A MODELING STUDY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) FORMED DURING THE PYROLYSIS OF HYDROCARBONS – APPLICATION TO LOW-PRESSURE GAS CARBURIZING PROCESSES

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Abstract

Hydrocarbon pyrolysis in low-pressure gas carburizing conditions drives to gas phase reactions which lead to the production of Polycyclic Aromatic Hydrocarbons (PAHs). These PAHs are afterwards responsible for soot formation. A detailed kinetic model was implemented to predict the formation of sixteen PAHs considered as priority pollutants by the Environmental Protection Agency in the United States (US EPA). Some of them, such as benzo(a)pyrene, are carcinogens (cf. International Agency for Research on Cancer). The model was validated using experimental data from the literature. It was used to compare the pyrolysis of different reactants. Flux analyses were realized in order to determine the main reaction pathways leading to PAHs.

Keywords

PAHs, Low-pressure gas carburizing, Detailed kinetic modeling.

Introduction

Low-pressure gas carburizing is a heat treatment process used to harden surface of steel by enriching the metal with carbon atoms coming from the pyrolysis of hydrocarbons. Unfortunately, at the same time, a wide variety of molecules and radicals are also formed in the gas phase. They react together, leading to the formation of Polycyclic Aromatic Hydrocarbons (PAHs), which are soot precursors. Released into the atmosphere or adsorbed on soot, PAHs are toxic to humans and hazardous to the environment. Sixteen have been classified as priority pollutants by the Environmental Protection Agency in the United States (EPA-PAHs). Some of them, such as benzo(a)pyrene, are known carcinogens (cf. International Agency for Research on Cancer). Understanding PAH formation is important to make safer the low-pressure carburizing processes, as other processes which can produce PAHs by pyrolysis, such as atmosphere carburizing and carbonitriding, or by combustion.

A detailed kinetic model was developed in order to describe hydrocarbon pyrolysis in gas carburizing conditions, i.e. at low pressure and at temperature ranging between 900 and 1000°C. It focuses on the prediction of the formation of the sixteen EPA-PAHs: 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-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene.

The closest work realized on this subject is that of Noringa et al. It includes experimental data (Norinaga et al., 2006) and kinetic modeling (Norinaga et al., 2009). They studied acetylene, ethylene and propylene pyrolysis in a plug-flow reactor at 900°C under low pressure. They measured thirteen EPA-PAHs and the model details PAH formation up to seven aromatic rings (coronene). Their experimental data and others (Sánchez et al., 2012; Ziegler et al., 2005) were used to validate our model.

Modeling

A model of ethylbenzene and anisole combustion (Nowakowska et al., 2014) containing the reactions of pyrolysis and oxidation for hydrocarbons including up to six carbon atoms and the formation of six EPA-PAHs was used as a starting point. It was completed by nine EPA-PAHs with their formation reactions coming from Norinaga et al.'s model. The sixteenth EPA-PAH is dibenzo(a,h)anthracene, for which no model of formation has been proposed in the literature. Reactions were written based on those for benzo(a)anthracene. The added pathways take into account the formation of this species from phenanthrene, benzo(a)anthracene and by recombination of species with a five-membered ring.

The model was then improved by the addition of some new reaction pathways for the formation of cyclopentadiene, benzene, styrene, indene and many PAHs. Kinetic constants were updated to take into account pathways, which could be negligible in the initial oxidation mechanism. The final model contains 364 species and 1245 reactions, most of them reversible.

Results and Discussions

Figure 1 shows the concordance of the model with experimental points obtained by Norinaga et al. (2006) for acetylene pyrolysis at 900°C and low pressure in a plug-flow reactor. The inlet stream is composed of 98% acetylene, 0.2% methane and 1.8% acetone. Figure 1 presents the evolution of acetylene, vinylacetylene, benzene, naphthalene, phenanthrene and benzo(a)pyrene as

a function of the residence time. The variations of these species are fairly well described by the model. For comparison, simulations in the same conditions with the model of Norinaga et al. (2009) are also represented.
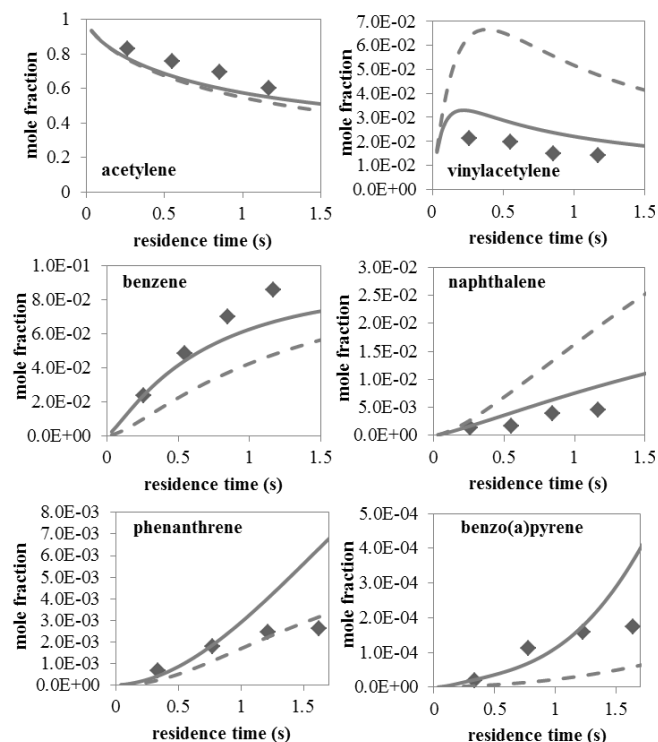

Figure 1. Mole fraction profiles during acetylene pyrolysis at 900°C and 8 kPa (for acetylene, vinylacetylene, benzene and naphthalene) or 15 kPa (for phenanthrene and anthracene)
Points refer to experiments, solid lines to modeling and dashed lines to Norinaga et al.'s model

The proper description of these species by the model is important since they are key species in the pyrolysis of acetylene and in the formation of PAHs. Flux analysis shows that vinylacetylene is the main primary product and is an important intermediate in benzene formation. Benzene is the first aromatic ring. It is at the basis of the formation of the majority of PAHs and it plays an important role in PAH growth, as acetylene. Naphthalene and phenanthrene mainly come from benzene and lead to many heavier PAHs. For example, the main reaction pathway of benzo(a)pyrene formation is the Hydrogen Abstraction C_2H_2 Addition (HACA) mechanism from benzo(a)anthracene which mainly comes from anthracene by phenylacetylene addition.

The model was used to compare different reactants: acetylene, ethylene and propane. Figure 2 presents the mole fractions of the sixteen EPA-PAHs brought back to the fraction of consumed reactant (selectivities) for these three reactants at 900°C, 15 kPa and a residence time of 1 s. In these conditions, acetylene produces more PAHs than ethylene and propane. It may be because of the importance of the HACA mechanism in the growth of PAHs.
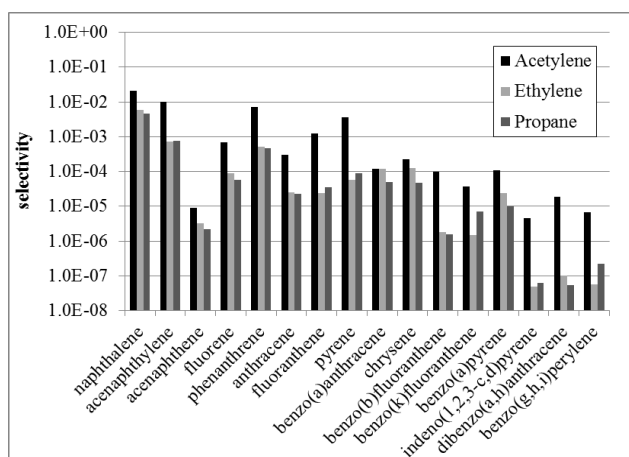

Figure 2. Comparison of EPA-PAH formation during acetylene, ethylene and propane pyrolysis at 900°C, 15 kPa and residence time of 1 s

Conclusions

A model was developed to describe the formation of PAHs during different hydrocarbon pyrolysis. It is mainly focused on the formation of the sixteen EPA-PAHs at low pressure. The aim is to use the model to evaluate the potential of toxicity of a process. The model was validated thanks to various experimental data from the literature. It reproduces reasonably well the orders of magnitude for PAHs. The model was used to realize flux analysis in order to determine the main reaction pathways, and to make comparisons between reactants and between different operating conditions (variations of pressure, temperature, etc.). Experiments will be performed, allowing a better validation of the model.

References

Norinaga, K., Deutschmann, O., Hüttinger, K. J. (2006), Analysis of gas phase compounds in chemical vapor deposition of carbon from light hydrocarbons. *Carbon*, *44*, 1790–1800.

Norinaga, K., Deutschmann, O., Saegusa, N., Hayashi, J. (2009), Analysis of pyrolysis products from light hydrocarbons and kinetic modeling for growth of polycyclic aromatic hydrocarbons with detailed chemistry. *J. Anal. Appl. Pyrol.*, *86*, 148–160.

Nowakowska, M., Herbinet, O., Dufour, A., Glaude, P.-A. (2014), Detailed kinetic study of anisole pyrolysis and oxidation to understand tar formation during biomass combustion and gasification. *Combust. Flame*, *161*, 1474–1488.

Sánchez, N. E., Callejas, A., Millera, Á., Bilbao, R., Alzueta, M. U. (2012), Polycyclic Aromatic Hydrocarbon (PAH) and Soot Formation in the Pyrolysis of Acetylene and Ethylene: Effect of the Reaction Temperature. *Energ. Fuels*, *26*, 4823–4829.

Ziegler, I., Fournet, R., Marquaire, P.-M. (2005), Pyrolysis of propane for CVI of pyrocarbon: Part II. Experimental and modeling study of polyaromatic species. *J. Anal. Appl. Pyrol.*, *73*, 231–247.