

Modeling the Detailed Chemical Kinetics of NO_x Sensitization for the Oxidation of a Model fuel for Gasoline

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ABSTRACT

At temperatures below 1100 K, the oxidation of nitric oxide (NO) impacts the oxidation of hydrocarbons, causing a sensitization effect in fuel combustion. This effect can be important in engine operations, especially those involving high levels of exhaust-gas recirculation (EGR). Many researchers have observed this NO sensitization for the oxidation of hydrocarbons in HCCI engines as well as stirred reactors. They used several model-fuel components relevant to gasoline, such as *n*-heptane, *iso*-octane, and toluene. As found in stirred reactor experiments, NO tends to increase the extent of oxidation for high-octane fuel components, such as *iso*-octane and toluene. However, for the low-octane component *n*-heptane, NO has an inhibiting effect on hydrocarbon oxidation, particularly at low temperatures corresponding to the negative temperature coefficient (NTC) region. In this study, a detailed reaction mechanism for the combustion of complex gasoline surrogates has been extended to incorporate the sensitization effect of NO_x on the oxidation of hydrocarbons. The NO_x sub-mechanism incorporates recent updates in the kinetics literature for the hydrogen cyanide and related chemistry, as well as various production pathways that lead to NO_x emissions from fuel combustion. The gasoline-NO_x mechanism contains 1833 species and 8764 elementary reaction steps, including formation of several polycyclic aromatic hydrocarbons (PAH) species.

The extended self-consistent surrogate mechanism has been validated against available stirred-reactor measurements that cover a range of pressures, temperatures, and equivalence ratios for various small and large hydrocarbon components included in the mechanism. It successfully captures NO's inhibiting effect for *n*-heptane at temperatures below 650 K

as well as its promoting effects at higher temperatures. Though validation data are not available for all the components of a complex gasoline surrogate, self-consistency of the mechanism that is built on rate-rules should guarantee the predictive capability for other components as well as their blends. In addition to the validation using the limited fundamental experimental data available, modeling using the detailed reaction mechanism has been performed for a typical gasoline HCCI engine using an eight-component gasoline surrogate. Higher levels of NO are predicted to significantly advance the combustion phasing due to the sensitization effect. The expected effect of exhaust gas recirculation (EGR) on combustion phasing and emissions has also been discussed.[CN1]

INTRODUCTION

Many researchers observed the sensitization effect of nitric oxides (NO_x) on oxidation of hydrocarbons [1,2,3,4] under HCCI engine conditions. Ricklin et al. [1] observed that addition of nitrogen dioxide (NO₂) as little as 10 ppm to an Homogeneous Charge Compression Ignition (HCCI) engine running on methane fuel can have catalytic effect. Risberg et al. [2] found that addition of NO to primary reference fuel (PRF), toluene reference fuel (TRF), and gasoline with research octane number (RON) of 84 generally advance combustion phasing represented by CA50. They also observed in case of PRF84 and boosted pressure conditions, very high concentrations of NO may retard the combustion phasing. However, Sjöberg and Dec [3] only observed the advancing of combustion phasing in their HCCI engine due to NO addition to PFR mixtures with various octane ratings. In addition to engine studies, several fundamental experimental studies focused on NO sensitization on oxidation of hydrocarbons [5,6,7,8]. In three different studies,

Dagaut et al. [4, 5, 7] quantified NO_x sensitization effects on various hydrocarbons using jet-stirred reactors. They used methane, ethane, ethylene, *n*-heptane, *iso*-octane, and toluene as fuels and measured outlet species concentrations. Sivaramakrishnan et al. [8] used high pressure shock tube to study the effect of NO on the oxidation of methane doped with ethane. It was found that the impact of NO on hydrocarbon oxidation varies with the temperature regime as well as structure of the hydrocarbon fuel. For high-octane components, such as *iso*-octane and toluene, NO has a promoting effect on their oxidation for temperatures up to 1100 K. At higher temperatures, this sensitization effect diminishes. The effect of NO on low-octane components with significant negative temperature coefficient (NTC) behavior, such as *n*-heptane, is much more drastic. For these components, at very low temperatures below 650 K, NO inhibits hydrocarbon oxidation. Conversely, between 650 K and 1100 K, NO increases the rate of hydrocarbon oxidation. The temperature range of sensitization effects of NO on hydrocarbon oxidation coincides with that of the operation of HCCI engines.

Several reaction mechanisms are available in literature that can capture the sensitization of NO_x on oxidation of hydrocarbons. Among many, Farvelli et al. [9], Glaude et al. [10], and Dagaut and Nicolle [6] developed reasonably accurate detailed reaction mechanisms for smaller hydrocarbons including methane, ethane, ethylene, propane, *n*-butane, and *n*-pentane. But, it is only recently that the low temperature sensitization chemistry for methane and ethane has been described in detailed by Rasmussen et al. [11]. They developed a detailed reaction mechanism for NO-methane oxidation that is valid over a wide range of pressures. Despite availability of several reaction mechanisms, no single self-consistent, accurate, and validated mechanism is available for simulation of complex gasoline surrogates under the conditions of HCCI engine. We have developed a self-consistent detailed reaction mechanism to describe the combustion of gasoline under engine conditions [12]. The mechanism is built based on established literature mechanisms [13, 14] using rate-rules based approach for. This mechanism has been extensively validated using many available fundamental data in literature [15, 16]. The main goal of this work is to extend the established gasoline surrogate mechanism to include a comprehensive NO_x chemistry sub-mechanism and to capture the NO_x -hydrocarbon sensitization effect on gasoline oxidation at lower temperatures.

GASOLINE SURROGATE AND ITS MECHANISM DEVELOPMENT

A surrogate for a typical U.S. street gasoline has been proposed in a companion publication by Naik et al. [17]. The surrogate composition was determined by optimizing a match

between the surrogate-fuel properties and the gasoline street fuel properties. The blend captures chemical and physical properties of a URL gasoline in the USA, as shown in Table 1. The composition of the gasoline surrogate is also shown in Table 1.

Table 1. Model fuels for typical U.S. gasoline based on the proposed methodology [17] and the data collected. Some of the blend properties are also shown. Composition is in mole %.

Components	Surrogate
1-Pentane	8.7
<i>n</i> -Propylbenzene	19.3
Toluene	11.6
Methylcyclohexane	7.6
<i>iso</i> -hexane	19.9
<i>iso</i> -Octane	21.3
<i>n</i> -Pentane	7.4
<i>n</i> -Heptane	4.1
Research Octane Number	90.6
Motor Octane Number	85.8
Molar H/C Ratio	1.89
Lower heating value (MJ/kg)	43.8

In addition to defining the blend, we have developed a detailed self-consistent reaction mechanism that includes many hydrocarbon fuel components for use in surrogate blends for gasoline. These components and the initial sources of the kinetics data used in the mechanism are listed in Table 2. Through attention to self-consistency across fuel sub-mechanisms, thermodynamic reversibility, and addition of missing reaction paths and new sub-mechanisms, we have significantly improved the predictions of the comprehensive mechanism for many components compared to their initial literature sources. Improvements to the smaller hydrocarbon core mechanism and its validation, for example, has been discussed elsewhere [16].

Building on this validated gasoline surrogate mechanism, we then extended it to include a comprehensive reaction mechanism for NO_x that is applicable over a wide range of conditions found in internal combustion engines. Several recently published mechanisms have been included in the comprehensive NO_x sub-mechanism. As seen in Table 3, three main sources of mechanism data provide the dominant NO_x chemistry effects under different temperature ranges. The GRI-mech 3.0 NO_x sub-mechanism includes major NO_x formation pathways for thermal and prompt NO. However, these pathways were validated only for high-temperature flame conditions. Dagaut et al. [18] reviewed the HCN chemistry and developed a mechanism containing formation pathways including N_2O and NNH pathways that are important for producing prompt-NO and for nitrogen-containing fuels. This chemistry is important for the medium-temperature regime. The Dagaut et al. mechanism was added

Table 2. Components in gasoline surrogate mechanism and their sources of initial mechanism.

No.	Component	Component class	Mechanism source
1	<i>n</i> -Butane	<i>n</i> -alkane	Curran et al. [13]
2	<i>n</i> -Pentane	<i>n</i> -alkane	Curran et al. [13]
3	<i>n</i> -Hexane	<i>n</i> -alkane	Curran et al. [13]
4	<i>n</i> -Heptane	<i>n</i> -alkane	Curran et al. [13]
10	<i>iso</i> -Pentane	<i>iso</i> -alkane	Curran et al. [14]
11	<i>iso</i> -Hexane	<i>iso</i> -alkane	Curran et al. [14]
12	<i>iso</i> -Octane	<i>iso</i> -alkane	Curran et al. [14]
14	1-pentene	Olefin	Naik et al. [12]
15	2-pentene	Olefin	Naik et al. [12]
16	1-hexene	Olefin	Naik et al. [12]
17	2-hexene	Olefin	Mehl et al. [19]
18	3-hexene	Olefin	Mehl et al. [19]
19	MCH	Cyclo-paraffin	Pitz et al. [20]
20	Toluene	1-ring aromatics	Naik et al. [21]
21	n-Propylbenzene	1-ring aromatics	Naik et al. [12]
22	o-Xylene	1-ring aromatics	ENSIC [22]
23	m-Xylene	1-ring aromatics	ENSIC [22]
24	p-Xylene	1-ring aromatics	ENSIC [22]
26	Ethanol	Oxygenates	Marinov et al. [23]
A	NO _x		Multiple sources [11, 18, 24]
B	PAH		Multiple sources [25-27]

Table 3. The literature sources considered for the comprehensive NO_x sub-mechanism.

No.	Mechanism source	Included NO _x chemistry	Temperature range of importance
1	GRI 3.0 [28]	Thermal-NO _x , Prompt NO, Reburn chemistry	High
2	Dagaut et al. [18]	HCN chemistry, N ₂ O and NNH chemistry	Medium
3	Rasmussen et al. [11]	NO _x -hydrocarbon chemistry	Low

to the GRI-based NO_x sub-mechanism. Rasmussen et al. [11] developed a mechanism focused only on sensitization effects of NO on methane and ethane oxidation at low temperatures over a broad range of pressures. The NO_x chemistry from these three mechanisms was extracted and systematically merged to create a new comprehensive reaction set included in the gasoline mechanism, which was then used as a starting point for further improvement.

<table 2, 3 here>

For modeling gasoline combustion in engines, it is important to consider the interactions of NO_x with the larger hydrocarbon components of the surrogate, which was not addressed in previous studies. Such reactions could have a significant impact at low temperatures, and under these conditions the NO-sensitization effect may not be sufficiently captured by only including NO_x reactions with methane and ethane. Therefore, reactions of larger hydrocarbons with NO_x are included in the current gasoline surrogate mechanism. The low- to mid- temperature (600-1100 K) NO_x-HC chemistry can be described by the scheme shown in Table 4. Here, R· represents alkyl and phenyl radicals and RO₂·

represents their peroxy radicals. Reactions 2, 6, and 7 are important for inhibition effects of NO of hydrocarbon oxidation. Reaction 6 represents the inhibition reaction in the reverse direction. These reactions scavenge OH, HO₂, and R· radicals produced at very low temperatures below 650K. At low temperatures, HONO acts as a sink for OH radicals, as in Reaction 6. In the range of 650K to 1100K, NO is converted to NO₂ via Reaction 1 and 2. NO₂ is then converted to HONO via Reaction 3 to 5. Reaction 5 also converts formaldehyde into the more reactive formyl radical. HONO then acts as a source of OH via the dissociation path of Reaction 6 and also regenerates NO. Since NO₂ is recycled back to NO, it has a catalytic effect on hydrocarbon oxidation. At higher temperatures Reactions 8 and 9 become important and the production of NO₂ via Reactions 1 and 2 diminishes. This reduces the catalytic effect of NO_x on hydrocarbon oxidation. Since NO - NO₂ conversion is very fast and reaches partial equilibrium quickly, the impact on hydrocarbon oxidation is indistinguishable for similar ppm levels of NO or NO₂ under HCCI engine conditions. Therefore, when we refer to NO_x-hydrocarbon sensitization effect, it usually apply to both NO or NO₂ as NO_x.

Table 4. The low- to mid-temperature NO_x-hydrocarbon sensitization scheme. R• represents alkyl and phenyl radicals and RO₂• represents their peroxy radicals.

No.	Reaction
1	NO+RO ₂ • = NO ₂ +RO•
2	NO+HO ₂ = NO ₂ +OH
3	NO ₂ +HO ₂ = HONO+O ₂
4	NO ₂ +CH ₃ O• = HONO+CH ₂ O
5	NO ₂ +CH ₂ O = HONO+HCO
6	HONO(+M) = NO+OH(+M)
7	R•+NO ₂ = RNO ₂
8	R•+NO ₂ = RO•+NO
9	NO ₂ +H = NO+OH

To apply the NO_x-hydrocarbon scheme discussed above to higher hydrocarbons, rate rules for several types of reactions were derived (Table 5). In the current mechanism, reaction types shown in Table 5 were included for all alkyl radicals up to C₅. Additional alkyl radicals for only parent fuel species heptyl, octyl, and phenyl were considered. New species included in the updated mechanism are shown in Table 6 with reference values for their respective thermodynamic data. Thermodynamic data were estimated based on group additivity. The new NO_x mechanism contains 50 species and 354 reactions. Reactions of NO_x with higher hydrocarbons for components of diesel surrogates may be important and will require further extensions to the NO_x sub-mechanism.

Table 5. Proposed rate-rules for extending the NO_x-hydrocarbon kinetics to higher hydrocarbons. Rate constants are given by modified Arrhenius equation as $k=A \cdot T^n \cdot \exp(-E_a/RT)$. Units are mol, cm, K, cal. R• represents alkyl and phenyl radicals and RO₂• represents their peroxy radicals.

Reaction Type	A	n	E _a
RO ₂ •+NO = RO•+NO ₂	1.60E+12	0	-755
R•+NO ₂ = RO•+NO	4.00E+13	-0.2	0
R•+NO ₂ = RNO ₂ †	6.00E+12	0	0
RNO ₂ +•OH = ROH+NO ₂	2.00E+10	0	-1000

†Considers high-pressure limits for C3 and higher alkyl- and phenyl-NO₂ systems.

Table 6. New species added in the current NO_x sub-mechanism and their estimated thermodynamic properties.

Species name	Molecular Structure	ΔH _f ²⁹⁸ (kcal/mol)	S ²⁹⁸ (cal/mol-K)
c2h3no2		8.00	72.04
c6h5ch2no2		6.91	98.95
c7h15no2-1		-49.96	122.94
c7h15no2-2		-55.93	120.99
c7h15no2-3		-55.93	120.99
c7h15no2-4		-55.93	120.99
nc3h7no2		-30.23	85.26
pc4h9no2		-35.16	94.68
c5h11no2-1		-40.09	104.10