

Nitric Oxide Circumstances in Nitrogen-Oxide Seeded Low-Temperature Powling-Burner Flames

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Abstract

Flat low-temperature two-stage flames were established on a Powling burner using rich diethyl-ether/air or n-heptane/air mixtures, and nitrogen monoxide NO was added into the fuel-air mixtures with a concentration of 240 ppm. The temperature development and chemical-species histories, especially of NO, nitrogen dioxide NO₂ and hydrogen cyanide HCN were examined associated with an emission-spectrum measurement from the low-temperature flames. Nitrogen monoxide was consumed in the cool-flame region, where NO was converted to the NO₂. The NO₂ generated, however, fell suddenly in the cool-flame degenerate region, in which the HCN superseded. In the blue-flame region the NO came out again and developed accompanied with remained HCN in the post blue-flame region. The NO seeding into the mixture intensified the blue-flame luminescence probably due to the cyanide increase.

Introduction

It has been indicated that some nitrogen-related compounds closely take part in the ignition promotion/retardation phenomena.

1. The NO_x generation was plausible during the preflame reactions prior to the hot ignition [1].
2. The behavior of cool- and blue-flame onsets was different between the mixtures whether N₂ or Ar was included as an inert diluting agent for the oxidizer [2].
3. Hot-flame occurrence caused by mixture compression could be eliminated by low-volatile compound-vapor addition in the mixture, but when the 21O₂/79Ar synthetic air was used instead of natural air as oxidizer, no eliminating effect could be found [3].

The burned gases are always included in the fresh mixtures in the reciprocating piston engines. The exhaust gas recirculation is a popular measure for reducing nitric oxide emission. On the nitrogen-oxide contained mixtures the ignition delays has been reported [4], but no details has been informed on the low-temperature oxidation-reaction processes.

Flat low-temperature Powling-burner flames with/without nitrogen-oxide seeding into the mixtures have been examined as to the emission spectrum and chemical-species history, to elucidate the effects of

nitrogen oxides on low-temperature oxidation of fuel-air mixtures in the most simple, undoubted system, and to find out ignition control procedures to realize premixed compression-ignition (HCCI) engines.

Experimental

A modified Powling burner at atmospheric pressure was used to stabilize flat two-stage low-temperature flames of rich diethyl-ether/air mixtures in vertically-flowing laminar streams. An outline is shown in Fig. 1. The details are shown in our paper formerly published [5], though the present apparatus was improved for a higher-level flame stabilization. A fuel/air mixture flowed with almost uniform velocity distribution from an inner burner tube surface, which was a porous ceramic honeycomb plate. An outer quartz shielding tube (inner diameter: 105 mm, height: 172 mm) supported a stabilizing ceramic screen at the top way-out position. The stabilizing screen was a ceramic-fiber matrix including heaters electrically controlled in temperature. The low-temperature cool and blue flames are stabilized within the quartz shielding tube.

Fuel used for the Powling burner was diethyl-ether or n-heptane. The equivalence ratio of mixtures was set to be 2.0 or 3.0. The nitrogen-balanced 5000-ppm nitrogen-monoxide reference gas was supplied into the fuel/air mixtures. Pure nitrogen gas was added in the

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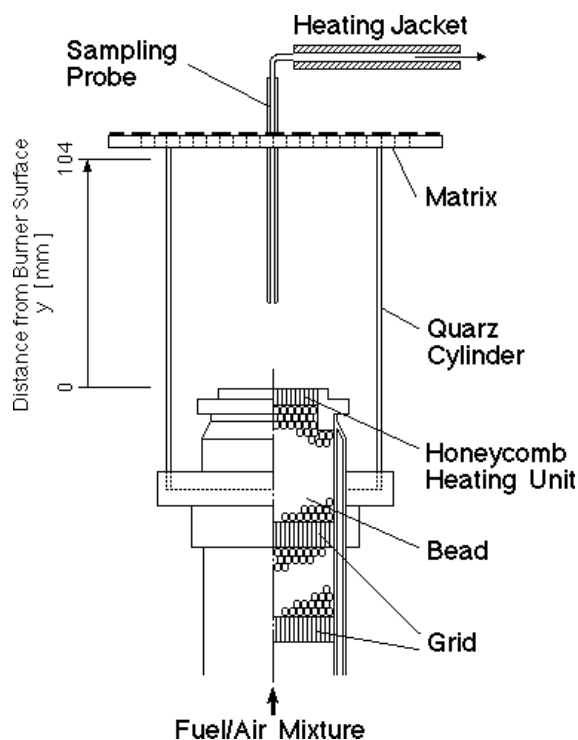


Fig. 1. Schematics of Powling burner and gas sampling device.

NO-nonseeding case to keep an identical inert-gas dilution ratio.

Temperature profiles in the two-stage flames were measured with a type K thermocouple having 50 μm in diameter, coated with SiO_2 to eliminate catalytic effects on the wire surface.

Gas samples were aspirated continuously through a quartz probe kept 105°C and then introduced into a cooler kept -21°C to remove water vapor. The concentration of each nitrogen related compound was determined by using a chemiluminescence type NO_x analyzer (Beckmann: 951) for nitrogen monoxide NO, by Salzman absorption luminosity method (JIS K 0104) for nitrogen dioxide NO_2 , by Zinc-reducing naphthylethylenediamine Zn-NEDA method (JIS K 0104) for nitric oxide NO_x , and by Dräger tubes for hydrogen cyanide HCN respectively.

Light emission was focused onto a slit of a monochromator (Japan Spectroscopy: CT-25N) to obtain emission spectra, and was detected by a cooled photomultiplier (Hamamatsu Photonics: R3896, 190~900 nm). The slit width was set to be 50 μm except for the cool-flame observation with 200 μm in width. The spatial resolution was less than 1 mm. For the wave length higher than 620 nm, a red-color glass filter (Toshiba: R-62) was used to eliminate the secondary reflection.

Results and Discussion

Typical low-temperature flames could be obtained easily by a diethyl-ether/air mixture with an equivalence ratio of 3.0; cool and blue flames were visible to the naked eye and the cool-flame degeneration was given as a recognizable distance between cool and blue flames [6]. The temperature development in this case is shown in the lower part of Fig. 2. The nitrogen monoxide was so added to this mixture as to be 240 ppm, the initial seeding NO concentration.

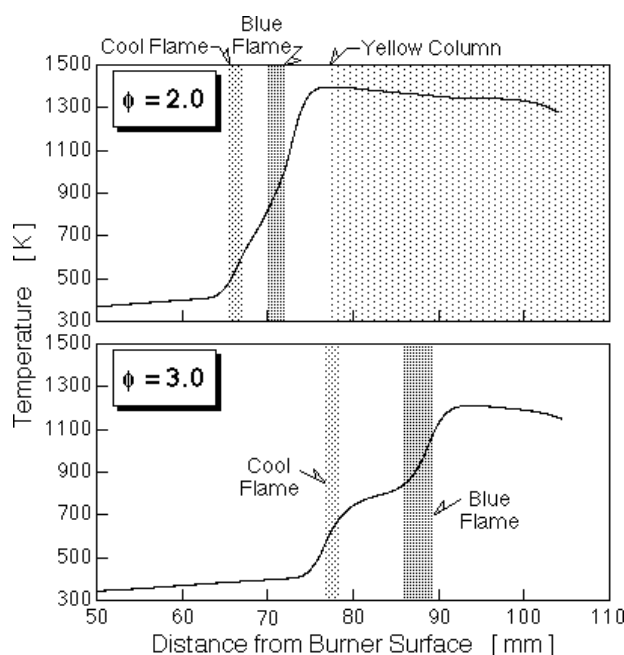


Fig. 2 Temperature development of diethyl-ether/air low-temperature flames with equivalence ratio of 2.0 and 3.0.

The concentration histories of NO, NO_2 and HCN are shown in Fig. 3. The abscissa is the height from the burner honeycomb surface. A temperature rise due to cool flame appearance could be recognized from around 75-mm height in Fig 2. At about 69-mm position just before the cool flame onset the NO concentration has been slightly reduced to be 220 ppm and the amount of NO_2 detected has been 16 ppm.

The NO was consumed drastically in the cool flame period. Corresponding to the NO consumption, NO_2 was generated during the cool flame and showed a peak at 77-mm position within the luminous zone of cool flame. All of the consumed NO in cool flame was not converted to NO_2 . It was not until the cool-flame that the HCN appeared.

The NO_2 decreased steeply in the cool-flame degenerate region. At the 79-mm height the NO_x

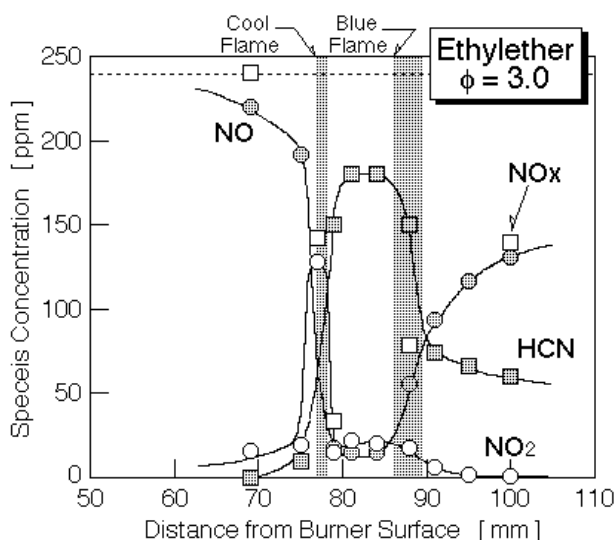


Fig. 3. NO, NO₂, HCN concentration histories in diethyl-ether/air low-temperature flames with an equivalence ratio of 3.0.

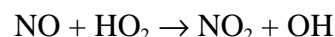
concentration was 33 ppm. It was close to the sum of NO (15 ppm) and NO₂ (15 ppm) which were separately measured, but was far from the original NO amount of 240 ppm. The HCN accounted for a greater part of nitrogen-related compound in the cool-flame degenerate region, where the amounts of NO, NO₂ and HCN were unperturbed.

At around 87-mm height the temperature was raised again as shown in Fig. 2; the blue flame appearance. In the blue flame the HCN was consumed almost to half. After the blue flame appeared the amount of NO increased gradually. The difference between the NO_x concentration and the sum of NO and NO₂ was a negligible one of 8 ppm at the 100-mm position.

In the post blue-flame region the NO concentration

was restored only to 54 per cent of the initial charge, while the HCN decreased to the 34 per cent of its maximum level. The sum of NO_x and HCN did not attain to the 240 ppm; the NO initially charged.

The degeneration of cool flame has led a NO consumption/NO₂ generation, which would be derived through an oxidation reaction of NO:



It has been reported that the nitrogen-oxide oxidation to the nitrogen dioxide would be promoted under hydrocarbon coexistence [7]. The nitrogen-oxide addition into the mixture would result in the nitrogen-dioxide supply for the blue-flame onset. The NO and NO₂ would react with organic radicals such as alkoxy radical and formed a nitrous acid or alkylnitrate in and after the blue flame. The alkylnitrate is the typical one of cetane rating improvers for the hydrocarbon fuels.

It could be possible to hypothesize that the NO would be generated from the decomposition of nitrous acid or alkylnitrate. The hypothesis could explain why the blue-flame reactions have high fuel-decomposition potency.

The spectroscopic emission distribution in this case is shown in Fig. 4. The emission spectra shown were the ones of the middle position of each flame on the centerline of the burner tube. The abscissa and ordinate are the wavelength and photomultiplier current respectively. The chemical species corresponding to principal emission peaks are indicated in the figure. The ultraviolet to visible spectrum of cool-flame emission is the one of the «Emel us's Cool Flame Bands» overlapped with «Carbon Monoxide Flame Bands». The almost all emission are originated from the formaldehyde.

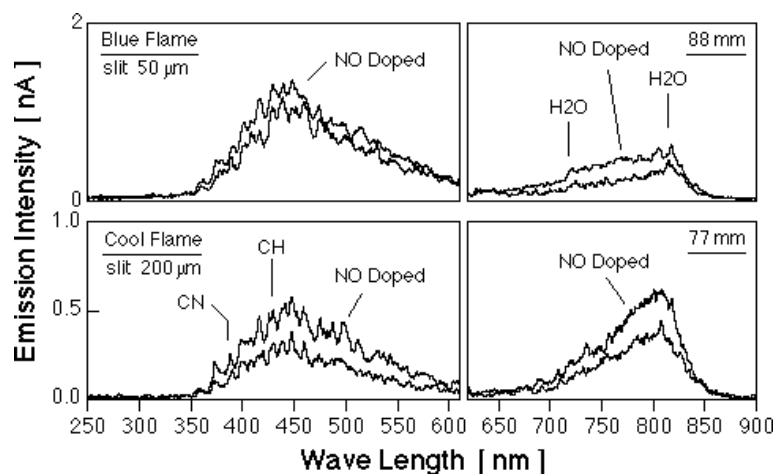


Fig. 4. Spectral emission distribution in diethyl-ether/air low-temperature flames with an equivalence ratio of 3.0.

No characteristic change due to NO addition in the mixture was found on the cool-flame emission spectrum, through the emission was slightly intensified over the ultraviolet, visible and near-infrared wave length. Also on the blue-flame spectrum no change in characteristic and intensity except as to a manifestation of near-infrared 716- and 809-nm «H₂O Vibration-Rotation Spectrum».

Even in the NO-nonseeded low-temperature flame an emission in 388-nm wave length (equivalent to the «CN Violet System») could be found. The HCN content measured in the NO-nonseeded cool flame with a 3.0 equivalence ratio was 160 ppm, which amount was similar to the 150 ppm HCN in the NO-nonseeded cool flame shown in Fig. 3.

When the equivalence ratio of the diethyl-ether/

air mixture was reduced to 2.0, a thin nonluminous «Dark Zone» and a bright luminous «Yellow Column» zone [8] followed in the post blue-flame region. Under the 2.0 equivalence ratio, the NO addition up to 240 ppm in the mixture weakened the yellow-column intensity. When the NO addition was decreased to 180 ppm a bright luminous yellow column came up again. The temperature development is shown in the upper part of Fig. 2. The spectral emission distribution from the low-temperature flames of the diethyl-ether/air mixture with an equivalence ratio 2.0 is shown in Fig. 5 with/without the initial NO charge of 180 ppm. The blue-flame spectrum was intensified in the near-infrared bandwidth. The yellow column became brighter with the 180-ppm NO addition.

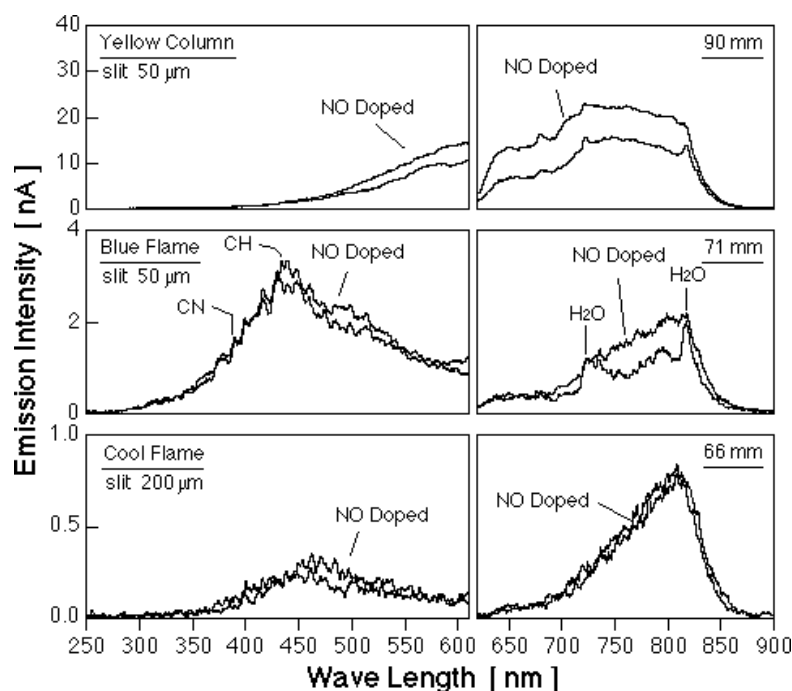


Fig. 5. Spectral emission distribution in diethyl-ether/air low-temperature flames with an equivalence ratio of 2.0.

The diethyl-ether is a convenient fuel to get stabilized low-temperature flames. It is not, however, the normal hydrocarbon fuel used in piston engines but the oxygenated one. n-Heptane/air stabilized low-temperature flames were realized herewith with an equivalence ratio of 3.0. The NO, NO₂, HCN consumption/generation histories in a normal hydrocarbon low-temperature flames with an initial content of 200-ppm NO seeding was examined, and the results are shown in Fig. 6.

The interval between cool and blue flames, *i.e.*,

cool-flame degenerate region, are shorter than in the diethyl-ether case. The spatial resolution for gas sampling was narrowly permissible. The n-heptane/air mixture with the 3.0 equivalence ratio gave us a yellow column. Characteristic with/without NO addition in the mixture did not change significantly the cool- and blue flame emission spectra and intensity, except the near-infrared emission intensity of blue flame.

The NO and NO₂ histories of n-heptane originated low-temperature flames were almost identical in the

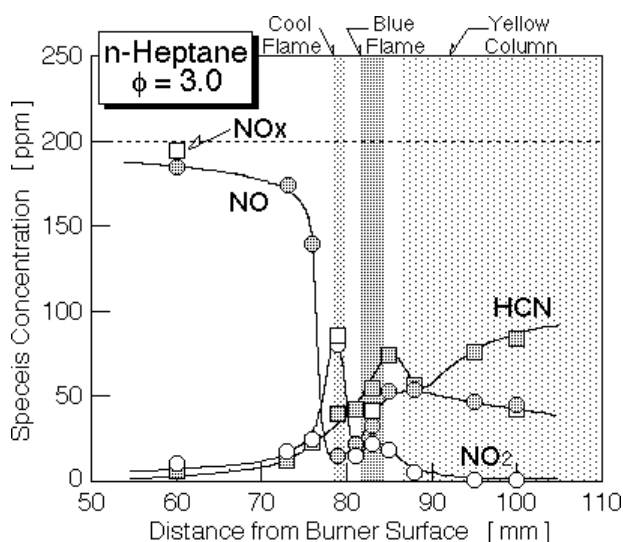


Fig. 6. NO, NO₂, HCN concentration histories in n-heptane/air low-temperature flames with an equivalence ratio of 3.0.

consumption/generation trends with the diethyl-ether cases. The HCN, however, increased continuously up to the dark zone just before the yellow column, decreased once and then increased again gradually in the yellow column. This behavior differs from the diethyl-ether case.

Prepared the diethyl-ether/air mixture with an equivalence ratio of 2.0, the HCN concentration was measured in and after the blue flame under the initial NO seeding of 180 ppm, to differentiate the reason whether the fuel type or the equivalence ratio determines the HCN history after the dark zone. Detected were the 140-ppm HCN in the blue flame, 32-ppm HCN in the dark zone and the 66-ppm HCN in the yellow column at the 90-mm position. It can be recognized that the HCN history after the blue flame depends on the equivalence ratio and/or the yellow column existence.

Conclusions

We have obtained the consumption/generation histories of NO, NO₂ and HCN in low-temperature Powling-burner flames with a relatively low content of 240-ppm NO seeding, associated with the temperature development and emission spectrum measurements. The features of this paper are as follows:

- Initially seeded NO was consumed and NO₂ was generated in the cool flame.
- The NO₂ generated in the cool flame was consumed in the cool-flame degenerate region.

- The differences caused by NO addition are due not to the initially seeded NO itself but to the products formed through the reactions with NO. The products would intensify the low-temperature oxidation and fuel decomposition reactions in blue flame.
- The nitrogen-oxide addition into the mixture would result in the nitrogen-dioxide supply for the blue-flame onset.
- The information obtained using an oxygenated ether as fuel is effective to understand the low-temperature oxidation processes of normal hydrocarbon fuels.

Even in the NO-nonseeded low-temperature flames an emission of CN system can be found, and the HCN is detected in the sampled gases. It seems that the HCN generation has no dependence on the initial NO seeding. Active oxygenate radicals, such as O atom, is necessary for the NO generation. In the low-temperature oxidation processes a similar generation reaction mechanism is plausible to progress.

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