APPENDIX A. Changes in the original mechanisms

Original low pressure methanol oxidation mechanism, without NO_x chemistry:

SPECIES CONSIDERED

1. CH3OH	10. HO2	19. CH3O
2. CO	11. H2O	20. CH2OH
3. CO2	12. H2O2	21. CH2O
4. CH4	13. HOCO	22. HCO
5. H	14. CH3	23. CH3OOH
6. O	15. CH2	24. CH3OO
7. OH	16. CH2(S)	25. CH2OOH
8. H2	17. CH	26. AR
9. O2	18. C	27. N2

REACTIONS CONSIDERED		A	β	E
H_2/O_2 subset				
1. H+O2=O+OH		3.60E+15	-0.4	16600.0
2. H+H+M=H2+M		7.00E+17	-1.0	0.0
N2	Enhanced by	0.000E+00		
H2O	Enhanced by	0.000E+00		
H2	Enhanced by	0.000E+00		
3. H+H+N2=H2+N2		5.40E+18	-1.3	0.0
4. H+H+H2=H2+H2		1.00E+17	-0.6	0.0
5. H+H+H2O=H2+H2O		1.00E+19	-1.0	0.0
6. H+O+M=OH+M		6.20E+16	-0.6	0.0
H2O	Enhanced by	5.000E+00		
7. H+O2(+M)=HO2(+M)		1.50E+12	0.6	0.0
Low pressure limit:		0.35000E+17	-0.41000E+00	-0.11160E+04
TROE centering:		0.50000E+00	0.10000E-29	0.10000E+31
N2	Enhanced by	0.000E+00		
AR	Enhanced by	0.000E+00		
H2O	Enhanced by	1.100E+01		
H2	Enhanced by	2.000E+00		
O2	Enhanced by	7.800E-01		
8. H+O2(+AR)=HO2(+AR)		1.50E+12	0.6	0.0
Low pressure limit:		0.90400E+20	-0.15000E+01	0.49000E+03
TROE centering:		0.50000E+00	0.10000E-29	0.10000E+31
9. H+O2(+N2)=HO2(+N2)		1.50E+12	0.6	0.0
Low pressure limit:		0.63700E+21	-0.17200E+01	0.52000E+03
TROE centering:		0.80000E+00	0.10000E-29	0.10000E+31
10. O+O+M=O2+M		1.90E+13	0.0	-1788.0
N2	Enhanced by	1.500E+00		
O2	Enhanced by	1.500E+00		
H2O	Enhanced by	1.000E+01		
11. O+H2=OH+H		3.80E+12	0.0	7948.0
Declared duplicate reaction...				
12. O+H2=OH+H		8.80E+14	0.0	19175.0
Declared duplicate reaction...				

REACTIONS CONSIDERED	A	β	E
13. OH+OH=O+H2O	4.30E+03	2.7	-1822.0
14. OH+H+M=H2O+M	4.50E+22	-2.0	0.0
AR Enhanced by 3.800E-01			
H2 Enhanced by 7.300E-01			
H2O Enhanced by 1.200E+01			
15. OH+H2=H+H2O	2.10E+08	1.5	3449.0
16. H2+O2=HO2+H	7.40E+05	2.4	53502.0
17. HO2+H=OH+OH	8.40E+13	0.0	400.0
18. HO2+H=H2O+O	1.40E+12	0.0	0.0
19. HO2+O=OH+O2	1.60E+13	0.0	-445.0
20. HO2+OH=H2O+O2	3.60E+21	-2.1	9000.0
Declared duplicate reaction...			
21. HO2+OH=H2O+O2	2.00E+15	-0.6	0.0
Declared duplicate reaction...			
22. HO2+OH=H2O+O2	-2.2E+96	-24.0	49000.0
Declared duplicate reaction...			
23. HO2+HO2=H2O2+O2	1.90E+11	0.0	-1408.0
Declared duplicate reaction...			
24. HO2+HO2=H2O2+O2	1.00E+14	0.0	11034.0
Declared duplicate reaction...			
25. H2O2(+M)=OH+OH(+M)	4.00E+11	0.0	37137.0
Low pressure limit:	0.22910E+17	0.00000E+00	0.43638E+05
TROE centering:	0.50000E+00	0.10000E-29	0.10000E+31 0.10000E+31
H2O Enhanced by 1.200E+01			
H2 Enhanced by 2.500E+00			
AR Enhanced by 6.400E-01			
26. H2O2+H=H2O+OH	1.00E+13	0.0	3580.0
27. H2O2+H=HO2+H2	1.70E+12	0.0	3760.0
28. H2O2+O=HO2+OH	9.60E+06	2.0	3970.0
29. H2O2+OH=H2O+HO2	1.90E+12	0.0	427.0
Declared duplicate reaction...			
30. H2O2+OH=H2O+HO2	1.60E+18	0.0	29410.0
Declared duplicate reaction...			

CO/CO_2 subset

31. CO+O(+M)=CO2(+M)	1.80E+10	0.0	2384.0
Low pressure limit:	0.13500E+25	-0.27900E+01	0.41910E+04
TROE centering:	0.10000E+01	0.10000E-29	0.10000E+31 0.10000E+31
H2 Enhanced by 2.500E+00			
H2O Enhanced by 1.200E+01			
CO Enhanced by 1.900E+00			
CO2 Enhanced by 3.800E+00			
32. CO+O2=CO2+O	4.70E+12	0.0	60500.0
33. CO+HO2=CO2+OH	1.60E+05	2.2	17943.0
34. CO+OH=CO2+H	8.00E+10	0.0	0.0
Declared duplicate reaction...			
35. CO+OH=CO2+H	8.80E+05	1.8	954.0
Declared duplicate reaction...			
36. CO+OH=HOCO	6.00E+26	-5.6	2881.0

REACTIONS CONSIDERED	A	β	E
37. HOCO=CO2+H	3.50E+56	-15.0	46500.0
Declared duplicate reaction...			
38. HOCO=CO2+H	2.50E+69	-18.0	60000.0
Declared duplicate reaction...			
39. HOCO+OH=CO2+H2O	4.60E+12	0.0	-89.0
Declared duplicate reaction...			
40. HOCO+OH=CO2+H2O	9.50E+06	2.0	-89.0
Declared duplicate reaction...			
41. HOCO+O2=CO2+HO2	9.90E+11	0.0	0.0

CH_2O subset

42. CH2O(+M)=HCO+H(+M)	8.00E+15	0.0	87726.0
Low pressure limit:	0.37340E+16	0.00000E+00	0.73479E+05
43. CH2O(+M)=CO+H2(+M)	3.70E+13	0.0	71969.0
Low pressure limit:	0.56610E+16	0.00000E+00	0.65849E+05
44. CH2O+H=HCO+H2	4.10E+08	1.5	2444.0
45. CH2O+O=HCO+OH	4.20E+11	0.6	2760.0
46. CH2O+O2=HCO+HO2	2.40E+05	2.5	36461.0
47. CH2O+OH=HCO+H2O	7.80E+07	1.6	-1055.0
48. CH2O+HO2=HCO+H2O2	4.10E+04	2.5	10206.0
49. CH2O+CH3=HCO+CH4	3.20E+01	3.4	4310.0
50. HCO=H+CO	9.90E+11	-0.9	16755.0
51. HCO+H=CO+H2	1.10E+14	0.0	0.0
52. HCO+O=CO+OH	3.00E+13	0.0	0.0
53. HCO+O=CO2+H	3.00E+13	0.0	0.0
54. HCO+OH=CO+H2O	1.10E+14	0.0	0.0
55. HCO+O2=CO+HO2	3.40E+12	0.0	0.0
56. HCO+HO2=CO2+OH+H	3.00E+13	0.0	0.0
57. HCO+HCO=CO+CH2O	2.70E+13	0.0	0.0

CH_4 subset

58. CH3+H(+M)=CH4(+M)	2.10E+14	0.0	0.0	
Low pressure limit:	0.64670E+24	-0.18000E+01	0.00000E+00	
TROE centering:	0.63760E+00	0.10000E-29	0.32300E+04	0.10000E+31
CH4 Enhanced by	1.900E+00			
59. CH4+H=CH3+H2	4.10E+03	3.2	8755.0	
60. CH4+O=CH3+OH	4.40E+05	2.5	6577.0	
61. CH4+OH=CH3+H2O	1.00E+06	2.2	2506.0	
62. CH4+HO2=CH3+H2O2	4.70E+04	2.5	21000.0	
63. CH4+CH2=CH3+CH3	4.30E+12	0.0	10030.0	
64. CH4+CH2(S)=CH3+CH3	4.30E+13	0.0	0.0	
65. CH2+H(+M)=CH3(+M)	3.80E+16	-0.8	0.0	
Low pressure limit:	0.48000E+28	-0.31400E+01	0.12300E+04	
TROE centering:	0.68000E+00	0.78000E+02	0.19950E+04	0.55900E+04
N2 Enhanced by	1.000E+00			
H2O Enhanced by	6.000E+00			
AR Enhanced by	7.000E-01			
66. CH3+H=CH2+H2	9.00E+13	0.0	15100.0	

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
67. CH2(S)+H2=CH3+H	7.20E+13	0.0	0.0	
68. CH3+O=CH2O+H	6.90E+13	0.0	0.0	
69. CH3+O=H2+CO+H	1.50E+13	0.0	0.0	
70. CH3+OH=CH2+H2O	1.10E+03	3.0	2780.0	
71. CH2(S)+H2O=CH3+OH	3.00E+15	-0.6	0.0	
72. CH3+HO2=CH4+O2	1.80E+03	2.8	-3730.0	
73. CH3+HO2=CH3O+OH	2.00E+13	0.0	1075.0	
74. CH3+O2=CH3O+O	7.50E+12	0.0	28297.0	
75. CH3+O2=CH2O+OH	1.90E+11	0.0	9842.0	
76. CH3+O2=CH3OO	5.00E+22	-3.9	2000.0	
77. CH3+HCO=CH4+CO	2.80E+13	0.0	0.0	
78. CH2+M=CH+H+M	5.60E+15	0.0	89000.0	
79. CH2+M=C+H2+M	5.80E+12	0.5	68500.0	
80. CH2+H=CH+H2	1.00E+18	-1.6	0.0	
81. CH2+O=CO+H+H	5.00E+13	0.0	0.0	
82. CH2+O=CO+H2	3.00E+13	0.0	0.0	
83. CH2+OH=CH2O+H	3.00E+13	0.0	0.0	
84. CH2+OH=CH+H2O	1.10E+07	2.0	3000.0	
85. CH2+O2=CO+H2O	2.20E+22	-3.3	2867.0	
86. CH2+O2=CO2+H+H	3.30E+21	-3.3	2867.0	
87. CH2+O2=CH2O+O	3.30E+21	-3.3	2867.0	
88. CH2+O2=CO2+H2	2.60E+21	-3.3	2867.0	
89. CH2+O2=CO+OH+H	1.60E+21	-3.3	2867.0	
90. CH2+CO2=CO+CH2O	1.00E+11	0.0	1000.0	
91. CH2(S)+M=CH2+M	1.00E+13	0.0	0.0	
N2 Enhanced by	0.000E+00			
H2O Enhanced by	0.000E+00			
AR Enhanced by	0.000E+00			
H Enhanced by	0.000E+00			
92. CH2(S)+N2=CH2+N2	1.30E+13	0.0	430.0	
93. CH2(S)+AR=CH2+AR	1.50E+13	0.0	884.0	
94. CH2(S)+H=CH2+H	2.00E+14	0.0	0.0	
95. CH2(S)+H=CH+H2	3.00E+13	0.0	0.0	
96. CH2(S)+O=CO+2H	3.00E+13	0.0	0.0	
97. CH2(S)+OH=CH2O+H	3.00E+13	0.0	0.0	
98. CH2(S)+O2=CO+OH+H	7.00E+13	0.0	0.0	
99. CH2(S)+H2O=CH2+H2O	3.00E+13	0.0	0.0	
100. CH2(S)+CO2=CH2O+CO	1.10E+13	0.0	0.0	
101. CH+H=C+H2	1.50E+14	0.0	0.0	
102. CH+O=CO+H	5.70E+13	0.0	0.0	
103. CH+OH=HCO+H	3.00E+13	0.0	0.0	
104. CH+OH=C+H2O	4.00E+07	2.0	3000.0	
105. CH+O2=HCO+O	3.30E+13	0.0	0.0	
106. CH+H2O=CH2O+H	5.70E+12	0.0	-755.0	
107. CH+CO2=HCO+CO	8.80E+06	1.8	-1040.0	
108. C+OH=CO+H	5.00E+13	0.0	0.0	
109. C+O2=CO+O	2.00E+13	0.0	0.0	

REACTIONS CONSIDERED	A	β	E

Different reactions between low and high pressure mechanisms

110. CH3OH(+M)=CH2OH+H(+M)	2.70E+16	-0.1	98940.0
Low pressure limit:	0.23400E+41	-0.63300E+01	0.10310E+06
TROE centering:	0.77300E+00	0.69300E+03	0.53330E+04
111. CH3OH+H=CH2OH+H2	1.70E+07	2.1	4868.0
112. CH3OH+H=CH3O+H2	4.20E+06	2.1	4868.0
113. CH3OH+O=CH2OH+OH	3.90E+05	2.5	3080.0
114. CH3OH+OH=CH2OH+H2O	1.40E+06	2.0	-3510.0
115. CH3OH+OH=CH3O+H2O	6.30E+06	2.0	6300.0
116. CH3OH+HO2=CH2OH+H2O2	1.00E+12	0.0	10040.0
117. CH3OH+O2=CH2OH+HO2	2.10E+13	0.0	44900.0
118. CH3OH+CH3=CH2OH+CH4	3.20E+01	3.2	7170.0
119. CH3OH+CH3=CH3O+CH4	1.50E+01	3.1	6940.0
120. CH2O+H(+M)=CH3O(+M)	5.40E+11	0.5	2600.0
Low pressure limit:	0.15400E+31	-0.48000E+01	0.55600E+04
TROE centering:	0.75800E+00	0.94000E+02	0.15550E+04 0.42000E+04
N2 Enhanced by	1.430E+00		
H2O Enhanced by	8.580E+00		
121. CH3O+H=CH2O+H2	2.00E+13	0.0	0.0
122. CH3O+O=CH2O+OH	1.00E+13	0.0	0.0
123. CH3O+OH=CH2O+H2O	1.00E+13	0.0	0.0
124. CH3O+O2=CH2O+HO2	6.30E+10	0.0	2600.0
*125. CH3O+HO2=CH2O+H2O2	3.00E+11	0.0	0.0
126. CH3O+CO=CH3+CO2	1.60E+13	0.0	11800.0
*127. CH3O+CH3=CH2O+CH4	2.40E+13	0.0	0.0
128. CH3O+CH2O=CH3OH+HCO	1.00E+11	0.0	3000.0
**129. CH3O+HCO=CH3OH+CO	9.00E+13	0.0	0.0
**130. CH3O+CH3OH=CH3OH+CH2OH	3.00E+11	0.0	4100.0
*131. CH3O+CH3O=CH3OH+CH2O	6.00E+13	0.0	0.0
132. H+CH2O(+M)=CH2OH(+M)	5.40E+11	0.5	3600.0
Low pressure limit:	0.91000E+32	-0.48200E+01	0.65300E+04
TROE centering:	0.71870E+00	0.10300E+03	0.12910E+04 0.41600E+04
N2 Enhanced by	1.430E+00		
H2O Enhanced by	8.580E+00		
CO Enhanced by	2.000E+00		
CO2 Enhanced by	3.000E+00		
H2 Enhanced by	2.000E+00		
133. CH2OH+H=CH2O+H2	4.80E+13	0.0	0.0
134. CH2OH+O=CH2O+OH	6.50E+13	0.0	-700.0
135. CH2OH+OH=CH2O+H2O	1.00E+13	0.0	0.0
136. CH2OH+O2=CH2O+HO2	1.60E+15	-1.0	0.0
Declared duplicate reaction...			
137. CH2OH+O2=CH2O+HO2	7.20E+13	0.0	3577.0
Declared duplicate reaction...			
138. CH2OH+HO2=CH2O+H2O2	3.60E+13	0.0	0.0
139. CH2OH+HCO=CH3OH+CO	1.20E+14	0.0	0.0
140. CH2OH+HCO=CH2O+CH2O	1.80E+14	0.0	0.0
141. CH2OH+CH2O=CH3OH+HCO	5.50E+03	2.8	5860.0
142. CH2OH+CH2OH=CH3OH+CH2O	5.00E+12	0.0	0.0
*143. CH2OH+CH3O=CH3OH+CH2O	2.40E+12	0.0	0.0

REACTIONS CONSIDERED	A	β	E
End of differences			
144. CH3OOH=CH3O+OH	2.00E+35	-6.7	47450.0
145. CH3OOH+H=CH2OOH+H2	5.40E+10	0.0	1860.0
146. CH3OOH+H=CH3OO+H2	5.40E+10	0.0	1860.0
147. CH3OOH+H=CH3O+H2O	1.20E+10	0.0	1860.0
148. CH3OOH+O=CH2OOH+OH	1.60E+13	0.0	4750.0
149. CH3OOH+O=CH3OO+OH	8.70E+12	0.0	4750.0
150. CH3OOH+OH=CH3OO+H2O	1.10E+12	0.0	-437.0
151. CH3OOH+OH=CH2OOH+H2O	7.20E+11	0.0	-258.0
152. CH3OOH+HO2=CH3OO+H2O2	4.10E+04	2.5	10206.0
153. CH3OO+H=CH3O+OH	1.00E+14	0.0	0.0
154. CH3OO+O=CH3O+O2	1.60E+13	0.0	-445.0
155. CH3OO+OH=CH3OH+O2	2.00E+15	-0.6	0.0
156. CH3OO+OH=CH3O+HO2	4.00E+11	0.6	0.0
157. CH3OO+HO2=CH3OOH+O2	2.50E+11	0.0	-1490.0
158. CH3OO+CH3=CH3O+CH3O	5.10E+12	0.0	-1411.0
159. CH3OO+CH4=CH3OOH+CH3	4.70E+04	2.5	21000.0
160. CH3OO+HCO=CH3O+H+CO2	3.00E+13	0.0	0.0
161. CH3OO+CO=CH3O+CO2	1.60E+05	2.2	17940.0
162. CH3OO+CH2O=CH3OOH+HCO	4.10E+04	2.5	10206.0
163. CH3OO+CH3O=CH2O+CH3OOH	3.00E+11	0.0	0.0
164.CH3OO+CH3OH=CH3OOH+CH2OH	4.00E+13	0.0	19400.0
165. CH3OO+CH3OO=CH3O+CH3O+O2	1.10E+18	-2.4	1800.0
Declared duplicate reaction...			
166. CH3OO+CH3OO=CH3O+CH3O+O2	7.00E+10	0.0	800.0
Declared duplicate reaction...			
167.CH3OO+CH3OO=CH3OH+CH2O+O2	2.00E+11	-0.6	-1600.0
168. CH2OOH=>CH2O+OH	2.40E+12	-0.9	1567.0

*Reactions with the same parametrization in low and high pressure mechanisms
**Only low pressure reactions

NOTE: A units mole-cm-sec-K, E units cal/mole

Original high pressure methanol oxidation mechanism and kinetic data, without NO_x chemistry, since the reaction 110 where the differences start:

REACTIONS CONSIDERED	A	β	E
**110. CH3OH(+M)=CH3+OH(+M)	2.10E+18	-0.6	92540.0
Low pressure limit:	0.26000E+50	-0.88000E+01	0.10150E+06
TROE centering:	0.76560E+00	0.19100E+04	0.59510E+02 0.93740E+04
111. CH3OH+H=CH2OH+H2	2.90E+09	1.2	4491.0
112. CH3OH+H=CH3O+H2	5.10E+08	1.2	4491.0
113. CH3OH+O=CH2OH+OH	2.10E+13	0.0	5305.0
**114. CH3OH+O=CH3O+OH	3.70E+12	0.0	5305.0
115. CH3OH+OH=CH2OH+H2O	1.50E+08	1.4	113.0
116. CH3OH+OH=CH3O+H2O	2.70E+07	1.4	113.0
117. CH3OH+HO2=CH2OH+H2O2	3.98E+13	0.0	19419.0
118. CH3OH+O2=CH2OH+HO2	6.00E+13	0.0	46600.0
**119. CH3OH+O2=CH3O+HO2	6.00E+13	0.0	54800.0
120. CH2OH(+M)=CH2O+H(+M)	2.80E+14	-0.7	32820.0
Low pressure limit:	0.60100E+34	-0.53900E+01	0.36200E+05
TROE centering:	0.96000E+00	0.67600E+02	0.18550E+04 0.75430E+04
H2 Enhanced by	2.000E+00		
H2O Enhanced by	5.000E+00		
CO Enhanced by	2.000E+00		
CO2 Enhanced by	3.000E+00		
121. CH2OH+H=CH2O+H2	1.40E+13	0.0	0.0
**122. CH2OH+H=CH3+OH	6.00E+12	0.0	0.0
123. CH2OH+H(+M)=CH3OH(+M)	4.30E+15	-0.8	0.0
Low pressure limit:	0.38440E+38	-0.62100E+01	0.13330E+04
TROE centering:	0.25000E+00	0.21000E+03	0.14340E+04 0.10000E+31
124. CH2OH+O=CH2O+OH	6.60E+13	0.0	-693.0
125. CH2OH+OH=CH2O+H2O	2.40E+13	0.0	0.0
126. CH2OH+HO2=CH2O+H2O2	1.20E+13	0.0	0.0
127. CH2OH+O2=CH2O+HO2	7.20E+13	0.0	3736.0
Declared duplicate reaction...			
128. CH2OH+O2=CH2O+HO2	2.90E+16	-1.5	0.0
Declared duplicate reaction...			
129. CH2OH+HCO=CH3OH+CO	1.00E+13	0.0	0.0
130. CH2OH+HCO=CH2O+CH2O	1.50E+13	0.0	0.0
131. CH2OH+CH2O=CH3OH+HCO	5.50E+03	2.8	5862.0
132. CH2OH+CH2OH=CH3OH+CH2O	4.80E+12	0.0	0.0
*133. CH2OH+CH3O=CH3OH+CH2O	2.40E+12	0.0	0.0
134. CH2OH+CH4=CH3OH+CH3	2.20E+01	3.1	16227.0
135. CH3O(+M)=CH2O+H(+M)	6.80E+13	0.0	26154.0
Low pressure limit:	0.18670E+26	-0.30000E+01	0.24291E+05
TROE centering:	0.50000E+00	0.10000E+04	0.20000E+04
136. CH3O+H=CH2O+H2	5.30E+13	0.0	745.0
**137. CH3O+H=CH3+OH	4.60E+12	0.0	745.0

REACTIONS CONSIDERED	A	β	E
**138. CH3O+H(+M)=CH3OH(+M)	2.40E+12	0.5	50.0
Low pressure limit:	0.46600E+42	-0.74400E+01	0.14080E+05
TROE centering:	0.70000E+00	0.10000E+03	0.90000E+05 0.10000E+05
N2 Enhanced by	1.000E+00		
H2 Enhanced by	2.000E+00		
H2O Enhanced by	6.000E+00		
CH4 Enhanced by	2.000E+00		
CO Enhanced by	1.500E+00		
CO2 Enhanced by	2.000E+00		
139. CH3O+O=CH2O+OH	3.80E+12	0.0	0.0
140. CH3O+OH=CH2O+H2O	1.80E+13	0.0	0.0
*141. CH3O+HO2=CH2O+H2O2	3.00E+11	0.0	0.0
142. CH3O+O2=CH2O+HO2	2.20E+10	0.0	1749.0
143. CH3O+CO=CH3+CO2	9.50E+25	-4.9	9080.0
*144. CH3O+CH3=CH2O+CH4	2.40E+13	0.0	0.0
145. CH3O+CH4=CH3OH+CH3	1.30E+14	0.0	15073.0
146. CH3O+CH2O=CH3OH+HCO	1.00E+11	0.0	2981.0
*147. CH3O+CH3O=CH3OH+CH2O	6.00E+13	0.0	0.0

End of differences

148. CH3OOH=CH3O+OH	2.00E+35	-6.7	47450.0
149. CH3OOH+H=CH2OOH+H2	5.40E+10	0.0	1860.0
150. CH3OOH+H=CH3OO+H2	5.40E+10	0.0	1860.0
151. CH3OOH+H=CH3O+H2O	1.20E+10	0.0	1860.0
152. CH3OOH+O=CH2OOH+OH	1.60E+13	0.0	4750.0
153. CH3OOH+O=CH3OO+OH	8.70E+12	0.0	4750.0
154. CH3OOH+OH=CH3OO+H2O	1.10E+12	0.0	-437.0
155. CH3OOH+OH=CH2OOH+H2O	7.20E+11	0.0	-258.0
156. CH3OOH+HO2=CH3OO+H2O2	4.10E+04	2.5	10206.0
157. CH3OO+H=CH3O+OH	1.00E+14	0.0	0.0
158. CH3OO+O=CH3O+O2	1.60E+13	0.0	-445.0
159. CH3OO+OH=CH3OH+O2	2.00E+15	-0.6	0.0
160. CH3OO+OH=CH3O+HO2	4.00E+11	0.6	0.0
161. CH3OO+HO2=CH3OOH+O2	2.50E+11	0.0	-1490.0
162. CH3OO+CH3=CH3O+CH3O	5.10E+12	0.0	-1411.0
163. CH3OO+CH4=CH3OOH+CH3	4.70E+04	2.5	21000.0
164. CH3OO+HCO=CH3O+H+CO2	3.00E+13	0.0	0.0
165. CH3OO+CO=CH3O+CO2	1.60E+05	2.2	17940.0
166. CH3OO+CH2O=CH3OOH+HCO	4.10E+04	2.5	10206.0
167. CH3OO+CH3O=CH2O+CH3OOH	3.00E+11	0.0	0.0
168.CH3OO+CH3OH=CH3OOH+CH2OH	4.00E+13	0.0	19400.0
169. CH3OO+CH3OO=CH3O+CH3O+O2	1.10E+18	-2.4	1800.0
Declared duplicate reaction...			
170. CH3OO+CH3OO=CH3O+CH3O+O2	7.00E+10	0.0	800.0
Declared duplicate reaction...			
171.CH3OO+CH3OO=CH3OH+CH2O+O2	2.00E+11	-0.6	-1600.0
172. CH2OOH=>CH2O+OH	2.40E+12	-0.9	1567.0

*Reactions with the same parametrization in low and high pressure mechanisms

**Only high pressure reactions

APPENDIX B. Merged methanol oxidation mechanism

Merged methanol oxidation mechanism, kinetic data and uncertainty limits of each reaction:

SPECIES CONSIDERED

1. CH3OH	10. HO2	19. CH3O
2. CO	11. H2O	20. CH2OH
3. CO2	12. H2O2	21. CH2O
4. CH4	13. HOCO	22. HCO
5. H	14. CH3	23. CH3OOH
6. O	15. CH2	24. CH3OO
7. OH	16. CH2(S)	25. CH2OOH
8. H2	17. CH	26. AR
9. O2	18. C	27. N2

REACTIONS CONSIDERED		A	β	E	Δlog(*k*)
1. H+O2=O+OH		3.60E+15	-0.4	16600.0	0.2
2. H+H+M=H2+M		7.00E+17	-1.0	0.0	0.5
N2	Enhanced by	0.000E+00			
H2O	Enhanced by	0.000E+00			
H2	Enhanced by	0.000E+00			
3. H+H+N2=H2+N2		5.40E+18	-1.3	0.0	1.0
4. H+H+H2=H2+H2		1.00E+17	-0.6	0.0	0.5
5. H+H+H2O=H2+H2O		1.00E+19	-1.0	0.0	1.0
6. H+O+M=OH+M		6.20E+16	-0.6	0.0	1.0
H2O	Enhanced by	5.000E+00			
7. H+O2(+M)=HO2(+M)		1.50E+12	0.6	0.0	1.0
Low pressure limit:		0.35000E+17	-0.41000E+00	-0.11160E+04	
TROE centering:		0.50000E+00	0.10000E-29	0.10000E+31	
N2	Enhanced by	0.000E+00			
AR	Enhanced by	0.000E+00			
H2O	Enhanced by	1.100E+01			
H2	Enhanced by	2.000E+00			
O2	Enhanced by	7.800E-01			
8. H+O2(+AR)=HO2(+AR)		1.50E+12	0.6	0.0	0.2
Low pressure limit:		0.90400E+20	-0.15000E+01	0.49000E+03	
TROE centering:		0.50000E+00	0.10000E-29	0.10000E+31	
9. H+O2(+N2)=HO2(+N2)		1.50E+12	0.6	0.0	0.2
Low pressure limit:		0.63700E+21	-0.17200E+01	0.52000E+03	
TROE centering:		0.80000E+00	0.10000E-29	0.10000E+31	
10. O+O+M=O2+M		1.90E+13	0.0	-1788.0	0.5
N2	Enhanced by	1.500E+00			
O2	Enhanced by	1.500E+00			
H2O	Enhanced by	1.000E+01			
11. O+H2=OH+H		3.80E+12	0.0	7948.0	0.2
Declared duplicate reaction...					
12. O+H2=OH+H		8.80E+14	0.0	19175.0	0.2
Declared duplicate reaction...					
13. OH+OH=O+H2O		4.30E+03	2.7	-1822.0	0.5

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
14. OH+H+M=H2O+M	4.50E+22	-2.0	0.0	0.5
AR Enhanced by 3.800E-01				
H2 Enhanced by 7.300E-01				
H2O Enhanced by 1.200E+01				
15. OH+H2=H+H2O	2.10E+08	1.5	3449.0	0.3
16. H2+O2=HO2+H	7.40E+05	2.4	53502.0	0.9
17. HO2+H=OH+OH	8.40E+13	0.0	400.0	0.3
18. HO2+H=H2O+O	1.40E+12	0.0	0.0	0.5
19. HO2+O=OH+O2	1.60E+13	0.0	-445.0	0.5
20. HO2+OH=H2O+O2	2.89E+13	0.0	-497.0	1.0
21. HO2+HO2=H2O2+O2	1.90E+11	0.0	-1408.0	0.5
Declared duplicate reaction...				
22. HO2+HO2=H2O2+O2	1.00E+14	0.0	11034.0	0.5
Declared duplicate reaction...				
23. H2O2(+M)=OH+OH(+M)	4.00E+11	0.0	37137.0	0.9
Low pressure limit:	0.22910E+17	0.00000E+00	0.43638E+05	
TROE centering:	0.50000E+00	0.10000E-29	0.10000E+31	0.10000E+31
H2O Enhanced by 1.200E+01				
H2 Enhanced by 2.500E+00				
AR Enhanced by 6.400E-01				
24. H2O2+H=H2O+OH	1.00E+13	0.0	3580.0	0.3
25. H2O2+H=HO2+H2	1.70E+12	0.0	3760.0	0.5
26. H2O2+O=HO2+OH	9.60E+06	2.0	3970.0	0.3
27. H2O2+OH=H2O+HO2	1.90E+12	0.0	427.0	0.5
Declared duplicate reaction...				
28. H2O2+OH=H2O+HO2	1.60E+18	0.0	29410.0	0.5
Declared duplicate reaction...				
29. CO+O(+M)=CO2(+M)	1.80E+10	0.0	2384.0	1.0
Low pressure limit:	0.13500E+25	-0.27900E+01	0.41910E+04	
TROE centering:	0.10000E+01	0.10000E-29	0.10000E+31	0.10000E+31
H2 Enhanced by 2.500E+00				
H2O Enhanced by 1.200E+01				
CO Enhanced by 1.900E+00				
CO2 Enhanced by 3.800E+00				
30. CO+O2=CO2+O	4.70E+12	0.0	60500.0	4.0
31. CO+HO2=CO2+OH	1.60E+05	2.2	17943.0	1.2
32. CO+OH=CO2+H	8.00E+10	0.0	0.0	0.7
Declared duplicate reaction...				
33. CO+OH=CO2+H	8.80E+05	1.8	954.0	0.7
Declared duplicate reaction...				
34. CO+OH=HOCO	6.00E+26	-5.6	2881.0	2.0
35. HOCO=CO2+H	3.50E+56	-15.0	46500.0	1.0
Declared duplicate reaction...				
36. HOCO=CO2+H	2.50E+69	-18.0	60000.0	1.0
Declared duplicate reaction...				
37. HOCO+OH=CO2+H2O	4.60E+12	0.0	-89.0	0.6
Declared duplicate reaction...				
38. HOCO+OH=CO2+H2O	9.50E+06	2.0	-89.0	0.6
Declared duplicate reaction...				
39. HOCO+O2=CO2+HO2	9.90E+11	0.0	0.0	0.2

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
40. CH2O(+M)=HCO+H(+M)	8.00E+15	0.0	87726.0	0.5
Low pressure limit:	0.37340E+16	0.00000E+00	0.73479E+05	
41. CH2O(+M)=CO+H2(+M)	3.70E+13	0.0	71969.0	2.0
Low pressure limit:	0.56610E+16	0.00000E+00	0.65849E+05	
42. CH2O+H=HCO+H2	4.10E+08	1.5	2444.0	0.5
43. CH2O+O=HCO+OH	4.20E+11	0.6	2760.0	0.5
44. CH2O+O2=HCO+HO2	2.40E+05	2.5	36461.0	0.7
45. CH2O+OH=HCO+H2O	7.80E+07	1.6	-1055.0	0.3
46. CH2O+HO2=HCO+H2O2	4.10E+04	2.5	10206.0	0.4
47. CH2O+CH3=HCO+CH4	3.20E+01	3.4	4310.0	0.4
48. HCO=H+CO	9.90E+11	-0.9	16755.0	1.0
49. HCO+H=CO+H2	1.10E+14	0.0	0.0	0.3
50. HCO+O=CO+OH	3.00E+13	0.0	0.0	0.3
51. HCO+O=CO2+H	3.00E+13	0.0	0.0	0.3
52. HCO+OH=CO+H2O	1.10E+14	0.0	0.0	0.3
53. HCO+O2=CO+HO2	3.40E+12	0.0	0.0	0.2
54. HCO+HO2=CO2+OH+H	3.00E+13	0.0	0.0	1.0
55. HCO+HCO=CO+CH2O	2.70E+13	0.0	0.0	0.2
56. CH3+H(+M)=CH4(+M)	2.10E+14	0.0	0.0	0.2
Low pressure limit:	0.64670E+24	-0.18000E+01	0.00000E+00	
TROE centering:	0.63760E+00	0.10000E-29	0.32300E+04	0.10000E+31
CH4 Enhanced by	1.900E+00			
57. CH4+H=CH3+H2	4.10E+03	3.2	8755.0	0.2
58. CH4+O=CH3+OH	4.40E+05	2.5	6577.0	0.3
59. CH4+OH=CH3+H2O	1.00E+06	2.2	2506.0	0.2
60. CH4+HO2=CH3+H2O2	4.70E+04	2.5	21000.0	0.2
61. CH4+CH2=CH3+CH3	4.30E+12	0.0	10030.0	0.2
62. CH4+CH2(S)=CH3+CH3	4.30E+13	0.0	0.0	0.3
63. CH2+H(+M)=CH3(+M)	3.80E+16	-0.8	0.0	1.0
Low pressure limit:	0.48000E+28	-0.31400E+01	0.12300E+04	
TROE centering:	0.68000E+00	0.78000E+02	0.19950E+04	0.55900E+04
N2 Enhanced by	1.000E+00			
H2O Enhanced by	6.000E+00			
AR Enhanced by	7.000E-01			
64. CH3+H=CH2+H2	9.00E+13	0.0	15100.0	0.3
65. CH2(S)+H2=CH3+H	7.20E+13	0.0	0.0	0.3
66. CH3+O=CH2O+H	6.90E+13	0.0	0.0	0.1
67. CH3+O=H2+CO+H	1.50E+13	0.0	0.0	0.1
68. CH3+OH=CH2+H2O	1.10E+03	3.0	2780.0	0.2
69. CH2(S)+H2O=CH3+OH	3.00E+15	-0.6	0.0	0.5
70. CH3+HO2=CH4+O2	1.80E+03	2.8	-3730.0	0.5
71. CH3+HO2=CH3O+OH	2.00E+13	0.0	1075.0	0.5
72. CH3+O2=CH3O+O	7.50E+12	0.0	28297.0	0.7
73. CH3+O2=CH2O+OH	1.90E+11	0.0	9842.0	0.5
74. CH3+O2=CH3OO	5.00E+22	-3.9	2000.0	1.5
75. CH3+HCO=CH4+CO	2.80E+13	0.0	0.0	0.7
76. CH2+M=CH+H+M	5.60E+15	0.0	89000.0	0.7
77. CH2+M=C+H2+M	5.80E+12	0.5	68500.0	1.2
78. CH2+H=CH+H2	1.00E+18	-1.6	0.0	1.0
79. CH2+O=CO+H+H	5.00E+13	0.0	0.0	0.3
80. CH2+O=CO+H2	3.00E+13	0.0	0.0	0.3

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
81. CH2+OH=CH2O+H	3.00E+13	0.0	0.0	0.4
82. CH2+OH=CH+H2O	1.10E+07	2.0	3000.0	2.0
83. CH2+O2=CO+H2O	2.20E+22	-3.3	2867.0	0.7
84. CH2+O2=CO2+H+H	3.30E+21	-3.3	2867.0	0.7
85. CH2+O2=CH2O+O	3.30E+21	-3.3	2867.0	0.7
86. CH2+O2=CO2+H2	2.60E+21	-3.3	2867.0	0.7
87. CH2+O2=CO+OH+H	1.60E+21	-3.3	2867.0	0.7
88. CH2+CO2=CO+CH2O	1.00E+11	0.0	1000.0	0.5
89. CH2(S)+M=CH2+M	1.00E+13	0.0	0.0	0.3
N2 Enhanced by	0.000E+00			
H2O Enhanced by	0.000E+00			
AR Enhanced by	0.000E+00			
H Enhanced by	0.000E+00			
90. CH2(S)+N2=CH2+N2	1.30E+13	0.0	430.0	0.3
91. CH2(S)+AR=CH2+AR	1.50E+13	0.0	884.0	0.2
92. CH2(S)+H=CH2+H	2.00E+14	0.0	0.0	0.3
93. CH2(S)+H=CH+H2	3.00E+13	0.0	0.0	0.6
94. CH2(S)+O=CO+2H	3.00E+13	0.0	0.0	0.5
95. CH2(S)+OH=CH2O+H	3.00E+13	0.0	0.0	0.4
96. CH2(S)+O2=CO+OH+H	7.00E+13	0.0	0.0	0.5
97. CH2(S)+H2O=CH2+H2O	3.00E+13	0.0	0.0	0.3
98. CH2(S)+CO2=CH2O+CO	1.10E+13	0.0	0.0	0.3
99. CH+H=C+H2	1.50E+14	0.0	0.0	0.6
100. CH+O=CO+H	5.70E+13	0.0	0.0	0.5
101. CH+OH=HCO+H	3.00E+13	0.0	0.0	1.0
102. CH+OH=C+H2O	4.00E+07	2.0	3000.0	1.0
103. CH+O2=HCO+O	3.30E+13	0.0	0.0	0.5
104. CH+H2O=CH2O+H	5.70E+12	0.0	-755.0	1.0
105. CH+CO2=HCO+CO	8.80E+06	1.8	-1040.0	0.3
106. C+OH=CO+H	5.00E+13	0.0	0.0	1.0
107. C+O2=CO+O	2.00E+13	0.0	0.0	0.4
108. CH3OH(+M)=CH3+OH(+M)	2.10E+18	-0.6	92540.0	2.0
Low pressure limit:	0.26000E+50	-0.88000E+01	0.10150E+06	
TROE centering:	0.76560E+00	0.19100E+04	0.59510E+02	0.93740E+04
109. CH3OH+O=CH3O+OH	3.70E+12	0.0	5305.0	0.2
110. CH3OH+O2=CH3O+HO2	6.00E+13	0.0	54800.0	2.5
111. CH2OH+H=CH3+OH	6.00E+12	0.0	0.0	0.3
112. CH3O+H=CH3+OH	4.60E+12	0.0	745.0	0.6
113. CH3O+H(+M)=CH3OH(+M)	2.40E+12	0.5	50.0	1.0
Low pressure limit:	0.46600E+42	-0.74400E+01	0.14080E+05	
TROE centering:	0.70000E+00	0.10000E+03	0.90000E+05	0.10000E+05
N2 Enhanced by	1.000E+00			
H2 Enhanced by	2.000E+00			
H2O Enhanced by	6.000E+00			
CH4 Enhanced by	2.000E+00			
CO Enhanced by	1.500E+00			
CO2 Enhanced by	2.000E+00			
114. CH3O+HCO=CH3OH+CO	9.00E+13	0.0	0.0	0.3
115. CH3O+CH3OH=CH3OH+CH2OH	3.00E+11	0.0	4100.0	0.2
116. CH3OH+H=CH2OH+H2	2.20E+08	1.7	4680.0	0.4
117. CH3OH+H=CH3O+H2	4.60E+07	1.7	4680.0	0.4

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
118. CH3OH+O=CH2OH+OH	2.90E+09	1.2	4193.0	0.2
119. CH3OH+OH=CH2OH+H2O	1.40E+07	1.7	-1699.0	0.5
120. CH3OH+OH=CH3O+H2O	1.30E+07	1.7	3207.0	0.3
121. CH3OH+HO2=CH2OH+H2O2	6.30E+12	0.0	14730.0	1.4
122. CH3OH+O2=CH2OH+HO2	3.50E+13	0.0	45750.0	0.2
123. CH2OH+H=CH2O+H2	2.60E+13	0.0	0.0	0.3
124. CH2OH+O=CH2O+OH	6.50E+13	0.0	-697.0	0.4
125. CH2OH+OH=CH2O+H2O	1.50E+13	0.0	0.0	0.2
126. CH2OH+O2=CH2O+HO2	3.40E+14	-0.5	1868.0	0.4
Declared duplicate reaction...				
127. CH2OH+O2=CH2O+HO2	1.40E+15	-0.8	1789.0	0.4
Declared duplicate reaction...				
128. CH2OH+HO2=CH2O+H2O2	2.10E+13	0.0	0.0	0.5
129. CH2OH+HCO=CH3OH+CO	3.50E+13	0.0	0.0	0.6
130. CH2OH+HCO=CH2O+CH2O	5.20E+13	0.0	0.0	0.6
131. CH2OH+CH2O=CH3OH+HCO	5.50E+03	2.8	5861.0	0.2
132. CH2OH+CH2OH=CH3OH+CH2O	4.90E+12	0.0	0.0	0.5
133. CH3O+H=CH2O+H2	3.30E+13	0.0	373.0	0.1
134. CH3O+O=CH2O+OH	6.20E+12	0.0	0.0	0.3
135. CH3O+OH=CH2O+H2O	1.30E+13	0.0	0.0	0.2
136. CH3O+O2=CH2O+HO2	3.70E+10	0.0	2175.0	0.3
137. CH3O+CO=CH3+CO2	3.90E+19	-2.5	10440.0	2.0
138. CH3O+CH2O=CH3OH+HCO	1.00E+11	0.0	2991.0	0.2
139. CH2OH(+M)=CH2O+H(+M)	1.20E+13	-0.1	18210.0	0.5
Low pressure limit:	0.60100E+34	-0.53900E+01	0.36200E+05	
TROE centering:	0.96000E+00	0.67600E+02	0.18550E+04	0.75430E+04
H2 Enhanced by	2.000E+00			
H2O Enhanced by	5.000E+00			
CO Enhanced by	2.000E+00			
CO2 Enhanced by	3.000E+00			
140. CH2OH+CH4=CH3OH+CH3	2.70E+01	3.1	11699.0	1.5
141. CH2OH+H(+M)=CH3OH(+M)	1.10E+16	-0.4	49470.0	1.0
Low pressure limit:	0.38440E+38	-0.62100E+01	0.13330E+04	
TROE centering:	0.25000E+00	0.21000E+03	0.14340E+04	0.10000E+31
142. CH3O(+M)=CH2O+H(+M)	6.10E+12	0.2	14377.0	0.5
Low pressure limit:	0.18670E+26	-0.30000E+01	0.24291E+05	
TROE centering:	0.50000E+00	0.10000E+04	0.20000E+04	
143. CH3O+CH4=CH3OH+CH3	4.40E+07	1.6	11007.0	0.9
144. CH2OH+CH3O=CH3OH+CH2O	2.40E+12	0.0	0.0	1.0
145. CH3O+HO2=CH2O+H2O2	3.00E+11	0.0	0.0	0.2
146. CH3O+CH3=CH2O+CH4	2.40E+13	0.0	0.0	0.2
147. CH3O+CH3O=CH3OH+CH2O	6.00E+13	0.0	0.0	0.2
148. CH3OOH=CH3O+OH	2.00E+35	-6.7	47450.0	1.0
149. CH3OOH+H=CH2OOH+H2	5.40E+10	0.0	1860.0	1.0
150. CH3OOH+H=CH3OO+H2	5.40E+10	0.0	1860.0	1.0
151. CH3OOH+H=CH3O+H2O	1.20E+10	0.0	1860.0	1.0
152. CH3OOH+O=CH2OOH+OH	1.60E+13	0.0	4750.0	0.3
153. CH3OOH+O=CH3OO+OH	8.70E+12	0.0	4750.0	0.3
154. CH3OOH+OH=CH3OO+H2O	1.10E+12	0.0	-437.0	0.3
155. CH3OOH+OH=CH2OOH+H2O	7.20E+11	0.0	-258.0	0.4
156. CH3OOH+HO2=CH3OO+H2O2	4.10E+04	2.5	10206.0	1.0

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
157. CH3OO+H=CH3O+OH	1.00E+14	0.0	0.0	0.2
158. CH3OO+O=CH3O+O2	1.60E+13	0.0	-445.0	0.4
159. CH3OO+OH=CH3OH+O2	2.00E+15	-0.6	0.0	0.4
160. CH3OO+OH=CH3O+HO2	4.00E+11	0.6	0.0	1.0
161. CH3OO+HO2=CH3OOH+O2	2.50E+11	0.0	-1490.0	0.6
162. CH3OO+CH3=CH3O+CH3O	5.10E+12	0.0	-1411.0	0.5
163. CH3OO+CH4=CH3OOH+CH3	4.70E+04	2.5	21000.0	1.0
164. CH3OO+HCO=CH3O+H+CO2	3.00E+13	0.0	0.0	1.0
165. CH3OO+CO=CH3O+CO2	1.60E+05	2.2	17940.0	1.0
166. CH3OO+CH2O=CH3OOH+HCO	4.10E+04	2.5	10206.0	0.5
167. CH3OO+CH3O=CH2O+CH3OOH	3.00E+11	0.0	0.0	0.2
168.CH3OO+CH3OH=CH3OOH+CH2OH	4.00E+13	0.0	19400.0	0.5
169. CH3OO+CH3OO=CH3O+CH3O+O2	1.10E+18	-2.4	1800.0	4.0
Declared duplicate reaction...				
170. CH3OO+CH3OO=CH3O+CH3O+O2	7.00E+10	0.0	800.0	4.0
Declared duplicate reaction...				
171.CH3OO+CH3OO=CH3OH+CH2O+O2	2.00E+11	-0.6	-1600.0	1.0
172. CH2OOH=>CH2O+OH	2.40E+12	-0.9	1567.0	1.0

Low pressure reactions, kinetic data and uncertainty limits:

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
173. H+O2(+M)=HO2(+M)	0.35000E+17	-0.41000E+00	-0.11160E+04	1.0
174. H+O2(+AR)=HO2(+AR)	0.90400E+20	-0.15000E+01	0.49000E+03	0.2
175. H+O2(+N2)=HO2(+N2)	0.63700E+21	-0.17200E+01	0.52000E+03	0.2
176. H2O2(+M)=OH+OH(+M)	0.22910E+17	0.00000E+00	0.43638E+05	0.5
177. CO+O(+M)=CO2(+M)	0.13500E+25	-0.27900E+01	0.41910E+04	1.7
178. CH2O(+M)=HCO+H(+M)	0.37340E+16	0.00000E+00	0.73479E+05	1.8
179. CH2O(+M)=CO+H2(+M)	0.56610E+16	0.00000E+00	0.65849E+05	5.0
180. CH3+H(+M)=CH4(+M)	0.64670E+24	-0.18000E+01	0.00000E+00	0.2
181. CH2+H(+M)=CH3(+M)	0.48000E+28	-0.31400E+01	0.12300E+04	1.0
182. CH3OH(+M)=CH3+OH(+M)	0.26000E+50	-0.88000E+01	0.10150E+06	2.0
183. CH3O+H(+M)=CH3OH(+M)	0.46600E+42	-0.74400E+01	0.14080E+05	1.0
184. CH2OH(+M)=CH2O+H(+M)	0.60100E+34	-0.53900E+01	0.36200E+05	0.5
185. CH2OH+H(+M)=CH3OH(+M)	0.38440E+38	-0.62100E+01	0.13330E+04	1.0
186. CH3O(+M)=CH2O+H(+M)	0.18670E+26	-0.30000E+01	0.24291E+05	0.5

NOTE: A units mole-cm-sec-K, E units cal/mole

APPENDIX C. Calculations of the uncertainty limits

Most of the uncertainty limits of the mechanism reactions were easily calculated as we could see in Chapter 3. Mainly, Baulch Evaluated Database was used to obtain these limits. When the reaction parameters were not available in Baulch Database, the resource used was NIST Chemical Kinetic Database. In those cases, where there is not recommended values available, the uncertainty interval was assumed in the order of magnitude. At the same time, pressure dependent reactions require special attention.

Here, we explain in details how the uncertainty limits were calculated for the merged mechanism.

The temperature dependence of the rate of some reactions in the mechanism is described by two Arrhenius equations. In the merged mechanism there are 7 declared duplicated reactions (word DUPLICATE should be used in CHEMKIN format to indicate such reactions). As an example, Reactions 11 and 12 in Appendix B is detailed following:

O+H2=OH+H (R11, Appendix B)
O+H2=OH+H (R12, Appendix B)

The Arrhenius parameters of this reaction are the following:

$A_{11} = 3.80 \cdot 10^{12}$ cm^3 mol^{-1} s^{-1}, $\beta_{11} = 0$, $E_{11} = 7948$ cal mol^{-1}

$A_{12} = 8.80 \cdot 10^{14}$ cm^3 mol^{-1} s^{-1}, $\beta_{12} = 0$, $E_{12} = 19175$ cal mol^{-1}

Since there are two reactions available, the rate reaction is the sum of both, parameters of Reaction 11 and Reaction 12. The preferred values and reliability according Baulch Evaluated Data are:

> $k = [6.34 \cdot 10^{-12} \exp(-4000/T) + 1.46 \cdot 10^{-9} \exp(-9650/T)]$ *cm^3 molecule^{-1} s^{-1} over the range 298-3300 K.*
> $\Delta \log k = \pm 0.2$ *over the range 298-3300 K.*

The Arrhenius parameters calculated from these data:

> $A = 3.81858 \cdot 10^{12}$ *cm^3 mol^{-1} s^{-1},* $\beta = 0$, $E = 7943.508$ *cal mol^{-1}*
> $A = 8.79358 \cdot 10^{14}$ *cm^3 mol^{-1} s^{-1},* $\beta = 0$, $E = 19163.71$ *cal mol^{-1}*

Plotting the recommended values and its uncertainty together the values used in the merged methanol mechanism (Figure 1), it is possible to check if the value used in the methanol mechanism fall between the Baulch evaluation uncertainty limits over the whole temperature interval.

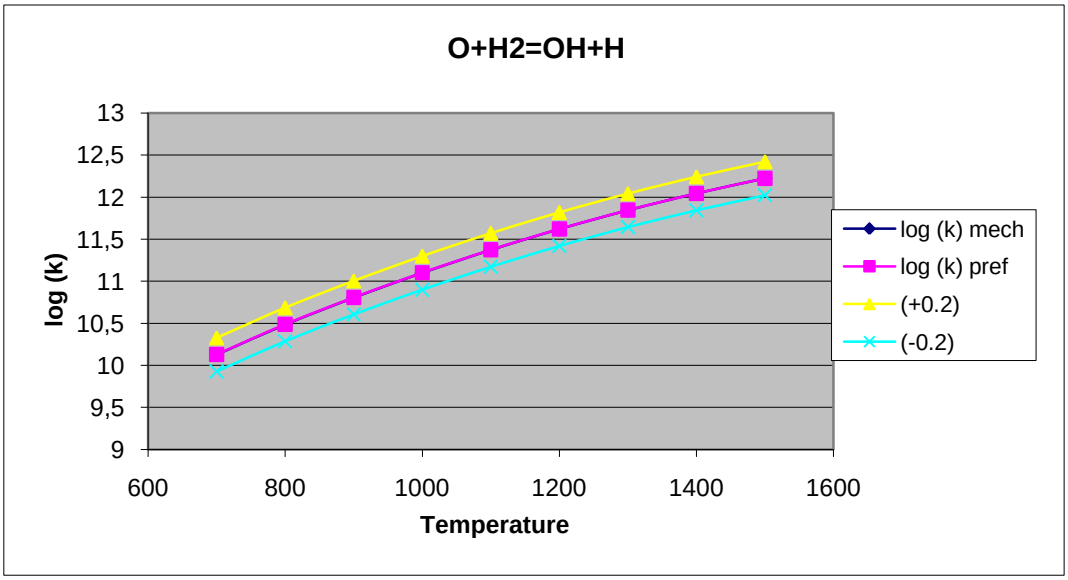


Figure 1. Temperature [K] vs. log (k[$cm^3mol^{-1}s^{-1}$]) of merged mechanism (diamonds), the Baulch preferred values (squares) and the uncertainty limits assigned to the merged mechanism values (triangles and crosses)

In this case, the rate coefficient in the merged mechanism and recommended by Baulch et al. are very similar all over the temperature range and fall between the uncertainty limits.

If the represented curve does not fall within the expected range, that range is extended to keep the two curves within the limits. Next example shows this situation, where the preferred error limits are very narrow and the uncertainty of the rate reaction should be increased. Reaction 119 is presented as an example:

CH3OH+OH=CH2OH+H2O (R119, Appendix B)

The Arrhenius parameters of this reaction are the following:

$A = 1.4 \cdot 10^7$ cm^3 mol^{-1} s^{-1}, $\beta = 1.7$, $E = -1699$ cal mol^{-1}

The preferred values and its reliability according Baulch Evaluation Data are:

$k = 1.03 \cdot 10^{-17}$ $T^{1.92}$ $exp(144/T)$ cm^3 $molecule^{-1}$ s^{-1} over the range 240-2000 K.
$\Delta log\ k$ = ± 0.1 at 300 K, rising to ± 0.2 at 240 K and to ± 0.3 at 2000 K.

The Arrhenius parameters calculated from this data:

$A = 5.27 \cdot 10^6$ cm^3 mol^{-1} s^{-1}, $\beta = 1.92$, $E = 285.9663$ cal mol^{-1}

In this work, temperature independent uncertainty limits were uses. Thus, the reliability was choose initially as ± *0.3* but, as Figure 2 show, this value was not enough to cover the reaction rate used in the merged mechanism over the whole temperature range. For this cause, the uncertainty was raised to until the preferred values fall between the limits.

In this case, if the reliability is increased until ± *0.5*, both rate parameters are in agreement with the uncertainty limits (Figure 3).

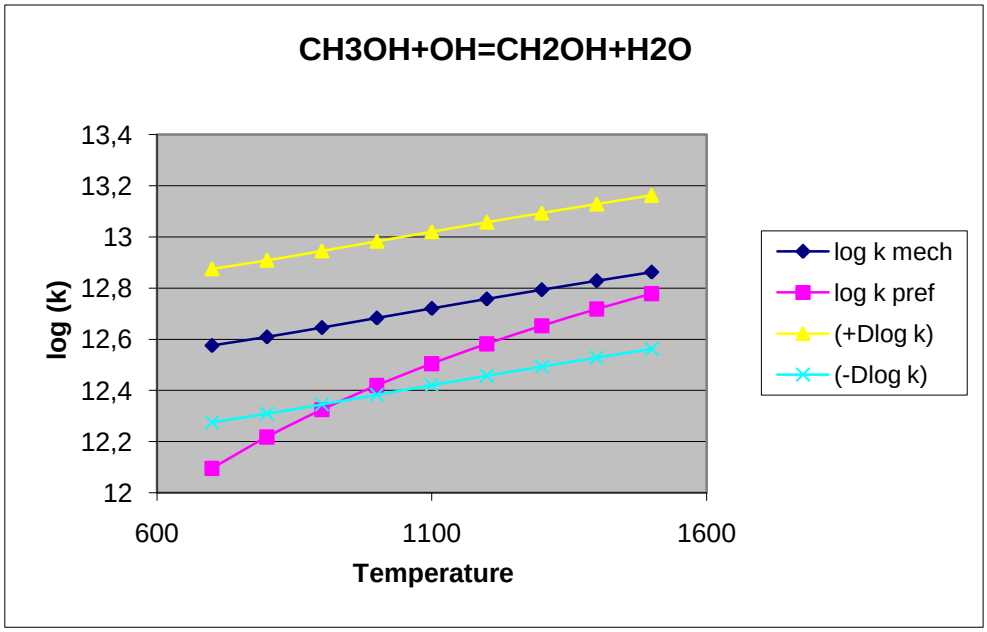


Figure 2. Temperature [K] vs. log (k[$cm^3mol^{-1}s^{-1}$]) of reaction 119 of merged mechanism (rhombus), the Baulch preferred values (squares) and the uncertainty limits assigned to the preferred values (triangles and crosses)

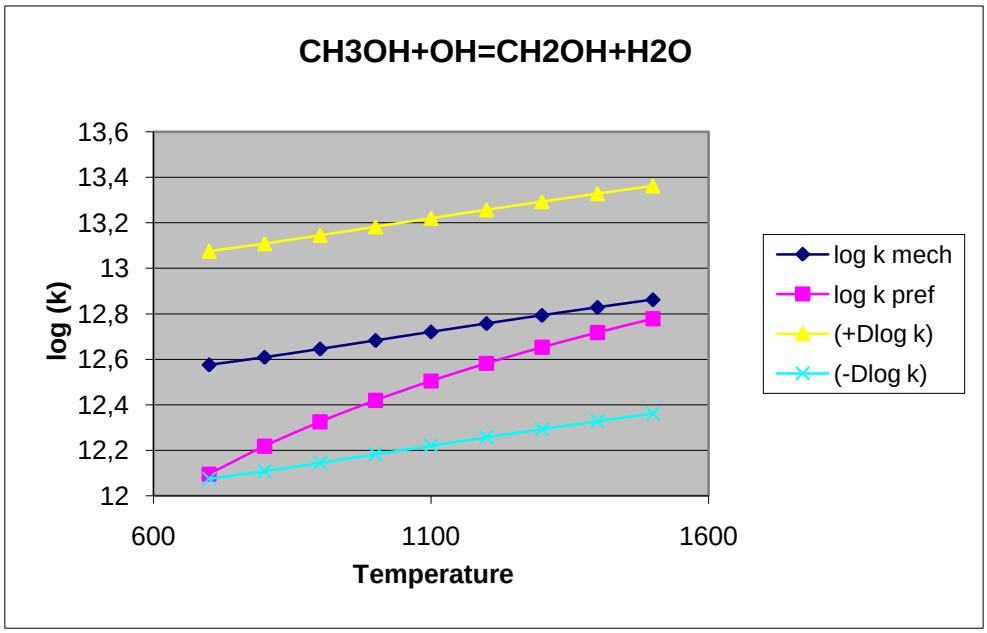


Figure 3. Temperature [K] vs. log (k[$cm^3mol^{-1}s^{-1}$]) of merged mechanism (diamonds), the Baulch preferred values (squares) and the uncertainty limits assigned to the merged mechanism values (triangles and crosses)

There are several cases where the uncertainty is quite large, as it happens in Reaction 30:

CO+O2=CO2+O (R30, Appendix B)

The Arrhenius parameters of the reaction are:

$A = 4.70 \cdot 10^{12}$ cm^3 mol^{-1} s^{-1}, $\beta = 0$, $E = 60500$ cal mol^{-1}

The preferred values according NIST Chemical Kinetic Database are:

1991KOI1726-1730

T = 1000 - 1400 2.09x10^{-11} [cm^3/molecule s] e$^{-197\ [kJ/mole]/RT}$
A = 1.26·10^{13} cm^3 mol^{-1} s^{-1}, β = 0, E = 47050.39 cal mol^{-1}

1986TSA/HAM1087

T = 300 - 2500 4.2x10^{-12} [cm^3/molecule s] e$^{-200\ [kJ/mole]/RT}$
A = 2.53·10^{12} cm^3 mol^{-1} s^{-1}, β = 0.17, E = 47766.9 cal mol^{-1}

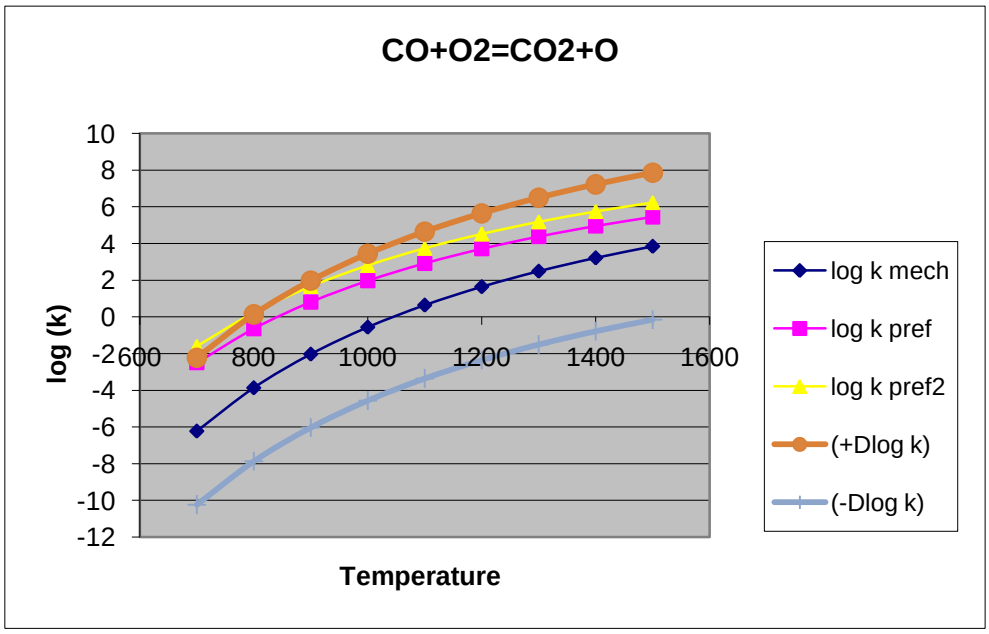


Figure 4. Temperature [K] vs. log (k[cm^{3}mol^{-1}s^{-1}]) of merged mechanism (rhombus), the reaction rates coming from the NIST database (2 references, squares and triangles) and the uncertainty limits assigned to the merged mechanism values (circles and lines)

Plotting the data from the NIST database and the original reaction rate (Figure 4), the uncertainty interval can be obtained. The uncertainty interval was increased till it covered all experiments coming from the NIST Database. In this case, this lead to the value ± 4.

Finally, the details of the calculation of the rate coefficient of pressure dependent reactions are shown below. Under certain conditions, some reaction rate expressions depend on pressure as well as temperature. Several reactions in the Baulch Evaluation have pressure dependence. As an example let we see Reaction 23 of the merged mechanism. Note that Reaction 23 is the reaction number, and Reaction 176 corresponds to its low pressure limit:

H2O2(+M)=OH+OH(+M) (R23 and R176, Appendix B)

The rate parameters of the reaction are:

High pressure: $A = 4.0\cdot10^{11}$ cm^3 mol^{-1} s^{-1}, $\beta = 0$, $E = 37137$ cal mol^{-1}
Low pressure: $A = 2.291\cdot10^{16}$ cm^3 mol^{-1} s^{-1}, $\beta = 0$, $E = 43638$ cal mol^{-1}
TROE / $\alpha = 0.5$, $T^{***} = 1.0E\text{-}30$, $T^{*} = 1.0E30$, $T^{**} = 1.0E30$ /

The high pressure rate parameter is k_∞, the low pressure one is k_0, and the pressure dependence is described using the Troe formalism with four Troe parameters, which are α, T^{***}, T^{*} and T^{**}. It is often that parameter T^{**} is not used.

The preferred values and their reliability according Baulch Evaluated Data are:

k_o = $2.0 \cdot 10^{-7}$ exp(-22900/T) cm^3 $molecule^{-1}$ s^{-1} for M = N_2 over the range 700-1500 K.
A = $1.2046 \cdot 10^{17}$ cm^3 mol^{-1} s^{-1}, β = 0, E = 45473.58 cal mol^{-1} (Arrhenius parameters)

k_∞ = $3.0 \cdot 10^{14}$ exp(-24400/T) s^{-1} over the range 1000-1500 K.
A = $3.0 \cdot 10^{14}$ s^{-1}, β = 0, E = 48500 cal mol^{-1} (Arrhenius parameters)

F_c = 0.5 for M = Ar over the range 1000-1500 K.

$\Delta \log k_o$ = ± 0.2 for M = N_2 over the range 700-1500 K.
$\Delta \log k_\infty$ = ± 0.5 over the range 700-1500 K.
$\Delta \log F_c$ = ± 0.1 for M = Ar over the range 700-1500 K.

For this kind reactions the reaction rate coefficient at a given temperature and pressure is calculated in the following way: In Arrhenius form, the parameters are given for the high-pressure limit k_∞ and the low-pressure limit k_o as follows:

$$k_0 = A_0 \, T^{\beta_0} \exp\left(\frac{-E_0}{R_c \, T}\right)$$

$$k_\infty = A_\infty \, T^{\beta_\infty} \exp\left(\frac{-E_\infty}{R_c \, T}\right)$$

The rate coefficient at any pressure is calculated as

$$k = k_\infty \left(\frac{P_r}{1 + P_r}\right) F$$

where the reduced pressure, P_r is given by

$$P_r = \frac{k_0 [M]}{k_\infty}$$

and [M] is the enhanced third body weighted concentration of the mixture.

For this example, note that the units for k are 1/sec, k_o are cm3/(mole · sec), and k_∞ are 1/sec.

In the Troe form F is given by

$$\log F = \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)}\right]^2\right]^{-1} \log F_c$$

The constant in this equation are

$$c = -0.4 - 0.67 \log F_c$$

$$n = 0.75 - 1.27 \log F_c$$

$$d = 0.14$$

And

$$F_c = (1 - \alpha)\exp\left(-T/T^{***}\right) + \alpha \exp(-T/T^{*}) + \exp(-T^{**}/T)$$

Using these equations, it is possible to calculate the pressure dependent rate coefficient *log (k)*, both for the preferred values of the Baulch Database and the values of the merged mechanism.

Figure 5 shows the Arrhenius plot of the reaction 23 for different pressure (1 bar, 20 bar, 50 bar and 100 bar). The results at each pressure should coincide or should fall between the limits. To visualize this, Figure 6 presents the results in details in four different plots (one at each pressure) including the uncertainty limits.

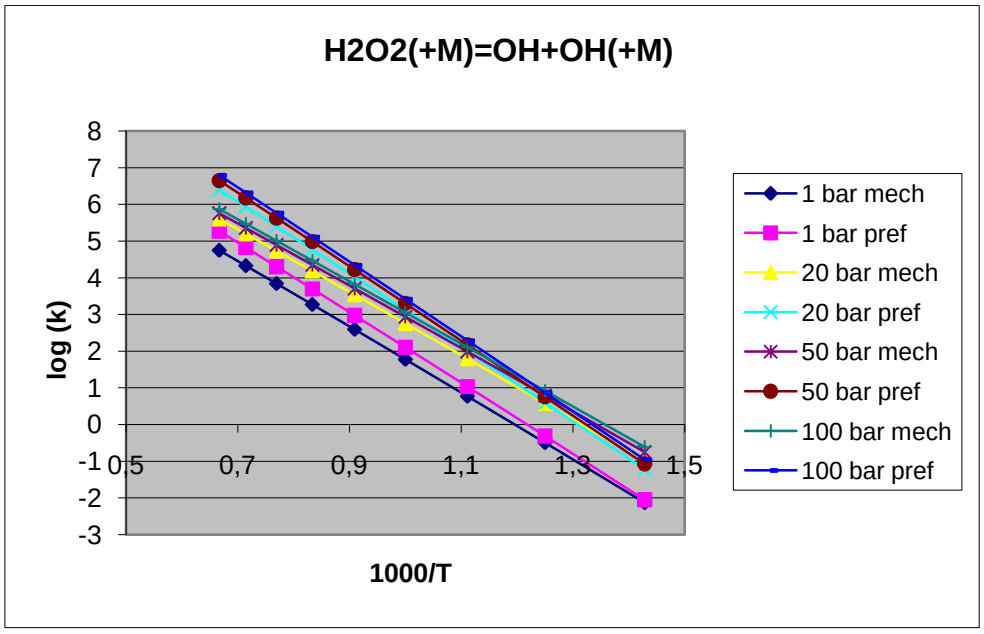
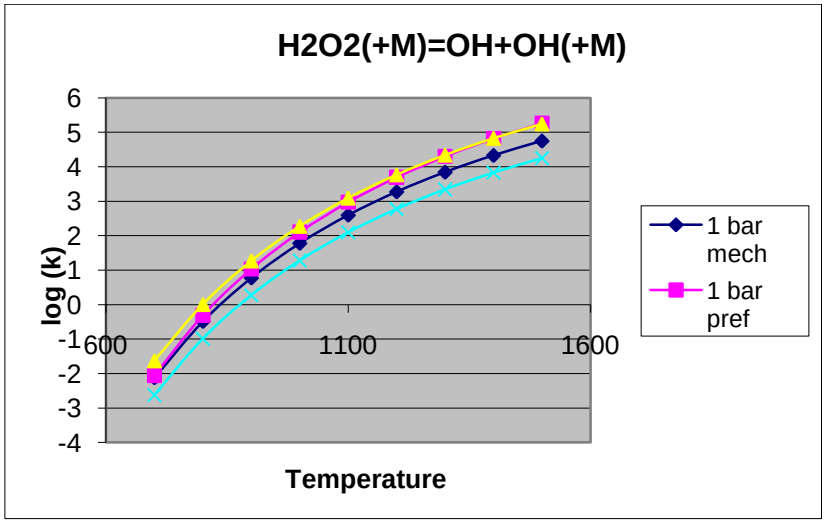


Figure 5. Arrhenius plots of different pressures for both rate parameters, merged mechanism and preferred values



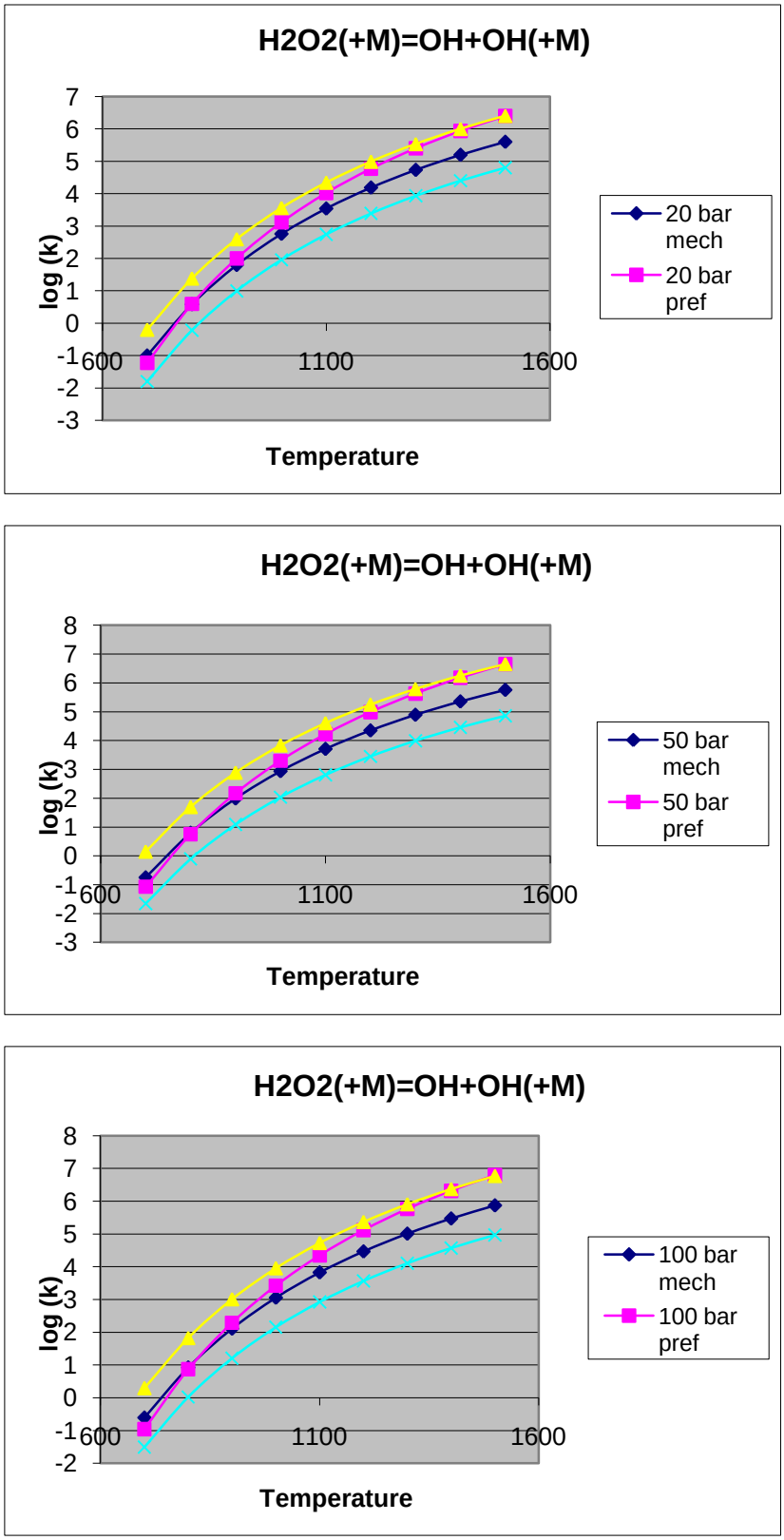


Figure 6. Temperature [K] vs. log (k[$cm^3mol^{-1}s^{-1}$]) of the merged mechanism values (diamonds) and preferred values (squares) and the reliability (triangles and crosses) for each pressure 1 bar, 20 bar, 50 bar and 100 bar

Uncertainty limits were the following: ±*0,5* for the low pressure limit and at 1 bar, ±*0,8* at 20 bar, and ±*0,9* at 50 and 100 bar.

APPENDIX D. Local Sensitivity Analysis

Sensitivity analysis allows quantitative understanding how the solution depends on the various parameters of a model. The results of the local sensitivity analysis for the four studied experimental sets were similar, but there are some details that should be commented.

As it was mentioned in Chapter 4, the input files of the program are: the mechanism to be simulated, and the initial conditions included in the xml files (due to technical reasons, the species involved in the mechanism should be provided in a separated file, too). When the program is ready to make the simulations, in Matlab, the instructions to run the program are

>> main_flowsens (step in temperature, parameter of the residence time)

where the first parameter is the step in temperature, usually 50 K step, this means how close the points of the calculations are done in temperature. The smaller value used, the better plots and functions can be obtained, but the calculations could be too slow. For this reason, 50 K was found to be optimal for most cases. The second argument is the parameter correspond to the calculation of the residence time, for example, in Set 1, residence time is 180K/T, then the number 180 is included here.

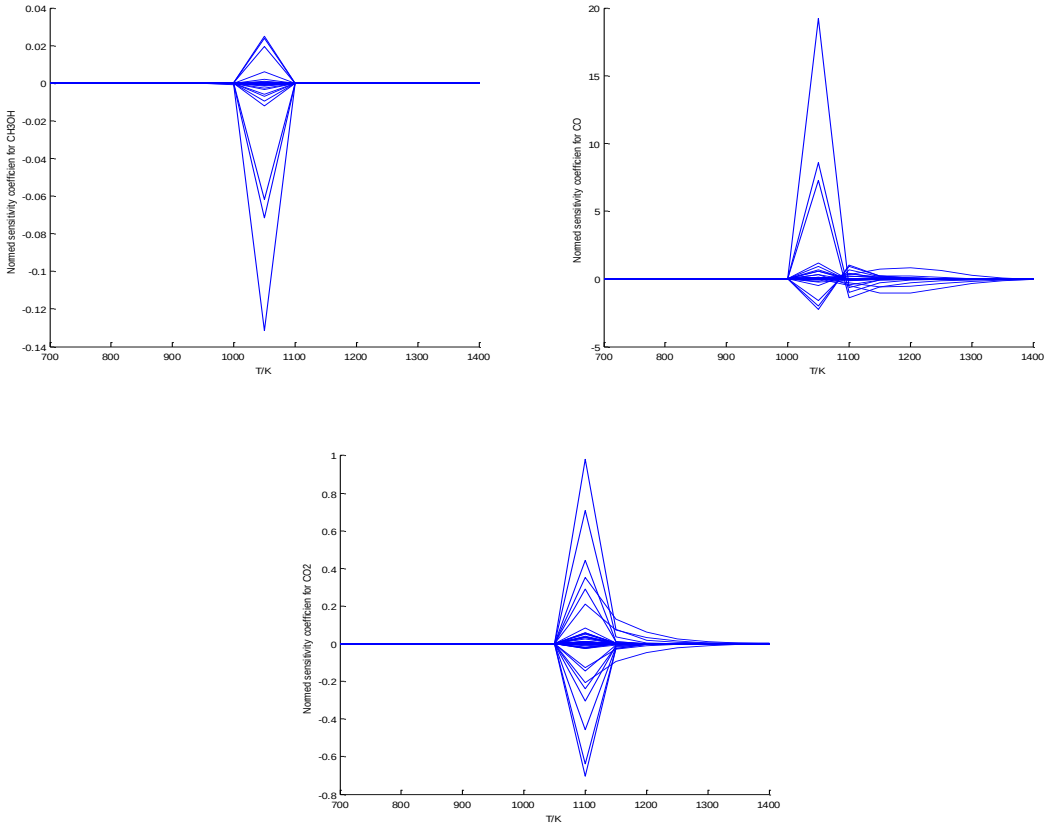


Figure 7. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set 1

Figure 7 shows the local sensitivity indices vs. temperature functions for the Set 1 simulations, and in Table D.1**¡Error! La autoreferencia al marcador no es válida.**, the local sensitivity coefficients and the most sensitive reactions are listed.

Table D.1. The most sensitive reactions and the relative sensitivities (>5%) belong Set 1 for methanol (a), carbon-monoxide (b) and carbon-dioxide (c)

CH3OH T=1050 K
Highest absolute sensitivity: -1.314084e-001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 5.45133e-001
Number of reaction: 1 Relative sensitivity : 4.68975e-001
Number of reaction: 126 Relative sensitivity : -1.88438e-001
Number of reaction: 116 Relative sensitivity : -1.82657e-001
Number of reaction: 127 Relative sensitivity : -1.49354e-001
Number of reaction: 176 Relative sensitivity : 9.15978e-002
Number of reaction: 182 Relative sensitivity : 7.37272e-002
Number of reaction: 122 Relative sensitivity : 5.38901e-002

CO T=1050 K
Highest absolute sensitivity: 1.923726e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 4.46452e-001
Number of reaction: 1 Relative sensitivity : 3.78291e-001
Number of reaction: 116 Relative sensitivity : -1.16839e-001
Number of reaction: 126 Relative sensitivity : -1.03324e-001
Number of reaction: 127 Relative sensitivity : -8.40255e-002
Number of reaction: 176 Relative sensitivity : 6.04467e-002

CO2 T=1100 K
Highest absolute sensitivity: 9.798240e-001

Number of reaction: 1 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 7.21996e-001
Number of reaction: 116 Relative sensitivity : -7.17712e-001
Number of reaction: 126 Relative sensitivity : -6.51625e-001
Number of reaction: 127 Relative sensitivity : -4.67029e-001
Number of reaction: 121 Relative sensitivity : 4.51105e-001
Number of reaction: 33 Relative sensitivity : 3.61254e-001
Number of reaction: 16 Relative sensitivity : -3.09621e-001
Number of reaction: 17 Relative sensitivity : 2.96090e-001
Number of reaction: 15 Relative sensitivity : -2.45087e-001
Number of reaction: 32 Relative sensitivity : 2.15366e-001
Number of reaction: 14 Relative sensitivity : -2.09258e-001
Number of reaction: 20 Relative sensitivity : -1.49025e-001
Number of reaction: 175 Relative sensitivity : -1.29861e-001
Number of reaction: 182 Relative sensitivity : 8.44683e-002
Number of reaction: 176 Relative sensitivity : 6.08207e-002
Number of reaction: 45 Relative sensitivity : 5.93460e-002
Number of reaction: 119 Relative sensitivity : 5.63587e-002
Number of reaction: 108 Relative sensitivity : 5.13380e-002

Results of Set 2 (Figure 8 and Table D.2) are similar to Set 1, the largest sensitivities can be calculated at 1050 K for both the methanol, carbon-monoxide and carbon-dioxide output concentration.

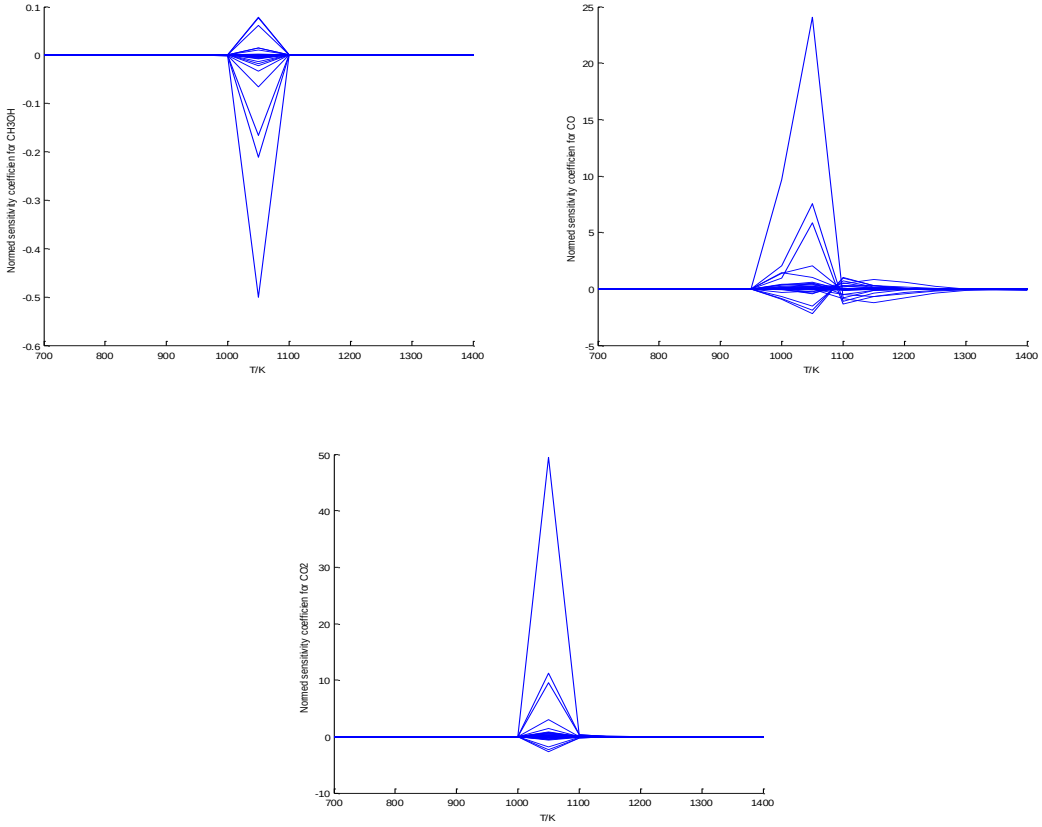


Figure 8. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set 2

Table D.2. The most sensitive reactions and the relative sensitivities (>5%) belong Set 2 for methanol (a), carbon-monoxide (b) and carbon-dioxide (c)

CH3OH T=1050 K
Highest absolute sensitivity, at T=1050 K : -5.000042e-001
Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 4.22213e-001
Number of reaction: 1 Relative sensitivity : 3.32583e-001
Number of reaction: 116 Relative sensitivity : -1.55711e-001
Number of reaction: 126 Relative sensitivity : -1.53303e-001
Number of reaction: 176 Relative sensitivity : 1.31037e-001
Number of reaction: 127 Relative sensitivity : -1.21243e-001
Number of reaction: 122 Relative sensitivity : 6.69670e-002

CO T=1050 K

Highest absolute sensitivity, at T=1050 K : 2.404512e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 3.14357e-001
Number of reaction: 1 Relative sensitivity : 2.42406e-001
Number of reaction: 116 Relative sensitivity : -9.11417e-002
Number of reaction: 176 Relative sensitivity : 8.40187e-002
Number of reaction: 126 Relative sensitivity : -7.88218e-002
Number of reaction: 127 Relative sensitivity : -6.38892e-002

CO2 T=1050 K

Highest absolute sensitivity, at T=1050 K : 4.948579e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 2.26944e-001
Number of reaction: 1 Relative sensitivity : 1.93627e-001
Number of reaction: 176 Relative sensitivity : 6.09340e-002
Number of reaction: 116 Relative sensitivity : -5.41176e-002

For Set 3, the results are very similar (Figure 9 and Table D.3).

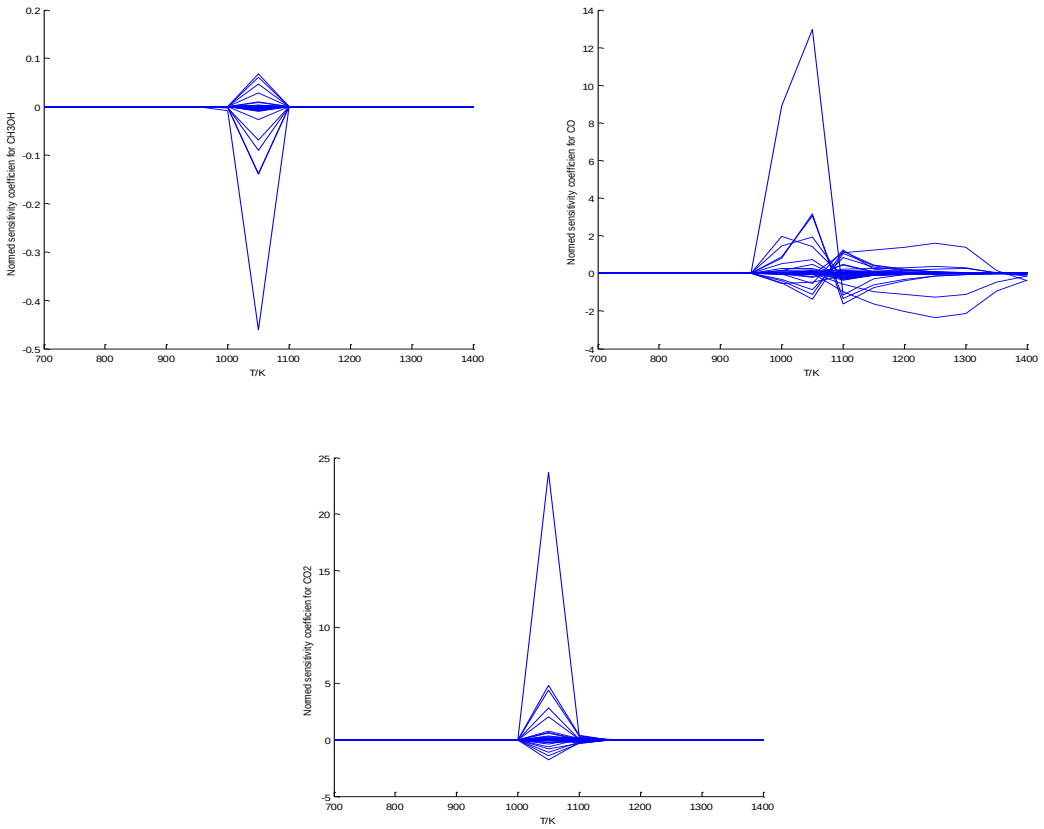


Figure 9. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set 3

Table D.3 The most sensitive reactions and the relative sensitivities (>5%) belong Set 3 for methanol (a), carbon-monoxide (b) and carbon-dioxide (c)

CH3OH T=1050 K
Highest absolute sensitivity, at T=1050 K : -4.610219e-001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 1 Relative sensitivity : 3.03312e-001
Number of reaction: 184 Relative sensitivity : 3.00187e-001
Number of reaction: 176 Relative sensitivity : 1.93966e-001
Number of reaction: 116 Relative sensitivity : -1.48930e-001
Number of reaction: 122 Relative sensitivity : 1.48090e-001
Number of reaction: 126 Relative sensitivity : -1.31334e-001
Number of reaction: 127 Relative sensitivity : -1.02593e-001
Number of reaction: 20 Relative sensitivity : -6.19697e-002
Number of reaction: 120 Relative sensitivity : 5.76245e-002

CO T=1050 K
Highest absolute sensitivity, at T=1050 K : 1.295595e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 1 Relative sensitivity : 2.44337e-001
Number of reaction: 184 Relative sensitivity : 2.35008e-001
Number of reaction: 176 Relative sensitivity : 1.48027e-001
Number of reaction: 122 Relative sensitivity : 1.10792e-001
Number of reaction: 116 Relative sensitivity : -1.04583e-001
Number of reaction: 126 Relative sensitivity : -8.54678e-002
Number of reaction: 127 Relative sensitivity : -6.76696e-002
Number of reaction: 45 Relative sensitivity : 5.75278e-002

CO2 T=1050 K
Highest absolute sensitivity, at T=1050 K : 2.367274e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 1 Relative sensitivity : 2.04879e-001
Number of reaction: 184 Relative sensitivity : 1.85230e-001
Number of reaction: 176 Relative sensitivity : 1.20068e-001
Number of reaction: 122 Relative sensitivity : 8.58484e-002
Number of reaction: 116 Relative sensitivity : -7.35500e-002
Number of reaction: 126 Relative sensitivity : -5.95128e-002

For the three low pressure cases, the most important reaction is Reaction 121, and the second and third reactions are 184 and 1, their order depend on the Set.

However, the graphs plotting the Set E4 results (see Figure 10) showed non-typical curves; therefore, instead of taking a step in temperature of 50 K, 20 K step was used to obtain a value closer to the temperature at which the species concentrations are the most sensitive to the reaction rate coefficients.

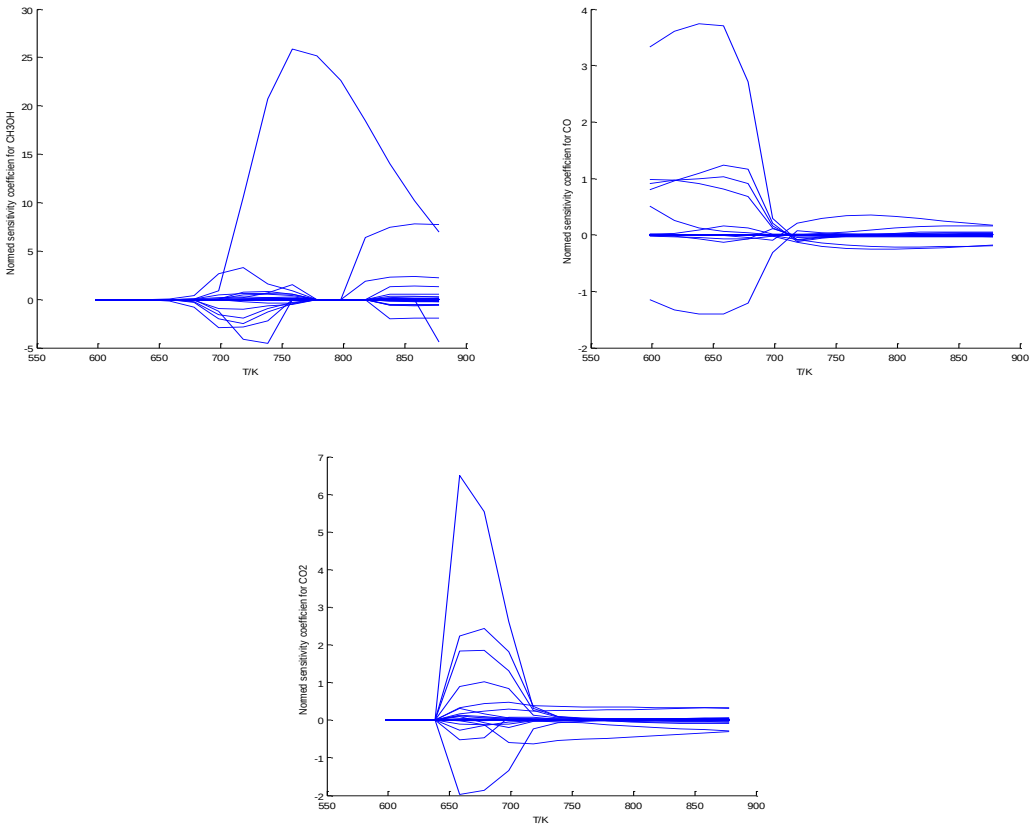
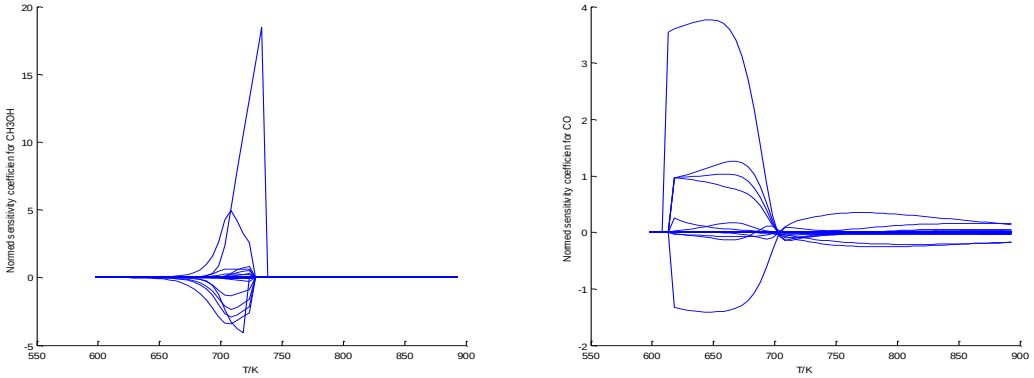


Figure 10. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set E4

In Figure 10 can sense the temperature at which there is greater sensitivity but the graphics are not very good. To avoid this problem even more steps were added to the study, which the simulation was performed with a temperature step of 5 K, obtaining much higher number of analysis points. Figure 11 and Table D.4 shows the results of this, final analysis.



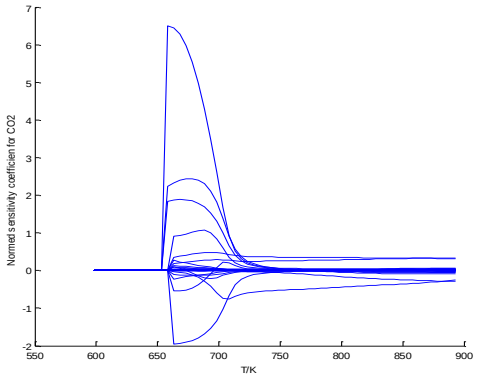


Figure 11. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set E4, five points

Table D.4. The most sensitive reactions and the relative sensitivities (>5%) belong Set E4 for methanol (a), carbon-monoxide (b) and carbon-dioxide (c)

CH3OH T=758 K
Highest absolute sensitivity, at T=7.581500e+002 K : 2.590607e+001
Number of reaction: 27 Relative sensitivity : 1.00000e+000
Number of reaction: 20 Relative sensitivity : 5.95936e-002
CO T=638 K
Highest absolute sensitivity, at T=6.381500e+002 K : 3.740528e+000
Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 21 Relative sensitivity : -3.74351e-001
Number of reaction: 23 Relative sensitivity : 2.92042e-001
Number of reaction: 176 Relative sensitivity : 2.67002e-001
Number of reaction: 46 Relative sensitivity : 2.44207e-001
CO2 T = 658 K
Highest absolute sensitivity, at T=6.581500e+002 K : 6.498186e+000
Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 23 Relative sensitivity : 3.44636e-001
Number of reaction: 21 Relative sensitivity : -3.02880e-001
Number of reaction: 176 Relative sensitivity : 2.83688e-001
Number of reaction: 46 Relative sensitivity : 1.37987e-001
Number of reaction: 119 Relative sensitivity : -7.91047e-002

Since the largest local sensitivity coefficients of different species appeared at different temperatures the global sensitivity analysis was done at two different temperatures (650 K and 750 K).

APPENDIX E. Monte Carlo Simulations

As seen in Chapter 5, Monte Carlo simulations were conducted with large number of random parameter sets. To get information about the convergence, reliability of the determined minimum and maximum values calculations were done using 1000, 3000 and 10000 parameter sets. In Chapter 5, we focused on the results obtained for the case of 10000 values for Set 2. Now, let's see the results for other sets in the case of 1000 values. The Figures 30, 31, 32 and 33 show the reliability of the results of the experimental sets 1, 3, E4 and 2 respectively (note that the Set 2 is in last place to compare it later with the 3000 and 10000 calculations). The reliability of the simulations is very poor although the average values are close to the experimental results.

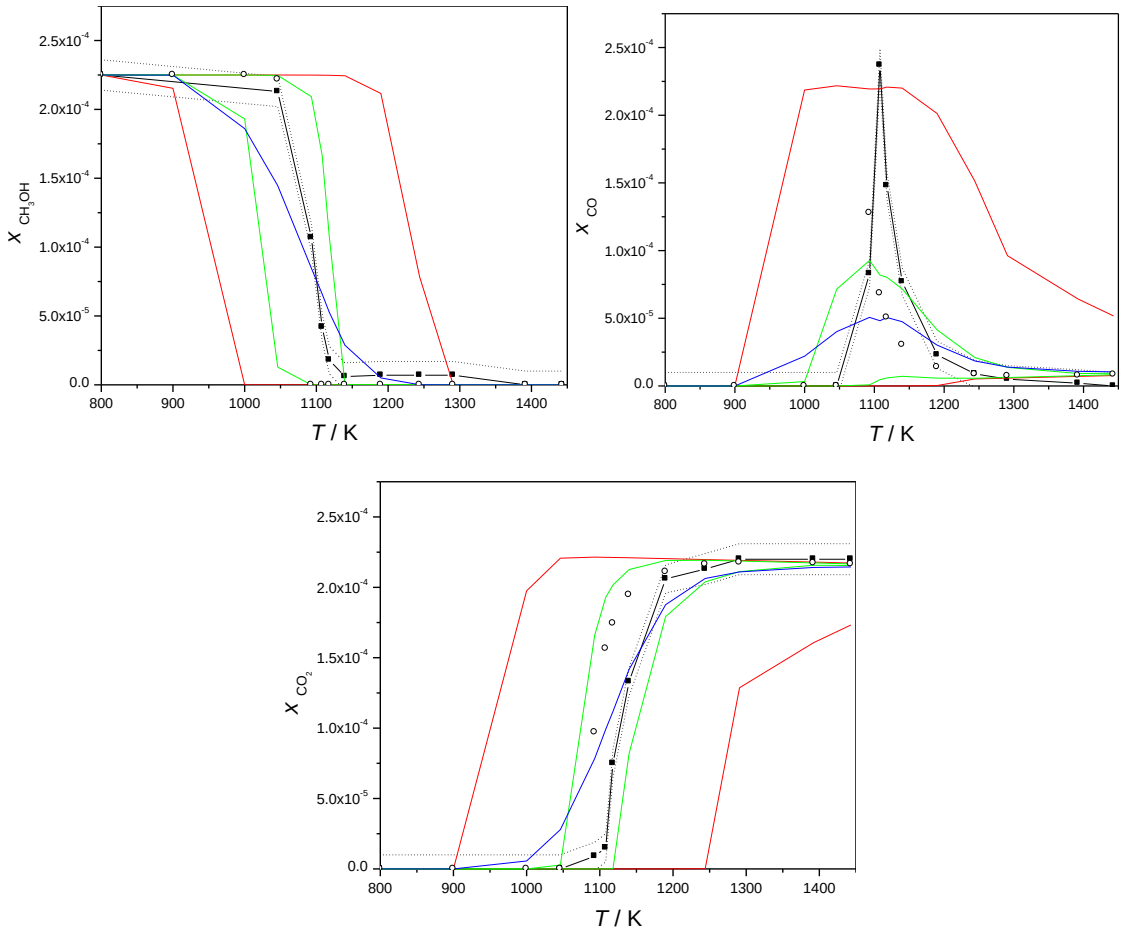


Figure 12. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 1 [2] and 1000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

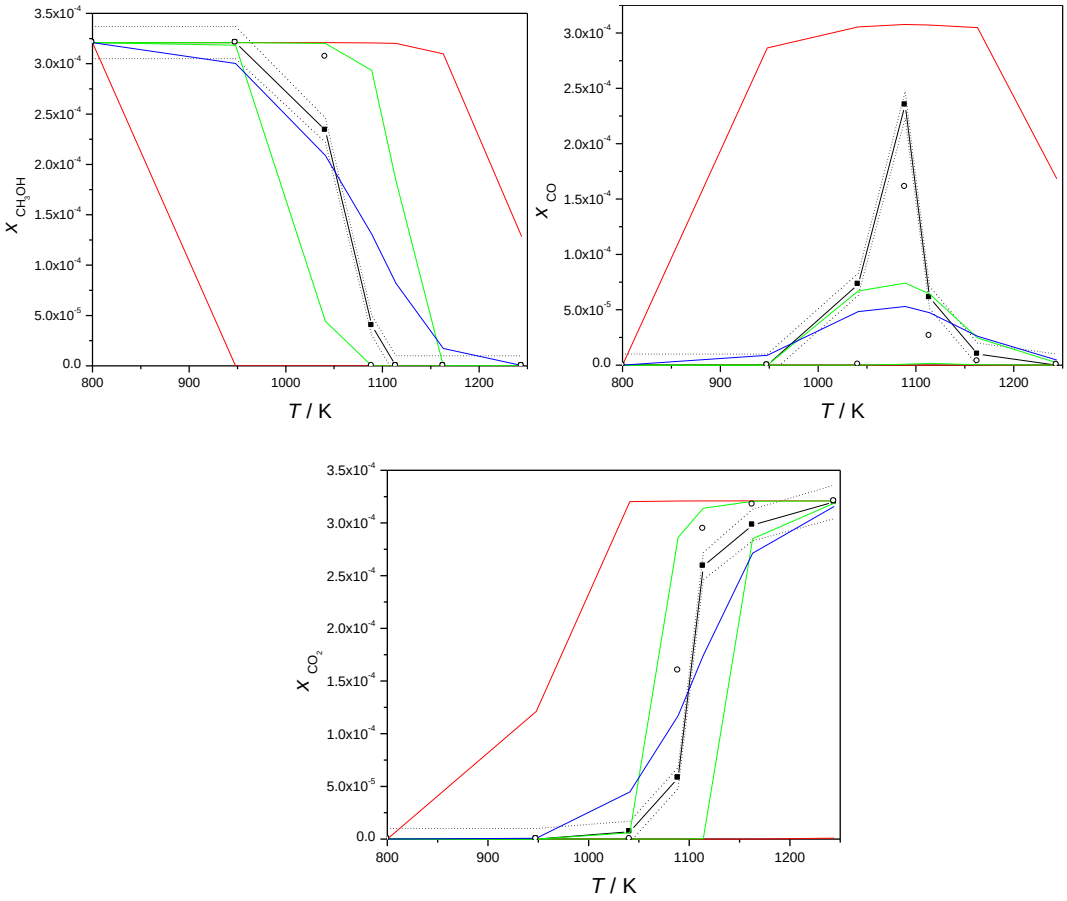
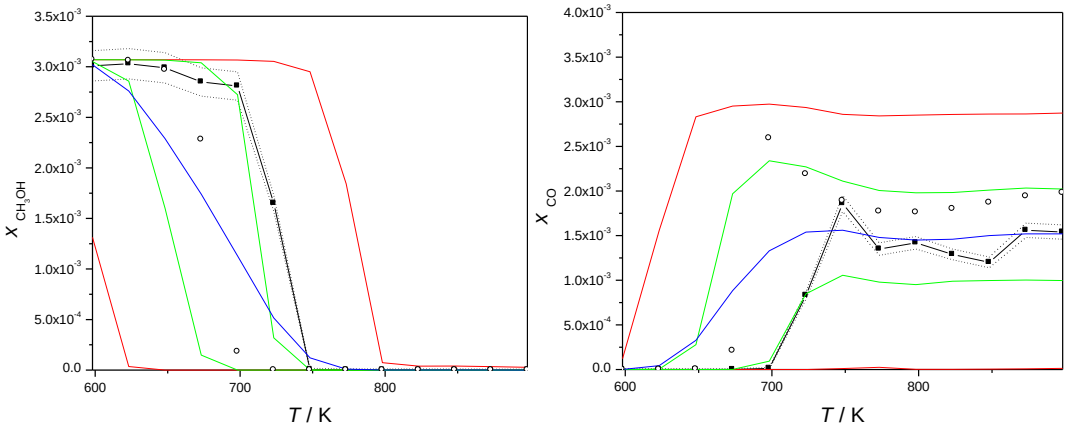


Figure 13. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 3 [2] and 1000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.



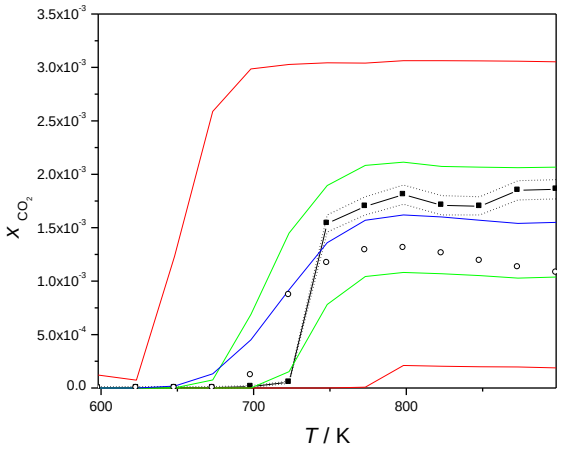


Figure 14- Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set E4 [2] and 1000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

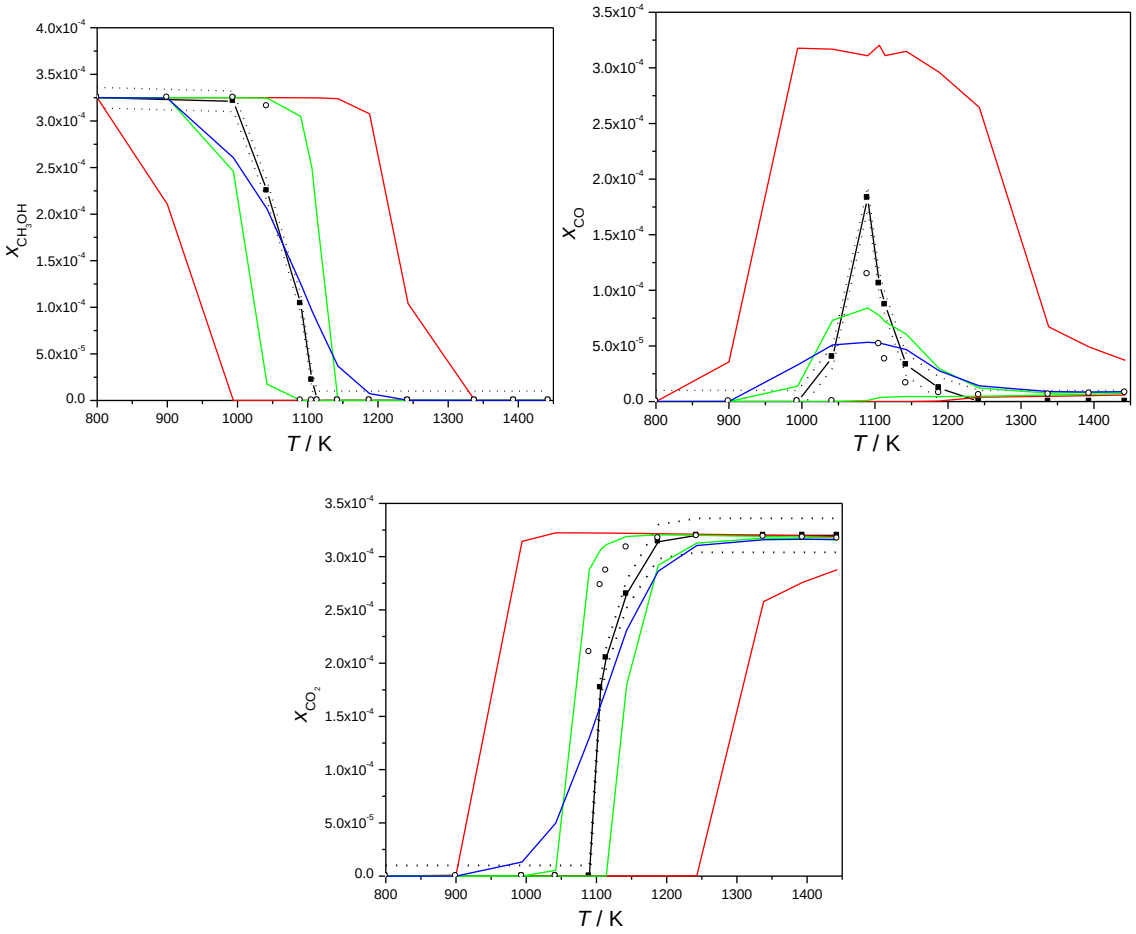


Figure 15. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2] for 1000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

Then, the results for the Set 2 for 1000 (Figure 15), 3000 (Figure 16) and 10000 (Figure 17) values were studied, and it was checked that the limits are almost the same for all three cases.

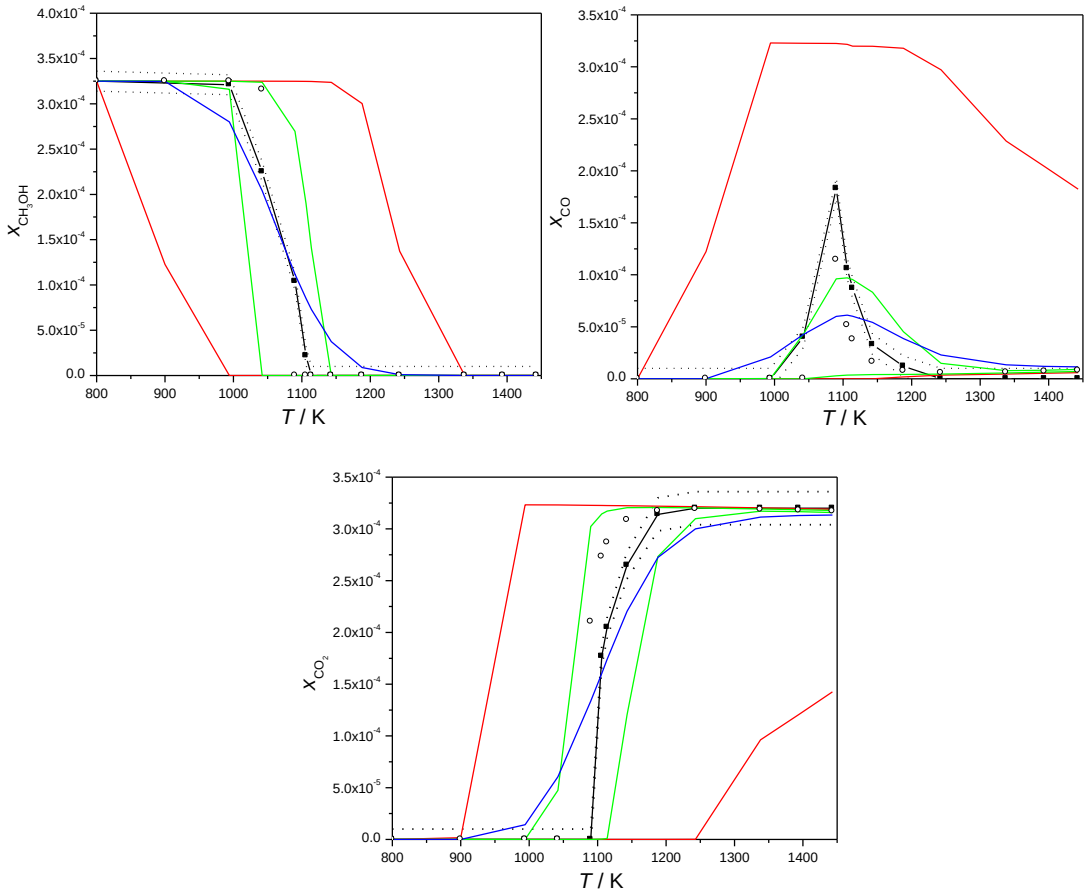


Figure 16. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2] for 3000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

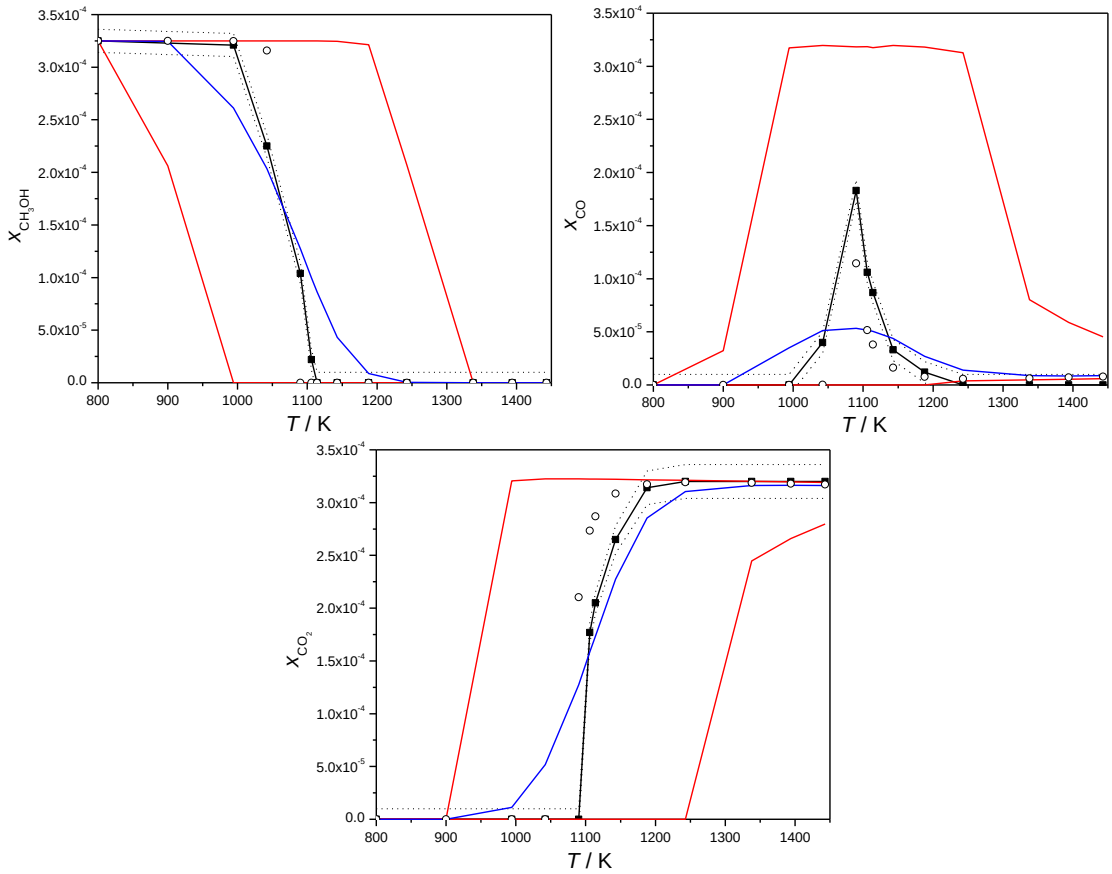


Figure 17. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2] for 10000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the mechanism keeping all parameters within their uncertainty limits.

APPENDIX F. Global Sensitivity Analysis

An uncertainty-based sensitivity index represents the contribution the uncertainty of model input to the overall uncertainty of the model output. In Table F.1-4, the sensitivity coefficients of the five most important reactions are shown.

Table F.1. Sensitivity indices for the five most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 1 [2]

CO							
1000							
Ranking	1	2	3	4	5		
Reaction	121	33	163	77	152		
SI	0,2563	0,0323	0,0241	0,0216	0,0211	Sum SI	0,8884
3000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	33	32		
SI	0,372	0,0226	0,0141	0,0104	0,0071	Sum SI	0,5975
10000							
Ranking	1	2	3	4	5		
Reaction	121	16	184	33	32		
SI	0,419	0,0175	0,0175	0,0138	0,0067	Sum SI	0,511
CO2							
1000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	1	126		
SI	0,1686	0,0654	0,064	0,0518	0,0405	Sum SI	1,1148
3000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	1	33		
SI	0,2304	0,1223	0,0626	0,0515	0,0317	Sum SI	0,7776
10000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	1	33		
SI	0,2459	0,1151	0,0637	0,0521	0,0362	Sum SI	0,6918
CH3OH							
1000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	137	33		
SI	0,5	0,0568	0,0188	0,0171	0,0165	Sum SI	1,0545
3000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	66	1		
SI	0,6024	0,0385	0,0257	0,0118	0,0113	Sum SI	0,8251
10000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	1	126		
SI	0,6544	0,0418	0,0261	0,011	0,0098	Sum SI	0,7944

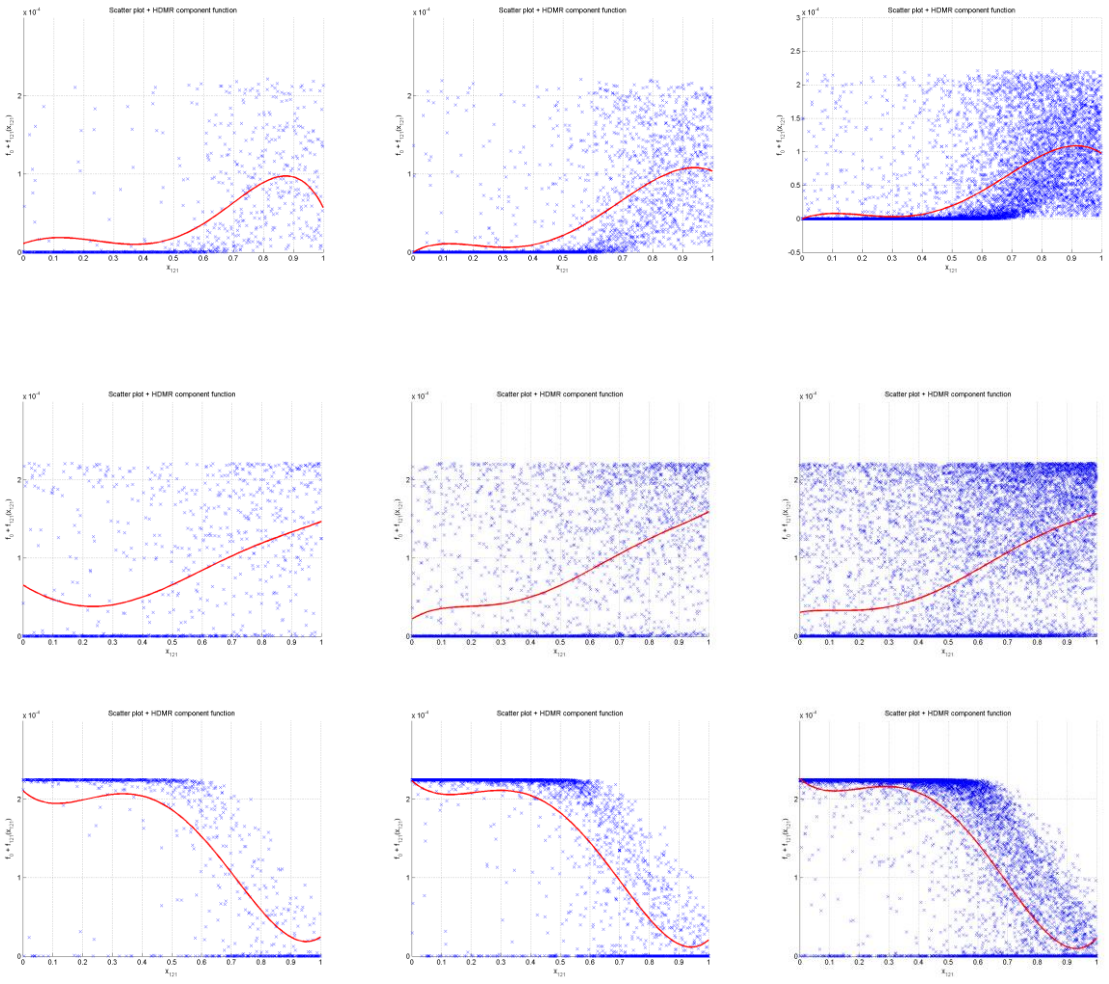


Figure 18. First-order component function and scatter plot of the (a) carbon-monoxide (first row), (b) carbon-dioxide (second row) and (c) methanol (third row) mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*), for 1000 calculations (first column), 3000 calculations (second column) and 10000 calculations (third column) for the conditions of Set 1 [2]

Figure 36 show the different results for the global sensitivity analysis depending on the number of calculations.

It is clear the most important reaction is R121. However, it does not determine alone the simulation result, several other reactions are sensitive more or less. Due to the large number of parameter varied parallel even the 10000 set run did not show converged global sensitivity values. However, this semi-quantitative information is enough to direct further mechanism development work.

Table F.2 Sensitivity indices for the five most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 2 [2]

CO							
1000							
Ranking	1	2	3	4	5		
Reaction	121	33	32	41	16		
SI	0,3055	0,0399	0,0202	0,0193	0,0176	Sum SI	0,8339
3000							
Ranking	1	2	3	4	5		
Reaction	121	141	168	164	65		
SI	0,0469	0,0095	0,0069	0,0058	0,0057	Sum SI	0,3032
10000							
Ranking	1	2	3	4	5		
Reaction	121	33	32	16	180		
SI	0,4083	0,0173	0,0098	0,0042	0,0032	Sum SI	0,4677

CO2							
1000							
Ranking	1	2	3	4	5		
Reaction	121	33	16	64	1		
SI	0,3189	0,0346	0,0326	0,0251	0,0217	Sum SI	1,2831
3000							
Ranking	1	2	3	4	5		
Reaction	121	1	81	67	33		
SI	0,0213	0,013	0,0128	0,0115	0,0112	Sum SI	0,5504
10000							
Ranking	1	2	3	4	5		
Reaction	121	16	184	20	32		
SI	0,3275	0,0591	0,0356	0,0266	0,0211	Sum SI	0,6451

CH3OH							
1000							
Ranking	1	2	3	4	5		
Reaction	121	184	18	44	98		
SI	0,579	0,0284	0,0166	0,013	0,013	Sum SI	0,9424
3000							
Ranking	1	2	3	4	5		
Reaction	121	37	152	176	19		
SI	0,0763	0,0121	0,0119	0,0095	0,0089	Sum SI	0,5662
10000							
Ranking	1	2	3	4	5		
Reaction	121	184	16	20	48		
SI	0,7268	0,0216	0,0211	0,0106	0,0086	Sum SI	0,8319

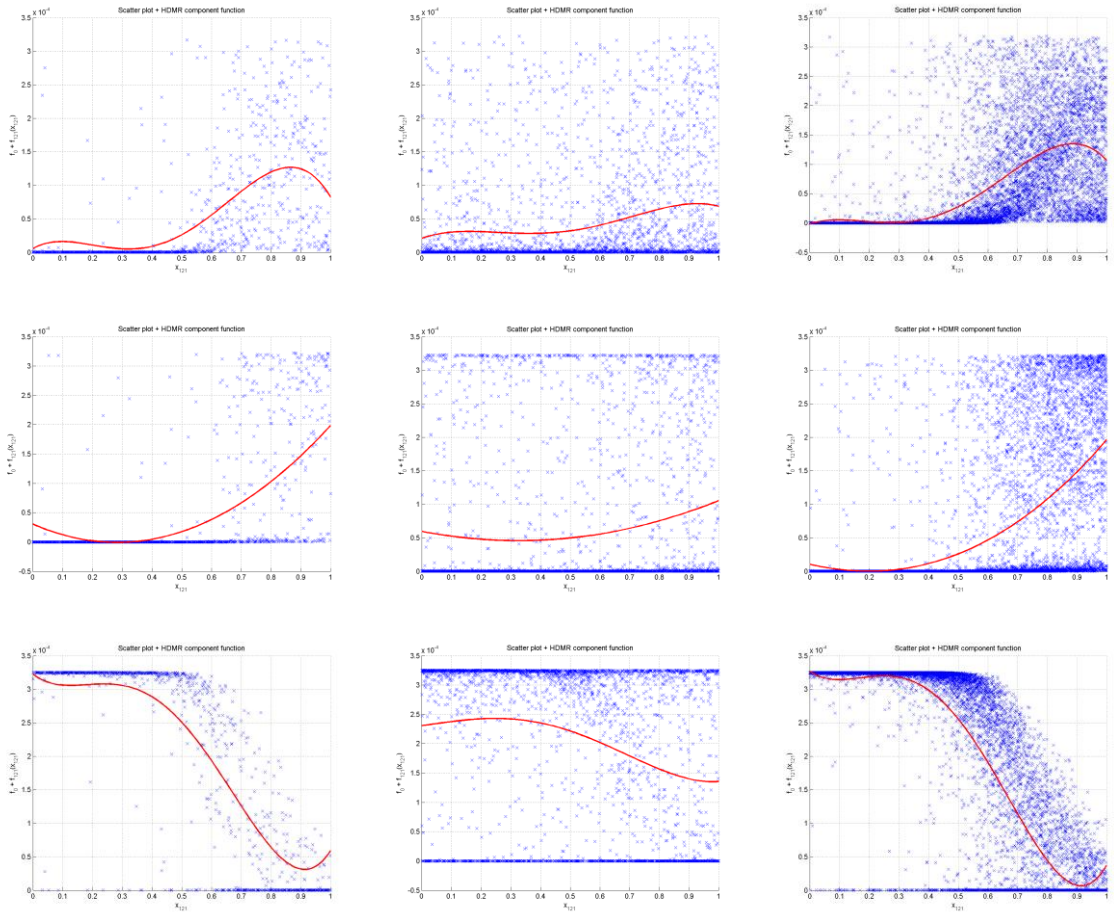


Figure 19. First-order component function and scatter plot of the (a) carbon-monoxide (first row), (b) carbon-dioxide (second row) and (c) methanol (third row) mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*), for 1000 calculations (first column), 3000 calculations (second column) and 10000 calculations (third column) for the conditions of Set 2 [2]

Table F.3. Sensitivity indices for the five most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 3 [2]

CO							
1000							
Ranking	1	2	3	4	5		
Reaction	121	185	151	18	38		
SI	0,2588	0,0201	0,0188	0,0179	0,0178	Sum SI	0,7701
3000							
Ranking	1	2	3	4	5		
Reaction	121	138	19	96	39		
SI	0,0641	0,0077	0,0061	0,0054	0,0053	Sum SI	0,2879
10000							
Ranking	1	2	3	4	5		
Reaction	121	33	20	32	173		
SI	0,4616	0,0154	0,0108	0,008	0,0055	Sum SI	0,5381

CO2							
1000							
Ranking	1	2	3	4	5		
Reaction	121	143	20	172	175		
SI	0,2507	0,0612	0,0392	0,0365	0,0302	Sum SI	1,3165
3000							
Ranking	1	2	3	4	5		
Reaction	121	119	33	32	160		
SI	0,0186	0,0125	0,0114	0,0101	0,01	Sum SI	0,5314
10000							
Ranking	1	2	3	4	5		
Reaction	121	20	48	16	33		
SI	0,3334	0,0817	0,00211	0,0159	0,0139	Sum SI	0,6412

CH3OH							
1000							
Ranking	1	2	3	4	5		
Reaction	121	20	184	93	152		
SI	0,6549	0,0184	0,0113	0,0093	0,0091	Sum SI	0,8742
3000							
Ranking	1	2	3	4	5		
Reaction	121	116	81	110	60		
SI	0,0836	0,0102	0,0094	0,0083	0,0075	Sum SI	0,4086
10000							
Ranking	1	2	3	4	5		
Reaction	121	20	184	170	94		
SI	0,8013	0,0303	0,007	0,0066	0,0054	Sum SI	0,8768

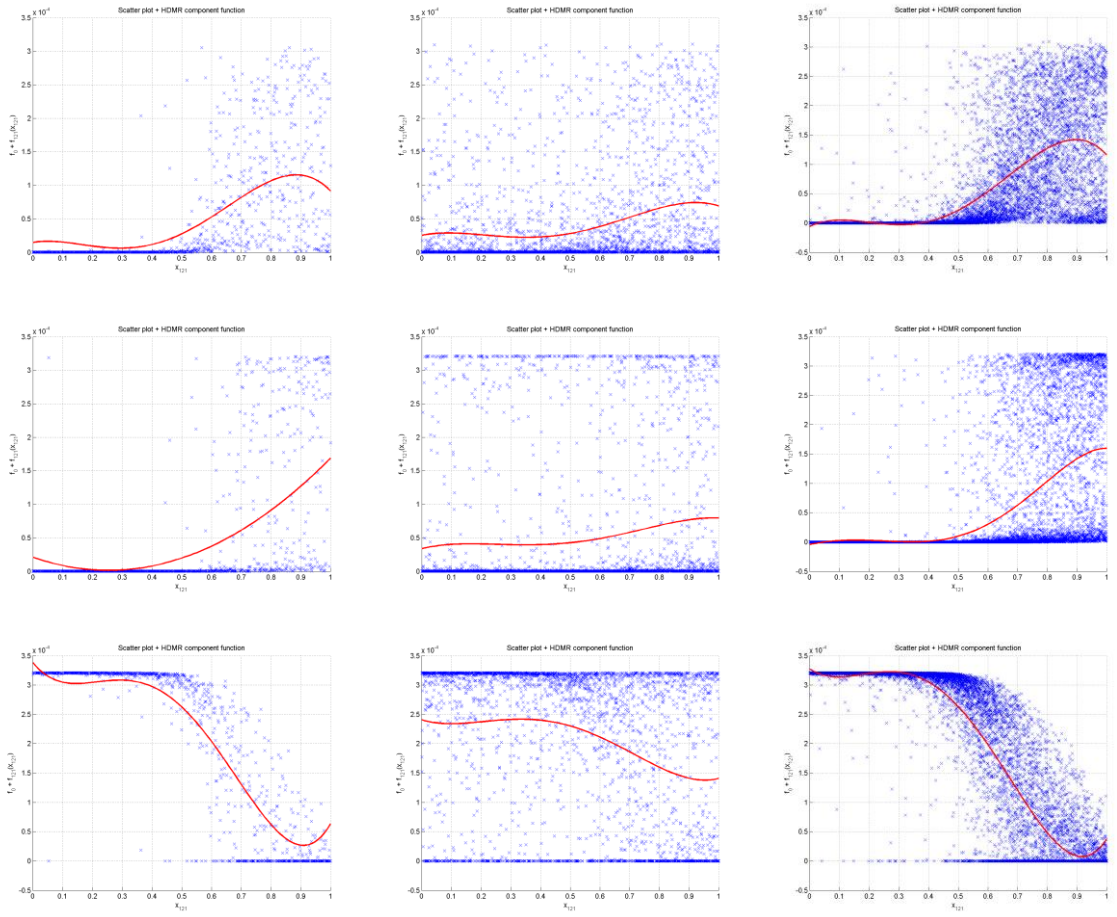


Figure 20. First-order component function and scatter plot of the (a) carbon-monoxide (first row), (b) carbon-dioxide (second row) and (c) methanol (third row) mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*), for 1000 calculations (first column), 3000 calculations (second column) and 10000 calculations (third column) for the conditions of Set 3 [2]

Table F.4. Sensitivity indices for the five most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 4 [3]

CO							
1000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	176	124		
SI	0,4663	0,0494	0,0327	0,0148	0,0113	Sum SI	0,717
3000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	81	13		
SI	0,1583	0,0137	0,0093	0,0042	0,0041	Sum SI	0,2959
10000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	176	46		
SI	0,6117	0,0588	0,0322	0,0208	0,0101	Sum SI	0,7369

CO2							
1000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	180	162		
SI	0,1642	0,0173	0,0161	0,0114	0,0111	Sum SI	0,4338
3000							
Ranking	1	2	3	4	5		
Reaction	121	23	108	9	124		
SI	0,0268	0,0083	0,0067	0,0039	0,0036	Sum SI	0,128
10000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	176	46		
SI	0,1769	0,0339	0,029	0,0165	0,0099	Sum SI	0,2803

CH3OH							
1000							
Ranking	1	2	3	4	5		
Reaction	121	21	23	135	32		
SI	0,7517	0,0237	0,022	0,0117	0,0059	Sum SI	0,9267
3000							
Ranking	1	2	3	4	5		
Reaction	121	78	39	21	158		
SI	0,195	0,0056	0,0047	0,0046	0,0042	Sum SI	0,3092
10000							
Ranking	1	2	3	4	5		
Reaction	121	23	21	176	…		
SI	0,876	0,0194	0,017	0,0072	…	Sum SI	0,9197

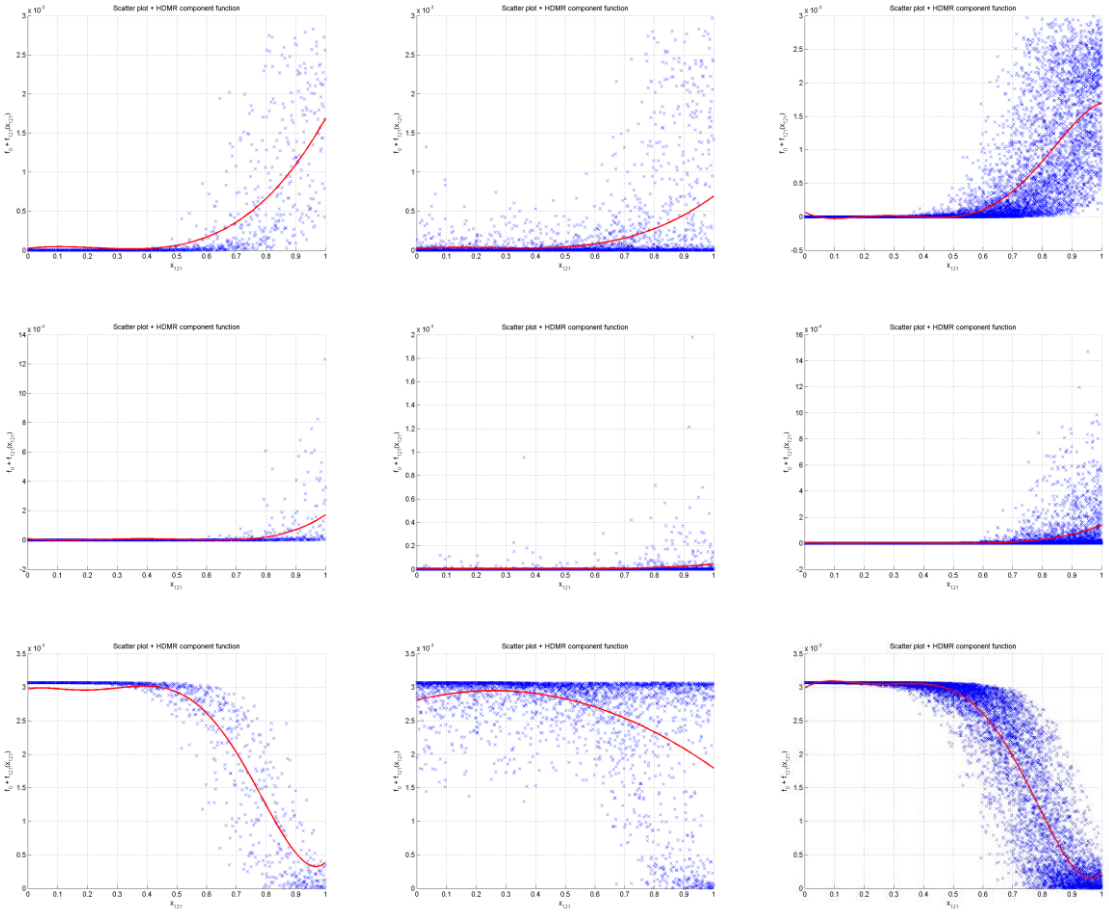


Figure 21. First-order component function and scatter plot of the (a) carbon-monoxide (first row), (b) carbon-dioxide (second row) and (c) methanol (third row) mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*), for 1000 calculations (first column), 3000 calculations (second column) and 10000 calculations (third column) for the conditions of Set 4 [3]

APPENDIX G. Sensitivity analysis of the improved mechanism

Similarly to the investigation of the merged mechanism, sensitivity analysis was carried out to this new improved mechanism.

First, local sensitivity analysis revealed the temperature of the largest local sensitivity indices.

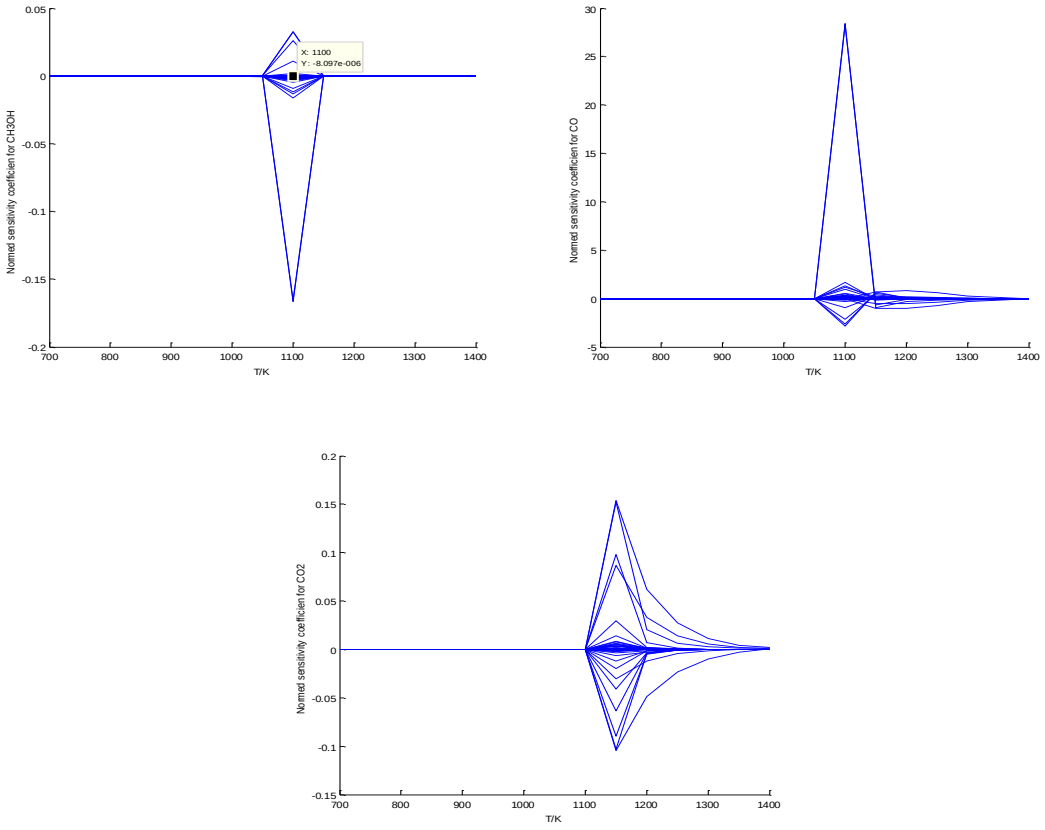


Figure 22. Normalized local sensitivity coefficients versus temperature of the mole fraction of methanol (a), carbon-monoxide (b) and carbon-dioxide (c) under the circumstances of Set 1 in the improved mechanism

The most important reaction has changed. In Table G.1 the relative sensitivities (>5%) of the most important reactions are detailed. Here, we focus in the temperature where the sensitivity is larger because the global sensitivity analysis has been carried out and the results will be discussed later.

With the improved mechanism, the temperature where the reactions are more sensitive has increased.

Table G.1 The most sensitive reactions and the relative sensitivities (>5%) belong Set 1 for methanol (a), carbon-monoxide (b) and carbon-dioxide (c) in the improved mechanism

CH3OH T=1100 K
Highest absolute sensitivity, at T=1100 K : -1.667175e-001

Number of reaction: 184 Relative sensitivity : 1.00000e+000
Number of reaction: 1 Relative sensitivity : 9.92033e-001
Number of reaction: 116 Relative sensitivity : -1.96515e-001
Number of reaction: 126 Relative sensitivity : -1.95146e-001
Number of reaction: 127 Relative sensitivity : -1.57079e-001
Number of reaction: 182 Relative sensitivity : 9.74307e-002
Number of reaction: 121 Relative sensitivity : 8.00430e-002
Number of reaction: 175 Relative sensitivity : 7.05817e-002
Number of reaction: 15 Relative sensitivity : -6.69069e-002
Number of reaction: 108 Relative sensitivity : 5.66512e-002

CO T=1100 K
Highest absolute sensitivity, at T=1100 K : 2.838301e+001

Number of reaction: 1 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 9.97141e-001
Number of reaction: 116 Relative sensitivity : -1.00894e-001
Number of reaction: 126 Relative sensitivity : -9.18954e-002
Number of reaction: 127 Relative sensitivity : -7.65983e-002
Number of reaction: 182 Relative sensitivity : 5.90170e-002

CO2 T=1150 K
Highest absolute sensitivity, at T=1150 K : 1.541187e-001

Number of reaction: 33 Relative sensitivity : 1.00000e+000
Number of reaction: 1 Relative sensitivity : 9.89768e-001
Number of reaction: 14 Relative sensitivity : -6.77646e-001
Number of reaction: 116 Relative sensitivity : -6.68404e-001
Number of reaction: 184 Relative sensitivity : 6.36640e-001
Number of reaction: 126 Relative sensitivity : -5.81063e-001
Number of reaction: 32 Relative sensitivity : 5.61402e-001
Number of reaction: 127 Relative sensitivity : -4.11448e-001
Number of reaction: 15 Relative sensitivity : -2.68105e-001
Number of reaction: 175 Relative sensitivity : -1.96238e-001
Number of reaction: 17 Relative sensitivity : 1.93696e-001
Number of reaction: 16 Relative sensitivity : -1.27024e-001
Number of reaction: 182 Relative sensitivity : 9.08828e-002
Number of reaction: 20 Relative sensitivity : -7.68494e-002
Number of reaction: 108 Relative sensitivity : 5.34469e-002

Monte Carlo simulations revealed the possible minimum and maximum concentrations. In this case, the predictions have been improved but the simulations still have large uncertainty.

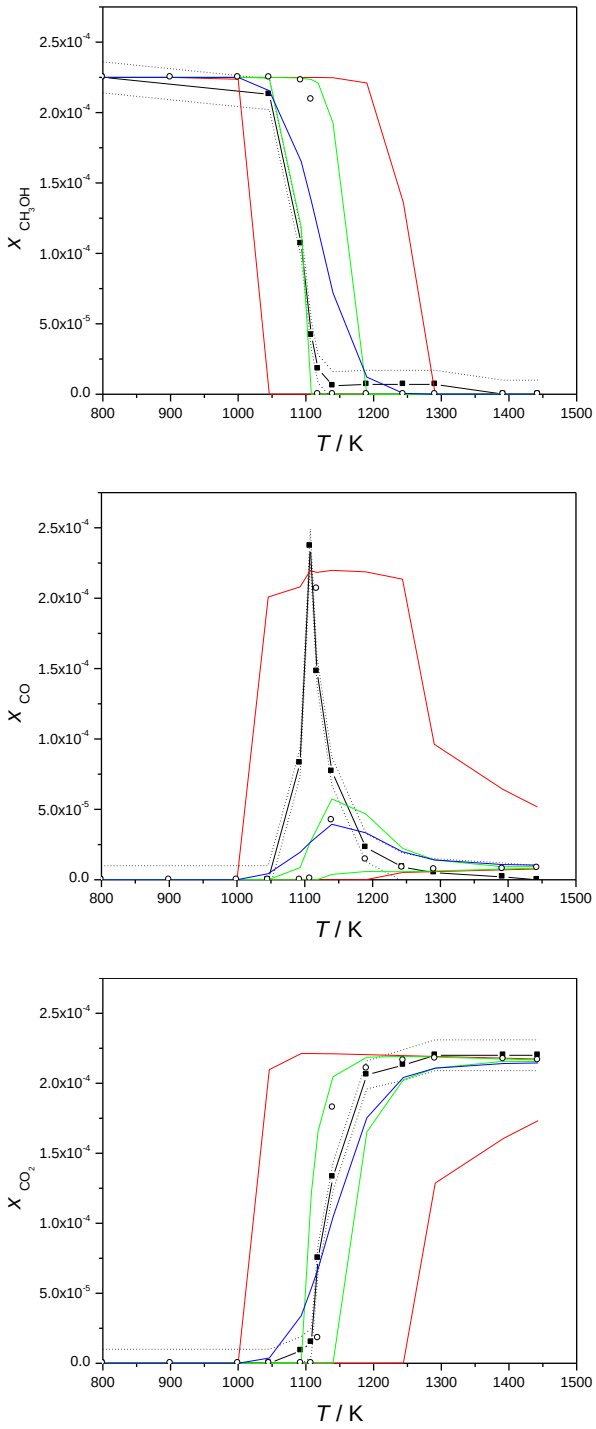


Figure 23. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 1 [2] and 10000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

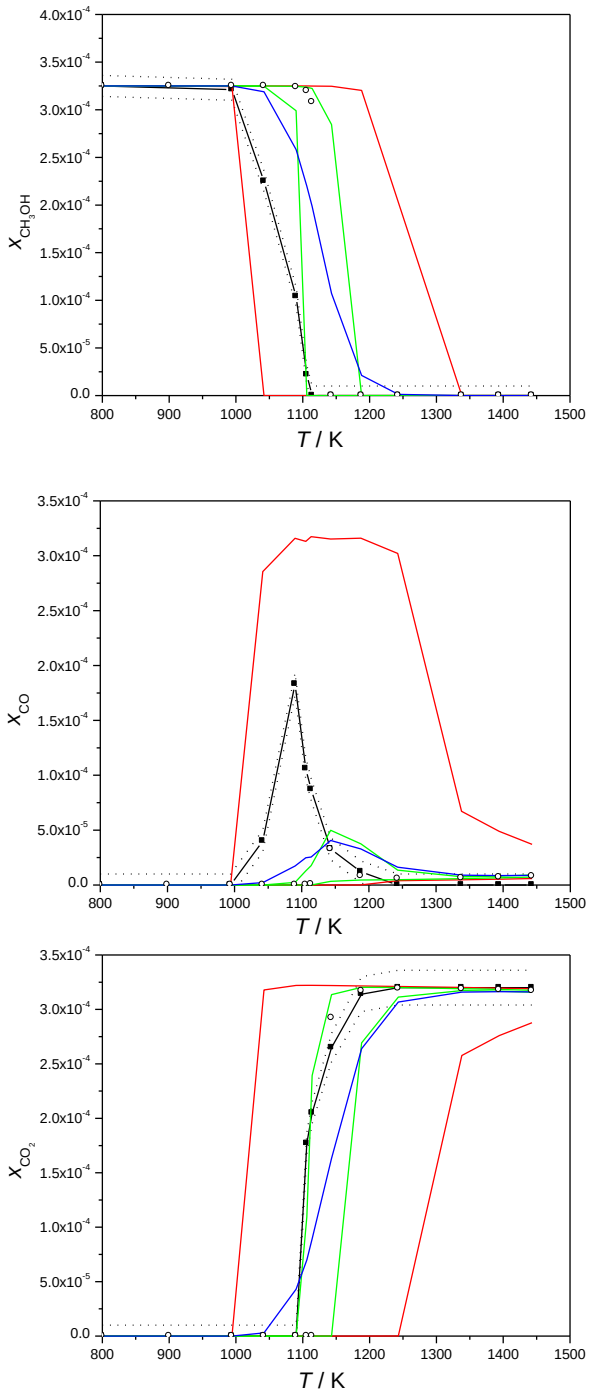


Figure 24. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2] and 10000 calculations. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

The global sensitivity analysis was carried out in two different temperatures to corroborate in which of them the sensitivity is the largest. Table G.2 show the comparative values of sensitivity between two temperatures and the largest one was selected (1108 K for CO and 1118 K for CO_2 and CH_3OH) to be plotted in Figure 25.

Table G.2 Sensitivity indices and temperature for the two most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 1 [2]

	CO		CO2		CH3OH	
	1108K	1118K	1108K	**1118K**	1108K	**1118K**
	1st order	1st order	1st order	1st order	1st order	1st order
sum Si	0,283	0,2794	0,6521	0,7097	0,7383	0,7952
1st reaction	184	184	184	184	184	184
Si	0,1045	0,0811	0,2385	0,2662	0,3056	0,3251
2nd reaction	33	33	1	1	116	116
Si	0,0373	0,0531	0,0713	0,075	0,0665	0,0617

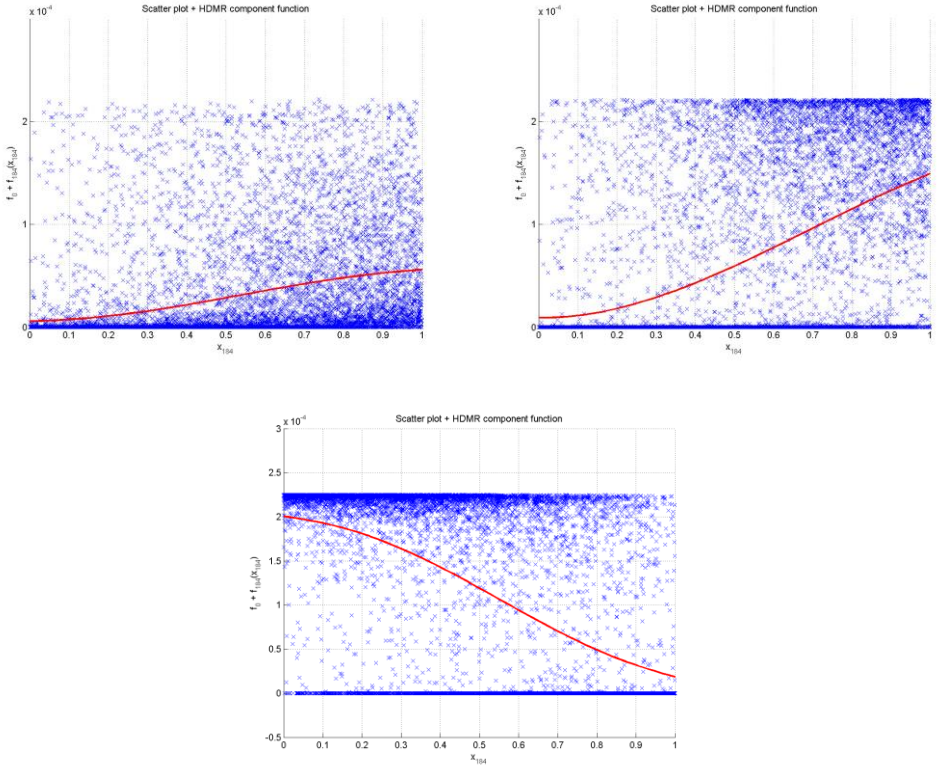


Figure 25. First-order component function and scatter plot of the (a) carbon-monoxide, (b) carbon-dioxide and (c) methanol mole fraction for Reaction 184 CH_2OH (+M) = CH_2O + H (+M) versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*) under conditions of Set 1 in [2]

Table G.3 Sensitivity indices and temperature for the two most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 2 [2]

	CO		CO2		CH3OH	
	1090K	1106K	1090K	**1106K**	1090K	**1106K**
	1st order	1st order	1st order	1st order	1st order	1st order
sum Si	0,2269	0,2173	0,6207	0,7508	0,5786	0,7318
1st reaction	184	184	184	184	184	184
Si	0,0886	0,0665	0,1831	0,2437	0,2317	0,279
2nd reaction	116	33	116	116	116	116
Si	0,0201	0,025	0,0654	0,0743	0,0728	0,0754

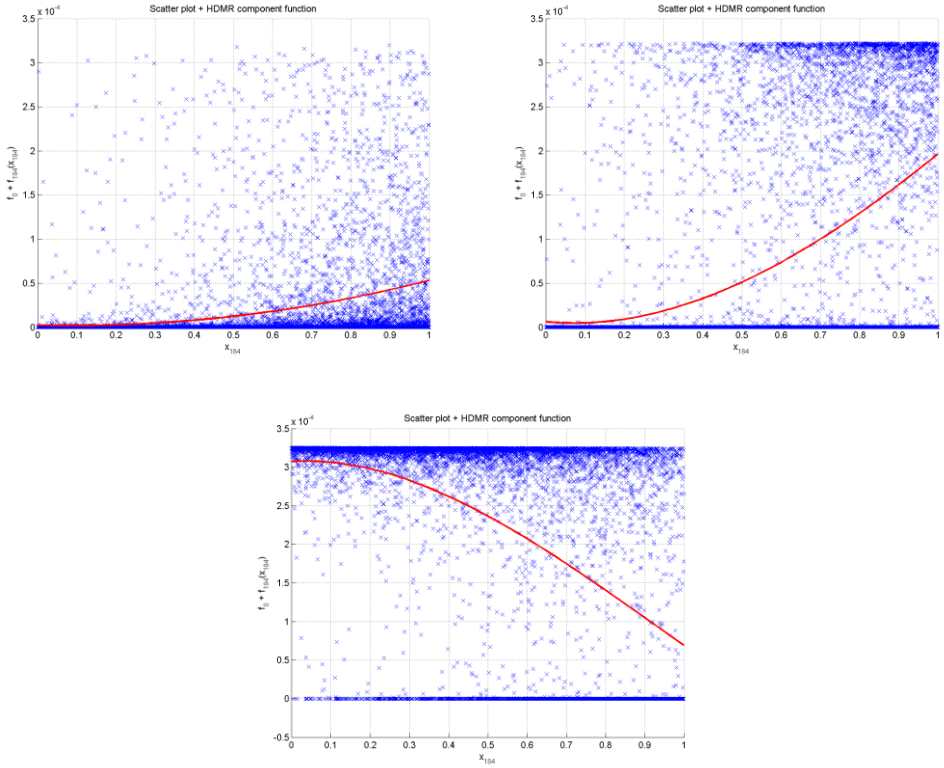


Figure 26. First-order component function and scatter plot of the (a) carbon-monoxide, (b) carbon-dioxide and (c) methanol mole fraction for Reaction 184 CH_2OH (+M) = CH_2O + H (+M) versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*) under conditions of Set 2 in [2]

Table G.4 Sensitivity indices and temperature for the two most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set 3 [2]

	CO		CO2		CH3OH	
	1089K	1114K	1089K	**1114K**	1089K	**1114K**
	1st order	1st order	1st order	1st order	1st order	1st order
sum Si	0,2262	0,22	0,4815	0,6319	0,5053	0,7067
1st reaction	184	184	184	184	184	184
Si	0,0709	0,0404	0,1296	0,2113	0,1938	0,2611
2nd reaction	116	33	126	20	116	20
Si	0,0221	0,0326	0,0383	0,0723	0,0551	0,0793

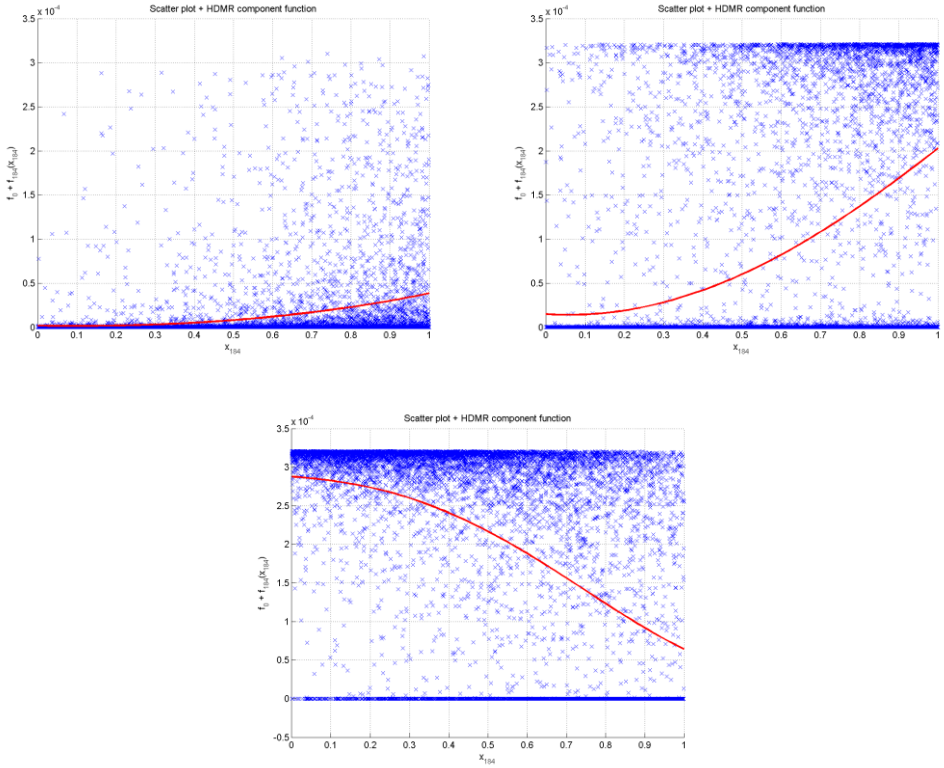


Figure 27. First-order component function and scatter plot of the (a) carbon-monoxide, (b) carbon-dioxide and (c) methanol mole fraction for Reaction 184 CH_2OH (+M) = CH_2O + H (+M) versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*) under conditions of Set 3 in [2]

The sensitivity indices obtained for carbon-monoxide at this temperature are too low, further investigation is needed here, since sensitivity index of 0.2 or less means not a really significant correlation between the result variable and the parameter.

Table G.5 Sensitivity indices and temperature for the two most sensitive reaction for CO (a), CO_2 (b) and CH_3OH (c) in Set E4 [2]

	CO	CO2	CH3OH
	748K	**748K**	**748K**
	1st order	1st order	1st order
sum Si	0,6136	0,6795	0,817
1st reaction	23	23	23
	0,3821	0,3439	0,5514
2nd reaction	21	176	176
	0,0551	0,0822	0,0819

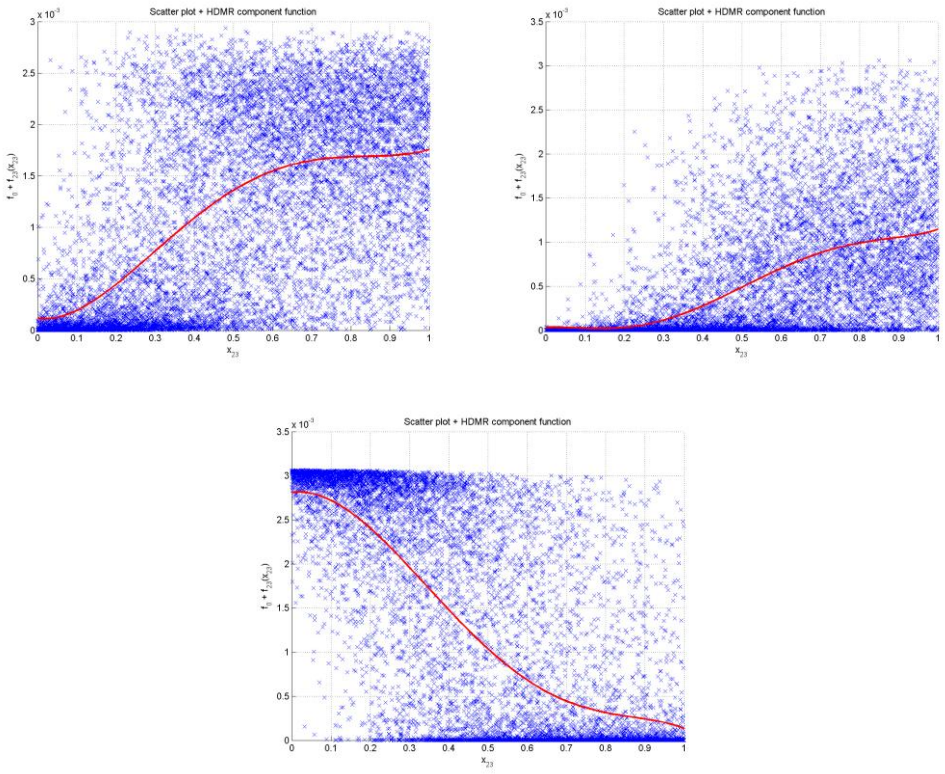


Figure 28, First-order component function and scatter plot of the (a) carbon-monoxide, (b) carbon-dioxide and (c) methanol mole fraction for Reaction 23 H2O2(+M)=OH+OH(+M) versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*) under conditions of Set E4 in [3]

Here, we can conclude that Reaction 23 H2O2(+M)=OH+OH(+M) is the most important reaction controlling these species concentrations. In the future, one should concentrate on the right place and slope of the methanol consumption, the same for CO2, and the good prediction of CO (since it is an important intermediate).

APPENDIX H. English version of the report

SUMMARY

Alcohols have been the most common examples of biofuels and have been the subject of considerable interest. Methanol is the simplest alcohol and even though it has been studied in the past, no mechanism has been able to reproduce the experimental data in a wide range of conditions. Due to the hierarchical model development, the oxidation of methanol is a part of the oxidation mechanisms for all higher alcohols as well as necessary to account for the combustion of a number of fuels under certain conditions.

This work is based on a (i) low pressure oxidation mechanism for simulating the conversion of methanol in a flow reactor at atmospheric pressure and (ii) a high pressure methanol oxidation mechanism for analyzing the conversion of methanol at high pressure up to 100 bar. Both reaction mechanisms describe the oxidation of methanol and the formation of nitric-oxides. Both reaction mechanisms perform well at the conditions where these were developed, but fail at the other pressure range. Development of a new mechanism is necessary for simulating the conversion of methanol throughout the pressure range.

The first version of a common methanol oxidation mechanism was created based on existing mechanisms. New parameters were considered for the 28 reactions which were different in the basis mechanisms. The experimentally measured concentration of methanol, carbon-monoxide and carbon-dioxide was compared to the simulation results of the low pressure, the high pressure and the merged mechanisms and the agreement was not satisfactory. To get some information how to improve the mechanism sensitivity analysis was carried out.

Local sensitivity analysis was performed for each experimental set on the concentration of methanol, carbon-monoxide and carbon-dioxide. The low pressure limits of the pressure dependent reactions were also included in the analysis. The merged mechanism contains 172 reactions, but 14 reactions are pressure dependent and have low pressure limit. Altogether, 186 parameters (pre-exponential factors) were varied. The temperatures having the largest local sensitivity values were selected for the global sensitivity analysis.

Global sensitivity analysis methods are widely used to investigate detailed combustion mechanisms. The uncertainty limits of each reaction rate parameter were estimated and Monte Carlo simulations were performed to predict the possible minimum and maximum concentrations calculated at different temperatures. High Dimensional Model Representation (HDMR) method was used to identify the global sensitivity coefficients and reveal the globally most sensitive reactions which can be modified to enhance the general performance of the mechanism.

The most important reaction in this mechanism under all the circumstances investigated was Reaction 121, $CH_3OH + HO_2 = CH_2OH + H_2O_2$, which controls both the methanol, carbon-monoxide and carbon-dioxide concentration. To improve the mechanism, the rate coefficient of this reaction was revised and a new mechanism was proposed.

The updated mechanism was investigated further. Results are seen to be improved significantly, suggesting that the new parameters recommendations should be present in an updated submechanism for methanol conversion.

Table of contents

1. INTRODUCTION

1.1.Preliminaries

1.1.1. The importance of methanol

Alcohols have been the most common examples of biofuels and have been the subject of considerable interest [1]. Nowadays, the oxygenated hydrocarbons are considered as an alternative to gasoline for transport purposes. Among those, methanol which is the simplest alcohol may be of interest because of its different possible production sources. Methanol is a comparatively clean fuel because of, among others, the presence of oxygen in its composition and the lack of C-C bonds in its structure limits the probability of incomplete combustion.

Methanol does not contain sulfur or complex organic compounds. The organic emissions (ozone precursors) from methanol combustion will have lower reactivity than gasoline fuels hence lower ozone forming potential. If pure methanol is used then the emission of benzene and PAHs is very low. Methanol gives higher engine efficiency and is less flammable than gasoline.

A chemical kinetic mechanism is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reaction proceeds. A mechanism is a proposal from which a rate law that agrees with the observed rate laws can be derived. The fact that a mechanism explains the experimental results is not a proof that the mechanism is correct. A mechanism is our rationalization of a chemical reaction.

Methanol is the simplest alcohol and even though it has been studied in the past, no mechanism has been able to reproduce the experimental data in a wide range of conditions. Due to the hierarchical model development, the methanol mechanism is a part of the oxidation mechanisms for all higher alcohols as well as necessary to account for the combustion of a number of fuels under certain conditions.

1.1.2. Original mechanisms

In this work, we utilized an already developed (i) low pressure oxidation mechanism [2] for simulating the conversion of methanol in flow reactor at atmospheric pressure in the 700-1500 K temperature range and (ii) a high pressure methanol oxidation mechanism [3] for analyzing the conversion of methanol at high pressure up to 100 bar.

Both reaction mechanisms describe the oxidation of methanol and the formation of nitrogen-oxides (NO_x). The atmospheric pressure mechanism contains 502 reactions of 68 species (27 species and 168 reactions without the nitrogen-oxide chemistry). The high pressure mechanism has 506 reactions of 68 species (without the NO_x chemistry 27 species and 172 reactions). Mechanisms without the NO_x chemistry are detailed in Appendix A.

1.1.3. Experimental sets

Table 1.1 and Table 1.2 details the two types of experimental data that were used for developing each mechanism: Table 1.1 presents the experimental conditions of the low pressure experiments (1 bar), corresponding Set 1–6. In Table 1.2 the details of the high pressure

experiments can be found, corresponding Set E1–E5. The experimental installation used in the methanol mechanism development is described in details in the cited work [2].

Table 1.1. Initial conditions and residence time for low pressure (1 bar) experiments

Experiment	CH_3OH(ppm)	O_2(ppm)	H_2O(%)	NO(ppm)	N_2(%)	λ	res.Time(s)
Set 1	225	206	1.75	0	98.2069	0.61	179/T
Set 2	325	429	1.87	0	98.0546	0.88	180/T
Set 3	321	3821	1.78	0	97.8058	7.94	180/T
Set 4	450	250	1.16	505	98.7195	0.37	188/T
Set 5	450	771	1.10	416	98.7363	1.14	182/T
Set 6	330	7256	0.94	3450	97.9564	14.66	185/T

Table 1.2. Initial conditions and residence time for high pressure experiments

Experiment	*p*(bar)	CH_3OH(ppm)	O_2(ppm)	NO(ppm)	N_2(%)	λ	res.Time(s)
E1	20	3070	921	0	99.6009	0,2	1317,36/T
E2	50	3070	921	0	99.6009	0,2	3293,39/T
E3	100	3070	921	0	99.6009	0,2	6586,79/T
E4	100	3070	4605	0	99.2325	1	6586,79/T
E5	100	3070	92100	0	90.483	20	6586,79/T

1.1.4. Sensitivity analysis

Chemical mechanisms are constantly being updated as new experiments and calculations yield improved kinetic data. Sensitivity analysis is an effective tool for the exploration of the relationship between the output of mathematical models and the input data, which comprise the values of parameters as well as the initial or boundary conditions.

Sensitivity analysis lets to improve the performance of chemical models that have proven unsatisfactory because of the inaccuracy of the rate coefficients. By means of a sensitivity analysis, those reactions having the higher influence on the results can be identified.

1.2.Aims

The low pressure and high pressure methanol oxidation mechanisms chosen for the present study perform well under the conditions they were developed but fail at the other pressure range. The mechanisms have slightly different species sets and use different reaction rate parameters for several reactions.

The aim of this project is to make an attempt to create a common methanol oxidation mechanism based on existing low and high pressure detailed reaction mechanisms, for simulating the conversion of methanol throughout the pressure range.

1.3.Outreach

This project is based on the results achieved in two former mechanism development works. Therefore, the first step was to analyze the reaction mechanisms in which the progress of the

project bases. First, a simplified mechanism version was considered to begin the analysis, leading a single unified mechanism. The two basis mechanisms were compared to select either those reactions which appear in both mechanisms but with different parameters, or those reactions that belong to only one of the mechanisms.

Then, new parameter values of the common reactions were calculated. For that purpose a simple average of the Arrhenius parameters were used. A more sophisticated estimation of the new rate parameters is desired in the future. This new mechanism was analyzed in the same way as the two original ones.

Once the new merged mechanism has been obtained, uncertainty limits of each reaction were assigned utilizing chemical kinetic evaluations and databases. Using these uncertainty limits, random values were created for the Monte Carlo (MC) simulation. From these simulations, beside the nominal concentration of methanol, carbon-monoxide and carbon-dioxide, the reliability of the simulations were revealed (i.e. the possible maximum and minimum concentration and the mean). The same simulation results were used in the subsequent global sensitivity analysis.

Local sensitivity analysis was performed to obtain the reactions which can cause the largest change of the calculated concentrations and the temperature where this sensitivity is the largest. These temperatures were used to perform global sensitivity analysis.

Finally, global sensitivity analysis was applied on the merged mechanism. High Dimensional Model Representation (HDMR method) was used to identify the global sensitivity coefficients and reveal the globally most sensitive reactions whose modifications can enhance the general performance of the mechanism.

Once the globally most sensitive reactions are known, the improvement of their rate parameters was the next step amending the mechanism to perform better against the experiments. Sensitivity analysis was applied using the new mechanism and the results were analyzed to expose the guidelines to obtain the best methanol oxidation mechanism possible.

1.4.Context and limitations

This project was made possible by an Erasmus exchange between the University of Zaragoza and the Eötvös Loránd University (Budapest, Hungary). University of Zaragoza has provided the basis reaction mechanisms, and the Eötvös University has brought his extensive knowledge and tools required for the analysis of these mechanisms.

Upon the completion of this project, the high pressure mechanism was in development, therefore, the available experimental data are limited to only one of the sets mentioned above, namely set E4, thereby preventing further comprehensive study of high-pressure mechanism, and consequently of the merged mechanism.

1.5. Methods used

It is necessary to create a new mechanism applies for both, high and low pressure, and for this, sensitivity analysis was carried out, which is a technique changing systematically the parameters of the model to determine the effects of such changes.

With the accumulation of knowledge about kinetic mechanisms under investigation and with the advance of power of modern computing technologies, detailed complex kinetic models are increasingly used as predictive tools and as aids for understanding the underlying phenomena. Sensitivity analysis has been proven to be a powerful tool to investigate complex kinetic models.

Sensitivity analysis can be used to identify the influential parameters which can be determined from available data while screening out the unimportant ones. Sensitivity analysis can also be used to identify redundant species and reactions allowing model reduction.

1.5.1. Parameterization and simulations of reactions mechanisms

The CHEMKIN program package is a collection of subroutines and simulation programs written in FORTRAN language for solving problems involving gas-phase kinetics, equilibrium and transport properties. In this project, the CHEMKIN -II [6] version was used. CHEMKIN -II can solve the differential equations of a detailed reaction mechanism, including thousand reactions of several species, thus can lead to a comprehensive understanding of a particular process, which might involve multiple chemical species, concentration ranges, and gas temperatures. The computational capabilities of CHEMKIN -II allow for a complex chemical process to be studied in detail, including intermediate compounds and trace compounds.

The rate coefficients of the reactions are generally assumed to have Arrhenius type temperature dependence. Since in most of the combustion processes wide temperature range is covered during the simulations the extended Arrhenius-expression is used:

$$k = A\,T^{\beta}\,\exp\left(\frac{-E}{R_c\,T}\right)$$

where A is the "pre-exponential factor" (note: not the same as in the classical, two parameter Arrhenius-equation), β the temperature exponent, and E the activation energy . These three parameters are required input of the GAS-PHASE KINETICS package for each reaction.

To create the merged mechanism these three values were modified, calculating the simple average between high pressure and low pressure mechanisms parameters.

1.5.2. Local Sensitivity Analysis

Local sensitivities are the partial derivatives of model output with respect to the parameters and describe the effect of small parameter perturbations around nominal parameter values. Due to its nature it takes into account the effect of the change of one parameter while all others are fixed at their nominal values. This analysis usually is done using the built-in sensitivity calculation features of the kinetic simulation programs.

The common reaction kinetic simulation program packages investigate the sensitivities with respect to the pre-exponential factors only. The calculation also can be done using the brute force method (modifying the pre-exponential factors of the reactions manually), but it is very rare that the impact of other parameters, for example the low pressure limits are investigated. However, the simulation results can be sensitive to the low pressure limit of some reactions. In this work, the low pressure sensitivities were also calculated. The simulations and computation

of the local sensitivity coefficients were done using an automatic program [4]. The program was written in MATLAB [5] and uses the CHEMKIN-II [6] package for the simulations. Since the program requires the experimental data in PrIMe data format [(http://www.primekinetics.org/)] all experiments were converted to xml files.

The experimental values and the simulation results should be compared regularly during the mechanism development procedure and the agreement is typically adjudged only qualitatively. Recently, plotting the experimental error becomes common, but presentation of the error or possible minimum and maximum values of the simulation results is still rare. However, the agreement can be quantitatively characterized using these measures [7].

1.5.3. Monte Carlo Simulations

The Monte Carlo Method is a series of simulations in which a deterministic model is evaluated using random number sets as inputs. This method is often used when the model is complex, nonlinear, or involves more than just a couple uncertain parameters.

Latin Hypercube Sampling (LHS) is a statistical method for generating a distribution of plausible collections of parameter values from a multidimensional distribution. The sampling method is often applied in uncertainty analysis. In the context of statistical sampling, a square grid containing sample positions is a Latin square if (and only if) there is only one sample in each row and each column. A Latin hypercube is the generalization of this concept to an arbitrary number of dimensions, whereby each sample is the only one in each axis-aligned hyperplane containing it. LHS ensures that the ensemble of random numbers is representative of the real variability whereas traditional random sampling (sometimes called brute force) is just an ensemble of random numbers without any guarantees.

1.5.4. Global Sensitivity Analysis

Global sensitivity analysis methods are widely used to investigate detailed combustion mechanisms. The high dimensional model representation (HDMR) method is a set of tools which can be used to construct a fully functional metamodel and to calculate variance based sensitivity indices very efficiently. The method was introduced by Rabitz and Alis [8] and applied in the field of reaction kinetics [9, 10]. An optimisation algorithm, which automatically determines the optimal order of the polynomials used in the HDMR expansion for the approximation of the component functions has been developed by Ziehn and Tomlin [10] as an extension to existing HDMR tools. Further, a threshold has been introduced by Ziehn and Tomlin [9] in order to exclude unimportant component functions from the HDMR expansion. This is particularly useful if the number of input parameters is larger than 20 which is the case in the methanol oxidation mechanism investigated here.

In this work, the MATLAB based GUI-HDMR software [11] was used to calculate the global sensitivity coefficients. The maximum order of the first-order component functions was 5, that of the second-order ones 3, correlation method was used to reduce the variance, and 0,1% relative threshold was used when the HDMR method was applied.

2. THE MERGED MECHANISM

2.1. Mechanism without Nitrogen

The reliability of a methanol oxidation mechanism is crucial for the accurate prediction of the nitrogen-oxides. Thus, the first step is the investigation of the pure methanol chemistry without NO_x species and reactions. The original reaction mechanisms contain the nitrogen chemistry therefore they were eliminated to get simplified mechanisms.

This means that experiments having added nitrogen-monoxide among the reactants cannot be simulated using this simplified mechanism. Therefore, only Sets 1, 2 and 3 of the low pressure experiments and Set E4 of the high pressure experiments were utilized.

2.2.Creation of the merged mechanism

2.2.1. New rate parameters

To create a merged reaction mechanism from the low pressure and the high pressure ones, it is necessary to create common species set as the union of the species involved in either mechanism. Fortunately, these methanol oxidation sub-mechanisms contain the same species set. However, they use different set of reactions. Most of the reactions were common, but there were 8 reactions which appeared only in either the low pressure (6 reactions) or in the high pressure (2 reactions) reaction mechanism. Additionally, a part of the common reaction set used different rate parameters, specifically, 28 reactions. All reactions of original mechanisms and their parameters appear in Appendix A.

As a first step to a common reaction mechanism, the two reaction mechanisms were merged to get a united reaction mechanism which will be used as the base mechanism of the further mechanism development. It contains 172 reactions of 27 species. The rate parameters of the common reactions were determined simply averaging the Arrhenius parameters used in the original low and high pressure mechanisms. Later, a more sophisticated determination of these rate parameters will be desired. Average values were made for the following calculations:

$$\frac{1}{2}\ln k_1 = \frac{1}{2}\left(\ln A_1 + \beta_1 \ln T - \frac{E_1}{R\,T}\right)$$

$$\frac{1}{2}\ln k_2 = \frac{1}{2}\left(\ln A_2 + \beta_2 \ln T - \frac{E_2}{R\,T}\right)$$

$$\ln(k_1 k_2)^{1/2} = \ln(A_1 A_2)^{1/2} + \frac{\beta_1 + \beta_2}{2}\ln T - \frac{E_1 + E_2}{2}\frac{1}{R\,T}$$

$$\ln k = \ln A + \beta \ln T - \frac{E}{R\,T}$$

Let's consider Reaction 119 as an example:

$CH_3OH+OH = CH_2OH+H_2O$ (R119, Appendix B)

Arrhenius parameters in the high pressure mechanism:

$A_h = 1.50 \cdot 10^8$ cm^3 mol^{-1} s^{-1}, $\beta_h = 1.4434$, $E_h = 113$ cal mol^{-1}

And in the low pressure mechanism:

$A_l = 1.40 \cdot 10^6$ cm^3 mol^{-1} s^{-1}, $\beta_l = 2$, $E_l = -3510$ cal mol^{-1}

The intermediate values utilized in the merged mechanism are:

$A_m = \sqrt{A_h \cdot A_i} = 14491377$ cm^3 mol^{-1} s^{-1},

$\beta_m = \frac{\beta_h+\beta_i}{2} = 1.7217$,

$E_m = \frac{E_h+E_i}{2} = -1698.5$ cal mol^{-1}

The different kinetic parameters considered for Reaction 119 are shown in Figure 29.

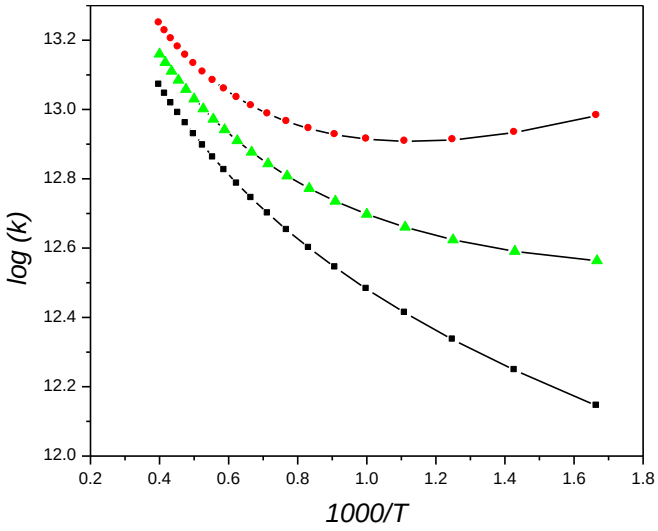


Figure 29. Arrhenius plot (T [K], k [cm^{3}mol^{-1}s^{-1}]) of the reaction $CH_3OH+OH=CH_2OH+H_2O$ with high pressure (squares), low pressure (circles) and intermediate values (triangles)

2.3. First simulations and comparison plots

Once the merged mechanism is defined, the first simulations of the experiments can start. SENKIN is a program that predicts the time-dependent chemical kinetics behavior of a homogeneous gas mixture in a closed system [17].

To solve a problem using SENKIN, the user must access the CHEMKIN thermodynamic data base, execute the CHEMKIN interpreter, and pass input keyword data to SENKIN.

The first step is to execute the CHEMKIN interpreter, which reads user-supplied information about the species and chemical reactions for a particular reaction mechanism. All

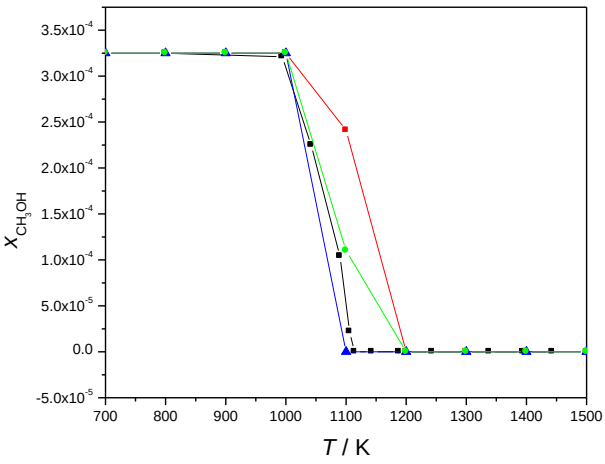
this information is stored in the CHEMKIN linking file, which is needed by the CHEMKIN subroutine library.

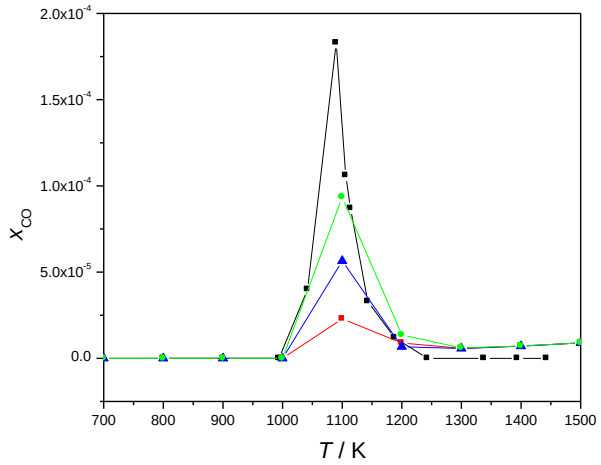
The input that defines a particular problem and the parameters needed to solve it are read by SENKIN from a text file. An example of input file is shown below:

```
CONT
PRES 1
TEMP 700
TIME 0.25714
TLIM 1800
DELT 1.0e-6
RTOL 1.0e-5
ATOL 1.0e-15
REAC CH3OH  0.0325
REAC O2  0.0429
REAC H2O 1.87
REAC N2  98.0546
END
```

This case corresponds to the conditions of Set 2. The temperature (TEMP) (700 K) is constant during the simulation (CONT), the pressure is 1 bar (PRES), residence time (TIME) is calculated with the expression *180/T*, where the residence time is in seconds and the temperature in Kelvin, and the initial mole fractions of the substances involved is detailed. The reactants (REAC) are defined in mole fraction. The simulations were carried out at different temperatures under the conditions of all sets, and the results of the different mechanisms used were compared.

The plots represent the experimental data obtained during the low pressure experiments (Sets 1, 2 and 3) and the high pressure experiment (Set E4). The simulations of high and low pressure experiments are carried out with both mechanisms. Also, the simulation of the merged mechanism is carried out to compare the new results and check if the new parameters are reasonable. Figure 30 and Figure 31 show the concentration of methanol, carbon-monoxide and carbon-dioxide for the simulations of low pressure, high pressure, merged mechanism and experimental results under the circumstances of a low pressure (Set 2) and a high pressure experimental (E2) set.





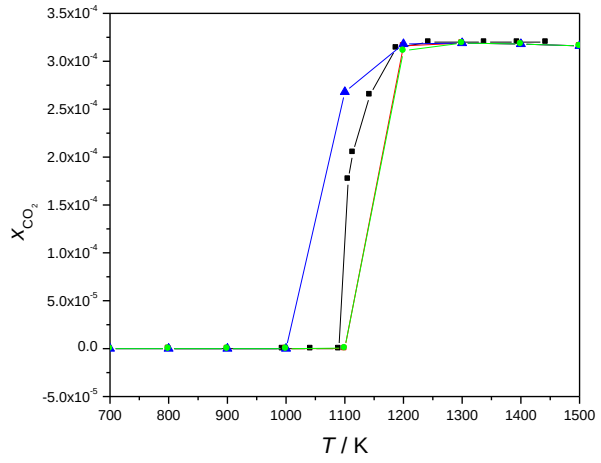


Figure 30. Mole fraction of CH_3OH, CO and CO_2 vs, temperature under the circumstances of Set 2. Black squares indicate the measured values, red squares high pressure mechanism results, green circle the low pressure ones and blue triangle the merged mechanism simulation results.

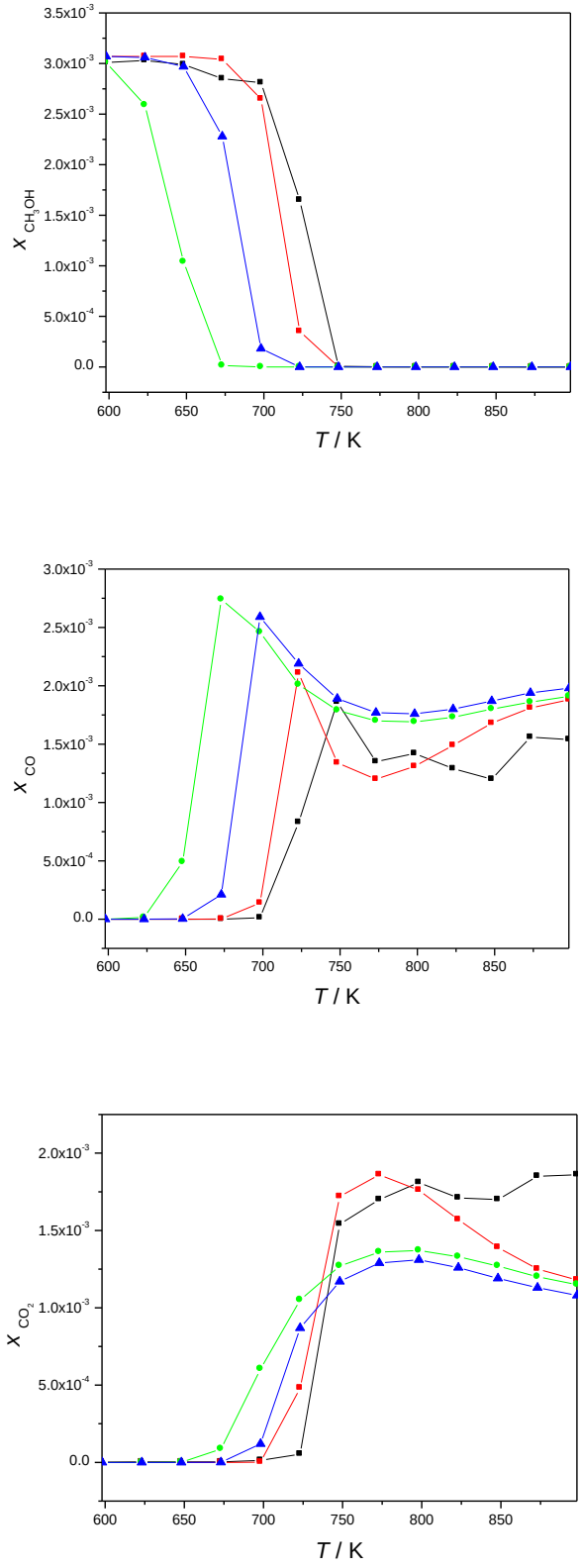


Figure 31. Mole fraction of CH_3OH, CO and CO2 vs, temperature under the circumstances of Set E4. Black squares indicate the measured values, red squares high pressure mechanism results, green circle low pressure and blue triangle show the merged mechanism simulation results.

The low pressure mechanism results explain better the conversion of those substances at low pressure (see Figure 2), while the high pressure mechanism is more effective at high pressure (see Figure 3). The first version of the merged mechanism is a good approximation to start the sensitivity analysis calculations.

2.4.Modifications

The temperature dependence of some reactions in the mechanism are described by two (7 reactions) or three (1 reaction) Arrhenius equations. One Arrhenius of the reaction (HO_2 + OH = H_2O + O_2) described by triple Arrhenius had negative *A*-factor. The sum of the three Arrhenius provided correct rate coefficient, but this kind of parameterization should be modified since negative *A*-factor cannot be handled in the logarithmic space. In this work a simple Arrhenius of Keyser [12] was used according to Dryer et al [13] instead of the triple Arrhenius description.

Parameterization in the original mechanism:

	A	**β**	**E**
20. HO2+OH=H2O+O2	3.6E21	-2.100	9000
DUPLICATE			
21. HO2+OH=H2O+O2	2.0E15	-0.600	0
DUPLICATE			
22. HO2+OH=H2O+O2	-2.2E96	-24.000	49000
DUPLICATE			

Modified parameterization:

	A	**β**	**E**
20. HO2+OH=H2O+O2	2.89E13	0.0	-497.0

The complete reaction mechanism, with all reactions and rate parameters, can be found in Appendix B.

3. THE UNCERTAINTY LIMITS

3.1.Databases utilized

An "uncertainty limit" means an estimate of the total error of a measurement or calculation. Since we cannot presume to know the "true" value of a measured quantity from the experiments, we can only estimate the error by observing the scatter of the results, which is the sign of random errors, and by studying the apparatus and the measuring process to discover likely sources of systematic error.

For the Monte Carlo simulations the uncertainty limits of the rate parameters were estimated on the bases of the latest Baulch et al. evaluation [14]. In this, Evaluated Kinetic Data for Combustion Modeling paper data sheets are presented setting out relevant thermodynamic data, rate coefficient measurements with references, and an assessment of the reliability of the data, and preferred values of the rate coefficients are suggested for several reactions. In addition, where appropriate, all of the data are displayed on an Arrhenius diagram. Generally, the recommended uncertainty factors of Baulch et al. are accepted, but if one value did not cover the rate coefficient used in the merged mechanism its value was increased till it did that.

For those reactions not having recommendation in the Baulch et al. evaluation, the NIST database [15] was utilized. There were 20 reactions which did not appear either in the Baulch et al. evaluation or in the NIST database. In these cases an order of magnitude uncertainty interval was assumed, $\Delta\log(k) = 1$, generally.

3.2. Determination of the uncertainty limits

Plotting the rate coefficient calculated from the Baulch evaluation preferred values together with its uncertainty and from the values used in methanol mechanism, it will get to know if the value used in the methanol mechanism fall between the Baulch evaluation uncertainty limits at any temperature.

Using these graphs, the uncertainty limits of each merged mechanism reaction can be analyzed.Let's consider Reaction 57 of the merged mechanism as an example:

$CH_4+H = CH_3+H_2$ (R57, Appendix B)

The Arrhenius parameters of this reaction are the following:

$A = 4.1\cdot10^3$ cm^3 mol^{-1} s^{-1}, $\beta = 3.156$, $E = 8755$ cal mol^{-1}

The preferred values and reliability according Baulch Evaluated Data are:

$k = 1.02\cdot10^{-18}\ T^{2.50}\ exp(-4825/T)$ cm^3 molecule^{-1} s^{-1} over the range 350-2500 K
$\Delta\log k = \pm 0.2$ at 1000 K, rising to ± 0.4 at 350 K and 2500 K

These values calculated according the units of this work are:

$A = 6.14E05$ cm^3 mol^{-1} s^{-1}, $\beta = 2.5$, $E = 9581.857$ cal mol^{-1}

Plotting the recommended rate coefficient and its uncertainty together that of values used in the merged methanol mechanism (Figure 4), it is possible to check if the value used in the methanol mechanism fall between the Baulch evaluation uncertainty limits at any temperature.

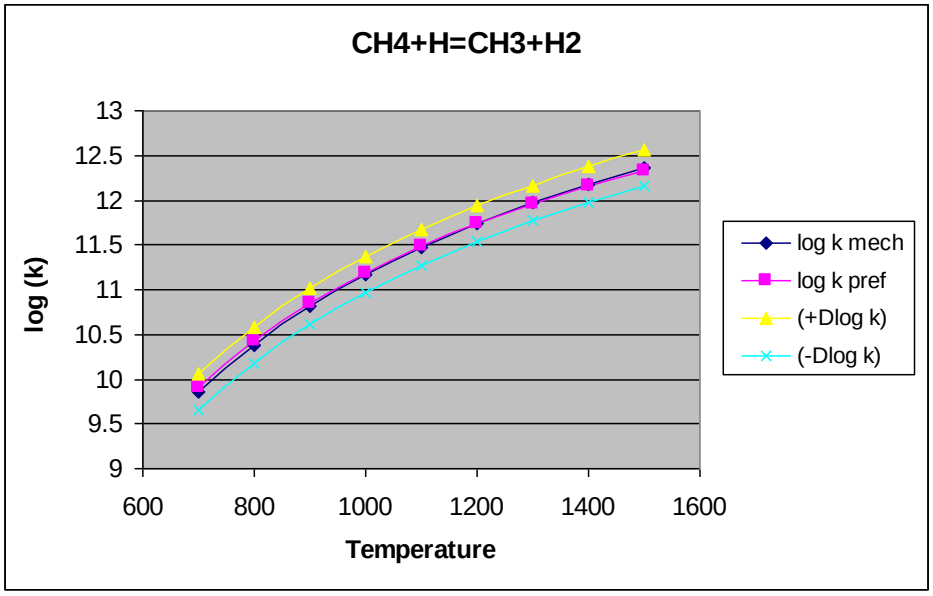


Figure 32. Temperature vs. log (k) of merged mechanism (blue squares), the Baulch preferred values (pink squares) and the uncertainty limits assigned to the merged mechanism values (triangles and crosses)

In this case, the rate coefficients are very similar and fall between the uncertainty limits. If the represented curve does not fall within the expected range, that range is extended to keep the two curves within the limits.

When a reaction is not available in Baulch Evaluated Data, the resource used is NIST Chemical Kinetic Database. Here, a compilation of kinetics data on gas-phase reactions can be found.

The uncertainty limits were determined to keep inside the rate measured coefficients over the whole temperature interval investigated. For example, the Reaction 16 of the merged mechanism is:

$H_2+O_2 = HO_2+H$ (R16, Appendix B)

And the Arrhenius parameters of the reaction are:

$A = 7.40 \cdot 10^5$ cm^3 mol^{-1} s^{-1}, $\beta = 2.433$, $E = 53502$ cal mol^{-1}

The preferred values and reliability according NIST Chemical Database are:

2000MIC/SUT1471-1478

T = 400 - 2300 1.28x10^{-12} [cm^3/molecule s] (T/298 K)$^{2.43}$ e$^{-224\ [kJ/mole]/RT}$
A = 7.49·10^5 cm^3 mol^{-1} s^{-1}, β = 2.43, E = 53498.93 cal mol^{-1}

1999KAR/OSH11918-11927

T = 298 - 1000 6.31x10^{-11} [cm^3/molecule s] (T/298 K)$^{0.17}$ e$^{-233\ [kJ/mole]/RT}$
A = 1.44·10^{13} cm^3 mol^{-1} s^{-1}, β = 0.17, E = 55648.44 cal mol^{-1}

1989KOI2480-2484

$T = 1000 - 1400 \quad 6.81x10^{-8}\ [cm^3/molecule\ s]\ e^{-285\ [kJ/mole]/RT}$

$A = 4.10 \cdot 10^{16}\ cm^3\ mol^{-1}\ s^{-1},\ \beta = 0,\ E = 68067.83\ cal\ mol^{-1}$

1986TSA/HAM1087

$T = 300 - 2500 \quad 2.41x10^{-10}\ [cm^3/molecule\ s]\ e^{-237\ [kJ/mole]/RT}$

$A = 1.45 \cdot 10^{14}\ cm^3\ mol^{-1}\ s^{-1},\ \beta = 0,\ E = 56603.77\ cal\ mol^{-1}$

Note that the parameters A, β and E are calculated because the rate coefficient, k has different units.

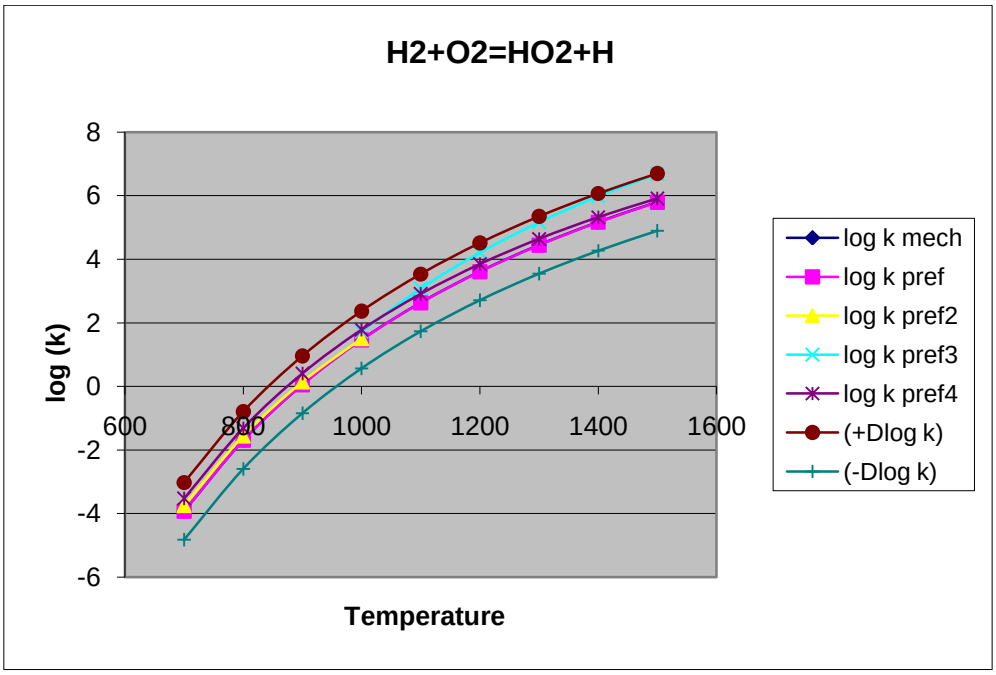


Figure 33. Temperature vs. log (k) of merged mechanism (diamonds), the reaction rates coming from the NIST database (4 references) and the uncertainty limits assigned to the merged mechanism values (circles and lines)

Plotting the data from the NIST database and the original reaction rate (see Figure 33), the uncertainty interval can be obtained. The limits are determined to keep all referenced parameters between them. Its value for this reaction is ±0.9.

Under certain conditions, some reaction rate expressions depend on pressure as well as temperature. Baulch Evaluated Data also include such reactions. As an example, Reaction 9 of the merged mechanism:

$H+O_2(+N_2) = HO_2(+N_2)$ (R9 and R175, Appendix B)

The parameters of the rate reaction are:

High pressure: $A = 1.5 \cdot 10^{12}$ cm^3 mol^{-1} s^{-1}, $\beta = 0.6$, $E = 0$ cal mol^{-1}
Low pressure: $A = 6.37 \cdot 10^{20}$ cm^3 mol^{-1} s^{-1}, $\beta = -1.72$, $E = 520$ cal mol^{-1}
TROE / 0.8 1.0E-30 1.0E30 /

The preferred values and reliability according Baulch Evaluated Data are:

$k_o = 7.3 \cdot 10^{-29}\ T^{-1.3}\ cm^6\ molecules^{-2}\ s^{-1}$ *for* $M = N_2$ *over the range 298-2000 K.*

$k_\infty = [0.32\ T^{0.56} + 2.9 \cdot 10^4] \cdot 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ *over the range 298-1500 K*

$F_c = 0.57$ *for* $M = N_2$ *over the range 298-1500 K.*

$\Delta \log k_o = \pm 0.1$ *at 298 K rising to* ± 0.2 *at 2000 K for M = Ar and for* $M = N_2$.

$\Delta F_c(Ar) = \Delta F_c(N_2) = \Delta F_c(H_2O) = \pm 0.1$ *over the range 298-1500 K.*

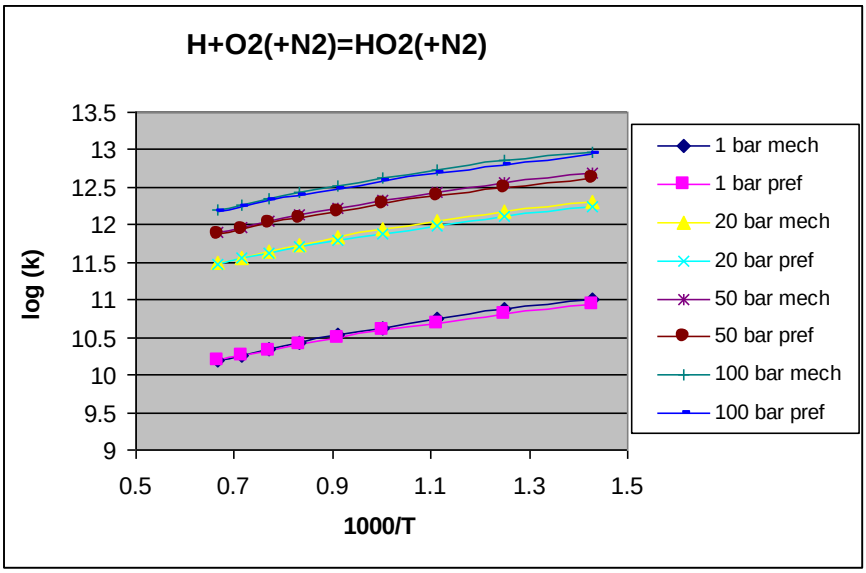


Figure 34. Arrhenius plots of different pressures for both rate parameters, merged mechanism and preferred values for Reaction 9

Figure 34 shows the Arrhenius plots of different pressures. Plotting the values for different pressure it is obtained the uncertainty for each one (see Figure 35).

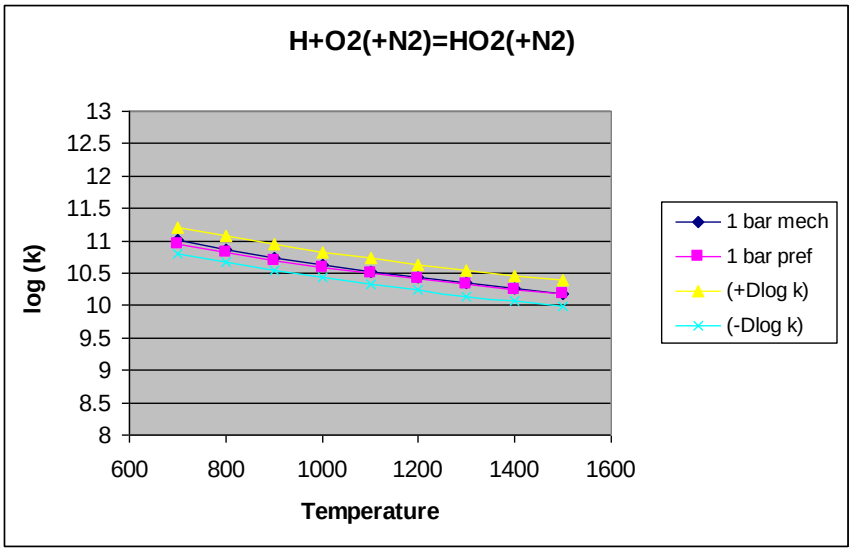


Figure 35. Temperature [K] vs. log (k[$cm^3 mol^{-1} s^{-1}$]) of the merged mechanism values (diamonds) and preferred values (squares) and the reliability (triangles and crosses) for one bar for Reaction 9

The complete list of the determined uncertainties is detailed in the last column (Δlogk) of Appendix B. The details of these calculations can be checked in Appendix C.

4. LOCAL SENSITIVITY ANALYSIS

4.1. Calculation of the local sensitivity coefficients

The kinetic simulations and the computation of the local sensitivity coefficients were done using an automatic program [4]. The program was written in MATLAB [5] and uses the CHEMKIN-II [6] package for the simulations. Automated local sensitivity analysis was performed for each experimental set. The low pressure limits were also included in the analysis. The merged mechanism contains 172 reactions and 27 species, but 14 reactions are pressure dependent and have low pressure limit. Altogether, 186 parameters (pre-exponential factors) were varied.

This program lets to obtain the concentration of methanol, carbon-monoxide and carbon-dioxide as well as the local sensitivity coefficients of the most sensitive reaction at each temperature and the relative sensitivities for the rest of reactions. Figure 36 presents typical results of the local sensitivity analysis.

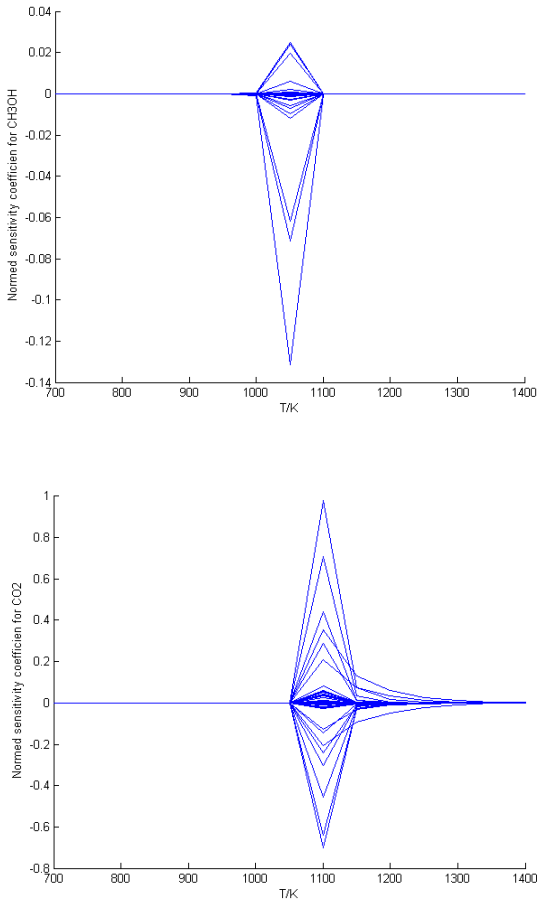


Figure 36. Normalized local sensitivity coefficients of the mole fraction of methanol (a) and carbon-dioxide (b) vs. temperature under the circumstances of Set 1 [2]. These plots were automatically generated using a MATLAB based program reported in [4]

4.2. The most sensitive reactions

Table 4.1. The most sensitive reactions and relative sensitivities (>5%) belong Set 1 [2] for methanol (a), carbon-monoxide (b) and carbon-dioxide (c)

CH3OH T=1050 K
Highest absolute sensitivity: -1.314084e-001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 5.45133e-001
Number of reaction: 1 Relative sensitivity : 4.68975e-001
Number of reaction: 126 Relative sensitivity : -1.88438e-001
Number of reaction: 116 Relative sensitivity : -1.82657e-001
Number of reaction: 127 Relative sensitivity : -1.49354e-001
Number of reaction: 176 Relative sensitivity : 9.15978e-002
Number of reaction: 182 Relative sensitivity : 7.37272e-002
Number of reaction: 122 Relative sensitivity : 5.38901e-002

CO T=1050 K
Highest absolute sensitivity: 1.923726e+001

Number of reaction: 121 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 4.46452e-001
Number of reaction: 1 Relative sensitivity : 3.78291e-001
Number of reaction: 116 Relative sensitivity : -1.16839e-001
Number of reaction: 126 Relative sensitivity : -1.03324e-001
Number of reaction: 127 Relative sensitivity : -8.40255e-002
Number of reaction: 176 Relative sensitivity : 6.04467e-002

CO2 T=1100 K
Highest absolute sensitivity: 9.798240e-001

Number of reaction: 1 Relative sensitivity : 1.00000e+000
Number of reaction: 184 Relative sensitivity : 7.21996e-001
Number of reaction: 116 Relative sensitivity : -7.17712e-001
Number of reaction: 126 Relative sensitivity : -6.51625e-001
Number of reaction: 127 Relative sensitivity : -4.67029e-001
Number of reaction: 121 Relative sensitivity : 4.51105e-001
Number of reaction: 33 Relative sensitivity : 3.61254e-001
Number of reaction: 16 Relative sensitivity : -3.09621e-001
Number of reaction: 17 Relative sensitivity : 2.96090e-001
Number of reaction: 15 Relative sensitivity : -2.45087e-001
Number of reaction: 32 Relative sensitivity : 2.15366e-001
Number of reaction: 14 Relative sensitivity : -2.09258e-001
Number of reaction: 20 Relative sensitivity : -1.49025e-001
Number of reaction: 175 Relative sensitivity : -1.29861e-001
Number of reaction: 182 Relative sensitivity : 8.44683e-002
Number of reaction: 176 Relative sensitivity : 6.08207e-002
Number of reaction: 45 Relative sensitivity : 5.93460e-002
Number of reaction: 119 Relative sensitivity : 5.63587e-002
Number of reaction: 108 Relative sensitivity : 5.13380e-002

Local sensitivity analysis shows (Table 4.1) that for Set 1 the most important reaction is the Reaction 121, $CH_3OH + HO_2 = CH_2OH + H_2O_2$ (Appendix B) for methanol and carbon-monoxide and the Reaction 1, $H+O_2=O+OH$ (Appendix B) for carbon-dioxide. At second place, Reaction 184, $CH_2OH(+M)=CH_2O+H(+M)$ (Appendix B) appears in the three cases. Therefore, by varying the pre-exponential factor of Reaction 121, the output concentrations of methanol and carbon monoxide vary more sharply, affecting output parameters.

The temperatures having the largest local sensitivity values were selected for the global sensitivity analysis. Note, that these temperatures vary with the sets and can be different for methanol, carbon-monoxide and carbon-dioxide. For example, the global sensitivity analysis for Set 1 and for the concentration of methanol was carried out at 1050 K, approximately. All results are showed in detail in Appendix D.

The local sensitivity analysis is only an approximation and the sensitivity indices correspond to the nominal values of the parameters, but can be used as first assumption and provided a good basis for the global sensitivity analysis.

5. MONTE CARLO SIMULATIONS

5.1. Generation of the random input values

In chapter 3, the uncertainty limits of each reaction rate parameter were estimated in such way that symmetrical intervals were applied in logarithmic scale. These intervals were sampled uniformly using the Latin hypercube method for the analysis. This sampling covers the parameter space with minimal sample size and in an unbiased manner. The number of runs was 1000, 3000 and 10000 calculations. Figure 37 shows an example of distribution of the random values. This Figure clearly shows that there was no correlation assumed between the parameters.

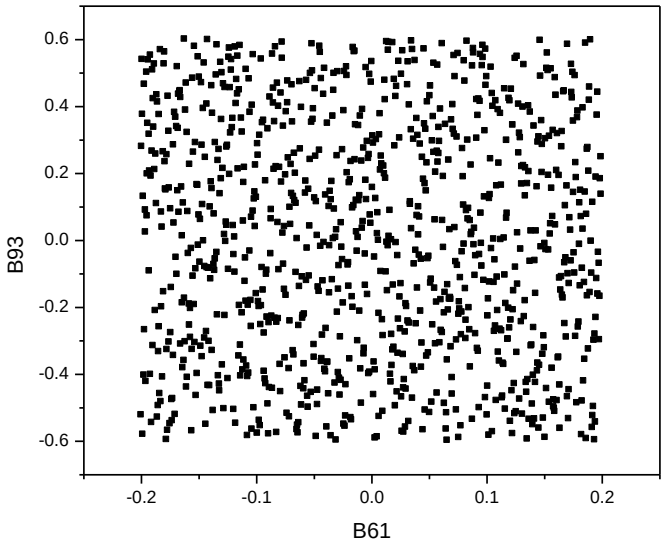


Figure 37. Random values with no correlation for 1000 calculations. B61 correspond Reaction 61 with uncertainty limits ±0.2 and B93 represent uncertainty limits ±0.6 of Reaction 93

5.2.The reliability of the results

The possible minimum and maximum values of the simulation results were determined using a 10000 parameter sets random sample. Figure 38 shows the mole fraction of CH_3OH (a), CO (b) and CO_2 (c) versus temperature under the circumstances of Set 2. The graphs of all other experimental sets were similar to this and can be checked in Appendix E. The calculations showed that the experiments and the simulations using the current merged reaction mechanism are in agreement, except the maximum concentration of carbon-monoxide under the circumstances of Set 1 at 1100 K (shown in Figure 39). The paper of Alzueta et al. [2] reported the experimental uncertainty as 5%, but not less than 10 ppm. These uncertainty intervals are also plotted on the figures with dotted lines. Also, the mean and the nominal values were plotted. One can conclude that the experimental uncertainties are much smaller than the simulation ones.

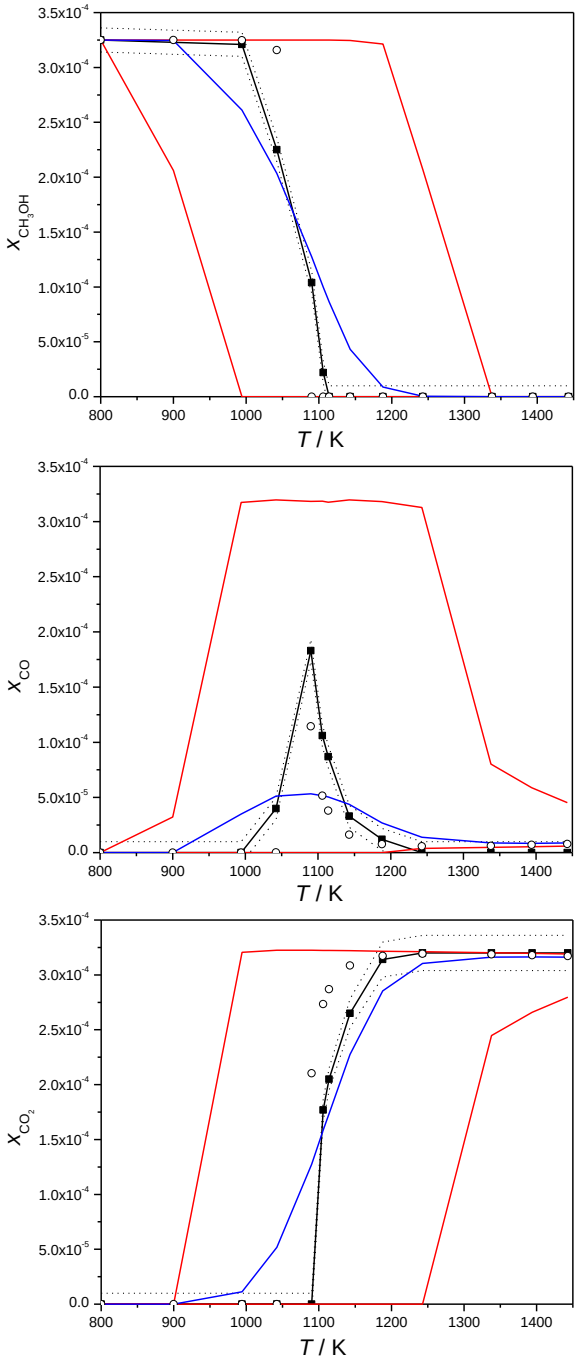


Figure 38. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2]. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits.

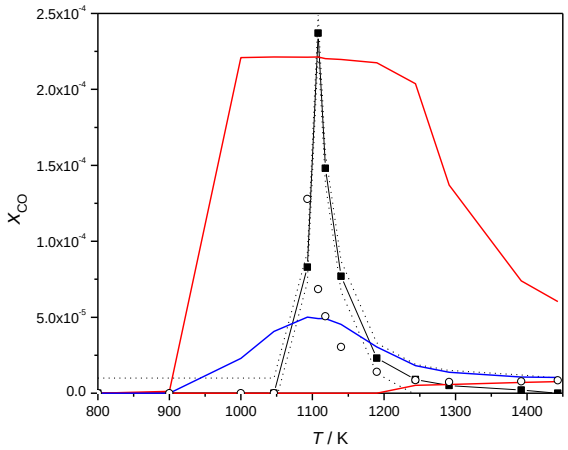


Figure 39. Mole fraction of CO vs. temperature under the circumstances of Set 1 [2]. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the nominal values, the blue line the mean values of the Monte Carlo simulations, the red lines the possible minimum and maximum values can be reached using the merged mechanism keeping all parameters within their uncertainty limits

The output files obtained during the Monte Carlo simulations were utilized as input files in the global sensitivity analysis.

6. GLOBAL SENSITIVITY ANALYSIS

6.1. The High Dimensional Model Representation (HDMR)

As we saw in the Monte Carlo simulations, the reliability of the simulations is poor. To reveal which reactions could cause this large uncertainty the High Dimensional Model Representation method (HDMR) was applied. Since all the kinetic parameters were sampled uniformly in the Monte Carlo simulations, the same calculations were used in the HDMR method.

The computation of the global sensitivity indices using the HDMR method requires much more computer time than the calculation of the local ones. Therefore, they were calculated only at one temperature for each set and species, at that temperature where the local sensitivity of the given species was the largest.

6.1.1. First order results

HDMR scatter plots and the first-order component functions are presented for all three species investigated under the circumstance of the low-pressure Set 2 in Figure 40 and the high-pressure Set E4 in Figure 41. In all cases the most sensitivity reaction is Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$.

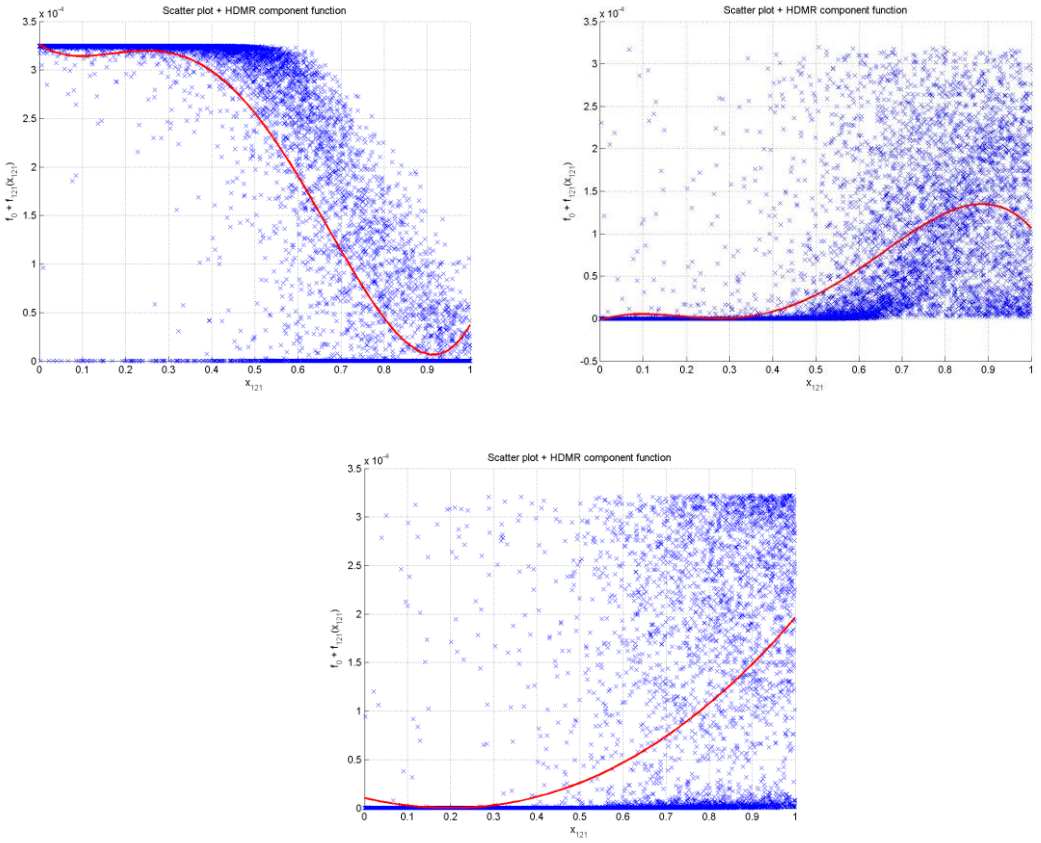


Figure 40. First-order component function and scatter plot of the (a) methanol, (b) carbon-monoxide, (c) carbon-dioxide mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus x (x ranges from 0 to 1 over the uncertainty range of k). This calculation was done at T = 1042 K under conditions of Set 2 in [2]

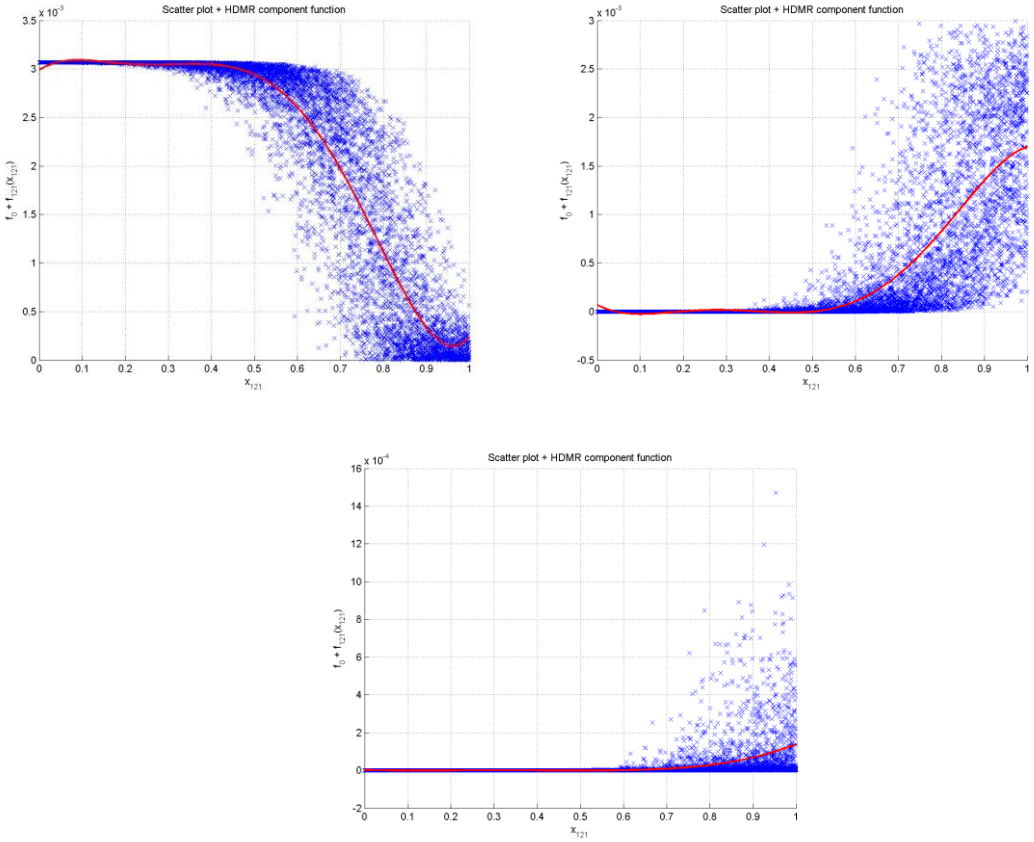


Figure 41. First-order component function and scatter plot of the (a) methanol, (b) carbon-monoxide, (c) carbon-dioxide mole fraction for Reaction 121 $CH_3OH + HO_2 = CH_2OH + H_2O_2$ versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*). This calculation was done at *T* = 648 K under conditions of Set E4 in [3]

6.1.2. Second order results

Second order effect means that the effect of the change of two parameter values depends on the values of both parameters (their effects are not independent). Strong second order effects were found in several cases, typical plots can be seen Figure 42. Under the circumstance of Set1 at 1093K one can conclude the following: when the rate coefficient of R121 is large increase of the rate coefficient of R184 increases the methanol concentration. However, when R121 has small values the maximum methanol concentration is calculated around the nominal value of R184 and its modification decreases the methanol concentration in both directions.

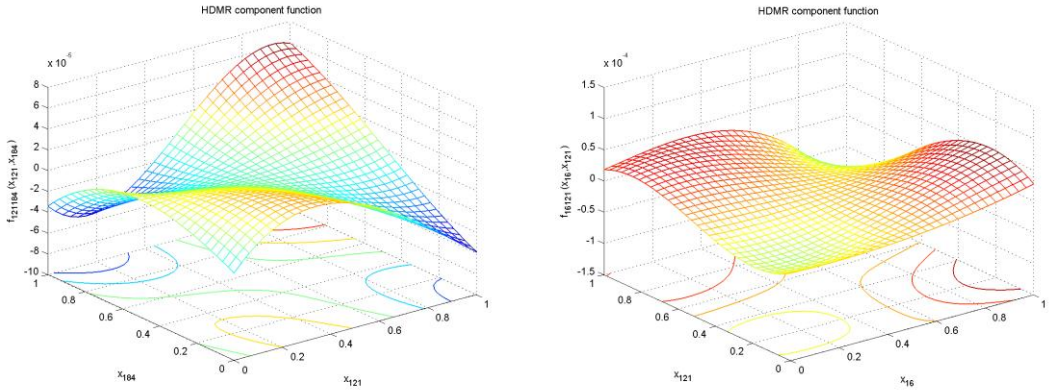


Figure 42. Second-order component function of the (a) methanol under conditions of Set1 at 1093K, (b) carbon-dioxide under conditions of Set2 at 1042K

For further information Appendix F is available.

6.2. Controlling reaction

After Global Sensitivity Analysis one can conclude that the most important reaction in the methanol oxidation mechanism is the Reaction 121 (Appendix B) $CH_3OH + HO_2 = CH_2OH + H_2O_2$, that controls both methanol, carbon-monoxide and carbon-dioxide concentration. This means that a small change in the parameters of the reaction rate significantly affects the output concentration.

The first step to improve the mechanism was to find better rate parameters of the most important reaction.

7. THE IMPROVED VERSION OF THE MECHANISM

7.1. New rate parameters

The most important reaction in the merged mechanism under all the circumstances investigated was Reaction 121, $CH_3OH + HO_2 = CH_2OH + H_2O_2$, which controls both the methanol, carbon-monoxide and carbon-dioxide concentration. The same reaction was found to be one of the most important controlling reaction of the methanol ignition in the paper of Skodje *et al.* [16]. The rate coefficient of this reaction was revised using this paper (see Figure 43) [16]. Note, that Reaction 122, $CH_3OH + O_2 = CH_2OH + HO_2$ was also updated using the recommendation of the same paper.

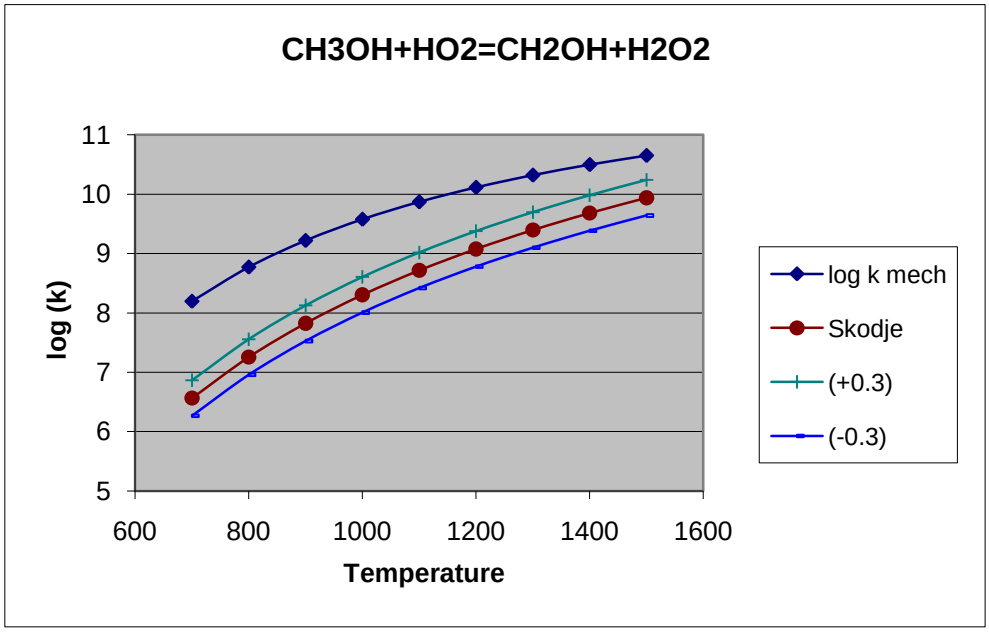


Figure 43. log (k[$cm^3mol^{-1}s^{-1}$]) vs. temperature [K] of Reaction 121, $CH_3OH + HO_2 = CH_2OH + H_2O_2$. Diamonds correspond to the merged mechanism value, circles are the modified one with its error limits adapted from Skodje et al. [16] (horizontal and vertical lines)

The new parameters are detailed in Table 7.1 and visual comparison can be revised in Figure 43 and Figure 44. The new parameters are very different but the global rate reaction is very close to the old parameters.

Table 7.1. Rate parameters of the merged mechanism, the preferred values and the new values

REACTIONS CONSIDERED	A	β	E	Δlog(*k*)
	Rate parameters in the merged mechanism			
121. CH3OH+HO2=CH2OH+H2O2	6.30E+12	0.0	14730.0	1.4
122. CH3OH+O2=CH2OH+HO2	3.50E+13	0.0	45750.0	0.2
	Preferred values in Nist Chemical Kinetic Database			
121. CH3OH+HO2=CH2OH+H2O2	9.64E+10	0.0	12569,86	
	1.00E+12	0.0	10028.66	
122. CH3OH+O2=CH2OH+HO2	2.05E+13	0.0	44900.88	
	New rate parameters in the paper of Skodje *et al.*			
121. CH3OH+HO2=CH2OH+H2O2	2.28E-05	5.06	10207.41	0.3
122. CH3OH+O2=CH2OH+HO2	3.58E+05	2.27	42736.07	0.3

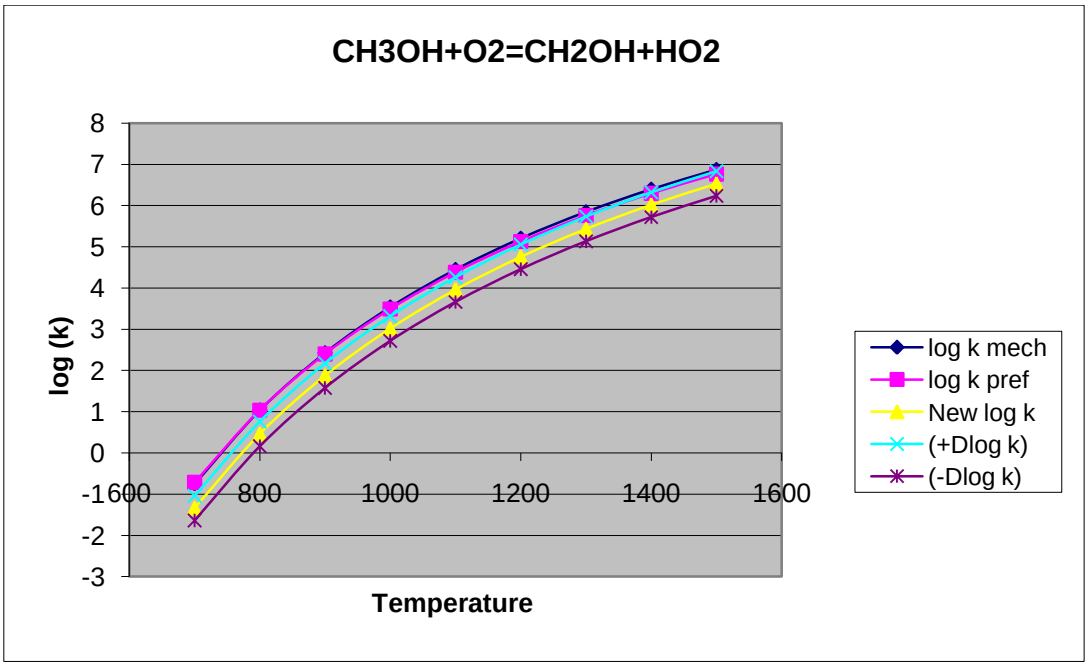


Figure 44. log (k[$cm^3mol^{-1}s^{-1}$]) vs. temperature [K] plot of Reaction 122, $CH_3OH + O_2 = CH_2OH + HO_2$. Diamonds correspond to the merged mechanism value, triangles are the modified one with its error limits (small lines) adapted from Skodje et al. [16], squares are NIST preferred values

7.2.Sensitivity analysis

Changing the parameters of reactions 121 and 122 a new improved mechanism was formed. This updated mechanism was investigated further. Similarly to the investigation of the merged mechanism local sensitivity analysis revealed the temperature of the largest local sensitivity indices, Monte Carlo simulations the possible minimum and maximum concentrations, and HDMR analysis the global sensitivity indices. For details, consult Appendix G, here, we focus on the results.

The analysis showed that the simulations still have large uncertainty, but the most sensitive reactions have changed. For example in Set 2 reaction $CH_3OH + HO_2 = CH_2OH + H_2O_2$ disappeared from the globally sensitive reactions and the previously second one, CH_2OH (+M) = CH_2O + H (+M) low-pressure limit become the most important in this case (as an example Figure 45 presents the first-order component function and scatter plot for this case). Appearance of low-pressure limits among the most sensitive reactions proved that these parameters cannot be neglected when sensitivity/uncertainty analysis of methanol oxidation mechanism is performed and it is important to focus on their appropriate values in the mechanism development, too.

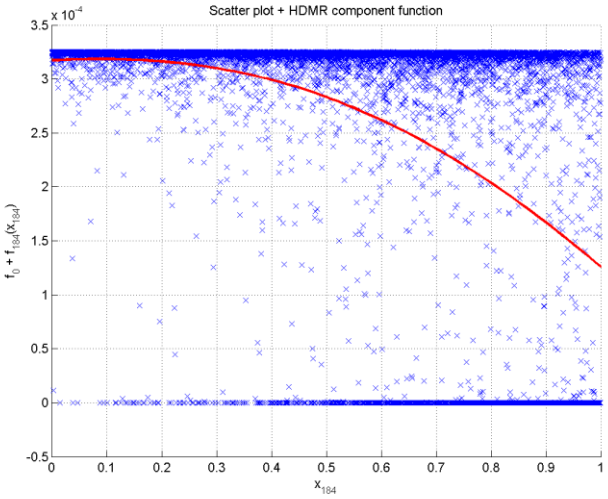


Figure 45. First-order component function and scatter plot of the methanol mole fraction for Reaction 184 CH_2OH (+M) = CH_2O + H (+M) low-pressure limit versus *x* (*x* ranges from 0 to 1 over the uncertainty range of *k*). This calculation was done at *T* = 1090 K under conditions of Set 2 in [2].

Overall, the results are seen to be improved significantly, suggesting that the recommendations of Skodje et al. [16] should be present in an updated subset for methanol conversion.

These modifications shifted the oxidation of methanol to higher temperatures and decreased the maximum CO concentration (see the concentration profiles of Set 2 in Figure 46). Taking into account only the change of the nominal values the description of most of the low pressure experiments seems to be worse, but the high pressure one better. It can be concluded that the overall performance of the mechanism became better.

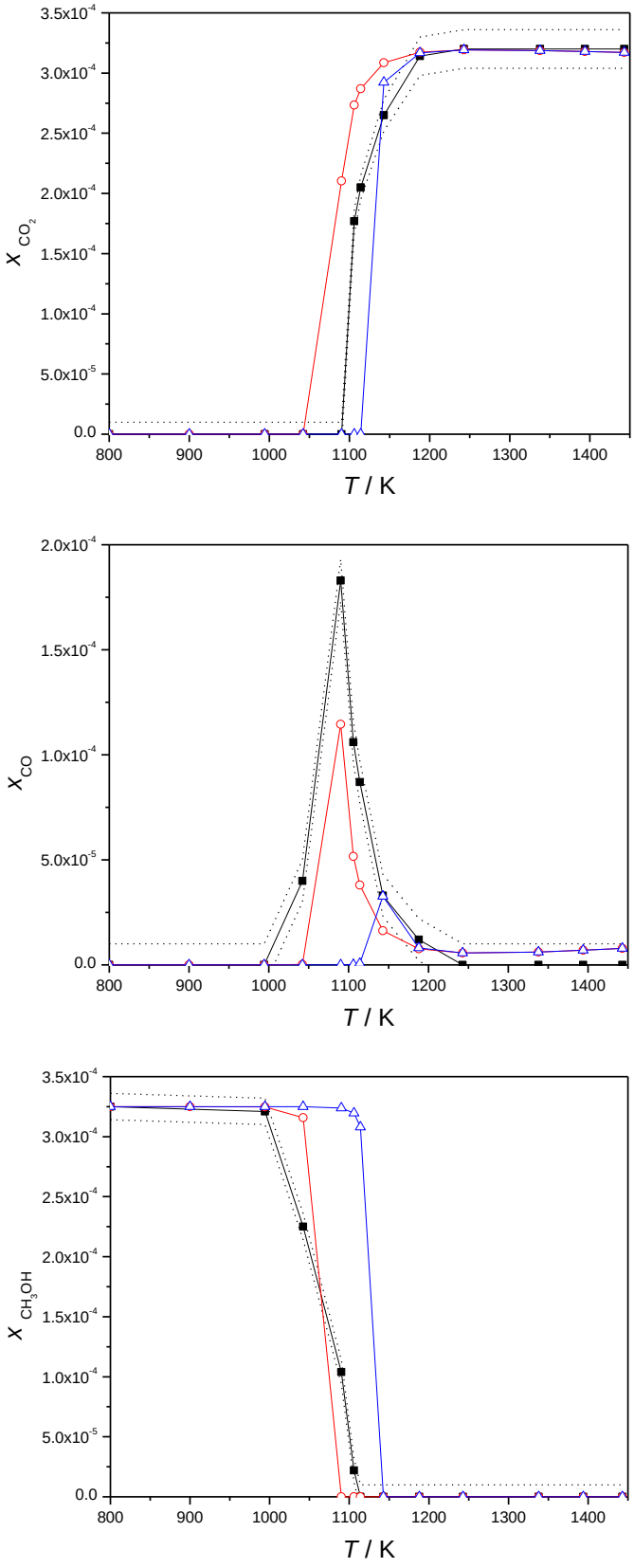


Figure 46. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set 2 [2]. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the merged mechanism, the interconnected triangles that of using the modified mechanism.

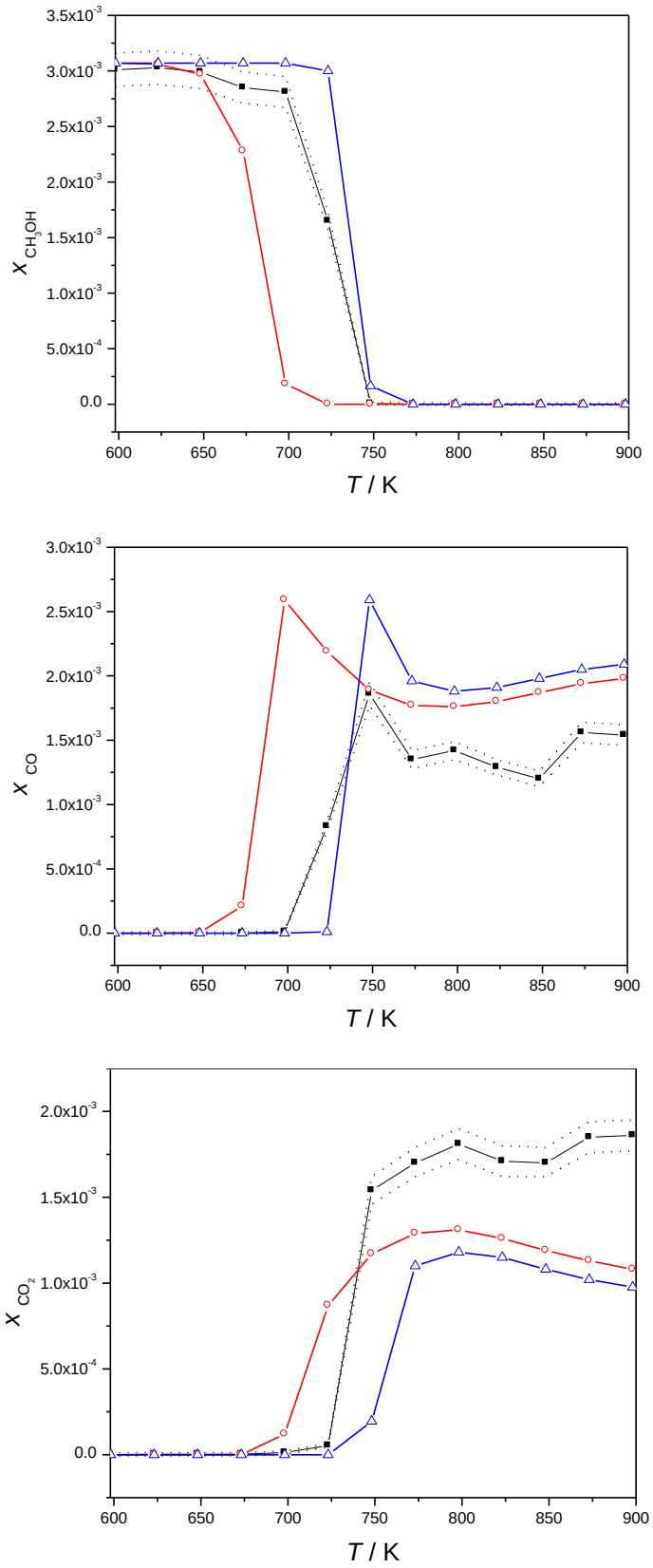


Figure 47. Mole fraction of CH_3OH (a), CO (b) and CO_2 (c) vs. temperature under the circumstances of Set E4 [3]. The interconnected solid squares indicate the measured values, the dotted lines the assumed experimental error limits, the interconnected open circles the simulation results using the merged mechanism, the interconnected triangles that of using the modified mechanism.

8. CONCLUSIONS

8.1. Summary of the results

A common methanol oxidation mechanism based on an existing low and a high pressure detailed mechanism was created. It contains 172 reactions of 27 species. Common species and reaction set was determined. The rate parameters of the common reactions were calculated simply averaging the Arrhenius parameters used in the original low and high pressure mechanism. The methanol, carbon-monoxide and carbon-dioxide concentrations were investigated.

Automated local sensitivity analysis was performed for each experimental set. The merged mechanism contains 172 reactions, but 16 reactions are pressure dependent and have low pressure limit. Altogether, 186 parameters (pre-exponential factors) were varied. The temperatures having the largest local sensitivity values were selected for the global sensitivity analysis.

The uncertainty limits of each parameter were estimated. These logarithmically symmetrical intervals were sampled uniformly for the Monte Carlo simulations. The possible minimum and maximum values of the simulation results were determined using 10000 parameter sets.

The calculations showed that the experiments and the simulations using the current merged reaction mechanism are in agreement, except the maximum concentration of carbon-monoxide under the circumstances of Set 1 at 1100 K. One can conclude that the experimental uncertainties are much smaller than the simulation ones. Despite the agreement of the experiments and the simulations, the uncertainty of the simulations should be significantly decreased.

To reveal which reactions could cause this large uncertainty the High Dimensional Model Representation method (HDMR method) was applied. Since all the kinetic parameters were sampled uniformly in the Monte Carlo simulations, the same calculations were used in the HDMR method. To get information about the reliability of the results this method was applied using 1000, 3000, 10000 samples.

The most important reaction in this mechanism under all the circumstances investigated was Reaction 121, $CH_3OH + HO_2 = CH_2OH + H_2O_2$, which controls both the methanol, carbon-monoxide and carbon-dioxide concentration. The same reaction was found to be one of the most important controlling reaction of the methanol ignition in the paper of Skodje *et al.* [16]. The rate coefficient of this reaction was revised using this paper. The updated mechanism was investigated further. Results are seen to be improved significantly, suggesting that the recommendations of Skodje et al. [16] should be present in an updated subset for methanol conversion.

These modifications shifted the oxidation of methanol to higher temperatures and decreased the maximum CO concentration. Taking into account only the change of the nominal values the description of most of the low pressure experiments seems to be worse, but the high pressure one better. It can be concluded that the overall performance of the mechanism became better. The simulations still have large uncertainty, but the most sensitive reactions have changed. For example in Set 2 reaction $CH_3OH + HO_2 = CH_2OH + H_2O_2$ disappeared from the globally

sensitive reactions and the previously second one, CH_2OH (+M) = CH_2O + H (+M) low-pressure limit become the most important in this case. Appearance of low-pressure limits among the most sensitive reactions proved that these parameters cannot be neglected when sensitivity/uncertainty analysis of methanol oxidation mechanism is performed.

8.2. Further research directions

These results can be improved in several different ways. At the time of ending the period at the host university, it was carrying out an improvement of the mechanism. The next step would be incorporation of an updated version of the Hydrogen subset (H_2/O_2) using recently published mechanism, e.g. by Hong et al. [18], that incorporates recent reaction rate determinations in shock tubes, which would increase the reliability of the results and improve the mechanism under study.

Another improvement could be adding the outstanding experimental sets of high pressure, with more information on the mechanism of high pressure better results could be found. A different extension of the work would be the inclusion in the analysis of the simulation of flame experiments.

Once the appropriate mechanism is performed using more high pressure experimental sets the nitrogen-oxide formation part of the mechanism should be investigated and in a similar way a joint mechanism should be created and tested.

8.3.Impact of development work

There are three aspects of this project that have been very interesting during the development. First, this was the first time during my studies I have carried out a real project with real applications. During the project I saw how it works outside the usual class work. What most struck me was the continual adjustment and feedback that occurs in the information, always seeking the latest published research and the latest results to improve the project itself.

Second, teamwork, depending on projects in other college friends and the aid received from my mates. And finally, the fact of working in a different country with different language has added difficulty to the project while extra motivation and effort required was greater.

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LIST OF TABLES

LIST OF FIGURES