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Control of combustion conditions - soot generator for liquid fuels

SOOT GENERATION FROM LIQUID FUELS. REACTIONS OF HEXANE SOOT WITH NO_2 AND THE IMPORTANCE OF CONTROL OF COMBUSTION CONDITIONS.

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We have examined the interaction of NO_2 with different types of soot. Both soot particles as well as NO_2 are mainly produced by fossil fuel and biomass burning which are therefore ubiquitous in the atmospheric boundary layer where they may react with each other. One possible product of this interaction is nitrous acid (HONO). HONO is an important trace gas in atmospheric chemistry because it is easily photolysed resulting in OH radical and NO. Thus the photolysis of HONO significantly enhances photooxidation processes especially early in the morning [1].

Soot samples usually have been prepared in our laboratory using a diffusion flame. The samples are analysed using BET isotherms and elemental analysis. Representative results are shown below for different kinds of soot together with literature results. However, the use of diffusion flames for the production of soot has several disadvantages: the thermal and chemical properties of the diffusion flame are varying both temporally as well as spatially, the combustion process depends more on the rate of mixing than on the chemical reaction rates, the fuel/air ratio may only be roughly estimated and the air flow must be continuously adjusted during sample collection in order to maintain a flame of constant appearance.

In the present study two different types of hexane soot have been produced. In order to improve the diffusion flame characteristics, we have adapted the Combustion Aerosol Standard device (CAST) for the combustion of liquid fuels in order to produce soot under controlled conditions. We have coupled the CAST burner unit, usually used in conjunction with gaseous fuel[2], to a setup which produces liquid fuel vapours .The adapted CAST includes the following elements: A constant flow of N_2, controlled by a flowmeter is maintained over liquid hexane at a rate allowing the establishment of the vapour-liquid equilibrium in the vessel, which seems to be a key parameter in the control of the soot generation process. An electronically controlled heating system regulates the temperature of hexane as well as the transfer line connecting the storage vessel with the inlet of the CAST burner. A check valve is located just before the inlet to the burner and protects the system of the possible return of the flame towards the storage vessel. **Figure 1**, presents the experimental system of soot generation and **Figure 2** illustrates the CAST burner unit. The connection tube temperature must always be approximately 10 degrees higher than the vapour production zone in order to avoid vapour condensation. As a result, we have a controlled mixed gas flow of N_2/hexane corresponding to the vapour-pressure of hexane at the chosen temperature. This flow feeds the burner across a fixed point as can be seen in **Figure 1** and **Figure 2** The air flow necessary for combustion is introduced into the burner across a second port and may be controlled using an additional flowmeter. By varying the temperature of the hexane storage vessel, that is the vapour pressure of hexane and changing the air flow we may obtain different mixtures of air/hexane. These two parameters have been varied in the present experiments in order to produce soot samples generated under combustion conditions at the following values:

F_{hexane}=140 ml/min, F_{o2}=270 ml/min: Fuel-rich conditions
F_{hexane}=30 ml/min, F_{o2}=300 ml/min: Fuel-lean conditions.

The surface chemical properties of the samples have been probed using the heterogeneous reaction of NO_2 interacting with soot . Kinetic measurements have been performed in a Knudsen cell, a low pressure flow reactor that operates under molecular flow conditions using modulated molecular beam mass spectrometry for the quantification of reactant uptake and product release into the gas phase. Design and operation of the Knudsen cell have been described in detail in the literature [3]. The apparatus is shown in **Figure 3** and consists of a vacuum line from which molecules are introduced into the reactor , the two-chamber Knudsen cell where the interaction of the gaseous species with the surfaces of interest takes place, and the vacuum chamber wherein the mass spectrometer is mounted.

Each soot sample has been pumped for 5 minutes prior to the uptake experiment. NO_2 is then introduced into the cell as a continuous flow (steady-state experiment). When the flow has stabilized, we lift the isolation plunger and follow the reaction. A large instantaneous rate of NO_2 uptake is observed and quickly saturates within a few minutes. At the same time, we observe product formation. We were able to distinguish different reactivities for the two different types of soot, that is for the fuel-rich and fuel lean flame. The air/fuel ratio is therefore a key parameter influencing the reactivity of soot towards NO_2.

Our preliminary conclusions regarding this work are:

- We have adapted an existing diffusion flame burner (CAST) to combustion of liquid fuels.
- We have obtained reproducible results in terms of two distinctly different types of soot.
- We have probed the two kinds of soot using NO_2 under molecular flow conditions.
- Whereas soot from a fuel-rich flame (grey hexane soot) leads to HONO with yields higher than 50% upon interaction with NO_2, only small amounts of HONO, but significant amounts of NO are formed in the presence of soot generated under fuel-lean conditions (black hexane soot). Typical experiments and results are shown in the following view graphs. Uptake coefficients γ are in the range of 0.7-1.7 x 10^{-4} depending on NO2 taken up.
- The reaction mechanism is different for the two types of soot, which means that depends on combustion conditions. We propose a reaction mechanism in which NO_2 is initially converted to HONO by a redox reaction which is subsequently quantitatively desorbed into the gas phase on grey hexane soot. However, HONO undergoes decomposition on the surface of black soot producing NO, which is instantaneously desorbed into the gas phase, and NO_2 which undergoes secondary reactions and is therefore not observed.
- We have measured particle size distributions of the two types of soot using a TSI Scanning Particle Sizer We observe important differences in both the diameter as well as the width of the distribution between both types of soot.

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- F. Caloz, F. F. Fenter, K.D. Tavor and M.J. Rossi. "Design and construction of a Knudsen-cell reactor for the study of heterogeneous reactions over the temperature range 130-750 K: Performances and limitations", *Rev. Sci. Instrum*. 1997, 68(8), 3172-3179.

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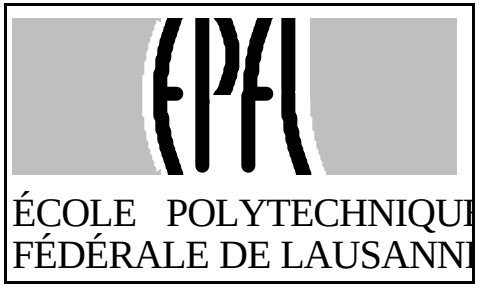

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Type of soot	Surf. Area $[m^2\ g^{-1}]$	Pressure range (P/P_0)	ΔH_{ADS} [kJ/molec]
«grey» decane soot «black» decane acetylene	69 218 72	0.0284-0.3000 0.0001-0.22 0.0258-0.297	8.3 10.1 8.9
n-hexane[D] keroxene[D]	46 91		
n-hexane[E]	89		

D,E- Other authors calculations

Type of soot	C[% weight] Mean	**s**	H[% weight] Mean	**s**	N[% weight] Mean	**s**	O[% weight] Mean	**s**
Acetylene (lean)	**98.26**	**0.08**	**0.15**	**0.02**	**0.16**	**0.08**	**1.41**	**0.02**
Acetylene	**98.57**	**0.27**	**0.20**	**0.01**	**0.33**	**0.11**	**0.90**	**0.26**
«black»decane	**96.39**	**0.22**	**0.19**	**0.01**	**0.27**	**0.09**	**3.22**	**0.25**
«grey»decane	**97.27**	**0.05**	**0.83**	**0.04**	**0.20**	**0.18**	**1.65**	**0.19**
n-hexane	**85.1-90.5**		**0.10-0.13**		-		**7.8-14.3**	

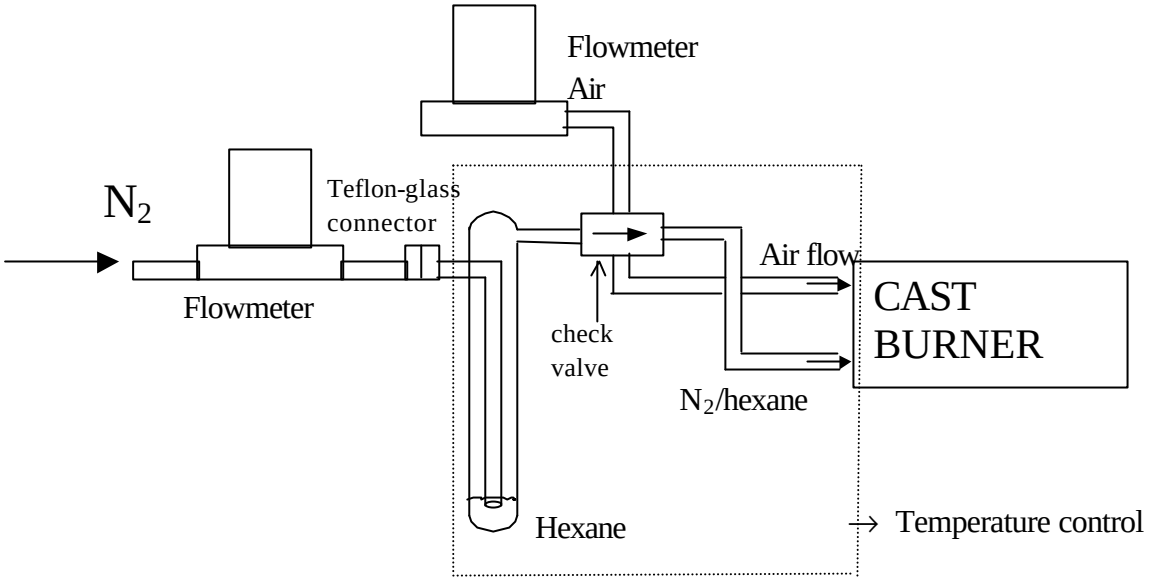


FIGURE 1.- Soot generation system for liquid fuels.

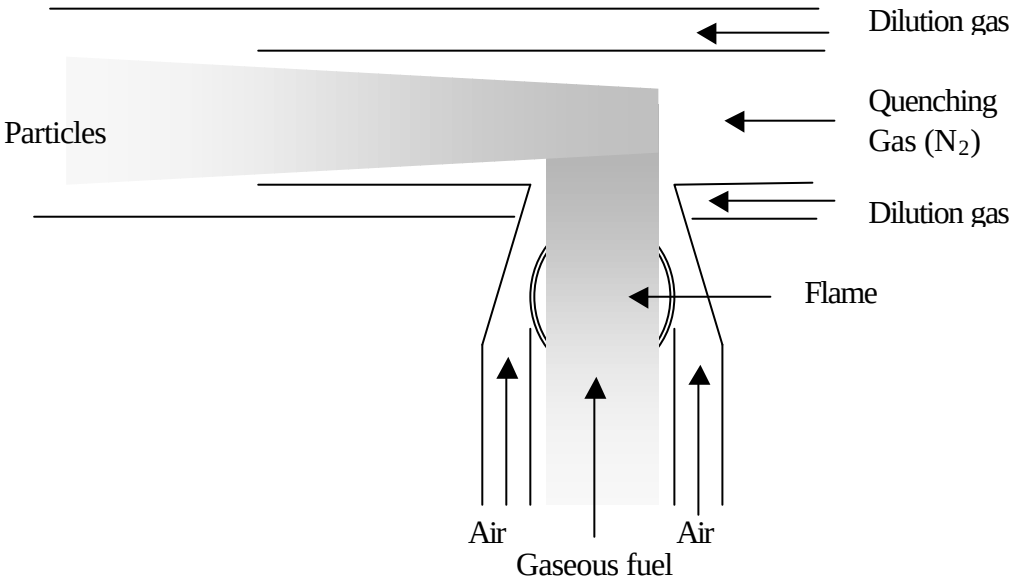


FIGURE 2.- CAST burner unit

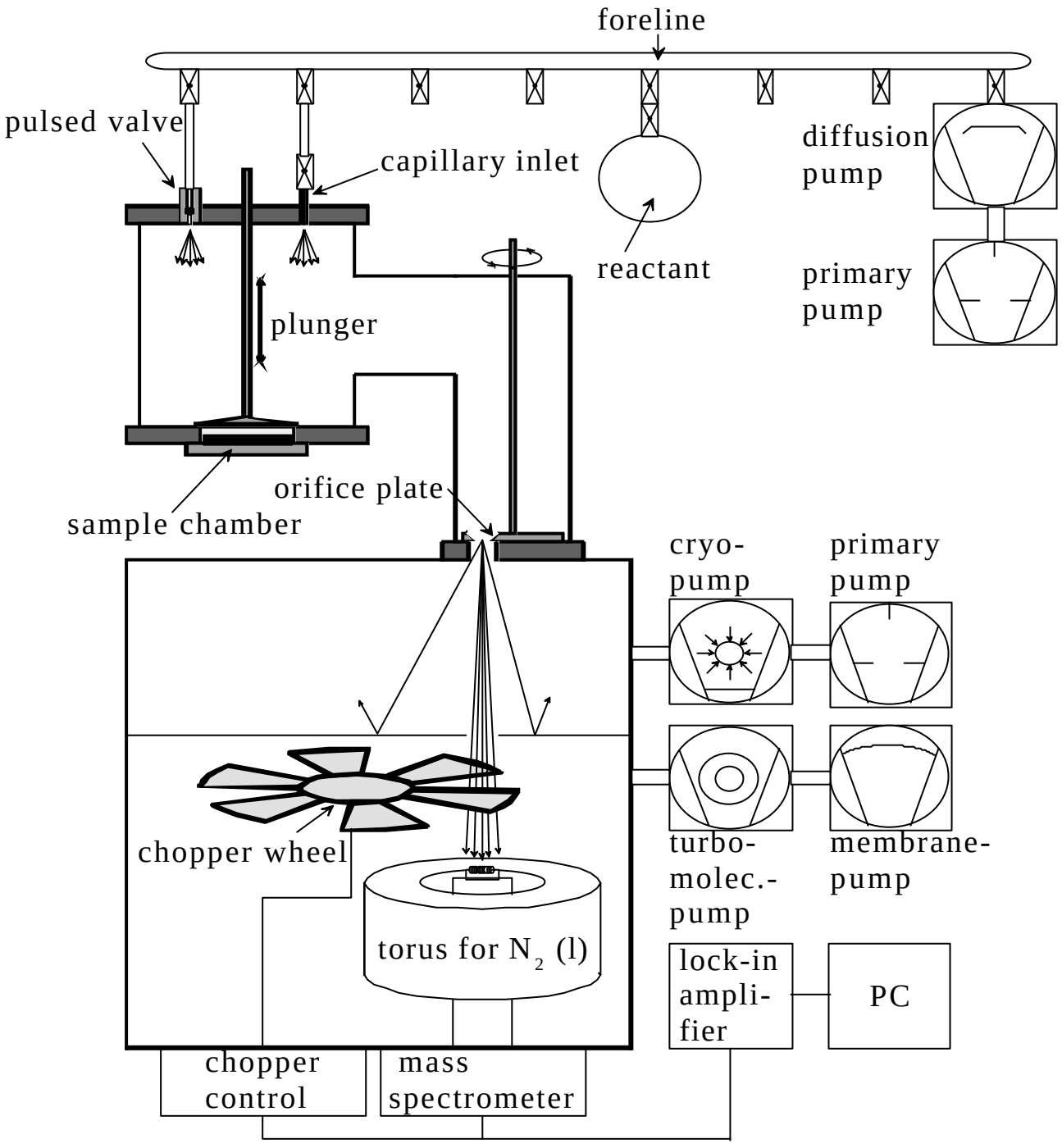
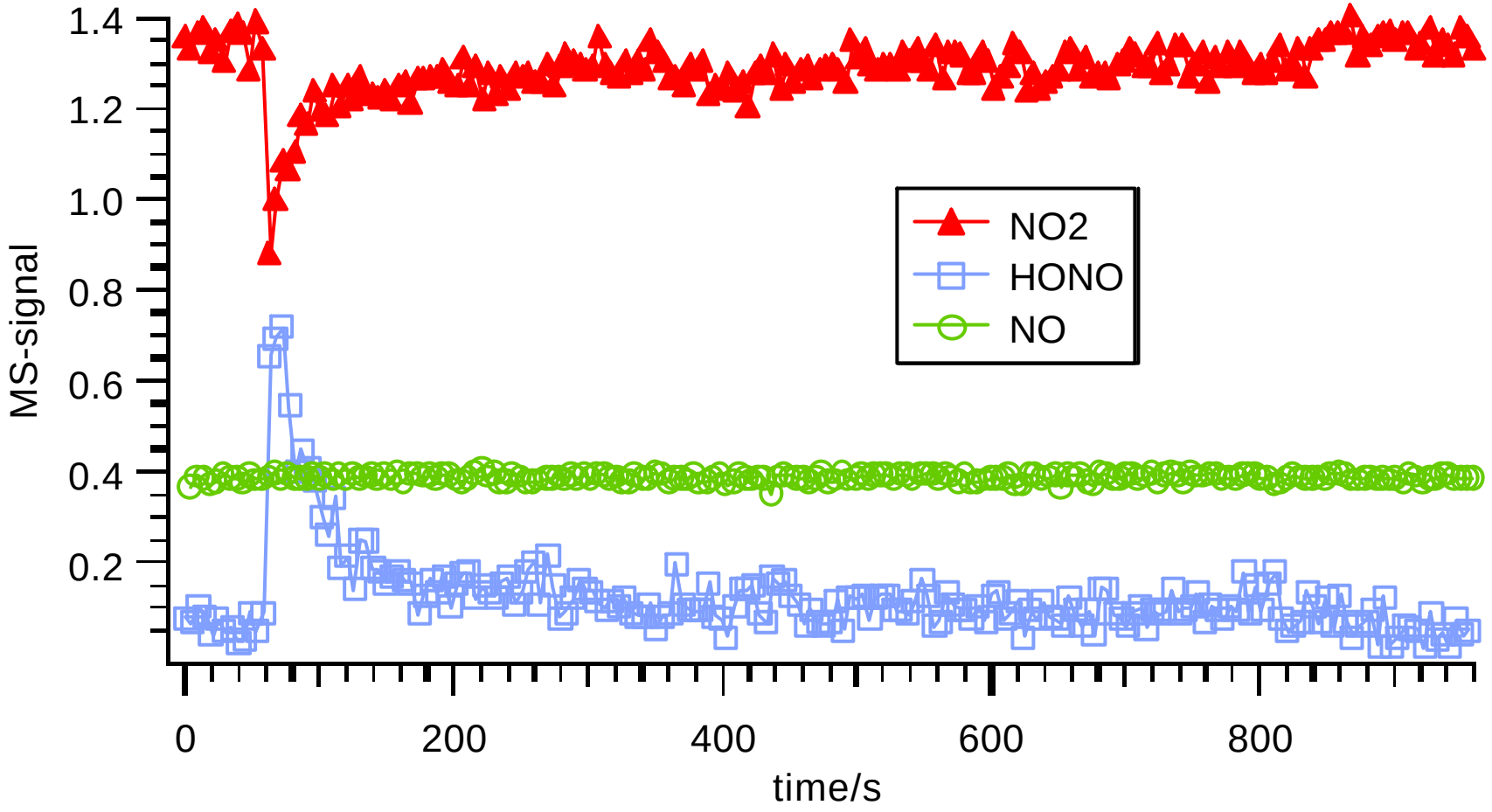
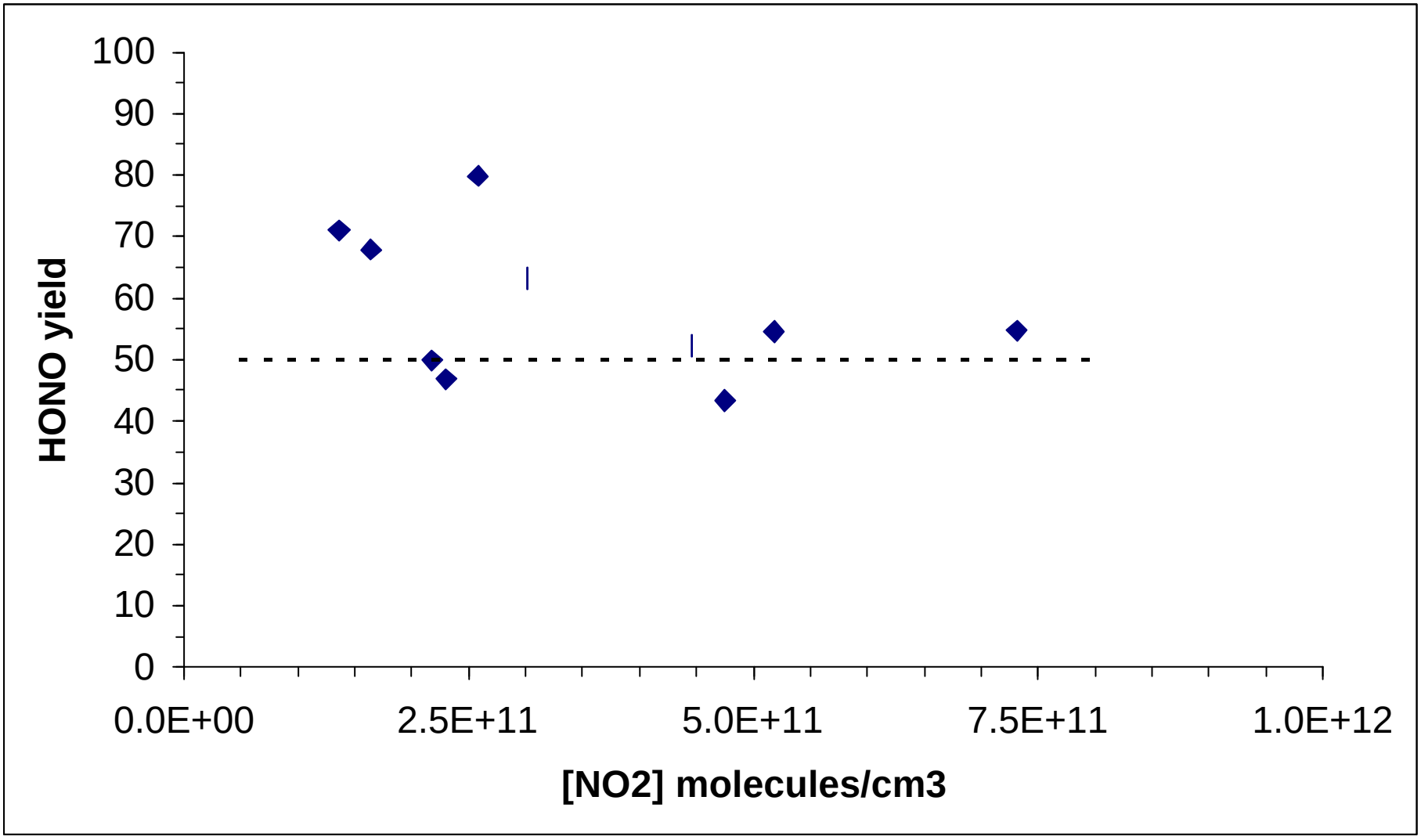


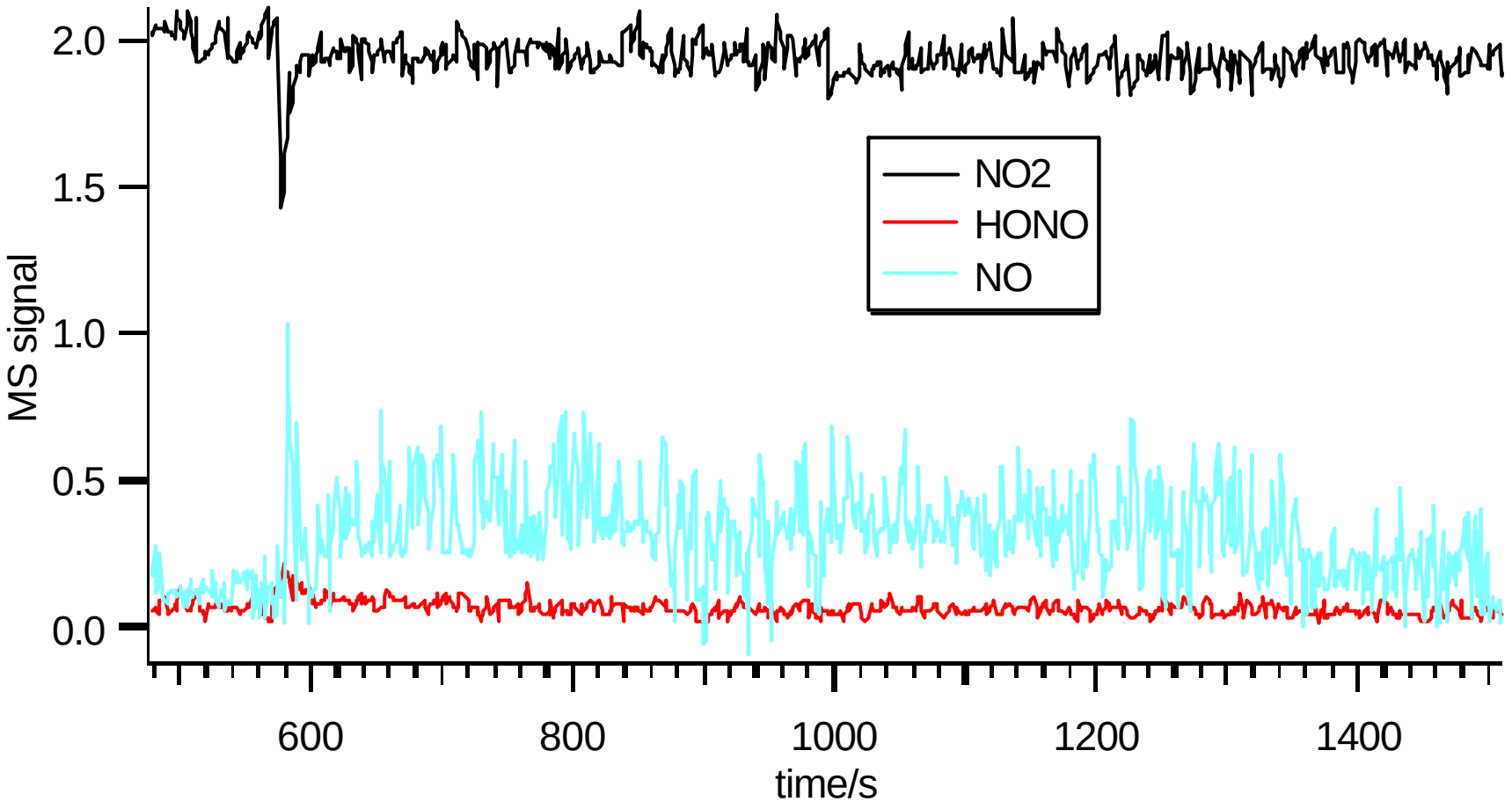
FIGURE 3.- Knudsen cell experiment



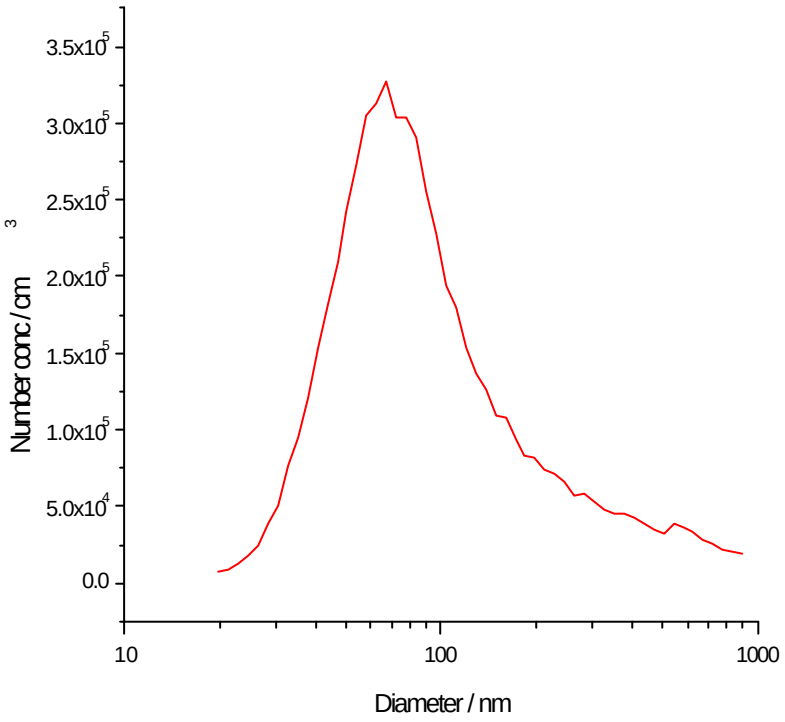
Typical uptake of NO_2 on «grey soot »



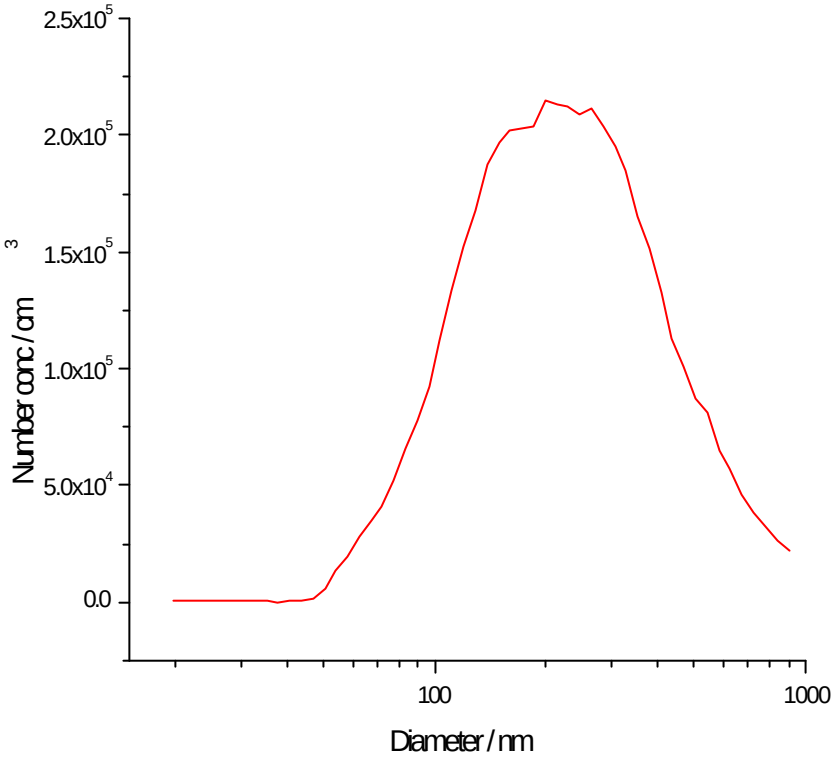
HONO YIELD vs NO_2 CONCENTRATION ON GREY SOOT EXPERIMENTS



Typical uptake of NO_2 and products release on black hexane soot



GREY HEXANE SOOT
MODE=62nm



BLACK HEXANE SOOT
MODE=198nm

PARTICLE SIZE DISTRIBUTION

PRELIMINARY CONCLUSIONS :

- **Soot production for liquid fuels in the laboratory achieved in a controlled and reproducible way.**

- **Combustion conditions affect the reactivity of soot particles with NO_2.**

- **Metrology of two types of hexane soot**