Supplementary Material

Table of Content

A.	Equivalence Ratio	6
B.	Soot precursor compositions extracted from the CHEMKIN calculations	9
C.	Rate analysis of for the pyrene growth reactions in Raj's mechanism	26
D.	Detection of Soot Structures from the ReaxFF calculations after 2ns	40

Table of Figures

Figures S1. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel
mixtures for initial temperatures of 1400K in the Chemkin calculation11
Figures S2. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel
mixtures for initial temperatures of 1600K in the Chemkin calculation12
Figures S3. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel
mixtures for initial temperatures of 1800K in the Chemkin calculation13
Figures S4. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel
mixtures for initial temperatures of 2000K in the Chemkin calculation14
Figures S5. Reaction Pathway diagramm of the growth of the PAHs considered for the precursor
pool21

Figures S6. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature Figures S7. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature Figures S8. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature Figures S9. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature Figures S10. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 100% Figures S11. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 60% n-decane and 40%

Figures S12. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an

equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 100% n-Figures S13. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 100% Figures S14. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 60% n-decane and 40% Figures S15. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 100% n-Figures S16. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1800K and a fuel mixture of 100% Figures S17. Percentage contribution of the rate of production for each of the reactions depicted in table S8 and the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1800K and a fuel mixture of 60% n-decane and 40%

Table of Tables

Table S1. Mole fractions of nitrogen, oxygen, toluene and n-decane for all tested equivalence
ratios and fuel mixtures
Table S2. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 100% n-decane and 0% toluene in the Chemkin calculations15

Table S3. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 80% n-decane and 20% toluene in the Chemkin calculations16
Table S4. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 60% n-decane and 40% toluene in the Chemkin calculations17
Table S5. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 40% n-decane and 60% toluene in the Chemkin calculations
Table S6. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 20% n-decane and 80% toluene in the Chemkin calculations19
Table S7. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition
of 0% n-decane and 100% toluene in the Chemkin calculations20
Table S8. Major reaction pathways for the production of A4 in Raj's mechanism
Table S9. Growth structure found for each of the ReaxFF simulations for a fuel composition of
0% n-decane and 100% toluene in the Chemkin calculations
Table S10. Growth structure found for each of the ReaxFF simulations for a fuel composition
of 20% n-decane and 40% toluene in the Chemkin calculations
Table S11. Growth structure found for each of the ReaxFF simulations for a fuel composition
of 40% n-decane and 60% toluene in the Chemkin calculations
Table S12. Growth structure found for each of the ReaxFF simulations for a fuel composition
of 60% n-decane and 40% toluene in the Chemkin calculations
Table S13. Growth structure found for each of the ReaxFF simulations for a fuel composition
of 80% n-decane and 20% toluene in the Chemkin calculations

Table S14.	. Growth struc	ture found for each	h of the ReaxF	F simulations for	r a fuel composition
of 100% n-	decane and 09	% toluene in the C	hemkin calculat	ions	47

A. Equivalence Ratio

The equivalence ratio Φ is the stoichiometric ratio between fuel and air, meaning an equivalence ratio of 1 would be a perfect stoichiometric mixture of the fuel and the air which theoretically leads to a complete oxidation. Values of Φ larger than 1 thus match situations where there is not enough oxygen for a complete combustion.

$$\boldsymbol{\Phi} = \frac{\left[\frac{n_{fuel}}{n_{Air}}\right]_{given}}{\left[\frac{n_{fuel}}{n_{Air}}\right]_{Stochiometric}}$$
(1)

The quantity of fuel and oxygen are defined above as number of atoms, but could also be defined as mass, mole fraction or concentration.

For pure compounds defining the equivalence ratio is straight forward. For mixtures it is more complicated, hence a short example is given for the fuel mixture (n-decane/toluene) used in this study. For this the stoichiometric formula for the combustion of n-decane ($C_{10}H_{22}$) and toluene (C_7H_8) with air is given below.

$$a C_{10}H_{22} + b C_7H_8 + c O_2 + 4c N_2 \rightarrow d CO_2 + e H_2O + 4c N_2$$
 (2)

a, *b*, *c*, d and *e* may be mole fraction, mole percentages or stoichiometric coefficients. For simplicity the ratio of nitrogen and oxygen is given as 4/1. In reality it is 79/21 but the amount of nitrogen does not play any role for the equivalence ratio calculation, hence the simplification.

As for every n-decane molecule 15.5 oxygen molecules and for each toluene molecule 9 oxygen molecules are consumed to completely oxidize the respective fuel molecule. Therefore in the complete oxidation shown in equation (2) the stoichiometric coefficient c must be (15.5a + 9b). Hence the denominator in the equivalence ratio equation has this relation between

 n_{fuel} and n_{02} , where $n_{fuel} = a C_{10}H_{22} + b C_7H_8$ and $n_{Air} = (15.5a + 9b) \times O_2 + 4 \times (15.5a + 9b) \times N_2$. If the enumerator has the same ratio between *a*, *b* and *c* in equation (1) the equivalence ratio is 1 and a different ratio between *a*, *b* and *c* in the enumerator yields equivalence ratios different than 1. As in the present study the equivalence ratios used are larger than one, the calculation of the equivalence ratio for the fuel mixtures are more complicated. The calculation of the equivalence ratio for the differing fuel ratios of toluene and n-decane used was done using the Chemkin software¹, the resulting mole fractions are depicted in table S1 for all equivalence ratios and fuel mixtures. The mole fractions are consistent over the tested temperatures.

Fuel	Mole fraction	Ф=2.5	Ф=3	Ф=3.5	Ф=4	Ф=4.5	Ф=5
0%	%mol N ₂	0.746456	0.738318	0.7303544	0.722561	0.714932	0.707462
100%	%mol O ₂	0.198425	0.196262	0.1941448	0.192073	0.190045	0.188059
C ₇ H ₉	%mol C7H9	0.055118	0.065421	0.0755007	0.085366	0.095023	0.104477
20%	%mol N ₂	0.751685	0.744464	0.7373811	0.7304309	0.7236105	0.716916
$C_{10}H_{22}$	%mol O ₂	0.199815	0.197895	0.1960127	0.1941652	0.1923522	0.190572
80% C-H	%mol C7H9	0.038799	0.046111	0.053285	0.0603231	0.0672298	0.074008
C/119	%mol C ₁₀ H ₂₂	0.009699	0.011527	0.013321	0.015080	0.016807	0.018502
40%	%mol N ₂	0.755793	0.749305	0.742926	0.736656	0.73049	0.724427
$C_{10}H_{22}$	%mol O ₂	0.200907	0.199182	0.197486	0.19582	0.194181	0.192569
60% C-H-	%mol C7H9	0.025979	0.030908	0.035751	0.040514	0.045197	0.049802
C7119	%mol C ₁₀ H ₂₂	0.017319	0.020605	0.023834	0.02701	0.030132	0.033202
60%	%mol N ₂	0.759106	0.753215	0.747414	0.741703	0.736078	0.730538
$C_{10}H_{22}$	%mol O ₂	0.201787	0.200222	0.198679	0.197162	0.195666	0.194194
40% C-H-	%mol C7H9	0.015642	0.018625	0.021562	0.024454	0.027302	0.030108
C7119	%mol C ₁₀ H ₂₂	0.023463	0.027938	0.032343	0.036681	0.040953	0.045161
80%	%mol N ₂	0.761833	0.75644	0.751121	0.745878	0.740707	0.735607
$C_{10}H_{22}$	%mol O ₂	0.202512	0.201079	0.199665	0.198271	0.196897	0.195541
20% C-H	%mol C7H9	0.007130	0.008496	0.009842	0.01117	0.012479	0.01377
C7119	%mol C ₁₀ H ₂₂	0.028522	0.033985	0.039370	0.044681	0.049917	0.055082
100%	%mol N ₂	0.764118	0.759145	0.754234	0.749388	0.744603	0.739879
$0^{0/2}$	%mol O ₂	0.203120	0.201798	0.200492	0.199204	0.197933	0.196676
C ₇ H ₉	%mol C ₁₀ H ₂₂	0.032761	0.039058	0.045272	0.051408	0.057464	0.063444

Table S1. Mole fractions of nitrogen, oxygen, toluene and n-decane for all tested equivalence

 ratios and fuel mixtures. The mole fractions for all mixtures are consistent over all temperatures.

B. Soot precursor compositions extracted from the CHEMKIN calculations

Pie charts of the soot precursor compositions that are extracted from the Chemkin calculations using Raj's mechanism² for the varying parameters are depicted in the figures S1 - S4, separated for the different temperatures and shown for all tested fuel mixtures and equivalence ratios. A tabular representation is given in the tables S2 - S7, with the first four rows giving the temperature, the equivalence ratio and percentage of n-decane in the n-decane/toluene fuel mixture, and percentage of toluene in the fuel mixture, respectively. The following rows are the number of PAHs of the respective species given in the first column that are present in the composition at the given conditions. Columns in which for all PAHs a 0 is marked down, are representing conditions for which the selection criteria for extracting the soot precursor pools have not been met, i.e. the pyrene concentration did not have a peak within 2ms or the pyrene concentration at half the maximum of the first peak was beneath the ppm level.

Figure S6 – S9 depict the mole fractions and rate of productions for the PAHS considered in the soot precursor compositions for the Chemkin calculations with an equivalence ratio of 3.5, temperatures of 1400K and 2000K, and pure aliphatic and pure aromatic fuel mixtures. The point at which the precursor pool composition is generated is depicted with a vertical line. Note that the mole fraction and rate of production of pyrene is beginning to rise in all calculations before other PAHs are formed. A reaction pathway diagram of the growth of the considered PAHs in Raj's mechanism is shown in figure S5 with the exception of pyrene. Production of pyrene is discussed in detail in chapter C. For better visualization several reaction steps, such as hydrogen abstraction and subsequent acetylene addition, are displayed in one reaction step. Note that hydrogen abstraction occurs by reaction with several smaller radicals, e.g. hydrogen radicals, oxygen radicals, hydroxyl radicals and methyl radicals. From the diagram it follows that the

growth of the majority of the larger PAHs is described by the hydrogen - abstraction - C_2H_2 - addition (HACA) mechanism and therefore result in consumption of smaller PAHs, most of them being linked to pyrene. The only PAHs considered for the soot precursor compositions that are not produced mainly through pyrene are fluoranthene, cyclopenta[1,2]phenalen and partly cyclopenta[cd]pyrene. None the less figures S6- S9 show that pyrene production precedes also the production of these species. Hence considering the maximum of pyrene as point of soot inception appears to be a valid choice. The reason for this is that a reduction of the pyrene mole fraction can be considered as a growth of species larger than pyrene for the studied equivalence ratios as oxidation reaction are hindered due to the low oxygen content in the gas phase.



Figure S1. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel mixtures for initial temperatures of 1400K in the Chemkin calculation.



Temperature = 1600 K

Figure S2. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel mixtures for initial temperatures of 1600K in the Chemkin calculation.



Temperature = 1800 K Fuel mixture

Figure S3. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel mixtures for initial temperatures of 1800K in the Chemkin calculation.



Figure S4. Pie chart of the soot precursor pool compositions at all equivalence ratios and fuel mixtures for initial temperatures of 2000K in the Chemkin calculation.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
% toluene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
pyrene	0	41	14	0	75	46	20	16	76	47	23	18	77	41	28	21	0	41	28	22	0	40	32	26
cyclopenta[1,2]phenalen	0	1	4	0	0	0	2	3	0	0	2	1	0	0	2	1	0	0	2	1	0	0	1	1
cyclopenta[cd]pyrene	0	17	24	0	6	14	19	17	5	12	17	15	5	14	14	14	0	14	14	13	0	13	12	11
fluoranthene	0	0	1	0	0	0	1	1	0	0	1	1	0	0	1	0	0	0	1	0	0	0	1	0
benzo[a]pyrene	0	5	8	0	3	5	8	8	4	5	7	7	4	6	6	6	0	7	6	6	0	7	6	5
1-(1-pyrenyl)acetylene	0	5	6	0	1	4	8	10	0	4	8	11	0	4	8	11	0	4	8	11	0	4	8	11
1-(2-pyrenyl)acetylene	0	18	10	0	8	18	15	13	8	18	17	15	7	19	19	17	0	19	19	17	0	19	19	18
1-(4-pyrenyl)acetylene	0	5	6	0	1	4	7	9	0	4	8	10	0	4	8	11	0	4	8	11	0	4	8	11
benzo[e]pyrene	0	1	2	0	1	1	2	3	2	1	2	3	2	2	2	2	0	2	2	2	0	3	2	2
benzo[ghi]perylene	0	0	2	0	0	0	2	2	0	0	1	2	0	0	1	2	0	0	1	1	0	0	1	1
anthan	0	3	13	0	0	2	9	9	0	2	7	8	0	3	5	6	0	2	5	5	0	2	3	4
coronene	0	0	2	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1
2-pyrenyl radical	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1
4-pyrenyl radical	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1

Table S2. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 100% n-decane and 0% toluene in the Chemkin calculations.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
% toluene	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
pyrene	81	46	25	0	80	49	27	27	79	52	31	23	79	53	33	25	79	53	35	26	79	54	37	29
cyclopenta[1,2]phenalen	0	0	0	0	0	0	0	4	0	0	0	2	0	0	0	2	0	0	0	1	0	0	0	2
cyclopenta[cd]pyrene	4	12	14	0	4	11	14	8	4	10	12	11	4	9	11	11	4	9	11	10	4	9	10	9
fluoranthene	2	3	3	0	2	2	3	2	2	2	2	1	2	2	2	1	1	2	2	1	1	2	1	1
benzo[a]pyrene	2	5	7	0	3	5	7	4	3	5	6	6	4	5	6	5	4	5	6	5	4	5	5	5
1-(1-pyrenyl)acetylene	0	3	7	0	0	3	7	8	0	3	7	10	0	3	7	11	0	3	7	11	0	3	7	10
1-(2-pyrenyl)acetylene	5	15	14	0	6	15	16	14	6	15	17	16	5	15	18	17	5	15	18	18	5	15	18	18
1-(4-pyrenyl)acetylene	0	3	7	0	0	3	7	8	0	3	7	10	0	3	7	10	0	3	7	10	0	3	7	10
benzo[e]pyrene	1	1	2	0	1	1	2	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
benzo[ghi]perylene	0	0	1	0	0	0	1	0	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1
anthan	0	1	4	0	0	1	4	1	0	1	3	3	0	1	3	3	0	1	2	3	0	1	2	2
coronene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	0	0	0	0	0	4	0	0	0	2	0	0	0	2	0	0	0	1	0	0	0	2
2-pyrenyl radical	0	0	0	0	0	0	0	3	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1
4-pyrenyl radical	0	0	0	0	0	0	0	4	0	0	0	2	0	0	0	2	0	0	0	1	0	0	0	2

Table S3. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 80% n-decane and 20% toluene in the Chemkin calculations.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
% toluene	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40
pyrene	77	47	36	36	78	50	40	35	78	53	44	34	77	54	47	33	78	58	46	35	78	60	51	38
cyclopenta[1,2]phenalen	0	0	1	8	0	0	1	6	0	0	1	4	0	0	1	3	0	0	1	3	0	0	1	3
cyclopenta[cd]pyrene	4	10	9	4	3	9	9	5	3	8	8	6	4	8	7	7	3	7	7	7	3	7	6	6
fluoranthene	3	4	3	2	3	3	2	1	3	3	2	1	3	2	2	1	3	2	1	1	2	2	1	0
benzo[a]pyrene	4	6	5	1	4	6	5	2	4	6	4	3	5	6	4	3	4	5	4	3	5	5	3	3
1-(1-pyrenyl)acetylene	0	3	6	5	0	3	6	7	0	3	6	8	0	3	5	9	0	2	6	9	0	2	5	9
1-(2-pyrenyl)acetylene	5	13	15	10	5	13	16	13	5	13	16	15	5	13	16	16	5	13	16	16	5	13	15	16
1-(4-pyrenyl)acetylene	0	3	6	5	0	3	6	7	0	3	6	8	0	3	5	9	0	2	6	9	0	2	5	8
benzo[e]pyrene	2	2	2	0	2	2	2	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1	1
benzo[ghi]perylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
anthan	0	1	1	0	0	1	1	0	0	1	1	1	0	1	1	1	0	0	1	1	0	0	0	1
coronene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	1	8	0	0	1	6	0	0	1	4	0	0	1	3	0	0	1	3	0	0	1	3
2-pyrenyl radical	0	0	1	7	0	0	1	5	0	0	1	3	0	0	1	2	0	0	0	2	0	0	0	2
4-pyrenyl radical	0	0	1	8	0	0	1	6	0	0	1	4	0	0	1	3	0	0	1	3	0	0	1	3

Table S4. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 60% n-decane and 40% toluene in the Chemkin calculations.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40
% toluene	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
pyrene	0	43	48	41	71	49	53	41	72	53	56	41	74	60	58	45	75	62	60	46	0	65	61	47
cyclopenta[1,2]phenalen	0	0	3	8	0	0	2	7	0	0	2	5	0	0	2	5	0	0	1	5	0	0	1	4
cyclopenta[cd]pyrene	0	9	6	3	4	8	5	4	3	8	5	4	3	6	5	4	3	6	4	4	0	5	4	4
fluoranthene	0	3	2	1	4	3	2	1	4	2	1	1	3	2	1	0	3	2	1	0	0	1	1	0
benzo[a]pyrene	0	9	3	1	8	9	3	1	7	8	3	2	7	6	2	1	7	6	2	1	0	5	2	1
1-(1-pyrenyl)acetylene	0	3	4	5	0	3	4	6	0	3	4	7	0	2	4	6	0	2	4	6	0	2	4	7
1-(2-pyrenyl)acetylene	0	12	13	10	5	12	13	11	4	12	13	13	4	11	12	13	4	11	12	13	0	10	12	13
1-(4-pyrenyl)acetylene	0	3	4	5	0	3	4	6	0	3	4	7	0	2	4	6	0	2	4	6	0	2	4	7
benzo[e]pyrene	0	4	1	0	4	4	1	0	4	4	1	0	3	3	1	0	3	3	1	0	0	2	1	0
benzo[ghi]perylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
anthan	0	1	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
coronene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	3	8	0	0	2	7	0	0	2	5	0	0	2	5	0	0	1	5	0	0	1	4
2-pyrenyl radical	0	0	2	7	0	0	2	5	0	0	1	4	0	0	1	4	0	0	1	3	0	0	1	3
4-pyrenyl radical	0	0	3	8	0	0	2	7	0	0	2	6	0	0	2	5	0	0	1	5	0	0	1	4

Table S5. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 40% n-decane and 60% toluene in the Chemkin calculations.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
% toluene	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
pyrene	0	56	61	49	0	64	65	46	0	66	66	56	0	70	67	54	0	69	67	55	0	71	69	53
cyclopenta[1,2]phenalen	0	0	4	8	0	0	3	8	0	0	2	6	0	0	2	5	0	0	2	5	0	0	2	4
cyclopenta[cd]pyrene	0	6	3	2	0	5	3	2	0	5	3	0	0	4	3	3	0	4	3	3	0	4	3	3
fluoranthene	0	1	1	1	0	1	1	0	0	1	1	3	0	1	0	0	0	1	0	0	0	1	0	0
benzo[a]pyrene	0	9	2	0	0	7	1	0	0	7	1	0	0	6	1	1	0	6	1	1	0	5	1	1
1-(1-pyrenyl)acetylene	0	2	3	4	0	2	3	4	0	2	3	1	0	1	3	5	0	1	3	5	0	1	3	6
1-(2-pyrenyl)acetylene	0	11	9	8	0	9	9	9	0	9	9	5	0	8	9	10	0	9	10	10	0	8	9	11
1-(4-pyrenyl)acetylene	0	2	3	4	0	2	3	4	0	2	3	10	0	1	3	5	0	1	3	5	0	1	3	6
benzo[e]pyrene	0	5	1	0	0	3	0	0	0	3	0	0	0	3	0	0	0	3	0	0	0	3	0	0
benzo[ghi]perylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
anthan	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
coronene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	4	8	0	0	3	8	0	0	2	6	0	0	2	5	0	0	2	5	0	0	2	4
2-pyrenyl radical	0	0	2	6	0	0	2	6	0	0	2	4	0	0	1	3	0	0	1	3	0	0	1	2
4-pyrenyl radical	0	0	4	8	0	0	3	8	0	0	2	6	0	0	2	5	0	0	2	5	0	0	2	4

Table S6. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 20% n-decane and 80% toluene in the Chemkin calculations.

T (10 ³ K)	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0	1.4	1.6	1.8	2.0
Φ	2.5	2.5	2.5	2.5	3	3	3	3	3.5	3.5	3.5	3.5	4	4	4	4	4.5	4.5	4.5	4.5	5	5	5	5
% n-decane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
% toluene	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
pyrene	94	83	73	59	93	83	70	62	94	84	71	57	94	85	69	64	94	84	74	66	0	85	70	62
cyclopenta[1,2]phenalen	0	0	3	5	0	0	2	5	0	0	2	4	0	0	1	4	0	0	1	3	0	0	1	3
cyclopenta[cd]pyrene	0	2	2	2	1	2	2	2	0	2	2	2	0	2	3	2	0	2	2	2	0	2	3	2
fluoranthene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
benzo[a]pyrene	1	1	0	0	2	1	0	0	1	1	0	0	1	1	1	0	1	1	0	0	0	1	1	0
1-(1-pyrenyl)acetylene	0	1	3	4	0	1	3	4	0	1	3	6	0	1	4	5	0	1	3	4	0	1	4	6
1-(2-pyrenyl)acetylene	1	5	7	8	1	5	8	7	1	5	8	10	1	5	9	8	1	5	8	7	0	5	10	9
1-(4-pyrenyl)acetylene	0	1	3	4	0	1	3	4	0	1	3	6	0	1	4	5	0	1	3	4	0	1	4	6
benzo[e]pyrene	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
benzo[ghi]perylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
anthan	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
coronene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-pyrenyl radical	0	0	3	5	0	0	2	5	0	0	2	4	0	0	1	4	0	0	1	3	0	0	1	3
2-pyrenyl radical	0	0	1	3	0	0	1	2	0	0	1	2	0	0	0	2	0	0	0	1	0	0	0	1
4-pyrenyl radical	0	0	3	5	0	0	2	5	0	0	2	4	0	0	1	4	0	0	1	3	0	0	1	3

Table S7. Soot precursor pool compositions for the ReaxFF simulations for a fuel composition of 0% n-decane and 100% toluene in the Chemkin calculations.



Figure S5. Reaction Pathway diagramm of the growth of the PAHs considered for the precursor pool. The main pathways for the production of pyrene are discussed in chapter C.



Figure S6. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 0% n-decane and 100% toluene. The vertical line depicts the point at which half of the maximum of pyrene was reached.



Figure S7. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature of 2000K and a fuel mixture of 0% n-decane and 100% toluene. The vertical line depicts the point at which half of the maximum of pyrene was reached.



Figure S8. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 100% n-decane and 0% toluene. The vertical line depicts the point at which half of the maximum of pyrene was reached.



Figure S9. The mole fractions and rate of productions of the PAHs considered for the soot precursor pools during the Chemkin calculations with an equivalence ratio of 3.5, a temperature of 2000K and a fuel mixture of 100% n-decane and 0% toluene. The vertical line depicts the point at which half of the maximum of pyrene was reached.

C. Rate analysis of for the pyrene growth reactions in Raj's mechanism

The major reaction pathways for the production of pyrene from smaller molecules in Raj's mechanism² are shown in table S8. Reaction 1 is the addition of a methylene radical to a 4methylenephenanthrenyl radical. Reactions 2, 3 and 4 can be seen as different intermediates of the H-abstraction - C_2H_2 – addition (HACA) mechanism. Reaction 5 is the reaction of activated acetylenated naphthalene with cyclobutadiene. Reactions 6 and 7 are dimerization reactions of a benzyl radical and an indenyl radical and two indenyl radicals, respectively.

The percentage contribution of each reaction to the total rate of production (ROP) of pyrene is shown in figures S10 to figure S21 for equivalence ratios of 3.5, all tested temperatures and fuel mixtures of 100% toluene, 60% n-decane/40% toluene and 100% n-decane. Reactions not shown in the graphs did not exceed a percentage contribution towards the total pyren ROP of 1%.

At temperatures of 1400K one finds that the reaction 6 is contributing the most at fuel mixtures of 100% toluene. At these temperatures and fuel mixture reaction 2, 4 and 7 contribute to the growth of pyrene at later times. In this region pyrene is also consumed by oxidation and further growth to larger PAH, however. With increasing n-decane content reaction 6 gains importance towards the production of pyrene at 1400K, while reactions 1 and 5 don't contribute significantly towards the growth of pyrene at all fuel mixtures at temperatures of 1400K. This is due to the fact that little fragmentation of the fuel molecules occurs at these temperatures and recombination reactions are frequent.

While reaction 7 remains the most important reaction towards pyrene growth at fuel mixtures with a high aliphatic content, reactions 2 and 4 gain importance with increasing temperatures due to a faster fragmentation of the fuel molecules. For the same conditions reaction 6 loses significance and the ROP of reaction 6 could not be detected anymore for conditions with a high aliphatic content in the fuel mixture. This is due to the fact that the benzyl radical concentration

Reaction#1	$\overset{CH_2}{\longleftrightarrow} + CH_2 \longrightarrow \overset{CH_2}{\longleftrightarrow} + H_2 + H_2$
Reaction#2	$+ C_2H_2 \longrightarrow + H$
Reaction#3	+H → ↔ +H
Reaction#4	
Reaction#5	→ + □ → ↔ + H
Reaction#6	$\bigcirc + \bigcirc^{CH_2} \longrightarrow \bigcirc + 2H_2$
Reaction#7	$2 \qquad \qquad \bullet \qquad \qquad \bullet \qquad \qquad + C_2H_2 + H_2$

Table S8. Major reaction pathways for the production of A4 in Raj's mechanism.

is too low and is mostly consumed by oxidation and fragmentation at high temperatures. Production reactions of the benzyl radical can't compensate for this at high temperatures and hence the reaction pathway does not contribute to the growth of pyrene at temperatures above 1800K and a fuel-mixture with more than 50% of toluene.

Also the reaction 1 and 5 undergo an interesting evolution. While for 1400K they do contribute at short times for both pure fuel compositions, their contribution diminishes for the pure toluene contributions at higher temperatures. For the pure n-decane they continue to contribute to the early growth of pyrene, indicating the different molecular compositions at higher n-decane compositions. As n-decane decomposes is goes through more stages than toluene. This explains the significance of reaction 5 at early stages of pyrene formation for intermediate temperatures, since the cyclobutadien can be formed from decomposed n-decane more easily than from toluene. This significance ceases at higher temperatures since there the cyclobutadien decomposes more easily.

Also for reaction 1 the production of methylene-radicals is crucial for the contribution of this reaction. Since n-decane can successively decompose into methylene-radicals its decomposition contributes more towards this reaction. Also toluene can form methylene-radicals by decomposing into a phenyl-radical and a methyl-radical, which in turn by H-dissociation can form methylene-radical. This is why reaction 1 also slightly contributes to the early stage of pyrene formation at pure toluene mixtures at intermediate temperatures.

Another interesting progression in the percentage contribution of reactions 2 and 4 is that the contributions of phenanthrene and the phenanthreneacetenyl are gain significance with increasing aliphatic content in the fuel mixture and increasing temperature. This indicates that the pyrene is overall consumed in this region, however. This is due to the fact that the HACA

mechanism, which reaction 2 to 4 are describing several transition steps of from phenanthrene to pyrene, is also responsible for the growth of the PAHs larger than pyrene. Hence while phenanthrene is consumed through the HACA mechanism forming pyrene, by further H-abstraction and acetylene-addition an equal amount of pyrene as generated through reactions 1 and 2 is consumed.

In order to simplify the presentation of the above presented reactions, one can group the reactions into two groups. The first group is the production of pyrene by subsequent addition of small aliphatic molecules to aromatics smaller than pyrene. This group is consists of reactions 1 to reaction 4. The second group is the production of pyrene by recombination of two aromatic molecules smaller than pyrene. This group consists of reaction 5 to reaction 6.

As described above this grouping of reactions give that while at 1400K the pathway of recombination by smaller aromatics is dominant, with increasing temperature the pathway of addition of small aliphatic molecules is becoming more significant. Furthermore with increasing temperature the significance of the pathway of recombination of smaller aromatic molecules is losing significance with increasing aliphatic fuel content.



Figure S10. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 100% toluene.



Figure S11. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 60% n-decane and 40% toluene.



Figure S12. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1400K and a fuel mixture of 100% n-decane.



Figure S13. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 100% toluene.



Figure S14. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 60% n-decane and 40% toluene.



Figure S15. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1600K and a fuel mixture of 100% n-decane.



Figure S16. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1800K and a fuel mixture of 100% toluene.



Figure S17. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1800K and a fuel mixture of 60% n-decane and 40% toluene.



Figure S18. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 1800K and a fuel mixture of 100% n-decane.



Figure S19. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 2000K and a fuel mixture of 100% toluene.



Figure S20. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 2000K and a fuel mixture of 60% n-decane and 40% toluene.



Figure S21. Percentage contribution of the rate of production for each of the reactions depicted in table S8 towards the total rate of production of pyrene for the Chemkin calculation at an equivalence ratio of 3.5, a temperature of 2000K and a fuel mixture of 100% n-decane.

D. Detection of Soot Structures from the ReaxFF calculations after 2ns

The PAH compositions generated with Raj's mechanism² are simulated with the SCM modeling suite³ using ReaxFF, employing the Chennoweth C/H/O force field⁴, and ran for 2 ns in an NVT-Ensemble at a temperature of 2500K with a Nose-Hoover-chain thermostat and a dumping rate of 10fs. For each extracted PAH composition from one of the CHEMKIN calculations, three individual calculations where performed with ReaxFF. At the end of each calculations each structure whose mole mass exceeded the initial maximal mole mass of the starting composition was detected as a growth structure and its structural features and reaction pathway has been investigated. The number of growth structures detected this way for all the calculations are given in table S9-S14.

The reason why the values shown in figure 5 are not a sum of the values of 7 and 8 is a difference in the recognition of just growth product and structural differentiation. In the case that a growth product is recognized at the end of a calculation, it was recognized and the average of growth products recognized is calculated for the three calculations for each composition. The average value for the averages is than calculated for each condition investigated in the CHEMKIN calculations and depicted in Figure 5.

For the structural recognition each structure recognized is further put into one of the classes ADLH, APPH, ALLH. Hence for each ReaxFF calculation the structure is again recognized and evaluated as one of the classes. Due to this additional step the check at the end of one ReaxFF calculation is not binary any more (is the a structure? Yes/no) but has 6 possible outcomes (is it ADLH? Yes/no. is it APPH? Yes/no. is it AALH? Yes/no.). This introduces outcomes, where the answer is there is no structure of this class found, since one structure can

only be in one class. An average of the structures found for each class is calculated. Again the average value of these calculated averages is displayed separated by the conditions it is averaged for in figure 7. Due to the introduction of new values, these average value drawn for the individual conditions tested with CHEMKIN cannot be summed up to give the average of the values of figure 5. The same argument holds for figure 8, where the structures have been identified on the criterion of the presence of a side chain.

Table S9.	Growth	structures	found fo	r each	of the	ReaxFF	simulation	ns for a	a fuel	compos	sition of
0% n-deca	ine and 1	00% tolue	ne in the	Chem	kin cal	culation	S.				

Temperature [K]	Equivalence Ratio Φ	n-decane (mol%)	Calculation #1	Calculation #2	Calculation #3
1400	2.5	0	1	0	0
1400	3	0	0	0	1
1400	3.5	0	0	0	1
1400	4	0	0	0	1
1400	4.5	0	0	1	2
1600	2.5	0	1	0	3
1600	3	0	1	0	0
1600	3.5	0	0	0	2
1600	4	0	0	2	0
1600	4.5	0	1	0	0
1600	5	0	2	0	0
1800	2.5	0	3	0	2
1800	3	0	1	1	1
1800	3.5	0	2	2	0
1800	4	0	1	1	1
1800	4.5	0	0	2	4
1800	5	0	1	0	1
2000	2.5	0	3	1	2
2000	3	0	0	3	1
2000	3.5	0	1	1	1
2000	4	0	1	2	1
2000	4.5	0	1	1	1
2000	5	0	3	1	0

Table S10. Growth structures found for each of the ReaxFF simulations for a fuel composition of 20% n-decane and 80% toluene in the Chemkin calculations.

Temperature [K]	Equivalence Ratio Φ	n-decane (mol%)	Calculation #1	Calculation #2	Calculation #3
1600	2.5	20	1	0	0
1600	3	20	1	0	0
1600	3.5	20	0	1	0
1600	4	20	0	0	0
1600	4.5	20	0	1	0
1600	5	20	1	0	0
1800	2.5	20	1	2	1
1800	3	20	1	1	0
1800	3.5	20	0	0	3
1800	4	20	1	1	0
1800	4.5	20	1	0	0
1800	5	20	3	3	0
2000	2.5	20	5	4	2
2000	3	20	3	1	5
2000	3.5	20	0	1	1
2000	4	20	1	2	3
2000	4.5	20	3	0	1
2000	5	20	2	0	2

Table S11. Growth structures found for each of the ReaxFF simulations for a fuel composition of 40% n-decane and 60% toluene in the Chemkin calculations.

Temperature [K]	Equivalence Ratio Φ	n-decane (mol%)	Calculation #1	Calculation #2	Calculation #3
1400	3	40	0	1	0
1400	3.5	40	0	0	1
1400	4	40	1	0	0
1400	4.5	40	1	0	0
1600	2.5	40	1	0	1
1600	3	40	0	1	0
1600	3.5	40	0	1	2
1600	4	40	0	1	0
1600	4.5	40	1	0	0
1600	5	40	0	0	0
1800	2.5	40	0	1	3
1800	3	40	1	0	1
1800	3.5	40	2	2	0
1800	4	40	1	0	1
1800	4.5	40	2	0	0
1800	5	40	1	3	3
2000	2.5	40	2	2	3
2000	3	40	1	3	4
2000	3.5	40	3	3	2
2000	4	40	3	2	1
2000	4.5	40	3	1	4
2000	5	40	1	2	0

Table S12. Growth structures found for each of the ReaxFF simulations for a fuel composition of 60% n-decane and 40% toluene in the Chemkin calculations.

Temperature [K]	Equivalence Ratio Φ	n-decane (mol%)	Calculation #1	Calculation #2	Calculation #3
1400	2.5	60	1	2	1
1400	3	60	0	2	0
1400	3.5	60	1	1	0
1400	4	60	0	0	0
1400	4.5	60	1	1	1
1400	5	60	0	1	0
1600	2.5	60	1	3	3
1600	3	60	0	1	0
1600	3.5	60	1	0	0
1600	4	60	2	1	2
1600	4.5	60	2	0	1
1600	5	60	0	0	2
1800	2.5	60	0	0	0
1800	3	60	1	0	4
1800	3.5	60	2	0	2
1800	4	60	1	1	1
1800	4.5	60	1	2	0
1800	5	60	0	0	2
2000	2.5	60	3	5	2
2000	3	60	1	2	2
2000	3.5	60	3	3	2
2000	4	60	3	0	2
2000	4.5	60	2	2	1

Table S13. Growth structures found for each of the ReaxFF simulations for a fuel composition of 80% n-decane and 20% toluene in the Chemkin calculations.

Temperature [K]	Equivalence Ratio Φ	n-decane (mol%)	Calculation #1	Calculation #2	Calculation #3
1400	2.5	80	0	0	0
1400	3	80	1	1	0
1400	3.5	80	1	0	0
1400	4	80	1	1	0
1400	4.5	80	0	0	1
1400	5	80	0	1	0
1600	2.5	80	0	0	0
1600	3	80	2	0	2
1600	3.5	80	0	1	0
1600	4	80	0	2	3
1600	4.5	80	1	0	0
1600	5	80	3	0	0
1800	2.5	80	2	2	1
1800	3	80	2	3	1
1800	3.5	80	2	2	2
1800	4	80	1	2	4
1800	4.5	80	2	1	2
1800	5	80	3	2	2
2000	3	80	4	3	2
2000	3.5	80	1	2	1
2000	4	80	4	3	3
2000	4.5	80	1	2	1
2000	5	80	2	1	1

Temperature	Equivalence Ratio Φ	n-decane	Calculation #1	Calculation #2	Calculation #3
լույ	ituito +	(110170)	11 1	112	115
1400	3.5	100	1	0	1
1400	4	100	2	3	1
1600	2.5	100	1	2	0
1600	3	100	0	3	1
1600	3.5	100	0	0	1
1600	4	100	1	2	2
1600	4.5	100	1	1	2
1600	5	100	0	0	1
1800	2.5	100	0	1	2
1800	3	100	1	3	1
1800	3.5	100	3	2	3
1800	4	100	2	1	1
1800	4.5	100	2	2	2
1800	5	100	1	1	2
2000	3.5	100	1	1	1
2000	4	100	0	2	3
2000	4.5	100	2	0	1
2000	5	100	1	1	3

Table S14. Growth structures found for each of the ReaxFF simulations for a fuel composition of 0% n-decane and 100% toluene in the Chemkin calculations.

References

(1) CHEMKIN-PRO; Reaction Design: San Diego, 2015.

(2) Raj, A.; Prada, I. D. C.; Amer, A. A.; Chung, S. H. A reaction mechanism for gasoline surrogate fuels for large polycyclic aromatic hydrocarbons. *Combust Flame* **2012**, *159*, 500–515.

(3) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders,

J. G.; Ziegler, T. Chemistry with ADF. J. Comput. Chem. 2001, 22, 931–967.

(4) Chenoweth, K.; van Duin, Adri C T; Goddard, W. A. 3. ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation. *J Phys Chem A* **2008**, *112*, 1040–1053.