Benchmarks of the CO_2 chemical kinetics model and evaluation of the stepwise model updates.

Supplemental material for the paper
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1 Models

The initial model was based on the PLASIMO input file taken from `https://plasimo.phys.tue.nl` (file `CO2_chemistry.gum`) which was translated into Fortran code. The results of the re-implemented model were compared with PLASIMO calculations, see DBD test below, Section 2.1.1. The source files of this initial model can be found here [6].

After that some technical mistakes were found and corrected in the PLASIMO input. The input file was then then translated into Fortran code with exactly same converter as the one which was used to create the first model. Meanwhile, the PLASIMO model on `https://plasimo.phys.tue.nl` is updated as well (file `CO2_chemistry_v2.gum`). The most important correction was fixing the mistake with double counting of the activation energy which practically diminished the reduction of the activation energy due to vibrations for reactions N1, N2, N5 (see the list of reactions in [1, 2]).

This second model was implemented with predecessor of REACNET. The Fortran files of the model were than re-written with REACNET [4]. Correctness of the re-factoring was ensured by a special test where all rate coefficients calculated for one combination of input parameters are compared one by one with coefficients produced by the pre-REACNET model. This benchmark is used as the standard integrated test of REACNET. The model which was produced in this way is called here Model 1. The sequence of updates of this model is described in the list below.

Model 2 is the Model 1 with slightly corrected energies and masses

Model 3 is the Model 2 with symmetric states added to reactant M for reactions V1, V2, V3, V5 (see the full list of reactions in [1, 2]).

Model 4 is the Model 3 without electron elastic energy losses, $Q^e_{elastic} = 0$

Model 5 is the Model 4 with rates of the electron impact processes calculated for the Maxwellian electron energy distribution

Model 6 is the Model 5 with electron-impact cross-sections for excited species re-calculated applying scalings described in [1, 2]). Some cross-sections, in particular for CO, are taken directly from [5] instead of applying the scaling relations

Model 7 is the Model 6 with electron-impact de-excitations added

Source files of the Models 3 and 7 can be found in [7] and [8] respectively.

2 Quantities

X is the conversion rate, for 1d model:

$$X = \frac{\Gamma_{CO}\left(x = x_{end}\right)}{\Gamma_{CO_2}\left(x = 0\right)}$$

here $\Gamma_{CO_2}\left(x = 0\right)$ is the influx of CO_2 (sum over all excited states) at inlet, $\Gamma_{CO}\left(x = x_{end}\right)$ is the outflux of CO (sum over all excited states) at the end of integration.

For 0d model:

$$X = \frac{n_{CO}^{t\to\infty}}{n_{CO_2}^{t=0}}$$

$n_{CO}^{t\to\infty}$ is the final density of produced CO (sum over all excited states), and $n_{CO_2}^{t=0}$ is the initial density of CO_2.

η is the energy efficiency

$$\eta = \frac{2.93\ \text{eV}}{SEI} \cdot X$$

SIE - see below - must be expressed in eV, 2.93 eV is the ideal cost of producing one CO molecule.

n_e^{max} is the maximum of the electron density on the interval from x to x_{end}

T_e^{max} is the maximum of the electron temperature on the interval from x to x_{end}

T_h^{max} is the maximum of the heavy particles temperature on the interval from x to x_{end}

T_v^{max} is the maximum of the CO_2 vibrational temperature. Vibrational temperature of the asymmetric modes is defined as:

$$T_v = -\frac{3382.6\ \text{K}}{\ln\left(\frac{n_{CO_2[v=1]}}{n_{CO_2[v=0]}}\right)}$$

where $n_{CO_2[v=0]}$ is the number density of the ground state molecules, $n_{CO_2[v=1]}$ is the number density of molecules in first asymmetric mode of vibrations

SEI is the specific energy input per one CO_2 molecule:

$$\text{SEI} = \frac{P_{in}}{\Gamma_{CO_2}\left(x = 0\right) \cdot A}$$

here P_{in} is the total input power into discharge in eV/s, $\Gamma_{CO_2}\left(x = 0\right)$ is the flux density and A is the cross sectional area of the discharge tube.

2.1 Benchmarks

2.1.1 DBD test

To check the implementation of the model [2, 3] in another technical format a test described in [2] was used. A set of equations is solved for the time-dependent species densities, and for the electron pressure:

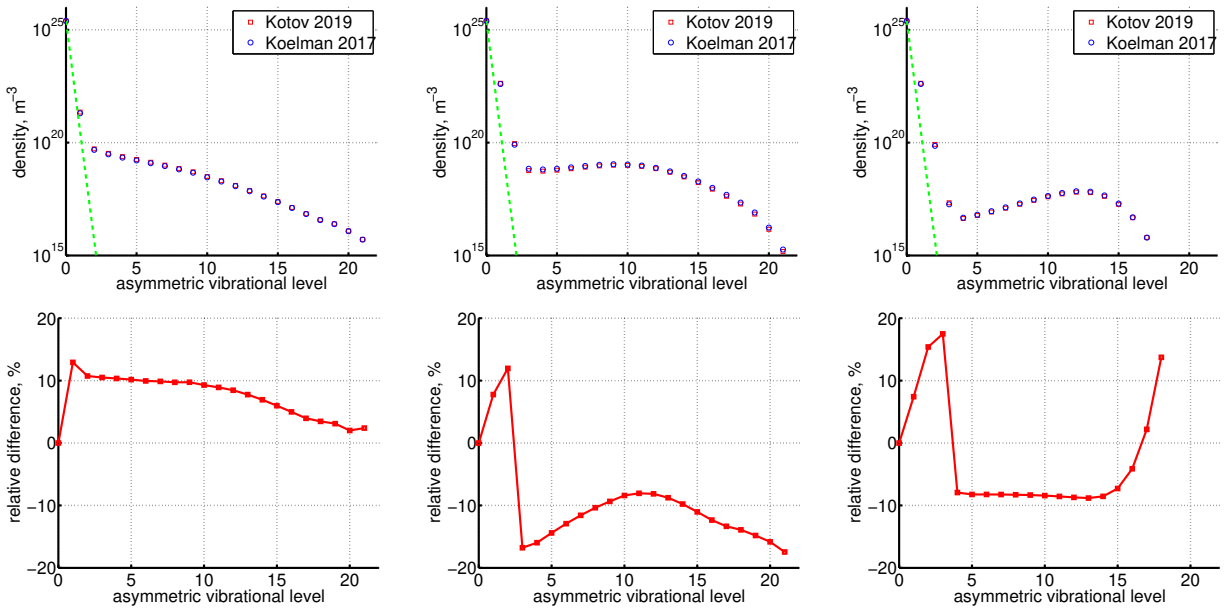
$$\frac{dn_i}{dt} = S_i, \ \frac{d}{dt}\left(\frac{3}{2} n_e T_e\right) = Q_{in} - Q^e_{inelastic} - Q^e_{elastic} \tag{1}$$

Here Q_{in} is the specific input power, $Q^e_{elastic}$ is the power lost by free electrons in elastic collisions, $Q^e_{inelastic}$ is the power lost in inelastic collisions. The electron density obeys quasineutrality $n_e = \sum_{i=1}^{N_s} Z_i n_i$. No energy balance equation is solved for heavy particles, their temperature is fixed at $T_h = const$=300 K. The pressure is p=1 bar. The input power Q_{in} is a triangular pulse: the power increases linearly between t=0 and t=15 ns from 0 to Q_{max}=2e11 W/m^3, then decreases linearly back to Q_{in}=0 at t=30 ns. The parameters of the pulse mimic approximately a Dielectric Barrier Discharge (DBD).

The plasma chemical model applied for the test is the original model [3] without corrections, translated into Fortran code [6]. Calculation of $Q^e_{elastic}$ is translated from the original model [3] as well. The initial concentrations of species are also taken from [3].

In figure 1 comparison of the calculated distributions of the asymmetric vibrational levels of CO_2 between the re-implemented model and the original model [2, 3] is presented. For the levels whose density is larger than 10^{15} m^{-3} shown in the figure the relative difference does not exceed 20 %. The difference gets larger for the time instant t=1000 ns (not shown), up to 34 % for asymmetric level 4. Vibrational temperature T_{vibr} differs by 1.3 % at maximum.

Technical mistakes found in the chemical model have tiny impact on the outcome of the DBD test. This is demonstrated in figure 2, where time tracings of the discharge parameters calculated with the original and corrected models are compared. The results obtained with "model 1" and with original model "Koelman 2017" cannot be distinguished, the difference between "Koelman 2017" and "model 3" is very small.



(a) t=6 ns (b) t=30 ns (c) t=100 ns

Figure 1: Comparison of the distribution of the asymmetric vibrational levels of CO_2 calculated in the DBD test, section 2.1.1, in the present work ("Kotov 2019") with results obtained in [2] ("Koelman 2017") for different time-instants t. Dashed line is the Boltzmann distribution at 300 K. Figures in the bottom row show relative difference between "Kotov 2019" and "Koelman 2017"

2.1.2 Microwave test

As a next benchmark it was tried to reproduce the microwave plasma test case of [1]. The problem is described by the same set of equations (1) as the previous one. The pressure is set to p =20 Torr, T_h is fixed at 300 K. Q_{in} exceeds zero only at $0 \leq t \leq t_{res}$, $Q_{in} = 0$ for $t > t_{res}$=9.13e-6 sec. The non-zero Q_{in} is constant in time, its value is determined by the prescribed Specific Energy Input (SEI) per CO_2 molecule, see Eq. (11) and (12) in [1]. Initial gas at t=0 is pure CO_2. The calculations are made with reaction kinetics "model 3", see section 1, the source code of this model can be found in [7].

In figure 3 the results of the calculations are compared with the numbers from [1], table 4. As one can see the agreement between two independent calculations can only be considered as qualitative. Quantitatively the results agree only withing a factor of 2. Here we restrict ourselves to documenting this difference, without attempting to further investigate its origin. Besides known differences in the reaction kinetics, see [2], it cannot be guaranteed that EEDFs used for calculations of the electron impact rate coefficients are same. Both model implementations agree in the principle statement that the maximal η is around 20-30 %.

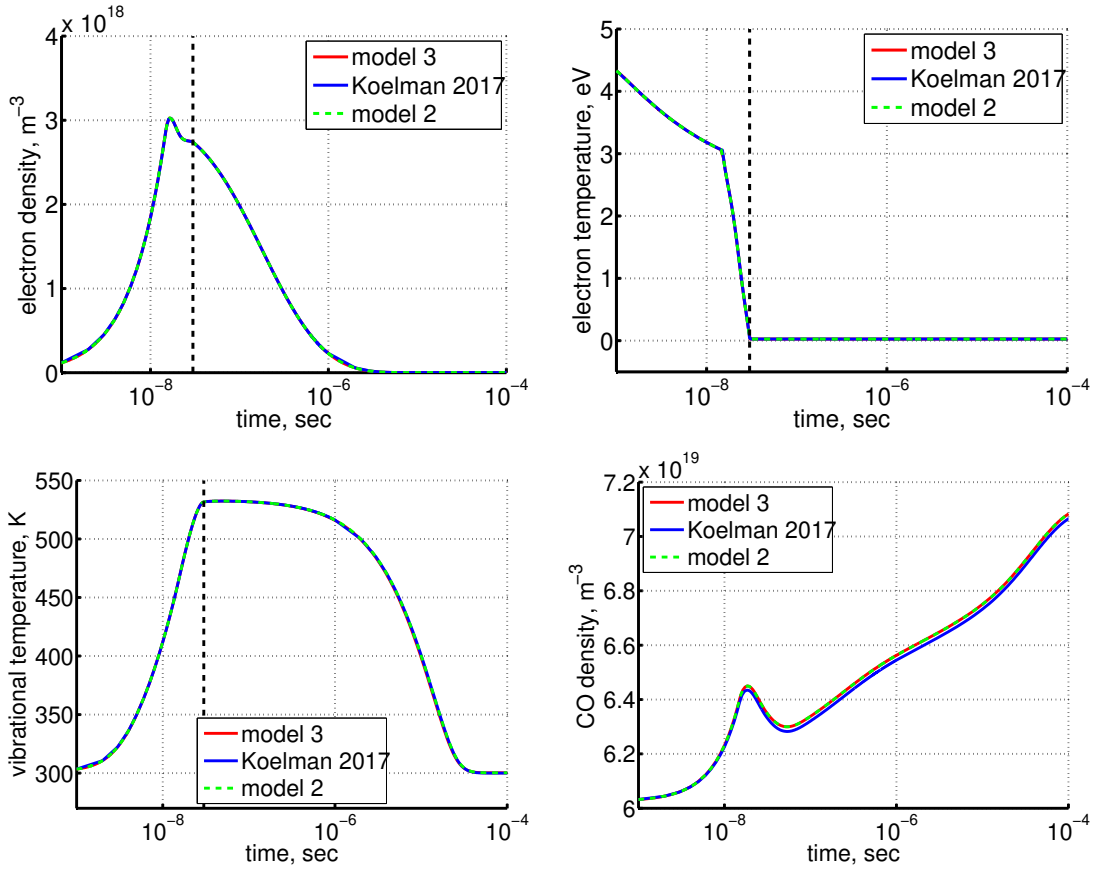
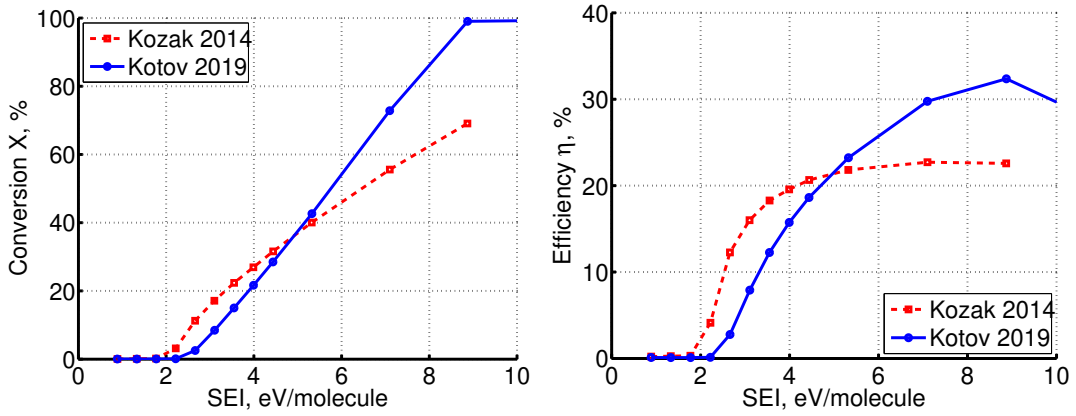


Figure 2: Comparison of the time tracings of discharge parameters in DBD test, section 2.1.1, calculated with the original model [2] ("Koelman 2017"), and the models with corrected technical mistakes: "model 3" and "model 1", see section 1



(a) (b)

Figure 3: 0D problem which mimics conditions in a microwave discharge [1]. Pressure p=20 Torr, fixed T_h=300 K, t_{res}=9.13e-6 sec. Solid lines ("Kotov 2019") are the calculations made in the present work with the plasma chemical model [7]. Dashed lines ("Kozak 2014") are numbers from [1], table 4

References

[1] Kozak T and Bogaerts A 2014 *Plasma Sources Sci. Technol* **23** 045004

[2] Koelman T et al. 2017 *Plasma Proceses and Polymers* **14** 1600155

[3] Koelman P et al., "PLASIMO Global Model for CO2 chemistry", `https://plasimo.phys.tue.nl/resources`

[4] `https://jugit.fz-juelich.de/v.kotov/reacnet.git`

[5] The Plasma Data Exchange Project, `https://fr.lxcat.net`

[6] `https://jugit.fz-juelich.de/reacflow/co2_model_koelman2016`

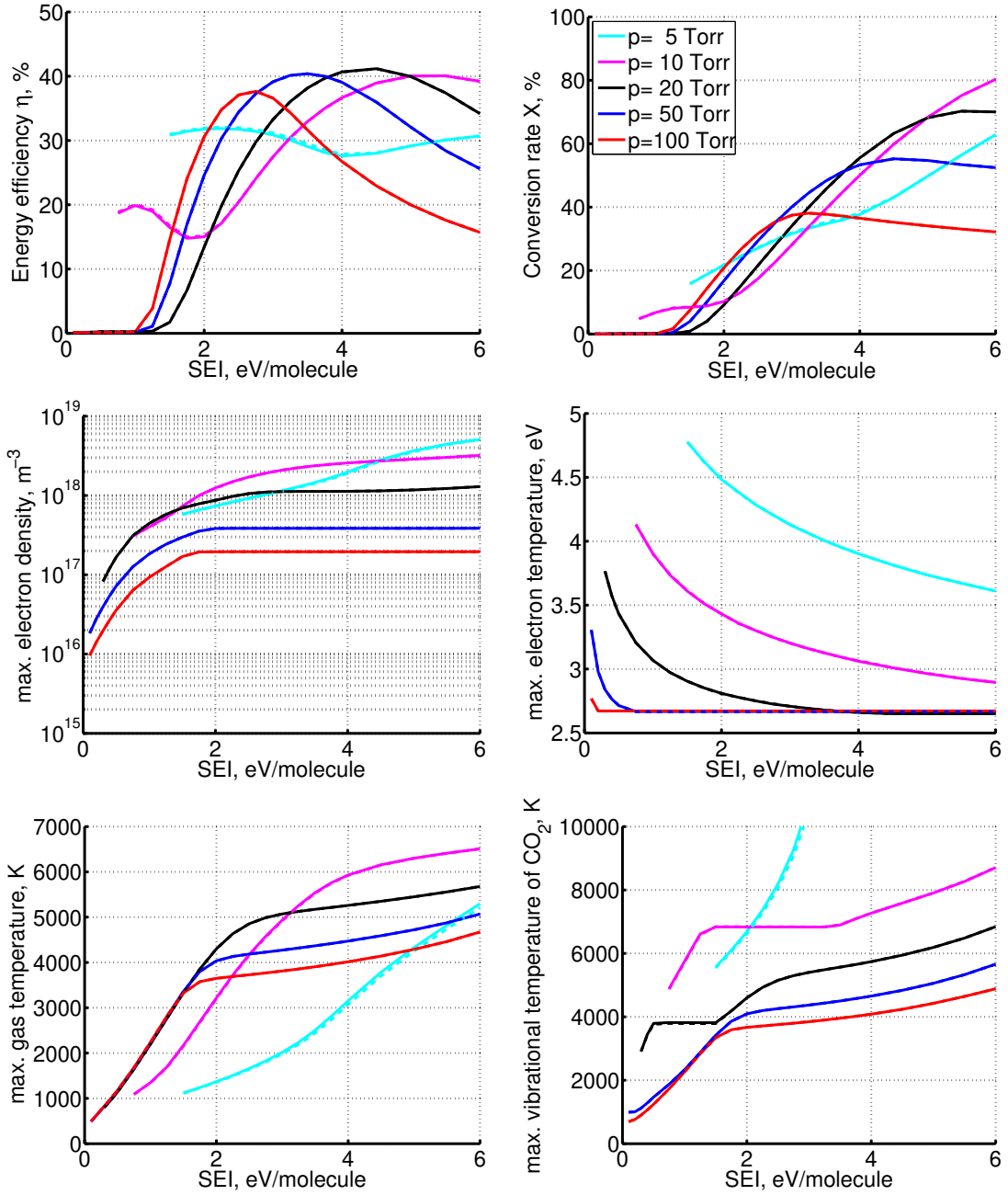
[7] `https://jugit.fz-juelich.de/reacflow/3`

[8] `https://jugit.fz-juelich.de/reacflow/7`

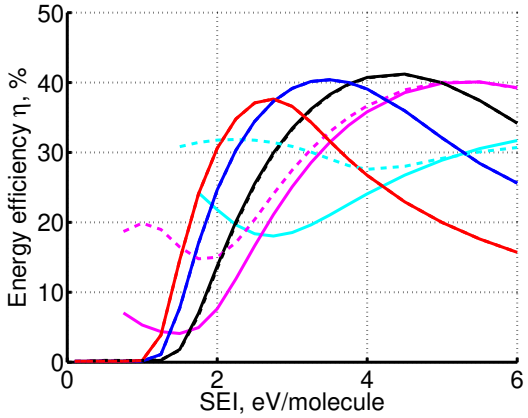
3 Evaluation of the of the stepwise model updates on the 1D plug flow solution

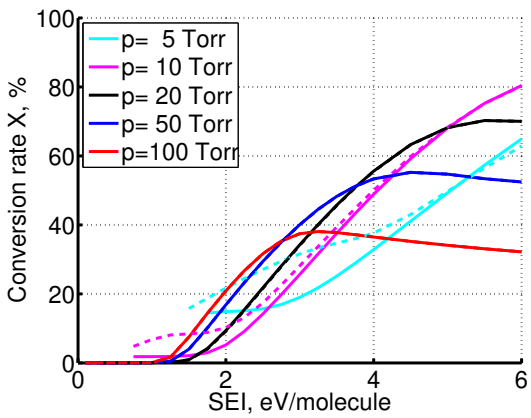
Reference model, see section 5.1 of the main paper.

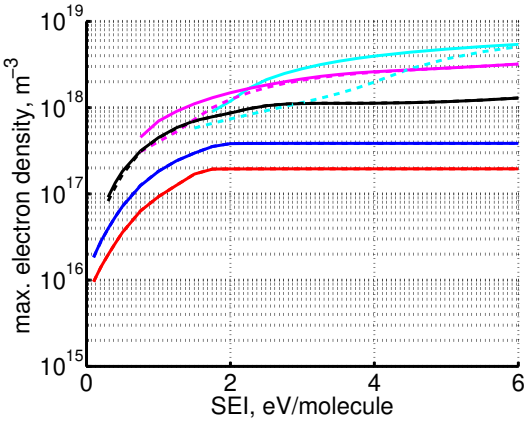
3.1 Model 2 (solid lines) versus Model 1 (dashed lines)

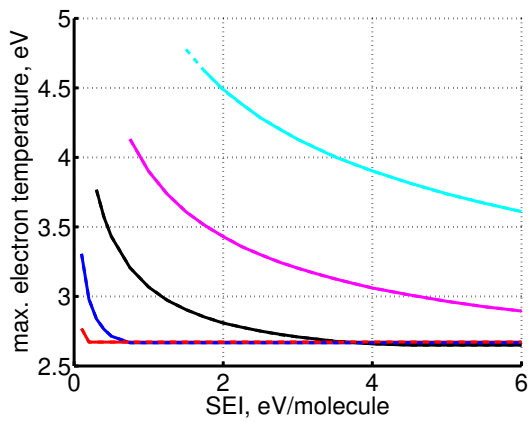


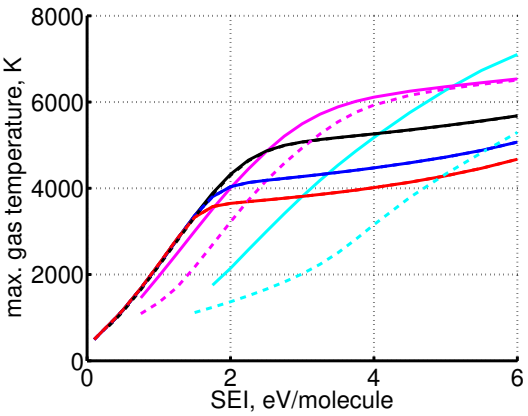
3.2 Model 3 (solid lines) versus Model 2 (dashed lines)

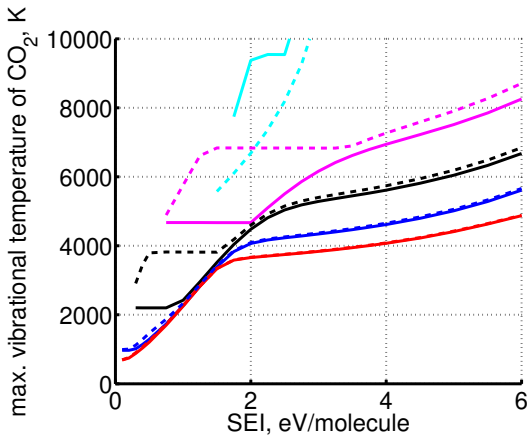




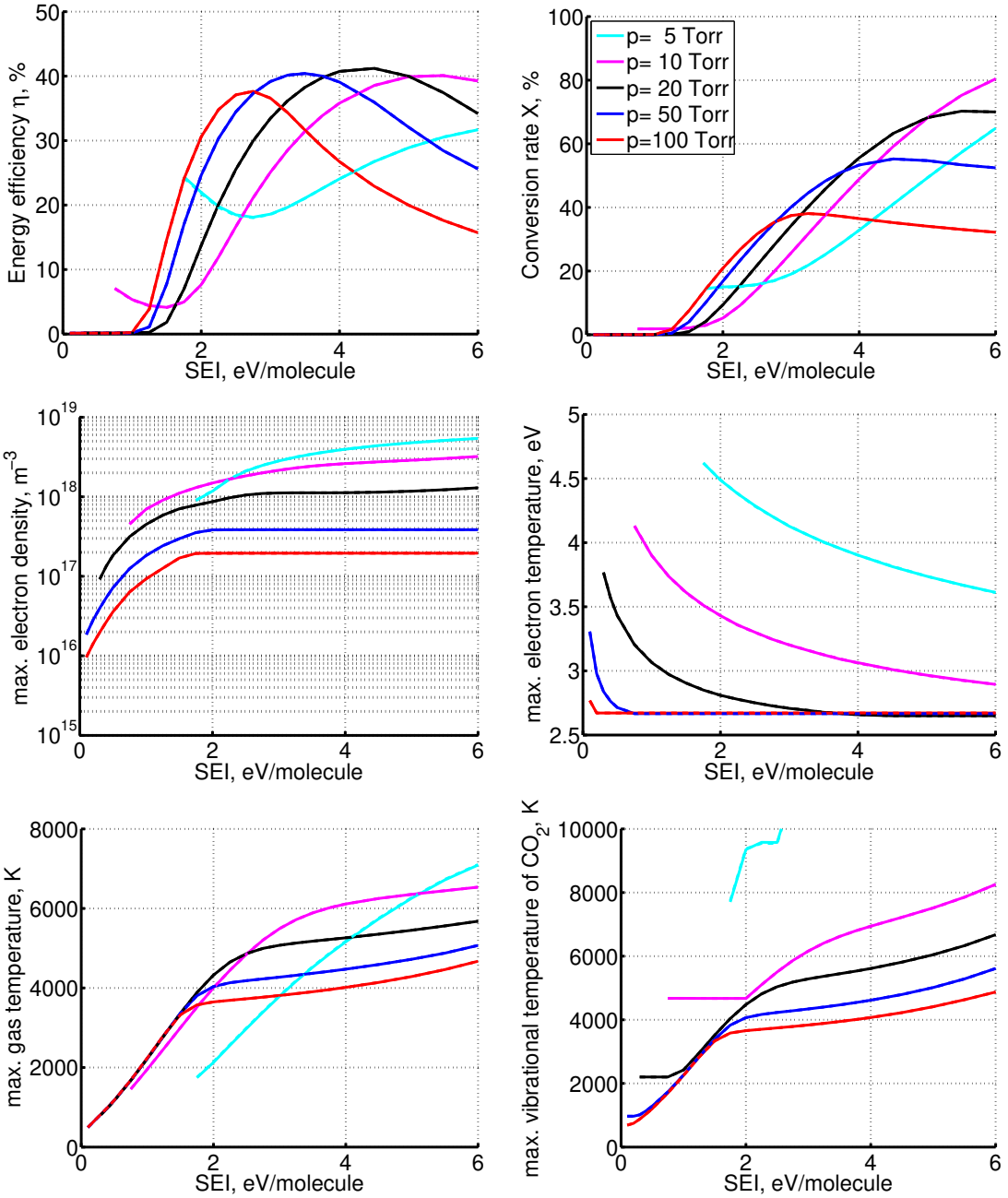




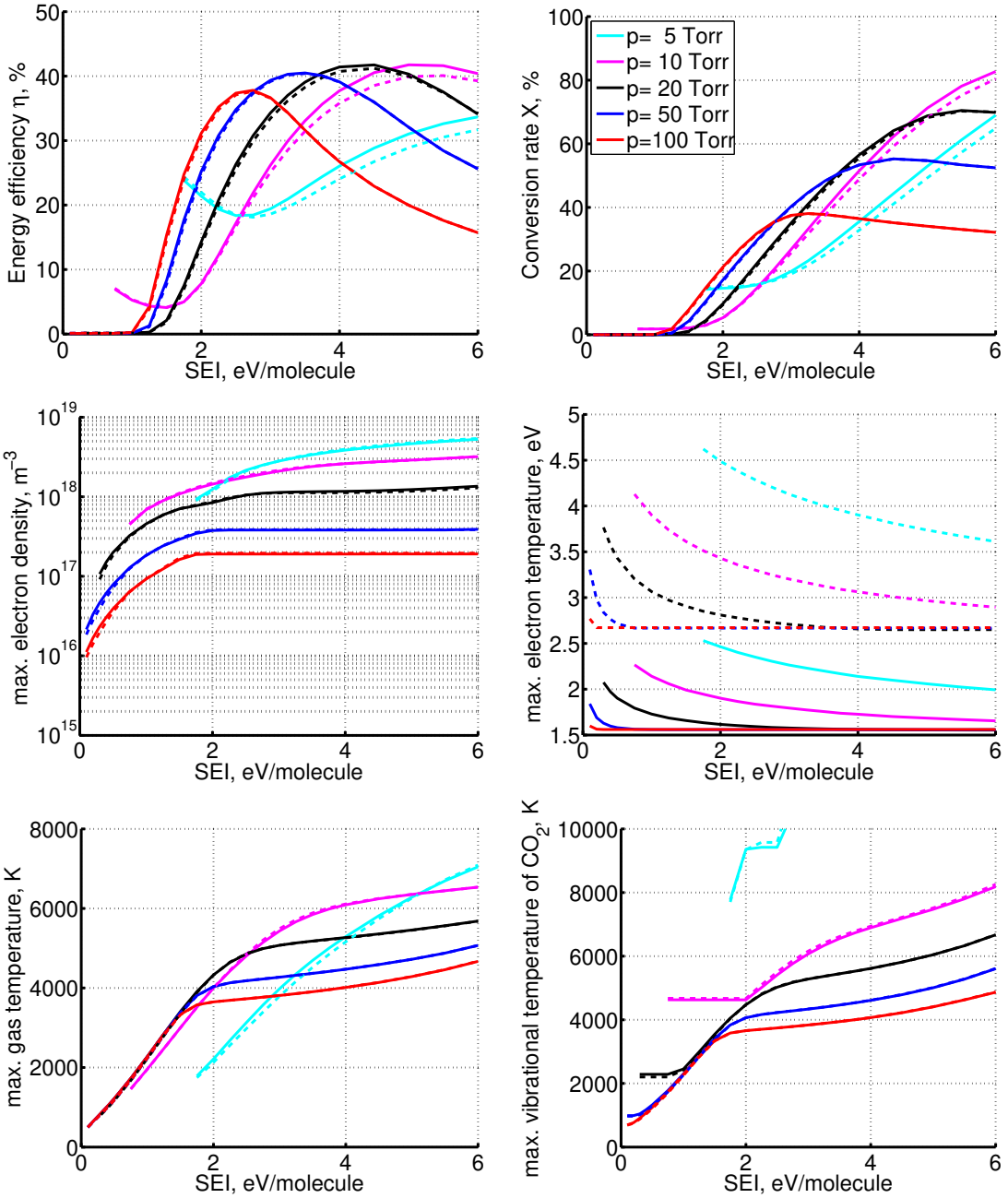




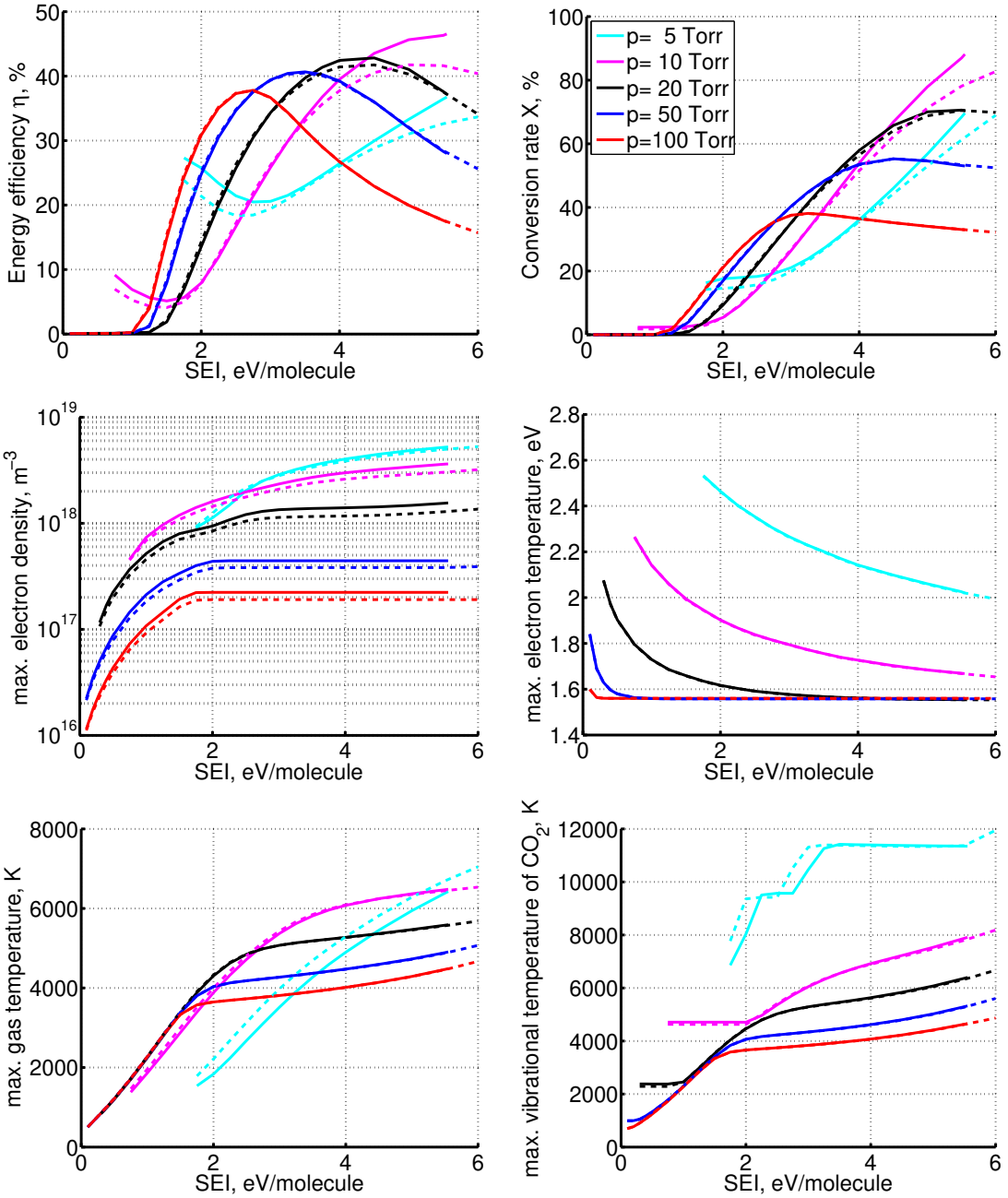
3.3 Model 4 (solid lines) versus Model 3 (dashed lines)



3.4 Model 5 (solid lines) versus Model 4 (dashed lines)



3.5 Model 6 (solid lines) versus Model 5 (dashed lines)



3.6 Model 7 (solid lines) versus Model 6 (dashed lines)