

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous air pollutants that are released into the atmosphere as a by-product of combustion processes. The gas-phase PAHs can be chemically transformed in the lower troposphere via reaction with the hydroxyl (OH) radical to produce a range of oxidised organic compounds and other pollutants such as ozone and secondary organic aerosol (SOA). Epidemiological studies have established that exposure to this type of air pollution is associated with damaging effects on the respiratory and cardiovascular systems, and can lead to asthma, oxidative stress, health deterioration and even death (1).

Despite their importance, relatively little is known about the atmospheric chemistry of the PAHs, mainly because of the variety and complexity of the reaction products. Indeed, although the atmospheric degradation of naphthalene, the simplest PAH, has been investigated on several occasions (2), the reported product yields are not in agreement and, on average, only around 50% of the reacted naphthalene is accounted for. Furthermore, the atmospheric degradation of naphthalene and other gas-phase PAHs is known to produce SOA, but the yield and chemical composition of the aerosol has not been determined. Therefore, the investigations into the atmospheric degradation of gas-phase PAHs are necessary.

## Experimental Setup

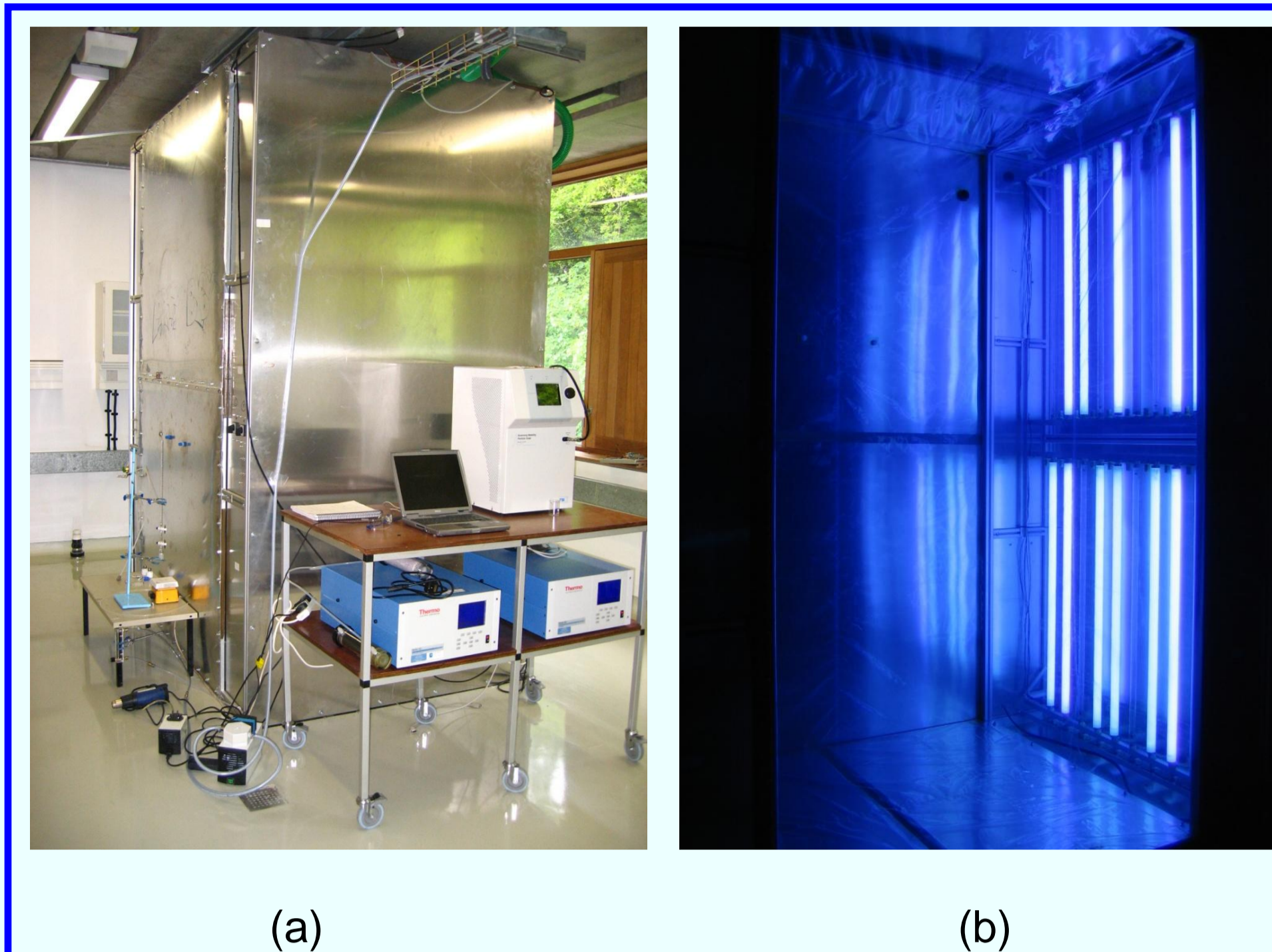


Figure 1. (a) Experimental setup for the 6500 litre FEP Teflon chamber; (b) inner view of the reactor

All of the experiments were performed in a 6500 litre FEP Teflon chamber (Figure 1) at atmospheric pressure and temperature. The reactor is equipped with 12 Philips TL05 (40 W) visible lamps ( $\lambda_{max}=360$  nm) and 12 Philips TL12 (40 W) UV lamps ( $\lambda_{max}=310$  nm) as photolysis sources.

The temperature, relative humidity and the water concentration were measured using a dewpoint meter (Vaisala DM70). Naphthalene was introduced through a heated impinger and its concentrations were monitored by a gas chromatography (GC Varian 3800) and a flame ionization detector (FID).

NO, NO<sub>2</sub> and hence NO<sub>x</sub> concentrations were measured with a chemiluminescence NO<sub>x</sub> analyzer (Thermo Model 42). Ozone concentration was measured with a UV photometric O<sub>3</sub> analyzer (Thermo Model 49).

The formation and evolution of particles in the range 10-470 nm was monitored using a scanning mobility particle sizer (SMPS, TSI Model 3034).

## Results and Discussion

Table 1 Experimental Conditions and Results

Expt. No.	RH (%)	Naphthalene (ppb)	NO <sub>x</sub> (ppb)	HC <sub>v</sub> /NO <sub>x</sub> (ppb/ppb)	$\Delta$ HC ( $\mu\text{g}/\text{m}^3$ )	M <sub>0</sub> ( $\mu\text{g}/\text{m}^3$ )	SOA yield (%)
30/01/08	0.2	1070	520	1.95	2198	285.5	13.0
31/01/08	0.6	1040	240	4.35	1797	330	18.4
05/02/08	0.8	1084	250	4.34	2202	380	17.3
09/02/08	0.7	1081	510	2.13	2135	237.3	11.1
12/02/08	0.8	830	690	1.20	1317	136	10.3
01/05/08	0.8	602	145	4.15	1470	248.5	16.9
06/05/08	1.9	508	500	1.02	954	63.4	6.64
09/05/08	1.3	611	202	3.02	1444	230.9	16.0
12/05/08	25	585	470	1.24	1022	118.6	11.6
13/05/08	25	593	540	1.01	926	103.8	11.2
15/05/08	25	532	520	1.02	1055	97.3	9.23
19/05/08	25	611	344	1.78	1408	229.4	15.5
20/05/08	25	626	517	1.21	1168	155	13.3
21/05/08	25	699	556	1.26	1745	271.3	15.5
22/05/08	50	629	590	1.07	1276	218.5	17.1
23/05/08	50	514	496	1.04	1064	159.4	15.0
26/05/08	50	602	370	1.63	1293	206.9	16.0
27/05/08	50	705	410	1.72	1611	302.4	18.8

Table 2 Aerosol Yield Parameters and Steady State OH Radical Concentrations

Data Group	$\alpha$	K	OH conc. ( $10^6 \text{ cm}^{-3}$ )
RH=0, HC <sub>v</sub> /NO <sub>x</sub> =1.0 ~ 2.2	0.1636	0.0113	2.1 ~ 2.4
RH=0, HC <sub>v</sub> /NO <sub>x</sub> =3.0 ~ 4.4	0.2198	0.0125	2.2 ~ 2.8
RH=25%, HC <sub>v</sub> /NO <sub>x</sub> =1.0 ~ 1.8	0.2324	0.0081	2.2 ~ 2.7
RH=50%, HC <sub>v</sub> /NO <sub>x</sub> =1.0 ~ 1.8	0.2548	0.0095	3.0 ~ 3.2

### Conclusion:

NO<sub>x</sub> level and relative humidity dependent SOA yields were observed in the photooxidation of naphthalene. The former could be explained by the peroxide radicals/NO<sub>x</sub> chemistry; the latter was attributed to the formation of HONO at higher water concentrations.

By fitting the experimental data to Odum's partitioning model the maximum SOA mass yields ( $\alpha$  values) found to correlate with the concentrations of OH radicals present in the reaction chamber.

In addition to OH radicals the role of the HO<sub>2</sub> radical in the SOA formation from the photooxidation of naphthalene is unclear.

### Future Work:

Identify and quantify the major gas and particle-phase degradation products from the photooxidation of naphthalene;

Study the photooxidation of other PAHs (acenaphthene, acenaphylene and phenanthrene);

Investigate the toxicological effects of the SOA produced from PAHs

### Effect of NO<sub>x</sub> level on SOA yields:

Table 1 summarizes the experiments on photooxidation of naphthalene. The SOA formation yield, Y, is defined as the fraction of the reactant, i.e. naphthalene, which is converted into aerosol.

It is clear from experiments 30/01/08 to 09/05/08 of Table 1 that under dry conditions (RH < 2%) experiments with higher HC<sub>v</sub>/NO<sub>x</sub> ratios led to higher SOA mass yields. Such an HC<sub>v</sub>/NO<sub>x</sub> ratio dependent SOA yields were also observed in monocyclic aromatics (3-5), that was attributed to peroxide radicals/NO<sub>x</sub> chemistry.

Figure 2 shows a typical time-concentration profile for the photooxidation of naphthalene from the experiment 05/02/08.

It is clear from Figure 2 that the SOA nucleation started while the NO concentration was as high as around 200 ppb. This would suggest that unlike photooxidation of monocyclic aromatics, where the SOA nucleation was observed only when the NO was nearly completely decayed (3-5), the primary gas phase products from the photooxidation of naphthalene may be partitioning into the particle phase.

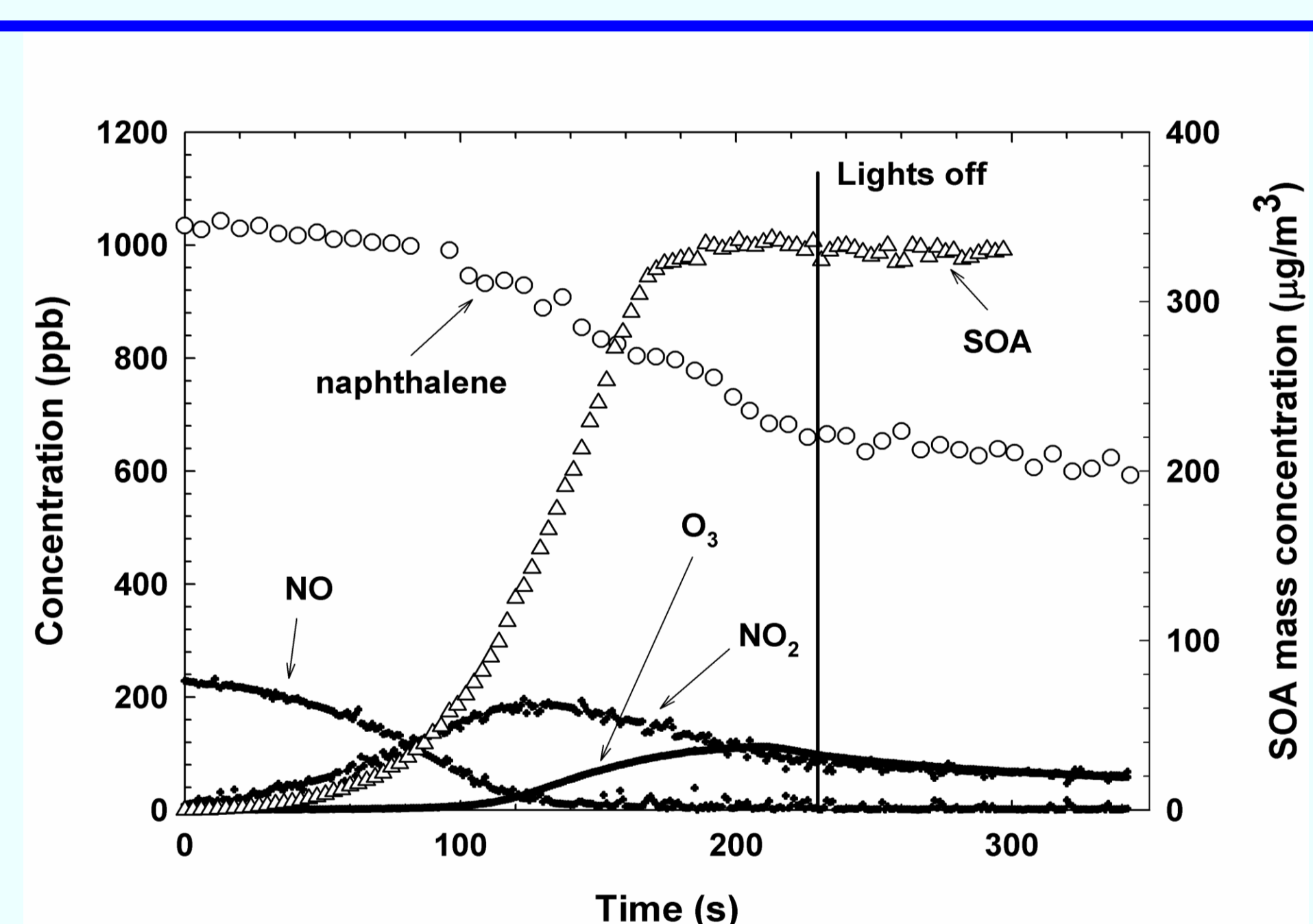


Figure 2. Typical time-concentration profile for the photooxidation of naphthalene (Expt. 05/02/08)

### Effect of relative humidity on SOA yields:

Figure 3 gives the yield curves of the experiments by assuming single product partitioning into the aerosol phase.

It is clear from Figure 3 that the data points fall into four categories. By fitting the data points to gas-particle partitioning model proposed by and Odum et al. (6), the yield parameters of  $\alpha_i$  and  $K_i$  values are listed in Table 2.

It is clear that the SOA yields are higher with the higher relative humidity, the maximum SOA yields increases by a factor of 1.5 over the relative humidity of 0-50%, which is attributed to the formation of higher concentrations of HONO.

A trend of the higher SOA mass yields with higher OH radicals present in the reaction chamber becomes clear (Table 2)

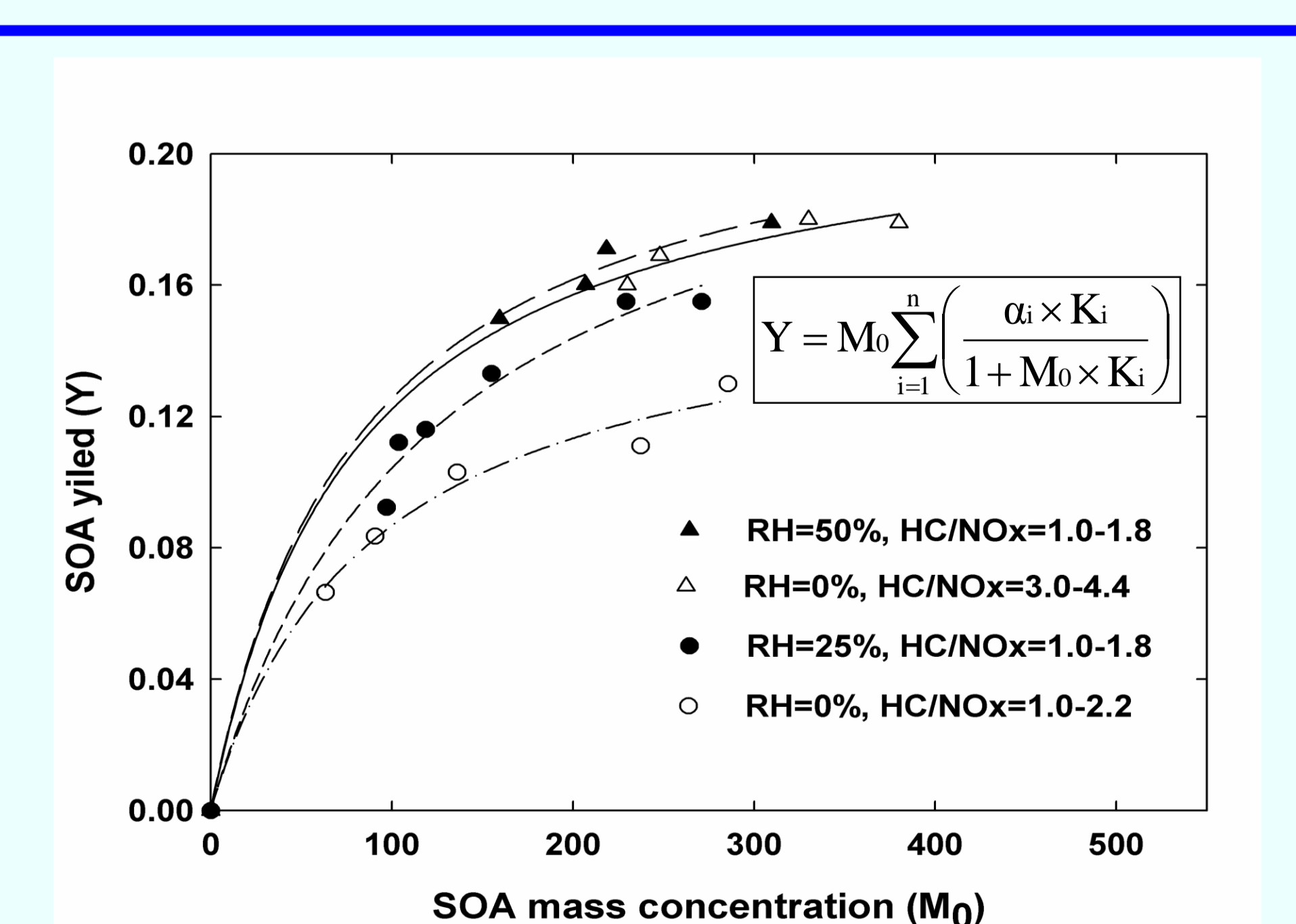


Figure 3. Yield curve for photooxidation of naphthalene experiments

### Literature

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