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Study of Polycyclic Aromatic Hydrocarbon (PAH) formation during acetylene pyrolysis in a perfectly stirred jet reactor - Application to the low pressure gas carburizing processes

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Highlights

- Pyrolysis experiments carried out for PAH formation study in gas carburizing conditions.
- CFD simulations performed to characterize CSTR hydrodynamic: RTD calculated
- Comparison of PAH and light hydrocarbon formation between experiments a kinetic model.

1. Introduction

In the course of a study on the chemical risk of generating Polycyclic Aromatic Hydrocarbons (PAHs) during a low-pressure gas carburizing operation, laboratory experiments were conducted in a gas-jet spherical reactor. Low-pressure gas carburizing is a heat treatment process used to harden surface of steel by enriching the metal with carbon atoms coming from pyrolysis of hydrocarbons like acetylene. Unfortunately, at the same time PAHs were formed. These compounds are toxic to humans and hazardous to the environment[1]. Some of them, like benzo[*a*]pyrene ($C_{20}H_{12}$), are known carcinogens (IARC). The aim of the study is to understand the pathways of PAH formation to find operating conditions to improve the occupational hazard prevention of the low-pressure gas carburizing process. Therefore on the one hand CFD simulations were performed to characterize the reactor hydrodynamic to confirm the hypothesis of perfect mixing and the other hand experiments carried out into the perfectly agitated jet reactor to show the influence of the residence time on the generation of PAHs. The detailed kinetic model which was developed earlier allowed to describe PAHs formation in other gas carburizing conditions after being validated by ours experiments.

2. Methods

The reactor was constituted by a sphere (D = 58 mm), into which the gas was injected in four different directions from nozzles (d=300 µm) disposed as shown in Figure 1. This reactor is mainly used for combustion and pyrolysis gas reactions but its hydrodynamic has been studied at room temperature and atmospheric pressure. Therefore, simulations of the CFD type were conducted to study how the hydrodynamic conditions varied as a function of these two parameters. The reactor was modeled using "Meshing" and "Design Modeler" (ANSYS) as the software. The entire reactor was simulated using a complete CFD model (Fluent®): the RNG k-epsilon model.

Experiments of acetylene pyrolysis were carried out in conditions close to low-pressure gas carburizing processes, at 900°C, 8 kPa and using pure acetylene. They were performed in a quartz continuous gas-jet spherical reactor [1]. At the outlet of the reaction zone, light products of pyrolysis ($<C_7$) were analyzed on-line by gas chromatography (TCD and FID detectors). Heaviest products and PAHs were recovered in a cold trap with liquid nitrogen. They were then analyzed off-line by gas chromatography (MS and FID detectors). Among other products, the sixteen EPA-PAHs were observed. Influence of residence time (between 0.5 and 1.75 s) on the amount of PAH was studied.

3. Results and discussion

[1] Sixteen PAH were classified as priority pollutants by the United States Environmental Protection Agency (US EPA): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo[*ghi*]perylene.

The numerical Residence Time Distribution of the gas shows a certain degree of matching with the ideal reactor relationship (Figure 1). This result proves that the behavior of the reactor is close to a continuous stirred-tank reactor (CSTR). However other conditions shall be satisfied to use this reactor [2] like a turbulent flow near the nozzle outlet, a sufficient recycling rate and a jet velocity lower than the sound speed. This work showed the influence of temperature and pressure on its hydrodynamic behavior.

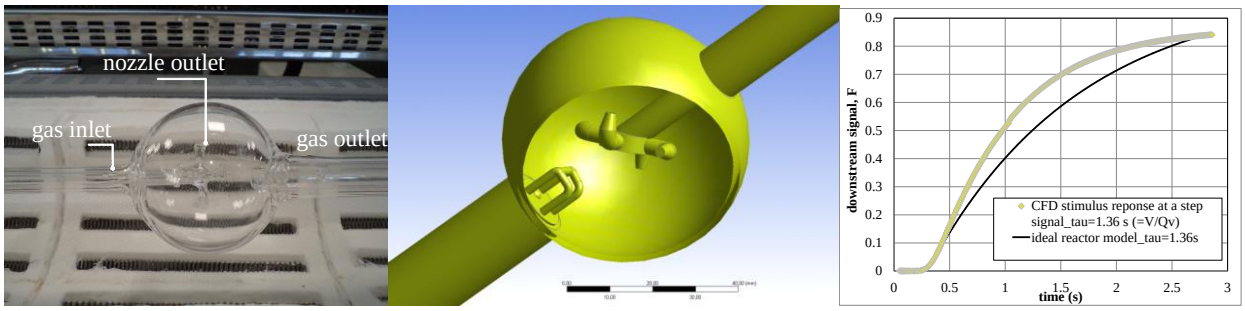

Figure 1: Perfectly Stirred Reactor (Matras & Villermaux, 1973) – Part carried out with Design Modeler software (ANSYS®) – RTD study : the stimulus is a step signal (P=8kPa – T=900°C – τ=1.36s)

Experimental results were compared to those obtained with a detailed kinetic model [3]. This model was developed in order to describe PAH formation during light hydrocarbon pyrolysis in gas carburizing conditions, i.e. at low pressure and high temperature. It was validated by experimental data from the literature [4]. The good agreement between model predictions and experimental data from this study was achieved for light products (Figure 2). For heaviest products and PAHs the difference between concentration values can depend on the preparation of the sample to be analyzed off-line with GC MS or because of the gap to ideal hydrodynamic conditions of reactor experimentally used.

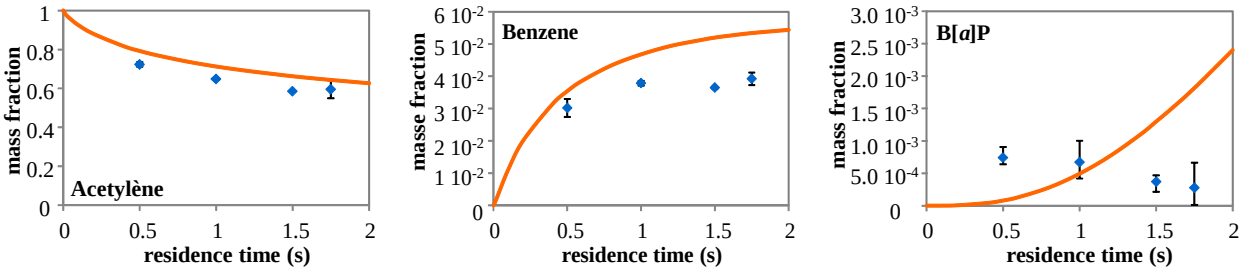

Figure 2: Mass fraction profiles of acetylene, benzene en B(a)P during pure acetylene pyrolysis (at 900°C and 8 kPa) - points refer to experiments and solid lines to simulations [2]

4. Conclusions

The agreement between model and experimental data is obtained. But some differences are observed. They depend on different parameters like the preparation of samples, analysis carried out or the gap to ideal hydrodynamic conditions of reactors experimentally used. But the model has to be improved too: some reaction pathways are still missing or wrongly evaluated. However the orders of magnitude obtained for PAHs are broadly correct. To decrease the occupational risk in this process further experiments are planned with an iron part into the reactor to show the influence of surface reactions on the generation of PAHs.

References

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Keywords

pyrolysis; acetylene; CSTR; PAH