An Updated Reaction Model for the High-Temperature Pyrolysis and Oxidation of Acetaldehyde

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This supplemental material presents the complete preliminary evaluation of the Aramco 2.0 with respect to ignition delay-time and species profiles data. The corresponding preliminary sensitivity analyses are also presented.

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1. Preliminary kinetics modeling and analyses

To make a preliminary assessment of the predictive capability of reference reaction models and determine important reactions for acetaldehyde pyrolysis and oxidation, Aramco 2.0 has been employed. The choice of this reaction model is motivated by the specific validation performed for acetaldehyde in Metcalfe et al. [1].

1.1. Characteristic time of reaction

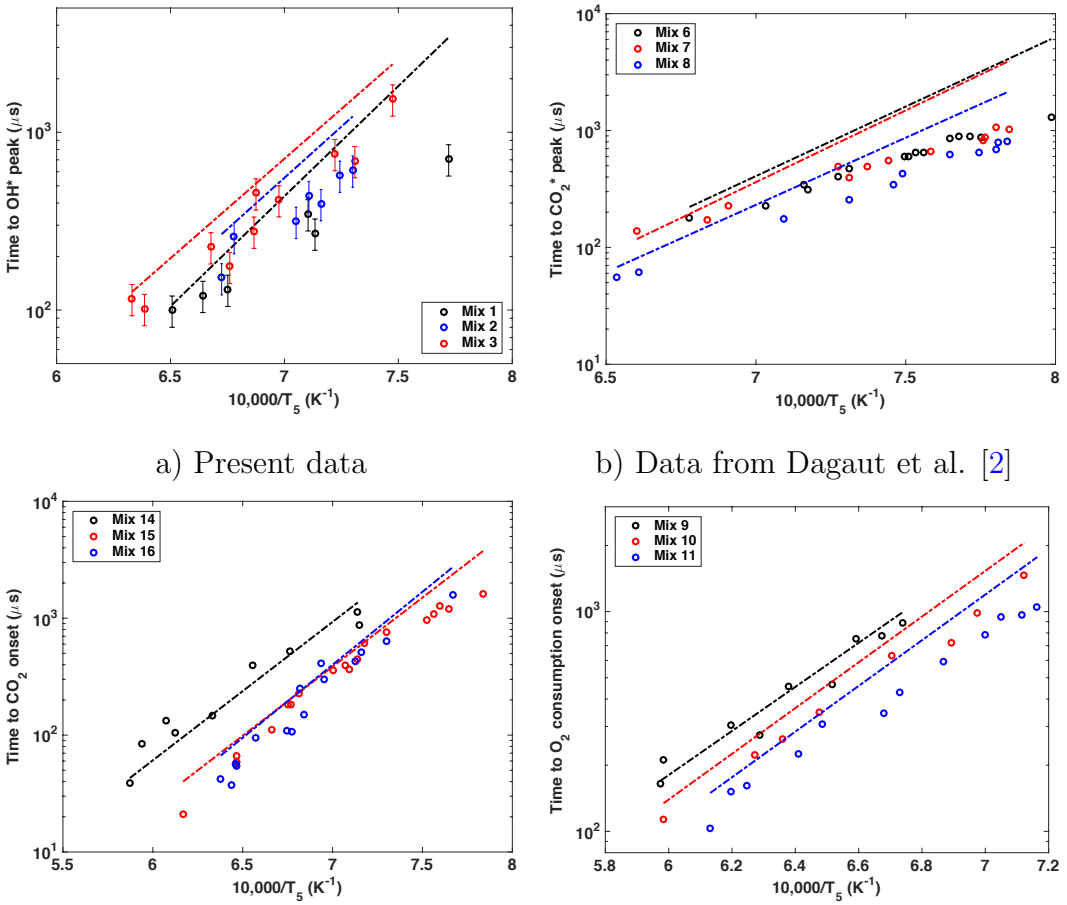
Figure 1 presents a comparison between the experimental results (present data and data from [2–4]) and the predictions of Aramco 2.0. The reaction model tends to over-estimates (90 to 120% error) the characteristic time of reaction based on emission signals (see Figure 1 a) and b)). The characteristic time of reaction based on CO_2 and O_2 (see Figure 1 c) and d)) are better reproduced but still overall over-estimated with mean errors of 42% and 31%, respectively.

Figure 2 presents sensitivity analyses performed under oxidative conditions. The analyses performed on temperature, CO_2*, CO_2, and O_2 are consistent with each other and demonstrate the primary importance of acetaldehyde decomposition, $CH_3CHO(+M)=CH_3+HCO(+M)$, the branching reaction $H+O_2=OH+O$, and $CH_3CHO+H=CH_3CO+H_2$. The later reaction acts as a sink of H atom which would be otherwise formed by the rapid decomposition of HCO. The sensitivity analyses also show the importance of methyl radicals chemistry.

1.2. IR and UV absorption and emission profiles

In Figure 3, the absorption and emission profiles have been calculated according to the procedure described in Yasunaga et al. [4]. Briefly, the absorption/emission profiles were calculated by including the contributions of the relevant species in each case, considering the concentrations predicted by the reaction models and the absorption/emission "cross-section" for each species provided by Yasunaga et al.

In Figure 3 a) and b), the experimental [4] and simulated absorption profiles at 3.39 μm obtained under pyrolytic and oxidative conditions are displayed. This



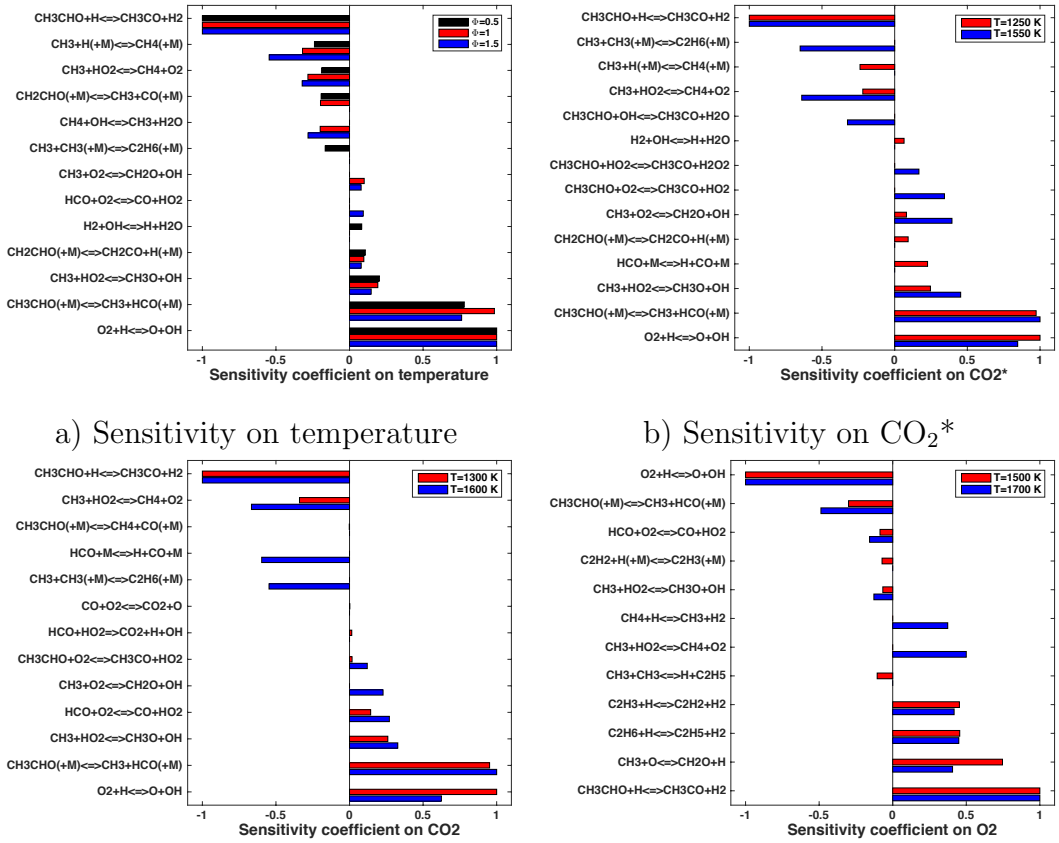
a) Present data

b) Data from Dagaut et al. [2]

c) Data from Yasunaga et al. [4]

d) Data from Hidaka and Suga [3]

Figure 1: Comparison between the experimental (present study and [2–4]) and the predicted (Aramco 2.0) ignition delay-time for CH_3CHO-O_2-Ar mixtures.



a) Sensitivity on temperature

b) Sensitivity on CO_2*

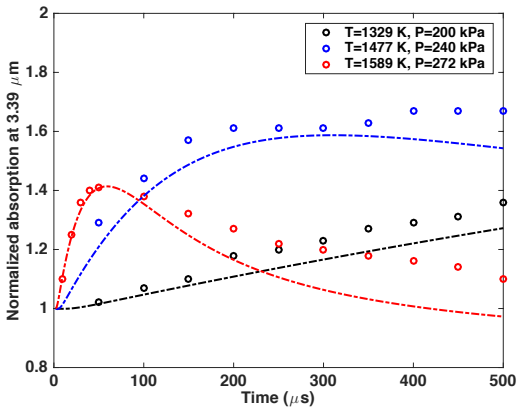
c) Sensitivity on CO_2

d) Sensitivity on O_2

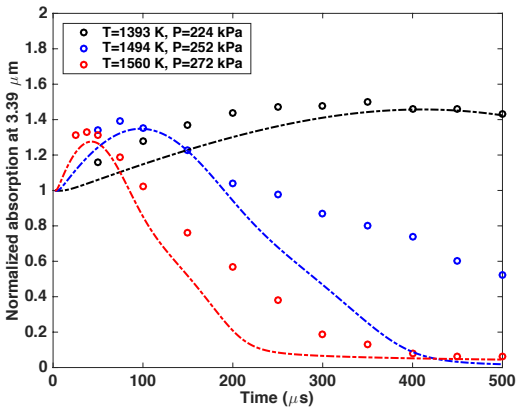
Figure 2: Sensitivity analyses during the oxidation of CH_3CHO performed with Aramco 2.0. In a): mixture 1-3; T_5=1450 K; P_5=300 kPa. In b): mixture 8; T_5=1325 and 1550 K; P_5=500 kPa. In c): mixture 15; T_5=1300 and 1600 K; P_5=200 kPa. In d): mixture 9; T_5=1500 and 1700 K; P_5=40 kPa.

parameter is representative of the C—H bond consumption rate. Overall, the predictions of Aramco 2.0 qualitatively and quantitatively match the experimental profiles. In Figure 3 c) and d), the experimental and predicted emission profiles at 4.68 μm are shown. This wavelength corresponds to a strong absorption/emission band of carbon monoxide [5]. However, Yasunaga et al. report that for the mixtures studied, the emission due to ketene, CH_2CO, plays a major role in reproducing the experimental profiles. Whereas Aramco 2.0 captures the shape of the profiles, discrepancies are observed in terms of amplitude, especially under pyrolytic conditions.
Figure 3 e) and f) present the experimental and simulated UV absorption profiles, around 200 nm. These profiles are representative of the absorption by CH_3 radicals and CH_2CO. The Aramco mechanism does not capture the shape nor the amplitude of the profiles under pyrolytic conditions. Under oxidative conditions, the amplitude of the profile is captured but not the overall shape.

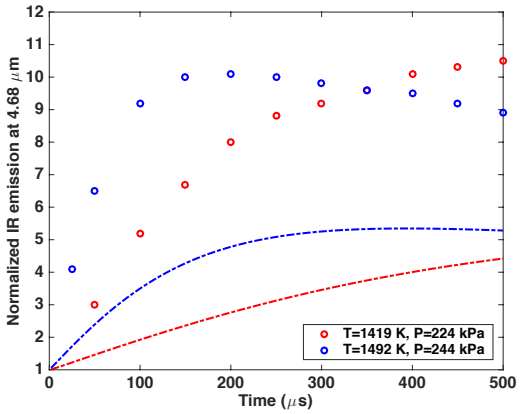
As a complement to the analyses shown in Figure 2 for oxidative conditions, Figure 4 presents sensitivity analyses performed under pyrolytic conditions for CH_4, CO, and CH_2O. These species have been selected due to their primary contribution to the IR and UV absorption and emission signals obtained by Yasunaga et al. [4]. These analyses confirm the important role of acetaldehyde decomposition and of the reactions of methyl radical, especially its recombination to form ethane. In addition, the importance of the H-abstraction reactions (by H and CH_3) on the methyl group of acetaldehyde, and their competition with the H-abstraction reactions on the aldehyde group of CH_3CHO, are to be underlined. The IR and UV emission signals are also sensitive to the decomposition of CH_2CHO into CH_2CO and H.



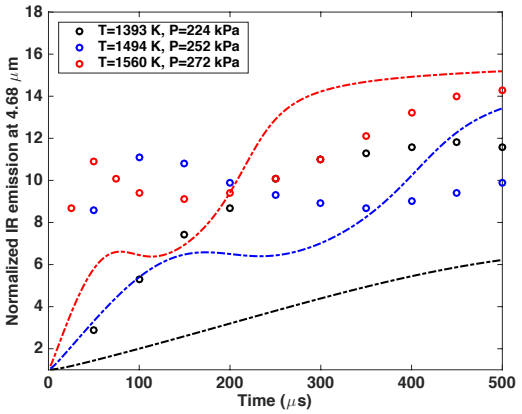
a) CH_3CHO pyrolysis: mixture 19



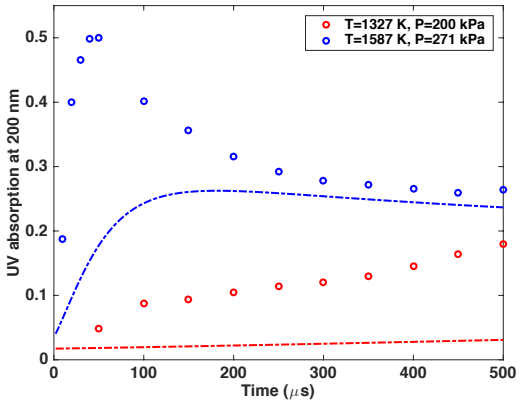
b) CH_3CHO oxidation: mixture 17



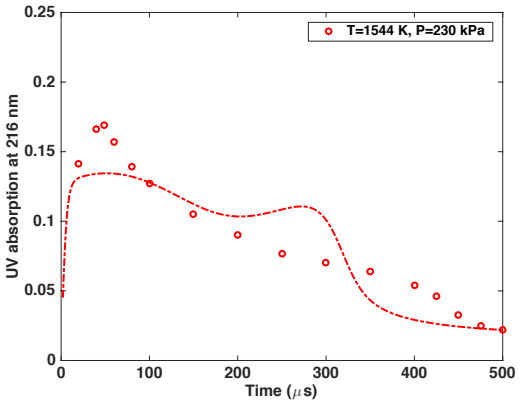
c) CH_3CHO pyrolysis: mixture 19



d) CH_3CHO oxidation: mixture 17

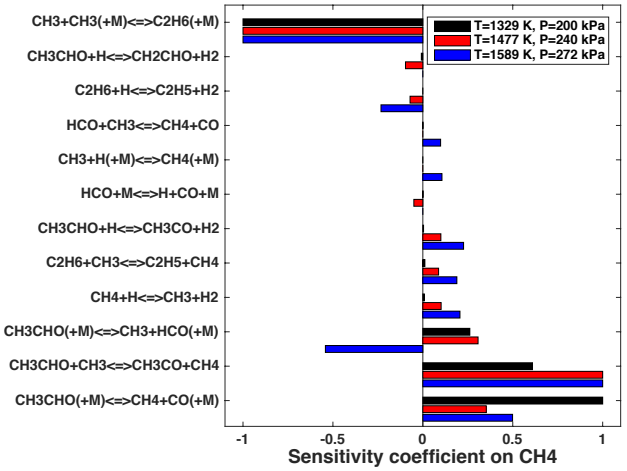


e) CH_3CHO pyrolysis: mixture 19

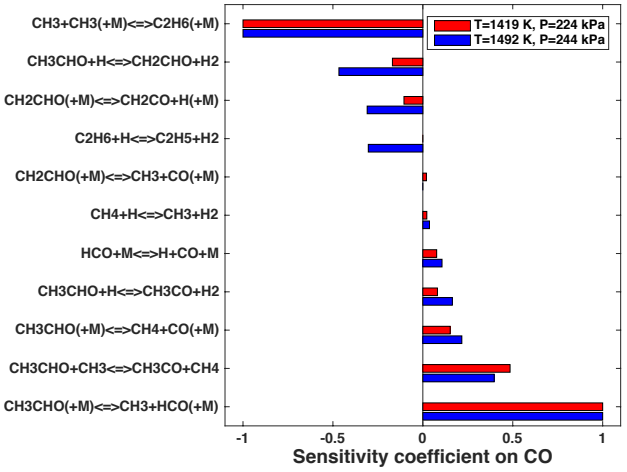


f) CH_3CHO oxidation: mixture 14

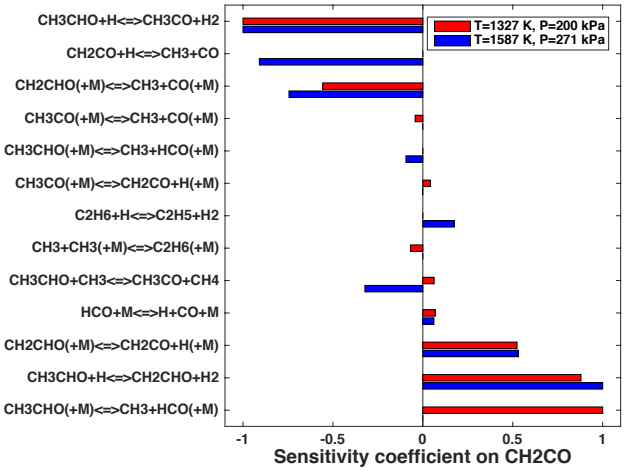
Figure 3: Comparison between the experimental [4] and the predicted (Aramco 2.0) IR and UV absorption/emission profiles during the pyrolysis and oxidation of CH_3CHO.



a) Sensitivity on CH_4



b) Sensitivity on CO



c) Sensitivity on CH_2CO

Figure 4: Sensitivity analyses during the pyrolysis of CH_3CHO performed with Aramco 2.0. In a), b) and c): mixture 19.

References

[1] W. Metcalfe, S. Burke, S. Ahmed, C. H.J., International Journal of Chemical Kinetics 45 (2013) 638–675.

[2] P. Dagaut, M. Reuillon, D. Voisin, M. Cathonnet, M. M. Guinness, J. Simmie, Combustion Science and Technology 107 (1995) 301–316.

[3] Y. Hidaka, M. Suga, Journal of the Mass Spectrometry Society of Japan 35 (1987) 74–83.

[4] K. Yasunaga, S. Kubo, H. Hoshikawa, T. Kamesawa, Y. Hidaka, International Journal of Chemical Kinetics 40 (2008) 73–102.

[5] L. S. Rothman, A. Barbe, D. C. Benner, L. R. Brown, C. Camy-Peyret, M. R. Carleer, K. Chance, C. Clerbaux, V. Dana, V. M. Devi, A. Fayt, J. M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, K. W. Jucks, W. J. Lafferty, J. Y. Mandin, S. T. Massie, V. Nemtchinov, D. A. Newnham, A. Perrin, C. P. Rinsland, J. Schroeder, K. M. Smith, M. A. H. Smith, K. Tang, R. A. Toth, J. Vander Auwera, P. Varanasi, K. Yoshino, Journal of Quantitative Spectroscopy and Radiative Transfer 82 (2003) 5–44.