Experimental Investigation of Non-Catalytic Soot Particle Oxidation: A contribution for understanding the complex Flame Chemistry

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Abstract

Experimental investigation of oxidation of soot generated from ethylene/air pre-mixed flame was performed in a flow reactor. Effect of different parameters like temperature (300-1400 K), oxygen concentration (0-30 %) and residence time was studied on oxidation kinetics. Soot was analyzed with nano-DMA, condensation particle counter and experiments were performed with two different particle size distributions with mean diameters 20 and 28 nm. A clear effect of oxidation was observed at temperatures above 1050 K. The activation energies calculated with a simple Arrhenius expression were found to be 120 kJ/mol for PSDs with mean size 20 nm and 126 kJ/mol for PSDs with mean size 28 nm.

Introduction

Soot particle oxidation is an important integral class of various chemical reactions involved in the flame chemistry. Soot oxidation occurs in parallel to the soot formation and growth reactions. Particle oxidation in flames occurs by O_2, OH and other gas phase species and is relatively less understood. Most of the works already done on soot oxidation are either with catalysts [1,2] or with soot surrogates like pyro-graphite [3]. The work by *Higgins et al*. involves the oxidation study of soot generated from a diffusion flame [4].

Experimental

DLR- soot generator is used as the stable soot source. It is basically an ethylene/air flame and particle size distributions (PSD) of different mean sizes can be generated by varying the operating air fuel ratio. The flame extracted particles were diluted and made to pass through a series of diffusion sieves before entering the reactor. The flow reactor is made of material quartz and is heated using tube ovens. It has three side branches using which the soot is sent into the reactor and to the analyzing equipment SMPS, from the reactor. The soot particles sent to the reactor were mixed with preheated reacting medium. Experiments were done with different reaction media: air, N_2 and N_2+O_2 mixtures of varying O_2 concentrations and the reactions were studied in the temperature range 300-1400 K.

The activation energies were calculated using a simple Arrhenius fit for rate of diameter decrease with oxidation at different temperatures. Here, the geometric mean diameters of the PSDs were considered.

$$\text{Rate of } (\Delta D_p)_{Oxid.} = AT^{0.5} \exp(-E_a/RT) \quad (1)$$

The fit resulted in activation energies of 120 kJ/mol for 20 nm and 126 kJ/mol for 28 nm. Also, the specific surface burnout rates calculated for the PSDs examined in the experiments were observed to be slightly higher than what is reported in most of the literature [3,4].

Effect of oxygen concentration of the reactants on oxidation kinetics was studied by varying the O_2 content of reaction medium in the range 0-30%. A rapid increase in the particle diameter reduction was observed with increase in the oxygen concentration till 5%. But

further increase in the oxygen concentration till 30% could reduce the particle diameter by only ~ 5% more. Higher oxidation rates at higher temperatures with equal oxygen concentrations indicate temperature dependent active sites on the surface of soot particles.

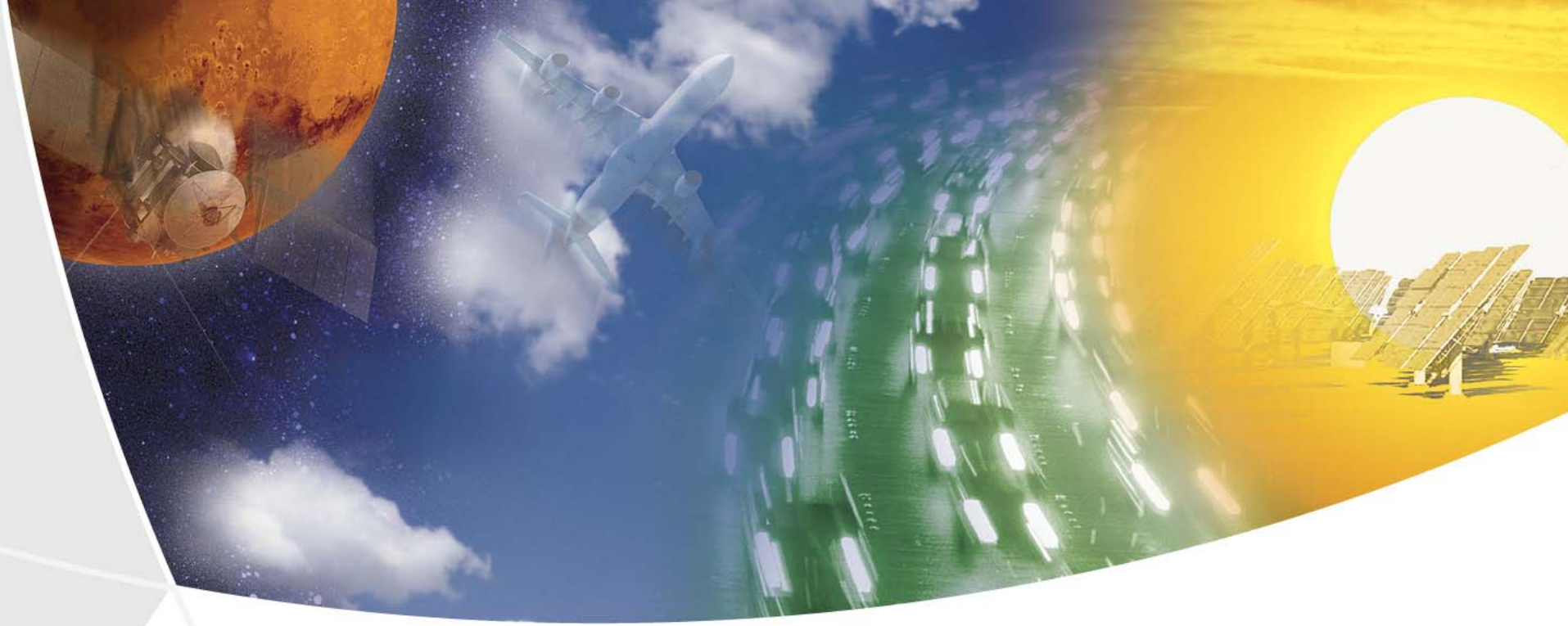
A modified reactor setup with multiple side branches was employed to study the temporal changes in soot particles with oxidation. These additional side branches give the opportunity to sample soot from the flow reactor at different reaction times. A delay in the initiation of soot oxidation and increased oxidation rate as the reaction proceeds was observed. This result is being studied in depth using other analyzing techniques like TEM and REM.

Conclusions

Oxidation of soot nanoparticles was studied in a flow reactor. A clear effect of different parameters like reaction temperature, oxygen concentration and reaction time was observed on particle oxidation. The surface specific burnout rate of the soot particles was observed to be following the similar pattern reported in literature, while the activation energy (E_a) from the experimental results was observed to be lesser than reported in most of the literature (140-160 kJ/mol). Particle size reduction was observed to be increasing with increase in the oxygen concentration in the range 0-5%. Further increase in the O_2 concentration could reduce the particle size by only 5% more.

Literature

1. Neeft J.P.A., Nijhuis T.X., Smakman E., Makkee M., Moulijn J.A., *Kinetics of the oxidation of diesel soot.* Fuel 1997, 76(12): 1129-36.
2. Lahaye J., Boehm P., Chambrion P., Ehrburger p., Influence of cerium oxide on the formation and oxidation of soot. Combust Flame 1996, 104: 199-207.
3. Nagle J., Strickland-Constable R.F., *Oxidation of carbon between 1000-2000°C.* Fifth Carbon Conference, Permagon, Oxford (1962) Vol. 1: pp. 154-164.
4. Higgins K.J., Jung, H., Kittelson D.B., Roberts J.T., Zachariah M.R., *Size-selected nanoparticle chemistry: kinetics of soot oxidation. J.Phys. Chem. A 2002*, 106: 96-103.



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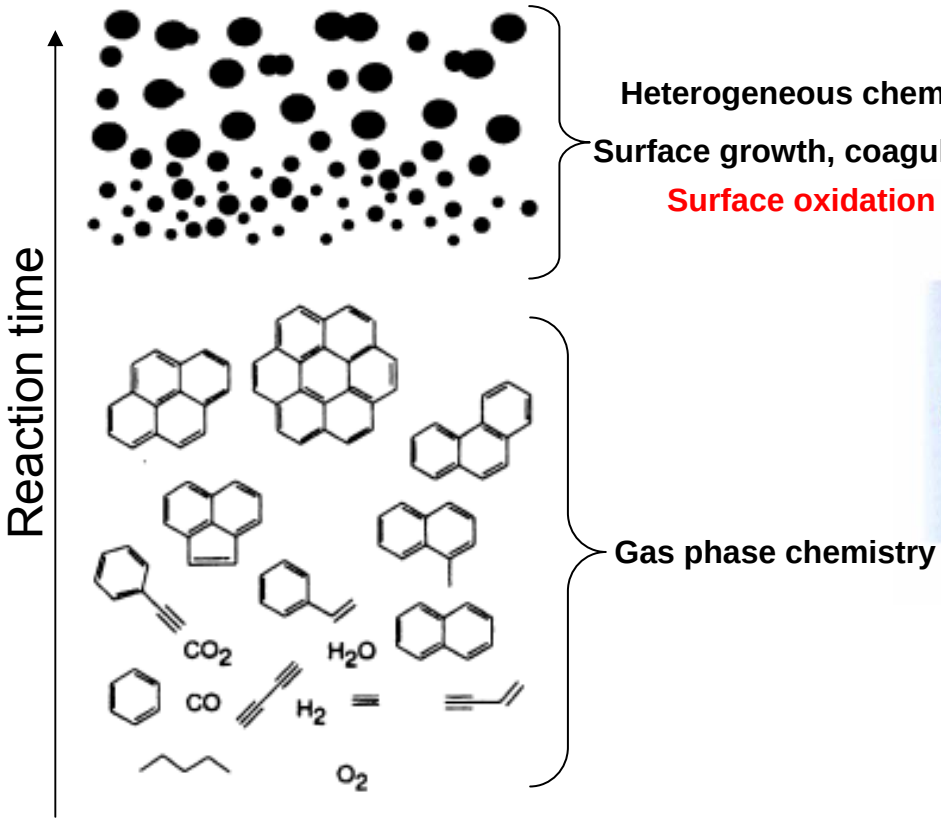
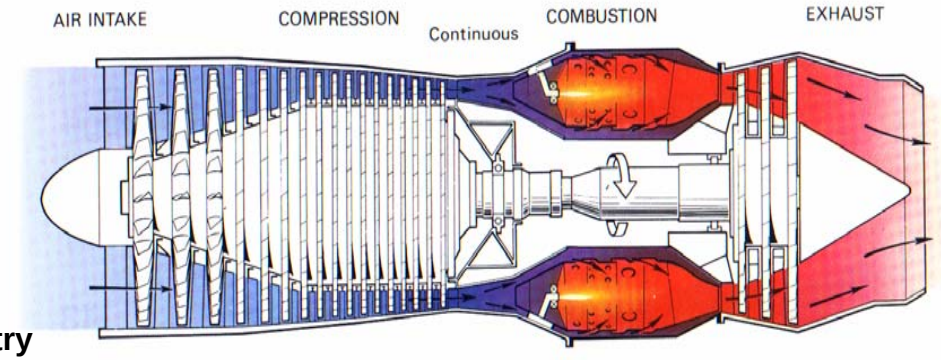
Motivation



Mechanism of soot formation in pre-mixed flames ***Bockhorn 1995***



Technical Combustion systems

Non-premixed flames

Soot formed in a local rich zone is oxidized in the next leaner zone

Total amount of soot = $S_{Nucleation} + S_{Surface\ growth} - S_{Oxidation}$

Previous work - Literature survey

- Nagle and Strickland-Constable [1]:

  Oxidation of pyrographite with O_2 in the temperature range from 1273 K – 2273 K and pressures from 0.1 – 0.6 atm. The results were based on the analyses of reactant and product gas concentrations

- Neoh, Howard and Sarofim [2]:

  Soot-laden gas from a methane flame is partially cooled, mixed with oxygen containing gas and burned in a downstream premixed flame at temperatures of 1575 K – 1865 K and O_2 mole fractions of 10^{-5} to 0.05. The soot oxidation rate was measured using light scattering and absorption techniques

- Higgins, Kittelson and Roberts [3]:

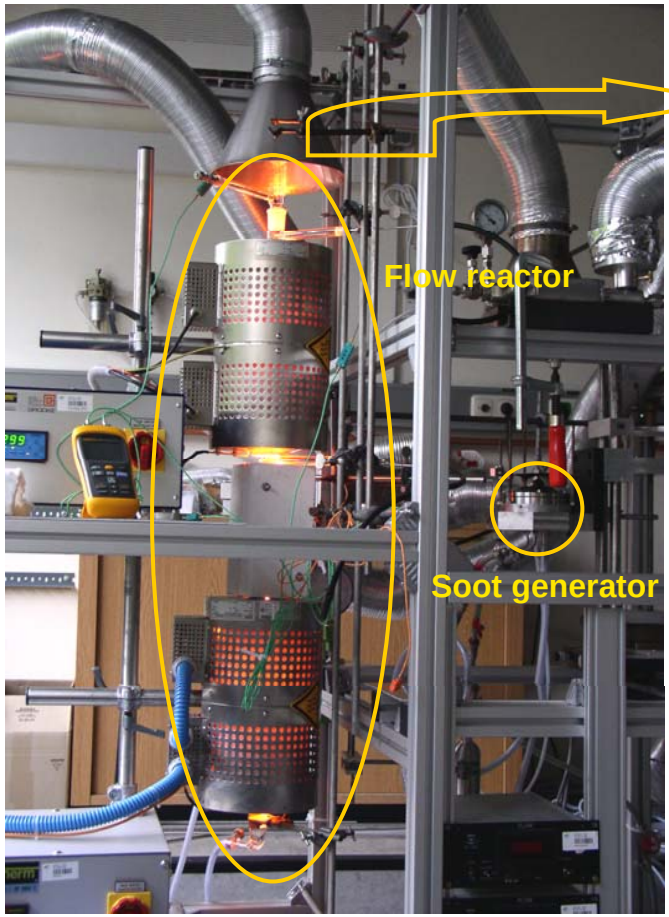
  Soot particles from a diffusion flame as the source and O_2 as the oxidant in the temperature range from 1073 K – 1400 K. Experiments based on measurement of mobility diameter with SMPS technique

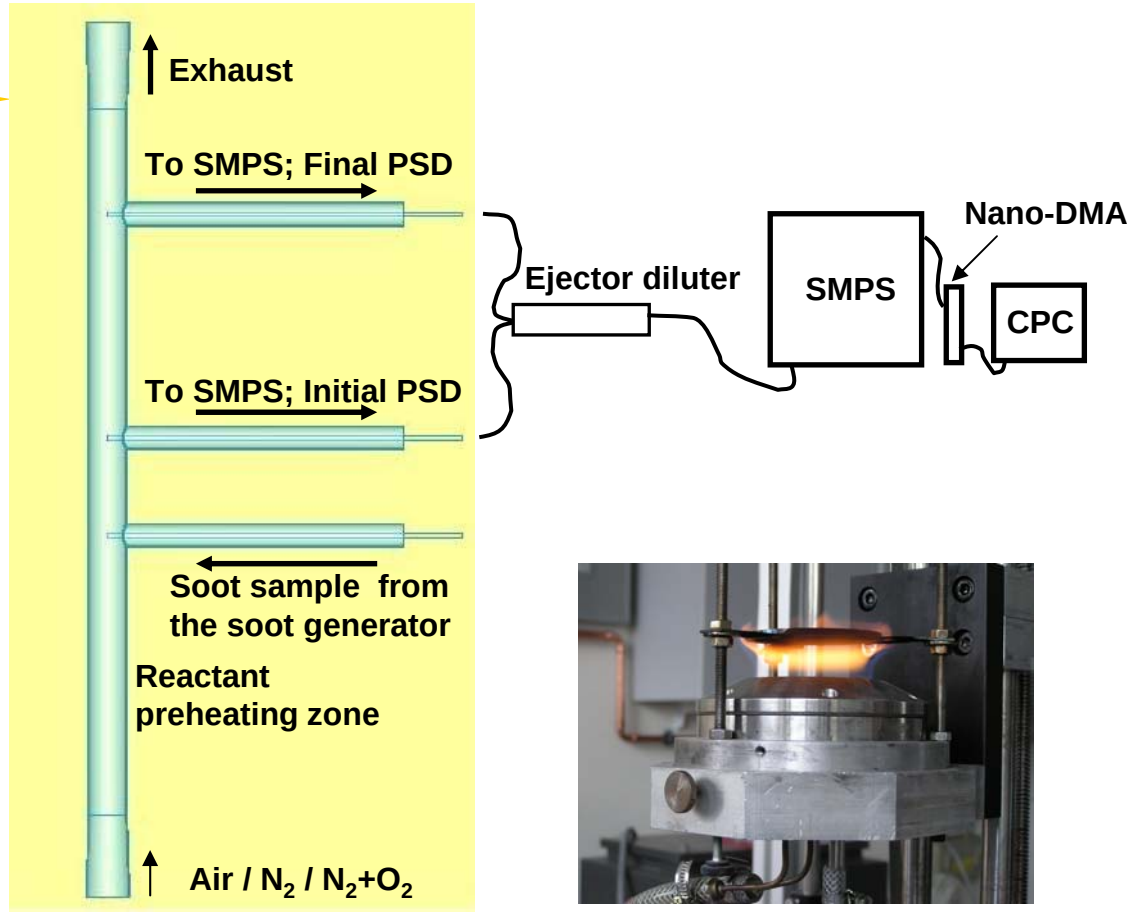
[1]. Nagle, J. and Strickland-Constable, R. F., *Fifth Carbon Conference,* Vol. 1, pp. 154-164, Permagon, Oxford (1962)

[2]. Neoh, K.G., Howard, J.B., Sarofim, A.F., Particulate carbon formation during combustion, Plenum Press, London 1981

[3]. Higgins, K. J., jung, H., Kittelson, D.B., Roberts, J.T.and Zachariah, *J.Phys. Chem. A 2002*, 106, 96-103

Experimental Setup

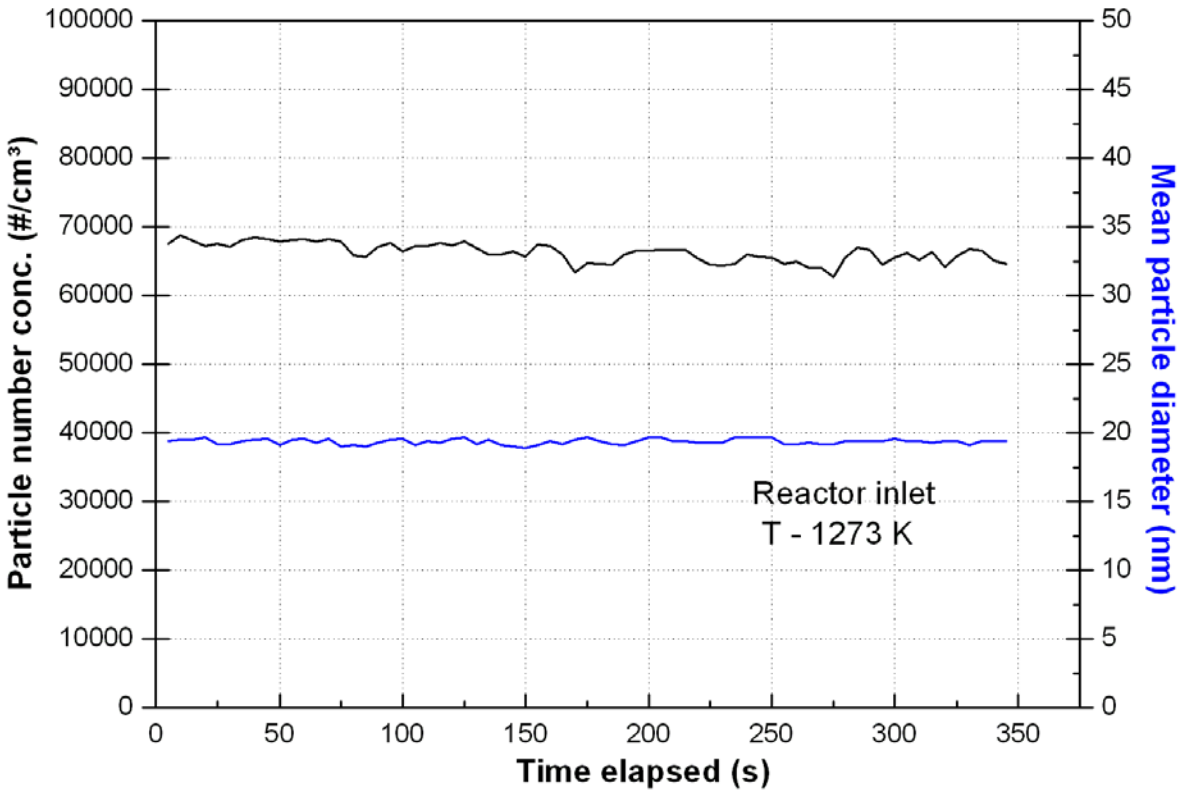




Experimental test bench | **Flow reactor** | **Soot generator**

Soot Particle Generator - Stability

EEPS Measurement of soot particle size distributions at the reactor inlet to verify the stability of the soot generator with time



Max. variation in particle number conc. ~ ± 8%

Max. variation in particle mean diameter ~ ± 0.4 nm

The soot generator is very stable and highly reliable to study soot oxidation

Experimental Details

Two different particle size distributions with mean diameters 20 nm, 28 nm

Air / Fuel ratio of soot generator

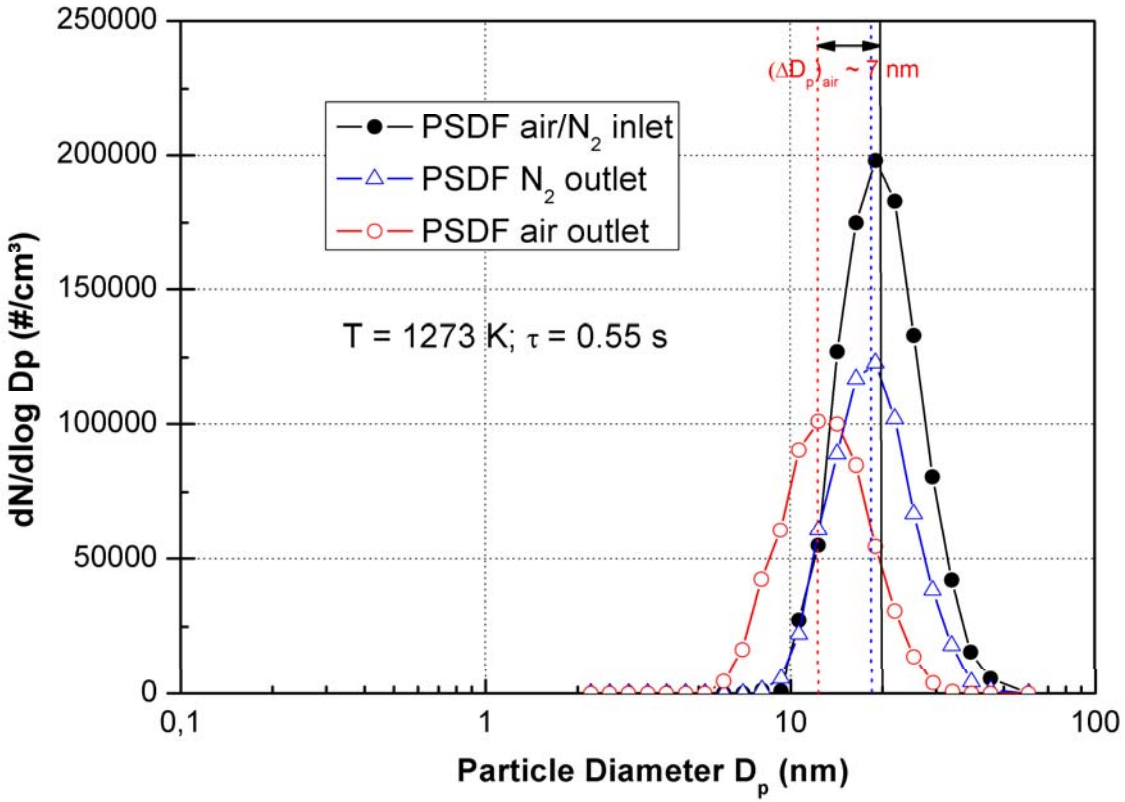
At various temperatures 300 K – 1400 K

Set point temperature of oven

At each operating point, experiments were conducted with three different reaction media - Air ; N_2 and N_2+O_2 mixtures with different O_2 Conc.

Results & Analyses

Effect of reaction media on soot particles



$(\Delta D_p)_{air}$ = 35%

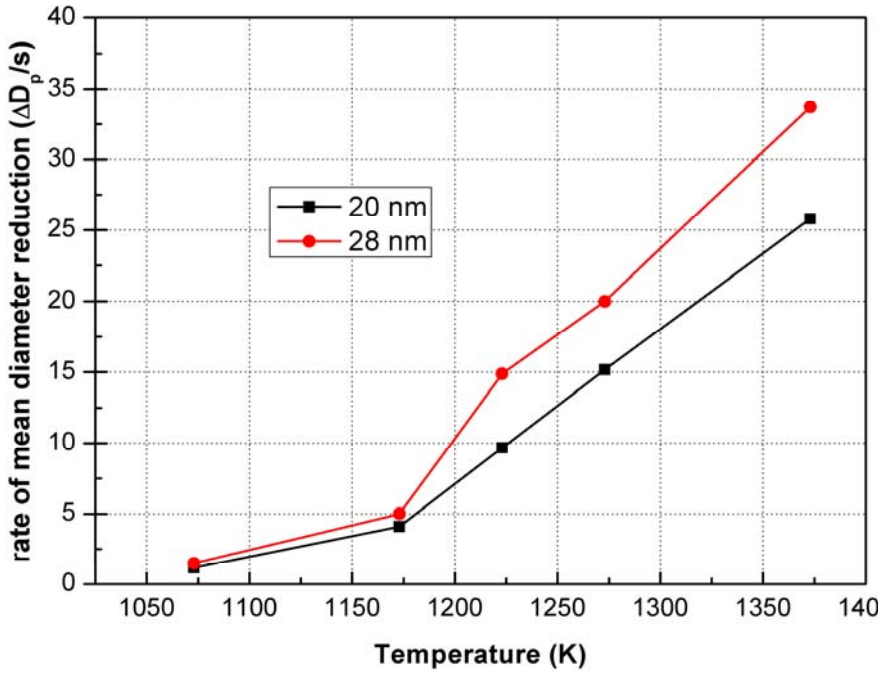
$(\Delta D_p)_{N2}$ = 6.5%

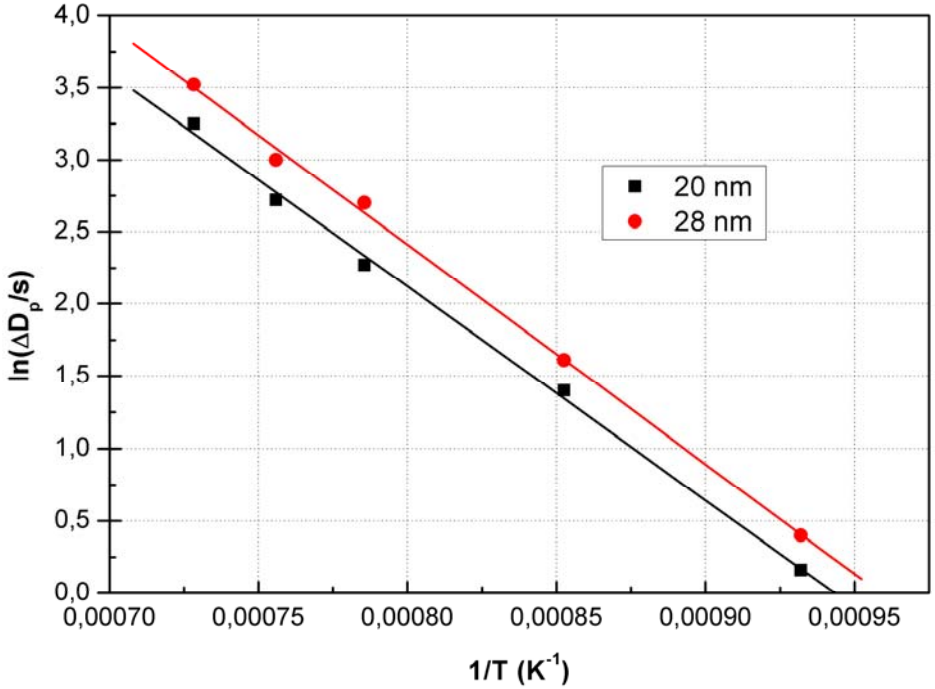
$(\Delta D_p)_{Oxid.} = (\Delta D_p)_{air} - (\Delta D_p)_{N2}$

Decrease in the particle size in reaction with N_2 is due to the vaporization of semi-volatile compounds

Results & Analyses

Effect of temperature on soot particle oxidation





Rate of $(\Delta D_p)_{Oxid.} = AT^{0.5} \exp(-E_a/RT)$

Activation Energy (E_a) (kJ/mol) 20 nm - 120; 28 nm - 126

Pre-exponential factor *(A)* ($nmK^{-0.5}s^{-1}$) 20 nm - 3.5 E04; 28 nm - 6.54E04

Results & Analyses

Effect of Temperature on soot particle oxidation

$$r_w = \frac{1}{A}\frac{dm}{dt}$$

$$r_w = \frac{1}{N\pi d_m^2 \exp\left[2\sigma^2\right]}\frac{d}{dt}\left(N\frac{\pi\rho}{6}d_m^3 \exp\left[\frac{9}{2}\sigma^2\right]\right)$$

r_w = surface specific burnout rate

A = available surface area (m^2/m^3)

m = mass concentration of soot

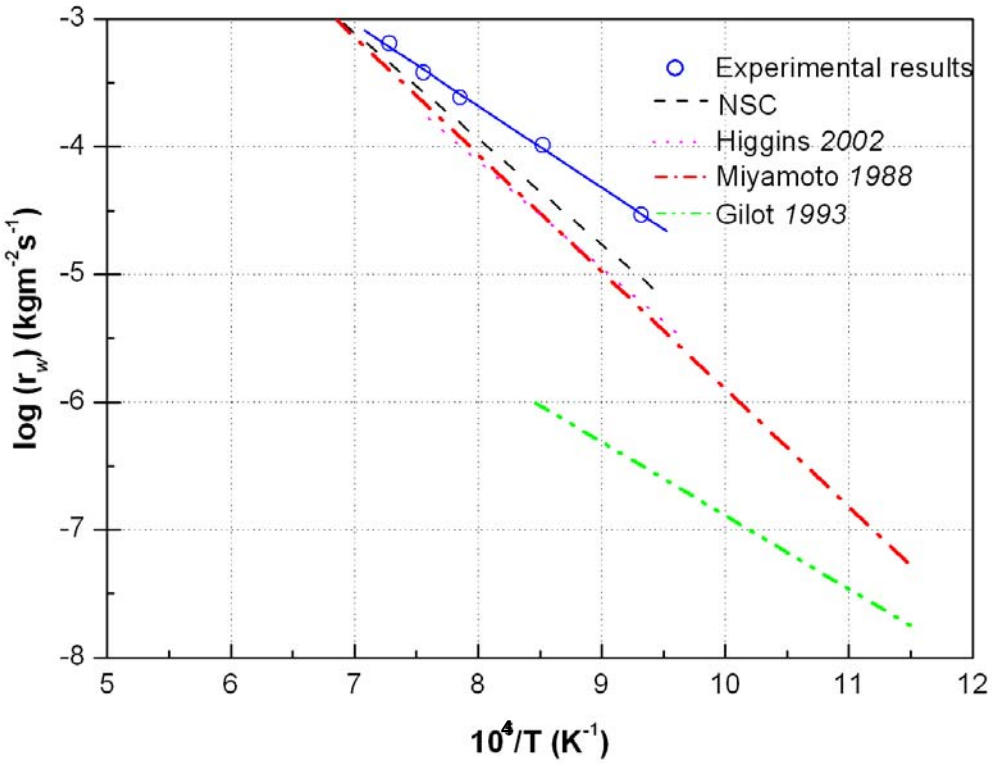
t = time

d_m = geometric mean diameter

σ = Standard deviation

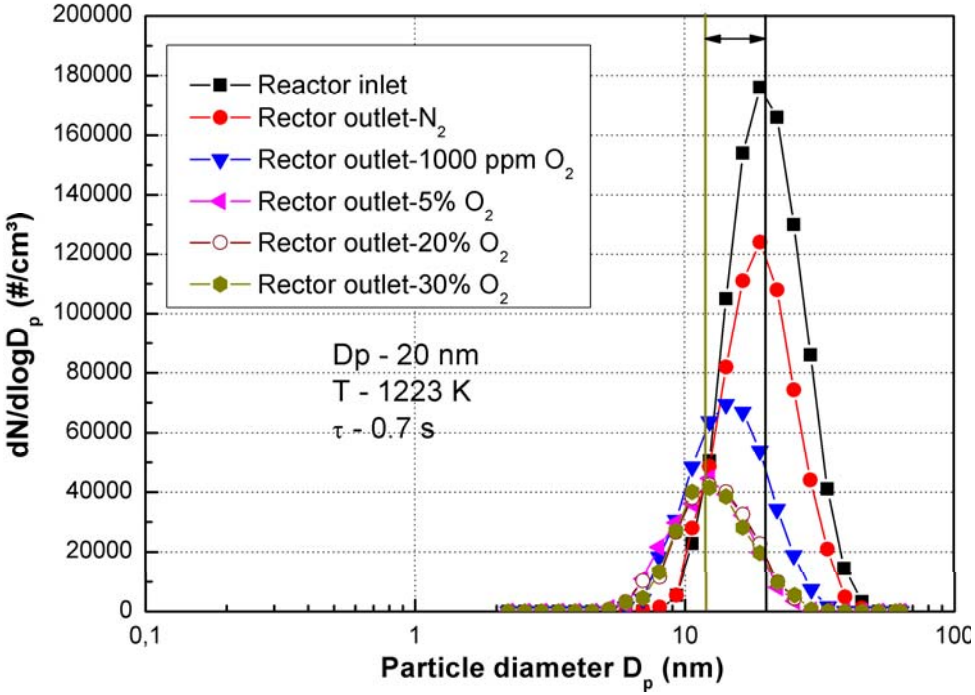
N = Number conc. ($\#/cm^3$)

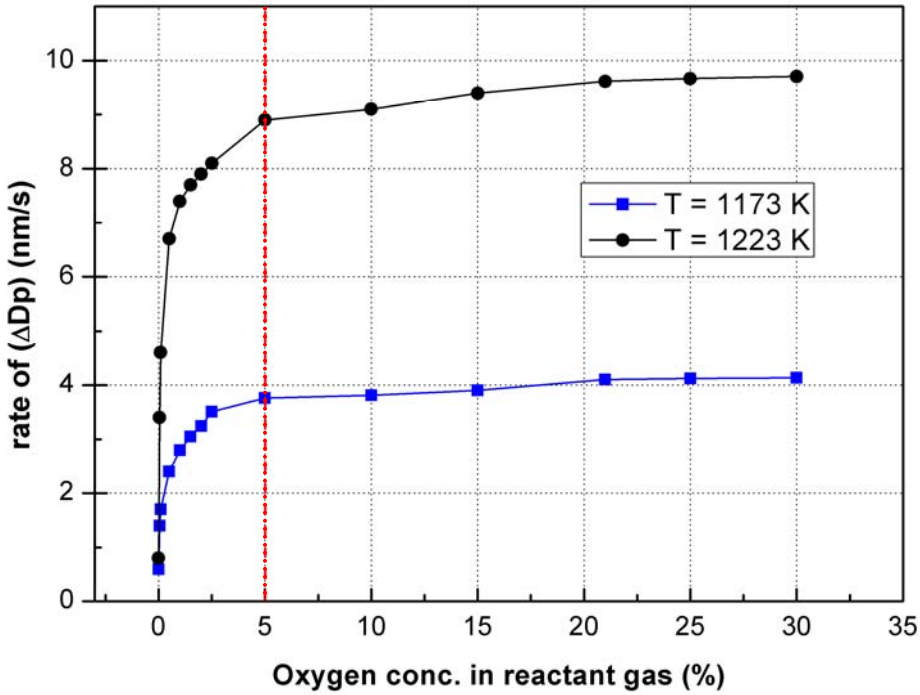
ρ = Density of soot



Results & Analyses

Effect of oxygen conc. of reacting gas





Experiments were performed by varying the oxygen conc. from 0-30%

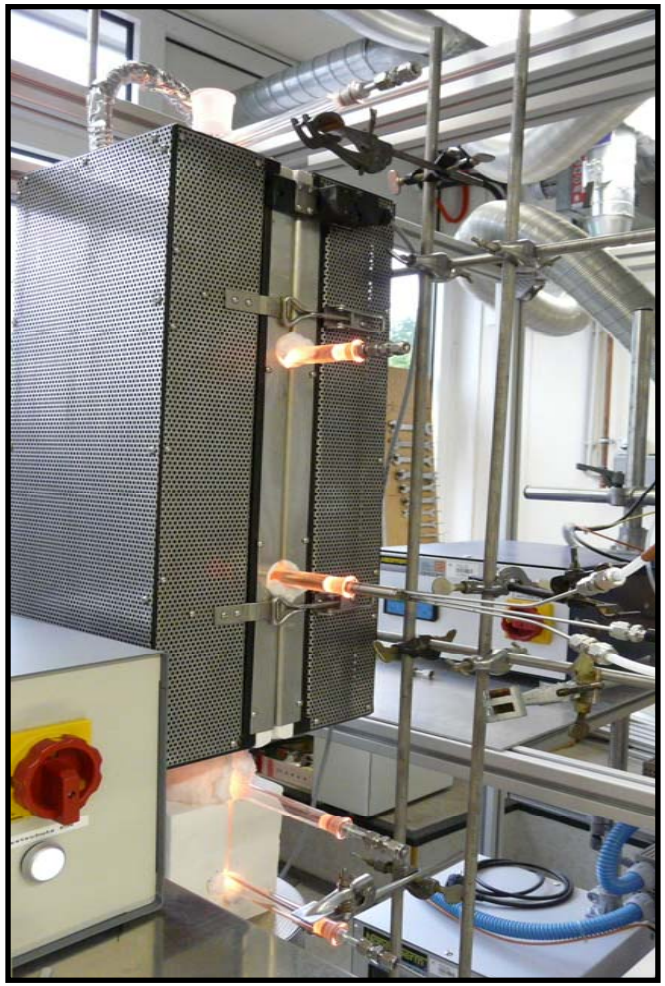
Rapid increase in rate of oxidation in the O_2 conc. range ~ 0-5%

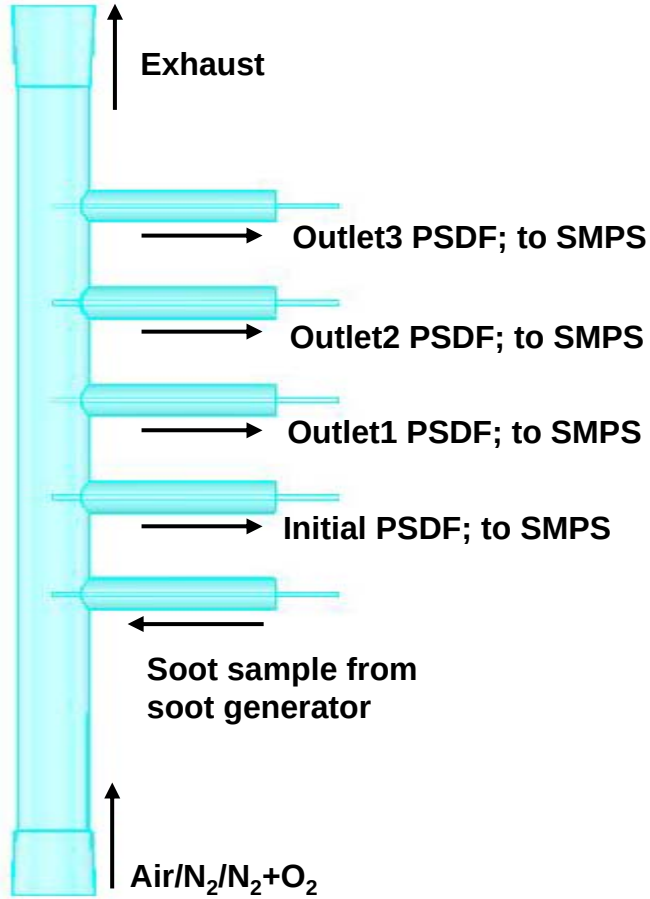
Further increase in O_2 has very little effect

⇒ Temperature dependent active sites on particle surface

Results & Analyses

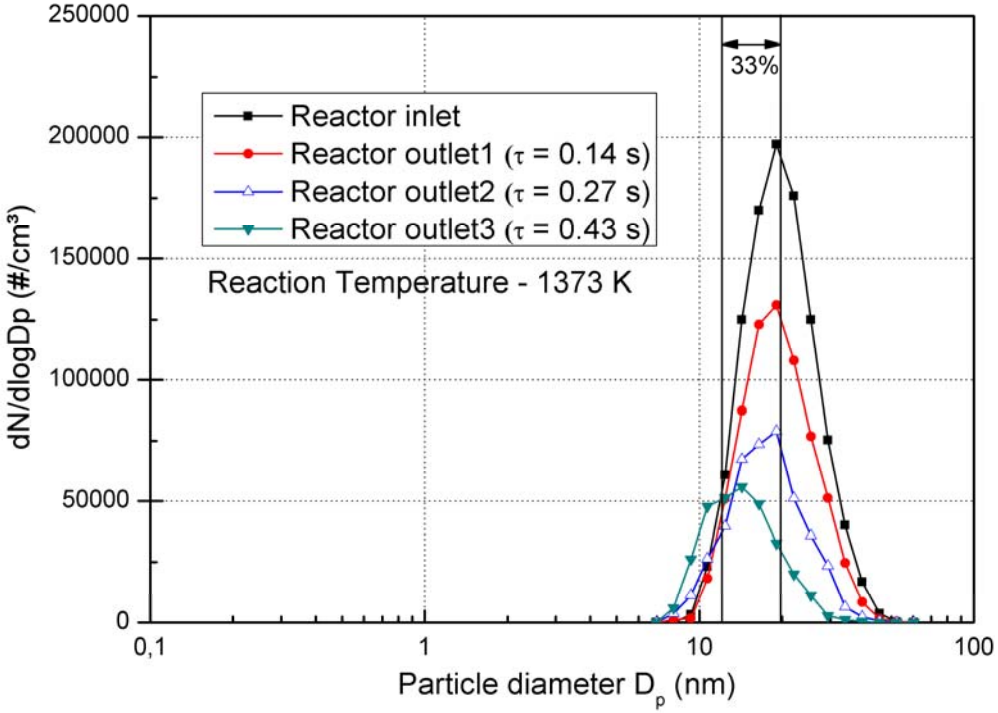
Flow reactor to study the temporal changes in soot particle size with oxidation

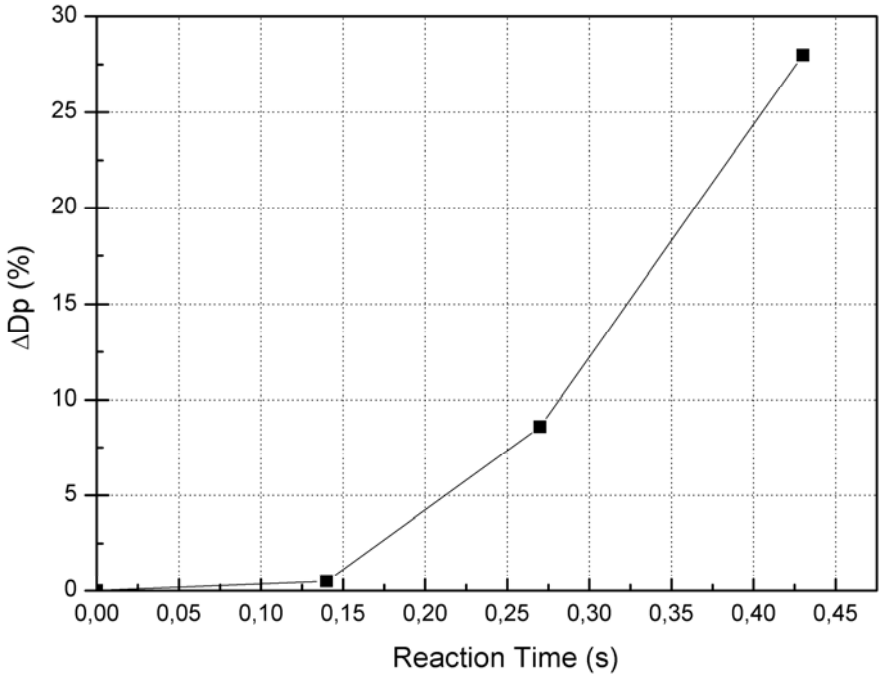




Results & Analyses

Effect of residence time on soot particle size with oxidation





A delay in the initiation of soot oxidation and increased oxidation rate as the reaction proceeds was observed

Conclusions

- Oxidation of soot nanoparticles separated from soot formation process was studied
- A clear effect of parameters like temperature, particle residence time, oxygen conc. was observed on soot oxidation
- The rate of surface oxidation is following the similar pattern reported in most of the literature, while the activation energy (E_a) from the experimental results was observed to be lesser than reported in the literature (Ea ~ 140-160 kJ/mol)
- A rapid increase in the particle diameter reduction was observed with increase in the oxygen concentration till 5%. But further increase in the oxygen concentration till 30% could reduce the particle diameter by only ~ 5% more.
- Temporal changes in soot particles with oxidation is planned to be studied using TEM, SEM.

Thanks for your attention!!!