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Improving a Reactive MD Potential for Phenolic Shock

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Problem and Motivation

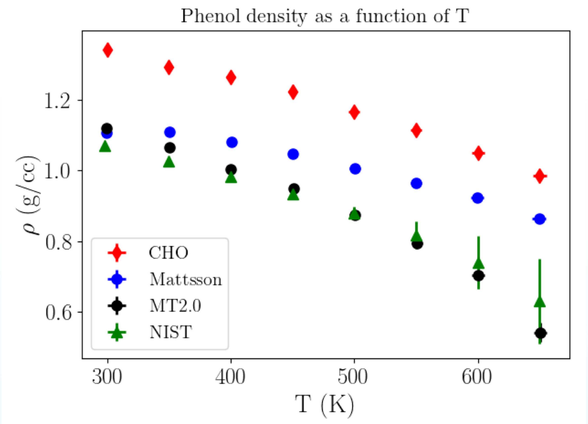
Phenolics are used in composite materials in many different contexts, oftentimes exposed to extreme conditions like heating and shock. Their chemistry under shock is therefore of interest. Non-reactive molecular dynamics (MD) has been utilized in the past to study phenolics under shock [5], and reactive MD has been employed to study pyrolysis [3, 4]. Our goal is to use reactive MD to study phenolics under shock. Accurate kinetic models describing the chemistry of phenolics under extreme conditions are also lacking. Reactive MD can provide unique insight into the chemical processes that occur under shock. In this work, we explore the capabilities of a new hybrid reaxFF parametrization and demonstrate that it is the appropriate choice for reactive shock studies.

Density

The density and other properties of phenolics can vary significantly, depending on cure time, cure temperature, formaldehyde:phenol (F:P) ratio, and other synthesis parameters. To simplify the problem of finding a potential that correctly predicts densities, we tested phenol, one of the two starting materials in the polymerization, across a range of temperatures, with 3 force fields, using the LAMMPS MD code [6] under constant pressure and temperature, in order to determine which force field yielded densities in closest agreement with the NIST model, REFPROP.

Three reaxFF parametrization candidates

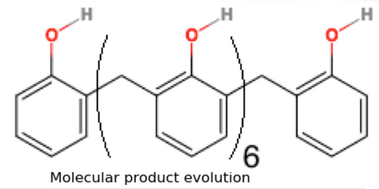
- ffield.reax.CHO: The standard for reactive C/H/O systems.
- ffield.reax.mattsson: Used successfully in previous C/H shock studies.
- ffield.reax.hm (**HM**). ffield.reax.mattsson, with the H-bonding parameters replaced with the H-bonding parameters from the CHO potential.



As can be seen in the figure above, the densities predicted by our new potential, **HM**, show the greatest agreement with the NIST densities over a range of temperatures. The NIST program, REFPROP (wtt-pro.nist.gov), is based on the most accurate pure fluid and mixture models currently available. Experimental data were unavailable, aside from the 298 K data point, which is experimental data.

Reactivity

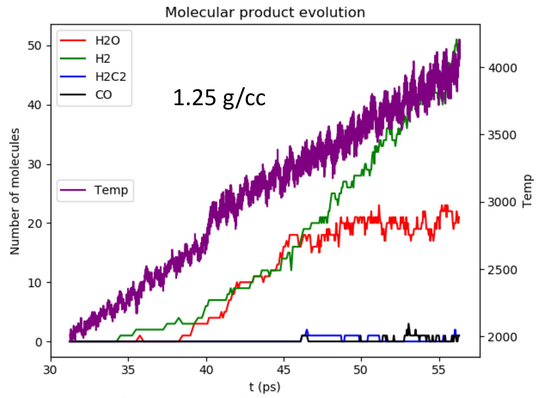
We conducted constant volume pyrolysis on a linear phenolic system (image to the right) containing 16 chains with the **HM** potential at 2 densities: 1.25 and 1.19 (ambient) g/cc in order to observe the evolution of major pyrolysis products: H_2O and H_2, and to evaluate their activation energies for formation. In refs [1, 2], four pyrolytic regimes were identified experimentally, each with its own gaseous product distribution and assigned global activation energies, which were compared with the activation energies calculated in this work.

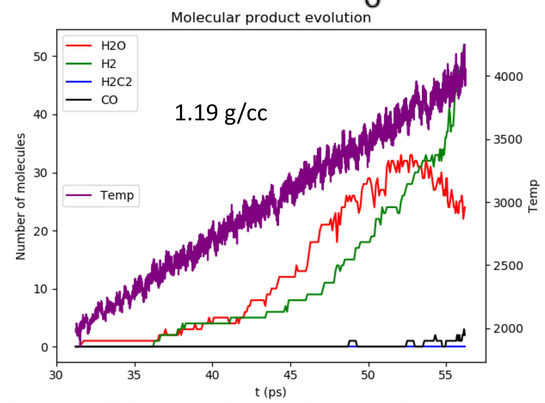


Molecular species evolution

Species evolved experimentally in individual reaction regimes (molar percentage). Table 2 - [2]

Regimes 1-2	Regime 3	Regime 4
H_2O – 49.8 %	H_2 – 59.4 %	H_2 – 85.7 %
Phenol and cresol – 50.1 %	CH_4 – 14.9 %	CO – 9.5 %
	CO – 12.7 %	H_2O – 4.7
	H_2O 12.7 %	
T = 300-550 K	T = 400-800 K	T = 560-900 K

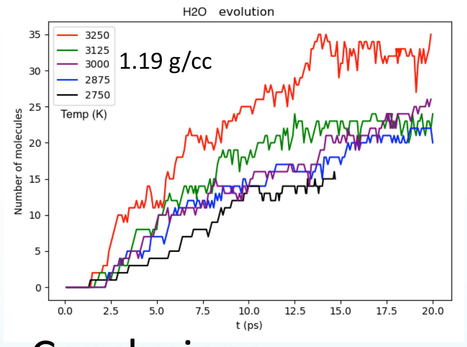


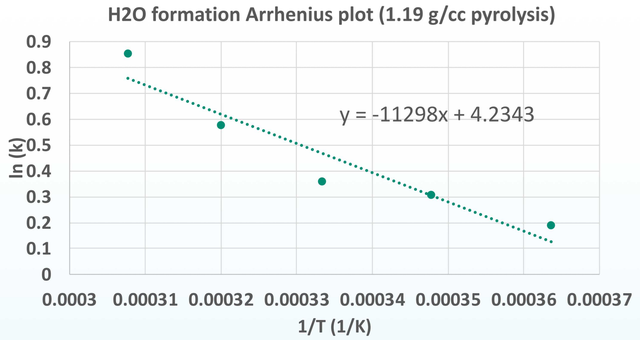


The figures above show the thermal ramp to 4000 K at a rate of 0.08 K/fs, for both simulations. H_2O and H_2 formation begin at ~2500 K, and they are the most abundant products, in agreement with experimental results. H_2O formation comes to completion as H_2 formation continues. This is consistent with experimental species evolution data and the fact that the majority of the H_2O is evolved in the lower temperature regimes (1-2), whereas H_2 evolution proceeds at higher temperatures.

H_2O activation energies of formation

Pyrolysis was carried out at 5 different temperatures to determine activation energies for H_2O formation, which were related back to the experimental data. Rate constants at each temperature were extracted from the proportionality between number of molecules and time (plot shown below,), which allowed the construction of Arrhenius plots (shown below), from which activation energies could be calculated. These energies lie in the range of experimentally determined global activation energies, and are also closer to the lower end of the range than previous work [3,4], which is where water formation occurs.





Study	H_2O E_a (kJ/mol)
This work (1.19 g/cc)	94 +/- 18
This work (1.25 g/cc)	96 +/- 43
Experimental [1]	74 - 199
Jiang, van Duin [3]	144 +/- 28
Desai [4]	124 +/- 20

Conclusions

The new reactive potential, **HM** is appropriate for future shock studies, due to its ability to:

- Accurately predict the density of phenol across a range of temperatures.
- Yield the two most abundant byproducts of phenolic pyrolysis, H_2 and H_2O, as its most abundant byproducts.
- Predict activation energies of formation for H_2O within the experimental range of activation energies.

References
[1]. K. A. Trick et al. *Carbon* **35**(3), 393-401 (1997).
[2]. K. A. Trick et al. *Carbon* **33**(11), 1509-1515 (1995).
[3]. D. Jiang et al. *J. Phys. Chem. A* **113**(25), 6891-6894 (2009).
[4]. T. G. Desai et al. *Polymer* **52**, 577-585 (2011).
[5]. B. Arman et al. *J. Appl. Phys.* **109**, 013503 (2011).

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