Kinetic modeling for PAH formation in a counterflow diffusion flame of isobutane

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1 Abstract

In the purpose of understanding the complex chemistry of aromatic hydrocarbon formation in diffusion flames of isobutane oxidation, mechanism that consists of 300 species and 11790 reactions is employed for verifying experimental measurements. The kinetic mechanism is incorporated into a 1-D axisymmetric laminar finite-rate model of a counterflow flame to compute the species profiles. Furthermore, the reaction pathway diagram produced by rate of production analysis illustrates the correlation between the decomposition of isobutane and formation of the target species.

Keywords: isobutane, counterflow diffusion flame, paromatic hydrocarbon, chemical kinetic modeling

2 Introduction

Isobutane (iC_4H_{10}) is an isomer of butane and flammable gas. Although it is not ideal fuel on its own, this species plays a role in the oxidation of large hydrocarbon fuels and is used in liquified natural gas (LNG) [1]. The detailed kinetic mechanism of isobutane combustion contains dozens of species and hundreds of reactions. When a kinetic mechanism is applied to a reaction source term of species transport equations, the computational solutions can be used to describe reactive flows and species distribution in multidimensional reactors. This kind of numerical modeling permits designers and analysts to evaluate emissions and performance of fuels in reactors or combustors.

Dagaut et al.[2] reported improved kinetic schemes (979 reversible reactions and 130 species) that are used to model the reduction of nitric oxide (NO) by isobutane in a jet-stirred reactor condition. That consistency between the experimental and modeling data is obtained. Wilk et al.[3, 4] investigated the effect of molecular structure effect on the knock of engine combustion using n-butane and isobutane. The authors also employed detailed chemical kinetic mechanism that consists of 138 and 833 species to be used with interpret the experimental results. The authors identified that chain branching reactions in isobutane oxidation depend on the H atom extraction reactions involving HO₂ and CH₃O₂ radicals, which occur at a higher temperature than the RO₂ isomerization reaction. Healy et al.[1] conducted compressor and shock

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tube ignition experiments for an equivalent fuel/air isobutane mixture. The experimental results were verified with a detailed chemical kinetic model consisting of 1328 reactions and 230 species. In recent years, kinetic mechanisms of hydrocarbon fuel oxidation and pyrolysis have extensively included chemical kinetics of formation of polycyclic aromatic hydrocarbons (PAHs).

PAHs are the precursors in the soot formation process in combustion [5-8]. PAH have gained attention recently since the United States Environmental Protection Agency (USEPA) [9] had classified 16 of the PAH compounds as the carcinogenic and mutagenic to human health. The group of CRECK modeling has published a mechanism [10-13] that describes formation of light-weight PAHs in oxidation of several hydrocarbon fuels including n-butane, isobutane, n-decane and n-dodecane.

Motivated by the experimental study of Singh et al.[14], we attempt to utilize the kinetic mechanism [10-13] to predict the formation of aromatic species in a counterflow diffusion flame of isobutane. This study simulation the four target species pyrene, benzene, acetylene and propargyl, the simulation data is quite consistent with the experiment to verify the ability of this mechanism and to show the rate of production of formation of aromatic species.

3 Methodology

By means of linking a plug-in finite-rate chemistry CHEMKIN-CFD into FLUENT package[15, 16], the reaction rates and mole fractions of 300 species profiles along the 1-D axial direction between two ports are numerically solved. 50,000 grid number is used while the convergence criterion for species equations is set to 10^-6. Figure 1 shows the boundary conditions of the 1-D counterflow flame of isobutane based on the experimental study of Singh et al. [14]. The 1-D species equations and the reaction rates for a species are listed below:

Energy equation:

$$\rho v_{x} \frac{dT}{dx} - \frac{1}{c_{p}} \frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) + \frac{\rho}{c_{p}} \sum_{i} c_{p_{i}} Y_{i} V_{i} \frac{dT}{dx} + \frac{1}{c_{p}} \sum_{i} h_{i} \dot{\omega}_{i}$$
(1)

where ρ is mixture density; λ is thermal conductivity of the gas mixture; T is temperature; Y_i is mass fraction of the species i; V_i is diffusion velocity of the species i; c_p is constant-pressure specific heat capacity of the gas mixture; h_i is specific enthalpy of the species i; $\dot{\omega}_i$ is molar rate of production of the species; x is the spatial coordinate along the principal and radial flow direction.

Species conservation equation:

$$\rho v_x \frac{dY_i}{dx} + \frac{d}{dx} (\rho Y_i V_i) - \dot{\omega}_i W_i = 0 \qquad i = 1, \dots, N$$
(2)

where W_i is molecular weight of the species i; v_x is axial velocity.





4 Results and discussion

4.1. Predictions of mole fractions

As shown in Figure 2, while fuel is primarily consumed, the flame temperature at around 800 K, which is relatively low. This area near 0.3 cm from the fuel port is the place where most of the light-weight PAHs reach their peaks. At the location where the oxygen is completely destroyed and the flame temperature reaches its maximum, the PAHs are seen to be composed or oxidized. Acetylene and propargyl radicals are the key precursors of PAHs and their profiles are highly correlated with the formation of PAHs. Specifically, the propargyl radical is formed and destroyed within a relatively short distance at 4 cm from the fuel port. According to the profile of the benzene formation, it is not highly dependent on the formation of PAHs.



Figure 2. Mole fraction profiles of iC₄H₁₀, O₂, temperature, acetylene, propargyl and four aromatics in the counterflow diffusion flame of isobutane.

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Table 1. Comparison between e	xperiments and si	mulations for r	nole fraction o	f acetylene, j	propargyl, ł	penzene and
pyrene of Singh and Sung [14]						

Name	Experiment	Present data
acetylene (C_2H_2)	0.04753	0.04743819
propargyl (C ₃ H ₃)	0.00135	0.001334262
benzene (C_6H_6)	0.00452	0.004584357
pyrene ($C_{16}H_{10}$)	0.00017	0.00017504

4.2. Reaction pathways of the isobutane

Figure 3 the reaction pathways forming benzene (A1), naphthalene (A2) and phenanthrene (A3) from the decomposition of isobutane at maximum gradient of fuel consumption where it is located at 0.28 cm from the fuel port and 38.95% of isobutane is consumed. The corresponding reaction temperature is 842 K. At this condition, isobutane is dissociated to form (iC₄H₉T and iC₄H₉P) via H atom abstraction reactions by several radicals, including Methyl (CH₃). The fuel radical, iC₄H₉P, further undergo β -scission reactions to form propene (C₃H₆) that further lead to a propenyl radical CH₂CHCH₂ via H-atom abstraction reactions. The propenyl radical further cyclizes with iC₄H₇ to form benzene (A1) that leads to pyrene (A4) (see Fig 3a). Naphthalene (A2) seen in Fig 3b is formed by cyclization of benzene and addition of H atom to a A2 radical. The A2 radical is seen to be formed by the cyclization of acetylene and C₆H₄C₂H, where the acetylene is formed by the β -scission reactions of another fuel radical, iC₄H₉T. Regarding phenanthrene (A3), it is primarily formed by 1-ethynylnaphthalene (C₁₂H₇) via three cyclization reactions with different small hydrocarbons including acetylene, propargyl radicals and vinyl radicals.





Figure 3. Rate of production (ROP) analysis from isobutane to aromatic hydrocarbon formation (PAH): (a) pyrene,
(b) naphthalene and (c) phenanthrene. The pathways are captured at x = 0.282606 cm where 38.95% of isobutane, which corresponds to the maximum fuel consumption gradient. The percentage shown in the image indicates the degree of a reactant consumed in a reaction that mainly produces the products.

5 Conclusions

This study predicts the formation of unsaturated hydrocarbons which were previously measured by mass spectroscopy in a counter-flow flame. The mechanism consisting of 300 and 11790 reactions shows good agreement with the measured C_6H_6 and $C_{16}H_{10}$. The 1-D profiles of PAH mole fractions indicate the locations where the peaks of PAHs are formed. With the help of rate-of-production analysis, the pathways from the decomposition of isobutane to the formation of naphthalene, phenanthrene and pyrene are separately identified.

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