Fuel 235 (2019) 495–503

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The impact of nitric oxide on knock in the octane rating engine

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ARTICLE INFO

Keywords:
Nitric oxide
Engine knock
Autoignition
CFR engine

ABSTRACT

Nitric oxide (NO) is a trace species that is always present in reciprocating engines, and can significantly affect fuel autoignition. This work presents a systematic investigation of the impact of NO on fuel autoignition in a standard, octane rating engine. Knock onset timing is investigated over a wide range of equivalence ratios, intake temperatures, and fuel compositions with increasing levels of NO added via the engine intake. NO is observed to both promote and retard autoignition in different cases. In particular, NO added via the engine intake can often promote autoignition when the engine is operated at sufficiently rich conditions such that there is negligible, combustion-induced residual NO in the fresh charge. Increasing the intake air temperature with iso-octane fuelling further enhances NO's promoting effect. The promoting effect of NO is also found to be stronger for fuels containing higher toluene and ethanol content rather than paraffins, suggesting that the autoignition of fuels with higher octane sensitivity is also more sensitive to NO addition. These observed impacts of NO are discussed using a current understanding of the interaction chemistry between NO and the studied fuels. This suggests that new, fuel-specific NO mechanisms are required as an integral part of the kinetic modelling of engine combustion.

1. Introduction

Knock in spark ignition (SI) engines fundamentally limits engine efficiency, and is a process that results from the interaction of the fuel autoignition chemistry and the thermo-chemical conditions inside the engine cylinder. For reciprocating engines, these in-cylinder conditions commonly involve the products of combustion as part of the auto-igniting mixture due to the presence of residual gases. The increasing use of exhaust gas recirculation (EGR) to control engine emissions and to enable advanced, low temperature combustion [1] also makes the residual combustion products even more significant in the engine autoignition process.

Amongst the various combustion products, nitric oxide (NO) has been reported to have a pronounced and complex impact. NO was reported to promote autoignition (and therefore knock) of iso-octane in SI engines [2–5] and in homogeneous charge compression ignition (HCCI) engines [6–9]. For example, Sheppard et al. [3] reported that knock onset of iso-octane in an optical SI engine was monotonically advanced with increasing NO addition up to 387 ppm. Contino et al. [9] studied the impact of NO (from 0 to approximately 500 ppm) in an HCCI engine and found that the CA50 (50% mass fraction burnt point) of iso-octane was consistently advanced as more NO was added.

This promoting effect of NO was, however, generally observed at low levels of NO addition or high autoignition temperatures, with high levels of NO addition at low temperatures found to retard autoignition [2,3,6,7,10]. For example, Prabhu et al. [11] conducted a motored engine study using PRF81 (iso-octane/n-heptane mixture at 81:19 ratio by volume), and reported that for intake temperatures below 70 °C, NO addition up to 100 ppm promoted the fuel autoignition as indicated by the CO formation, but higher levels of NO addition inhibited the reactivity. A similar, non-monotonic impact was reported by Dubreuil et al. in an HCCI engine [6] fueled with n-heptane and the mixtures of n-heptane/iso-octane and n-heptane/toluene with research octane numbers (RON) of 25 and 24, respectively. They found that the first-stage ignition (low temperature heat release) was advanced with NO addition up to 100 ppm but was delayed by further NO addition. The second-stage ignition (hot ignition) was also advanced with NO addition up to 100 ppm but remained almost unaffected at higher NO levels.

The impact of NO has also been reported to be fuel dependent. Sheppard et al. [3] reported that NO tended to suppress the autoignition of fuels with strong negative temperature coefficient (NTC) behaviors (e.g. paraffins), but promote the autoignition of fuels with weak NTC behaviors (e.g. aromatics). More fundamental experiments have also been conducted in flow reactors, jet stirred reactors, and a rapid compression machine to understand the chemistry between NO and C1-C5 hydrocarbons [12–19], n-heptane, iso-octane and toluene [6,20,21]. Similar to the engine studies, the impact of NO in these experiments exhibited a complex dependence on temperature, NO concentration and

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https://doi.org/10.1016/j.fuel.2018.08.039
Received 21 April 2018; Received in revised form 13 July 2018; Accepted 9 August 2018
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fuel composition [21].

Such investigations show that the impact of NO in SI engines is complex and challenging to study experimentally. This is in part because NO in the residual gases varies with engine operating conditions. Techniques such as skip-firing [2,3] and Ar-O_2 combustion [4] have been used to remove the impact of residual NO at the cost of altering the engine combustion environment. Also, production engines are often unable to withstand continuous knocking combustion, and the borderline knocking condition commonly used in these engines makes it difficult to examine the impact of NO on engine autoignition.

To address such issues, this study therefore uses a Cooperative Fuel Research (CFR) engine, which is the standard octane rating engine [22,23] and is designed for continuous knocking operation. Fuel rich conditions are a focus in order to suppress combustion generated NO, thereby enabling study of the impact of NO addition via the engine intake. Although these conditions differ from normal, stoichiometric SI engine operation, they permit continuous firing and thus maintain more realistic temperatures for the cylinder walls and residual gases, both of which are important to autoignition. The adjustable compression ratio of the CFR engine further allows knocking to be studied over a wide range of operating conditions, particularly the varied intake temperatures, equivalence ratios and fuel compositions that are considered in this work.

2. Experimental methods

2.1. Engine setup

A Waukesha CFR engine is used in this work. The engine is in the standard setup for octane number testing with minor modification for this study. Engine specifications are shown in Table 1. A schematic of the setup is shown in Fig. 1. Ambient air is dehumidified by a chiller operating at 3.5 ± 1.5 °C. NO (10 vol% in N_2) is injected into the air flow upstream of a surge tank. Pure O_2 (99.999%) is added at the same location to maintain the intake O_2 at the same level as air (20.95%). The gases are mixed in the 10-L surge tank, where turbulence blades are used to facilitate mixing. An electrical heater is installed downstream of the surge tank to control the gas temperature (± 1 °C) for the mixed air and NO. A fraction of this gas mixture is sent to a Horiba exhaust emission bench for NO and O_2 measurement.

The fuel is supplied via a carburetor downstream of the heater, as per the standard setup of the CFR engine. The gas temperature past the carburetor is reduced due to fuel vaporization. The equivalence ratio (ϕ) is measured with a Bosch LSU 4.9 wideband universal exhaust gas oxygen sensor and a MoTeC Professional Lambda Meter. The detonation pickup and knock-meter are used to determine the baseline operating condition. The detonation pickup is then replaced by a Kistler (6125C) pressure transducer for the in-cylinder pressure measurement at 0.1 crank angle degree (CAD) resolution. Data acquisition is achieved with an in-house LabVIEW program.

Table 1
Specifications of the CFR engine.

Engine type	Single-cylinder, unthrottled, spark ignition
Combustion chamber shape	Pancake
Spark plug location	Side-mounted
Compression Ratio	Adjustable from 4:1 to 18:1
Cylinder Bore	82.55 mm
Connecting Rod	254.0 mm
Stroke	114.3 mm
Displacement	611.7 cm3
Fuelling	Carburettor
Number of Valves	2
Inlet Valve Closing	146°BTDC
Exhaust Valve Opening	140°ATDC

2.2. Definition of knock onset timing

The impact of NO on fuel autoignition is quantified by the resulting changes in knock onset timing. At each operating condition, the knock onset timing is determined from a single, representative cycle selected from the 600 cycles sampled. To ensure that the selected cycle is representative of the operating condition, the following cost function is used for which the minimum value is reached by the representative cycle

$$\mathrm{COST} = \left(\frac{MFB50_i - MFB50_{avg}}{MFB50_{avg}}\right)^2 + \left(\frac{KP_i - KP_{avg}}{KP_{avg}}\right)^2 \quad (1)$$

where MFB50 is the crank angle for 50% mass fraction burned and KP is the 'knock onset point'. Subscripts *i* and *avg* denote the value for the ith cycle and the average of all 600 cycles respectively. The MFB50 is evaluated with the approach developed by Rassweiler and Withrow [24]. The 'knock onset point' is defined as the crank angle where the second derivative of the pressure vs. CAD first equals 2000 kPa/deg^2 [25]. Figure 2 shows an example of a representative trace at the standard knock intensity (SKI) condition for iso-octane's RON test.

2.3. O_2 compensation

Since the NO used in this study is 10 vol% in N_2, the intake O_2% will be reduced as NO is added. To examine the impact of reduced O_2%, an O_2 displacement test is conducted, where pure N_2 is added at the engine intake to simulate the O_2 dilution from using the NO/N_2 mixtures. Experiments are conducted using PRF91 at a compression ratio of 6.73 and an intake temperature of 52 °C. Figure 3(a) shows representative pressure traces at different O_2 displacement levels. Retarding of the knock onset timing is observed as in Fig. 3(b). For example, a delay of knock onset by approximately 0.4 CAD results as O_2% drops from 20.95% to 20.75%, equivalent to 900 ppm NO addition. This is comparable to the effect of NO reported in previous engine studies [2,3]. Therefore, O_2 compensation is considered necessary and thus used throughout this study to maintain 20.95% O_2 at the engine intake.

2.4. NO-NO_2 conversion

The residence time of the NO/air mixture in the CFR engine intake system is approximately 5 s, during which NO could be potentially converted to NO_2. To evaluate the extent of conversion, tests are conducted with different NO addition levels at the intake air temperature (IAT) of 52 °C and 200 °C. Measurements are conducted between the point of NO addition and a point approximately 40 cm before the intake port (Fig. 1). The results are shown in Fig. 4, where the NO_2 formation is indicated by the difference between the NO_x and NO.

It is evident that NO_2 is only produced significantly at high temperature and high NO addition levels. NO_2 production is low for NO addition below 600 ppm where most of the experiments in this work are conducted. NO to NO_2 conversion in the engine intake is therefore considered insignificant in this study.

2.5. Test conditions

The CFR engine experiments adopt the RON-like conditions for all cases studied in this work. The conditions shared by these experiments are shown in Table 2.

2.5.1. Impact of NO at different engine operating conditions

Two engine operating parameters, the equivalence ratio and the intake temperature, are swept to study the impact of NO on the autoignition of iso-octane (Table 3). The equivalence ratio is first varied from 0.91 to 1.43 with a fixed intake air temperature of 52 °C (Set 1). Second, the IAT is varied from 52 °C to 200 °C with a fixed ϕ of 1.43 (Set

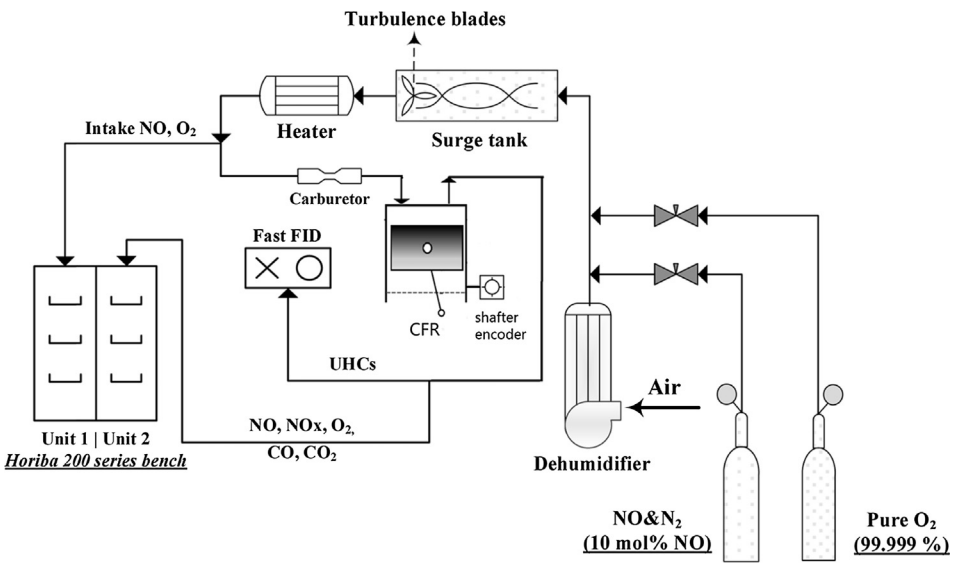

Fig. 1. Schematic of the experimental setup.

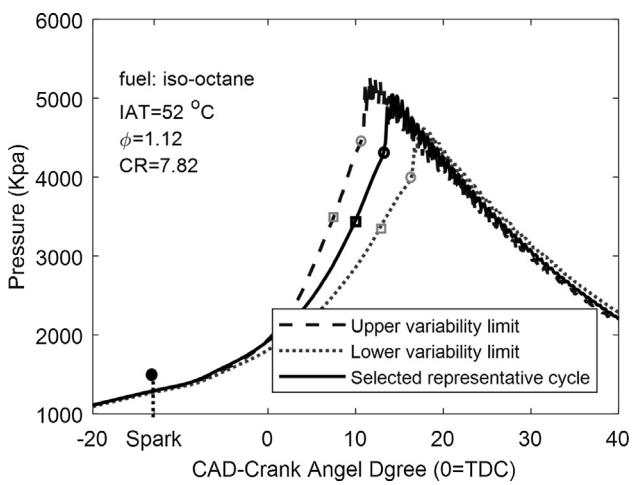

Fig. 2. In-cylinder pressure traces with MFB50 points (rectangles) and the knock-onset points (circles) shown.

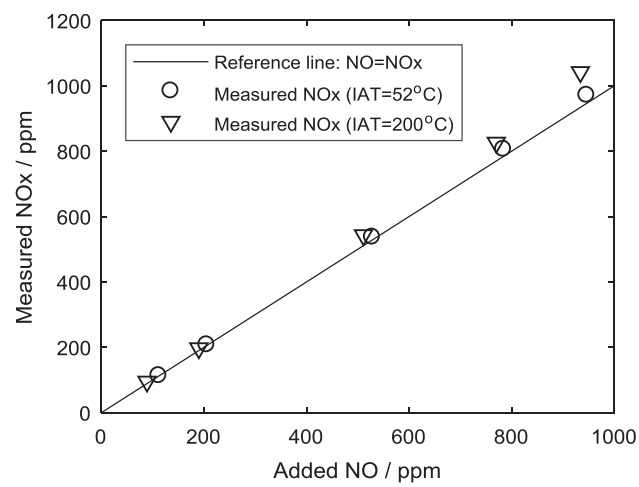

Fig. 4. Measured NO_x concentration at various levels of NO addition.

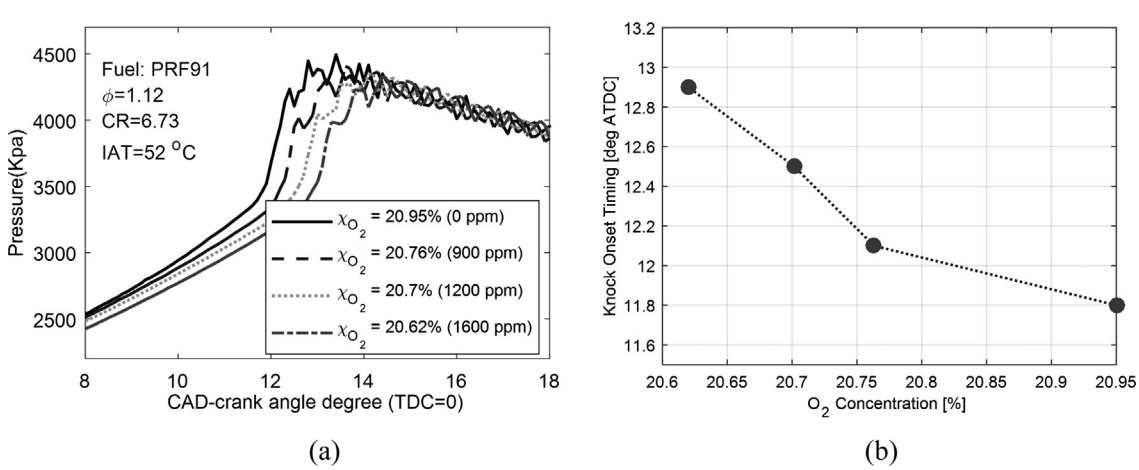

Fig. 3. (a) Representative pressure traces at different intake O_2% with ϕ = 1.12, CR = 6.73 and a constant spark timing of 13 CAD BTDC, which are equivalent to NO additions of 0 (—), 900 (– –), 1200 (· ·) and 1600 ppm (– ·) from a NO/N2 = 10/90 vol mixture, and (b) associated change of knock-onset timing.

Table 2
Engine operating conditions.

Engine speed	600 ± 6 rpm
Intake air pressure	atmospheric
Spark timing	13 CAD BTDC
Air temperature, dehumidified	3.5 ± 1.5 °C
Coolant temperature	100 ± 1.5 °C

Table 3
Test matrix for investigating the impact of NO under different operating conditions.

	IAT (°C)	ϕ	CR
Set1	52	1.43	8.55
		1.12[a]	7.82
		1	8.29
		0.91	8.83
Set 2	52	1.43	8.55
	100		8.64
	150		8.72
	200		9.33
Set 3	150	1.43	8.72
		1.12	8.19
		1	8.44
		0.91	8.81

[a] The 0 ppm NO condition of this case corresponds to that in the standard RON test of iso-octane.

2). Finally, a ϕ-sweep is conducted using IAT = 150 °C (Set 3). For each of the 12 cases in Table 3, NO is added at the intake from 0 to 800 ppm. The engine compression ratio is adjusted so that the knock-meter reads the standard knock intensity (50 ± 2) at all the baseline cases (0 ppm NO). The compression ratio is then kept constant for that case as various amount of NO is added.

2.5.2. Impact of NO with different fuels

To investigate the impact of NO on different fuel compositions, several gasoline surrogates are tested. This includes primary reference fuels (PRFs, mixture of iso-octane and n-heptane), toluene reference fuels (TRFs, toluene + PRFs), and ethanol reference fuels (ERFs, ethanol + TRFs). For TRFs and ERFs, toluene and ethanol are blended at 15, 30, and 45 vol% with iso-octane and n-heptane. In total, seven fuels are tested, and all have a RON of approximately 91. The composition of these fuels is shown in Table 4. The constant octane number allows a fixed compression ratio to be used. The knock onset timing and the impact of NO can therefore be investigated under comparable conditions.

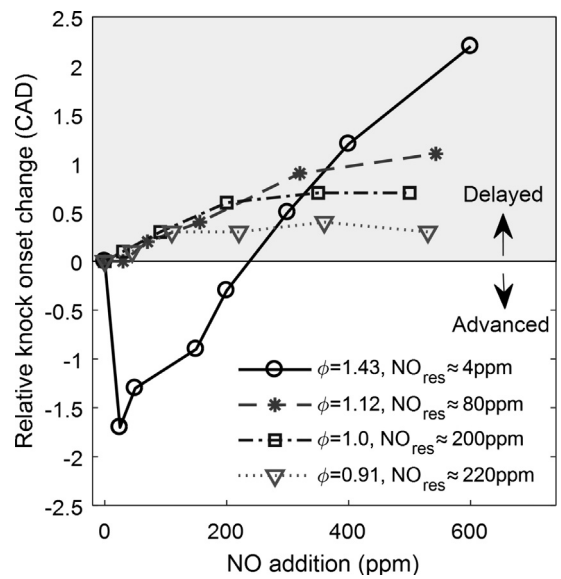

Fig. 5. Impact of NO on the knock onset timing of iso-octane at different ϕ with IAT = 52 °C.

To eliminate the impact of fuel vaporization on the knock onset, a constant intake mixture temperature (IMT) of 32 °C, measured downstream of the carburetor, is used for all test fuels. This is particularly important for ethanol-containing mixtures for which charge cooling varies significantly with ethanol content. The constant IMT of 32 °C is realized by adjusting the IAT as demonstrated in our previous study [27]. The 32 °C is used as it is the IMT of iso-octane tested at ϕ = 1.43 and IAT = 52 °C. This temperature is also consistent with the IMT = 36 °C reported by Foong et al. [27] for iso-octane's RON tests at a leaner condition (ϕ = 1.12).

3. Results and discussion

3.1. Impact of NO on iso-octane autoignition

3.1.1. Variation of the impact of NO with equivalence ratio (IAT = 52 °C)

The impact of NO on iso-octane autoignition is first studied at equivalence ratios at 0.91, 1.0, 1.12 (standard RON condition) and 1.43 with the intake air temperature fixed at 52 °C. Figure 5 shows the changes of knock onset timings from the 0 ppm NO baseline cases as a function of NO addition levels. For ϕ = 0.91, 1.0 and 1.21, NO addition delays the knock timing for all cases relative to the baseline. The maximum delay occurs at the higher levels of NO addition, which is

Table 4
Fuel matrix for investigating the impact of NO.

Fuel	PRF91	TRF91-15	TRF91-30	TRF91-45	ERF91-15	ERF91-30	ERF91-45
RON*	91	90.7	90.2	90.9	90.2	90.2	91.8
MON*	91	87.7	84.6	83.1	85.8	84.2	83.9
S	0	3	5.6	7.8	4.4	6	7.9
Toluene (v/v%)	0	15	30	45	0	0	0
Ethanol (v/v%)	0	0	0	0	15	30	45
Iso-octane (v/v%)	91	72.6	53	34.7	64.6	40	18
n-Heptane (v/v%)	9	12.4	17	20.3	20.4	30	37
IAT (°C)	55	60	67	74	69	76	82
IMT (°C)	32						
ϕ	1.43						
CR	7.4						

* RON and MON of TRFs and ERFs are calculated using correlations proposed in [26].
PRF – primary reference fuels, mixture of iso-octane and n-heptane.
TRF – toluene reference fuels, mixture of iso-octane, n-heptane and toluene.
ERF – ethanol reference fuels, mixture of iso-octane, n-heptane and ethanol.

0.4–1.2 CAD later than the baseline. The inhibiting effect appears to be weakened as equivalence ratio decreases.

However, for the richest case (ϕ = 1.43), a non-monotonic effect is observed. At the low NO levels, iso-octane's knock onset is advanced. A maximum promoting effect occurs around 25 ppm NO addition where the knock onset is advanced by approximately 1.7 CAD. As more NO is added, the knock onset is delayed, similar to the leaner cases. For > 200 ppm NO addition, the knock onset timing becomes later than the baseline, and the largest delay, approximately 2.2 CAD, is observed at the highest NO addition, ~600 ppm.

Figure 5 shows some noteworthy differences to the literature, in that NO does not promote iso-octane autoignition except for a few cases of ϕ = 1.43. In particular, as noted in the Introduction, Sheppard et al. [3] found that for stoichiometric iso-octane combustion, knock onset was always advanced further as more NO was added. Their study was conducted in a skip-firing engine, where the engine fired every 7 cycles to remove the 'residual gases' so that the in-cylinder NO was the same as that added in the intake. In our experiments, however, residual NO is always present and varies with equivalence ratio. For example, at ϕ = 1.12, the exhaust NO is about 800 ppm, which corresponds to about 80 ppm residual NO given a residual fraction of 10%, as estimated in [28]. The residual NO fractions are even higher for ϕ = 0.91 and 1.0 cases. For these cases, therefore, the potential NO promoting effect (as observed for the ϕ = 1.43 case) is likely concealed by the residual NO, and the externally added NO only further suppresses iso-octane's autoignition. On the other hand, the richest case (ϕ = 1.43) produces a minimal amount of NO (i.e. about 40 ppm exhaust and 4 ppm residual), and therefore the promotion effect is exhibited.

3.1.2. Variation of the impact of NO with intake temperature

Previous experiments [11,17,20,21] and modeling [18,29,30] have shown that temperature has an important impact on NO related chemistry. To investigate this issue, four intake air temperatures, 52, 100, 150 and 200 °C, are studied with iso-octane and different amounts of NO. All the tests are performed at ϕ = 1.43 to minimize the effect of residual NO. In addition, the compression ratio is adjusted to achieve the standard knock meter reading (50 ± 2) at different IATs (Table 3). It is noted in Table 3 that the case with a higher IAT also requires a higher compression ratio to reach the same knock meter reading, suggesting that the end gas autoignition exhibits the negative temperature coefficient behavior at these intake temperatures. As a result, even higher temperatures are resulted for end gas autoignition, due to the simultaneously increased compression ratios and IATs.

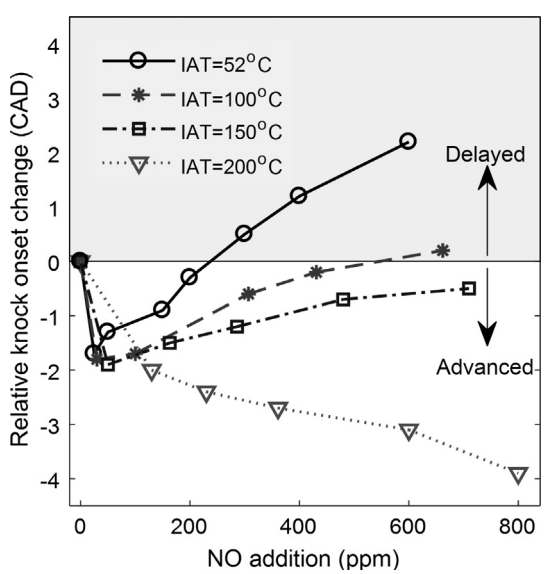

Fig. 6. Impact of NO on the knock onset timing of iso-octane at different IAT with ϕ = 1.43 (NO_{res} ≈ 4–6 ppm for all cases).

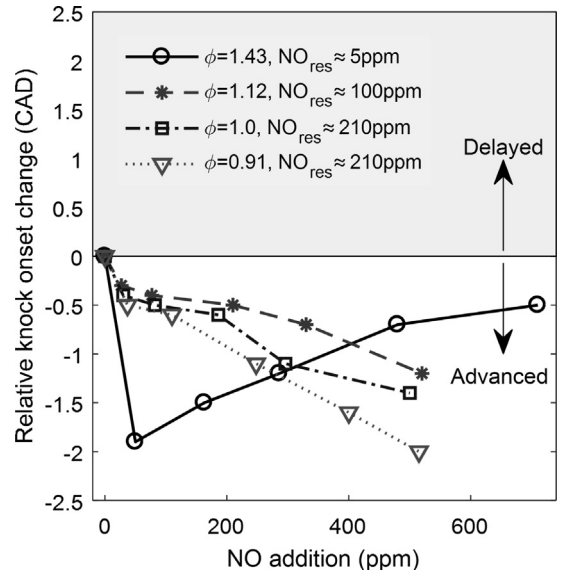

Fig. 7. Impact of NO on the knock onset timing of iso-octane at different ϕ with IAT = 150 °C.

Figure 6 summarizes the impact of NO on iso-octane knock onset at various IATs. With an IAT of 100 °C, a non-monotonic trend similar to that at 52 °C is observed, but the inhibiting impact is apparently weakened. At 150 °C, all knock onsets are advanced relative to the 0 ppm NO case, although the strongest promotion impact is still at ~25 ppm NO. At IAT of 200 °C, a monotonic promoting effect is finally observed, where the strongest promotion occurs at the highest NO addition of 800 ppm and the knock onset is advanced by approximately 4 CAD.

3.1.3. Variation of the impact of NO with equivalence ratio (IAT = 150 °C)

Further experiments are conducted to examine the equivalence ratio effect at a higher IAT of 150 °C. Figure 7 now shows a mostly promoting effect at this higher intake temperature. Particularly, monotonic promoting trends are observed at all equivalence ratios except ϕ = 1.43, despite the fact that significant amounts of residual NO exist in the three leaner cases. This different effect from the case at 52 °C (Fig. 5) is likely because at IAT of 150 °C, the NO/hydrocarbon reactions take place in a regime where more NO always further promotes knock, as observed typically at high temperatures, e.g. [11,17,20,21].

It is noted that for ϕ = 0.91, 1.0 and 1.12, leaner mixtures produce stronger promoting effect, which is consistent with Fig. 5 in that leaner mixtures produce weaker inhibiting effects. These results, however, need to be understood in the context that the residual NO fraction is higher at leaner conditions. Also, the species composition of residual gases varies with equivalence ratios. Detailed understanding of these factors is beyond the scope of this work and will be the topic of future studies.

3.2. Variation of the impact of NO with fuel composition

3.2.1. Toluene reference fuels

To investigate the impact of NO on different fuels, PRF91 and three TRF91 are tested under similar engine conditions as listed in Table 4. The results are shown in Fig. 8. With ϕ = 1.43 and IAT = 52 °C, an overall similar trend is observed for these fuels in that the low NO additional levels promote autoignition, but further NO additions reduce the promotion effect and even inhibit knock onset at the highest NO levels in some cases (e.g. PRF91 and TRF91-15). This non-monotonic trend is similar to that observed for iso-octane at the same IAT and equivalence ratio (Fig. 5).

It is also evident that the impact of NO strongly depends on fuel

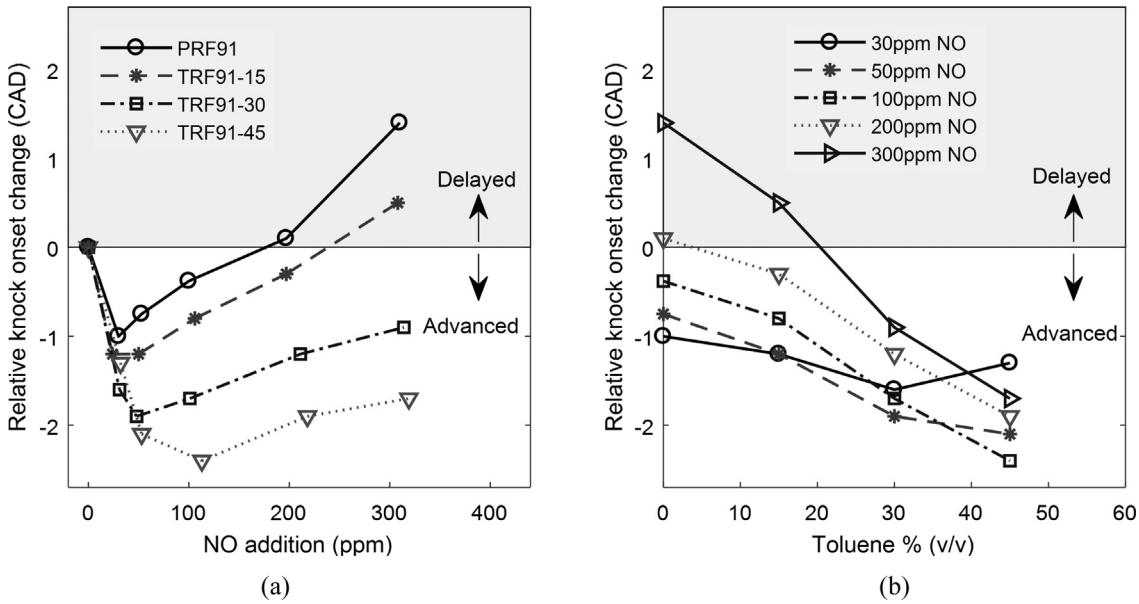

Fig. 8. Impact of (a) NO concentration and (b) toluene content on knock onset of different TRFs with ϕ = 1.43, IMT = 32 °C and constant CR of 7.4.

composition. The promotion effect is apparently stronger for fuels of higher toluene content, despite the similar RONs. This is evidenced by TRF91-45 producing the largest advance in knock onset timing. Figure 8(b) replots these results to further illustrate the influence of toluene content. It is observed that the promoting effect of NO is enhanced as the toluene content increases from 0 to 45%. Nevertheless, the effect of toluene content is apparently dependent on NO addition levels. For example, at 30 ppm NO addition, the knock onset is promoted similarly by approximately 1 CAD for PRF91 and the three TRFs. However, at 300 ppm NO addition, the knock onset of PRF91 is *inhibited* by about 1.5 CAD whereas that of TRF91-45 is *promoted* by 2.5 CAD. Such results could be useful in understanding the knocking behaviors of different gasoline in SI engine combustion.

3.2.2. Ethanol reference fuels

Three ethanol/PRF mixtures, ERF91-15, ERF91-30 and ER91-45, are now tested under the same operating conditions (Fig. 9). Similar to the toluene cases, lower levels of NO addition significantly promote knock onset but further NO addition reduces the promotion effect or has little extra effect. Figure 9(b) demonstrates the effect of ethanol content on the impact of NO where, similar to the TRFs, the impact of NO is nearly invariant with the ethanol content at 30 ppm NO, but becomes increasingly sensitive to the ethanol content as more NO is added. In particular, at 300 ppm NO addition, the knock onset of ERF91-45 is advanced by approximately 3 CAD whereas that of PRF91 is retarded by approximately 1.5 CAD.

These results indicate that NO is more effective in promoting the autoignition of fuels containing more aromatics or alcohol at the engine operating conditions studied. Contino et al. [9] reported that the NO promotion effect in an HCCI engine was more pronounced with increased octane number. However, since the seven fuels studied here have a similar RON, other fuel properties should be important. A major difference between toluene/ethanol and paraffins is the octane sensitivity (S) which is the difference in the Research and Motor octane number (MON), as shown in Table 4. Therefore, the impact of NO is plotted against the S values of the TRFs and ERFs in Fig. 10, where the

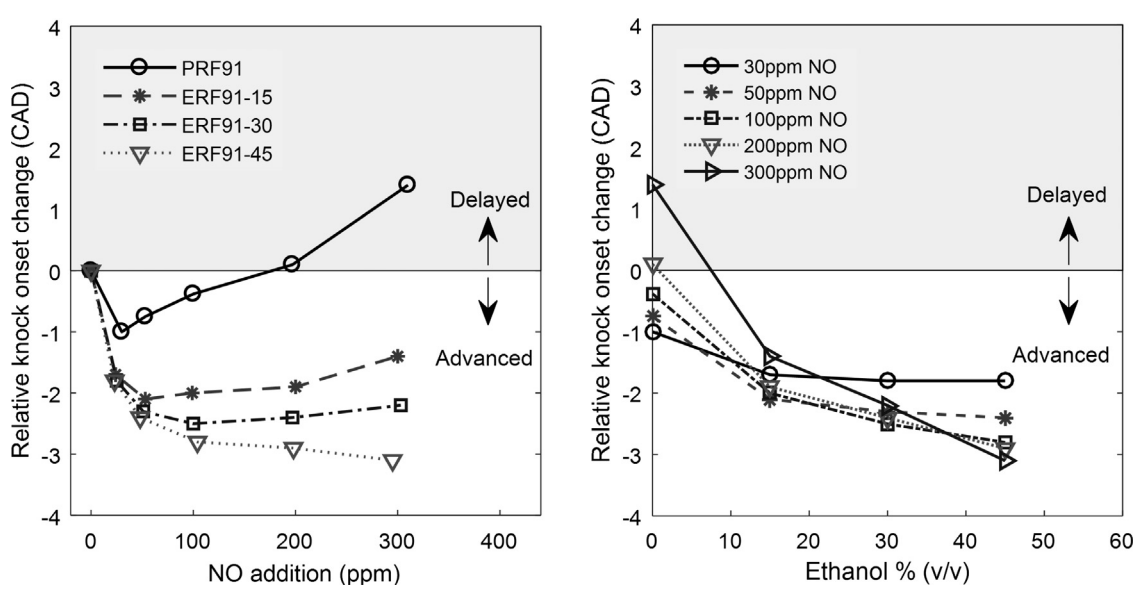

Fig. 9. Impact of (a) NO concentration and (b) ethanol content on knock onset of different ERFs with ϕ = 1.43and IMT = 32 °C and constant CR of 7.4.

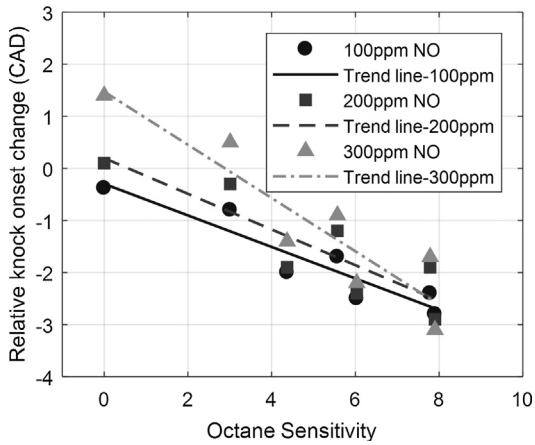

Fig. 10. Knock onset timing as a function of octane sensitivity (reploted from the TRFs and ERFs data in Figs. 8 and 9).

NO promoting effect on knock onset becomes increasingly prominent as S increases. The trend is not surprising given the results shown in Figs. 8(b) and 9 (b), and is consistent with Sheppard et al. [3] who proposed that NO tends to promote the autoignition of fuels with weak NTC behavior (e.g. aromatics and ethanol) and suppress the autoignition of fuels with strong NTC behavior (e.g. paraffins). It was also interesting to note that the fuels of high octane sensitivity are also more sensitive to the NO promotion effect in their autoignition. Discussion on NO's stronger promotion effect on toluene and ethanol is conducted in the following.

3.3. Discussion on NO/fuel interaction chemistry

It should be noted that the NO addition can potentially affect both the end gas autoignition and the flame propagation. The knock onset timings measured reflect the combined impact of NO on both processes. The impact of NO on flame speed is therefore examined by investigating the variation of the CA50 of the CFR engine combustion with increasing NO addition. Results for iso-octane at different IATs with $\phi = 1.43$ are shown in Fig. A1 in the Appendix, which indicate that the CA50 at all IATs is much less affected by NO addition than the knock onset timing. Similar results appear for the TRFs and ERFs studied, as shown in Figs. A2 and A3. Together, these results provide good evidence that NO has a smaller impact on flame propagation than on the autoignition chemistry. Therefore, the discussion in the following is focused on the impact of NO on the autoignition chemistry. Note that such impact has been explained in detail in the literature, e.g. [6,9,21,29–31]. This section applies the existing understanding to qualitatively interpret the trends of the impact of NO observed in this work.

3.3.1. Temperature effect

Figure 11 summarizes the impact of NO on the oxidation/autoignition of hydrocarbons [21]. In the absence of NO, hydrocarbon oxidation starts with H-abstraction from the fuel (RH), followed by the ROO and QOOH steps, leading to degenerate chain branching. Adding NO introduces new reactions. For example, NO can react with HO_2 (R1) and produce a reactive OH radical to accelerate oxidation. On the other hand, NO can also react with OH (R2) and produce a low reactivity HONO radical to slow down the oxidation. Another type of reaction is NO with RO_2 radicals (R3), which in some cases promote ignition, due to RO_2 being converted to a more reactive RO radical, but in other cases inhibit ignition, due to consumption of the ROO radical which could otherwise react in the low temperature branching channel to accelerate autoignition.

$$NO + HO_2 \leftrightarrow NO_2 + OH \quad (R1)$$

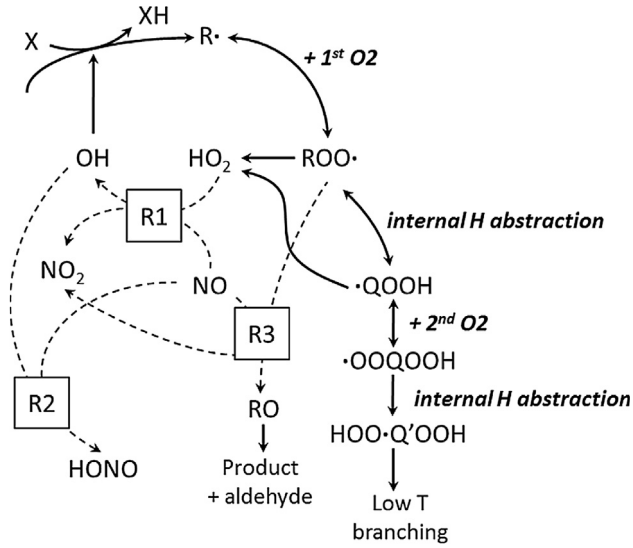

Fig. 11. Schematic of low temperature hydrocarbon oxidation without NO (solid line) and with NO (dashed line) [21] .

$$NO + OH + M \leftrightarrow HONO + M \quad (R2)$$

$$NO + RO_2 \leftrightarrow NO_2 + RO \quad (R3)$$

The variation of the impact of NO with temperature, as shown in Fig. 6, can also be understood using these reactions. For example, at the IAT of 52 °C, the addition of the first 25 ppm NO can react with HO_2 via R1, producing OH and promoting the autoignition of iso-octane. With further NO addition, NO starts to react via R2, which inhibits the chain reactions. R3 can also be inhibiting as the conversion of $C_8H_{17}O_2$ to $C_8H_{17}O$ bypasses the low temperature degenerate branching and consequently slows down the autoignition process. This can be particularly important at high NO addition levels, e.g. ≥ 300 ppm cases in Fig. 6. As the IAT increases, higher compression ratio is required for maintaining a same knock intensity (Table 3), suggesting that the end gas autoignition overall experiences the NTC behavior. During this, less RO_2 is formed as the higher temperatures favors RO_2 decomposition. Consequently, more HO_2 is formed from the decomposition of QOOH and ROO radicals [32]. With abundant HO_2 in the mixture, R1 can remain important even at high NO addition levels and thus produce stronger promotion impact. Moreover, higher temperatures favor the reverse reaction of R2 and produce OH instead of consuming OH [33]. R3 in this case is less relevant due to the decomposition of RO_2.

3.3.2. Fuel composition effect

Ignoring the impact of NO on the flame propagation (as indicated by Figs. A2–A3), the variation of the impact of NO with the TRFs and ERFs can be attributed to the low temperature oxidation chemistry of toluene and ethanol. Toluene oxidation at low temperatures is primarily via the resonance-stabilized benzyl radicals (C_6H_5-CH_2), which is inherently slow. In the presence of NO and NO_2, however, other reaction pathways can be opened, i.e. R4 and R5, as suggested by Anderlohr et al. [29]

$$Benzyl + NO_2 \rightarrow C_6H_5CH_2\ O + NO \quad (R4)$$

$$Benzyl + NO_2 \rightarrow C_6H_5CH_2NO_2 \quad (R5)$$

Reaction R(4) converts a stable benzyl radical to a more reactive benzyloxy radical (C_6H_5-CH_2O), which accelerates the overall oxidation in two ways. First, it accelerates the production of benzyloxy radical, which is considered as a key step in toluene oxidation [29]. Second, it converts NO_2 back to NO which can react via R1 again to produce another OH in a catalytic manner. This argument is consistent with the observation that higher toluene content further enhances the NO promoting effect in the previous and the present studies [20,33]. On the

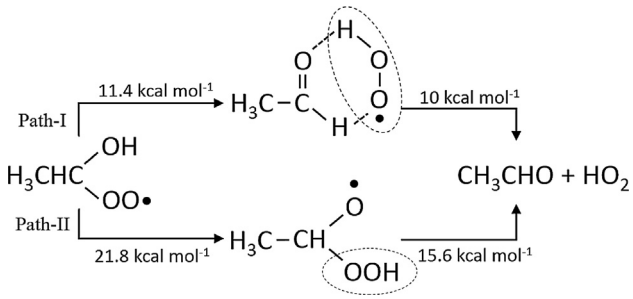

Fig. 12. C–H bond dissociation energies for ethanol (kcal mol^{-1}) [34] .

other hand, benzyl radicals can also be combined with NO_2 to form a $C_6H_5CH_2NO_2$ through R5, competing with R4 and inhibiting the autoignition [29]. However, this channel appears to be less significant under conditions investigated in this work.

Ethanol also exhibits low reactivity in the low temperature oxidation. This is due to the preferred HO_2 formation during ethanol's low temperature oxidation. Ethanol's low temperature oxidation starts most likely via the hydrogen abstraction on the α-carbon (the carbon connected to –OH) due to the weak α-C–H bonds. Following the O_2 addition, the formed α-hydroxy-ethylperoxy radical ($CH_3CHO_2{\cdot}OH$) can readily lose an HO_2 radical and form acetaldehyde (CH_3CHO). This can be achieved via multiple pathways and some have a particularly low energy barrier, as shown in Fig. 12 [34]. This results in abundant HO_2 and acetaldehyde in the ethanol reaction mixture, which are relatively stable at low temperatures and is a primary reason for the superior anti-knock performance of ethanol in SI engine combustion. However, in the presence of NO, the stable HO_2 radicals can react with NO and produce reactive OH radicals via R1, thus accelerating the oxidation. A similar argument has been proposed by Alzueta et al. [35].

3.4. Implications for kinetic modelling of engine combustion

These results are thought to have some significant implications on the kinetic modeling of engine combustion. First, the data suggest that the interaction chemistry between NO and fuel should be included as an integral part of a fuel's combustion mechanism. This considers the ubiquitous existence of NO in practical engines (including gas turbines) making NO a natural constituent of the reacting mixtures for engine autoignition. On the other hand, engine combustion behaviors, particularly those related to autoignition, should be understood in the context of NO presence. For example, RON and MON should be regarded as a property of not only the fuel, but also a property dependent on the in-cylinder NO concentration when the fuel is tested, as well as on the engine operating conditions (e.g. charge temperature, pressure, equivalence ratio) that can affect the NO and fuel interactions. Related studies by the group (e.g. [25]) suggest that these effects of NO are significant in determining fuel octane.

It is also expected that NO/fuel interaction chemistry should be developed on an individual basis for different fuels, given the different results for PRF, TRFs, and ERFs under similar conditions. This additional onus on mechanism development comes from the need to include fuel specific species, e.g. RO_2 radicals (R3) or benzyl radical for toluene (R4 and R5), to describe the interaction chemistry, and also from the need to calibrate the HO_2 and OH formations that are critical for the impact of NO but unlikely to be modelled by the baseline fuel mechanism to the required accuracy. Such fuel specific development of the NO mechanism is not trivial but highlights the need for quality experiments in fundamental reactors and in engines, as well as consistent mechanism development to minimize the chances of imprudent mechanism tuning.

4. Conclusion

This work investigated the impact of NO on knock onset in a CFR octane rating engine under constant knocking, continuous firing conditions. The influences of engine intake temperature, charge equivalence ratio, and fuel composition on the impact of NO were investigated with 0–800 ppm NO added via the engine intake. Major conclusions of this work are as follows.

- Temperature strongly affected the impact of NO on fuel iso-octane. With an engine intake temperature of 52 °C, NO advanced the knock onset of iso-octane ($\phi = 1.43$) only up to 200 ppm, with a peak promotion at 25 ppm, and then inhibited it as more NO was added. The promotion effect became much stronger as temperature increased, where the knock onset is monotonically advanced with increasing levels of NO at the intake temperature of 200 °C.
- The impact of NO on iso-octane autoignition was affected by the mixture equivalence ratio. This effect, however, was complicated by the varying amounts of residual NO at different equivalence ratios and also strongly affected by the charge temperature.
- The impact of NO varied with fuel chemical composition. The seven gasoline surrogate fuels of a similar octane number showed that higher contents of toluene and ethanol led to stronger promotion effects which correlated to an increase of the octane sensitivity in these fuels.

These observed impacts of NO were attributed to the interaction between NO and autoignition chemistry of the fuels, and then interpreted by the current understanding on this topic from the literature. This suggested that new, fuel-specific NO mechanisms are required as an integral part of the kinetic modeling of engine combustion.

Acknowledgement

This project is supported by the Australian Research Council, Australia (DP140100846).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.fuel.2018.08.039.

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