

REMOVAL OF MULTIPLE AIR POLLUTANTS BY GAS-PHASE REACTIONS OF HYDROGEN PEROXIDE

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INTRODUCTION

Hydrogen peroxide is a large-volume chemical with a wide range of applications in different industries. If properly stored, hydrogen peroxide solutions in water are stable, with no loss of the effective substance. Environmental applications have become a major area of use for hydrogen peroxide because it is not itself a source of pollution, and water and oxygen are the only reaction by-products. There is a variety of developed or developing environmental technologies which use H₂O₂ as an active reagent: detoxification and deodorization of industrial and municipal effluents; low temperature removal of nitrogen oxides, sulfur dioxide, cyanides, chlorine, hydrogen sulfide, organic compounds; low temperature treatment for catalytic NO-to-NO₂ conversion, etc.

This study develops a novel concept of high-temperature H₂O₂ injection into combustion gases or other off-gases followed by gas-phase reactions of H₂O₂ with NO, SO₃, CO, and organic compounds. Experimental and modeling data show that a water solution of hydrogen peroxide injected into post-combustion gases converts NO to NO₂, SO₃ to SO₂, and improves the removal of CO and organic compounds due to chain reactions involving OH and HO₂ radicals. The existence of the chemical reaction between NO and hydrogen peroxide has been proven earlier experimentally by Azuhata et al.¹ at long residence times of approximately 12 sec which are not applicable to air pollution control. In this study effective NO-to-NO₂ and SO₃-to-SO₂ conversion, as well as CO and CH₄ oxidation, was predicted by kinetic modeling and measured experimentally in the temperature range 600-1100 K in a practical range of reaction times (t_r) from 0.2 to 2.0 s.

EXPERIMENTAL

In the current work, the bulk of experiments were carried out in a flow system which consists of four parts, a gas blending system, a liquid injection system, a reactor, and an analytical train. The gas blending system is a set of rotameters capable of preparing a flowing mixture of O₂ with addition of NO, CO or CH₄ in N₂ as a carrier gas. The liquid injection system includes a burette containing 3% H₂O₂/H₂O solution and a precision metering pump for delivery of the solution through a capillary tube to the heated reaction zone. For the study of the SO₃/H₂O₂ reaction, dilute sulfuric acid was added into 3% H₂O₂ solution. At a temperature of 500-600 K H₂SO₄ is converted into H₂O and SO₃ and this is a convenient means of producing a gas mixture containing known amounts of H₂O and SO₃. The rates of pumping the water solutions of H₂O₂ and H₂SO₄ were chosen so as to provide the desired concentrations of H₂O₂ and SO₃ in the gas mixture.

The prepared gas and liquid mixtures go to the reactor which was located in a 1 m three zone electrically heated furnace. The first and the third zones (25 cm each) were heated to 450-600 K to evaporate the liquid, to preheat the gas mixture and to avoid condensation of the reaction products in the reactor. In the second heating zone (50 cm long) which was the reaction zone, the temperature was varied from 450 to 1300 K. All tests with air pollutants were performed with a 2.7 cm ID quartz reactor. The experimental gas mixture could be passed through the reactor and then sent to analysis, or it could be sent directly to analysis. The analytical train included a Thermolectron Chemiluminescent NO/NO_x analyzer, a Thermolectron Gas Filter Correlation CO analyzer, a Thermolectron Pulsed Fluorescence SO₂ analyzer, Flame Ionization Total Hydrocarbon analyzer, and permanganate titration of H₂O₂.

In addition to the laboratory-scale experiments done with synthetic gas mixtures, a set of experiments on NO-to-NO₂ conversion was also carried out at pilot scale in a 1 MBtu/hr Boiler Simulator Facility (BSF) burning natural gas with stoichiometric ratio of 1.2. The furnace has two sections: a vertically down-fired tower (56 cm in diameter and 6.7 m height) and a horizontal convective pass (20 x 20 cm cross section, 14.2 m long) simulating typical temperature profiles of full-scale utility boilers. Solutions of hydrogen peroxide, methanol or their mixtures (15% in water) were injected by a fluid nozzle into the convective pass at different temperatures. Flue gas was sampled downstream in the convective pass at different temperatures with residence times from 0.2 to 2.0 s. Most experiments were conducted with sampling at about 500 K and analysis by NO_x and CO meters.

The Chemkin-II kinetic program² and a reaction mechanism based on Miller and Bowman review paper³ were used for kinetic modeling.

LABORATORY-SCALE RESULTS

Gas phase reactions of H_2O_2 are complicated by heterogeneous processes, and therefore, a preliminary set of experiments was done for a mixture without air pollutants (1100 ppm H_2O_2 - 7.3% H_2O - balance air) to define the degree of H_2O_2 heterogeneous decomposition under different experimental conditions and to estimate how much H_2O_2 will be available for the useful homogeneous reactions with air pollutants. A water cooled impinger with a known amount of $KMnO_4$ solution was installed at the exit of the reactor. The concentrations of hydrogen peroxide leaving the reactor were defined by "on-line titration", e.g. by measuring time for which the gas passes through the $KMnO_4$ solution until decoloration. Results show that about 75% H_2O_2 decomposes at temperatures which are lower than the threshold temperature for homogeneous decomposition. The measured heterogeneous rate constant was $5.5 \exp(-1.250/T) s^{-1}$, and it was included in modeling. A substantial excess of H_2O_2 was used for the tests with air pollutants. It is worth noting, however, that in the scope of scaling up the process the surface chemistry becomes less important in large size industrial installations. All concentrations of hydrogen peroxide, shown in this Section, are calculated values after subtraction of the heterogeneously decomposed H_2O_2 before the reaction zone from initial H_2O_2 concentrations.

NO-to- NO_2 Conversion. Two set of tests were performed to demonstrate the NO to NO_2 conversion in the presence of H_2O_2 : variation of temperature and variation of reaction time. Two initial gas mixture compositions were used for the tests with different temperatures: (1) 100 ppm NO - (160-220) ppm H_2O_2 - 4.2% O_2 - 4.8% H_2O - balance N_2 and (2) 100 ppm NO - (90-120) ppm H_2O_2 - 4.4% O_2 - 1.7% H_2O - balance N_2 . The flow rates of the H_2O_2 solution were 0.05 and 0.14 ml/min correspondingly and reaction time $t_r=1-2$ s. Experimental and modeling results for the same conditions are presented in Figure 1. One can see that experimental and modeling results agree at least qualitatively and that at H_2O_2/NO ratios equal to 1.6-2.2 and 0.9-1.2, the achievable NO-to- NO_2 conversions are 95 and 80%. In the next set, the experiments were conducted at 820 K, and air was added to the mixture (1) in order to increase the gas flow rate and decrease the reaction time. The concentrations of NO and H_2O_2 were adjusted to the same levels as in previous tests. Concentrations of H_2O and O_2 were 4.7-7.0% and 4.2-15%. Five various air flow rates from 2.5 to 10.0 l/min were checked, and there were no visible difference in the final NO concentration: it was in the range of 10-12 ppm at $t_r=0.4-1.4$ s.

SO_3 -to- SO_2 Conversion. Average gas mixture composition for these experiments was 100 ppm SO_3 - (160-220) ppm H_2O_2 - 4.2% O_2 - 4.8% H_2O - balance N_2 and the reaction times were between 1.0 and 1.6 s. Under certain conditions SO_3 reacts with H_2O_2 to form SO_2 . No sulfur dioxide was formed at $T=600-1100$ K when hydrogen peroxide was absent in the mixture. SO_2 measurements and modeling for different H_2O_2 concentrations are shown in Figure 2. One can conclude that SO_3 is converted to SO_2 in a temperature range of 800-1100 K with up to 75-85% efficiency.

Oxidation of CO Promoted by H_2O_2 . The goal of this set of experiments was to show the improvement of the CO oxidation in the presence of H_2O_2 . In other words, it was expected according to kinetic calculations that H_2O_2 will make it possible to reduce CO concentrations at lower temperatures than that without H_2O_2 . The results of experiments and calculations are compared in Figure 3 at $t_r=1.0-1.5$ s for three mixtures: (1) 90 ppm CO - 4.2% O_2 - (160-220) ppm H_2O_2 - 4.8% H_2O - balance N_2 , (2) the same mixture but without H_2O_2 , and (3) the same mixture but without H_2O_2 and H_2O . Modeling for the mixture (3) was done at 10 ppm H_2O in the mixture because in experiments it was prepared without special drying. It is clear that experiments and modeling well agree and that H_2O_2 promotes CO oxidation but at rather low extent, about 20% at 860-960 K.

Oxidation of CH_4 Promoted by H_2O_2 . In the presence of H_2O_2 the temperature limit of CH_4 removal is substantially shifted to lower temperatures. This is shown in Figure 4 at $t_r=1.0-1.8$ s for three mixtures: (1) 90 ppm CH_4 - 4.2% O_2 - (160-220) ppm H_2O_2 - 4.8% H_2O - balance N_2 , (2) 90 ppm CH_4 - 4.4% O_2 - (90-120) ppm H_2O_2 - 1.7% H_2O - balance N_2 , and (3) the same mixture as (1) but without H_2O_2 and H_2O . In the temperature range from 790 to 1060 K, the addition of H_2O_2 can provide from 20 to 90% CH_4 removal. Maximum performance is observed at $T = 900 - 1040$ K.

PILOT-SCALE RESULTS

An attractive method of NO-to- NO_2 and SO_3 -to- SO_2 conversion by injection of methanol into the flue gas was described by Lyon et al.⁴ In pilot-scale experiments recently performed by Evans et al.⁵, 87% NO-to- NO_2 conversion was achieved. Unfortunately, a problem with using methanol is the formation of CO as a by-product. Each molecule of NO or SO_3 converted into NO_2 and SO_2 produces a molecule of CO, and CO is not oxidized to CO_2 at methanol injection temperatures.

Results of NO and CO measurements after injection of H_2O_2 and CH_3OH are shown in Figure 5 for two initial NO levels of 400 (Figure 5a) and 200 ppm (Figure 5b). For all tests the molar ratio of $[Agent]/[NO]$ was 1.5, and O_2 concentration in flue gas was 3.8%. Maximum NO-to- NO_2 conversion

was in the range of 80-87% for H₂O₂ injection and 87-92% for CH₃OH injection. For comparison, in the previous tests⁵, 87% NO-to-NO₂ conversion was achieved by CH₃OH injection. The minimum of the temperature window is shifted to lower temperatures in the case of H₂O₂ injection as predicted by kinetic calculations. The mechanisms of NO-to-NO₂ conversion by H₂O₂ and CH₃OH injection are similar, and therefore the slight decrease in performance of H₂O₂ can be explained by the heterogeneous decomposition which might be still noticeable in the 20 x 20 cm duct.

As for CO measurements, the H₂O₂ injection almost does not affect 24 ppm CO exiting the furnace tower, which is consistent with the laboratory-scale tests for low H₂O₂ levels. Methanol injection generates high CO emissions of about 600 and 300 ppm as shown in Figure 5.

Methanol is less expensive than H₂O₂. Therefore, if CO emissions are considered to be the primary drawback of CH₃OH injection, one strategy might be to add as much CH₃OH as possible within CO limits, and then add enough H₂O₂ to obtain target NO conversion. In light of this, several tests were performed in which the agent consisted of various combinations of CH₃OH and H₂O₂. In Figure 6 measured NO and CO concentrations are shown at different agent injection temperatures for various [H₂O₂]/[CH₃OH] mixtures. Initial NO and CO levels for these tests were 70 and 30 ppm respectively, and total CH₃OH+H₂O₂ concentration was always 105 ppm. At H₂O₂/CH₃OH=1:1 (52.5 ppm H₂O₂) NO-to-NO₂ conversion was approximately the same as for pure CH₃OH injection, and then NO conversion decreases incrementally as [H₂O₂]/[CH₃OH] ratio increases. The CO emissions increase also incrementally as CH₃OH concentration grows (Figure 6b). The temperature window for NO-to-NO₂ conversion had about the same minimum for all H₂O₂/CH₃OH mixtures and incremental temperature shift was not observed. This is explained by appearance of OH radicals at lower temperatures in the presence of H₂O₂. The NO and CO concentrations shown in Figure 6b were measured at the minimum point of the H₂O₂/CH₃OH temperature window, 800 K, except for the NO and CO concentrations after injection of pure methanol ([H₂O₂]=0). These concentrations were measured at 866 K, the minimum point of the CH₃OH temperature window.

DISCUSSION

It is known that NO₂ is much more soluble in water than NO. Kobayashi et al.⁶ demonstrated that NO₂ can be removed by aqueous solutions of various inorganic and organic reagents. Senjo et al.⁷ reported several methods of NO₂ removal by sodium salts. It was also proven by Zamansky et al.⁸ that NO₂ can be removed efficiently in modified calcium-based SO₂ scrubbers. Since flue gas desulfurization systems are increasingly required for SO₂ removal after combustion of sulfur containing fuels, the conversion of relatively inert NO into much more reactive NO₂ and corrosive SO₃ into SO₂ becomes promising for combined NO_x and SO_x removal.

Hydrogen peroxide injection is a "green" process. It is not dangerous for the atmosphere, there is no additional soot, CO or nitrogen compounds formation as may be expected from urea, cyanuric acid or methanol injection. H₂O₂ can be injected as a water solution at various concentrations. The products of the H₂O₂ decomposition at high temperatures are H₂O and O₂ which are environmentally acceptable. Therefore, hydrogen peroxide can be applied in any reasonable excess to air pollutants for their complete or partial removal depending on current needs without risk of ammonia, CO or other dangerous compound breakthrough.

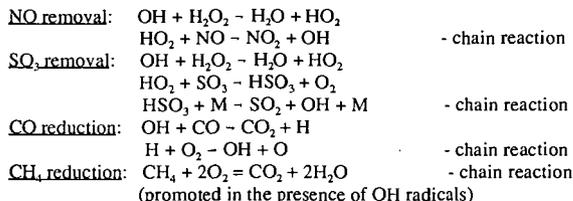
In the homogeneous H₂O₂ decomposition the total amount of OH radicals increases due to dissociation: H₂O₂ + M → 2 OH + M. The hydroxyl radicals formed have several reaction routes, including (1) the reaction with H₂O₂ molecules to form HO₂ radicals: OH + H₂O₂ → H₂O + HO₂; (2) chain termination steps, such as OH + HO₂ → H₂O + O₂; and (3) interaction with carbon-containing compounds, such as CO, CH₄ and other organics: OH + CO → CO₂ + H, OH + CH₄ → H₂O + CH₃, etc. The total CH₄-O₂ reaction, CH₄ + 2O₂ = CO₂ + 2H₂O, is promoted in the presence of OH radicals. As known from the literature⁹, H₂O₂ enhances oxidation of some other organic compounds due to the chain processes involving OH and other active species. Cooper et al.⁹ found that injection of H₂O₂ in dilute air mixtures of heptane and isopropanol increases the rate of their destruction at T = 910-1073 K and t_r = 0.26-0.94 s.

The HO₂ radicals, formed in the reaction of OH radicals with H₂O₂, play an important role in pollutants removal. The interaction of HO₂ radicals with NO, HO₂ + NO → NO₂ + OH, is the only rapid NO reaction at low and moderate temperatures, and this is the principal route of NO-to-NO₂ conversion. The HO₂ species react also with SO₃ followed by HSO₃ thermal decomposition: HO₂ + SO₃ → HSO₃ + O₂ and HSO₃ + M → SO₂ + OH + M.

Both modeling and experimental results show that NO is not converted to NO₂ in the absence of H₂O₂, but SO₃, CO, and CH₄ are converted to SO₂ and CO₂ at higher temperatures even without H₂O₂ addition. However, in non-ideal practical combustion systems all these pollutants, SO₃ and carbon-containing compounds, are present in flue gas, and H₂O₂ injection will reduce their concentrations.

The position of the H_2O_2 temperature window is defined by chemical nature of H_2O_2 reactions. At temperatures lower than 600 K the homogeneous H_2O_2 decomposition is very slow and OH and HO_2 radicals are not formed. At temperatures higher than 1100 K, concentrations of all radicals in the system become very high, and the rate of recombination reactions which are quadratic on radical concentration prevails over the rate of their reactions with molecules. An important factor is also the decomposition of HO_2 radicals at temperatures higher than 1000 K. Thus, H_2O_2 is active only in the temperature range of 600-1100 K.

It is believed that four chain reactions are involved in removal of air pollutants:



Thus, the single reagent can remove multiple air pollutants.

One can use H_2O_2 injection in combination with other NO_x control technologies, such as reburning, ammonia or urea injection, etc. to reduce NO to a very low level. In this case rather low NO concentrations (100-200 ppm) will react with H_2O_2 , which reduces the cost for the additive and reduces the residual (after scrubbing) NO_2 concentration, preventing the NO_2 brown plume. For example, in the COMBINOX process which includes reburning, urea injection, methanol injection and SO_2/NO_2 scrubbing, H_2O_2 could either completely or partially replace methanol to meet CO regulatory limits. Assuming 90% NO-to- NO_2 conversion by H_2O_2 injection and taking into account the pilot-scale results in other COMBINOX steps the total process will reduce NO_x emissions by 96%.

CONCLUSIONS

This paper demonstrates the feasibility of multiple pollutants removal (NO , SO_3 , CH_4 , and CO) by hydrogen peroxide injection within reaction times (0.2-2.0 s), temperatures (600-1100 K), and other conditions which are in the practical range for its application in boilers, furnaces, engines and other combustion installations. In the presence of H_2O_2 , maximum NO-to- NO_2 conversion was 95% in the flow system and 87% in pilot-scale at $H_2O_2/NO = 1.5$. SO_3 was effectively converted to SO_2 with up to 85% efficiency. CO-to- CO_2 conversion was slightly enhanced by about 20% at temperatures of about 900 K. Formation of carbon monoxide is incrementally increases when methanol is added to H_2O_2 . Mixtures of methanol and hydrogen peroxide can be injected to remove NO and to meet CO regulations at reduced cost for the additive. In the presence of H_2O_2 , CH_4 is effectively (70-90%) removed from flue gas at 1000 K and at $H_2O_2/NO = 0.9-2.2$. Kinetic modeling describes quantitatively or at least qualitatively all substantial features of NO , SO_3 , CO and CH_4 reactions with H_2O_2 .

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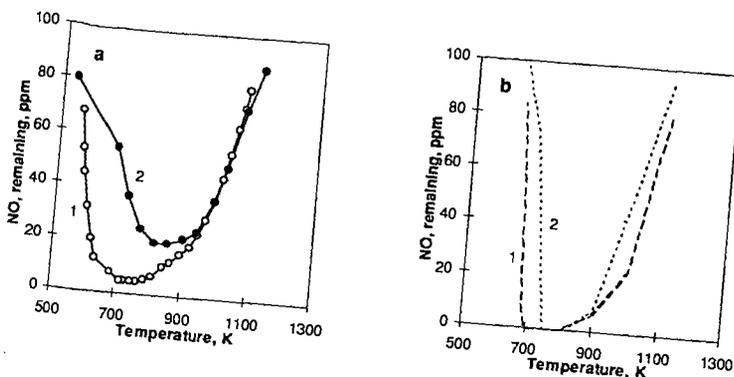


Figure 1. NO-to-NO₂ conversion by H₂O₂ injection. (a) - experimental and (b) - modeling data for $\tau = 1.0-2.0$ s; mixture (1): 100 ppm NO - (160-220) ppm H₂O₂ - 4.2% O₂ - 4.8% H₂O - balance N₂; mixture (2): 100 ppm NO - (90-120) ppm H₂O₂ - 4.4% O₂ - 1.7% H₂O - balance N₂.

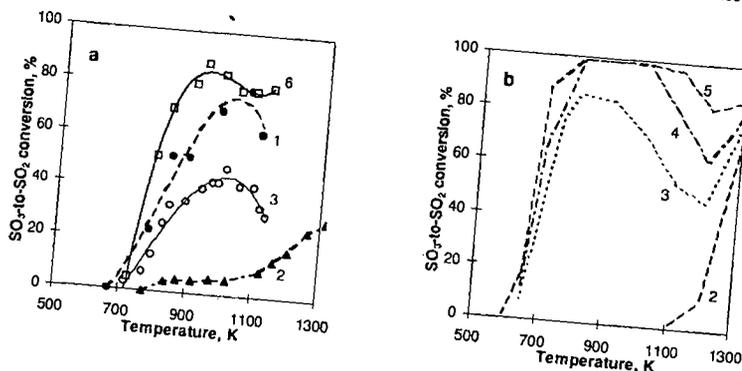


Figure 2. SO₃-to-SO₂ conversion by H₂O₂ injection. (a) - experimental and (b) - modeling data for $\tau = 1.0-1.6$ s; mixture (1): 100 ppm SO₃ - (160-220) ppm H₂O₂ - 4.2% O₂ - 4.8% H₂O - balance N₂; mixtures (2-5) are the same but with different amounts of H₂O₂: (2) - without H₂O₂, (3) - 100 ppm H₂O₂, (4) - 200 ppm H₂O₂, (5) - 500 ppm H₂O₂.

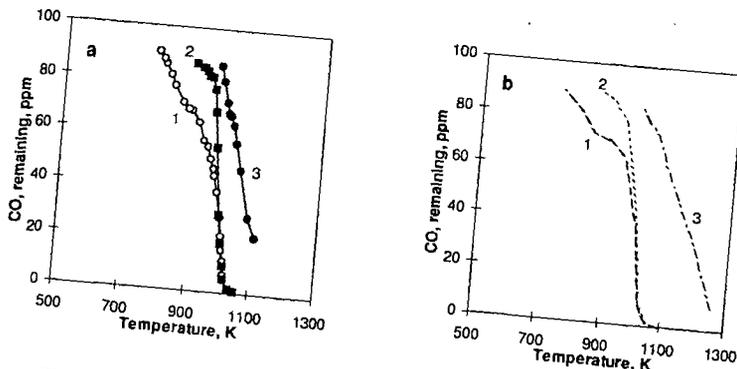


Figure 3. CO oxidation by H₂O₂ injection. (a) - experimental and (b) - modeling data for $\tau = 1.0-1.5$ s; mixture (1): 90 ppm CO - (160-220) ppm H₂O₂ - 4.2% O₂ - 4.8% H₂O - balance N₂; mixture (2): 90 ppm CO - 4.2% O₂ - 4.8% H₂O - balance N₂; mixture (3): 90 ppm CO - 4.2% O₂ - balance N₂ (10 ppm H₂O in modeling).

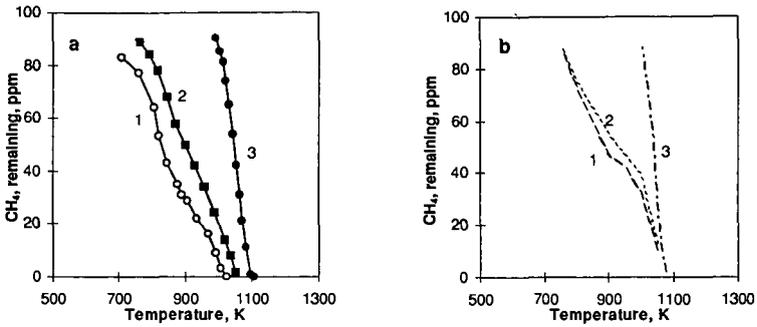


Figure 4. CH₄ oxidation by H₂O₂ injection. (a) - experimental and (b) - modeling data for $\tau = 1.0-1.8$ s; mixture (1): 90 ppm CH₄ - (160-220) ppm H₂O₂ - 4.2% O₂ - 4.8% H₂O - balance N₂; mixture (2): 90 ppm CH₄ - (90-120) ppm H₂O₂ - 4.4% O₂ - 1.7% H₂O - balance N₂.

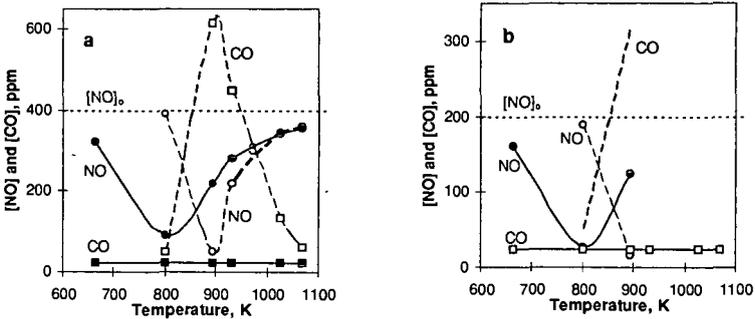


Figure 5. NO and CO concentrations after pilot-scale injection of H₂O₂ (solid curves) and CH₃OH (dash curves). $[Agent]/[NO]=1.5$. (a)- $[NO]_0=400$ ppm, (b)- $[NO]_0=200$ ppm.

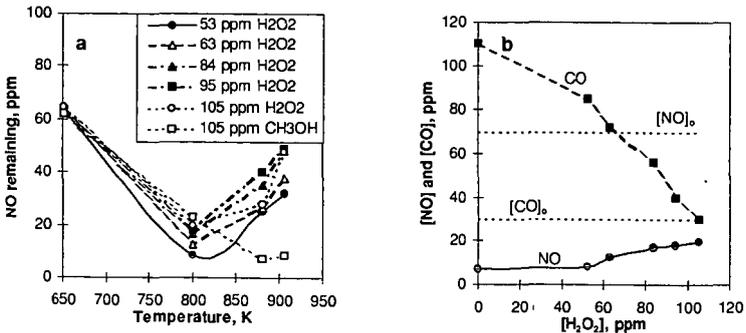


Figure 6. NO and CO concentrations after pilot-scale injection of H₂O₂/CH₃OH mixtures. $([H_2O_2]+[CH_3OH])/[NO]=1.5$, $[NO]_0=70$ ppm. (a) - temperature windows for various H₂O₂/CH₃OH mixtures, (b) - NO and CO concentrations at 800 K (at $[H_2O_2]=0$ data are shown for 866 K).