to the formation of the first soot nuclei as a function of the fuel and the thermodynamic conditions, with particular focus on the role of the polyynes routes and their interaction with the PAH intermediates.

The proposed chemical kinetic model constitutes a detailed and comprehensive base simulation of the pyrolytic formation of carbon nanoparticles, as well as the production of carbon black in furnaces. Further developments of the model will be essential for its use in other practical applications, e.g., for modeling free and confined flame propagation or energy production systems.

Keywords: chemical kinetic modeling, soot formation, carbon nanoparticle, polycyclic aromatic hydrocarbons, polyynes, shock tube, discrete sectional model.

Résumé

La chimie impliquée dans la formation de nanoparticules de carbone dans les dispositifs de combustion est un sujet complexe et difficile, impliquant de nombreuses étapes souvent mal caractérisées. Le développement des modèles cinétiques chimiques associés a évolué au fil du temps, passant de mécanismes empiriques simples comprenant quelques réactions pour la simulation de paramètres globaux à des modèles détaillés capables de reproduire l'évolution des précurseurs en phase gazeuse et de la cinétique des particules. Cependant, les modèles actuels rencontrent encore de nombreux défis liés à la description du processus de nucléation et à la définition des facteurs influençant la croissance des particules. Cela limite leur utilisation en tant qu'outils prédictifs pour la conception de dispositifs de combustion plus propres et pour la synthèse de matériaux fonctionnels à base de carbone par flamme. Le présent travail utilise la modélisation cinétique chimique pour approfondir notre compréhension fondamentale des éléments clés de la chimie de la formation de suie à partir de la pyrolyse de combustibles aliphatiques et aromatiques.

Premièrement, le générateur automatisé du mécanisme de suie (SMAuG) a été conçu et construit. SMAuG est un environnement Python convivial capable de générer automatiquement des sous-modèles cinétiques chimiques des particules en se basant sur les classes et règles de réaction, avec le modèle sectionnel discret utilisant des espèces BIN pseudo-lumpées comme méthode pour décrire la distribution des particules. La chimie des particules est couplée à un sous-mécanisme en phase gazeuse défini par l'utilisateur, dans ce cas, le modèle cinétique ICARE PAH a été choisi pour la simulation des précurseurs gazeux des particules.

Le modèle développé dans le cadre de cette thèse comporte plusieurs avancées par rapport à des modèles similaires dans la littérature : i) une nouvelle chimie en phase gazeuse pour la pyrolyse du C_2H_2 et la formation de polyynes ; ii) de nouveaux mécanismes pour la formation d'hydrocarbures aromatiques polycycliques à partir de réactions entre molécules de polyynes et radicaux ; iii) de nouvelles réactions synergiques combinant la chimie des HAP et des polyynes ; iv) la mise en œuvre d'une nouvelle classe d'intermédiaires BIN activés ; v) des paramètres de vitesse de réaction optimisés pour les processus de nucléation

et de croissance en fonction de la phase gazeuse utilisée dans ce travail. Le modèle a été validé par des expériences réalisées dans un tube à choc à l'ICARE, sur une variété de molécules de combustible, allant de l'acétylène, choisi pour étudier la chimie des polyynes appliquée à la formation de suie, à des combustibles aromatiques tels que le benzène et le toluène, pour la validation des réactions impliquant des composés HAP. Les résultats de la simulation montrent un excellent accord et une excellente concordance entre les profils temporels expérimentaux des fractions volumiques de suie et ceux obtenus par simulation, ce qui constitue une réussite remarquable compte tenu de la complexité de la tâche. D'autres cibles de validation incluaient les profils de la fraction volumique de suie en fonction de la température, les temps d'induction de la suie, et les taux de croissance de la suie. Cet excellent accord a aussi été obtenu pour des résultats issus de la littérature. Les performances du modèle ont également été testées pour différents combustibles, allant des alcanes (éthylène, propylène, propyne, cyclopentène) aux aromatiques (éthylbenzène, styrène), ainsi que pour des mélanges contenant du toluène, du benzène, du cyclopentène et des intermédiaires C2/C3. Des analyses cinétiques chimiques ont été réalisées pour identifier les principaux mécanismes conduisant à la formation des premiers noyaux de suie en fonction du combustible et des conditions thermodynamiques, avec une attention particulière portée au rôle des voies polyne et à leur interaction avec les intermédiaires HAP.

Le modèle cinétique chimique proposé constitue une simulation détaillée et complète de la formation pyrolytique de nanoparticules de carbone, ainsi que de la production de noir de carbone dans les fours. Son développement ultérieur sera essentiel pour son utilisation dans d'autres applications pratiques, par exemple pour modéliser la propagation de flammes libres ou confinées, ou encore les systèmes de production d'énergie.

Mots-clés : modélisation cinétique chimique, formation de suie, nanoparticule de carbone, hydrocarbures aromatiques polycycliques, polyynes, tube à choc, modèle sectionnel discret.

Introduction

Les sociétés modernes, aussi avancées en technologie soient-elles, restent fortement dépendantes de l'utilisation de combustibles à base de carbone, tels que les combustibles conventionnels ou de nouveaux vecteurs énergétiques comme les e-combustibles, les biocombustibles, les carburants durables pour l'aviation, etc. Malgré les différentes propensions des combustibles à base de carbone à produire des nanoparticules de carbone (NPC) et de la suie, les technologies de combustion devront évoluer vers de nouvelles solutions capables de réduire l'impact des émissions de suie. En effet, comme le montrent des réglementations internationales de plus en plus strictes, la présence dans l'atmosphère de particules issues des dispositifs de combustion, dont le noyau est constitué de particules de suie agrégées en structures fractales complexes, a été associée à de graves conséquences sur la santé humaine et l'environnement. Les stratégies d'atténuation reposent sur l'utilisation d'outils de simulation précis, intégrant une description plus ou moins détaillée de la cinétique chimique de la formation de NPC. Le développement de modèles cinétiques chimiques précis pour la formation de la suie favorisera également les secteurs où l'objectif est de maximiser et de contrôler la synthèse par combustion de matériaux fonctionnels, tels que le noir de carbone. Le but du présent travail est de développer et de valider un nouveau modèle cinétique chimique détaillé, complet, pour la formation de NPC en conditions pyrolytiques.

État de l'art

La formation de suie lors de la combustion est un processus complexe impliquant plusieurs étapes cinétiques. Bien que certaines de ces étapes soient encore mal comprises, le consensus actuel général est que deux mécanismes principaux et concurrents pilotent la nucléation et la croissance des particules, à savoir la chimie des précurseurs des HAP et celle des polyynes. La chimie des HAP a fait l'objet de nombreuses recherches expérimentales, théoriques et de modélisations récentes. Selon la molécule de combustible et les conditions thermodynamiques, plusieurs voies de croissance complémentaires ont

été proposées, allant du mécanisme HACA classique et des processus de coagulation réactifs (réactions aromatiques + aromatiques) à une description détaillée des étapes impliquant divers intermédiaires, tels que le vinylacétylène et le radical vinyl (HAVA), les radicaux méthyle (MAC), les espèces di-radicalaires (CAF), les radicaux stabilisés par résonance, etc. L'un des modèles cinétiques chimiques les plus complets et avancés est le modèle ICARE HAP, basé sur des résultats expérimentaux obtenus dans des tubes à choc à impulsion unique. Cependant, la chimie des HAP, seule, s'est avérée insuffisante pour expliquer certains résultats expérimentaux dans des conditions spécifiques, notamment en pyrolyse. C'est pourquoi la chimie des polyynes a été proposée comme un élément central dans la formation de la suie, d'abord sur la base de résultats expérimentaux, puis par des activités de modélisation détaillée.

Après les études sur les molécules précurseurs, les activités cinétiques dans la littérature se sont concentrées sur la chimie de la nucléation et de la croissance des particules. La nucléation de particules marque la transition entre de grands précurseurs en phase gazeuse et la formation des premiers noyaux de particules (processus de nucléation). Les différents processus chimiques et physiques proposés dans la littérature comme responsables de cette étape illustrent la complexité associée, mais reflètent aussi le manque de compréhension fondamentale dû à notre capacité limitée à étudier ces processus insaisissables par des techniques expérimentales ou théoriques. La croissance ultérieure des particules inclut des réactions hétérogènes, la condensation, ainsi que des réactions entre particules, par exemple le mécanisme HACA, la croissance chimique par les HAP, la condensation des HAP sur les particules primaires, la polymérisation rapide des polyynes, la coalescence et l'agglomération. Divers modèles ont été développés pour décrire tous ces processus, qu'ils soient empiriques, semi-empiriques ou basés sur des formulations détaillées stochastiques (résolution des équations de bilan de population par Monte Carlo ou dynamique moléculaire) ou déterministes (méthode des moments et modèle sectionnel discret). Parmi ces propositions, le modèle sectionnel discret se distingue par sa capacité supérieure à fournir des prédictions détaillées dans l'étude de la formation de la suie, le modèle du groupe CRECK du Politecnico di Milano étant une référence dans le domaine.

Configuration expérimentale

L'utilisation d'un tube à choc dans les études cinétiques chimiques s'est avérée essentielle pour faire progresser notre compréhension fondamentale dans de nombreux domaines, allant de la spéciation détaillée et de la mesure des constantes de vitesse de réaction à la détermination des paramètres globaux de combustion et de détonation. Les tubes à choc sont des réacteurs idéaux où les mélanges d'intérêt sont comprimés et chauffés par le passage d'une onde de choc générée par la rupture d'une membrane initialement séparant le mélange d'intérêt d'un autre gaz à des pressions beaucoup plus élevées. La théorie derrière l'utilisation des techniques de tubes à choc est bien établie. En résolvant les équations de conservation, il est possible de calculer avec une grande précision les conditions thermodynamiques derrière les ondes de choc incidentes et réfléchies, en connaissant l'état initial du mélange et la vitesse de l'onde de choc incidente. Parmi les différents tubes à choc présents à l'ICARE, le Tube à Choc Chauffé (TCC) a été équipé d'une section finale permettant un accès optique via des techniques laser (extinction et diffusion de Rayleigh). En particulier, des études antérieures ont porté sur la mesure des fractions volumiques de suie à haute température (1500 K à 2000 K), à des pressions d'environ 16-19 bar, avec un temps de réaction de 1,3 ms, sur des mélanges composés de nombreux combustibles purs ou en mélanges dans un gaz porteur, l'argon. Ces résultats, ainsi que des données issues de la littérature, constituent la référence de validation pour le développement des modèles.

Soot Mechanism Automated Generator (SMAuG) – framework

Le générateur automatisé du mécanisme de suie (SMAuG) a été conçu et construit à l'ICARE pour permettre la rédaction des sous-mécanismes des particules. Cela est essentiel en raison du grand nombre de réactions et d'espèces chimiques impliquées. SMAuG est un environnement Python convivial capable de générer des sous-modèles cinétiques chimiques pour les particules, basés sur les espèces, les classes de réactions et les règles de taux définies par l'utilisateur. Le modèle à sections discrètes avec des espèces BIN pseudo-lumpées, tel que développé par le groupe CRECK, a été choisi comme méthode pour décrire la distribution des particules.

Modélisation cinétique en conditions pyrolytiques

Le modèle cinétique chimique développé dans le cadre de cette thèse est constitué de différents sous-mécanismes : i) la chimie de formation des hydrocarbures aromatiques polycycliques à partir du modèle ICARE HAP ; ii) la chimie gazeuse mise à jour pour la pyrolyse de C_2H_2 et la formation de polyynes, validée par des données de tubes à choc dans la littérature (profils de espèces et spéciation par tube à choc à impulsion unique) ; iii) de nouvelles voies pour la formation des HAP ramifiés à partir de réactions entre molécules de polyynes et radicaux, suivies d'additions C_2H_2/C_4H_2 et de cyclisations ; iv) de nouvelles réactions synergiques combinant la chimie des PAH et des polyynes ; v) la mise en œuvre d'une nouvelle classe d'espèces BIN activées ; vi) la chimie des particules avec des classes de réactions pour les mécanismes d'initiation et de croissance générés avec SMAuG. Les paramètres de constantes de vitesse de réaction de référence pour les différentes classes de réactions, qu'elles soient conventionnelles ou nouvellement proposées, sont discutés dans ce chapitre, notamment en relation avec la logique derrière leur utilisation.

Résultats et discussions

Les paramètres et mécanismes du modèle ont été optimisés dans ce travail en se basant sur la validation des profils temporels de la fraction volumique de suie (fv) et des paramètres cinétiques dérivés tels que les temps d'induction et les taux de croissance pour des combustibles sélectionnés. En général, toutes les simulations ont été ajustées par un facteur de 2,2 pour une meilleure concordance avec les résultats. Cela résulte d'un compromis sur la précision dans la simulation des profils en termes de forme et de quantité.

Le modèle a d'abord été validé avec des données sur la pyrolyse de l'acétylène (C_2H_2). L'acétylène n'est pas seulement un intermédiaire clé dans les environnements à haute température, mais aussi un précurseur de la formation et de la croissance des polyynes. Comme la formation de composés aromatiques à partir des réactions classiques $C_4 + C_2$, $C_3 + C_3$, et $C_5 + C_1$ est très limitée dans la pyrolyse de C_2H_2 , il a été possible d'isoler la contribution de la chimie des polyynes et d'optimiser les sous-mécanismes correspondants. Le modèle est capable de reproduire les profils expérimentaux sur toute la plage de températures initiales de 1603 à 1989 K, avec 0,245 % et 0,35 % d'acétylène dans l'argon,

ainsi que ceux issus de la littérature à différentes pressions et concentrations initiales de combustible. Les analyses du taux de production (ROP) ont montré que les espèces BIN initiales se forment principalement par des réactions entre les HAP ramifiés et les polyynes, tandis que la croissance est principalement alimentée par des réactions impliquant des polyynes. Le rôle des polyynes de taille plus grande devient de plus en plus important avec l'augmentation de la température initiale expérimentale.

Deux combustibles aromatiques, tels que le benzène (C_6H_6) et le toluène (C_7H_8), ont ensuite été sélectionnés afin d'étudier les mécanismes de formation de la suie impliquant respectivement des aromatiques à radicaux σ et des HAP, ainsi que des intermédiaires stabilisés par résonance, y compris leur interaction avec les polyynes. Le modèle est capable de reproduire avec une précision satisfaisante les résultats expérimentaux obtenus avec 0,082 % de benzène et 0,07 % de toluène dans un gaz porteur d'argon, sur une large gamme de températures initiales. Des données bibliographiques à différentes conditions thermodynamiques et concentrations de combustible ont également été utilisées comme cibles de validation. Les analyses cinétiques pour le cas du benzène indiquent qu'à basse température, les réactions entre HAP et, entre HAP ramifiés et polyynes contribuent toutes deux à la formation du BIN1, tandis que la croissance du BIN1-5 est alimentée par le mécanisme HACA et par les réactions de C_4H_2 . À des températures plus élevées, la chimie des particules est dominée par les réactions impliquant de grands polyynes avec des HAP ramifiés et des radicaux BIN. Ces résultats ont été confirmés pour le toluène, où un déplacement encore plus marqué de la chimie est observé. Dans ce cas, les analyses ROP montrent qu'à basse température, la formation des premières particules de suie est principalement due au mécanisme HACA et aux réactions de C_7H_7 et des espèces de PAH (principalement stabilisées par résonance, par exemple le radical indenyle, et d'autres molécules), et la contribution des polyynes se fait via C_4H_2 . À très haute température, la chimie des polyynes + HAP domine la formation des particules de suie.

Le modèle a également été testé sur une variété de mesures avec différents combustibles, dans des conditions similaires de T, P, et de concentrations en atomes de carbone (sauf pour l'éthylène, pour lequel des concentrations plus élevées ont dû être utilisées). Le modèle a montré d'excellentes capacités de prédiction pour les combustibles aromatiques,

le styrène et l'éthylbenzène, tandis qu'une légère surestimation à des températures plus basses des profils expérimentaux a été observée pour l'éthylène, le cyclopentène, le propylène et la propyne. Cela se traduit par un léger décalage du profil de modélisation de f_v en fonction de T vers des températures plus basses. Concernant le cas spécifique du propylène et du propyne, un facteur de correction de 1,2 est préféré. Les capacités du modèle ont également été testées pour des résultats sur des mélanges de combustibles, par exemple le toluène, le benzène, le cyclopentène + espèces C2, ainsi que le toluène + espèces C3, dans des conditions similaires de T , P et de concentrations en atomes de carbone. En général, le modèle est capable de reproduire avec une grande précision les données avec l'ajout d'acétylène, tout en sous-estimant les données obtenues avec des mélanges contenant de l'éthylène. La chimie du toluène + C3 pour la formation de suie est bien représentée par les résultats de la simulation.

Conclusions

Le présent travail propose un nouveau modèle cinétique chimique détaillé, complet, pour la simulation de la formation de suie en conditions pyrolytiques. Ce modèle constitue un outil clé pour la prédiction de la synthèse de CNP et sert de base pour de futurs développements via le code SMAuG récemment élaboré. Parmi ces développements, on prévoit une optimisation supplémentaire du schéma cinétique et l'ajout de la chimie d'oxydation en vue d'applications dans la production d'énergie.

Introduction

Modern societies, no matter how high-tech, are still strongly dependent on the use of carbon-based fuels, e.g., conventional fuels or new energy vectors as e-fuels, biofuels, sustainable aviation fuels, etc. Despite the different propensities of the carbon-based fuels to produce carbonaceous nanoparticles (CNP) and soot, combustion technologies will have to evolve towards new solutions capable of reducing the impact of soot emissions. Indeed, as reflected in more and more stringent International regulations, the presence in the atmosphere of particulate matter from combustion devices, whose core is constituted by soot particles aggregated in complex fractal structures, has been linked to severe consequences on human health and the environment. Mitigation strategies rely on the use of accurate simulation tools, which include a more-or-less detailed description of the chemical kinetics of CNP formation. The development of accurate chemical kinetic models for soot formation will also favor sectors where the scope is to maximize and control the flame-based synthesis of functional materials, such as carbon black. The goal of the present work is to develop and validate a new, detailed, comprehensive chemical kinetic model for CNP formation in pyrolytic conditions.

State of the art

Soot formation in combustion is a complex process involving several kinetic steps. Although certain of these steps are still poorly understood, the current general consensus is that two main competing mechanisms drive the nucleation and growth of the particles, e.g., PAH precursor molecules and polyynes chemistry. PAH chemistry has been the focus of many recent experimental, theoretical, and modeling activities. Depending on the fuel molecule and thermodynamic conditions, several complementary growth pathways have been proposed, from the classical HACA mechanism and reactive coagulation processes (aromatic + aromatic reactions) with to detailed description of steps involving a variety of intermediates, such as vinylacetylene and vinyl radical (HAVA), methyl radicals (MAC), diradical species (CAF), resonantly stabilized radicals, etc. One of the most complete and

advanced chemical kinetic models is the ICARE PAH model, implemented based on single-pulse shock tube experimental results. The PAH chemistry alone, though, has been demonstrated to be insufficient to describe experimental results for selected conditions, especially in pyrolytic conditions. For this reason, the polyynes chemistry has been proposed as central in soot formation, first based on experimental evidence, and then through detailed modeling activities.

Following the studies on the precursor molecules, the kinetic activities in the literature have focused on the chemistry of the CNP inception and growth. Particle inception marks the passage from large gas-phase precursors to the first particle nuclei (nucleation process). The different chemical and physical processes proposed in the literature as responsible for inception demonstrate the related complexity, but also reflect the lack of fundamental understanding due to our limited capability to study such elusive processes by experimental or theoretical techniques. The subsequent particle growth includes heterogeneous reactions and condensation as well as reaction between particles, e.g., HACA mechanism, chemical growth by PAHs, PAHs condensation on primary particles, polyynes rapid polymerization, coalescence, and agglomeration. Different modeling approaches have been developed in the past to describe all these processes, empirical, semi-empirical, or detailed formulations of stochastic (solution of the population balance equations through Monte Carlo or molecular dynamics) and deterministic types (method of moments and discrete sectional model). Among the various propositions, the discrete sectional model stands out for its superior capacity to provide detailed predictions in soot formation studies, with the model by the CRECK group at Politecnico di Milano being a reference in the field.

Experimental set-up

The use of a shock tube in chemical kinetic studies has been proven essential to advance our fundamental understanding in many fields, from detailed speciation and reaction rate constant measurements to the determination of global combustion parameters and detonation. Shock tubes are ideal reactors where the mixtures of interest are compressed and heated by the passage of a shock wave generated by the rupture of a diaphragm initially separating the mixture of interest from another gas at much higher pressures. The theory

behind the use of shock tube techniques is well established. Solving the conservation equations, it is possible to calculate with high accuracy the thermodynamic conditions behind incident and reflected shock waves, knowing the initial state of the mixture and the velocity of the incident shock wave.

Among the various shock tubes present at ICARE, the Heated Shock Tube (HST) has been equipped with an end-section for optical access through laser-based techniques (extinction and Rayleigh scattering). In particular, previous studies have focused on the measurement of soot volume fractions at high temperature conditions (1500 K to 2000 K), pressures around 16-19 bar, 1.3 ms reaction time, with mixtures composed of numerous fuels and blends in argon bath gas. Such results, together with data from the literature, constitute the validation benchmark for model development.

Soot Mechanism Automated Generator (SMAuG) – framework

The Soot Mechanism Automated Generator (SMAuG) was designed and constructed at ICARE to allow for the writing of the particle sub-mechanisms. This is essential due to the large number of reactions and chemical species involved. SMAuG is a user-friendly Python framework capable of generating particle chemical kinetic sub-models based on the species, reaction classes, and rate rules defined by the end-user. The discrete sectional model with pseudo-lumped BIN species, as developed by the CRECK group, was chosen as a method to describe the particle distribution.

Kinetic modeling under pyrolytic conditions

The chemical kinetic model developed in the present thesis work is constituted by different sub-mechanisms: i) chemistry for the formation of polycyclic aromatic hydrocarbons from the ICARE PAH model; ii) updated gas-phase chemistry for C_2H_2 pyrolysis and polyynes formation validated against shock tube data in the literature (species profiles and single-pulse shock tube speciation); iii) new pathways for the formation of branched PAHs starting from reactions between polyynes molecules and radicals, followed by C_2H_2/C_4H_2 addition and cyclization; iv) new synergistic reactions combining PAH and polyynes chemistry; v)

implementation of a new class of activated BIN species; v) particle chemistry with reaction classes for inception and growth mechanisms generated with SMAuG. The reference reaction rate constant parameters of the different reaction classes, conventional or newly proposed, are discussed in this chapter, especially in relation to the rationale behind their use.

Results and discussions

The model parameters and mechanisms were optimized in this work based on validation against soot volume fraction f_v time-history profiles and derived kinetic parameters such as induction times and growth rates for selected fuels. In general, all simulations were scaled by a factor of 2.2 for better agreement with the results. This was the result of a compromise between accuracy in the simulation of the profiles in terms of shape and quantity.

The model was first validated against data on acetylene (C_2H_2) pyrolysis. Acetylene is not only a key intermediate in high-temperature environments, but also a precursor of polyynes formation and growth. As the formation of aromatic species from classical $C_4 + C_2$, $C_3 + C_3$, and $C_5 + C_1$ reactions is very limited in C_2H_2 pyrolysis, it was possible to isolate the contribution of the polyynes chemistry and optimize the corresponding sub-mechanisms. The model is capable of reproducing the experimental profiles over the entire initial temperature range 1603-1989 K with both 0.245% and 0.35% acetylene in argon, as well as the data in the literature at different pressures and initial fuel concentrations. The rate-of-production (ROP) analyses showed how the initial BIN species are formed mainly through reactions between branched PAHs and polyynes, while the growth is driven by reactions involving polyynes. The role of larger polyynes becomes more and more prominent with the increase in the initial experimental temperature.

Two aromatic fuels, such as benzene (C_6H_6) and toluene (C_7H_8), were then selected in order to probe the mechanisms of soot formation involving σ -radical aromatics and PAHs and resonantly stabilized intermediates, respectively, including their interaction with polyynes. The model is capable of reproducing with quite good accuracy the experimental results obtained with 0.082% benzene and 0.07% toluene in argon bath gas over a wide range of

initial temperatures. Literature data at different thermodynamic conditions and fuel concentrations were also used as validation targets. The kinetic analyses for the benzene case indicate that, in the low temperature range, the PAH + PAH reactions and the reactions between branched PAH species and the polyynes both contribute to the formation of the BIN1, while the BIN1-5 growth is driven by HACA and the reactions of C_4H_2 . At higher temperatures, the particle chemistry is dominated by the reactions involving large polyynes with branched PAHs and BIN radicals. These results have been confirmed for toluene, where an even more marked shift in chemistry is observed. In this case, the ROP analyses show that at low temperatures, the formation of the first soot particles is mainly driven by the HACA mechanism and the reactions of C_7H_7 and PAH species (mainly resonantly stabilized, e.g., the indenyl radical, and molecules), and the contribution of polyynes is via C_4H_2 . At very high temperatures, the polyyne + PAH chemistry dominates the formation of soot particles.

The model was also tested against a variety of measurements with different fuels, at similar T, P conditions, and carbon atom concentrations (except for ethylene, for which higher concentrations had to be employed). The model showed excellent prediction capabilities concerning the aromatic fuels, styrene and ethylbenzene, while a slight overprediction at lower temperatures of the experimental profiles was obtained for ethylene, cyclopentene, propylene, and propyne. This translates into a slight shift of the f_v vs T modeling profile towards lower temperatures. Concerning the specific case of propylene and propyne, a correction factor of 1.2 is preferred. The model capabilities were also tested against results on fuel blends, e.g., toluene, benzene, and cyclopentene + C2 species as well as toluene + C3 species, at similar T, P conditions and carbon atom concentrations. In general, the model is capable of quite accurately reproducing the data with acetylene addition, while it underpredicts the data obtained with mixtures containing ethylene. The toluene + C3 chemistry for soot formation is well captured by the simulation results.

Conclusions

The present work provides a new, detailed, comprehensive chemical kinetic model for the simulation of soot formation in pyrolytic conditions. The model constitutes a key tool for the prediction of CNP synthesis and the base for future developments through the newly developed SMAuG code. Such developments include further optimization of the kinetic scheme and the addition of oxidation chemistry for use in energy production applications.

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1. Introduction

This chapter provides an in-depth examination of soot formation processes, emphasizing their critical role in environmental and human health concerns. Soot, a byproduct of combustion and pyrolytic reactions driven by both human activities and natural phenomena, presents significant challenges and opportunities. Its ecological and health hazards necessitate a thorough understanding, while its potential applications in various technological domains highlight its importance in scientific research and development.

1.1 General overview of global energy sources and emissions.

Despite the start of a marked energy transition to renewable energy sources from fossil fuels during the first two decades of the third millennium, combustion science and technology remain important for energy supply and production of flame-based materials, due to their essential role and influence on many aspects of everyday life. The sustainable energy transition is clearly finding great public consensus and vast applications, but traditional combustion still offers an easy and relatively low-cost source of energy, in a global market constituted by different socio-economic and geopolitical contexts. Old and new challenges in the combustion field need to be addressed by the scientific community in order to lay the base for the design of next-generation technologies.

Overall, combustion can be described as an exothermic, oxidoreductive, self-sustaining process, in either multiphase or monophasic conditions, between a fuel (solid, liquid, or gaseous) and an oxidizer (usually atmospheric oxygen), resulting in the development of combustion products, thermal energy, and electromagnetic radiation. Starting simplistically from the given definition, it is possible to understand its broad spectrum of applications. In fact, since ancient times, humankind has lit fires to protect themselves, illuminate, heat, cook, and produce utensils and goods of various kinds. Over the centuries, the significant epochal change occurred in the 1700s with the first industrial revolution through the introduction of steam engines and the creation of industrial processes, up to the present day, with the fourth industrial revolution and the development and evolution of modern thermal engines in aerospace, aviation, terrestrial, and maritime fields, and, in the

industrial domain, new furnaces and combustion system technologies, contextualized in an innovative and AI integrated development for better efficiency and control of combustion processes. So, it is evident how, over the years, combustion has played a crucial role in energy supply, and it has been a vital component of the global energy landscape. As illustrated in **Figure 1.1.1** [1], the combination of oil, gas, and coal has constituted a significant portion of energy resource consumption from 1965 to 2023, including the latest generation of biofuels. Primary energy refers to the energy contained in natural resources before conversion, such as raw coal, oil, or uranium, including the energy used by end consumers (for electricity, transport, and heating) and the losses that occur during the transformation into usable forms. In this context, the substitution method is applied to measure non-fossil energy, considering the inefficiencies typical of fossil fuel power generation: it is possible to estimate the amount of fossil fuel required to produce the same amount of electricity, applying a standard efficiency factor (typically around 0.4). Following this method, it is possible to conduct a more consistent comparison between fossil and non-fossil energy sources, including nuclear energy. The category “other renewables” includes geothermal, biomass (excluding traditional biomass, e.g., wood fuel or agricultural by-products), waste, wave, and tidal. Even though there has been a significant increase in the use of renewable energy sources over the years, the continuous dominance of fossil fuels can mostly be due to their widespread use and availability, and their high calorific value. Combustion has historically contributed, and continues to contribute, to the huge worldwide demand for the energy supply.

Considering that fossil fuels are a significant source of energy on a large scale, their use has been tailored in accordance with international protocols and legislations, albeit unevenly at the geopolitical level. In particular, such legislation provides limitations to the primary emissions of pollutants that are hazardous to humans and the environment, especially in relation to the current climate change caused by the greenhouse effect. These include NO_x, CO_x, VOCs, SO_x, soot, and atmospheric particulate matter in general. An overview of the data from [2] reveals the origin of pollutant emissions from traditional combustion technologies associated with different human activities and energy sources (**Figures 1.1.2**), including a detailed analysis of the emissions by regions (**Figures 1.1.3**).

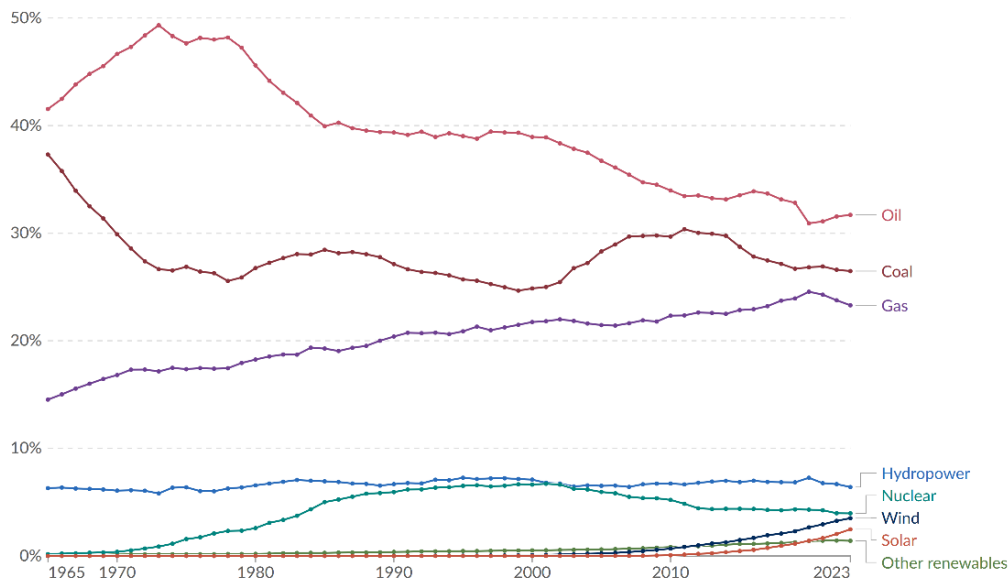


Figure 1.1.1 – World share of energy consumption by source, measured as a percentage of primary energy, using the substitution method. Energy Institute - Statistical Review of World Energy (2024). OurWorldinData.org/energy | CC BY [1].

This overview reflects the information contained in various inventories available in the literature, as the one from the Community Emissions Data System (CEDS) [3], which has been updated in [4] to create a new global emission database known as CEDS_{GBD-MAPS}. This inventory encompasses emissions of seven key atmospheric pollutants: NO_x, CO, SO₂, NH₃, non-methane volatile organic compounds (NMVOCs), black carbon (BC), and organic carbon (OC) for the period from 1970 to 2017. It presents annual country-specific total emissions categorized by 11 anthropogenic sectors—namely agriculture, energy generation, industrial processes, on-road and non-road transportation, separate residential, commercial, and other sectors (RCO), waste management, solvent use, and international shipping—as well as four fuel categories: total coal, solid biofuel, the combined emissions from liquid-fuel and natural-gas combustion, and residual process-level emissions.

The global trends show an alarming increase in the emissions of NO_x, non-methane volatile organic compounds, NH₃, black carbon, and organic carbon, mainly driven by the developing countries. The main sectors contributing to carbon pollutant emissions are industry, residential areas, and transportation. In terms of emissions, the sources cited

frequently quantify carbon pollutants in terms of black carbon (BC), which can be defined as light-absorbing refractory carbonaceous matter. Generally, the major component of black carbon is constituted by soot particles from the incomplete fuel combustion.

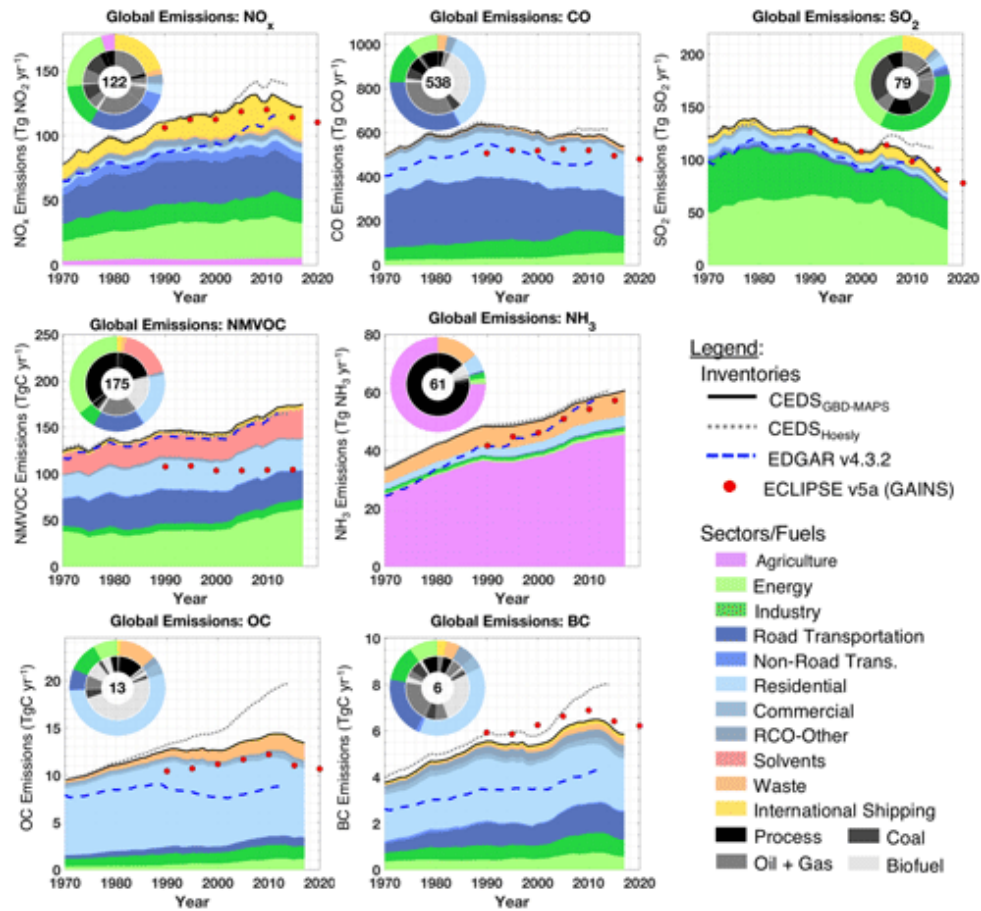


Figure 1.1.2 – Time series of global annual emissions of NO_x (as NO₂), CO, SO₂, NMVOCs, NH₃, BC, and OC for all sectors and fuel types [2].

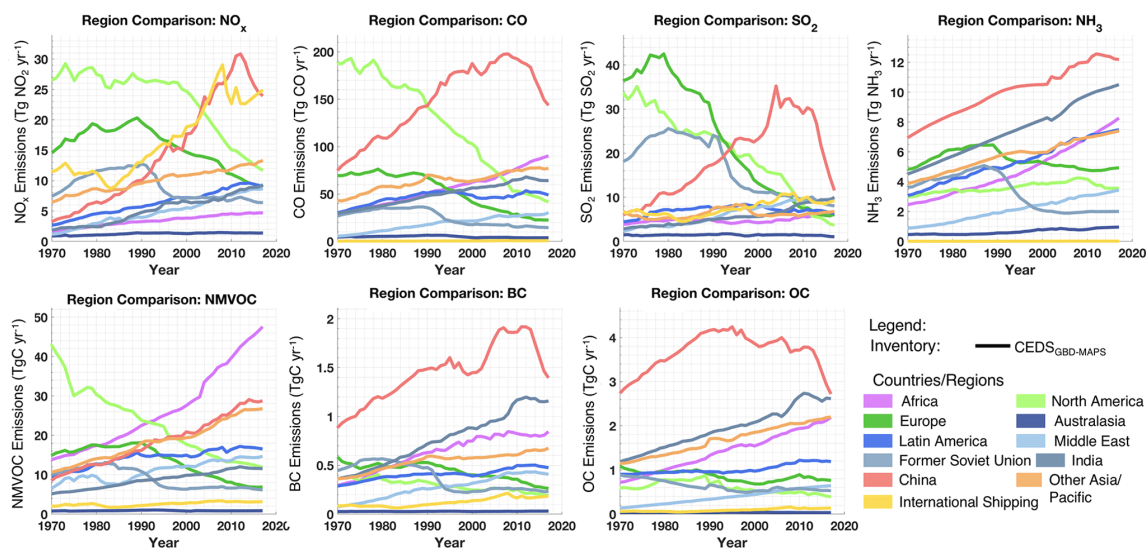


Figure 1.1.3 – Time series of global annual emissions of NO_x (as NO₂), CO, SO₂, NMVOCs, NH₃, BC, and OC for all sectors and fuel types [2].

1.2 General overview of soot carbon nanoparticles.

Before proceeding to the description of the chemistry involved in the process of carbon nanoparticle formation, it is appropriate to make some terminological distinctions. In the available literature, soot is generally referred to as a carbonaceous condensed-phase particulate formed from molecular gas-phase precursors. It is predominantly composed of elemental carbon, but it also contains a significant amount of hydrogen. It exists in condensed phase, as a solid or liquid [5]. In the combustion research, the investigations on soot chemistry encompass a broad range of carbon structures as a function of the fuel, the thermodynamic conditions, the residence time, and varying case-selective formation mechanisms.

On the other hand, as already mentioned, in the context of atmospheric emissions, the definition of Black Carbon (BC) is often used to describe light-absorbing carbon aerosols that are now recognized as key climate-altering agents across a range of emission sources, e.g., fossil fuel combustion. Another component of the black carbon is the so-called "Brown Carbon" (BrC), which derives from the combustion of biofuels and biomass [6,7]. In fact, since the early 2000s, this kind of differentiation in terminology has been of

considerable importance with respect to the different properties (e.g., composition, morphology, etc.) and the consequent environmental and human effects.

In the field of technology, the definition of Carbon Black (CB) is also widely recognized. As outlined in [8], carbon black is produced under controlled conditions mainly for use in the rubber, painting, and printing industries. In contrast, soot is an undesirable byproduct from burning carbon-based materials to generate energy, heat, or for waste disposal. The terms carbon black and soot are often used interchangeably; however, carbon black is physically and chemically different from soot, despite the two often sharing similar formation chemistry. Over 97% of carbon black is made up of elemental carbon arranged as small particles. The large-scale, flame-based synthesis of carbon black constitutes a material engineering challenge, with the goal of optimizing combustion technologies to control the properties of carbon nanoparticles (crystallinity, particle size, aggregation, etc). In this work, the study of "soot" is addressed in a general context, deliberately avoiding the unnecessary complexity of specific terminological differences related to size, morphology, composition, or quality. In addition, the model activities will focus on the simplified case of soot particles fundamentally composed of primary particles and pure carbon aggregates, explicitly excluding advanced aging, oxidation phases, and interactions with other pollutants. The objective is to develop and validate a robust model capable of accurately predicting the formation of soot nanoparticles during the initial stages of pyrolytic processes (nucleation, growth, coalescence, and aggregation). Modeling is designed to predict fundamental primary structures that can be effectively extended to the formation of more complex, mature carbon structures.

1.3 Soot as an anthropological hazard.

Soot is the carbonaceous core and main constituent of Atmospheric Particulate Matter (PM) from combustion emissions. Indeed, PMs include other components such as dust, ashes, sand, organic and metal compounds, sulfides, and other substances present as solid particles and liquid droplets in the atmosphere.

Particulate matter is classified based on its average size distribution [9]. The three major classes are $PM_{0.1}$ (particles with a diameter smaller than $0.1\ \mu m$), $PM_{1.0}$ (particles smaller than $1.0\ \mu m$), $PM_{2.5}$ (particles smaller than $2.5\ \mu m$), and PM_{10} (particles smaller than $10\ \mu m$). Generally, the fractions corresponding to such classification are identified as ultrafine particles ($\leq PM_{0.1}$), submicron particles ($\leq PM_1$), fine particles ($\leq PM_{2.5}$), coarse particles ($> PM_{2.5}$, $< PM_{10}$), and large particles ($\geq PM_{10}$). This denomination is generally employed in the legislations and in the related tools, such as the integrated GAINS (Greenhouse gas – Air pollution Interactions and Synergies) model [10], which has been developed to support key negotiations on air pollution control agreements in Europe based on the estimated emissions of air pollutants and greenhouse gases (GHGs; i.e., carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the three F gases), their dispersion in the atmosphere, and their consequences for the environment and human health.

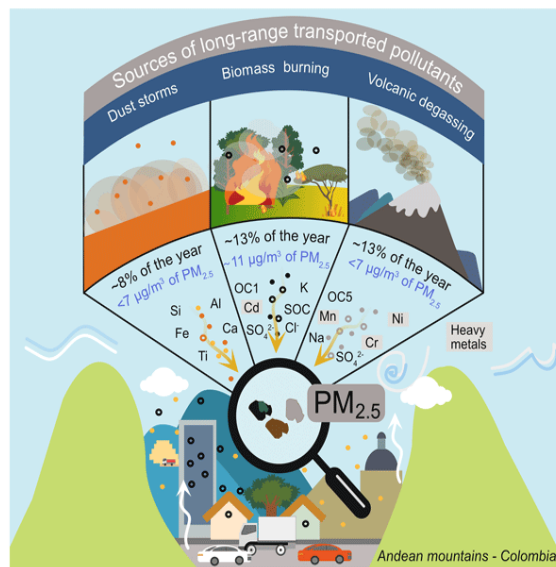


Figure 1.3.1 – Long-range transport of natural air pollutants increases the concentration of hazardous components of $PM_{2.5}$ [11].

Although fine-matter particulate matter is produced from anthropogenic sources, such as emissions, or accidental fires, pool fires, explosions, or even natural resource extraction activities, the contribution that also comes from natural events, such as volcanic eruptions or wildfires, should not be underestimated. For example, the comparative study presented

in **Figure 1.3.1** [11] shows how the emissions of air pollutants from biomass burning in South America affect the formation of small PMs to the greatest extent, but the effects of long-range transported pollutants from dust storms or volcanic degassing are clearly not negligible, if not predominant, when combined. The anthropological sources across different geographic areas are reported in **Figure 1.3.2**, for both PM_{2.5}, and PM₁₀ emissions [12], including from road transportation, industry, and domestic heating.

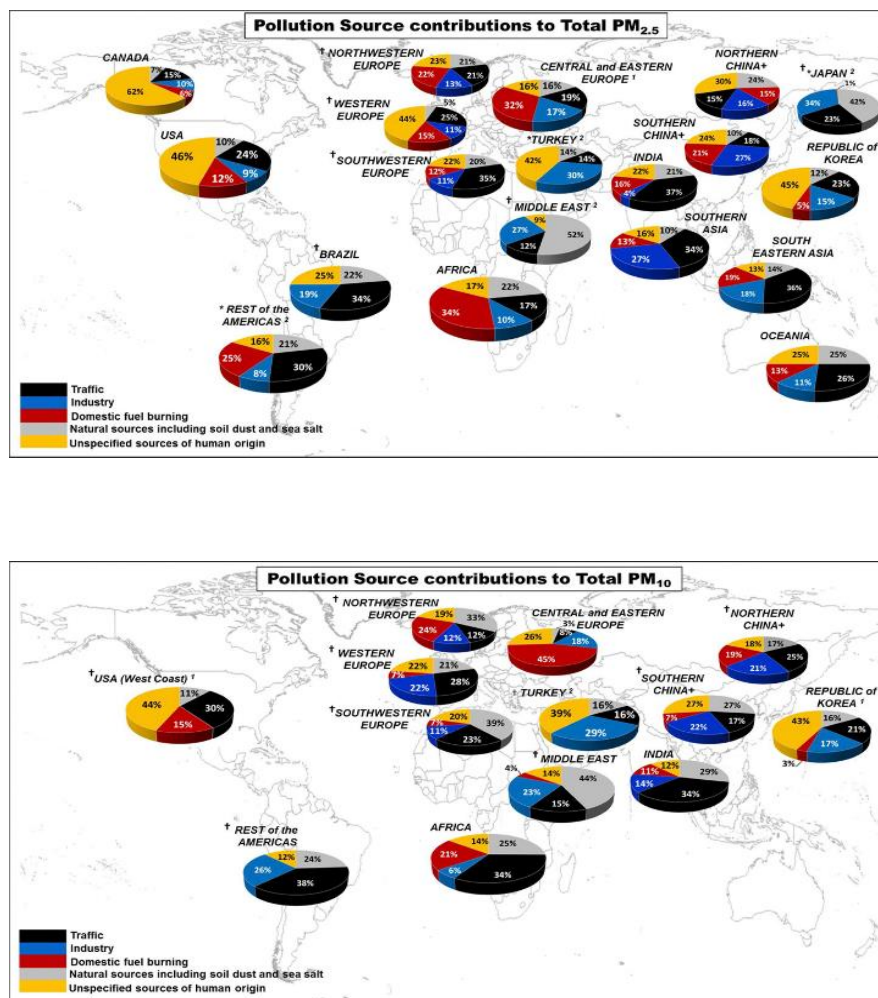


Figure 1.3.2 – Population-weighted averages for relative source contributions to total PM₁₀ in urban sites [12].

Exposure to PM in the atmosphere is associated with significant human health hazards, and the consequences depend strongly on particle size. The smallest ultrafine particles are the most dangerous, as they can enter the bloodstream through the respiratory system, bind to red blood cells, and thus prevent the normal exchange of oxygen, and also carry several highly harmful condensed substances, including PAHs and heavy metals.

As reported by the EPA (United States Environmental Protection Agency) [13] and as confirmed by the World Health Organization [14], exposure to such particles can affect both the lungs and the heart's functioning. Numerous scientific studies have linked particle pollution exposure to a variety of problems, including premature death in people with heart or lung disease, nonfatal heart attacks, irregular heartbeat, aggravated asthma, decreased lung function, increased respiratory symptoms, such as irritation of the airways, coughing or difficulty breathing, and cancer [13,15–18].

Globally, populations living in socio-economically and geopolitically degrading environments are more susceptible to the adverse effects of particulate pollution. In many communities, stringent laws or policies to manage and mitigate pollution are nonexistent, which allows harmful practices to persist unchecked. Additionally, the general population may not fully understand the long-term consequences of environmental degradation on health and ecosystems, which can lead to complacency and inaction. This combination of inadequate regulatory frameworks governing environmental pollution emissions and limited awareness about their impacts creates a cycle that perpetuates environmental harm and hinders efforts toward sustainable practices. According to recent WHO data [14], the largest concentrations of PM_{2.5} and PM₁₀, as shown in **Figures 1.3.3** and **1.3.4**, respectively, are concentrated unevenly, but mainly in developing countries, including China, the Middle East, and India. This reflects the associated risks to the population and the environment in these regions.

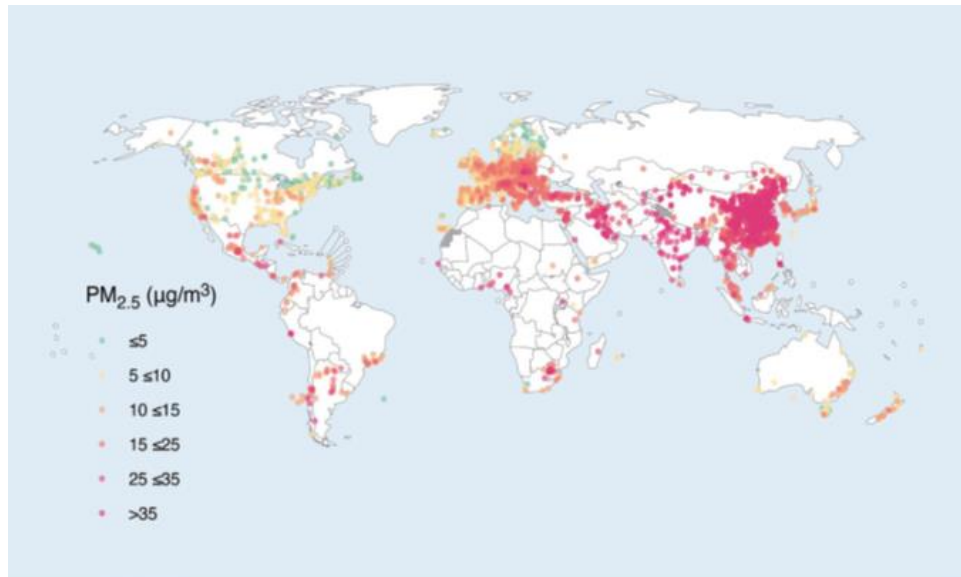


Figure 1.3.3 – Global concentration per area of PM_{2.5} in 2022 [14].

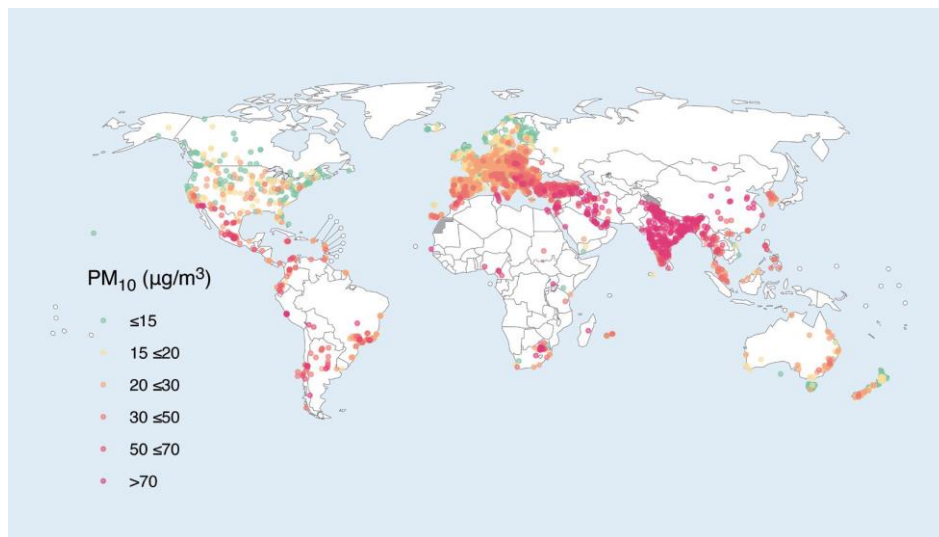


Figure 1.3.4 – Global concentration per area of PM₁₀ in 2022 [14].

1.4 Soot as environmental risk.

Soot emissions pose a serious threat to the environment. In fact, it is one of the main contributors to climate change and naturally absorbs light because of its black color.

From an environmental perspective, therefore, the effects of particulate matter combined with other pollutants influence atmospheric dynamics and sunlight filtering, thereby impacting land and water levels through climate change, as reported by [19] and shown in **Figure 1.4.1**. Widely established effects are: making lakes and streams acidic, changing the nutrient balance in coastal waters and large river basins, depleting the nutrients in soil, damaging sensitive forests and farm crops, affecting the diversity of ecosystems, and contributing to acid rain effects [13], and deposition on ice, favoring its melting [20,21]. Concerning direct light absorption by PMs suspended in the atmosphere, this is somewhat controversial. Indeed, many studies proposed that black carbon is one of the main contributors to global warming [19], while others suggest that soot is characterized by a warming potential that varies significantly during its atmospheric lifetime [22].

In the latter study, the authors show how the fast aging of soot particles, driven by their complex fractal morphology, promotes rapid capillary condensation of secondary vapors derived from VOC oxidation [23,24]. This aging process can substantially modify the particles' optical properties, sometimes enhancing light scattering and thereby reducing their net warming potential [25–27].

Of course, the modification of the particle properties through aging also affects other aspects related to their efficiency as nuclei for cloud droplets and possibly ice nuclei, their atmospheric lifetime as well as dispersion and vertical distribution, and effects on human health [19].

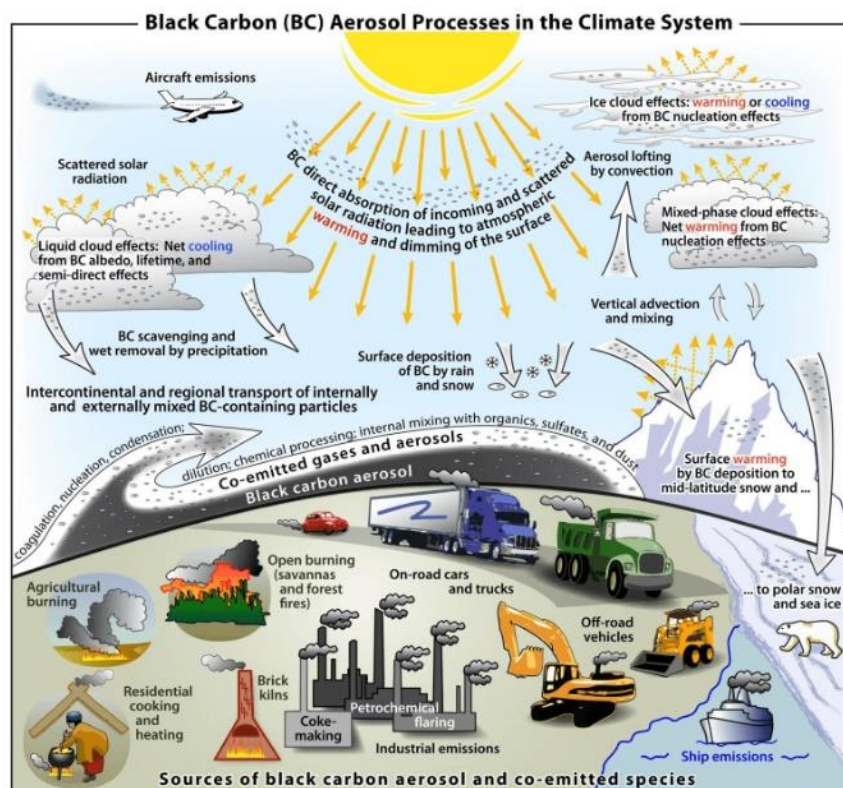


Figure 1.4.1 – Schematic overview of the primary black-carbon emission sources and the processes that control the distribution of black carbon in the atmosphere and determine its role in the climate system [19].

1.5 Carbonaceous nanoparticles, an innovative technology for novel materials.

Carbon nanoparticles (CNP) are not only harmful to the environment and humans, but when synthesized or properly used, they can have beneficial applications in the production of materials for everyday life or advanced specialty materials. As reported by [28], a large family of carbonaceous nanoparticles can be experimentally obtained, as illustrated in **Figure 1.5.1** (adapted from [11]). This figure depicts crystalline forms of carbon, such as diamond and graphite, as well as nanoforms like fullerene and carbon nanotubes (CNTs). Additionally, various carbon forms exhibit an amorphous structure, such as cokes, carbon black, and charcoal. In particular, amorphous carbon nanomaterials, e.g., carbon black, are produced in furnaces through pyrolytic reactions of selected fuels (often natural gas). The chemistry of carbon black formation is then very similar to that of soot in combustion devices. Carbon black is widely used in everyday products, for example, as a pigment or

reinforcement in vehicle tires, enhancing properties such as viscosity, strength, and conductivity, as well as facilitating the vulcanization process of natural rubber. Carbon particles such as nanotubes and graphene can provide polymer matrices with multifunctional properties, making them suitable for advanced applications in aerospace, electronics, and automotive industries. Recycled soot, after proper heat treatment, can be reused as a conductive material in lithium-ion batteries, solar evaporation devices, and as an adsorbent for removing pollutants from air and water. Hydrophilic carbon particles made from soot are also used in inkjet printer ink [29]. **Figure 1.5.2** illustrates some of the many applications of materials engineered with soot nanoparticles.

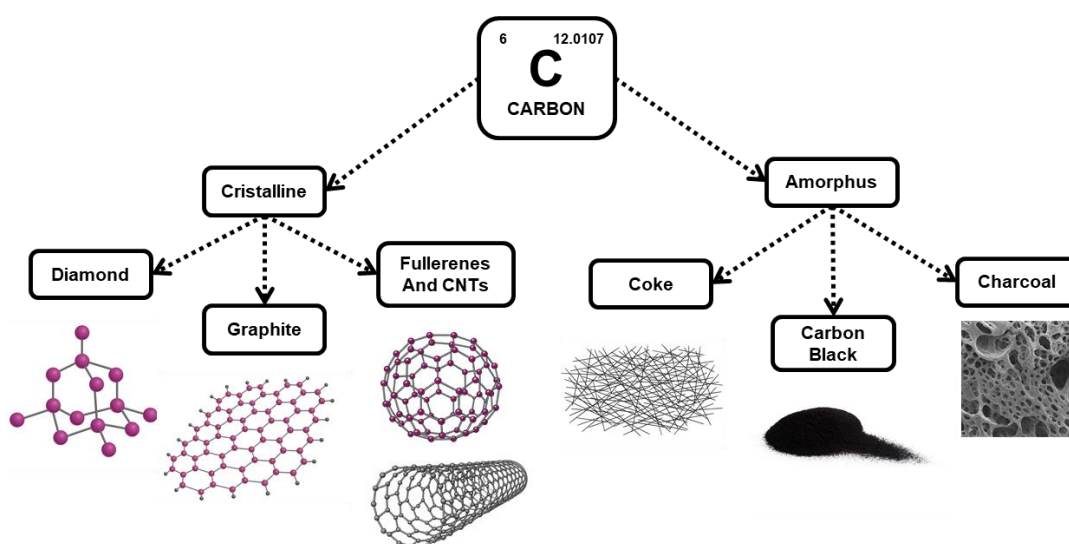


Figure 1.5.1 – Scheme of possible structures in the CNP family adapted from [11].



Figure 1.5.2 – CNP flame-based synthesis applied to novelty materials.

Additionally, beyond the practical use of soot starting from the synthesis of CNPs, other studies suggest that at the quantum level, it is possible to synthesize materials with even more advanced characteristics. Unlike common inorganic materials with known quantum behavior, it is possible to produce the so-called carbon dots, which possess specific features [30–33] such as non-toxicity, stability, biocompatibility, and hydrophobicity, with low-cost synthesis processes. These are very small CPNs, different from regular soot, with unique forms and structures, and they are used in various high-tech applications, including electronics, photonics, biomedical diagnostics and manipulation techniques, nanotechnology, and more, as shown in **Figure 1.5.3** for carbon dots [34] and **Figure 1.5.4** for different types of morphology [32].

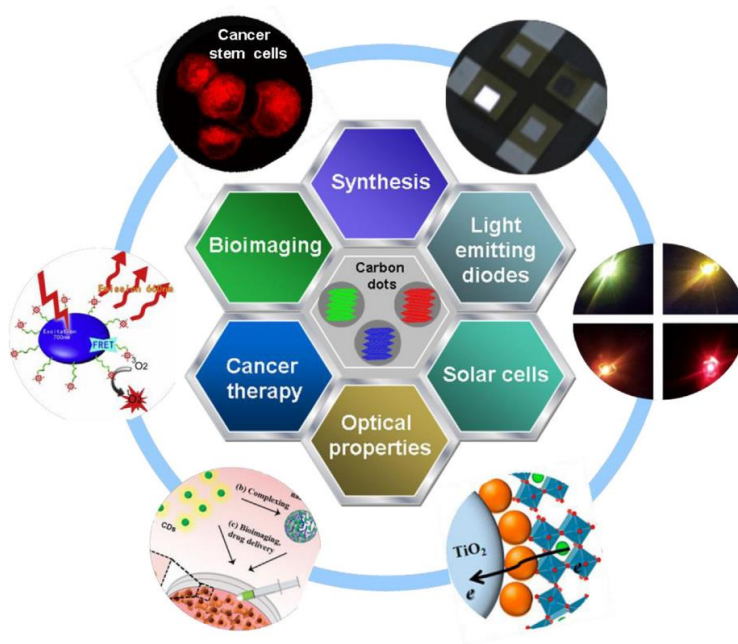


Figure 1.5.3 – CNP flame-based synthesis applied to novelty materials [35].

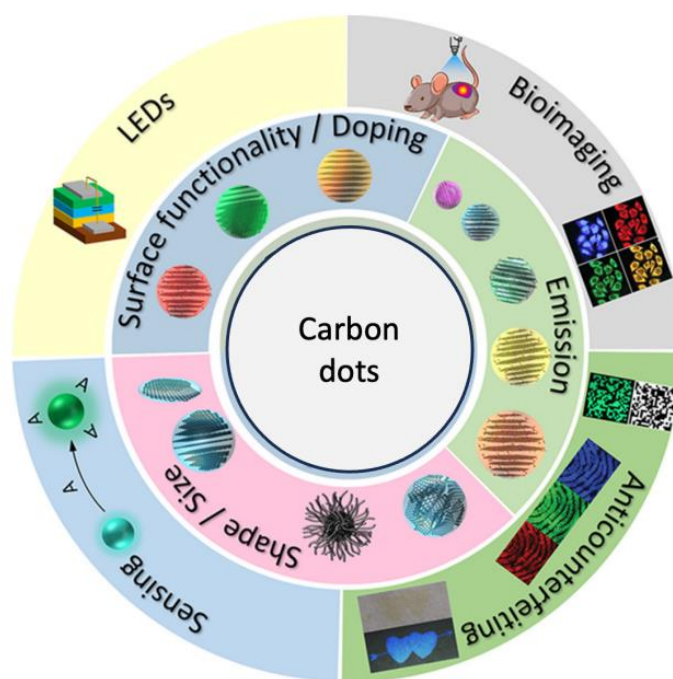


Figure 1.5.4 – CNP flame-based synthesis applied to novelty materials [32].

1.6 Goal and thesis organization.

The aim of this thesis is to develop an advanced kinetics model for soot formation under pyrolytic conditions for both aromatic and aliphatic fuels, implementing the sectional method for the description of the particle chemistry. The model development, realized through a Python framework, is based on an updated gas-phase mechanism from earlier groundbreaking work at ICARE on the chemistry of polycyclic aromatic hydrocarbons (PAHs) in highly diluted conditions. In particular, the major updates concern the chemistry of polyynes and their interaction with the PAH chemistry. This part of the model, previously not developed, has been identified as a significant mechanism for producing soot from aromatic fuels, such as benzene and toluene, as well as from aliphatic compounds, including acetylene and ethylene. In addition, the gas-phase formation of resonantly-stabilized intermediates from the reactions between polyacetylene molecules and radicals has been implemented for the first time as a preliminary step for the formation of aromatic soot precursors in the case of acetylene pyrolysis. The validation of this enhanced model was conducted using shock tube experiments on time history soot volume fraction measurements, including kinetic properties such as soot induction delay times and growth rates. The model is set to qualitatively and quantitatively describe soot production from common aromatic and aliphatic fuels, including blends. The comprehensive validation against fuels with very different structures is essential to provide a solid foundation for the new implementations and the subsequent kinetic analyses. The model constitutes an advanced fundamental tool to improve our understanding of the complex processes involved in soot formation, with the potential to support the development of next-generation clean combustion technologies and optimized syntheses of advanced carbon nanomaterials.

The thesis starts with Section 2, containing a brief literature overview on the state of the art concerning the kinetics of particle precursors. The shock tube technique used for soot measurements is then presented in Section 3, followed by details on the Soot Mechanism Automated Generator (SMAuG) developed as part of this thesis (Section 4). The optimized model, including the updates on the gas-phase section and the particle chemistry, is then described in Section 5, while Section 6 contains the simulation results for the different fuels

considered, as well as kinetic analyses for selected cases. The manuscript will be concluded with a summary of the work performed as well as the main perspectives.

2. State of the art

In this chapter, the thermodynamics and chemistry underlying the formation of soot carbonaceous nanoparticles are examined. The soot formation process is typically characterized by four major reactive steps occurring under pyrolytic conditions, as illustrated in **Figure 2.1**: nucleation, surface growth by chemical reactions, dehydrogenation, and coalescence/aggregation. A crucial aspect of understanding this process is addressing the knowledge gap regarding the formation of the initial soot core, which is significantly influenced by gas-phase precursors, particularly large polycyclic aromatic hydrocarbons (PAHs). Consequently, accurate modeling of PAH formation mechanisms serves as a key basic foundation for modeling the overall process of soot formation. Thus, the latest advancements in understanding the kinetic pathways leading to the creation of typical gas-phase precursors under purely pyrolytic conditions are presented below.

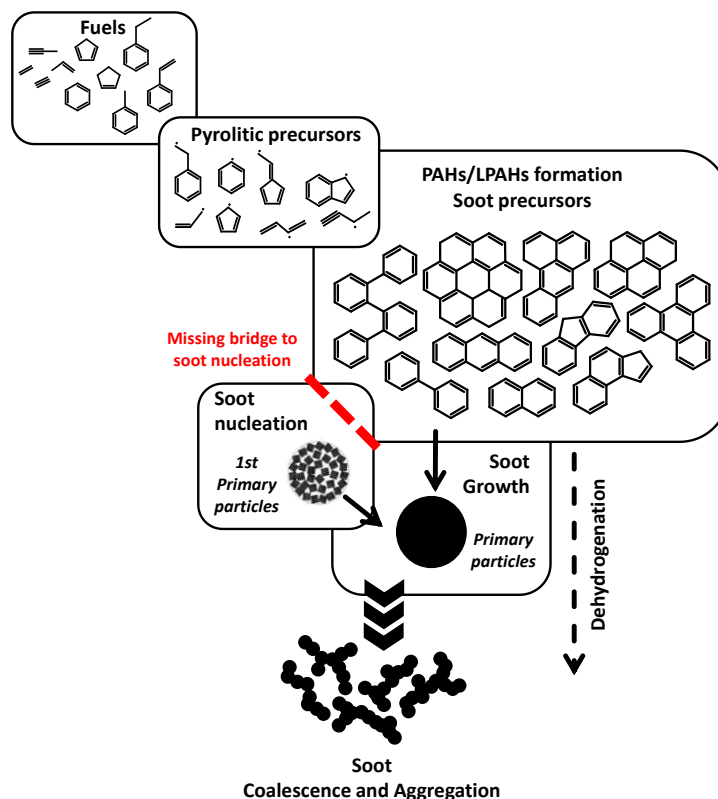


Figure 2.1 – Scheme of the main steps of soot formation process from fuels under pyrolytic conditions.

The current knowledge on soot formation is comprehensively summarized in several established review papers [5,36–41]. These papers highlight the key aspects of the phenomena as they are nowadays understood, even though two key steps still remain unclear due to limitations in experimental and theoretical capabilities, e.g., the soot initiation process and the mechanisms behind the formation of low molecular weight polycyclic aromatic hydrocarbons to large PAHs (LPAHs), which are crucial building blocks for carbon nanoparticle nucleation. These steps constitute the transition from the gas phase precursors to a liquid-like phase matter and subsequently to primary solid particles, the main constituent of large aggregates.

Generally, the pathways for forming the first aromatic ring, the base for the growth to PAHs and LPAHs, vary depending on whether the initial fuels are aromatic or aliphatic. For aliphatic fuels, the small intermediates from the fuel fragmentation are primarily represented by C₂, C₃, and C₄ species, which can recombine to form the aromatic ring (e.g., through reactions such as C₃H₃ + C₃H₃, or C₄H₅ + C₂H₂) [38,42]. For the case of aromatic fuels, the thermal fragmentation of the fuel leads to aromatic products, such as benzene, the phenyl radical, or the benzyl radical, which can directly react to form PAH compounds [38].

In the complex process of soot formation, a well-known mechanism called HACA (Hydrogen Abstraction Carbon Addition) has been identified as a major contributor to both PAH chemistry and particle inception and surface growth. Initially suggested in [43] and later defined and depicted in [44], HACA has been recognized as crucial for soot modeling, supported by other experimental and theoretical studies (e.g., [45–47]). However, several researchers have noted that HACA alone is insufficient to drive the CNP formation process due to its slow nature [44,45], requiring multiple reactive steps, including H-abstraction and acetylene addition, for a significant increase in PAH size.

For this reason, complementary growth mechanisms involving PAH molecules and radicals have been proposed for the quick growth of aromatic rings, based on gas-phase prototypical reactions (active coagulation processes) [38,46]s. On the other hand, at high temperatures, the applicability of PAH-only mechanisms becomes limited, as PAH formation becomes less favorable due to the thermal decomposition and ring-opening

reactions of the single-ring structures, e.g., phenyl or benzyl [37,47]. For example, high-pressure single-pulse shock tube experiments show that the maximum PAH concentrations are reached around 1450-1550 K for most species, with a marked decrease at higher temperatures (e.g. [48–50]). As a consequence, models relying exclusively on PAH chemistry tend to underpredict soot precursor formation at elevated temperatures [46,51–53].

To address this issue, attempts have been made to propose faster reactive pathways, including radical-radical and radical-molecule interactions, as proposed by [54] and further developed in subsequent studies, e.g., [38,42,55,56]. Other theories based on ion-radical mechanisms [57,58] have now been rejected by the current common understanding. The main PAH growth pathways, including the HACA route, will be presented in more detail below.

In the exploration of pathways responsible for the formation of the first soot particles from both aromatic and aliphatic fuels, researchers have also identified those leading to the formation of polyacetylenic species, commonly referred to as polyynes. The contribution of polyynes to soot formation was first proposed in pioneering works such as [38,59]. Given that polyacetylenes derive from aliphatic fuels, particularly through the acetylene pathway, subsequent studies have highlighted their importance for aromatic fuels as well, as investigated by [60] and further supported by [61–63] in their studies on incipient soot particles. According to [59], the current descriptions of polyynes-based processes indicate that these compounds serve as key components that promote rapid polymerization, thereby enhancing soot formation. The thermal stability of polyacetylenes compensates for the thermal fragmentation of PAH precursors at high-temperature conditions. Indeed, the role of polyynes is complementary to the main PAH mechanisms involved in soot formation for both aromatic and aliphatic fuels, acting as an enhancing factor due to the corresponding rapid kinetics and abundance of acetylenic species. Both the PAH and the polyynes mechanisms may contribute to different extents depending on specific thermodynamic conditions and fuel formulations. For instance, the thermal decomposition of aromatic fuels generates small $C_{2n}H_2$ intermediates that support PAH and particle growth, while polyynes precursors recombine to form complex PAH structures, which serve as building blocks for

soot particle inception. Investigations on different fuels and intermediates under pyrolytic conditions have proven valuable for simplifying the complex oxidation chemistry and often decoupling the various mechanisms involved.

2.1 Thermodynamics of soot carbon nanoparticle formation.

The formation of soot carbon nanoparticles takes place from the gas-phase formation of PAH precursors. Generally, forming the first aromatic ring is considered one of the most critical steps in the process. Still, it is not the only bottleneck in the inception of the first soot particle. Several limiting or alternative kinetic steps are interconnected, making the understanding of the complex process difficult. On the other hand, certain trends and general behaviors can be explained based on pure thermodynamic considerations [64].

Figure 2.1.1 illustrates the overall implications of the thermodynamic process of solid carbon C(s) formation in relation to soot formation, as proposed by [65]. When considering the pyrolysis of C₃H₈ at 1600 K, the initial process can be divided into two phases: acetylene formation and the formation of aromatic rings. Acetylene formation is the initial reactive step and exhibits a large endothermic nature, with a significant ΔG° decrease due to the negative entropy change. In the second phase, which involves the formation of the benzene aromatic ring, the process becomes exothermic, with a positive entropic change due to the ring formation and the dehydrogenation (loss of H₂). The change in Gibbs free energy is still negative. This dehydrogenation process continues throughout, culminating in the formation of C(s), while still exhibiting a steady decrease in Gibbs free energy. According to this scheme, considering the formation of PAHs, LPAHs from benzene, up to the formation of graphitic carbon C(s), the process is regarded as reversible [37].

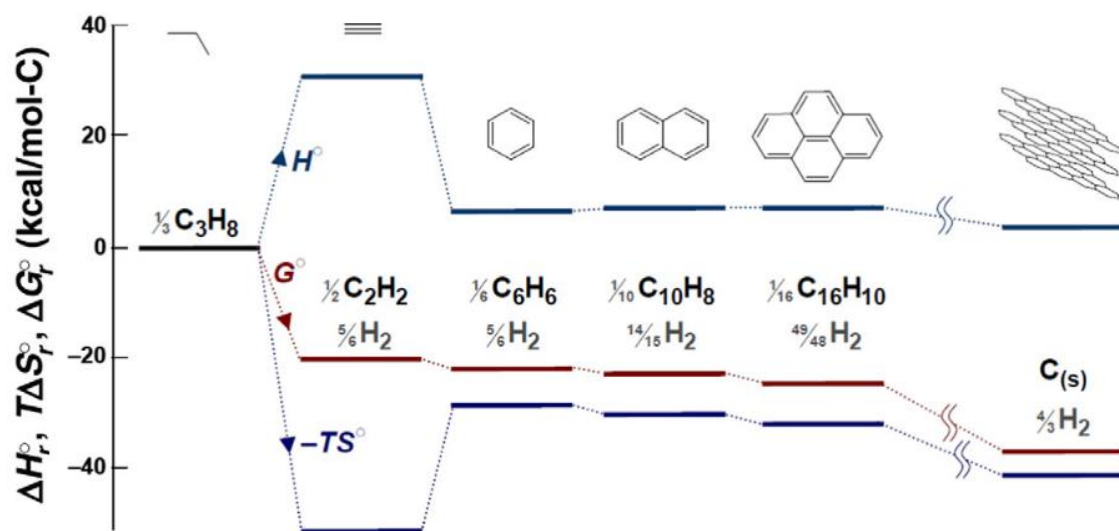


Figure 2.1.1 – Enthalpy and entropy contributions to Gibbs free energy at 1600 K for the formation of solid carbon from propane [65].

Considering another example, **Figure 2.1.2** shows the thermodynamics of soot formation for a fuel that is heavier than C_3H_8 , such as $C_{11}H_{22}$, at temperatures in the flame where the fuel kinetics favor the formation of smaller species, i.e., alkenes [66]. For the first three steps up to the formation of alkynes, the thermal decomposition of the fuel and the subsequent dehydrogenization steps are driven by an increase in entropy as fuels are broken into smaller species. Enthalpy then drives the formation of the first ring (step 4). Further growth of aromatics (steps 5 and 6), which will be discussed later, is also seen to be driven by entropy as hydrogen is released.

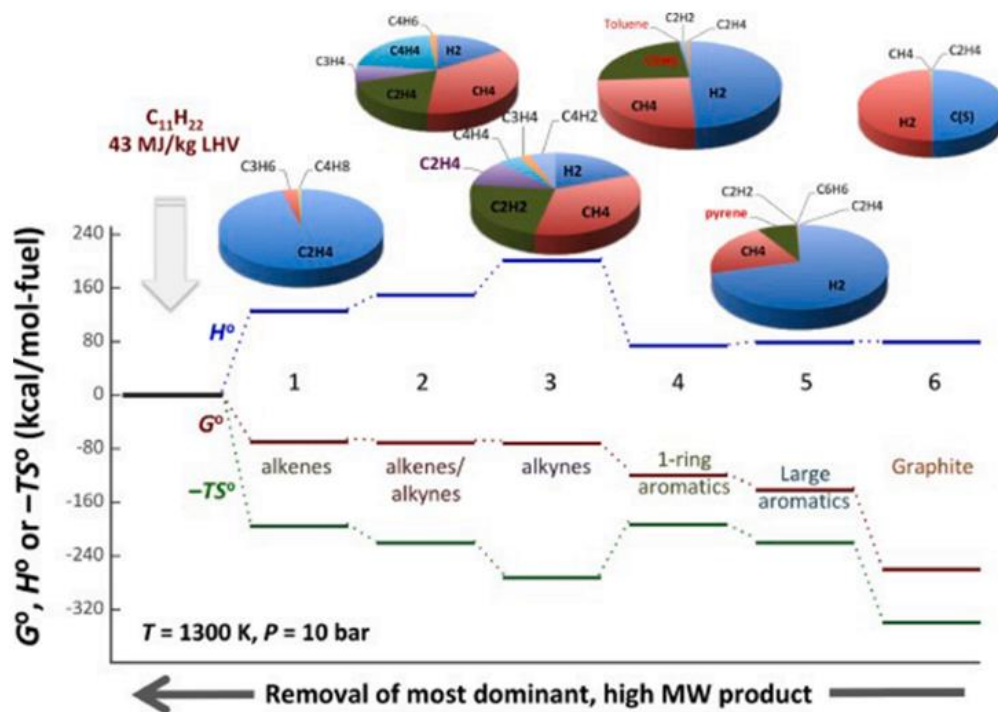


Figure 2.1.2 – Enthalpy and entropy contributions to Gibbs free energy at 1600 K for the formation of solid carbon from propane [66].

2.2 Main pathways to soot precursors.

This section discusses the classical mechanisms that lead to the formation of PAH soot precursors, which are recognized as essential intermediates for CNP inception and growth. The goal is not to provide a comprehensive picture of the entire PAH chemistry as reported in various reviews [38,41,42,67–69], but to introduce the main pathways and general considerations.

2.3.1 HACA mechanism (hydrogen-abstraction-carbon-addition).

The HACA is a repetitive kinetic scheme in which hydrogen abstraction is followed by acetylene addition on the radical site and by ring closure. This mechanism was initially developed by Bockhorn et al. [70] and Frenklach et al. [30], and later refined through

additional research, including Frenklach and Wang [46], Appel et al. [71], and Frenklach [47]. An example of a classical HACA pathway leading to the formation of 2- or 3-ring structures is shown in **Figure 2.3.1.1**. The acetylene addition mechanism exhibits a low energy barrier with high exothermicity. The addition of acetylene to a PAH radical involves an energy barrier of around 2-6 kcal/mol with an exothermicity of around 30-40 kcal/mol (e.g., phenyl + C₂H₂ to phenylacetylene). The subsequent H-abstraction at the ring carbon adjacent to the C₂H moiety involves a relatively high energy barrier, with the possibility of some reversibility of the process. The additional acetylene addition and ring closure is characterized by an energy barrier of around 2-5 kcal/mol and an exothermicity of around 30-50 kcal/mol. The resulting naphthyl radical can react with an H atom to form naphthalene (usually a minor reaction due to the relatively low abundance of H), or react with another acetylene. Such addition occurs in a zigzag structure, thus it can lead to the 5-member ring closure (to acenaphthylene) or lose a H to form a C₂H moiety. The H-loss to form C₂H moieties, e.g., phenyl + acetylene to phenylacetylene, is the favored reaction path at high temperatures. At lower temperatures, the intermediate radical (C₆H₅C₂H₂) has a lifetime sufficiently long to allow migration of the radical from the C₂H₂ moiety to the ring (C₆H₄C₂H₃), as proposed by Moriarty et al. [72] in the modeling of acenaphthylene formation from styrene. C₆H₄C₂H₃ can react with acetylene to form naphthalene. The HACA route can then proceed with additional subsequent abstraction/addition steps, with the products defined based on the presented scheme, function of the reaction site on the PAH molecule.

Despite its undeniable role in high-temperature chemistry, the HACA mechanism alone has been proven to be insufficient to model the aromatic formation process, in particular due to the numerous steps required for the growth of PAHs and particles. Additional competing mechanisms will be presented for further discussion.

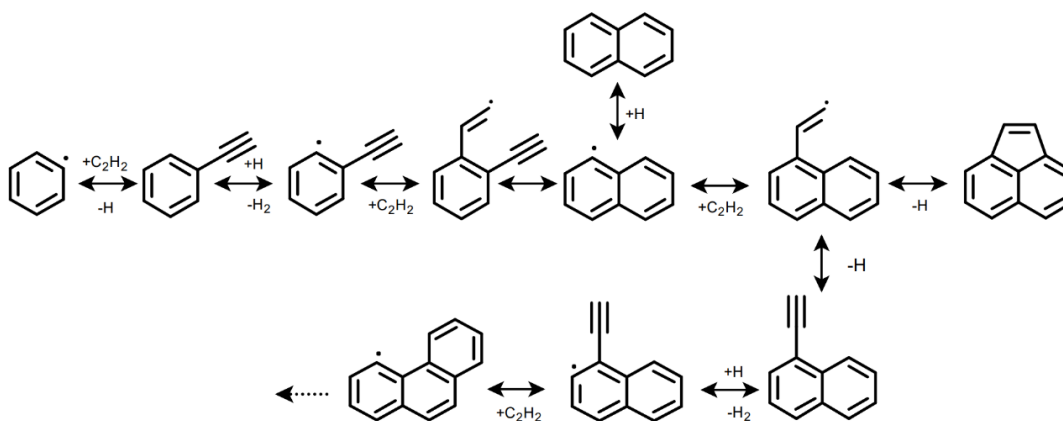


Figure 2.3.1.1 – Formation of naphthyl, naphthalene, and acenaphthylene by the HACA mechanism [72].

2.3.2 HAVA mechanism (Hydrogen Abstraction and Vinyl/Vinylacetylene Addition).

An alternative route to the HACA route, recently proposed by Shukla and Koshi [73], is the Hydrogen Abstraction and Vinyl Addition (HAVA) mechanism. This pathway was initially investigated for C_2H_4 pyrolysis carried out in a quartz tube and combined with the time-of-flight mass spectrometer (TOFMS) technique. The subsequent addition of vinyl radicals has been proposed as the main PAH growth mechanism, as depicted in **Figure 2.3.2.1**, with measurements up to fluoranthene. On the other hand, the concentrations of vinyl radicals are very low, especially at flame conditions where the fragmentation to acetylene + H dominates; thus, the mechanism is not very efficient in practical applications. A different but related pathway involves reactions with vinylacetylene with aromatic and PAH radicals [43]. On the other hand, at high temperature conditions, the ring-formation path is not favored compared to the addition/fragmentation, e.g., $C_6H_5 + C_4H_4 = C_6H_5C_4H_3 + H$ [74] .

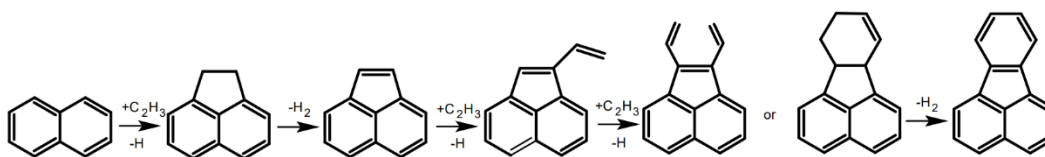


Figure 2.3.2.1 – PAH growth process via vinyl radical addition from ethylene [73].

2.3.3 Phenyl Addition.

The mechanism of phenyl addition and cyclization (PAC) is another key pathway for PAH formation. This pathway, previously proposed by Howard [75] and Richter [38] as the addition of an aromatic radical to an aromatic molecule, has recently been reconsidered by Shukla [76] and Shukla and Koshi [77]. They studied benzene under pyrolytic conditions to examine the role of the phenyl radical, with or without acetylene addition, in a flow reactor using TOFMS techniques. **Figure 2.3.3.1** illustrates examples of PAH structure formation. PAC is an efficient mechanism, offering a different approach from HACA and serving as a complementary path for fast growth. Indeed, one single addition can result in the direct growth of the number of rings, e.g., phenanthrene (3 rings) + phenyl (1 ring) to a 5-ring PAH. The addition site will influence the kind of structure that results from the specific reaction and its symmetry.

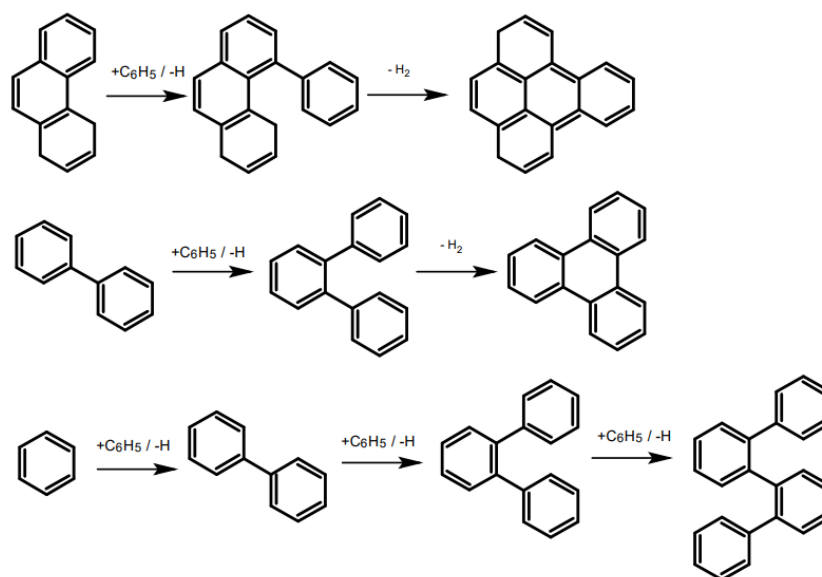


Figure 2.3.3.1 – Examples of phenyl addition-cyclization [78]

2.3.4 Diradical Cycloaddition Fragmentation (CAF).

The Diradical Cycloaddition Fragmentation (CAF) mechanism was first proposed by Comandini and Brezinsky [79] and Shukla et al. [80], who proposed the importance of the 1,4-cycloaddition of o-benzyne to benzene, followed by fragmentation, leading to the

formation of naphthalene and acetylene. Comandini et al. [81] demonstrated how, in the case of phenyl radical pyrolysis, naphthalene is mainly formed from the CAF mechanism. Later, Comandini and Brezinsky [82] and Comandini et al. [83] extended this concept to theoretical investigations on the radical/ π -bond addition reaction involving o-benzyne + C5 cyclic hydrocarbons and PAH molecules, respectively. This conceptualization is schematized in **Figure 2.3.4.1**, starting from the prototypal $C_6H_6 + C_6H_4$ reaction (a) to larger reactions (b and c), where anthracene and benz[a]anthracene are produced, respectively.

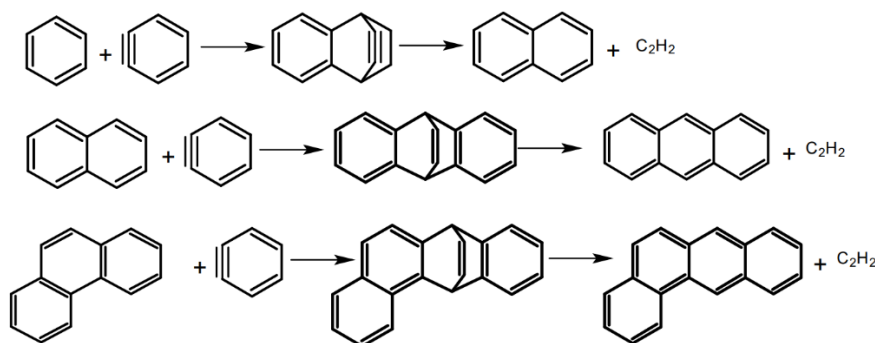


Figure 2.3.4.1 – Examples of CAF [79,82,83].

2.3.5 Methyl Addition/ Cyclization (MAC).

Wellman et al. [84] proposed that the addition of a methyl radical is a contributing mechanism to the growth of PAHs and soot formation. This is because the methyl group is produced in significant quantities along with acetylene during the pyrolysis and/or oxidation of most aliphatic fuels and alkyl aromatic hydrocarbons. Subsequently, this mechanism was further investigated by Shukla et al. [85], who analyzed products from the pyrolysis of toluene and toluene/acetone mixtures. An illustration of how this mechanism proceeds is provided in **Figure 2.3.5.1**. The process begins with an aromatic molecule, followed by the addition of a methyl group, then further methyl additions and the loss of an H atom, until cyclization occurs through a 5-ring carbon structure. The final step involves the loss of H_2 and isomerization through ring expansion, which results in the

formation of an additional aromatic ring. This process of ring expansion, facilitated by methyl addition, has also been reported by other authors such as McEnally et al. [67, 68] and Lifshitz et al. [88], and studied theoretically by several authors, e.g., [89–91]. Although the MAC mechanism contributes to the formation of aromatic structures and soot, it does not appear to be as efficient as HACA or PAC. This is mainly due to the lower mass of CH_3 compared to C_2H_2 or C_6H_5 , and the need for many addition reactions for the formation of an extra aromatic ring.

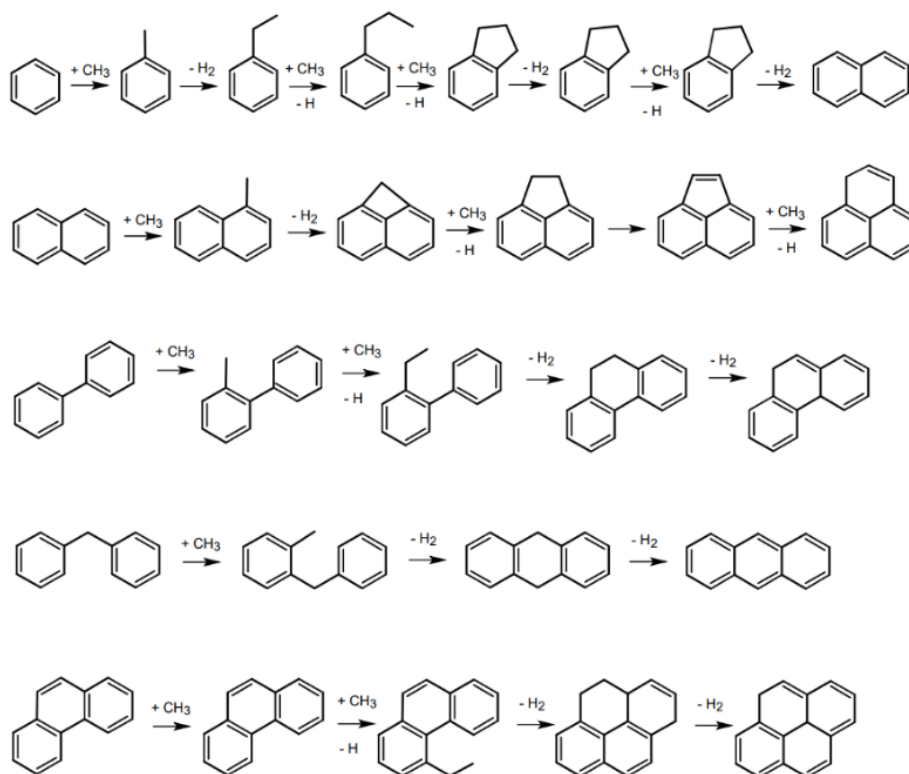


Figure 2.3.5.1 – Formation of aromatics by the MAC mechanism.

2.3.6 Role of resonantly stabilized radicals.

Resonant stable radicals are chemical intermediates found in abundance under combustion conditions because of their high stability; thus, they usually play a key role in PAH formation pathways. Among these species, the most common are C_3H_3 , C_3H_5 , C_5H_5 (cyclopentadienyl), $\text{C}_6\text{H}_5\text{CH}_2$ (benzyl), and C_9H_7 (indenyl). Several studies have been

carried out over the years to verify their contribution to PAH formation chemistry. Indeed, Castaldi et al [92] have identified C_5H_5 as playing a key role in the formation of naphthalene. Lu and Mulholland [93] have found that recombination of the indenyl radical is involved in the formation of $C_{18}H_{12}$ isomers such as chrysene, benzophenanthrene, and benzoanthracene. Colket et al. [75] and Marinov et al. [76], have identified an alternative pathway for naphthalene formation via the addition of the propargyl radical to styrene ($C_3H_3 + C_6H_5CH_2$). Recently, a study by K.O. Johansson et al. [94] demonstrated that RSRs are not only implicated in the formation of PAHs but also provide an effective pathway for high-temperature soot formation through a rapid molecular clustering process. RSR species were detected by an ultraviolet aerosol mass spectrometer (VUV-AMS) from particles extracted from ethylene-oxygen flames, as shown in **Figure 2.3.6.1**. Kinetic analyses indicate that RSRs react with other hydrocarbons to form complex covalent bonds, promoting the formation and growth processes of the RSRs themselves through a low-energy barrier for H-abstraction and H_2 loss.

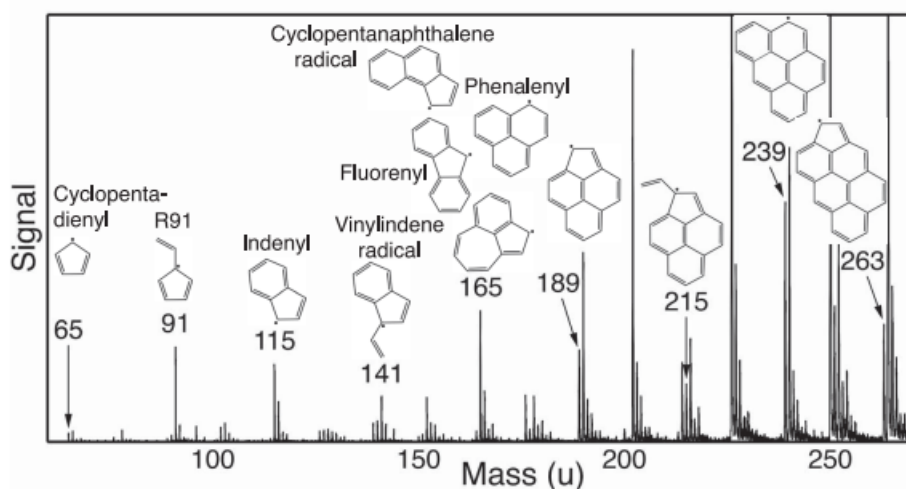


Figure 2.3.6.1 – VUV-AMS spectrum of an atmospheric-pressure laminar premixed ethylene-oxygen flame using a photon energy of 9.4 eV. Masses from species posited to drive the CHRCCR mechanism [93].

2.3.7 Overall mechanisms of PAH formation and growth.

In reality, the various mechanisms presented for PAH formation are complementary and may occur at the same time. The contributions of the various pathways to the formation and growth of aromatic structures depend on the operating conditions, such as temperature

and pressure, or even on the type of fuel and its intrinsic nature. Chemical kinetic models for PAH chemistry need to include such pathways and must be validated against tailored experiments capable of probing the different mechanisms.

2.3 Overview of polyyn chemistry: gas-phase precursors for high-temperature soot formation.

Polyynes, also known as polyacetylenes, linear carbon chains featuring alternating single and triple bonds, represent key transient species in combustion environments. Their unique reactivity and thermodynamic properties make them crucial intermediates in the gas-phase chemistry that precedes soot nucleation at high temperatures.

Polyynes, with the molecular formula $C_{2n}H_2$, and radicals ($C_{2n}H$), originate from acetylene chemistry through decomposition and recombination reactions. Currently, the literature documents several studies under combustion or pyrolysis conditions that confirm the presence of linear polyacetylene chains [95–99], generally up to 12–14 carbon atoms, 18 carbons under specific conditions. Regarding the particle chemistry, polyynes have gained increasing interest due to their implications in soot formation under high-temperature pyrolytic conditions for aliphatic and aromatic fuels. The definition of the alternative polyyn pathways for soot formation has evolved slowly over the course of a century, with a notable qualitative advancement of the fundamental understanding only in the last 40 years, as shown in **Figure 2.3.1**.

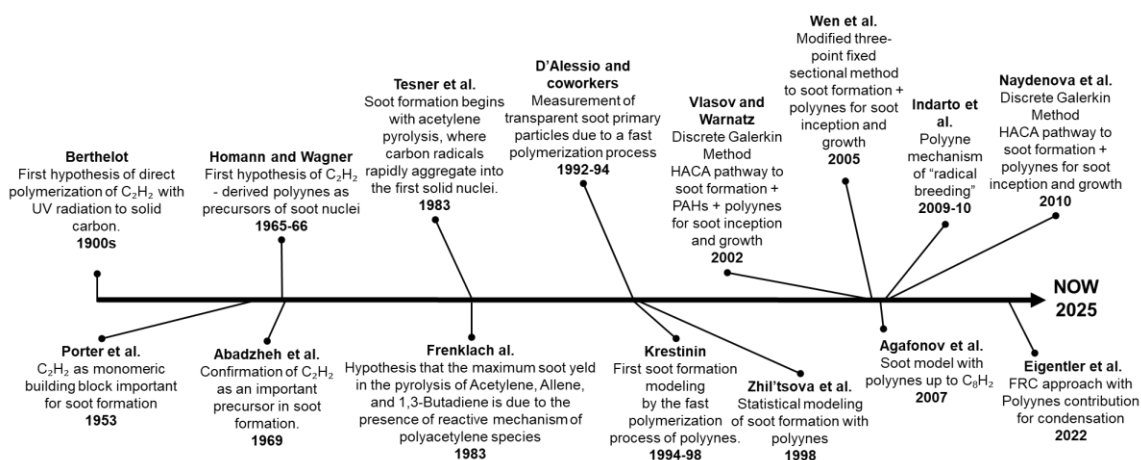


Figure 2.3.1 – Polyyn chemistry applied to soot formation.

Starting from the late 19th century and the early 20th century, Marcellin Berthelot realized that acetylene could give rise to solid carbon through a polymerization process mediated by UV rays [100]. It was not until 1953, thanks to Porter et al.[101], that acetylene was proposed as a key monomeric building block in the process of soot formation. From there, in 1965-66, the first hypothesis by Homann and Wagner [102] about polyynes derived from acetylene and precursors to soot formation was introduced. The year 1969 marks the time when Abadzheh et al. [103] confirmed the role of acetylene as an important precursor in soot formation, but it was only in the early 1980s that a breakthrough occurred. In 1983, Tesner et al. [104] proposed that soot formation initiates with the pyrolysis of acetylene, where rapidly-forming carbon radicals aggregate to form the first solid nucleus. In the same year, Frenklach [105] demonstrated through shock tube pyrolysis experiments with acetylene, allene, and 1,3-butadiene that the maximum soot production is determined by the reactive mechanism of polyacetylene species. During 1992-94, D'Alessio and coworkers [61–63] found another clue regarding the contribution of polyynes in soot formation, observing measurements of primary transparent soot particles. These entities were linked to a rapid polymerization process caused by the presence of polyacetylenes. In the same timeframe, from 1994 to 1998, Krestinin [106,107] reviewed the previous findings on the kinetics of polyynes in soot formation, proposing a fast polymerization process of polyacetylene species as illustrated in **Figure 2.3.2**. In this way, Krestinin defined a mechanism where the polyynes contribute to the appearance of the initial solid soot nuclei through the formation of broad plane structures, which increase in size due to attachment and lateral growth facilitated by the presence of polyyn chains.

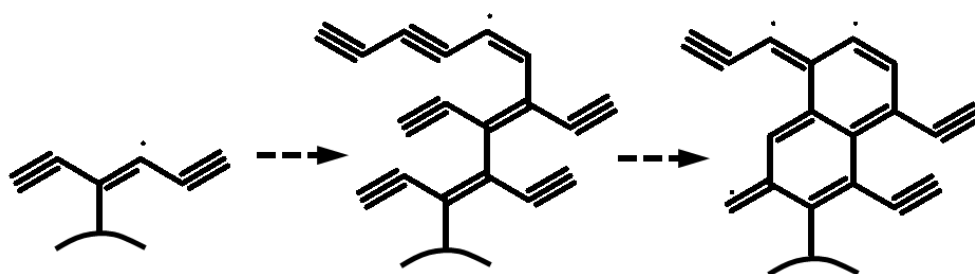


Figure 2.3.2 – Fast polymerization process of polyynes adapted from [106].

In 1998, a statistical implementation of a model for soot formation was developed by Zhilt'sova et al. [108] based on Krestinin's proposal. Krestinin proposed his own model implementation in 2000, including a process of rapid soot inception and surface growth [109].

In 2005, Wen et al. [110] proposed a new approach to soot formation, using a sectional method for discretizing soot species, combined with polyynes chemistry in a rapid inception and surface growth process. In 2007, Agafonov et al. [111] published an additional kinetic model, implemented with polyynes chemistry and validated through shock tube experiments on benzene and acetylene under pyrolytic conditions, while in 2009, Indarto et al. [98] developed a model for polyynes growth. In 2010, Naydenova et al. [112] developed the first model implemented using the discrete sectional Galerkin method [113], which combines the gas-phase kinetics of PAHs with a polyynes-driven process for producing soot precursors and the initial soot nuclei. Surface growth reactions with PAHs and polyynes were also considered. In 2022, Eitengler et al. [114] developed a new kinetic modeling approach incorporating a revised PAH gas phase sub-mechanism and an updated sub-model for polyynes chemistry.

In light of what has been reported and the evolution in the formulation of the mechanism for the formation of polyacetylene precursors, as well as their inclusion in the descriptive process of soot formation, it is observed that, to date, no scientific publication has directly linked the chemistry of PAHs with that of the polyynes. The two research areas have remained separate until now, evolving in parallel and independently. Currently, no model has incorporated interactions between polyynes and PAHs in the process of LPAH formation, the key step for the formation of the first solid soot nuclei and primary carbon nanoparticles.

2.4 Overview of the ICARE gas-phase.

The ICARE gas-phase kinetic mechanism is a comprehensive pyrolysis model developed at the laboratory ICARE (CNRS Orléans) on the chemistry of PAH formation and growth,

based on several versions of the CRECK mechanism from the Politecnico di Milano [115–119]. Starting from the CRECK model, several reactions were integrated and/or updated based on theoretical studies and experimentally observed formation and decomposition pathways. Validation of the mechanism was conducted against single-pulse shock tube speciation data under pyrolytic conditions, at a nominal pressure of 20 bar, in a temperature range of 950 to 1800 K, with a reaction time of about 4 ms. Species profiles up to four-ring structures were modeled. Several fuels were studied to probe the different reaction mechanisms, including propylene [120], propyne [120], benzene [48], toluene [48], phenylacetylene [49], linear C₈–C₁₀ alkylbenzenes [121], xylenes [122], n-heptane [123], cyclopentene [124], and mixtures between selected fuels and C₂/C₃ hydrocarbons [add refs]. The summary of the results achieved and the validation targets for the mentioned studies are summarized in **Table 1**, as an outline of the main capabilities of the ICARE gas-phase model.

Table 1 – Summary table of implementations of gas-phase PAH chemistry in the ICARE model on PAHs.

Fuels	SPST Conditions	Ref.
n-Heptane	900–1700 K, 100–2000 ppm C ₇ H ₁₆	[123]
Benzene & Toluene	1100–1800 K, ~200 ppm C ₆ H ₆ and C ₆ H ₅ CH ₃	[48]
Cyclopentene /+C₂H₂	940–1650 K, 108 ppm and 326 ppm cyC ₅ H ₈ ; 111 ppm cyC ₅ H ₈ + 517 ppm C ₂ H ₂	[124]
Benzene + C₂/C₃ Unsaturated Species	1030–1800 K, 109 ppm C ₆ H ₆ ; 108 ppm C ₆ H ₆ + 532 ppm C ₂ H ₄ ; 108 ppm C ₆ H ₆ + 500 ppm C ₂ H ₂ ; 110 ppm C ₆ H ₆ + 531 ppm C ₃ H ₆ ; 108 ppm C ₆ H ₆ + 508 ppm pC ₃ H ₄	[125]
Propylene/Propyne	1050–1650 K, 518 ppm C ₃ H ₆ ; 509 ppm pC ₃ H ₄	[120]
Toluene + C₃H₆ / C₃H₄	1050–1700 K, 105 ppm C ₇ H ₈ ; 106 ppm C ₇ H ₈ + 513 ppm C ₃ H ₆ ; 108 ppm C ₇ H ₈ + 557 ppm pC ₃ H ₄	[120]
Toluene + C₂H₂ / C₂H₄	1150 – 1650 K, ~100 ppm C ₇ H ₈ + 50–469 ppm C ₂ H ₂ , + 516 ppm C ₂ H ₄	[126]
Styrene /+C₂H₂	1100 – 1730 K, 92 ppm C ₈ H ₈ ; 97 ppm C ₈ H ₈ + 500 ppm C ₂ H ₂	[50]
Xylene isomers (-o,-m,-p)	1150 – 1650 K, 113 ppm o-C ₈ H ₁₀ ; 106 ppm m-C ₈ H ₁₀ ; 101 ppm p-C ₈ H ₁₀ ;	[122]
C8–C10 Linear Alkylbenzenes	950–1700 K, ~100 ppm C ₆ H ₅ C ₂ H ₅ , C ₆ H ₅ C ₃ H ₇ and C ₆ H ₅ C ₄ H ₉	[121]
Phenylacetylene + C₂H₂/ C₂H₄	1100–1700 K, 103 ppm C ₆ H ₅ C ₂ H, 104 ppm C ₆ H ₅ C ₂ H + 415 ppm C ₂ H ₂ , 105 ppm C ₆ H ₅ C ₂ H + 504 ppm C ₂ H ₄	[49]

2.5 Formation of large gas-phase soot precursor.

The chemistry of soot formation is closely determined by the initial fuels and how the gas-phase chemistry proceeds, either in combustion regimes or under purely pyrolytic

conditions. In this process, which, at high temperatures, starts with pyrolytic reactions, the fuel fragments into smaller molecules that, through different reactive steps, form a variety of more and more complex aromatic structures of different size and morphology, following pathways similar to the one presented in Section 2.3 for small PAHs. The diversity of the LPAHs produced in flame conditions is well represented in **Figure 2.5.1** for the case study in [127] concerning LPAHs deposited on incipient soot particles collected at $Z = 8$ mm. In this case, the measurements were performed by Laplacian-filtered constant-height CO-tip AFM images.

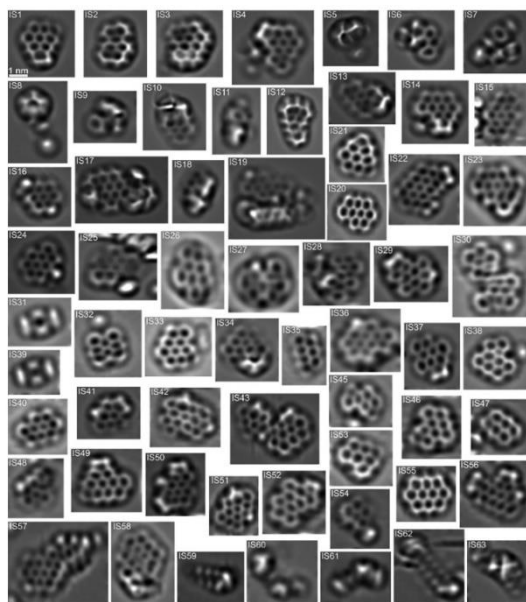


Figure 2.5.1 – LPAHs produced in flame conditions from [127].

Early modeling efforts [128–131] already considered LPAH species with 4-6 peri-condensed rings, such as pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$), as major precursors responsible for carbon particle formation due to their relative abundance and relative stability. Their formation is mainly driven by the HACA mechanism [46,60]. Subsequent studies have provided a more detailed picture of the main soot precursor molecules. Indeed, LPAHs differ not only in size but also in whether they have even or odd numbers of carbon atoms, as shown by Keller et al. [132] in premixed benzene/oxygen flames. **Figure 2.5.2**, from Nobili et al. [117], shows measurements on an ethylene flame by resonance-enhanced multiphoton ionization (REMPI) combined with time-of-flight molecular beam mass spectrometry. PAHs with even numbers of carbon atoms are represented by closed-shell

molecules, while those with odd numbers are mostly stable radicals. These results reveal that below $C < 25$, the concentration of PAHs decreases linearly with the number of carbon atoms, with even C-number PAHs being more prevalent. Conversely, for $C > 25$, the behavior shifts to follow an exponential trend, with similar molar fractions for even and odd C-number PAHs. The peak concentration occurs around $C = 50$ for both, then decreases around $C = 70$. These findings, obtained for large PAHs up to 70 carbon atoms, were also observed in a low-pressure premixed acetylene/oxygen flame ($P = 2.67$ kPa, $C/O = 0.70$ - 1.06) [133].

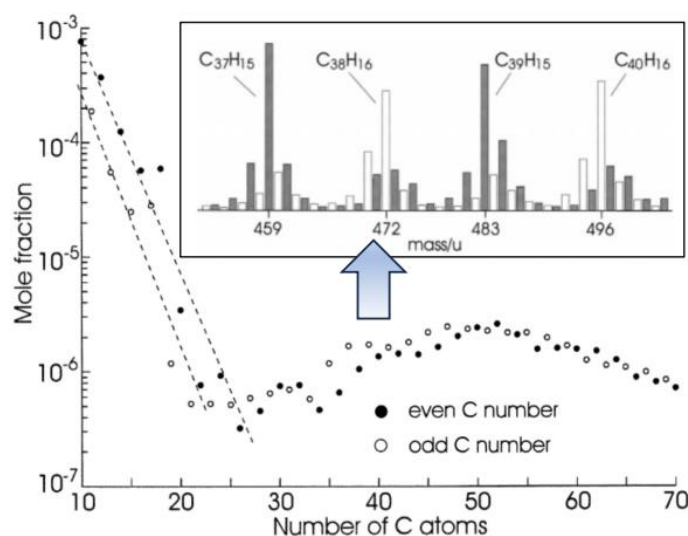


Figure 2.5.2 – LPAHs produced in flame conditions from [132].

Based on the results in [132], the highest comparable fraction between closed- and open-shell LPAHs can be explained considering open-shell LPAHs as stable π -radicals rather than σ -radicals. The formation of π -radicals is mainly linked to unimolecular processes and structural rearrangements, which enhance the formation rate of larger PAH molecules relative to smaller aromatic compounds [132,134]. This explains the leveling off of the exponential decline in mole fraction for species with less than 25 C atoms.

An important detail to consider is that Keller et al. [132] found, based on flame data, that LPAHs do not require activation for further growth through H-abstraction reactions to form σ -radicals, and that the structure of LPAHs influences their reactivity more than their

molecular or radical character. The higher stability of π -radicals compared to σ -radicals has also been examined by Faravelli et al [135], supporting Keller et al [132]'s claim that the tendency to form π -radicals increases as PAHs grow larger.

2.6 Soot chemistry in pyrolytic conditions

In combustion, soot modeling is a highly complex process involving numerous detailed physical and chemical steps. These processes begin in the gaseous phase, primarily driven by the chemistry of aromatic and aliphatic molecules. The main mechanisms of soot formation — such as inception (initial soot particle nucleation), surface growth, coagulation, agglomeration, and oxidation (not present in pyrolytic conditions) — are then implemented. Broadly, two macro-mechanisms can be identified: inception and growth. The production of soot precursors in the gas phase has been extensively discussed in the previous sections. Here, the emphasis is on exploring the primary mechanisms responsible for the formation of the solid carbon particles.

2.6.1 Inception.

The inception process refers to a series of mechanisms involved in the transition from the gas phase of aromatic and aliphatic molecules to the formation of the initial carbonaceous nanoparticles. This process is highly intricate and remains only partially understood, posing a significant challenge in elucidating the mechanisms of soot formation. This is due mainly to the lack of experimental techniques capable of probing such elusive processes, as well as the impossibility of performing high-level theoretical calculations on such large systems. Current understanding suggests that this process predominantly involves the formation of precursor species that subsequently lead to the generation of Large Polycyclic Aromatic Hydrocarbons (LPAHs), which in turn contribute to the nucleation of the first carbon nanoparticles. Historically, this pathway has been regarded as more efficient in soot formation compared to the polyynes pathway, which was previously presented in the

literature as an alternative 'new route' for soot production. Over the years, this mechanism has been extensively investigated, stimulating numerous research proposals.

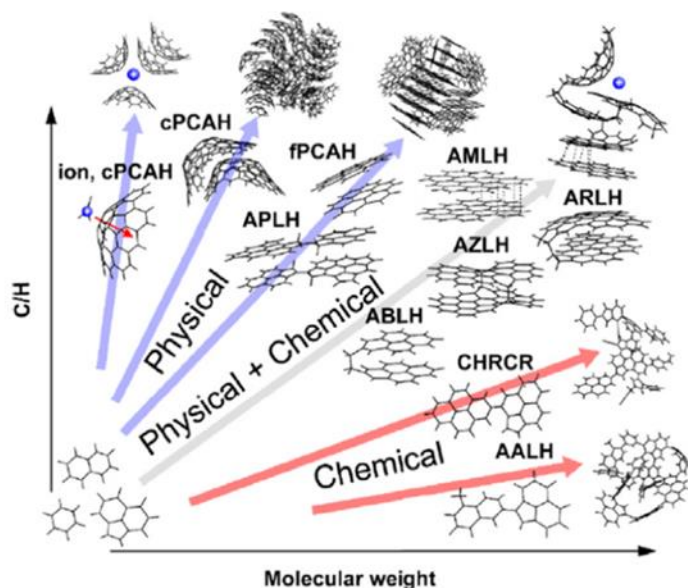


Figure 2.6.1.1 – Inception mechanism related to C/H vs. PAHs molecular weight. Adopted from [5,136].

Figure 2.6.1.1 suggests several pathways, both chemical and physical, that are proposed in the literature as suggested by Violi et al. [51]. These mechanisms can be purely physical or chemical, or a combination of both.

Following the work of Violi et al. [51], Thompson et al. [136] and Martin et al. [5] extended the analyses of these mechanisms. Within the physical inception mechanism, Homann [137] suggested a grouping toward fullerene and soot through a process of formation of pericondensed aromatic hydrocarbons (cPACHs), which allow the complete closure of pentagonal rings and the formation of aromatic structures. Unlike classic planar aromatics, cPACHs can have ionic interactions due to their polarity, which can induce a force-driven mechanism guided by ionic forces. However, it has also been shown that the formation of fullerene is inherently disfavored in combustion processes under both atmospheric and high-pressure flame conditions [5]. Another widely known mechanism is the sticking of PAH islands due to van der Waals forces. This purely physical mechanism was initially

proposed by [128] and later used in various studies [5,129,138–140], although it has been the subject of extensive debate due to the weak influence it demonstrates under high-temperature conditions. Over time, another proposed interaction was the chemical-physical combination, which is not thermodynamically favored in flames, proposed by Sabbah et al. [141] and Kolghy et al. [142], involving a reversible clustering interaction of PAHs with the formation of chemical bonds. In a subsequent study, the key role of aromatic aliphatic-linked hydrocarbons (AALH) has been suggested by Chung and Violi [143]. Based on this formulation, covalent bonds can be formed through aliphatic chains, connecting PAH compounds and providing the base for particle formation. Another possibility, emerging from Wang's work [65], is the realization of a diradical ambivalence in two dimensions, concerning PAHs — the nature of PAHs with an even number of carbons and zigzag edges — as a predisposition to increase the number of aromatic rings. Similarly, it has also been verified that linear acenes can transition from closed-shell structures to open-shell structures in singlet or triplet states with an increase in fused benzene rings [144,145]. Considering pentacenes, that is, acenes with five rings, they demonstrate significantly greater reactivity, being capable of spontaneous dimerization in a solvent at ambient temperature [146]. Another inception proposition concerns the mechanism of aromatic rim-linked hydrocarbons (ARLH) for π radicals, proposed by Martin et al. [5], which leads to the formation of stacked structures with high bond energy. To demonstrate the importance of stabilized resonant structures, Johansson et al. [94] also supported the contribution of these species by the influence of Small Resonantly Stabilized Radicals (RSRs) during the inception process, thereby developing the clustering hydrocarbon radical chain reaction (CHRCR) mechanism previously presented in section 2.3.6. In addition to these propositions, Shao et al. [147] proposed that the soot inception process is primarily driven by a physical mechanism, supported by experimental evidence from various flame studies under different conditions. This assertion was made because the mass spectrum peak of non-organic carbon particles originating from premixed flames has been correlated with planar PAHs with an even number of H and C atoms through stochastic simulations and theoretical calculations, without identifying these rings as pentagonal rings or aliphatic branches.

In this process, it has been highlighted that the most favored chemical species are those with 6 to 14 aromatic rings, which undergo physical dimerization via van der Waals forces. Of course, all these propositions demonstrate the clear complexity of the process, due to the coexistence of processes that together contribute to the formation of the first nanocarbon particles and to the variety of radical and molecular PAH structures involved. They also demonstrate a lack of clarity regarding the transition from the gas phase to the solid phase.

2.6.2 Soot Growth.

Soot inception sets the stage for the subsequent growth process, marking the transition from molecular clustering to particle coalescence and aggregation. In general, the soot growth process plays a fundamental role in the soot formation process [148] as it strongly affects the quantity of produced soot. This observation has been confirmed through experimental flame tests. In fact, Wagner [149] showed that the carbon deposition rate in flames follows first-order kinetics, proportional to surface growth processes, with typical values ranging from 30 to 500 s⁻¹. Conversely, from a numerical perspective, D'Alessio et al. [150] compared detailed particle formation mechanisms with experimental data, finding good agreement when soot growth reactions were neglected in flames with a C/O ratio below 0.8. For richer conditions (C/O = 0.92), however, they observed that about 60% of the soot carbon mass results from surface growth, while the remaining part comes from the transformation of chemical species into solid particles.

In reality, soot growth is a broad process that is a function of the conditions within flames and the fuels in general. Until now, within this complexity, the mechanisms recognized as responsible for the growth process can be formally referred to as follows:

1. Carbon Addition – chemical growth – promoted by C₂H₂;
2. Chemical growth by PAHs (biaryl recombination);
3. PAHs condensation on primary particles;
4. Polyynes rapid polymerization process;
5. Coalescence and agglomeration mechanism of soot particles.

Generally, mechanisms 1, 2, 3, and 4 are attributable to surface growth reactions that increase the total amount of soot. Instead, the coalescence and aggregation mechanisms regulate the production of particles of different sizes and their number.

Regarding chemical growth via Carbon Addition, commonly known as acetylene addition, this occurs via the HACA mechanism [64,64,71]. Similarly to what happens in the gas phase, for this process to occur, Carbon Addition requires the abstraction of an H atom to form an aryl radical, after which the subsequent addition of C_2H_2 increases the mass. The rate at which this process occurs is directly controlled by the density of active sites, which is proportional to the number of hydrogen atoms [65]. However, this process has limitations as the size of the particles involved increases [64,71]. This deceleration behavior could be due to two reasons: 1) reduction of the available surface area; 2) aging of the surface. In addition, as the particle becomes larger, each addition of C_2H_2 leads to a very small increment in the total number of carbons. Supporting the idea that HACA becomes inefficient as particle size increases, there is experimental evidence [151,152] from premixed flames showing that the mass of soot continues to increase even in the post-flame region, where regionally there is a decrease in the presence of carbon atoms in terms of concentration. Additionally, the HACA mechanism alone cannot explain some structural characteristics of soot, particularly the aliphatic shell observed in soot particles [153–155]. Clearly, this analysis highlights the need to introduce additional mechanisms. In particular, phenomena of adsorption and desorption of gaseous species on particle surfaces can also occur.

A growth mechanism is represented by the reactions between particles and PAHs. The reference reaction is the recombination of two aryl radicals forming biaryls, followed by rearrangement to a more stable compound. This behavior is especially identified in specific fuels such as coal and wood, as indicated by Sarofim et al. [156]. PAH condensation also occurs, involving a rapid carbonization process that promotes the growth of soot particles. In fact, it consists of the adsorption of gaseous species onto the surface of the particles, occurring via small monomeric aromatic species [157,158].

Although some studies have indicated the high-temperature instability of small PAHs, such as pyrene and coronene, in flames [141,159], other experiments suggest that PAHs stack

as building blocks of soot [51,159]. This modeling has been adopted by many studies over time [138,160,161].

The polyynes mechanism is another pathway proposed as a soot particle growth mechanism, as introduced in section 2.3, supported by various experimental evidence over time [61,63,105]. The polyynes chemistry is especially favored at high temperatures, where the production of large polyynes is favored.

Based on this evidence, Krestinin [106,107,162] proposed that soot particles grow through rapid surface interactions with polyynes.

As the number of soot particles increases, they also enter a collision regime that leads to coagulation, which can occur simultaneously with the surface growth mechanism. Unlike the surface growth process, which operates from a quantitative perspective, coagulation affects qualitative aspects of soot production such as morphology, number density, particle size, and distribution. Within coagulation, two mechanisms are distinguished: 1) coalescence between two particles that collide and fuse to form a single larger particle, similar to two liquid drops colliding.

As particles coalesce, they tend to reduce their free surface area, thereby minimizing their energy, and are characterized by smooth, spherical surfaces. For small particles, the process can be sufficiently fast. However, for larger particles, it is slower because they are more rigid and graphitic; 2) agglomeration between two soot particles that, upon collision, stick together, forming chain-like fractal structures where each particle remains distinguishable. The structures resulting from this process are called aggregates. Supporting the definition of these structures, TEM analyses show that these aggregates include primary particles that are nearly spherical.

The coagulation rate can be defined using the Smoluchowski equation, which depends on the Knudsen number (Kn), defined as the ratio of the mean free path of gas molecules to the particle radius. However, this relationship implies that every collision between particles necessarily results in coagulation.

In standard models of the soot formation process, based on an inception mechanism and surface growth primarily governed by PAH chemistry and the contribution of the HACA mechanism, particle growth is traditionally represented according to the scheme shown in **Figure 2.6.2.1** from [163].

In the present work, an additional soot growth pathway has been introduced, based on kinetic mechanisms associated with polyynes chemistry.

For this purpose, specific reactive species generated by this kinetics have been considered and modeled according to the approach proposed by Naydenova et al. [112].

Details will be elaborated in the following chapters. This alternative growth pathway is illustrated in **Figure 2.6.2.2**, showing the development in this work compared with [163].

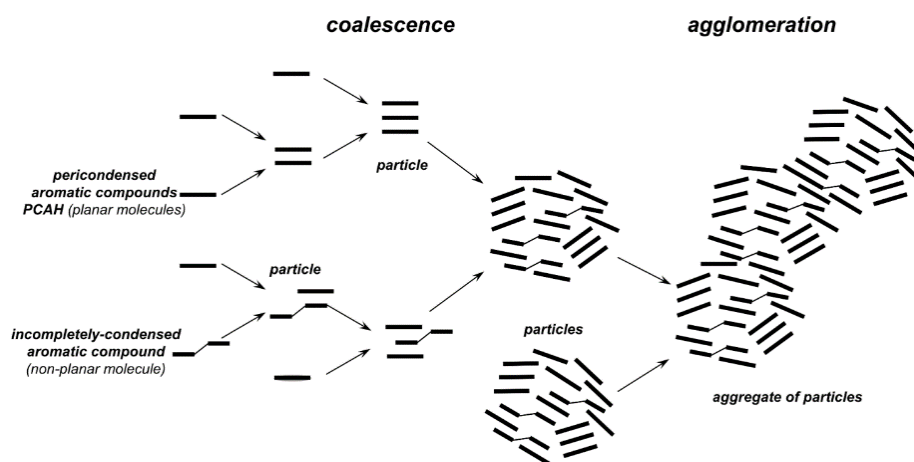


Figure 2.6.2.1 – Scheme of coagulation processes - growth [163].

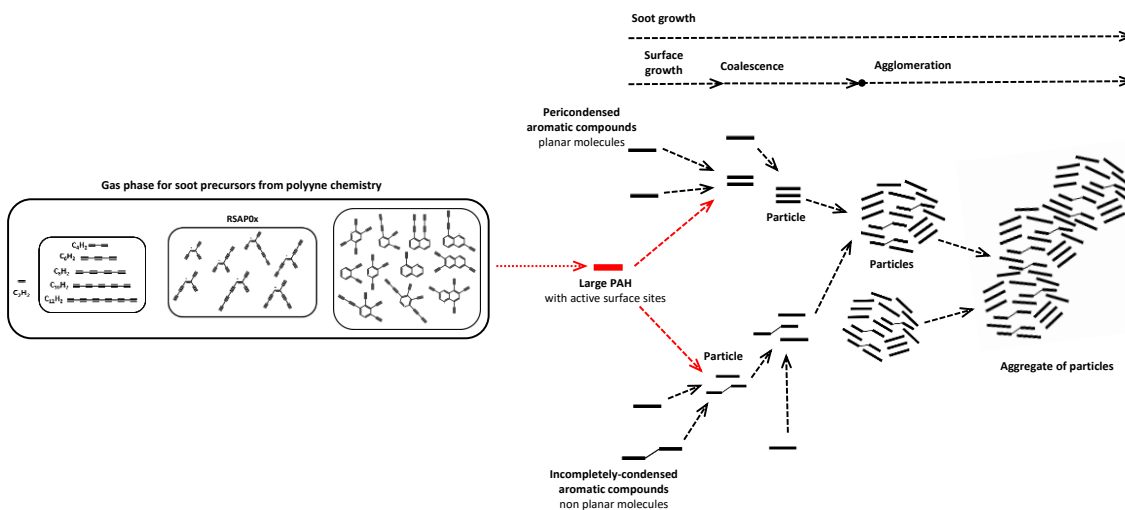


Figure 2.6.2.2 – Scheme of coagulation and growth processes proposed in this work.

2.7 Soot modeling approaches.

In the domain of combustion and pyrolytic processes, soot formation is recognized as a highly intricate phenomenon characterized by multiscale interactions involving a series of interconnected chemical and physical reactions. Over the past several decades, extensive experimental investigations have been conducted to elucidate the key aspects of this process, leading to the development of theoretical models that aim to elucidate its fundamental mechanisms. Nevertheless, substantial gaps in knowledge persist, particularly concerning the dynamics involved in the transition from gas-phase chemistry to solid carbon formation [5,65,136]. The governing processes may also vary qualitatively under different thermodynamic conditions, adding complexity to the overall picture.

From a modeling perspective, in order to develop realistic and reliable models that are chemically and physically scientifically sound, as well as with suitable structures capable of defining the entities that constitute soot, the first step is to adopt a gas-phase model as the initial basis. As previously mentioned, the gas phase represents a fundamental element in the modeling process because it allows for an effective setup of the main precursors involved in soot particle formation (sections 2.2 to 2.6). Starting from the choice of a gas phase model, one can proceed to model the solid carbon phase.

In the literature, various types of models for soot have been developed, which Kennedy [164] primarily classifies into three main categories:

- ⊗ **Empirical models:** These represent the earliest modeling approaches developed, based on correlations of experimental data, e.g., soot yield, within the range of the investigated operating conditions. Such approaches essentially involve using a simplified global mechanism to predict soot formation, usually through the use of one or two transport equations. Their simplicity allows for quantitative predictions regarding the amount of soot produced, also resulting in lower computational cost, although they lack the capacity to qualitatively describe the process. In practical applications, such as predicting soot in engines, for example, as reported by Calcote and Manos [165], it is possible to calculate the soot threshold index (TSI) from 0 to 100, based solely on the fuel's propensity to form soot and its molecular structure;

- ⊗ **Semi-empirical models:** unlike purely empirical approaches, they incorporate additional input parameters such as specific chemical and physical properties of soot, while accounting for production and oxidation rates with global steps. These models also integrate experimental correlations to facilitate reliable predictions across a range of operating conditions. An illustrative example within this category is provided by studies conducted by Leung, Lindsted, and Jones [166], which introduce simplified modeling frameworks for solving transport equations related to the mass and numerical density of soot particles. Notably, these models are characterized by high computational efficiency and robustness, enabling their calibration to closely match experimental data. Nonetheless, a critical limitation is their dependence on specific calibration parameters, coupled with an overly simplified structure that constrains their applicability across diverse scenarios and their use in extrapolating simulations to conditions outside their validation;

- ⊗ **Detailed models:** the most complex and detailed category allows for a deeper understanding of soot formation, considering both the chemical and physical aspects of the process and the species involved. Although these models ensure a high level of fidelity as well as greater quality and descriptive capability, they entail higher computational costs compared to empirical or semi-empirical models. Detailed models for soot formation can employ both stochastic and deterministic approaches.

Among the various modeling approaches, the discrete element model of stochastic and Lagrangian type, as proposed by Kelesidis et al. [167], is notably valuable for conducting detailed analyses of soot morphology. Generally, other advanced models are categorized into stochastic and deterministic types. Stochastic models are often implemented using the Monte Carlo method or molecular dynamics simulations, whereas deterministic models typically employ the moment method or the discrete sectional method (Eulerian approach). The latter is utilized both for field simulations and, within computational fluid dynamics

(CFD) applications, in a reduced or indirect manner. It is also prevalent in the literature to observe that detailed models are frequently applied stochastically, commonly through the solution of the population balance equation (PBE) across various application contexts. The pioneering application of PBEs dates back to the studies by Hulburt and Katz [168], as well as Randolph [169], which aimed to describe the number density function (NDF) [170]. This implementation finds applications in various engineering systems such as crystallization and granulation [171]. In particular, NDFs are capable of describing populations of discrete elements in a dispersed phase distributed over a certain spectrum of characteristic properties [170]. Regarding the engineering applications that arise in the field of soot formation, NDFs are used to represent the Particle Size Distribution Function (PSDF), which is the number density function used to describe the population in terms of soot particle sizes. Generally, NDF $f(\xi) = f(t, \mathbf{x}; \xi)$ in fuel-rich premixed flames is represented by the following transport equation:

$$\text{Eqn(2.7.1):} \quad \frac{\partial f(t, \mathbf{x}; \xi)}{\partial t} + \frac{\partial (u_i f(t, \mathbf{x}; \xi))}{\partial x_i} - \frac{\partial}{\partial x_i} D_x \left(\frac{\partial f(t, \mathbf{x}; \xi)}{\partial x_i} \right) = S_\xi(t, \mathbf{x}; \xi)$$

where $\mathbf{x}$ and ξ , respectively represent the vectors of the external coordinates (physical space) and internal coordinates. Some properties of soot particles are highlighted, such as diameter, fractal dimension, volume, area, age, etc. u_i is the velocity of the fluid relative to the i -th velocity, while D_x corresponds to the diffusion coefficient. The term S_ξ represents the chemical and physical processes involved in the formation of soot particles.

2.7.1 Stochastic Approach

As previously mentioned, the stochastic approach refers to the solution of the Population Balance Equations (PBE), which is adopted through numerical methods such as Monte Carlo (MC) or molecular dynamics (MD). This approach allows for the efficient computational generation of a set of representative particles. Thanks to these methods, it is possible to track the dynamics of entities generated by the growth of precursor species in the gas phase, up to the formation of carbon nanoparticles, considering chemical interactions with other entities. Models that employ this methodology can potentially

predict various properties of soot particles beyond just solving the Particle Size Distribution Function; however, they have a significant disadvantage in terms of high computational costs, which is why they are often used as post-processing strategies, as common in flames [172].

In the context of detailed modeling, numerous research groups have adopted stochastic approaches. Violi et al. [158] developed a combined Monte Carlo-molecular dynamics (KMC-MD) kinetics, known as the Atomistic Model for Particle Inception (AMPI), aimed at predicting the transition from PAH chemistry to carbon nanoparticle chemistry. This methodological integration enables the tracking of the most probable evolution of particles through the KMC algorithm, while simultaneously ensuring the equilibrium of the predicted structures. Such a complex approach enables the evaluation of two different time scales: the time between one Monte Carlo event and the next can be significantly longer than that typical of molecular dynamics, which operates on much shorter time scales. For this reason, Izvekov and Violi [173] also implemented agglomeration processes on large length and time scales, using a multiscale coarse-graining (MS-CG) method to effectively address the prediction of soot aggregation. Similarly, Violi and Venkatnathan [174] applied this methodology to predict the inception of soot particles in low-pressure premixed flames, providing detailed information on the structural properties of the produced particles. Along the same lines, Balthasar and Kraft [175] utilized the Monte Carlo method to model soot in laminar acetylene flames at low pressure. Building on the work of Singh et al. [139], the entire coagulation process was extended to the continuum regime and validated under various conditions of low-pressure premixed flames, successfully highlighting the decrease in surface activity of mature soot particles — a phenomenon strongly dependent on local temperature and residence time. Further studies were conducted using Monte Carlo techniques, including the kinetic MC aromatic site (KMC-ARS) method [176], to describe the growth of PAHs with different surface activities. Among these studies are those by Totton et al. [177] on investigating soot nucleation from PAHs, Raj et al. [178] on the collision efficiency of PAHs during inception and coagulation of soot, and Hou et al. [172] on the structural prediction of aggregates based on the work of Mitchell and Frenklach [179] on polydisperse primary particles.

2.7.2 Method of Moments

Among the methods discussed, the method of moments is notable for its computational efficiency. Instead of solving the NDF directly, it evaluates certain lower-order moments of the distribution, offering insights into average quantities. Typically, the source term related to m_0 corresponds to the most significant part of the particle number distribution, influenced by mechanisms like inception and coagulation that cause variations in particle numbers. Another key term, m_3 , pertains to the soot volume fraction, f_v , and reflects processes such as inception, growth, and oxidation during combustion. Each moment has its own transport equation, with the source term expressed through pseudo-reactions calculated via moment closure approximations, which are based on assumed PSDFs.

Regarding the choice of these closure models, various schemes have been proposed over time, such as those by Frenklach and Harris [180], and the Method of Moments with Interpolative Closure (MOMIC) [181]—where unknown moments are estimated through the interpolation of known ones. This strategy has been applied both in calculations related to the free molecular regime [181] and in the continuum regime [182]. Additionally, this technique has been used to scale the relationships between soot aggregate particles, starting from the Monte Carlo method developed by Balthasar and Frenklach [175]. Thanks to its low computational cost, this method has also been extended to simulation levels such as Large Eddy Simulation (LES) [183] and Direct Numerical Simulations (DNS) [184].

The Quadrature Method of Moments (QMOM) represents an alternative method to achieve closure, particularly useful when the NDF function is unknown and can be approximated using a set of Dirac delta functions or kernel density functions [185]. This methodology has led to numerous applications over time, including:

- Direct Quadrature Method of Moments (DQMOM) [186];
- Hybrid Method of Moments (HMOM)[161];
- Extended Quadrature Method of Moments (EQMOM) [185];
- Conditional Quadrature Method of Moments (CQMOM) [187];
- Split-based Extended Quadrature Method of Moments (S-EQMOM)[188].

2.7.3 Discrete Sectional Methods (DSM)

The Discrete Sectional Methods, among the various models previously discussed, is distinguished by its superior capacity to provide detailed predictions in soot formation studies. This methodology enables the development of comprehensive kinetic models by discretizing the continuous domain of precursor species and particles into sections defined by parameters such as mass or the number of carbon/hydrogen atoms. These sections, which are finite in number, are established based on experimental evidence and calibrated using stochastic modeling data. Typically, properties such as the number of carbon atoms, H/C ratio, and characteristic size are assigned to each section, often referencing average values. Mirroring the structure of gas-phase kinetic models, the sectional discretized approach involves specific reaction classes associated with each section, to which relevant kinetic parameters and, optionally, rate rules are attributed, depending on the reactive mechanisms considered. Notably, the predictive accuracy of this approach is directly proportional to the number of sections implemented, a factor that inherently leads to increased computational costs.

Conventionally, sectional discrete methods necessitate the implementation of at least 20 sections, with the number of potential reactions ranging from hundreds to thousands, depending on the specific modeling approach employed. Although this modeling approach incurs high computational costs, it offers the advantage of simultaneously solving the Population Balance Equation (PBE) along with gas-phase kinetics and the flow field. Furthermore, it enables the comprehensive tracking of particle dynamics across a broad spectrum of operating conditions, thereby providing a significant improvement over alternative detailed methodologies.

Gelbard and Seinfeld pioneered this technique [189], initially applying it to aerosol dynamics with the development of the MAEROS code, which predicts multicomponent and polydisperse coagulation in aerosols. The first attempt to combine this technique, using MAEROS, with a detailed kinetic mechanism proposed by Colket and Hall [39,190], aimed to predict soot with just a few sections, providing a quantitative estimate of soot volume fraction in premixed counterflow flames. This approach showed that accurately predicting particle number density or sizes requires implementing a sufficiently high number of

reactions. As a result of these efforts, other applications started to emerge gradually, featuring more sections. For instance, Smoke et al. [191] developed a version with 12 combined sections, and Pope et al. [192] created the Simultaneous Particle and Molecule Modeling (SPAMM) technique to study elementary gas phase kinetics in laminar flames within co-flow diffusion. Thanks to Richter et al. [138], an initial substantial expansion of the sectional model framework has been realized through the introduction of a comprehensive kinetic sectional model designed to predict soot formation from polycyclic aromatic hydrocarbons (PAHs). This model incorporates 295 gas-phase species alongside 20 pseudo-lumped species, termed BINs (Binary species of carbon and hydrogen), to enhance predictive accuracy. Richter's approach was then extended by D'Anna and Kent [129] through the validation of a model capable of predicting soot for laminar co-flow diffusion flames. This latter contribution was further expanded by Sirignano et al. [193] through an enhancement of the discretization level of species in terms of H/C for the sections. In this same implementation, different structures of molecular clusters and types of aggregates, including chain-like ones, were also introduced, providing a structural variety of species involved in the soot formation process.

Another important upgrade of the latest modeling mentioned was the proposal to include different reactive pathways of crucial importance for describing soot formation, such as inception, PAH adsorption, growth, coagulation, surface oxidation, and oxidation-induced fragmentation. An approach based on size and temperature was also used to implement coagulation efficiency, allowing for the appropriate use of different rates for coalescence and aggregation. This model has been validated in the field of laminar flames [193,194].

Another noteworthy proposal was put forward by Thompson and colleagues [195,196], building upon their predecessor work by Park et al. [130], who employed a sectional discrete methodology for soot prediction. This methodological framework incorporated both fixed and mobile sections. Theoretically, the fixed sections were characterized by just two variables: the count of soot clusters and the number of primary particles. In contrast, the mobile sections additionally considered the volume of the clusters. This approach facilitated analytical simplifications related to the variation in the definition of the sections, which, in the context of surface growth phenomena and particle dynamics, remain invariant. The moving-section model represents an effective approach to avoid problems

related to numerical diffusion [197], which is instead a typical critical issue of fixed-section models. However, the application of this method is limited to ideal systems, since in spatially non-homogeneous systems it is necessary to keep the section boundaries unchanged in all positions to ensure computational consistency [130]. To partially overcome the limitations of fixed-section models, a 'three-point corrected' method has been proposed, capable of significantly reducing numerical diffusion [198]. The results obtained from numerical simulations related to soot formation and growth processes in ideal reactors have shown that the fixed-section approach with the corrected method provides performance entirely comparable to that of the moving-section model, both in terms of soot mass prediction and regarding the numerical density and size distribution of particles [130]. Other authors have improved the use of this technique. For example, Zhang et al. [195,199] proposed a method to avoid the overestimation of soot in laminar coflow diffusion flames, caused by PAH condensation. Also in the field of combustion, Dworkin et al. [200] tested their soot model with different gas phase sub-mechanisms to verify the strong dependence of the results on the type of initial gas phase used; Eaves [201] implemented reversible nucleation and condensation processes, validated and further developed by other authors such as Veshkini et al. [160], Kholgy et al. [142], and Naseri et al. [202].

Currently, the leading developers of DSM models are represented by the CRECK modeling group at Politecnico di Milano, starting from their earlier works [116–119,140,203]. The latest updated version of the CRECK model was carried out in the work of Nobili et al. [118], which considers i) the particular reactivity of large aromatic structures up to carbon nanoparticles, as highlighted by recent experimental and theoretical studies, and ii) an improved description of the morphology of carbon particles through the introduction of polydispersity of aggregates. Another recent DSM model from the literature, which introduces innovations in the implementation of coagulation efficiency, is that of Huo et al. [204].

The soot model presented in the current work was built based on recent work by the CRECK group [117].

Initially, the CRECK model's descriptive capabilities were verified, as shown in **Figure 2.7.3.1**, by comparing the simulation results against shock tube data on benzene pyrolysis obtained in the present work at ICARE. The figure indicates that the model in [114]

requires a factor of 10 to match the maximum experimental soot volume fractions, more importantly, exhibiting a notable temporal shift relative to the onset of soot production. This shift results from modeling soot formation chemistry solely based on PAH chemistry, as previously noted. Nonetheless, the basic structure and global rules of the CRECK model were chosen as it allows a detailed description of the particle chemistry through the use of pseudo-lumped species sections that discretize the entities involved in soot formation, along with a clear methodology for rate-rules and kinetic parameter assignment. In this thesis, this model has been appropriately refined to develop a new detailed kinetic soot sectional model applicable across various fuels and operational conditions in pyrolytic environments, based on shock tube data. The novelty of this detailed kinetic model for soot lies in the combination of gas-phase chemistry with polyynes chemistry, as already introduced in the previous sections of this chapter. In light of existing sectional approaches to polyynes chemistry [110,112,162], this thesis introduces new gas-phase precursors and a new combined PAH-polyynes kinetics, extended also to the interactions within the soot model concerning inception and growth.

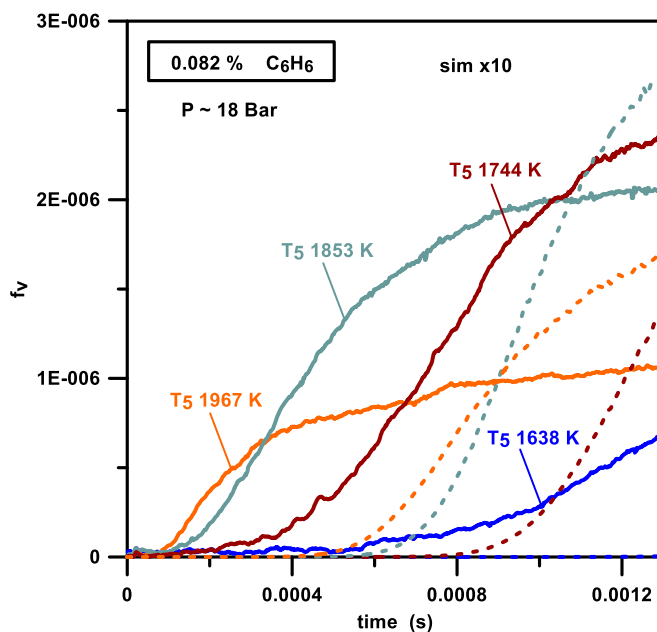


Figure 2.7.3.1 – CRECK Model [117] performance against benzene pyrolysis data obtained at ICARE in shock tube experiments. Experiments: continuous lines; CRECK model: dashed lines.

3. Experimental set-up

3.1 Shock tube theory.

The shock tube is a tubular reactor that belongs to the ideal reactor family and is used for a wide range of chemical kinetics studies [148,205–207]. It operates based on the physics of shock waves, which are disturbances that can occur in either a closed or open space within a gaseous medium due to a local perturbation. This work explains the shock wave phenomenon and the operation of the shock tube, from the classical discussion by A. G. Gaydon and I. R. Hurle [206]. Unlike a classical sound wave, a shock wave causes a significant adiabatic, isentropic compression in a gaseous medium and travels at a velocity greater than the local speed of sound of the medium, as defined by (Eq 3.1.1) when considering an ideal gas. This results in a rapid, local, substantial, and irreversible increase in the medium's thermodynamic properties, such as pressure, temperature, and density.

$$\text{(Eq 3.1.1)} \quad a = \sqrt{\frac{\gamma \cdot P}{\rho}} = \sqrt{\frac{\gamma \cdot R \cdot T}{M}}$$

In (Eq 3.1.1), γ is the specific heat of the gas considered, ρ the density, and P the pressure. Since it is an ideal gas, it is possible to express P and ρ as functions of the ideal gas constant R , the temperature T , and the molecular weight M .

When a shock wave is generated, it propagates with a velocity $u \gg a$, causing the brutal perturbation to move the molecules of the gaseous medium following the direction of propagation. By means of (Eq 3.1.3), it is possible to introduce the so-called Mach number, which consists of the ratio of the velocity u of a generic disturbance or flow in a gas to the local velocity of sound in the same gas.

$$\text{(Eq 3.1.3)} \quad \text{Ma} = \frac{u}{a}$$

In general, if $\text{Ma} > 1$, the regime is supersonic, while if $\text{Ma} < 1$, it is subsonic.

In practice, a plane shock wave can be imagined according to the representation of Becker et al. [208] of 1922, whereby we consider a tube possessing a piston at one end, as in **Figure 3.1.1.a**, that is capable of performing an acceleration whereby it reaches a velocity v greater than the speed of sound in the gaseous medium. As in **Figure 3.1.1.b**, a small increase in dv in the piston velocity is then reached, which generates a weak compression wave at velocity a . The gas between the piston and the wave front has been uniformly and adiabatically compressed, having acquired another infinitesimal increase in velocity. As shown in **Figure 3.1.1.c**, the piston has reached a velocity $2dv$, and the resulting disturbance travels at a velocity $a+da$. Subsequent accelerations of the piston generate subsequent compression waves of increasing velocity. The compression waves finally merge into a single shock wave front, as shown in **Figure 3.1.1.e**, that moves at the velocity W_s . The column of gas moving between the piston and the shock front travels at velocity v . The wave front is planar and normal to the tube walls, and is capable of producing abrupt changes in pressure, density, and temperature as it travels across the shock tube through an irreversible process.

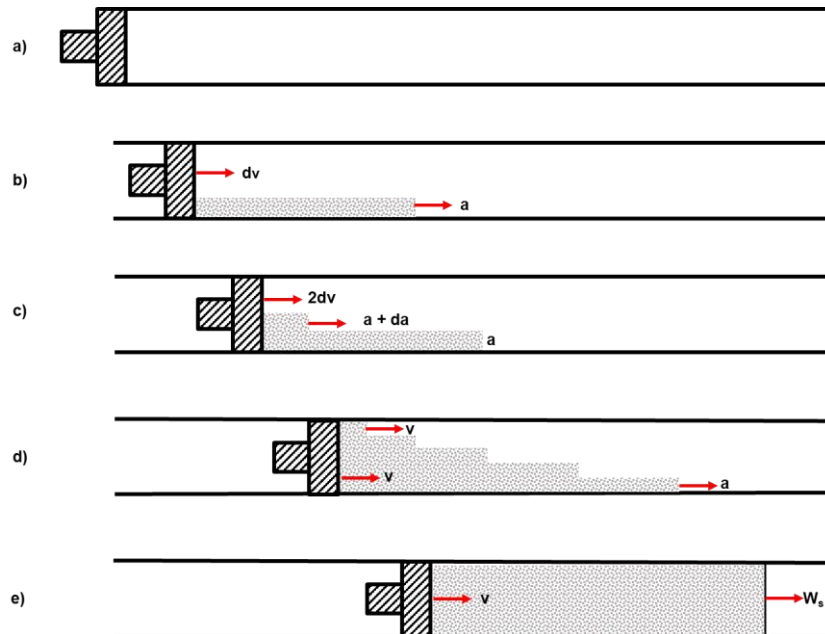


Figure 3.1.1 – Schematic model of shock wave formation adapted from [206].

Since a shock wave is capable of generating an isoentropic adiabatic transformation, the shock tube can be defined as an adiabatic reactor capable of achieving, via shock waves, defined pressure and temperature conditions. Energy exchange and molecular diffusion in the wall regions are negligible, as are heterogeneous reactions at the walls, due to the presence of the boundary layers. All these features make the shock tube particularly suitable for following the dynamics of chemical reactions or physical processes.

A shock tube, as schematized in **Figure 3.1.2**, generally consists of two main sections: a high-pressure (HP) section and a low-pressure (LP) section, separated by a diaphragm, as shown in **Figure 3.1.2**. Certain shock tubes implement the use of one diaphragm, others two (double diaphragm technique, DD). The LP section contains the gas under study, commonly called “Driven gas,” at the pressure and temperature states P_1 and T_1 . On the other side, the HP section contains an inert gas, called “Driver gas,” which is used to drive the gas expansion and the generation of the shock wave. The driver gas is initially at a state of pressure and temperature P_4 and T_4 . The DD dividing zone between HP and LP is generally at a pressure state P_{DD} and T_{DD} , which are about $P_4 \cdot 0.5$ and $T_{DD} = T_4$, respectively.

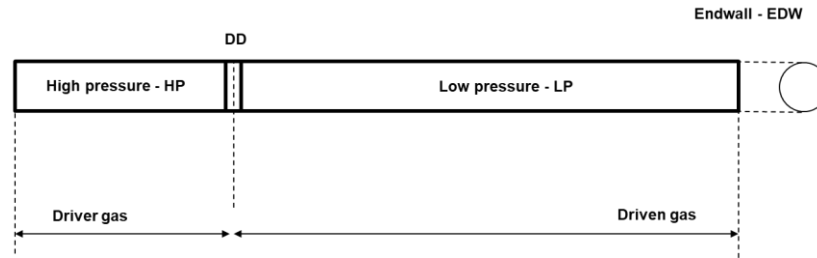


Figure 3.1.2 – Shock tube schematic.

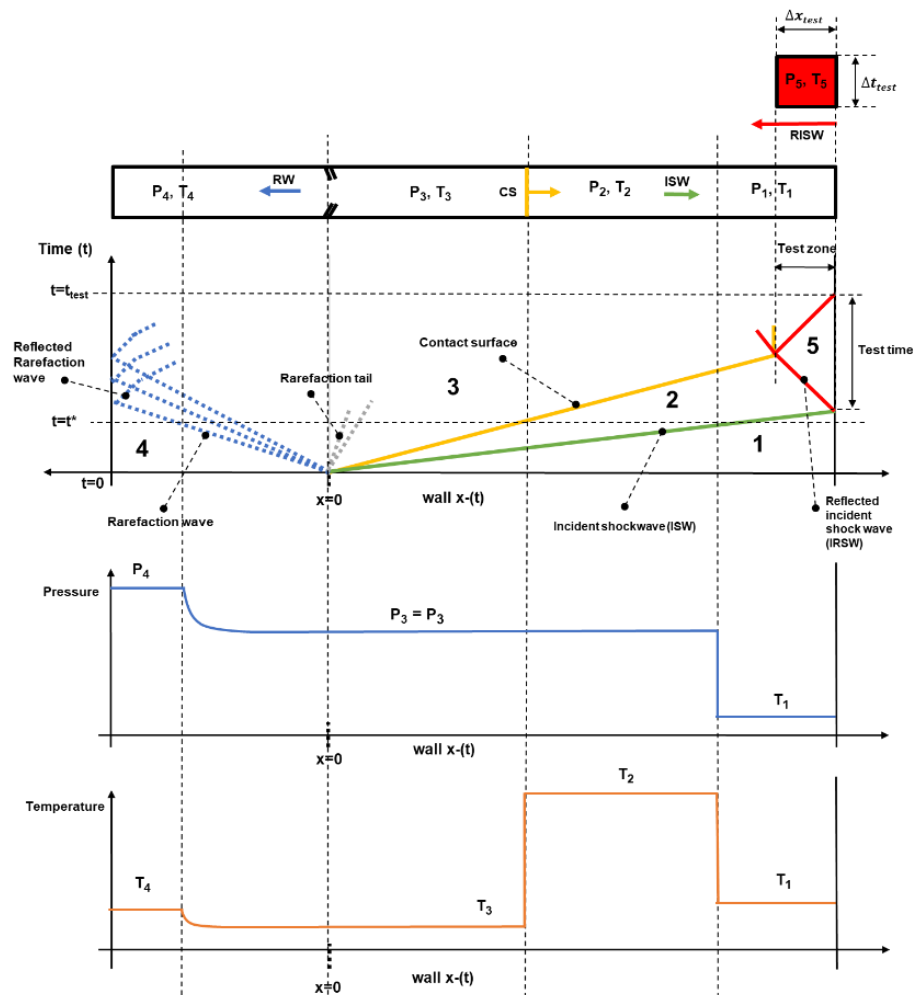


Figure 3.1.3 – Diagram of shock tube gas dynamics.

Figure 3.1.3 contains a diagram of the gas dynamics of the shock tube, in particular, the position in time of the different waves, the temperature, and the pressure along the shock tube (thus, as a function of the x-axis, $x = 0$ corresponding to the location of the diaphragm section). Once the gases in the driver and driven sections are loaded, the diaphragm ruptures, and a shock wave is generated in the driven section after the coalescence of the compression waves. The incident shock wave ISW arrives at the end-wall, and it is reflected as the reflected shock wave RSW. At the same time as the compression waves are generated, rarefaction waves are formed and travel along the driver section in the opposite direction. The speed of the second rarefaction wave is lower than that of the first, the speed of the third is lower than that of the second, and so on. The rarefaction waves finally form a rarefaction wave fan with increasing distance between the head and the tail.

Five regions are distinguished:

1. test gas, driven gas, or undisturbed low-pressure gas at the initial pressure and temperature values P_1 and T_1 ;
2. region between the shock front and contact surface CS at P_2 and T_2 ;
3. region between the contact surface and the rarefaction tail at P_3 and T_3 ;
4. driver gas, or high-pressure inert gas at P_4 and T_4 ;
5. zone behind the reflected shock wave at P_5 and T_5 .

It is possible to describe the gas dynamics of the shock tube by starting from the definition of the regions of interest and the corresponding gas properties, such as pressure, temperature, gas density, and velocity of the gas molecules, as shown in **Figure 3.1.4.a**. Generally, for the test gas region, the velocity v_1 is considered to be zero even if there is a non-stationary condition in front of the shock wave front. $\mathbf{W}_s$ is defined as the velocity of the shock front in the tube. Often, it is convenient to use as a convention the definition of relative velocities $\mathbf{u}_1$ and $\mathbf{u}_2$ as in **Figure 3.1.4.b**. In common terminology, $\mathbf{u}$ is denoted as the gas velocity measured in shock-fixed coordinates, while $\mathbf{v}$ is relative to the coordinates of the experimental apparatus:

$$\text{(Eq 3.1.5)} \quad u_1 = W_s - v_1$$

$$\text{(Eq 3.1.6)} \quad u_2 = W_s - v_2$$

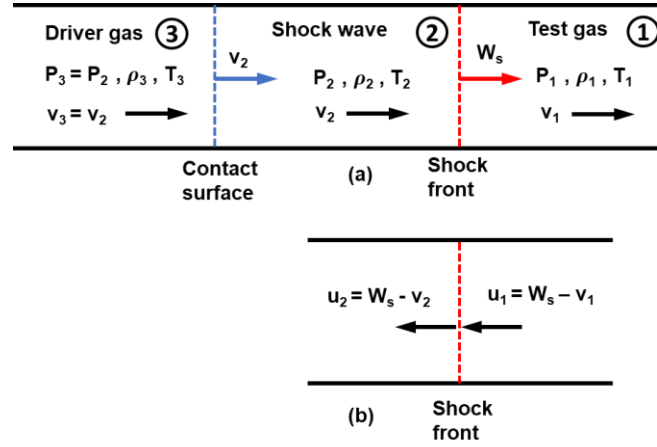


Figure 3.1.4 – Gas parameters associated with the shock wave in the two basic coordinate systems.
Adapted from [206].

Considering the introduced relative velocities u_1 and u_2 , it is possible to write the continuity equations to describe the system as follows:

(Eq 3.1.7) mass conservation: $\rho_1 u_1 = \rho_2 u_2$

(Eq 3.1.8) conservation of momentum: $P_1 + \rho_1 u_1^2 = P_2 + \rho_2 u_2^2$

(Eq 3.1.9) energy conservation: $h_1 + \frac{1}{2} u_1^2 = h_2 + \frac{1}{2} u_2^2$

h_1 and h_2 are the enthalpies of the initial and final states per unit mass for the gas involved, respectively. This analysis assumes that there is no heat exchange during the compression of the gases due to the shock wave, which is reasonable because the compression occurs over a distance of a few mean free paths. Radiative losses are negligible because of the gas's low emissivity, and convection at the walls is zero if the gas flow is not viscous. The conservation equations can then be solved for the ratios P_2/P_1 , ρ_2/ρ_1 , and T_2/T_1 .

The enthalpy is defined as in (Eq 3.1.10).

(Eq 3.1.10): $H = U + RT$

Since the magnitudes are considered per unit mass, they are defined as $h = \frac{H}{m}$ where m is the mass of the gas.

Pointing out that for ideal gases, c_v and c_p are constant and independent of temperature, it is possible to define enthalpy as $H = c_p T$. Considering also that $c_p = c_v + R$, it is also possible to introduce the parameter γ , the heat capacity ratio. From here, using the definition of h , it is possible to rewrite the enthalpy equation as:

$$\text{(Eq 3.1.11): } h = \left(\frac{\gamma}{\gamma-1} \right) RT = \left(\frac{\gamma}{\gamma-1} \right) \frac{P}{\rho}$$

3.1.1 Derivation of parameters for shock wave gas dynamics behind incident shock waves.

Rewriting the energy conservation equation (Eq 3.1.9) using the equation (Eq 3.1.11), it is possible to remove the presence of u_1 and u_2 , when also using the mass conservation equation, so:

$$\text{(Eq 3.1.1.1)} \quad \left(\frac{\gamma}{\gamma-1} \right) \frac{P_1}{\rho_1} + \frac{1}{2} u_1^2 = \left(\frac{\gamma}{\gamma-1} \right) \frac{P_2}{\rho_2} + \frac{1}{2} u_2^2 \rightarrow \text{(Eq 3.1.1.2)} \quad \frac{\rho_1 P_2 - \rho_2 P_1}{\rho_2 P_2 - \rho_1 P_1} = \frac{\gamma-1}{\gamma+1}$$

By rearranging (Eq 3.1.1.2), the following is obtained:

$$\text{(Eq 3.1.1.3)} \quad \frac{P_2}{P_1} = \frac{1 - \left(\frac{\gamma-1}{\gamma+1} \right) \frac{\rho_1}{\rho_2}}{\frac{\rho_1}{\rho_2} - \frac{\gamma-1}{\gamma+1}}$$

then:

$$\text{(Eq 3.1.1.4)} \quad \frac{\rho_1}{\rho_2} = \frac{\left(\frac{\gamma-1}{\gamma+1} \right) \frac{P_2}{P_1} + 1}{\left(\frac{\gamma-1}{\gamma+1} \right) \frac{P_2}{P_1} + 1} = \frac{u_1}{u_2}$$

(Eq 3.1.1.3) and (Eq 3.1.1.4) effectively expresses the ratio of shock wave parameters. This writing is known as the Rankine-Hugoniot formulation [209].

Moreover, by then combining (Eq 3.1.1.3) into (Eq 3.1.1.4), a simpler relationship can be obtained by expressing P_2/P_1 as:

$$(Eq\ 3.1.1.5) \quad \frac{P_2}{P_1} = 1 + \left(\frac{\rho_1 u_1^2}{P_1} \right) \left(1 - \frac{\rho_1}{\rho_2} \right)$$

From this point, the Mach number previously introduced is considered. Since the gas in front of the shock wave is in a steady state, still unperturbed by the disturbance, e.g., $v_1 = 0$ and $u_1 = W_s$. It follows that:

$$(Eq\ 3.1.1.6) : \quad M_1 = \frac{W_s}{a_1} = u_1 \left(\frac{\rho_1}{\gamma P_1} \right)^{\frac{1}{2}}$$

Substituting (Eq 3.1.1.6) for (Eq 3.1.1.5):

$$(Eq\ 3.1.1.7) \quad \frac{P_2}{P_1} = 1 + \gamma M_1^2 \left(1 - \frac{\rho_1}{\rho_2} \right)$$

Combining then (Eq 3.1.1.4) and (Eq 3.1.1.7) :

$$(Eq\ 3.1.1.8) \quad \frac{P_2}{P_1} = \frac{2\gamma M_1^2 - (\gamma - 1)}{\gamma + 1}$$

Equalizing (Eq 3.1.1.7) with (Eq 3.1.1.8) :

$$(Eq\ 3.1.1.9) \quad \frac{\rho_2}{\rho_1} = \frac{(\gamma + 1)M_1^2}{(\gamma - 1)M_1^2 + 2}$$

By then relying on the ideal gas law, the expression of the T_2/T_1 ratio is also obtained:

$$(Eq\ 3.1.1.10) \quad \frac{T_2}{T_1} = \frac{\left(\gamma M_1^2 - \frac{\gamma-1}{2}\right) \left(\frac{\gamma-1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma-1}{2}\right)^2 M_1^2}$$

The last three equations for pressure, temperature, and density can be used to derive the thermodynamic conditions behind the incident shock wave, knowing the initial state of the gas and W_s . It should be pointed out that the strength of the shock wave depends on the pressure ratio P_4/P_1 , thus on the pressure differential across the diaphragm. The maximum allowed pressure differential is a function of the type of diaphragm used (thickness, material, scoring, single vs DD).

It is also useful for design purposes to have expressions that express the properties of the driven gas and the driver gas as functions of properties of the incident shock wave, e.g., the shock wave velocity. Considering an isentropic process for ideal gases:

$$(Eq\ 3.1.1.12) \quad PV^\gamma = cost \rightarrow \frac{2a}{\gamma-1} + v = cost$$

Then:

$$(Eq\ 3.1.1.12) \quad \frac{2a_4}{\gamma_4-1} + v_4 = \frac{2a_3}{\gamma_3-1} + v_3$$

In (Eq 3.1.1.12), $v_3 = v_2$. Moreover, for continuity, $P_3 = P_2$ and $\gamma_3 = \gamma_4$. Then (Eq 3.1.1.12) becomes:

$$(Eq\ 3.1.1.13) \quad \frac{2a_4}{\gamma_4-1} = \frac{2a_3}{\gamma_4-1} + v_2$$

From the adiabatic law of the gases:

$$(Eq\ 3.1.1.14) \quad \frac{P_4}{P_3} = \left(\frac{a_4}{a_3}\right)^{\frac{2\gamma_4}{\gamma_4-1}} = \frac{P_4}{P_2}$$

Hence:

$$(Eq\ 3.1.1.15) \quad \frac{P_4}{P_2} = \left(\frac{a_4}{a_4 - \frac{\gamma_4-1}{2}v_2}\right)^{\frac{2\gamma_4}{\gamma_4-1}}$$

In addition, considering the equation of conservation of mass, energy, and momentum applied to (Eq 3.1.20), it is obtained:

$$(Eq\ 3.1.1.15) \quad v_2 = \frac{2a_1}{\gamma_1-1} \left(M_1 - \frac{1}{M_1}\right)$$

In this way, P_4/P_1 can be rewritten according to Mach number:

$$(Eq\ 3.1.1.17) \quad \frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left[1 - \frac{\gamma_4 - 1}{\gamma_1 - 1} \frac{a_1}{a_4} \left(M_1 - \frac{1}{M_1}\right)\right]^{\frac{2\gamma_4}{\gamma_4-1}}$$

(Eq 3.1.1.17) can be used to estimate the velocity of the incident shock tube for selected P_4/P_1 ratios. The ratio that guarantees the maximum shock strength is given for $\frac{P_4}{P_1} \rightarrow \infty$, resulting in:

$$\left\{1 - \frac{\gamma_4 - 1}{\gamma_1 - 1} \frac{a_1}{a_4} \left(M_1 - \frac{1}{M_1}\right)\right\} \rightarrow 0$$

Then, it follows (Eq 3.1.1.18):

$$M_1 \rightarrow \frac{\gamma_4 - 1}{\gamma_1 - 1} \frac{a_1}{a_4}$$

Generally, therefore, when strong shocks are desired, it is preferred to opt for driver gases that have a high speed of sound propagation and a low specific heat ratio, such as He or H₂. Another way to increase the strength of the shock is to increase the temperature of the driver gas. For these reasons, many facilities have driver gas heating systems.

3.1.2. Parameters behind the reflected shock wave in an ideal gas.

To derive the fundamental expressions of the parameters characterizing the state behind the reflected shock wave, it is essential to recall the schematization in **Figure 3.1.2.1**, which illustrates the velocities in the incident and reflected shock waves near the end wall.

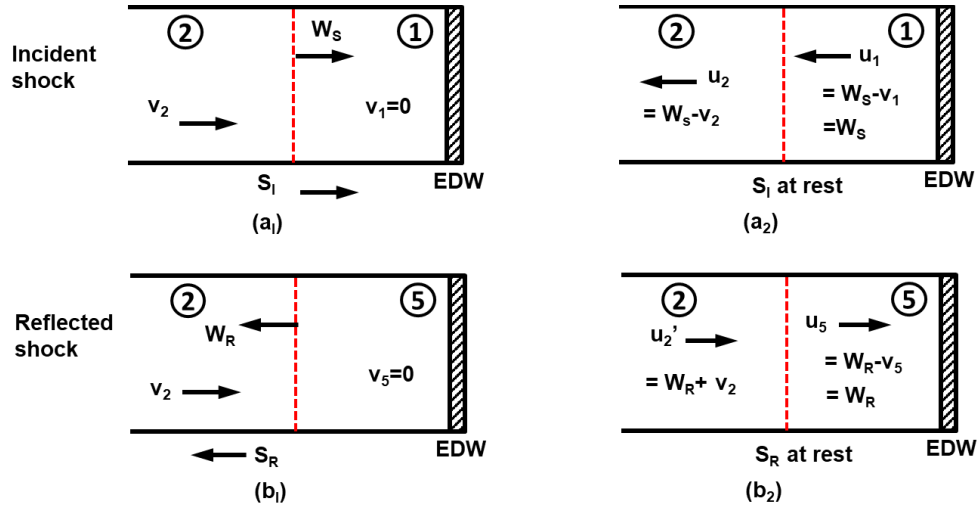


Figure 3.1.2.1 – Comparison between the particle-flow velocities before and after the reflection of a shock wave from a rigid wall. Adapted from [206].

Figures 3.1.2.1.a1 and 3.1.2.1.a2 The incident shock wave is initially propagating through region 1. When the front S_I , moving at velocity W_s relative to the tube, reaches the wall W , it is reflected as the front S_R , which travels back into region 2 with a reduced speed W_R . **Figure 3.1.2.1.b1.** The gas flows in region 2, speed u'_2 is:

$$(Eq\ 3.1.2.1) \quad u'_2 = W_R + v_2$$

From here, considering that after reflection, the wave velocity becomes zero, $v_5 = 0$. The reflected shock moves in the opposite direction to the end-wall. Referring to **3.1.2.1.b2** it is possible to rewrite the velocity of the particles relative to the reflected shock front and the Mach number as:

$$(Eq\ 3.1.2.2) \quad u_5 = W_R - v_5$$

$$(Eq\ 3.1.2.3) \quad u'_2 = W_R + v_2$$

$$(Eq\ 3.1.2.4) \quad M_R = \frac{u'_2}{a_2}$$

Similarly used in the previous discussion, using the equations of conservation of mass, momentum, and energy combined with (Eq 3.1.1.18):

$$(Eq\ 3.1.2.5) \quad u_1 - u_2 = v_2 - v_1 = \frac{2a_1}{\gamma-1} \left(M_1 - \frac{1}{M_1} \right)$$

Therefore, revaluating (Eq 3.1.2.2) and (Eq 3.1.2.3):

$$(Eq\ 3.1.2.6) \quad u'_2 - u_5 = v_2 + v_5 = \frac{2a_2}{\gamma-1} \left(M_R - \frac{1}{M_R} \right)$$

Considering that the gas initially in the shock tube is at rest, so $v_1 = 0$, and $v_5 = 0$, the following equation is obtained:

$$(Eq\ 3.1.2.7) \quad v_2 = \frac{2a_1}{\gamma-1} \left(M_1 - \frac{1}{M_1} \right) = \frac{2a_2}{\gamma-1} \left(M_R - \frac{1}{M_R} \right)$$

The first part of the equation (Eq 3.1.2.7) is the velocity behind the incident shock wave relative to the shock tube, which is also that of the contact surface. Considering the equation:

$$(Eq\ 3.1.2.8) \quad \left(\frac{a_2}{a_1}\right)^2 = \frac{P_2}{P_1} \cdot \frac{\rho_1}{\rho_2}$$

and substituting $\frac{\rho_2}{\rho_1}$:

$$(Eq\ 3.1.2.9) \quad \left(\frac{a_2}{a_1}\right)^2 = \frac{P_2}{P_1} \left(1 + \frac{\gamma-1}{\gamma+1} \cdot \frac{P_2}{P_1}\right) \left(\frac{\gamma-1}{\gamma+1} + \frac{P_2}{P_1}\right)^{-1}$$

Using the analogy with (Eq 3.1.1.7):

$$(Eq\ 3.1.2.10) \quad \frac{P_5}{P_2} = \frac{2\gamma M_R^2 - (\gamma-1)}{\gamma+1}$$

Solving (Eq 3.1.2.5) - (Eq 3.1.2.10), the equation that determines the ratio $\frac{P_5}{P_2}$, so:

$$(Eq\ 3.1.2.11) \quad \frac{P_5}{P_2} = \frac{\frac{\gamma+1}{\gamma-1} + 2 - \frac{P_1}{P_2}}{1 + \frac{\gamma+1}{\gamma-1} \cdot \frac{P_1}{P_2}}$$

Using the ideal gas law:

$$(Eq\ 3.1.2.12) \quad \frac{T_5}{T_2} = \frac{P_5}{P_2} \left\{ \frac{\frac{\gamma+1}{\gamma-1} + \frac{P_5}{P_2}}{1 + \frac{\gamma+1}{\gamma-1} \cdot \frac{P_5}{P_2}} \right\}$$

(Eq 3.1.2.11) and (Eq 3.1.2.12) make it possible to determine the conditions behind the reflected shock wave also by means of $\frac{P_2}{P_1}$, so it is possible to define:

$$(Eq\ 3.1.2.13) \quad \frac{P_5}{P_1} = \left\{ \frac{2\gamma M_1^2 - (\gamma - 1)}{\gamma + 1} \right\} \left\{ \frac{(3\gamma - 1)M_1^2 - 2(\gamma - 1)}{(\gamma - 1)M_1^2 + 2} \right\}$$

$$(Eq\ 3.1.2.14) \quad \frac{P_5}{P_2} = \frac{\{2(\gamma - 1)M_1^2 + (3\gamma - 1)\} \{(3\gamma - 1)M_1^2 - 2(\gamma - 1)\}}{(\gamma + 1)M_1^2}$$

And finally, the relationship between $\frac{W_R}{W_S}$ can be determined as:

$$(Eq\ 3.1.2.15) \quad \frac{W_R}{W_S} = \frac{2 + \frac{2}{\gamma - 1} \frac{P_1}{P_2}}{\frac{\gamma + 1}{\gamma - 1} \frac{P_1}{P_2}}$$

3.1.3. Test time definition.

Test time can be defined as the time between the incident shock wave arrival at the end-wall at coordinates x_1 , t_1 , and the time when the reflected shock wave hits the contact surface at coordinates x_2 , t_2 . In fact, the interaction between RSW and the contact surface generates compression or rarefaction waves that travel towards the end-wall, modifying the reaction zone conditions.

$$(Eq\ 3.1.3.1) \quad \Delta\tau = x_1 \left(\frac{W_S - v_2}{W_R - v_2} \right)$$

Expressing W_R in terms of $W_S = M_1 a_1$, and reconsidering the expression of $\frac{P_2}{P_1}$ and v_2 as a function of the Mach number, the test time can be expressed as:

$$(Eq\ 3.1.3.2) \quad \Delta\tau = \frac{x_1}{M_1 a_1} \left(\frac{\gamma - 1}{2\gamma} \right)$$

This approximation is valid if the shock is strong and $M_1^2 \gg 1$. For tailored conditions, when $\rho_2 \cdot a_2 = \rho_3 \cdot a_3$, no wave is reflected by the contact surface. In this case, the uniform conditions would, in theory, persist until the arrival of the reflected rarefaction head.

3.2 ICARE heated shock tube - HST.

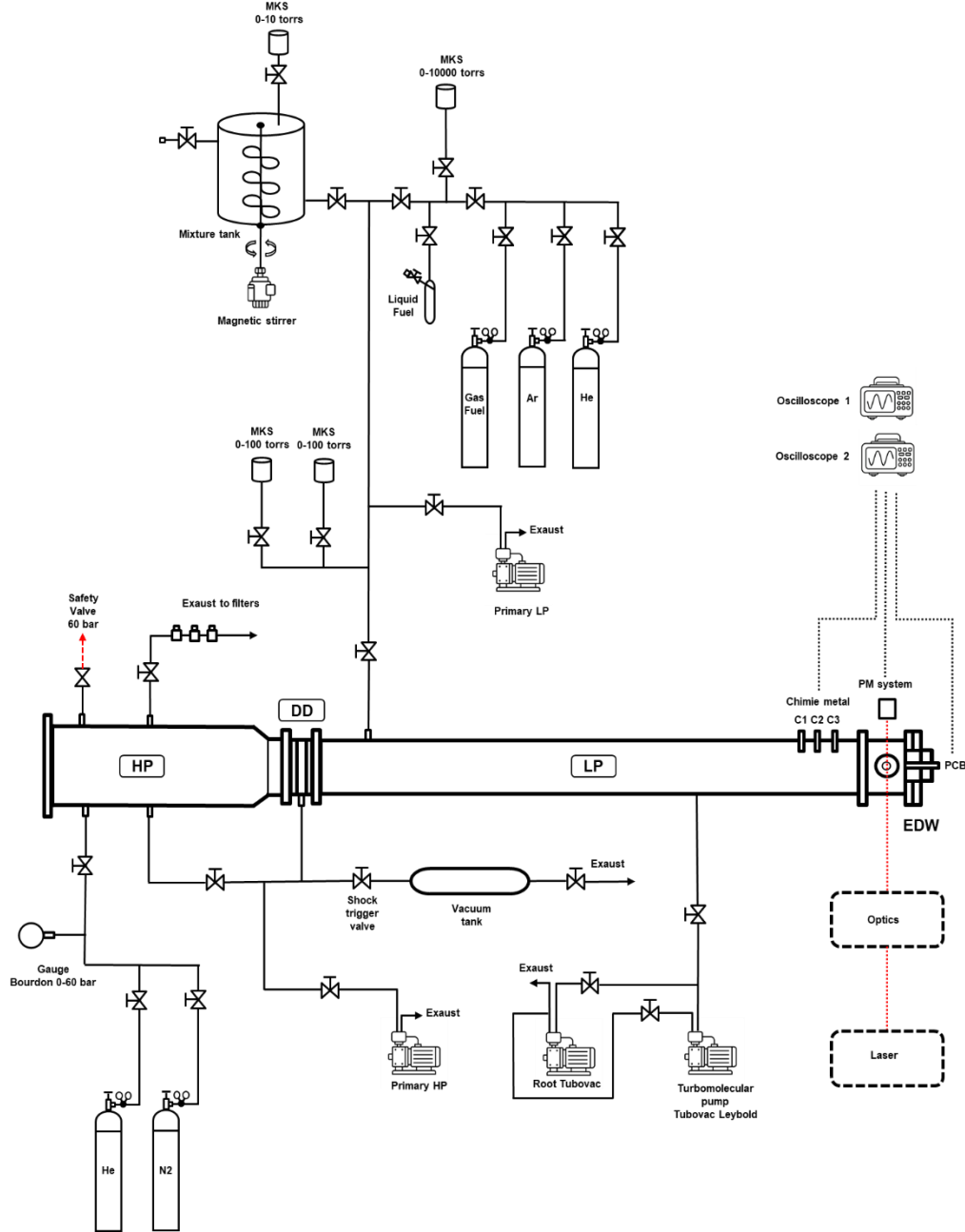


Figure 3.2.1 – Schematic diagram of the ICARE Heated Shock Tube (HST) set-up.

Figure 3.2.1 schematizes the heated shock tube facility at ICARE. The HST has been widely used for high-temperature kinetic studies, especially on soot formation [210–212]. The setup typically includes a heating system starting from the end of the high-pressure section close to the DD and covering the entire low-pressure section, and another separate heating system for the tank for mixture preparation and the transfer lines. The heating systems were not used for the experiments presented here.

Once the preparation is complete, the mixture is transferred to the driven section. Specifically, for the test gas loading procedure, a process known as 'passivation' of the surfaces is performed. This procedure involves the following steps:

1. Creating a vacuum in the low-pressure section using a primary pump followed by a turbomolecular pump;
2. Loading the driven section with 1 atm of mixture to let the fuel molecules adsorb into the metallic surface (passivation); the loading pressure of 1 atm prevents any air entrance during the loading time (around 3 minutes);
3. Fast evacuation of the driven section with the primary pump down to 1 Torr;
4. Loading the driven section with the desired amount of test gas mixture.

3.2.1 High-pressure section.

The high-pressure section, also commonly called the driver section, is 2 m long and 114.3 mm in diameter. It contains the gas that drives the shock, initially at a high pressure, denoted as P_4 , and temperature T_4 . Inert gases are generally used, even if different compositions can be selected to tailor the experimental conditions. A combination of He, in the majority, and N_2 is generally used for typical experiments with the HST. A safety valve is placed with a limit value of 50 bar to evacuate the gas in case of accidental overloading.

3.2.2 Double diaphragm section.

The double diaphragm section consists of a stainless steel element with a cylindrical cross-section, which holds two diaphragms creating a small chamber. The diaphragms are constituted by terphane membranes of various thicknesses, depending on operating conditions, between 20 and 420 μm . They are locked to the DD section by steel portholes with O-rings to maintain the seal. The chamber between the diaphragms is loaded with the driven gas at the pressure $P_{\text{DD}} \sim P_4/2$. It is also connected through a flexible tube and a ball valve to a cylinder, which is initially under vacuum. When the experimental setup is ready for firing, the ball valve is opened, abruptly decreasing the pressure inside the DD chamber. This will result in the breaking of the diaphragms and the generation of the shock wave.

3.2.3 Low-pressure section.

The low-pressure section, also called the driven section, is 5.15 m long and has an inner diameter of 5.4 mm. The inner side of the LP has been finely polished to minimize molecular adsorption and, equally importantly, to prevent flow perturbations behind the shock wave caused by the side wall's interaction with the boundary layer. The loading of the low-pressure section occurs in two different moments: 1) the test mixture with the fuel is loaded to around 100-200 Torr and let inside the shock tube for around 5 minutes for saturation of its inner surface; indeed, adsorption of heavy fuels can occur on the inner surface as the shock tube was unheated; 2) after pumping the driven section to around 1-2 Torr, the test mixture is loaded to the desired P_1 condition.

3.2.4 Vacuum pumping system.

The pumping system is composed of:

- 1) 1 EDWARDS rotary pump for the HP and DD sections, down to a pressure of approximately 10^{-2} Torr;
- 2) 1 ALCATEL rotary pump connected to the LP section and the mixture preparation rig. The low-pressure section is also pumped through a Leybold Turbovac 361

molecular turbopump, which is used to achieve a vacuum level of 10^{-4} mbar. The mixture preparation rig can also be pumped by means of the turbopump through the LP section, if needed.

3.2.5 Test time and conditions.

Optical access to the shock tube is ensured by the presence of quartz windows located 10 mm from the end wall. The measurements are performed behind the reflected shock waves, where the gases are quiescent and uniformly shock-heated. In order to calculate P_5 and T_5 through the classical shock wave equations, it is necessary to measure the velocity of the incident shock wave together with the initial T_1 and P_1 conditions. This is done through signals collected by three CHIMIE METAL A25L05B piezoelectric sensors located toward the end of the LP, and a PCB sensor mounted at the end-wall (PIEZOTRONICS Model 482C series). The signals are collected by three Rohde & Schwarz RTB 2004 oscilloscopes, together with the signals from the laser diagnostic. CHIMIE METAL's sensors, C3, C2, and C1, are spaced 150 mm, 152 mm, and 160 mm from each other. Their response time is very short, of the order of microseconds, providing an accurate estimate of the shock wave passage. Their surface is flush with the inner wall of the tube to reduce interference with the passage of the shock wave. The PCB sensor is shielded with a layer of RTV to reduce the effects of heating, which drifts the signal, and it is used to record the time-history pressure signal over time in the test zone. **Figure 3.2.5.1** shows the signals of CHIMIE METAL and PCB for calculating the incident shock speed, which is used to determine P_5 and T_5 .

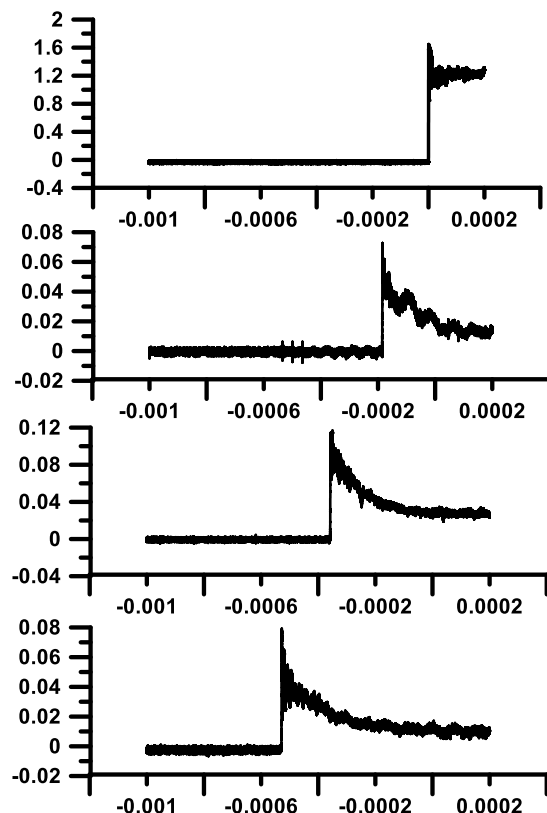


Figure 3.2.5.1– Pressure signals vs time. 0.35 % acetylene in argon $T_5 = 1742\text{ K}$, $P_5 = 17.6\text{ bar}$.

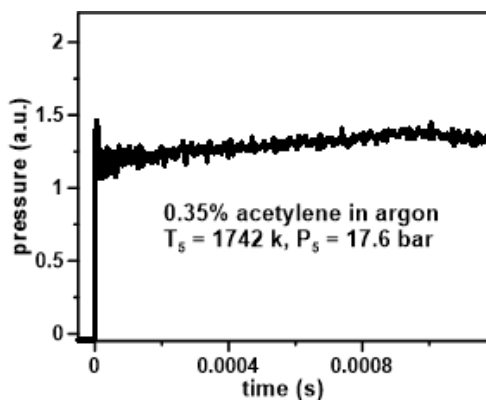


Figure 3.2.5.2– A typical example of a PCB signal of the ICARE Heated Shock Tube (HST) set-up.

The length of the shock tube affects the determination of the test time. However, the thermodynamic properties of the gases are also relevant. In particular, in successive kinetic studies over the years, techniques of “tailoring” test gas conditions have emerged for conventional shock tube techniques [213,214]. These techniques aim at reducing the effects

of the interaction between the contact surface and RSW, as well as delaying the arrival of the rarefaction head in the reaction zone. In addition, the use of a buffer gas has been tested as useful for removing the typical bumps observed in the pressure time-histories due to such interaction [213,214]. For the HST at ICARE, the following optimal conditions were experimentally determined:

- in the T_5 range 1520-1750K, 20-23% He of buffer gas in the gas test, 12.5-20% N_2 in the driver gas complemented by He;
- in the T_5 range 1520-1750K, 23-25% He of buffer gas in the gas test, 10% N_2 in the driver gas complemented by He.

As shown in **Figure 3.2.5.2**, to achieve reliable measurements, the f_v values are effectively treated as a 1.3 ms time limit, consistent with the pressure profile provided. This decision is based on the fact that this interval captures the moment before the contact surface and rarefaction waves arrive, allowing for accurate measurement of P_5 and T_5 . s

3.2.6 End wall.

For the measurements of soot volume fractions and particle diameters, a new type of end-section was designed. The end-section contains five windows positioned at the angles 0° , 90° , 180° , 225° , and 335° , with two additional plugs for the installation of windows or sensors. The end-wall plug can be removed and replaced to collect deposited soot particles at the end of the experiment, without removing the PCB sensor. The entire end-section has been blackened to avoid possible light reflection inside the shock tube. More details about this can be found in [215].

3.2.7 Laser and Optics.

The HST was appropriately set up to make simultaneous laser extinction and multi-angle Rayleigh scattering measurements. As shown in **Figure 3.2.7.1**, two types of lasers were implemented: 1) Helium-Neon laser @ $\lambda = 633$ nm to perform extinction measurements; 2) Quantum laser, OPUS 532 @ $\lambda = 538$ nm for multi-angle scattering measurements. The

optical system consists of mirrors (M1, M2, M3), lenses (L1, L2), and dichroic mirrors (DM1, DM2). Additionally, photodetectors PH1 and PH2 are installed (HAMAMATSU R5938P) connected to a high-voltage system HV1 and HV2. The 532 nm laser system is equipped with a chopper capable of modulating the signal intensity up to 40 kHz.

A system of photomultiplier tubes (PMT) HAMAMATSU R5938P is positioned at the windows to acquire signals, connected through a high-voltage system HV1 and HV2, and interfaced with two Rohde & Schwarz oscilloscopes, RTB2004.

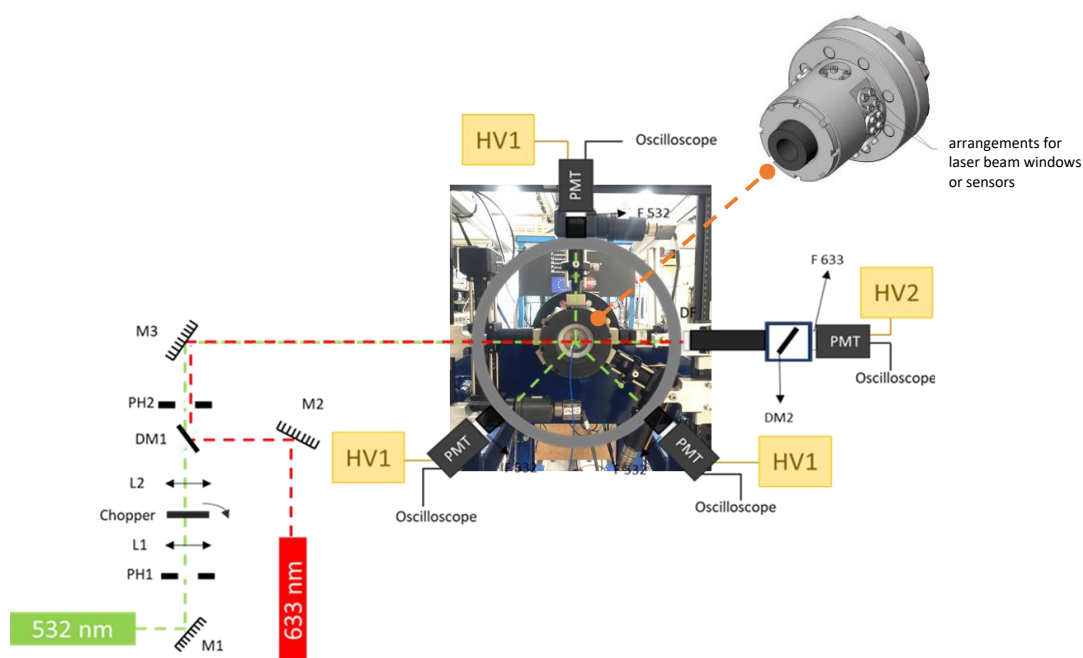


Figure 3.2.7.1– End-section and laser set-up for the HST at ICARE.

3.2.8 Mixture tank.

The mixture is prepared in a stainless-steel tank with a volume of 30 L, featuring an integrated stirring system driven by a magnetic stirrer with a holder equipped with six blades. Its pressure limit is about 4 bar. Under pyrolytic conditions, the prepared mixtures consist of one or two fuels diluted in Ar, introduced subsequently into the tank. Fuels can be introduced in three ways:

- 1) if the fuel is gaseous, through a flexible line from the fuel cylinder to the tank, isolated by a valve;
- 2) if the fuel is liquid and the vapor pressure is sufficiently high, the fuel is loaded into a bulb connected to the mixing rig through a valve, which is opened to allow the vapor to enter the tank;
- 3) if the fuel is liquid and the vapor pressure is not sufficient, the fuel is injected with a syringe through a septum installed on the tank.

Four capacitive MKS pressure manometers, of different ranges (0-10 Torrs, 0-100 Torrs, 0-1000 Torrs, 0-10000 Torrs), are used during mixture preparation to accurately measure the partial pressure of each component, with minimal error in the composition.

3.2.9 Experimental conditions.

The mixtures and associated experimental conditions examined in this study are detailed in **Table 2**. The initial fuel mole fractions were carefully selected to maintain a consistent carbon concentration across all investigated cases. Toluene served as the reference compound; its concentration was chosen to have nearly 90% of the maximum extinction of the laser signal at the selected conditions. Notably, the preliminary tests on acetylene and ethylene indicated the need for increased carbon concentrations to attain enough soot for accurate measurements. Thus, several sets with different initial mole fractions were obtained for acetylene, and only one set for ethylene with even larger carbon concentrations. Ethylene, propylene, propyne, argon, and helium were provided by Air Liquide, with a purity level exceeding 99.999%. For stability, acetylene from Air Liquide is dissolved in acetone. To effectively remove any residual acetone, a Matheson filter was used in conjunction with a flame arrestor for enhanced safety. Toluene, benzene, and cyclopentene were provided by Sigma-Aldrich, with purities greater than 99.7%.

Based on **Table 2**, it is evident that multiple fuels have been selected according to a clear hierarchy to probe for different soot formation pyrolytic mechanisms.

C₂H₂ was specifically examined for its kinetic role as a fundamental component in soot formation, not only through the HACA mechanism, but also as a precursor of

polyacetylenic compounds (polyynes). As PAH formation is very limited at high temperatures (the kinetic pathways to the first ring are not favorable in these conditions), the polyynes mechanisms can thus be isolated by considering acetylene alone.

C_2H_4 , on the other hand, is a fuel involved in the chemistry of C_2/C_3 species, particularly at high temperatures, and fundamental in the pathways of vinyl chemistry formation. The effects of the different hydrogenation levels compared to acetylene can be evaluated.

C_3 species, such as C_3H_4 -P (propyne) and C_3H_6 (propylene), are fundamental in the mechanisms of aromatic compound formation, as they generate propargyl radicals (C_3H_3) under pyrolytic conditions. These radicals are recognized as key intermediates in the synthesis of the first benzene ring. Through recombination and isomerization reactions, these radicals promote the transition from aliphatic to aromatic chemistry, significantly contributing to the initiation of PAH growth. The role of small resonantly stabilized radicals can then be verified.

Benzene (C_6H_6) represents the first stable aromatic ring and is a key fuel for understanding PAH chemistry in soot formation (PAH+PAH reactions), as it promotes the formation of the main precursors of PAH/LPAH, which contribute to the soot inception process.

Toluene is a reference substituted aromatic in the study of soot formation, as the presence of the methyl group promotes the formation of the benzyl radical, a resonance-stabilized species that accelerates the initial stages of PAH growth. Under pyrolytic conditions, toluene is more reactive than benzene and contributes more efficiently to the formation of PAH precursors through the chemistry of resonantly stabilized PAHs.

The CYC_5H_8 represents a key fuel whose chemical mechanism acts as a bridge between aliphatic and aromatic chemistry, thanks to the formation of small stabilized resonant cyclopentadienyl radicals C_5H_5 that enable the rapid formation of benzene and naphthalene. The role of small cyclic intermediates can then be highlighted.

Finally, ethylbenzene is the simplest among the alkylbenzenes, key components of real fuels. As its decomposition promotes the formation of the benzyl radical, validation of the model allows verification of the corresponding chemistry for a more complex molecule compared to toluene, for application to surrogate fuel chemistry. Similarly, styrene chemistry was selected for its central role in soot formation from real fuels.

The examined binary mixtures were also considered to evaluate the synergies between the C2/C3 aliphatic and key aromatic fuels, in relation to soot formation, compared to the case of pure aromatic/cyclic fuel.

Table 2 - List of the gas mixtures used in the heated shock tube considered in this work.

Mixtures	Temperature T _s , K	Pressure P _s , bar	[C]x10 ¹⁷ atoms/cm ³
0.07%C ₇ H ₈ +99.93%Ar	1518-1990	16.4-18.2	3.03-3.92
0.03%C ₇ H ₈ +0.15%C ₂ H ₂ +99.82%Ar	1607-1916	17.0-18.0	3.34-3.87
0.03%C ₇ H ₈ +0.15%C ₂ H ₄ +99.82%Ar	1571-1978	16.2-18.6	3.05-3.68
0.02%C ₇ H ₈ +0.11%C ₃ H ₆ +99.87%Ar	1609-1978	16.7-18.9	3.24-4.07
0.02%C ₇ H ₈ +0.11%C ₃ H ₄ +99.87%Ar	1562-1960	16.3-18.7	3.20-4.16
0.082%C ₆ H ₆ +99.918%Ar	1537-1967	16.4-18.3	3.06-3.90
0.03%C ₆ H ₆ +0.15%C ₂ H ₂ +99.82%Ar	1582-1975	16.7-18.6	3.23-3.85
0.03%C ₆ H ₆ +0.15%C ₂ H ₄ +99.82%Ar	1645-2017	16.1-18.7	3.10-3.71
0.098%CYC ₅ H ₈ +99.902%Ar	1551-1968	16.6-18.6	3.21-3.85
0.03%CYC ₅ H ₈ +0.16%C ₂ H ₂ +99.81%Ar	1576-1953	16.6-18.6	3.27-3.81
0.245%C ₂ H ₂ +99.755%Ar	1750-1989	16.8-18.1	3.09-3.63
0.35%C ₂ H ₂ +99.65%Ar	1603-1980	16.7-18.2	4.47-5.55
0.7%C ₂ H ₄ +99.3%Ar	1685-2017	16.9-20.7	8.95-11.2
0.16%C ₃ H ₆ +99.84%Ar	1598-1968	16.0-18.6	3.07-3.99
0.16%C ₃ H ₄ +99.84%Ar	1586-1951	16.8-19.4	3.32-4.11
0.06% Ethylbenzene+99.94%Ar	1560-1939	16.56-18.9	3.23-4.0
0.06% Styrene+99.94%Ar	1567-1942	17.35-18.5	3.17-3.98

3.2.10 Mixture preparation.

Mixture preparation is a key process in determining the desired experimental conditions in a kinetic study. For pyrolytic conditions, the experimental mixture contains no oxygen, and the fuel is diluted purely in Ar. For fuels in the liquid state, whose vapor pressure is used to fill the tank, a purification procedure is carried out. The liquid fuel to be purified is

placed in a Schlenk tube and subjected to subsequent freezing and thawing cycles for the removal of the initial air present in the bulb and light impurities. Usually, the procedure is repeated 3 times, or until no more gases are present when the fuel is frozen. In the mixture preparation procedure, the tank is pumped with a rotary pump down to around 0.1 Torr. The tank is then flushed with argon to remove any residual from the previous mixture and then pumped down once again. The partial pressure method is used to determine the initial composition.

3.2.11 Induction delay time and growth rate definition.

The experimental and modeling profiles were also used to extract additional kinetic parameters characterizing the soot formation process, as shown in **Figure 3.2.11.1**, such as the soot induction times and the surface growth rates.

The induction time, τ_{ind} , is commonly defined as the time required for the appearance of the first solid nuclei, and it can be estimated as the time between the passage of the reflected shock wave at the observation point and the time obtained by extrapolating the f_v profile at the baseline. The surface growth rate is the rate at which the mass or volume of soot particles increases due to chemical reactions occurring on their surface, obtained by fitting the experimental profile at the location of maximum $df_v(t)/dt$.

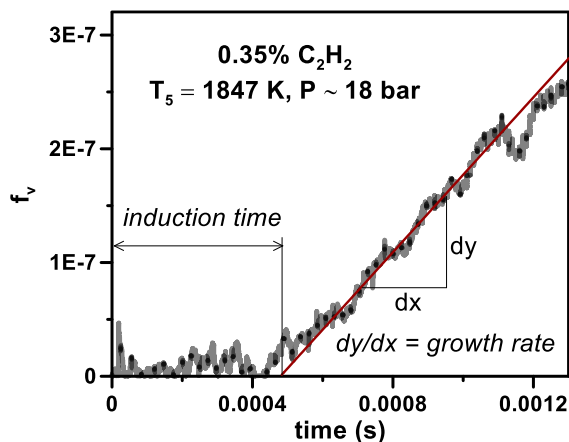


Figure 3.2.11.1– Induction delay time and growth rate definition.

3.2.12 Experimental uncertainties.

Regarding experimental uncertainties, there are two primary sources concerning the f_v quantification. The error in $E(m)$ is the main factor. Compared to the value selected in this work (0.37), other studies in the literature have used different properties to extract the experimental f_v , e.g., in [212]. More importantly, $E(m)$ varies not only with the type of soot produced but also over time as the particles grow. $E(m)$ values for nascent particles are expected to be very different from those for mature soot. A priori, at each time, the average particle size distribution and properties, and the associated $E(m)$ should be known. Introducing a constant $E(m)$ introduces an error. Considering all this, the estimated uncertainty in the soot volume fractions is at least 50%. The second source of error for f_v is the characterization of the particle density, again a function of time. For example, evidence shows that nascent particles have a density of around 1.1 g/cm³, while mature soot has a density close to 1.85 g/cm³ [118].

In addition, the estimated errors in the temperature and pressure conditions are 1% and 1.5%, respectively, based on the error in the measurement of the incident shock wave velocity (around 1%).

An example of uncertainty analysis will be provided in **section 6.1.1**.

4. Soot Mechanism Automated Generator (SMAuG) - framework.

In this chapter, the mechanism generator designed to produce the detailed thermodynamics and kinetics of the soot mechanism is presented. The acronym SMAuG stands for Soot Mechanism Automated Generator, a comprehensive Python-based framework designed for soot kinetic models employing the discrete sectional method. The mechanisms generated need to be coupled to the gas-phase section as close to the specific fuels of interest, including the thermal decomposition steps and the growth to small PAH compounds.

4.1 The features of SMAuG.

The initial version and overall architecture of SMAuG were specifically designed to facilitate the management and optimization of the model generation. As illustrated in **Figure 4.1.1**, the framework comprises a central core responsible for the main operations, complemented by dedicated modules for rate rule methods and reaction classification. Activation of the generator occurs via the execution of the SMAuG.py script, which enables users to generate reaction classes and input the relevant kinetic parameters. Additionally, this script incorporates features for tuning the reaction parameters through correction coefficients. The framework also includes a simulation environment developed with Cantera [216], supporting zero-dimensional (0-D) constant-pressure simulations, and it is equipped with an intuitive graphical user interface (GUI). Supplementary tools are provided for post-processing simulation data, facilitating data comparison, and managing experimental datasets.

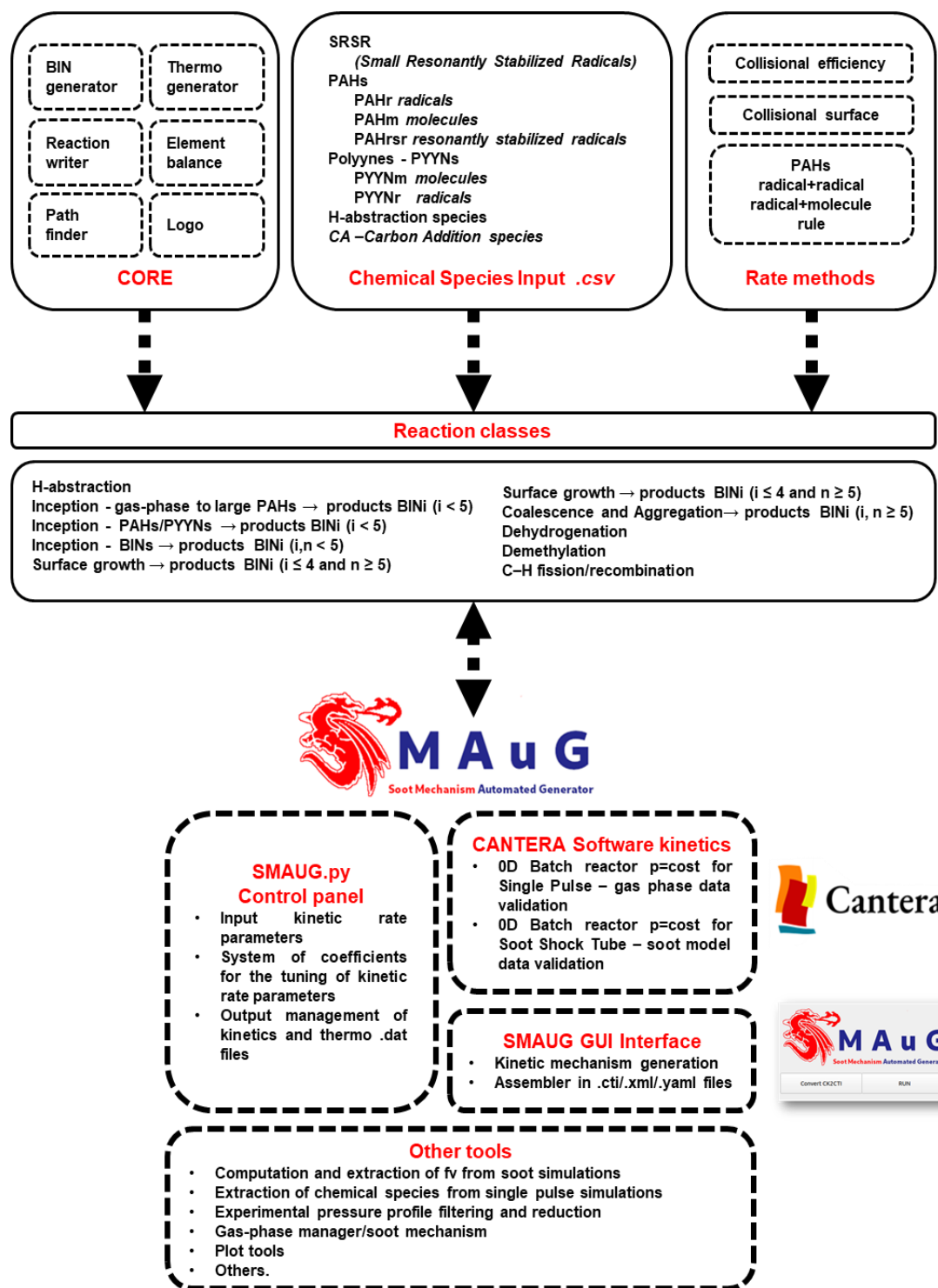


Figure 4.1.1– Overview of the framework's primary features.

4.2 Core.

This is the core code of the mechanism generator. It contains the fundamental scripts:

- **BIN Generator:** it creates BINs either by using Python functions or by importing BIN details from a .csv file into the framework, using the properties for each BIN section as input. These properties include the number of carbon, hydrogen, H/C ratio, characteristic dimension of the BIN entities, and atomic mass.
- **Thermo Generator:** it calculates and generates the thermodynamic properties of BIN species using the group additivity method described in the relevant section.
- **Reaction Writer:** it allows writing kinetic mechanism reactions for reactants, products, and kinetic parameters in a kinetic output ".dat" file.
- **Element Balance:** it checks and calculates the carbon and hydrogen content for reactants and products. It also allows for the adjustment of the hydrogen balance in the products when necessary, such as adding hydrogen in the form of radical H or molecule H₂, depending on the type of reactions. It is closely linked to the reaction class scripts, utilizing the lever method to maintain carbon and hydrogen balance through evaluation of the H/C ratio (see the relevant section).
- **Pathfinder:** a simple script used to define script paths within the generation logic.
- **Logo:** It displays the SMAuG logo once the mechanism generation process has started.
- **Chemical species input:** a collection of gas phase chemical species input files, in standard .csv format, used by reaction classes to define and write soot inception and growth reactions. Each input file concerns a family of chemical species, radicals, or molecules, and contains their name, number of carbon and hydrogen atoms, and H/C ratio. The files in the framework concern: chemical species involved in the HACA mechanism, PAH radicals and molecules, resonantly stabilized PAH radicals, small resonantly stabilized radicals, polyynes radicals and molecules.

4.3 Rate methods.

Rate methods are used in the framework for different processes, including dimerizations, molecule-molecule interactions (with collision efficiency), surface growth reactions, and interactions between polycyclic aromatic hydrocarbons (PAHs) involving radical-radical or radical-molecule dynamics. Rate methods are techniques that, within a general rate rule, adjust interactions between chemical species by calculating a correction coefficient. This coefficient is applied to the pre-exponential factor A of the Arrhenius equation (or to the temperature exponential). In contrast, a rate rule is a broader concept that defines how to express the reaction rate for a specific class of reactions. For example, a rate rule might specify that reference kinetic parameters like A , n , or E_a are used without any correction. Specifically, a rate method applies a parametric correction based on the characteristic size of the species involved and the type of their interactions, whether radical-radical, radical-molecule, or molecule-molecule.

4.4 Reaction classes.

Several classes of reactions are incorporated within the framework, as shown in **Figure 4.1.1**. Their operation varies depending on the kinetic contributions they make to the model, but all follow a typical pattern, illustrated in **Figure 4.4.1**. Reactions can be unimolecular, bimolecular, or trimolecular. Specifically, trimolecular reactions are generated in a few cases when the addition of a hydrogen atom is needed for specific hydrogen balancing challenges. In this case, the reaction order is effectively reduced to a bimolecular reaction by using the FORD option. For each reactant, the following information is defined: the name, the number of carbon (C) and hydrogen (H) atoms, the H/C ratio, and its type (radical or molecule). Based on this data and the reaction type, the total carbon and hydrogen content of the reactants is calculated and verified in the core using the `element_balance.py` module. The implementation of the leverage rule, which involves selecting the appropriate hydrocarbon (HC) species and the type of products generated (radical-radical, molecule-radical, or molecule-molecule), enables the determination of the reaction products. These products can be further modified by adding

radical or molecular hydrogen species, depending on the reaction. After completing the element balance and formulating the reaction equation, the rate rule for the reaction class is applied. Depending on whether this rule specifies fixed kinetic parameters or allows for corrections using a particular rate method, the final kinetic parameters are assigned based on the initial input.

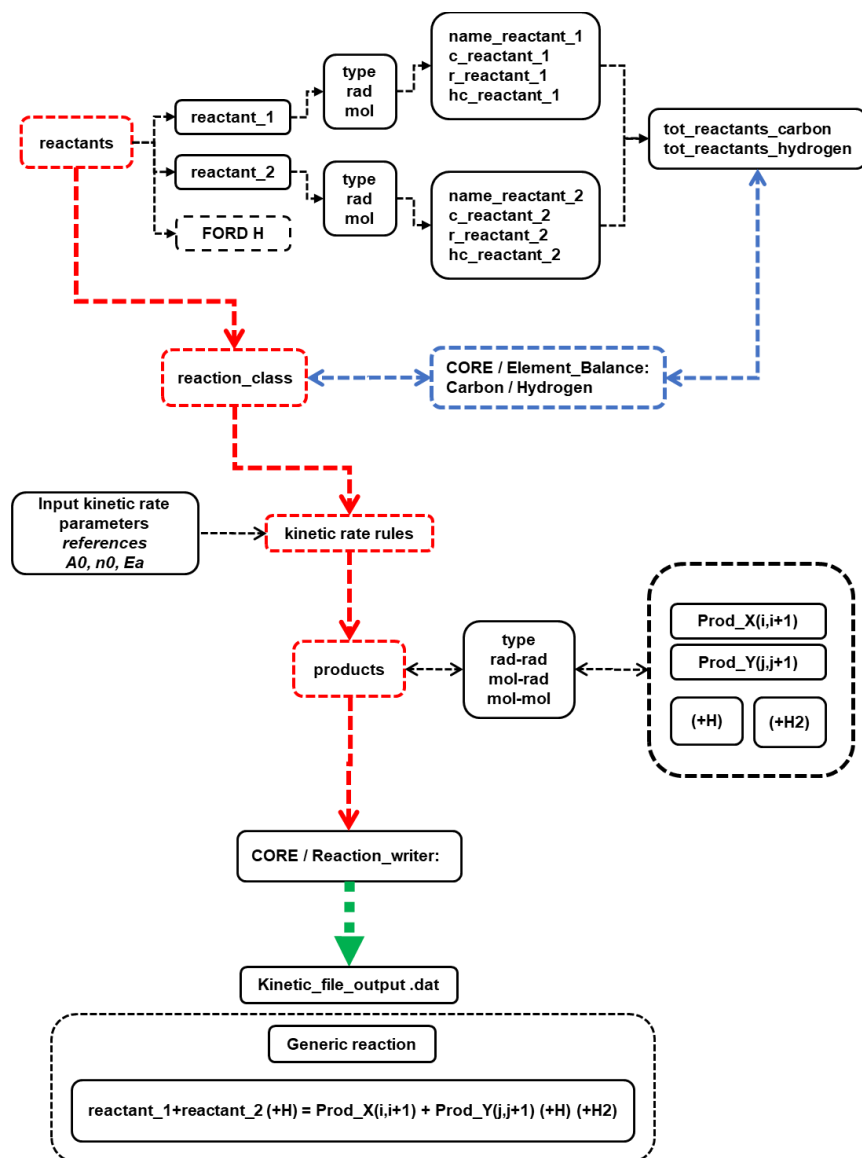


Figure 4.4.1– Logical diagram of reaction assembly in SMAuG.

4.5 SMAuG.py and Kinetic parameters input.

The SMAuG.py file allows the generation of the kinetic model by the following functions:

- calling the BIN creation function;
- generating the thermo file;
- writing the kinetic mechanism file;
- selecting the reaction classes;
- inserting the kinetic parameters;
- applying manual tuning coefficients to the kinetic parameters.

The tuning coefficients of the kinetic parameters are adjustment factors that are manually calibrated during the validation procedure against experimental data, with the support of rate-of-production (ROP) analyses performed with CHEMKIN [217] or brute-force sensitivity with SMAuG. SMAuG can be launched from a terminal within Ubuntu or Windows environments or accessed via a simple GUI (Graphical User Interface).

In general, the reaction classes, which correspond to the main mechanisms involved in soot formation, such as HACA, inception, growth, dehydrogenation, C-H scission, methylation, and demethylation, are called in SMAuG.py through a function that can be generalized as follows:

```
Reaction_class("reactant_species_list_1","reactant_species_list_2",
              hydrogen_radical = value, hydrogen_molecule = value,
              product_type = 'type',
              A0_value = A0_ref_f(reactants),
              n0_value = n0_ref_f(reactants),
              Ea0_value = Ea0_ref_f(reactants),
              set_op=NF,
              file_name=CKI).function_name_reaction_assembler()
```

In this generic example, *reactant_species_list_1* and 2 correspond to the groups of involved reactants, such as 'PAH+PAH' (radicals/molecules) or 'PAH+BINs', 'BINs+BINs', and so on. *hydrogen_radical* and *hydrogen_molecule* are corrections to the stoichiometry in terms of hydrogen balance, which results in the addition of H and/H₂ in the products consistently with the number of radicals in the reactants. The kinetic parameters A_0 , n_0 , and E_{a0} correspond to the reference kinetic parameters, depending on the type of chemical or physical mechanism. *set_op* considers the variable NF , which, depending on its value (0 or 1), allows writing of the reaction rates at selected temperatures in the model, when needed for evaluation during the parametric optimization of the reference kinetic constants. *file_name* manages the printing of the reactions called during compilation/storing in a dedicated kinetic file. *function_name_reaction_assembler* is the function that allows the reaction class to assemble reactants/products and rate rules that modify the kinetic constants based on the type of reactants, considering chemical or physical interactions, H/C ratio of reactants, or their characteristics.

4.6 Manual tuning procedures for rate kinetic parameters.

The SMAuG.py file includes a structure for adding correction coefficients related to reference kinetic parameters such as A , n , and E_a . These coefficients are primarily designed to adjust the kinetic parameters concerning:

- a specific reaction class;
- the reactivity of a specific group of chemical species, across one or more reaction classes;
- on specific interactions that can be related to radical-radical, radical-molecule, molecule-molecule. Additionally, such corrections can also be made based on the reactivity of the reacting species, for example, if a radical is a resonance-stabilized radical, etc...

This structure aims to favor the optimization of the kinetic parameters.

4.7 Mechanisms assembler.

A script for managing kinetic and thermodynamic files, which combines both the kinetics files and the thermodynamics files of the gas phase and the soot model into a single unified kinetic mechanism / thermodynamic file.

4.8 GUI – Graphic User Interface.

SMAuG provides a user-friendly graphical interface. Currently, there are two main options available: one for automatic generation of the mechanism and the other for conversion to Cantera format for simulations.

4.9 Integrated Cantera environment.

This section provides a brief overview of the tools implemented in Cantera related to the active simulation environment. Within the SMAuG framework, the Cantera software's kinetic environment is utilized to perform 0-D reactions using the IdealGasReactor function within a batch reactor system. The reactor operation diagram can be found in [218]. The IdealGasReactor has been properly modified to meet the simulation needs, allowing simulations at constant volume. The generated data is exported in .csv format to support standard post-processing, and a pandas DataFrame has been created for this purpose.

The soot volume fractions are calculated based on knowledge of the mass fraction of species BINJ(5-25), the density of the soot, and the density of the gas in the reactor, according to Eqn(4.1) as proposed by [203]:

$$\text{Eqn(4.1): } f_v = \frac{\rho_i \sum_{i=5}^{25} w_i}{1.85 \text{ g/cm}^3}$$

Since f_v is a time-dependent function, it is calculated up to a simulation time extension of 1.3 ms. From the time profile, f_v can also be evaluated at selected times, such as 0.5 ms and 1.0 ms.

Additional functional scripts have been implemented as tools for extracting f_v at different times from the simulations, reducing the experimental pressure profiles, extracting chemical species from an output file, managing the kinetic mechanism, and plotting.

5. Soot chemical kinetic model for pyrolytic conditions.

This section provides an in-depth description of the implementation aspects developed in this work, with particular attention to the kinetic modeling of the soot formation process under pyrolytic conditions for a variety of fuels, including both aromatic and aliphatic compounds, as well as some of their binary mixtures. The first part of the chapter illustrates the extension and validation of the gas-phase kinetic mechanism, specifically referring to the reactive pathways leading to the formation of polyynes up to species containing twelve carbon atoms (C_{12}), starting from acetylene chemistry. The reference model used as a basis is the one developed by Hamadi et al. [50] at ICARE, appropriately modified and refined to meet the objectives of this study. The detailed kinetic mechanism proposed in this work is based on the concept of pseudo-grouped binary species of carbon/hydrogen (BINs), in accordance with the CRECK scheme [115–117] under pyrolytic conditions, and also incorporates the same thermodynamic and structural properties of precursors and soot particles. In the new proposed model, the contribution of the gas-phase chemistry of polycyclic aromatic hydrocarbons (PAHs) has been integrated with that of polyynes to more comprehensively describe the formation mechanisms of soot precursors. The interaction between the two reactive pathways has also been included in the solid-phase modeling, extending to surface growth processes of the soot particles.

5.1 Upgrade of ICARE gas-phase chemistry.

The gas-phase chemistry of acetylene thermal decomposition and polyynes growth up to $C_{12}H_2$ has been revised compared to the original CRECK model [117] and ICARE PAH model [50], which contained reactions up to only C_4H_2 and C_6H_2 , the main polyynes deriving from the pyrolysis of the aromatic and aliphatic fuels in highly diluted conditions. The main reaction rate parameters for the polyynes chemistry are reported in **Table 3**.

Table 3 - Reaction and reaction rate parameters for polyynes formation and growth. Units in mol cm s K cal. These parameters are evaluated in $k=A \cdot T^n \cdot \exp(-E_a/RT)$

Reaction	A	n	E _a	Ref.
$C_2H+H(+M) = C_2H_2(+M)$	1.0E+17	-1.0	0	[115], k_∞
$C_{2x}H+H = C_{2x}H_2$ ($x>1$)	1.0E+14	0	0	est.
$C_{2x}H+C_{2y}H = C_{2(x+y)}H_2$	1.2E+14	0	0	[108]*
$C_2H+C_{2x}H = C_{2x+2}H+H$	1.2E+14	0	0	[219]x1.2
$C_{2x}H_2+C_{2y}H_2 = C_{2(x+y)}H_2+H_2$	1.51E+13	0	42700	[219]
$C_{2x}H_2+C_{2y}H_2 = C_{2(x+y)}H_2+2H$	1.51E+14	0	56000	[219]
$C_{2x}H_2+C_{2y}H = C_{2(x+y)}H_2+H$	1.0E+13	0	0	[115]/1.5**
$C_{2x}H_2+C_{2y}H = C_{2x}H+C_{2y}H_2$	5.0E+13	0	0	[219]*2.5
$C_{2x}H+H_2 = C_{2x}H_2+H$	4.9E+05	2.5	560	[115]

* Adjusted to maintain analogy with similar reactions; ** Reference for $C_2H_2 + C_2H = C_4H_2 + H$

The validation of the gas-phase model for acetylene pyrolysis was conducted using representative data sets extracted from established literature works. **Figure 5.1.1** illustrates the time-history profiles of species consumption and formation, based on a study by Aghsaee et al. [220], performed under pyrolytic conditions in a shock tube. The objective of this study was to investigate acetylene pyrolysis at nearly atmospheric pressures and temperatures exceeding 2200 K. The molar fractions of acetylene are 5% in **Figure 5.1.1a** and 2% in **Figure 5.1.1b**. In **Figure 5.1.1a**, the model predicts the consumption of C_2H_2 . C_4H_2 and C_6H_2 are simulated using a correction factor of 2. For these species, the model demonstrates good agreement with experimental trends during the initial production phases. However, deviations become apparent at longer reaction times, with the experimental data diverging from the simulated results. In **Figure 5.1.1b**, which considers a lower fuel mole fraction but similar temperature and pressure conditions, an improvement in the model's predictive performance is observed regarding both consumption of the fuel

and formation of the products. In this case, no correction factor is necessary. Nonetheless, at extended timescales, a divergence persists in the behavior of C_4H_2 , which initially exhibits production followed by subsequent consumption, tending toward a steady state that is slightly lower than the experiments.

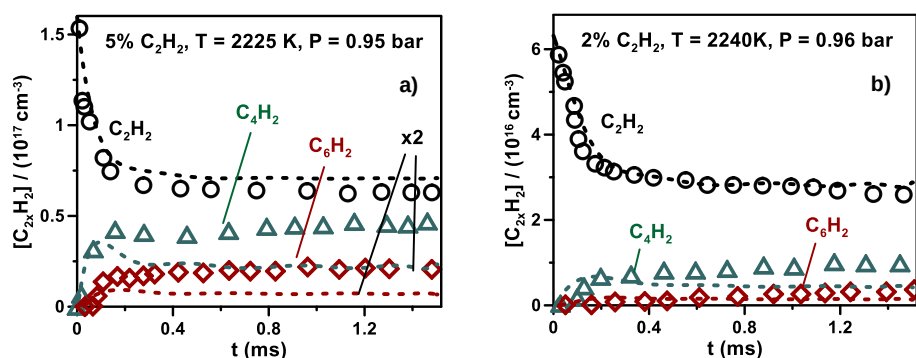


Figure 5.1.1 – Shock tube time-histories of 2% and 5% C_2H_2 at $P \sim 1$ atm. Symbols: experiments from [220]; lines: simulations.

Figure 5.1.2 presents a further comparison between the proposed model and the experimental observations related to the time histories of shock tube data, using the data provided by Wu et al. [221], under conditions of lower pressure compared to the previous example, equal to 0.41 atm, with an initial molar fraction of acetylene of 3.2% and temperatures ranging from 2030 K to 2430 K. As highlighted, the model's performance shows a significant dependence on thermal conditions. Regarding acetylene, the predictions are generally in agreement both qualitatively and quantitatively with the experiments, although a slight deviation at higher temperatures is observed, characterized by a slightly higher fuel consumption at the longer times. For the C_4H_2 species, as shown in **Figures 5.1.2a** and **5.1.2b**, the production rate is slightly faster than the experimental data. **Figure 5.1.2a**, which shows a behavior that is qualitatively and quantitatively plausible up to 0.3 ms, indicates that above such time the experimental and modeling trends differ, resulting in an underprediction of the diacetylene experimental profile. On the other hand, in **Figure 5.1.2b**, the model's behavior for C_4H_2 more closely aligns with the experimental data. At higher temperatures, as shown in **Figure 5.1.2c**, diacetylene production is predicted with reasonable accuracy, but at longer times, the experimental

measurement is underestimated by a factor of approximately 50%. Finally, for the C_6H_2 species, the predictions are overall reliable, with a single exception in **Figure 5.1.2a**, where an overestimation is noted compared to the experimental data.

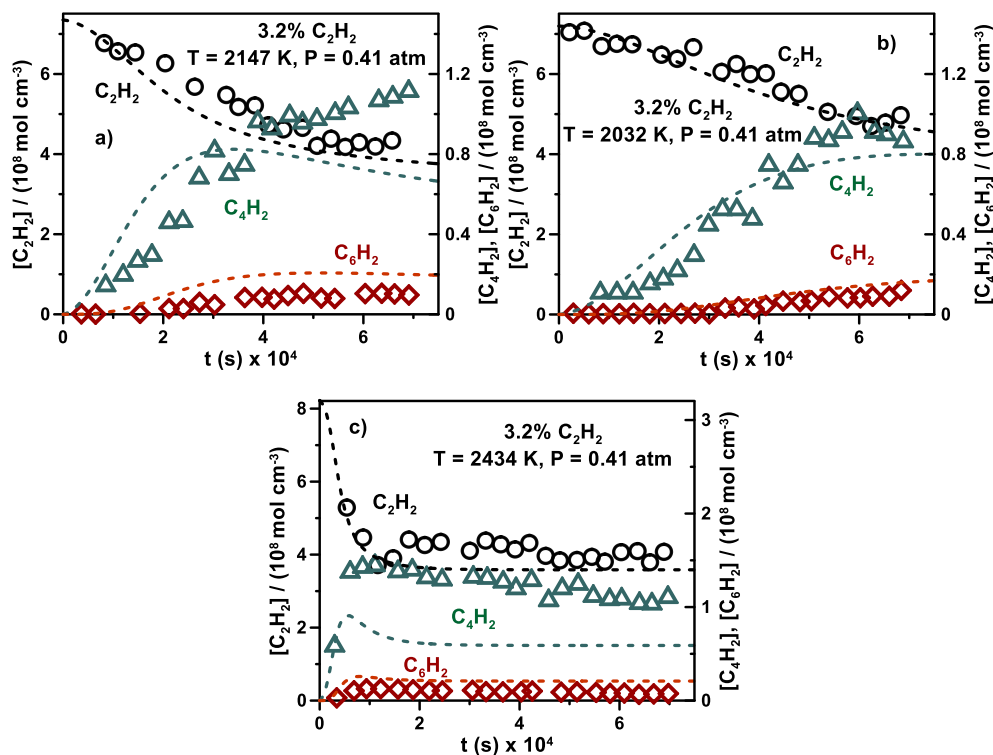


Figure 5.1.2 – Shock tube time-histories of 3.2% C_2H_2 at $P = 0.41$ atm at different temperatures. Symbols: experiments from [221]; lines: simulations.

In addition to the previously presented time-history results, the model has been further validated against speciation studies conducted in single-pulse shock tubes. Specifically, **Figure 5.1.3** illustrates the comparison with experimental data obtained by Colket et al. [222], which include measurements for both benzene and phenylacetylene, as shown in **Figure 5.1.3b**. Regarding acetylene consumption, **Figure 5.1.3a** illustrates the model's predictions starting from an initial concentration of 3.7% at a pressure of 8.1 bar within a temperature range of 1200 to 2400 K. The model predicts a slightly faster fuel consumption rate compared to experimental observations. Uncertainties in the temperature estimation are not provided by the author. Though the experimental temperatures are higher than usual ranges for chemical thermometers, uncertainties up to 50 K are expected.

The prediction of diacetylene formation is overall accurate; however, it exhibits a slight premature onset relative to the experimental data. The C_6H_2 species profile is simulated with accuracy. **In Figure 5.1.3**, the modeled benzene profile has a significant shift in the formation temperature, but a global trend that reflects the experimental profile; the vinylacetylene simulations align well with experimental observations. The modeled production of phenylacetylene (C_8H_6) corresponds with the experimental trend up to approximately 1500 K, beyond which a peak at 1600 K is observed in the simulations, followed by a decline in concentration, which is not observed in the experiments.

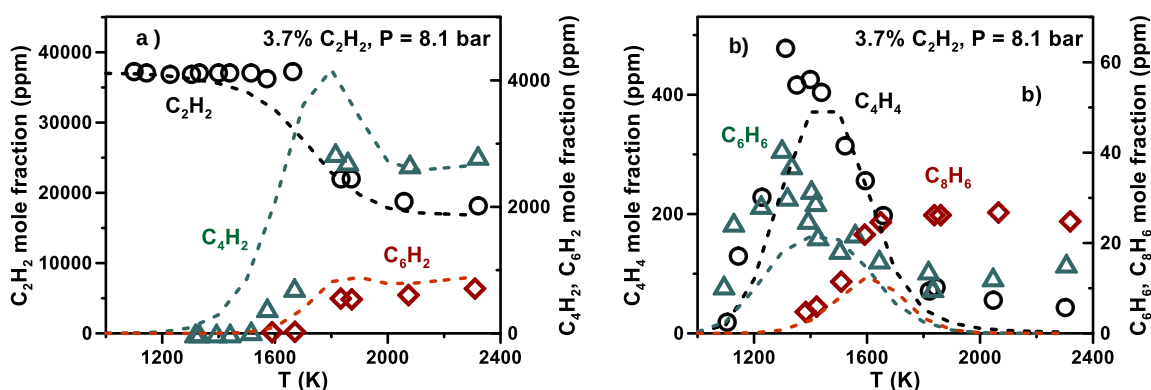


Figure 5.1.3 – Single Pulse shock tube data, 3.7 % C_2H_2 at $P = 8.1$ bar. Symbols: experiments from [222]; lines: simulations..

An additional dataset from single-pulse shock tube experiments, derived from the work of Hidaka et al. [223], has been used for model validation, as illustrated in **Figure 5.1.4**. Specifically, the experimental profiles were obtained with a molar concentration of 2.5% C_2H_2 and an initial pressure of 1.85 atm. The results demonstrate that the model accurately predicts acetylene consumption, though it slightly underestimates the values near 1800 K. Detailed evaluation of the model performances would require knowledge of the time-history pressure profiles, which are not provided in the work and which could affect the experimental results. The formation of diacetylene occurs earlier in the simulation compared to the experimental observations, but overall exhibits a consistent trend with the empirical data. Additionally, the model underestimates the concentration of C_6H_2 by

approximately 50%, despite correctly predicting the temperatures at which the production begins.

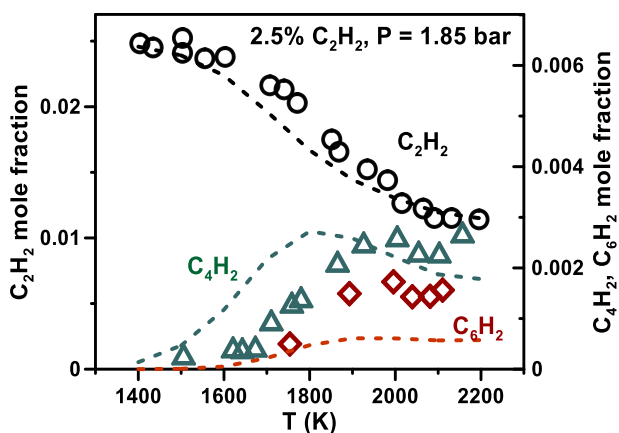


Figure 5.1.4 – Single Pulse shock tube data, 2.5 % C_2H_2 at $P = 1.85$ bar. Symbols: experiments from [223]; lines: simulations.

Based on the experimental and modeling data on acetylene pyrolysis presented, overall, the predictions for the fuel decay are found to be accurate and reliable. Concerning C_4H_2 , there is a notable tendency toward early predictions for its production. Except for the two cases in **Figures 5.1.2 and 5.1.2c**, the amount of diacetylene produced is quantitatively well reproduced. Additionally, the general simulation trends for triacetylene (C_6H_2) are consistent with empirical data. To further investigate the validity of the implementations related to the chemistry of polyynes in the gas phase, a comparison was made with time-history pyrolytic data obtained in shock tube experiments for 1% C_4H_2 , as reported by Kern et al. [224], at a pressure of 0.32 atm for two different temperatures, 1882 K and 1993 K (**Figure 5.1.5**).

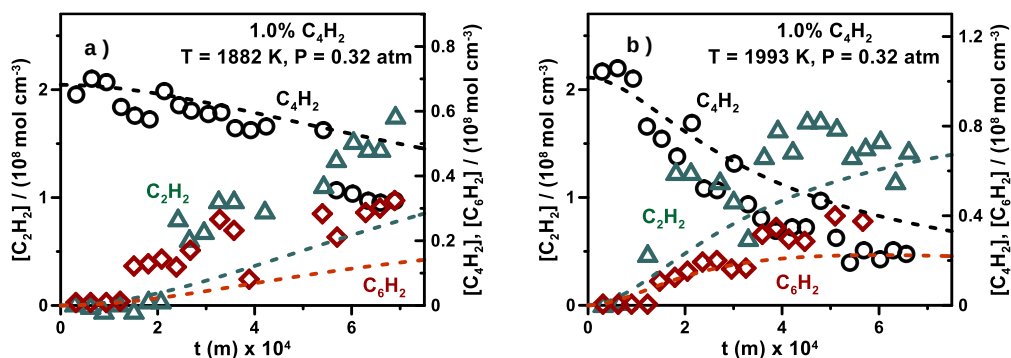


Figure 5.1.5 – Shock tube time-histories of 1% C_4H_2 at $P = 0.32$ atm. Symbols: experiments from [224]; lines: simulations.

In the case of **Figures 5.1.5a** and **5.1.5b**, the model generally demonstrates a robust capability to replicate diacetylene consumption across various temperatures. However, both datasets exhibit a pronounced step change in experimental measurements around 0.55 ms, with notable scattering in the data. An examination of the overall trend suggests that these fluctuations may be attributable to inherent experimental variability. Regarding the predicted C_2H_2 concentration at $T = 1882$ K, the model underestimates the concentration by approximately 50%, although it captures the overall linear trend. For the 1993 K simulation, the onset of acetylene formation is successfully predicted, albeit with a slight underestimation of the quantity produced, consistent with experimental fluctuations. These fluctuations suggest that the model's predictions remain relatively reliable within the experimental uncertainties. Concerning the triacetylene modeling profiles, the behavior depicted in **Figures 5.1.5a** and **5.1.5b** exhibits close qualitative and quantitative agreement with the consideration of the acetylene production, reflecting similar patterns and responses in the experimental and simulated data.

5.1.1 Polyacetylenes as gas-phase soot precursors.

In the first stage of the soot formation modeling process, regarding the generation of pseudo-lumped BIN species, two main mechanisms were considered and implemented based on the CRECK methodology [115–119]. The first concerns the formation mechanism of polycyclic aromatic hydrocarbon (PAH) precursors from the gas phase, through a direct growth involving the formation of the first aromatic ring up to the generation of large PAH precursors, contributing to the formation of the first primary soot particle. The second mechanism involves the direct formation of BIN species starting from relatively long polyacetylene chains ($C_{10}H_2$, $C_{12}H_2$), with the contribution of the related radicals, as proposed by Krestinin's modeling [106,107,109], following the scheme $PAH_m + PAH_m$, $PAH_m + PAH_r$, and $PAH_r + PAH_r$.

In this initial phase, applying a model strictly based on the contribution of PAH precursors produced volumetric soot estimates that were significantly lower than experimental data,

underestimating them by about two orders of magnitude. Consequently, tests were performed increasing the kinetic parameters for surface growth, coalescence, and aggregation to much larger values compared to the common estimates, in order to compensate for the insufficient route through the PAH growth. In addition to being fundamentally incorrect, this approach led to a substantial overestimation of soot volume fractions produced starting with aromatic fuels, such as benzene.

As an additional attempt to improve the simulation results, the adoption of direct nucleation steps between long-chain polyacetylenic species, as proposed by Krestinin, was also considered, but this strategy did not yield satisfactory results. Following the above, numerous attempts have been made using different reactive schemes and kinetic parameter optimizations both in the gas phase and in the sub-mechanisms of the solid phase. Despite these efforts, the following was observed: 1) for predicting soot formation in the low-temperature range of our experiments (below 1800 K), it was necessary to adopt higher reaction rates for reactions involving polyynes, which led to significant overestimations in aromatic pyrolysis data; 2) the irreversible nature of the nucleation steps leading to the formation of BIN structures, along with the high stability of polyynes at elevated temperatures, hindered the modeling of the experimentally observed decrease in volume fraction (f_v) at high temperatures. As a confirmation of this, constant-pressure simulations of f_v versus T , applied to acetylene pyrolysis, showed peaks around 3000 K, in contrast to the experimental maximum observed around 2000 K (current data and literature data). Moreover, additional attempts to incorporate reverse reactions from BIN and BINJ back to polyynes proved just as unsuccessful.

In light of these issues, a new mechanism for the formation of PAHs has been proposed based on the suggestion by Frenklach et al. [60], using stable radical structures of polyynes that lead to cyclization. In this case, all elementary reaction steps are considered reversible, and the thermodynamic data for various intermediates have been estimated using RMG.

In **Figure 5.1.1.1**, the simplest initiation reactions between polyynes to form the new intermediates are illustrated. This scheme is based on the hypothesis that the radical can react with the terminal carbons to grow the polyyne chain or any internal carbon except the carbon next to the terminal one, to form branched chair-type species, which are also

resonantly-stabilized radical structures, here called RSAP0x (*Resonantly Stabilized Acetylinic Precursors*).

The reaction rate constants for the steps that produce RSAP0x are set at 1×10^{13} , similar to the reactions $C_2xH_2 + C_2yH \rightarrow C_2(x+y)H_2 + H$, which represent insertion into the terminal carbon atoms. The radical RSAP0x can react with a hydrogen atom, thus forming the corresponding molecular species RSAP0xH. Reactions $RSAP0xH + H \rightarrow RSAP0x + H_2$ are also considered, implemented similarly to $H + C_4H_4 \rightarrow H_2 + C_4H_3$. Similar to the cyclization step $C_4H_3 + C_2H_2 = C_6H_5$ [225], the addition of a C_2H_2 of a C_4H_2 molecule to the RSAP0x radicals can lead to the formation of cyclic structures, as shown in **Figure 5.1.1.2**.

The production of larger PAHs has been modeled based on the HACA mechanism, similar to the steps observed for single-ring aromatics. Specifically, the cyclization steps were modeled based on the reaction $C_6H_4C_2H + C_2H_2(+M) = C_{10}H_7-1(+M)$ [226], while the addition of the ethynyl group was described through a mechanism similar to $C_6H_4C_2H + C_2H_2 = C_6H_4(C_2H)_2 + H$ [226]. The choice of this modeling approach is based on the consideration that high-temperature conditions, acetylene, and diacetylene are major products from the gas-phase chemistry in combustion environments. Although this mechanism can be extended to longer polyacetylene species, it has not yet been implemented in the model for the initial growth process of PAHs. The HACA steps lead to the formation of “branched” species containing multiple ethynyl groups. In particular, these species are denoted as PAH_{mHB} for larger molecules and PAH_{mB} for smaller ones.

The distinction between branched and unbranched radicals has not been made because, in both cases, the assumption of reactions occurring at the aromatic ring was hypothesized.

To ensure the consistency of the reaction pathways, additional reactions have been added to the model scheme, as illustrated in **Figure 5.1.1.2**, through the HACA mechanism pathway, where deemed necessary.

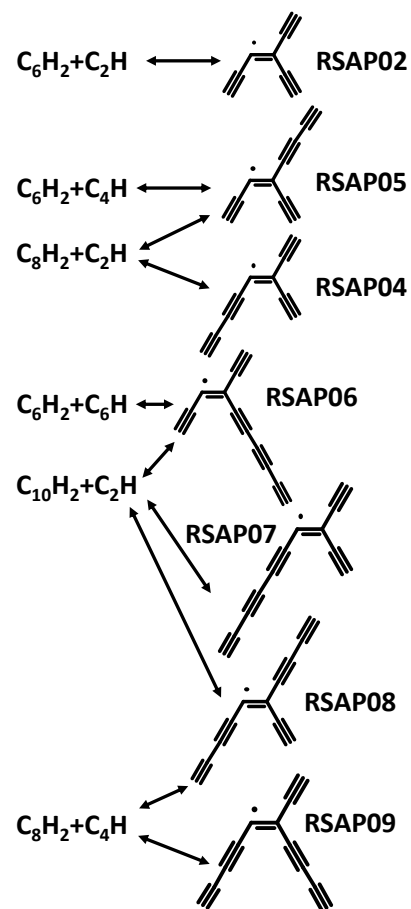


Figure 5.1.1.1 – Initial insertion steps to diradical structures.

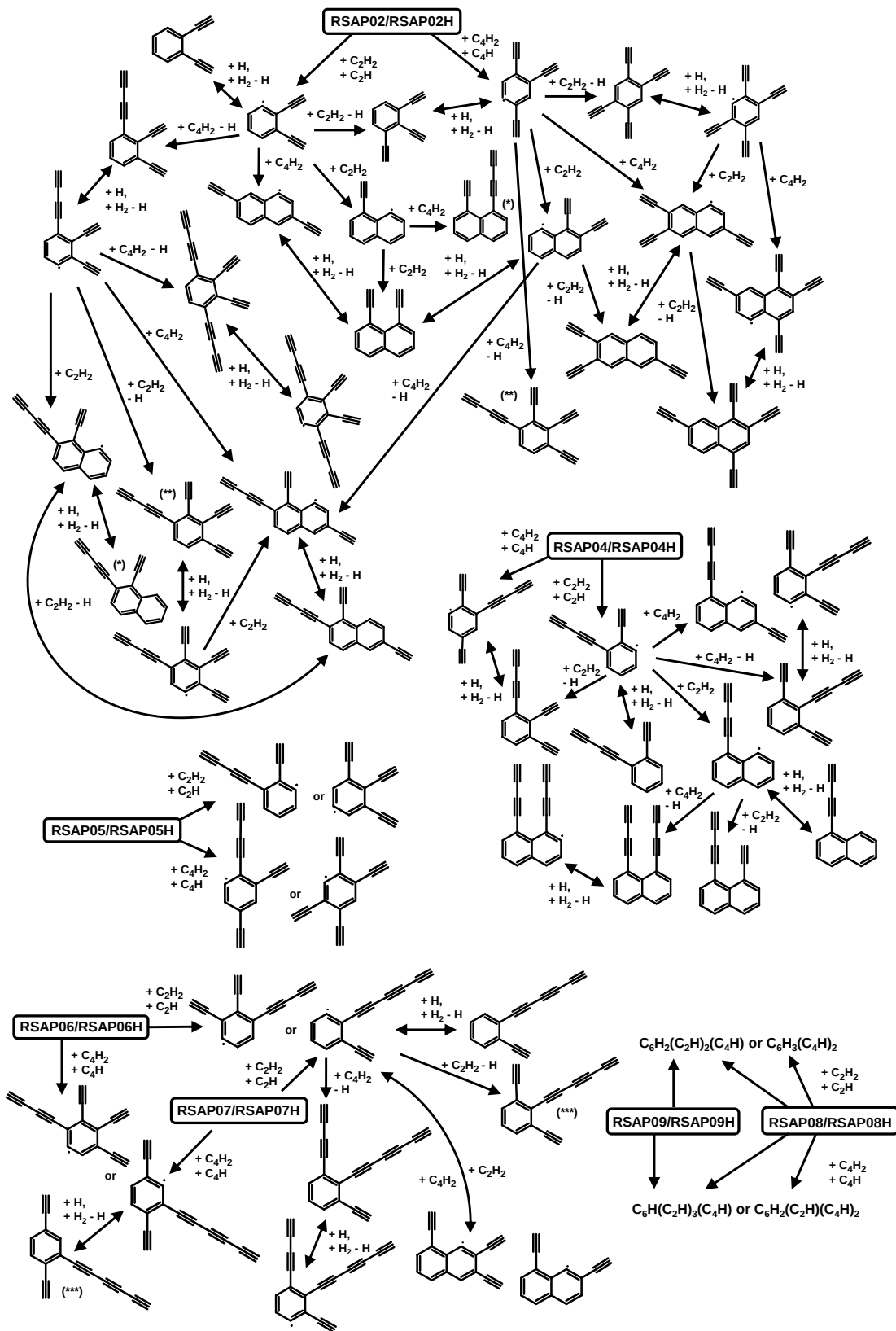


Figure 5.1.1.2 – Reaction mechanism of aromatic formation and growth in acetylene pyrolysis.

5.1.2 Single Pulse shock tube data on benzene pyrolysis.

Following the development of novel kinetic pathways for the gas phase aimed at predicting polyacetylenic species up to C₁₂, with validation against experimental data up to C₆H₂, particularly with respect to pyrolysis of acetylene, and simulating PAH formation from polyynes + polyynes radical insertion reaction, it became necessary to evaluate the performance of the gas-phase model against pyrolysis data obtained at ICARE using the single-pulse shock tube (SPST) technique. This validation step is crucial for assessing the modifications introduced by the new modeling approach in comparison to the prior polycyclic aromatic hydrocarbons (PAHs) model, which served as a reference framework at ICARE. The original widely-validated PAH model was not significantly modified. Thus, for the purposes of this thesis, only one dataset was used to test the model.

In particular, **Figure 5.1.2.1** compares the simulation trends from the ICARE shock tube data for 109 ppm benzene under pyrolytic conditions at around 20 bar. In **Figure 5.1.2.1a**, it is shown that the model can accurately and reliably replicate benzene consumption, as well as the formation of acetylene. For C₄H₂, the predictions align with experimental data up to approximately 1600 K, where a slight overestimation begins. The profile of C₆H₂ is correctly captured (both experiments and simulations are multiplied by a factor). In **Figure 5.1.2.1b**, the major products are presented, e.g., phenylacetylene (C₆H₅C₂H), which is predicted with good accuracy, though a minor overestimation of peak production exists. C₁₀H₈ is modeled with qualitative consistency, but the model tends to overpredict the peak by about 40%. Lastly, C₁₂H₈ is modeled with high accuracy, closely following the experimental trend.

Concerning larger minor intermediates, in **Figure 5.1.2.1c**, the phenanthrene (P-C₁₄H₁₀) is well predicted by the model. Indene (C₉H₈) is underestimated by around 40% compared to experimental results, while C₆H₅CCC₆H₅ is simulated with reasonable accuracy. In **Figure 5.1.2.1d**, ethynylnaphthalene (C₁₀H₇C₂H) and anthracene (A-C₁₄H₁₀) are predicted with high accuracy. For fluoranthene (F-C₁₆H₁₀), the model predicts an earlier production peak, overestimating by about 2.4 times compared to experimental results. In **Figure 5.1.2.1e**, the mole fractions of C₁₂H₇C₂H isomers are well reproduced by the simulations, while the model underestimates C₁₀H₆(C₂H)₂. Overall, certain discrepancies still exist in the

simulations, but the PAH model is capable of providing the necessary base for coupling with the particle chemistry. It is worth noting that, for various PAH products, the new modifications on the PAH chemistry improved the accuracy of the model with respect to the original version in [50].

Overall, certain discrepancies still exist in the simulations,

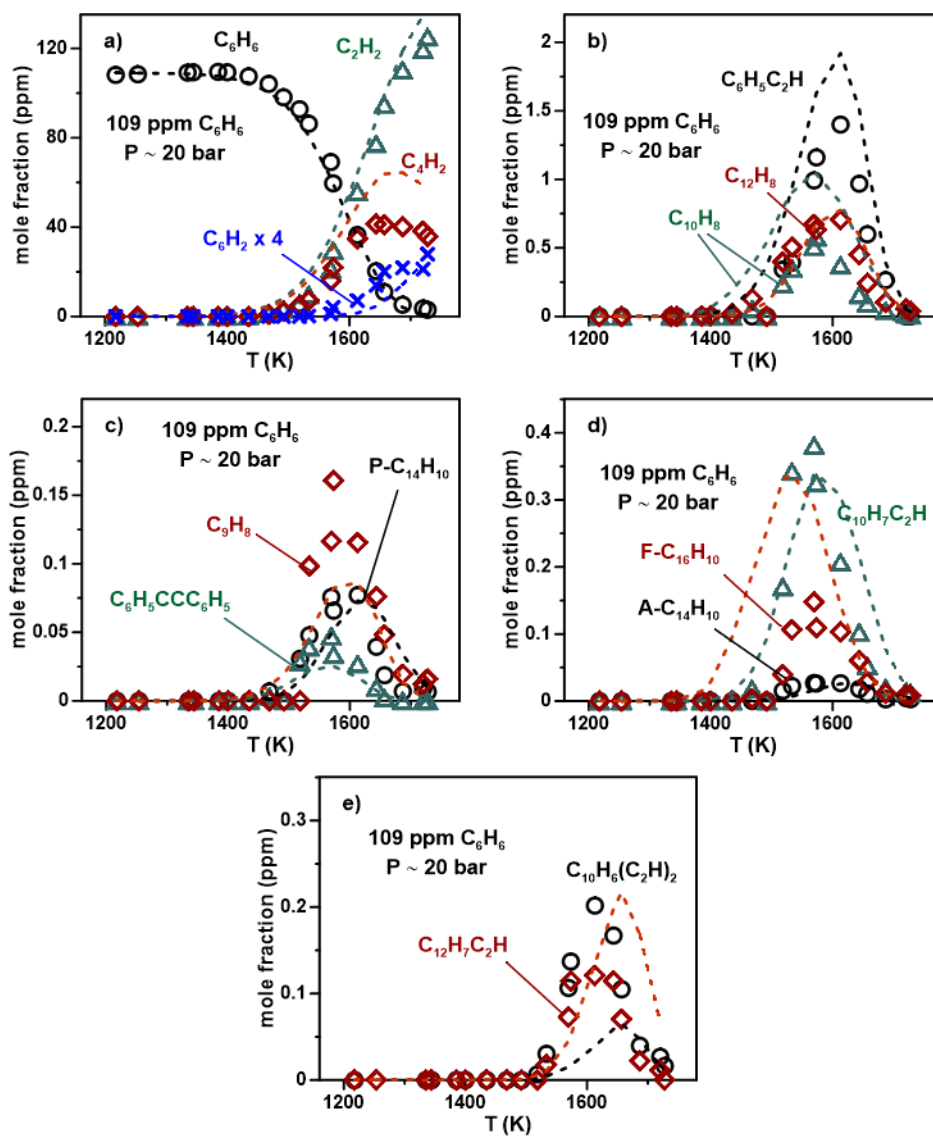


Figure 5.1.2.1 – ICARE Single Pulse Shock 109 ppm of benzene in Ar at P ~ 20 bar. Symbols: experiments from [125]; lines: simulations.

5.1.3 Model testing under low-temperature conditions.

To analyze the pyrolysis of acetylene over a wider temperature and reaction time range, the most recent flow-reactor experimental results by Sánchez et al. [227] were examined to further test the model capabilities. In these data, a quartz flow reactor with an internal diameter of 4.5 cm and an overall length of 80 cm was placed inside an electric furnace, which allows temperature regulation. Additionally, the reactor's outlet section is movable to adjust the reagents' residence time. At the reactor outlet, the products are directed to a quartz filter to collect carbonaceous particulate matter, followed by a resin trap to sample polycyclic aromatic hydrocarbons (PAHs) in the gaseous phase. Light species, PAHs, and soot were analyzed using specific analytical techniques.

These results are particularly significant as feedback on model performance under low-temperature operating conditions and for the availability of detailed information on PAH intermediates in this regime, considering also that the experiments were conducted under soot formation conditions. **Figures 5.1.3.1 and 5.1.3.2** show the comparison between experimental data and model predictions as a function of reaction temperature for two initial acetylene concentrations (10,000 ppm and 30,000 ppm), residence times of 1.5 ± 0.3 seconds.

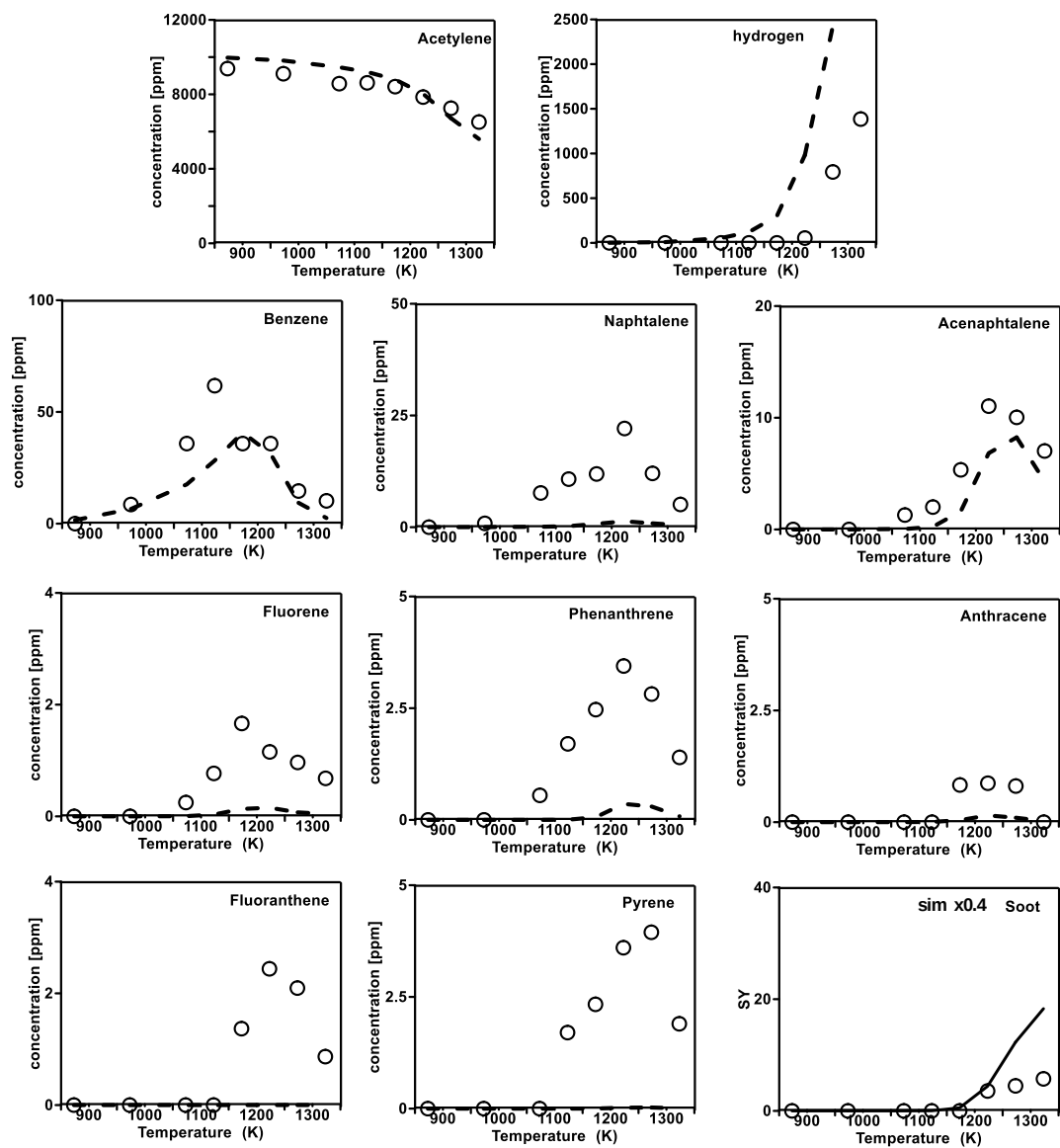


Figure 5.1.3.1 Nitrogen-diluted 10000 ppm of C_2H_2 pyrolysis a flow reactor at atmospheric pressure. Experimental data (symbols) and ICARE-SMAuG (lines) results at 1.5 ± 0.3 s.

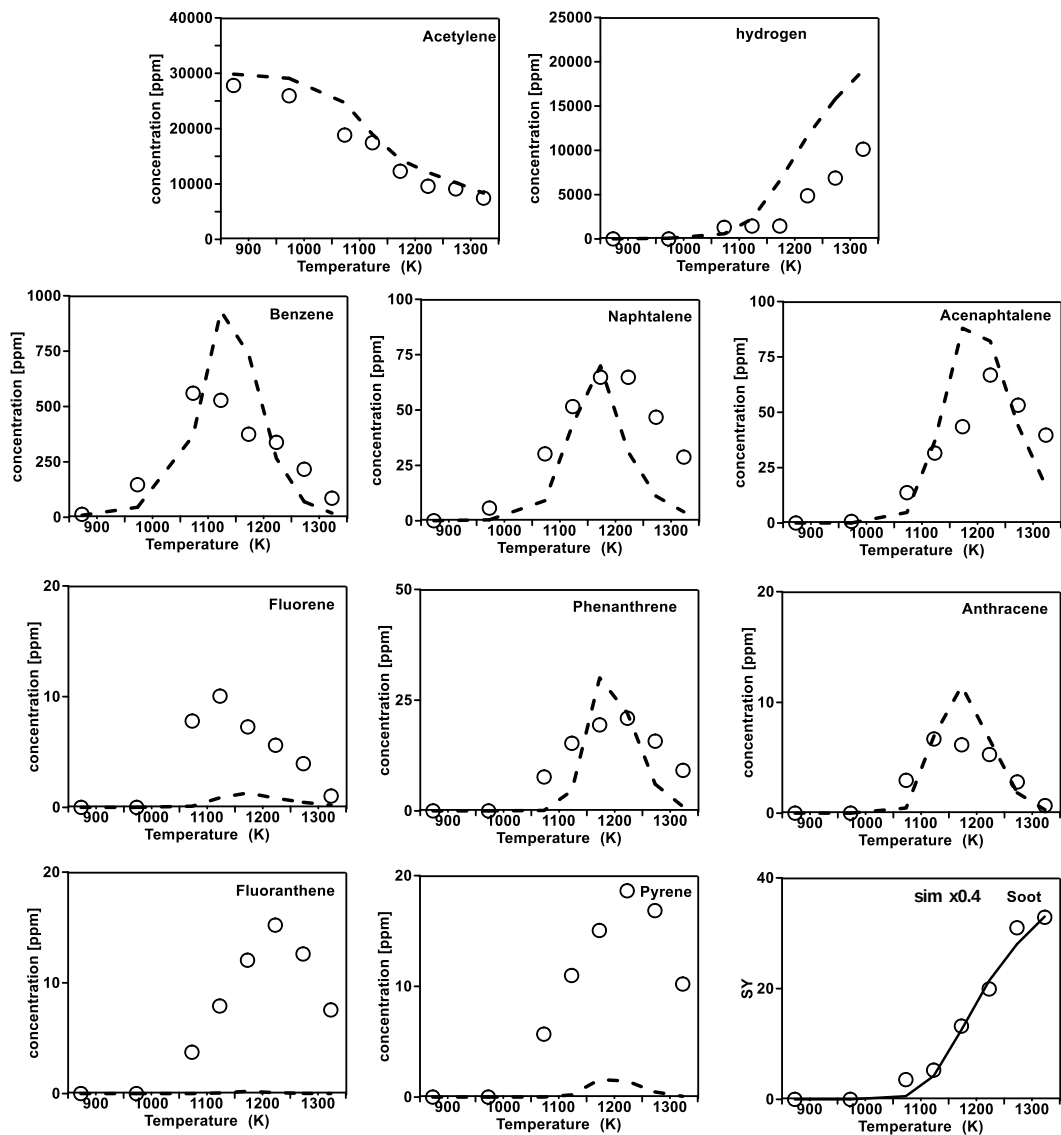


Figure 5.1.3.2 Nitrogen-diluted 30000 ppm of C_2H_2 pyrolysis in a flow reactor at atmospheric pressure. Experimental data (symbols) and ICARE-SMAuG (lines) results at 1.5 ± 0.3 s.

In **Figure 5.1.3.1**, the model has good predictive capability for acetylene, benzene, and acenaphthene, and shows a slight shift for hydrogen. The other PAHs are, under these conditions, underestimated. The model predicts soot formation, in terms of soot volume fraction (SY), with a correction factor of 0.4 and shows a tendency to overpredict as temperatures increase. Conversely, in **Figure 5.1.3.1**, the model consistently predicts acetylene consumption and hydrogen production under the verified condition of 10,000 ppm. Overall, the simulations of benzene, naphthalene, acenaphthene, phenanthrene, and

anthracene concentrations are well predicted. The remaining PAHs simulated are virtually absent. The prediction of soot formation within the considered temperature range is performed with a correction factor of 0.4, consistent with experimental data.

5.2 Soot kinetic model.

The kinetic model for soot proposed in this work was implemented starting from the existing gas phase developed at ICARE in previous studies, based on the latest update [50], including the kinetics of PAH formation up to C18. Starting from this basis, the gas phase mechanism has been expanded with the kinetics involving polyynes, as relevant to soot formation at high temperatures for aromatic and aliphatic fuels.

The modeling approach used is the discrete sectional method. The guidelines for this approach have their origins in the models developed in [129] and [30,228]. The structure of the current sectional model is taken from the works of the CRECK Modeling Group [110,112-114].

The kinetic model for soot is generated by implementing the Python framework SMAuG (Soot Mechanism Automated Generator), which is discussed in Chapter 4.

5.1 Binary carbon/hydrogen pseudo species – BINs.

Carbon/hydrogen binary species are grouped, discretized pseudo-species based on aerosol dynamics theory [118]. In this work, the BIN pseudo-species mirror the structure of [49] for soot modeling, aligning with the CRECK proposition. A total of 25 pseudo-species sections are considered, including Large PAHs, soot particles, and soot aggregates. The pseudo-lumped BIN species range from 20 carbon atoms up to approximately 10^8 . Mass (amu), diameter (nm), and hc (hydrogen/carbon ratio) are assigned to each section. J radical species differ from molecular species by one H atom.

The pseudo lumped species sections are related by a spacing factor f_s , separating them equidistantly by carbon atoms, as for Eq 4.3.1, where $i \in [1,24]$.

$$(Eq\ 5.3.1) \quad nC_{i+1} = f_s nC_i$$

LPAHs, listed in **Table 4**, can be mainly distinguished into radicals and molecules, BINJ and BIN, from 20 to 160 carbon atoms. Only for BIN1-3 species, the distinction between molecules and σ -radicals subsists, while after BIN4J, only the persistent radical form applies. BIN5J represents the first carbonaceous particle, 320 C-atoms with a diameter of 2 nm [152,229,230]. BIN and BINJ species are the main products from PAH chemistry, consistent with the CRECK model [117].

Furthermore, an additional implementation of LPAH species called BINPJs was carried out for sizes 1-3, based on the proposition from Naydenova et al. [108] in terms of the general scheme and reactivity. These species are also listed in **Table 4**. The new species were modeled based on guidelines from [112], representing precursor molecules formed from polyynes reactions, which are considered activated products that cannot be stabilized. For this scheme, the BINPJs are generated by reactions between polyynes and branched aromatics or PAHs. This is different from the kinetics in [112], where the activated species originate solely from reactions between polyynes molecules. The validation of the BINPJ pathways will be performed against data from acetylene pyrolysis, for which the fluxes of BINs and BINJs are negligible compared to BINPJs. Three groups of BINPJs — BIN1PJs, BIN2PJs, and BIN3PJs — are identified; each exhibits characteristics similar to those of their respective BINJs in terms of size and H/C ratios.

BIN(5-12) primary soot particles, as shown in **Table 5**, are assumed to be spherical with a constant density of 1500 kg/m³. BIN12J is the last stabilomer of primary particles, listed in **Table 5**, with a particle diameter d_p of 10 nm. BIN(13-25) soot aggregates, detailed in **Table 6**, have fractal characteristics, N_p representing the number of primary particles, and their collisional diameters.

As shown in the CRECK scheme, the present modeling assumes that the density of spherical carbonaceous particles increases with their size, from 1100 kg/m³ for BIN5J to 1850 kg/m³ for BIN22J, based on [231]. The hc levels of BIN primary particles and aggregates allow reconstructing the different types of dehydrogenation and maturation of entities from different fuels [232,233]. Increasing the size of pseudo lumped species decreases the hc ratio. The hc ratio is also an index of the reactivity of the structures, depending on the size and thermal range of prediction. In soot predictions under pyrolytic

conditions in shock tube experiments, the average soot density is 1850 kg/m^3 , as in the works [111,234]. This average soot density is also found in other experimental investigations, e.g. [233,235–237].

Table 4 - Soot Precursors – Large PAHs pseudo-lumped species.

Large PAHs - soot heavy precursors - BIN(1-4)											
Carbon number	Molecular Mass (a.m.u)	Equivalent Spherical Diameter ESD (nm)	hc ratio								
			A	B	C	AJ	BJ	CJ	aPJ	bPJ	cPJ
20	250	0.81	0.8	0.5	0.25	0.75	0.45	0.2	0.75	0.45	0.2
40	500	1.02	0.775	0.4	0.2	0.75	0.375	0.175	0.75	0.375	0.175
80	1000	1.28	0.75	0.3	0.1	0.7375	0.2875	0.0875	0.7375	0.2875	0.0875
160	2000	1.6	0.725	0.2	0.0625	0.71875	0.19375	0.05625	-	-	-

Table 5 - Soot Primary Particles properties.

Soot Primary Particles BIN(5-12)					
Carbon number	Molecular Mass (a.m.u)	Equivalent Spherical Diameter ESD (nm)	hc ratio		
			AJ	BJ	CJ
3.20E+02	4.00E+03	2.02	0.696875	0.196875	0.053125
6.40E+02	8.00E+03	2.55	0.673438	0.198438	0.051563
1.25E+03	1.55E+04	3.18	0.6496	0.1992	0.0512
2.50E+03	3.00E+04	4.01	0.6248	0.1996	0.05
5.00E+03	6.00E+04	5.05	0.5998	0.1998	0.05
1.00E+04	1.20E+05	6.37	0.5749	0.1999	0.05
2.00E+04	2.45E+05	8.02	0.54995	0.19995	0.05
4.00E+04	4.90E+05	10.11	0.524975	0.199975	0.05

Table 6 - Soot Aggregates properties.

Soot Aggregates - BIN(13-25)							
Carbon number	Molecular Mass (a.m.u)	Equivalent Spherical Diameter ESD (nm)	Collisional Diameter (nm)	Np	hc ratio		
					AJ	BJ	CJ
8.00E+04	9.70E+05	12.73	13.15	2	0.499988	0.199988	0.05
1.60E+05	1.95E+06	16.04	19.32	4	0.474994	0.199994	0.05
3.20E+05	3.90E+06	20.21	28.38	8	0.449997	0.199997	0.05
6.40E+05	7.80E+06	25.47	41.7	16	0.424998	0.199998	0.05
1.25E+06	1.51E+07	31.83	60.46	32	0.399999	0.199999	0.05
2.50E+06	3.02E+07	40.11	88.82	64	0.375	0.2	0.05
5.00E+06	6.02E+07	50.53	130.49	128	0.35	0.2	0.05
1.00E+07	1.21E+08	63.66	191.72	256	0.325	0.2	0.05
2.00E+07	2.41E+08	80.21	281.67	512	0.3	0.2	0.05
4.00E+07	4.82E+08	101.06	413.98	1024	0.3	0.2	0.05
8.00E+07	9.64E+08	127.33	608.44	2048	0.3	0.2	0.05
1.60E+08	1.93E+09	160.42	894.25	4096	0.3	0.2	0.05
3.20E+08	3.86E+09	202.12	1314.31	8192	0.3	0.2	0.05

5.2 Thermodynamics.

The thermodynamics of the lumped pseudo-species are estimated using the method of group additivity (GA) [115], considering that they are composed of functional groups as described in the works of [238–240]. The values of $C_{p,T}$, $\Delta H^0_{f,298K}$, and $S^0_{f,298K}$ are provided in **Table 7**. Similar properties have been used for the determination of the thermodynamic properties of BINPJs.

Table 7 - Group additivity values [176,177] of functional groups considered to compute BINs thermodynamic properties.

Groups	ΔH^0_f [kcal/mol]	S^0 [cal/mol/K]	$C_{p,T}$ [cal/mol/K]					
			300 K	400 K	500 K	600 K	800 K	1000 K
A CB-(H)	3.3	11.53	3.24	4.44	5.46	6.3	7.54	8.41
B CBF-(CB) ₂ (CBF)	4.8	-5	2.99	3.66	4.22	4.64	5.23	5.55
C CBF-(CB)(CBF) ₂	3.7	-5	2.99	3.66	4.22	4.64	5.23	5.55
D CBF-(CBF) ₃	1.45	1.82	2.08	2.85	3.5	4.03	4.75	5.14
E CB-C(CB) ₂	5.51	-7.69	2.67	3.14	3.68	4.15	4.96	5.44
F C-CB(H) ₃	-10	30.41	6.19	7.84	9.4	10.79	13.02	14.77
G CB-CB	4.96	-8.64	3.33	4.22	4.89	5.27	5.76	5.95

The representation in **Figure 5.2.1** within a structure of LPAHs provides a general example of the functional contribution of groups.

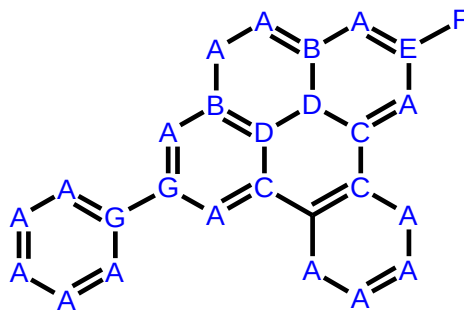


Figure 5.2.1– Example of functional groups in a large PAH from [117].

According to [117], all groups are identified through a center represented by a carbon atom. Basic considerations can be made based on **Table 7**. Depending on the type of molecular structures, the combination of one or more functional groups is identified:

- A-D, in pericondensed aromatic hydrocarbons;
- E-G, in oligomers that are not fully condensed and found in substituted aromatics and radicals;
- A, symbolic of the benzene C-H group, having a carbon bonded to an H atom at the edge of the aromatic structure;
- B, typical of the naphthalene structure with a fused carbon atom (CBF) in the central position;
- C is seen in phenanthrene and has a central fused carbon atom that can be connected to an A group and two fused carbon atoms that can be of the C or D group;
- D is typical of graphite layer structures;
- E is associated with substituted aromatics such as the phenyl radical;
- F is commonly a methyl group;
- G are typically connecting bridges as in biphenyl-like structures.

The methodology adopted in [117] was based on the assumptions of [115] to determine the number of functional groups present in the pseudo lumped species BIN, through discrimination based on hc thresholds, hydrogen-to-carbon ratio hc:

for $hc \leq 0.6$:

- group A = n° H-atoms
- groups B+C = 0.5 (group A)
- group B = 0.78 (group B+C)
- group C = 0.22 (group B+C)
- group D = n° C-atoms - (group A) - (group B) - (group C)
- group E = group F = group G = 0

for $hc > 0.6$:

- group A = 0.5 n° C-atoms
- group B = group C = group D = 0

→ group E = group F = 0.33 [n° H-atoms - (group A)]

→ group G = n° C-atoms - (group A) - (group E) - (group F)

Heat capacity Eqn(5.4.1), enthalpy Eqn(5.4.2), and entropy Eqn(5.4.3) for pseudo-lumped species are calculated as a function of temperature dependence, according to polynomial expressions, and include the contribution of functional groups.

$$\text{Eqn(5.4.1):} \quad \frac{C_{p,i}^0}{R} = a_{i,1} + a_{i,2}T + a_{i,3}T^2 + a_{i,4}T^3 + a_{i,5}T^4$$

$$\text{Eqn(5.4.2):} \quad \frac{\Delta H_{f,i}^0}{R} = a_{i,1} + \frac{a_{i,2}}{2}T + \frac{a_{i,3}}{3}T^2 + \frac{a_{i,4}}{4}T^3 + \frac{a_{i,5}}{5}T^4 + \frac{a_{i,6}}{T}$$

$$\text{Eqn(5.4.3):} \quad \frac{S_i^0}{R} = a_{i,1} \ln T + a_{i,2}T + \frac{a_{i,3}}{3}T^2 + \frac{a_{i,4}}{4}T^3 + \frac{a_{i,5}}{5}T^4 + a_{i,7}$$

The estimation of polynomial coefficients from $a_{i,1}$ to $a_{i,5}$ was performed by polynomial regression on heat capacity as function of temperature. According to the CRECK scheme, for $T > 1000$ K the heat capacity ratio is summarized in **Table 8**.

Table 8- Heat capacity ratio for $T > 1000$ K adopted from [117].

T[K]	Cp/Cp@1000K
1500	1.13
2000	1.2
2500	1.24
3000	1.26
3500	1.27

$a_{i,6}$ to $a_{i,7}$ in the polynomials are calculated from the additivity contribution of the groups via **Table 8**, and **Table 9** and **Table 10**, which each contain, respectively, two sets of seven coefficients for each functional group evaluated for a range of low (≤ 1000 K) and high (≥ 1000 K) temperature.

Table 9 - Fitting coefficients for the low-T range of each functional group from the group additivity analysis for BINs [117].

Group	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	a ₇
A	-7.09E-01	8.94E-03	-3.14E-06	-2.81E-09	1.95E-12	8.27E+02	7.34E+00
B	2.92E-02	6.17E-03	-4.46E-06	8.62E-10	1.90E-13	1.40E+03	-4.33E+00
C	2.92E-02	6.17E-03	-4.46E-06	8.62E-10	1.90E-13	1.05E+03	-4.33E+00
D	-4.03E-01	5.31E-03	-8.22E-07	-3.09E-09	-1.59E-12	-2.64E+02	1.69E+00
E	-1.10E+00	-1.39E-03	-1.01E-05	-1.05E-08	3.34E-12	1.30E+03	-1.01E+01
F	9.61E-01	4.58E-03	1.40E-05	2.03E-08	8.15E-12	-3.56E+03	8.00E+00
G	-1.08E+00	-1.39E-02	-1.93E-05	-1.30E-08	-3.50E-12	1.41E+03	-1.57E+00

Table 10 - Fitting coefficients for the high-T range of each functional group from the group additivity analysis for BINs [117].

Group	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	a ₇
A	2.02E+00	3.22E-03	-1.19E-06	1.98E-10	-1.23E-14	-4.72E+01	-7.25E+00
B	1.33E+00	2.13E-03	-7.86E-07	1.31E-10	-8.14E-15	1.12E+03	-1.08E+01
C	1.33E+00	2.13E-03	-7.86E-07	1.31E-10	-8.14E-15	7.68E+02	-1.08E+01
D	1.23E+00	1.97E-03	-7.28E-07	1.21E-10	-7.54E-15	-7.40E+02	-6.89E+00
E	1.30E+00	2.08E-03	-7.70E-07	1.28E-10	-7.98E-15	1.02E+03	-1.22E+01
F	3.54E+00	5.66E-03	-2.09E-06	3.48E-10	-2.17E-14	-4.83E+03	-7.67E+00
G	1.43E+00	2.28E-03	-8.42E-07	1.40E-10	-8.73E-15	1.07E+03	-1.31E+01

The seven low- and high-temperature coefficients for BIN_j related to the functional groups are evaluated by the equation Eqn(5.4.4):

$$\text{Eqn(5.4.4): } \sum_{k=A}^G [a_{i,k}(\text{number of groups } j \text{ in BIN}_j)]$$

The heat capacity and entropy of radicals are considered as those of the respective molecules. The enthalpy of formation is increased by 60 kcal/mol for the lumped σ -radical species of sections (1-3), as found for pyrenyl, phenanthrenyl, and naphthalenyl radicals compared with their respective molecules. As pseudo-lumped chemical species, BINs can participate only to irreversible reactions due to their structure and thermodynamic properties used to evaluate energy balances in the simulation environment.

5.3 Stoichiometric balances.

Stoichiometric balances with BIN species were calculated using the CRECK methodology from the works [110, 112, 113] via the lever rule. Since the present model was developed only under pyrolytic conditions, the writing of the balances involved only hydrogen and carbon atoms. The conceptual scheme of the implemented methodology is depicted in **Figure 5.3.1**. Defined two generic reactants, BIN_i and BIN_j , with $i, j \in [1, 24]$, radicals or molecules, two different H/C ratios are assigned. Three levels of H/C are available in the model according to the CRECK assignment, as shown in the **Tables (4, 5, 6)** for radicals and molecules. The reactants form a generic BIN (BIN_{prod}), determining the total amount of carbon and hydrogen, as well as the relative total H/C ratio. The carbon and hydrogen are split in the determination of four BIN products that respond to two different sections, $BIN_{X,K1/2}$, and $BIN_{Y,K3/4}$, where K represents their H/C (A, B, or C), $X=i$ and $Y=i+1$. In general, the choice of the H/C of the four possible BINs produced must be such that the H/C of BIN_{prod} is within or equal to the range of the H/C of $BIN_{X,K1} - BIN_{X,K2}$, and $BIN_{Y,K3} - BIN_{Y,K4}$.

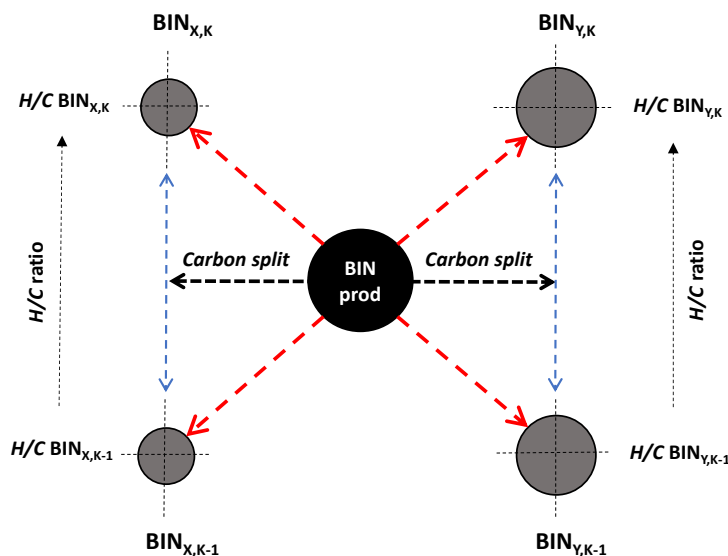


Figure 5.3.1 – Balance methodology based on the CRECK's method.

5.4 Soot model kinetic rate parameters

This section illustrates the kinetic rate parameters optimized during the development of the soot model presented in this work. The list of the main implemented PAH and polyne species in the new soot inception and growth mechanisms (gas-phase to LPAHs precursors - BINs) are:

⊗ **PAH molecules – PAH_m:**

C₆H₆, C₇H₈, C₇H₆, C₆H₅C₂H₃, XYLENE, C₆H₅C₂H₅, C₉H₈, C₆H₅C₃H₃P₋₁, C₁₀H₆₋₁₂, C₁₀H₆₋₂₃, C₁₀H₈, CH₃C₉H₇, C₁₀H₇CH₃₋₁, C₁₀H₇CH₃₋₂, C₁₂H₈, C₆H₅C₆H₅, BENZO, C₆H₄C₆H₄, C₁₀H₇C₂H₃, R₅C₁₂H₁₀, R₅C₁₂H₈, C₁₃H₁₀, C₆H₅CH₂C₆H₅, C₁₀H₇CCCH₃, C₁₀H₇CCCH₃₋₂, C₁₀H₇CHCCH₂₋₂, C₁₀H₇CYC₅₋₂, C₁₀H₇CYC₅, C₁₄H₈, C₆H₅CCC₆H₅, C₁₃H₈CH₂, C₁₄H₁₀, AC₁₄H₁₀, C₁₃H₉CH₃, PC₁₄H₈, C₁₂H₇CH₂CCH, C₁₂H₇CH₂CCH₂, C₁₂H₇CH₂CCH₃, A₂AR₅, C₁₆H₁₀, FC₁₆H₁₀, AAC₁₆H₁₀, C₁₀H₇C₆H₅, C₁₄H₉C₂H₃, C₁₈H₁₀, CC₁₈H₁₂, R₅C₁₈H₈, A₂AR₅A;

⊗ **PAH molecules branched – PAH_{mB}:**

C₆H₅C₂H, CH₃C₆H₄C₂H, C₆H₄(C₂H)₂, C₆H₃(C₂H)₃, C₂HC₆H₄C₄H, C₁₀H₇C₂H₋₁, C₁₀H₇C₂H₋₂, C₆H₅(C₆H), C₆H₄(C₂H)C₆H₅, C₁₀H₆(C₂H)₂, C₁₂H₇C₂H, C₁₂H₇C₂H₋₂, C₁₂H₇C₂H₋₃, C₁₂H₇C₂H₋₄, C₁₂H₇C₂H₋₁, C₆H₂(C₂H)₄, (C₂H)₂C₆H₃C₄H, C₆H₄(C₄H)₂, C₁₀H₇C₄H, C₆H₄(C₆H)C₂H, C₁₄H₉C₂H, C₁₂H₇C₄H, C₁₀H₅(C₂H)₃, C₂HC₁₀H₆C₄H, C₆H₂(C₂H)₃(C₄H), C₆H₃(C₂H)(C₄H)₂, C₆H₄(C₆H)C₄H, C₆H₃(C₆H)(C₂H)₂, C₁₀H₇C₆H, C₆H₂(C₂H)₂(C₄H)₂, C₆H₃(C₄H)₃, C₁₀H₄(C₂H)₄, C₁₀H₅(C₂H)₂(C₄H), C₁₀H₆(C₄H)₂, C₆H₄(C₆H)₂, C₆H₃(C₆)(C₄)C₂, C₆H₂(C₆H)(C₂H)₃, C₁₀H₆C₆HC₂H;

⊗ **PAH molecules heavy – PAH_{mH}:**

C₁₆H₁₀, FC₁₆H₁₀, AAC₁₆H₁₀, C₁₀H₇C₆H₅, C₁₄H₉C₂H₃, C₁₈H₁₀, CC₁₈H₁₂, R₅C₁₈H₈, A₂AR₅A;

⊗ **PAH molecules heavy branched – PAH_{mHB}:**

C₆H₄(C₂H)₂, C₆H₃(C₂H)₃, C₂HC₆H₄C₄H, C₁₀H₇C₂H₋₁, C₁₀H₇C₂H₋₂, C₆H₅(C₆H), AR₅MC₂H, C₆H₄(C₂H)C₆H₅, C₁₀H₆(C₂H)₂, C₁₂H₇C₂H, C₁₂H₇C₂H₋₂, C₁₂H₇C₂H₋₃, C₁₂H₇C₂H₋₄, C₁₂H₇C₂H₋₁, C₆H₂(C₂H)₄, (C₂H)₂C₆H₃C₄H, C₆H₄(C₄H)₂, C₁₀H₇C₄H, C₆H₄(C₆H)C₂H, C₁₃H₉C₂H, C₁₄H₉C₂H, C₁₂H₇C₄H, C₁₀H₅(C₂H)₃, C₂HC₁₀H₆C₄H, C₆H₂(C₂H)₃(C₄H), C₆H₃(C₂H)(C₄H)₂, C₆H₄(C₆H)C₄H, C₆H₃(C₆H)(C₂H)₂, C₁₀H₇C₆H, C₁₃H₉C₄H, C₁₃H₈(C₂H)₂, A₂AR₅C₂H, C₆H₂(C₂H)₂(C₄H)₂, C₆H₃(C₄H)₃, C₁₀H₄(C₂H)₄, C₁₀H₅(C₂H)₂(C₄H), C₁₀H₆(C₄H)₂, C₆H₄(C₆H)₂, C₆H₃(C₆)(C₄)C₂, C₆H₂(C₆H)(C₂H)₃, C₁₀H₆C₆HC₂H, C₁₃H₉C₆H, C₁₃H₈C₂HC₄H, A₂R₅C₂HA₁, A₂AR₅C₄H;

⊗ **PAH radicals – included branched radicals – PAH_r:**

C₆H₅, C₆H₅CHCH₃, C₆H₅C₂H₄, C₆H₅CHCH, C₆H₄C₂H, C₆H₄C₄H, C₆H₃(C₂H)₂, C₂HC₆H₄CHCH, C₁₀H₇₋₂, C₁₀H₇₋₁, cC₁₁H₉, C₁₀H₆CH₃, C₁₀H₆C₂H₋₈, C₁₂H₉, C₁₀H₇CHCH, C₁₀H₆C₂H₋₁, C₁₀H₆C₂H₋₂, C₁₀H₆C₂H₋₃, C₁₀H₆C₂H₋₄, C₁₀H₆C₂H₋₅, C₁₀H₆C₂H₋₆, C₁₀H₆C₂H₋₇, C₁₂H₇₋₄, C₁₂H₇₋₃, C₁₂H₇₋₂, C₁₂H₇₋₁,

C₁₂H₇, C₆H₂(C₂H)₃, C₂HC₆H₃C₄H, C₆H₄(C₆H), PC₁₃H₉R₁, C₁₀H₇CYC₅R₂, C₁₀H₇CYC₅R, C₁₄H₉, AC₁₄H₉, C₁₃H₈CH, C₁₀H₅(C₂H)₂, (C₂H)₂C₆H₂C₄H, C₆H(C₂H)₄, C₆H₃(C₄H)₂, C₆H₃(C₆H)C₂H, C₁₂H₇C₃H_{2_3}, C₁₂H₇C₃H_{2_2}, C₁₂H₇C₃H₂, C₁₆H₉, C₂HC₁₀H₅C₄H, C₆H(C₂H)₃(C₄H), C₆H₂(C₂H)(C₄H)₂, C₁₀H₄(C₂H)₃, C₁₀H₆C₄H, C₆H₃(C₆H)C₄H, C₆H₂(C₆H)(C₂H)₂, C₁₀H₆C₆H, C₁₈H₉, C₁₈H₁₁, R₅C₁₈H₇, C₆H(C₂H)₂(C₄H)₂, C₆H₂(C₄H)₃, C₁₀H₃(C₂H)₄, C₁₀H₄(C₂H)₂(C₄H), C₁₀H₅(C₄H)₂, C₆H₃(C₆H)₂, C₆H₂(C₆)(C₄)C₂, C₆H(C₆H)(C₂H)₃, C₁₀H₅C₆HC₂H;

⊗ **Small Resonantly Stabilized Radicals – SRSR:**

C₃H₃, C₄H₃, C₄H₅, C₅H₅;

⊗ **PAH resonantly stabilized radicals – PAH_rsr:**

C₇H₇, c-C₇H₇, C₆H₅CCH₂, C₉H₇, CH₂C₆H₄C₂H, C₉H₆C₂H, C₁₀H₇CH_{2_1}, C₁₀H₇CH_{2_2}, AR₅MC₂HR, C₁₃H₉, C₁₃H₈C₂H, A₂AR₅R, C₁₃H₈C₄H, C₁₃H₇(C₂H)₂, A₂AR₅C₂HR, C₁₃H₈C₆H, C₁₃H₇C₂HC₄H, A₂R₅C₂HA₁R, A₂AR₅C₄HR, A₂AR₅AR;

⊗ **Polyynes molecules – PYYN_m:**

C₄H₂, C₆H₂, C₈H₂, C₁₀H₂, C₁₂H₂;

⊗ **Polyynes radicals – PYYN_r:**

C₄H, C₆H, C₈H, C₁₀H, C₁₂H.

The kinetic parameters are presented in two separate tables. **Table 11** focuses on the fundamental pathways for soot formation from aromatic fuels. **Table 12** details the chemistry involved in soot formation involving the polyynes routes.

Table 11 - Reference reaction rate constant parameters for the soot model under pyrolytic conditions. Units in mol, cm, s, K, cal. These parameters are evaluated in $k=A \cdot T_n \cdot \exp(-E_a/RT)$. Rate rules based on the CRECK scheme [115–117].

Reaction classes	A	n	E _a	References
H-abstraction				
H+BIN _i →H ₂ +BINJ _i (i ≤ 3)	4.8E+6	2	10500	[115–117]
Carbon addition				
C _x H _y +BINJ _i →products (i ≤ 3)	1.0E+12	0	5000	[115–117]
C _x H _y +BINJ _i →products (i > 3)	1.0E+12	0	10000	[115–117]
Inception - gas-phase to large PAHs → BIN_i (i < 5)				
SRSR+PAH _r	2.474E+58	-12.29	60005	[50]
SRSR+PAH _m	6.26E+9	2.61	56500	[50]
SRSR+PAH _{mB}	6.26E+9	2.61	56500	[50]
PAH _r +PAH _r	3.09E+12	0.036	-1703	[50]
PAH _{rsr} +PAH _{rsr}	1.204E+39	-6.855	54539.3	[50]
PAH _r +PAH _m	5.6E+12	-0.076	7550	[50]
PAH _r +PAH _{mB}	1.12E+13	-0.076	7550	[50]x2
PAH _{mH} +PAH _{mH}	1.6E+10	0.5	0	[140]
PAH _{mH} +PAH _{mHB}	1.6E+10	0.5	0	[140]
PAH _{mHB} +PAH _{mHB}	8.0E+13	0	42700	p.w. see text
PAH _{rsr} +PAH _r	1.66E+64	-14.68	33262	[50]
PAH _{rsr} +PAH _m	4.0E+11	0	19000	[115–117]
PAH _{rsr} +PAH _{mB}	4.0E+11	0	19000	[115–117]
PAH _{rsr} +PYYN _r	4.0E+12	0	0	p.w. see text
PAH _{rsr} +PYYN _m	1.0E+12	0	18000	[140]
PYYN _m +PAH _r	1.0E+14	0	0	[112] x2
PYYN _r +PAH _r	1.0E+14	0	0	[112]x2
PYYN _r +PAH _m	2.0E+13	0	0	[112]
C ₂ H ₂ +PYYN _r	4.49E+82	-20.02	51830	[50]
PAH _{mH} +PYYN _m	8.0E+11	0	22500	[50]x5
Inception - PAHs/PYYNs → BIN_i (i < 5)				
SRSR+BINJ _i	2.474E+58	-12.29	60005	[50]
PAH _r +BINJ _i	3.09E+12	0.036	-1703	[50]
PAH _{rsr} +BINJ _i	1.66E+64	-14.68	33262	[50]
SRSR+BIN _i	6.26E+9	2.61	56500	[50]
PAH _{rsr} +BIN _i	1.0E+12	0	19000	[115–117]
PAH _r +BIN _i	5.6E+12	-0.074	7550	[50]
PAH _m +BINJ _i	5.6E+12	-0.074	7550	[50]
PAH _{mH} +BIN _i	1.6E+10	0.5	0	[140]
PYYN _r +BINJ _i	1.0E+14	0	0	[112]x2
PYYN _m +BINJ _i	8.0E+13	0	12010	p.w. see text
PYYN _r +BIN _i	5.0E+13	0	0	[112]x1.25
PYYN _m +BIN _i	8.0E+11	0	22500	[122]x5
Inception - BINs → BIN_i (i,n < 5)				
BINJ _i +BINJ _n	4.0E+13	0	0/3000	[50]x2.5
BIN _i +BINJ _n	4.0E+13	0	8000	[50]x2.5
BIN _i +BIN _n	1.6E+10	0.5	0	[140]
Surface growth → for BIN_i and BINJ_n (i ≤ 4 and n ≥ 5)				
SRSR+BINJ _i	6.26E+09	2.61	56500	[50]
PAH _{rsr} +BINJ _i	5.0E+14	0.5	6000	p.w
PAH _r +BINJ _i	5.0E+14	0.5	3000	p.w
PAH _m +BINJ _i	5.0E+14	0.5	23000	[115–117]
BINJ _i +BINJ _n	4.0E+13	0.5	0	[115–117]
BIN _i +BINJ _n	4.0E+12	0.5	0	[115–117]
Coalescence and Aggregation → BINJ_{i,n} (i, n ≥ 5)				
BINJ _i +BINJ _n	4.0E+13	0.5	0	[115–117]
Dehydrogenation				
BINJ _i →H ₂ +BINJ _i	1.0E+8	0	32000	[115–117]
BINJ _i →H·+BINJ _i (i ≤ 3)	1.0E+11	0	12000	[115–117]
Demethylation				
H·+BINJ _i →CH ₃ ·+products	1.2E+13	0	5000	[115–117]
C–H fission/recombination				
BIN _i →H·+BINJ _i (i ≤ 3)	1.5E+17	0	114000	[115–117]
H·+BINJ _i →BIN _i (i ≤ 3)	1.0E+14	0	0	[115–117]

* For a detailed description of the selection of kinetic rate parameters, refer to the text.

Table 12 - Reference reaction rate constant parameters for the soot model relevant to acetylene pyrolysis. Units in mol, cm, s, K, cal. These parameters are evaluated in $k=A \cdot T_n \cdot \exp(-E_a/RT)$. Rate rules based on the CRECK scheme [241].

Reaction classes	A	n	Ea	References
Inception - gas-phase to large PAHs (BINJ_iP)				
C ₂ H ₂ +PAH _{mB}	8.0E+13	0	42700	p.w. *
PYYN _m +PAH _{mB}	A ₁	0	E _{a1}	p.w. *
PYYN _m +PAH _{rB}	8.0E+13	0	E _{a2}	p.w. **
PYYN _r +PAH _{mB}	5.0E+13	0	0	p.w.
Inception - reactions BINJ_iP with gas phase intermediates				
PAH _{mB} +BINJ _i P	1.12E+13	-0.074	7550	[222]
PAH _{rB} +BINJ _i P	3.09E+12	0.036	-1703	[222]
PYYN _r +BINJ _i P	5.0E+13	0	0	[112]x1.2
C ₂ H ₂ +BINJ _i P	4.49E+82	-20.02	51830	p.w.
PYYN _m +BINJ _i P	5.0E+13	0	E _{a2}	[112]x1.2 **
Inception - BINs/BINJs/BINPs				
BINJ _i P+BINJ _n P	4.0E+13	0	0	[50]x2.5
BINJ _i P+BINJ _{n,n<4}	4.0E+13	0	0/3000	[50]x2.5
BINJ _i P+BIN _n	4.0E+13	0	8000	[50]x2.5
Surface growth (n≥5)				
PAH _{mB} /PAH _{rB} +BINJ _n	5.0E+14	0.5	23000/3000	[115–117]
PYYN _r +BINJ _n	2.0E+13	0	0	[112]/2
C ₂ H ₂ +BINJ _n	1.0E+12	0	10000	p.w. ***
PYYN _m +BINJ _n	1.0E+12	0	5000	p.w. ***
BINJ _i P+BINJ _n	4.0E+13	0.5	0	[115–117]x2.5

* A₁ is scaled with respect to A_{1,ref} of the C₂H₂ + PAH_{mB} reactions as it follows: for C₄H₂, A₁ = A_{1,ref} x 0.5; for C₆H₂ and C₈H₂, A₁ = A_{1,ref} x 0.25; for C₁₀H₂, A₁ = A_{1,ref} x 0.5; for C₁₂H₂, A₁ = A_{1,ref}. E_{a1} is scaled with respect to E_{a1,ref} of the C₂H₂ + PAH_{mB} reactions as it follows: for C₄H₂, E_{a1} = E_{a1,ref} x 0.5; for C₆H₂, E_{a1} = E_{a1,ref} x 0.33; for C₈H₂, E_{a1} = A_{1,ref} x 0.25; for C₁₀H₂, E_{a1} = A_{1,ref} x 0.2; for C₁₂H₂, E_{a1} = A_{1,ref} x 0.17. ** E_{a2} as proposed by Naydenova et al. [112]; *** reactions with C₂H₂ based on HACA [115–117]; E_a divided by 2 for polyynes for increased reactivity.

5.4.1 Kinetic parameters for soot aromatic chemistry

This section relates to the implemented work regarding soot chemistry formation from aromatics under pyrolytic conditions. Table 11 reports the reaction classes and the reference kinetic parameters adopted. The HACA mechanism (H-abstraction, Carbon Addition) has been parametrically adopted from the CRECK modeling group [116,140,241]. The classic inception and condensation reactions have been mainly calibrated on the ICARE gas phase [50]. More details about the specific reaction rate parameters can be found in related publications in the literature on the ICARE PAH model (see [50] and previous publications).

The interaction of reacting chemical species in the gas phase that are capable of forming at least 20 carbon atoms can initiate the formation of LPAHs, pseudo-lumped BINs, and BINJs. The inception reactions between SRSR+PAH_r were parametrically modeled in analogy to C₆H₅+C₃H₃ = C₉H₈ with P-dependent expression (at 100 atm of A = 2.474x10⁵⁸,

$n = -12.29$, and $E_a = 60005$ cal/mol), while the reactions $\text{SRSR} + \text{PAH}_m$ by analogy with the reaction $\text{C}_6\text{H}_6 + \text{C}_3\text{H}_3 = \text{C}_9\text{H}_8 + \text{H}$, using the parameters $A = 6.26 \times 10^9$, $n = 2.61$, and $E_a = 56000$ cal/mol. An addition of a small resonantly radical in a similar manner has also been considered for $\text{SRSR} + \text{PAH}_{mB}$ with identical parameters.

$\text{PAH}_r + \text{PAH}_r$ was implemented with the classic phenyl + phenyl reference taken from the gas phase implementation: $A = 3.09 \times 10^{12}$, $n = 0.036$, and $E_a = -1703$ cal/mol (100 atm of [242]). $\text{PAH}_{rsr} + \text{PAH}_{rsr}$ was modeled similarly to the gas phase with $A = 1.209 \times 10^{39}$, $n = -6.855$, $E_a = 54539.3$ cal/mol for $\text{C}_7\text{H}_7 + \text{C}_7\text{H}_7 = \text{C}_6\text{H}_5\text{C}_2\text{H}_3\text{C}_6\text{H}_5 + \text{H}$. $\text{PAH}_r + \text{PAH}_m / \text{PAH}_{mB}$ are modeled as $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5 = \text{H} + \text{C}_6\text{H}_5\text{C}_6\text{H}_5$ in the gas phase with $A = 5.6 \times 10^{12}$, $n = -0.076$, $E_a = 7550$ cal/mol. To $\text{PAH}_r + \text{PAH}_{mB}$, however, a correction factor of 2 was applied to A .

For molecule + molecule reactions, only the non-branched PAH_m molecules starting from C16 were considered as reagents (called PAH_{mH} , where H conventionally stands for – heavy – to indicate larger PAH molecules), while for branched PAH_{mB} from C14 (PAH_{mHB}). $\text{PAH}_{mH} + \text{PAH}_{mH}$ and $\text{PAH}_{mH} + \text{PAH}_{mHB}$ are analogous to the implementation of [115] where $A = 1.6 \times 10^{10}$, $n = 0.5$, and $E_a = 0$ cal/mol. The $\text{PAH}_{mHB} + \text{PAH}_{mHB}$ interactions have been assimilated to the reaction $2\text{C}_2\text{H}_2 = \text{C}_4\text{H}_2 + \text{H}_2$ based on Kiefer et al. [219], considering a reaction mechanism involving the branched polyacetynyl chains, with increased reactivity compared to a normal aromatic molecule without branches. In this case, $A = 8.0 \times 10^{13}$, $n = 0$, and $E_a = 42700$ cal/mol. $\text{PAH}_{rsr} + \text{PAH}_r$ is analogous to the gas-phase reaction $\text{C}_6\text{H}_5 + \text{C}_7\text{H}_7 = \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5$ with $A = 1.66 \times 10^{64}$, $n = -14.68$, $E_a = 33262$ cal/mol, while $\text{PAH}_{rsr} + \text{PAH}_m / \text{PAH}_{mB}$ are similar to the gas-phase reactions $\text{CRECK } \text{C}_3\text{H}_3 + \text{C}_9\text{H}_8 = \text{H} + \text{C}_6\text{H}_5\text{C}_6\text{H}_5$, with $A = 4.0 \times 10^{11}$, $n = 0$, and $E_a = 19000$ cal/mol.

$\text{PAH}_{rsr} + \text{PYYN}_r$ is estimated as constant ($A = 4.0 \times 10^{12}$, $n = 0$, $E_a = 0$ cal/mol), while $\text{PAH}_{rsr} + \text{PYYN}_m$ is similar to $\text{C}_7\text{H}_7 + \text{C}_2\text{H}_2 = \text{C}_9\text{H}_8 + \text{H}$ in Saggese et al. [115]. $\text{PYYN}_m + \text{PAH}_r$ and $\text{PYYN}_r + \text{PAH}_r$ are modeled as in Naydenova et al [112], considering analogous interactions with soot precursors multiplied by a factor of 2, so $A = 1.0 \times 10^{14}$, $n = 0$, and $E_a = 0$ cal/mol. $\text{PYYN}_r + \text{PAH}_m$ is taken from Naydenova et al [112], divided by a factor of 2. These values are derived from the model adjustment based on simulations, which will be presented in the next sections. Reactions between $\text{C}_2\text{H}_2 + \text{PYYN}_r$ are considered similar to $\text{C}_6\text{H}_4\text{C}_2\text{H} + \text{C}_2\text{H}_2 (+M) = \text{C}_{10}\text{H}_{7-1} (+M)$ in analogy with the gas phase, so $A = 4.49 \times 10^{82}$, $n =$

-20.02, and $E_a = 51830$ cal/mol, while the $\text{PAH}_{\text{mH}} + \text{PYYN}_{\text{m}}$ reactions are similar to $\text{C}_6\text{H}_6 + \text{C}_4\text{H}_2 = \text{C}_{10}\text{H}_8$, with a pre-exponential multiplied by a factor of 5.

Furthermore, parametric optimization has been implemented concerning the condensation process of PAH/PYYNs+BINs reactions. These modifications are calibrated either in accordance with gas-phase parameters or by developing novel reactive pathways involving polyynes. Conceptually, several reactions have been modeled parametrically in analogy with those of the gas-phase to LPAHs step, including:

- ⊗ $(\text{SRSR} + \text{BINJ}_i)_{i < 5} \leftrightarrow (\text{SRSR} + \text{PAH}_r);$
- ⊗ $(\text{SRSR} + \text{BIN}_i)_{i \leq 3} \leftrightarrow (\text{SRSR} + \text{PAH}_m);$
- ⊗ $(\text{PAH}_r + \text{BINJ}_i)_{i < 5} \leftrightarrow (\text{PAH}_r + \text{PAH}_r);$
- ⊗ $(\text{PAH}_{\text{rsr}} + \text{BINJ}_i)_{i < 5} \leftrightarrow (\text{PAH}_{\text{rsr}} + \text{PAH}_r);$
- ⊗ $(\text{PAH}_m + \text{BINJ}_i)_{i < 5} \leftrightarrow (\text{PAH}_m + \text{PAH}_r);$
- ⊗ $(\text{PAH}_{\text{mH}} + \text{BIN}_i)_{i \leq 3} \leftrightarrow (\text{PAH}_{\text{mH}} + \text{PAH}_{\text{mH}});$
- ⊗ $(\text{PYYN}_r + \text{BINJ}_i)_{i < 5} \leftrightarrow (\text{PYYN}_r + \text{PAH}_r);$
- ⊗ $(\text{PYYN}_m + \text{BIN}_i)_{i \leq 3} \leftrightarrow (\text{PYYN}_m + \text{PAH}_{\text{mH}}).$

The $\text{PYYN}_m + \text{BINJ}$ reaction pathways were modeled based on the analogy with the study by Naydenova et al.[112], scaling the activation energies of reactions involving polyynes according to their number of carbon atoms. However, for this reaction class, the CRECK reactivity criteria are also used. These criteria vary depending on whether the reaction involves BINJ from sections 1-3 or π -radical BINJ from section 4. The kinetic parameters for C_4H_2 have been determined, with $A = 8.0 \times 10^{13}$, $n = 0$, and $E_{a0} = 12010$ cal/mol. For the other polyynes, only the activation energies have been scaled, considering their reactivity based on the number of carbons and their interaction with BINJ species:

- $\text{BINJ}_\sigma \rightarrow E_{a\sigma}: \text{C}_6\text{H}_2 \rightarrow E_a = E_{a0} * 0.667, \text{C}_8\text{H}_2 \rightarrow E_a = E_{a0} * 0.251, \text{ and if } C \geq 10 E_a = 0;$
- $\text{BINJ}_\pi \rightarrow E_{a\pi}: \text{C}_4\text{H}_2 \rightarrow E_a = E_{a\sigma} * 2; , \text{C}_6\text{H}_2 \rightarrow E_a = E_{a\sigma, \text{C}_6\text{H}_2} * 2, \text{C}_8\text{H}_2 \rightarrow E_a = E_{a\sigma, \text{C}_8\text{H}_2} * 2, \text{ and if } C \geq 10 E_{a\pi} = E_{a\sigma, \text{C}_8\text{H}_2}.$

The $\text{PYYN}_r + \text{BIN}$ were implemented similarly to Naydenova [112], reactions of precursor soot reagents with polyacetylene radicals, but using a correction factor of 1.25 for A.

Regarding the BIN/BIN inception, the reactions $\text{BINJ}_i + \text{BINJ}_j$, $\text{BIN}_n + \text{BINJ}_j$, and $\text{BIN}_n + \text{BIN}_m$ are considered, with $i, j \in [1-4]$ and $n, m \in [1-3]$, finally leading to the

formation of primary particles BIN_{5J}. Concerning the BIN_i+BIN_j and BIN_n+BIN_j interactions, the same CRECK rules were used with A increased by a factor of 2.5, as from [118]. BIN_n+BIN_m were modeled using the kinetic parameters taken from [115].

For the reactions related to the surface growth process by reactions, the reactions PAH_{rsr}+BIN_j, PAH_r+BIN_j, PAH_m+BIN_j, BIN_i+BIN_j and BIN_n+BIN_j were implemented using the kinetic parameters of [118], except for SRSR+BIN_j, which were assigned parameters similar to those in inception but for BIN_j sizes (1-4), with $i \in [1-4]$, $j \in [5-24]$ and $n \in [1-3]$.

Coalescence and aggregation BIN_i+BIN_j $i, j \in [5-24]$, dehydrogenation, demethylation, and C–H fission/recombination follow the CRECK parameters [116,117,140].

5.4.2 Kinetic parameters for soot polyene chemistry

To model the chemistry of soot particles for the pathway of soot formation from pyrolytic conditions in acetylene, a method closely paralleling the approach used by Naydenova et al. [105] has been employed, both in terms of the reaction schemes and reactivity. Similar to [105], precursor molecules arising from polyene reactions are considered activated products that cannot be stabilized into molecular form. To implement this scheme, new large PAHs termed BINPJs are introduced alongside BINs and BINJs from the CRECK model. In the current scheme, BINPJs are generated from reactions between polyenes and branched aromatic compounds and PAHs, which differs from Naydenova et al. [105], where reactions between polyene molecules are regarded as the initial step in forming activated precursors. BINs and BINJs remain the dominant products in PAH chemistry within the model, consistent with the CRECK model [115–118]. Regarding acetylene pyrolysis, analysis indicates that the reaction fluxes through BINs and BINJs are negligible compared to those through BINPJs; thus, these pathways are not discussed in detail here. The soot formation chemistry involving aromatic fuels has been validated against shock tube data across multiple fuels, which will be elaborated on in future publications. The model considers three groups of BINPJs (BIN1JPs, BIN2JPs, BIN3JPs), each with three hydrogenation levels and with carbon atom counts and C/H ratios similar to their respective BINJs.

The key reaction parameters relevant to this study are summarized in **Table 12**. Major reactions involve C_2H_2 and polyynes during both the initial phase and particle growth. Naydenova et al. [112] considered two contributions for the reactions of these species with precursors from the polyyne pathway and activated solid particles: the first accounts for the formation of precursor molecules + H, with fixed reaction rate parameters ($A = 8.0 \times 10^7$, $n = 1.56$, $E_a = 3794$ kcal/mol). The second pathway involves forming precursor molecules + H_2 , with an activation energy that varies depending on the polyyne size—31800 kcal/mol for C_2H_2 , 12000 kcal/mol for C_4H_2 , 8000 kcal/mol for C_6H_2 , 3000 kcal/mol for C_8H_2 , and 0 kcal/mol for larger polyynes—using a fixed pre-exponential factor of 4.0×10^{13} . Incorporating both pathways to model C_2H_2 and polyynes reactions with BINJP's data results in a substantial overestimation of soot volume fraction profiles at the low temperatures considered in this study, mainly due to the C_2H_2 reactions. The reference reaction rate constants for C_2H_2 +BINJPs were obtained from gas-phase chemistry, similar to the reaction between $C_6H_4C_2H$ and C_2H_2 . This yields rate constants between the two contributions listed in [242] (at 2000 K, 8.0×10^{10} vs. 4.3×10^{12} and 1.4×10^{10}). For polyynes, the relevant reaction rate parameters were taken from [105], considering contributions with variable activation energies but slightly higher pre-exponential factors (by a factor of 1.2). Similar rates were applied for reactions between polyynes and PAH radicals, with the pre-exponential factor increased by 1.5 to better match experimental profiles.

The assumption that reactivity increases with the number of carbons in the polyyne chains was also considered for reactions involving branched PAH_{mB} species and $C_{2x}H_2$, leading to the formation of BINJPs. Initial analysis focused on acetylene reactions. The pre-exponential factor was set to 8.0×10^{13} , matching that for reactions between polyynes and PAH radicals. The activation energy of 42700 kcal/mol is comparable to that of $C_{2x}H_2 + C_{2y}H_2$ in gas-phase chemistry, assuming the reaction occurs at the side chain moiety. Activation energies for reactions involving polyynes were scaled proportionally to the number of carbons. Pre-exponential factors were adjusted accordingly to ensure that reaction rate ratios for different polyynes mirror those for reactions between polyynes and BINJPs/PAH radicals, as reported in [105]. The rate constants for reactions between polyyne radicals and PAH_{mB} species were set at 5.0×10^{13} . The reference reaction rate constants for C_2H_2 +BINJPs were obtained from gas-phase chemistry, similar to the

reaction between $C_6H_4C_2H$ and C_2H_2 . This yields rate constants between the two contributions listed in [242] (at 2000 K, 8.0×10^{10} vs. 4.3×10^{12} and 1.4×10^{10}). For polyynes, the relevant reaction rate parameters were taken from [105], considering contributions with variable activation energies but slightly higher pre-exponential factors (by a factor of 1.2). Similar rates were applied for reactions between polyynes and PAH radicals, with the pre-exponential factor increased by 1.5 to better match experimental profiles.

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Concerning other reactions of the BINJP's, the rate parameters for BINJP's + PAH_{mB} 's / PAH_{rB} 's are based on the addition reaction at the carbon atom on the ring between phenyl and phenylacetylene and the phenyl + phenyl reaction, respectively. The reactions between polyyne radicals and BINJP's have rates increased by a factor of 1.2 compared to [112], similarly to the polyynes + BINJP's reactions. Finally, the reactivity of BINJP's with BINJP's, BINJ's, and BIN's has been taken similarly to the CRECK model, with an increment of a factor 2.5 in the pre-exponential factor. A similar increment is considered for the reactions between BINPJ's and BINJ's in surface growth and the coagulation/agglomeration reactions between BINJ's, which have the same reaction parameters.

The surface growth chemistry relevant to this study involves reactions of BINJs with PAH_{mB} and PAH_{rB} , which have rate constants similar to those in the CRECK model [108,110,241] for PAH and PAH radicals + BINJs. $PYYN_r + BINJ$ reactions are in analogy

with the equivalent reactions of [105], with a correction factor of 0.5 in the pre-exponential. Additionally, the HACA parameters from the CRECK model are used for reactions with acetylene, while the increased reactivity of the larger polyynes is accounted for, reducing the activation energy by half.

5.5 Reaction classes rate rules for soot kinetic modeling.

In developing the SMAuG generator, the rate rule system from the CRECK model methodology was implemented. This section briefly describes the rate rules for each reaction class in the proposed soot model.

5.6.1 HACA mechanism.

It is recognized that the H-abstraction and acetylene addition (HACA) mechanism contributes dually to the growth of PAHs and soot particles. The hydrogen abstraction mechanism promotes the formation of reactive sites on both PAHs and soot particles, resulting in the release of H₂.

The chemical species that are involved in the H-abstraction mechanism are:

H, CH₃, C₂H₅, C₃H₅-A, NC₃H₇, IC₃H₇, C₂H₃, C₃H₃, C₃H₃, C₄H₃, C₄H₅, C₃H₅-S, C₃H₅-T, C₆H₅, C₅H₇, C₇H₇, CH₃C₆H₄, C₉H₇, C₁₀H₇₋₁, C₁₀H₆CH₃, C₁₀H₆CH₃, C₆H₅CCH₂, C₆H₅CHCH.

In agreement with the modeling of [117], with the assumption of persistence of radical structures with carbon number > 100 atoms, abstraction is considered to occur up to BIN_i ≤ 3.

For the acetylene addition, for σ-radicals BIN_i ≤ 3 references of [115] are implemented, while for BIN_i > 3 π-stabilized resonant radicals, those related to C₂H₂ + C₇H₇ are adopted [243]. An activation energy of 10 kcal/mol is applied for the addition of C₂H₂ on BIN_i > 3 π-stabilized resonant radicals, while 5 kcal/mol is used for the σ-radicals BIN_i ≤ 3. The Arrhenius pre-exponential, A, is scaled as a function of H/C of the BIN reactants and is adjusted for the different morphology and structure of the LPAHs. The implemented

corrections on $A_{0,ref}$ are 1.0×10^{12} for $H/C < 0.35$, 1.2×10^{12} for $0.35 \leq H/C \leq 0.65$ and 1.4×10^{12} for $H/C > 0.65$. At the same time, a pre-exponential correction law is introduced as a function of particle type and size by introducing the diameter d_p for primary particles BIN(5-12)J (Eqn(5.6.1.1)) and, for aggregates BIN(13-24)J, the number N_p and size of primary particles (Eqn(5.6.1.2)).

$$\text{Soot primary particles Eqn(5.6.1.1):} \quad \frac{A}{A_{ref}} = 1 + \frac{d^2 H/C}{d_{ref}^2}$$

$$\text{Soot aggregates Eqn(5.6.1.2):} \quad \frac{A}{A_{ref}} = 1 + N_p \frac{d^2 H/C}{d_{ref}^2}$$

Where d_{ref} is the reference diameter at soot inception for BIN5J, i.e, ~ 1.91 nm, considering the value of [115].

5.6.2 Extended Carbon Addition (CA).

The HACA mechanism was enhanced in Carbon Addition by other carbon species besides C_2H_2 , such as C_4H_4 , C_3H_4 -P, C_3H_4 -A, and C_5H_6 . This was conceived as an extension of either the acetylene or vinylacetylene addition mechanism using masses of small gas-phase molecules detected under pyrolytic conditions. HACA kinetic rate parameters and rate rules were analogously taken from the model of [118], both for hydrogen abstraction and carbon addition. The rate corrections for the extended species in CA are adjusted using scaling factors based on gas-phase analogies, similar to the CRECK rate rule for CA.

5.6.3 Gas-phase precursors bridging to soot inception.

Concerning soot inception, fundamental reaction classes were implemented in this work, expanding the original CRECK scheme, as a result of iterative integration of the polyynes gas phase reactions with that of PAHs of the ICARE gas-phase:

PAH_{rsr}+PYYN_r/PYYN_m, PYYN_m+PAH_r, PYYN_r+PAH_r/PAH_m/PAH_{mB}, C₂H₂+PAH_{mB}, C₂H₂+PYYN_r, PAH_{mH}+PYYN_m, PYYN_m+PAH_{mB}, PYYN_m+PAH_{rB}, PYYN_r+PAH_{mB}.

These reactions have fixed parameters except for certain classes where a scaling factor for E_a is applied, as mentioned in previous section (5.4.1). This scaling on the activation energy is given as Eqn(5.6.3.1):

$$\text{Eqn(5.6.3.1): } E_a = \frac{E_{a0}}{\left(\frac{n^\circ (C_2H_2) \text{ atom carbon}}{n^\circ \text{ carbon atoms of } C_2H_2} \right)}$$

Regarding reactions involving PAHs+PAHs species by radical-radical and radical-molecule interaction, such as PAH_r+PAH_r, PAH_{rsr}+PAH_{rsr}, PAH_r+PAH_m/PAH_{mB}, PAH_{rsr}+PAH_r, PAH_{rsr}+PAH_m/PAH_{mB}, the correction based on the collision frequency was implemented. In PAH_r are also considered PAH_r of branched type – (PAH_{rB}). Such a scheme is derived from the theory of aerosol dynamics [132,133] and follows the rule of variation presented in the CRECK, where the Arrhenius pre-exponential is corrected according to the ratio of the collision frequency C_f to that of the reference reaction. It is possible to define:

$$\text{Eqn(5.6.3.2): } \frac{A_{ref}}{A_{ref,0}} = \frac{C_{ref}}{C_{ref,0}} = \delta \text{ dove } C_{ref} = \sigma^2 \sqrt{\frac{8\pi k_b T}{\mu_r}}$$

where k_b is the Boltzmann constant, T the temperature, μ_r is the relative mass, and σ is the average collision diameter. In the case of the interactions, PAHs+PAHs radical-radical, and radical-molecule, only the pre-exponential $A = A_0\delta$ is corrected by having n and E_a fixed. The molecule-molecule interactions, PAH_m+PAH_m, on the other hand, are governed by a rate rule using the collisional efficiency γ , Eqn(5.6.3.3), according to [244] and as implemented in the CRECK works. For PAH_m+PAH_m reactions, only molecules with $C>16$ atoms are considered.

$$\text{Eqn(5.6.3.3):} \quad \gamma = 1 - \left(1 + \frac{\Phi_0}{k_b T}\right) \exp\left(-\frac{\Phi_0}{k_b T}\right)$$

The collisional efficiency is a function of the well depth potential Φ_0 , the temperature T, and the Boltzmann constant. Φ_0 is defined by Eqn(5.6.3.4) as in [115–117], which is a function of Hamaker's constant A, while R1 and R2 are the radii of the colliding entities, D is the separation distance.

Eqn(5.6.3.4):

$$\Phi_0 = \frac{A}{6} \left\{ \frac{2R_1 R_2}{(2R_1 + 2R_2 + D)D} + \frac{2R_1 R_2}{(2R_1 + D)(2R_2 + D)} + \ln \frac{(2R_1 + 2R_2 + D)D}{(2R_1 + D)(2R_2 + D)} \right\}$$

Given Eqn(5.6.3.3, 5.6.3.4), the rate rule for this type of interaction is written as Eq(5.6.3.5):

$$\text{Eqn(5.6.3.5):} \quad k = A\gamma(hc, d_p, T) T^n \exp\left(-\frac{E_a}{RT}\right) hc^{1/6} \text{ cm}^3/(\text{mol s})$$

γ is a function of the colliding entities, the hydrogen/carbon ratio, and temperature. The rate expression is also corrected for the hc of the species involved. The temperature exponential is corrected with a power law fit over a thermal range and collisional efficiency, as in CRECK work. For SRSR+PAH_r, SRSR+PAH_m reactions, the parameters were assigned without any variation or correction for the original references. Resonantly stabilized radical pathways have been highlighted for their importance in soot condensation and growth [39].

5.6.4 Soot inception.

The BINJ+BINJ, BIN+BINJ, BINJP+BIN, and BINJP+BINJ (LPAHs) reactions follow the same rate rules already presented for PAHs gas-phase precursors, bridging to the soot

inception reaction class. The BIN-BIN, molecule-molecule interactions are governed by the collisional efficiency γ . The BINJ(1-3) σ -radicals species and BINJ(4) π -radical, as the model of [118], have an adjusted assigned activation energy of 0/3000 and 8000 cal/mol for σ radical- σ radical/ σ radical- π radical and radical-molecule interactions, respectively. The choice of pre-exponential values is in line with CRECK surface growth/coagulation/aggregation reactions.

5.6.5 Surface growth.

Surface growth involves BINJ_i with $i \geq 5$. The involved molecules and radicals are the same as in the PAHs/PYYNs inception. SRSR+BINJ_i reaction has the same inception rate rule. While PYYN_m+BINJ_i are scaled according to the Carbon Addition CRECK rule, PYYN_r+BINJ_i have fixed kinetic parameters. PAH_{rsr}+BINJ_i, PAH_r+BINJ_i, and PAH_m/PAH_{mB}+BINJ_i rate rules consider the asymptotic values of the reference pre-exponential factor for the largest lumped aggregate BIN20 ($A = 5 \times 10^{14}$ cm³/mol/s) with scaling based on the mean collision diameter (σ):

$$\text{Eqn(5.6.3.6): } k = A_0 T^{0.5} \frac{10^2 + \sigma^{6.5}}{10^5 + \sigma^{6.5}}$$

The BINJ_i/BINi/BINJP_i + BINJ_i reactions were modeled in continuity with the already presented molecular collisional efficiency. This is also in line with [193,204].

5.6.6 Coalescence and Aggregation, Dehydrogenation, Demethylation, C-H fission/recombination.

The remaining classes completely follow the CRECK model in parameters and rate rules [241].

6. Results and discussions.

This chapter presents the main results concerning the proposed model implementation, which includes the kinetics of polyynes reactions as the key main reactive pathways to soot formation. An overall validation and testing of the model is performed on different types of fuels and binary fuel mixtures under pyrolytic conditions, comparing the results with experimental data obtained with the ICARE HST shock tube at ICARE. Finally, the performance of the model is also evaluated by comparing it with experimental data from the literature under pyrolytic conditions. ROP analyses are reported to understand the fundamental reactive pathways involved in soot formation at different temperature conditions for the most representative fuels.

6.1 Soot model validation vs ICARE HST shock tube data.

In this section, the model validation for soot formation is performed against experimental pyrolysis data for different aromatic and aliphatic fuels obtained using the ICARE HST shock tube. The measurements, presented in previous thesis work [215], have been performed in collaboration with T. Viola and partially re-analyzed as needed. The measurement of the soot volume fraction produced by each fuel was carried out using the laser extinction technique previously described in section 3. In general, the shock tube experiments for both cyclic and acyclic fuels are characterized by bell-shaped curves of f_v versus temperature at fixed times, in accordance with what Graham et al. suggested in 1975 [244] (**Figure 6.1.1**), highlighting the competition between two main pathways. This behavior is due to the fact that at high temperatures, fragmentation reactions become predominant, while at lower temperatures, condensation reactions between aromatics and between aromatics and small fragments prevail.

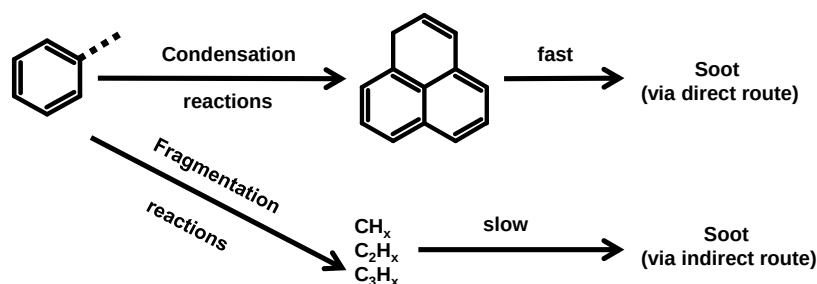


Figure 6.1.1 – Reaction scheme of soot formation from [245].

According to the information reported in Section 2.4 from literature studies, the reactive pathways of polyynes might have a key role in soot formation under various thermal conditions. In particular, the abundance of acetylene at high temperatures — resulting from the fragmentation of PAHs in aromatic fuels — favors soot production by such fast mechanisms, which involve the formation of a supersaturated vapor phase of polyynes. The diagram by Graham et al. can be modified as in **Figure 6.1.2**. The model activities presented in this work will confirm or refute such a hypothesis, including the role of the initiation reactions between polyynes and polyynyl radicals to aromatic precursors of soot.

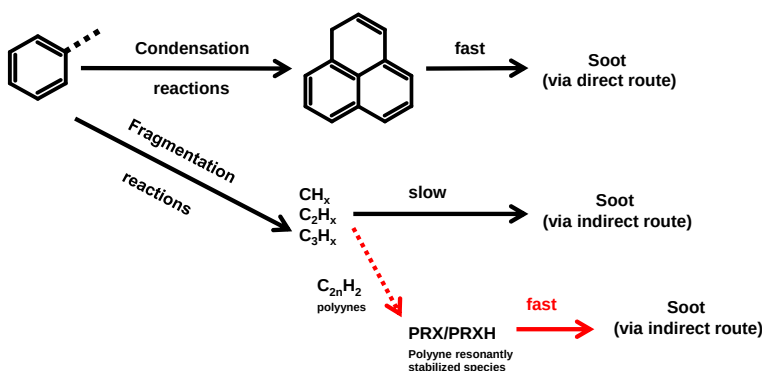


Figure 6.1.2 – Reaction scheme of soot formation ICARE-SMAuG adapted from [245].

6.1.1 Acetylene pyrolysis.

The comparative evaluation of the model's performance against experimental pyrolysis data on acetylene pyrolysis from HST of ICARE represents a critical component in

validating the proposed modeling framework. This analysis provides a rigorous assessment of the implemented gas-phase mechanisms, with a particular emphasis on modeling the polyynic chemistry and the new pathways to polycyclic aromatic hydrocarbons (PAHs), which are crucial in the soot inception process and subsequent surface growth steps. The current section presents comparative results for two distinct volumetric ratios of acetylene (C_2H_2) in argon: 0.35% (**Figure 6.1.1.1**) and 0.245% (**Figure 6.1.1.2**). These results are evaluated as functions of the time-history soot volume fraction (f_v), or as f_v measured at two different times, 0.5 ms and 1.0 ms. In both cases, the model proves to be reliable within a factor of approximately 2.2.

In **Figure 6.1.1.1a**, the model accurately reproduces both qualitatively and quantitatively the formation of soot, including its nucleation and the subsequent temporal evolution at the three selected temperatures: 1742 K, 1847 K, and 1954 K. Of particular interest is the model's capacity to capture the crossing time between the two high-temperature profiles, which occurs shortly after 0.8 ms. The validity of the model's performance in this context is further confirmed in **Figure 6.1.1.1b**, where the model accurately reproduces the trends recorded at 0.5 ms and 1.0 ms. In the dataset, the pressure P_5 varies between 16.7 and 18.2 bar, while the atomic carbon concentration $[C]$ spans from 4.47×10^{17} to 5.55×10^{17} atoms/cm³.

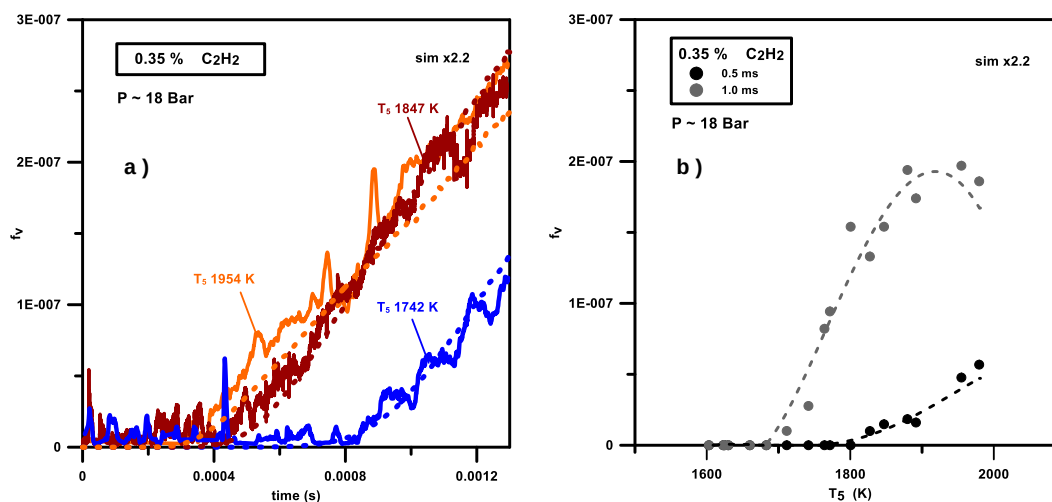


Figure 6.1.1.1 – 0.35% C_2H_2 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

Figure 6.1.1.2 presents the data corresponding to a C_2H_2 concentration of 0.245% in argon, collected within the temperature range T_5 1750 K - 1989 K. The pressure P_5 varies between 16.8 and 18.1 bar, while the atomic carbon concentration $[C]$ spans from 3.09×10^{17} to 3.63×10^{17} atoms/cm³. Analysis of the f_v profiles over time reveals that, under these conditions, the experimental data exhibit a notably increased noise level, which was mitigated through temporal averaging. In **Figure 6.1.1.2a**, the theoretical model accurately and consistently replicates the experimental trends observed at 1832 K and 1989 K. It is important to note that f_v values are not reported at lower temperatures, as soot formation under these conditions is negligible or absent, and the measurements cannot be considered reliable. Even at 0.245% C_2H_2 in argon, the model accurately captures the crossing point of soot volume fractions (f_v) at the two different temperatures. Examining **Figure 6.1.1.2b**, the model is capable of reproducing both qualitatively and quantitatively the profiles at 0.5 ms and 1.0 ms, but more experimental scatter is observed, stemming from the low initial acetylene concentration. Notably, the measured soot amount is quite low, approximately 6×10^{-8} . For both analyzed acetylene concentrations under pyrolytic conditions, the model demonstrates a high predictive capability.

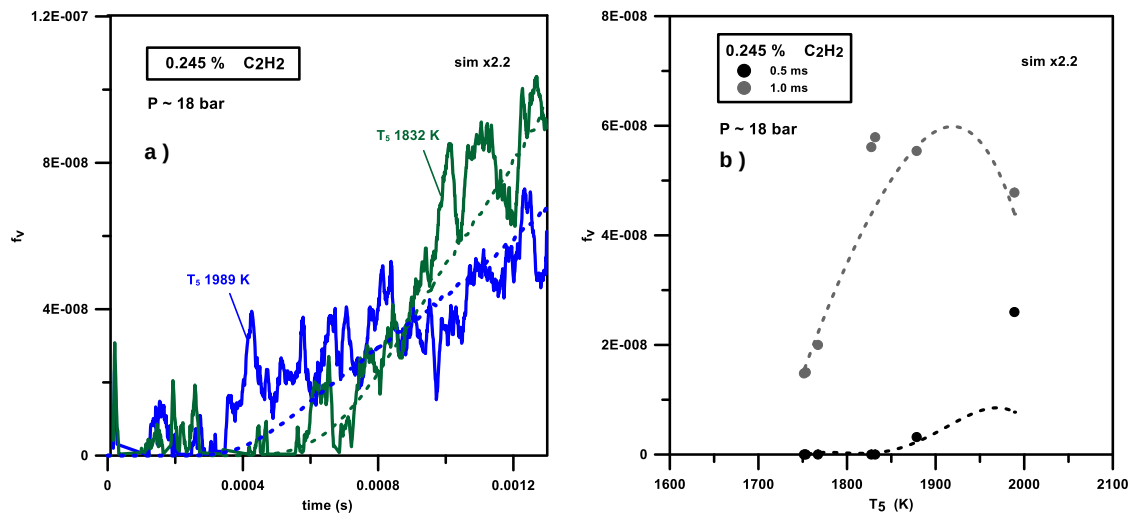


Figure 6.1.1.2 – 0.245% C_2H_2 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

The experimental and modeling profiles were also used to extract other kinetic parameters that characterize the soot formation process, such as the soot induction times (**Figure**

6.1.1.3 a) and the surface growth rates (**Figure 6.1.1.3 b**). In general, the results obtained with 0.35% C₂H₂ are perfectly reproduced by the kinetic model. The experimental and modeling global activation energies for induction are 26 kcal/mol and 29 kcal/mol, respectively, while those for the growth rate are -6 kcal/mol and -8 kcal/mol, respectively. Concerning the set with 0.245% C₂H₂, there are more discrepancies between model and experiments, but in this case, the smaller signal/noise ratio profiles might provide larger uncertainties in the experimental results. The experimental and modeling global activation energies for the induction are 32 kcal/mol and 25 kcal/mol, respectively, while those for the growth rate are -3 kcal/mol and -15 kcal/mol, respectively. In the latter case, the growth rates are slightly underpredicted, especially at higher temperatures. At 1878 K, the highest temperature for which the growth rate could be accurately determined, the underprediction is by a factor of 1.25. The simulated growth rates are multiplied here by a factor of 2.2 to obtain the f_v values.

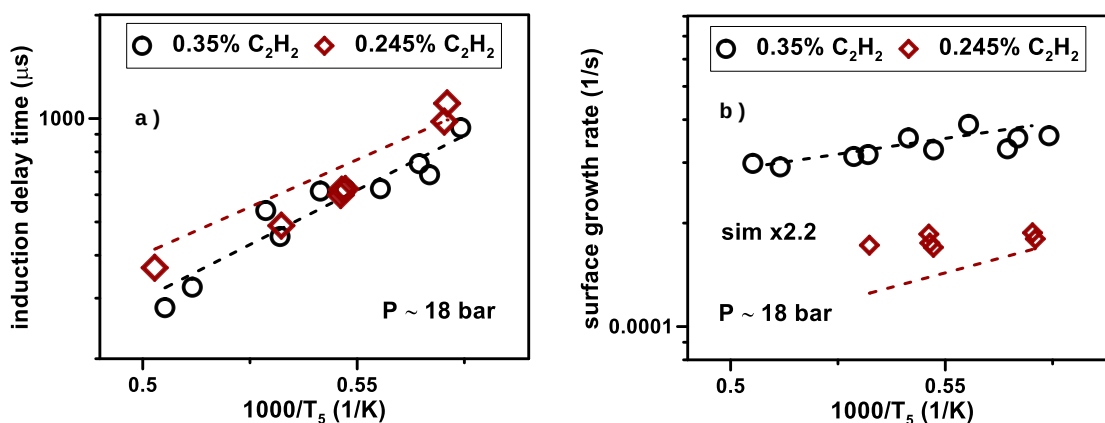


Figure 6.1.1.3 – Induction delay times and soot growth rates for the two acetylene mixtures.

To better understand the experimental uncertainties associated with $E(m)$, soot density, and T_5 , already discussed in **section 3.2**, a representative case is presented in **Figure 6.1.1.4**. This example illustrates how the modeling results are affected by these uncertainties, with the goal of having a better understanding of the global uncertainty in the measurements compared to the correction factor used to match the profiles in **Figure 6.1.1.2** and below for the other fuels. For this purpose, the modeling results (dashed lines) are not corrected.

In **Figure 6.1.1.4a**, the highlighted areas show the uncertainty on $E(m)$ on the experimental measurements, which can reach up to 50%. In **Figure 6.1.1.4b**, the simulation uncertainty resulting from the uncertainty in T_5 is analyzed, together with the uncertainty in the soot density. For the latter, the density of primary particles was considered to vary linearly between 1.1 g/cm³ for BIN5J and 1.85 g/cm³ for BIN22J, according to [230].

Globally, a discrepancy of up to a factor of 3 between modeling and experimental results is generally acceptable. Reproducing the shape of the time-history profiles at the different T_5 becomes essential.

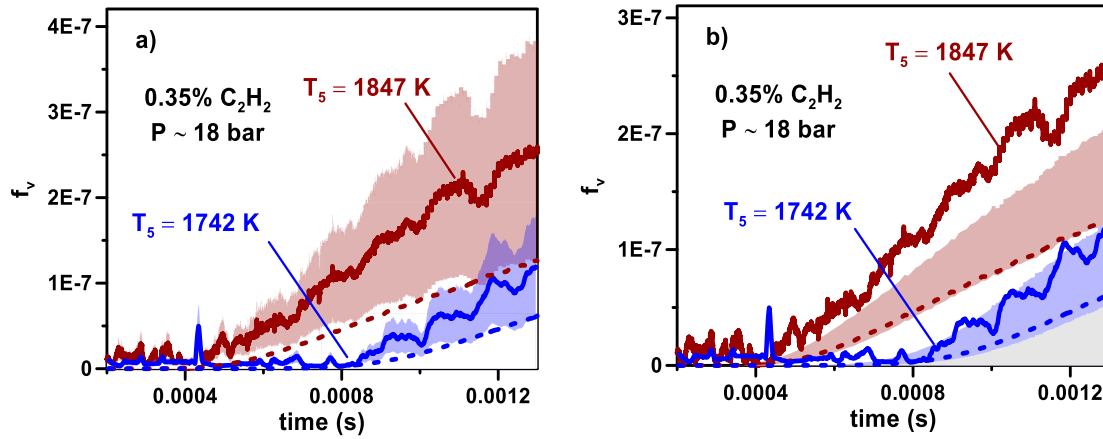


Figure 6.1.1.4 – Example of uncertainties in a) the experimental results due to the definition of $E(m)$; b) the simulations due to uncertainties in T_5 and soot density. The modeling profiles were not multiplied by any factor

6.1.2 Benzene pyrolysis.

The acetylene data presented in 6.1.1 provide an excellent benchmark for validating the polyynes routes. In addition, the chemistry of the aromatic fuels needs to be evaluated. Benzene is one of the key single-ring aromatics in combustion environments. Pyrolytic data for a mixture of benzene (C_6H_6) at a concentration of 0.082% in argon are here considered. The temperature range for this analysis spans from 1537 K to 1967 K (T_5), while the pressure range extends from 16.4 bar to 18.3 bar (P_5). Regarding carbon concentration, the values considered lie within the interval $3.06\text{--}3.90 \times 10^{17}$ atoms/cm³. In **Figures 6.1.2.1a** and **6.1.2.1b**, the predictive performance of the ICARE model for soot formation is compared to experimental f_v data. **Figure 6.1.2.1a** presents a comparison between simulations and experimental time-history profiles up to 1.3 ms. The model outputs have been corrected by a factor of 2.2 to align with the experimental data. At 1638 K, the model profile is qualitatively consistent with the experimental data, exhibiting a slight underestimation and a slight delay. At 1744 K, the profile demonstrates a similar qualitative behavior, with a minor increase in soot production rate starting around 0.4 ms, while overall matching the quantity of soot produced over the entire timeframe. At higher temperatures, the initial formation of the soot particles starts to diverge between simulations and experiments. At 1853 K, the simulated profile starts approximately 0.1 ms after the experimental data but maintains a qualitatively accurate and parallel shape, consistent both qualitatively and quantitatively. This delay remains evident at 1967 K; however, the slope of the simulation profile remains parallel and comparable to the experimental data, indicating good qualitative agreement. At this temperature, the model accurately reproduces the amount of soot formed up to 1.3 ms with high quantitative precision. Overall, the model demonstrates reliable predictive capability across the entire temperature range for soot formation initiated by benzene, particularly when the applied correction factor is considered.

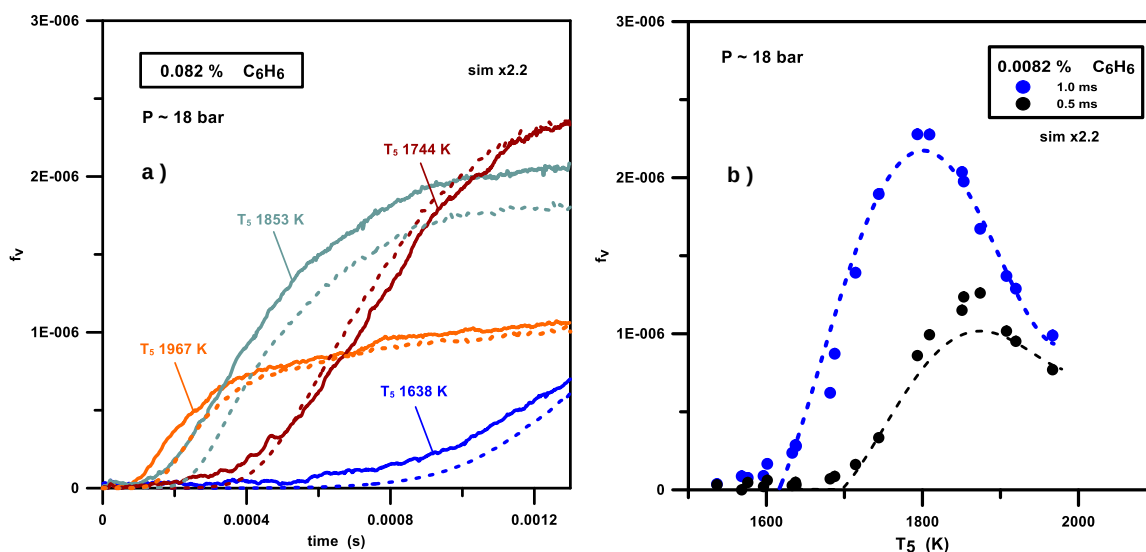


Figure 6.1.2.1 – 0.082% C_6H_6 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

A comprehensive overview of the model's performance across the entire temperature range relevant to soot formation from benzene pyrolysis is provided by the curves of f_v at 0.5 ms and 1.0 ms in **Figure 6.1.2.1b**, again employing a correction factor of 2.2 for the simulations. The model accurately predicts soot formation at both 0.5 ms and 1.0 ms across various temperature ranges. At 1.0 ms, the model fits very well, with a slight overestimation of the volume fractions within the temperature range of 1600-1750 K, which can be interpreted as a minor shift of the peak by 20-30 K relative to experimental data. In the 1900-2000 K range, the model tends to slightly underestimate soot production. Overall, for the two series examined, the model's predictions align well with experimental results, both qualitatively and quantitatively. At 1.0 ms, the model is capable of reproducing the experimental data trend very well, being able to also catch the temperatures at which the maximum soot volume fraction occurs. The model closely matches the experimental data at 0.5 ms but slightly underestimates soot production around the peak at 1870 K.

As for the case of acetylene, a more detailed analysis of the induction delay times and soot growth rates is presented (**Figure 6.1.2.2**). From an experimental point of view, the results

on the induction delay time have been divided into two parts, with a temperature limit around 1750 K (**Figure 6.1.2.2a**). At lower temperatures, the global activation energy of the induction process is around 40 kcal/mol; at higher temperatures, it is around 56 kcal/mol. This behavior is also present in other literature investigations on benzene pyrolysis, as it will be shown in the section 6.3 related to the validation against literature data. The modeling results are reasonable in terms of absolute induction values, although they are characterized by a single slope similar to the one observed in the experiments below 1750 K. The global activation energy is around 38 kcal/mol. The maximum discrepancy between the simulation and the experiments is nearly a factor of 2 at the highest temperature conditions (1967 K). This discrepancy is also clear from the delay in the simulation profiles compared to the experiments in **Figure 6.1.2.1**. As is common to other aromatic fuels, e.g., toluene (**section 6.1.3**), styrene (**section 6.2.3**), and ethylbenzene (**section 6.2.2**), the possible explanation could lie in the selected parameters for the relevant PAH/polyne interactions and surface growth by polyne reactions. The key role of these reaction classes is confirmed by the analyses of **section 6.4.4**. Though improvement of the current simulation capabilities could not be obtained without a deterioration of the results at other conditions.

The soot growth rate can also be extracted from the f_v profiles as presented in **Figure 6.1.2.2 b**. Once again, the experimental results indicate two different regimes for the lower and the higher temperature conditions. The temperature threshold separating the two regimes is around 1750 K, as for the induction delay times. The global activation energy of the growth below such temperature is around 51 kcal/mol, while above, the growth rate is nearly constant. The model is capable of reproducing the experimental behavior. The simulated global activation energy of the soot surface growth below 1750 K is 61 kcal/mol, around 10 kcal/mol lower than the experimental value, while above 1750 K, it is slightly negative. The growth rate at high temperature is underpredicted by a factor of 1.16 on average. To be noted, the growth rate has been multiplied by a factor of 2.2 in the simulations.

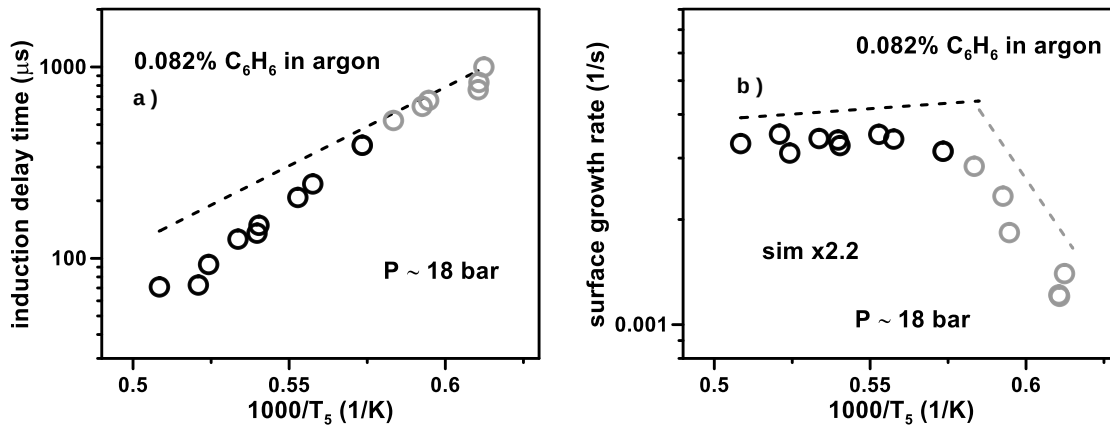


Figure 6.1.2.2 – Induction delay times and soot growth rates for the 0.082% benzene.

6.1.3 Toluene pyrolysis.

Toluene is another important aromatic in real fuels and surrogates. Its decomposition leads to the formation of the resonantly stabilized benzyl radical, an intermediate that is a key participant in various growth mechanisms. Thus, it is important to validate the model against data for this fuel. The experimental data were collected at a concentration of 0.07% C_7H_8 in argon, over a temperature range of 1518–1990 K, at a pressure of 16.4–18.2 bar, and with $[C]$ of $3.03\text{--}3.92 \times 10^{17}$ atoms/cm³. In **Figure 6.1.3.1**, the experimental results are presented and compared with the ICARE soot model. Specifically, **Figure 6.1.3.1a** shows the temporal trends of f_v up to 1.3 ms, while **Figure 6.1.3.1b** illustrates the values of f_v at 0.5 and 1.0 ms.

The model appears to be consistent with the experimental data, within a correction factor of 2.2. In **Figure 6.1.3.1a**, at a temperature of 1538 K, the model accurately reproduces the observed trend, with a slight overestimation of approximately 20% at around 1.2 ms. At 1649 K, the modeling curve qualitatively resembles the experimental one, though with some discrepancies. The model-predicted onset of soot formation is delayed relative to the initial phase of the experimental curve. Between 0 and 0.8 ms, the model underestimates the amount of soot produced; however, beyond this threshold, a trend inversion occurs, with an overestimation of up to 50% of the soot amount. At 1748 K, with a slight delay in initiation, the model demonstrates good agreement with experimental data. As temperatures increase, the model's ability to reproduce the exponential data becomes less

accurate. At 1855 K and 1939 K, the model behaves similarly, producing qualitatively accurate profiles but with delayed ignition and underestimating soot by about 50%. Overall, the observation in **Figure 6.1.3.1a** is confirmed across the entire temperature range shown in **Figure 6.1.3.1b**. At both 0.5 ms and 1.0 ms, the model qualitatively reproduces soot formation under the measured conditions, although a shift of approximately 50 K is observed in the peak of maximum soot production. This shift reflects the model's overestimation in the temperature range between 1600 and 1700 K, with a progressive underestimation at higher temperatures. For both 0.5 ms and 1.0 ms, starting from 1800K, the model underestimates the high-temperature range between 1800 and 1900K. Subsequently, it adapts to the trend at the extremes of f_v at higher temperatures. Overall, the model provides a good reproduction of the soot formation chemistry for toluene pyrolysis, in addition to the case of acetylene and benzene presented in the previous sections.

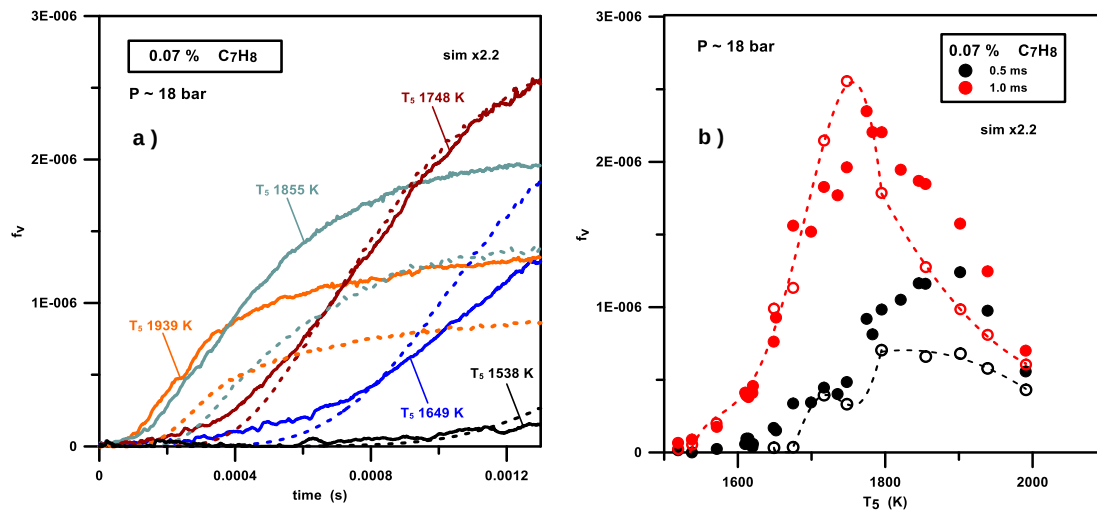


Figure 6.1.3.1 – 0.07% C₇H₈ in Ar at P ~ 18 bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2 Soot model performance vs ICARE HST shock tube data.

The chemical kinetic model was mainly validated against data on acetylene for the polyynene chemistry, benzene for the aromatic chemistry, and toluene for the influence of resonantly stabilized radicals. Moreover, the model was tested against similar time-history soot volume fraction profiles obtained with the HST at ICARE on other fuel molecules and mixtures. Below are the main results.

6.2.1 Ethylene pyrolysis.

Following the analysis of soot formation data for acetylene, ethylene is probably the most studied C₂ component. C₂H₄ decomposes quickly at high temperatures to the vinyl radical (C₂H₃) + H. The vinyl radical can decompose to acetylene + H, but it can also react with another ethylene molecule to form C₄ intermediates. This opens a pathway to the formation of the aromatic ring that is not available in the acetylene case. Evaluating soot formation from ethylene pyrolysis can then be important for testing both the aromatic and the acetylenic pathways. Soot formation from 0.7% C₂H₄ in argon was examined under conditions spanning temperatures from 1685 K to 2017 K (T₅), pressures from 16.9 bar to 20.7 bar (P₅), and carbon concentration ranges between 8.5×10^{17} and 11.2×10^{17} atoms/cm³. The results are depicted in **Figure 6.2.1.1**, with panel (a) illustrating the time history of f_v , and panel (b) displaying f_v at 0.5 ms and 1.0 ms across the examined temperature range. A correction factor of 2.2 is applied to the simulation results in all comparisons. At 1799 K, the model overestimates f_v and predicts an earlier onset of soot formation compared to experimental observations. At 1857 K, the model closely replicates the temporal evolution of soot production, albeit with an underestimation above 1.0 ms; this trend persists at 1954 K, with underpredictions of the experimental results by around 30%. In **Figure 6.2.1.1b**, which presents f_v at 0.5 ms and 1.0 ms over the temperature range, the model underestimates the experimental peaks. Notably, for the data at 0.5 and 1.0 ms, the simulation exhibits a rising trend rather than the bell-shaped profile observed experimentally.

Overall, discrepancies exist in ethylene pyrolysis; the model demonstrates acceptable quantitative agreement. At the same time, non-negligible experimental scatter is reported in the data.

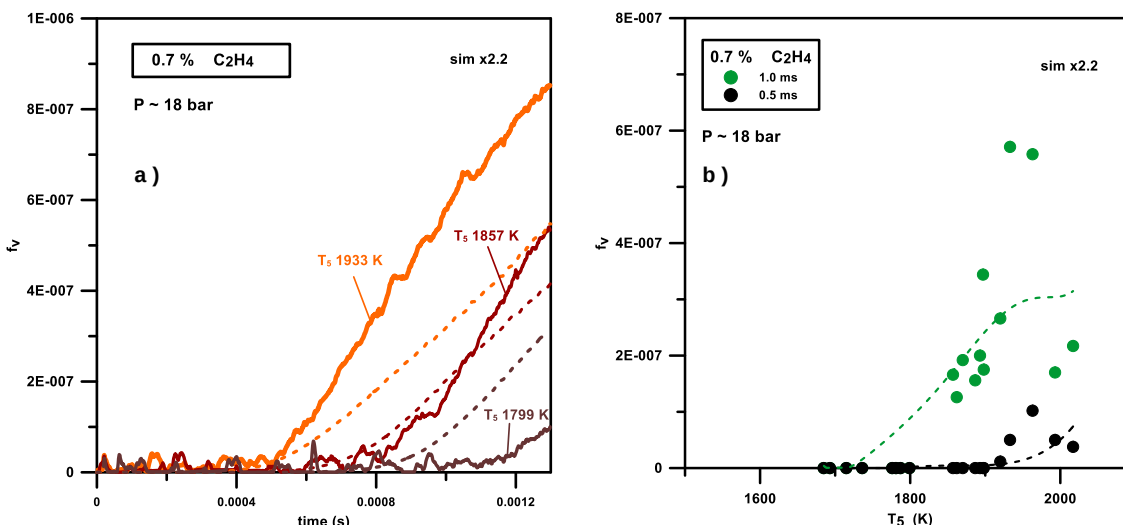


Figure 6.2.1.1 – 0.07% C_7H_8 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2.2 Ethylbenzene pyrolysis.

Ethylbenzene is the simplest of the alkylbenzenes, a main constituent of conventional fuels. Its decomposition leads to the formation of benzyl radicals and styrene, the latter being an intermediate compound for the formation of the second ring through the HACA mechanism and phenanthrene by reaction with the phenyl radical.

Figure 6.2.2.1 shows the comparison of the modeling simulations (corrected by the usual factor 2.2) with the experimental data for 0.06% ethylbenzene ($C_6H_5C_2H_5$) in argon, evaluated over a temperature range of 1560 to 1931 K, a pressure range of 16.56 to 18.9 bar, and a concentration $[C]$ spanning from 3.24 to 5.06×10^{17} atoms/cm³. **Figure 6.2.2.1** presents the comparison of the model with the experimental soot data with a correction factor of 2.2. At 1640 K (**Figure 6.2.2.1a**), the model exhibits a slight delay in capturing soot formation, intersecting the experimental curve around 0.9 ms and subsequently overestimating the value until approximately 1.3 ms. The model accurately reproduces the

f_v profile at 1764 K, despite an initial delay in soot production. At elevated temperatures, specifically 1862 K and 1939 K, the simulations show a qualitative agreement with experimental data, with persistent delays at the onset of soot formation and an underestimation of the asymptotic values at late times by approximately 20-30%. Considering the data at 0.5 ms and 1.0 ms, the model predictions accurately reproduce the profiles observed in the experimental scattering, with no significant discrepancies observed (**Figure 6.2.2.1b**). At 0.5 ms, a slight underprediction is observed, which remains constant across the entire simulated range.

Overall, the model demonstrates both qualitative and quantitative capabilities to replicate experimental results for ethylbenzene pyrolysis across the entire temperature range, further supporting the validity of the chemistry involving the benzyl radical in soot formation.

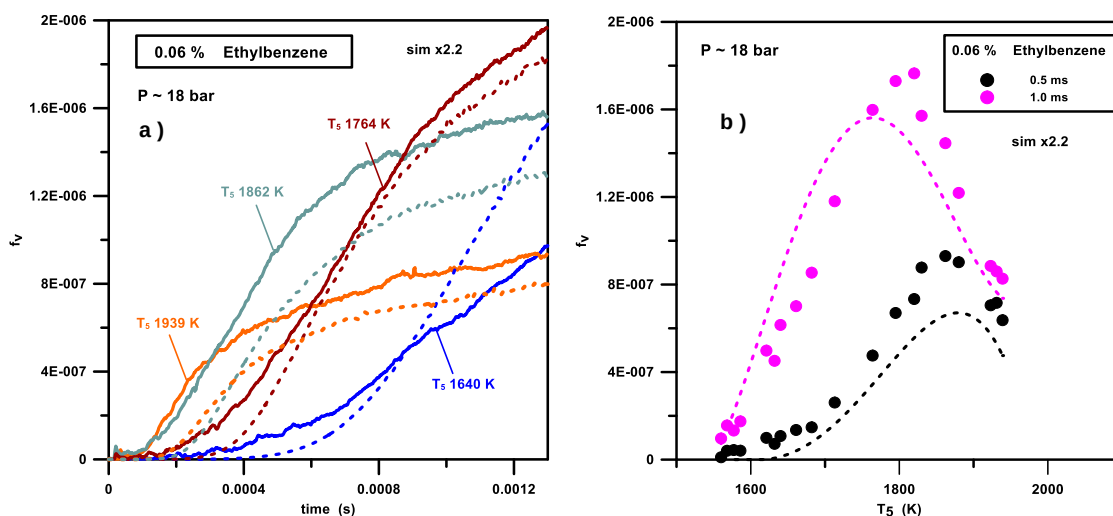


Figure 6.2.2.1 – 0.06% Ethylbenzene in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2.3 Styrene.

Styrene represents an important intermediate in pyrolytic processes, serving as a precursor to PAHs and aliphatic compounds; thus, it plays a significant role in soot formation. Following the modeling study on ethylbenzene, whose decomposition leads to a high styrene concentration, the role of the styrene side chain can be investigated and compared

with the saturated case. **Figure 6.2.3.1** shows the comparison between the model predictions (corrected by the factor 2.2) and experimental data with a mixture of 0.6% styrene ($\text{C}_6\text{H}_5\text{C}_2\text{H}_3$) in argon, highlighting the temporal trends of the soot volume fraction (f_v) (**Figure 6.2.3.1a**), and the data extracted at 0.5 and 1.0 ms (**Figure 6.2.3.1b**). The operating conditions involve temperatures between 1576 and 1942 K, pressures ranging from 17.4 to 18.2 bar, and $[\text{C}]$ of the order of 3.48×10^{17} to 5.68×10^{17} atoms/cm³. In **Figure 6.2.3.1a**, the f_v profiles over time up to 1.3 ms are illustrated, as previously analyzed in earlier studies. All compared profiles show a temporal delay in the model, with a more or less pronounced delay depending on the temperature considered. At 1647 K, the model exhibits behavior qualitatively similar to the experimental data, with a slight overestimation after 1.0 ms. At 1741 K, the simulation maintains good agreement and convergence up to 1.3 ms, resulting in a quantitative match with the experimental trend. At 1845 K, a smaller delay is observed, with predicted values very close to the experimental ones and a slight overestimation after 0.8 ms. At 1942 K, an even further reduction in delay compared to the experimental data is noted. In addition, despite an overestimation of about 50% in the soot volume fraction above 0.4 ms, the model remains qualitatively consistent with the experimental observations. The variation in induction delay for the profiles is reflected in **Figure 6.2.3.1b**, which compares the models at 0.5 and 1.0 ms within the analyzed temperature range. This behavior is particularly evident at 0.5 ms before 1750 K, with the maximum soot production shifting to the right by about 50 K, corresponding to a delay of approximately 0.2 ms based on estimates from the modeling results. At 1.0 ms, the simulation behavior more closely aligns with the experiments, despite a slight overestimation between 1500-1650 K and 1800 and 1850 K.

The model is shown here to accurately reproduce soot formation from styrene pyrolysis, another important confirmation of the accurate kinetics for aromatic fuels proposed in this work.

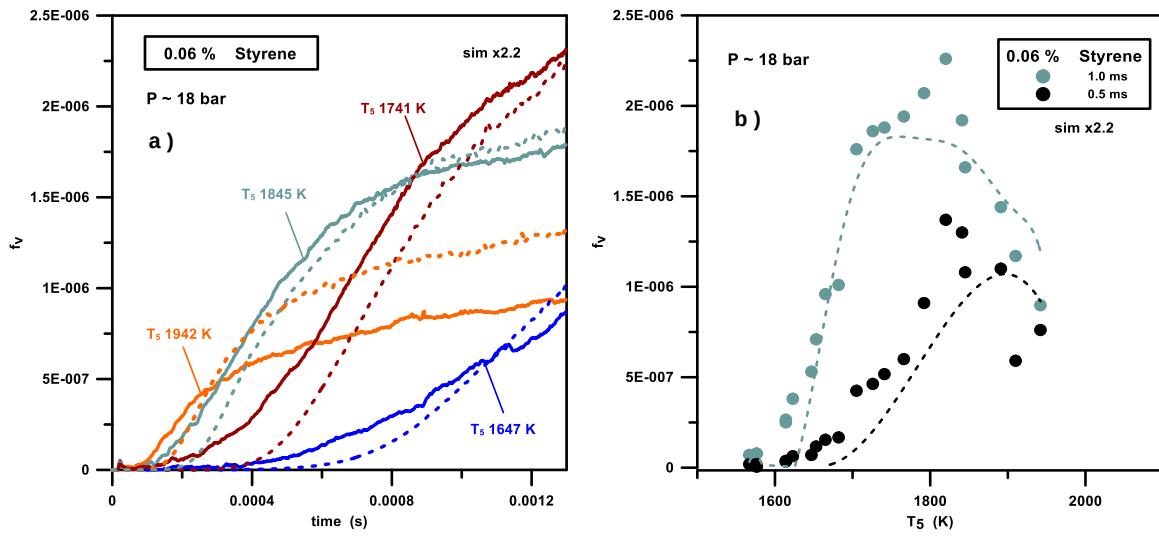


Figure 6.2.3.1 – 0.06% Styrene in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2.4 Cyclopentene pyrolysis.

An additional analysis of the model's performance was conducted using data related to soot formation from the pyrolysis of cyclopentene. The latter is a significant fuel as a precursor of cyclopentadiene and cyclopentadienyl radicals, whose addition and recombination represent critical pathways in the formation of small PAH compounds such as naphthalene in flames. The kinetics of resonantly stabilized radicals applied to soot formation is once again tested here. Experiments were conducted with a mixture containing 0.098% cyC_5H_8 in argon. The experimental conditions include temperatures T_5 ranging from 1551 to 1968 K, pressures P_5 varying between 16.4 and 18.7 bar, and concentrations $[C]$ ranging from 3.10 to 3.71×10^{17} atoms/cm³. The proposed model proved to be accurate, with a correction factor of 2.2 compared to the experimental data as reported in **Figure 6.2.4.1**. In this figure, the variations of f_v over time at different temperatures are shown. At 1625 K, the model fairly accurately reproduces the experimental trend of f_v , with a slight increase observed after 1.0 ms. At 1748 K, the soot formation predicted by the simulation closely follows the experimental data, overestimating it starting from 0.7 ms. Overall, the simulation and experimental trends are qualitatively similar. At 1826 K, the model shows a delay and increasing deviation, underestimating the quantities by about 20-30%. This delay becomes more pronounced with increasing temperature, as observed at 1962 K, although the deviation from the experimental values reduces with time. The profiles of f_v as a function of T_5 , illustrated in **Figure 6.2.4.1b**, show that at 0.5 ms, the peak around 1900 K is underestimated. At 1.0 ms, the simulation profile shows a very accurate agreement in the range between approximately 1600 and around 1770 K, while between 1800 and 2000 K, a slight underestimation is observed, with a peak shift of about 50 K. Overall, the observed trends are consistent with the experimental data, although accompanied by slight quantitative discrepancies.

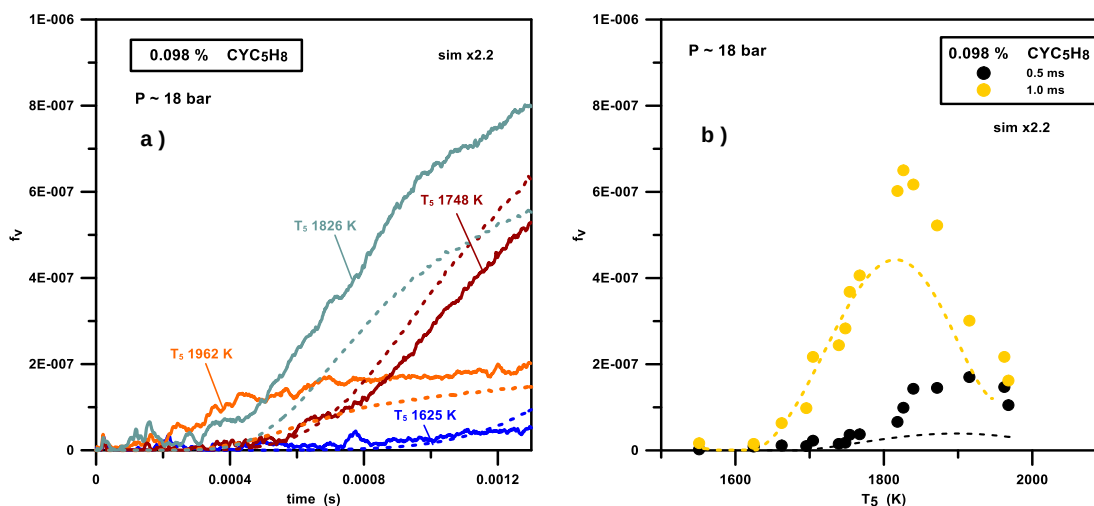


Figure 6.2.4.1 – 0.098% CYC₅H₈ in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2.5 Propylene pyrolysis.

The gas-phase of ICARE was developed based on single pulse shock tube experiments aimed at validating reactive pathways starting with the thermal fragmentation of C₃ unsaturated hydrocarbons, contributing to PAH formation mainly through the allyl and propargyl radicals. Soot formation experiments were performed at ICARE with a concentration of approximately 0.1633% C₃H₆ in argon, for T_5 ranging from 1598 to 1968 K, P_5 between 16.0 and 18.6 bar, and a concentration $[C]$ $3.10\text{--}3.71 \times 10^{17}$ atoms/cm³. **Figure 6.2.5.1** compares the model with f_v time-histories and f_v at 0.5 and 1.0 ms. The simulations are adjusted with a factor of 2.2. In **Figure 6.2.5.1a**, the temporal evolution of the simulated f_v profiles is shown. At 1636 K, the model prediction closely matches the experimental profile, with a slight increase around 1.1 ms. At 1742 K, minor experimental noise is observed, but the simulation begins producing soot with a delay of 0.2 ms and exhibits a significant growth from 0.8 ms, overestimating soot quantity by about 50%. This behavior diminishes at higher temperatures; at 1839 K, the simulation aligns well both qualitatively and quantitatively with the experimental trend, with a slight f_v overestimation starting at 0.9 ms. At 1968 K, a delay of approximately 0.1 ms is observed, with the

simulation slope remaining parallel to the experimental data. From 0.8 ms onward, soot production increases quite rapidly. **Figure 6.2.5.1b** presents the overall trend of f_v at 0.5 and 1.0 ms across the investigated temperature range.

At 0.5 ms, the model performs qualitatively well, albeit with a slight, constant underestimation of the experimental data across low to high temperatures. At 1.0 ms, between 1650 K and 1900 K, there is a slight overestimation that shifts the maximum soot production peak to the left by about 50 K. However, the high-temperature trend is faithfully reproduced.

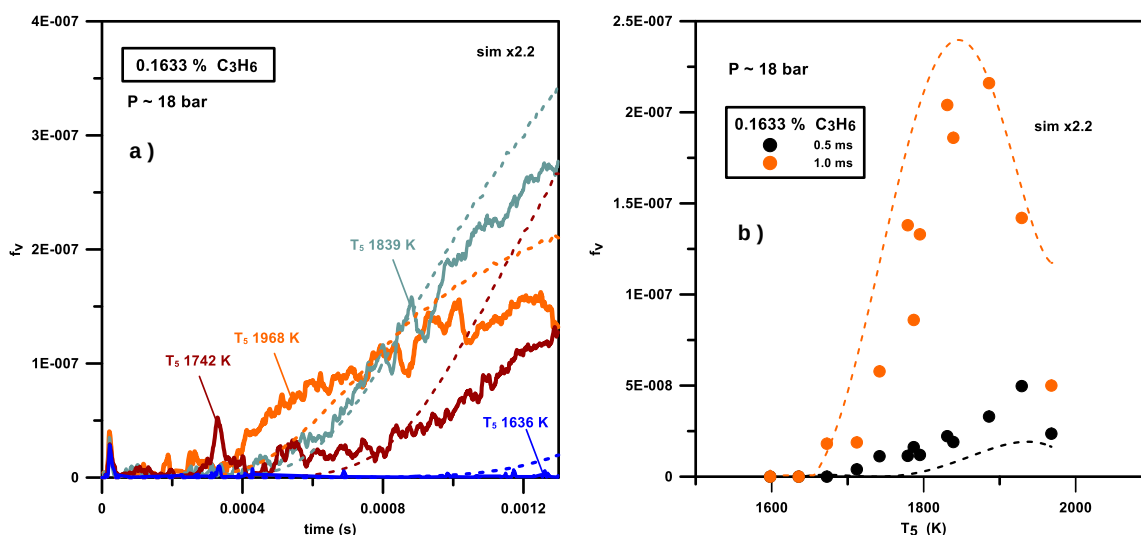


Figure 6.2.5.1 – 0.1633% C_3H_6 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

6.2.6 Propyne pyrolysis.

Along the same line of study related to propylene, measurements of the soot volume fraction were conducted starting from propyne, which is a direct precursor of the resonantly stabilized propargyl radical, a species fundamental for benzene formation in flames and, consequently, for the precursors of polycyclic aromatic hydrocarbons involved in the soot process. Specifically, soot measurements were performed under pyrolytic conditions, with a concentration of 0.166% pC_3H_4 in argon, at temperatures ranging from 1586 to 1951 K,

pressures from 16.8 to 19.4 bar, and a concentration $[C]$ of the order of $3.10\text{--}3.71 \times 10^{17}$ atoms/cm³. A correction factor of 2.2 was applied to the model.

Figure 6.2.6.1 illustrates the comparisons between the results from the ICARE-soot model and the experimental data. **Figure 6.2.6.1a** shows how f_v changes over time, up to 1.3 ms. At 1621 K, the model predicts a faster growth than observed experimentally and about three times the f_v at 1.3 ms compared to the experimental value. At 1764 K, the timing of soot production in the simulation nearly matches the experimental onset, though it overestimates by roughly 1.3 times. At 1857 K, the model's predictions are quite inaccurate, significantly overestimating the growth and soot production rate. At 1954 K, both experimental and simulated data agree on the time of soot nucleation, but the model estimates asymptotic soot quantity approximately 50% higher than the measurements. These differences are also evident in **Figure 6.2.6.1b**, which shows f_v extracted at 0.5 and 1.0 ms within the temperature range. The peak at 0.5 ms is slightly shifted upward by about 50 K, and the one at 1.0 ms is at lower temperatures, with predicted formation of soot particles below 1650 K, where the experimental data are nearly zero. Though the model overestimates by about 50% the f_v in both cases, reproducing the proportion between the two sets correctly.

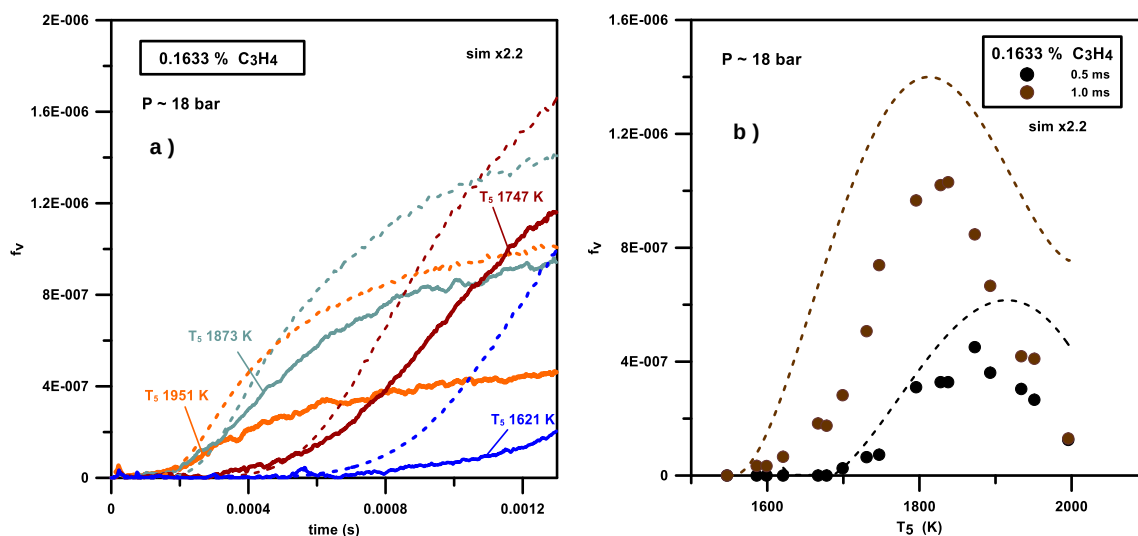


Figure 6.2.6.1 – 0.1633% C_3H_4 in Ar at $P \sim 18$ bar. a) Experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

After comparing the data in **Figure 6.2.6.1**, it is evident that the correction factor of 2.2 used for soot simulation from C_3H_4 significantly overestimates the experimental results. Therefore, a comparison of the model with experimental data is also presented in Figure 6.2.6.2 using a different factor, specifically 1.5.

Figure 6.2.6.2 shows a significantly improved performance for C_3H_4 , thanks to a correction factor of 1.5. At 0.5 ms, the model overall reproduces the experimental range well up to about 1850 K, although a shift of the peak toward higher temperatures of approximately 50 K is observed. At 1.0 ms, the peak match is very accurate, with a slight overestimation both to the left and right of the peak itself. Overall, the model's performance is better for this fuel with a correction factor of 1.5.

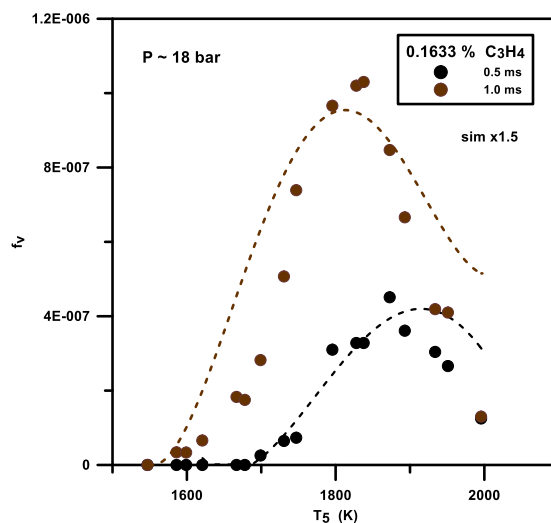


Figure 6.2.6.2 – 0.1633% C_3H_4 in Ar at $P \sim 18$ bar. Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations $\times 1.5$.

6.2.7 Global fuels performance.

In this section, a comprehensive and summarized comparison of the performance of the developed model is presented, analyzed across all types of fuel, considering the volumetric fractions of soot at 0.5 ms and 1.0 ms within the range of operational conditions described. This comparison is illustrated in **Figure 6.2.7.1a** for 0.5 ms and in **Figure 6.2.7.1 b** for 1.0 ms.

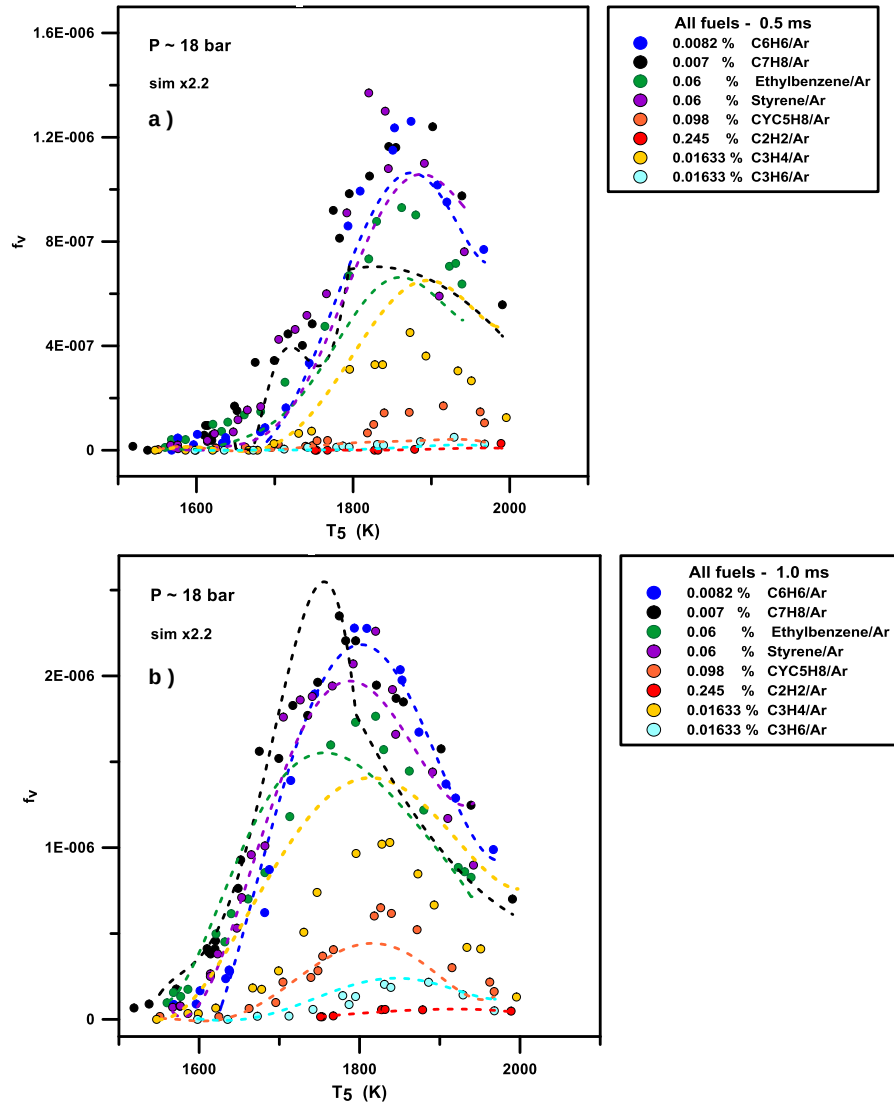


Figure 6.2.7.1 – Global comparison of Experimental f_v at 0.5ms a) and 1.0 ms b) vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations x 1.5.

The model proves to be generally reliable for both 0.5 ms and 1.0 ms f_v , demonstrating good performance both quantitatively and qualitatively, except for the overestimation of f_v for C_3H_4 , as previously presented.

6.2.8 Aromatic + aliphatic mixtures.

In this section, the predictive capability of the model regarding soot formation in binary mixtures composed of C_6H_6 , C_7H_8 , and CYC_5H_8 blended with C2-C3 compounds, namely C_2H_2 , C_2H_4 , C_3H_4 , and C_3H_6 , is analyzed. As for the single-component cases, comparisons are provided concerning the temporal trend of the f_v value, considering detection times of 0.5 and 1.0 ms within the analyzed temperature range. Additionally, comparisons between single-component data and results obtained with the mixtures are presented

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6.2.8.1 Benzene + C_2 unsaturated hydrocarbons

Figure 6.2.8.1.1 shows the comparisons between the modeling results and the experimental data related to the mixtures $C_6H_6 + C_2H_2/C_2H_4$. In **Figures 6.2.8.1.1(a)** and **(c)**, the time history of f_v for each binary mixture is presented, while in Figures (b) and (d), the same is shown at 0.5 and 1.0 ms as a function of T_5 . Specifically, in **Figures 6.2.8.1.1(a)** and **(b)**, the model predictions for a mixture containing 0.0306% C_6H_6 and 0.154% C_2H_2 in argon are illustrated, at temperatures T_5 ranging from 1582 to 1975 K, pressures P_5 between 16.7 and 18.6 bar, and a concentration $[C]$ $3.23\text{--}3.85 \times 10^{17}$ atoms/cm³. The correction factor applied to the model relative to the experimental data is 2.2, for consistency with the single-

component cases. Better agreement between experiments and simulations would have been obtained by applying a different factor for the different mixtures, but this would have led to an erroneous evaluation of the model capabilities.

In Figure 6.2.8.1.1a, at 1625 K, the model accurately and consistently predicts soot production up to 1.3 ms. At 1766 K, the simulation captures the induction time of soot formation but overestimates the values by a factor between 20% and 30%, increasing with time, while maintaining a general shape consistent with the experimental data. Similar considerations apply for the profile at 1860 K: despite the initial rise being correctly captured, the simulated f_v 's start diverging from the experimental profile at about 0.4 ms, while preserving the profile shape. The overestimation becomes more pronounced at higher temperatures; in fact, at 1950 K, a more pronounced increase in the modeling profile is observed, with an overestimation starting around 0.3 ms of factor 2 compared to the experiments. Despite these differences, in all four profiles analyzed, qualitative simulation trends are observed to faithfully reproduce the characteristics of the experimental curves. This behavior is reflected in the simulations of the f_v at 0.5 and 1.0 ms, as shown in Figure 6.5.6.1.1b. At 0.5 ms, the f_v simulated values reproduce the experimental trend in the initial part of the profile, below 1850 K, but they diverge at higher T_5 's, with an approximate deviation of 100 K at the peak of production. Concerning the f_v values at 1.0 ms, although a quantitative difference in terms of model overestimation is evident (around 50% more soot in the simulations), the general profile, in terms of the position of the soot volume fraction peak (about 1820 K) and starting temperature for soot production (about 1680 K), is well reproduced by the model.

A different, opposite behavior was observed for the second mixture containing ethylene (C_2H_4). **Figures 6.2.8.1.1 (b) and (c)** present similar evaluations performed on the previously discussed mixtures. Specifically, a mixture composed of 0.0306% benzene (C_6H_6) and 0.154% ethylene (C_2H_4) in argon bath gas was examined across a temperature range T_5 from 1645 K to 2017 K, P_5 between 16.1 and 18.7 bar, and a $[C]$ from 3.10 to 3.71×10^{-7} atoms/cm³. The correction factor used for the model is 2.2.

In Figure 6.2.8.1.1c, the model's behavior at 1645 K aligns with experimental data both in terms of quantity and quality up to 1.3 ms. At 1753 K, the model-predicted soot production

shows a slight delay relative to the experimental data, but it reproduces both the trend and the magnitude observed. At 1843 K, the model's prediction is also delayed, with an underestimation of up to 50%, yet it maintains a trend shape consistent with the experimental data. In 1977 K, the model shows a further delay in the onset of soot production, but there is quantitative agreement between the model and experimental maximum soot yield. The observed underestimation of the f_v 's for this mixture is also confirmed in **Figure 6.2.8.1.1d** for the data at 0.5 ms; the estimated quantities are lower than the experimental data, and the peak is shifted by about 100 K towards higher temperatures. At 1.0 ms, for temperatures below 1750 K, the predicted trend approaches the experimental one, with the maximum simulated peak centered compared to the experiments and underestimated by a factor of 2.2. For temperatures above 1950 K, however, the predicted trend aligns both quantitatively and qualitatively with the experimental data, with a very limited underestimation. Reactive pathways involving C_2H_2 and C_2H_4 with aromatics for soot growth might be missing, as the model is capable of quite correctly reproducing the experimental data for the two fuels (sections 6.1.1 and 6.2.1).

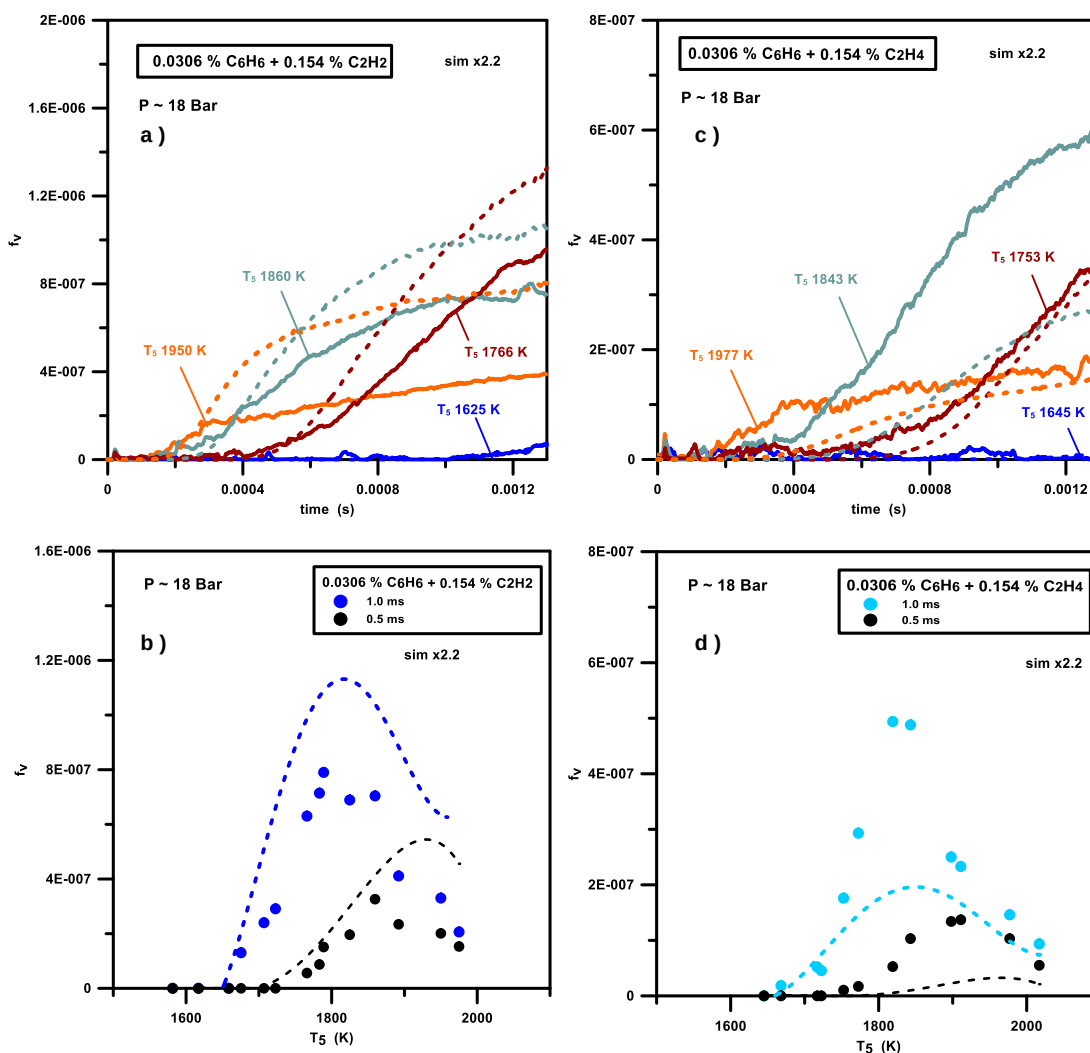


Figure 6.2.8.1.1 –a) 0.0306% C₆H₆ + 0.154% C₂H₂ in Ar at P ~ 18 bar and b) 0.0306% C₆H₆ + 0.154% C₂H₄ in Ar at P ~ 18 bar : experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) 0.0306% C₆H₆ + 0.154% C₂H₂ in Ar at P ~ 18 bar and c) 0.0306% C₆H₆ + 0.154% C₂H₄ in Ar at P ~ 18 bar : experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

To provide a comprehensive overview of how C₂ compounds influence soot formation from benzene under pyrolytic conditions, **Figure 6.2.8.1.2** compares soot volume fractions (f_v) at 0.5 and 1.0 ms across the examined temperature range. This comparison considers soot produced from pure C₆H₆ pyrolysis and in the presence of C₂H₂ and C₂H₄.

Generally, within the differences between model simulations and experiments highlighted in previous sections, the decrease in soot volume fractions from benzene to benzene + C₂H₂ and to benzene + C₂H₄ is well reproduced, especially for the data at 1 ms, where a better reproduction of the experimental profiles is obtained.

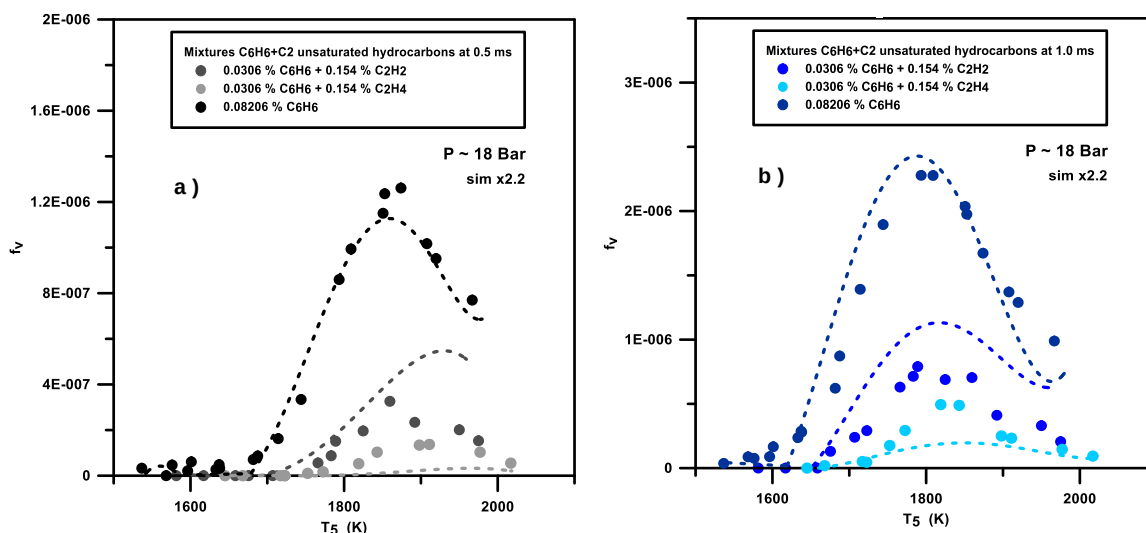


Figure 6.2.8.1.2 – Global comparison of 0.08206% C₆H₆ / 0.0306% C₆H₆ + 0.154% C₂H₂ / 0.0306% C₆H₆ + 0.154% C₂H₄ in Ar at P ~ 18 bar. : Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model - dots: experiments- dashed lines: simulations - respectively a) 0.5 ms and b) 1.0 ms.

6.2.8.2 Toluene + C₂ unsaturated hydrocarbons

This section analyzes the simulations of the co-pyrolysis of toluene with unsaturated hydrocarbon mixtures C₂, as shown in **Figure 6.2.8.2.1**. The model simulations are once again corrected by a factor of 2 for consistency with the previous analyses. **Figures 6.2.8.2.1 (a) and (c)** show the model simulations versus experimental data for C₂ mixtures in terms of f_v time histories up to 1.3 ms. **Figures 6.2.8.2.1 (b) and (d)** present comparisons for individual mixtures at 0.5 and 1.0 ms. Overall, the results show similar behavior to the benzene + C₂ cases.

In **Figure 6.2.8.2.1 (a) and (b)**, the model simulation is shown for a mixture containing 0.029% C₇H₈ + 0.15% C₂H₂, with a T_5 range between 1518 and 1990 K, P_5 pressure

between 16.4 and 18.2 bar, and a concentration $[C]$ of $3.03\text{--}3.92 \times 10^{17}$ atoms/cm³. In **Figure 6.2.8.2.1a**, at 1629 K, the model accurately simulates the profile except fast increment above 1.1 ms. At 1754 K, the model simulates the experimental f_v profile with a slight initial delay, with an overestimation starting around 0.7 ms and reaching up to +40% at 1.3 ms. As temperatures increase, the model maintains a slight delay in soot formation initiation, but the profiles at 1860 and 1953 K are generally qualitatively consistent with the experiments, despite an overproduction reaching up to +50% within the 1.3 ms time window, starting at around 0.4 ms. This trend is reflected in the results presented in **Figure 6.2.8.2.1b**, showing f_v at 0.5 and 1.0 ms. At both times, the model predictions align both quantitatively and qualitatively with the experimental data, predicting the peak production zone around 1900 K (0.5 ms) and 1750–1800 K (1.0 ms). The simulations just overpredict the experimental curves by around 50%.

Figures 6.2.8.2.1 (c) and (d) present the comparison related to the mixture containing 0.029% C₇H₈ and 0.145% C₂H₄, within the temperature range T_5 1571–1978 K, pressure P_5 between 16.2 and 18.6 bar, and concentration $[C]$ of approximately $3.05\text{--}3.68 \times 10^{17}$ atoms/cm³. In **Figure 6.2.8.2.1c**, the model's performance in terms of the f_v time histories shows some limitations in the quantitative description, which also result in quite large qualitative discrepancies at high temperatures. At 1626 K, the model shows, aside from a slight constant underestimation, a good qualitative correlation with experimental data. At 1738 K, the model's predictive capability improves, showing overall agreement with the experimental f_v data. At temperatures of 1861 K and 1927 K, the proportionality between the two profiles is maintained, as in the experiments. However, the simulations are quantitatively more than a factor of 2 lower than the experimental measurements across the entire time range, despite the application of the correction factor. This behavior is further illustrated in **Figure 6.2.8.2.1d**, where at 0.5 ms, a significant underestimation of the experimental values is evident, without a marked peak in soot production. At 1.0 ms, the model accurately reproduces the soot production up to 1770 K qualitatively, as shown in the f_v time history graph, and the production peak shifts to the left by about 80 K at higher temperatures, with a marked underprediction of the dataset. These results are in support of the hypothesis of missing reactive routes for aromatic + C₂H₄/C₂H₃ chemistry as proposed in the previous section.

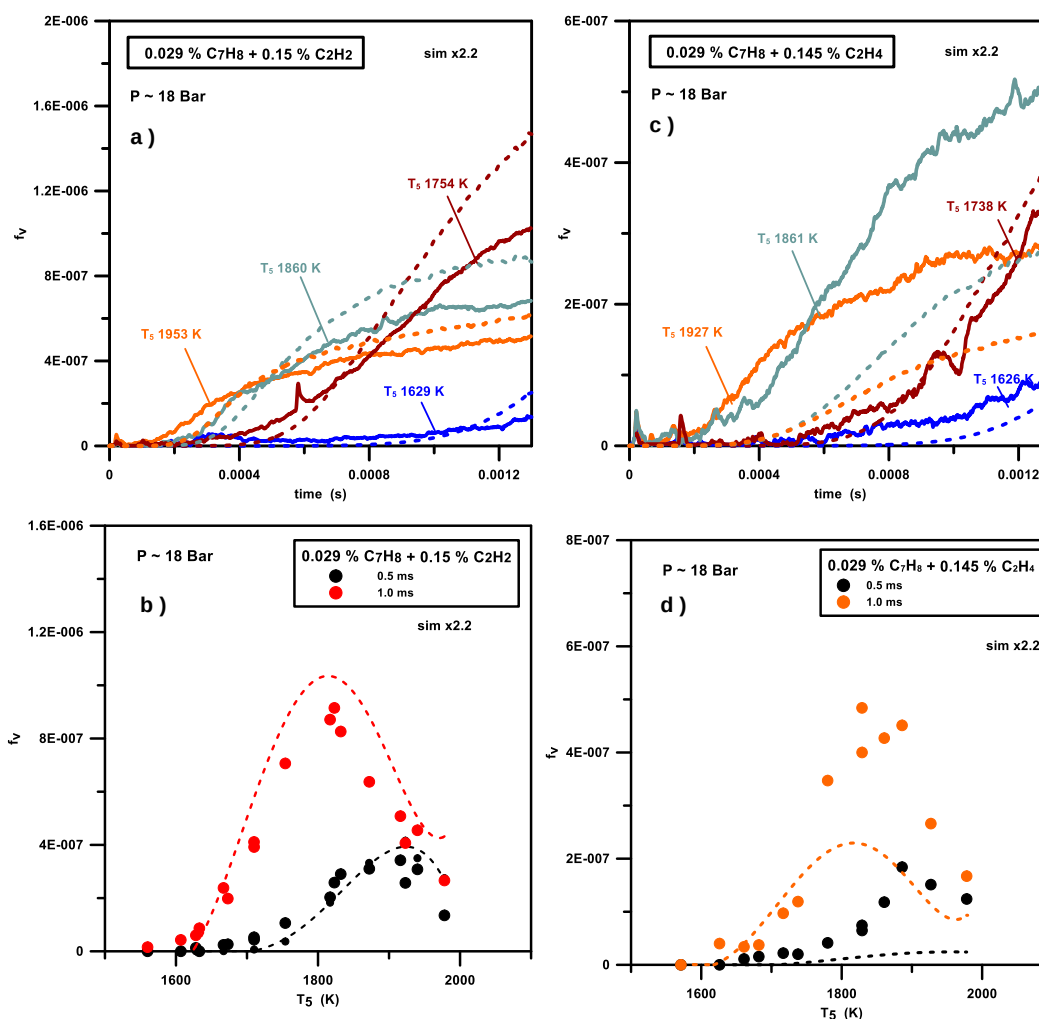


Figure 6.2.8.2.1 –a) 0.029% C_7H_8 + 0.15% C_2H_2 in Ar at $P \sim 18$ bar and b) 0.029% C_7H_8 + 0.145% C_2H_4 in Ar at $P \sim 18$ bar : experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) 0.029% C_7H_8 + 0.15% C_2H_2 in Ar at $P \sim 18$ bar and c) 0.029% C_7H_8 + 0.145% C_2H_4 in Ar at $P \sim 18$ bar : experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

In **Figure 6.2.8.2.2**, the overall effect of adding unsaturated hydrocarbons C2 to toluene under pyrolytic conditions is evaluated. As for the case of benzene, the overall trend in soot produced in the different cases is similar in the modeling and experimental results, keeping in mind the discrepancies presented above, in particular concerning the underprediction of the results with ethylene addition.

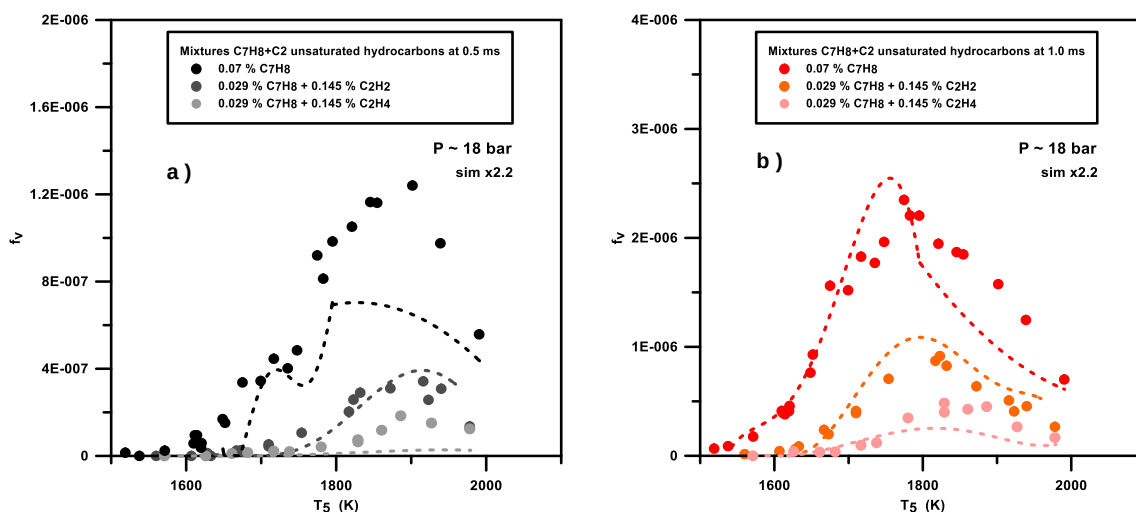


Figure 6.2.8.2.2 – Global comparison of 0.07% C₇H₈ / 0.029% C₇H₈ + 0.15% C₂H₂ / 0.029% C₇H₈ + 0.145% C₂H₄ in Ar at P ~ 18 bar. : Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model - dots: experiments- dashed lines: simulations - respectively a) 0.5 ms and b) 1.0 ms.

6.2.8.3 Toluene + C3 unsaturated hydrocarbons

This section provides a comprehensive analysis of the influence of the addition of unsaturated C3 hydrocarbons, specifically C₃H₆ and C₃H₄, to C₇H₈ under pyrolytic conditions, as depicted in **Figure 6.2.8.3.1**. The simulation results have been multiplied by a factor of 2.2 for consistency with the toluene data. **Figures 6.2.8.3.1 (a) and (c)** illustrate the comparison between the simulated and experimental data for C3 mixtures, focusing on f_v time histories up to 1.3 ms. Conversely, **Figures 6.2.8.3.1 (b) and (d)** depict the comparisons at 0.5 and 1.0 ms, respectively.

In **Figures 6.2.8.3.1 (a) and (b)**, the model simulation pertains to a mixture containing 0.0224% C₇H₈ + 0.112% C₃H₄, with temperature ranges T_5 1537-1960 K, pressures P_5 between 16.3-18.7 bar, and concentration $[C]$ approximately $3.20\text{--}4.16 \times 10^{17}$ atoms/cm³. Notably, in **Figure 6.2.8.3.1a**, at $T_5 = 1605$ K, the model tends to overestimate soot production by approximately threefold starting from 0.8 ms for this mixture. At an operating temperature of 1749 K, the model predicts the onset of soot formation and exhibits a more pronounced growth between 0.45 and 1.3 ms, with an overestimation of roughly 40%. Higher temperature scenarios display improved agreement between

simulations and experiments: at 1853 K, the model qualitatively and quantitatively replicates soot formation with only slight delays, whereas at 1941 K, the delay diminishes further with a slight overproduction observed starting at 0.4 ms. Overall, the model demonstrates robust capability in predicting soot production at elevated temperatures. **Figure 6.2.8.3.1b** reveals that the trends observed in **(a)** are consistent across the investigated temperature range. At 0.5 ms, the model accurately captures the corresponding soot volume fractions within the experimental scattering. At 1.0 ms, the simulations predict production of soot particles at lower temperature than the experiments: the peak is shifted approximately 50 K to lower temperatures compared to the experimental data, resulting in an overestimation of f_v in the temperature range of 1530–1750 K. Beyond 1750 K, the simulated f_v reproduces the experimental trend at higher temperatures.

Figures 6.2.8.3.1 (c) and (d) illustrate the simulation of the model for a mixture composed of 0.0224% C_7H_8 + 0.112% C_3H_6 , analyzed within the temperature range T_5 between 1609 and 1978 K, with pressures P_5 between 16.7 and 18.9 bar, and concentrations of $[C]$ of $3.24\text{--}4.07 \times 10^{17}$ atoms/cm³. In **Figure 6.2.8.3.1c**, at 1605 K, the model accurately reproduces the experimental f_v , while at 1749 K, it is able to predict the start time of f_v production, although it overestimates the values from 0.5 ms up to 1.3 ms, with a maximum discrepancy of around 50%. At higher temperatures, the model shows a delay in the onset of soot production: indeed, the predictions at 1853 K and 1941 K are both delayed by approximately the same interval (0.2 ms). In **Figure 6.2.8.3.1d**, this behavior is observed in the f_v profiles at 0.5 and 1.0 ms. At 0.5 ms, the model predicts the experimental f_v consistently up to about 1800 K, after which it shows an underestimation compared to the experimental values. The peak at 0.5 ms is shifted toward higher temperatures by approximately 50 K. At 1.0 ms, similarly with the toluene + pC_3H_4 data, the model predicts production of soot at lower temperatures compared to the experiments. The maximum simulated f_v is in agreement with the experimental data despite the peak is shifted by approximately 100 K. Between 1800 K and 1920 K, soot production is underestimated by the model.

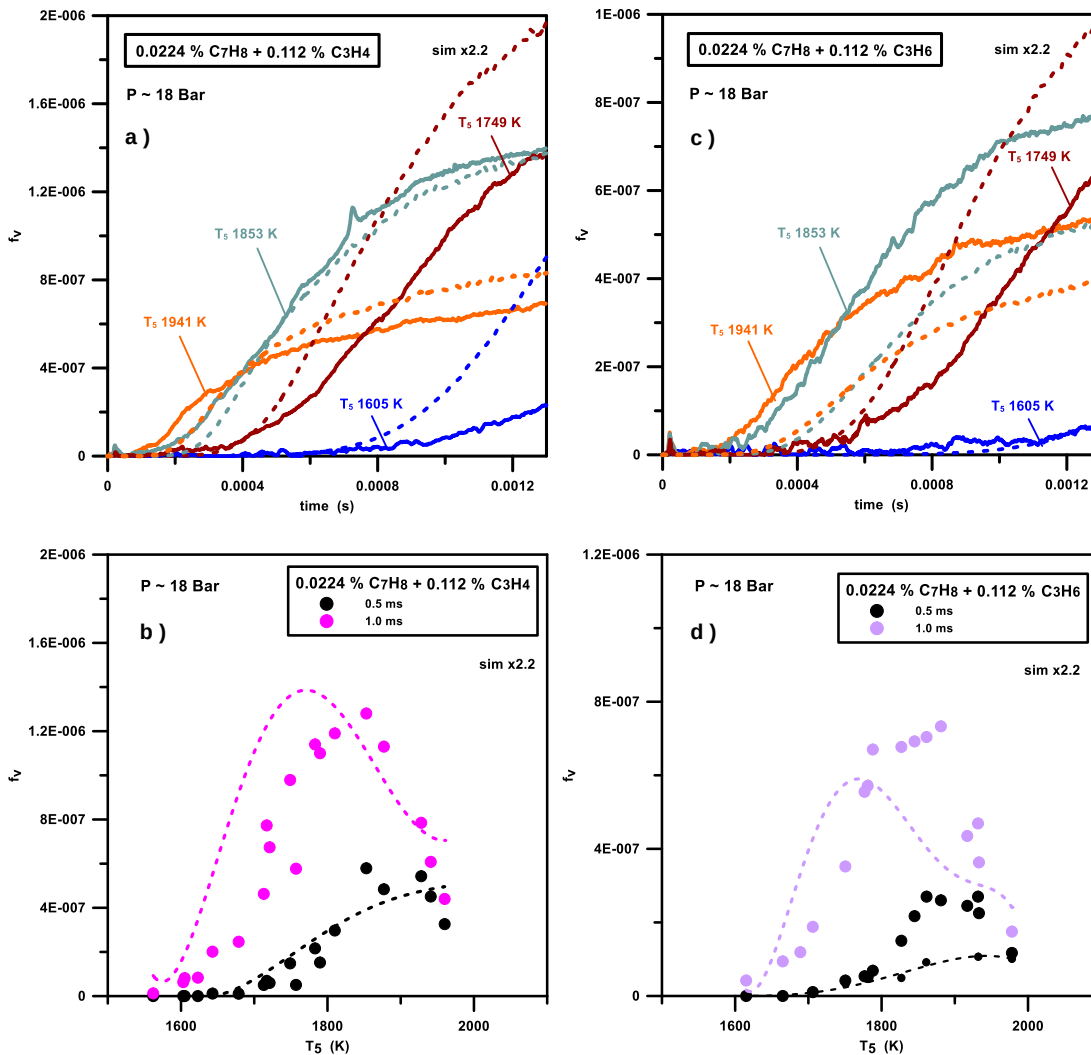


Figure 6.2.8.3.1 –a) 0.0224% C_7H_8 + 0.112% C_3H_4 in Ar at $P \sim 18$ bar and b) 0.0224% C_7H_8 + 0.112% C_3H_6 in Ar at $P \sim 18$ bar: experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) 0.0224% C_7H_8 + 0.112% C_3H_4 in Ar at $P \sim 18$ bar and c) 0.0224% C_7H_8 + 0.112% C_3H_6 in Ar at $P \sim 18$ bar: experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

Figures 6.2.8.3.2 (a) and (b) show the overall performance of the model compared to C_7H_8 under pure pyrolysis conditions, also with the addition of C3 hydrocarbons. Overall, the soot formation model reproduces the experimental data in their proportions, with quite a good representation of the amount of the maximum amount of soot produced for the

different cases. The peaks at 1 ms are though moved towards lower temperatures, with a more marked discrepancy for the mixtures.

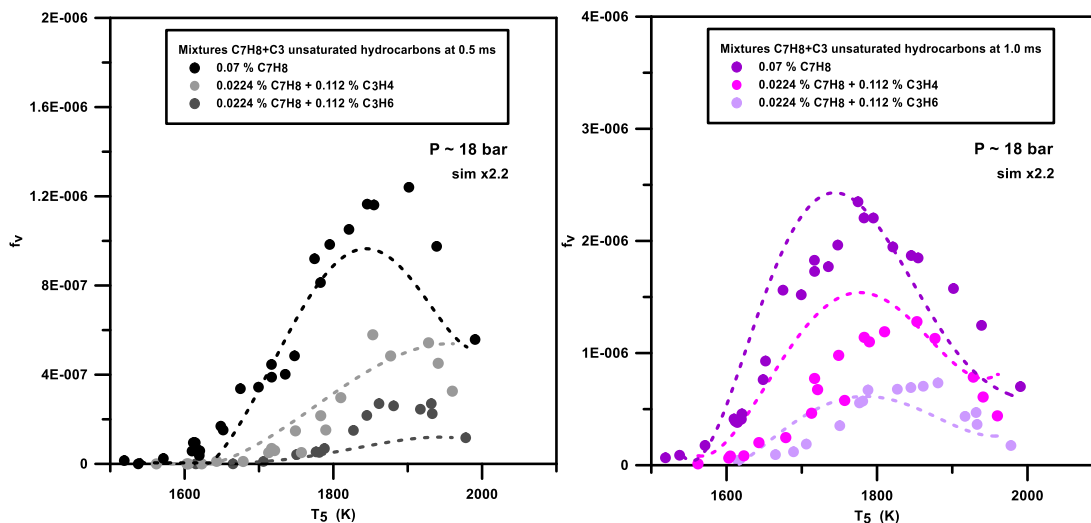


Figure 6.2.8.3.2 – Global comparison of 0.07% C₇H₈ / 0.0224% C₇H₈ + 0.112% C₃H₄ / 0.0224% C₇H₈ + 0.112% C₃H₆ in Ar at P ~ 18 bar. : Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model - dots: experiments- dashed lines: simulations - respectively a) 0.5 ms and b) 1.0 ms.

6.2.8.4 Cyclopentene + acetylene.

This section analyzes the effect of adding C₂H₂ to CYC₅H₈ under pyrolytic conditions. **Figure 6.2.8.4.1** illustrates the soot formation model predictions related to the time histories in panel a, and the values of f_v at 0.5 and 1.0 ms in panel b across the investigated temperature range. The correction factor is still 2.2. The experimental conditions involve a mixture containing 0.033% CYC₅H₈ and 0.164% C₂H₂, with a temperature T₅ ranging from 1576 to 1953 K, a pressure P₅ between 16.6 and 18.6 bar, and a concentration [C] spanning 3.27 to 3.81×10¹⁷ atoms/cm³. According to the model predictions in **Figure 6.2.8.4.1a**, soot formation initiates at approximately 1629 K, aligning with experimental observations and indicating an absence of soot production below this temperature. At 1753 K, the simulation predicts a faster onset of soot formation than observed experimentally, overestimating soot yields by roughly threefold, although the trend shape remains consistent with experimental data. At 1860 K, the model accurately captures the onset and

subsequent evolution of soot formation, with a slight overprediction in soot quantity above 0.6 ms. Similar behavior is observed at 1977 K, where the experimental soot volume fraction is overestimated by up to 50% at 1.3 ms. Overall, as depicted in **Figure 6.2.8.4.1b**, the model demonstrates acceptable predictive capability at 0.5 ms, within the experimental scattering, closely following experimental trends. At 1.0 ms, the modeled production of soot at lower temperatures compared to the experiments is reflected in a shift of the peak towards lower temperatures, but the model effectively reproduces the maximum quantity.

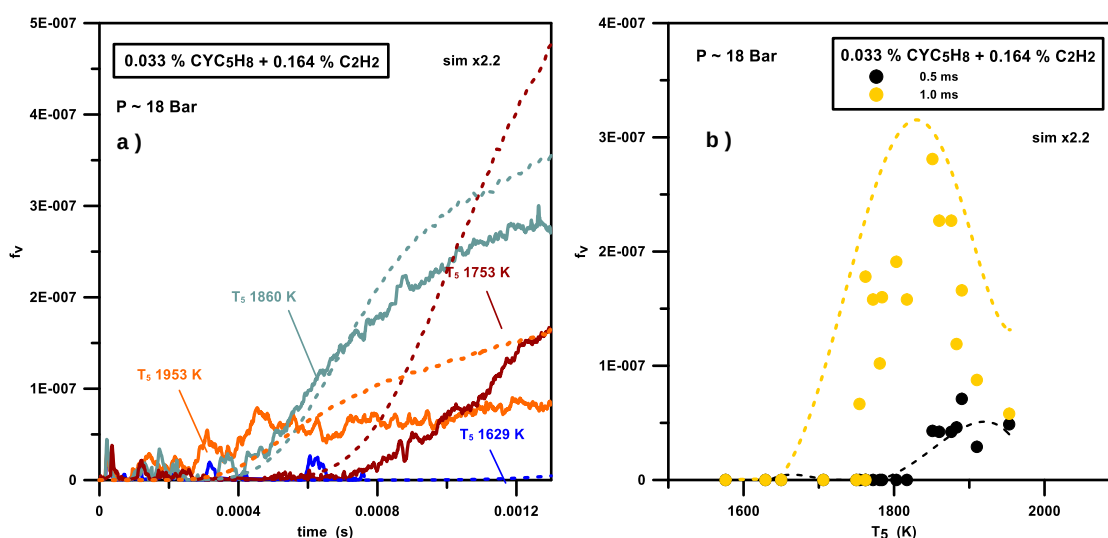


Figure 6.2.8.4.1 –a) 0.033% CYC₅H₈ + 0.164% C₂H₂ in Ar at P ~ 18 bar: experimental f_v time-histories at different temperatures vs ICARE-SMAuG model; b) 0.033% CYC₅H₈ + 0.164% C₂H₂ in Ar at P ~ 18 bar: experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model: dots: experiments; dashed lines: simulations.

To get an idea of the impact of acetylene addition on CYC₅H₈, a comparative analysis with pure fuel under pyrolytic conditions is presented in **Figure 6.2.8.4.2**. Panel (a) displays the data at 0.5 ms, while panel (b) at 1.0 ms, both within the simulated experimental temperature range. The model demonstrates a qualitatively consistent performance with experimental observations at 0.5 ms, albeit with a slight underestimation. Notably, at 1.0 ms (**Figure 6.2.8.4.2b**), the relative quantities are very well reproduced, and the peak soot volume fractions moved to lower temperature in a similar fashion in the two cases. The

overall trend aligns relatively well with experimental data, and the quantitative prediction is generally plausible.

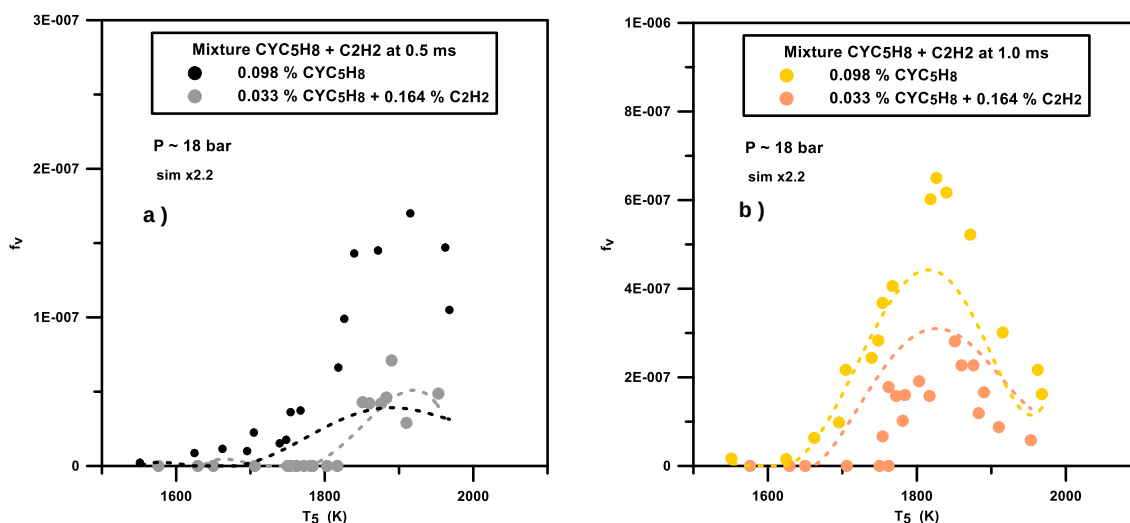


Figure 6.2.8.4.2 – Global comparison of 0.098% CYC_5H_8 / 0.033% CYC_5H_8 + 0.164% C_2H_2 in Ar at $P \sim 18$ bar. : Experimental f_v at 0.5 and 1.0 ms vs ICARE-SMAuG model - dots: experiments- dashed lines: simulations - respectively a) 0.5 ms and b) 1.0 ms.

6.3 Soot model validation vs shock tube literature data.

In addition to being validated against the ICARE HST datasets, the results from literature works have also been used as comparative benchmarks, especially in relation to acetylene, benzene, toluene, and ethylene. The results of such analyses are presented in this section.

6.3.1 Acetylene pyrolysis.

A substantial part of the present work has focused on understanding the chemistry involved in soot formation for the case of acetylene pyrolysis. To further investigate the descriptive capability of the ICARE soot model, comparisons were made with various literature data related to soot formation from acetylene under pyrolytic conditions behind reflected shock waves, for different pressure conditions, acetylene concentrations, and temperatures. The simulations were performed at constant pressure conditions, and the model was corrected by a factor of 1.4 to match the experimental data values. For the calculation of f_v , $E(m) = -$

0.36 was used. The literature data considered in this study, among those available, include: f_v at a reaction time of 1.0 ms for a molar acetylene concentration of 2% at approximately 4.5 bar pressure [246] **Figure 6.3.1.1a**; datasets at reaction times of 0.5 and 1.0 ms for pressures around 2.15 bar and an initial acetylene concentration of 10% [247] **Figure 6.3.1.1b**; f_v at 1.0 ms and pressures of about 3.75 bar for different acetylene concentrations ranging from 1.5% to 5% [248] **Figure 6.3.1.1c**. The model successfully reproduces the experimental datasets presented in the literature. Along with these comparisons, additional ones based on pyrolytic data at various acetylene concentrations from Frencklach et al. [105] were also included, as shown in **Figures 6.3.1.1d, e, and f**. For these data, different mixtures are presented: A, B, C, D, and E, with initial molar fractions of acetylene and average pressures of 1.09% and 3.0 bar, 1.09% and 6.2 bar, 4.65% and 0.7 bar, 4.65% and 1.8 bar, and finally 4.65% and 1.7 bar, respectively. From **Figures 6.3.1.1d and 6.3.1.1f**, it emerges that the model correctly estimates the peaks of maximum soot production as a function of the initial C_2H_2 concentration. In particular, the profiles at different times shown in **Figure 6.3.1.1e** suggest that the kinetics are well reproduced, especially for predicting the soot peaks within the temperature ranges. However, a shift of about 150-200 K between experiments and simulations is observed. The reason for this is unclear, especially since **Figures 6.3.1.1a, 6.3.1.1b, and 6.3.1.1c** show accurate predictions of the datasets. Nevertheless, in [105], there is no mention of some issues related to non-idealities observed in the shock tube used or pressure time-history profiles. Maybe the constant pressure hypothesis is not valid in this case.

An additional validation target provided in the literature works concerns the induction delay times, as shown in **Figure 6.3.1.2**. In this case, the induction times have been normalized based on the carbon concentration for better comparison. Considering the different measurements, there is a decreasing trend with the carbon concentration (**Figure 6.3.1.2a**), and our data are in line with such behavior. The measurements in the literature include data at temperatures higher than 2000 K, showing a marked change in slope in the curve. Such a change in slope is not captured by the model (**Figure 6.3.1.2b**), but the simulations are accurate for lower temperatures.

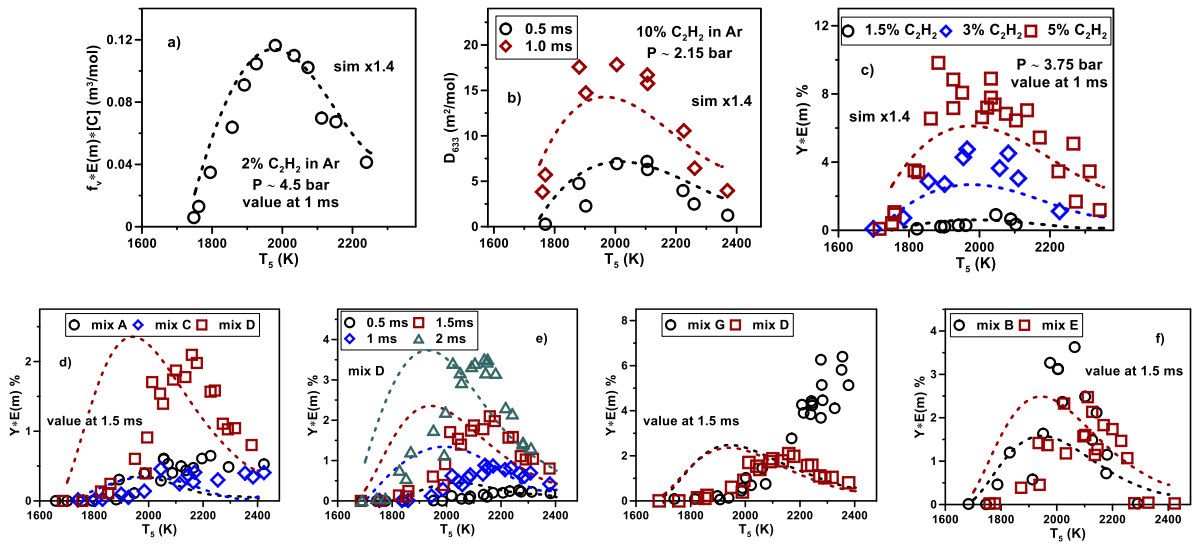


Figure 6.3.1.1 – Soot volume fraction measurements from literature: a) [246]; b) [247]; c) [248]; d)-f) [105].

Lines: simulations with the current model.

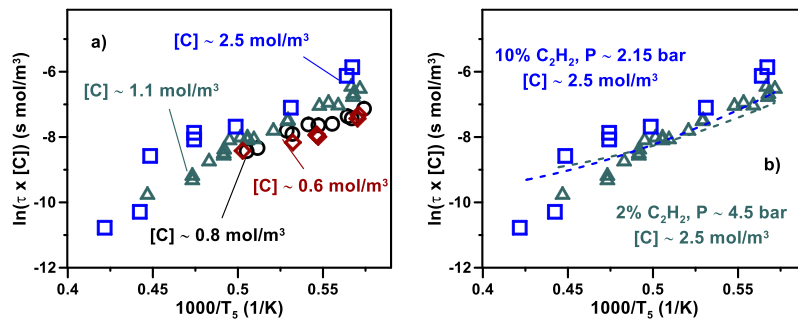


Figure 6.3.1.2 – Induction delay times from literature: $\square$ [247]; Δ [246]; $\circ$ p.w. 0.35% C_2H_2 ; $\diamond$ p.w. 0.245% C_2H_2 . Lines: simulations with the current model.

6.3.2 Benzene pyrolysis.

In this section, the capability of the ICARE soot model to reproduce experimental pyrolytic shock tube data from literature for soot formation from benzene behind reflected shock waves is tested under various conditions of concentrations, temperature, and pressure. The model has been corrected with a factor of 1.4 to better quantitatively capture the experimental trends. For the calculation of f_v , an $E(m)$ of -0.36 was used. The literature data considered, among those available, are: D_{633} (m^2/mol) at a pressure of 2.15 bar at 0.7 ms for 1 and 2% C_6H_6 in Ar [247]; D_{633} (m^2/mol) at 0.7 and 1.0 ms at a pressure of 1.4 bar for 2% C_6H_6 in Ar [249]; soot yield multiplied by $E(m)$ at 1.5 ms for 0.175-0.467-0.62-1.05% C_6H_6 in Ar [250]; soot yield at 1.0 ms at a pressure of 50 bar for 0.02-0.04-0.05% C_6H_6 in Ar [251]; soot yield at a pressure of 1.2 bar at 1.3 ms for 0.5-1-2% C_6H_6 in Ar [112]. The model successfully reproduces the presented data, except for discrepancies in **Figures 6.3.2.1 a and d**. In these cases, the experimental results are incorrect, as they show a similar amount of soot production by changing the fuel concentration (1% to 2% in **Figure 6.3.2.1**, 0.2% to 0.05%, and 0.04% in **Figure 6.3.2.1d**). Nevertheless, the model reproduces the bell-shaped form of the experimental curves, as well as reasonable quantities.

Another comparison to assess the robustness and quality of the model's match with literature data is provided through the example shown in **Figure 6.3.2.2**. In **Figure 6.3.2.2a**, the induction times measured at ICARE with the HST shock tube are first compared to those derived from literature data [247,251]. This comparison was made based on the normalization of carbon concentrations from 0.4 mol/m³ to 4 mol/m³. The HST data from ICARE are consistent with the literature trend. **Figure 6.3.2.2b** shows the simulation of the same literature induction times for: 0.02% and 0.05% C_6H_6 at 50 bar pressure for $[C]$ 0.4-4 mol/m³; 1% and 2% C_6H_6 at 2.15 bar pressure for 0.8-1.6 mol/m³. In **Figure 6.3.2.2b**, it can be seen that for the data in [247] in red, the model underestimates the induction delay time linearly for $1000/T_5$ between 0.625 and 0.58 (1/K), and overestimates it for lower values of 0.55 as temperature increases. This behavior is more pronounced when moving from 1% to 2% benzene. Conversely, for the induction delay times in [251],

the model reproduces these times accurately and quite precisely. This serves as further positive feedback on the overall performance of the model relative to the literature data.

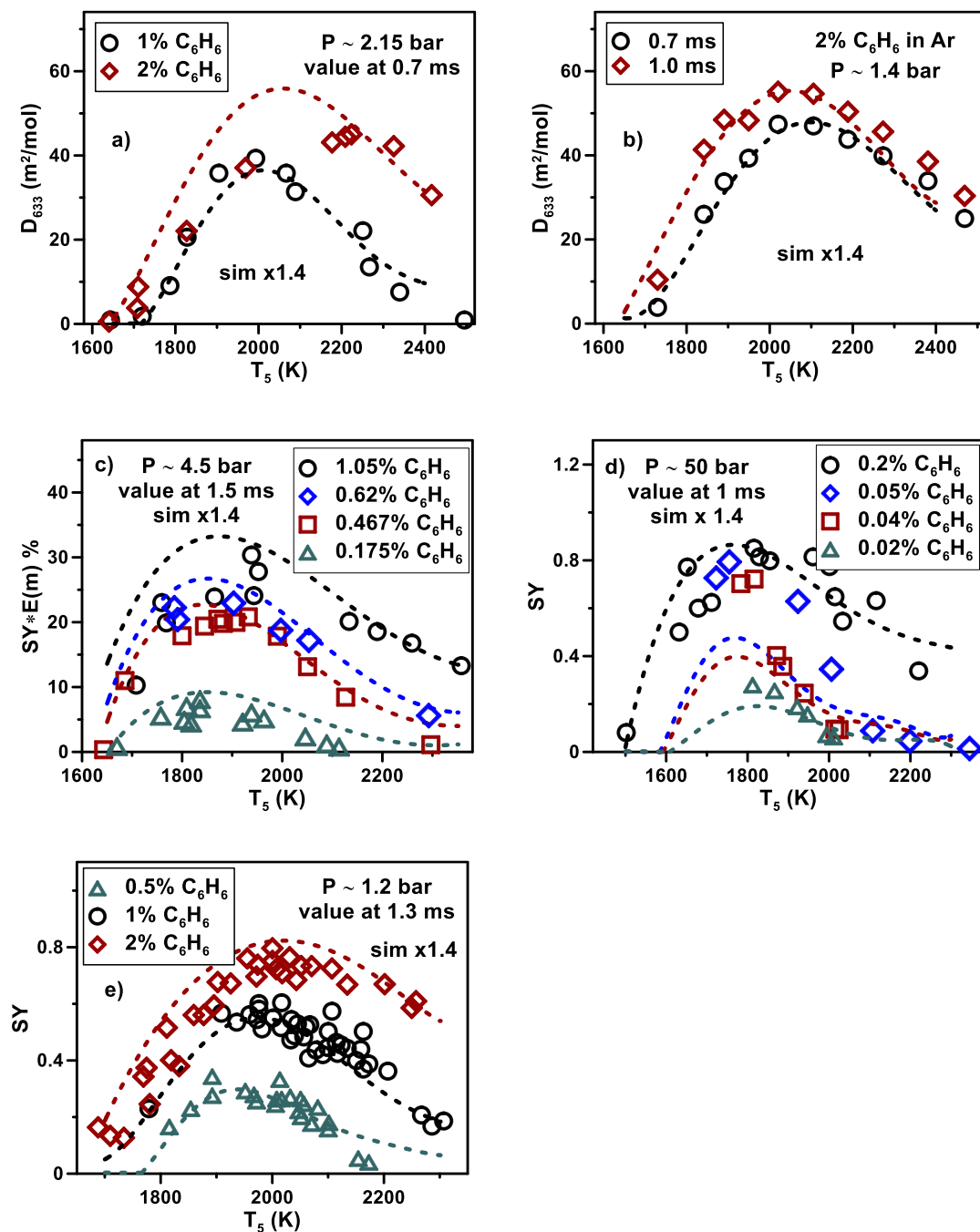


Figure 6.3.2.1 – Experimental soot measurements from literature: a) [247]; b) [249]; c) [248]; d) [251]; e) [112] vs Lines: simulations with the current model.

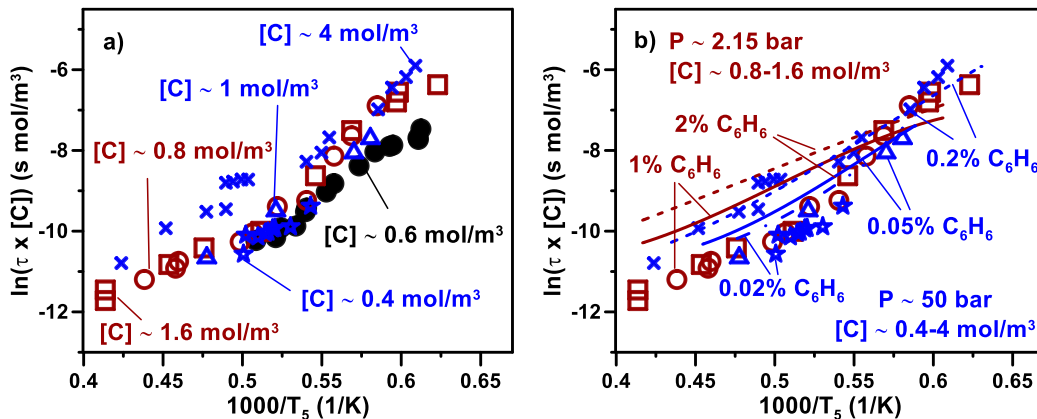


Figure 6.3.2.2 – a) Experimental soot induction delay time from literature (red: [247], blue [251]) vs HST ICARE data (black); b) experimental soot induction delay time from literature (red: [247], blue [251]) vs. lines - simulations with the current model.

6.3.3 Toluene pyrolysis.

Another opportunity to test the model's capabilities is provided by comparison with pyrolytic data from shock tube literature studies related to soot formation from toluene, as shown in **Figure 6.3.3.1**. In **Figure 6.3.3.1a**, soot yield data in percentage (SY%), with $E(m) = -0.6$, are reported by Agafonov et al. [111] at a pressure P_5 of 3.0 bar for various concentrations of C_7H_8 in molar fractions (0.097%, 0.15%, 0.17%, 0.25%, 0.5%, and 0.9%). For these data, a correction factor of 2.0 was found appropriate, which is similar to the one used for the shock tube data from the ICARE HST (2.2). For the lower concentrations of 0.097%-0.15%-0.17%, the model underestimates the experimental trends, and the peaks of production are shifted to higher T_5 by about 150 K. Starting from 0.25% of C_7H_8 , the model begins to provide a greater quantitative and qualitative description of the experimental profiles, with a peak shift of about 50 K, underestimating the soot produced between 1700-2000 K by 50%. At 0.5%, soot prediction becomes more accurate, quantitatively matching the f_v range up to about 1900 K, then showing an underestimation of about 16% between 2000 and 2400 K. At 0.9% of C_7H_8 , the model anticipates soot production within the 1600-1950 K range, effectively shifting the peak about 80 K to lower temperatures. The high-temperature trend is reproduced with a slight underestimation starting from 2100 K. Overall, the model reasonably simulates the trends,

with a temperature shift of the peak toward higher temperatures for higher concentrations (0.9%) and toward lower temperatures for the remaining lower concentration range. In **Figure 6.3.3.1b**, pyrolytic data by Alexiou et al. [252] are shown, in terms of $SY \cdot E(m)\%$ at 2.0 ms, with $E(m) = -0.253$, for three different molar fractions of C_7H_8 at different pressures: 0.5% at 2.5 bar, 1.0% at 3.3 bar, and 1.5% at 3.5 bar in argon. In this case, the model reproduces the experimental data with a correction factor of 1.4. For 0.5% C_7H_8 , the model shows a strong shift of the maximum production peak to lower temperatures by about 200 K, while still predicting the high-temperature trend for values above 2000 K. For 1.0% C_7H_8 , the model shows a reduced temperature shift of about 100 K compared to the lower percentage of toluene data. The trend is accurately predicted between 1850-2400 K. The peak shift disappears at 1.5% C_7H_8 , with the model accurately reproducing the 1750-2400 K range. In **Figure 6.3.3.1c**, a comparison with data from previous ICARE HST shock tube studies by Douce et al. [253] is shown, in terms of $SY \cdot E(m)\%$ at 2.0 ms, for a molar fraction concentration of 0.5% C_7H_8 , with an indicative operating pressure of 14 bar, and $E(m) = -0.19$ used for measurements. Douce et al. [253] data show that the model can be corrected with a factor of 2.2 to accurately approximate the experimental measurements, the same factor used for current measurements. The model predicts the experimental trend quite accurately, both qualitatively and quantitatively, with a slight overestimation at higher temperatures. Finally, in **Figure 6.3.3.1d**, the model simulation of data from Nativel et al. [234] is shown, regarding soot production from a 2% C_7H_8 in argon mixture, expressed as $D_{633nm} \text{ m}^2/\text{mol}$, using $E(m) = -0.36$, at an indicative pressure of 3.6 bar. The model is corrected with a factor of 1.4. The simulations indicate that the model accurately predicts soot data within the temperature ranges of 1500-1800 K and 2550-2700 K. It is unclear why, between 1800-2550 K, the experimental data show a behavior which is completely different from the other sets, with a double peak in f_v which the authors explain as due to the competing chemistry of resonantly stabilized radicals and HACA route. The model is not able to capture such a trend. Possible doubts arise about the experimental results. In the HST set-up, the 0.07% toluene was chosen in order to have below 90% of signal extinction for the specific carbon concentrations ($3.03\text{-}3.92 \times 10^{17} \text{ atoms/cm}^3$). This guarantees a linear behavior in the signal response of the laser. The carbon concentration in [234] is $1.1 \text{ to } 2.4 \times 10^{18} \text{ atoms/cm}^3$, so at least a factor of 3 with respect to our data. Considering that the

soot volume fraction goes as the square of the carbon concentration, the soot volume fraction should be 10 times ours. Doubts arise in the possibility of measuring such a quantity in a linear regime of the signal, though, depending on the laser used.

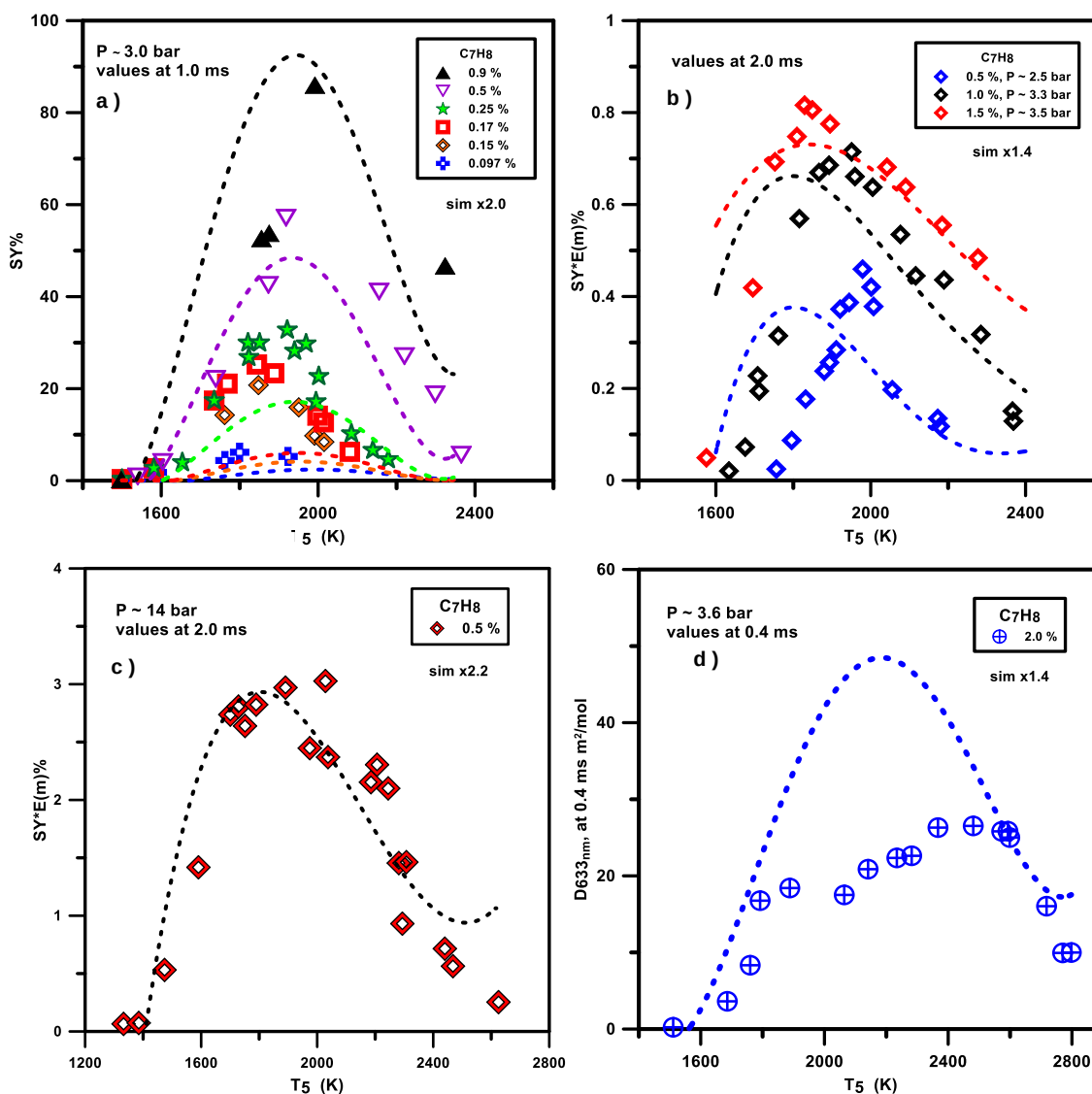


Figure 6.3.3.1 – Experimental soot measurements from literature: a) [111]; b) [252]; c) [253]; d) [234] vs Lines: simulations with the current model.

6.3.4 Ethylene pyrolysis.

This section presents a performance test of the ICARE soot model compared to literature data on soot formation from the pyrolysis of ethylene in a shock tube. The comparison

shown in **Figure 6.3.4.1** is based on data from Agafonov et al. [248] in terms of $SY^*E(m)\%$ at 1.0 ms, with $E(m) = -0.36$, for three different concentrations expressed as molar fractions of C_2H_4 in argon, namely 5%, 3.0%, and 1.0% in argon, at an average pressure of 3.75 bar. Similar to the data from ICARE HST, the model here is corrected by a factor of 2.0 to approximate the experimental measurements. At 1.5% C_2H_4 , the model aligns with the experimental trend. At 3.0%, soot prediction is underestimated by 50%, with a better descriptive accuracy above 2300 K, resulting in a temperature shift of the soot production peak of about 100 K to higher T_5 . A similar situation occurs at 5% C_2H_4 , where the model shows a peak shift of 100 K to higher temperatures, and it tends to have greater predictive accuracy at temperatures above 2300 K, while underestimating at lower values. Overall, for all three cases, the proportionality of the $SY^*E(m)\%$ profiles for different conditions, the quantities (although with a temperature shift), and the shape of the profiles are successfully predicted.

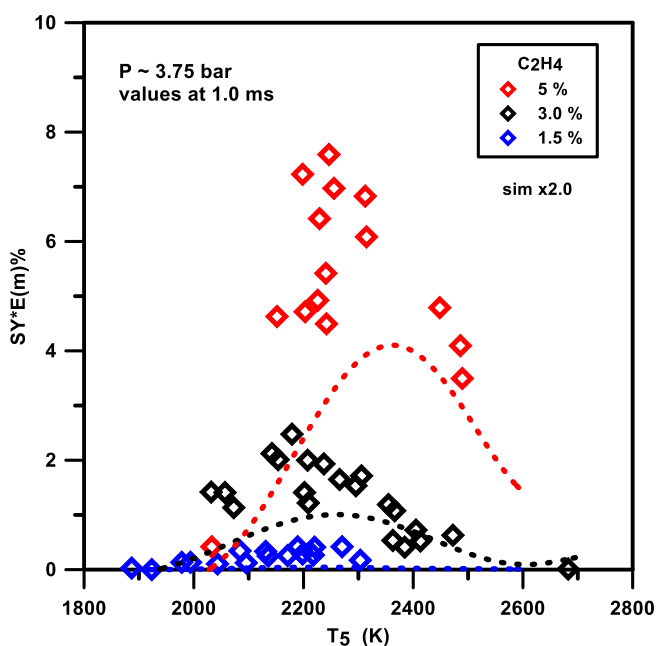


Figure 6.3.4.1 – Ethylene experimental soot measurements at different concentrations in argon from literature: [248] vs Lines: simulations with the current model.

6.4 Chemical kinetic analysis

6.4.1 Effects of polyynes chemistry implementation on soot formation from acetylene pyrolysis.

In order to understand the role of the polyne chemistry as implemented in this work and identify the key intermediate species of the process leading to the formation of the first soot particle in the case of acetylene pyrolysis, time-dependent rate-of-production (ROP) analyses were performed on the pyrolysis of 0.35% C_2H_2 mixture for two conditions, $T_5 = 1742$ K and $T_5 = 1954$ K. These temperatures were selected to represent the low-temperature and the high-temperature range of the experimental dataset. The integrated rates are presented in **Figure 6.4.1.1** for the two temperature conditions (respectively, left and right graphs). From the figure, it appears that the reactive pathway leading to the formation of the first BIN species involves reactions between polyacetylenic species and branched aromatic hydrocarbons. The pathways leading to the formation of BINJ's, although present in the model, are significantly less prominent compared to those that produce BINPJ. In fact, the total flux of BINJ formation is about 1% of the flux to BINP1J species. For this reason, the kinetics of BIN1J to BIN3J are not represented in the figure.

C4H2+C10H5(C2H)3	5 %
C6H2+C10H6(C2H)2	20 %
C6H2+C10H5(C2H)2	4 %
C8H2+C10H6(C2H)2	18 %
C8H2+C6H2(C2H)3	8 %
C8H2+C10H7C2H_1	4 %
C8H2+C6H3(C2H)(C4H)	4 %
C8H2+C6H2(C2H)2(C4H)	2 %
C8H2+C10H5(C2H)2	4 %
C8H2+C6H3(C2H)2(C4H)	1 %
C8H2+C6H3(C6H)(C2H)	1 %
C8H2+C6H4(C2H)(C4H)	3 %
C10H2+C6H2(C2H)2(C4H)	1 %
C10H2+C6H3(C2H)(C4H)	1 %
C10H2+C6H2(C2H)3	2 %
C10H2+C6H3(C2H)2	14 %
C10H2+C10H6(C2H)2	7 %
C12H2+C6H3(C2H)2	1 %

C6H2+C10H6(C2H)2	1 %
C8H2+C6H2(C2H)3	11 %
C8H2+C6H3(C2H)(C4H)	9 %
C8H2+C6H4(C2H)(C4H)	4 %
C8H2+C6H2(C2H)2(C4H)	7 %
C8H2+C6H3(C6H)(C2H)	7 %
C8H2+C10H6(C2H)2	1 %
C10H2+C6H3(C2H)2	22 %
C10H2+C6H2(C2H)3	9 %
C10H2+C6H2(C2H)2(C4H)	6 %
C10H2+C6H3(C2H)(C4H)	8 %
C10H2+C6H3(C6H)C2H	6 %
C12H2+C6H2(C2H)3	2 %
C12H2+C6H3(C2H)2	7 %

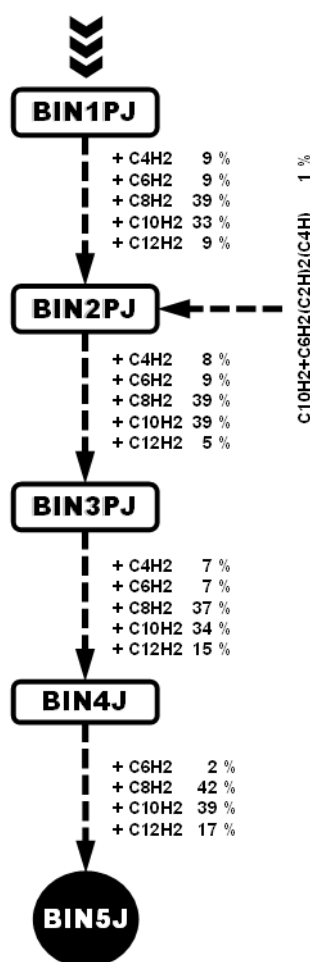
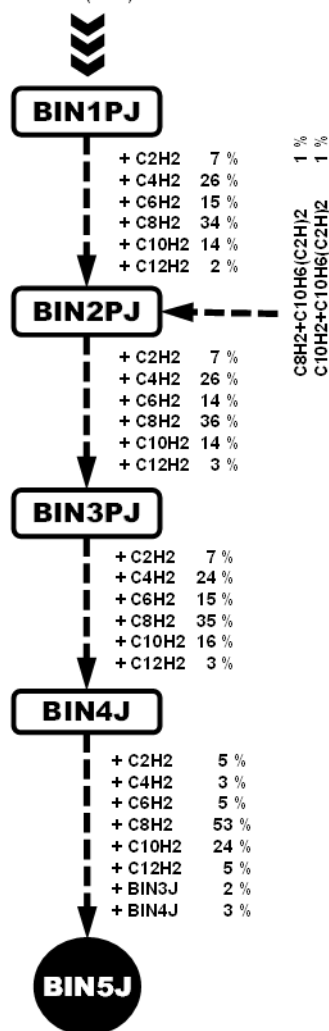


Figure 6.4.1.1 – Integrated rate-of-production analyses, 0.35% C₂H₂, T₅ = 1742 K (left) and 1954 K (right).

At a temperature of 1742 K, reactions involving single-ring and two-ring aromatic species with C_6H_2 (which accounts for 24% of the total flux), C_8H_2 for 45%, and $C_{10}H_2$ for 25% are the most significant contributors to the formation of BIN1PJ. In particular, among the branched single-ring species, $C_6H_3(C_2H)_2$ and $C_6H_2(C_2H)_3$ are the intermediates mainly involved in the formation of BIN1PJ (15% and 10% of the total flux, respectively), with smaller contributions from $C_6H_4(C_2H)(C_4H)$ (3%) and its radical counterpart $C_6H_3(C_2H)(C_4H)$ (5%), $C_6H_3(C_2H)_2(C_4H)$ (1%) and its radical $C_6H_2(C_2H)_2(C_4H)$ (3%), and more marginally from $C_6H_4(C_2H)(C_6H)$ (1%). Overall, the cumulative percentage of these reactions accounts for 38% of the total ring formation flux. For this reason, a rate-of-production analysis was also performed on the related aromatic intermediates, represented schematically in **Figure 6.4.1.2**. The pathways related to the C4+C2 and C4+C4 reactions resulting in ring formation are indicated in blue and are taken from the CRECK model. The percentages are the integrated ROPs (regular font for 1742 K, italics for 1954 K), while the fluxes are reported only for the ring formation reactions.

At lower temperature conditions, $C_6H_2(C_2H)_3$ is primarily formed through two reactive pathways involving RSAP02 + diacetylene, contributing 43%, and RSAP05 + acetylene, contributing 41%. The process of H-abstraction by H on triethynylbenzene ($C_6H_3(C_2H)_3$) also leads to the formation of $C_6H_2(C_2H)_3$. The most influential reactive pathway leading to the formation of triethynylbenzene involves reactions of RSAP02 with acetylene, forming diethynylbenzene ($C_6H_3(C_2H)_2$) radicals, followed by an addition of C_2H_2 . As further exemplified in the next paragraph, the reaction $C_6H_3(C_2H)_2 + C_2H_2$ also represents the most influential pathway contributing to the formation of second-ring structures. Finally, triethynylbenzene can also be formed through the classic addition of H to its corresponding radical.

The RSAP05 + C_2H_2 reaction previously mentioned promotes the process toward the formation of $C_6H_3(C_2H)(C_4H)$, with only a small contribution from RSAP04 + C_2H_2 . The reactions of $C_6H_3(C_2H)(C_4H)$ with H (recombination) and H_2 (abstraction) produce the stable molecule $C_6H_4(C_2H)(C_4H)$ (72% of the ROP), while the remaining reactive pathways come from reactions of phenylacetylene with C_4H (18%) and the corresponding radical ($C_6H_4C_2H$) with diacetylene (8%). $C_6H_4C_2H$ is produced through thermal fragmentation of phenylacetylene and H-abstraction by H, as well as by the reaction C_4H_3

+ C_4H_2 (25% of the ROP). Regarding $C_6H_5C_2H$, it appears that the HACA step, starting from C_6H_5 , is responsible for its production, with the phenyl radical mainly formed from reactions $C_4H_3 + C_2H_2$ (45%), $C_4H_2 + C_2H_3$ (22%), and H abstraction from benzene (8%). The total integrated flux related to cyclization reactions starting from the diradical species $PR0x$ is about $4e-11$ mol/(cm³s) (around 31%), against approximately $9e-11$ mol/(cm³s) for the previously mentioned cyclization reactions between $C_4 + C_2$ and $C_4 + C_4$ (69%, including fluxes toward benzene originating from $C_4H_4 + C_2H_2$, $C_4H_5 + C_2H_2$, $C_4H_2 + C_2H_4$). Nonetheless, another factor contributing to the formation mechanism of BIN precursors is the thermal stability of the intermediates. Aromatic compounds containing ethynyl groups are relatively stable compared to the phenyl radical, which thermally fragments into acetylene or diacetylene through a mechanism involving ring-opening steps and β -scission. For this reason, more detailed analyses are proposed below regarding the different contributions and their influence on soot production and thus on f_v .

Concerning reactions involving polyynes and PAHs to BIN1JP, as shown in **Figure 6.4.1.1**, about 45% of the total BIN1JP flux produced relates to diethynylnaphthalene ($C_{10}H_6(C_2H)_2$), particularly in combination with triacetylene (20%), C_8H_2 (18%), and $C_{10}H_2$ (7%). The diethynylnaphthalene radical ($C_{10}H_5(C_2H)_2$) also plays an important role as a PAH precursor, reacting mainly with C_6H_2 and C_8H_2 . These reactions account for about 4% of the total flux converging into BIN1PJ. The contribution from triethynylnaphthalene ($C_{10}H_5(C_2H)_3$) + diacetylene is approximately 5%, while that from $C_{10}H_7C_2H_1 + C_8H_2$ is about 4%. To investigate the central role of diethynylnaphthalene chemistry and its radical, **Figure 6.4.1.3** provides a detailed representation of the corresponding ROP analyses at $T_5 = 1742$ K. The species highlighted are single-ring intermediates derived from **Figure 6.4.1.2**. The kinetics attributed to $C_{10}H_5(C_2H)_2$ are relatively straightforward, considering it is produced from reactions of $C_6H_2(C_2H)_3$ with acetylene (62% of the ROP) and $C_6H_3(C_2H)_2$ with diacetylene (38%). Its recombination with H atoms and H abstractions with H_2 are important resources for $C_{10}H_6(C_2H)_2$ (20% of the total ROP). Despite this, the most influential pathway forming diethynylnaphthalene involves the formation of the ethynylnaphthalene radical through the reaction of $C_6H_3(C_2H)_2$ with acetylene and subsequent addition of C_2H_2 . Additionally, a smaller contribution comes from the reaction of $C_{10}H_6(C_2H)(C_4H)$ with H (addition) and H_2 (H-

abstraction), accounting for about 6% of the total ROP. The reactive pathways leading to the formation of $C_{10}H_6(C_2H)(C_4H)$ are also depicted in **Figure 6.4.1.3**.

This molecule is produced from the reaction of $C_{10}H_6(C_2H)$ with C_4H_2 (40% of the total ROP); from reactions of $C_{10}H_6(C_4H)$ and $C_{10}H_7(C_4H)$ with C_2H_2 and its radical C_2H , respectively (35% of the total ROP); from reactions of $C_{10}H_5(C_2H)(C_4H)$ with H (addition) and H_2 (H-abstraction), together accounting for 24% of the combined ROP. $C_{10}H_5(C_2H)(C_4H)$ is formed from the reaction of $C_6H_3(C_2H)(C_4H)$ with C_2H_2 , while $C_{10}H_6(C_4H)$ is formed [65] through the reactions of $C_6H_3(C_2H)(C_4H)$ with C_4H_2 and $C_6H_2(C_2H)_2(C_4H)$ with C_2H_2 (12% and 88% of the ROP, respectively). $C_{10}H_7(C_4H)$ is produced via several multiple pathways, the main one being the reaction of $C_{10}H_6$ with C_2H_2 , followed by reactions of $C_{10}H_6(C_4H)$ with H (addition) and H_2 (H-abstraction), and the naphthyl radical with acetylene. $C_{10}H_6$ mainly originates from the thermal decomposition of ethynylnaphthalene (78%) and from the reaction between $C_6H_4C_2H$ and C_2H_2 (22%), while the phenyl radical is formed from reactive pathways starting with the reaction of $C_6H_4C_2H + C_2H_2$.

As the temperature T_5 increases, the pathways promoting second-ring aromatic formation become progressively less influential, while larger polyynes start playing a key role. In fact, at 1954 K, most of the formation flow of BIN1PJ is contributed by $C_{10}H_2$ (51% of the total ROP), C_8H_2 (39%), and $C_{12}H_2$ (9%), in order of increasing importance. Clearly, the fast polyyne kinetics promote the presence of substantial concentrations of large polyacetylenes at short reaction times, and their reactions with single-ring species to produce BINs. Simultaneously, in this case, the reactions with intermediate PAHs are less significant compared to those with single-ring aromatics. In particular, reactions with $C_6H_3(C_2H)_2$ contribute 29% to the total BIN1PJ flow, followed by $C_6H_2(C_2H)_3$ (22%), $C_6H_3(C_2H)(C_4H)$ (17%), and their respective molecules $C_6H_4(C_2H)(C_4H)$ (4%), $C_6H_2(C_2H)_2(C_4H)$ (13%), and $C_6H_3(C_6H)(C_2H)$ (13%). The kinetic mechanism leading to these chemical species is similar to that already described at lower temperatures (**Figure 6.4.1.2**), but some key differences can still be distinguished.

The first concerns the role of pathways involving RSAP species compared to the so-called “conventional” pathways through benzene and phenyl. At 1954 K, there is a significant reduction in the latter pathways, especially those involving C_4H_4 , C_4H_5 , and C_2H_4 , which quickly decompose under these conditions. These related flows, through reactions forming the phenyl radical ($C_4H_3 + C_2H_2$, $C_4H_2 + C_2H_3$), are consequently lower than at 1742 K, although still influential. However, the reaction of the phenyl radical with C_2H_2 is significantly disfavored compared to its thermal fragmentation at high temperatures, due to both the reduced availability of acetylene and faster decomposition rates. At 1742 K, the reaction $C_6H_5 + C_2H_2$ accounts for 45% of the total integrated rate of consumption of C_6H_5 , compared to only 8% at 1954 K. The production of $C_6H_4C_2H$ from $C_4H_3 + C_4H_2$ is also reduced, further preventing the formation of diphenylbenzene and $C_6H_4(C_2H)(C_4H)$ via phenylacetylene and phenylacetylene radicals. Regarding reactions involving RSAP intermediates, the flows through RSAP02 (from $C_6H_2 + C_2H$) at 1954 K are evidently lower compared to the lower temperature case at $T_5 = 1742$ K. The total flow from reactions PR05 + C_2H_2 and C_4H_2 does not change significantly, while there is a notable increase in addition reactions leading to larger RSAP radicals (e.g., $C_6H_2 + C_6H$, $C_{10}H_2 + C_2H$, $C_8H_2 + C_4H$). As further evidence of the relative importance of $C_6H_5 / C_6H_4C_2H$ chemistry at different temperatures, **Figure 6.4.1.4** compares the previously described time-history profiles for 0.35% C_2H_2 with simulations obtained by removing the reactions forming RSAP intermediates from the original kinetic model. First, the result of the simulations had to be scaled by a factor of 7 to match the temperature profiles at lower temperatures. Even at 1742 K, the soot formation predicted by the modified model is about 3.5 times lower than that of the original model. This behavior is mainly due to two key factors: 1) the removal of RSAP pathways; 2) the low thermal stability of the phenyl radical, which effectively hampers the $C_4 + C_2$ chemistry compared to RSAP chemistry, despite higher overall fluxes (as already discussed, $9e-11$ vs $4e-11$ mol/(cm³s)). Additionally, the modeled profiles significantly underestimate the experimental soot volume fractions at high temperatures, and thus, the overall trend is not accurately reproduced. An example is the f_v at 1.3 ms, which decreases from 1742 K to 1847 K, and even at higher values like 1954 K, which is not consistent with the behavior already observed and expected. The profile at 1954 K is therefore lower than that at 1847 K, except for short time scales after the induction time,

further confirming the dominant and significant role of RSAP species chemistry at very high temperatures.

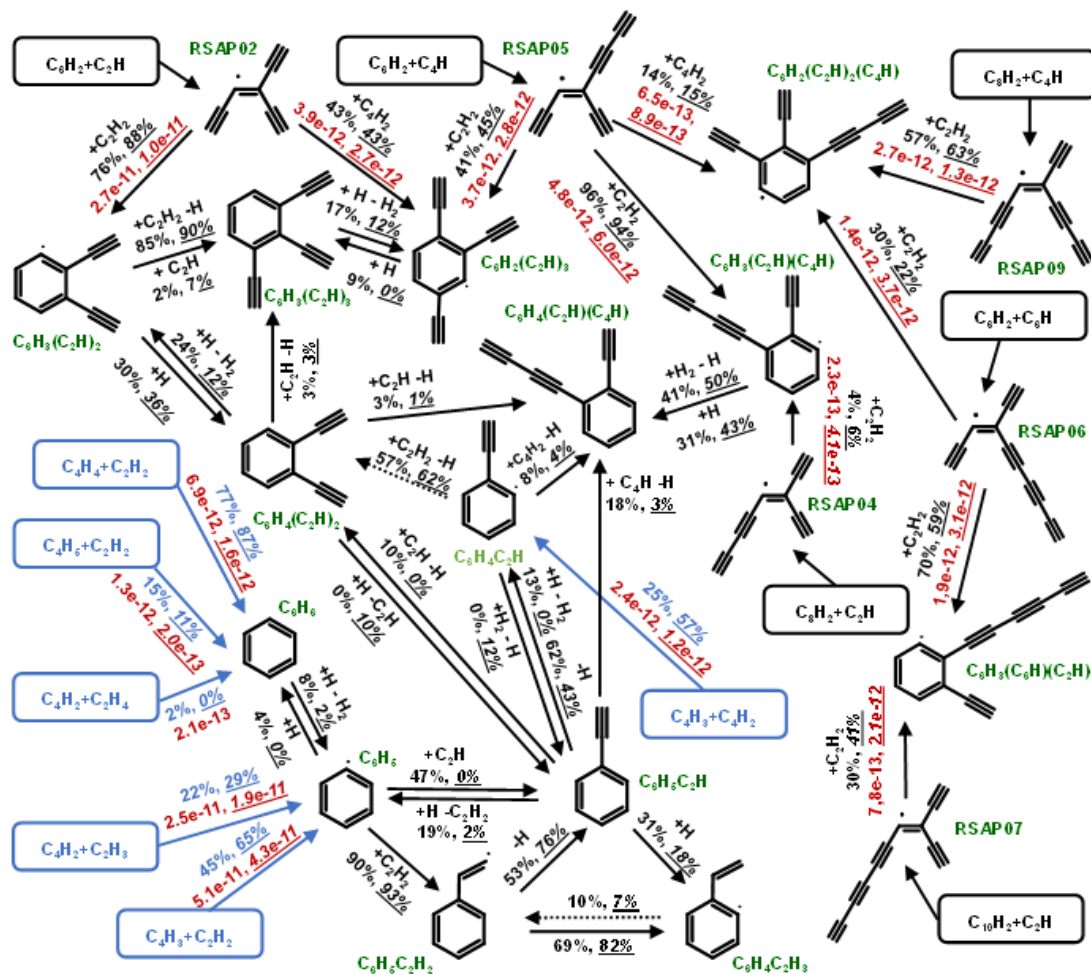


Figure 6.4.1.2 – Schematic of the kinetics of the key single-ring aromatics involved in the formation of BIN1PJ. Integrated rate-of-production percentages for 0.35% C_2H_2 , $T_5 = 1742$ K (regular font) and 1954 K (italic font). In red, integrated fluxes (moles / (cm³ s)).

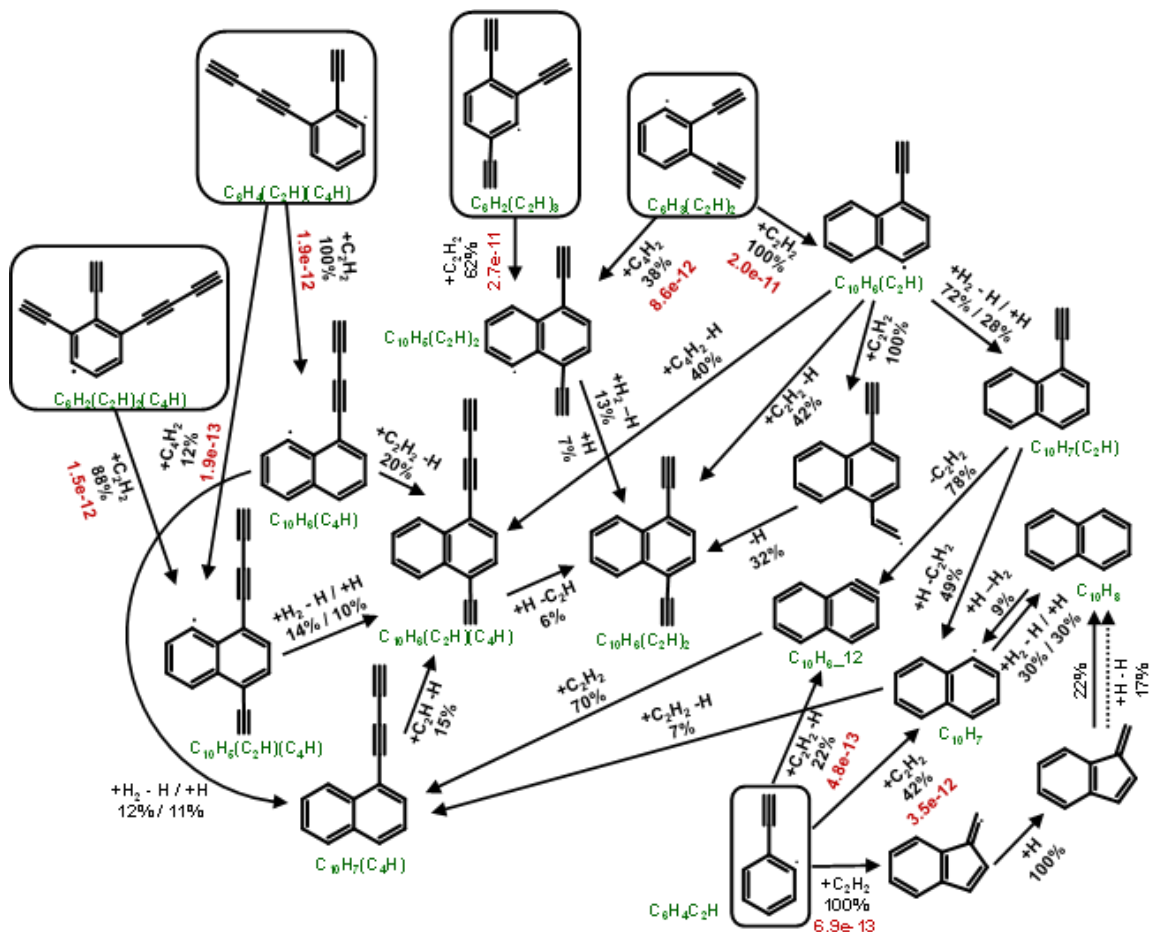


Figure 6.4.1.3 – Schematic of the kinetics to key second-ring aromatics involved in the formation of BIN1PJ. Integrated rate-of-production percentages for 0.35% C_2H_2 , $T_5 = 1742$ K. In red, integrated fluxes (moles / (cm³ s)).

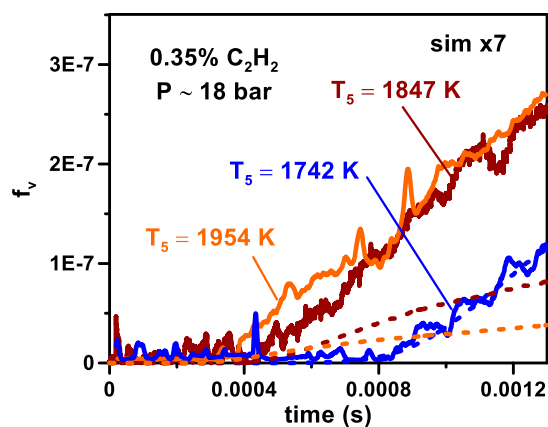


Figure 6.4.1.4 – Simulations of experimental profiles from the present work and simulations with the chemical kinetic model after removal of the PR formation reactions (dashed lines). Simulations multiplied by 7.

After the formation of BIN1JP species, their growth continues mainly through reactions involving acetylene and polyynes until the first primary particle BIN5J. At 1742 K, it is observed that more than 90% of the total flux from BIN1JP to BIN4JP comes from reactions with C_2H_2 (7%), C_4H_2 (24-26%), C_6H_2 (14-15%), C_8H_2 (34-36%), $C_{10}H_2$ (14-16%), and $C_{12}H_2$ (2-3%). As temperatures increase, reactions involving longer chains of polyynes, especially $C_{10}H_2$, begin to become more significant compared to those with acetylene, which starts to become negligible; diacetylene (reduced to 7-9%); and triacetylene (7-9%). The remaining contributions are from C_8H_2 (37-39%), $C_{10}H_2$ (33-39%), and $C_{12}H_2$ (5-15%). This behavior can be explained by considering that at relatively low temperatures, acetylene only partially decomposes, so the formation of longer polyyne chains is mainly activated at higher temperatures, where the growth of polyynes is actually favored. An equivalent observation applies to the reactions from BIN4J to BIN5J, where a further increase in the contribution of $C_{12}H_2$ is observed (17% at 1954 K vs. 5% at 1742 K). In light of this, it is interesting to note that at lower temperatures, reactions between BINJ species begin to play a role in the growth process (5% of the total ROP flux).

6.4.2 Kinetic analysis for soot formation from benzene pyrolysis.

In order to further improve our understanding of the combination of the gas phase of PAHs with that of polyynes in the formation of soot from aromatic fuels, an analysis of the integrated time-dependent production rates (ROP) is proposed for three experimental conditions studied in this work. These include the experimental condition of $T_5 = 1638$ K up to 1.3 ms, in the low-temperature range of the study (**Figure 6.4.2.1**), 1744 K up to 0.7 ms, specifically chosen as corresponding to the discontinuity in the growth rate and induction delay time curves as shown in section 6.1.1 (**Figure 6.4.2.2**), and at 1967 K at 0.2 ms, for the high-temperature range (**Figure 6.4.2.3**). In these figures, the reactions marked in blue relate to the formation of BINPJ, in black to the formation of BIN/BINJ. The PAH formation chemistry of the main gas-phase BIN precursors is not detailed here as already largely discussed in the publications concerning benzene pyrolysis [48,125].

For the condition studied at $T_5 = 1638$ K, in **Figure 6.4.2.1**, the BINJ/PJ and BIN species are produced in a ratio ~ 6.0 to 1 with fluxes of 1.20×10^{-10} mol/cm³-sec and 7.68×10^{-10} mol/cm³, respectively. Under these temperature conditions, both molar fluxes are significant. The BIN1J/PJ species are mainly formed from the contribution of polyynes molecules + PAH_r (radicals or branched radicals) or PAH_m (molecules) or PAH_{mB} (branched molecules), or from PAH_r + PAH_m. Notably, a large portion of the molar flux forming the first BIN radicals results in activated BIN1PJ species from the contribution of polyynes + PAHs (in blue). Specifically, the predominant reactions contributing to BIN1J production are: C₄H₂ + C₁₂H₇C₄H (34%), C₄H₂ + C₁₈H₉ (9%), + C₁₄H₉C₂H (5%); C₆H₂ + C₁₀H₇C₄H (9%), C₆H₅ + C₁₀H₇C₄H (5%). In the formation of BIN1J σ -radicals, the main contribution comes from H-abstraction from BIN1 by H (20%) and a minor 7% from PAH_r + PAH_m reactions (mainly naphthyl radical + biphenyl, naphthalene, acenaphthylene). BIN1 molecules are mainly formed through PAH_{rsr} (resonantly stabilized radicals) + PAH_r reactions. The contribution of the indenyl radical + PAH_r is notable, especially C₉H₇ + PC₁₃H₉R₁, accounting for 10% of the total flux. The contribution of C₂H₂ + C₁₈H₉ is also significant (14%). BIN1 can also be formed via reactions of BIN1PJ with C₆H₅ (2%) and C₉H₇ (8%), or through BIN1J σ -radicals + C₂H₂ (44%), a contribution from the HACA route. The kinetic growth of BIN1J σ -radicals and activated BIN1JP species promotes the formation of the next size species, BIN2J and BIN2PJ. For BIN2J, the main contribution comes from the reactions of BIN1PJ with polyynes, especially C₄H₂ (36%) and C₂H₂ (4%). Also important is the formation of BIN2J radicals via reactions of BIN1J with C₄H₂ (16%) and C₆H₆ (4%). The formation pathways to BIN2J also involve H-abstraction from BIN by H and, in a smaller percentage (3%), by the propargyl radical. There is also a small contribution from BIN1 + BIN1PJ (2%). For BIN2 formation, carbon addition plays a significant role via BIN1J + C₂H₂ (4%) and BIN2J + C₂H₂ (63%). Reactions of BIN2PJ (6%), BIN2J (8%), and BIN1PJ (6%) with the indenyl radical also contribute notably. The recombination of BINPJ species via BIN1PJ + BIN1PJ starts contributing to BIN2 formation (9%). As the growth proceeds, the formation of BIN3J σ -radicals occurs mainly through BIN2J + C₄H₂ (29%) and C₆H₆ (7%), with H-abstraction by H and C₃H₃ from BIN3 contributing 28% in total. The contribution of activated species from BIN2PJ, especially through addition of C₄H₂ (20%) and C₆H₆ (5%), is significant. BIN3 is mainly

formed through carbon addition: $\text{BIN2J} + \text{C}_2\text{H}_2$ (5%) and $\text{BIN3J} + \text{C}_2\text{H}_2$ (68%). Contributions from $\text{BIN2J} + \text{C}_9\text{H}_7$ (2%) and $\text{BIN2PJ} + \text{C}_9\text{H}_7$ (2%) are also present. The reactions between BINJ/PJ species, such as $\text{BIN2J} + \text{BIN2J}$ (6%) and $\text{BIN2PJ} + \text{BIN2J}$ (8%), are becoming more evident.

The formation of the last large PAH, BIN4J, is primarily driven by reactions of $\text{BIN3J} + \text{C}_4\text{H}_2$ (40%) and $\text{BIN3PJ} + \text{C}_4\text{H}_2$ (12%), followed by $\text{BIN3J} + \text{C}_6\text{H}_6$ (15%). Other contributions to BIN4J include BINPJ - BIN3J reactions, accounting for 16% overall, and finally, $\text{BIN3PJ} + \text{BIN}$ (4%). The first primary particle, BIN5J, is mainly formed by additions to BIN4J with: C_6H_6 (29%), C_9H_7 (5%), $\text{C}_6\text{H}_5\text{C}_2\text{H}$ (4%), with a significant flux from additions of BINPJ (20%), BINJ (sizes 2 to 4) (12%), and BIN (16%).

From the analysis at 1638 K, it is evident that the process of particle formation starts with reactions between PAHs + PAHs and PAHs + polyynes, while the growth is driven by two processes: 1) H-abstraction and carbon addition, which promote the formation of σ radicals and their respective molecules; 2) reactions of C_4H_2 with BINJs and BINPJs. Among the single-ring and PAH species contributing to addition reactions on BINs are $\text{C}_6\text{H}_5/\text{C}_6\text{H}_6$, C_9H_7 , $\text{C}_6\text{H}_5\text{C}_2\text{H}$, and $\text{C}_{10}\text{H}_7\text{C}_4\text{H}$.

Regarding **Figure 6.4.2.2**, the integrated ROP analyses at the temperature of 1744 K up to 0.7 ms indicate that the molar fluxes of BIN1J/PJ and BIN1 in this case show a ratio of about ~ 17 to 1, with fluxes of $6.49\text{e-}10$ mol/cm³-sec and $3.90\text{e-}11$ mol/cm³-sec, respectively. In this case, the pathways to BIN1PJ are predominant compared to those to BIN1J. Among these reactions, the ones involving polyynes + PAH_m and PAH_r stand out. The most influential reactions for the formation of BIN1PJ are $\text{C}_4\text{H}_2 + \text{C}_{12}\text{H}_7\text{C}_4\text{H}$ (38%) and $\text{C}_6\text{H}_2 + \text{C}_{10}\text{H}_7\text{C}_4\text{H}$ (16%). Following these, among other significant contributions, are $\text{C}_6\text{H}_2 + \text{C}_{12}\text{H}_7\text{C}_4\text{H}$ (5%), $\text{C}_8\text{H}_2 + \text{PC}_{13}\text{H}_9\text{R1}$ (5%), and $\text{C}_8\text{H}_2 + \text{C}_{10}\text{H}_7\text{C}_4\text{H}$ (5%). BIN1J σ -radicals are mainly formed by H-abstraction from BIN1 by H and C_3H_3 (16%). BIN1 is directly formed from $\text{C}_2\text{H}_2 + \text{C}_{18}\text{H}_9$ (9%) and $\text{C}_9\text{H}_7 + \text{PC}_{13}\text{H}_9\text{R1}$ (8%); it is then mainly formed via $\text{BIN1PJ} + \text{C}_6\text{H}_5$ (2%), + C_9H_7 (15%), + C_3H_3 (5%), + $\text{C}_9\text{H}_6\text{C}_2\text{H}$ (3%), with a significant contribution from carbon addition through $\text{BIN1J} + \text{C}_2\text{H}_2$ (46%).

BIN2J/PJ is produced from reactions involving $\text{BIN1PJ} + \text{C}_2\text{H}_2$ (4%), + C_4H_2 (51%), + C_6H_2 (10%), + C_8H_2 (7%), + C_6H_6 (4%), and $\text{BIN1J} + \text{C}_4\text{H}_2$ (6%), as well as contributions from $\text{BIN2} + \text{H}$ (13%) and $\text{BIN2} + \text{C}_3\text{H}_3$ (4%) via H-abstraction. At the same time, BIN2

is mainly produced through carbon addition $\text{BIN2J} + \text{C}_2\text{H}_2$ (63%), $+ \text{BIN1PJ}$ (5%), $+ \text{C}_9\text{H}_7$ (3%), as well as the reactions $\text{BIN2PJ} + \text{C}_3\text{H}_3$ (4%), $+ \text{C}_9\text{H}_7$ (10%), $+ \text{C}_9\text{H}_6\text{C}_2\text{H}$ (3%), $+ \text{BIN1PJ}$ (3%). Reactions of BIN1PJ with C_9H_7 and BIN1PJ are also significant.

The formation of BIN3J shows an increasing contribution from BIN2J σ -radicals adding to polyynes molecules such as C_4H_2 (13%), C_6H_2 (2%), and C_8H_2 (2%) (17% total, vs 7% for formation of BIN2J), while H-abstraction reactions by BIN3 count for 22% of the total flux. BIN2PJ predominantly drives the growth process of BIN3PJ through additions of C_4H_2 (40%), C_6H_2 (8%), and C_8H_2 (5%). The BIN3 formation receives a significant contribution from C_2H_2 addition to BIN3J (69%) and growth reactions from BIN2PJ (mainly with BIN2J (10%), BIN2PJ (7%), BIN1PJ (3%), and C_9H_7 (3%)) and $\text{BIN2J} + \text{BIN2J}$ (2%).

The flow to BIN4J gains considerable contribution from the $\text{BIN3PJ}/\text{BIN3J} + \text{BINJ}/\text{BIN}$ reactions, with a total of 31% of the integrated ROP. In particular, $\text{BIN2PJ} + \text{BIN3J}$ (8%), $\text{BIN3PJ} + \text{BIN3PJ}$ (5%), $\text{BIN3PJ} + \text{BIN3J}$ (11%), and $\text{BIN3B} + \text{BIN3PJ}$ (5%) are main growth steps. Still dominant, the chemistry of polyynes involves reactions such as $\text{BIN3PJ} + \text{C}_4\text{H}_2$ (35%), $\text{BIN3PJ} + \text{C}_6\text{H}_2$ (8%), $\text{BIN3J} + \text{C}_4\text{H}_2$ (23%), and $\text{BIN3PJ} + \text{C}_8\text{H}_2$ (5%).

The formation of the initial primary particle, BIN5J , is mainly guided by inception reactions involving $\text{BIN4J} + \text{BIN}(1-3)\text{JP}$, representing 60% of the total flux, followed by $\text{BIN4J} + \text{BINJ}$ (3-4) at 16%, and $\text{BIN4J} + \text{BIN}(2-3)$ at 13%. Additional contributions to BIN5J formation arise from reactions of BIN4J with C_8H_2 (6%) and C_6H_6 (5%).

At 1744K, it is observed that HACA significantly influences the formation of BIN5J , mainly through the production of $\text{BIN}(1-3)$. The role of reactions involving polyynes, especially with longer chains, is also prominent. There is a noticeable shift from the influence of C_2H_2 and C_4H_2 at lower temperatures (1638 K) to a dominance of C_4H_2 , C_6H_2 , and C_8H_2 . Moreover, aromatic and PAH compounds like C_6H_6 , C_9H_7 , $\text{C}_{10}\text{H}_7\text{C}_4\text{H}$, $\text{C}_{12}\text{H}_7\text{C}_4\text{H}$, $\text{PC}_{13}\text{H}_9\text{R1}$, and $\text{C}_9\text{H}_6\text{C}_2\text{H}$ play a significant but reduced role compared to the low temperature case. This is clearly noticeable in the reduced formation of $\text{BIN1}/\text{BIN1PJ}$ from PAH+PAH reactions, or the formation of the first particles (BIN5J), which is now driven by reactions of BIN molecules and radicals with other BIN species and with polyynes (the contribution of PAH reactions is negligible in the latter case, vs 41% of the flux at 1638 K).

The analyses at 1938 K represent a typical temperature condition within the high-temperature range for soot formation starting from benzene pyrolysis. In this case, shown in **Figure 6.4.2.3**, it is already evident that the process of BIN formation is primarily governed by activated radical species. The fluxes to BIN1 and BIN1PJ/BIN1J show a ratio of about 47 to 1, with values of $9.18\text{e-}11$ mol/cm³-sec and $1.97\text{e-}12$ mol/cm³-sec, respectively. Looking into the details of the analysis, BIN1PJ are predominant compared to the corresponding BIN1J radicals, with main formation reactions $\text{C}_4\text{H}_2 + \text{C}_{12}\text{H}_7\text{C}_4\text{H}$ (17%), $\text{C}_6\text{H}_2 + \text{C}_6\text{H}_4(\text{C}_6\text{H})\text{C}_2\text{H}$ (6%), $\text{C}_8\text{H}_2 + \text{C}_6\text{H}_5(\text{C}_6\text{H})$ (17%), $\text{C}_8\text{H}_2 + \text{C}_6\text{H}_4(\text{C}_6\text{H})$ (11%), $\text{C}_8\text{H}_2 + \text{C}_2\text{HC}_6\text{H}_4\text{C}_4\text{H}$ (7%), $\text{C}_{10}\text{H}_2 + \text{C}_6\text{H}_5(\text{C}_6\text{H})$ (9%), and $\text{C}_{10}\text{H}_2 + \text{C}_6\text{H}_4(\text{C}_6\text{H})$ (3%). The contribution discussed pertains to the formation of BIN1PJ through polyynes + PAH_{rB} and polyynes + PAH_{mB} reactions. Additionally, there are also, in a reduced but significant manner, reactions of polyynes + PAH_r such as $\text{C}_6\text{H}_2 + \text{C}_{12}\text{H}_7\text{C}_3\text{H}_2\text{-}2$ (3%), $\text{C}_8\text{H}_2 + \text{C}_{12}\text{H}_7\text{-}2$ (4%), $\text{C}_8\text{H}_2 + \text{C}_{12}\text{H}_7\text{-}3$ (3%), $\text{C}_8\text{H}_2 + \text{PC}_{13}\text{H}_9\text{R1}$ (5%). Despite the entrance flux to BIN1 is much lower than that of BIN1J/PJ, it accounts for around 28% of the total BIN1 ROP. The main reactions in this process involve propargyl and indenyl radicals with PAH intermediates. The addition of these two resonantly stabilized radicals to BIN1PJ is also very relevant to the formation of BIN1, together with the C_2H_2 addition to BIN1J.

BIN2J/PJ is formed via BIN1PJ + C_2H_2 (2%), + C_4H_2 (4%), + C_6H_2 (5%), + C_8H_2 (7%), + C_{10}H_2 (3%), with a significant contribution from polyynes, especially of sizes C4-C8. Additionally, there is also a flux of BIN1PJ + C_6H_6 of about 4%. BIN1J + C_4H_2 (13%) and BIN1J + C_6H_2 (11%) also contribute to the formation of BIN2J. A major contribution comes from BIN2 by H-abstraction (31%). As for BIN1, BIN2 come mainly from reactions of BIN2PJ with C_3H_3 (28%) and C_9H_7 (3%) and BIN2J with C_2H_2 (63%).

Moving to the formation of BIN3J/PJ, the contribution from the polyyne chemistry becomes more significant through reactions BIN2J + C_4H_2 (3%), + C_6H_2 (17%), + C_8H_2 (24%), + C_{10}H_2 (1%). Simultaneously, the addition of polyynes is involved in the formation of BIN3PJ, notably BIN2PJ + C_4H_2 (32%), + C_6H_2 (17%), + C_8H_2 (24%), + C_{10}H_2 (11%), + C_{12}H_2 (2%). It is again observed that at higher temperatures, the contribution of larger polyynes becomes more important, especially C6-C10. BIN3 is mainly formed through the C_2H_2 addition to BIN3J. The BIN2J + BIN1PJ reactions have a minimal contribution in this case, only 5% of the total flow to BIN4J (much smaller compared to the lower T cases).

Similar considerations apply for the formation of BIN4J, with the predominance of the polyynes contribution to the growth.

Concerning BIN5J, again, the central role of polyynes is confirmed, in particular from reactions between BIN4J and C_6H_2 (5%), C_8H_2 (28%), and $C_{10}H_2$ (13%). The reactions of BIN4J with BIN(2-3)PJ and with BIN4J start becoming relevant, with a total percentage of 46% of the total flux to BIN5J.

What emerges from this analysis is that, at high temperatures, soot formation is primarily driven by the formation of large polyynes, which influence the BIN1 formation through reactions with branched PAHs, radicals, or molecules, and the growth to larger BINs. The contribution of the HACA process becomes less prominent compared to lower temperatures, while the PAH chemistry is minimal.

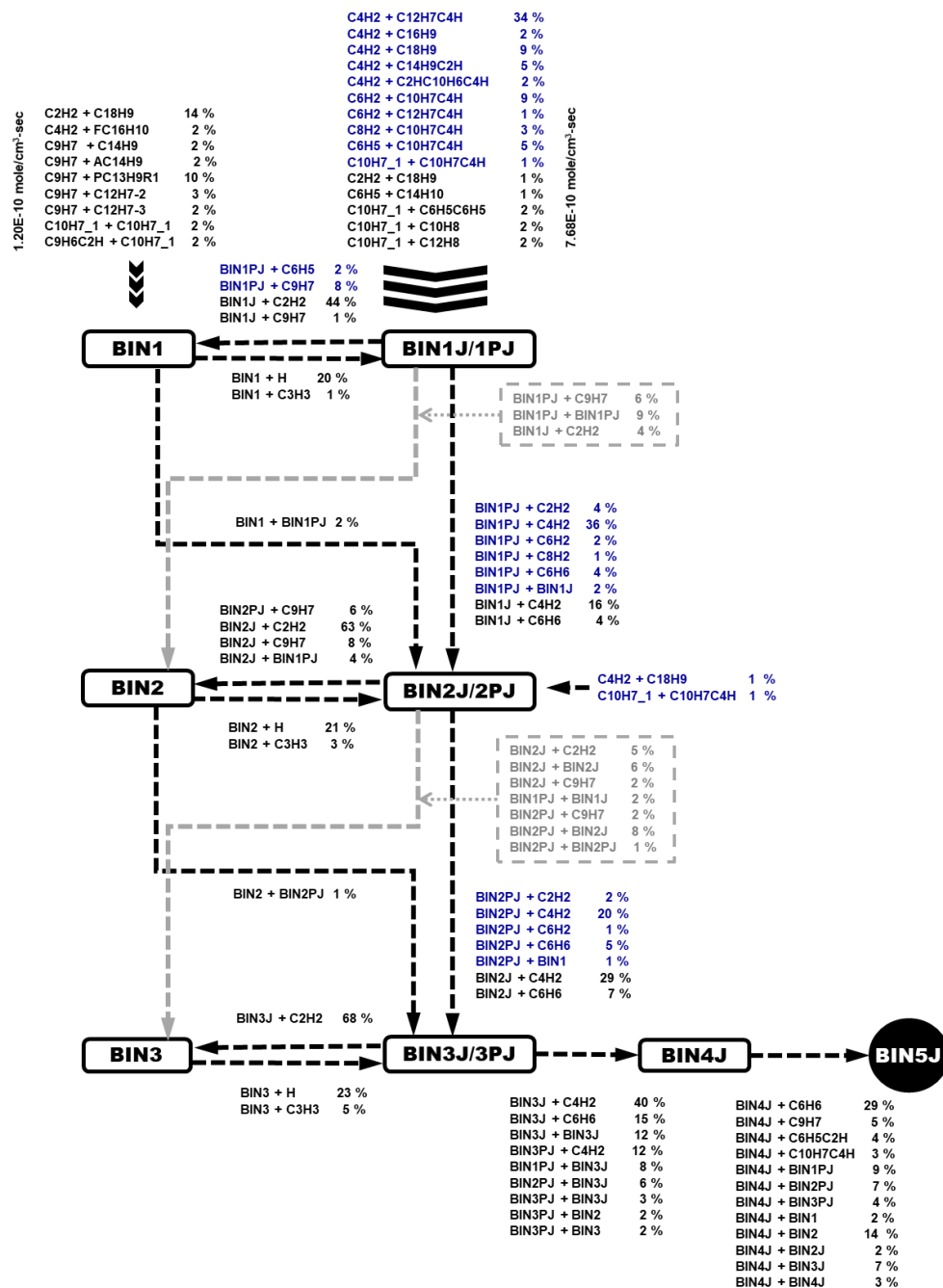


Figure 6.4.2.1 – 0.082% of C₆H₆ under pyrolytic conditions in argon, respectively, at T₅ = 1638 K at 1.3 ms.

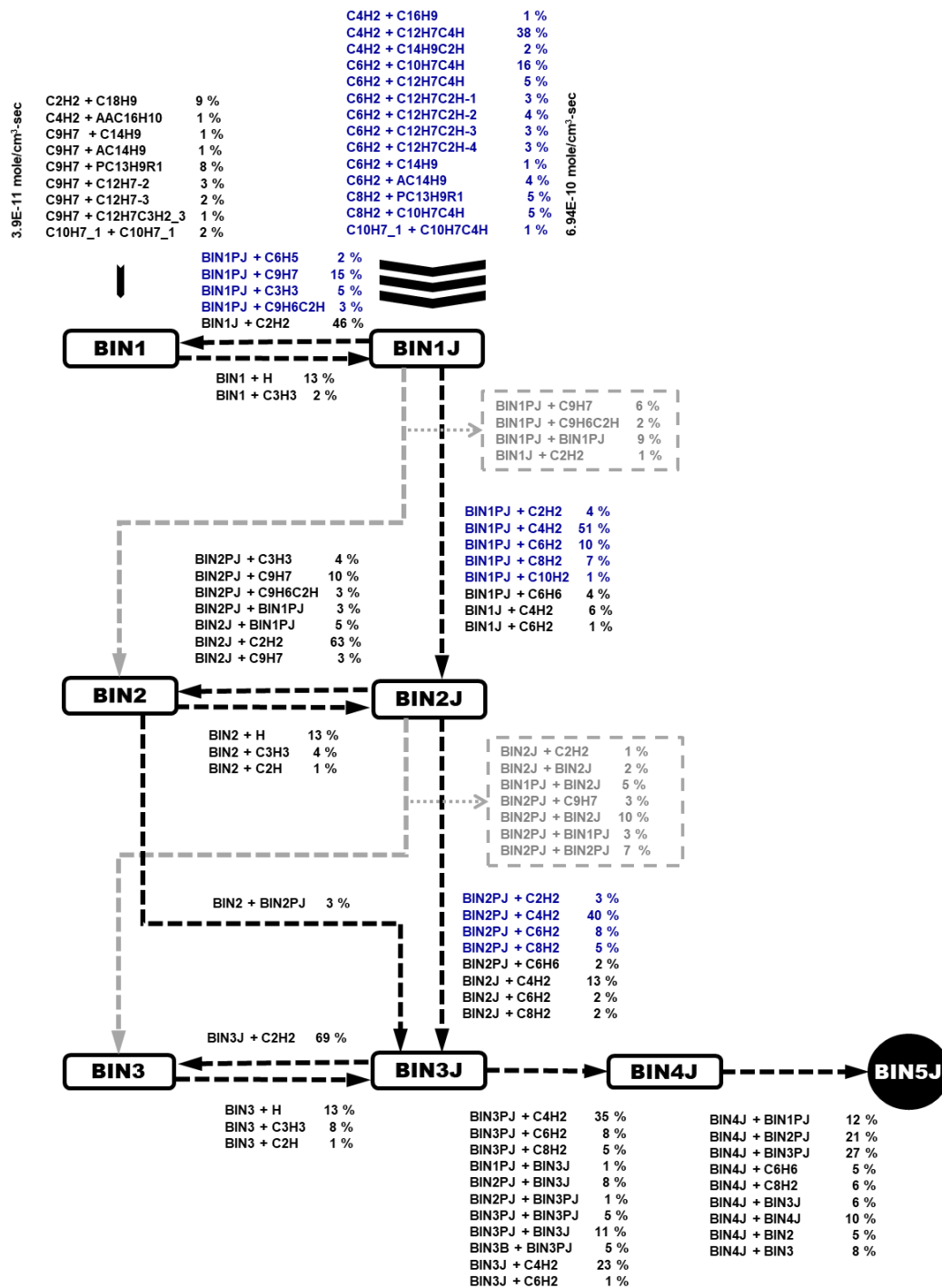


Figure 6.4.2.2 – 0.082% of C_6H_6 under pyrolytic conditions in argon, respectively, at $T_5 = 1744$ K at 0.7 ms.

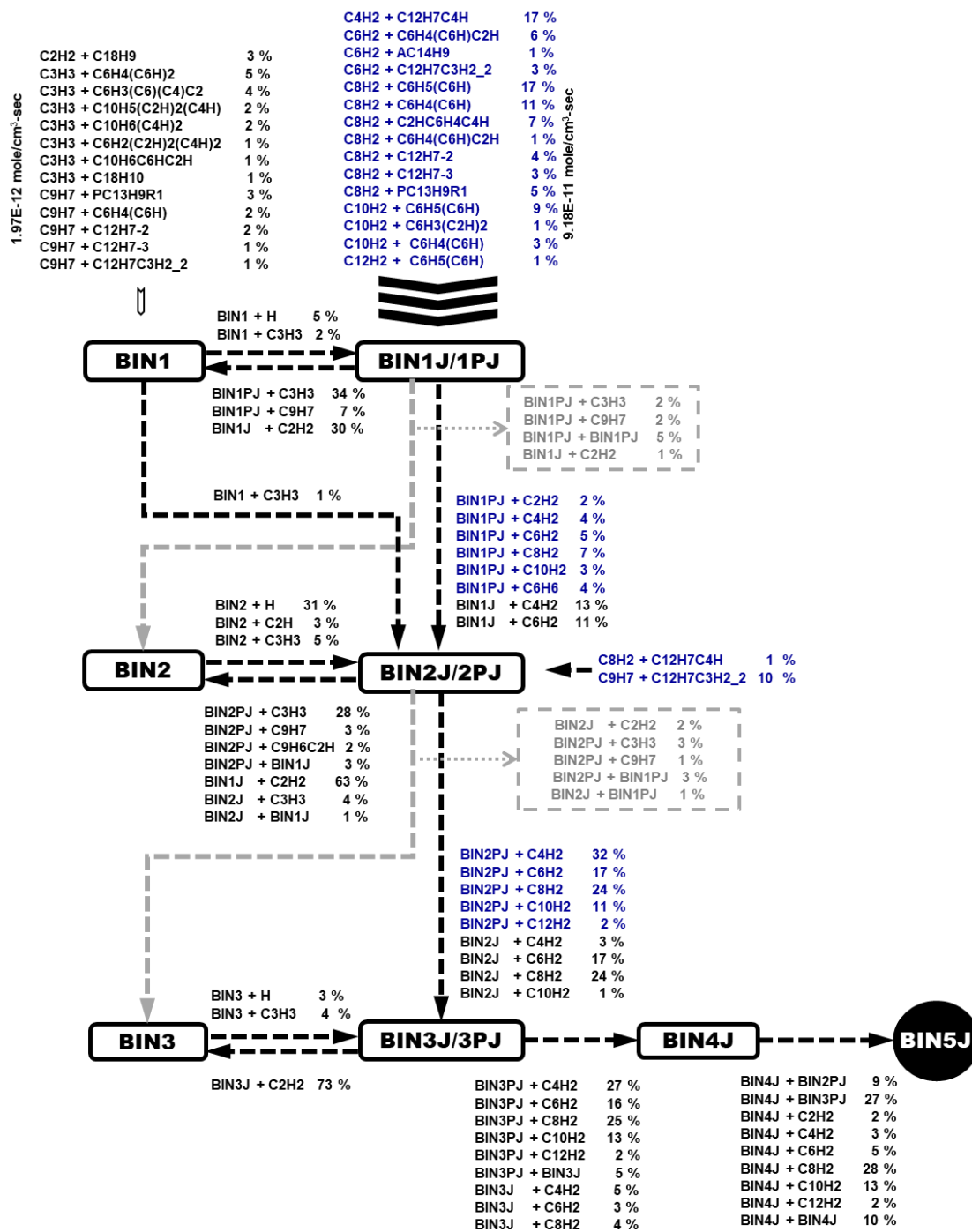


Figure 6.4.2.3 – 0.082% of C₆H₆ under pyrolytic conditions in argon, respectively, at T₅ = 1967 K at 0.2 ms.

6.4.3 Kinetic analysis for soot formation for toluene pyrolysis.

This section presents a detailed analysis of the main kinetic pathways leading to soot formation under pyrolytic conditions starting from toluene. Compared to the benzene case, toluene chemistry plays a key role in the formation of benzyl radicals and thus it facilitates the production of key PAH species such as indene, naphthalene, and fluorene, all important soot precursors. The role of such intermediates in BIN formation will be tested here.

The analyses were conducted with similar conditions as the experiments in section 6.1.3, specifically at $T_5 = 1538$ K for 1.3 ms (**Figure 6.4.3.1**), 1748 K for 0.7 ms (**Figure 6.4.3.2**), and 1939 K for 0.2 ms (**Figure 6.4.3.3**), with an average pressure of 18 bar. While the last two temperatures are similar to the intermediate- and high-temperature conditions considered for benzene pyrolysis, the 1538 K case is lower by 100 K compared to **Figure 6.4.2.1**. This is because toluene decomposition starts at a lower temperature compared to benzene, thus triggering the soot formation even below 1600 K. The corresponding integrated ROP analysis is shown in **Figure 6.4.3.1**.

BIN1J/PJ and BIN1 are produced with a molar flow ratio of 0.22, meaning that the production flow of pseudo-lumped BIN1 LPAHs is more than four times greater than the corresponding radical species BIN1J/PJ. This indicates that at low temperatures, the influence of PAH chemistry in the soot precursor formation process is very significant for toluene.

The key reactions in the formation of BIN1 are $C_7H_7 + PC_{13}H_9R1$ (29%) and $C_9H_7 + PC_{13}H_9R1$ (19%), followed by reactions $C_7H_7 + C_{14}H_9$ (7%), + $AC_{14}H_9$ (+9%). The role of the C_7H_7 and C_9H_7 resonantly stabilized radical is evident, as they are involved in almost all reactions forming BIN1. BIN1 formation occurs also by reactions $BIN1J + C_2H_2$ (8%) carbon addition and $BIN1J + C_7H_7$ (8%) and + C_9H_7 (4%). As the flux to BIN1 is predominant compared to the one to BIN1J/PJ, BIN1J is mainly formed by H-abstraction reactions by H (63%), CH_3 (5%), and C_3H_3 (5%). The formation of BIN1PJ accounts for 19% of the total flux, with major contributions from reactions of C_4H_2 (12% total). Other minor contributions from PAHr (mainly the naphthyl radical) + PAHm lead to the formation of BIN1J, accounting for 9%.

BIN2 is mainly formed through two pathways: i) BIN1J + resonantly stabilized radicals (C_7H_7 , 14%, and C_9H_7 , 11%); ii) reactions of BIN2J with C_2H_2 (17%) and C_7H_7 , (21%) and C_9H_7 (16%). Another smaller, but notable contribution comes from the reaction between indenyl radical with $PC_{13}H_9R1$ (6%). The H-abstraction reactions on BIN2 still represent the main pathway to BIN2J (46% of the total flow). Besides this, a significant portion of BIN2J is formed by BIN1J + C_4H_2 reactions (25%), + C_6H_6 (4%), and + C_7H_8 (4%). At the same time, there is a reduced flow through BIN1PJ + C_2H_2 (1%) and + C_4H_2 (5%).

BIN3J/PJ is mainly produced from the contributions of BIN2J and BIN3. The presence of C_4H_2 begins to become significant through the reaction $BIN2J + C_4H_2$, which produces 27% of BIN3J/PJ, followed by smaller contributions from $BIN2J + C_6H_6$ (6%) and + C_7H_8 (4%). The role of BIN/BIN reactions begins to become important, in particular the reactions $BIN2J + BIN1$ (14%) and + BIN2 (11%). For BIN3J/PJ, H-abstractions by H from BIN3 also play an important role, accounting for about 26%, along with a 5% contribution from abstraction by the propargyl radical. BIN3, on the other hand, is formed from both BIN2J and BIN3J. Considering BIN2J, contributions include the reaction with C_2H_2 (4% of the total flux), reactions involving the benzyl radical (18%) and indenyl (18%), as well as reactions with PAH radicals such as $C_{10}H_7CH_2_2$ (3%), and + $C_9H_6C_2H$ (2%). The BINs-BINs inception forms BIN3 through $BIN2J + BIN1J$ (4%) and $BIN2J + BIN2J$ (6%). An important part of BIN3 formation is also due to carbon addition steps with acetylene (36%) and ethylene (7%).

The production of BIN4J involves reactions of BINs with aromatics, PAHs, and polyynes, notably, the reactions $BIN3J + C_4H_2$ (22%), + C_6H_6 (6%), + C_7H_7 (14%), + C_9H_7 (5%). The BINs-BINs inception reactions are also important, including reactions of BIN3J with BIN1 (15%), BIN2 (10%), BIN3 (4%), BIN1J (4%), BIN2J (5%), and BIN3J (5%). There is no contribution from activated BINPJ species.

The reactions involving PAH_{rsr} and PAH_m compounds become even more central in the formation of the primary particle BIN5J, including reactions of BIN4J with C_9H_7 (20%), C_7H_7 (16%), C_6H_6 (8%), C_7H_8 (4%), and $C_{10}H_8$, $C_9H_6C_2H$, $C_{10}H_7CH_2_2$, each at 2% of the total flux. An important role is played by the addition to BIN4J of BIN1 (21%), BIN2 (14%), and BIN3 (5%), with a smaller flow (5%) from BINJ + BINJ.

From this initial analysis, it emerges that soot formation starting from C_7H_8 pyrolysis at 1538 K is influenced by the chemistry of PAH_{rsr} , PAH_m , and PAH_r . The contribution of activated species BINPJ is minimal, and the chemistry is mainly driven by HACA and PAHs, with the only contribution of polyynes via C_4H_2 . The formation of BIN molecules is favored under these conditions, highlighted by their role in the growth process.

For the temperature of 1748 K at 0.7 ms, the ROP analysis is reported in **Figure 6.4.3.2**. This temperature, as previously seen for benzene, is important as a crossing point of low-temperature kinetics mainly governed by PAH chemistry and HACA in soot formation, and that of polyynes at higher temperatures. In this case, the fluxes of BIN1 and BIN1J are respectively $3.05e-10$ mol/cm³-sec and $1.09e-9$ mol/cm³-sec. The ratio between the fluxes of BIN1J and BIN1 is about 3.5. An inversion of trend is observed here, where radicals begin to dominate in the formation of soot precursors with respect to the case at 1538 K. BIN1PJ are produced in larger amounts than BIN1J species, mainly thanks to reactions involving polyynes + PAH_{mB} , also with some radical contributions. Among these reactions, $C_4H_2 + C_{12}H_7C_4H$ (20%) and $+ C_{14}H_9C_2H$ (5%), $C_6H_2 + C_{10}H_7C_4H$ (10%), $C_8H_2 + PC_{13}H_9R1$ (12%) are the most influential. Simultaneously, the H-abstraction reactions by H, C_3H_3 , C_2H , and CH_3 on BIN1 account for 17% of the total integrated rate to BIN1J/PJ. The production of BIN1 is strongly driven by $C_9H_7 + PC_{13}H_9R1$, accounting for 26% of the total flux; followed mainly by contributions from $C_7H_7 + PC_{13}H_9R1$ (9%), $C_9H_7 + C_{10}H_7CYC5R$ (4%), and $+ C_{10}H_7CYC5R_2$ (4%). BIN1 is also formed through carbon addition on BIN1J, with a significant contribution of 33% from C_2H_2 addition. In the formation of BIN1, BIN1PJ + C_9H_7 also contributes, accounting for 5% of the total flux. BIN2PJ is mainly formed through reactions of BIN1PJ with C_2H_2 (3%) and polyynes: C_4H_2 (38%), C_6H_2 (5%), C_8H_2 (2%), as well as BIN1J with C_4H_2 (15%). H-abstraction reactions on BIN2 count globally for 33% of the total flux to BIN2J/PJ, BIN2 being formed mainly from carbon addition ($BIN2J + C_2H_2$, 61% of the integrated ROP). Other most influential reactions for BIN2 include the ones involving the indenyl radical with BIN1PJ (4%), BIN2J (5%), and BIN2PJ (7%), and $BIN1J + C_2H_2$ (3%). Simultaneously, there is a smaller flow from other PAH-PAH reactions contributing to BIN2 formation, particularly $C_9H_7 + PC_{13}H_9R1$ (3%).

For the production of BIN3J/PJ, the reactions between BIN2J/BIN2PJ and C₂H₂/polyynes are still the most influential, accounting for 60% of the total ROP. In particular, the C₄H₂ reactions with BIN2J and BIN2PJ account for 22% and 27%, respectively, the C₆H₂ reactions for 3% and 4%, respectively, with minor contributions from BIN2PJ + C₈H₂ and C₂H₂. The integrated rates of the H-abstraction reactions on BIN3 constitute 35% of the total rate of BIN3J/PJ. Regarding the formation of BIN3, carbon addition plays a decisive role, in particular from reactions of BIN3J with C₂H₂ and C₂H₄ (69% and 5% of the total ROP). Except few other smaller contributions, the remaining flow is primarily from BIN2J/PJ-BINJ/PJ inception reactions, with a cumulative percentage of 21%.

In the production of BIN4J, interactions mainly involve polyynes with BIN3J (C₄H₂ (33%), C₆H₂ (5%)) and with the activated species BIN3PJ (C₄H₂ (23%)), as well as inception reactions among LPAHs BINs such as BIN3J + BIN3J (8%), BIN3J + BIN1PJ (5%), BIN3J + BIN2PJ (8%), BIN3PJ + BIN3J (9%), and BIN3PJ + BIN3 (4%).

BIN5J is produced from contributions of inception reactions, notably from BIN4J + BINJP and BIN4J + BIN (molecules), with the most influential being: BIN4J + BIN1PJ (11%), + BIN2PJ (15%), + BIN3PJ (18%), + BIN3J (14%), + BIN2 (17%), and +BIN3 (12%). C₉H₇ is the most representative PAH that, interacting with BIN4J, influences the formation of BIN5J (7% of the ROP flow).

In the ROP performed at 1748 K, it is clear how, compared to the case at 1538 K, the formation of the first BIN species is mainly influenced by PAH_{rsr} + PAH_r and polyynes molecules + PAH_{mb} and PAH_r. The contribution of polyynes, mainly C₄H₂ and C₆H₂, increases, especially in the growth reactions with BINPJ species. HACA still has a significant influence, parallel to the pathway of polyynes. An important contribution is exerted by active BINPJ species in combination with BINJ radicals towards BIN5J. A balanced effect is observed in the participation of BIN5J formation, involving the contribution of BINJ/BINPJ/BIN.

To investigate the kinetics of soot formation from toluene at high temperature, a case ROP study was conducted at a temperature of 1939 K and a time of 0.2 ms. This analysis is shown in **Figure 6.4.3.3**. In this case, similar to the analysis done for benzene in the previous section, the ratio BIN1J/BIN1 is highly in favor of BIN1J, with a value close to 18. This means that, even for toluene, the kinetics are practically driven exclusively by the

BINs in their radical form, e.g., BIN(1-3)J, BIN(4-5)J, and activated species BINP(1-3)J. However, the BIN1J/BIN1 ratio for benzene at 1967 K is about 2.7 times larger than that for toluene. For toluene at 1939 K, the molar fluxes of BIN1J and BIN1 are 6.14×10^{-11} mol/cm³-sec and 3.52×10^{-12} mol/cm³-sec, respectively.

All the flux to radical species involves formation of BIN1PJ, from C₄H₂ + C₁₂H₇C₄H (13%), C₆H₂ + AC₁₄H₉ (7%), C₆H₂ + C₁₄H₉ (5%), C₆H₂ + C₁₂H₇C₄H (3%), C₆H₂ + C₁₂H₇C₃H₂_2 (3%), C₈H₂ + C₆H₅(C₆H) (8%), C₈H₂ + PC₁₃H₉R1 (22%), C₈H₂ + AC₁₄H₉ (5%), C₈H₂ + C₁₂H₇-2 (4%), C₁₀H₂ + C₆H₅(C₆H) (8%), and C₁₀H₂ + PC₁₃H₉R1 (8%). Specifically, these are polyynes + PAH_r/PAH_{rB} interactions. The polyynes contributing most to the formation of BIN1J(P) are primarily the C₄H₂ and C₈H₂. The BIN1 are mainly formed by reaction of C₁₈H₉ + C₂H₂ and reactions involving resonantly stabilized radicals such as C₃H₃, C₇H₇, and C₉H₇. H-abstraction reactions and reactions involving the HACA step and resonantly stabilized radicals connect BIN1 with BIN1J/PJ.

Following the growth of LPAHs, the formation of BIN2J/PJ and subsequently BIN3J/PJ is mainly influenced by the reactions of polyynes with BINPJ, with contributions for C₄H₂ from 32% to 40% of the total ROP, for C₆H₂ from 14% to 15%, for C₈H₂ from 19% to 22%, and for C₁₀H₂ of 9%. Polyynes reacting with BINJ also provide minor contributions, together with H-abstraction from BIN2 and BIN3. BIN2 is mainly produced by BIN2J + C₂H₂ and BIN2PJ + C₃H₃, while BIN3 from BIN3J + C₂H₂ and BIN2PJ + BIN2PJ.

The formation of BIN4J is mainly driven by polyyne reactions with BIN3PJ and BIN3J, with a contribution of 78% and 17% of the total rate, respectively. BINJ-BINJ reactions account for the remaining 5%. The reactions between BIN4J and BINJ/PJ become more relevant for the formation of BIN5J (36% of the ROP, in total), while the reactions of BIN4J with polyynes (in particular, C₈H₂ and C₁₀H₂) still dominate the growth process.

The analyses presented in **Figure 6.4.3.3** indicate that in the high-temperature range of this study, the polyyne chemistry coupled to PAH species and BINPJ dominates the formation of soot particles.

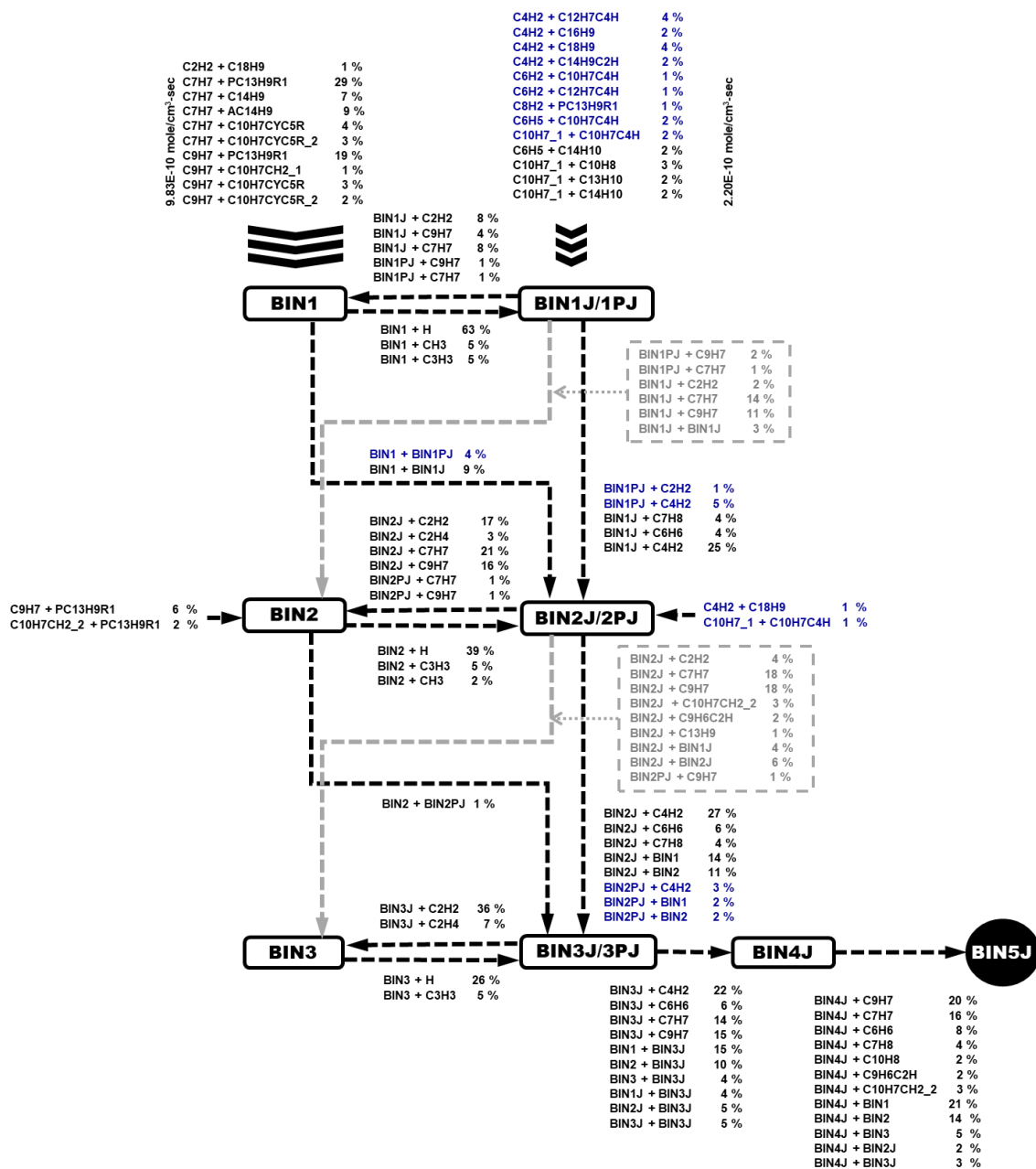


Figure 6.4.3.1 – 0.07% of C_7H_8 under pyrolytic conditions in argon, respectively, at $T_5 = 1538$ K at 1.3 ms.

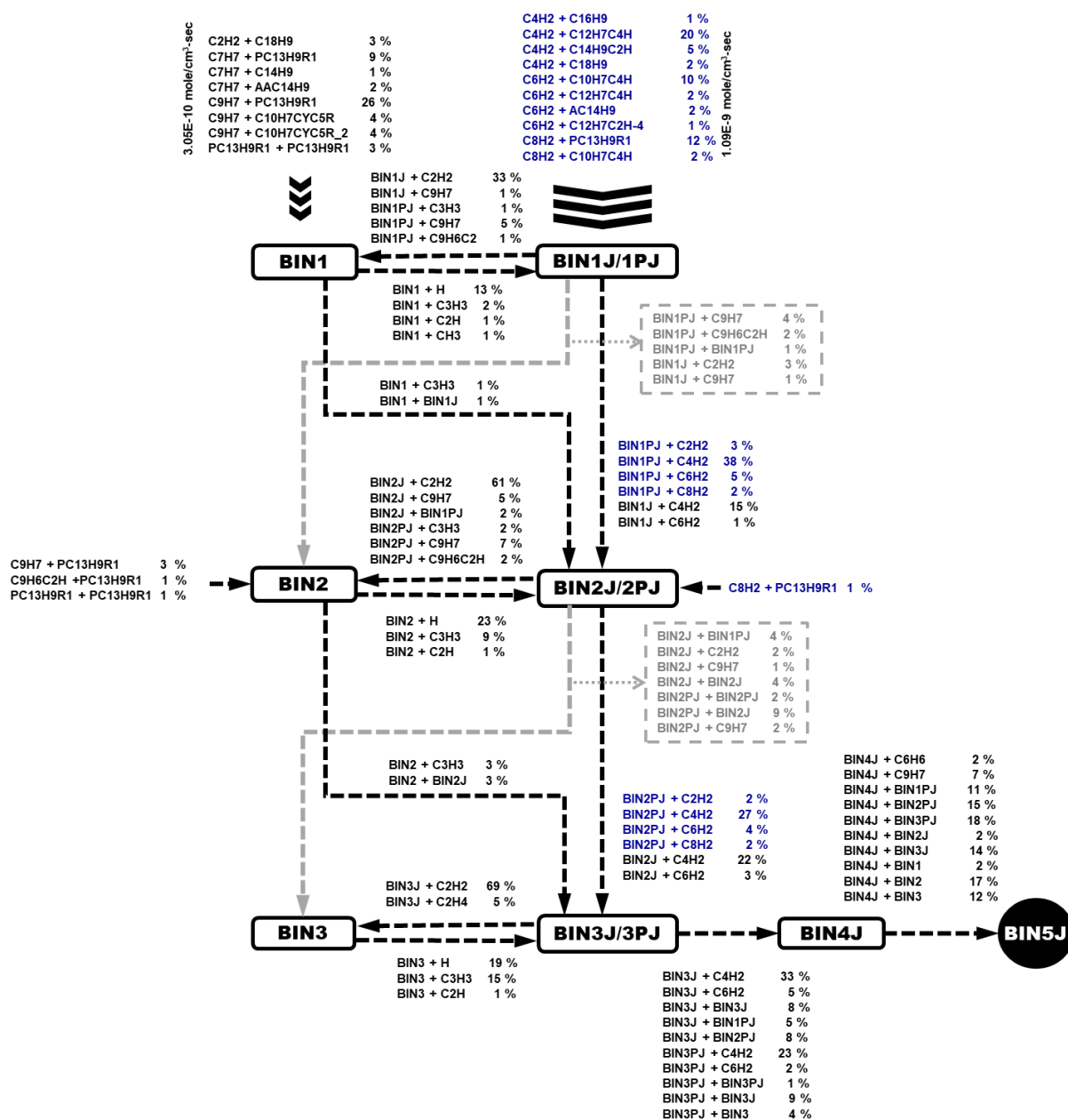


Figure 6.4.3.2 – 0.07% of C₇H₈ under pyrolytic conditions in argon, respectively, at T₅ = 1748 K at 0.7 ms.

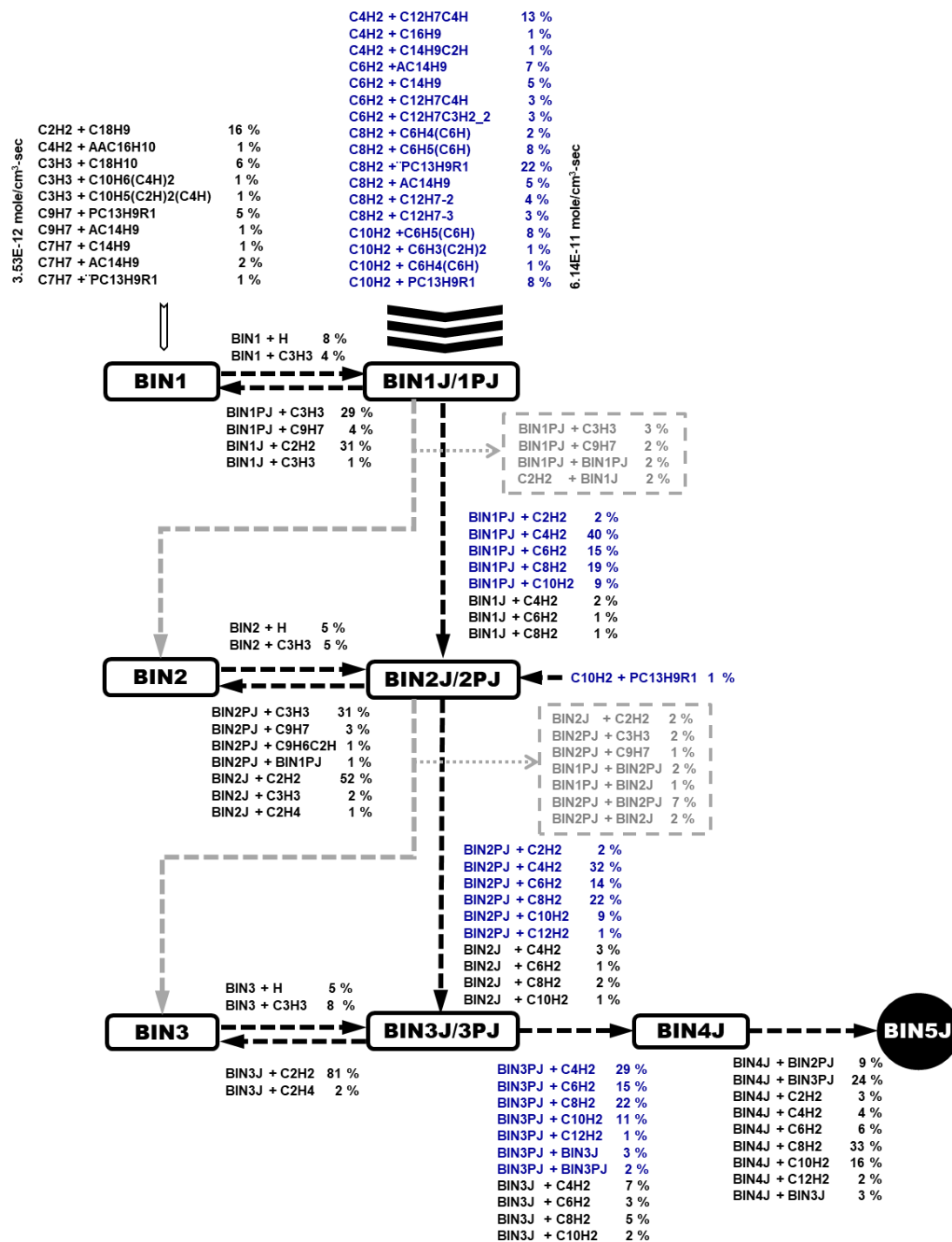


Figure 6.4.3.3 – 0.07% of C₇H₈ under pyrolytic conditions in argon, respectively, at T₅ = 1939 K at 0.2 ms.

6.4.4 Example of brute force sensitivity analysis: case study of soot formation for aromatic chemistry.

This section presents a brute-force sensitivity analysis of the main reaction classes in the mechanism, using benzene as a case study for soot formation from aromatic chemistry.

The main reaction classes, illustrated in **Figure 6.4.4.1**, were parametrically modified by increasing the Arrhenius pre-exponential factor A by a factor of 10, while using the correction factor 2.2 for the modeling results, as previously done for the original model. In the figure, the thick solid lines represent the experiments, the thin solid line the simulations with the original model, the dashed lines with the modified model. A test was also conducted by removing the precursors of polyynes chemistry to evaluate their impact on the performance of the kinetic mechanism.

As shown in **Figure 6.4.4.1**, removing the RSAP precursors in acetylene kinetics results in a drastic degradation of soot predictions at the different temperatures (underestimation of the soot volume fraction by 2 orders of magnitude + shift in the behavior as function of T_5). Increasing the rate constant for the HACA mechanism shows no significant influence; except within the mid-temperature range. The PAH growth and condensation mechanisms favor soot formation in the low- and mid-temperature range, as observed at 1638 K and 1744 K. Condensation of polyynes (PYYNs CONDENSATION) accelerates soot formation across the entire temperature range, with a more significant quantitative impact at 1744 K and 1853 K. Conversely, the soot growth mechanism via polyynes (PYYNs GROWTH) is highly influential both in accelerating soot formation and enhancing f_v across the entire investigated temperature range. Increasing the reaction rates of BIN+BIN inception reactions results in a quantitative decrease in global soot formation over time. If enhanced, the COALAGG mechanism does not significantly affect the predictions.

To conclude, what emerges is a particular sensitivity of the mechanism at the parametric level for PAH and polyyne condensation, as well as for growth, along with the fundamental importance of polyyne chemistry in sustaining the process chemistry.

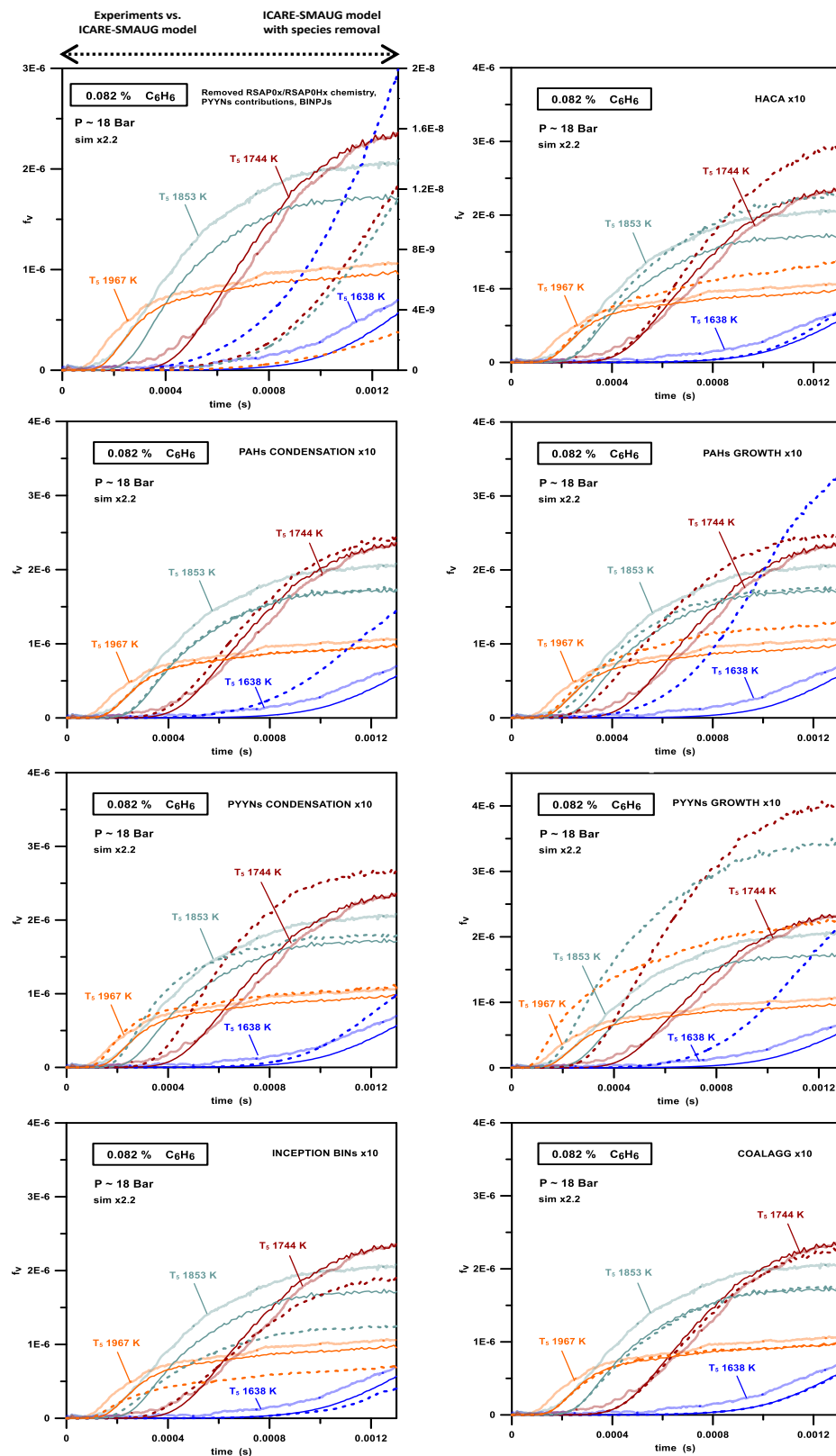


Figure 6.4.4.1 – Brute force sensitivity analysis for benzene.

7. Conclusion.

Understanding the processes that lead to the formation of carbonaceous particles and soot in combustion devices remains a puzzling challenge for the combustion community, although it is critical for the design of next-generation cleaner systems and the optimization of functional nanomaterial synthesis. Recent advances in the field have been made based on new experimental evidence and the development of modeling tools that couple the comprehensive gas-phase chemistry of the fuels and precursor molecules with the detailed kinetics of soot nucleation, growth, agglomeration, and oxidation. Recent chemical kinetic models have achieved excellent capabilities in reproducing experimental data in flame environments, but critical questions remain unresolved, especially regarding particle chemistry under pyrolytic conditions for certain key fuels.

The present work presents a new detailed chemical kinetic model (ICARE soot model) for soot particle pyrolytic chemistry validated against shock tube experimental data (time-history soot volume fraction, soot volume fraction as a function of temperature, induction delay time, soot growth rate). The experiments were taken from previous works at ICARE using laser-based techniques, considering various aromatic, cyclic, and aliphatic fuels, together with selected mixtures, as well as literature data, when available. The first key step in the development of the chemical kinetic model was the construction of a Python framework for the automatic generation of models. Such a framework, called Soot Mechanism Automated Generator (SMAuG), is constituted by a central core responsible for the main operations related to the writing of the reactions and associated reaction rate parameters, which are defined based on reaction classes and rules as set by the end-user, as well as on the discrete sectional model with pseudo-lumped BIN species. The framework also includes a simulation environment supporting zero-dimensional constant-pressure simulations, as well as supplementary tools for post-processing simulation data and managing experimental datasets.

Following the complexity of soot formation in terms of possible mechanistic pathways available as a function of the fuel chemistry and thermodynamic conditions, it was considered essential for developing a predictive, comprehensive tool to provide validation

against data on different and complementary fuels. Two main contributions have been highlighted in literature modeling activities: the route involving polycyclic aromatic hydrocarbons (PAHs) and the one based on the polyynes chemistry. The two mechanisms are complementary, and possible synergistic effects can arise in certain conditions. Acetylene (C_2H_2) was chosen as the first validation target with the goal of isolating the polyynes chemistry. Indeed, C_2H_2 is not only a major product in high-temperature combustion environments, but it is also the main building block for the formation of large polyynes chains. First, the gas-phase chemistry of acetylene pyrolysis and polyynes formation was revised based on literature data with shock tube techniques (time-history profiles and single-pulse shock tube data). After this, the preliminary modeling activities on the solid-phase chemistry confirmed a negligible contribution of PAHs in the case of pyrolysis of 0.245% and 0.35% acetylene in argon bath gas, over the temperature range 1603-1989 K, and pressures of 16.7-18.2 bar. In addition, the implementation of the mechanisms for the formation of the first BIN through direct reactions of polyynes-polyynes, as in literature works, could not lead to a satisfactory simulation of the experimental results. Thus, a new chemistry for the gas-phase soot precursors was proposed, which includes the formation of branched PAH species by the addition of polyynes radicals into polyynes molecules, followed by C_2H_2/C_4H_2 addition and cyclization. The HACA route links the different branched intermediates and provides the growth pathways to larger species. In addition, a new class of activated BIN species (BINPJ) was introduced to account for the fast kinetics of polyynes growth. Following optimization of the rate parameters for the different reaction classes, the model was capable of accurately reproducing the f_v profiles (with a correction factor of 2.2), as well as induction delay times and the soot growth rates. The ROP kinetic analyses showed how the initial BIN species are formed mainly through reactions between branched PAHs and polyynes, with the role of larger $C_{2n}H_2$ chains becoming more and more prominent with the initial temperature of the experiment. Similarly, the growth of the BINPJ and BINJ up to the first particle is driven by similar polyynes species. The model was also validated against literature data with different experimental conditions, pressures ranging from 0.7 to 6 bar, and fuel mole fractions from 1.09% to 10%.

Once the polyynes chemistry was validated, the contribution of the aromatic mechanisms had to be determined. For this, benzene was chosen as a reference fuel for its key role as a precursor of PAH species in all combustion environments. The chemistry of PAH formation from benzene pyrolysis was taken from the ICARE PAH model. The model was then completed with cross-reactions PAH/BIN – polyynes, and the corresponding rate parameters validated against soot volume fraction measurements with 0.082% benzene (C_6H_6) in argon bath gas, temperatures 1537-1967 K and pressures 16.4-18.3 bar. The model showed excellent capabilities to reproduce the experimental results (with a correction factor of 2.2), as well as other data from the literature at different conditions: 1 and 2% C_6H_6 at a pressure of 2.15 bar; 2% C_6H_6 at 1.4 bar; 0.175-0.467-0.62-1.05% C_6H_6 at 4.5 bar; 0.02-0.04-0.05% C_6H_6 at 50 bar; 0.5-1-2% C_6H_6 at 1.3 bar. The chemical kinetic analyses indicated the complexity of the chemistry involved in particle formation for the benzene case. In the low temperature range of the study, the PAH + PAH reactions and the reactions between branched PAH species and the polyynes both contribute to the formation of the BIN1. The growth of the large PAHs up to BIN5J is driven by H-abstraction and carbon addition, and the reactions of C_4H_2 with BINJs and BINPJs. As the temperature increases, the particle chemistry is more and more dominated by the reactions involving large polyynes, which influence the BIN1 formation through reactions with branched PAHs and the growth to larger BINs.

Another essential intermediate of PAH and soot chemistry is toluene (C_7H_8), which, together with the resonantly stabilized benzyl radical (C_7H_7), participates in many key mechanistic pathways. Shock tube experiments on 0.07% toluene in argon, temperatures 1518-1990 K, and pressures 16.4-18.2 bar were used as a benchmark to assess the influence of the resonantly stabilized radicals on soot formation. The chemistry of PAH formation from toluene pyrolysis was taken from the ICARE PAH model as the benzene case. The model simulated the experimental results quite accurately, using a correction factor of 2.2, with a slight underprediction in the high-temperature range of the study. A good correspondence was also found between simulations and experiments from other works in the literature. The experimental conditions of such works include pressures of 3.0 bar and C_7H_8 molar fractions of 0.097%, 0.15%, 0.17%, 0.25%, 0.5%, and 0.9% in argon; 0.5%

C₇H₈ at 2.5 bar, 1.0% C₇H₈ at 3.3 bar, and 1.5% C₇H₈ at 3.5 bar; 0.5% C₇H₈ at 14 bar. The ROP analyses performed at different temperatures showed a marked shift in the particle formation chemistry, moving from low-temperature conditions to the highest temperatures. At low temperatures, the formation of the first soot particles is mainly driven by the HACA mechanism and the reactions of C₇H₇ and PAH species (mainly resonantly stabilized, e.g., the indenyl radical and molecules). The contribution of activated species BINPJ is minimal, with the only contribution of polyynes via C₄H₂. At very high temperatures, the polyyne chemistry coupled to PAH species (branched and non-branched) becomes the main factor, and BINPJ dominates the formation of soot particles.

The model was also tested against a variety of f_v measurements with different fuels, including ethylene, cyclopentene, styrene, ethylbenzene, and C3 intermediates (propene and propylene), under similar P conditions and carbon atom concentrations (except for ethylene, for which higher concentrations were employed). The model showed excellent predictive performance for aromatic fuels, styrene, and ethylbenzene, always within a factor of 2.2. The formation of soot particles from ethylene was overpredicted at lower temperatures, as was that from cyclopentene, propylene, and propyne. This translates into a slight shift of the f_v vs T modeling profile towards lower temperatures. For propylene and propyne, a factor of 1.2 rather than 2.2 is preferred.

Concerning the fuel blends, toluene, benzene, and cyclopentene + C2 species, as well as toluene + C3 species, were considered at similar P conditions and carbon atom concentrations. In general, the model accurately reproduces the data with acetylene addition, but it underpredicts the data obtained with mixtures containing ethylene. This suggests the possibility of missing pathways involving C₂H₄ and C₂H₃. The toluene + C3 chemistry for soot formation is well captured by the simulation results.

Overall, the model developed in this work has been shown to be reliable for predicting soot formation under high-pressure, high-temperature conditions, with multiple fuels considered in the validation process. It is important to underscore that gas-phase chemistry is essential for the correct evaluation of the entire particle chemistry: coupling the solid-phase chemistry with a different PAH sub-model could yield very different results.

For a comprehensive understanding of the model's capabilities for tested pure hydrocarbons and binary mixtures, the performance summary is shown in **Figures 7.1 and 7.2**.

Pure hydrocarbons									
Small aliphatic hydrocarbons				5 ring	Aromatic hydrocarbons				
									
Acetylene	Propyne	Propylene	Ethylene	Cyclopentene	Benzene	Toluene	Ethylbenzene	Styrene	
✓	✓	✓		✓	✓	✓	✓	✓	

Figure 7.1 – General performance of ICARE-SMAuG prediction for pure fuels.

Binary mixtures Aliphatic and Aromatic Hydrocarbons	 Cyclopentene	 Benzene	 Toluene
 Acetylene	✓	✓	✓
 Ethylene	No info available	No info available	
 Propyne	No info available	No info available	✓
 Propylene	No info available	No info available	✓

Figure 7.2 – General performance of ICARE-SMAuG prediction for binary fuel mixtures.

Regarding the mechanistic analyses performed on selected fuels (benzene, acetylene, C3's, toluene), **Figures 7.3 and 7.4** highlight the main chemical pathways leading to the formation of BINs/BINPs of size 1 (first lumped LPAHs) and size 5 (the first primary particles), at low and high temperatures, respectively. Concerning BIN1 formation from aromatic fuels and C3's, the chemistry of PAHs (including branched ones) and their reactions with polyynes are dominant at low temperatures, with contributions from short polyynes, whereas at high temperatures, the reactions of branched PAHs with longer polyynes play a more significant role through the production of BINJPs. Unlike other fuels,

soot formation from C_2H_2 is mainly driven by polyynes, which are shorter at low temperatures and longer at high temperatures.

The PAH's + BIN and the BIN + BIN reactions are mainly contributing to the formation of BIN5J's at lower temperatures for all fuels except acetylene, while at higher temperatures, the role of PAHs is replaced by the polyynes.

	 Acetylene ■ 1742 K	 Benzene ■ 1638 K	 Propyne ■ 1667-1673 K	 Propylene ■ 1667-1673 K	 Toluene ■ 1538 K
 BIN1J σ -Radicals	—	$PAH_m + PAH_r$	—	—	—
 BIN1PJ Activated species	$PYYN + PAH_{rB,mB}$	$PYYN + PAH_{mB}$ $PAH_r + PYYN / PAH_{mB}$	$PYYN + PAH_{mB}$ $PYYN + PAH_r$	$PYYN + PAH_{mB}$ $PYYN + PAH_r$	$PYYN + PAH_{r,mB}$ $PAH_r + PAH_{m,mB}$
 BIN1 Molecules	—	$PAH_r + PAH_{rsr}$ $C_2H_2 + PAH_r$	$PAH_{rsr} + PAH_r$ $PAH_{mB,r} + PAH_r$	$PAH_{rsr} + PAH_r$	$PAH_{rsr} + PAH_r$
 BIN5J 1 st Primary Particle	$PYYN + BIN4J$	$PAH + BIN4J$ $BINJ + BINJ / PJ$	$C_2H_2 + BIN4J$ $PAH + BIN4J$ $BINJ + BINJ / PJ$	$C_2H_2 + BIN4J$ $PAH + BIN4J$ $BINJ + BINJ / PJ$	$PAH_{m,rsr} + BIN4J$ $PAH_{mB} + BIN4J$ $BINJ + BINJ / PJ$

Figure 7.3 – Behavior of ICARE-SMAuG model at low temperatures for validation fuel kinetics: formation of the first pseudo-lumped precursors of LPAHs and the primary particle BIN5J.

	 Acetylene ■ 1954 K	 Benzene ■ 1967 K	 Propyne ■ 1951-1968 K	 Propylene ■ 1951-1968 K	 Toluene ■ 1939 K
 BIN1PJ Activated species	$PYYN + PAH_{rB,mB}$	$PYYN + PAH_{mB}$ $PYYN + PAH_{rB,r}$	$PYYN + PAH_{mB}$ $PYYN + PAH_r$	$PYYN + PAH_{mB}$ $PYYN + PAH_r$	$PYYN + PAH_{r,mB}$ $PYYN + PAH_{rB}$
 BIN1 Molecules	—	—	$PAH_{rsr} + PAH_r$	$PAH_r + PAH_{rsr}$ $C_2H_2 + PAH_r$ $C_3H_3 + PAH_m$	$PAH_r + PAH_{rsr}$ $C_2H_2 + PAH_r$ $C_3H_3 + PAH_m$
 BIN5J 1 st Primary Particle	$PYYN + BIN4J$	$PYYN + BIN4J$ $BINJ + BINJ / PJ$	$C_2H_2 + BIN4J$ $PYYN + BIN4J$ $BINJ + BINJ / PJ$	$C_2H_2 + BIN4J$ $PYYN + BIN4J$ $BINJ + BINJ / PJ$	$PYYN + BIN4J$ $BINJ + BINJ / PJ$

Figure 7.4 – Behavior of ICARE-SMAuG model at high temperatures for validation fuel kinetics: formation of the first pseudo-lumped precursors of LPAHs and the primary particle BIN5J.

The results presented in this thesis suggest that the new ICARE soot model could serve as a comprehensive basis for further developments. In particular, future activities will focus on improving the kinetic parameters for certain fuels and fuel mixtures, for example, aromatic + ethylene mixtures. In addition, new fuels will be considered. In particular, recent industrial applications have focused on producing soot through methane pyrolysis. Methane pyrolysis is one of the most promising methods for low-CO₂-emission hydrogen production [254]; however, the process's success is hindered by the formation of solid carbon, which occurs via nucleation and growth mechanisms. In pyrolytic conditions, the dynamics of soot carbon formation simultaneously determine the methane conversion efficiency, the operational stability of the reactors, and the properties of the produced carbon, which is increasingly recognized as a valuable co-product.

Consequently, predictive modeling of soot formation from methane pyrolysis is a key element for understanding and controlling the genesis of carbon in strongly reducing environments, as well as for facilitating the development and scale-up of advanced methane pyrolysis processes, including the plasma-assisted ones [255,256].

In this perspective, the predictive capability of the ICARE soot model was also initially evaluated using shock tube data for methane pyrolysis under pyrolytic conditions, as shown in **Figures 7.5a** [257] and **7.5b** [250].

The performance resulting from this test is overall positive and promising for developing, testing, and validating the model in the context of methane pyrolytic kinetics.

An additional potential of the model is the future possibility of implementing kinetics related to soot formation in plasma-assisted processes, which could have significant implications for advanced materials synthesis applications.

Over a longer time frame, oxidation chemistry will also be targeted for both gas-phase and solid-phase mechanisms, with an extension of the SMAUG framework.

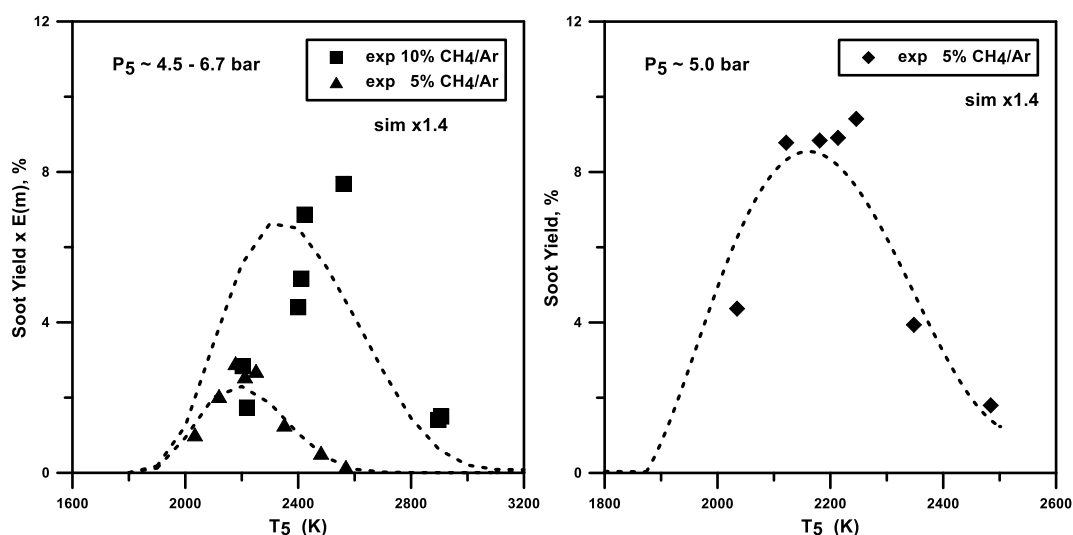


Figure 7.5 – Test of the potential of the ICARE-SMAuG model in methane pyrolysis. The symbols represent experimental data, while the dashed lines indicate the model.

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9. Appendix.

Table 1-A – Resonantly Stabilized Acetylenic Precursors.

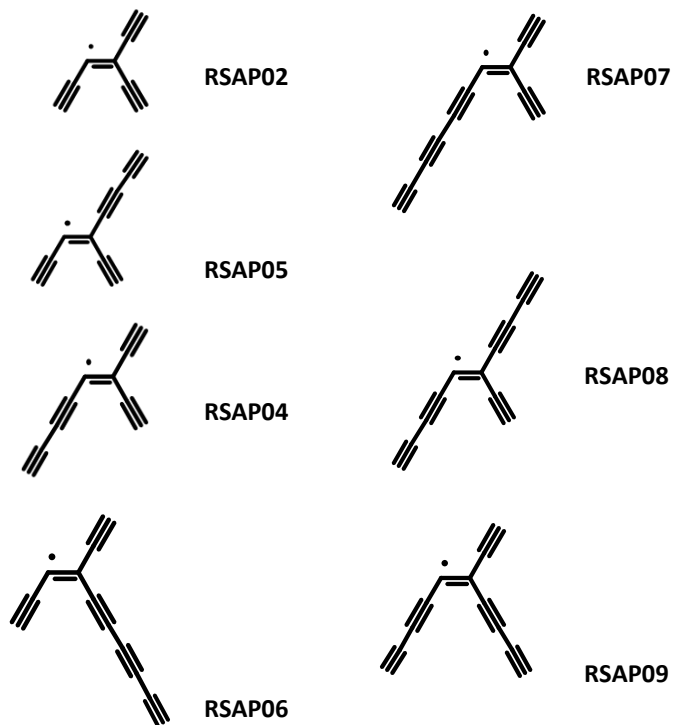


Table 2-A – PAH_{mB} - Polycyclic Aromatic Hydrocarbons molecules Branched – Examples of the most influential in the model.

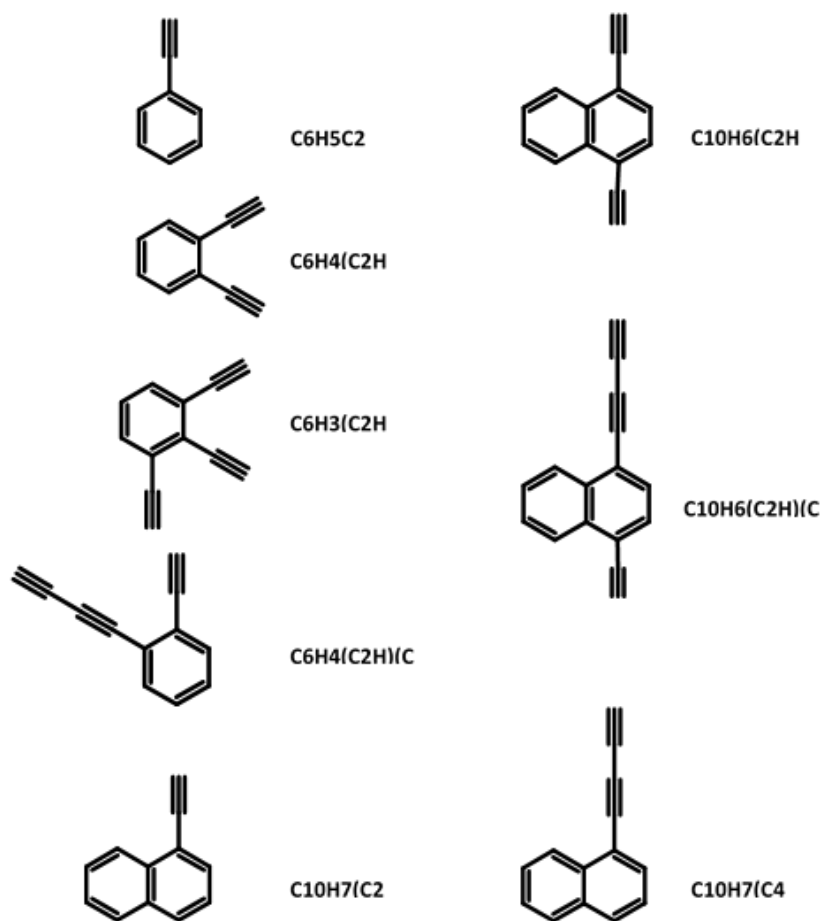


Table 3-A – PAH_{RB} - Polycyclic Aromatic Hydrocarbons radicals Branched - Examples of the most influential in the model.

