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Investigation of NO formation in premixed adiabatic laminar flames of H_2/CO syngas and air by saturated laser-induced fluorescence and kinetic modeling

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ABSTRACT

A series of experiments were performed to investigate the relationship between syngas composition ($H_2/CO/CO_2/N_2/O_2$) and NO formation. Laser-saturated fluorescence measurements of NO in a premixed syngas flat flame from a heat flux burner were recorded for various fuel compositions, dilution ratios and equivalence ratios. Quantitative measurements were compared with the predictions from CHEMKIN software using four different chemical mechanisms, i.e., GRI mech 3.0, Chemical Reaction Engineering and Chemical Kinetics 1407, GDF-Kin 3.0, and the Mendiara and Glarborg mechanism; each mechanism included reaction subsets for NO*x* formation. These models were validated against a CH_4 flame; the GDF-Kin 3.0 mechanism produced the best agreement with measurements. NO measurements for CO/H_2 syngas fuel with 50% CO_2 dilution at various equivalence ratios found the maximum NO production near stoichiometry. The majority of NO produced for these conditions is predicted to come from the combination of the NNH and N_2O pathways. Investigation of NO production during combustion of different CO/H_2 ratio syngas diluted with 60% N_2 showed that increasing the H_2 fraction decreased the total NO concentration. However, normalizing the NO production rate by the fuel mass consumption rate showed H_2 produces more NO per gram of fuel consumed. Predictions of temperature and NO rate of production along the flame axis showed that the syngas with high H_2 content had a flame front closer to the burner exit and NO production rate greater than the high CO case. Dilution of CO/H_2 syngas fuel with N_2 and CO_2 showed that CO_2 has a stronger reduction in NO emission than N_2. GDF-Kin 3.0 predicted that dilution with CO_2 caused a greater reduction in flame temperature than the same volume of N_2. Predicted NO rate of production and reaction sensitivity analysis predicted that the Zel'dovich pathway was dominant for undiluted syngas. However, as the flame temperature reduced, the Zel'dovich pathway was inhibited to a greater extent than the N_2O and NNH pathways so that, at high dilution, NO production was driven by the N_2O and NNH pathways.

1. Introduction

The economic development seen in transitional countries (e.g., China and India) has largely been powered by inefficient and/or environmentally damaging energy production methods. Concerns over public health and environmental conservation have become increasingly prominent, which has stimulated research into alternative means of energy production. Synthetic gaseous fuel (syngas) is an alternative energy source generated by gasification or pyrolysis of solid fuels like biomass and coal [1]. A properly designed, syngas-fueled system will be inherently fuel-flexible, allowing for syngas feedstock to be varied according to price or availability [2]. In addition to added flexibility of the energy pool, conversion of materials to syngas before combustion may have lower pollutant emission than direct combustion of the feedstock because of a cleaner combustion system or the ability to use more effective pollution after treatment.

The combustible components of syngas are typically H_2, CO and CH_4, the concentrations of which vary with the feedstock and production method. The H_2 content range varies from 32% to 67%, that of CO varies from 10% to 57%, and the CH_4, N_2, and CO_2 ratios are 0.1% to 14%, 0.6% to 23%, and 2% to 28%, respectively [3]. Given this variability, a combustion system operating on syngas must tolerate a wide range of combustion properties. The combustion of syngas with different compositions has dramatically different properties of ignition delay [4–6], intermediate species [7,8], flame burning velocity, etc. [9–14].

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Table 1
Volumetric fraction of fuel components used in experimental cases. Each dilution case was performed in duplicate; fuel was diluted with CO_2 and separately with N_2.

Series	Case	H_2	CO	CH_4	CO_2	N_2	Note
Calibration	Cali.	0	0	1	0	0	$\phi = 0.8$, NO seeding
Validation	Vali.	0	0	1	0	0	$\phi = 0.7 - 1.4$
Equivalence ratio	Eqrt.	0.167	0.333	0	0.5	0	$\phi = 0.7 - 1.5$
	Fuel 1	0.32	0.08	0	0	0.6	
	Fuel 2	0.267	0.133	0	0	0.6	
	Fuel 3	0.229	0.171	0	0	0.6	
CO–H_2	Fuel 4	0.2	0.2	0	0	0.6	$\phi = 1.0$
	Fuel 5	0.171	0.229	0	0	0.6	
	Fuel 6	0.133	0.267	0	0	0.6	
	Fuel 7	0.08	0.32	0	0	0.6	
Diluent CO_2/N_2	Dilu. 1	0.1	0.2	0	0.7/0	0/0.7	
	Dilu. 2	0.133	0.267	0	0.6/0	0/0.6	
	Dilu. 3	0.167	0.333	0	0.5/0	0/0.5	$\phi = 1.0$
	Dilu. 4	0.2	0.4	0	0.4/0	0/0.4	
	Dilu. 5	0.233	0.467	0	0.3/0	0/0.3	

Syngas has the potential to be a clean energy source; however, some amount of NO*x* will be produced during its combustion [15]. The effect of syngas composition on NO*x* formation is an area of active research, with experimental and kinetic studies to highlight selected characteristics of syngas combustion [16–18]. Several experimental studies have been conducted of syngas application in gas turbine engines and IGCC (Integrated gasification combined cycle) [19,20]. Meier et al. conducted simultaneous Raman/LIF measurements of major species and NO in turbulent H_2/air diffusion flames [21]. Hwang et al. measured NO*x* concentrations of non-premixed jet flames under turbulent conditions with four different syngas compositions [22]. Watson et al. performed a comparative study of syngas and biogas fuel blends, which comprised CH_4, H_2, CO, and CO_2, to validate current natural gas kinetic models and assess NO production from prompt, thermal, NNH, and N_2O formation pathways [2]. Sutton et al. studied NO emissions experimentally and statistically in a turbulent non-premixed jet flame [23].

Experimental data is necessary for generating accurate computational models of NO*x* production in combustion. Numerous chemical mechanisms (e.g., GRI mech 3.0 [24], CRECK [25], and GDF-Kin 3.0 [26]) include various NO*x* formation sub-mechanisms [27]; improvement of the model predictions is accomplished by validation against data from well-defined experiments. The experiments mentioned above were performed using diffusion flames, the low-NO*x* premix strategy has seldom been studied. Thus, our study investigates NO*x* formation for H_2/CO syngas premixed flames and compares NO concentrations, measured using laser saturated fluorescence (LSF), with the predictions of models from the aforementioned chemical kinetic mechanisms.

2. Experimental methods

2.1. Experimental setup

A comprehensive measurement set was devised to study NO formation during combustion of $H_2/CO/CO_2/N_2/O_2$. All flames investigated herein featured premixing of the fuel with synthetic air (21% O_2–79% N_2). The variables addressed were fuel-air equivalence ratio, fuel mixture composition and dilution of the syngas by N_2 and CO_2. N_2 and CO_2 dilution was included due to the significance of dilution in low-NO*x* combustion strategies used in clean energy development and IGCC. Calibration of the NO*x* measurement system was performed by seeding NO into a methane flame; predictions of NO production by various chemical kinetic mechanisms were validated against the measured NO concentration for CH_4 flames at a variety of equivalence ratios. The gases used in the experiments were supplied by Jingong Gas Co., Ltd., China: H_2 (99.999% purity), CO (99.95% purity), CO_2 (99.995% purity), N_2 (99.999% purity) and O_2 (99.999% purity). The flow rates were controlled by mass flow controllers (Alicat Scientific, Inc.). The fuel gas mixtures used for experiments were selected according to real syngas components [2], they are described in Table 1.

A modified heat flux burner was used to produce the experimental flame. The heat flux method and original heat flux burner were created by Goey et al. at the Eindhoven University of Technology [28–30]. The burner plate is a 2 mm thick, 30 mm diameter brass disk perforated by 0.5 mm diameter holes arranged in a hexagonal pattern with a 0.7 mm pitch. Two thermostatic water baths were installed in conjunction with the burner: one water bath (298 K) was connected to the mixture chamber where the premixed combustion gases were heated prior to combustion; the second bath (358 K) was connected to the burner head to balance the heat lost by the flame to the burner. The burner used for this paper was modified from the original design by substituting Teflon for certain metal portions of the body and burner-plate mount. The Teflon acts as insulation between the burner plate and burner body to reduce heat transfer between these two and allows for shorter burner start up times [31–33]. Seven T-type thermocouples are located at requisite positions in the underside of the burner plate to measure the temperature profile across the burner plate [29]. A data logger (Agilent 34970A, Agilent Technologies Inc.) was used to record the thermocouple probe readings. For each measurement case, the gas supply speed was adjusted until the temperature across the burner plate was uniform. Under this condition, the heat flux burner produces a flat, approximately 1D, stretchless and adiabatic flame. The heat flux burner is able to achieve these conditions for fuel/air mixtures with flame speeds between 10 and 60 cm/s. All the cases investigated were within the acceptable laminar flame speed limits of the heat flux burner.

2.2. Laser system

The flame NO concentration was measured in-situ using laser saturated fluorescence. In the saturated regime, fluorescence signal may be considered insensitive to fluctuations of the laser irradiance and the electronic quenching rate coefficients [34], which facilitates quantitative measurements of the target species. The absolute NO volumetric concentration, N_{abs}, can be computed from the calibrated LSF signal, N_{re}, using the following correction of local thermal variation between the calibration flame and measurement case [35]:

$$N_{abs} = \left(\frac{T}{T_C}\right) \cdot \left(\frac{f_B(T_c)}{f_B(T)}\right) \cdot N_{re} \tag{1}$$

where T is the local flame temperature at the measurement point (10 mm above the burner), T_C is the calibration flame temperature

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