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THE FORMATION OF NO AND NO₂ IN THE I. C. ENGINE COMBUSTION
OF METHYL ALCOHOL AND FUEL-NITROGEN DOPED METHYL ALCOHOL*

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ABSTRACT

Measurements of NO_x levels in the exhaust gas from a CFR engine fueled with methyl alcohol are reported. The results showed that the dominant form of NO_x for lean combustion conditions was NO_2 . The significance of this observation is discussed. Also, the conversion to NO_x of several added "fuel-nitrogen" compounds was studied. The data for the conversion of pyridine, di-ethylamine, and acetonitrile added to methyl alcohol were qualitatively similar showing $\geq 50\%$ conversion for lean operation but $< 50\%$ conversion for rich operation.

Introduction

A number of reports dealing with the mode of NO_x formation from "fuel-nitrogen" in both diffusion¹⁻³ and pre-mixed⁴⁻⁶ flames have appeared recently. These studies were directed not only toward practical aspects of pollution abatement but also toward the fundamental principals involved in the chemistry of NO_x production. To date, however, there appears to be no analogous study in which internal combustion engines have been utilized. In the present study, measurements were made of NO and NO_2 in the exhaust from a CFR engine running on methyl alcohol, both neat and doped with low levels (0.5 to 3.0% V/V) of several organic nitrogen compounds, viz. pyridine, diethylamine and acetonitrile. These nitrogen compounds cover a range of chemical and physical properties that could conceivably influence the extent of conversion to NO_x during the combustion process.

Experimental

The Cooperative Fuel Research (CFR) engine used in this study was set up for the Motor Octane test.⁷ The only exceptions to the ASTM specifications were the omission of the intake air ice tower⁸ and the lack of heating both the intake air and the intake mixture. In place of the ice tower, a calibrated orifice/surge tank⁹ was attached to the air intake line to measure the mass flow rate of inducted air. The compression ratio was maintained at 7.84 and the spark timing was 18° BTDC throughout the experiments. Under these conditions, the lean combustion limit for neat methyl alcohol was observed to occur at $\phi = 0.58$.

The engine exhaust was sampled using a known dilution technique to avoid condensation of water in the sample lines and the analytical equipment. Exhaust samples were withdrawn continuously from the exhaust surge tank through the side leg of an aspirator type flow line. A check valve was inserted between the dilution flow line and the sampling port to minimize pressure fluctuations. The entire sampling assembly was wrapped with electrical heating tape and maintained at $110 \pm 10^\circ\text{C}$. Dry nitrogen was used for the sample dilutions, except where noted. The sample (wet) volume flow rate was determined simply from the difference between the dilution gas flow rate and the diluted sample gas flow rate, as measured from calibrated rotometers. The precision of this sampling measurement was good to about $\pm 4\%$. The diluted sample was thence analyzed for NO and NO_x using the sensitive and specific chemiluminescence technique on an atmospheric pressure instrument (TECO model 44). Dry oxygen was supplied to the instrument for internal dilution and ozone production. The instrument calibration gas was 1030 ± 10 ppm NO in N₂ (MG Scientific Co.). Nitrogen dioxide (NO₂) in the calibration gas was less than 1% of the NO.

The organic nitrogen compounds used were of the following quality: the pyridine was Mallinckrodt analytical reagent grade; the diethylamine was from Eastman, 98% minimum purity; and the acetonitrile was Tridom (Fluka) puriss. grade, 99.5% minimum purity. All nitrogen compound/fuel mixtures were prepared by volume dilution, i.e. % V/V.

The equivalence ratios (fuel to air) were calculated from the measured CO_2 content of the exhaust gas (dry basis).¹⁰ This was necessary since the air mass flow measurement using the calibrated orifice/surge tank proved to have a relatively large systematic error (approx. 25%). The orifice was re-calibrated roughly against the CO_2 based equivalence ratio for purposes of estimating $\phi_{\text{F/A}}$, however all reported equivalence ratios were calculated from measurements of CO_2 in the exhaust gas.

Results and Discussion

Experiments were performed using neat methyl alcohol and mixtures of pyridine (0.5, 1.0, 2.0 and 3.0% V/V, diethylamine (1.0 and 2.0 % V/V) and acetonitrile (1.5% V/V) in methyl alcohol. Results are shown for neat methanol and the 1.0% pyridine mixtures in Figure 1 which gives the measured NO and NO_x levels in the exhaust gas as a function of the equivalence ratio ($\phi_{\text{F/A}}$). The curve for the neat fuel is in qualitative agreement with the results of Most and Longwell¹¹ and Harrington and Pilot¹², although there are some discrepancies in the magnitude of the peak NO_x ($\pm 30\%$) and the value of ϕ at peak NO_x (± 0.05). Large increases in both NO and NO_x are readily apparent for the fuel-nitrogen case. The results of the other fuel-nitrogen mixtures* were similar to those for 1% pyridine shown in Figure 1. Taking the difference between the NO_x curve for neat methyl alcohol and the NO_x curve for the mixture to represent the extent of conversion of "fuel nitrogen" to NO_x , one may calculate that something less than 100% of the pyridine was converted to NO_x . Indeed, the extent of conversion is only about 50% at the peak NO_x level ($\phi \approx 0.90$), while it is always greater than 50% on the fuel-lean side of that point and less than 50% on the fuel-rich side. Since this last

* Shown in Figures 2-7.

observation is subject to a degree of uncertainty due to the possible contributions of compounds such as HCN , NH_3 , and partially oxidized fuel-nitrogen to the NO_x measurement via reaction in the instrument's stainless steel; $\text{NO}_x \rightarrow \text{NO}$ converter, further discussion on this phase of the investigation will be deferred until more tractable experimental methods may be applied to the study. Nevertheless, the results of the present study show a similar behavior for fuel-nitrogen conversion as a function of ϕ compared to the pre-mixed burner investigations.³⁻⁶ This observation is significant in terms of the considerable differences in the conditions between the present engine experiments and the previous sub-atmospheric or atmospheric burner studies. In addition, in the present study, a large fraction of the nitrogen oxides formed in the I.C. engine combustion of both the neat fuel and the fuel-nitrogen mixtures was observed to be in the form of NO_2 . In the two often noted reports on methyl alcohol combustion^{11,12} this observation was not made since both of those studies employed non-dispersive infra-red (NDIR) detectors for NO . This observation is of sufficient importance, however, that it was deemed necessary to prove that the measured NO_2 arose from the combustion process alone and was not an artifact of the measurement procedure. Three steps were taken to accomplish this end. The first two involved: 1) moving the sample withdraw point on the surge tank closer to the engine exhaust port; and 2) replacing the N_2 sample dilution gas with dry air. In both cases the result was negative, i.e., the measured levels of NO and NO_x were identical (within the experimental uncertainty, $\approx \pm 5\%$) to the initial conditions. In the last test, the engine was operated at $\phi = 0.68$ on neat methanol and a small amount of the span gas (1030 ppm NO in N_2) was injected into the exhaust stream as close to the exhaust port as possible

(≈ 1 inch) and the sample withdraw point on the surge tank was moved to the farthest position away from the exhaust port (≈ 3 feet). The added NO and NO_x were calculated by difference, and 15 to 20% of the added NO was found to be converted to NO_2 . At $\phi = 0.68$, the NO and NO_2 were measured at about 15 ppm and 110 ppm, respectively; and thus at $\phi = 0.68$ the contribution of NO to NO_2 in the exhaust line was no more than about 3%. Based on the results of the tests just described, it is reasonable to ascribe the measured NO_2 to formation in the engine combustion chamber and not in the exhaust or sampling lines.

In Figure 1, it may also be noted that the ratio of NO_2 ($\text{NO}_x - \text{NO}$) to NO decreases monotonically with increasing ϕ , from ϕ equals 0.6 to 0.9. Since this behavior was noted for both the neat methyl alcohol and all of the nitrogen-compound doped methanol fuels, this observation suggests that the mechanism for NO_2 formation in the engine involves the oxidation of NO as opposed to direct formation of NO_2 . The observations of Merryman and Levy⁴⁻⁵ and Fenimore¹³ would therefore seem to apply generally rather than just to a specific experiment or combustion device.

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FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7