



Full Length Article

Numerical analysis of effects of iron pentacarbonyl as fuel additive for reducing NO and soot precursors from methane/air diffusion flame

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ABSTRACT

The present work focuses on improving our understanding of interactions of as-produced iron species, from thermal decomposition of iron pentacarbonyl during combustion, and major gaseous emissions from a methane/air counter-flow laminar flame. Numerical simulation explores underlying issues which are, otherwise, difficult to analyze by experimental means. Sensitivity analysis is carried out to investigate the influence of input parameters such as iron pentacarbonyl concentration and fuel fraction on emissions. Results demonstrate a proportional decline in most C_2H_x , commonly accepted soot precursors, and NO species with increasing the concentration of $Fe(CO)_5$. The decline in NO and C_2H_2 emissions is found to be more promising with increasing the fuel fraction. Beyond a certain threshold of the fuel fraction, however, the radical pool in the flame sufficiently overwhelms the additionally radical scavenging of iron species and consequently the emission reduction declines. In addition, a high flame temperature results in activation of new iron pathways which lead to a greater emission reduction.

1. Introduction

Crude oil derivatives and natural gas are currently the most utilized primary sources of energy, contributing to around 60% of the global energy consumption [1], and will continue to dominate the primary energy mix for the next 25 years [2]. Consequently greater efforts, directed towards restricting the carbon intensity as well as emissions of hydrocarbons, are required. While catalytic combustion had been found effective in achieving cleaner and more efficient combustion, it continues to remain cost-prohibitive due to expensive metal catalysts involved [3]. Iron presents itself as an abundantly available, environmentally benign and highly functional catalytic material capable of exhibiting different oxidation states. Iron pentacarbonyl ($Fe(CO)_5$) is a metal carbonyl compound having a high vapor pressure which makes it attractive to be used as a fuel-borne iron precursor. The high temperature encountered in the flame causes the decomposition of $Fe(CO)_5$ into constituent species and particles which catalyze the combustion process resulting in reduced emissions. Two key outcomes are expected out of iron assisted combustion: first, combustion efficiency may be changed due to change of the fuel/air ratio and mixing of different flow patterns (axial and radial flow) and secondly, catalytic combustion may be altered significantly due to the catalytic nature of the gas phase iron, iron oxide particles and iron clusters.

In the literature, most research has focused on the inhibition effects of $Fe(CO)_5$ on flame speed, the in-flame nanoparticle formation process and experimental soot reduction using fuel doped iron precursors in engines. However, challenges still exist in understanding the formation mechanism of iron oxide species in their condensed phase counterparts and their roles in emission reduction at the fundamental level. While the flame inhibiting characteristics of iron pentacarbonyl doping in the fuel have been documented for premixed H_2/O_2 flames [4], a comprehensive understanding of their interdependency along with the impact on emissions is lacking in the case of hydrocarbon fuels based diffusion flames. The knowledge of the interplay between the formation of iron species and the methane combustion mechanism will help develop better correlation between the operating parameters for combustors and optimal outputs in terms of fuel efficiency and emissions.

Rumminger et al. [5] developed a multi staged reaction mechanism describing: i) decomposition of $Fe(CO)_5$; ii) iron species formation and; iii) homogeneous reactions of the iron species scavenging radicals. This approach did not, however, consider possible polymerization of iron atoms to form clusters. Density Functional Theory (DFT) was employed by Wen et al. [6] for the estimation of kinetic parameters of a comprehensive iron pentacarbonyl decomposition mechanism which included iron carbonyls and iron cluster complexes. Kluge et al. [7] and Poliak et al. [8] have credited these iron clusters to be the precursors of

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Nomenclature

s	strain rate
$\rho_{fuel/ox}$	density of fuel/oxidizer stream
ρ	density
L	distance between the two burners
$v_{x/r}$	velocity in axial/ radial directions
$v_{fuel/ox}$	velocity of fuel/oxidizer stream
p	pressure
μ	viscosity
Y_i	mole fraction of i th species
$Y_{f/ox}$	mass fraction of fuel/oxidizer in the respective stream

x	spatial distance
r	radial distance
a_i	absorption coefficient of i th species in flame
c_p	specific heat at constant pressure
T	temperature
σ	Stefan-Boltzmann coefficient
$\dot{m}_i'''$	net mass production rate of i th species
$h_{f,i}^0$	formation enthalpy of i th species
T_b	far-field background temperature
D	diffusion coefficient
Z_f	mixture fraction
ν	stoichiometric mass ratio of oxygen to fuel

experimentally verified ‘prompt nanoparticles’ being formed close to the burner surface in a premixed laminar flat-flame. Wloka et al. [9] developed another sub-mechanism addressing the formation of iron oxide from iron atoms based on experimentally characterized concentrations of iron atoms and iron oxide particles while the formation of gas phase Fe_2O_3 was investigated both numerically and experimentally in a premixed H_2/O_2 mixture. Reinelt et al. [10] examined the impediment of flame propagation rates in premixed flames under the influence of lower concentrations of $Fe(CO)_5$, which was traced to the recombination of H, O and OH radicals. Linteris et al. [4] probed the outcome of $Fe(CO)_5$ addition to a flame and found that the inhibition effect only comes into picture at higher concentrations ($> 150 \mu L/L$) of iron compounds while, at lower concentrations as also illustrated by Park et al. [11], $Fe(CO)_5$ promotes ignition through the enhancement of the oxidizing radical pool (H, O, OH).

Realizing the potency of iron pentacarbonyl in altering sooting characteristics, Kim et al. [12] inquired into the soot emissions from a $Fe(CO)_5$ loaded isooctane flame from a combustor under realistic working conditions. Their conclusions appropriated the process of catalytic oxidation of soot by carbon coated iron particles, as proposed by Zhang et al. [13] and Rumminger et al. [14], to justify their findings. This mechanism elucidates the effect of $Fe(CO)_5$ addition on the particle inception and soot burnout regimes. Closer to the flame, the soot inception and growth process was found to be invigorated under the influence of $Fe(CO)_5$ due to enhanced surface area of iron particles. However, the soot concentration plummeted rapidly at locations further downstream of the flame as a result of augmented soot oxidation caused by the available O and OH species on iron catalyst surface [12]. This was also corroborated through the work of Nash et al. [15], which reported a decline of around 32% by weight in soot emissions from ferrocene loaded 2 kW diesel engine operation. Similar decline of around 25–42% was reported in the particulate matter concentration in the work of Skillas et al. [16] under iron precursor loaded diesel engine operation. Reichert et al. [17] and Fennell et al. [18] attributed the emission reduction characteristics to enhanced conversion of NO_x and soot to N_2 and CO_2 respectively, over Fe_2O_3 under excess O_2 conditions. The increased surface mobility within Fe_2O_3 results in an enhanced dissociative adsorption of NO at the soot-catalyst interface. Consequently, the dissociated atomic oxygen is readily available for the oxidation of soot while the atomic nitrogen atoms recombine and diffuse out. Song et al. [19] focused on fuel-borne-precursor (4:1 iron to strontium ratio) assisted particulate matter oxidation under varying engine loading conditions (from 25% to 75% of peak load) and identified the multiple-oxidation-state retaining capability of in-flame metal oxides to be a significant driving force for emission reduction. Thus, while the effectiveness of fuel-borne iron precursors in reducing emissions was demonstrated, the emission reduction mechanism warrants a further investigation.

In a previous work by the authors [20], the potency of iron pentacarbonyl in achieving C_2 and NO species reduction was established through an experimental analysis of the emissions and flame structure

of a methane flame using a counter-flow burner. Methane was selected due to its high NO formation and low sooting tendency which lowers the possibilities of iron oxide particle being covered with soot as well as because of its increasing use as a commercial fuel in various applications. Due to the unique geometry of the counter-flow burners and the location of the flat flame being close to the mid-plane (lying at an axial distance of 10 mm), it was observed that while the formation of particles, responsible for heterogeneous catalysis, was mainly restricted to the flame region, the gas phase iron species was expected to occur much upstream based on theoretical study. As a result, it remains important to assess the impact of both gas phase and heterogeneous reactions separately. The limitations of that work include its inability to distinguish the emission reduction either due to gas phase reactions or due to heterogeneous catalytic reactions between iron species and hydrocarbon combustion intermediates and products. While the species mole fraction was measured using Gas Chromatography and Fourier Transform Infra-Red Spectroscopy, experimental analysis was limited in terms of the absence of quantitative diagnostics for the iron species measurement.

The present study focuses on bridging the research gap through the analysis of formation processes of soot precursors, NO, iron, iron oxide, and iron hydroxide species, to develop a better understanding of their mutual dependency in a $Fe(CO)_5$ laden counter-flow methane diffusion flame. The numerical model utilizes the available gas phase mechanisms for methane combustion, iron pentacarbonyl decomposition, iron clusterization and iron species formation. The heterogeneous reactions between iron and absorbed hydrocarbons will be addressed in the future.

2. Counter-flow laminar flame geometry

A stable, planar axisymmetric methane flame front is desired as it provides ease in analyzing the catalytic combustion process through sampling of gases along the vertical axis [21]. Existing literature has underlined the appropriateness of counter-flow burner arrangement for achieving such flame to analyze high temperature oxidation kinetics at atmospheric pressure [22]. The qualitative and quantitative analysis of the consumption or evolution of various intermediate and minor products along the axial length, under both catalytic and non-catalytic conditions, provides an insight towards the impact of the fuel additive on the combustion process. This arrangement also provides flexibility to vary the injection orientation of reactants with respect to each other. Parameters like global flow strain rate (s) and mixture fraction (z_f) are normally used to characterize counter-flow flames. The strain rate ‘ s ’ is defined as the inverse of characteristic flow time and is mathematically defined as spatial gradient of the normal component of the flow velocity [23] as shown in the following equation

$$s = 2 \frac{|v_{fuel}|}{L} \left(1 + \frac{|v_{ox}| \sqrt{\rho_{ox}}}{|v_{fuel}| \sqrt{\rho_{fuel}}} \right) \quad (1)$$

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