Version of Record: https://www.sciencedirect.com/science/article/pii/S1540748922002553
Manuscript_fd2955b7b503a369362741fe44965f5e

Influence of NOx Chemistry on the Prediction of Natural Gas End-Gas Autoignition in CFD Engine Simulations

Diego Bestel, Daniel Olsen, Anthony Marchese, Bret Windom*

Colorado State University, Fort Collins, CO, USA
**Corresponding Author Email: Bret.Windom@colostate.edu*

Abstract

Natural gas (NG) represents a promising low-cost/low-emission alternative to diesel fuel when used in high-efficiency internal combustion engines. Advanced combustion strategies utilizing high EGR rates and controlled end-gas autoignition can be implemented with NG to achieve diesel-like efficiencies; however, to support the design of these next-generation NG ICEs, computational tools, including single- and multi-dimensional simulation packages will need to account for the complex chemistry that can occur between the reactive species found in EGR (including NOx) and the fuel. Research has shown that NOx plays an important role in the promotion/inhibition of large hydrocarbon autoignition and when accounted for in CFD engine simulations, can significantly improve the prediction of end-gas autoignition for these fuels. However, reduced NOx-enabled NG mechanisms for use in CFD engine simulations are lacking, and as a result, the influence of NOx chemistry on NG engine operation remains unknown. Here, we analyze the effects of NOx chemistry on the prediction of NG/oxidizer/EGR autoignition and generate a reduced mechanism of a suitable size to be used in engine simulations. Results indicate that NG ignition is sensitive to NOx chemistry, where it was observed that the addition of EGR, which included NOx, promoted NG autoignition. The modified mechanism captured well all trends and closely matched experimentally measured ignition delay times for a wide range of EGR rates and NG compositions. The importance of C2-C3 chemistry is noted, especially for wet NG compositions containing high fractions of ethane and propane. Finally, when utilized in CFD simulations of a Cooperative Fuels Research (CFR) engine, the new reduced mechanism was able to predict the knock onset crank angle (KOCA) to within one crank angle degree of experimental data, a significant improvement compared to previous simulations without NOx chemistry.

Keywords: hydrocarbon chemistry, NOx chemistry, natural gas, homogeneous autoignition, engine simulation

---

*Corresponding author:
bret.windom@colostate.edu

© 2022 published by Elsevier. This manuscript is made available under the Elsevier user license
https://www.elsevier.com/open-access/userlicense/1.0/

1. Introduction

Natural gas (NG) fueled internal combustion engines (ICE) represent promising alternatives to traditional diesel fuel-based powerplants, especially in difficult-to-electrify applications, including medium- and heavy-duty transportation sectors, off-road applications, remote power generation, and marine propulsion [1, 2]. The interest in NG fuel arises from its lower cost, on an energy-equivalent basis, compared to diesel fuel [1] and its potential to reduce CO_2-based greenhouse gas (GHG) emissions owning to its high mass-specific heating value and its low C/H ratio as a result of being primarily composed of Methane (CH_4). This potential can only be realized if NG ICEs can achieve diesel-like efficiencies, but, unfortunately, the efficiency, transient load response, and CH_4-based GHG emissions from state-of-the-art spark-ignited (SI) NG engines are inferior to their diesel counterparts. To mitigate these issues, high exhaust gas recirculation (EGR) rates coupled with advanced combustion modes such as Controlled End-Gas Autoignition (C-EGAI), i.e., where the unburned gas ahead of the flame is subjected to auto-ignition (similar to engine knock) while controlling the onset and pressure rise of the autoignition event to prevent destructive knocking, have been demonstrated and are proven strategies to achieve diesel-like efficiencies (~44%) and significantly reduce cylinder out CH_4 emissions [2-5]. Employing such combustion control strategies for multiple applications will require uniquely designed engine platforms and thus will necessitate an understanding and ability to accurately model the chemistry, including those with NOx species (present in the EGR), to accurately predict/control the onset of End-Gas Autoignition (EGAI) [3].

Research has shown that a small amount of NOx (NO and NO_2) can strongly influence hydrocarbon autoignition, both promoting and inhibiting autoignition, depending on the reactant thermodynamic conditions, composition, and NOx concentrations [6-8]. These previous works, which have primarily focused on gasoline-based fuels, including Primary Reference Fuels (PRF) (n-heptane, iso-octane, and toluene) and ethanol, have shown that NOx chemistry inhibits autoignition at low temperatures (<700 K) and higher concentrations (>30 ppm) as a result of NOx impeding the well-known low-temperature RO_2 ignition pathway. In contrast, faster ignition of PRFs at medium to high temperatures has been observed and attributed to the production of OH via $NO+HO_2=NO_2+OH$ (R1) [6]. However, this autoignition promotion becomes weaker as NOx concentrations are increased due to the decreased rate of formation of HO_2, which subsequently reduces the rate of formation of OH via R1 [6, 9]. There have also been a few fundamental chemical kinetic studies showing the influence of NOx chemistry on the autoignition of smaller HCs which make up NG, such as CH_4 [7], C_2H_6 [10-13], and C_3H_8 [14], with the degree of influence being unique to each fuel species as well as pressure- and temperature-dependent. Since NG is not constrained to specific reactivities, due to varying compositions, as is the case with gasoline, there is a need to understand and predict the combined influence of NOx with representative NG blend variations, composed of smaller and larger hydrocarbons that behave differently in the presence of NOx [7].

There is a growing body of evidence highlighting the importance of NOx chemistry on SI ICE operation via simulation with the majority of work also being conducted with PRFs [15, 16]. Chen et al. [17], using a Cooperative Fuel Research (CFR) engine fueled with iso-octane, found that the onset of knock varied significantly with intake charge temperature and NO concentration, where low levels of NO (<200 ppm) at an intake charge temperature of 52 °C promoted EGAI, i.e., advanced the onset of knock, but high levels of NO at lower temperatures suppressed (or retarded) the onset of EGAI. Morganti et al. [18] showed that NO addition in the residual gas strongly promoted liquefied petroleum gas (LPG) EGAI and that NO chemistry was necessary for their models to obtain good agreement with experimental data. However, to the best of the authors' knowledge, there have not been detailed kinetic studies exploring the importance of NOx chemistry on the autoignition tendencies of NG mixtures, especially while considering the variability in NG compositions that exist within the supply chain. Furthermore, a reduced chemical kinetic mechanism suitable for Computational Fluid Dynamics (CFD) ICE simulations is nonexistent, and thus the influence of NOx chemistry on NG engine operation remains unknown.

Mohr et al. [19, 20] investigated the effect of NG reactivity, EGR substitution rates, and EGR composition on homogeneous ignition delay times (IDT), laminar flame speeds, and EGAI for stoichiometric NG/oxidizer/EGR blends using a laser-ignited rapid compression machine (RCM). The study investigated three unique NG blends spanning reactivities representative of those experienced by NG compositions found in the United States. Each of these NG formulations was blended with varying levels of a non-reactive (NR-EGR) and reactive EGR (R-EGR), and the IDTs were measured at compressed pressures and temperatures ranging from 30-34 bar and 929-1019 K, respectively. For the NR-EGR, which was only composed of inert species (CO_2 and Ar), the homogeneous IDTs were suppressed as EGR rates increased while maintaining similar compressed temperatures and pressures. This trend was observed for all NG fuel blends. However, for the blends including R-EGR, which included NO and CO at concentrations mimicking those measured from complementary engine tests combined with the inert species of CO_2 and Ar, an opposite trend was observed with shorter homogeneous IDTs occurring at higher EGR rates (under similar compressed temperatures and pressures) for all NG fuel blends. Removing CO (and keeping NO) from the R-EGR blend had no noticeable effect on the fuels' IDTs, and measured flame speeds were indistinguishable between the R-EGR and NR-EGR blends (when the EGR rate and the compressed temperatures/pressures were fixed). These results, which were taken under a much more controlled setting of an RCM, signify the importance of NO ignition chemistry for EGAI of NG fuels and represent a valuable data set to support the construction of a predictive yet tractable chemical mechanism for use in NG engine simulation and design.

In this study, a reduced NG/oxidizer/NOx combustion mechanism was developed with the aim to be of suitable size for multi-dimensional CFD engine simulations while capturing the non-trivial interactions of varying NG blends/activities with NOx. To generate the new reduced NG/NOx mechanism, NOx chemistry was added to the previously developed reduced NG mechanism by Mohr et al. [19, 20] called ARIES82 and was validated using previously published IDT data [19, 20]. In this work, a brief discussion on the important species and reactions for NG/NOx oxidation is provided and the mechanism's performance is compared to state-of-the-art detailed mechanisms (i.e., NUIG Mech1.2 and ARAMCO 3.0). Finally, the newly generated reduced NG/NOx mechanism was employed in a multi-dimensional CFD ICE simulation and compared to experimental engine test data, highlighting the importance of NOx chemistry on NG EGAI prediction under engine-relevant conditions [3, 4].

2. Methods

2.1 Ignition Delay Measurements

The experimental data utilized in this study was gathered by Mohr et al. [19, 20] and is briefly described in this section. Utilizing the RCM described in [19], Mohr et al. tested three synthetic NG fuel compositions with varying concentrations of CH_4, C_2H_6, and C_3H_8 to simulate the spread in reactivity (quantified by the Methane Number) seen in the US NG supply chain. The three synthetic NG compositions referred by Mohr et al. as dry, mid, and wet are provided in Table 1, along with their calculated Methane Number (MN). Mohr et al. conducted tests with synthetic EGR substitution rates at 0%, 10%, 20%, and 30% by mass for each fuel composition. The synthetic R-EGR composition, shown in Table 2, was chosen to simulate a typical medium-duty SI NG engine EGR composition. Although EGR composition will change with engine operating conditions, the same composition was used across all test points to maintain consistency. Additionally, the mid fuel composition was also tested with an NR-EGR composition to assess the effect of reactive species in the EGR on NG homogeneous autoignition. The NR-EGR composition is also provided in Table 2.

Table 1
Fuel compositions utilized to analyze NOx influence on NG homogeneous autoignition. Concentrations are in Mol%.

Species	Dry	Mid	Wet
CH_4	99%	95%	82%
C_2H_6	0.5%	4%	15%
C_3H_8	0.5%	1%	3%
MN	95	86	68

Water was excluded from their tests to avoid condensation and ensure even mixing which, according to Mohr et al., had an accuracy of 0.25%. CO_2 concentration was increased to match the ratio of specific heats, γ, to an actual EGR blend containing H_2O. Argon (Ar) replaced N_2 to achieve higher compressed temperatures and pressures for the same compression ratio by increasing the mixture's γ.

Table 2
Synthetic EGR compositions utilized to analyze NOx influence on NG autoignition. Concentrations are in Mol%.

Species	Reactive EGR	Non-Reactive EGR
Ar	79.3%	80%
CO_2	20.0%	20%
CO	0.35%	-
NO	0.35%	-

Each fuel and EGR composition were tested at a fixed initial pressure of 1 bar and three different initial temperatures: 35 °C, 45 °C, and 55 °C. This approach resulted in multiple compressed temperatures (929-1019 K) at similar compressed pressures (30-34 bar). Only points with compressed temperatures within ±10 K of weighted average were selected for analysis. The homogeneous IDT was calculated as the time after the RCM's pistons reached top dead center (TDC) to the time corresponding to the maximum pressure gradient.

Mixture preparation was performed as described by Mohr et al. [19, 20], where, to ensure good mixing, NG/oxidizer/EGR mixtures were stored in mixing tanks for up to 2 hours. As noted in [7], extended storage of mixtures containing NO and O_2 can lead to NO conversion into NO_2 via $2NO+O_2 \Leftrightarrow 2NO_2$. In this study, constant volume calculations were performed to estimate the correct amount of NO converted into NO_2 after 2 hours of mixing, and this composition was used in the homogeneous IDT calculations. For the 30% R-EGR mixtures, roughly 90% of NO was consumed to NO_2 over the course of the 2-hour mixing duration. Results of these simulations and the impact of the NO to NO_2 conversion on predicted ignition delays are provided in the supplementary materials, Figures 2S-5S and Table 1S.

2.2 Chemical Mechanism Development

The reduced NG chemical mechanism ARIES82 [19, 20] (82 species and 518 reactions), which was generated by reducing ARAMCO 3.0 using the Directed Relation Graph with Error Propagation (DRGEP) method and proven to successfully capture NG autoignition in both 0-D simulations of the RCM and 3-D simulations of an engine without NOx [3, 4], was used as the base mechanism to subsequently incorporate NOx chemistry. The choice of starting from a reduced mechanism instead of reducing from a large, detailed mechanism came due to the fact that detailed mechanisms available at the time of conducting this study failed to accurately reproduce NG/NOx IDTs as shown later in the manuscript, whereas ARIES82 accurately captured NG IDTs times (without NOx species) and already had a suitable size for multi-dimensional engine simulations. The NOx-containing ARIES82 mechanism, hereafter referred to as ARIES82NOx, was generated by incorporating the NOx-chemistry subset from the mechanism developed by Dagaut and Dayma [21] and the complete C_3+NOx sub-mechanism from NUIG Mech1.1 [22-30]. The final ARIES82NOx reduced mechanism incorporated 141 species and 783 reactions, an acceptable size for use in full-cycle ICE CFD simulations. Although the focus of this work is the ARIES82NOx mechanism, this mechanism was further reduced to improve computational efficiency of multi-dimensional engine simulations using the DRGEP method and sensitivity analysis, targeting a 1% deviation in IDTs predicted by ARIES82NOx. The resultant further reduced mechanism, referred to as ARIES50NOx, contains 50 species and 257 reactions. IDT calculation results using ARIES50NOx are shown in the supplementary materials, Figure 6S.

2.3 Simulation Approach

The upgraded ARIES82NOx reduced mechanism was evaluated by comparing homogeneous IDT calculations for all three NG compositions, EGR compositions, and conditions tested in the previous RCM experimental campaign by Mohr et al. [19, 20]. Variable Volume 0-D Simulation toolbox available in CONVERGE version 3.0.25 [31] was used to perform all IDT calculations. The ‘adiabatic core hypothesis’ [32] was used to capture heat loss effects, and the procedures highlighted in [33] were used to calculate the time-dependent gas temperatures and the adiabatic core volume for use in IDT calculations. IDTs are subsequently plotted versus top dead center (TDC) temperatures for simplicity; however, the transient volume traces used to perform the IDT calculations and account for heat losses within the RCM experiments are available upon request. Ignition sensitivity analyses were performed with the ARIES82NOx mechanism using CONVERGE v3.0.25. IDT calculations and sensitivity analysis were also performed with the recently published NUIGMech1.2 detailed mechanism (2857 species, 11809 reactions) with updated CH_4-NOx chemistry [7] for comparison.

CFR engine simulations were then performed using ARIES82NOx with CONVERGE version 2.4.35 [31]. Boundary conditions matched those reported in previously published engine tests, which explored the role of varying EGR rates and controlled EGAI on NG SI ICE efficiency [3, 4].

3. Results and Discussion

3.3 Homogeneous Ignition Delay

Figure 1 compares the calculated IDTs plotted versus the inverse of the TDC temperature to the previously published experimental data from Mohr et al. [19, 20]. Cases with and without reactive EGR (R-EGR) for all three NG compositions are shown. Included are calculations using the newly developed reduced mechanism, ARIES82NOx, ARIES82 [19, 20] (for the cases without EGR addition), and the state-of-the-art detailed mechanisms NUIG Mech1.1 [22-30] and NUIG Mech1.2 [7]. While not shown, mixtures containing 10% and 20% R-EGR were simulated and compared to experimental data and used to assess mechanism errors. These intermediate R-EGR data did not show any unusual trends, except the large discrepancies with NUIG Mech1.1, and are provided in the supplementary materials, Figure 6S.

As can be seen in Figure 1, the addition of R-EGR to the NG/oxidizer mixtures enhances the chemical reactivity and shortens the IDTs of all NG mixtures. ARIES82 agrees well with the data absent of EGR (and NOx) whereas NUIG Mech1.1 shows the largest discrepancies for drier fuels in the presence of R-EGR, confirming our choice of using the ARIES82 mechanism as the foundation on which to add NOx-chemistry. Although the results shown in Figure 1 of IDTs from NUIG Mech1.1 seem promising, additional data shown in the supplementary materials (Figure 6S) show the large discrepancies for the Dry and Mid fuels with R-EGR addition. On the other hand, the results with the newly developed reduced mechanism, ARIES82NOx, show good agreement with the experimental data, demonstrating an average absolute error in calculated IDT of 19.1%. The average of the absolute errors found for the NUIG Mech1.2 was 18.5%, only slightly lower than that found with ARIES82NOx. Interestingly, ARIES82NOx and NUIG Mech1.2, generally followed similar trends when compared to the experimental data, for example, both calculating faster IDTs for the wet fuel than observed in the experiments. The general overlap between the reduced and detailed mechanism substantiates the robustness of the reduced mechanism in predicting NG IDTs in the presence of NOx species.

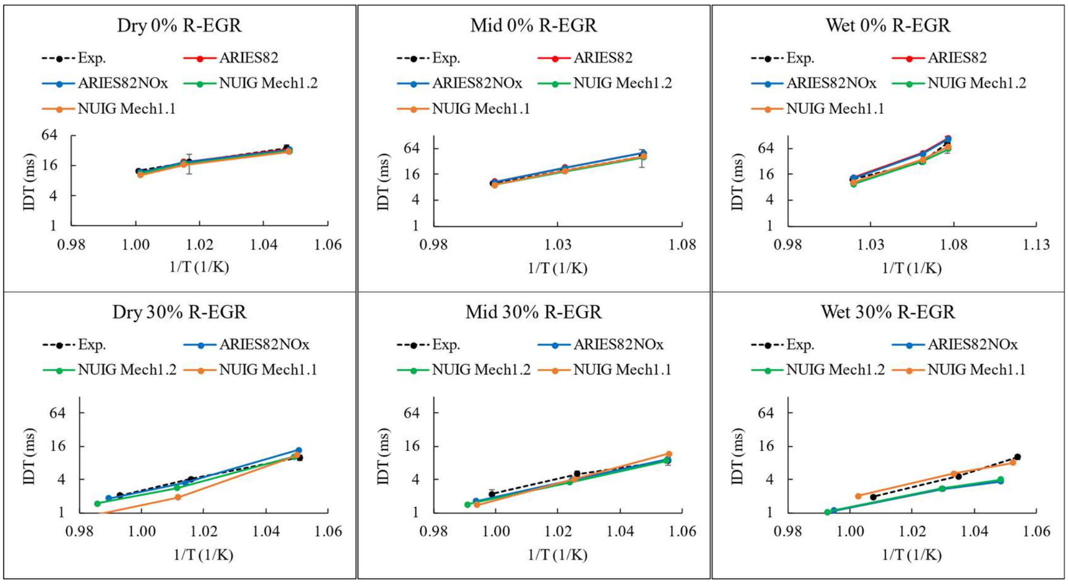

Figure 1: IDT calculation results for all fuels without (top row) and with 30% R-EGR (bottom row).

3.4 *Sensitivity Analysis*

A sensitivity analysis was performed using ARIES82NOx and compared to that of NUIG Mech1.2 mechanism to (1) expand on a recently published study investigating CH_4–NOx chemistry by highlighting the important reactions when C2-C3 species are present and (2) to further validate the chemistry being captured by the reduced ARIES82NOx mechanism by comparing it to a state-of-the-art, detailed chemical kinetic mechanism [7].

Figure 2 compares the ten most ignition-promoting (top) and inhibiting (bottom) reactions in the ARIES82NOx mechanism to that of NUIG Mech1.2 for the wet fuel with a 30% R-EGR substitution rate at TDC temperature of 948 K and TDC pressure of 32 bar. These analyses were conducted to match the RCM conditions and thus were performed using the updated composition after the mixture was allowed to sit for 2 hours (i.e., with the majority of the NO being converted to NO_2). As shown in Figure 2, although there are some slight differences in the normalized sensitivity coefficients between the detailed and reduced mechanism, as is expected due to the considerably different number of reactions in each, the leading reactions responsible for both promoting and inhibiting autoignition are essentially the same. As noted by Sahu et al. [7], $CH_3+NO_2 \Leftrightarrow CH_3O+NO$ is the most important NG ignition promoting reaction as it feeds the main hydrocarbon oxidation pathway of methane with the production of methoxide (CH_3O). However, the competing reaction, which occurs with a third body to form nitromethane (CH_3NO_2), is an endothermic reaction that is very sensitive to reducing system reactivity and extending IDTs.

For NG fuels, there are several reactions with C2-C3 species that are important, including $RH+NO_2 \Leftrightarrow R+HONO$ which enhance fuel consumption, and thus, autoignition. Additionally, for the wet fuels, NUIG Mech1.2 indicates that the formation of Nitroethane, $C_2H_5NO_2$, is important for inhibiting autoignition; however, this reaction does not appear in the ARIES82NOx sensitivity analysis since the sub-mechanism for the formation and oxidation of

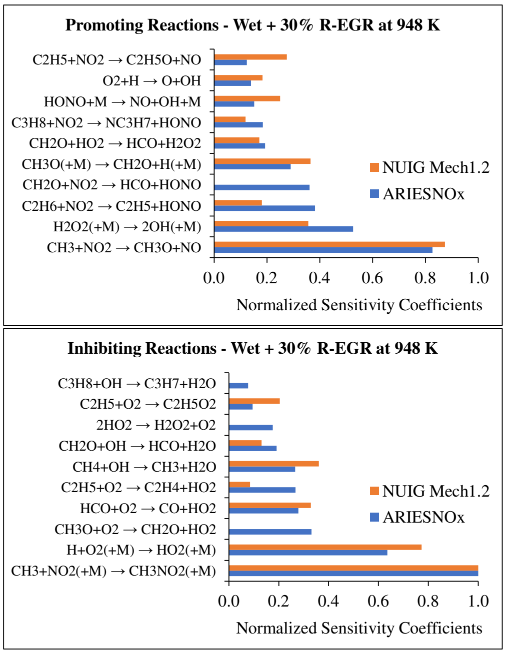

Figure 2: Sensitivity Analysis results for the Wet fuel with 30% R-EGR. The top graph shows ignition-promoting reactions, and the bottom graph shows inhibiting reactions.

$C_2H_5NO_2$ is not present in the reduced mechanism. Its addition would result in a considerable number of added reactions without considerably improving the IDT calculation accuracy. Sensitivity analyses were also performed for the dry NG composition (provided in supplementary materials, Figure 9S) and as expected, showed less sensitivity for the C2-C3 reactions on ignition than the wet fuel. Interestingly, for these conditions, the sensitivity analyses do not indicate R1 nor NOx obstruction on RO_2 chemistry as being important even for the wet NG fuels, despite their known sensitivity to the ignition of larger hydrocarbons.

A sensitivity analysis was also conducted using the unaffected composition (with all NOx being comprised of NO) as would be seen in an engine. Interestingly, with NO present the analysis shows that RO_2+NO reactions promote autoignition for methyl fuel radicals; however, the same class of reactions for C_3 and larger HCs result in inhibition. This can be explained due to the fact that RO_2+NO will form RO+NO_2, which is CH_3O+NO_2 for C_1 species, feeding the main HC oxidation pathway, whereas, for C_3, the pathway will ultimately form an olefin+HO_2. The results of these sensitivity and pathway flux analyses are provided in the supplementary materials (Figures 9S, 10S, and 11S).

3.5 *Laminar Flame Speed*

As a further validation on the robustness of ARIES82NOx in capturing NG combustion, Laminar Flame Speed (S_L) calculations were performed and compared to ARAMCO 3.0, the mechanism used to generate S_L lookup tables in [3, 4]. The excellent agreement of calculated S_L between the two mechanisms further validates its robustness and suitability to be used in NG engine simulations. These S_L results are shown in the supplementary materials, in Figure 7S. Figure 3 shows additional S_L calculations comparing the effect of R-EGR versus NR-EGR on S_L for stoichiometric Mid fuel combustion at varying temperatures and EGR ratios. Similarly to what was observed by Mohr et al., there is no noticeable difference between the effects of R-EGR and NR-EGR up to temperatures of 800 K; however, beyond 800 K the addition of R-EGR seems to enhance reactivity and increases S_L. The authors speculate that, due to the higher temperatures, H-abstraction is increased which, combined with higher rates of NO formation, enhances reactivity. Additionally, higher temperatures result in greater Nitromethane (CH_3NO_2) dissociation, whose formation, as shown in the previous section, is the most inhibiting reaction. Figure 8S in the supplementary materials shows mass fractions distributions supporting this speculation; however, this topic needs further analysis.

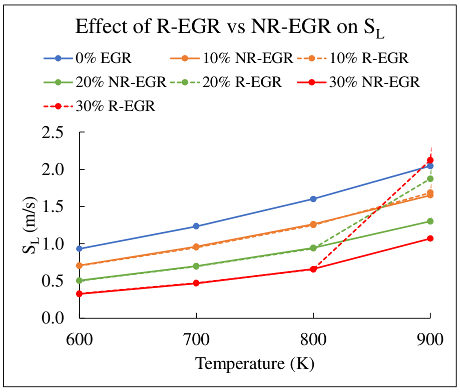

Figure 3: Effect of R-EGR versus NR-EGR on the Mid fuel's SL. The same SLs are observed up to 800 K, agreeing with Mohr et al. results. SLs at higher temperatures need further analysis.

4. Impact on Engine Simulations

Multi-dimensional CFR engine CFD simulations were carried out with both the ARIES82 and ARIES82NOx mechanisms and compared to experiments to explore the impact of NOx containing EGR on engine performance. The CFR engine CFD model developed in [3], calibrated using the ARIES82 mechanism, was used to analyze the effects of NOx chemistry on the prediction of NG EGAI. In this work, the model (originally run with ARIES82, without NOx) was rerun with the newly developed reduced mechanism, ARIES82NOx, while keeping the same boundary and initial conditions as well as the same calibration parameters, i.e., nothing was changed in the model except for the chemical mechanism and the EGR composition. The model was run with the intake, exhaust, and residual gas compositions updated to properly match the EGR composition that was experimentally observed, which contains NO and whose composition is shown in Table 3. Pipeline NG fuel with an MN of 69 was used. The detailed composition of which can be found in [3]. Due to the absence of NOx species in the ARIES82 mechanism, only complete combustion products had been assumed for the EGR composition in the previous work [3]. Two operating points were simulated with varying compression ratios, Indicated Mean Effective Pressures (IMEP), EGR ratios, and CA50s, all at a constant engine speed of 900 RPM. This sweep of parameters led to various values of knock onset crank angle (KOCA), or the crank angle at which EGAI occurs, and fractional end-gas autoignition (f-EGAI), which we define as the fraction of the energy released from the EGAI event normalized by the total heat release. Table 4 summarizes the experimental engine conditions for the selected simulated cases. Additionally, 'Case 1' was also run using ARIES50NOx to assess its accuracy and computational performance in multi-dimensional engine simulation.

Table 3
EGR composition used in the CFD ICE simulations.

Exhaust Composition	
Species	**Mol**
CH4 (THC)	0.09%
CO	0.06%
NO	0.14%
N2	74.52%
CO2	8.78%
H2O	16.09%

Figure 4 shows the simulated pressure (taken from a monitor point matching the position of the cylinder pressure transducer in the experiments) and the Apparent Heat Release Rate (AHRR) profiles for the two simulated cases with the respective individually resolved cycle (gray) and a representative cycle (black), chosen to be the cycle with the maximum cylinder pressure closest to the average of all cycles maximum pressure, from the experimental data. These plots also include: (1) The original simulation data with ARIES82 without NOx (red trace), (2) the

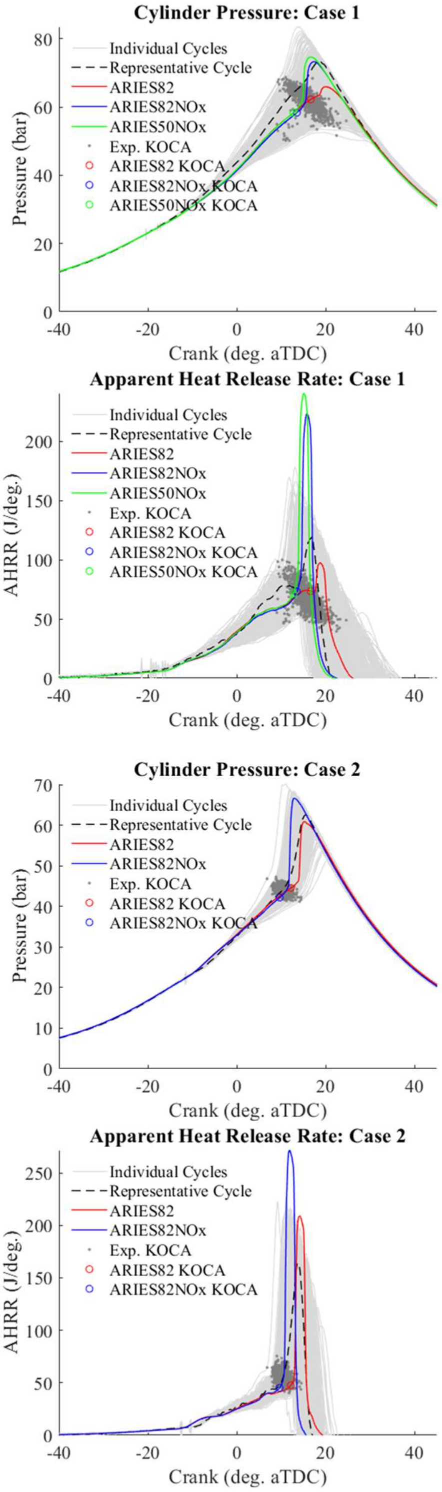

Figure 4: Cylinder pressure and AHRR with overlaid KOCA obtained from experimental data and CFD simulations using ARIES82 (red) and ARIES82NOx

simulation data using ARIES82NOx (blue trace), and (3) the simulation data using ARIES50NOx (green trace) with the experimentally observed EGR/residual gas composition. Also reflected are the measured and predicted KOCA noted by the overlaid symbols.

Table 1
Simulated engine operating conditions

Test Case	CR	Eng. Spd (RPM)	IMEP (bar)	EGR	Lambda	CA50 (° aTDC)	P_{in} (bar)	T_{in} (°C)
Case 1	9.55	903	12	17%	1.00	12	1.6	61
Case 2	12.30	900	8	0%	1.01	12	0.9	60

In both cases, the addition of NOx chemistry advances the onset of EGAI and leads to a better representation of the engine pressure data, and more accurately reflects the onset of EGAI indicated in the AHRR plots. Table 5 shows a comparison of the mean experimental KOCAs of all 1000 engine cycles and the predicted/simulated KOCA using ARIES82 and ARIES82NOx. As can be clearly seen, the results for KOCA significantly improve, allowing the CFR engine simulations to match KOCA within 1.0 crank-angle degree (°CA) of the experimental values when using the ARIES82NOx mechanism. Although not shown in Table 5, ARIES50NOx predicts a KOCA 1.28 deg. earlier than the experimental mean. Important to notice is the direction of the change. Similar to the RCM experiments, the system's reactivity when utilizing ARIES82NOx is enhanced, and the onset of EGAI is advanced by over 2 °CA. 'Case 2' further highlights the importance of using a NOx-containing mechanism even in cases without EGR, where the NOx formed during combustion remaining in the residual gas is sufficient to influence EGAI and improve the CFD simulations. Additionally, as observed by Mohr et al. and discussed in §3.2, NOx species do not seem to influence flame propagation in the CFD simulations since the pressure traces and AHRR before the onset of EGAI nearly overlap. Lastly, Figure 4 also shows the excellent agreement of ARIES50NOx with experimental data, showcasing its accuracy, while reducing simulation time during the combustion section by nearly 50%.

Table 2
Simulated KOCA results comparison between ARIES82 and ARIES82NOx.

Test Case	KOCA (deg. aTDC)				
	Experimental	ARIES82	Error	ARIESNOx	Error
Case 1	14.0	16.9	2.9	13.6	-0.4
Case 2	10.3	12.1	1.8	9.8	-0.5

Leveraging the CFD results and the predicted spatial distribution of CH_3, NO_2, NO, and OH concentrations at onset of EGAI (Figure 5, 'Case 2') one can visualize and better understand the mechanisms responsible for EGAI described in §3.2 that occur within the engine. Figure 5 illustrates that at the same location where the concentrations of CH_3 and NO_2 significantly decrease (top row), there is a corresponding increase in the concentrations of NO and OH, which is an indication of the reaction sequence $CH_3+NO_2 \Leftrightarrow CH_3O+NO$ and $NO+HO_2 \Leftrightarrow NO_2+OH$, the importance of which was previously discussed with the homogeneous IDT results and in [7]. If the subsequent timesteps were to be plotted, the same pattern of lower concentrations of CH_3 and NO_2 corresponding to the locations of higher concentrations of NO and OH would continue and indicate the areas undergoing EGAI.

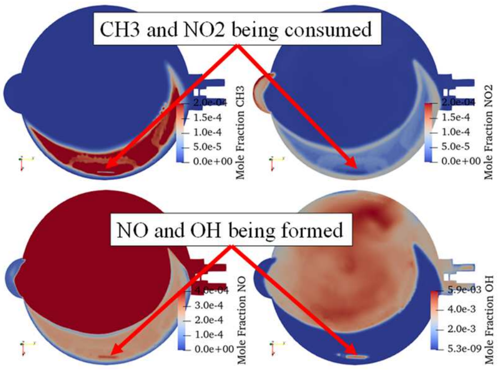

Figure 5: Spatial distribution of CH_3, NO_2, NO, and OH. Highlighted locations show the onset of EGAI.

5. Conclusions

In this study, the importance of accounting for NOx chemistry on the prediction of NG autoignition was assessed and a reduced mechanism suitable for engine simulations was generated and validated with published homogeneous ignition and engine test data. The reduced ARIES82NOx mechanism is comprised of 141 species and 783 reactions and was developed by including previously published NOx chemistry subsets with the previously published and validated ARIES82 reduced NG mechanism. The updated and reduced mechanism predicted shorter ignition delays with the addition of a reactive EGR containing NO & NO_2 for three different NG compositions/reactivities and reflected RCM data resulting in less than a combined 20% deviation between the predicted and measured IDTs. A sensitivity analysis was performed where it was noted that due to the presence of large amounts of methane in NG, ignition is generally promoted when NOx containing EGR is present due to key reactions that accelerate the oxidation of methyl radicals. In addition, both the detailed and the reduced mechanisms identified several new initiation reactions that become important with C_2 and C_3 species present in NG. Finally, the newly generated reduced mechanism was applied in CFD engine simulations where it was noticed that simulations which included NOx chemistry, even in cases without EGR, predicted an advanced KOCA that more closely matched the measured KOCAs compared to the simulations which excluded NOx.

Acknowledgments

This research is funded by the US Department of Energy under grant number DE-EE0008331. The authors would like to also thank Convergent Science for providing CONVERGE licenses for this study.

References

[1] R.H. Mitchell, D.B. Olsen, Extending Substitution Limits of a Diesel–Natural Gas Dual Fuel Engine, Journal of Energy Resources Technology 140 (2018) 052202.

[2] G.J. Hampson. High Efficiency Natural Gas Engine Combustion Using Controlled Auto-Ignition. In: editor^editors. ASME 2019 Internal Combustion Engine Division Fall Technical Conference; 2019: American Society of Mechanical Engineers Digital Collection. p.

[3] D. Bestel, S. Bayliff, A. Marchese, D. Olsen, B. Windom, H. Xu. Multi-Dimensional Modeling of the CFR Engine for the Investigation of SI Natural Gas Combustion and Controlled End-Gas Autoignition. In: editor^editors. ASME 2020 Internal Combustion Engine Division Fall Technical Conference; 2020: American Society of Mechanical Engineers Digital Collection. p.

[4] D. Bestel, S. Bayliff, H. Xu, A. Marchese, D. Olsen, B. Windom, Investigation of the end-gas autoignition process in natural gas engines and evaluation of the methane number index, Proceedings of the Combustion Institute (2020).

[5] S. Bayliff, EVALUATION OF CONTROLLED END GAS AUTO IGNITION WITH EXHAUST GAS RECIRCULATION IN A STOICHIOMETRIC, SPARK IGNITED, NATURAL GAS ENGINE, Mechanical Engineering, Colorado State University, Colorado State University, 2020, pp. 168.

[6] R. Fang, C. Saggese, S.W. Wagnon, AB Sahu, H.J. Curran, W.J. Pitz, C.-J. Sung, Effect of nitric oxide and exhaust gases on gasoline surrogate autoignition: iso-octane experiments and modeling, Combustion and Flame 236 (2022) 111807.

[7] AB Sahu, A.A.E.-S. Mohamed, S. Panigrahy, C. Saggese, V. Patel, G. Bourque, W.J. Pitz, H.J. Curran, An experimental and kinetic modeling study of NOx sensitization on methane autoignition and oxidation, Combustion and Flame (2021) 111746.

[8] Y. Chan, J. Bromly, A. Konnov, D. Zhang, The comparative and combined effects of nitric oxide and higher alkanes in sensitizing methane oxidation, Combustion science and technology 184 (2012) 114-132.

[9] Z. Chen, P. Zhang, Y. Yang, M.J. Brear, X. He, Z. Wang, Impact of nitric oxide (NO) on n-heptane autoignition in a rapid compression machine, Combustion and Flame 186 (2017) 94-104.

[10] A.V. Menon, S.-Y. Lee, M.J. Linevsky, T.A. Litzinger, R.J. Santoro, Addition of NO2 to a laminar premixed ethylene–air flame: effect on soot formation, Proceedings of the Combustion Institute 31 (2007) 593-601.

[11] F. Deng, H. Xu, X. Liu, Y. Wu, H. Zheng, Z. Li, Effect of nitrogen dioxide addition on ethane auto-ignition at different pressures and equivalence ratios: Experiments and chemical kinetic modeling, Fuel 285 (2021) 119042.

[12] F.E. Alam, F.M. Haas, T.I. Farouk, F.L. Dryer, Influence of trace nitrogen oxides on natural gas oxidation: Flow reactor measurements and kinetic modeling, Energy & Fuels 31 (2017) 2360-2369.

[13] X. Zhang, W. Ye, J. Shi, X. Wu, R. Zhang, S. Luo, Shock-induced ignition of methane, ethane, and methane/ethane mixtures sensitized by NO2, Energy & Fuels 31 (2017) 12780-12790.

[14] P. Gokulakrishnan, C.C. Fuller, M.S. Klassen, R.G. Joklik, Y.N. Kochar, S.N. Vaden, T.C. Lieuwen, J.M. Seitzman, Experiments and modeling of propane combustion with vitiation, Combustion and Flame 161 (2014) 2038-2053.

[15] A. Burluka, K. Liu, C. Sheppard, A. Smallbone, R. Woolley, The influence of simulated residual and NO concentrations on knock onset for PRFs and gasolines, SAE transactions (2004) 1873-1889.

[16] P. Roberts, C. Sheppard, The influence of residual gas NO content on knock onset of iso-octane, PRF, TRF and ULG mixtures in SI engines, SAE International Journal of Engines 6 (2013) 2028-2043.

[17] Z. Chen, H. Yuan, Y. Yang, M. Brear. The Effect of Nitric Oxide on Knock Onset of iso-Octane in a CFR Spark-Ignition Engine. In: editor^editors. 10th Asia Pacific Conference on Combustion; 2015. p.

[18] K.J. Morganti, M.J. Brear, G. da Silva, Y. Yang, F.L. Dryer, The autoignition of Liquefied Petroleum Gas (LPG) in spark-ignition engines, Proceedings of the Combustion Institute 35 (2015) 2933-2940.

[19] J. Mohr, The Effect of Fuel Reactivity and Exhaust Gas Recirculation on Knock Propensity of Natural Gas, Mechanical Engineering, Colorado State University, Colorado State University, 2020, pp. 175.

[20] J. Mohr, B. Windom, D.B. Olsen, A.J. Marchese. Homogeneous Ignition Delay, Flame Propagation Rate and End-Gas Autoignition Fraction Measurements of Natural Gas and Exhaust Gas Recirculation Blends in a Rapid Compression Machine. In: editor^editors. Internal Combustion Engine Division Fall Technical Conference; 2020: American Society of Mechanical Engineers. p. V001T003A012.

[21] P. Dagaut, G. Dayma, The high-pressure reduction of nitric oxide by a natural gas blend, Combustion and flame 143 (2005) 135-137.

[22] H. Ajrouche, O. Nilaphai, C. Hespel, F. Foucher, Impact of nitric oxide on n-heptane and n-dodecane autoignition in a new high-pressure and high-temperature chamber, Proceedings of the Combustion Institute 37 (2019) 3319-3326.

[23] Y. Wu, S. Panigrahy, AB Sahu, C. Bariki, J. Beeckmann, J. Liang, A.A. Mohamed, S. Dong, C. Tang, H. Pitsch, Understanding the antagonistic effect of methanol as a component in surrogate fuel models: A case study of methanol/n-heptane mixtures, Combustion and Flame 226 (2021) 229-242.

[24] A. Ramalingam, S. Panigrahy, Y. Fenard, H. Curran, K.A. Heufer, A chemical kinetic perspective on the low-temperature oxidation of propane/propene mixtures through experiments and kinetic analyses, Combustion and Flame 223 (2021) 361-375.

[25] M. Baigmohammadi, V. Patel, S. Nagaraja, A. Ramalingam, S. Martinez, S. Panigrahy, A.A.E.-S. Mohamed, K.P. Somers, U. Burke, K.A. Heufer, Comprehensive experimental and simulation study of the

ignition delay time characteristics of binary blended methane, ethane, and ethylene over a wide range of temperature, pressure, equivalence ratio, and dilution, Energy & Fuels 34 (2020) 8808-8823.

[26] SS Nagaraja, J. Liang, S. Dong, S. Panigrahy, A. Sahu, G. Kukkadapu, S.W. Wagnon, W.J. Pitz, H.J. Curran, A hierarchical single-pulse shock tube pyrolysis study of C2–C6 1-alkenes, Combustion and Flame 219 (2020) 456-466.

[27] S. Panigrahy, J. Liang, S.S. Nagaraja, Z. Zuo, G. Kim, S. Dong, G. Kukkadapu, W.J. Pitz, S.S. Vasu, H.J. Curran, A comprehensive experimental and improved kinetic modeling study on the pyrolysis and oxidation of propyne, Proceedings of the Combustion Institute (2020).

[28] A.A.E.-S. Mohamed, S. Panigrahy, AB Sahu, G. Bourque, H. Curran, An experimental and kinetic modeling study of the auto-ignition of natural gas blends containing C1–C7 alkanes, Proceedings of the Combustion Institute (2020).

[29] SS Nagaraja, J. Power, G. Kukkadapu, S. Dong, S.W. Wagnon, W.J. Pitz, H.J. Curran, A single pulse shock tube study of pentene isomer pyrolysis, Proceedings of the Combustion Institute (2020).

[30] S. Dong, K. Zhang, P.K. Senecal, G. Kukkadapu, S.W. Wagnon, S. Barrett, N. Lokachari, S. Panigaphy, W.J. Pitz, H.J. Curran, A comparative reactivity study of 1-alkene fuels from ethylene to 1-heptene, Proceedings of the Combustion Institute (2020).

[31] K.J. Richards, P.K. Senecal, E. Pomranin, CONVERGE 3.0, Convergent Science, Madison, WI, 2021.

[32] H. Hu, J. Keck, Autoignition of adiabatically compressed combustible gas mixtures, SAE transactions (1987) 592-604.

[33] C.-J. Sung, H.J. Curran, Using rapid compression machines for chemical kinetics studies, Progress in Energy and Combustion Science 44 (2014) 1-18.