

# On developing a post processing approach to investigate PAH evolution for industrial applications

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## Abstract

The use of detailed CFD simulations to predict PAH emission from industrial processes is impractical due to the very high computational overhead apart from the relatively high uncertainty in the input data. To address this, we propose a post processing approach to predict PAH evolution which uses the results of the CFD simulation of the major process gases based on a relevant skeletal mechanism as the input to PSR reactors (which is run on each cell in the domain) using detailed PAH chemistry. This work describes the underlying assumptions of the proposed approach and its implementation. The predictions from the proposed approach is compared with results of CFD simulation employing detailed PAH chemistry for the case of coflow burner burning a mixture of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> at various flue gas recycling levels and fuel inlet velocities. The results show that proposed approach can predict the PAH emission, at a reasonable accuracy and a fraction of computational cost, using an appropriate value of the tuning parameter used in the definition of the residence time of the PSR model.

Keywords: PAH, CFD, PSR, Post processing

## Introduction

The emission of Polycyclic Aromatic Hydrocarbons (PAH) from process (especially related to metal processing and production industries) is considered to originate from the combustion of the carbon materials in furnaces that contain PAH and aliphatic fuels. The evolution of PAH evolution during combustion of aliphatic fuels consists of the formation of the first aromatic ring (i.e. benzene), its growth into larger aromatic species eventually forming soot, and decomposition of some larger PAH, depending on temperature, into smaller aromatic species or even carbon dioxide. The reaction pathways that describes the evolution of PAH is a topic of active research and has been reviewed in the recent work by [1]. So understanding how PAH evolution within industrial systems is critical in the optimal design of the process to ensure the complete oxidation of PAH.

A way to predict and develop strategies to reduce emissions from from industrial processes is by using Computational fluid dynamics (CFD) based modelling. Use of CFD to model emissions (like CO<sub>2</sub> and NO<sub>x</sub>) from various industrial operational scenarios is well documented in literature like [2–4]. A major example is the framework to model thermal NO<sub>x</sub>, available in Fluent [5], which decouples the NO<sub>x</sub> evolution from the reactive flow of process gases thus enabling 'fast' post processing of the thermal NO<sub>x</sub> generated from the process. The use of this post processing approach is especially beneficial and computationally cheaper for modelling thermal NO<sub>x</sub> emission from industrial processes, especially for furnaces, as it is a complex transient phenomena due to furnace operations, turbulent reactive

flow of gases, NO<sub>x</sub> evolution is driven by intermediate species and their reactions (Zeldovich mechanism), additionally the mesh used typically consists of using millions of cells (see [2, 5]). Although this NO<sub>x</sub> post processing tool can capture the trends in NO emission with changes in the furnace conditions, it still does not match the experimental data as reported in the work by [2]. Additionally there is a the large uncertainty in the input data available for industrial processes, for example, the mass flow rate and composition of the process gases rising up from the charge surface is unknown in furnaces (see [2]). When compared to thermal NO<sub>x</sub>, PAH is generated from the reactions involve aliphatic and PAH bounded fuels. So to predict PAH emissions, knowledge of the amount and composition of the PAH bounded to the fuel species or aliphatic fuel needs to be known a priori. This is often difficult as PAH bounded to the carbon materials added to the furnace varies drastically, and depends on the operational conditions (see [6]). So modelling emissions from industrial processes typically looks for trends evolution of the pollutant species (like NO<sub>x</sub> and PAH) than its accurate prediction – so use of approximate models is very relevant in this context.

Inspired by the NO<sub>x</sub> post processing tool used in industrial modelling, a framework (based on CFD + 0D reactors) to predict the PAH evolution is presented in this work. The framework relies on decoupling the PAH evolution from the reactive flow of process gases as former is emitted in relatively very small amounts. Additionally when compared to thermal NO<sub>x</sub>, PAH evolution from aliphatic species is much more complex involving hundreds of species and thousands of reactions, see [7, 8], making the simulation involving the detailed mechanism for an industrial application very computationally expensive and impractical. So the underlying

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rationale behind developing the proposed approach is to predict the overall trends in PAH evolution for various operational scenarios with sufficient accuracy and a reasonable computational overhead.

### Proposed approach

The post processing approach proposed in this work essentially decouples the PAH evolution from the turbulent reactive flow of the major species in the process. This allows for CFD results of the reactive flow of major species to be used as input to model PAH evolution using 0D reactors. This approach is developed based on the following assumptions:

- impact of PAH evolution on the flow (velocity, turbulence and temperature distribution) is negligible - as amount of PAH emitted is much lower than the major/primary species emitted from the process,
- time averaged (or quasi-steady) solution obtained from the CFD simulation provides a reasonable representation of the process,
- the transport of PAH within the computational domain is not considered - could limit the ability of the proposed approach to capture the complexity of the phenomena as the PAH can grow/oxidize as it is transported within the domain.

In the proposed approach, the turbulent reactive flow of the major species relevant in the process is initially simulated using a skeletal (or reduced) mechanism (that does not treat PAH evolution) using the gaseous turbulent reactive flow solver in OpenFOAM, reactingFoam, which solves for governing equations corresponding to mass, momentum, energy and species conservation. The solver accounts for the generation or consumption of species due to chemical reactions (which is computed based on Eddy Dissipation Concept (EDC) model [9]) as well as the heat released/consumed due to chemical reactions. Additionally solver also models turbulent nature of these gaseous flow which in this work is based on the Standard  $k - \epsilon$  model. The model also accounts for the temperature dependent nature of transport (based on Sutherland viscosity model and modified Eucken thermal conductivity model) and thermodynamic (based on NASA 7-coefficient polynomials) properties of species as well as the equation of state of the gas mixture (using perfect gas model). It should be noted that the simulation is run until the solution reaches a time averaged or quasi-steady state solution and the results exported (to the next step - 0D reactors) are the mole fraction distribution of the species, pressure, temperature, density ( $\rho$ ), dynamic viscosity ( $\mu$ ) and turbulent dissipation rate ( $\epsilon$ ).

The result obtained from the CFD simulation in the previous step is subsequently used as input to Perfectly Stirred Reactor (PSR) model, or the 0D reactor, to predict the PAH evolution based on very detailed PAH chemistry and local composition, pressure, temperature and mean residence time in the control volume. It should be noted that these PSR model do not exchange any information with the neighbouring cells - so it does

not account for transport of species. The PSR model essentially solves for the conservation of species in each cell (in the domain used in the previous step) employing a detailed reaction mechanism describing PAH evolution based on

$$\frac{dY_k}{dt} = \frac{Y_k^* - Y_k}{\tau} + \frac{\dot{\omega}_k W_k}{\rho}$$

where  $\tau$  is the user-specified residence time,  $W_k$  is the molecular weight of  $k$ th species,  $\dot{\omega}_k$  is the chemistry driven molar rate of production of  $k$ th species per unit volume and  $Y_k^*$  is the inlet mass fraction of  $k$ th species (which is assumed to be equal to the prediction from step 1 for the same species). The definition of the mean residence time in each control volume ( $\tau$ ) is defined (inspired by the Eddy Dissipation Concept model) as a function of the  $\mu$ ,  $\rho$  and  $\epsilon$ :

$$\tau = A \left( \frac{\mu}{\rho \epsilon} \right)^{1/2} \quad (1)$$

where  $A$  is a tunable parameter.

The proposed approach relies on a streamlined workflow which can be summarized as: OpenFOAM simulation of the reactive flow involving the major species is performed and the quasi-steady state results are converted to VTK format (using *foamToVTK* utility), this VTK file is directly read into a Python script (using *pyvista* library [10]) and PSR model is run on each cell (based on input file containing information on local gas composition - based on mole fraction, temperature, pressure and  $\tau$ ), and once the PSR model is run on all the cells in the domain a new VTK file is written with results from the PSR model. The VTK files can be visualized using ParaView. As the species used in the CFD and PSR based modelling steps of the proposed approach are different, for compatibility, the thermodynamic data file (for the PAH evolution chemistry) used in PSR model is appended with species treated only in the reactive flow of major species simulated in the OpenFOAM simulation. It should be noted that to run very large meshes, the script that runs the PSR model is parallelized using *multiprocessing* library in python. Additionally the PSR is run only in cell which has local temperature  $\geq 500$  K and local mole fraction of  $O_2 > 10^{-8}$  (as PAH is considered to evolve only once the fuel species reacts).

### Simulation details

In order to investigate the ability of the proposed approach to predict PAH evolution, a simplified case of axisymmetric co-flow burner is used, see illustration in Fig.1. The fuel consisting of  $C_2H_2$ ,  $H_2$  and  $N_2$  is injected from a central nozzle of diameter around 4 mm. The fuel is introduced into the domain at a fixed velocity of 42.2 m/s at constant temperature of 1000 °C and its composition (defined based on mass fraction) is 24.5642% of  $C_2H_2$ , 4.6497% of  $H_2$  and 70.7861% of

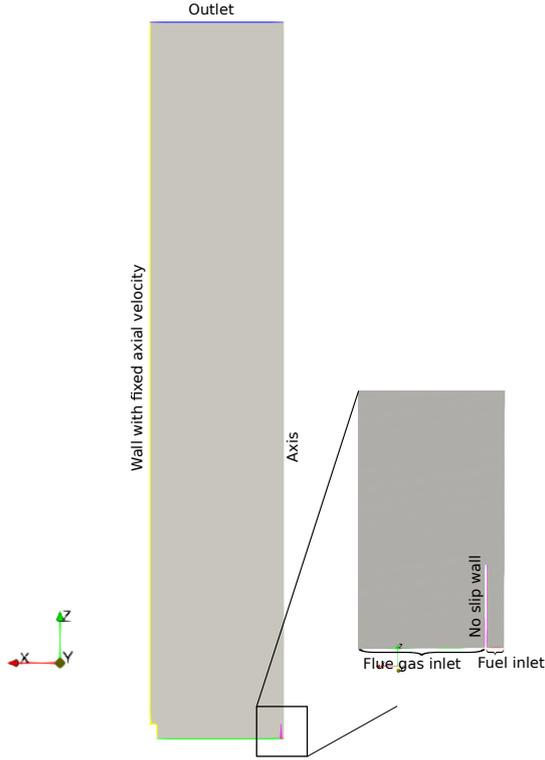


Figure 1: Illustration of the domain used in the simulations.

$N_2$ . The flue gases are added through nozzle surrounding the annulus (with inner and outer radii around 4.5 mm and 180 mm) at a velocity of 0.3 m/s and temperature of 300 K. The flue gas is considered to comprise (by mass fraction) of  $N_2$  (76.3149%), Ar (0.5008%),  $O_2$  (varied 23.1843%, 17.4318% and 11.6212%) and  $CO_2$  (remaining: 0.0 %, 5.7525%, 11.5631%). Larger amount of  $CO_2$  (or lower amount of  $O_2$ ) in the flue gas is representative of the larger levels of recycling flue gases. The flue gases and fuel are separated for the initial 20 mm after which they mix/react for the next 1 m (along with the outer radius of the domain is increased to 190 mm). Additionally, the inlets of fuel and flue gas are assigned with turbulence intensities of 8% and 2% respectively with turbulent mixing length scale of 5 mm. The top boundary is set a outlet, and fuel-flue gas separating walls are set as no-slip (or fixed value of 0 m/s) walls but the remaining walls are assigned a fixed axial velocity of 0.3 m/s. The geometry used for the simulation is meshed with 18226 cells and solver is run until the solution reaches a pseudo steady state (around 34000 iterations).

To model the reactive flow of the major species, which is performed in the first step of the proposed approach, the OpenFOAM simulation is performed based on reaction kinetics data and thermodynamic data of species described by GRI Mech 3.0 [11]. The mechanism contains 53 species and 325 reactions which considers oxidation of simple hydrocarbons ( $C_1$ - $C_3$ ). Based on the results from the simulation using GRI Mech 3.0, the PSR model is run on each cell with reaction mecha-

nism for PAH chemistry (proposed by [7] which has 112 species and 939 reactions with the largest PAH considered is a 5 ringed PAH - Benzo(a)pyrene). To compare the predictions from the proposed approach, the full or detailed CFD simulation is run using the detailed PAH reaction mechanism proposed by [7].

## Results

In order to investigate the ability of the proposed approach to predict trends in PAH emission during industrial operations, we investigate two operational scenarios: flue gas recycling, and fuel injection rates. The prediction from the proposed approach is compared against equivalent results from the full/detailed CFD simulation that employs the detailed PAH chemistry.

To compare the predictions from the different simulations, the emission of PAH (or rather the PAH generated) is computed quite simply as the average mole fraction of the monitored PAH which is calculated as

$$\langle X_i \rangle = \frac{\sum_{j=0}^{N-1} X_j V_j}{\sum_{j=0}^{N-1} V_j}, \quad (2)$$

where  $V_j$  is the volume of cell indexed  $j$  and  $X_i$  is the mole fraction of species  $i$ . For simplicity only some of the species (out of the 112 species described in the reaction mechanism of [7]) are monitored which for this work are: A1 ( $C_6H_6$  or Benzene), A2 ( $C_{10}H_8$  or Naphthalene), P2 ( $C_{12}H_{10}$  or Acenaphthene), A2C2H ( $C_{12}H_8$  or Acenaphthylene), A3 ( $C_{14}H_{10}$  or Anthracene/Phenanthrene), A4 ( $C_{16}H_{10}$  or Fluoranthene/Pyrene), C18H12 ( $C_{18}H_{12}$  or Benzo(a)anthracene/Chrysene), and BAPYR ( $C_{20}H_{12}$  or Benzo(a)pyrene).

*Impact of flue gas recycling:* With increasing levels of flue gas recycling (or recirculated gases has larger content of  $CO_2$  and lower amounts of  $O_2$ ), the detailed CFD simulation predicts a decrease in the flame temperature where as in the case where flue gas contains around 11.6% of  $O_2$  (and almost same amount of  $CO_2$ ) the combustion does not occur. The simulations using the GRI Mech 3.0 is able to predict the decrease in the flame temperature when  $O_2$  in the flue gas reduces from around 23.2% and 17.4%. The simulations using the GRI Mech 3.0 mechanism predicted the successful combustion of the fuel species when flue gases comprised of 11.6%  $O_2$ . As the reduced mechanism (which in this work is based on GRI Mech 3.0) based simulations was able to predict the major flow features reliably only for two scenarios, the PAH emission from these two simulations (where flue gases consisted of  $O_2$  around 23.2% to 17.4% and  $CO_2$  around 0.0 % and 5.75%) are compared in Fig.2 and Fig.3. Fig.2 shows that PAH species are generated locally within the flame but they are not transport away from the flame as these species get oxidized as they are convected through the high temperature region of flame. A possible reason for this prediction is a result of the PAH chemistry not account for even larger PAH species (and soot) which are more ther-

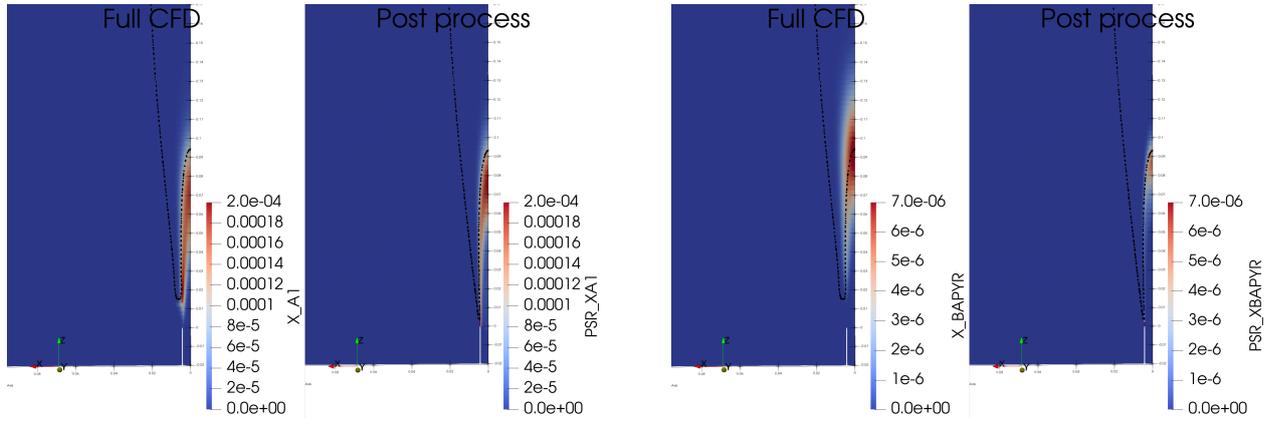


Figure 2: Comparison of the mole fraction of A1 ( $C_6H_6$  or Benzene) and BAPYR ( $C_{20}H_{12}$  or Benzo(a)pyrene) predicted using the Full CFD (with detailed PAH chemistry) and Post process (the proposed approach using  $A = 20$ ) for the scenario where the flue gas consists of  $O_2$  and  $CO_2$  around 17.4% and 5.75% (by mass fraction) respectively. Note that the image is zoomed to the section close to the fuel inlet where PAH species evolve. The black line in the images is the isotherm corresponding to 1750 K.

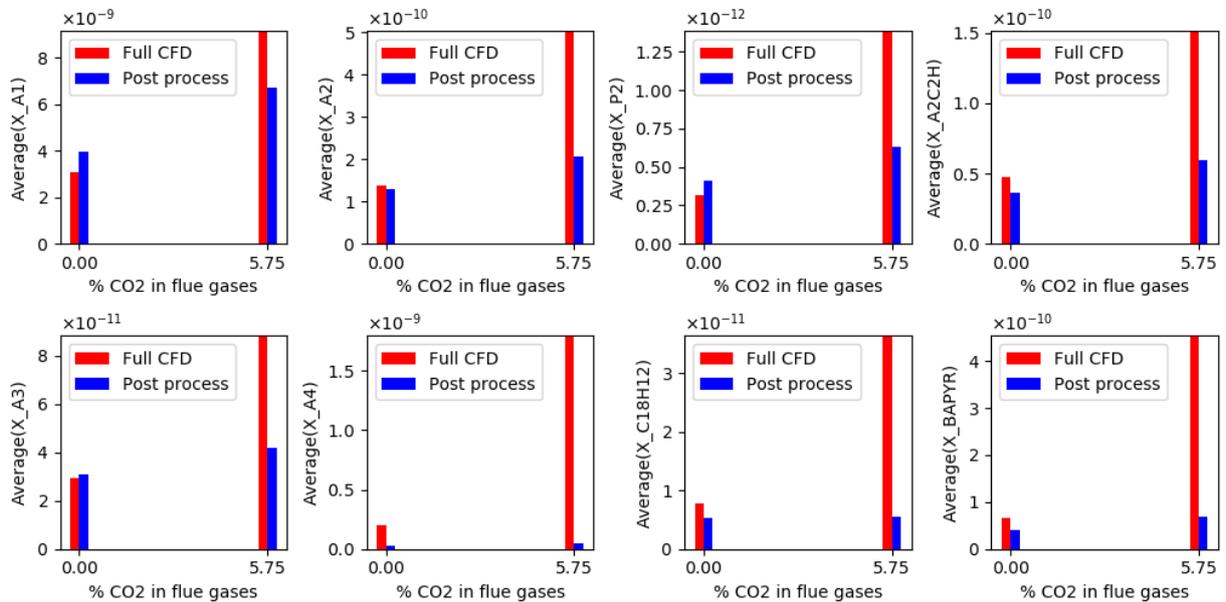


Figure 3: Comparison of the PAH predicted with the Full CFD (simulations with detailed PAH chemistry) and Post process (the proposed approach using  $A = 20$ ) for two scenarios of flue gas recycling (defined based on level on  $CO_2$  in the circulated gas). It should be noted that average mole fraction of specie, plotted on y-axes, is calculated based on Eq.2.

mally stable (than the species treat in this work) - as experiments have reported soot particles and PAH evolving from flames [12]. As seen in Fig.2 there are obvious differences in the spatial distribution of the species, but the post processing approach is able to predict the changes in the PAH with varying levels of flue gas recycling - the increase in PAH with increased levels of flue gas recycling, see Fig.3. Interestingly, the variation in the difference between the predictions of the post processing approach and the detailed/full simulation is different for the two levels of flue gas recycling - indicating the need to adjust  $A$  for a better agreement.

*Impact of fuel injection velocities:* The flow rate by which the fuel is injected into the domain, governs the combustion of the fuel in the control volume as it impacts the the way in which fuel mixes and reacts with the air within the turbulent structures of the flow [9]. So to investigate if the proposed approach can reliably predict this, the simulation using air (with no CO<sub>2</sub> and O<sub>2</sub> around 23.2%) is injected at 0.3 m/s and fuel injected at two different velocities (of 42.2 m/s and 21.1 m/s) is used. It should be noted that both these simulations uses the same turbulence intensity and mixing length scale (defined earlier in the paper) to describe the fuel inlet turbulence conditions. Fig.4 compares the PAH predicted using the CFD simulation using detailed PAH chemistry and the proposed approach (using two values of the tuning parameter ( $A$ )). Both the detailed CFD simulations and the proposed post processing approach predicted a decrease in PAH with the larger fuel flow rate (or inlet velocity). Further investigation is needed to understand the underlying reason for this trend. The overall predictions of the post processing approach is in better agreement with the full CFD simulation when using  $A = 10$  instead of  $A = 20$ .

*On the choice of the tunable parameter ( $A$ ):* The results in Fig.3 and Fig.4 shows that  $A$  needs to be adjusted for a better agreement between the post processing approach and full CFD simulation indicating a universally applicable  $A$  value is improbable. So we hypothesize that  $A$  as an complex function that is a function of the inlet conditions of the fuel and flue gases. The idea is to develop a correlation of  $A$  which can be defined based on knowledge of the inlet boundary conditions of the fuel and flue gases like the inflow velocities, turbulence parameters, composition and temperature which can be represented as  $A = f(U, k, \epsilon, T, X)$ . Although the dependence of  $A$  on the inlet composition and inlet velocities of fuel is illustrated in Fig.3 and Fig.4, the work to develop such a inlet condition based correlation for  $A$  will be undertaken in future works.

*Computational overhead:* The proposed approach (for the case with no CO<sub>2</sub> in the flue gases and fuel injected at 42.2 m/s) took around 35 hours for the CFD simulation using the skeletal or reduced mechanism (which in this work is the GRI Mech 3.0 with 53 species and 325 reactions) and around 0.5 h to run the PSR model to obtain PAH species in each cell (us-

ing PAH mechanism reported by [7]) which is much faster than the CFD simulation employing detailed PAH chemistry (proposed by [7]) which took around 104 h. It should be noted that the reduced mechanism used in this work is the GRI Mech 3.0, but for practical furnace modelling the reaction mechanisms used are comprise of few global reactions describing the reactions involving the major species. So when using such reduced mechanisms, the runtime for the CFD simulation (first step of the proposed approach) will be relatively low. But future investigations should also look into the ability of the proposed approach to predict PAH emission when the CFD simulation employs skeletal mechanisms which has very few global reactions.

## Conclusions

A post processing approach, motivated by the need to obtain 'fast' and reasonably accurate predictions of trends in PAH emission from processes for industrial applications, is proposed in this work. The proposed approach uses a skeletal (or reduced) mechanism to predict the critical characteristics of the process (like temperature, turbulence, and distribution of major species) which is used as input for PSR model (for in each cell in the domain) that uses a detailed PAH chemistry to predict the PAH produced locally. The main drawback of the approach is that it does not account for the transport of PAH within domain which can limit the predictive ability - as PAH formed in a region can evolve (or get oxidized) as it is transported. The tunable parameter  $A$  employed in the definition of the residence time used in the PSR model ( $\tau$ ), see Eq.1, is seen to significantly impact the solution obtained from the proposed approach. From the simulations performed in this work,  $A$  needs to be modified depending on the fuel inlet velocities and composition of flue gases to provide a more accurate estimate of the 8 PAH species monitored. So we have hypothesized  $A$  to be a complex correlation which can be written based on inlet boundary conditions of fuel and flue gases, like  $A = f(U, k, \epsilon, T, X)$ , which is a subject that will be explored in future investigations. Despite the simplifications used to develop the post processing approach, its predictions of the eight monitored PAH species (when using the appropriate  $A$ ) are comparable to the CFD simulation employing detailed PAH chemistry. And more importantly, the proposed approach is able to capture overall trends in the PAH evolution for various levels of flue gas recycling and fuel inlet velocities, and it runs much faster than a CFD simulation that uses detailed PAH reaction mechanism.

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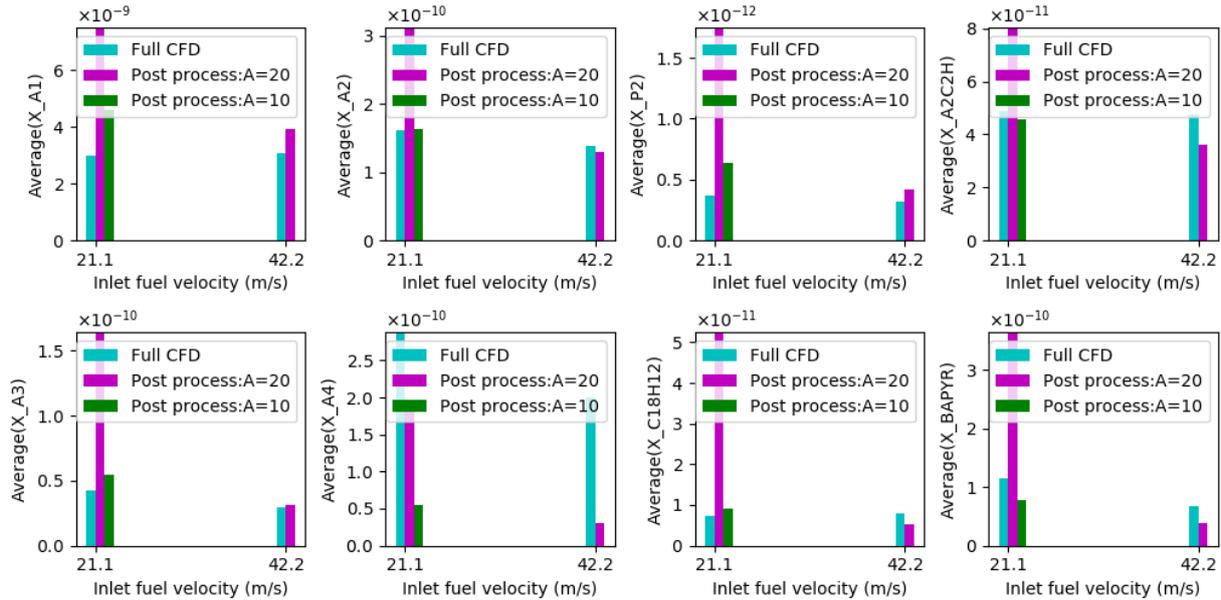


Figure 4: Comparison of the PAH predicted with the Full CFD (simulations with detailed PAH chemistry) and Post process (the proposed approach using  $A = 10$  and  $A = 20$ ) for two fuel inlet velocities for flue gas recycling scenario that contains no  $\text{CO}_2$  in the recirculated gas. It should be noted that average mole fraction of specie, plotted on y-axes, is calculated based on Eq.2.

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