PLASMA REMEDIATION OF NO_X FROM DIESEL EXHAUSTS : EFFECTS OF PROPENE AND PROPANE

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AGENDA

- Research Goals
- Research Plan
- Description of the model
- Reaction kinetics in the propene system
- Simulation results of the propene system
- Effects of the addition of propane
- Conclusions and Future Work

RESEARCH GOALS

- Investigate the effect of hydrocarbons (e.g., propane, propene, i-butane, dodecane, toulene) on the reaction mechanisms of NO_X
- Incorporate the effects of surface reactions in the plasma chemistry module and analyze the final exit gas characteristics and composition.
- Study the effect of particulates on the reaction mechanisms of NO_X
- Determine optimal conditions and propose strategies for the complete removal of NO_X from diesel exhausts.

RESEARCH DONE TO DATE

- Studied and identified the basic underlying reactions driving the plasma chemistry in the systems containing NO_X and
  - Propene
  - Propane
  - n-Butane
  - iso-Butane

- Implementation of the reaction scheme into the global kinetics module and simulation of the plasma remediation of NO_X in the presence of these HCs.

RESEARCH PLANS

- Quantify and compare the effect of multiple pulses in the plasma remediation process with that of the single pulse input.

- The general trend in the plasma chemistry for other alkenes or alkanes will closely resemble that of propene or propane.
  Our next task will be therefore to study the role of surface reactions in these systems

- Develop a representative reaction mechanism for investigating the surface reaction kinetics in the NO_X processing of diesel exhausts.

ISSUES IN MODELLING ALKANES AND ALKENES

- Alkanes are in general much less reactive when compared to alkenes due to the absence of double bond. Hence, one would always expect more formation of the products along the alkene degradation line than the alkane one.

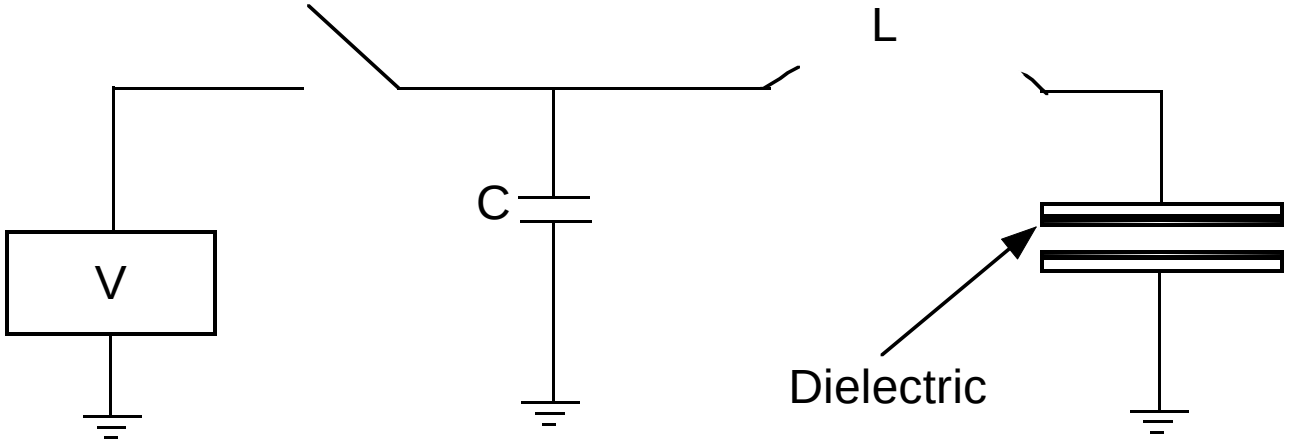
- As one analyzes higher hydrocarbons, the reaction chemistry becomes more involved and complicated. The branching ratios become more uncertain.The species of any given reaction are more in number. This is further complicated by the increased occurances of isomerizations in such systems.

- Unavailability of reaction rate data for higher hydrocarbons restricts the analysis to lower hydrocarbon systems.

THE EXPERIMENTAL SETUP MODELLED

- A dielectric barrier discharge reactor has been modelled with the following characteristics.

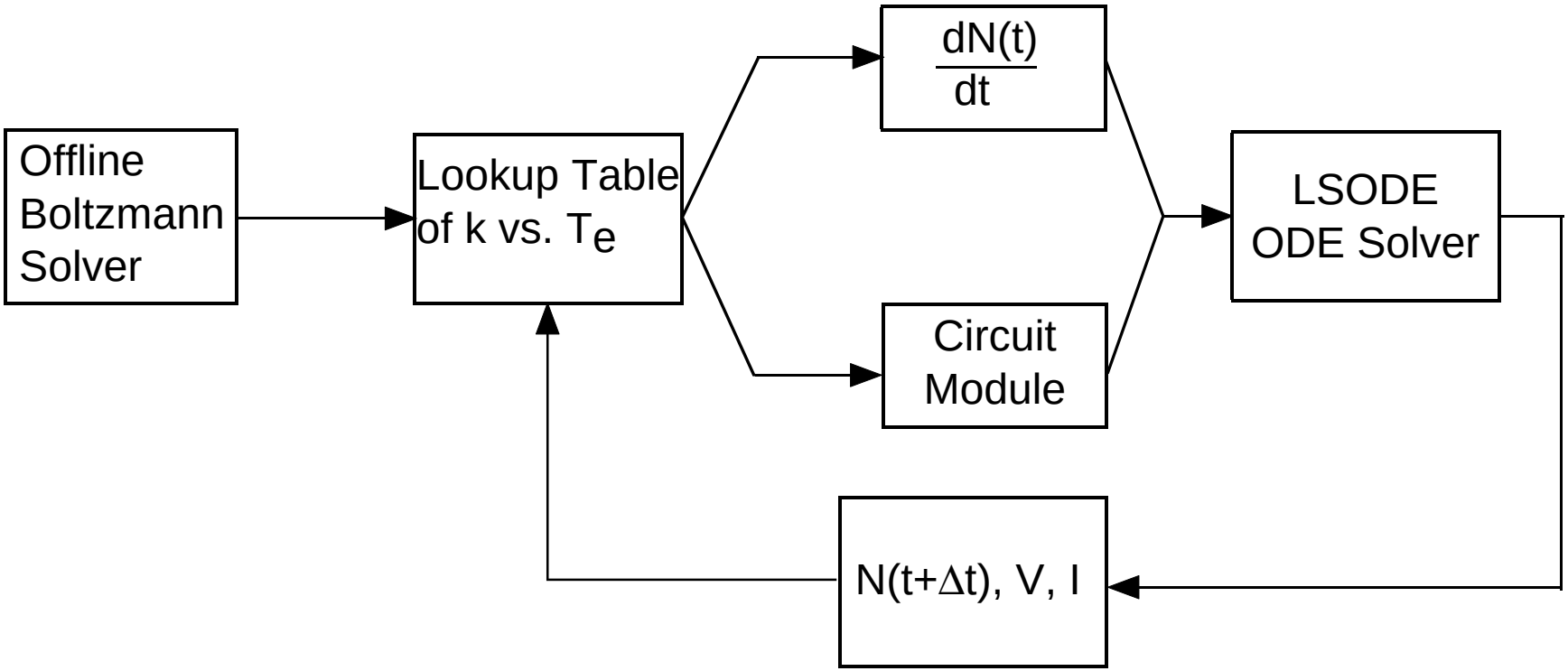
  - Dielectric discharge height = 2.5 mm
  - Reactor pressure = 1 atm
  - Single pulse input



Schematic of the device modelled

DESCRIPTION OF THE MODEL

- The basis of the model is to integrate the non-linear ordinary differential equations describing the reaction chemistry over the residence time with the simultaneous solution of the equations for the circuit parameters.
- The rate coefficients for the electron impact reactions are obtained from a lookup table produced by an offline Boltzmann solver.



Block diagram representation of the model

REACTOR OPERATING CONDITIONS

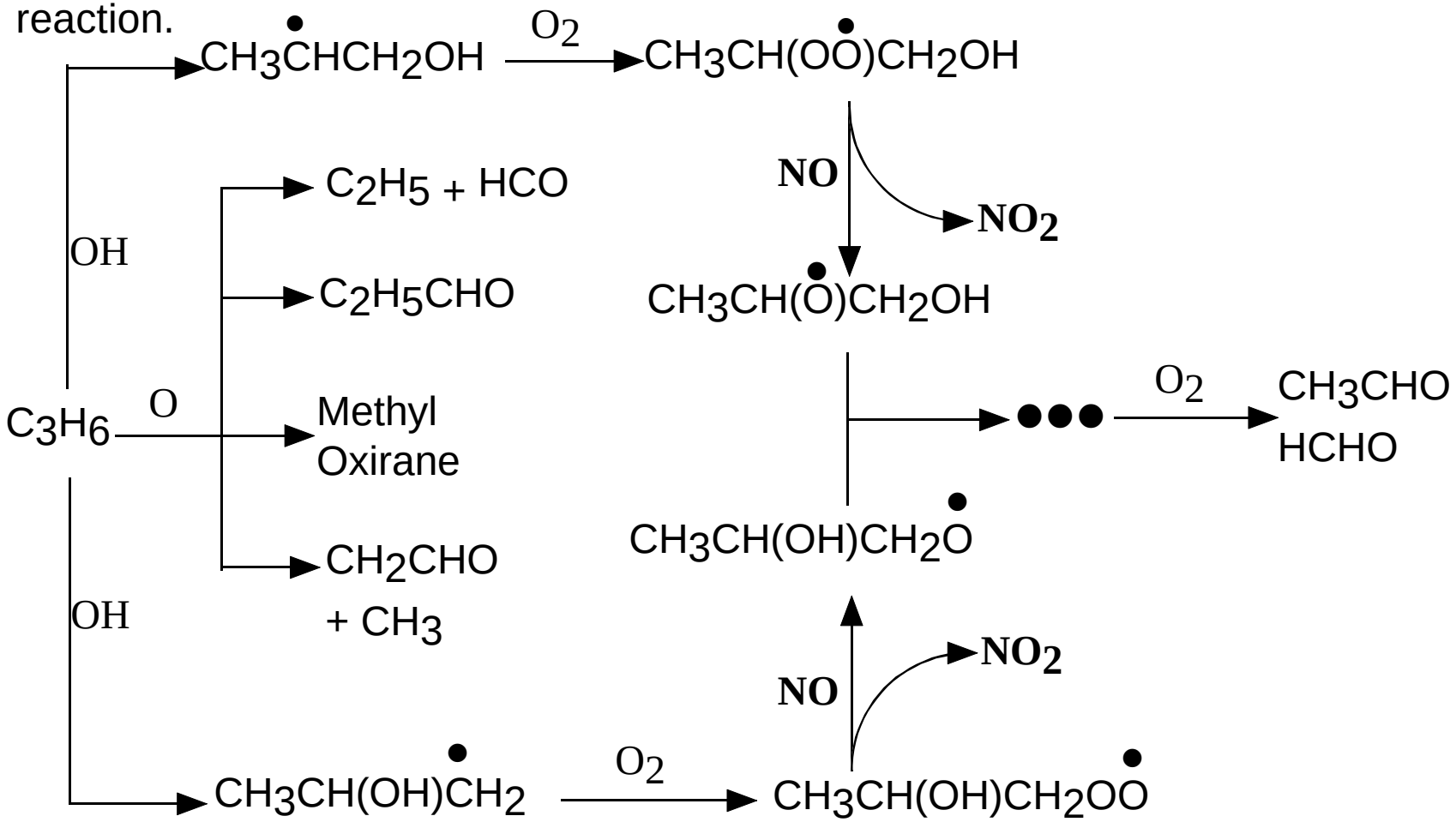
- Basic composition of the gas at reactor entrance :

CO_2 = 7%	O_2 = 8%	H_2O = 6%
CO = 400 ppm	NO = 260 ppm	H_2 = 133 ppm
C_3H_6 = 0 -1100 ppm	C_3H_8 = 0 - 600 ppm.	
N_2 = Balance		

- Temperature = 453 K
- Pressure = 1 atm
- Applied voltage = 14 - 25 V

PROPENE AS A CONSTITUENT IN THE INLET GAS

- The presence of propene affects the reaction mechanism significantly.
- One of the major sources for the NO consumption is the peroxy radical produced by the reaction of O_2 with the products of the OH-propene reaction.



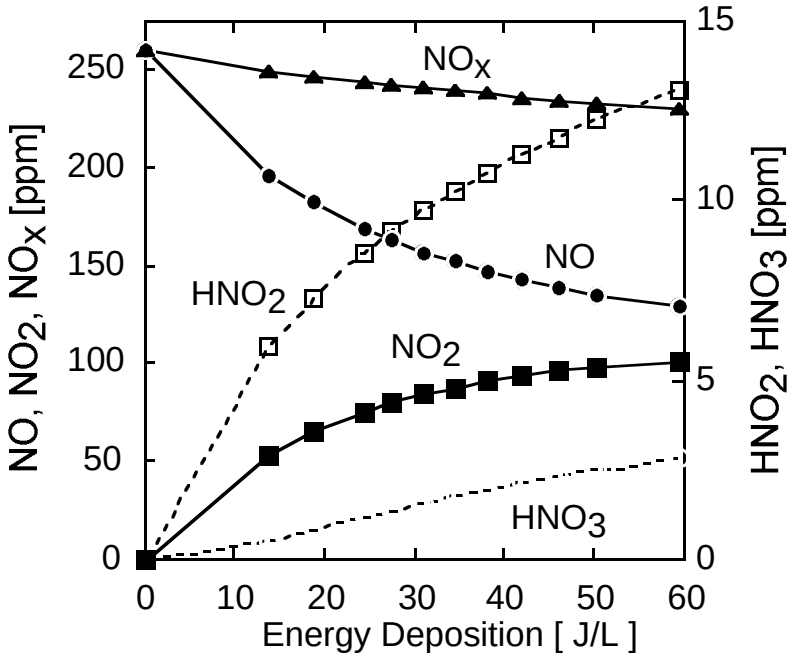
Reaction Mechanisms For Propene - NO_X

BASIC ELECTRON IMPACT REACTIONS TRIGGERING THE PLASMA PROCESSING

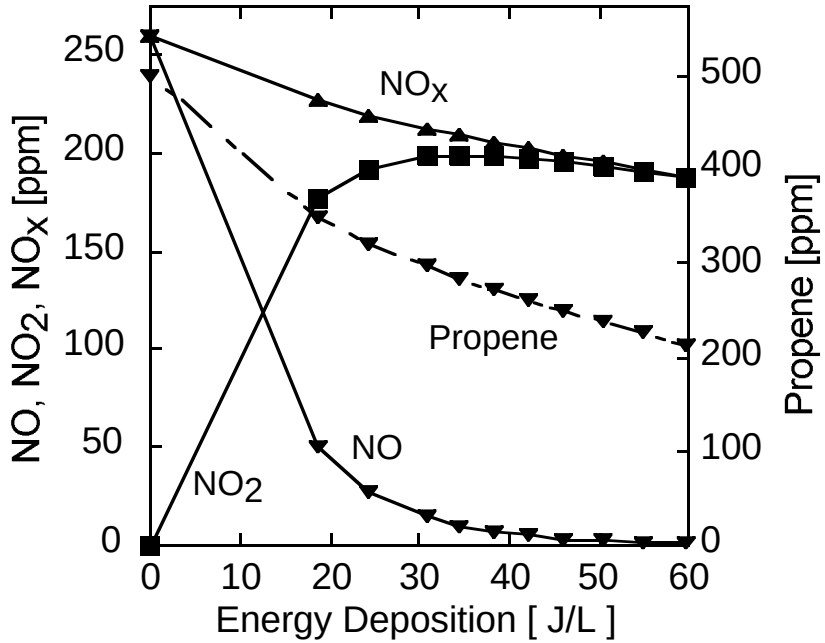
- The basic electron impact reactions are :
  - $e + O_2 \longrightarrow O + O + e$
  - $e + N_2 \longrightarrow N + N + e$
  - $e + H_2O \longrightarrow OH + H + e$
- OH radicals are also generated by the reactions of $O(^1D)$ with water
  - $O(^1D) + H_2O \rightarrow OH + OH$

EFFECTS OF INPUT ENERGY ON PROPENE-NO_X SYSTEM

- In the absence of propene, increasing input energy results in an increased rate of NO reduction, but a much lesser rate of NO_X removal.
- The same trend continues with propene included in the system, except that the NO_X removal increases quite a bit.



NO_X processing in the absence of propene

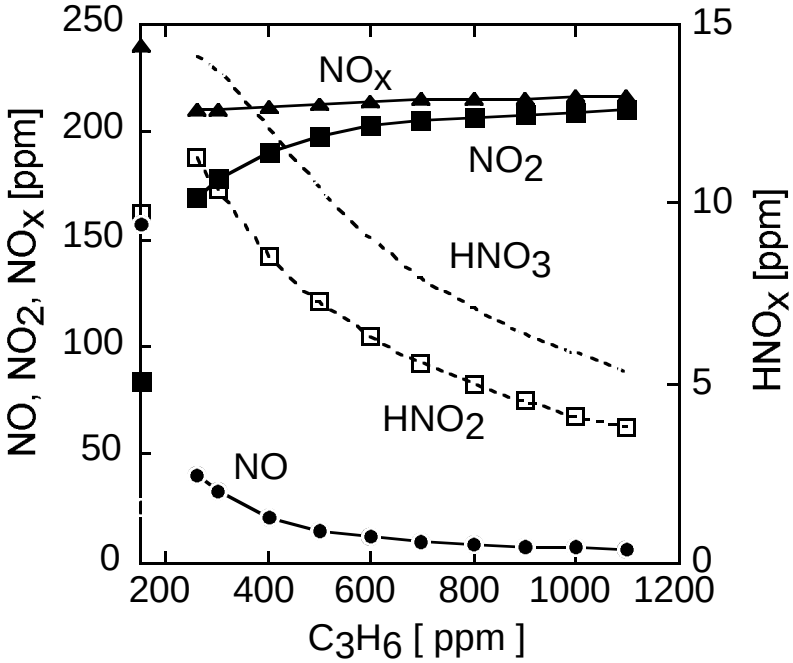


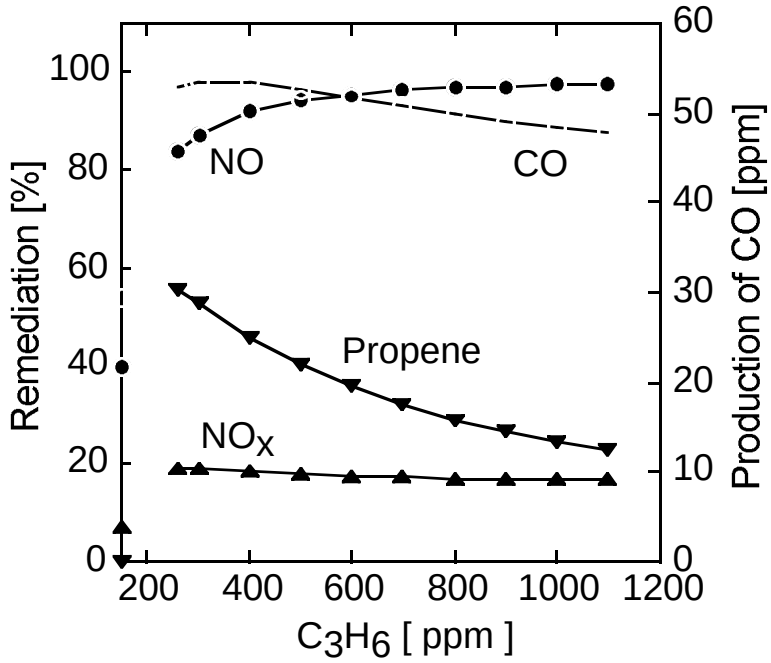
NO_X processing in the presence of propene

EFFECT OF PROPENE CONCENTRATION

- Increasing amounts of the hydrocarbon in the inlet gas results in an increased conversion of NO to NO_2 and hence, the NO_X removal doesn't get affected.

- More amount of inlet hydrocarbon effectively reduces the concentration of the radicals available to other species in the reactor. This is evident from the decrease in the concentration of HNO_X with propene.



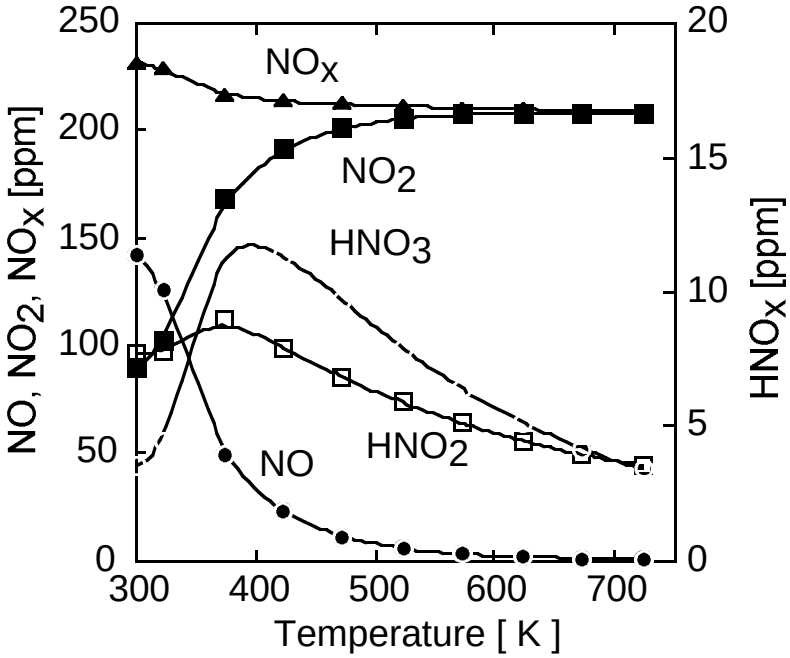


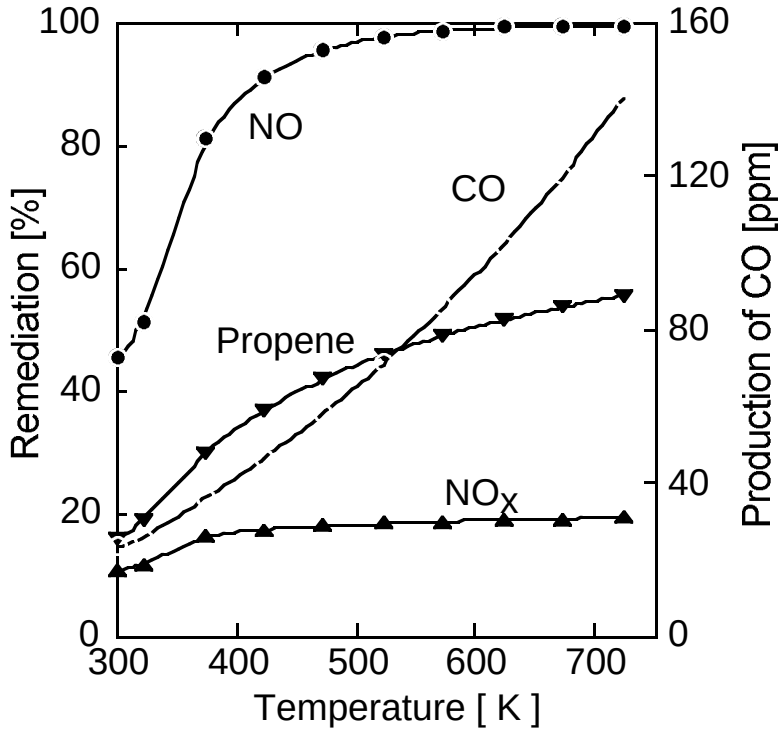
- There is also a decrease in the propene conversion because the radicals such as OH, O are present in limiting quantities.

EFFECT OF GAS TEMPERATURE ON NO_X CONVERSION

- Increasing the gas temperature seems to affect the NO_X concentration minimally.

- There is however an increase in the exit concentration of CO and other propene-initiated reaction products with reactor gas temperature.





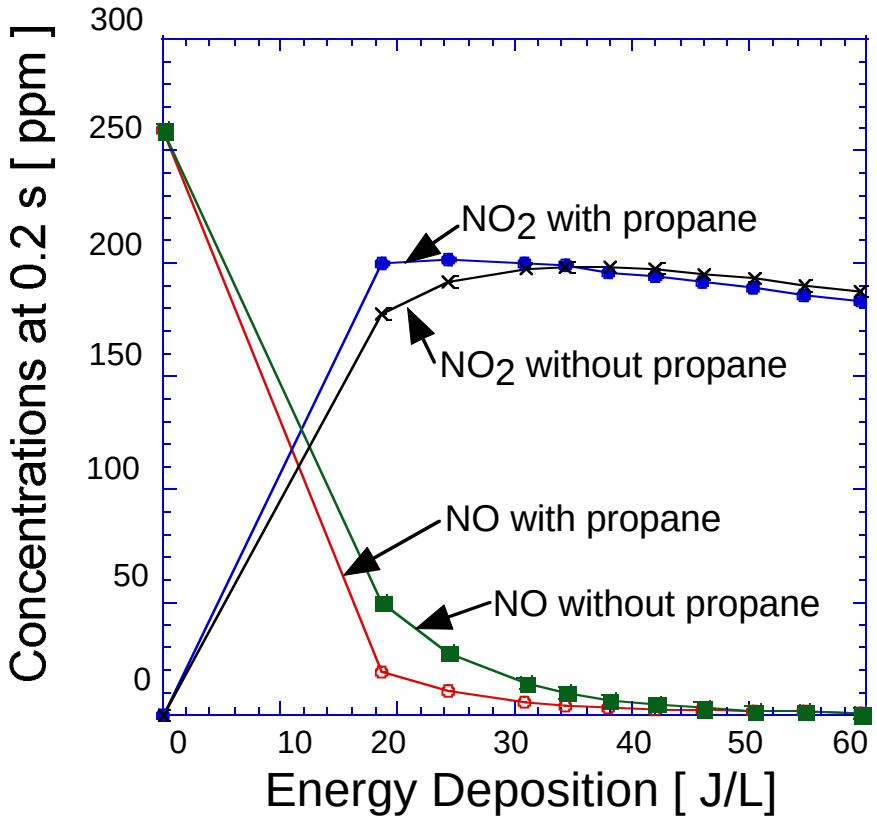
Effect of gas temperature on the concentration of species in the DBD reactor

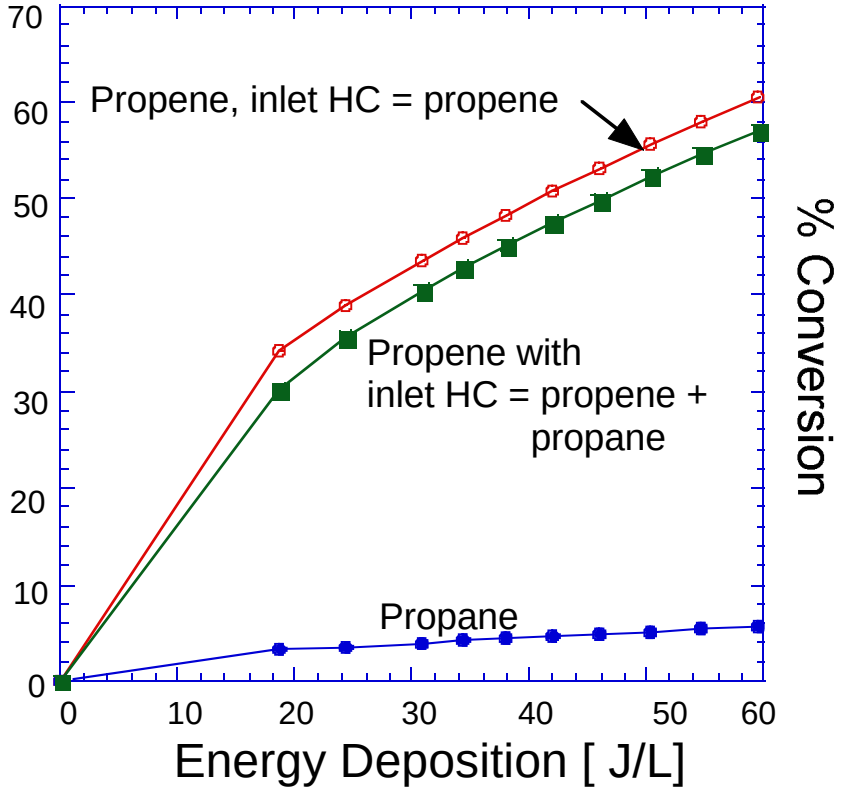
ADDITION OF PROPANE TO THE PROPENE-NO_X SYSTEM

- Under atmospheric conditions, the usual loss processes for alkanes are the reactions with OH and NO_3 radicals.
- The introduction of propane into the inlet gas results in a further decrease in the NO exit concentration, though it's effect on the NO_X is insignificant.
- The alkanes branch down along the reaction tree to produce the alkyl radicals by the H-abstraction reaction with OH, which then react with O_2 to form the peroxy radicals. These peroxy radicals then react with NO to convert it into NO_2.
- Thus, there is no direct elimination of NO_X by the addition of propane to the system.

EFFECTS OF PROPANE ON NO, NO_2 AND HC CONVERSION

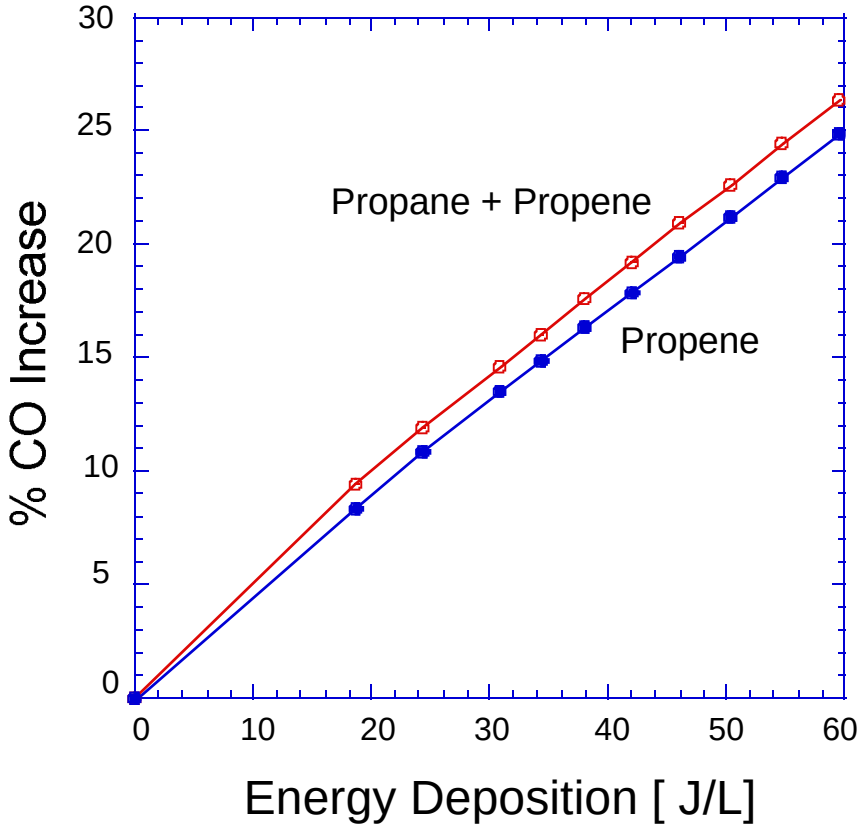
- NO conversion increases to a small extent. Most of the extra NO converted is due to the addition of propane and goes into forming NO_2
- Propene conversion goes down in the presence of propane, since the available radicals are then shared between the two hydrocarbons. However, this effect is quite small since C_3H_8 is much less reactive compared to C_3H_6

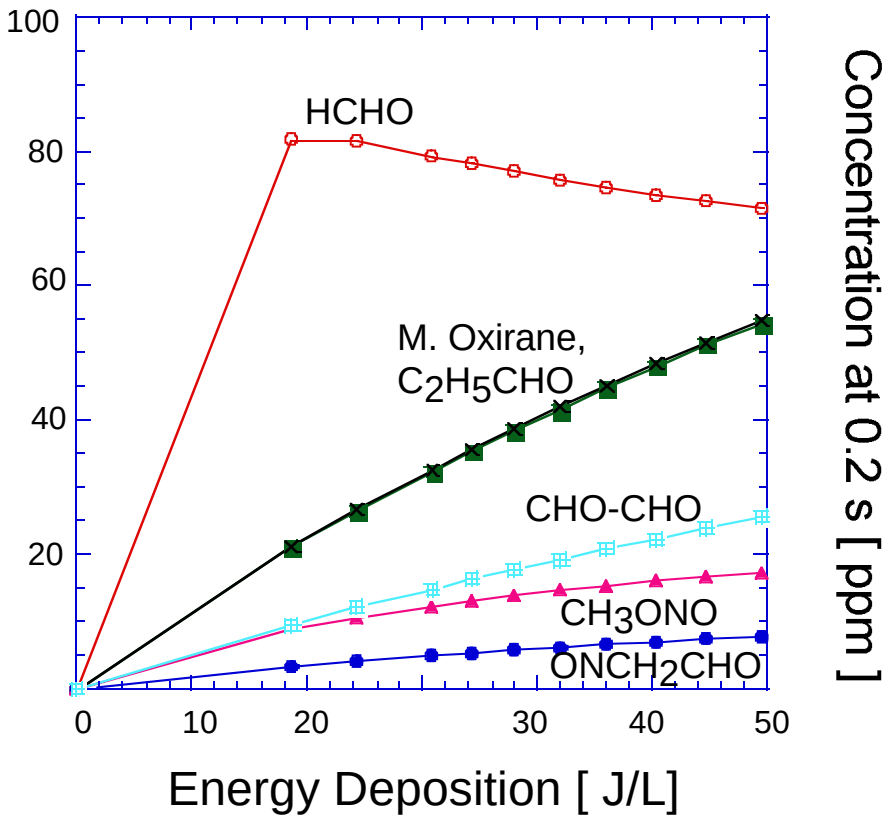




EFFECTS OF PROPANE ADDITION (Contd...)

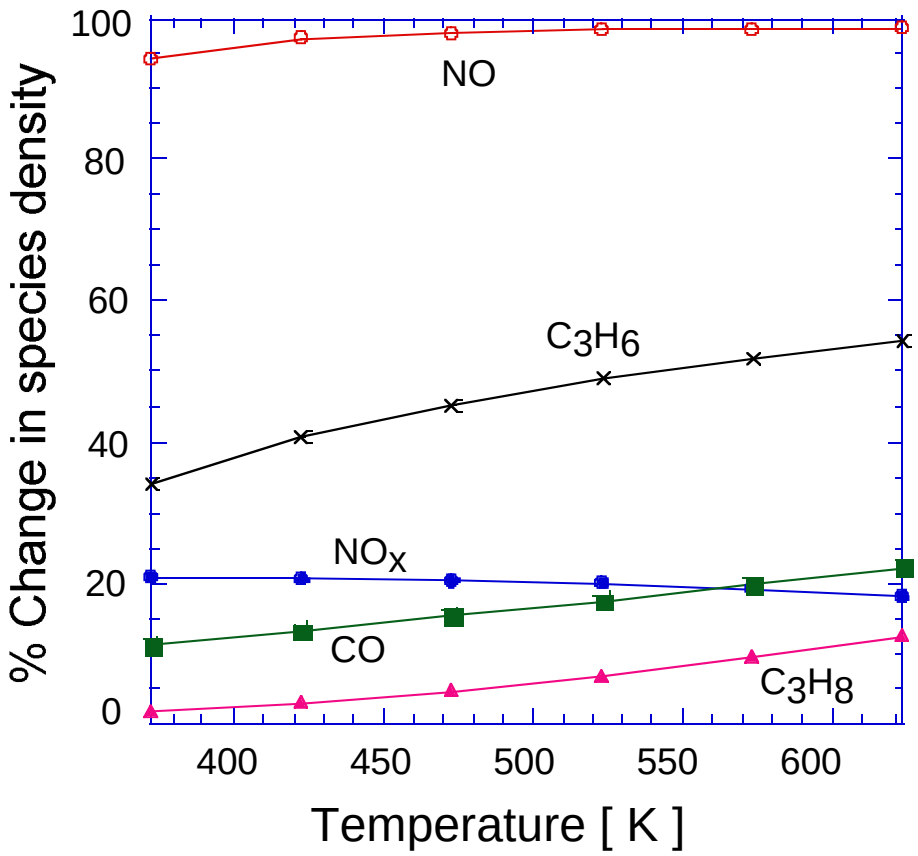
- Propane has a few % effect on the CO production.
- The final end-products generated in significant amounts include HCHO, oxirane, propionaldehyde, glyoxal and methyl nitrite.

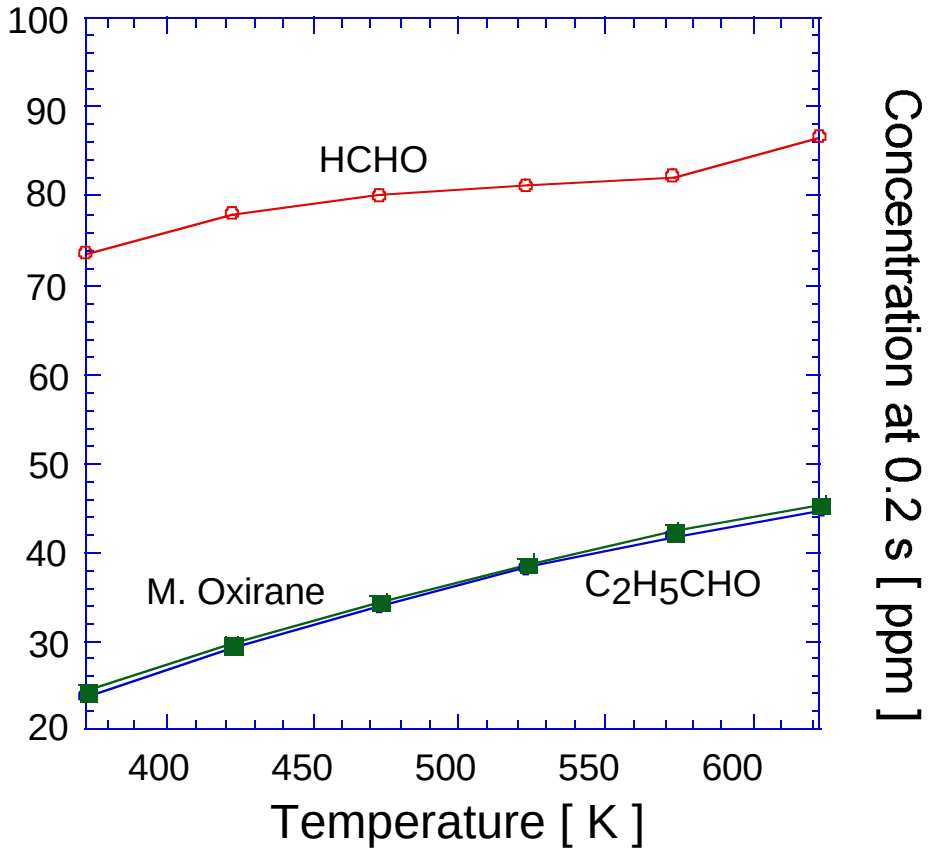




EFFECTS OF TEMPERATURE ON PROPANE + PROPENE SYSTEM

- Temperature has a small effect on NO as well as NO_X conversion, but has a noticeable effect on the concentration of propene, C_3H_8 and CO
- In general, the concentration of the major end-products increases with increasing inlet gas temperature.





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OPTICAL AND DISCHARGE PHYSICS

THE $ONCH_2CHO$ CONTROVERSY (?) !!!

- Rate coefficients for the reaction of O with C_3H_6

Reaction	Rate Coefficient (cm^3/molecule/s) at 298 K	Source
$O + C_3H_6 \rightarrow$ Products	4.79e-12	J.P.C.R.D., 1991, **20** 221-224
$O + C_3H_6 \rightarrow$ Methyl Oxirane	4.81e-12	Gaedtke *et.al.*, Symp. (Int.) Combust., [Proc.]_1973,**14**,295
$O + C_3H_6 \rightarrow CH_2CHO + CH_3$	0.3 x (4.79e-12)	Knyazev *et.al.*, Int. J. Chem. Kinet., 1992 **24**,545-561.
$CH_2CHO + O_2 \rightarrow$ Products	2.6e-13	J.P.R.C.D., 1991, **21** 411-429.
$CH_2CHO + O_2 \rightarrow HCHO + CO + OH$	3.0e-14	-- Do --

- Since reactions of CH_2CHO with O_2 are so significant, the products need to be determined

THE $ONCH_2CHO$ CONTROVERSY (?) !!! (Contd...)

- The reaction products were unknown during initial parameterization (not that they are now), and so only the reaction with O_2 to give HCHO was included.

- There is evidence from the OH radical initiated reaction of acetylene that OH radicals are produced. Therefore the possible reaction products could be HCHO and/or glyoxal. [Atkinson, J.P.R.C.D.,1997, **26**, 2, 215-290]

$$CH_2CHO + O_2 \rightarrow [OOCH_2CHO] \rightarrow \begin{cases} HCHO + CO + OH \\ (CHO)_2 + OH \end{cases}$$

- When this reaction scheme is incorporated, then net reaction of CH_2CHO with NO is reduced to about 20%.

CH_3ONO - WHY WAS THIS NOT PREDICTED EARLIER(?)

- One another classic case of disparity in the reaction rates reported by the NIST Standard Reference Data.
- The reaction of concern is : $CH_3ONO \longrightarrow HCHO + HNO$

	Source	Rate Coefficient (cm^3/molecule/s)	Order	Reaction Rate (molecule/cm^3/s)
	Ohmori *et.al*	7.70e-12	2	= 7.70e-12 x [CH_3ONO] x [M]
1 →	Bull. Chem. Soc. Jpn., 1993, **66,** 51-56.			
	Batt *et. al.*	2.067e-08	1	= 2.07e-8 x [CH_3ONO]
2 →	Int. J. Chem. Kinet., 1975,**7**,441.			

Ratios of rates as given by sources 1 and 2 = 10^{15} (!!!!)

CONCLUSIONS

- Alkenes, in general contribute more towards NO_X processing when compared to alkanes.
- Important end-products of the HC-NO_X include aldehydes, ketones, oxiranes, CO and NO_2.
- If one could come up with a method for consuming NO_2 effectively, then the present use of the process would suffice.
- The presence of higher HCs would complicate matters much more since the products of their reactions with other species are highly uncertain. Hence, the modelling of higher HCs is subject to a higher percentage of error.
- Increasing the energy input to the reactor improves the NO_X conversion, but at a high cost because the energy efficiency decreases with increasing energy deposition.

FUTURE WORK

- Investigate the effects of multiple pulse input on the reactor output characteristics.
- Include the surface reaction module in the present global kinetics module and study the effect of surface reactions on NO_X degradation
- Incorporate the particulate effects in the system as a further step towards approaching the real-time situations.
- Study the combined effect of all of the above implementations and finally propose a practical, optimal and hence an efficient way of removing NO_X from the automobile emissions.