

NO formation in premixed H₂/CH₄/CO/C₆H₆-air flat flames at low pressure: an experimental and numerical study

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Nitrogen oxides (NO_x and N₂O) are harmful atmospheric pollutants, mostly emitted by high-temperature combustion processes [1]. Extensive research activity on NO_x control is being driven by increasingly stricter emission limits and the need of fuel flexible combustion systems. In this context, Coke Oven Gas (COG), a valuable by-product of coal carbonization, remains an attractive energy source [2,3]. After being cleaned from tar residues and other impurities; COG mostly contains H₂, CH₄, CO and small percentages of aromatic compounds, of which benzene is the most abundant one [2,4]. The proper exploitation of COG in combustion processes requires a detailed kinetic characterization, to assess both the combustion efficiency and pollutants emissions. This work aims to shed light on the effect of benzene on NO_x formation in low pressure premixed H₂/CH₄/CO-air flames doped with benzene (0 to 1% in the fuel), as COG surrogates. A joint experimental and numerical study was performed at three different equivalence ratios (0.8, 1 and 1.2). The investigated flames, listed in Tab.1, were stabilized on a movable Spalding-Botha burner, with a diameter of 8 cm, at fixed dilution ratio $D=O_2/(O_2+N_2)=0.21$ and constant flow rate of the fresh mixture, $Q=13\text{ nL/min}$. Species detection was performed by gas chromatography through PoraPLOT Q and Molsieve 5 Å capillary columns while NO was measured by chemiluminescence. The kinetic modeling was carried out by using the CRECK kinetic framework [5].

Table 1: Investigated premixed flames compositions – $p=7.5$ kPa, dilution ratio $D=O_2/(O_2+N_2)=0.21$, $Q_{\text{inlet}}=13$ nL/min.

Flame	H ₂ % vol.	CH ₄ % vol.	CO% vol.	O ₂ % vol.	N ₂ % vol.	C ₆ H ₆ % vol.	Eq. ratio, ϕ
L1	11.01	4.06	0.96	17.63	66.34	-	0.8
L2	10.86	4.01	0.95	17.67	66.49	0.03	
L3	10.46	3.86	0.91	17.78	66.89	0.11	
L4	10.17	3.75	0.89	17.86	67.17	0.17	
S1	13.23	4.88	1.15	16.95	63.78	-	1
S2	13.05	4.82	1.14	17.00	63.96	0.04	
S3	12.59	4.64	1.10	17.12	64.42	0.13	
S4	12.25	4.52	1.07	17.21	64.75	0.20	
R1	15.29	5.64	1.33	16.33	61.42	-	1.2
R2	15.09	5.57	1.31	16.38	61.61	0.04	
R3	14.57	5.37	1.27	16.51	62.12	0.15	
R4	14.19	5.23	1.24	16.61	62.50	0.23	

NO measurements showed that it is mainly produced at the flame front and that its concentration increases progressively with the amount of benzene (Figure 1.1).

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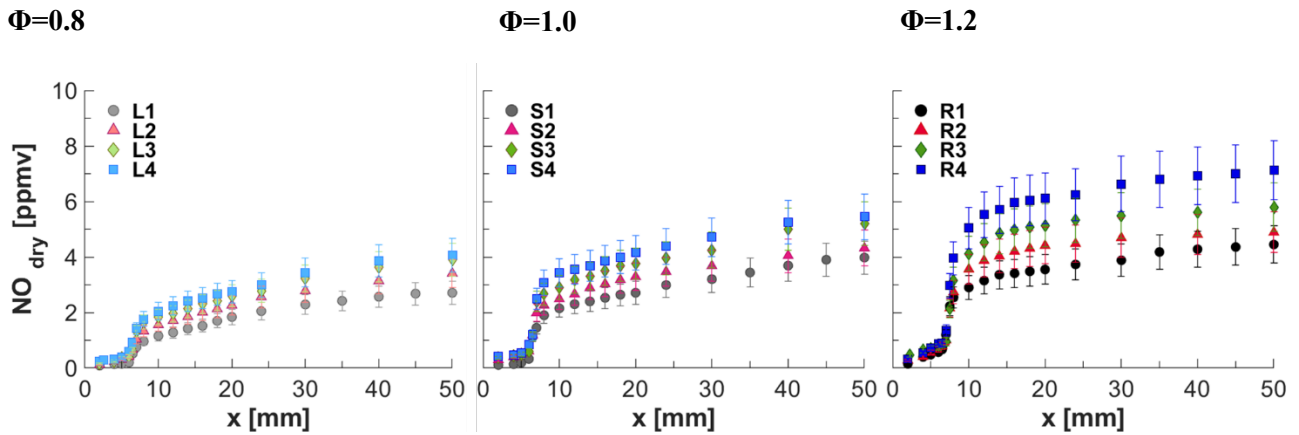


Figure Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.1.1: Experimental NO mole fraction profiles measured in the investigated flames the equivalence ratios: $\Phi=0.8$, $\Phi=1.0$ and $\Phi=1.2$.

Although the increase of NO with the addition of benzene is well reproduced in the simulations, the comparison between the simulated and the measured NO concentration profiles, reported in Figure 1.2, shows that while at the flame front the experimental trend is reasonably reproduced at all the equivalence ratios, and in the post-flame region of the rich flames, significant NO overestimations are observed in the post-flame of the stoichiometric and lean flames. This is due to the high sensitivity of the thermal NO mechanism, which is the main pathway contributing to NO formation at $\Phi=0.8$ and $\Phi=1.0$ with respect to $\Phi=1.2$, given both the higher flame temperatures ($T_{\max}(\Phi=1.2)$: 1819-1867 K, $T_{\max}(\Phi=0.8)$: 1925-1949 K, $T_{\max}(\Phi=1)$: 1929-1957 K) and the higher O_2 and N_2 availability.

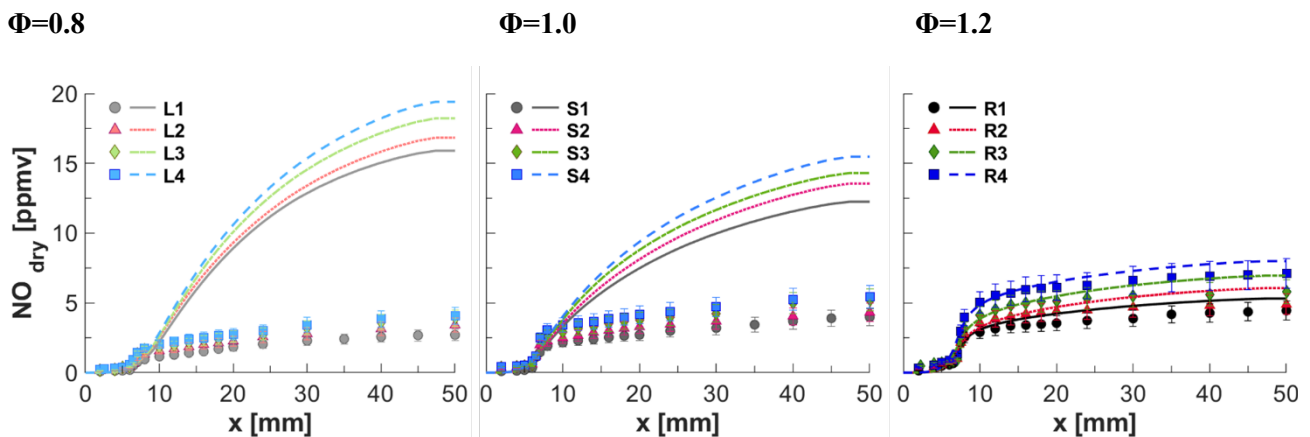


Figure Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.2.2: - Experimental NO mole fractions vs simulations with the CRECK kinetic model at the equivalence ratios: $\Phi=0.8$, $\Phi=1.0$ and $\Phi=1.2$. Symbols: experiment, lines: simulations.

The combined numerical and experimental study allowed to identify the main NO formation pathways and the interactions between benzene oxidation and NO formation at different equivalence ratios in $H_2/CH_4/CO$ -air flames. C_6H_6 was found to increase NO, mainly through the prompt NO route due to additional reaction paths coming from different intermediates of C_6H_6 oxidation, which contribute to higher peaks of ethylene (C_2H_4), acetylene (C_2H_2), ketene (CH_2CO), vinoxy radical (CH_2CHO), vinyl radical (C_2H_3), ethynyl radical (C_2H) and ultimately HCCO. Therefore, the interactions between benzene oxidation and prompt NO chemistry, ultimately involve the ketylenyl radical (HCCO), and acetylene (C_2H_2). This leads to an increase of singlet CH_2 ($CH_2(S)$) and CH_2 with consequent modification of CH profile, via $HCCO \rightarrow CH_2(S) \rightarrow CH_2 \rightarrow CH$ and $C_2H_2 \rightarrow CH_2 \rightarrow CH$. As a result, the higher available CH radical enhances the prompt NO route through its key reaction: $CH+N_2=H+NCN$. In presence of benzene NO formation increased also because of the thermal NO route increase.