Kinetic modelling of NO_x formation and consumption during Methanol and Ethanol oxidation

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Supplement Material

Additional validation plots for Methanol and Ethanol

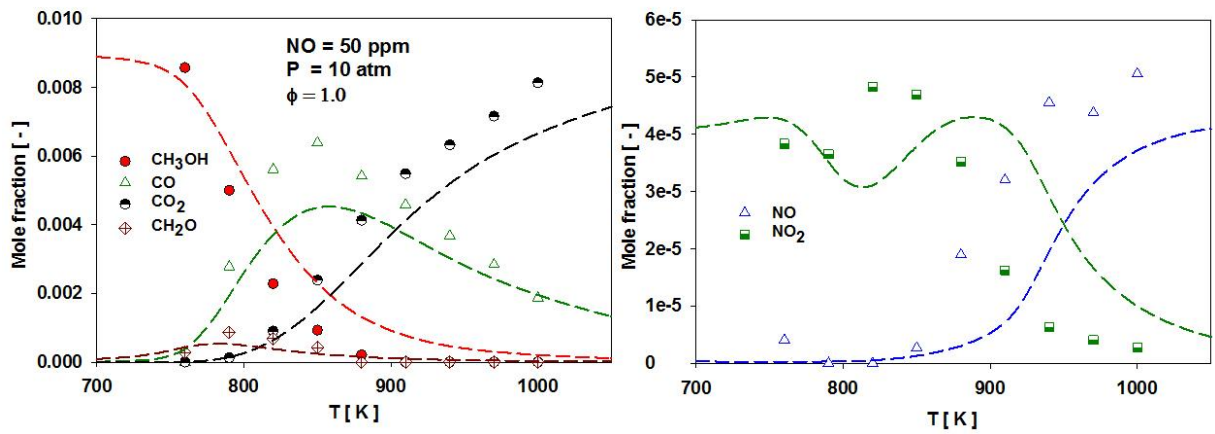


Figure S1: CH_3OH 0.9%/O_2 1.35%/N_2/NO 0.005% oxidation in JSR at 10 atm, $\phi = 1.0$ and $\tau = 1.0$ s. Symbols: experimental data (Moréac *et al.*, 2006), lines: this model prediction.

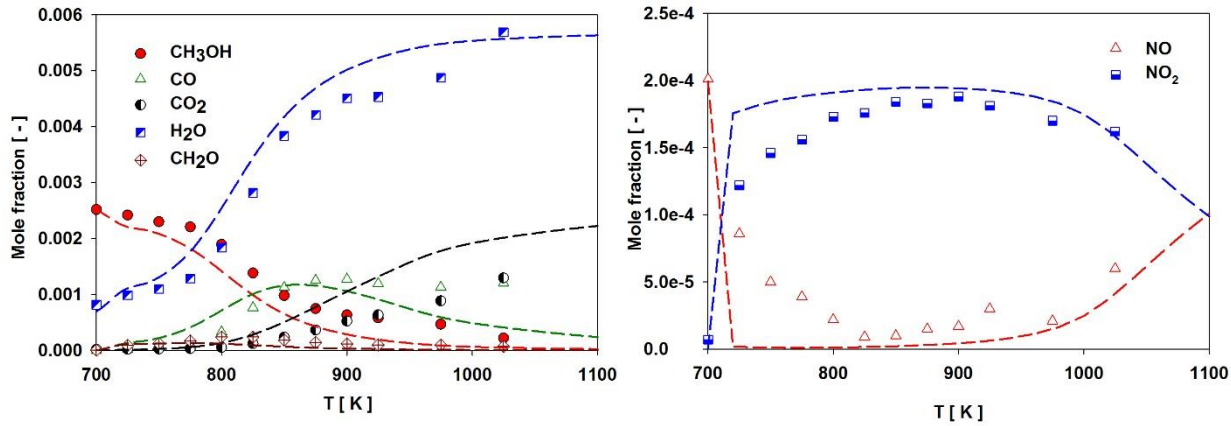


Figure S2: 200 ppm of NO on methanol oxidation (ϕ =0.3, 2500 ppm of CH_3OH, 12500 ppm of O_2, 700 ppm of H_2O, τ =0.8 s. Symbols: experimental data (Dayma *et al.*, 2007), lines: this model prediction.

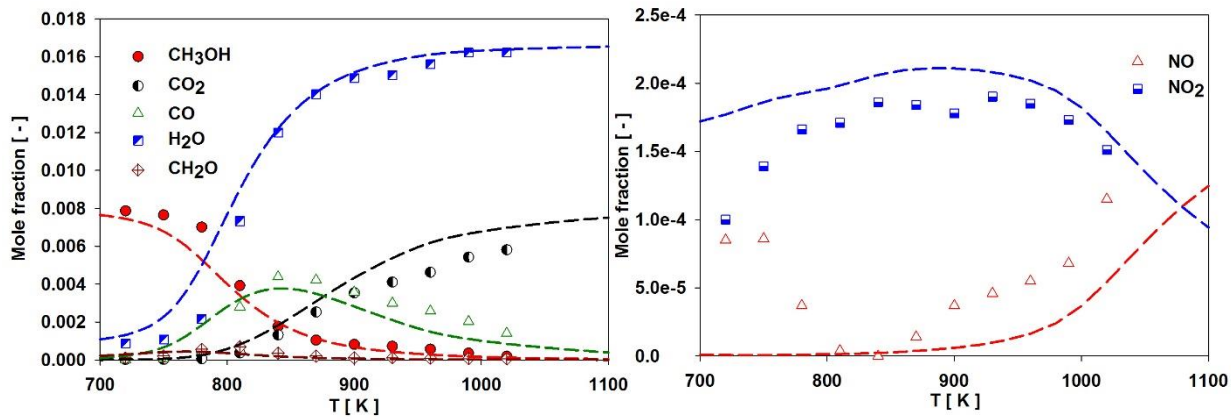


Figure S3: 220 ppm of NO on methanol oxidation (ϕ =0.6, 8000 ppm of CH_3OH, 20000 ppm of O_2, 700 ppm of H_2O, τ =1.0 s. Symbols: experimental data (Dayma *et al.*, 2007), lines: this model prediction.

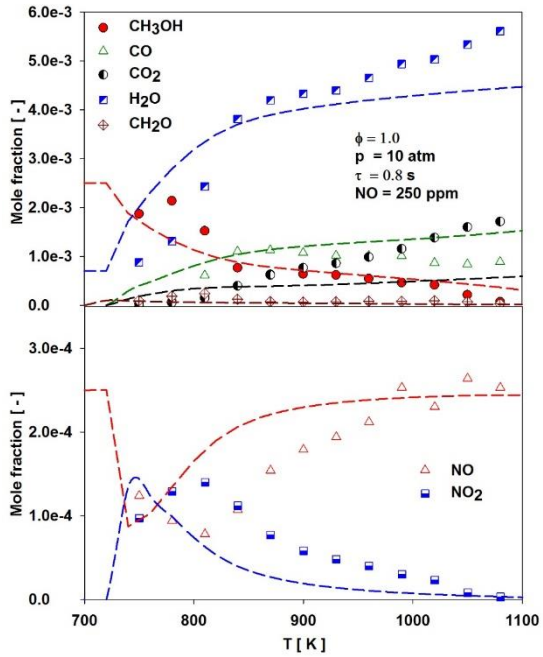


Fig. S4: 250 ppm of NO on methanol oxidation (ϕ =1.0, 2500 ppm of CH_3OH, 3750 ppm of O_2, 700 ppm of H_2O, τ = 0.8 s. Symbols: experimental data (Dayma *et al.*, 2007), lines: this model prediction.

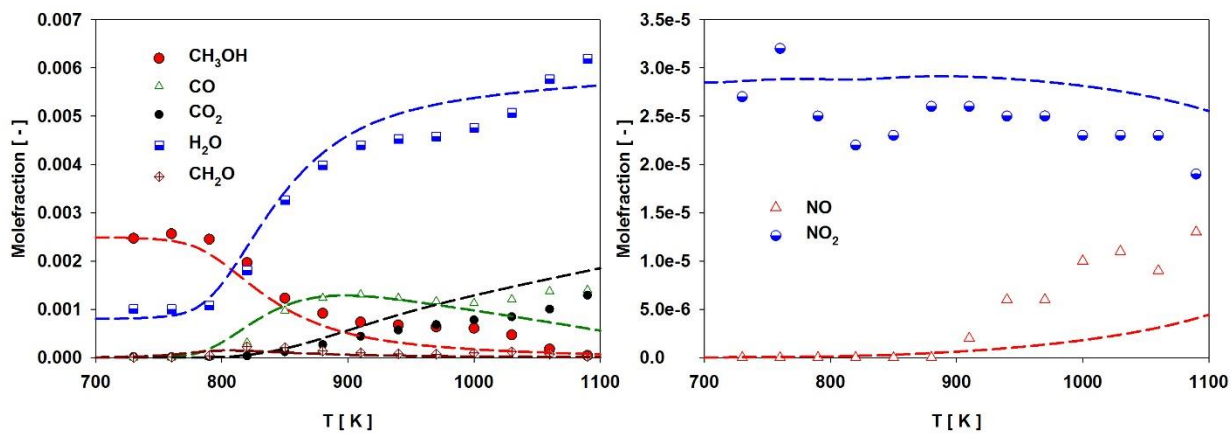


Figure S5: 30 ppm of NO_2 on methanol oxidation (ϕ = 0.3, 2500 ppm of CH_3OH, 12500 ppm of O_2, 800 ppm of H_2O, τ =0.8 s. Symbols: experimental data (Dayma *et al.*, 2007), lines: this model prediction.

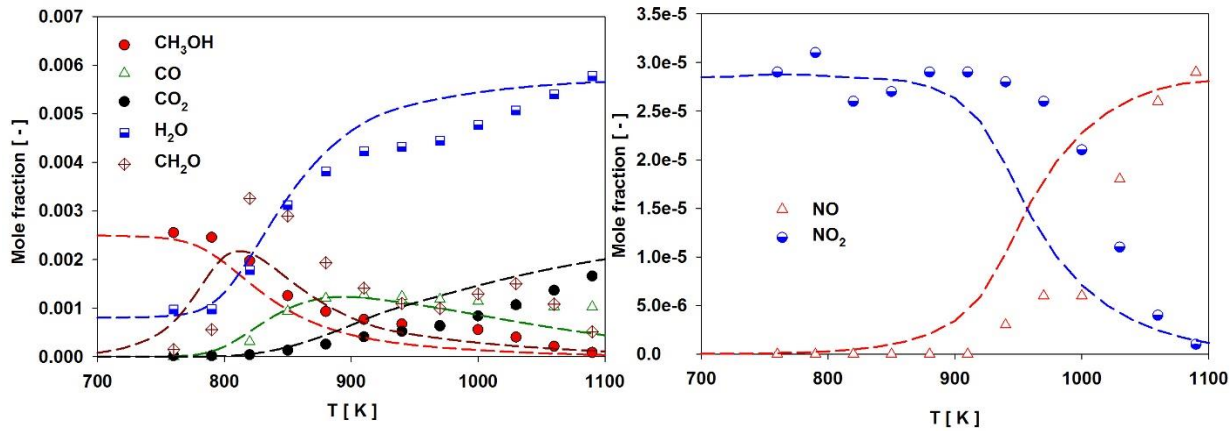


Figure S6: 30 ppm of NO_2 on methanol oxidation (ϕ = 1.0, 2500 ppm of CH_3OH, 3750 ppm of O_2, 800 ppm of H_2O, τ = 0.8 s. Symbols: experimental data (Dayma *et al.*, 2007), lines: this model prediction.

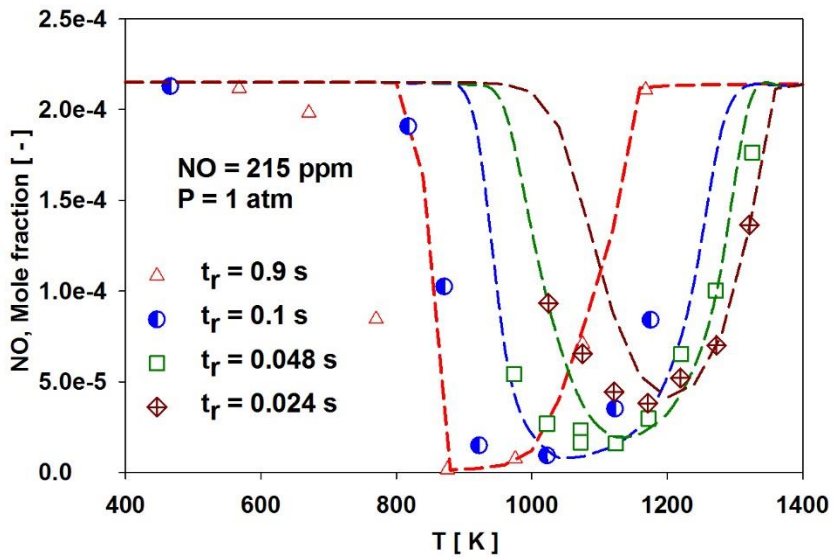


Figure S7: Methanol oxidation in flow (5 % O_2, CH_3OH 400 ppm, NO 215 ppm, balance He). Symbols: experimental data (Lyon *et al.*, 1990), lines: this model prediction.

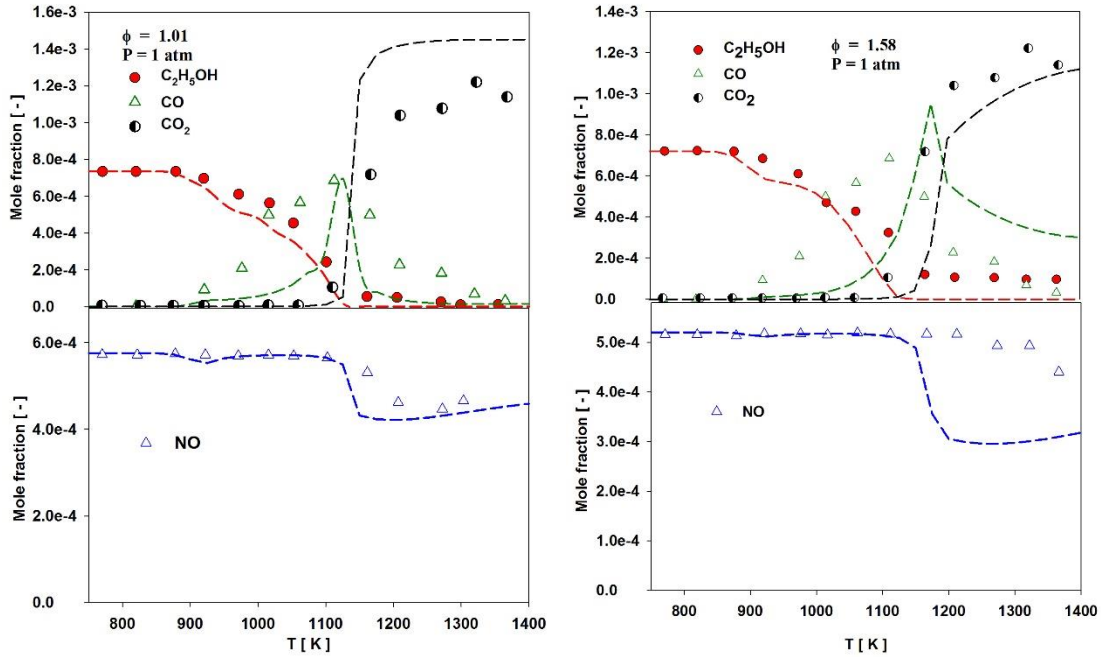


Figure S8: Ethanol oxidation in presence of NO, ϕ = 1.01, NO 576 ppm, 735 ppm CH_3OH, 0.64 % H_2O (set 4) and ϕ = 1.58, NO 520, 720 ppm CH_3OH, 0.96 % H_2O (set 2). Symbols: experimental data (Alzueta and Hernández, 2002), lines: this model prediction

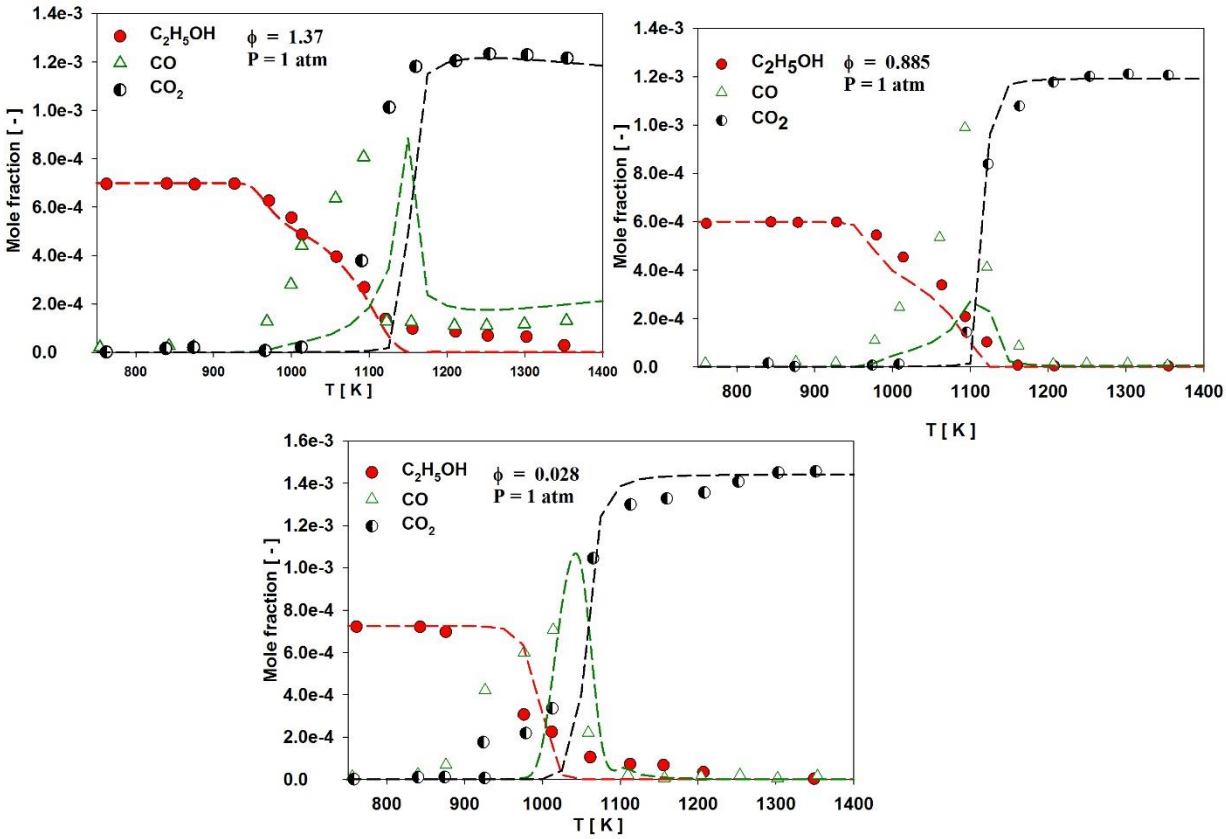


Figure S9: $C_2H_5OH/O_2/H_2O/N_2$ oxidation in flow reactor. Symbols: experimental data (set 1, set 3 and set 5) (Alzueta and Hernández, 2002), lines: this model prediction.

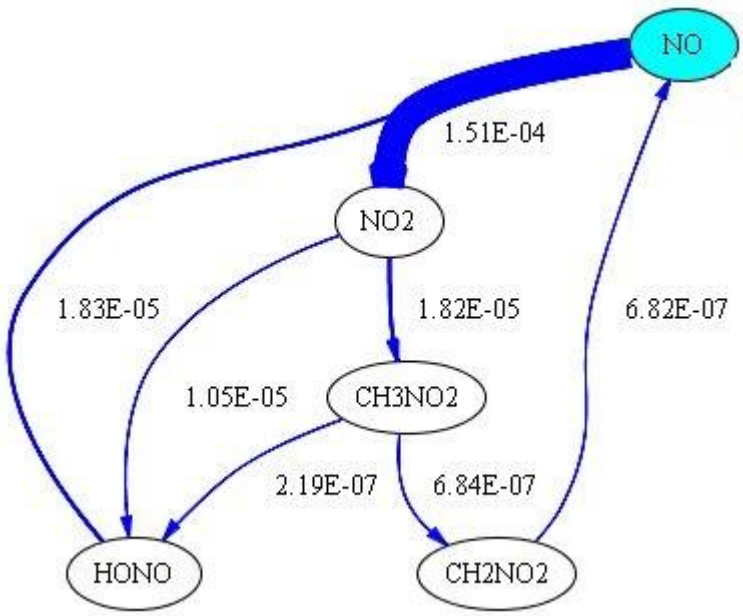


Figure S10: Flow analysis for ethanol oxidation in presence of NO, ϕ = 1.01, NO 576 ppm, 735 ppm CH_3OH, 0.64 % H_2O (set 4) in Figure S8.

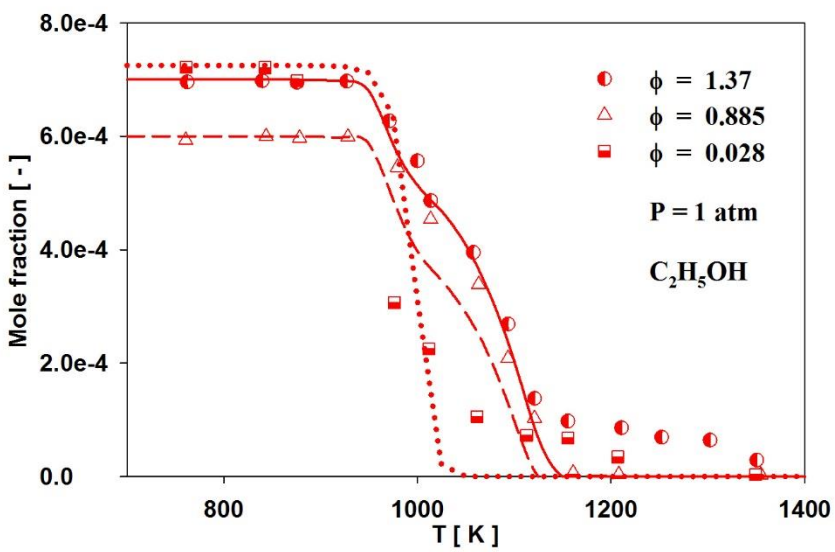


Figure S11 $C_2H_5OH/O_2/H_2O/N_2$ oxidation in flow reactor. Symbols: experimental data (set 1, set 3 and set 5) (Alzueta and Hernández, 2002), lines: this model prediction.

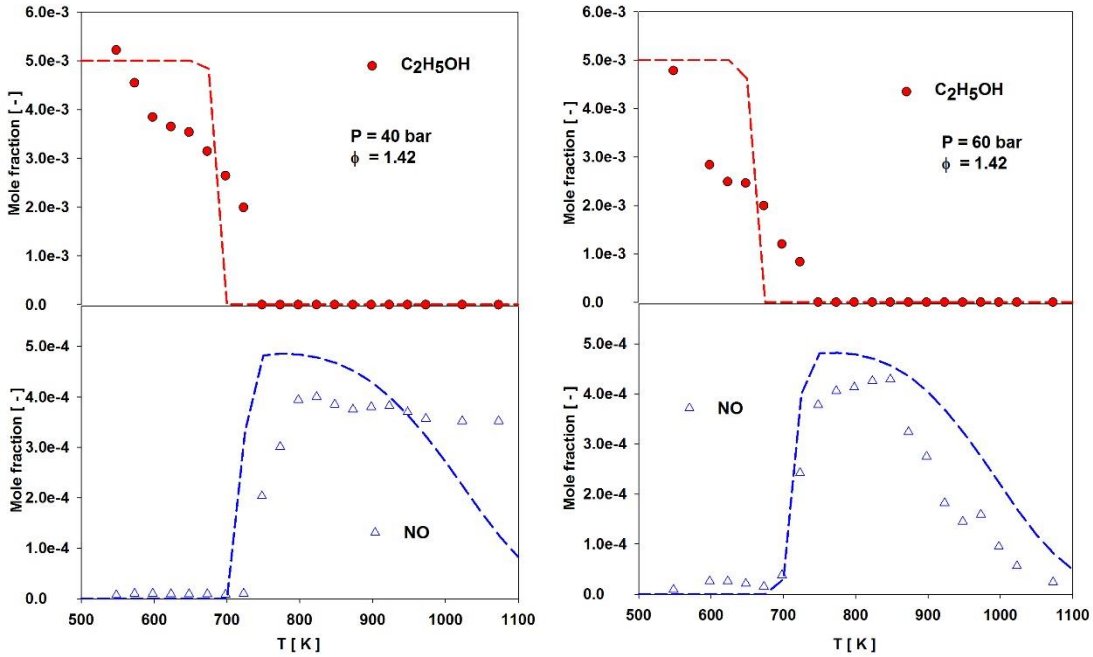


Figure S12: Ethanol oxidation in presence of NO in flow reactor 5000 ppm C2H5OH/O2/N2/ 500 ppm NO at 40 and 60 bar. Symbols: experimental data from (Marrodán *et al.*, 2018), lines: this model prediction.

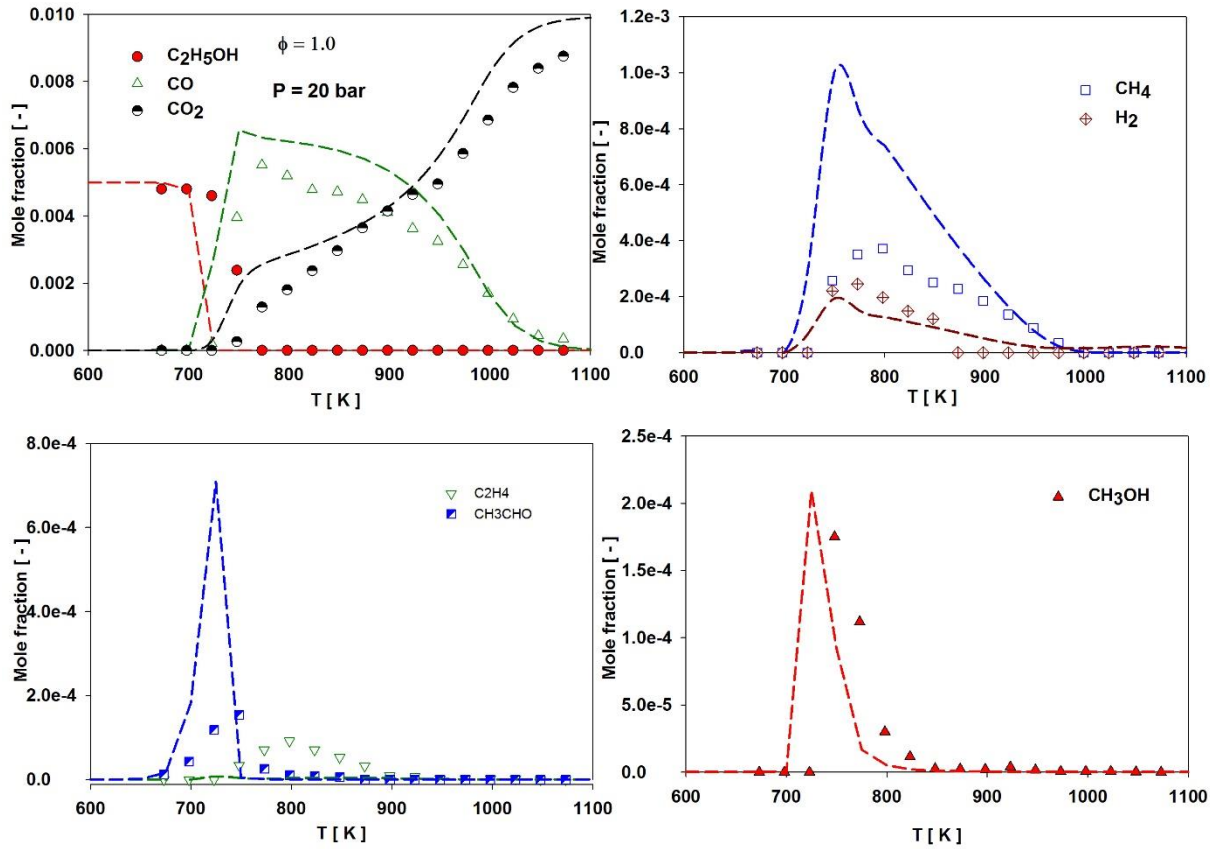


Figure S13: Ethanol oxidation in flow reactor 5000 ppm C2H5OH/O2/N2/ at 20 bar (set 4). Symbols: experimental data from (Marrodán *et al.*, 2018), lines: this model prediction.

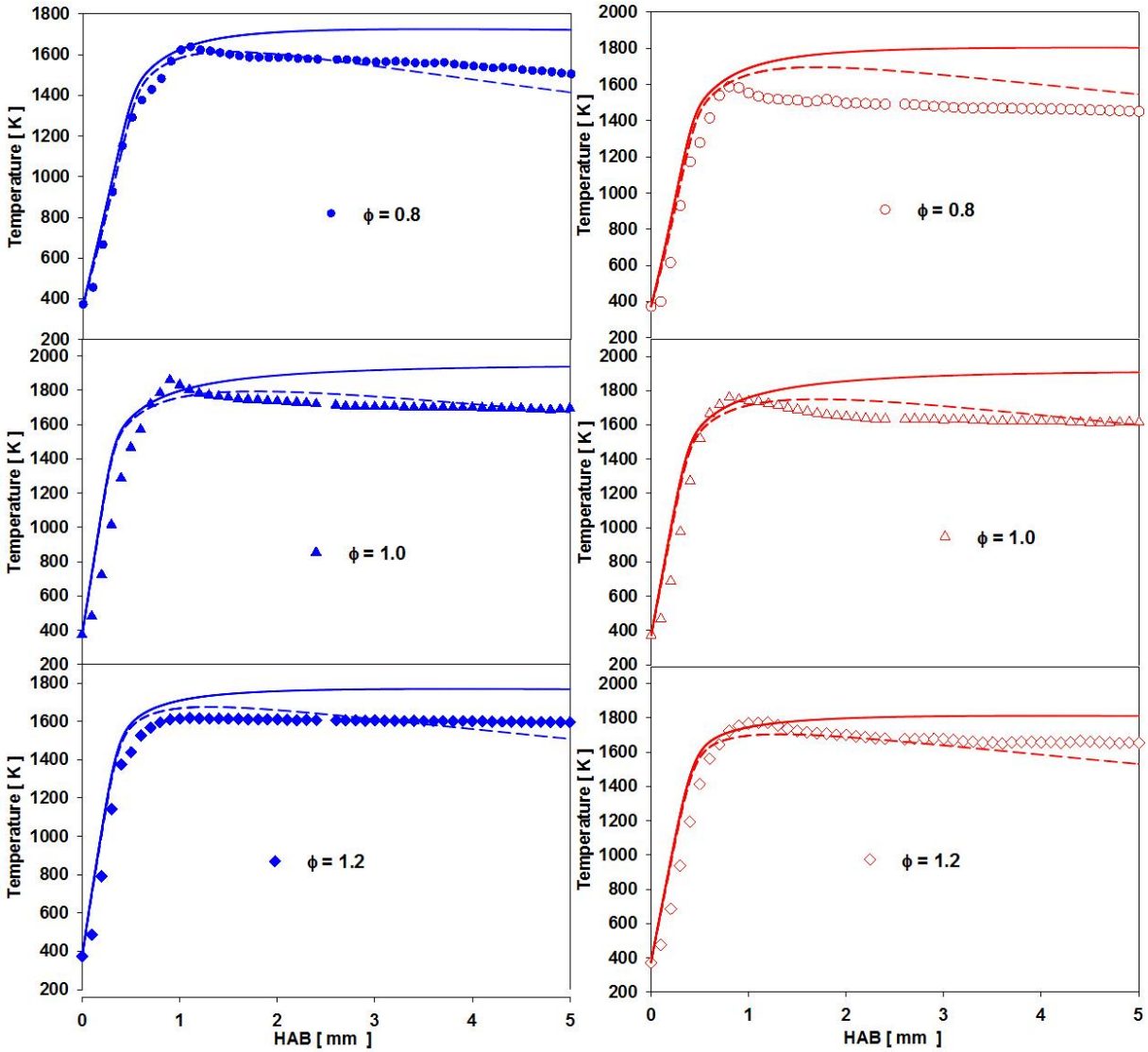
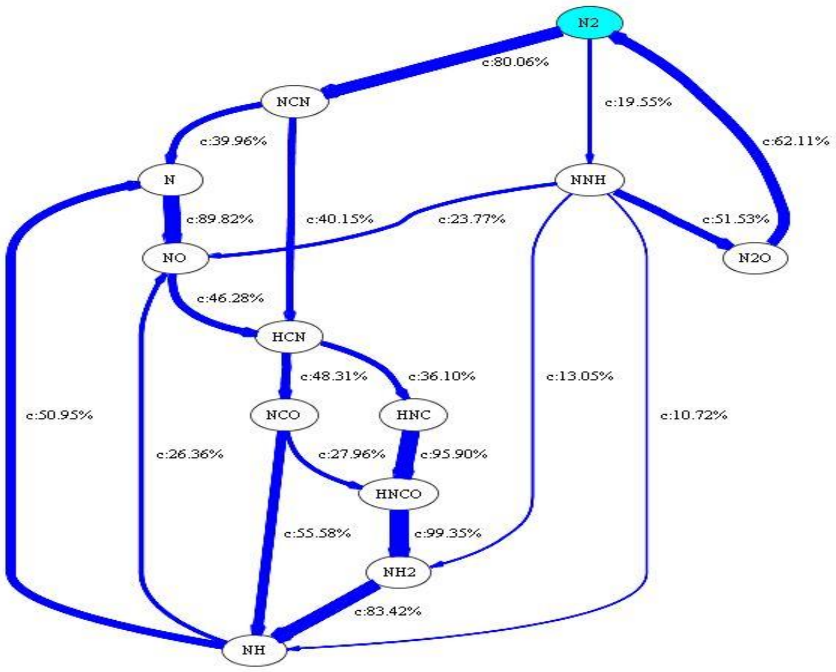


Figure S14: Temperature profile in burner stabilized premixed flames methanol/air (left) and ethanol/air (right) at three different equivalence ratio (ϕ = 0.8, 1.0 and 1.2), 1atm and 373K for flame shown in Figure 9. Symbols: experimental data (Bohon *et al.*, 2018; Myles D. Bohon 2018, personal communication, 27 July), lines: calculated temperature solving energy conservation equation. Solid lines: taking radiation factor = 0.5 (standard), dash lines: using radiation factor = 8.0.


N2
c:80.06%
c:19.55%
c:62.11%
NCN
c:39.96%
N
NNH
c:89.82%
c:40.15%
c:23.77%
c:51.53%
NO
N2O
c:46.28%
HCN
c:48.31%
c:36.10%
c:13.05%
c:50.95%
NCO
HNC
c:10.72%
c:26.36%
c:27.96%
c:95.90%
HNCO
c:55.58%
c:99.35%
NH2
c:83.42%
NH

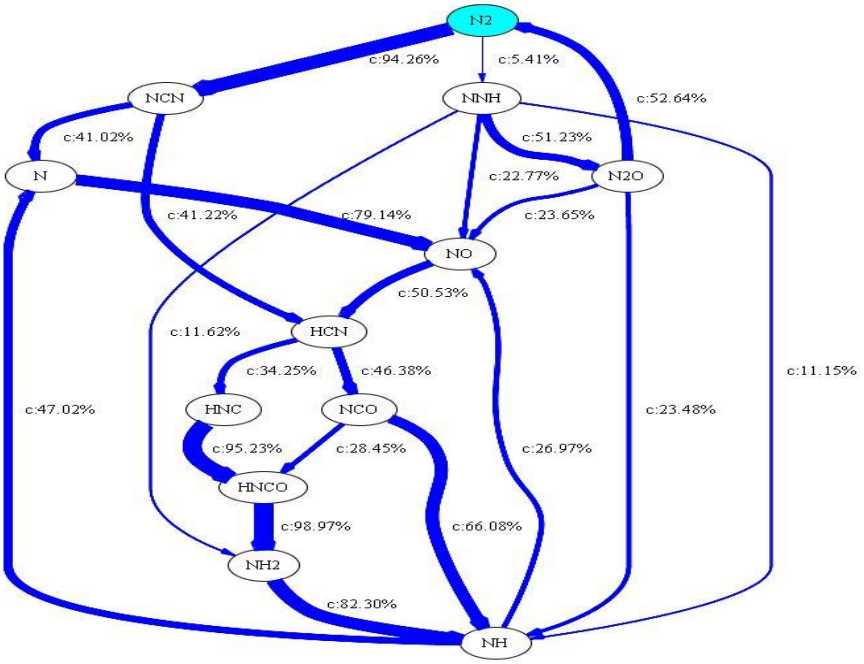
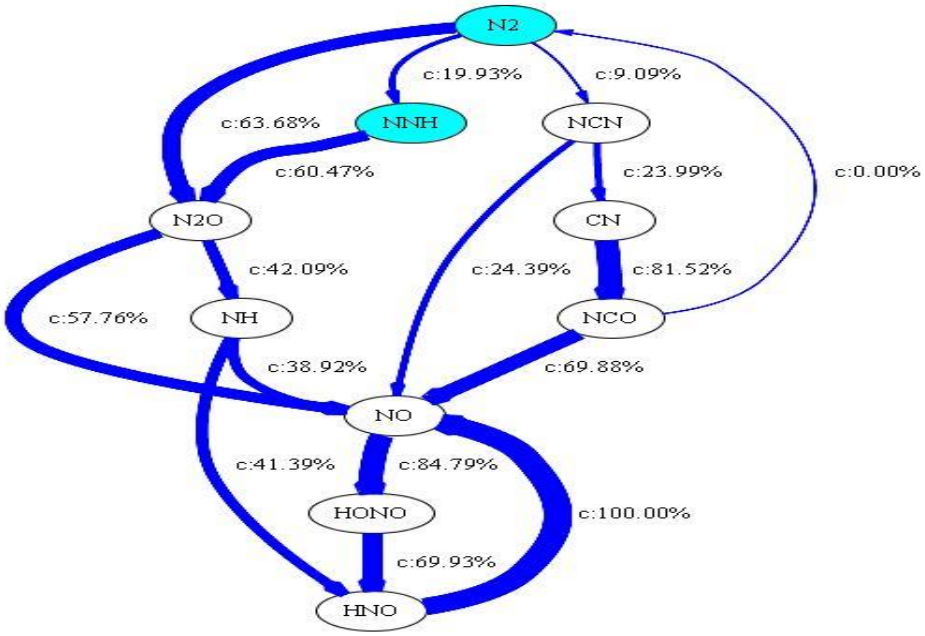

N2
c:94.26%
c:5.41%
NCN
NNH
c:52.64%
c:41.02%
c:51.23%
N
c:22.77%
N2O
c:41.22%
c:79.14%
c:23.65%
NO
c:50.53%
c:11.62%
HCN
c:34.25%
c:46.38%
c:11.15%
c:47.02%
HNC
NCO
c:23.48%
c:95.23%
c:28.45%
c:26.97%
HNCO
c:98.97%
c:66.08%
NH2
c:82.30%
NH

Figure S15: Flow analysis for flame shown in Figure 9. Methanol/air (ϕ = 1.2, top), Ethanol/air (ϕ = 1.2, bottom).



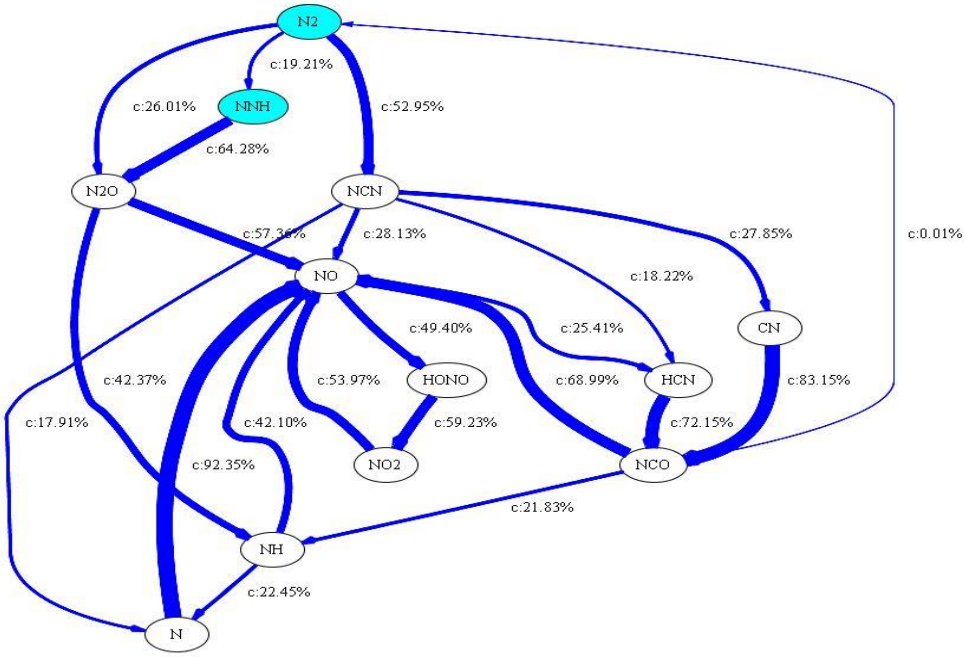


Figure S16: Flow analysis for flame shown in Figure 9. Methanol/air (ϕ = 0.8, top), Ethanol/air (ϕ = 0.8, bottom).

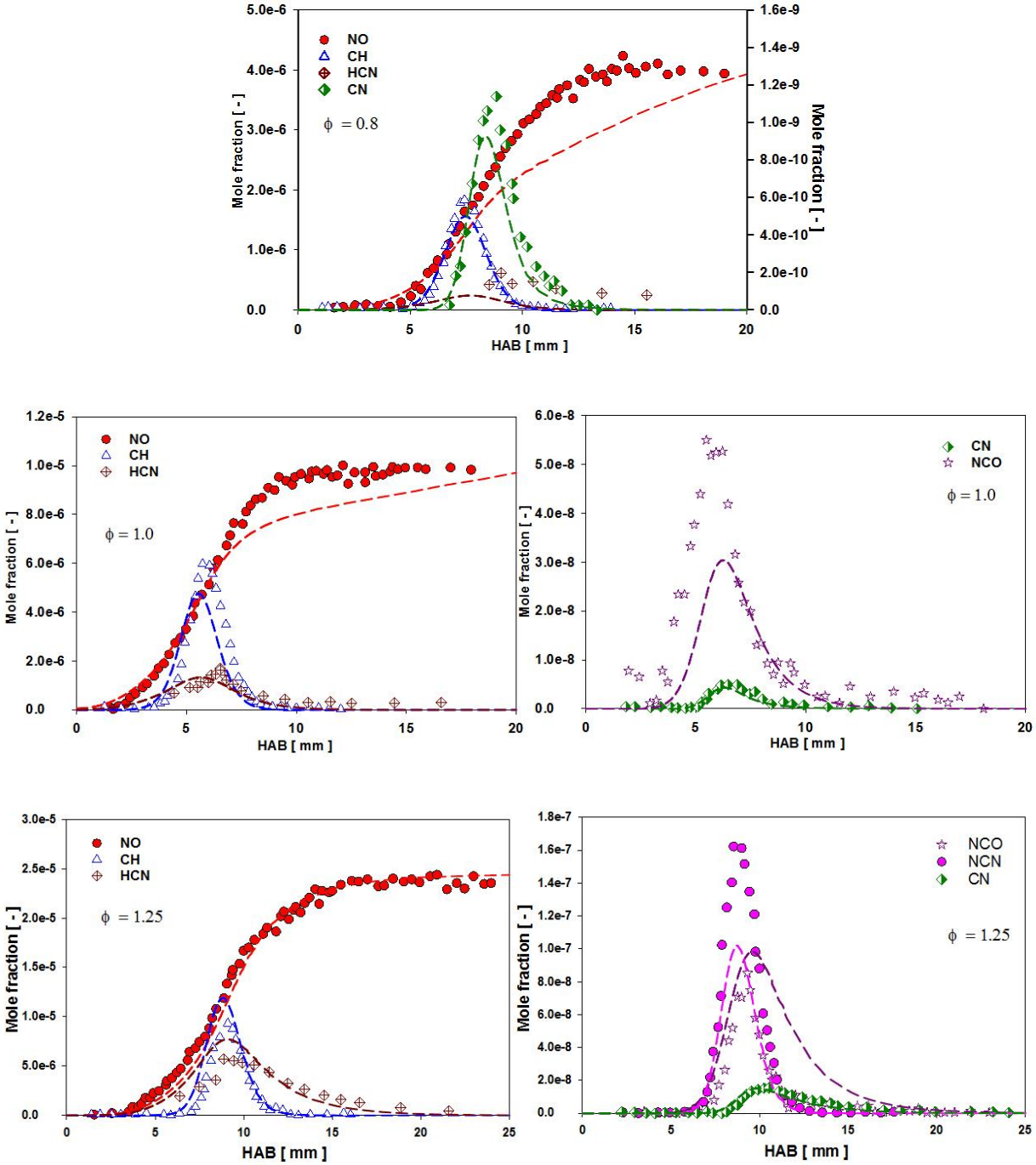


Figure S17: Speciation in burner stabilized premixed flame for $CH_4/O_2/N_2$ at three different equivalence ratio at 5.3 kPa and 273.15 K, top (ϕ = 0.8), middle (ϕ = 1.0) and bottom (ϕ = 1.25).

Symbols: experimental data from Lamoureux *et al.* (2016); lines: model prediction imposing experimental temperature profile.

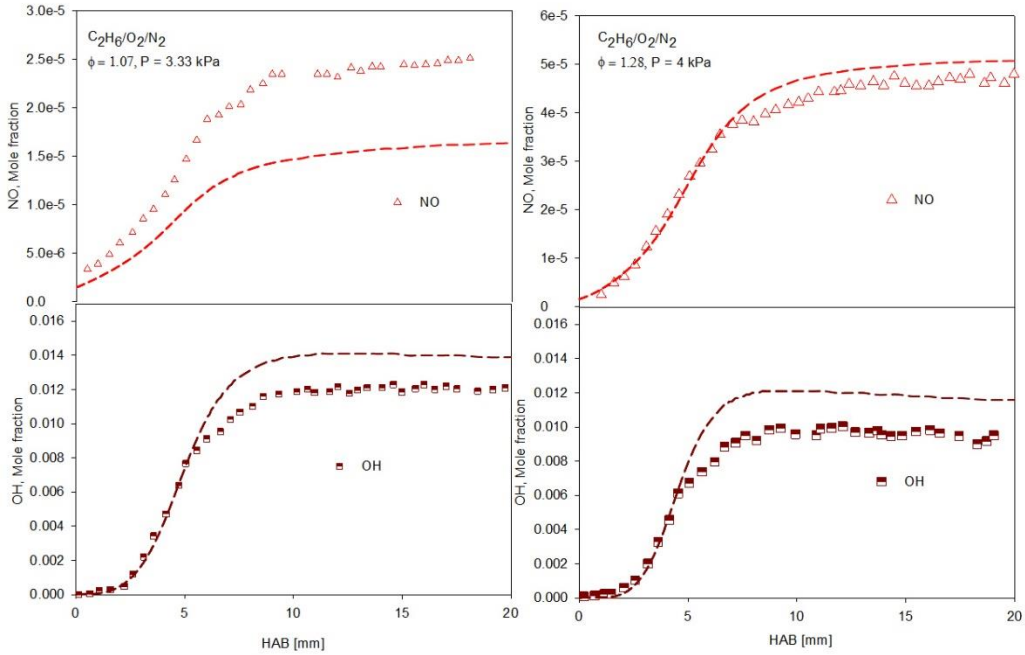


Figure S18: Speciation in burner stabilized premixed flame for $C_2H_6/O_2/N_2$ at 3.33 kPa and ϕ = 1.07 (left), at 4.0 kPa and ϕ = 1.28 (right). Symbols: experimental data from Sutton *et al.* (2012); lines: model prediction imposing experimental temperature profile.

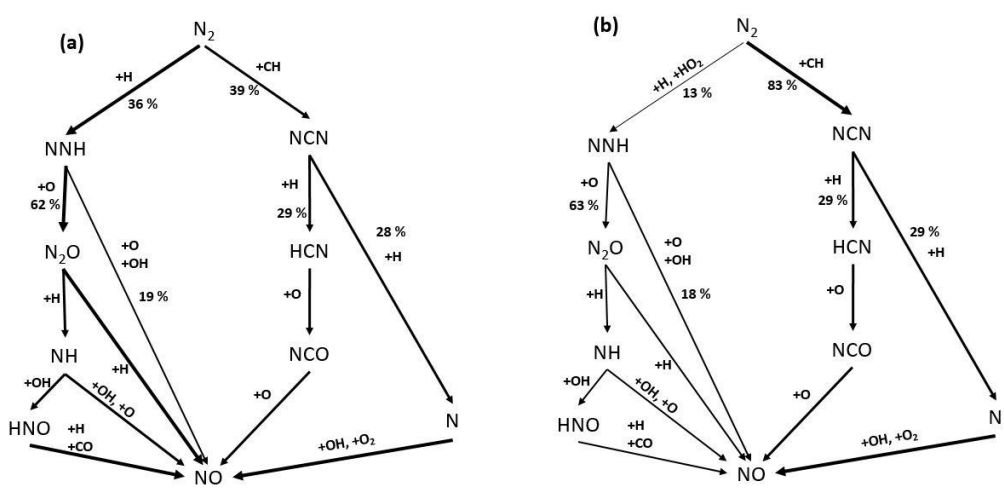


Figure S19: Reaction flow analysis based on the nitrogen atom at ϕ = 1.0 for the burner stabilized laminar premixed methanol/air (a) and ethanol/air (b) flames shown in Figure 9 at HAB = 1 mm.

Additional model validation for pure fuels

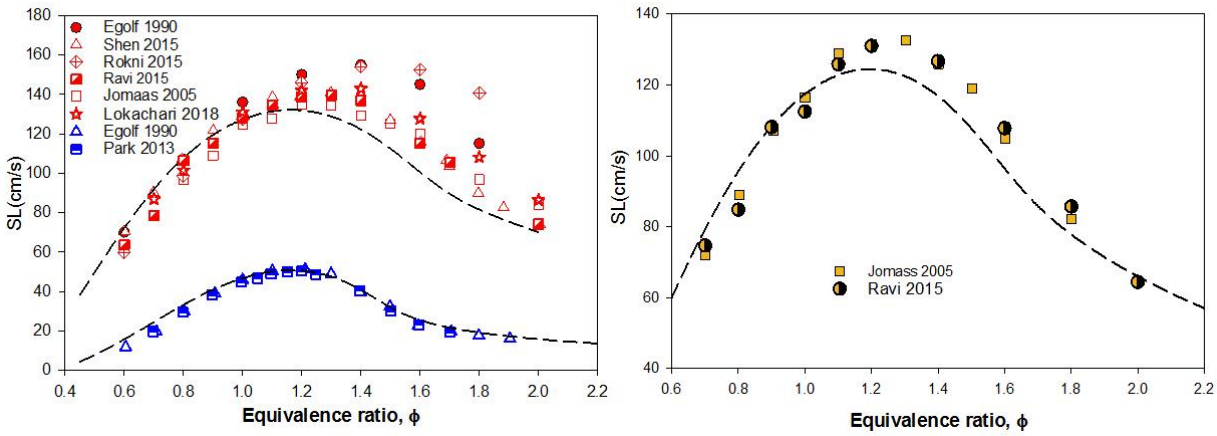


Figure S20: Laminar flame speed of C_2H_2/air at standard condition (298 K, 1 atm), left and at 298K and 2 atm, right. Lines: model prediction from this study. Symbols: experimental data(Egolfopoulos et al., 1990, Jomaas et al., 2005, Park et al., 2013, Ravi et al., 2015, Rokni et al., 2015, Shen et al., 2015, Lokachari et al., 2018)

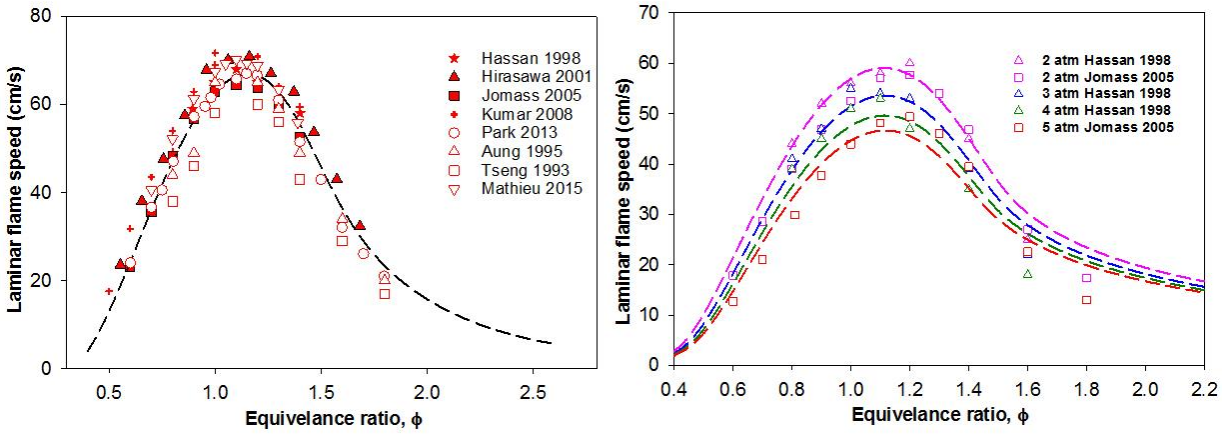


Figure S21: Laminar flame speed of C_2H_4/air at standard condition (298 K, 1 atm), left figure and at 298K and elevated pressure, right figure. Lines: model prediction from this study. Symbols: experimental data(Tseng et al., 1993, Aung et al., 1995, Hassan et al., 1998a, Hirasawa et al., 2002, Jomaas et al., 2005, Kumar et al., 2008, Park et al., 2013, Mathieu et al., 2015)

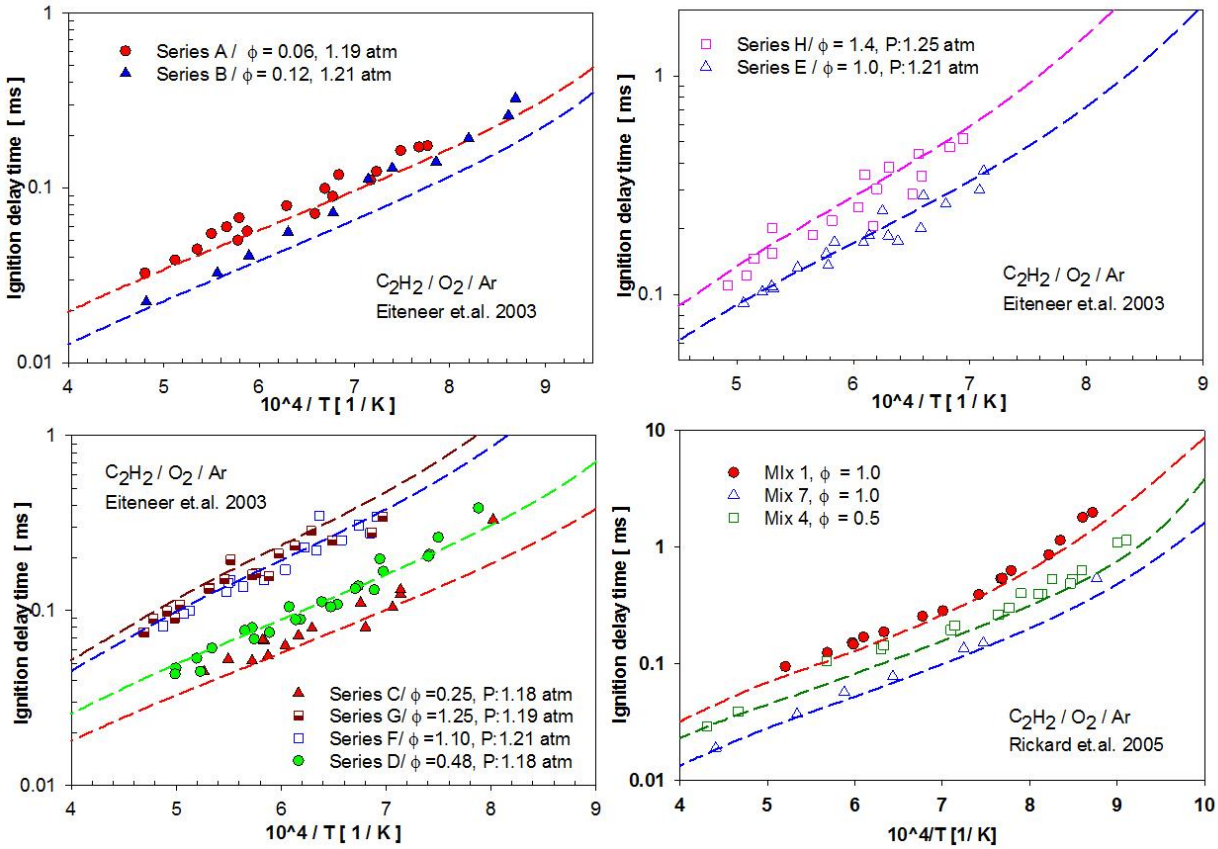


Figure S22: Ignition delay time comparison between model predictions against experimental data for $C_2H_2/O_2/Ar$ in shock tube. Lines: model prediction from this study. Symbols: experimental data ((Eiteneer and Frenklach, 2003, Rickard et al., 2005)

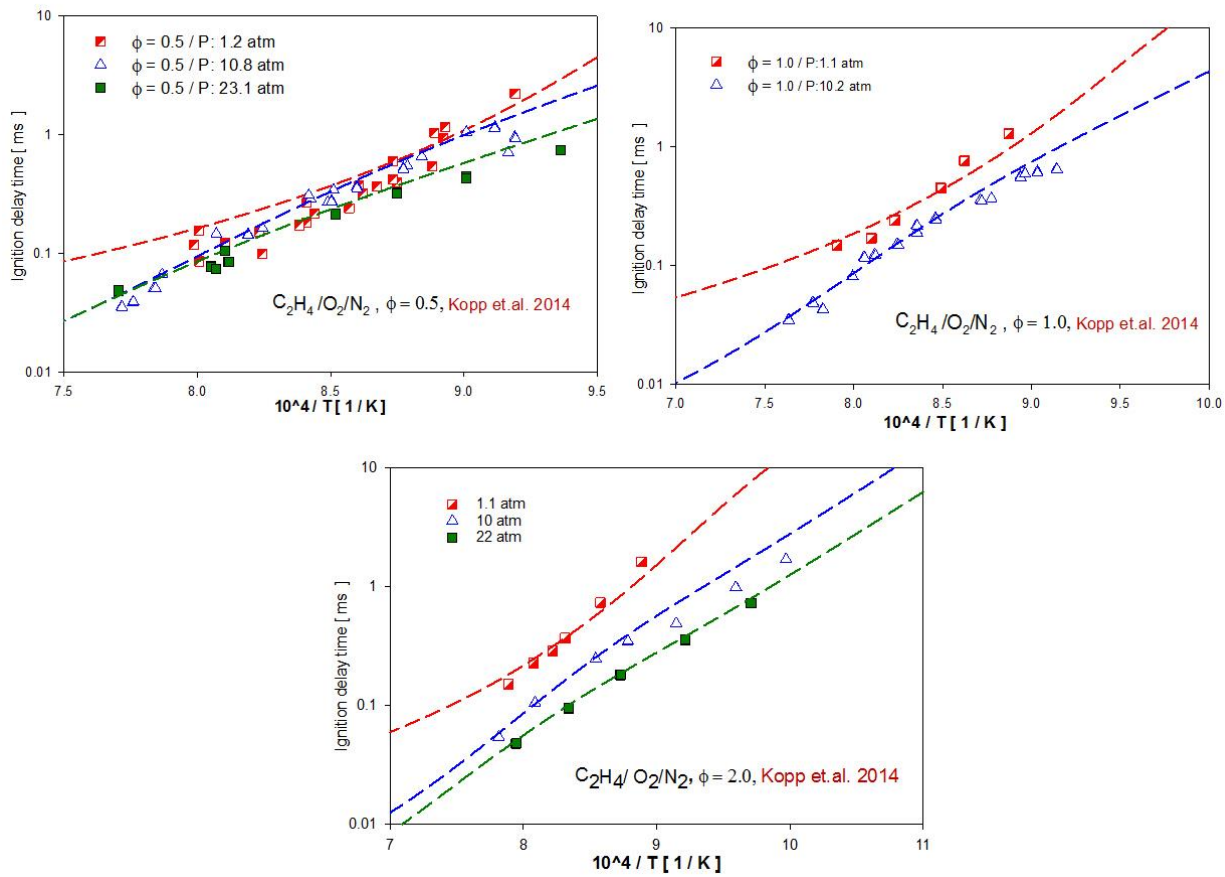


Figure S23: Ignition delay time comparison between model predictions against experimental data for $C_2H_4/O_2/N_2$ in shock tube. Lines: model prediction from this study. Symbols: experimental data(Kopp et al., 2014).

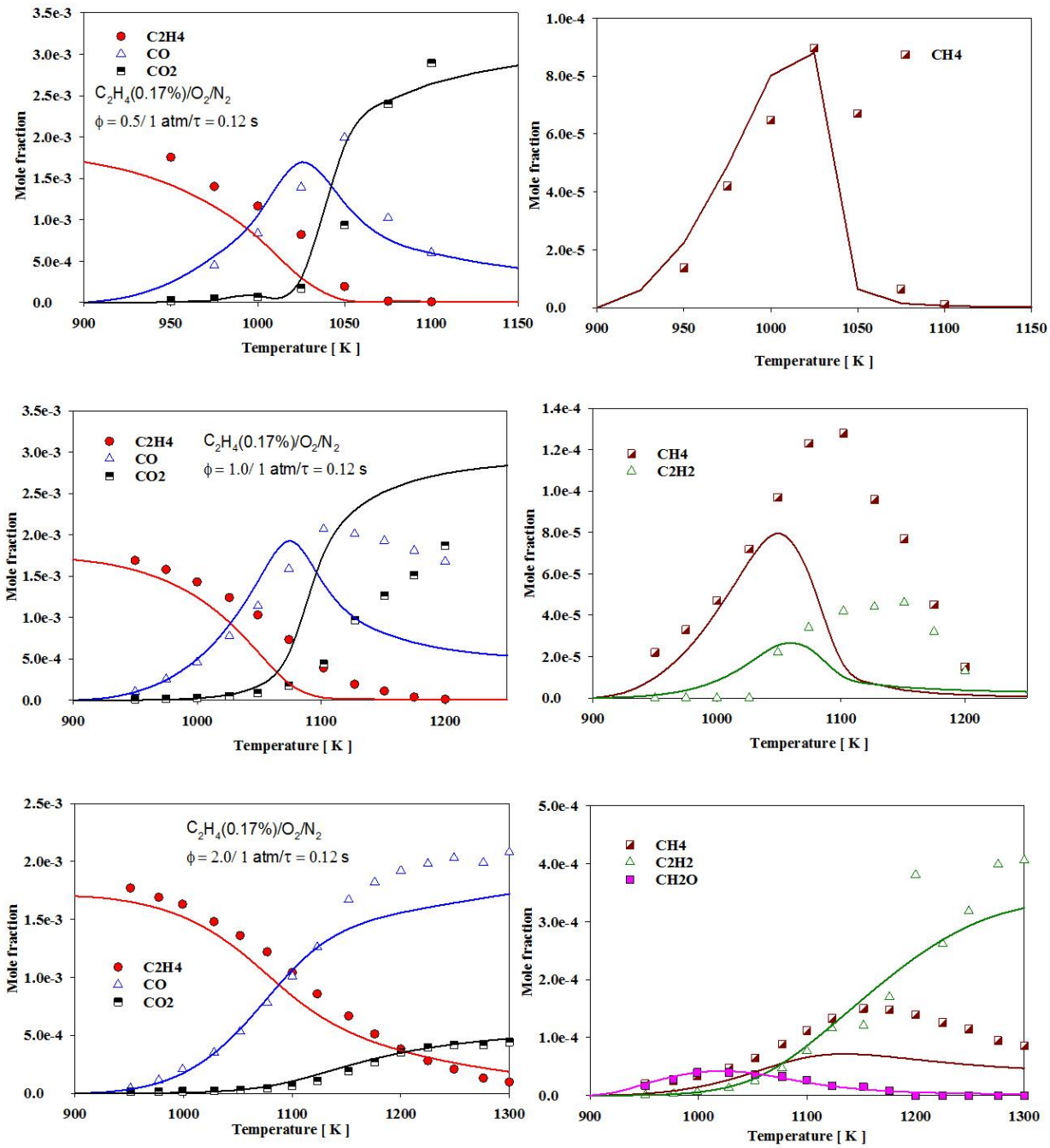


Figure S24: Speciation of $C_2H_4/O_2/N_2$ oxidation in JSR, comparison between model predictions against experimental data. Lines: model prediction from this study. Symbols: experimental data (Le Cong et al., 2010).

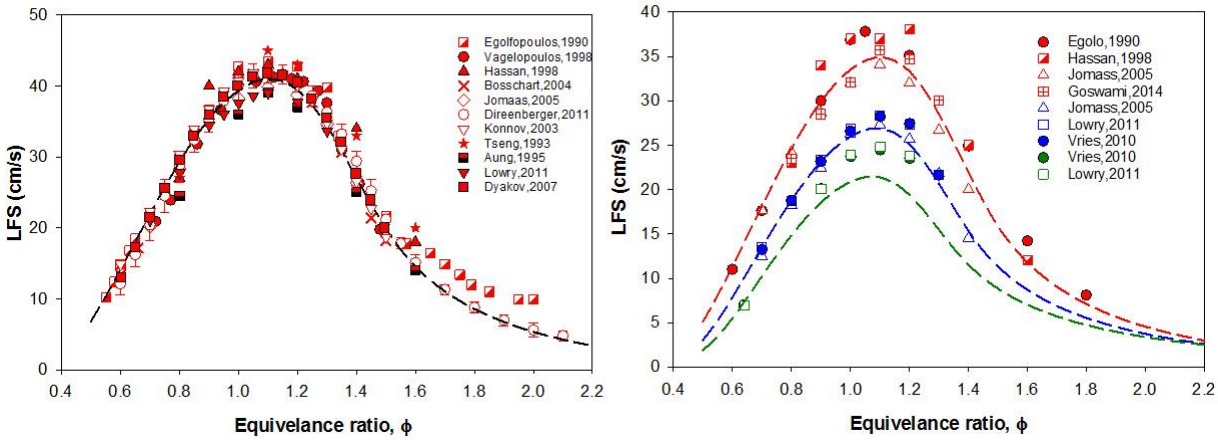


Figure S25: Laminar flame speed of C_2H_6/air at standard condition (298 K, 1 atm), left figure and at 298K and elevated pressure (2 atm, red; 5 atm, blue; and 10 atm, green), right figure. Lines: model prediction from this study. Symbols: experimental data (Egolfopoulos et al., 1990, Tseng et al., 1993, Aung et al., 1995, Hassan et al., 1998b, Vagelopoulos and Egolfopoulos, 1998, Konnov et al., 2003, Jomaas et al., 2005, Dyakov et al., 2007, Dirrenberger et al., 2011, Lowry et al., 2011)

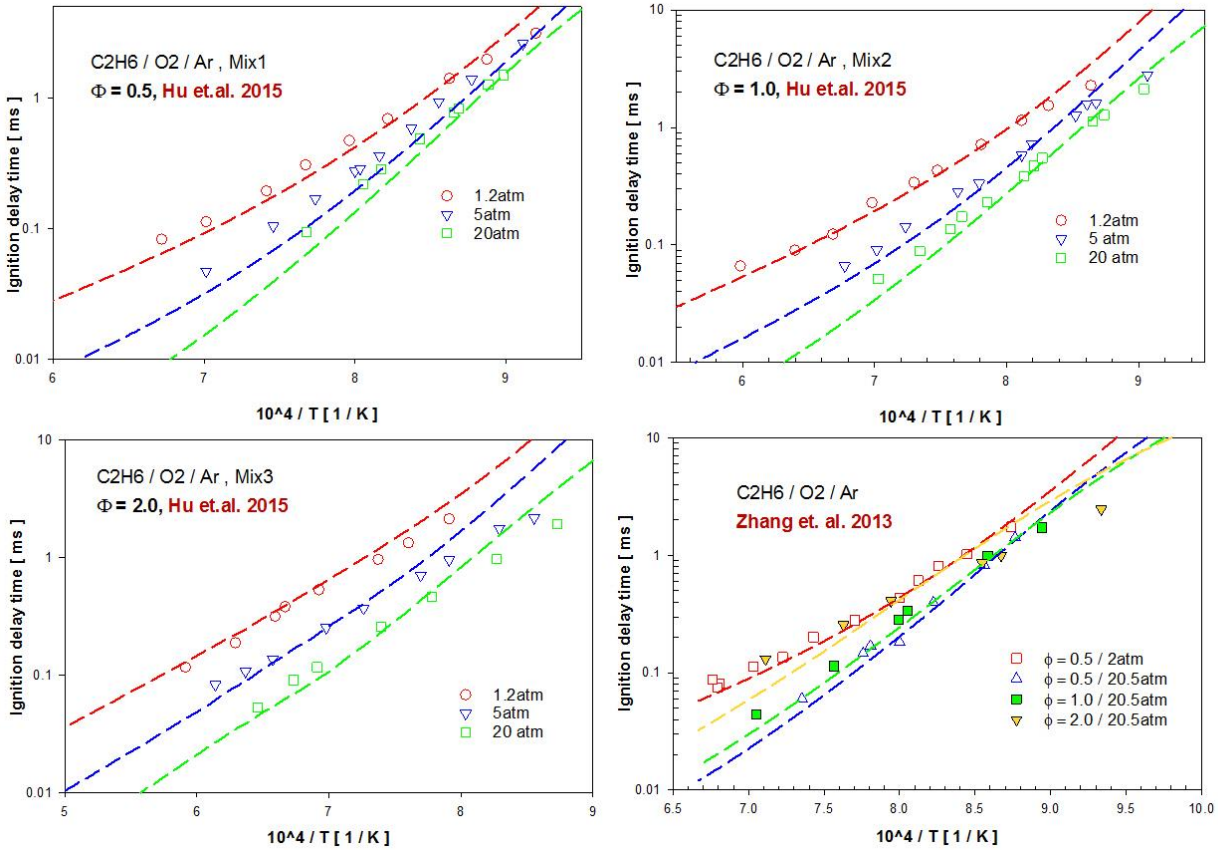


Figure S26: Ignition delay time comparison between model predictions against experimental data for $C_2H_6/O_2/Ar$ in shock tube. Lines: model prediction from this study. Symbols: experimental data (Zhang et al., 2013, Hu et al., 2015)

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