

## An Experimental Investigation of the Effect of Nitric Oxide (NO) on Knock Onset in a Spark-Ignition Engine

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### Abstract

This paper studies the effect of nitric oxide (NO) on the onset of knock in a cooperative fuel research (CFR) engine. The experiments are conducted at both the standard knock intensity (SKI) condition for research octane number (RON) tests, as well as at a richer operating condition of a similar knock intensity but a higher compression ratio. Iso-octane is the fuel. The experiments show clearly that knock onset is consistently suppressed with increasing NO additions at the SKI condition. However, different trends are seen at the richer condition, with increased NO addition first advancing knock onset and then retarding it. Using established chemical models of the interaction between NO and hydrocarbons from the literature, these differing results are argued as most likely due to the different concentrations of residual NO at these different engine operating conditions. The authors' planned kinetic modelling at these conditions will confirm whether these arguments are correct.

### Introduction

The past century has witnessed enormous progress in engine research and development, particularly in recent decades in response to the increasing concerns of air pollution, energy efficiency, and greenhouse gas emissions. A number of advanced techniques have been employed to address these issues in SI engines, among which exhaust gas recirculation (EGR) has the advantage of reducing combustion temperature and thus limiting NO<sub>x</sub> emissions.

Nonetheless, engine knock remains as an important factor limiting the development of SI engines [1]. SI engine knock is generally accepted as being caused by the propagating flame compressing the unburned fuel/air mixture until it autoignites. The autoignition process is highly dependent on the fuel chemical structure and the temperature/pressure history of the unburned gas [2]. Also, autoignition kinetics are sensitive to trace components in the unburned gas. Thus, the species in EGR can be important for determining knock.

Among these species, nitric oxide (NO) is of particular interest due to its complicated impact on autoignition. An SI engine study by Stenlass et al. showed that with NO addition, knock onset of gasoline was advanced [3]. A similar effect was found in [4], which showed the knock onset of iso-octane was advanced with NO. Studies in homogeneous charge compression ignition (HCCI) engines have also observed similar impact on autoignition [5–8]. However, contradictory results have also been reported in the literature [4, 9–12], where autoignition (knock) can be either suppressed or promoted by trace amounts of NO addition. These studies suggested that effect of NO could vary with fuel structures [4, 9] and engine operating conditions [10, 13].

The chemical origin underlying the NO impact on the oxidation of hydrocarbons has been proposed [14–17]. The knock promoting effect is attributed to the reaction  $\text{HO}_2 + \text{NO} = \text{OH} + \text{NO}_2$ , where a reactive OH radical is produced from a less reactive  $\text{HO}_2$  via NO. The knock inhibiting effect is attributed to  $\text{OH} + \text{NO} + \text{M} = \text{HONO} + \text{M}$  reaction, where the reactive OH radical is removed via NO. However, due to the limited experiments available and the widely different experimental conditions used, further studies are needed for a comprehensive understanding of the NO-Hydrocarbon interaction mechanisms.

This paper therefore studies the influence of NO on the onset of knock in a CFR engine. Iso-octane is the fuel used. Experiments are conducted at two operating conditions: standard knock intensity conditions (SKI) for the research octane number (RON) tests and a quasi-SKI condition (details presented later in this paper). The effect of NO on knock onset is studied by adding 0–1000 ppm NO into the engine intake. The observed influence of NO addition on knock-onset and the related chemical reasons responsible are then discussed.

### Experimental Setup

#### CFR Engine

All experiments in this study were performed using a standard single-cylinder CFR engine at the University of Melbourne. The specification of the engine is detailed in Table 1. Standard knock rating instruments, including the detonation pickup and the knock meter, were used to set a baseline knocking condition for studying the NO effect. An air dehumidifier was used to control the humidity of the intake air. All experiments were performed at an engine speed of 600 rpm and an intake air temperature of 52 °C, and the ignition timing was set to be 13° crank angle before top dead centre (CA BTDC).

#### Fuel Supply

The fuel supply in the CFR engine was achieved by a carburettor and the fuel flow rate was controlled by adjusting the height of the fuel reservoir. A lambda sensor was installed at the exhaust manifold to measure the A/F ratio.

#### Air, NO & O<sub>2</sub> Supply

A schematic of the gas supply system is shown in Figure 1. The NO/N<sub>2</sub> (10%mol NO) and O<sub>2</sub> (99.999% purity) from gas cylinders were added into the intake air stream at separate locations. An air dehumidifier was installed upstream of the mixing point of air/NO/N<sub>2</sub>/O<sub>2</sub> to control the humidity of the intake air. Needle valves were used to control the flow rates of the NO/N<sub>2</sub> and O<sub>2</sub> flows such that the injected N<sub>2</sub> and O<sub>2</sub> had the same concentrations as the displaced air. To achieve homogeneous mixing, the gas mixture passed through a ~10 litre surge tank before entering the engine. Turbulence blades were

also placed upstream of the heater to enhance turbulence in the intake flow. A good mixing of the intake gas mixture is obtained by these two measures. The gas mixture was then heated by an electric heater to the required temperature.

Downstream of the heater, the intake mixture was sampled and analysed by a Horiba emission bench for the NO and O<sub>2</sub> concentrations. In this study, the NO concentration was varied from 0~1000 ppm and the O<sub>2</sub> concentration was maintained constant at 20.96%.

Table 1 Engine specification and test conditions

Test Engine		CFR engine
Compression Ratio	Adjustable 4:1 to 18:1	
Cylinder Bore (mm)	82.55	
Stroke (mm)	114.3	
Displacement (cm <sup>3</sup> )	611.7	
Equivalence Ratio	Adjustable	
Fuelling Method	Carburettor	
Throttle	Wide open	
Intake Air Temperature (°C)	52	
Engine Speed (rpm)	600	
Ignition Timing (° CA BTDC)	13	
Intake Air Humidity	Controlled by dehumidifier (Air chilled to ~2°C)	
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Fuel	iso-octane	
RON/MON	100/100	
A/F stoich	15.13	
Test Conditions	SKI	Quasi-SKI
Lambda	0.89	0.7
Compression Ratio	8.03	8.36

### Data Acquisition

In-cylinder knock intensity was measured using a detonation pickup and knock meter. In-cylinder pressures were then measured by a Kistler pressure transducer using the same port on the cylinder head as the detonation pickup. The output of the pressure transducer was amplified by a Kistler charge amplifier. The crank angle was measured using a shaft encoder connected to the engine crankshaft. Oil temperature, coolant temperature, intake temperature, exhaust temperature, manifold absolute pressure (MAP) pressure, spark timing, and in-cylinder pressure were measured and displayed using the data acquisition system consisting of data acquisition boards and the LabView programme from National Instruments.

A Horiba 200 Series Emissions bench was used to measure the concentrations of intake and exhaust mixtures. O<sub>2</sub> was measured by a magneto-pneumatic method, CO and CO<sub>2</sub> by non-dispersive infrared (NDIR) absorption, NO by chemiluminescence and HC by a flame ionisation detector (FID).

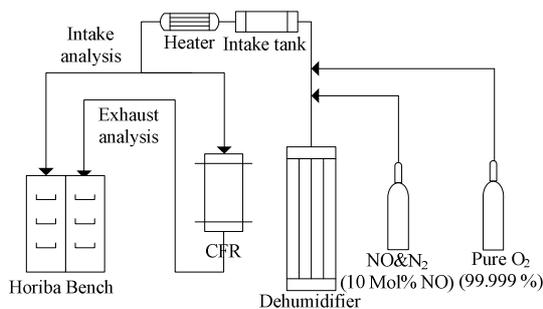


Figure 1 Gas Supply System

### Testing Conditions and Fuel

Engine testing conditions and relevant fuel properties are shown in Table 1. In the SKI tests, the operating conditions were maintained as in the standard RON test. For a fuel with known octane number (ON), e.g. iso-octane ON = 100, the compression ratio was predetermined in the standard RON test for producing a medium-intensity knock where the knock meter reading is 50. At this condition lambda was 0.89. A Quasi-SKI condition was also examined in the present study, where lambda=0.7 was specified and then the compression ratio was adjusted to produce a knock intensity of “50” indicated by the knock meter, same as in the standard RON test.

### Results and Discussion

#### Oxygen Displacement Experiments

Since the NO bottle contains only 10 mol% NO (N<sub>2</sub> balance), dilution was induced as NO was added to the engine intake. Therefore an O<sub>2</sub> displacement test was first conducted to examine the impact of N<sub>2</sub> dilution on knock onset. The test was conducted by adding different amount of pure N<sub>2</sub> to the intake mixture, which corresponds to NO addition from 0 ppm to 1600 ppm using the NO/N<sub>2</sub> mixture.

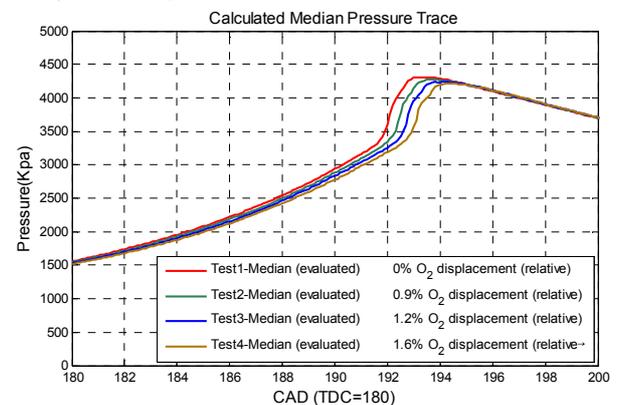


Figure 2 O<sub>2</sub> displacement effect on calculated median pressure traces

Cylinder pressure traces at various levels of O<sub>2</sub> displacement were analysed and compared in Fig. 2. For each case, a ‘median’ trace is shown. Figure 3 shows that knock onset was suppressed with N<sub>2</sub> addition. More specifically, decreasing the O<sub>2</sub> concentration by 0.2%, corresponding to the effect of 900 ppm NO addition, resulted in a delay of knock onset time by approximately 0.3~0.4 CAD, which is in the same order of observed NO effect on knock onset in previous studies [4, 9]. Therefore, the O<sub>2</sub> displacement effect on knock cannot be ignored, and oxygen was added to the intake air to maintain the O<sub>2</sub> concentration in air.

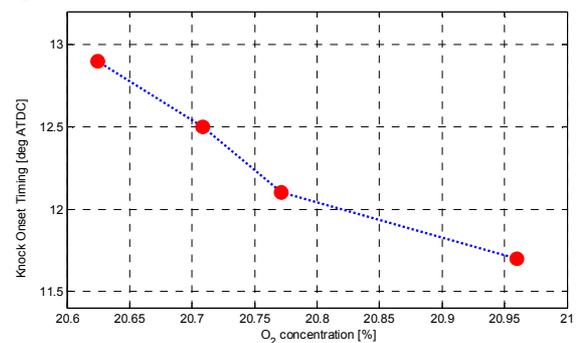


Figure 3 Effect of O<sub>2</sub> displacement on knock onset

### NO impact at SKI conditions

Experiments on the impact of NO were first conducted at the SKI condition, which was under the standard RON test condition. Figure 4-(a) and 4-(c) show the influence of NO addition under SKI experimental conditions. With 25 ppm NO, knock onset was nearly the same as the baseline (without NO addition). With NO higher than 25 ppm, knock onset started to be retarded, where this inhibition increased with higher NO concentration. With NO higher than 200 ppm, only weak knock was observed. Thus, the inhibition by NO appeared to reach a ‘saturation-point’, where more NO did not induce more obvious difference.

Similar results have also been reported previously [9], where knock onset of iso-octane was also found to be suppressed with NO addition. However, the NO promoting effect for autoignition found in other studies [4, 7, 8] are not observed here.

The impact of NO on autoignition can be generally understood through the following reactions [14-17]:



Reaction (1) is the key reaction leading to the promoting effect of NO on hydrocarbon oxidation, which can convert an unreactive HO<sub>2</sub> to a reactive OH, consequently increasing the reactivity of the reacting system. Reaction (2) is responsible for the inhibiting effect of NO, by transforming a reactive OH into a relatively stable intermediate HONO. Low NO addition can enhance the oxidation process through reaction (1); while excess NO addition may induce inhibition by scavenging OH in the radical pool through reaction (2).

That the inhibiting effect of NO was observed in the SKI experiments is likely due to the NO in the engine residual gas, which can be estimated from the NO measured in the exhaust to be ~70 ppm given an estimated residual fraction of 10%. The NO level in the residual under SKI operating conditions might therefore be already high enough to promote autoignition, with additional NO in the intake leading to the observed inhibition.

### NO impact at quasi-SKI conditions

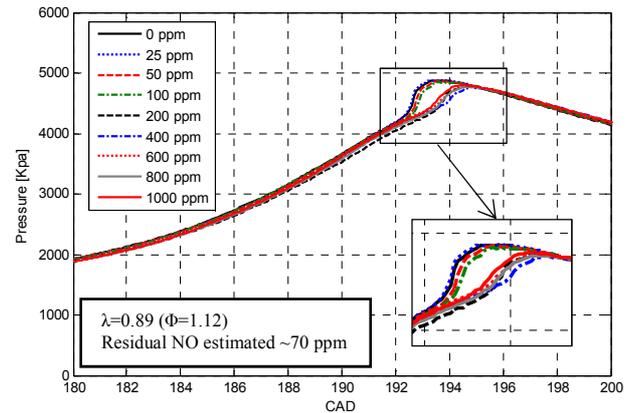
In order to understand the impact induced by the residual NO, quasi-SKI experiments using significantly richer mixtures (lambda=0.7) were therefore conducted to reduce the combustion NO formation. Figure 4-(b) and 4-(c) show the influence of NO addition under quasi-SKI experimental conditions. In this case, NO formation is substantially inhibited, with only ~50 ppm NO measured in the exhaust, corresponding to about ~5 ppm NO at inlet valve closure.

Results show that low concentrations of NO (< 200 ppm) now advance knock onset, and higher concentrations (> 200 ppm) retard knock onset. The largest promoting effect of NO is at around 29 ppm NO addition. Further, knock onset appears to be largely suppressed at 608 ppm, which was the highest NO concentration tested.

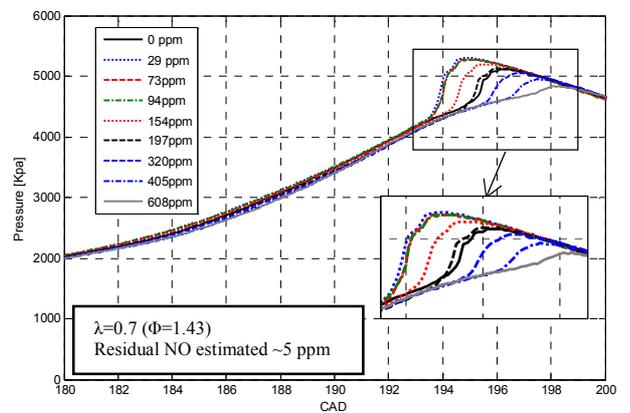
Due to the very low NO concentration in the engine’s residual gas, the initial, promoting effect of NO is now observed in these quasi-SKI tests. Moreover, interesting non-monotonic behaviour exists, in which NO addition first promotes knock and then suppresses it. Such behaviour has also been observed in HCCI experiments by others [12-13], where combustion produces very low amounts of NO, similar to this quasi-SKI condition.

These other studies also explain these trends by reference to equations 1 and 2. The authors’ planned kinetic modelling at

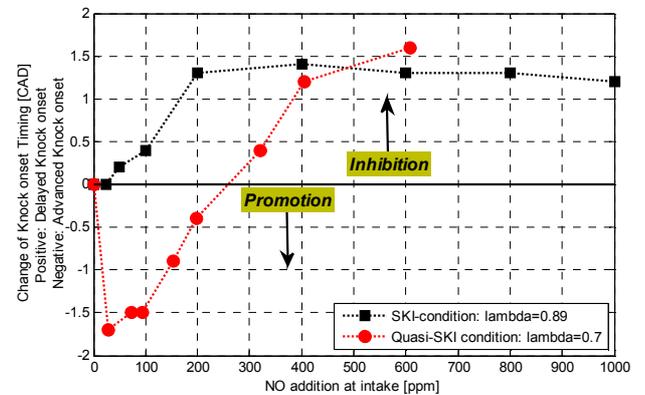
these conditions will confirm whether these arguments are correct.



(a) NO effect on knock onset at SKI conditions



(b) NO effect on knock onset at quasi-SKI conditions



(c) NO effect on change of knock onset

Figure 4 Median pressure trace out of 600 cycles for iso-octane with variable added NO concentration in the intake (600 rpm, Intake air temperature = 52 °C, TDC = 180 CAD, Spark= 13 CAD BTDC)

### Conclusions

This paper studied the effect of nitric oxide (NO) on the onset of knock in a cooperative fuel research (CFR) engine. The experiments were conducted at both the standard knock intensity (SKI) condition for research octane number (RON) tests, as well as at a richer operating condition of a similar knock intensity but a higher compression ratio. Iso-octane was the fuel.

Results showed that knock onset was always delayed with NO addition at the SKI condition (lambda=0.89 and CR=8.03). However,

different trends are seen at the richer condition ( $\lambda=0.7$  and  $CR=8.36$ ), with increased NO addition first advancing knock onset and then retarding it. In this case, smaller amounts of NO addition (below 200 ppm) advanced knock-onset, but higher concentrations of NO (over 200 ppm) again retarded knock.

The differing effects of NO at the SKI and quasi-SKI cases were argued to be likely due to their different residual NO concentrations. The residual NO is roughly 5 ppm at the richer condition. When NO is added into the engine intake, it is therefore the dominant source of NO, likely allowing it to promote autoignition via conversion of the less reactive  $HO_2$  to reactive OH radicals. However, at the SKI condition, combustion produces much more NO itself, and the residual NO concentration is an order of magnitude higher ( $\sim 70$  ppm) than the richer case. Thus, any promoting effect of NO may have largely already occurred without any NO added into the intake, and additional NO is primarily converted to HONO. This starves the unburnt mixture of reactive OH radicals, thereby inhibiting knock onset. The authors' planned kinetic modelling at these conditions will confirm whether these arguments are correct.

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