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CO Formation from Soot and CO_2 in the Hot Gas Layer

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Abstract

In this study the formation of CO from soot in the hot gas layer has been examined. The investigation has been made predominantly for rich mixtures, with equivalence ratios from 1.0 to 3.0. To study the soot particle growth as a function of equivalence ratio and residence time, equivalence ratios from 0.5 to 4.0 and residence times from 0.25 s to 10 s, respectively, have been used. The gas phase chemistry has been calculated using the Sandia CHEMKIN code [1]. The perfectly stirred reactor (PSR) concept has been used to model the hot gas layer. The input gas temperature, equivalence ratio and residence have been varied to investigate the thermochemical environment at a given location in the gas layer. Ethene, C_2H_4, was chosen as the fuel, as it has the necessary carbon/hydrogen ratio to form soot precursors.

The chemical kinetic model used consists of gas phase chemistry including reactions for aromatic chemistry, soot particle coagulation, soot particle aggregation and soot surface growth.

The gas phase chemistry has been calculated using the GRI-Mech 1.2 scheme [2] for smaller hydrocarbon reactions. The reaction scheme was modified to take higher hydrocarbon reactions (aromatic chemistry) into account. Benzene and phenyl formation are modelled by reactions of C_4H_x with acetylene and by cyclization reactions of C_6H_x species and recombination of propargyl radicals [3]. Reactions up to four aromatic rings, i.e. pyrene are included in the gas phase aromatic chemistry [4]. The pyrene formation is started from benzene following the HACA (hydrogen abstraction – carbon addition) reaction sequence via formation of biphenyl (i.e. "ring-ring condensation"). The total number of reaction steps is 542 in the gas phase scheme.

The soot particle coagulation dynamics is described by the method of moments [5] having altogether 6 moments. The soot surface growth mechanism is described using a 6-step reaction mechanism, which resembles the HACA mechanism for PAH [3, 6].

Soot formation starts at an equivalence ratio of 1.0 and increases linearly with equivalence ratio. The particle size increases with increased residence time. Reaction between soot and CO_2, resulting in CO, occurs at temperatures higher than 950 °C. The higher the temperature and equivalence ratio the higher is the CO formation via this mechanism. Addition of extra CO_2 into the mixture increases the formation of CO and decreases the soot volume fraction. This effect increases with increasing temperature and equivalence ratio.

Identification this "new" source of CO increases our knowledge of the production of CO in hot gas layers. The results can be used to predict CO formation in vitiated room fires.

Key words: CO formation, soot formation, chemical kinetics, gas layer, and under-ventilated fires.

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Table of contents

Sammanfattning

I denna studie har bildning av CO från sot i det heta gaslagret, som bildas i en rumsbrand, undersökts. Undersökningen har i huvudsak fokuserats på rika bränsle-luft blandningar, d v s underventilerade förhållanden. Vid undersökning av ekvivalenskvotens och uppehållstidens inverkan på sotbildning har ekvivalenskvoter från 0,5 till 4,0 och uppehållstider från 0,25 till 10 s studerats.

Sandias CHEMKIN program har använts för att beräkna gasfaskemin [1]. En s k "perfectly stirred reactor" (PSR) metod har använts för att modellera gaslagret. De parametrar som har varierats för att undersöka de olika termokemiska förhållanden som råder i olika delar av gaslagret är bl a gastemperaturen på inflöde, ekvivalenskvoten samt gasens uppehållstid i reaktorn. Eten (C_2H_4) valdes som bränsle eftersom den har de nödvändiga förutsättningarna för bildning av sot, d v s har tillräckligt hög kol/väte kvot samt att dess sönderdelningsprodukter leder till bildning av ämnen som är specifika för introduktion av sotpartikelbildning.

Den använda kemisk kinetiska modellen består av en gasfaskemimodell som inkluderar aromatisk kemi, sotpartikelkoagulation, partikelaggregation och yttillväxt.

GRI-Mech 1.2 reaktionsmodellen [2] har använts för beräkning av kemin för mindre kolväten. Modellen har kompletterats för att inkludera reaktioner för aromatiska kolväten. Bildning av bensen och fenyl modelleras genom reaktion av C_4H_x med acetylen och med reaktioner för ringbildning från C_6H_x – ämnen samt genom rekombination av propargylradikaler [3]. Polyaromater upp till fyra ringar har inkluderats i den aromatiska kemin [4]. Bildning av pyren utgår från bensen som följer en s k HACA sekvens (väte abstraktion – kol addition) via bildning av bifenyl (s k ring-ring – kondensation). Schemat inkluderar totalt 542 reaktionssteg.

Dynamiken av sotpartikelkoagulation beskrivs med hjälp av momentmetoden som innehåller totalt 6 moment [5]. Yttillväxten av sotpartiklar inkluderar 6 reaktionssteg, en mekanism som liknar HACA mekanism för polyaromater [3,6].

Sotbildningen startar vid ekvivalenskvoten 1.0 och ökar linjärt med ökad ekvivalenskvot. Sotpartikelstorleken ökar med längden av uppehållstiden. Reaktionen mellan sot och CO_2, som producerar CO, sker vid temperaturer på 950 °C och högre. Ju högre temperaturen är desto högre är CO produktionen på detta sätt. Addition av extra CO_2 in i blandningen ökar CO produktionen och minskar volymfraktionen av sot. Denna effekt ökar med ökning av temperatur och ekvivalenskvot.

Identifieringen av denna "nya" källa av CO ökar vår kunskap om CO produktion i det heta gaslagret. Resultaten kan användas för att bättre kunna förutsäga CO produktion i underventilerade rumsbränder.

Nomenclature

c_p	Specific heat
R	Molar gas constant
H^o	Enthalpy
S^o	Entropy
T	Temperature
a_i	i:th polynomial coefficient in enthalpy, entropy and heat capacitivity polynomial
A_f, A_b	Arrhenius pre-exponential factors in forward and backward rates
$C_{\phi i}$	Concentration of species ϕ_i
E_f	Activation energy in forward reaction
E_b	Activation energy in backward reaction
k_f	Rate constant of forward chemical reaction
k_b	Rate constant of backward chemical reaction
M_r	r:th moment (soot formation model)
NS	Total number of species in chemical model
N_{gas}	Number of gas phase species in the mixture
$N_{moments}$	Number of moments in soot model
N	Sum of N_{gas} and $N_{moments}$
Q_r	Formation rate of r:th moment
R_f	Forward chemical reaction rate
R_b	Backward chemical reaction rate
t	Time
W_k	Molecular weight of the k:th specie
Y_k	Mass fraction of the k:th specie
Y_k^*	Mass fraction of the k:th specie after chemical reaction
β_f, β_b	Temperature exponents in forward and backward reaction rates
γ_f	Third body reaction exponent in forward reaction
γ_b	Third body reaction exponent in backward reaction
ϕ	Equivalence ratio
ω_k	Production rate of k:th specie
ρ	Mean density
ν	Stoichiometric oxidiser-to-fuel ratio
τ	Residence time
σ_m	Reciprocal of mean molecular weight
σ_i	Number of species i
ν_i'	Stoichiometric coefficient of specie i appearing as reactant
ν_i''	Stoichiometric coefficient of specie i appearing as product

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Introduction

Carbon monoxide (CO) is the major product that causes deaths in fires. Fire fatalities due to CO often occur at remote locations from the room of fire origin. CO is formed in many combustion processes, such as fires. Combustion in spaces with a restricted oxygen supply reduce the combustion efficiency, which in turn increases the formation of the incomplete products of combustion, such as CO. The CO may also be formed in the hot gas layer depending on the chemical composition and the temperature of the gases. CO thus formed can easily be transported to other locations in the building, which are not involved to fire and in that way may reap more fire victims.

CO formation in the hot gas layer is a very complicated process as there usually are many different species (foremost incomplete products of combustion) present. The number of possible pathways for formation (and destruction) of CO is therefore great.

The production of large amounts of soot also poses a major problem in fires. Radiation from soot contributes to the drastic spread of the fire. Depending on the fire situation and fuel type 1-20 wt-% of the fuel is converter to soot. Under certain conditions CO is formed from this soot. The products of incomplete combustion and smoke particles in the gas layer prevent oxygen molecules from reacting with the fuel, which further enhances the formation of incomplete combustion products and soot. In general soot and CO are present in significant amounts under similar conditions in a fire. In this investigation the formation of CO from soot is of special interest, because CO plays an important roll in fire fatalities.

In this study the formation of CO from soot as a reaction with CO_2 has been investigated. CO_2 is, together with H_2O, the main product of complete combustion in hydrocarbon combustion. It is a stable molecule up to about below the temperature 900 °C. At higher temperatures it begins to dissociate partly and hence is able to react with other species.

There are simple models for soot formation that are working well for simple fuels. Soot formation models are, however, far from complete, i.e. they have large uncertainties for example, in flames and in the hot gas layer due to the large number of intermediate species present. However, the models can be used to calculate trends of soot formation as a function of the influence of certain parameters, such as temperature, equivalence ratio or species concentration.

In Chapter 1 a short description of the CHEMKIN code used in this study is given. The modelling has been described in Chapter 2, which includes a description of PSR, gas phase chemistry and soot modelling. The gas phase chemistry is clarified with respect to the most important pathways leading to the production of soot including some main pathways for the formation of acetylene, and aromatic species (benzene) and the further growth of form poly-aromatic hydrocarbons (PAH) up to four aromatic rings, i.e., pyrene. Soot surface growth is modelled according to the HACA sequence starting from pyrene, using the Frenklach model of surface growth.

1 CHEMKIN Code

CHEMKIN contains about 100 subroutines that have been used to model the gas phase chemical kinetics [1]. These subroutines are extremely flexible and can be effectively modified to simulate a large range of chemically reacting flow systems. The gas phase subroutines return all pertinent information about the elements, species, reactions, the equations of state, thermodynamics, the rates of species production, sensitivity parameters, the derivatives of chemical production rates, etc. The code can be used for a wide variety of problems that require solving the detailed chemistry, such as premixed flames, well stirred reactors, shock tubes and plug flow reactors. In addition the users can easily write their own routines to utilise the code to best suit their needs, such as the coding of special routines taking particles influence (such as soot or aerosol) into consideration or enhancing the model for more detailed heterogeneous (surface) chemistry.

CHEMKIN is mainly composed of four pieces: the Thermodynamic Database, the Interpreter, the Linking File and the Gas-Phase Subroutines.

The Thermodynamic Database contains the coefficients for polynomial fits to specific heat, standard states of enthalpies and the standard states of entropies. The polynomial fits are made to two polynomials of seven coefficients: one for the cold and one for the hot range. The common temperature connecting these temperature regions is typically 1000 K. Altogether 14 coefficients for each species are stored in the database and can be used for fitting equations in following form

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{1}$$

$$\frac{H^o}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \tag{2}$$

$$\frac{S^o}{R} = a_1 \ln(T) + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \tag{3}$$

where c_p is the specific heat, H^o is the enthalpy, S^o is the entropy, R is the molar gas constant, T is the temperature and a_1 through a_7 are polynomial coefficients.

If there are chemical reactions involved, a reaction mechanism is needed. The reaction mechanism contains a symbolic description of the chemical reactions of all species involved together with the relevant Arrhenius parameters for calculation of the rate of chemical reactions.

The interpreter checks that all in the reaction mechanism and Arrhenius parameters are correct and all the symbol names are correctly spelled and that they are found in the database. Once a successful run has taken place the binary linking file is created, which can then be used in the ensuing modules in CHEMKIN.

In this study the perfectly stirred reactor was used to calculate gas phase chemistry. A subroutine for soot formation was linked to the program to calculate the heterogeneous chemistry occurring during soot formation and destruction.

2 Modelling

In this study the calculations were made using the perfectly stirred reactor concept (PSR), which is a mathematical representation of a continuously stirred tank (CSTR). The gas phase chemistry was calculated using the detailed chemical kinetic scheme of Wang and Frenklach [7], with modified aromatic chemistry by Appel, Bockhorn and Frenklach [3]. Similarly, soot calculations were made using detailed chemical kinetic models for soot formation of Appel, Bockhorn and Frenklach [3, 6], which includes soot particle coagulation, soot particle aggregation, and soot surface growth.

2.1 Perfectly-Stirred Reactor Model

A perfectly stirred reactor (PSR) is a chemical kinetic simulator under conditions of high intensity turbulent mixing and spatially uniform reactant and temperature distribution in the reactor. The reactor is characterised by the reactor volume, residence time or mass flow rate, heat loss or temperature. One can say that the PSR method is the simplest non-trivial (zero-dimensional) transport analysis of a reacting system. The concentrations are the same everywhere in the reactor, which means that there are no gradients in the reactor (no gradients = “zero-dimensional”). Such a model is able to predict the chemical composition and temperature at the reactor outlet, for example, for any given initial substances the mass flow rate, temperatures, residence time in the reactor, value of the heat losses and reaction mechanism.

This concept has been used for many years to study the chemistry of various chemical processes such as combustion. In PSR the initial substances are introduced in such a way that high intensity turbulent mixing leads to uniform reactants and temperature distribution in the reactor volume. The chemical reaction rates inside the reactor are not limited by mass or heat transfer processes, i.e. diffusion or other mixing processes proceed much more rapidly than consumption and removal. An additional assumption, which is required for the application of the PSR model, is a steady state character of the process.

PSR can predict the steady state temperature and chemical composition under the assumptions mentioned above, taking into account the detailed elementary chemical reactions that can effect the species concentration and temperature.

The flows of reactants in this case must be steady or change insignificantly during the residence time in the process vessel. For gas phase chemistry in this application we are seeking the solution of the set of steady state conservation equations in the form:

$$\sum_{k}^{N_{gas}}\left(\frac{1}{\tau}\left(Y_k - Y_k^*\right) - \frac{\dot{\omega}_k W_k}{\rho}\right) = 0 \qquad (4)$$

where τ is the residence time, Y_k and Y_k^* are the inlet and outlet mass fractions, respectively, of the k*th* gas-phase, $\dot{\omega}_k$ is the production rate of the k*th* species, W_k is the molecular weight of the k*th* species, ρ is the mean density of the mixture and N_{gas} is the number of gas-phase species in the mixture. The additional set of equations required to find a solution for the soot formation and destruction is

$$\sum_{r}^{N_{moments}} \left(\frac{1}{\tau} \left(M_r - M_r^* \right) - Q_r \right) = 0 \tag{5}$$

where M_r is the r*th* moment, Q_r is the formation rate of the r*th* moment, and $N_{moments}$ is the number of moments. The moments are very large numbers and hence it is convenient to rewrite the equation (5) as

$$\frac{1}{\tau}\left(1 - \frac{\exp(Y_k^*)}{\exp(Y_k)}\right) - \frac{Q_r}{\exp(Y_k)} = 0, k = N_{gas} + 1, N \tag{6}$$

where $N = N_{gas} + N_{moments}$ and

$$Y_{r+1+N_{gas}} = \log(M_r). \tag{7}$$

2.2 Gas phase chemistry

2.2.1 Chemical mechanism

Soot formation is a very complicated process. It requires an accurate description of the gas phase chemistry of formation of quite complicated species, such as poly-aromatic hydrocarbons (PAH). In this study, the gas phase chemical kinetics scheme includes the pyrolysis and oxidation of C_1 and C_2 species and the formation of higher linear hydrocarbons up to C_6 species, the formation of benzene and further growth of small PAHs leading to pyrene, as well as the oxidation pathways of the aromatic species.

An important species for soot growth is acetylene (C_2H_2). There are many pathways to form acetylene. From the fuel we used in this study, C_2H_4, formation of C_2H_2 occurs the following way: C_2H_4 looses its first H-atom to form a vinyl, C_2H_3, at sufficiently high temperatures H^+ and OH^- radicals in the mixture react with C_2H_3 via the following reactions to form acetylene:

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \tag{R1}$$
$$C_2H_3 + OH \rightarrow C_2H_2 + H_2O \tag{R2}$$

If oxygen is present then acetylene can also be formed as a result for vinyl oxidation [10]:

$$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2 \tag{R3}$$

The vinyl is also oxidised by at least two other reactions: one producing formyl radicals (CHO) and formaldehyde (CH_2O) [3,9,10], and one forming C_2H_3O [3], i.e.,

$C_2H_3+O_2 \rightarrow CHO+ CH_2O$ (R4)
$C_2H_3+O_2 \rightarrow C_2H_3O + O$ (R5)

Formyl radicals then decompose thermally or through H-atom abstraction by H radicals or O_2, to form CO. Formaldehyde is thermally dissociated to formyl and hydrogen atoms or CO and molecular hydrogen [10, 11].

Returning to fuel consumption, other pathways for the consumption of C_2H_4 include:

$C_2H_4+H \rightarrow C_2H_5$ (R6)
$C_2H_4+O \rightarrow CH_3+ CHO$ (R7)
$C_2H_4+OH \rightarrow CH_3+CH_2O$ (R8)

resulting in ethyl radicals (C_2H_5), methyl radicals (CH_3), formaldehyde and formyl radicals. As thermal decomposition of formyl leads to formation CO, the vinyl consumption reaction, (R4), and C_2H_4 consumption reactions (R7) and (R8) are potential sources of CO.

Recombination reactions between two methyl radicals result in the formation of ethane (C_2H_6). Similarly the recombination of ethyl and methyl radicals will form propane (C_3H_8). These fuels, which are intermediate products of combustion of the fuel (C_2H_4) chosen in our study, will dissociate or thermally decompose to smaller fragments in similar ways. The fragments continue, in part to form smaller intermediates, for example CO and C_2H_2 (as in C_2H_4 combustion) and partly recombine to C_3 or higher hydrocarbons.

As this study also investigates soot formation possibilities the higher hydrocarbons are included in the gas phase chemistry. Thus the reaction scheme contains cyclic and polycyclic aromatic hydrocarbons.

When a hydrocarbon molecule is long enough it will react with itself. This means that both ends of the molecule react as two species resulting in a ring through a so-called cyclization reaction. The gas phase reaction scheme included in this study contains cyclization reactions of C_6H_x (x refers to the number of hydrogen atoms in a species), resulting in benzene, C_6H_6. Two other main pathways for the formation of benzene and phenyl are included in the reaction mechanism, i.e., by reactions of C_4H_x with acetylene, and by recombination of propargyl radicals (H_2C-C-CH) [3].

Benzene is then the starting specie for the formation of polyaromatic hydrocarbons. This is assumed to follow so called HACA (hydrogen-abstraction/carbon-addition) reaction sequence along with ring-ring-condensation [3, 12], i.e. via the formation of biphenyl. Species consisting of up to four 'benzene' rings are taken into account in the chemical model in this study. Species like benzene (named A_1, in the reaction scheme), phenyl (A_1 -), naphthalene (A_2), acenaphthalene (A_2R5), phenanthrene (A_3), and pyrene (A_4) are produced. Pyrene is of special interest because it is a precursor for soot particle nucleation. The suffix on "A" refers to the number of benzene rings in the aromatic molecule.

2.2.2 Mathematical model

The chemistry of the gas layer in this study was calculated using a 542 elementary step reaction mechanism involving 101 species. The reactions are of the form:

$$\sum_{i=1}^{N} \nu'_i \phi_i \overset{k_f}{\underset{k_b}{\longleftrightarrow}} \sum_{i=1}^{N} \nu''_i \phi_i \tag{8}$$

where ϕ_i is a chemical symbol for species i, and υ'_i and $\upsilon''_i$are the stoichiometric coefficients of species i appearing as reactant and product, respectively. Forward and backward reaction rates R_f and R_b are calculated using:

$$R_f = k_f (\rho\sigma_m)^{\gamma_f} \prod_{i=1}^{NS} (\rho\sigma_i)^{\nu'_i} \tag{9a}$$

$$R_b = k_b (\rho\sigma_m)^{\gamma_b} \prod_{i=1}^{NS} (\rho\sigma_i)^{\nu''_i} \tag{9b}$$

where σ_m is the reciprocal of the mean molecular weight of the mixture, and γ_f and γ_b have values of unity if the reactions occur on the third body, otherwise γ_f, $\gamma_b = 0$, σ_i is the number of species i, k_f and k_b are the forward and backward rate constants respectively for the reaction according to the Arrhenius expressions:

$$k_f = A_f T^{\beta_f} e^{-E_f/RT} \tag{10a}$$

$$k_b = A_b T^{\beta_b} e^{-E_b/RT} \tag{10b}$$

where E_f and E_b are the activation energies for forward and backward reactions, respectively, A_f and A_b are the Arrhenius pre-exponential factors, and β_f and β_b are the temperature exponents.

The net changes of concentration of species ϕ_i according to the reaction (8) can be calculated from equation:

$$\frac{dC_{\phi_i}}{dt} = (\nu''_i - \nu'_i) k_f \prod_{j=1}^{N} C_{\phi_j}^{\nu'_j} + (\nu'_i - \nu''_i) k_b \prod_{j=1}^{N} C_{\phi_j}^{\nu''_j} \tag{11}$$

The detailed reaction mechanism is shown in Appendix.

2.2.3 Soot particle growth

The soot formation is calculated by a separate FORTRAN routine linked to routines that calculate the gas phase and surface chemistry [3, 6]. Species responsible for soot nucleation and those taking part in surface reactions are included in an array in the program with indices for each species. In the current version of the program C_2H_2, CO, H, H_2, H_2O, O_2 and OH are included.

Acetylene has been found to be the most important surface growth species. According to measurements by Harris and Weiner [13] in laminar premixed flames the soot surface growth is proportional to soot surface area and the soot volume fraction is strongly dependent on the chemical structure of the fuel and that acetylene is the most important species. Wagner [14] found that a first-order rate law in soot volume fraction could express soot surface growth and the soot volume fraction is dependent on the chemical structure of the fuel, pressure, temperature and equivalence ratio.

Later work by Franklach and Wang [15] is based on a different kinetic formulation of the surface growth of soot particles. In such model the surface reactions are treated in analogy with the gas phase reaction kinetics, as the growth of PAH, using the HACA reaction sequence. On molecular scale the soot particles have enormous areas on which several reactions can occur in the same time. This surface growth mechanism is applied in this study.

The first part of the HACA sequence, hydrogen abstraction, is assumed to occur in analogy with hydrogen abstraction from benzene. The abstraction goes via the H atom (reaction S1) or hydroxyl radical, OH (reaction S2). The second part, the carbon addition (reaction S4), goes via acetylene-addition. For example, the rate of the H-abstraction from the soot particle is obtained through the division of the gas phase reaction rate (H with the benzene) by 6. This accounts for the six C-H sites of a benzene ring, each of them are presumed equivalent to a C-H site on a polyaromatic edge of the soot surface.

At the moment the soot surface growth and oxidation is calculated using the following subscheme of 6 reaction steps [3]:

$$C_{soot} - H + H = C_{soot}^{*} + H_2 \qquad \text{(S1)}$$

$$C_{soot} - H + OH = C_{soot}^{*} + H_2O \qquad \text{(S2)}$$

$$C_{soot}^{*} + H \rightarrow C_{soot} \qquad \text{(S3)}$$

$$C_{soot}^{*} + C_2H_2 = C_{soot}^{*} + H \qquad \text{(S4)}$$

$$C_{soot}^{*} + O_2 \rightarrow 2CO + products \qquad \text{(S5)}$$

$$C_{soot} + OH \rightarrow CO + products \qquad \text{(S6)}$$

Surface oxidation of soot is assumed to occur by molecular oxygen (reaction S5) and by hydroxyl radical (reaction S6).

3 Results

3.1 PSR simulations

PSR simulations were made using C_2H_4 as the fuel. The inlet gas to the PSR was a mixture of the fuel and air. As PSR means that at every point inside the reactor has the same physical condition, i. e. the temperature, species concentration, pressure, etc., have the same value everywhere inside the reactor at given time, every PSR run is restricted to a specific region in space, in which these variables do not vary much.

This inlet flow corresponds to the plume inflow, which enters into the upper hot gas layer that develops in room fires. The mixture of these inlet species was varied to suit different equivalence ratios. Although the PSR concept cannot be valid in the whole gas layer the chemistry, different locations can be calculated assuming that spatial variations of physical parameters are small.

The residence time was varied from 0.25 s to several seconds. Temperatures between 1200 K and 1500 K wre used. Varying amounts of extra CO_2 were added to the reactor inlet for every equivalence ratio, residence time and temperature.

3.1.1 Influence of residence time

The influence of residence time, τ was simulated with equivalence ratio, $\phi = 2.0$ for temperature T = 1500 K. The soot volume fraction, as expected, increases with increasing residence time. At $\tau = 0.25$ s the soot volume fraction is 0.9×10^{-6}, which increases to 1.47×10^{-6} (about 60 %) when τ is increased to 10 s, see Fig. 1a).

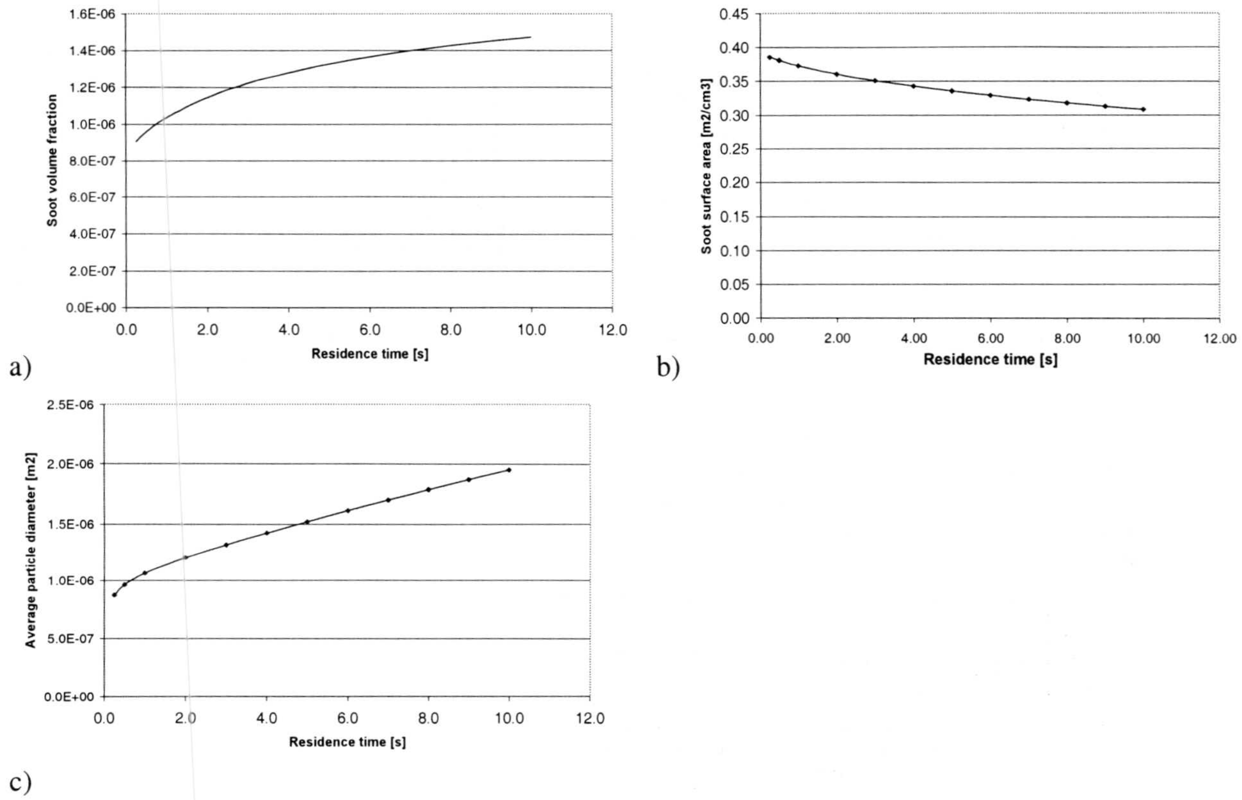


Figure 1. a) Soot volume fraction, b) soot surface area per cm^3 fire gas and c) average particle diameter, as a function of residence time. Equivalence ratio 2.0 and temperature 1500 K.

The soot surface area per cm^3 fire gas decreases about 25 % (Fig. 1b) while the average soot particle diameter increases from 0.8 μm to about 2.0 μm with the same increase of residence time (Fig. 1c). This indicates that the soot particles become fewer and larger with increasing residence time.

3.1.2 Influence of equivalence ratio

To examine the effect of the equivalence ratio the residence time of 5 s and temperature of 1500 K was used for varying equivalence ratio from 0.5 s to 4.0. The soot volume fraction is practically equal to zero below the ϕ = 1.0 and increases linearly to value 3.3 x 10^{-6} for ϕ = 4.0, see Fig 2a). The soot surface area per cm^3 fire gas increases also linearly from about zero at ϕ = 1.0, and increases to about 0.7 m^2 in a volume of 1 cm^3 fire gas, see Fig 2b). The average soot particle diameter increases rapidly at ϕ = 1.0 to a maximum size about 4.0 μm at ϕ = 1.45. Between equivalence ratio 1.5 and 2.0 the particle size decreases rapidly to 1.2 μm and is constant at that size up to ϕ = 4.0, see Fig. 2c).

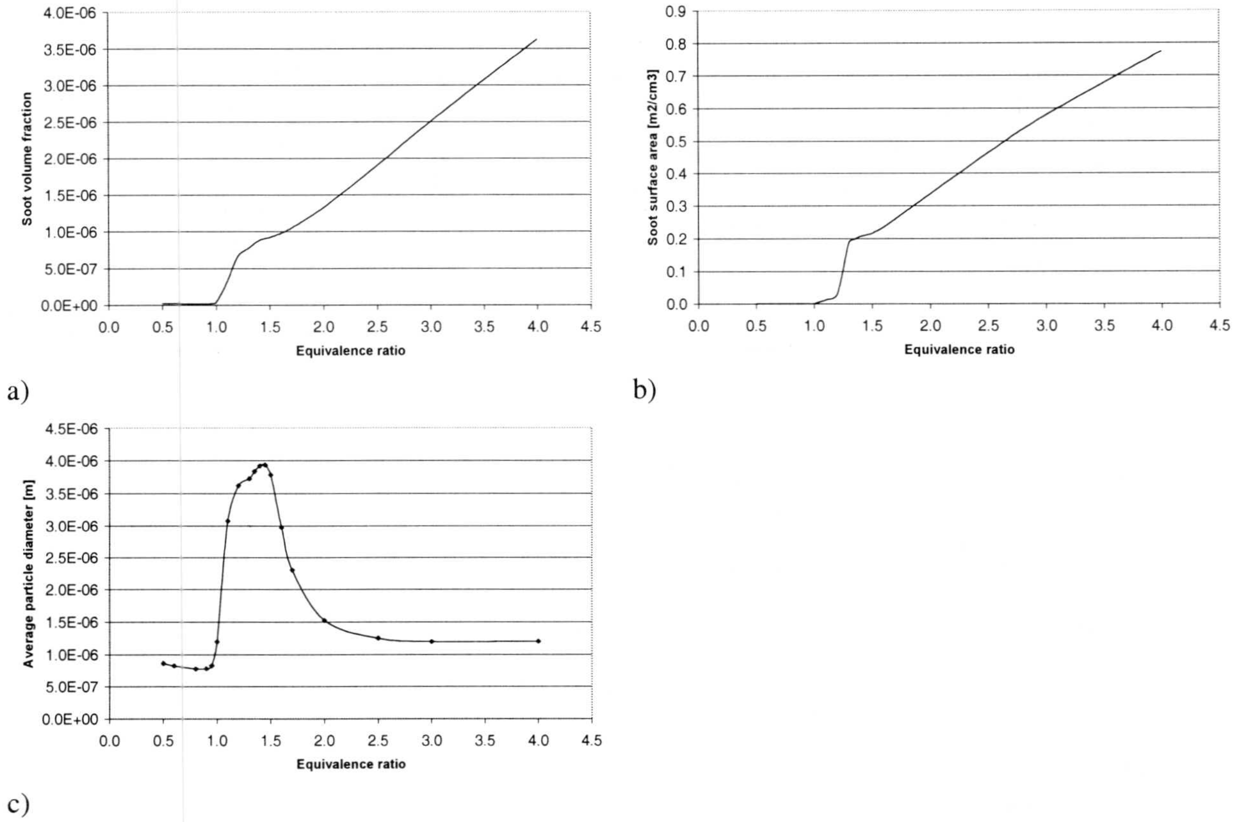


Figure 2.a) Soot volume fraction, b) soot surface area and c) average particle diameter, as a function of equivalence ratio. Residence time 5 s and temperature 1500 K.

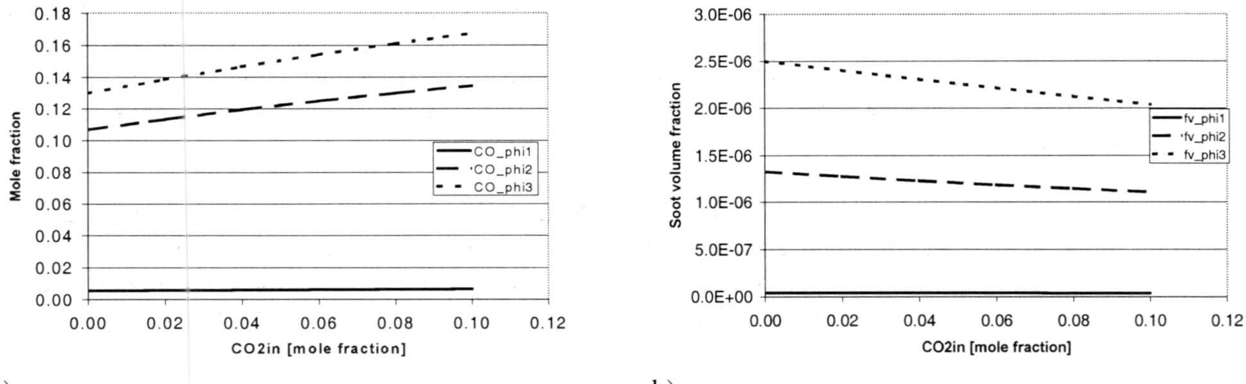
This indicates that below $\phi = 1.0$ essentially no soot is formed and that the amount of soot formed increases steadily as ϕ increases.

3.1.3 Influence of added CO_2

The influence of extra CO_2 was examined for a residence time of 5 s, for $\phi = 1.0$, 2.0 and 3.0 and temperatures 1200 K, 1300 K , 1400 K, and 1500 K. Adding extra CO_2 into the mixture makes the soot volume fraction decrease and the concentration of CO increase, which indicates that a reaction between soot and CO_2 occurs resulting CO. This effect is larger for higher temperatures and higher equivalence ratio. At $\phi = 1.0$ the mixture contain very little soot, and hence this effect is not seen, regardless of temperature. Also, at the temperature of 1200 K this effect is not seen even for higher equivalence ratios, because the soot does not react with CO_2 at so low temperatures.

For $\phi = 3.0$ and T = 1500 K the increase of CO is from 13.0 % to 16.8 % with increasing additional input of CO_2 from 0 to 10%. For $\phi = 2.0$ the CO concentration increases from 11.7 % to 13.5 % when CO_2 is increased from 0 to 10 %. At equivalence ratio $\phi = 1.0$ there both the soot and CO concentrations are so low that this effect is not noticeable, see Fig 3a.

Under the same conditions, the decrease in the soot volume fraction is about 20 % (from 2.5 x 10^{-6} to 2.0×10^{-6}) for $\phi = 3.0$ and about 16 % (from 1.33×10^{-6} to 1.1×10^{-6}) for $\phi = 2.0$, and negligible for $\phi = 1.0$, see Fig. 3b.

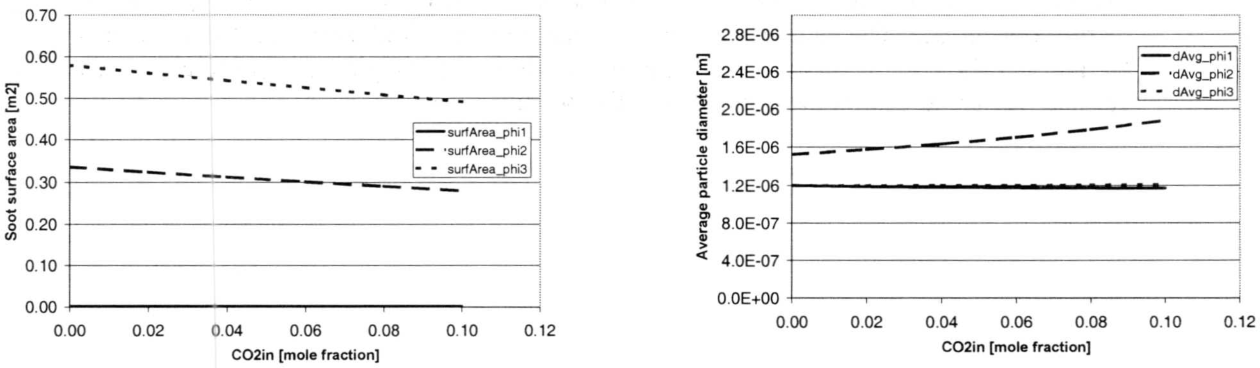


a) b)

Figure 3. *CO concentration a) and soot volume fraction b) as a function of added CO_2 input in the mixture. Temperature 1500 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*

At 1400 K the effect of CO increase and decrease of soot volume fraction is smaller as a function of CO_2 input in the mixture than for T=1500K. For 1300 K this effect is very small and at 1200K it is negligible. The result for 1400 K and 1300 K are shown in Appendix B.

The soot surface area decreases as a function of CO_2 input. The soot concentration is higher at higher equivalence ratios, thus the effect of the reduction is larger for high equivalence ratios as a function of CO_2 input, see Fig. 4 a. At $\phi = 3.0$ the soot surface area per volume fire gas is nearly 0.58 m^2/cm^3 when no extra CO_2 is added to the mixture. A 10 % addition of CO_2 in to the mixture reduces the soot surface area to about 0.50 m^2/cm^3. The average soot particle diameter is constant at about 1.2 μm at equivalence ratio 1.0 and 3.0 and does not vary with the addition of CO_2 into mixture. Hence the number of soot particles decrease as a function of the added CO_2. However, for equivalence ratio, $\phi = 2.0$ the soot particles are on average larger at about 1.6–1.9μm, the highest values when 10 % CO_2 is added in the mixture as shown in Fig 4b.



a) b)

Figure 4. a) *Soot surface area and b) average soot particle diameter as a function of added CO_2 input in the mixture. Temperature 1500 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*

Adding of CO_2 has a considerably smaller effect on the soot surface area than on the production of CO and the soot volume fraction. One can notice that there is a considerably lower amount of soot at 1400 K than 1500 K, but that the relative reduction of soot volume fraction and surface area are noticeable smaller with increase of CO_2 into the mixture, indicating that the rate of reaction between soot and CO_2 is larger at higher temperatures. The results for 1400 K and 1300 K are shown in Appendix B.

The acetylene concentration is shown in Fig. 5 and follows the soot volume fraction, i.e. it is higher for higher equivalence ratio (for $\phi < 1.0$ it is near zero) and decreases with increasing CO_2 input. For lower temperatures the decrease of acetylene concentration is smaller as a function of increase of CO_2 into the mixture. For temperatures 1400 K and 1300 K see Appendix B.

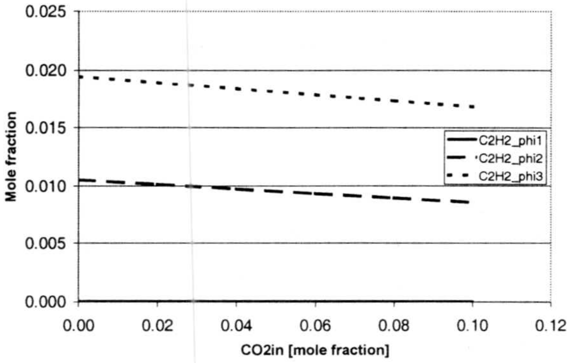
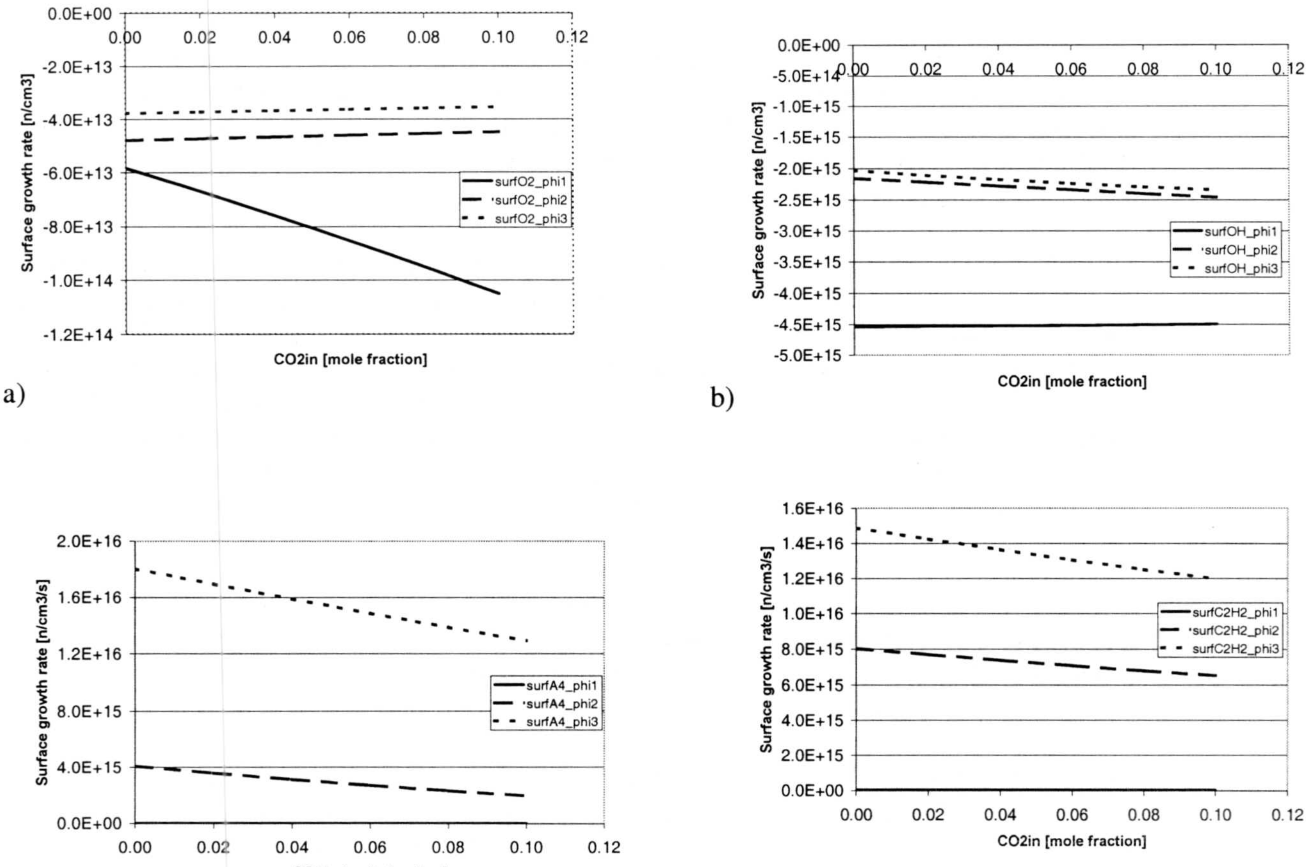


Figure 5. *Acetylene concentration as a function of added CO_2 input in the mixture. Temperature 1500 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*

The soot surface growth is assumed to occur in analogy to the hydrogen abstraction and carbon addition for benzene. Hydrogen abstraction is described via reactions S1-S3 and carbon addition by reaction S4. Four important species responsible in surface reactions are shown in Fig. 6: O_2, OH, A_4 and C_2H_2. The species A_4, pyrene, actually is not included in the six-step reaction scheme for surface growth, but is important in PAH condensation reactions leading to soot particles. This reaction also occurs on the soot particle surface, yielding the increase of surface growth.

Figures 6a) and 6b) show the number of O_2 and OH, respectively, per cm^3 fire gas and, reacting on the soot surface. The negative sign denotes that mass is withdrawn from the surfaces. Figures 6c) and 6d) show the number of surface species pyrene and acetylene, respectively per cm^3 fire gas and that are added on the soot surface (the positive sign).



a)

b)

c)

d)

Figure 6. *Surface species a)O_2, b) OH, c) A_4 (pyrene) and d) C_2H_2 as a function of added CO_2 input in the mixture. Temperature 1500 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*

Soot surface growth rates due to acetylene and pyrene are considerably lower at lower temperatures. The decrease of the rates due to CO_2 addition is smaller at the lower temperature. Similarly the rates of surface reactions involving O_2 and OH are lower with lower temperatures, but CO_2 addition has no effect in the reaction rates except for surface O_2 reactions at low equivalence ratio. Results are shown in Appendix B.

3.1.4 Onset of reaction between soot and CO_2

In order for soot and CO_2 to react with each other both components are needed in the mixture at a sufficiently high temperature and equivalence ratio. To form soot particles pyrene must be formed in the mixture. Pyrene consists of four aromatic rings and is assumed to be a precursor for soot. Below 1200 K the formation of a soot nucleus does not occur to any great degree even at as high equivalence ratio as ϕ = 3.0. The nucleation starts when the temperature is slightly above 1200 K and increases rapidly with temperatures higher than 1260 K.

Study of nucleation as a function of the equivalence ratio shows that nucleation rate starts at ϕ = 1.0 and increases rapidly with increased ϕ. The effect of extra CO_2 addition to the mixture is small. An extra 10 % CO_2 addition reduces slightly the nucleation rate. This can be understood as slowing the reaction rate forming the pyrene due to increased number of collision with CO_2.

4 Discussions and conclusions

Carbon monoxide formation from soot in the presence of CO_2 has been investigated. The calculations have been made to relevant for the reactions expected in the hot gas layer which develops in the room fires. Modelling includes the calculation of gas phase chemistry including the formation of aromatics, further growth of PAHs and soot formation, including nucleation, coagulation, surface growth and oxidation.

The calculations correspond to the chemistry in the gas layer indicating the residence time for the calculations should be long. In this study the representative residence time was chosen to be 5 s, which is used for most of the simulations when investigating the influence of other parameters on the chemistry and soot calculations. Both shorter, (from 0.25s) and longer (up to 10 s) residence times have been used in studying the influence of the residence time itself on the chemistry. However, in the gas layer, especially in the rooms with low ventilation, the residence times for gas 'particles' to pass the hot layer is much longer, from 30 s to several minutes. Investigating the chemistry within a part of the gas layer where the temperature and many other important parameters are somewhat unchanged, however shorter residence times are reasonable.

Soot particle nucleation is very rapid compared to the residence times considered in these calculations. Most nucleation occurs in the first milliseconds and will decay after longer time, although it will occur when the conditions for it are right. Therefore, nucleation is not presented in this study, although it is included in the calculations.

Soot surface growth, followed by nucleation; occurs all the time in the gas layer provided that there is 'material' to produce soot, i.e. carbon in the form mostly as acetylene, which can react with the soot surface. The soot volume fraction and particle size increases as the surface area decreases as a function of the increase of residence time. This indicates that the rate of nucleation decreases; i.e. fewer new particles per time unit are formed with longer residence time.

Results show that soot formation starts at an equivalence ratio of 1.0 and increases linearly with increasing equivalence ratio. The simulations were run up to equivalence ratios of 4.0. The soot surface area increases in the same fashion with the increased equivalence ratio, except at equivalence ratio 1.2 where there is very steep increase of surface area (this rapid increase can be seen also in the volume fraction, although the increase is not as steep). The rapid increase of surface area is due to a rapid increase in the particle size between equivalence ratios 1.1 and 1.3. The particle size has its maximum at an equivalence ratio of 1.45 (about 4 μm). Between equivalence ratio 2.0 and 4.0 the average particle size is constant about 1.2μm as a function of equivalence ratio.

At higher equivalence ratios the temperature in the flames should naturally go down due to slower chemistry, which would reduce the formation of the soot nuclei and possible lead to growth of the existing soot particles instead. In this study, however, the soot formation is calculated at the conditions that may occur in a fully developed room fire where the temperature is high and thus is held constant at high values up to 1500 K. Such high temperatures will "force" the chemistry to form more radicals leading to an increase in PAH and soot nuclei, with the equivalence ratio. This is a possible reason for the smaller soot particles at higher equivalence ratio. More intensive soot particle formation then increases the collision frequency between particles, which opposes the further increase of particle size.

The soot volume fraction increases and surface area decreases as a function of the residence time. The particle size increases with increasing residence time, which can be expected because the surface growth has more time to occur. At equivalence ratio 2.0 and temperature 1500 K the particle size is 0.8 μm after residence time 0.25 s. After 10 s residence time the soot particles are increased to about 2.0 μm. Within the same increase of residence time the soot volume fraction increases about 60 %.

Finally, an increase of CO_2 concentration in the hot products containing soot increases the formation of CO and decreases the soot volume fraction. The higher the temperature the greater this effect. In these calculations the temperatures ranging from 1200 K to 1500 K were used to investigate the effect of CO_2 addition up to 10 % in the combustion products. At 1500 K and an equivalence ratio of 3.0 the 10 % addition of CO_2 increases CO production from 13 % to nearly 17 %, i.e. 25% of the produced CO is due to reactions between soot and CO_2. Thus, in fully developed room fires with fuel producing large amount of soot the CO production may be very large. Then the high concentrations CO due to fire-induced flows could be transported to other locations far away from the source of the fire compounding the destructive potential of the fire gases.

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Appendix A – Gas phase reaction mechanism

A 542-step reaction scheme used in PSR simulations

```
                                            (k = A T**b exp(-E/RT))
      REACTIONS CONSIDERED                      A          b          E

  1.  H+O2=O+OH                             8.30E+13     0.0     14413.0
  2.  O+H2=H+OH                             5.00E+04     2.7      6290.0
  3.  OH+H2=H+H2O                           2.16E+08     1.5      3430.0
  4.  OH+OH=O+H2O                           3.57E+04     2.4     -2110.0
  5.  H+H+M=H2+M                            1.00E+18    -1.0         0.0
  6.  H+H+H2=H2+H2                          9.00E+16    -0.6         0.0
  7.  H+H+H2O=H2+H2O                        6.00E+19    -1.2         0.0
  8.  H+H+CO2=H2+CO2                        5.50E+20    -2.0         0.0
  9.  H+OH+M=H2O+M                          2.20E+22    -2.0         0.0
 10.  O+H+M=OH+M                            5.00E+17    -1.0         0.0
 11.  O+O+M=O2+M                            1.20E+17    -1.0         0.0
 12.  H+O2+M=HO2+M                          2.80E+18    -0.9         0.0
 13.  H+O2+O2=HO2+O2                        3.00E+20    -1.7         0.0
 14.  H+O2+H2O=HO2+H2O                      9.38E+18    -0.8         0.0
 15.  H+O2+N2=HO2+N2                        3.75E+20    -1.7         0.0
 16.  OH+OH(+M)=H2O2(+M)                    7.40E+13    -0.4         0.0
 17.  HO2+H=O+H2O                           3.97E+12     0.0       671.0
 18.  HO2+H=O2+H2                           2.80E+13     0.0      1068.0
 19.  HO2+H=OH+OH                           1.34E+14     0.0       635.0
 20.  HO2+O=OH+O2                           2.00E+13     0.0         0.0
 21.  HO2+OH=O2+H2O                         2.90E+13     0.0      -500.0
 22.  HO2+HO2=O2+H2O2                       1.30E+11     0.0     -1630.0
 23.  HO2+HO2=O2+H2O2                       4.20E+14     0.0     12000.0
 24.  H2O2+H=HO2+H2                         1.21E+07     2.0      5200.0
 25.  H2O2+H=OH+H2O                         1.00E+13     0.0      3600.0
 26.  H2O2+O=OH+HO2                         9.63E+06     2.0      4000.0
 27.  H2O2+OH=HO2+H2O                       1.75E+12     0.0       320.0
 28.  H2O2+OH=HO2+H2O                       5.80E+14     0.0      9560.0
 29.  CO+O+M=CO2+M                          6.02E+14     0.0      3000.0
 30.  CO+OH=CO2+H                           4.76E+07     1.2        70.0
 31.  CO+H2(+M)=CH2O(+M)                    4.30E+07     1.5     79600.0
 32.  CO+O2=CO2+O                           2.50E+12     0.0     47800.0
 33.  CO+HO2=CO2+OH                         1.50E+14     0.0     23600.0
 34.  C+OH=CO+H                             5.00E+13     0.0         0.0
 35.  C+O2=CO+O                             5.80E+13     0.0       576.0
 36.  CH+H=C+H2                             1.10E+14     0.0         0.0
 37.  CH+O=CO+H                             5.70E+13     0.0         0.0
 38.  CH+OH=HCO+H                           3.00E+13     0.0         0.0
 39.  CH+H2=CH2+H                           1.11E+08     1.8      1670.0
 40.  CH+H2O=CH2O+H                         5.71E+12     0.0      -755.0
 41.  CH+O2=HCO+O                           3.30E+13     0.0         0.0
 42.  CH+CO(+M)=HCCO(+M)                    5.00E+13     0.0         0.0
 43.  CH+CO2=HCO+CO                         3.40E+12     0.0       690.0
 44.  HCO+H(+M)=CH2O(+M)                    1.09E+12     0.5      -260.0
 45.  HCO+H=CO+H2                           7.34E+13     0.0         0.0
 46.  HCO+O=CO+OH                           3.00E+13     0.0         0.0
 47.  HCO+O=CO2+H                           3.00E+13     0.0         0.0
 48.  HCO+OH=CO+H2O                         5.00E+13     0.0         0.0
```

49.	HCO+M=CO+H+M	1.87E+17	-1.0	17000.0
50.	HCO+O2=CO+HO2	7.60E+12	0.0	400.0
51.	CH2+H(+M)=CH3(+M)	2.50E+16	-0.8	0.0
52.	CH2+O=HCO+H	8.00E+13	0.0	0.0
53.	CH2+OH=CH2O+H	2.00E+13	0.0	0.0
54.	CH2+OH=CH+H2O	1.13E+07	2.0	3000.0
55.	CH2+H2=H+CH3	5.00E+05	2.0	7230.0
56.	CH2+O2=CO2+H+H	1.32E+13	0.0	1500.0
57.	CH2+HO2=CH2O+OH	2.00E+13	0.0	0.0
58.	CH2+C=C2H+H	5.00E+13	0.0	0.0
59.	CH2+CO(+M)=CH2CO(+M)	8.10E+11	0.5	4510.0
60.	CH2+CH=C2H2+H	4.00E+13	0.0	0.0
61.	CH2+CH2=C2H2+H2	3.20E+13	0.0	0.0
62.	CH2*+N2=CH2+N2	1.50E+13	0.0	600.0
63.	CH2*+H=CH+H2	3.00E+13	0.0	0.0
64.	CH2*+O=CO+H2	1.50E+13	0.0	0.0
65.	CH2*+O=HCO+H	1.50E+13	0.0	0.0
66.	CH2*+OH=CH2O+H	3.00E+13	0.0	0.0
67.	CH2*+H2=CH3+H	7.00E+13	0.0	0.0
68.	CH2*+O2=H+OH+CO	2.80E+13	0.0	0.0
69.	CH2*+O2=CO+H2O	1.20E+13	0.0	0.0
70.	CH2*+H2O(+M)=CH3OH(+M)	2.00E+13	0.0	0.0
71.	CH2*+H2O=CH2+H2O	3.00E+13	0.0	0.0
72.	CH2*+CO=CH2+CO	9.00E+12	0.0	0.0
73.	CH2*+CO2=CH2+CO2	7.00E+12	0.0	0.0
74.	CH2*+CO2=CH2O+CO	1.40E+13	0.0	0.0
75.	CH2O+H(+M)=CH2OH(+M)	5.40E+11	0.5	3600.0
76.	CH2O+H(+M)=CH3O(+M)	5.40E+11	0.5	2600.0
77.	CH2O+H=HCO+H2	2.30E+10	1.1	3275.0
78.	CH2O+O=HCO+OH	3.90E+13	0.0	3540.0
79.	CH2O+OH=HCO+H2O	3.43E+09	1.2	-447.0
80.	CH2O+O2=HCO+HO2	1.00E+14	0.0	40000.0
81.	CH2O+HO2=HCO+H2O2	1.00E+12	0.0	8000.0
82.	CH2O+CH=CH2CO+H	9.46E+13	0.0	-515.0
83.	CH3+H(+M)=CH4(+M)	1.27E+16	-0.6	383.0
84.	CH3+O=CH2O+H	8.43E+13	0.0	0.0
85.	CH3+OH(+M)=CH3OH(+M)	6.30E+13	0.0	0.0
86.	CH3+OH=CH2+H2O	5.60E+07	1.6	5420.0
87.	CH3+OH=CH2*+H2O	2.50E+13	0.0	0.0
88.	CH3+O2=O+CH3O	2.67E+13	0.0	28800.0
89.	CH3+O2=OH+CH2O	3.60E+10	0.0	8940.0
90.	CH3+HO2=CH4+O2	1.00E+12	0.0	0.0
91.	CH3+HO2=CH3O+OH	2.00E+13	0.0	0.0
92.	CH3+H2O2=CH4+HO2	2.45E+04	2.5	5180.0
93.	CH3+C=C2H2+H	5.00E+13	0.0	0.0
94.	CH3+CH=C2H3+H	3.00E+13	0.0	0.0
95.	CH3+HCO=CH4+CO	2.65E+13	0.0	0.0
96.	CH3+CH2O=CH4+HCO	3.32E+03	2.8	5860.0
97.	CH3+CH2=C2H4+H	4.00E+13	0.0	0.0
98.	CH3+CH2*=C2H4+H	1.20E+13	0.0	-570.0
99.	CH3+CH3(+M)=C2H6(+M)	2.12E+16	-1.0	620.0
100.	CH3+CH3=H+C2H5	4.99E+12	0.1	10600.0
101.	CH3O+H(+M)=CH3OH(+M)	5.00E+13	0.0	0.0
102.	CH3O+H=CH2OH+H	3.40E+06	1.6	0.0
103.	CH3O+H=CH2O+H2	2.00E+13	0.0	0.0
104.	CH3O+H=CH3+OH	3.20E+13	0.0	0.0
105.	CH3O+H=CH2*+H2O	1.60E+13	0.0	0.0
106.	CH3O+O=CH2O+OH	1.00E+13	0.0	0.0
107.	CH3O+OH=CH2O+H2O	5.00E+12	0.0	0.0
108.	CH3O+O2=CH2O+HO2	4.28E-13	7.6	-3530.0
109.	CH2OH+H(+M)=CH3OH(+M)	1.80E+13	0.0	0.0

110.	CH2OH+H=CH2O+H2	2.00E+13	0.0	0.0
111.	CH2OH+H=CH3+OH	1.20E+13	0.0	0.0
112.	CH2OH+H=CH2*+H2O	6.00E+12	0.0	0.0
113.	CH2OH+O=CH2O+OH	1.00E+13	0.0	0.0
114.	CH2OH+OH=CH2O+H2O	5.00E+12	0.0	0.0
115.	CH2OH+O2=CH2O+HO2	1.80E+13	0.0	900.0
116.	CH4+H=CH3+H2	6.60E+08	1.6	10840.0
117.	CH4+O=CH3+OH	1.02E+09	1.5	8600.0
118.	CH4+OH=CH3+H2O	1.00E+08	1.6	3120.0
119.	CH4+CH=C2H4+H	6.00E+13	0.0	0.0
120.	CH4+CH2=CH3+CH3	2.46E+06	2.0	8270.0
121.	CH4+CH2*=CH3+CH3	1.60E+13	0.0	-570.0
122.	CH3OH+H=CH2OH+H2	1.70E+07	2.1	4870.0
123.	CH3OH+H=CH3O+H2	4.20E+06	2.1	4870.0
124.	CH3OH+O=CH2OH+OH	3.88E+05	2.5	3100.0
125.	CH3OH+O=CH3O+OH	1.30E+05	2.5	5000.0
126.	CH3OH+OH=CH2OH+H2O	1.44E+06	2.0	-840.0
127.	CH3OH+OH=CH3O+H2O	6.30E+06	2.0	1500.0
128.	CH3OH+CH3=CH2OH+CH4	3.00E+07	1.5	9940.0
129.	CH3OH+CH3=CH3O+CH4	1.00E+07	1.5	9940.0
130.	C2H+H(+M)=C2H2(+M)	1.00E+17	-1.0	0.0
131.	C2H+O=CH+CO	5.00E+13	0.0	0.0
132.	C2H+OH=H+HCCO	2.00E+13	0.0	0.0
133.	C2H+O2=HCO+CO	5.00E+13	0.0	1500.0
134.	C2H+H2=H+C2H2	4.90E+05	2.5	560.0
135.	HCCO+H=CH2*+CO	1.00E+14	0.0	0.0
136.	HCCO+O=H+CO+CO	1.00E+14	0.0	0.0
137.	HCCO+O2=OH+2CO	1.60E+12	0.0	854.0
138.	HCCO+CH=C2H2+CO	5.00E+13	0.0	0.0
139.	HCCO+CH2=C2H3+CO	3.00E+13	0.0	0.0
140.	HCCO+HCCO=C2H2+CO+CO	1.00E+13	0.0	0.0
141.	C2H2+H(+M)=C2H3(+M)	5.60E+12	0.0	2400.0
142.	C2H2+O=HCCO+H	1.02E+07	2.0	1900.0
143.	C2H2+O=C2H+OH	4.60E+19	-1.4	28950.0
144.	C2H2+O=CH2+CO	1.02E+07	2.0	1900.0
145.	C2H2+OH=CH2CO+H	2.18E-04	4.5	-1000.0
146.	C2H2+OH=HCCOH+H	5.04E+05	2.3	13500.0
147.	C2H2+OH=C2H+H2O	3.37E+07	2.0	14000.0
148.	C2H2+OH=CH3+CO	4.83E-04	4.0	-2000.0
149.	CH2CO+H=HCCO+H2	5.00E+13	0.0	8000.0
150.	CH2CO+H=CH3+CO	1.13E+13	0.0	3428.0
151.	CH2CO+O=HCCO+OH	1.00E+13	0.0	8000.0
152.	CH2CO+O=CH2+CO2	1.75E+12	0.0	1350.0
153.	CH2CO+OH=HCCO+H2O	7.50E+12	0.0	2000.0
154.	HCCOH+H=CH2CO+H	1.00E+13	0.0	0.0
155.	C2H3+H(+M)=C2H4(+M)	6.08E+12	0.3	280.0
156.	C2H3+H=C2H2+H2	4.00E+13	0.0	0.0
157.	C2H3+O=CH2CO+H	3.00E+13	0.0	0.0
158.	C2H3+OH=C2H2+H2O	2.00E+13	0.0	0.0
159.	C2H3+O2=C2H2+HO2	1.12E+08	0.9	200.0
160.	C2H3+O2=C2H3O+O	3.64E+11	0.3	101.0
161.	C2H3+O2=HCO+CH2O	4.58E+16	-1.4	1015.0
162.	C2H4(+M)=H2+C2H2(+M)	8.00E+12	0.4	88770.0
163.	C2H4+H(+M)=C2H5(+M)	1.08E+12	0.5	1820.0
164.	C2H4+H=C2H3+H2	1.33E+06	2.5	12240.0
165.	C2H4+O=CH3+HCO	1.92E+07	1.8	220.0
166.	C2H4+OH=C2H3+H2O	3.60E+06	2.0	2500.0
167.	C2H4+CH3=C2H3+CH4	2.27E+05	2.0	9200.0
168.	C2H5+H(+M)=C2H6(+M)	5.21E+17	-1.0	1580.0
169.	C2H5+H=C2H4+H2	2.00E+12	0.0	0.0
170.	C2H5+O=CH3+CH2O	1.32E+14	0.0	0.0

171.	C2H5+O2=C2H4+HO2	8.40E+11	0.0	3875.0
172.	C2H6+H=C2H5+H2	1.15E+08	1.9	7530.0
173.	C2H6+O=C2H5+OH	8.98E+07	1.9	5690.0
174.	C2H6+OH=C2H5+H2O	3.54E+06	2.1	870.0
175.	C2H6+CH2*=C2H5+CH3	4.00E+13	0.0	-550.0
176.	C2H6+CH3=C2H5+CH4	6.14E+06	1.7	10450.0
177.	HCCO+OH=C2O+H2O	3.00E+13	0.0	0.0
178.	C2O+H=CH+CO	5.00E+13	0.0	0.0
179.	C2O+O=CO+CO	5.00E+13	0.0	0.0
180.	C2O+OH=CO+CO+H	2.00E+13	0.0	0.0
181.	C2O+O2=CO+CO+O	2.00E+13	0.0	0.0
182.	CH2CO+H=C2H3O	5.40E+11	0.5	1820.0
183.	C2H3O+H=CH2CO+H2	1.00E+13	0.0	0.0
184.	C2H3O+O=CH2O+HCO	9.60E+06	1.8	220.0
185.	C2H3O+O=CH2CO+OH	1.00E+13	0.0	0.0
186.	C2H3O+OH=CH2CO+H2O	5.00E+12	0.0	0.0
187.	CH3+HCCO=C2H4+CO	5.00E+13	0.0	0.0
188.	CH3+C2H=C3H3+H	2.41E+13	0.0	0.0
189.	CH4+C2H=C2H2+CH3	1.81E+12	0.0	500.0
190.	C2H2+CH=C3H2+H	3.00E+13	0.0	0.0
191.	C2H2+CH2=C3H3+H	2.40E+13	0.0	6620.0
192.	C2H2+CH2*=C3H3+H	4.00E+13	0.0	0.0
193.	C2H2+CH3=AC3H4+H	5.72E+20	-2.4	31500.0
194.	C2H2+CH3=PC3H4+H	2.72E+18	-2.0	20200.0
195.	C2H2+C2H=C4H2+H	9.60E+13	0.0	0.0
196.	C2H2+C2H=n-C4H3	4.50E+37	-7.7	7100.0
197.	C2H2+C2H=i-C4H3	2.60E+44	-9.5	14650.0
198.	C2H2+C2H3=C4H4+H	2.00E+18	-1.7	10600.0
199.	C2H2+C2H3=n-C4H5	9.30E+38	-8.8	12000.0
200.	C2H2+C2H3=i-C4H5	1.60E+46	-11.0	18600.0
201.	C2H4+C2H=C4H4+H	1.20E+13	0.0	0.0
202.	C2H4+C2H3=C4H6+H	2.80E+21	-2.4	14720.0
203.	C2H2+HCCO=C3H3+CO	1.00E+11	0.0	3000.0
204.	C2H4+O2=C2H3+HO2	4.22E+13	0.0	60800.0
205.	C2H3+H2O2=C2H4+HO2	1.21E+10	0.0	-596.0
206.	C2H3+HCO=C2H4+CO	2.50E+13	0.0	0.0
207.	C2H3+CH3=C2H2+CH4	3.92E+11	0.0	0.0
208.	C2H3+C2H3=C4H6	1.50E+42	-8.8	12483.0
209.	C2H3+C2H3=i-C4H5+H	1.20E+22	-2.4	13654.0
210.	C2H3+C2H3=n-C4H5+H	2.40E+20	-2.0	15361.0
211.	C3H2+O=C2H2+CO	6.80E+13	0.0	0.0
212.	C3H2+OH=HCO+C2H2	6.80E+13	0.0	0.0
213.	C3H2+O2=HCCO+CO+H	5.00E+13	0.0	0.0
214.	C3H2+CH=C4H2+H	5.00E+13	0.0	0.0
215.	C3H2+CH2=n-C4H3+H	5.00E+13	0.0	0.0
216.	C3H2+CH3=C4H4+H	5.00E+12	0.0	0.0
217.	C3H2+HCCO=n-C4H3+CO	1.00E+13	0.0	0.0
218.	C3H3+H(+M)=AC3H4(+M)	3.00E+13	0.0	0.0
219.	C3H3+H(+M)=PC3H4(+M)	3.00E+13	0.0	0.0
220.	C3H3+O=CH2O+C2H	2.00E+13	0.0	0.0
221.	C3H3+OH=C3H2+H2O	2.00E+13	0.0	0.0
222.	C3H3+OH=C2H3+HCO	4.00E+13	0.0	0.0
223.	C3H3+O2=CH2CO+HCO	3.00E+10	0.0	2878.0
224.	C3H3+HO2=AC3H4+O2	1.00E+12	0.0	0.0
225.	C3H3+HO2=PC3H4+O2	1.00E+12	0.0	0.0
226.	C3H3+HCO=AC3H4+CO	2.50E+13	0.0	0.0
227.	C3H3+HCO=PC3H4+CO	2.50E+13	0.0	0.0
228.	C3H3+CH=i-C4H3+H	5.00E+13	0.0	0.0
229.	C3H3+CH2=C4H4+H	2.00E+13	0.0	0.0
230.	i-C4H5+H=C3H3+CH3	2.00E+13	0.0	2000.0
231.	C3H3+CH3(+M)=C4H612(+M)	1.50E+13	0.0	0.0

232.	C3H3+C3H3=>A1	5.00E+12	0.0	0.0
233.	AC3H4+H=C3H3+H2	5.75E+07	1.9	7530.0
234.	AC3H4+O=CH2CO+CH2	2.00E+07	1.8	1000.0
235.	AC3H4+OH=C3H3+H2O	5.30E+06	2.0	2000.0
236.	AC3H4+C2H=C2H2+C3H3	1.00E+13	0.0	0.0
237.	PC3H4+H=C3H3+H2	1.15E+08	1.9	7530.0
238.	PC3H4+OH=C3H3+H2O	3.54E+06	2.1	870.0
239.	PC3H4+C2H=C2H2+C3H3	1.00E+13	0.0	0.0
240.	C4H+H(+M)=C4H2(+M)	1.00E+17	-1.0	0.0
241.	C4H+C2H2=C6H2+H	9.60E+13	0.0	0.0
242.	C4H+O=C2H+C2O	5.00E+13	0.0	0.0
243.	C4H+O2=HCCO+C2O	5.00E+13	0.0	1500.0
244.	C4H+H2=H+C4H2	4.90E+05	2.5	560.0
245.	C4H2+H=n-C4H3	1.10E+42	-8.7	15300.0
246.	C4H2+H=i-C4H3	1.10E+30	-4.9	10800.0
247.	C4H2+O=C3H2+CO	2.70E+13	0.0	1720.0
248.	C4H2+OH=H2C4O+H	6.60E+12	0.0	-410.0
249.	C4H2+OH=C4H+H2O	3.37E+07	2.0	14000.0
250.	C4H2+CH=C5H2+H	5.00E+13	0.0	0.0
251.	C4H2+CH2=C5H3+H	1.30E+13	0.0	6620.0
252.	C4H2+CH2*=C5H3+H	2.00E+13	0.0	0.0
253.	C4H2+C2H=C6H2+H	9.60E+13	0.0	0.0
254.	C4H2+C2H=C6H3	4.50E+37	-7.7	7100.0
255.	H2C4O+H=C2H2+HCCO	5.00E+13	0.0	3000.0
256.	H2C4O+OH=CH2CO+HCCO	1.00E+07	2.0	2000.0
257.	H2C4O+O=CH2CO+C2O	2.00E+07	1.9	200.0
258.	n-C4H3=i-C4H3	4.10E+43	-9.5	53000.0
259.	n-C4H3+H=i-C4H3+H	2.50E+20	-1.7	10800.0
260.	n-C4H3+H=C2H2+C2H2	6.30E+25	-3.3	10014.0
261.	i-C4H3+H=C2H2+C2H2	2.80E+23	-2.5	10780.0
262.	n-C4H3+H=C4H4	2.00E+47	-10.3	13070.0
263.	i-C4H3+H=C4H4	3.40E+43	-9.0	12120.0
264.	n-C4H3+H=C4H2+H2	1.50E+13	0.0	0.0
265.	i-C4H3+H=C4H2+H2	3.00E+13	0.0	0.0
266.	n-C4H3+OH=C4H2+H2O	2.50E+12	0.0	0.0
267.	i-C4H3+OH=C4H2+H2O	5.00E+12	0.0	0.0
268.	i-C4H3+O2=HCCO+CH2CO	7.86E+16	-1.8	0.0
269.	n-C4H3+C2H2=l-C6H4+H	2.50E+14	-0.6	10600.0
270.	n-C4H3+C2H2=n-C6H5	2.70E+36	-7.6	16200.0
271.	n-C4H3+C2H2=A1-	9.60E+70	-17.8	31300.0
272.	n-C4H3+C2H2=c-C6H4+H	6.90E+46	-10.0	30100.0
273.	C4H4+H=n-C4H5	1.30E+51	-11.9	16500.0
274.	C4H4+H=i-C4H5	4.90E+51	-11.9	17700.0
275.	C4H4+H=n-C4H3+H2	6.65E+05	2.5	12240.0
276.	C4H4+H=i-C4H3+H2	3.33E+05	2.5	9240.0
277.	C4H4+OH=n-C4H3+H2O	3.10E+06	2.0	3430.0
278.	C4H4+OH=i-C4H3+H2O	1.55E+06	2.0	430.0
279.	C4H4+O=PC3H4+CO	3.00E+13	0.0	1808.0
280.	C4H4+C2H3=l-C6H6+H	2.80E+21	-2.4	14720.0
281.	n-C4H5=i-C4H5	1.50E+67	-16.9	59100.0
282.	n-C4H5+H=i-C4H5+H	3.10E+26	-3.4	17423.0
283.	C4H6=i-C4H5+H	5.70E+36	-6.3	112353.0
284.	C4H6=n-C4H5+H	5.30E+44	-8.6	123608.0
285.	n-C4H5+H=C4H4+H2	1.50E+13	0.0	0.0
286.	i-C4H5+H=C4H4+H2	3.00E+13	0.0	0.0
287.	n-C4H5+OH=C4H4+H2O	2.50E+12	0.0	0.0
288.	i-C4H5+OH=C4H4+H2O	5.00E+12	0.0	0.0
289.	n-C4H5+O2=>C2H4+CO+HCO	4.16E+10	0.0	2500.0
290.	i-C4H5+O2=CH2CO+C2H3O	7.86E+16	-1.8	0.0
291.	n-C4H5+C2H2=n-C6H7	1.10E+14	-1.3	2900.0
292.	n-C4H5+C2H2=c-C6H7	5.00E+24	-5.5	4600.0

293.	n-C4H5+C2H2=l-C6H6+H	5.80E+08	1.0	10900.0
294.	n-C4H5+C2H2=A1+H	1.60E+16	-1.3	5400.0
295.	C4H6+H=n-C4H5+H2	1.33E+06	2.5	12240.0
296.	C4H6+H=i-C4H5+H2	6.65E+05	2.5	9240.0
297.	C4H6+OH=n-C4H5+H2O	6.20E+06	2.0	3430.0
298.	C4H6+OH=i-C4H5+H2O	3.10E+06	2.0	430.0
299.	C4H6+C2H3=C6H8+H	2.80E+21	-2.4	14720.0
300.	C4H612+H=C4H6+H	2.00E+13	0.0	4000.0
301.	C4H612+H=i-C4H5+H2	1.70E+05	2.5	2490.0
302.	C4H612+H=AC3H4+CH3	8.00E+13	0.0	1000.0
303.	C4H612+O=CH2CO+C2H4	1.20E+08	1.6	327.0
304.	C4H612+O=i-C4H5+OH	1.80E+11	0.7	5880.0
305.	C4H612+OH=i-C4H5+H2O	3.10E+06	2.0	-298.0
306.	C5H2+OH=>C4H2+H+CO	2.00E+13	0.0	0.0
307.	C5H2+CH=C6H2+H	5.00E+13	0.0	0.0
308.	C5H2+O2=H2C4O+CO	1.00E+12	0.0	0.0
309.	C5H3+OH=C5H2+H2O	1.00E+13	0.0	0.0
310.	C5H3+CH=C6H2+H+H	5.00E+13	0.0	0.0
311.	C5H3+CH2=l-C6H4+H	5.00E+13	0.0	0.0
312.	C5H3+O2=H2C4O+HCO	1.00E+12	0.0	0.0
313.	C6H+H(+M)=C6H2(+M)	1.00E+17	-1.0	0.0
314.	C6H2+H=C6H3	1.10E+30	-4.9	10800.0
315.	C6H+O=C4H+C2O	5.00E+13	0.0	0.0
316.	C6H+H2=H+C6H2	4.90E+05	2.5	560.0
317.	C6H2+O=C5H2+CO	2.70E+13	0.0	1720.0
318.	C6H2+OH=>C2H+C2H2+C2O	6.60E+12	0.0	-410.0
319.	C6H2+OH=C6H+H2O	3.37E+07	2.0	14000.0
320.	C6H3+H=C4H2+C2H2	2.80E+23	-2.5	10780.0
321.	C6H3+H=l-C6H4	3.40E+43	-9.0	12120.0
322.	C6H3+H=C6H2+H2	3.00E+13	0.0	0.0
323.	C6H3+OH=C6H2+H2O	5.00E+12	0.0	0.0
324.	C6H3+O2=>CO+C3H2+HCCO	5.00E+11	0.0	0.0
325.	l-C6H4+H=n-C6H5	5.90E+39	-8.2	15600.0
326.	l-C6H4+H=A1-	1.70E+78	-19.7	31400.0
327.	l-C6H4+H=c-C6H4+H	1.40E+54	-11.7	34500.0
328.	l-C6H4+H=C6H3+H2	6.65E+06	2.5	9240.0
329.	l-C6H4+OH=C6H3+H2O	3.10E+06	2.0	430.0
330.	c-C6H4+H=A1-	2.40E+60	-13.7	29500.0
331.	n-C6H5=A1-	5.10E+54	-13.1	35700.0
332.	n-C6H5=c-C6H4+H	1.30E+59	-13.6	62000.0
333.	n-C6H5+H=i-C6H5+H	2.50E+20	-1.7	10800.0
334.	n-C6H5+H=C4H4+C2H2	6.30E+25	-3.3	10014.0
335.	i-C6H5+H=C4H4+C2H2	2.80E+23	-2.5	10780.0
336.	n-C6H5+H=l-C6H6	2.00E+47	-10.3	13070.0
337.	i-C6H5+H=l-C6H6	3.40E+43	-9.0	12120.0
338.	n-C6H5+H=l-C6H4+H2	1.50E+13	0.0	0.0
339.	i-C6H5+H=l-C6H4+H2	3.00E+13	0.0	0.0
340.	n-C6H5+OH=l-C6H4+H2O	2.50E+12	0.0	0.0
341.	i-C6H5+OH=l-C6H4+H2O	5.00E+12	0.0	0.0
342.	n-C6H5+O2=>C4H4+CO+HCO	4.16E+10	0.0	2500.0
343.	i-C6H5+O2=>CH2CO+CH2CO+C2H	7.86E+16	-1.8	0.0
344.	l-C6H6+H=n-C6H7	1.50E+16	-1.7	1600.0
345.	l-C6H6+H=c-C6H7	4.70E+27	-6.1	3800.0
346.	l-C6H6+H=A1+H	2.00E+18	-1.7	4500.0
347.	l-C6H6+H=n-C6H5+H2	6.65E+05	2.5	12240.0
348.	l-C6H6+H=i-C6H5+H2	3.33E+05	2.5	9240.0
349.	l-C6H6+OH=n-C6H5+H2O	6.20E+06	2.0	3430.0
350.	l-C6H6+OH=i-C6H5+H2O	3.10E+06	2.0	430.0
351.	n-C6H7=c-C6H7	1.20E+31	-8.0	8900.0
352.	n-C6H7=A1+H	3.20E+26	-5.0	15500.0
353.	n-C6H7+H=i-C6H7+H	2.40E+49	-10.7	15100.0

354.	i-C6H7+H=C6H8	1.80E+39	-7.6	11000.0
355.	n-C6H7+H=C6H8	5.60E+48	-10.5	14700.0
356.	n-C6H7+H=l-C6H6+H2	1.50E+13	0.0	0.0
357.	i-C6H7+H=l-C6H6+H2	3.00E+13	0.0	0.0
358.	n-C6H7+OH=l-C6H6+H2O	2.50E+12	0.0	0.0
359.	i-C6H7+OH=l-C6H6+H2O	5.00E+12	0.0	0.0
360.	n-C6H7+O2=>C4H6+CO+HCO	4.16E+10	0.0	2500.0
361.	i-C6H7+O2=>CH2CO+CH2CO+C2H3	7.86E+16	-1.8	0.0
362.	C6H8+H=n-C6H7+H2	1.33E+06	2.5	12240.0
363.	C6H8+H=i-C6H7+H2	6.65E+05	2.5	9240.0
364.	C6H8+OH=n-C6H7+H2O	6.20E+06	2.0	3430.0
365.	C6H8+OH=i-C6H7+H2O	3.10E+06	2.0	430.0
366.	A1+H=c-C6H7	1.40E+51	-11.9	16100.0
367.	A1+H=A1-+H2	2.50E+14	0.0	16000.0
368.	A1+OH=A1-+H2O	1.60E+08	1.4	1450.0
369.	A1-+H(+M)=A1(+M)	1.00E+14	0.0	0.0
370.	n-C4H3+C4H2=A1C2H-	9.60E+70	-17.8	31300.0
371.	A1+C2H=A1C2H+H	5.00E+13	0.0	0.0
372.	A1-+C2H2=n-A1C2H2	7.00E+38	-8.0	16400.0
373.	A1-+C2H2=A1C2H+H	3.30E+33	-5.7	25500.0
374.	A1C2H+H=n-A1C2H2	3.00E+43	-9.2	15272.0
375.	A1C2H+H=i-A1C2H2	3.00E+43	-9.2	15272.0
376.	A1C2H+H=A1C2H*+H2	2.50E+14	0.0	16000.0
377.	A1C2H+H=A1C2H-+H2	2.50E+14	0.0	16000.0
378.	A1C2H+OH=A1C2H*+H2O	1.60E+08	1.4	1450.0
379.	A1C2H+OH=A1C2H-+H2O	1.60E+08	1.4	1450.0
380.	A1C2H-+H(+M)=A1C2H(+M)	1.00E+14	0.0	0.0
381.	A1C2H*+H(+M)=A1C2H(+M)	1.00E+14	0.0	0.0
382.	A1+C2H3=A1C2H3+H	7.90E+11	0.0	6400.0
383.	A1-+C2H4=A1C2H3+H	2.51E+12	0.0	6190.0
384.	A1-+C2H3=A1C2H3	1.20E+27	-4.2	7235.0
385.	A1-+C2H3=i-A1C2H2+H	8.50E-02	4.7	18424.0
386.	A1-+C2H3=n-A1C2H2+H	9.40E+00	4.1	23234.0
387.	A1C2H3=i-A1C2H2+H	5.30E+27	-3.6	109332.0
388.	A1C2H3=n-A1C2H2+H	1.10E+32	-4.8	119483.0
389.	A1C2H3+H=A1C2H3*+H2	2.50E+14	0.0	16000.0
390.	A1C2H3+OH=A1C2H3*+H2O	1.60E+08	1.4	1450.0
391.	A1C2H3*+H(+M)=A1C2H3(+M)	1.00E+14	0.0	0.0
392.	A1C2H3+H=n-A1C2H2+H2	6.65E+06	2.5	12240.0
393.	A1C2H3+H=i-A1C2H2+H2	3.33E+05	2.5	9240.0
394.	A1C2H3+OH=n-A1C2H2+H2O	3.10E+06	2.0	3430.0
395.	A1C2H3+OH=i-A1C2H2+H2O	1.55E+06	2.0	430.0
396.	n-A1C2H2+H=A1C2H+H2	1.50E+13	0.0	0.0
397.	i-A1C2H2+H=A1C2H+H2	3.00E+13	0.0	0.0
398.	n-A1C2H2+H=i-A1C2H2+H	9.90E+04	3.4	22040.0
399.	n-A1C2H2+OH=A1C2H+H2O	2.50E+12	0.0	0.0
400.	i-A1C2H2+OH=A1C2H+H2O	5.00E+12	0.0	0.0
401.	A1C2H*+C2H2=A2-1	2.20E+62	-14.6	33100.0
402.	A1C2H*+C2H2=A1C2H)2+H	1.80E+19	-1.7	18800.0
403.	A1C2H*+C2H2=naphthyne+H	5.70E+64	-14.4	57000.0
404.	A1C2H)2+H=A2-1	1.40E+64	-14.6	29900.0
405.	A1C2H)2+H=naphthyne+H	1.90E+73	-16.3	60900.0
406.	naphthyne+H=A2-1	4.90E+52	-12.4	33000.0
407.	A1C2H+C2H=A1C2H)2+H	5.00E+13	0.0	0.0
408.	A1C2H3*+C2H2=A2+H	1.60E+16	-1.3	6600.0
409.	n-A1C2H2+C2H2=A2+H	1.60E+16	-1.3	5400.0
410.	A2+H=A2-1+H2	2.50E+14	0.0	16000.0
411.	A2+H=A2-2+H2	2.50E+14	0.0	16000.0
412.	A2+OH=A2-1+H2O	1.60E+08	1.4	1450.0
413.	A2+OH=A2-2+H2O	1.60E+08	1.4	1450.0
414.	A2-1+H(+M)=A2(+M)	1.00E+14	0.0	0.0

415.	A2-2+H(+M)=A2(+M)	1.00E+14	0.0	0.0
416.	A2-1+H=A2-2+H	2.40E+24	-1.8	45281.0
417.	A2+C2H=A2C2HA+H	5.00E+13	0.0	0.0
418.	A2+C2H=A2C2HB+H	5.00E+13	0.0	0.0
419.	A2-1+C2H2=A2C2H2	1.70E+43	-9.1	21100.0
420.	A2-1+C2H2=A2C2HA+H	1.30E+24	-3.1	22600.0
421.	A2C2HA+H=A2C2H2	5.90E+46	-10.0	19100.0
422.	A2C2H2+H=A2C2HA+H2	1.50E+13	0.0	0.0
423.	A2C2H2+OH=A2C2HA+H2O	2.50E+12	0.0	0.0
424.	A2C2HA+H=A2C2HA*+H2	2.50E+14	0.0	16000.0
425.	A2C2HB+H=A2C2HB*+H2	2.50E+14	0.0	16000.0
426.	A2C2HA+OH=A2C2HA*+H2O	1.60E+08	1.4	1450.0
427.	A2C2HB+OH=A2C2HB*+H2O	1.60E+08	1.4	1450.0
428.	A2C2HB*+H(+M)=A2C2HB(+M)	1.00E+14	0.0	0.0
429.	A2C2HA*+H(+M)=A2C2HA(+M)	1.00E+14	0.0	0.0
430.	A2C2HB*+C2H2=A3-1	1.10E+62	-14.6	33100.0
431.	A2C2HB*+C2H2=A2C2H)2+H	1.80E+19	-1.7	18800.0
432.	A2C2H)2+H=A3-1	6.90E+63	-14.6	29900.0
433.	A2C2HA*+C2H2=A3-4	1.10E+62	-14.6	33100.0
434.	A2C2HA*+C2H2=A2C2H)2+H	1.80E+19	-1.7	18800.0
435.	A2C2H)2+H=A3-4	6.90E+63	-14.6	29900.0
436.	A2C2HA+C2H=A2C2H)2+H	5.00E+13	0.0	0.0
437.	A2C2HB+C2H=A2C2H)2+H	5.00E+13	0.0	0.0
438.	A3+H=A3-1+H2	2.50E+14	0.0	16000.0
439.	A3+H=A3-4+H2	2.50E+14	0.0	16000.0
440.	A3+OH=A3-1+H2O	1.60E+08	1.4	1450.0
441.	A3+OH=A3-4+H2O	1.60E+08	1.4	1450.0
442.	A3-1+H(+M)=A3(+M)	1.00E+14	0.0	0.0
443.	A3-4+H(+M)=A3(+M)	1.00E+14	0.0	0.0
444.	A3-1+H=A3-4+H	3.80E+40	-6.3	61782.0
445.	A1-+C4H4=A2+H	3.30E+33	-5.7	25500.0
446.	A2-1+C4H4=A3+H	3.30E+33	-5.7	25500.0
447.	A2-2+C4H4=A3+H	3.30E+33	-5.7	25500.0
448.	A2R5+H=A2R5-+H2	2.50E+14	0.0	16000.0
449.	A2R5+OH=A2R5-+H2O	1.60E+08	1.4	1450.0
450.	A2R5-+H(+M)=A2R5(+M)	1.00E+14	0.0	0.0
451.	A2-1+C2H2=A2R5+H	9.70E+30	-5.3	21600.0
452.	A2C2HA+H=A2R5+H	4.60E+37	-7.0	23100.0
453.	A2C2H2=A2R5+H	1.56E+46	-10.3	41300.0
454.	A1C2H*+A1=A3+H	1.10E+23	-2.9	15890.0
455.	A1-+A1C2H=A3+H	1.10E+23	-2.9	15890.0
456.	A3+C2H=A3C2H+H	5.00E+13	0.0	0.0
457.	A3-4+C2H2=A3C2H2	8.00E+61	-14.5	34800.0
458.	A3-4+C2H2=A3C2H+H	1.20E+26	-3.4	30200.0
459.	A3-4+C2H2=A4+H	6.60E+24	-3.4	17800.0
460.	A3C2H+H=A3C2H2	1.90E+64	-15.1	29300.0
461.	A3C2H+H=A4+H	9.00E+38	-7.4	20700.0
462.	A3C2H2=A4+H	2.00E+63	-15.3	43200.0
463.	A4+H=A4-+H2	2.50E+14	0.0	16000.0
464.	A4+OH=A4-+H2O	1.60E+08	1.4	1450.0
465.	A4-+H=A4	1.00E+14	0.0	0.0
466.	A1+A1-=P2+H	1.10E+23	-2.9	15890.0
467.	A1+A1-=P2-H	3.70E+32	-6.7	9870.0
468.	P2-H=P2+H	3.80E+37	-8.0	27880.0
469.	A1-+A1-=P2	2.00E+19	-2.0	2900.0
470.	A1-+A1-=P2-+H	2.30E-01	4.6	28950.0
471.	P2=P2-+H	1.10E+25	-2.7	114270.0
472.	P2+H=P2-+H2	2.50E+14	0.0	16000.0
473.	P2+OH=P2-+H2O	1.60E+08	1.4	1450.0
474.	P2-+C2H2=A3+H	4.60E+06	2.0	7300.0
475.	A1+O=C6H5O+H	2.20E+13	0.0	4530.0

476.	A1+OH=C6H5OH+H	1.30E+13	0.0	10600.0
477.	A1-+O2=C6H5O+O	2.10E+12	0.0	7470.0
478.	C6H5O=CO+C5H5	2.50E+11	0.0	43900.0
479.	C6H5O+H=CO+C5H6	3.00E+13	0.0	0.0
480.	C6H5O+O=HCO+2C2H2+CO	3.00E+13	0.0	0.0
481.	C6H5O+H(+M)=C6H5OH(+M)	2.50E+14	0.0	0.0
482.	C6H5OH+H=C6H5O+H2	1.15E+14	0.0	12400.0
483.	C6H5OH+O=C6H5O+OH	2.80E+13	0.0	7352.0
484.	C6H5OH+OH=C6H5O+H2O	6.00E+12	0.0	0.0
485.	C5H5+H(+M)=C5H6(+M)	1.00E+14	0.0	0.0
486.	C5H5+O=n-C4H5+CO	1.00E+14	0.0	0.0
487.	C5H5+OH=C5H4OH+H	5.00E+12	0.0	0.0
488.	C5H5+HO2=C5H5O+OH	3.00E+13	0.0	0.0
489.	C5H6+H=C5H5+H2	2.20E+08	1.8	3000.0
490.	C5H6+O=C5H5+OH	1.80E+13	0.0	3080.0
491.	C5H6+OH=C5H5+H2O	3.43E+09	1.2	-447.0
492.	C5H5O=n-C4H5+CO	2.50E+11	0.0	43900.0
493.	C5H5O+H=CH2O+2C2H2	3.00E+13	0.0	0.0
494.	C5H5O+O=CO2+n-C4H5	3.00E+13	0.0	0.0
495.	C5H4OH=C5H4O+H	2.10E+13	0.0	48000.0
496.	C5H4OH+H=CH2O+2C2H2	3.00E+13	0.0	0.0
497.	C5H4OH+O=CO2+n-C4H5	3.00E+13	0.0	0.0
498.	C5H4O=CO+C2H2+C2H2	1.00E+15	0.0	78000.0
499.	C5H4O+O=CO2+2C2H2	3.00E+13	0.0	0.0
500.	A1C2H+OH=>A1-+CH2CO	2.18E-04	4.5	-1000.0
501.	A1C2H)2+OH=>A1C2H-+CH2CO	2.18E-04	4.5	-1000.0
502.	A2C2HA+OH=>A2-1+CH2CO	2.18E-04	4.5	-1000.0
503.	A2C2HB+OH=>A2-2+CH2CO	2.18E-04	4.5	-1000.0
504.	A3C2H+OH=>A3-4+CH2CO	2.18E-04	4.5	-1000.0
505.	A1C2H+OH=>C6H5O+C2H2	1.30E+13	0.0	10600.0
506.	A1C2H3+OH=>C6H5O+C2H4	1.30E+13	0.0	10600.0
507.	A1C2H)2+OH=>C4H2+C6H5O	1.30E+13	0.0	10600.0
508.	A2+OH=>A1C2H+CH2CO+H	1.30E+13	0.0	10600.0
509.	A2C2HA+OH=>A1C2H+H2C4O+H	1.30E+13	0.0	10600.0
510.	A2C2HB+OH=>A1C2H+H2C4O+H	1.30E+13	0.0	10600.0
511.	A3+OH=>A2C2HB+CH2CO+H	6.50E+12	0.0	10600.0
512.	A3+OH=>A2C2HA+CH2CO+H	6.50E+12	0.0	10600.0
513.	A3C2H+OH=>A2C2HA+H2C4O+H	6.50E+12	0.0	10600.0
514.	A3C2H+OH=>A2C2HB+H2C4O+H	6.50E+12	0.0	10600.0
515.	A4+OH=>A3-4+CH2CO	1.30E+13	0.0	10600.0
516.	A1C2H+O=>HCCO+A1-	2.04E+07	2.0	1900.0
517.	A1C2H)2+O=>HCCO+A1C2H-	2.04E+07	2.0	1900.0
518.	A1C2H3+O=>A1-+CH3+CO	1.92E+07	1.8	220.0
519.	A2C2HA+O=>HCCO+A2-1	2.04E+07	2.0	1900.0
520.	A2C2HB+O=>HCCO+A2-2	2.04E+07	2.0	1900.0
521.	A1C2H+O=>C2H+C6H5O	2.20E+13	0.0	4530.0
522.	A1C2H3+O=>C2H3+C6H5O	2.20E+13	0.0	4530.0
523.	A1C2H)2+O=>C6H5O+C4H	2.20E+13	0.0	4530.0
524.	A2+O=>CH2CO+A1C2H	2.20E+13	0.0	4530.0
525.	A2C2HA+O=>A1C2H)2+CH2CO	2.20E+13	0.0	4530.0
526.	A2C2HB+O=>A1C2H)2+CH2CO	2.20E+13	0.0	4530.0
527.	A3+O=>A2C2HA+CH2CO	1.10E+13	0.0	4530.0
528.	A3+O=>A2C2HB+CH2CO	1.10E+13	0.0	4530.0
529.	A3C2H+O=>A2C2HA+H2C4O	1.10E+13	0.0	4530.0
530.	A3C2H+O=>A2C2HB+H2C4O	1.10E+13	0.0	4530.0
531.	A4+O=>A3-4+HCCO	2.20E+13	0.0	4530.0
532.	A1C2H*+O2=>l-C6H4+CO+HCO	2.10E+12	0.0	7470.0
533.	A1C2H-+O2=>l-C6H4+CO+HCO	2.10E+12	0.0	7470.0
534.	A1C2H3*+O2=>l-C6H6+CO+HCO	2.10E+12	0.0	7470.0
535.	n-A1C2H2+O2=>A1-+CO+CH2O	1.00E+11	0.0	0.0
536.	A2-1+O2=>A1C2H+HCO+CO	2.10E+12	0.0	7470.0

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537. A2-2+O2=>A1C2H+HCO+CO             2.10E+12    0.0       7470.0
538. A2C2HA*+O2=>A2-1+CO+CO            2.10E+12    0.0       7470.0
539. A2C2HB*+O2=>A2-2+CO+CO            2.10E+12    0.0       7470.0
540. A3-4+O2=>A2C2HB+HCO+CO            2.10E+12    0.0       7470.0
541. A3-1+O2=>A2C2HA+HCO+CO            2.10E+12    0.0       7470.0
542. A4-+O2=>A3-4+CO+CO                2.10E+12    0.0       7470.0
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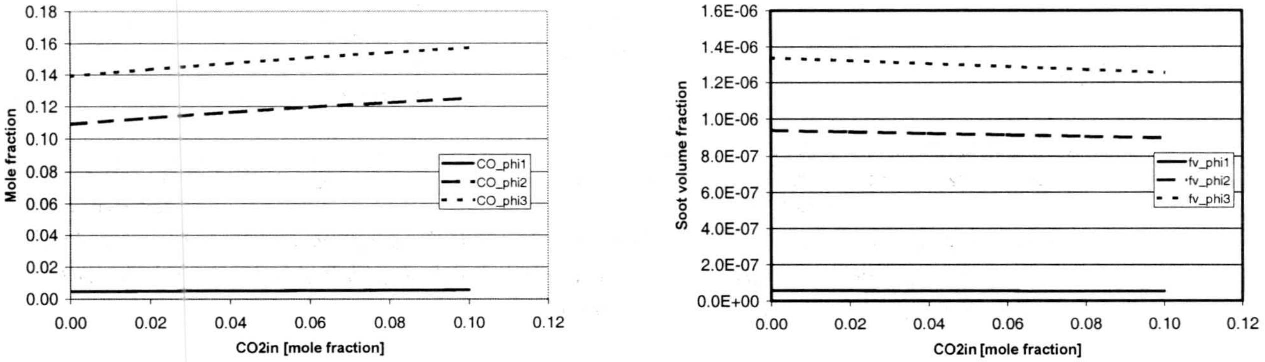
Appendix B – Results from temperatures 1400 K and 1300 K



a) b)

Figure B1. CO concentration a) and soot volume fraction b) as a function of added CO_2 input in the mixture. Temperature 1400 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.

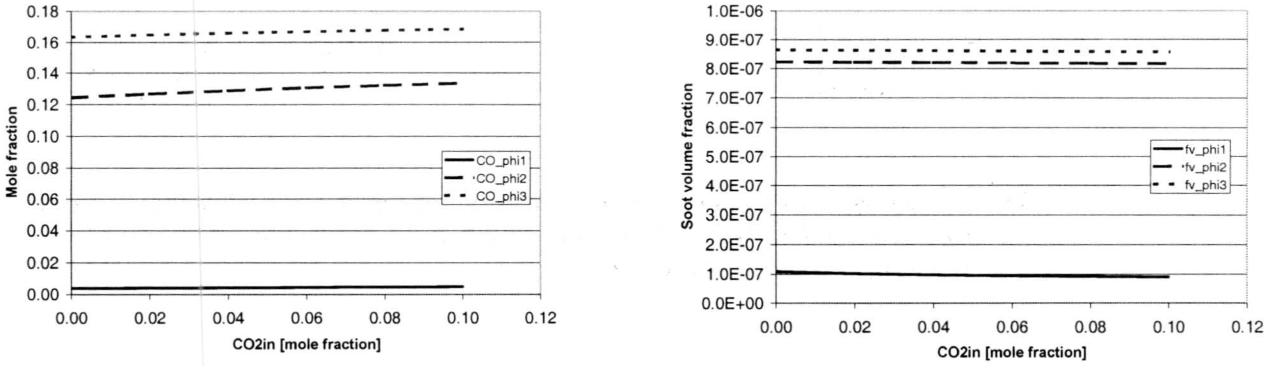


Figure B2. CO concentration a) and soot volume fraction b) as a function of added CO_2 input in the mixture. Temperature 1300 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.

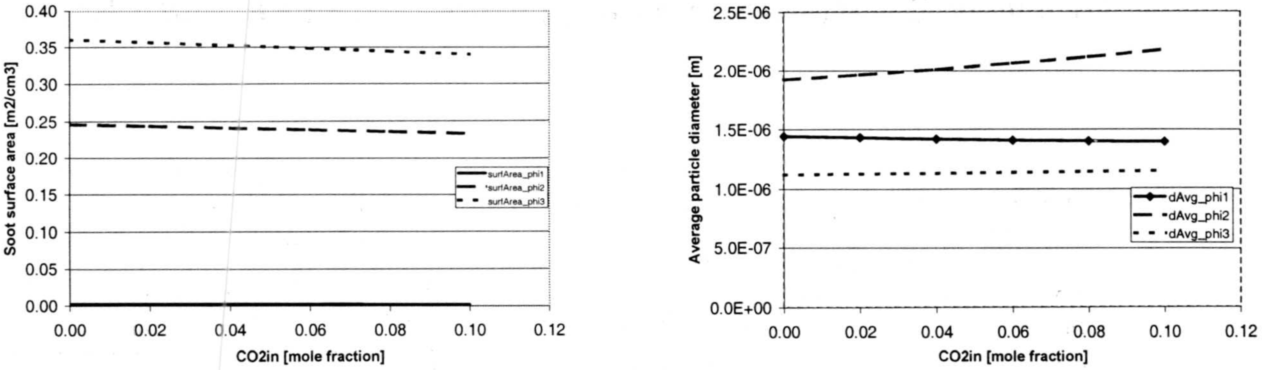
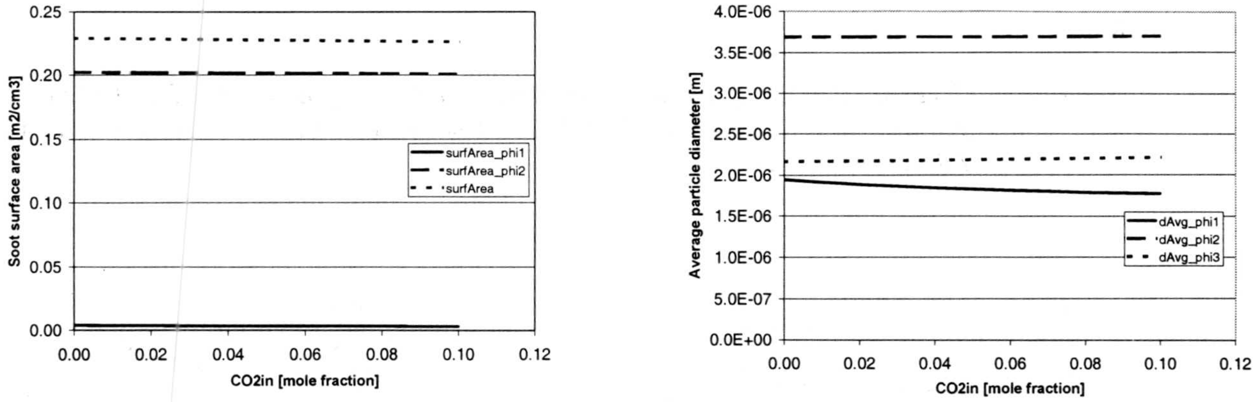


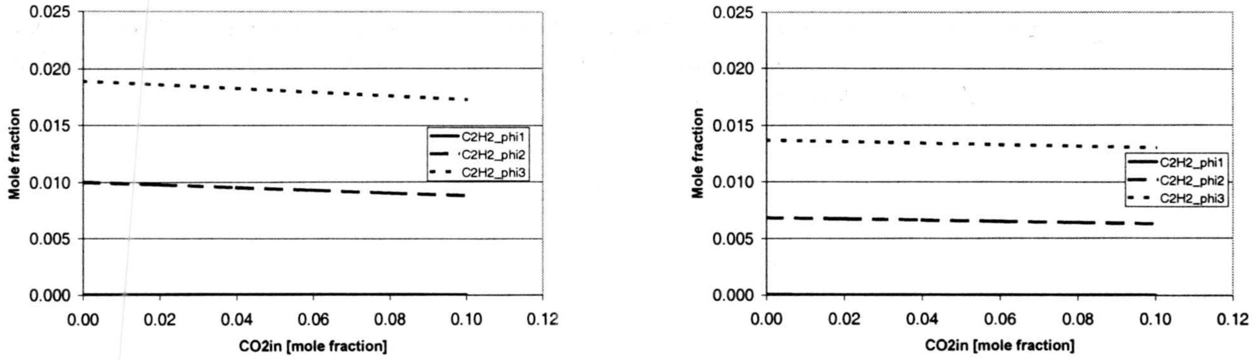
Figure B3. a) *Soot surface area and b) average soot particle diameter as a function of added CO_2 input in the mixture. Temperature 1400 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*



a)

b)

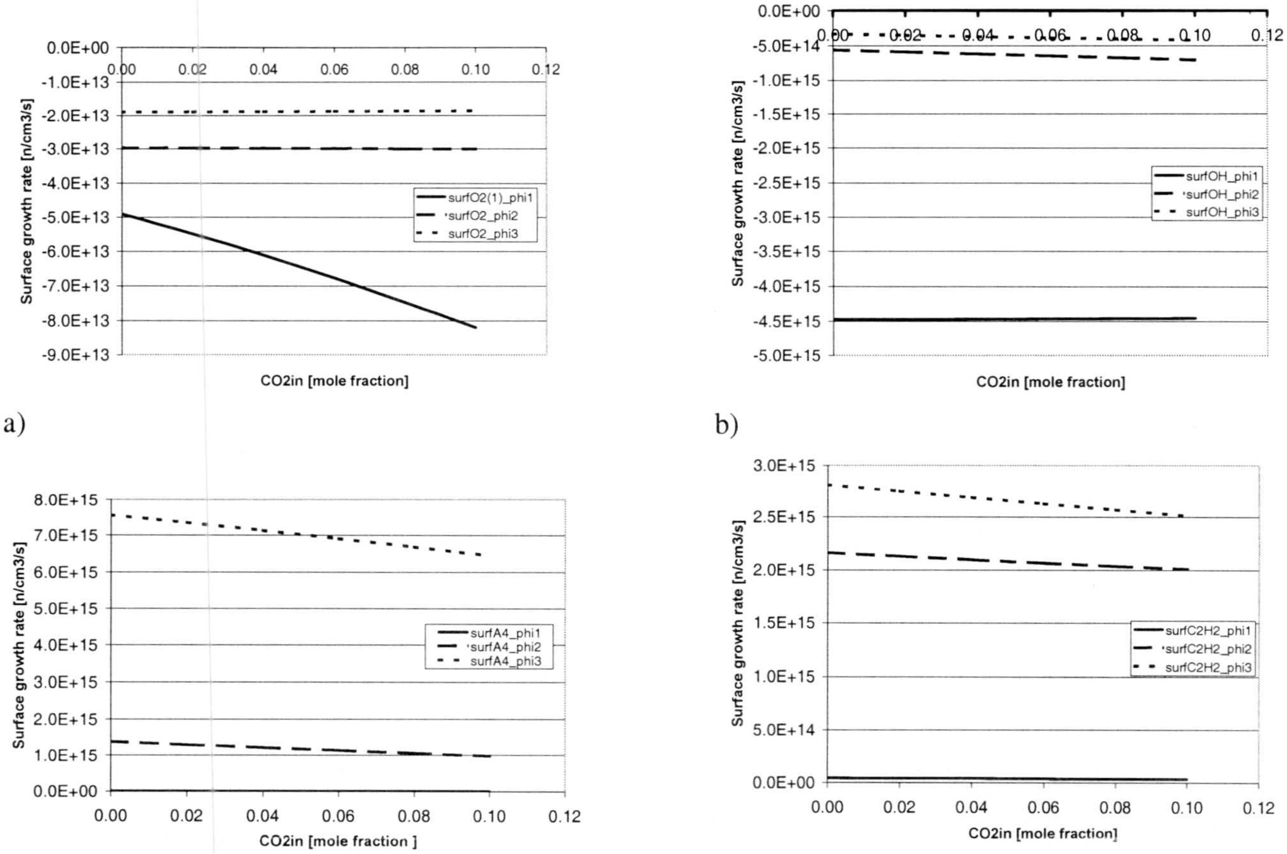
Figure B4. a) *Soot surface area and b) average soot particle diameter as a function of added CO_2 input in the mixture. Temperature 1300 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*



a)

b)

Figure B5. Acetylene concentration as a function of added CO_2 input in the mixture. a) Temperature 1400 K, b) temperature 1300 K. Residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.



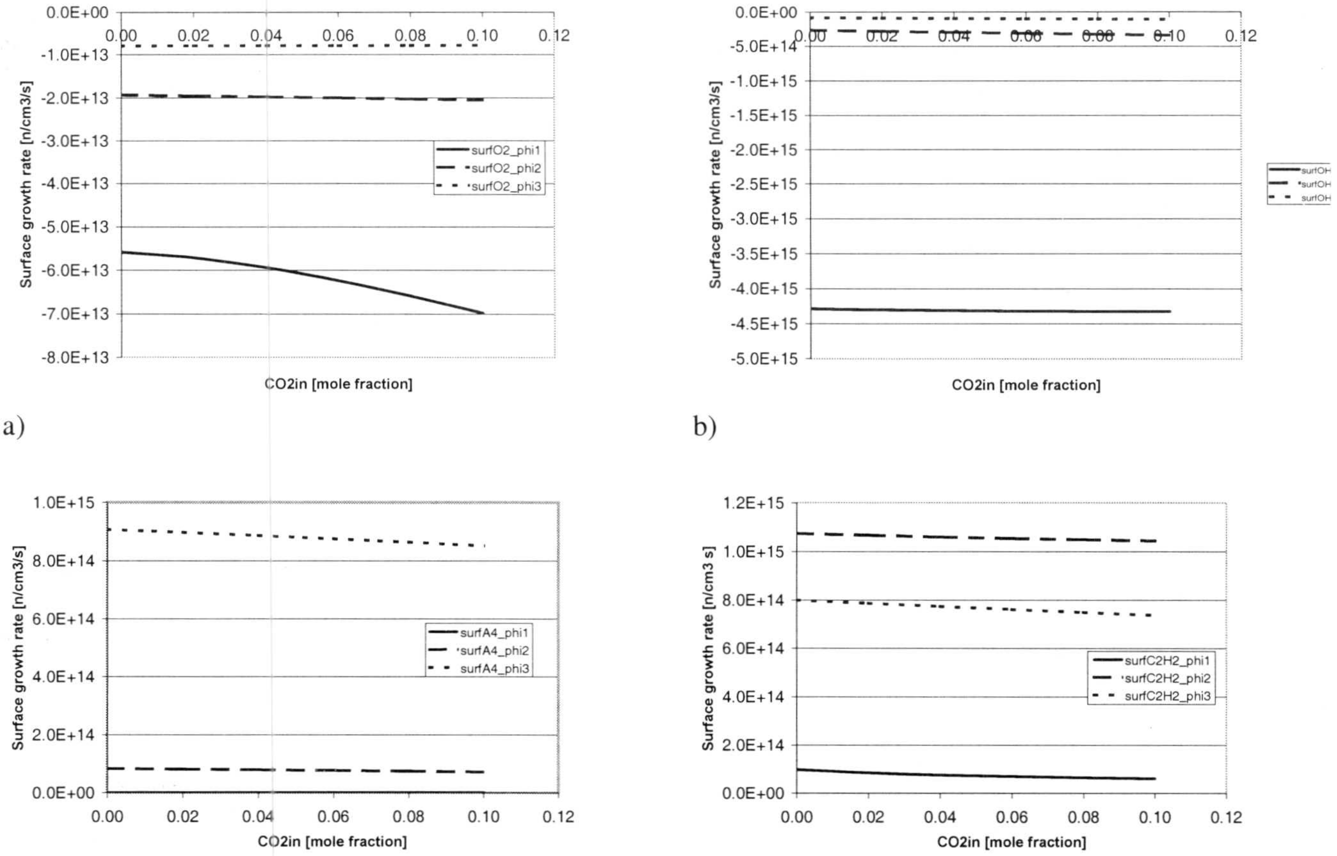
a)

b)

c)

d)

Figure B6. Surface species a)O_2, b) OH, c) A_4 (pyrene) and d) C_2H_2 as a function of added CO_2 input in the mixture. Temperature 1400 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.



a) b) c) d)

Figure B7. *Surface species a)O_2, b) OH, c) A_4 (pyrene) and d) C_2H_2 as a function of added CO_2 input in the mixture. Temperature 1300 K, residence time 5s and equivalence ratios 1.0, 2.0, and 3.0 respectively.*