

Effect of propene on the remediation of NO_x from engine exhausts

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ABSTRACT

Plasma treatment of diesel exhausts has been investigated in recent years due to its potential for remediating NO_x in emissions. Hydrocarbons in the exhausts have been found to play an important role in the reaction chemistry during remediation. In this paper, we report on a computational study of the plasma treatment of simulated exhausts containing propene to investigate the effects of hydrocarbons on the conversion pathways for NO_x.

INTRODUCTION

Increasingly stringent regulations on the emission levels of NO_x in automotive exhausts has led to a reexamination of efficient methods of NO_x removal. The use of low-temperature plasmas followed by a downstream catalytic converter has been found to efficiently remove NO_x for select conditions [1, 2]. Dielectric barrier discharge (DBD) reactors have, in particular, been studied extensively for plasma remediation of these gases [3-7]. Accompanying experimental studies have investigated the consequences of reactor parameters such as packing material, electrode diameter, voltage, frequency, temperature and gas composition, that affect the NO_x conversion process [10, 12]. Computer modeling of plasma remediation of NO_x using DBD reactors has also improved understanding of the elementary processes [8-9,11]. Hydrocarbons in the exhausts have been found to play an important role in the NO_x conversion chemistry. Earlier studies on the effects of alkenes such as ethene [11] and propene [2] have suggested that there is a positive effect of hydrocarbons on the NO_x removal process.

The present study investigates the consequences of propene (C₃H₆) on the conversion mechanism of NO_x by applying a spatially homogeneous plasma chemistry model. The goals of this investigation are to quantify the

reaction mechanism, and determine the consequences of hydrocarbons on the remediation process. A brief description of the model followed by a discussion of the reaction mechanisms follow.

DESCRIPTION OF THE MODEL

A spatially homogenous/plug flow plasma chemistry model has been developed to investigate DBD discharges for the remediation of NO_x. The plasma chemistry model consists of an electrical circuit module, a solution of Boltzmann's equation for the electron energy distribution and a set of coupled ordinary-differential equations which are integrated in time and produce the time evolution of species densities. The model uses a lookup table produced by an offline Boltzmann solver to obtain the rate coefficients of electron impact processes as a function of electron temperature. These electron impact coefficients and the current E/N (electric field/gas number density) are used to solve the electron energy equation which provides the electron temperature. A total of 750 reactions make up the mechanism for the plasma chemistry of NO_x with the inclusion of propene, of which 76 are electron impact processes. The system of equations is implicitly integrated using LSODE to allow both the current pulse (10s ns) and reactor residence time (0.2 s) to be resolved. A temperature of 0.5 eV is assumed for the seed electrons and then the electron density and temperature are allowed to vary with time. Typically, the electron temperature peaks during the pulse to around 3 eV.

The parameters which have been varied to determine their effect on NO_x conversion are input energy, gas temperature and the inlet hydrocarbon concentration. Energy deposition was varied by changing the voltage applied to the DBD reactor.

The species in the initial feed to the reactor are shown in Table 1. Although all possible species that may be in

actual exhausts are not included, the input composition is representative of typical exhaust stoichiometry. All simulations were performed at 1 atm over a period of 0.2 seconds (residence time of the gas) with a single discharge pulse. A large portion of the temperature dependent reaction rate coefficients was obtained from the NIST Chemical Kinetics Database [13].

Species	Inlet Concentration
O ₂	8%
CO ₂	7%
H ₂ O	6%
CO	400 ppm
NO	260 ppm
H ₂	133 ppm
C ₃ H ₆	0-1100 ppm
N ₂	Balance

Table 1. Inlet concentrations to the DBD reactor.

REACTION MECHANISMS AND REMEDIATION

REMEDICATION VS INPUT ENERGY

Earlier studies have shown that at moderate energy input and low E/N, plasma remediation in the absence of hydrocarbons dominantly results in the conversion of NO to NO₂ and HNO_x with a small amount of NO getting reduced to form N₂ [14-15]. In order to establish a baseline for comparison to cases with hydrocarbons in the exhaust, simulations were first performed without propene. The temperature and pressure are 453 K and 1 atm respectively. The dielectric gap is 2.5 mm.

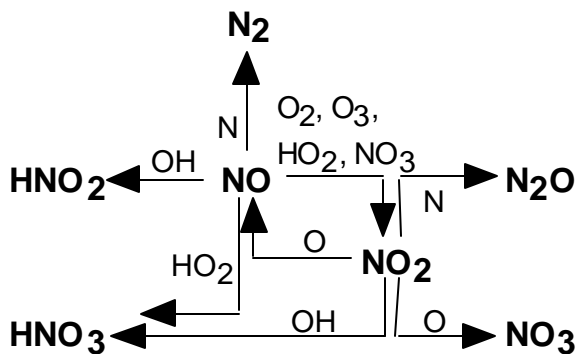
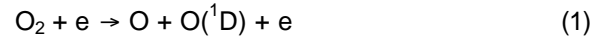


Figure 1 - Reaction mechanism for NO_x remediation in the absence of hydrocarbons.

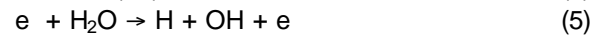
In this paper, remediation refers to the elimination of NO_x with no value judgement on the products. For example, HNO_x is undesirable in the control of diesel exhausts but may be desirable in other contexts, such as coal fired power plants.

In the absence of hydrocarbons, the most important reactions for NO_x remediation are shown in Fig. 1. A detailed discussion of the mechanisms are in Refs. [14] and [15]. The primary sink of NO is NO₂. Electron

impact processes result in the production of radicals such as O, OH and N, which react with NO to yield NO₂, HNO₃, and N₂. The main electron impact processes are those which produce O and N atoms.



OH is formed primarily by the reaction of H₂O with O(¹D) and by the electron impact dissociation of H₂O,



N atoms produced by the electron impact dissociation of N₂ effectively reduce NO to N₂.



N atoms are also involved in the conversion of NO₂ into N₂O,



Oxidation of NO takes place by a number of reactions, the main ones being,



The reaction of N atoms with O regenerates NO,

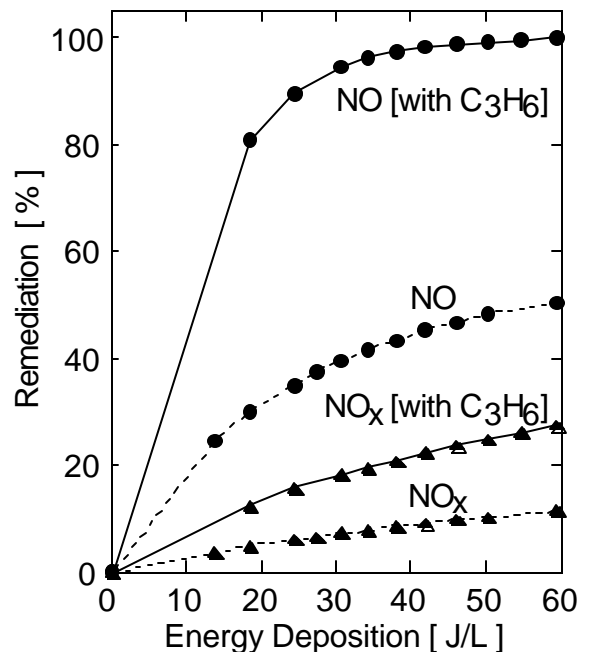


Figure 2 - Remediation of NO_x as a function of energy deposition with and without propene.

The fractional remediation of NO and NO_x and their concentrations are shown in Figs. 2 and 3 as a function of input energy deposition. NO conversion increases much more rapidly than the NO_x conversion with increasing energy deposition owing to the fact that most of the NO that gets converted goes into forming NO₂. At high energy inputs, as much as 15 ppm of NO_x is removed in the form of HNO_x. The CO concentration as a function of energy deposition is shown in Fig. 3. Almost 60 ppm of additional CO is produced at an input energy of 60 J/L. It is found that as high as 40% of the CO produced at the higher energy inputs is due to electron impact reactions with CO₂.



Reactions of CO₂ with N also lead to the formation of CO, and regeneration of NO.



CO production due to the presence of CO₂ has also been discussed in Ref. 16.

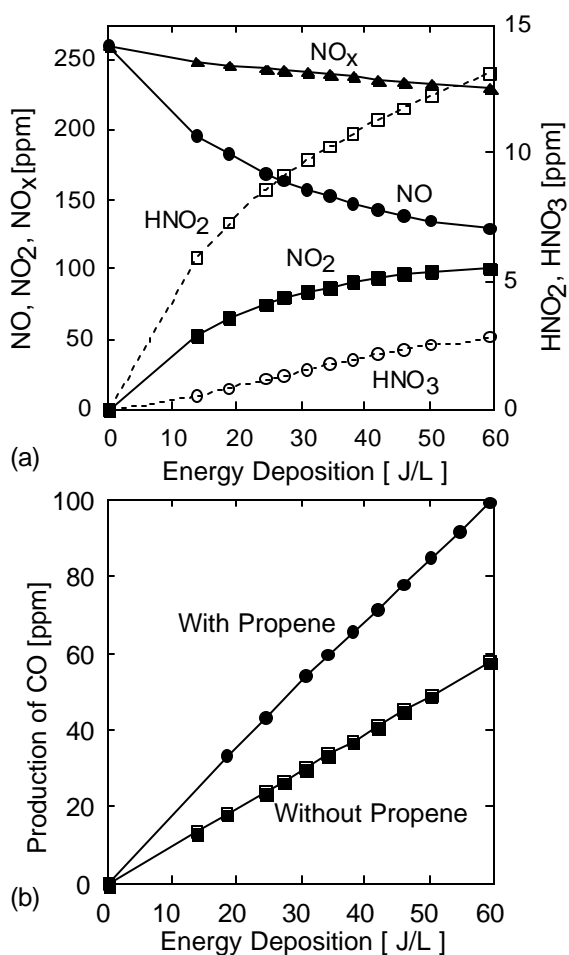
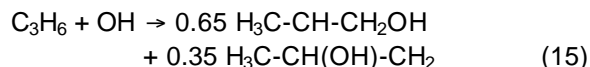


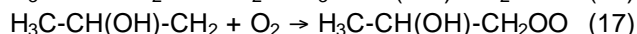
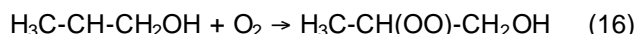
Figure 3 – Concentrations as a function of energy deposition. a) Exit values for NO_x and HNO_x without propene. b) Production of CO with and without propene.

REMIEDIATION VS INPUT ENERGY WITH PROPENE

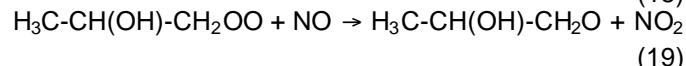
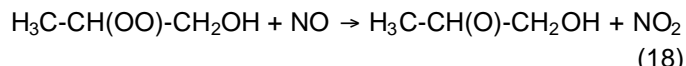
The addition of hydrocarbons changes the reaction mechanism significantly. Simulations were performed at 453 K, 1 atm and with an initial [C₃H₆] of 500 ppm. The breakdown of propene proceeds primarily by the addition of OH to form the corresponding β-hydroxyalkyl radicals. [17]



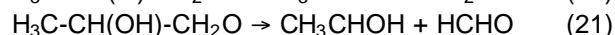
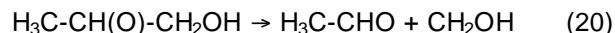
These species further react with O₂ to form the peroxy radicals,



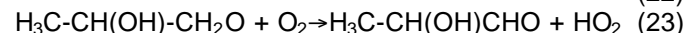
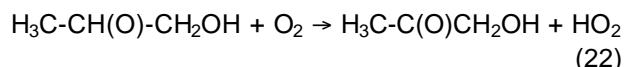
The rate constants for these processes have been discussed by Miyoshi et al. [18]. The peroxy radicals are ultimately the species which react with NO to convert it into NO₂.



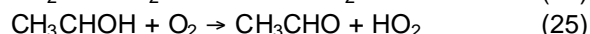
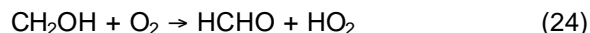
The resulting alkoxy radicals either decompose or react with O₂ to form the final products. It has been reported that decomposition of the alkoxy radicals is the major pathway that explains the experimentally observed products of the DBD processing with C₃, C₄ alkenes [19, 20]. Therefore, we include the decomposition of the alkoxy radicals as the final step in the reaction mechanism.



The reaction of the alkoxy radicals with O₂ proceeds via the following reactions.



The α-hydroxy radicals formed from the decomposition of the β-hydroxyalkoxy radicals react rapidly with O₂ to form aldehydes.



The formation of nitrates/nitrites by the reaction of β-hydroxyalkyl peroxy radicals with NO has also been included though they have been found to account only for a small fraction of the total reactions with NO [21].

Results for NO remediation in the presence of propene with varying input energy are shown in Fig. 4. The inclusion of the hydrocarbon reactions has significantly

reduced the NO concentration and has also improved the NO_x conversion.

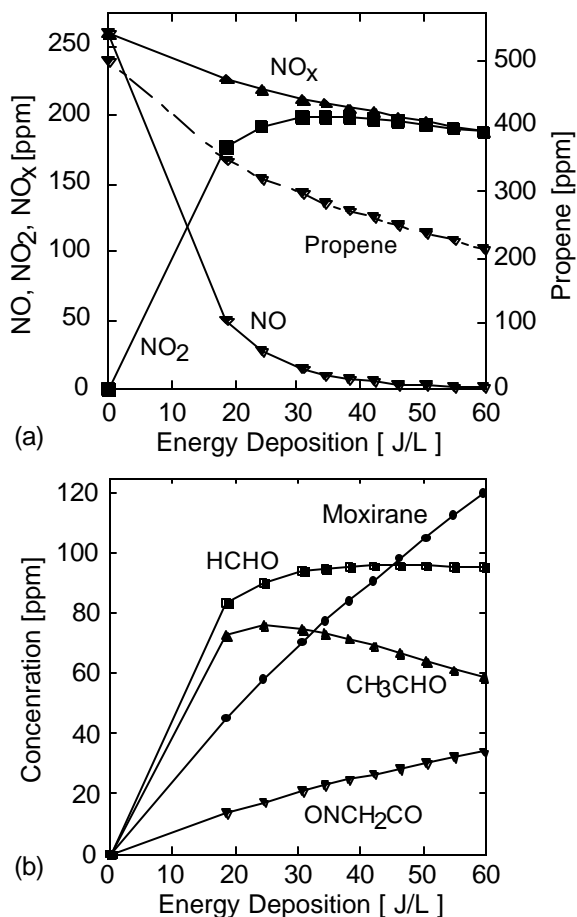
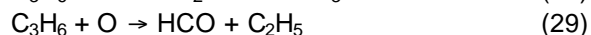
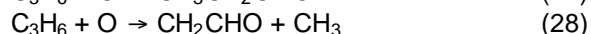


Figure 4 – Concentrations as a function of energy deposition with propene. a) Exit values for NO_x and propene b) Hydrocarbon species.

O attack on C₃H₆ mainly proceeds by the following pathway [17].



These products of the reaction of O with propene then further react with other species in the system. In particular, the CH₂CHO which is produced in the system reacts with NO and O₂.

The extra NO_x removal as, compared to the case without hydrocarbons, mainly comes from the reaction,



where, the CH₂CHO is produced by reaction (28).

When including the reaction of CH₂CHO with O₂, the net production of ONCH₂CHO decreased from a value of around 18 ppm to around 6 ppm at 30 J/L. Though experiments have been performed to estimate the high pressure rate constant for the reaction of CH₂CHO with

O₂, the products of the reaction have not been directly monitored. Since the products of this reaction are unclear, further study of this reaction pathway is required.

Increased energy deposition produces more O atoms. This leads to an increased production of CH₂CHO, which consumes more NO to form ONCH₂CHO resulting in NO_x removal.

Increased energy deposition produces more removal of NO, though less so for NO_x as shown in Fig. 4. Only about 18 ppm of NO remains after processing with 30 J/L. However, most of the NO removed appears as NO₂. As the energy deposition is increased, more NO is channeled along reaction (30) to produce ONCH₂CHO. The consumption of propene also increases with increasing input energy because of the increased production of OH radicals and O atoms.

The concentrations of the major end products of the hydrocarbon-NO_x system are shown in Fig. 4. One of the major end products is the aldehydes — namely formaldehyde and acetaldehyde, which are produced by reactions (24) and (25). Methyl oxirane as discussed earlier is also produced in significant amounts at higher energies because of the increased production of O atoms.

It is worthwhile noting that in all the simulations performed, ozone(O₃) does not build to significant amounts due to its reaction with NO to give NO₂ and O₂.

The presence of propene increases the production of CO, as shown in Fig. 3. Though produced in smaller amounts when compared to other end products, this production of CO may be of concern at higher energy inputs. As much as 100 ppm of CO is produced with an energy input of 60 J/L.

PROPENE CONCENTRATION

The inlet hydrocarbon concentration was varied while keeping the applied voltage and the initial temperature fixed. All the results for this parameterization were obtained at 453 K, 1 atm, and 30.9 J/L. The variations of NO and NO₂ with inlet propene concentration are shown in Fig. 5. More propene results in an increased rate of reaction (15), which accelerates every step further down the reaction pathway, thereby leading to an increased conversion of NO. However, the NO_x conversion does not significantly change owing to the main conversion of NO by the peroxy radical pathway rather than by CH₂CHO, as shown in Fig. 6. At high propene concentration O atoms are the species present in smaller quantities and its production is dominated by energy deposition, which is fixed. Therefore this reaction pathway should not be significantly affected by the increase in propene concentration.

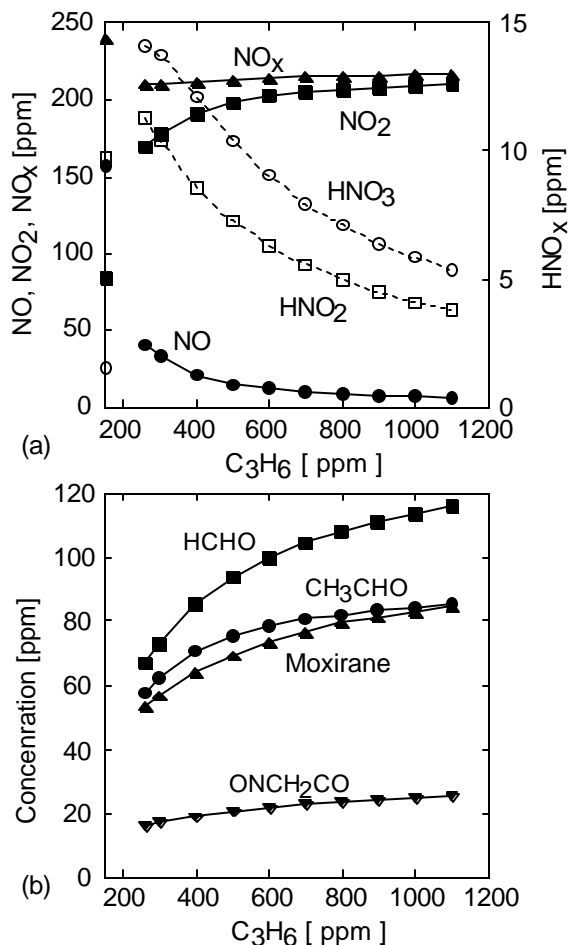


Figure 5 – Concentrations as a function of propene concentration. a) Exit values for NO_x and HNO_x b) Hydrocarbon species. The values on the vertical axis are for no propene.

The concentrations of $HCHO$, CH_3CHO and methyl oxirane at the end of the process as a function of the inlet hydrocarbon concentration are shown in Fig. 5. As the propene concentration increases, more total propene is consumed [but a smaller fraction of the feed gets converted] and, as a result, the final products also are generated in larger quantities. The $[HNO_2]$ and $[HNO_3]$ decrease with the increase in $[C_3H_6]$ because, as $[C_3H_6]$ increases, more of the available OH reacts with C_3H_6 . The effective production of these two acids is then reduced since the amount of OH available for the reactions with NO decreases.

The percentage consumption of propene decreases with increasing initial propene concentration. At higher concentrations of propene, larger energy deposition is required to generate more radicals to react with the hydrocarbons. Energy deposition remaining fixed, the percentage consumption of propene decreases as a result, as shown in Fig. 6. CO production decreases moderately.

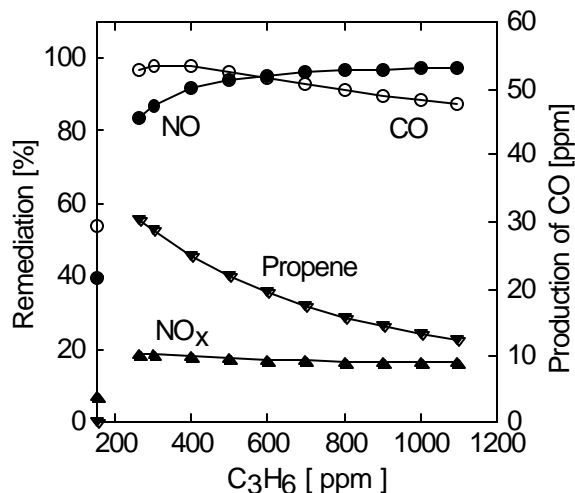


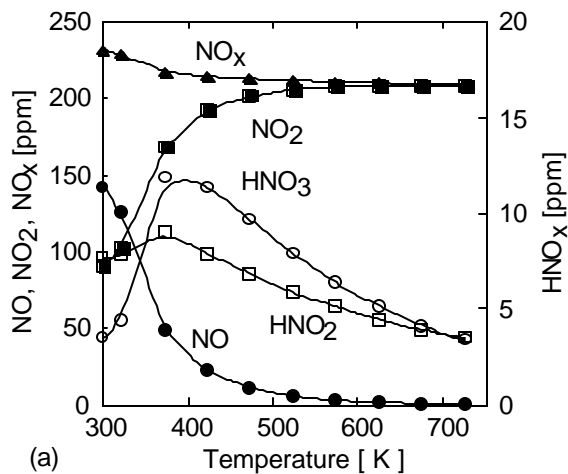
Figure 6 – Remediation of NO_x , consumption of propene and production of CO as a function of initial propene concentration. The values on the vertical axis are for no propene.

TEMPERATURE DEPENDENCE

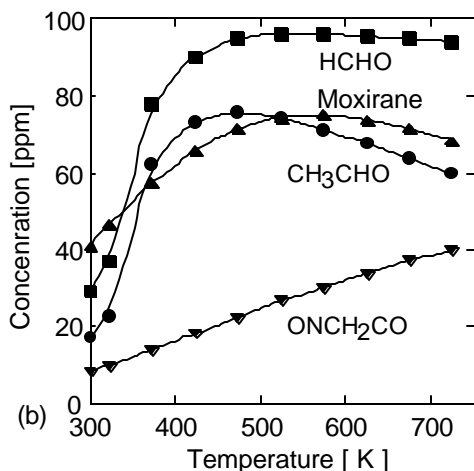
The effect of temperature on the conversion of NO_x with a constant energy deposition of 30.9 J/L and inlet $[C_3H_6]$ of 500 ppm was investigated. The temperature has a small effect on the NO_x conversion though it has a significant effect on the NO conversion as shown in Fig. 7. The increase in NO conversion obtained with increasing temperature is counteracted by the increase in $[NO_2]$ resulting in an almost constant NO_x level.

The effect of temperature on the concentration of major end products is also shown in Fig. 7. There are maxima for the production of end products, rising from the complex reaction mechanisms involved in their production and the highly non-linear nature of their rate coefficients with temperature. At high temperatures ($T > 650$ K), the $CH_3CH(OH)CH_2$ and $CH_3CH_2CH_2OH$ radicals decompose rapidly to their reactants and the OH radical addition reaction effectively will not occur. Rather, the reaction proceeds by H-atom abstraction to yield CH_2CHCH_2 . Given these dependencies, some control of end products can be obtained by choice of operating temperature.

The net effects of temperature on conversion/ production are shown in Fig. 8. NO conversion increases with temperature and, in fact, reaches to as high as 99% around 550 K. However, NO_x removal remains nearly constant. The CO concentration increases with temperature.



(a)



(b)

Figure 7 – Concentrations as a function of gas temperature. a) Exit values for NO_x and HNO_x . b) Hydrocarbons.

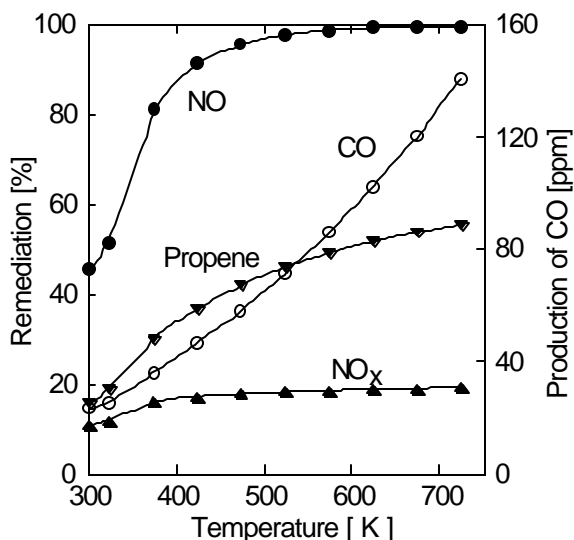


Figure 8 – Remediation of NO_x , consumption of propene and production of CO as a function of gas temperature.

CONCLUDING REMARKS

The effect of propene on the remediation of NO_x in a humid gas mixture using a dielectric barrier discharge has been investigated. Parameters affecting the NO_x

conversion, such as energy deposition, initial propene concentration and temperature were varied and their effects on NO_x removal were quantified. NO_x removal improves with increasing input energy, though temperature and inlet propene concentration have a smaller effect on the NO_x conversion. However, all the three parameters have been found to significantly affect the concentration of all the other species in the reactor, particularly NO. Production of CO as a side-product is moderate and should be considered in post plasma catalysis systems.

Though methyl nitrate has been reported as one of the major end-products of the plasma processing of gases of a slightly differing composition, the present model does not predict its production. It remains as an object of further investigation to determine whether the surface reactions or some other mechanisms play the important role of steering the reaction pathway towards the formation of methyl nitrate. [22]

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