TAMPERE UNIVERSITY OF TECHNOLOGY

Mikko Poikkimäki

SOA formation yields in chamber

Updated: 16.8.2013

TABLE OF CONTENTS

1. INTRODUCTION

2. THEORY

2.1 Diffusion in binary mixtures

Diffusion illustrates mass convection in medium from greater consentration to lower consentration. Fick's law states diffusion flux

$$J = -D_{AB}\frac{dn}{dx}, \tag{2.1}$$

where D_{AB} is binary diffusion coefficient and n molecule number consentration.

Diffusion coefficient for binary gasmixtures can be calculated from Reid et al. (1987)

$$D_{AB} = 0.001 \cdot T^{1.75}\frac{\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}}{p(V_A^{1/3}+V_B^{1/3})^2}, \tag{2.2}$$

where unit of diffusion coefficient is cm^2/s, temperature T is Kelvin, molar masses M are g/mol and pressure p is bar. Diffusion volumes V can be calculated from values for atomic diffusion volumes which are for carbon C 15.9, for hydrogen 2.31, for oxygen 6.11, for nitrogen 4.54, for heterocyclic ring -18.3 and for air 19.7.

Diffusion related vapor mean free path according to Pirjola and Kulmala (1998)

$$\lambda = \frac{3D_{AB}}{\overline{c}_A}, \tag{2.3}$$

where $\overline{c}_A$ is velocity of gas molecules

$$\overline{c}_A = \sqrt{\frac{8RT}{\pi M_A}}, \tag{2.4}$$

where R is ideal gas constant 8.31446 J/Kmol.

For example $C_{10}H_{16}O_{10}$ molecule ($M_A \approx 300$) with one heterocyclic ring, diffusion volume $V_A \approx 250$. Diffusion coefficient of this molecule in air in temperature 290 K and pressure 1 atm is 0.0489 cm^2/s. Related mean free path λ is 102.65 nm. Few more examples are presented in figure 2.1.

Vapors in figure 2.1 are proposed to form SOA (Ehn et al. 2013).

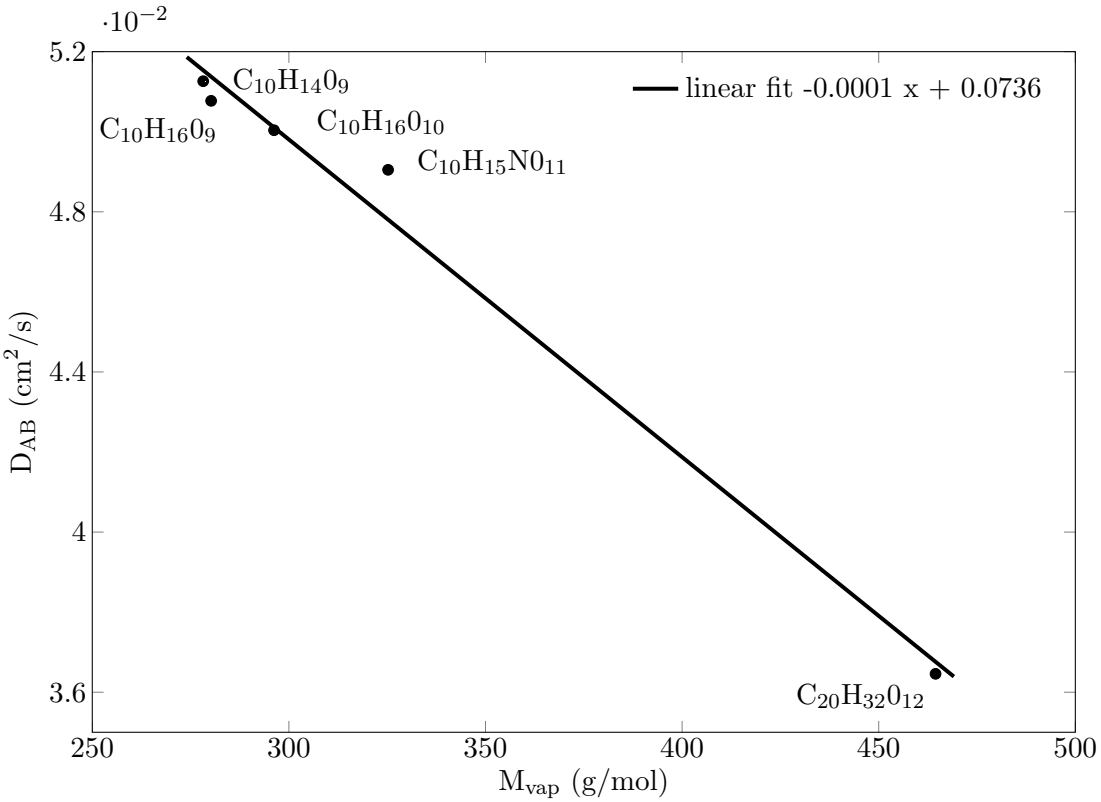

Figure 2.1: Binary diffusion coefficients as function of molar mass for different organic vapors calculated from equation 2.2.

2.1.1 Alternative

Mäkelä,J. kalvot

vapor(A) and air (B) have dilute mixture. For this two gases binary mixture we have to determine free path λ and diffusion coefficient D for both components.

vapormolecule diffusion coefficient in the air

$$D_{AB} = \frac{3}{8\pi} \frac{[\pi k_B^3 T^3 (1 + z_{AB})/(2m_A)]^{1/2}}{\rho \sigma_{AB}^2 \Omega_{AB}^{(1,1)}}, \tag{2.5}$$

and related vapor molecule free path

$$\lambda_{AB} = \frac{32}{3\pi(1 + z_{AB})} \frac{D_{AB}}{\overline{c}_A}, \tag{2.6}$$

before it collides next time to air molecule.

Average collosion area

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}, \tag{2.7}$$

Ratio of molemasses

$$z_{AB} = \frac{M_A}{M_B}, \tag{2.8}$$

collision integral $\Omega_{AB}^{(1,1)} = 1$ for hard spheres

Chapman-Enskog 1939 for more info

Chapman, Sydney, and Thomas George Cowling. The mathematical theory of non-uniform gases: an account of the kinetic theory of viscosity, thermal conduction and diffusion in gases. Cambridge university press, 1970.

S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases (Cambridge University Press, Cambridge, 1952).

Marrero, T.R. and Mason E.A. 1972 comment to Chapman-Enskog on page 8 section 2.2b

Mass

$$m = \rho V \Rightarrow V = \frac{m}{\rho}, \tag{2.9}$$

Otherwise

$$m = nM = \frac{N}{N_A}M, \tag{2.10}$$

Now considering one molecule (N =1)

$$m = nM = \frac{M}{N_A}, \tag{2.11}$$

Considering molecule as sphere, volume

$$V = \frac{\pi}{6}d_p^3 \Rightarrow d_p = \sqrt[3]{\frac{6V}{\pi}}, \tag{2.12}$$

Equation 2.11 to equation 2.9

$$V = \frac{M}{\rho N_A}, \tag{2.13}$$

Then equation 2.13 to equation 2.12, diameter of spherical molecule

$$d_p = \sqrt[3]{\frac{6M}{\pi\rho N_A}}, \tag{2.14}$$

Example for molecule which mass = 300 g/mol and density $\rho = 1.1$ g/cm^3

$$d_p = \sqrt[3]{\frac{6 \cdot 300 \cdot 10^{-3} kg/mol}{\pi \cdot 1100 kg/m^3 \cdot 6.022 \cdot 10^{23} 1/mol}} \approx 0.95nm, \tag{2.15}$$

Example for sulfuracid H_2SO_4 molecule which mass = 98.08 g/mol and density ρ = 1.84 g/cm^3

$$d_p = \sqrt[3]{\frac{6 \cdot 98.08 \cdot 10^{-3} kg/mol}{\pi \cdot 1840 kg/m^3 \cdot 6.022 \cdot 10^{23} 1/mol}} \approx 0.553nm, \tag{2.16}$$

Example for airmolecule which mass = 29 g/mol and density

$$\rho = \frac{Mp}{RT} = \frac{29 \cdot 10^{-3} kg/mol \cdot 101300 Pa}{8.31446 JK^{-1} mol^{-1} \cdot 290K} = 1.22 g/cm^3 \tag{2.17}$$

$$d_p = \sqrt[3]{\frac{6 \cdot 29 \cdot 10^{-3} kg/mol}{\pi \cdot 1220 kg/m^3 \cdot 6.022 \cdot 10^{23} 1/mol}} \approx 0.42nm, \tag{2.18}$$

according to Mäkelä, J. $d_{p_{air}}$ = 0.37 nm

Wikipedia S. Chapman, T. G. Cowling (1970) The Mathematical Theory of Non-uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction and Diffusion in Gases, Cambridge University Press (3rd edition), ISBN 052140844X.

for rigid spheres

$$D_{AB} = \frac{3}{8n(d_1 + d_2)^2} [\frac{k_B T(m_1 + m_2)}{2\pi m_1 m_2}]^{1/2}, \tag{2.19}$$

2.2 Condensation sink

Condensation sink represents rate how rapidly condensable vapor molecules condenses on existing aerosol in units 1/s. It can be calculated from

$$CS = 2\pi D \int_0^\infty d_p \beta(d_p) n(d_p) \, \mathrm{d}d_p = 2\pi D \sum_i \beta d_{pi} N_i, \tag{2.20}$$

where d_{pi} is the diameter of a particle in size class i, N_i is corresbonding particle number consentration (Dal Maso et al., 2002) and D is diffusion coefficient of condensing vapor. Transition regime correction factor β_m according to Fuchs and Sutugin (1971) is

$$\beta_m = \frac{1 + Kn}{1 + \left(\frac{4}{3\alpha_m} + 0.337\right) Kn + \frac{4}{3\alpha_m} Kn^2} \tag{2.21}$$

where α_m is the sticking coefficient which represents probability of molecule to

stick in to the particle. Dimensioless Knudsen number is

$$Kn = \frac{2\lambda}{d_p}, \tag{2.22}$$

where λ is the effective mean free path of the condensing vapor molecules in the gas. Knudsen number is the ratio of two lenght scales. Mean free path λ characterizes the gas with respect to the transport of mass and particle diameter d_p characterizes the droplet.

One can semiempirically represent condensation sink as a function of aerosol mass as follows

$$CS = 2 \cdot 10^{-4} \cdot N^{0.37} M^{0.63}, \tag{2.23}$$

where N is particle number and M particle mass.

2.3 Proposed chemical reaction of monoterpene, SLLV source

Monoterpene reaction with ozone produces SLLV product with mass yield of α and other products with mass yields of β_i

$$\mathrm{MT} \xrightarrow[\mathrm{O_3}]{\mathrm{k}} \alpha \mathrm{C_{vap}} + \textstyle\sum_{\mathrm{i}} \beta_{\mathrm{i}} \mathrm{C_i} \tag{2.24}$$

Source of SLLV vapor is then

$$Q = \alpha k P, \tag{2.25}$$

where $P = P_0 e^{-kt}$ is precursor (monoterpene) consentration and overall reaction rate $k = k'[0_3]$ is reaction rate of ozone times ozone consentration.

Proposed SLLV product sinks

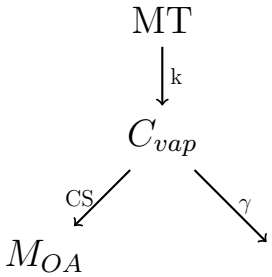

Figure 2.2: Proposed routes for monoterpene precursor MT reaction (rate k) SLLV product C_{vap}. To aerosol M_{OA} with rate CS or to walls or other losses with rate γ

3. METHODS

Particle size distribution varies in time through different processes as nucleation, condensation, coagulation, sedimentation and dilution. These changes can be modelled with general dynamic equation (GDE) (Seinfeld and Pandis, 1998)

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \mathrm{K}(v-q,q)n(v-q,t)\,\mathrm{d}q - n(v,t)\int_0^\infty \mathrm{K}(q,v)n(q,t)\,\mathrm{d}q \\ -\frac{\partial}{\partial v}[I(v)n(v,t)] + J_0\delta(v-v_0) + S(v) - R(v), \qquad (3.1)$$

where I is particle volume changing rate, J_0 is nucleation rate, K is coagulation coefficient, n is size distribution function, R particle loss rate, S particle sources emission rate, t is time, v and $q = v + dv$ are particle volumes and $\delta(v - v_0)$ is Dirac's delta function which is one whenever $v = v_0$ and otherwise zero. Two first term of equation represents coagulation, third term condensation, fourth nucleation, fifth other particle sources and the last other particle sinks like deposition.

3.1 Used sectional model

In sectional model particle size distribution is divided in desired amount of size sections which are characterized with two parametres: particle size and consentration. Particle population is considered monodispersive in each section. In this study moving center model was used where section borders are fixed but particle sizes can vary inside sections (Korhonen, 2004). Model takes into account particle coagulation and dilution, vapor condensation in to the particles, vapor dilution and loss to walls (or other places).

Coagulation is modelled with parts of discrete general dymanic equation (Seinfeld and Pandis, 1998)

$$\frac{dN_k}{dt} = \frac{1}{2}\sum_{j=g^*}^{k-g^*} K_{j,k-j}N_jN_{k-j} - N_k\sum_{j=g^*}^{\infty} K_{k,j}N_j, \qquad (3.2)$$

where first term represents increase of particles in section k and second term reduction of particles through coagulation.

Condensation growth of particles is modelled by growing section size using growth

rate (Seinfeld and Pandis, 1998)

$$\frac{dd_p}{dt} = \frac{2M_{vap}I}{\pi\rho d_p^2 N_A}, \tag{3.3}$$

where M_{vap} is condensing vapor molecular mass, ρ particle density, N_A Avogadro's number and I flux of molecules to the particle phase. It is obtained from

$$I = 2\pi d_p D C_{vap} \beta_m, \tag{3.4}$$

where D is diffusion coefficient, C_{vap} consentration of condensing vapor and β_m obtained from equation 2.21.

Dilution of particle consentration is modelled with equation

$$\frac{dN_k}{dt} = -\gamma_{dil} N_k, \tag{3.5}$$

where γ_{dil} is dilution coefficient in units 1/s. It is inverse value of aerosol lifetime τ.

Used condensing vapor consentration gradient

$$\frac{dC_{vap}}{dt} = Q - CS \cdot C_{vap} - \gamma C_{vap} - \gamma_{dil} C_{vap}, \tag{3.6}$$

takes into account vapor source rate Q, vapor loss rate to particles CS and to walls γ and vapor dilution rate γ_{dil}.

See connection with CS and I

$$CS = \sum_i I_i N_i. \tag{3.7}$$

This is connection between particle growth and vapor loss to particles. These differential equations 3.2, 3.3,3.5 and 3.6 are solved numerically using Runge-Kutta-method (Dormand and Prince, 1980) and time evolution of number distibution function dN/dd_p gained among other results.

3.2 How model was used

In this study batch type aerosol chamber was modelled with 60 size sections between sizes 1 nm and 1 µm. Different aerosol mass seeds M_0 and monoterpene consentrations P_0 was used for two particle sizes and two SLLV wall loss coefficient resulting 4x4x2x2 = 64 model runs. Used constants and variables are presented in table 3.1.

Aerosol total numbers for model presented in table 3.1 are calculated from aerosol

Table 3.1: Used values in modelling. Those values kept same in each model run are presented first and then values that changed between are under.

Constant	Symbol	Unit	Value
Stoichiometric yield of SLLV	α	-	0.3
Sticking coefficient	α_m	-	1
Dilution coefficient	γ_{dil}	1/s	$5\cdot 10^{-5}$
SLLV vapor mean free path	λ	nm	102.65
Particle density	ρ	g/cm^3	1.4
Geometric mean deviation GMD	σ	-	1.3
Diffusion coefficient of SLLV	D_{AB}	cm^2/s	0.0489
Reaction rate of ozone	k'	1/s	$2\cdot 10^{-16}$
Molar mass of SLLV	M_{vap}	g/mol	300
Molar mass of monoterpene	M_{MT}	g/mol	137
Ozone consentration	$[0_3]$	ppb	60
Pressure	p	atm	1
Temperature	T	K	290
Time vector	t	s	0 - 36000

Variable	Symbol	Unit	Value
SLLV wall loss coefficient	γ	1/s	0.02, 0.002
Count median diameter CMD	μ	nm	10, 80
Aerosol mass seed (10 nm particles)	M_{10nm}	ng/m^3	3, 15, 30, 100
Related number (10 nm particles)	N_{10nm}	10^3 1/cm^3	$\sim$ 4, 20, 41, 137
Aerosol mass seed (80 nm particles)	M_{80nm}	µg/m^3	1, 5, 10, 30
Related number (80 nm particles)	N_{80nm}	10^3 1/cm^3	$\sim$ 2.7, 13, 27, 80
Initial monoterpene consentration	P_0	ppb	10, 50, 100, 200

mass seed using count median diameter as size of particles

$$N = \frac{m}{\rho(\pi/6)\mu^3}. \tag{3.8}$$

Then lognormal distribution is produced with CMD, GMD and N.

Conversion of ppb to 1/cm^3 is done multipling with $p/kT = 2.5331\cdot 10^{19}$ air molecules/cm^3.

3.3 Analysing tools for results, how to get α and γ?

Aerosol mass yield

$$Y = \frac{\Delta M}{\Delta P}, \tag{3.9}$$

where ΔM is formed aerosol mass and ΔP is used precursor mass. Formed aerosol mass can be calculated

$$\Delta M = M_{tot} - M_0 + M_{dil}, \tag{3.10}$$

where M_{tot} is aerosol total mass, M_0 initial aerosol mass and M_{dil} diluted aerosol mass. From particle number distribution dN/dd_p, total aerosol number N_{tot}, volume V_{tot} and mass M_{tot} is integrated considering spherical particles with density $\rho = 1.4$ g/cm^3. Diluted aerosol number N_{dil} is calculated by model from differential equation 3.5. From N_{dil} diluted mass M_{dil} can be calculated and formed aerosol mass got.

Used precursor ΔP is calculated from

$$\Delta P = \int_0^{t_{end}} kP \, \mathrm{d}t, \tag{3.11}$$

where t_{end} is elapsed time, k is formation rate and P is precursor consentration presented in equation 2.25.

Condensation sink was calculated from equation 2.20 using particle number distribution dN/dd_p and values of table 3.1.

Proposed relation for yield and condensation sink

$$Y_{end} = \frac{\alpha}{1 + \dfrac{\gamma}{CS_{end}}}. \tag{3.12}$$

Using equation 2.23, this relation can be presented as function of aerosol mass

$$Y_{end} = \frac{\alpha}{1 + \dfrac{\gamma}{2 \cdot 10^{-4} \cdot N^{0.37} M^{0.63}}}. \tag{3.13}$$

Fitting these functions to yield data results knowledge of stoichiometric coefficient of SLLV product α and chamber wall losses γ.

4. RESULTS

4.1 Results using H_2SO_4 values

To get an idea how condensation sink and secondary organic aerosol mass varies throughout modelling time, in figures 4.1 and 4.2 are presented four examples of condensation sink and aerosol mass with different initial conditions in batch chamber. All other condensation sinks and aerosol masses of 60 cases are between or near of those lines in figures 4.1 and 4.2.

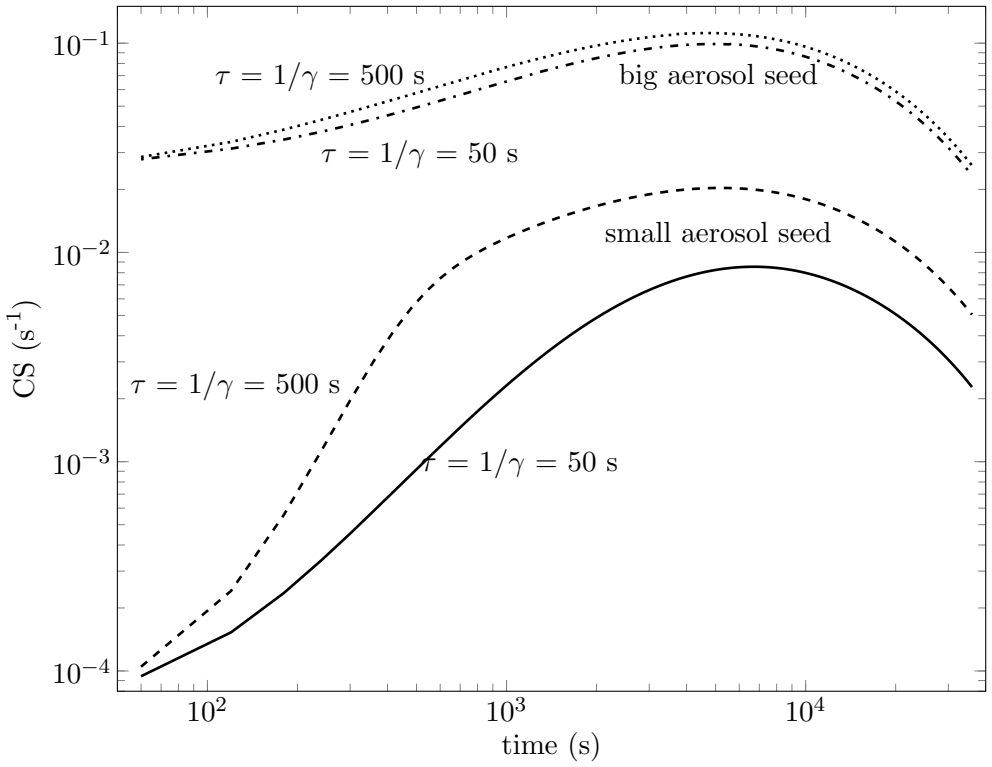

Figure 4.1: Condensation sink as function of modelling time in four different cases. Two lines for small ($D_p = 10$ nm, $M_{OA} = 3$ ngm^{-3}) and two lines for big ($D_p = 80$ nm, $M_{OA} = 10$ μgm^{-3}) secondary organic aerosol mass seeds are presented with two different SLLV product lifetimes τ.

Both condensation sink and aerosol mass grow until dilution loss is bigger than gain from aerosol growth. That happens near 10^4 seconds which is about 3 hours and near the times when aerosol mass yield values are stabilized, see figure 4.3.

Exactly: Yield Y and condensation sink CS values was chosen at times 6960 s

for 80 nm particles and 11280 s for 10 nm particles and final values for yield Y_{end} and condensation sink CS_{end} got.

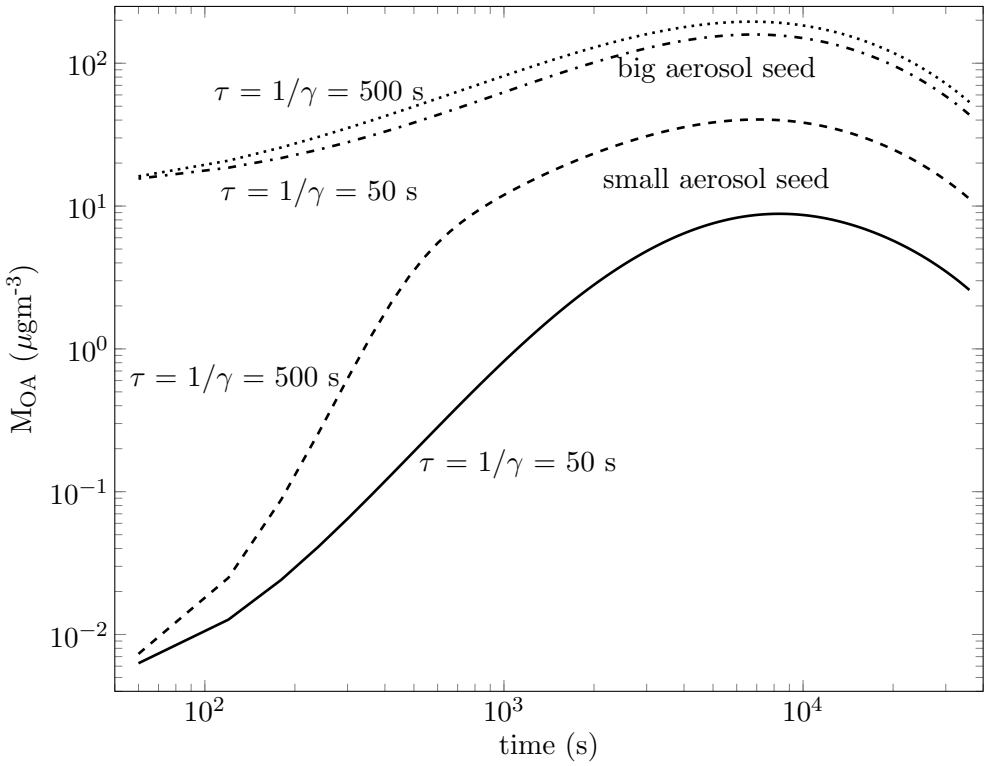

Figure 4.2: Secondary organic aerosol mass as function of modelling time in four different cases. Two lines for small (D_p = 10 nm, M_{OA} = 3 ngm^{-3}) and two lines for big (D_p = 80 nm, M_{OA} = 10 μgm^{-3}) secondary organic aerosol mass seeds are presented with two different SLLV product lifetimes τ.

In figure 4.4 are aerosol mass yield values at time when they have reached constant value, see figure 4.3, as function of aerosol condensation sink. Times needed to stabilise yields are in this modelling from two to three hours. That time is considered as end time t_{end}.

One can see, comparing data points with different SLLV lifetimes in figure 4.4, that aerosol mass yields are lower when lifetime is shorter. With short vapor lifetime, there is not enough time for aerosol to grow bigger sizes (bigger CS). When condensation sink remains low then also achieved yield is low.

What comes to goodness of formula 3.12, red lines in figure 4.4 show that yield values are over estimated. That is because of vapor dilution (neglible?? 5e-5) and... other? And fits better to those values with greater seed aerosol mass and condensation sink. Thus chamber wall loss is bigger when aerosol mass (condensation sink) is small. vapor goes to wall in the beginning (of experiment) because it has no other place to go resulting bigger wall loss coefficient γ.

Both black and blue lines fit to data really good and better than red ones. One can see, comparing vapor loss coefficients γ of red and blue fits, that blue one, which

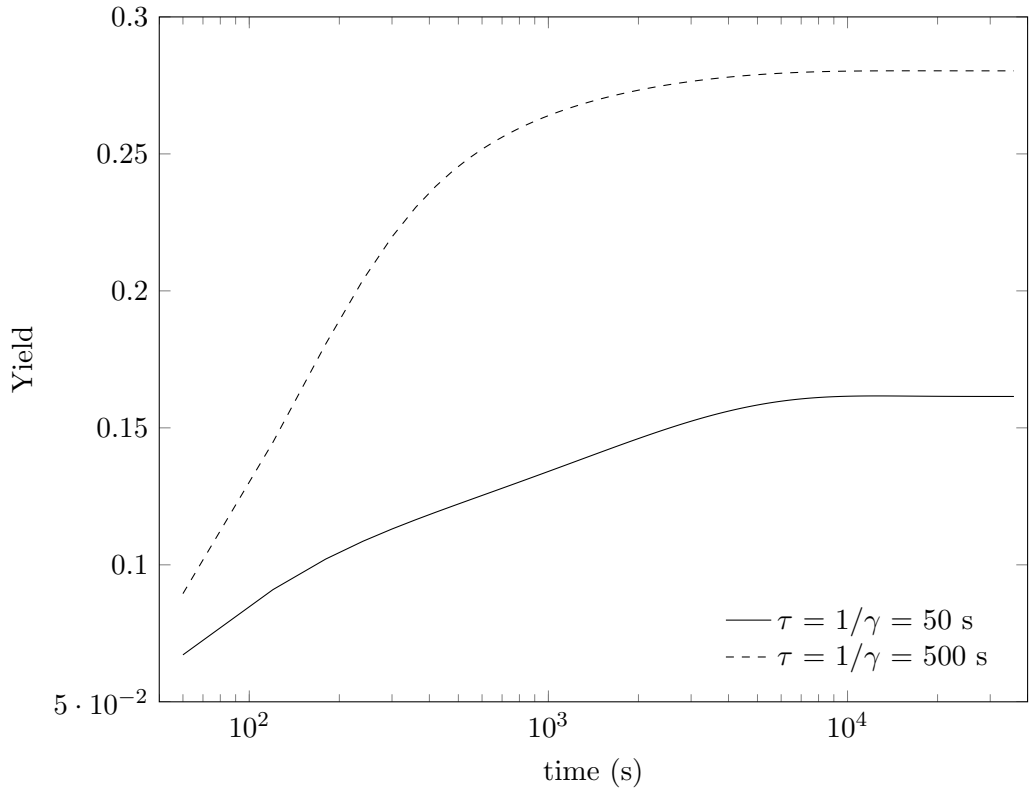

Figure 4.3: Aerosol mass yield as function of modelling time for two SLLV lifetimes τ. Model initial values were $D_p = 80$ nm, $M_{OA} = 5$ μgm^{-3} and $P_0 = 50$ppb.

agrees better to data, has greater loss coefficient. (Thus this result agrees with earlier conclusion...)

Other reason, why red line fits better to data points with bigger mass, is that it is assumed that condensation sink stays roughly constant during aerosol mass growth (see supplementary). Really CS isn't constant but increases during aerosol growth resulting to bigger values for wall loss coefficient γ.

Increase of CS is relatively bigger for small seeds than for bigger seeds as one can see from figure 4.1. Thus this assumption (red line) is better for bigger aerosol seeds when CS doesn't change so much.

One can get rough values for α and γ fitting formula 3.12 to CS data...

If also Vtot figure then α and γ values from distribution data (if density known and spherical particles). If Mtot known then you get

Problem still $N^{0.37}$

But how mentel or odum or shilling got Yield pictures as function of aerosol mass without problem but we have?

Questions in calculation

CS calc with H2S04 values (CS general function) diff coeff and molemass

Mass calc with H2SO4 molemass, density

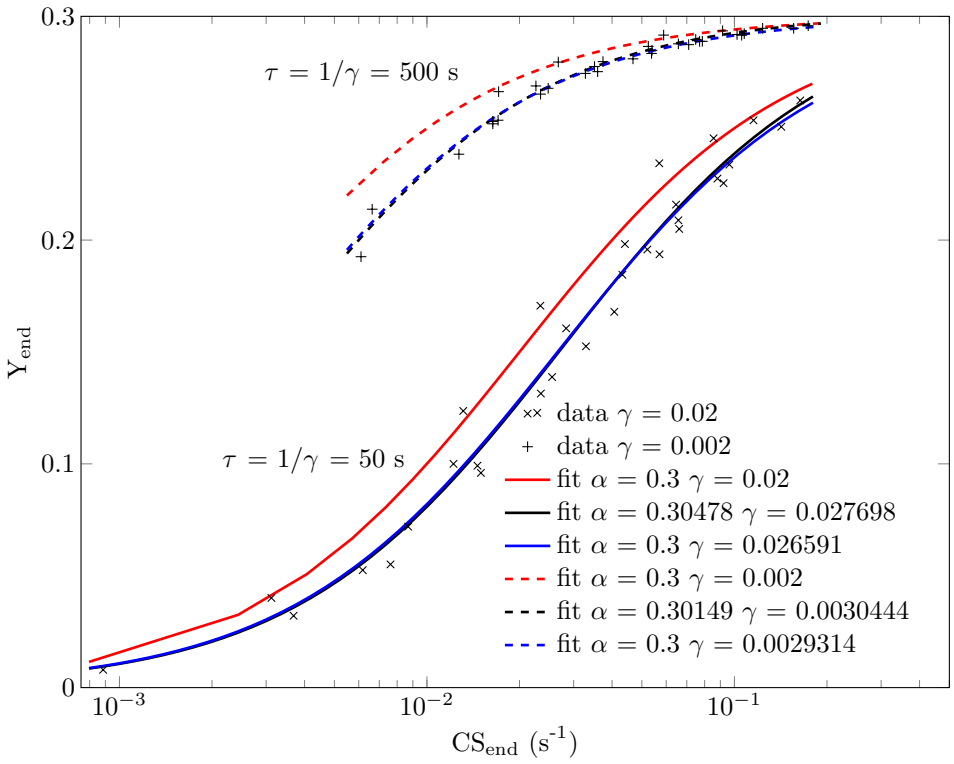

Figure 4.4: Presented data points are yield values as function of condensation sink for two different SLLV product lifetimes τ used in modelling. Lifetime is inverse of chamber loss rate γ. Data points are fitted to $\alpha/(1+\gamma/CS)$ with three different ways. Red lines are fitted with constant values for α and γ which are the same used in model. Black and blue lines are fitted to data using least square method with two parametres α and γ (black) or one parameter γ and constant α (blue). Used fitting parametres are shown in legend.

Model run with H2SO4

Diff coeff in model and CS calculation is for H2SO4...

Should we change those closer to condensating vapor values?

4.2 Results using $C_{10}H_{16}O_{10}$ values

Changed D, λ, molar mass of monoterpene precursor M_{MT} and condensing vapor M_{vap}, density of particles ρ

To get an idea how condensation sink and secondary organic aerosol mass varies throughout modelling time, in figures 4.5 and 4.6 are presented four examples of condensation sink and aerosol mass with different initial conditions in batch chamber model. All other condensation sinks and aerosol masses of 60 cases are between or near of those lines in figures 4.5 and 4.6.

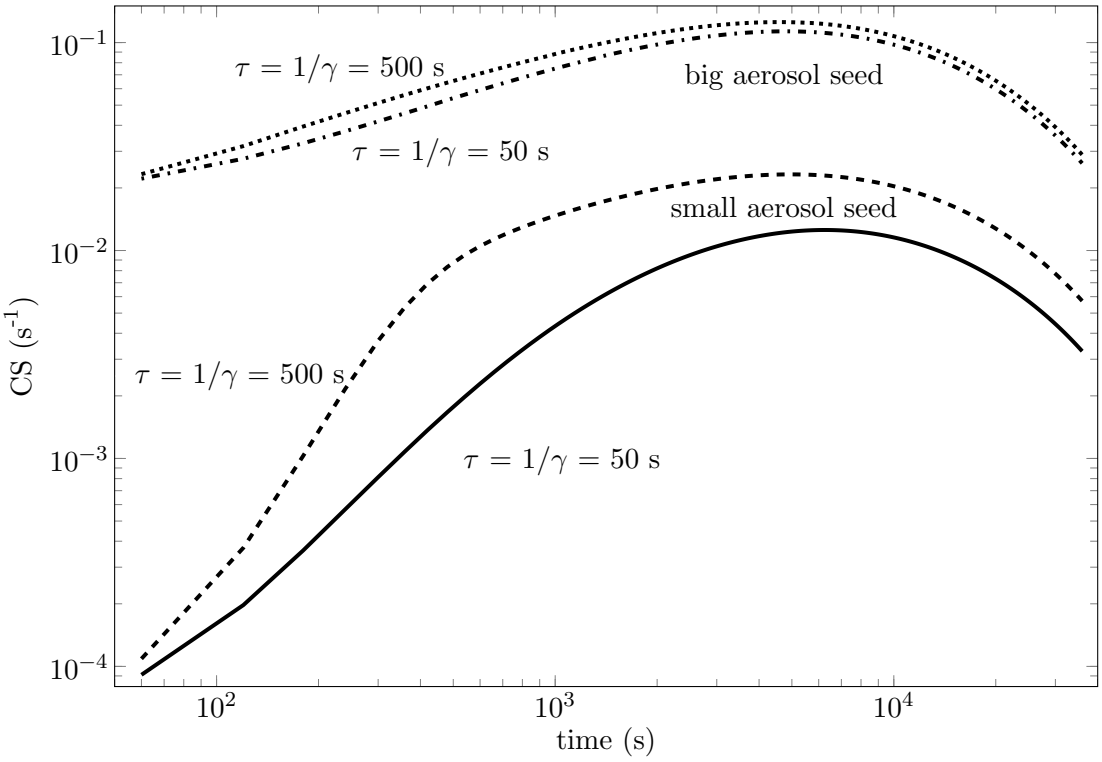

Figure 4.5: Condensation sink as function of modelling time in four different cases. Two lines for small ($D_p = 10$ nm, $M_{OA} = 3$ ngm^{-3}) and two lines for big ($D_p = 80$ nm, $M_{OA} = 10$ μgm^{-3}) secondary organic aerosol mass seeds are presented with two different SLLV product lifetimes τ.

Both condensation sink and aerosol mass grow until dilution loss is bigger than gain from aerosol growth. That happens near 10^4 seconds which is about 3 hours and near the times when also aerosol mass yield values are stabilized, see figure 4.7.

In figure 4.8 are aerosol mass yield values, at time when they have reached constant values, as function of aerosol volume. Times needed to stabilise yields are in this modelling from two to three hours, see figure 4.7. That time is considered as end time t_{end}.

From figure 4.8 can be seen that it not possible to fit all data points to same curve/graph. Yield values increase as aerosol mass seed increases and data points fit

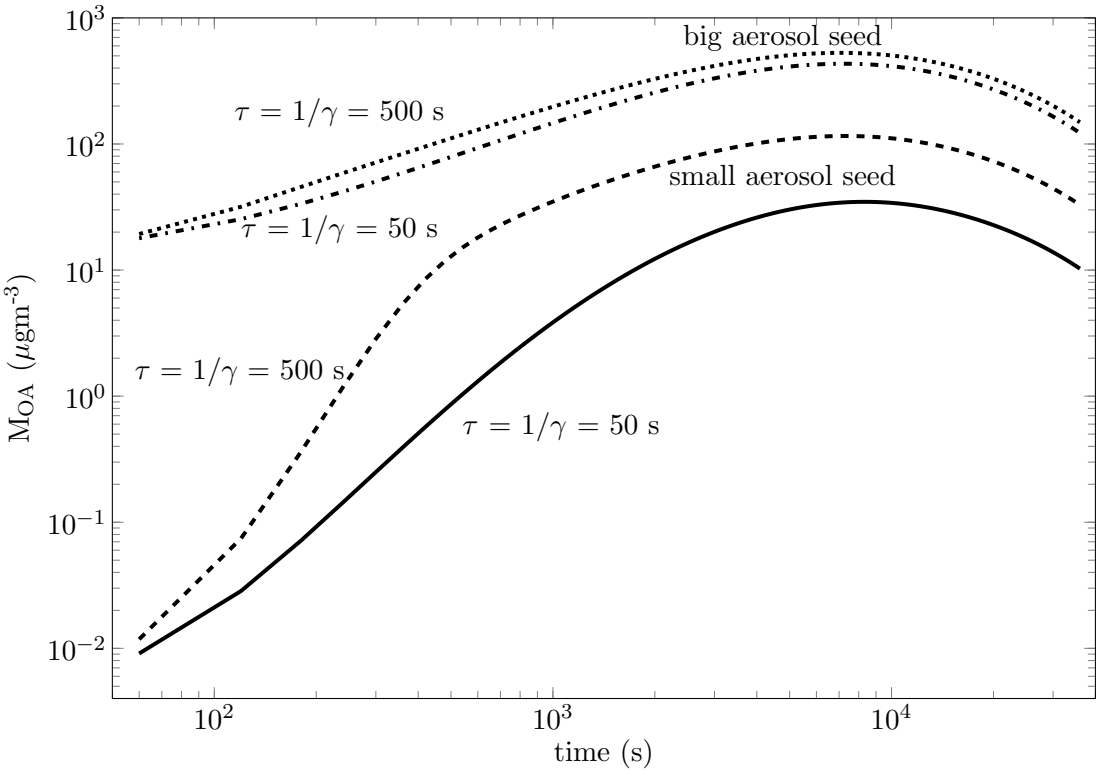

Figure 4.6: Secondary organic aerosol mass as function of modelling time in four different cases. Two lines for small (D_p = 10 nm, M_{OA} = 3 ngm^{-3}) and two lines for big (D_p = 80 nm, M_{OA} = 10 μgm^{-3}) secondary organic aerosol mass seeds are presented with two different SLLV product lifetimes τ.

to different graphs (see red arrow). One can see same effect for both chamber loss rate γ values (blue and black lines). Those points with particle size 10 nm behave similarly because they have pretty much same particle number N as 80 nm data points.

Table 4.1: Used final particle number values N_{end} in fitting figure 4.8. Values are averages of four data points with nearly equal number consentrations presented in different graphs in figure 4.8.

M_0 (µg/cm^3)	N_{end} (1/cm^3)
1	∼1900
5	∼9000
10	∼17000
30	∼44000

That's the reason why we propose that yield values should be presented as a function of condensation sink instead of aerosol mass or volume. All data points fit better to one graph as seen in figure 4.9.

One can see, comparing data points with different SLLV lifetimes in figure 4.9, that aerosol mass yields are lower when lifetime is shorter. With short vapor lifetime,

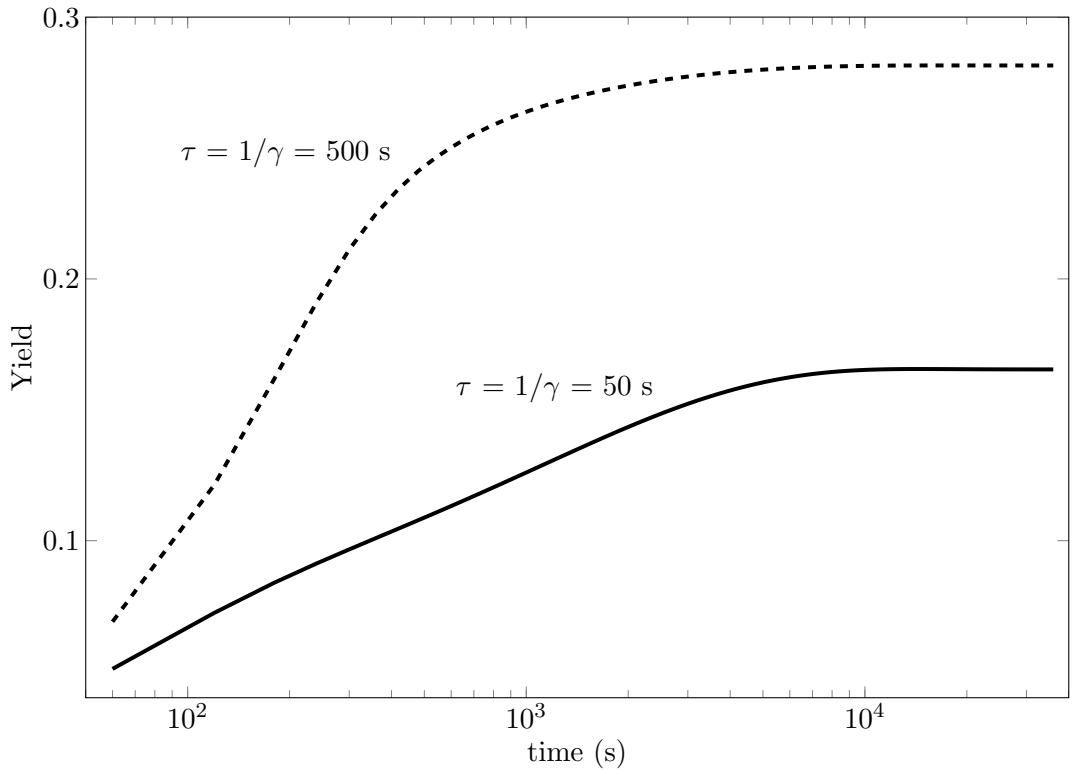

Figure 4.7: Aerosol mass yield as function of modelling time for two SLLV lifetimes τ. Model initial values were $D_p = 80$ nm, $M_{OA} = 5$ µgm^{-3} and $P_0 = 50$ ppb.

there is not enough time for aerosol to grow bigger sizes (bigger CS). This happens mainly in chamber studies but shifting to athmosphere, where vapor lifetime is assumed to be much longer, it results bigger yield values. This transfer is presented with black arrows in figure 4.9.

What comes to goodness of formula 3.12, red lines in figure 4.9 show that yield values are overestimated. And fits better to those values with greater seed aerosol mass and condensation sink. Thus chamber wall loss is bigger when aerosol mass (condensation sink) is small. Vapor goes to wall in the beginning of experiment because it has no other place to go, resulting bigger wall loss coefficient γ.

Both black and blue lines fit to data really good and better than red ones. One can see, comparing vapor loss coefficients γ of red and blue fits, that blue one, which agrees better to data, has greater loss coefficient. This result agrees with earlier conclusion.

Other reason, why red line fits better to data points with bigger mass, is that it is assumed that condensation sink stays roughly constant during aerosol mass growth (see supplementary). Really CS isn't constant but increases during aerosol growth resulting to bigger values for wall loss coefficient γ when CS is small.

Third reason is that increase of CS is relatively bigger for small seeds than for bigger seeds as one can see from figure 4.5. Thus this assumption (red line) is better

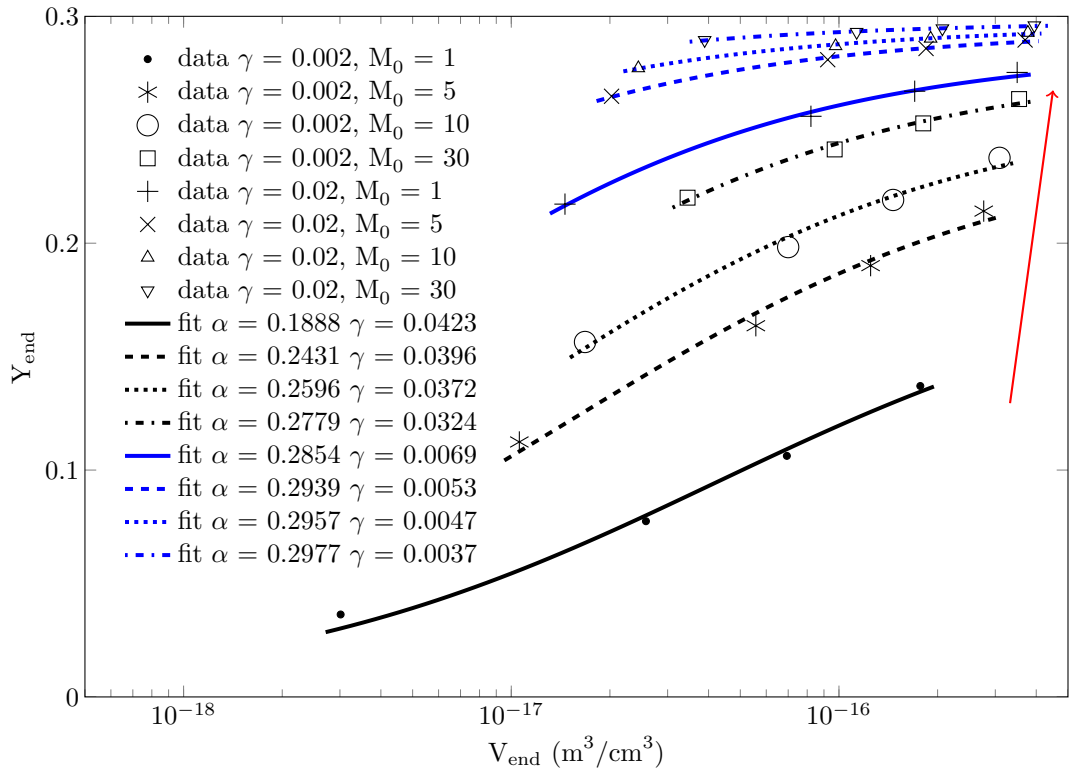

Figure 4.8: Presented data points are yield values as function of aerosol particles total volume V_{tot} for 80 nm particles with four different mass seeds M_0 ($\mu g/cm^3$) and two different SLLV product lifetimes τ used in modelling. Lifetime is inverse of chamber loss rate γ (s^{-1}). Data points are fitted to $\alpha/(1+\gamma/(2{\cdot}10^{-4}{\cdot}N_{end}^{0.37}M_{end}^{0.63}))$, where $M_{end} = \rho V_{end}$. Lines are fitted to data using least square method with two parametres α and γ. Parameter values are shown in legend and used N_{end} values in table 4.1. Red arrow represents growth of mass seed M_0.

for bigger aerosol seeds when CS doesn't change so much.

One can get rough values for α and γ fitting formula 3.12 to CS data.

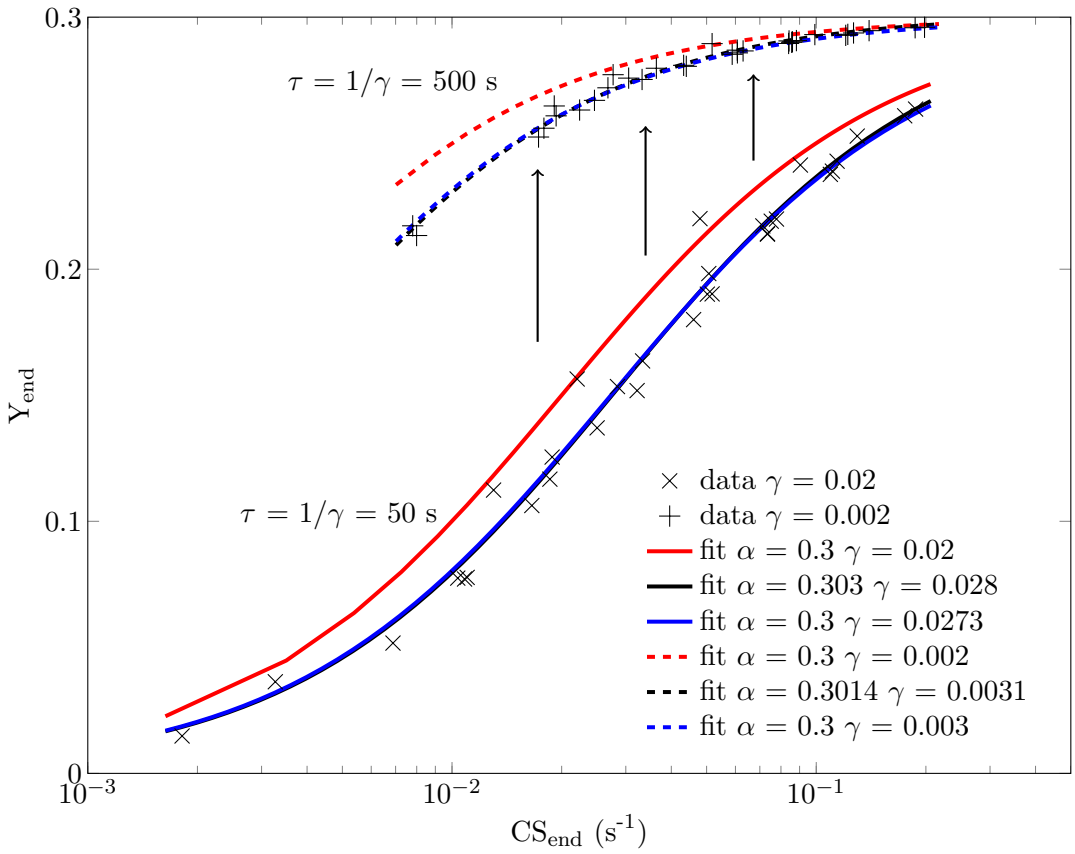

Figure 4.9: Presented data points are yield values as function of condensation sink for two different SLLV product lifetimes τ used in modelling. Lifetime is inverse of chamber loss rate γ. Data points are fitted to $\alpha/(1+\gamma/CS)$ with three different ways. Red lines are fitted with constant values for α and γ which are the same used in model. Black and blue lines are fitted to data using least square method with two parametres α and γ (black) or one parameter γ and constant α (blue). Used fitting parametres are shown in legend. Black arrows represents what happens when vapor lifetime grows.

4.2.1 Mass-α figures

In this section yields are calculated using precursor molar mass $M_{MT} = 137$ g/mol to calculate lost precursor mass. In previous section it was 300 g/mol.

From figures 4.10 and 4.11 can be seen that mass yields are higher than molecular/stoichiometric yields (figures 4.8 and 4.9). If stoichiometric coefficient α of equation 2.24 is wanted, one should use molecular yield. Althought mass yields are those which are measured. From stoichiometric α_{st} to mass α_{mass}

$$\alpha_{mass} = \alpha_{st} \cdot \frac{M_{vap}}{M_{MT}} = 0.3 \cdot \frac{300}{137} = 0.657. \tag{4.1}$$

In conclusion stoichiometric coefficients are not straight seen from mass yields but from stoichiometric yields.

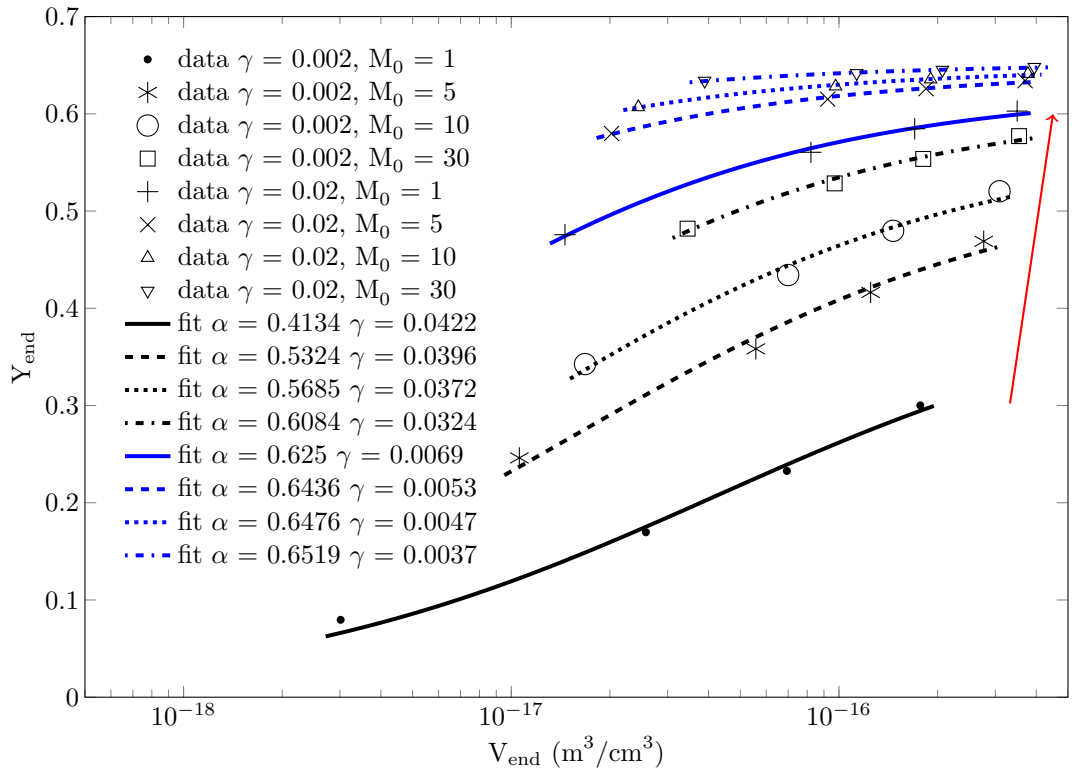

Figure 4.10: Presented data points are yield values as function of aerosol particles total volume V_{tot} for 80 nm particles with four different mass seeds M_0 ($\mu g/cm^3$) and two different SLLV product lifetimes τ used in modelling. Lifetime is inverse of chamber loss rate γ (s^{-1}). Data points are fitted to $\alpha/(1+\gamma/(2{\cdot}10^{-4}{\cdot}N_{end}^{0.37}M_{end}^{0.63}))$, where $M_{end} = \rho V_{end}$. Lines are fitted to data using least square method with two parametres α and γ. Parameter values are shown in legend and used N_{end} values in table 4.1. Red arrow represents growth of mass seed M_0.

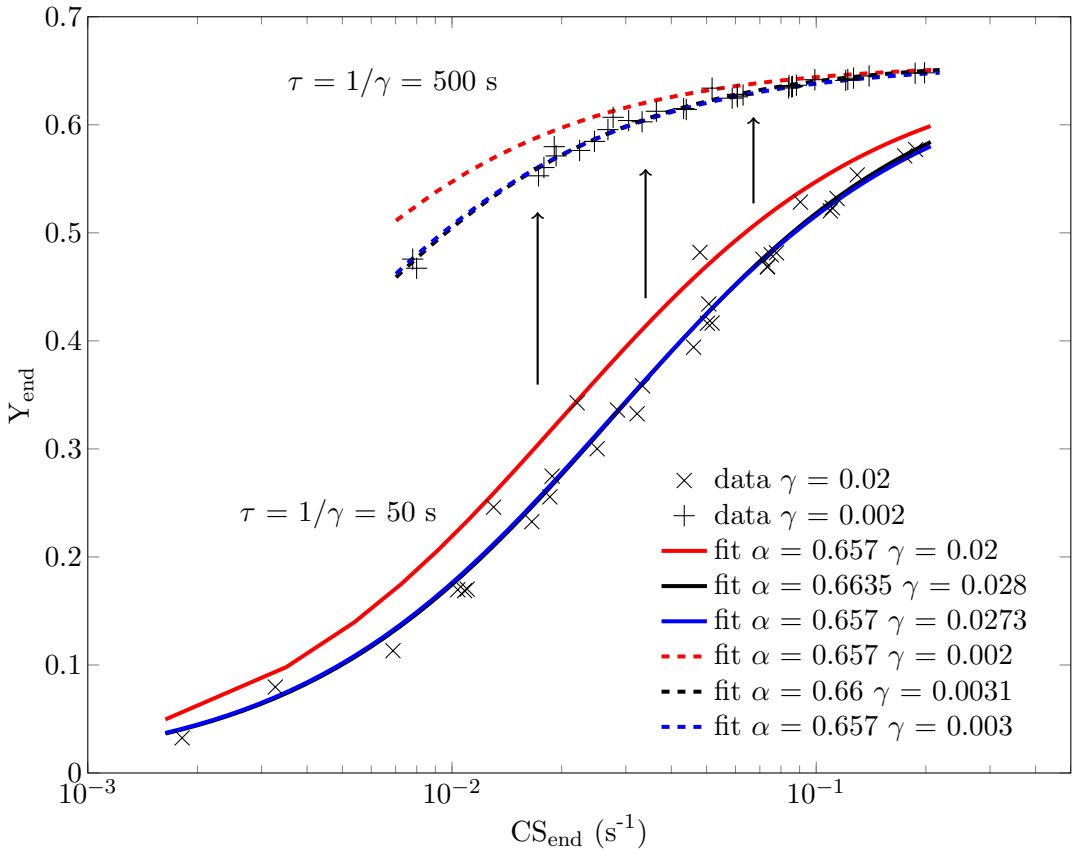

Figure 4.11: Presented data points are yield values as function of condensation sink for two different SLLV product lifetimes τ used in modelling. Lifetime is inverse of chamber loss rate γ. Data points are fitted to $\alpha/(1+\gamma/CS)$ with three different ways. Red lines are fitted with constant values for mass-α and γ which are the same used in model. Black and blue lines are fitted to data using least square method with two parametres mass-α and γ (black) or one parameter γ and constant mass-α (blue). Used fitting parametres are shown in legend. Black arrows represents what happens when vapor lifetime grows.

5. MATLAB SCRIPTS AND DATA FILES

Datafiles are located in GitHub path:

For 10 nm particles

\GitHub\AECHAMO\Results and scripts_mp\SOA formation\Batch \Fixed_diff_molemass\10nm\fixed correct lambda\fixed correct density \run_20130726T203251

And for 80 nm particles

\GitHub\AECHAMO\Results and scripts_mp\SOA formation\Batch \Fixed_diff_molemass\80nm\fixed correct lambda\fixed correct density \run_20130726T200039

Calculations was done with script:

\GitHub\AECHAMO\calculate and plot\SOA_calculation_Yend_CSend.m

Also all used functions are found in this folder or AEROTOOLS\development repository.

This documentation pdf latex origin:

\GitHub\AECHAMO\documentation_mp\chamber

Diffusion coefficient variation figure 2.1 made with: \GitHub\AECHAMO\calculate and plot

6. CONCLUSION

6.1 What next?

DONE-Writing down methods (and theory):

- DONE-How model works? Aerosol processes, equations, used coefficients
- DONE-How calculations are done? What are calculated from dN/dD_p?
- How one gets α and γ from dN/dD_p?
- DONE-Ask Jyrki for diffusion coefficient, find out D
- DONE-Draw pictures $Yend(Vtot)$ and fits
- DONE-$C_{10}H_{16}O_{10}$ pictures with right values
- DONE-yield pictures with precursor P molarmass M = 137 g/mol -> α to 0.657
- DONE-explain differense between mass yield and molecular yield
- DONE-used Nend values
- DONE-uniform terminology
- DONE- Diff. figure
- DONE- references

REFERENCES

Dal Maso, M., Kulmala, M., Lehtinen, K. E. J., Mäkelä, J. M., Aalto, P., and O'Dowd, C. D. (2002). Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers. *Journal of Geophysical Research D: Atmospheres*, 107(19):1–10.

Dormand, J. R. and Prince, P. J. (1980). A family of embedded Runge-Kutta formulae. *Journal of Computational and Applied Mathematics*, 6:19–26.

Korhonen, H. (2004). Model studies on the size distribution dynamics of atmospheric aerosols. *Doctoral thesis. University of Helsinki.*

Pirjola, L. and Kulmala, M. (1998). Modelling the formation of H_2SO_4-H_2O particles in rural, urban and marine conditions. *Atmospheric Research*, 46(3-4):321–347.

Reid, R., Prausnitz, J., and Poling, B. (1987). *The properties of gases and liquids.* McGraw Hill Book Co., New York.

Seinfeld, J. H. and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics - From Air Pollution to Climate Change.* John Wiley & Sons, New York.