



Development of Computational Framework for Design of Ablative Materials

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Outline



- ◆ Background
- ◆ Understanding Pyrolysis process through Reactive Molecular Dynamics simulations
 - Thermal degradation of EPDM rubber
 - ‘Resin-to-char’ process in phenolic resins
- ◆ Accelerated Molecular Dynamics method for pyrolysis
- ◆ Summary



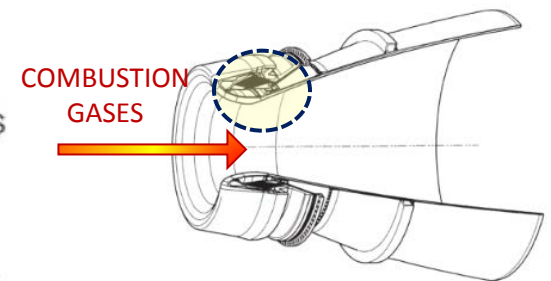
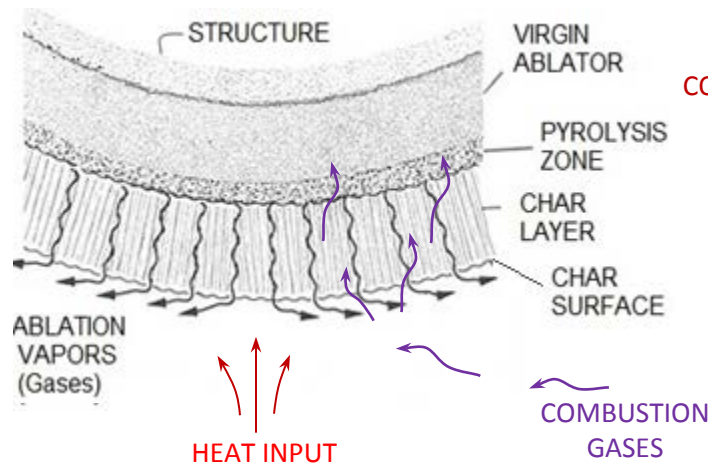
Background: Ablative Thermal Protection Systems



- ◆ Ablative materials used in TPS remove heat by undergoing pyrolysis (thermal degradation) to form a foamy char.
- ◆ Thermal insulation layer = Char layer + decomposing layer + virgin composite



Re-entry vehicles



Solid rocket motor nozzle

- ◆ Strong and stable char is needed to retain insulation.
- ◆ Optimal design needed to reduce payload.
- ◆ **Current tools and methods cannot accurately predict material response of ablative composites under extreme conditions.**
- ◆ **Need to develop tools to understand the complex phenomenon.**



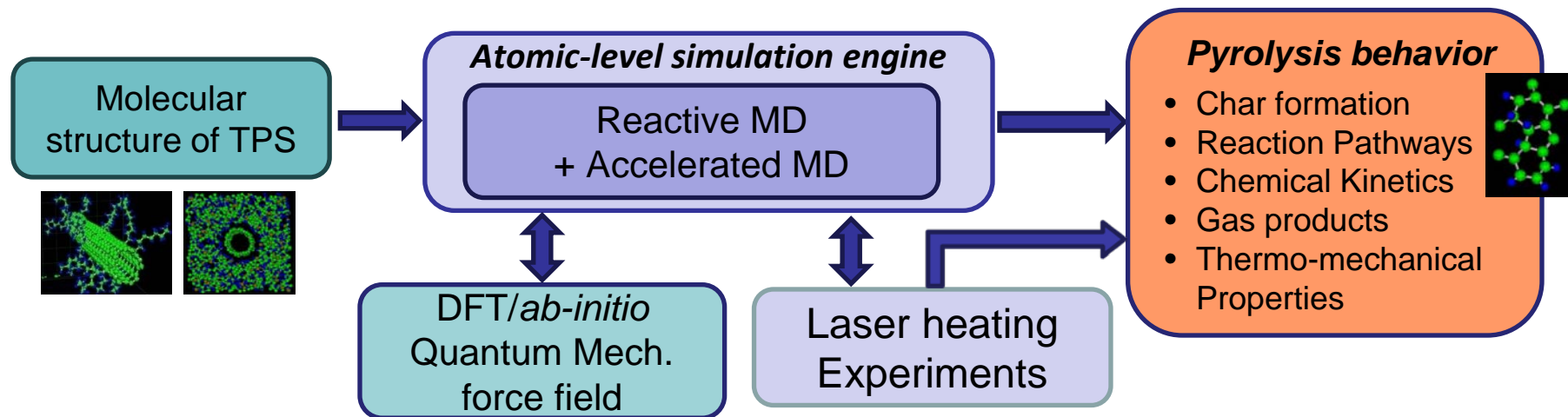
Goal – Computational Materials Development



To obtain detailed understanding of complex reactions mechanisms leading to formation of char and chemical interactions at the surface of the TPS (due to combustion gases), under extreme conditions.

ACT is developing a multi-scale computational tools to:

- Develop atomistic level details on methodology of char formation (complete carbonization)
- Analyzing effect of reinforcements on char formation and structure
- Obtain detail chemical pathways for reactions between char, pyrolysis gases and combustion edge gases, at high temperature, pressure.
- Predict the thermal and mechanical properties of the ablative TPS.



Computational framework for atomistic level modeling of ablative TPS materials



Reactive Force Fields



- ◆ Reactive force fields, ReaxFF, allows for bond-order based bond breaking and formation to simulate chemical reactions.
 - Parameters are derived solely from Quantum Mechanics, providing accurate unbiased reaction chemistry.
 - No need to predefine reactive sites or reaction pathways; potential functions automatically handle coordination changes associated with chemical reactions.
 - Smooth transition from non-bonded to single, double and triple bonded systems based on a bond length/bond order relationship.
 - All connectivity-dependent interactions (torsion, valence) are made bond-order dependent

(Chenoweth et.al., J. Phys. Chem. A, 112, 1040, 2008)

- ◆ Method successfully applied to study a variety of chemical problems:
 - Thermal degradation of polymers
 - Transition metal catalyzed reactions
 - Hydrocarbon Oxidation
 - H₂ adsorption in Mg-hydrides
 - Pyrolysis of Phenolic resins
 - Segregation and diffusivity estimation



Reactive Force Fields: Energy Contributions

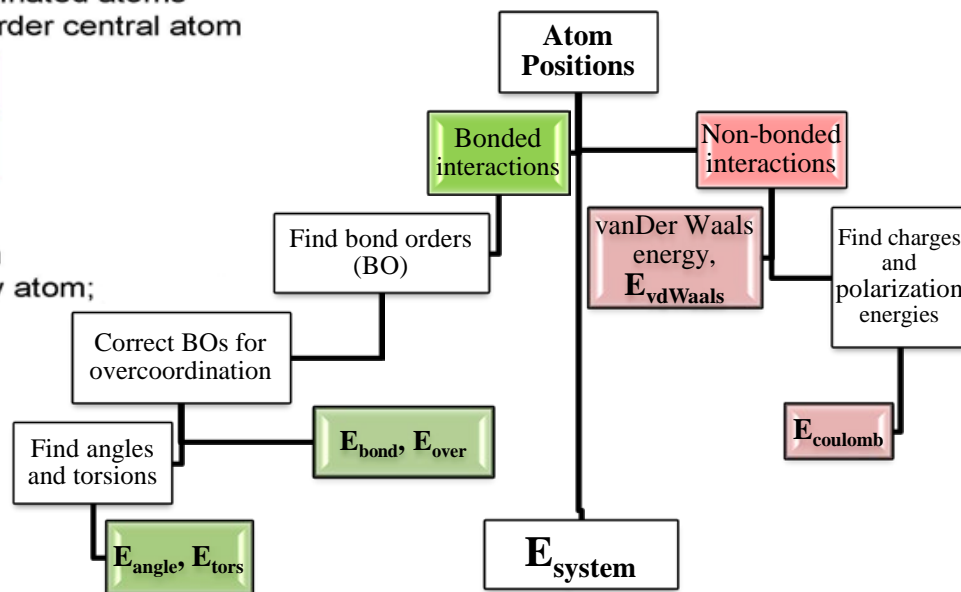


- ◆ System energy obtained from various partial energy contributions,

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{c2}} \\ + E_{\text{lp}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{H-bond}} + E_{\text{vdWaals}} + E_{\text{coulomb}}$$

- E_{bond} : bond energy; attractive term, directly derived from bond orders
- E_{lp} : Lone pair energy; penalty for breaking up lone pairs in O, N
- E_{over} : Overcoordination energy: penalty for overcoordinating atoms
- E_{under} : Undercoordination energy: stabilizes undercoordinated atoms
- E_{val} : Angle strain; equilibrium angle depends on bond order central atom
- E_{pen} : Penalty for 'allene'-type molecules ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$)
- E_{coa} : Angle conjugation; stabilizes $-\text{NO}_2$ groups
- E_{C2} : C_2 correction: destabilizes $\text{C}=\text{C}$
- E_{tors} : Torsion energy: bond-order dependent V_2 -term
- E_{conj} : Torsion conjugation: general conjugation stability
- $E_{\text{H-bond}}$: Hydrogen bond
- E_{vdWaals} : van der Waals: calculated between every atom
- E_{Coulomb} : Coulomb interaction: calculated between every atom;

(Chenoweth et. al, J. Phys. Chem A, 112, 1040, 2008
Adri van Duin et. al, J. Phys. Chem. A, 105, 9396, 2001)



Computation of system energy in ReaxFF from individual components, updated every iteration



Reactive MD Simulation of Pyrolysis

Thermal degradation of EPDM rubber*
(at high temperature)

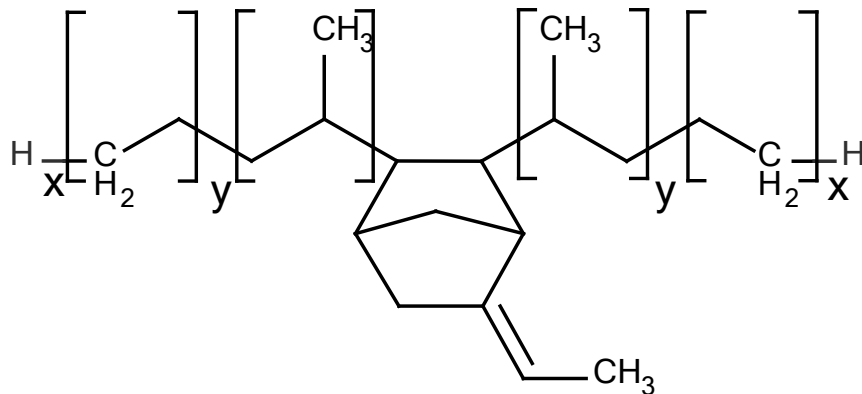
* Work supported by NAVAIR-WC



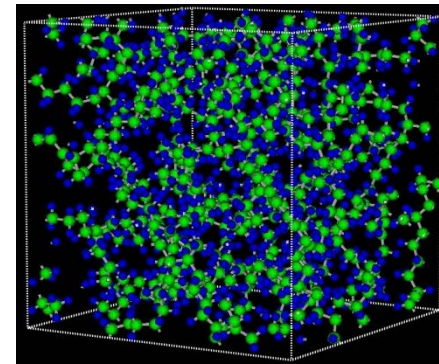
Structure of EPDM Rubber



- ♦ Ethylene Propylene Diene Monomer (EPDM) based rubber composites are commonly used for insulation of case-bonded solid rocket motor engine.
- ♦ Molecular models of EPDM were constructed using the monomer compositions.



Schematic of EPDM molecule



C : green atom
H : blue atom

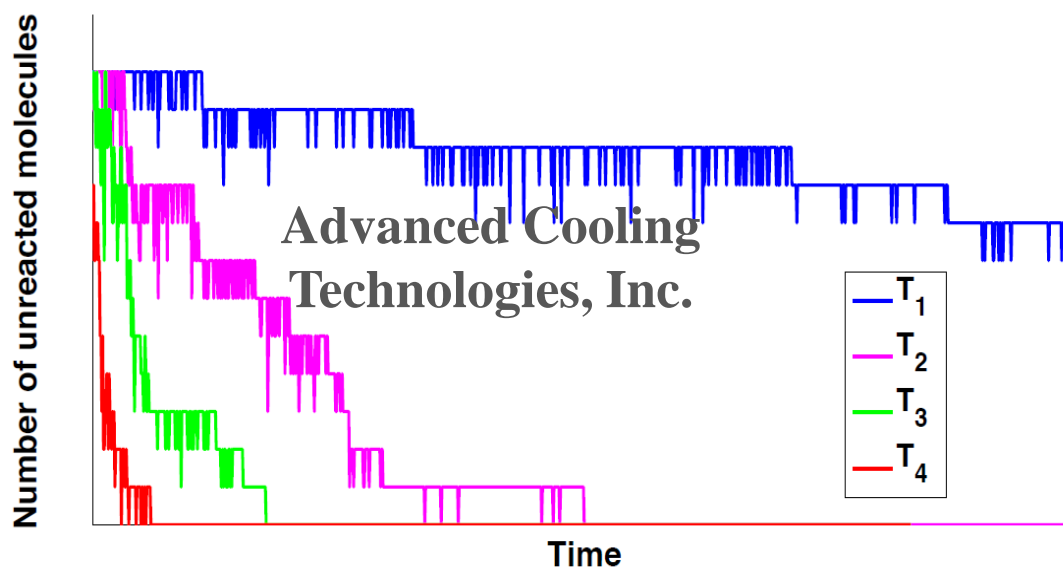
Simulation box packed with EPDM molecules

- ♦ Simulation cell: EPDM molecules packed and relaxed (~1600 atom system)
 - Sequence of equilibration and annealing cycles performed (at 300K ↔ 1500K) to relax chains.



Thermal Degradation (Pyrolysis) of EPDM

- ♦ Pyrolysis simulations performed using the equilibrated EPDM system
 - Isothermal reactive MD simulations at over temperatures of 1750K ~ 2500K.
- ♦ Degradation rate, products formed and chemical reaction pathways are analyzed



EPDM degradation rate as function of simulation time

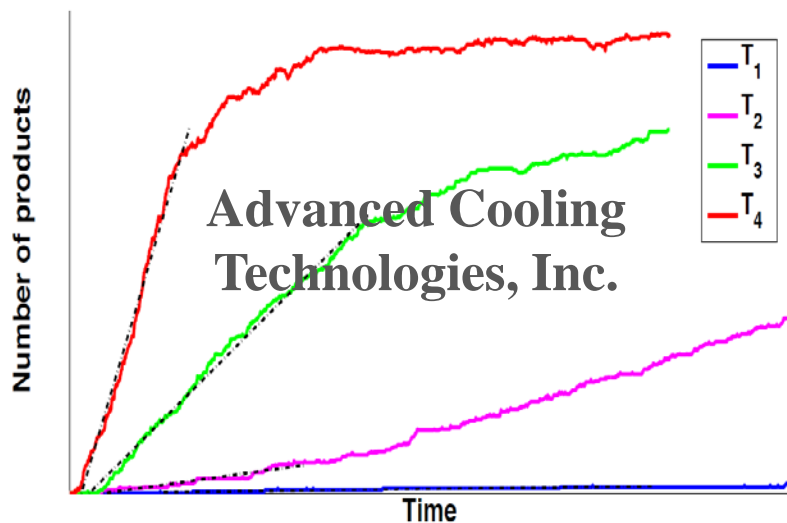
- ♦ Degradation rate increases with temperature
 - $T_1 < T_2 < T_3 < T_4$
 - At low temperatures, the molecules are mostly intact (till 300ps)



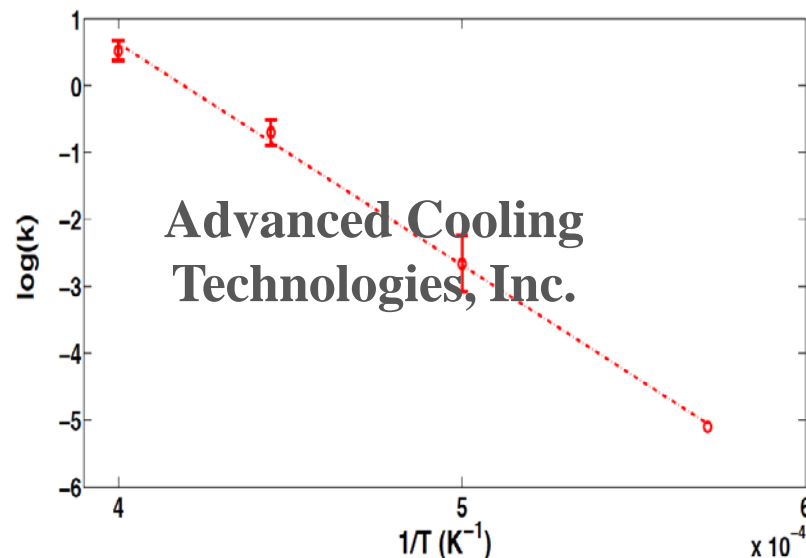
Products formed: rate & chemical pathways



- ◆ Products formed: lighter hydrocarbons like ethylene (C_2H_4), propylene (C_3H_6), methane (CH_4) etc.



Product formation with time (example)



Arrhenius plot of product formation (example)

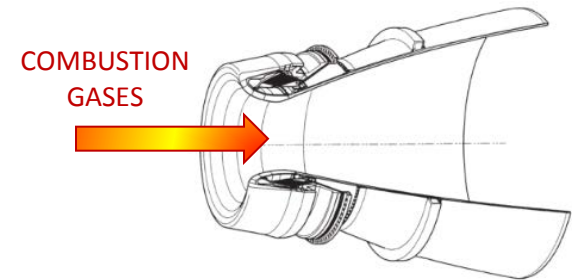
- ◆ The formation rate of products is estimated at different temperatures and used to compute the activation energy
- ◆ MD trajectories monitored to obtain chemical reactions undergone by the EPDM chains (major step in development of chemical kinetics).



Summary (1)



- ◆ Thermal degradation behavior of EPDM studied using reactive MD simulations
 - Degradation mechanisms, products formed, activation energies and chemical reaction pathways are discussed
- ◆ Reaction chemistry is much more complex in edge gas environments
 - High temperature, pressure, oxidizing environment
 - Reactions of combustion edge gases (Cl, Al, CO, H₂) mixture with of char and EPDM.
- ◆ Currently, we are also developing reactive force fields from Quantum Mechanical calculations to accurately capture the char – edge gas reactions



Solid rocket motor nozzle



Reactive MD simulation of Pyrolysis

Char formation in phenolic resins*

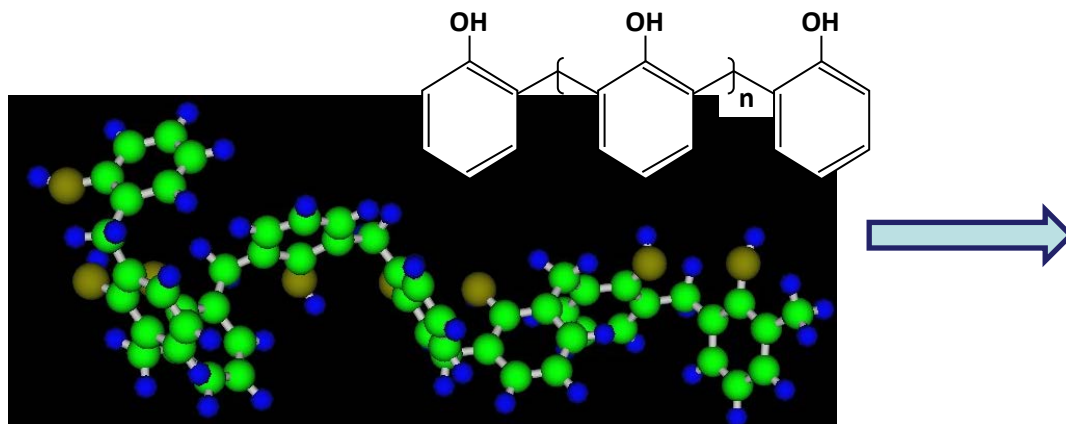
* Work supported by NASA-Ames



Structure of Non-crosslinked Phenolic Resin

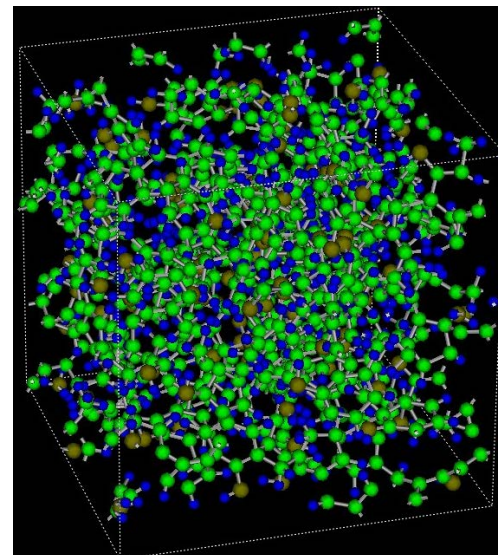


- ♦ Polymer chain of non-crosslinked phenol formaldehyde resin with 8 repeating units in ortho-ortho sequence (methyl terminated at one end)



Phenol formaldehyde chain $C_{56}H_{50}O_8$

C: Green, H: Blue, O: Brown



Simulation cell with 16 polymer chains at 300K

- ♦ Simulation cell adjusted to match experimental density 1.25gm/cc.
- ♦ Sequence of annealing steps performed to relax the chains. Followed by long equilibration at 2000K for 250ps (no reactions were found during these steps)

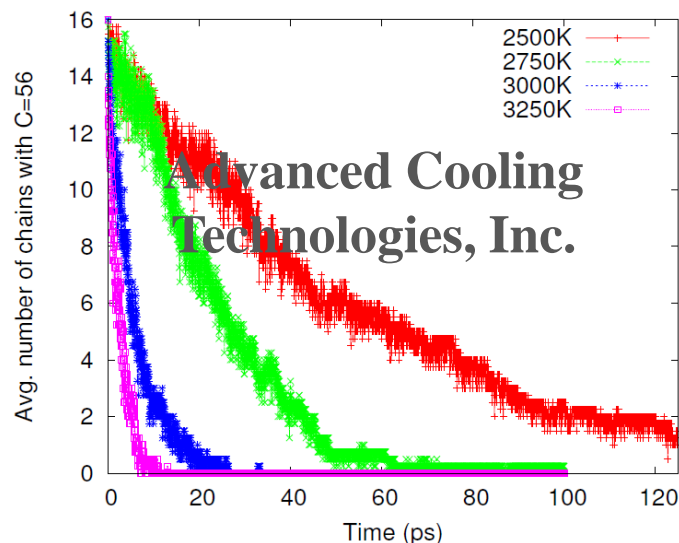
Desai et.al., Polymer 52 (2011) 577



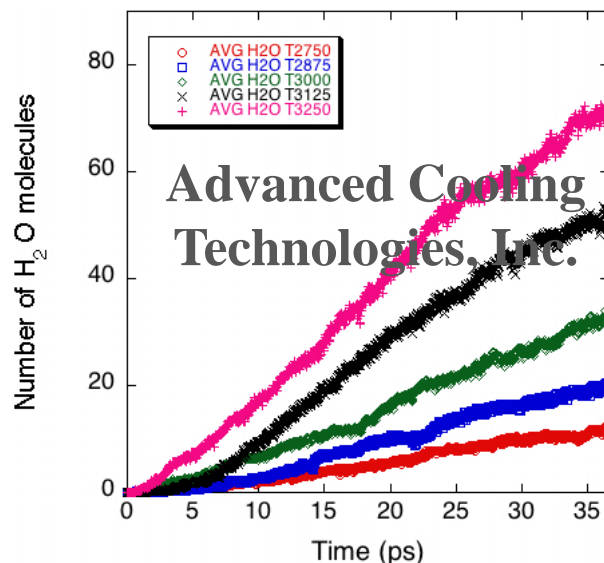
Thermal Degradation Study of Phenolic Resin



- ◆ Thermal degradation study on equilibrated phenolic resin system
 - Isothermal NVT reactive MD simulations at temperature 2500K to 3350K
- ◆ Degradation rate, products formed and chemical reaction pathways were analyzed



Degradation rate at different temperatures



No. of H₂O molecules formed with time

- ◆ Degradation rate increases with temperature. At 2500K, degradation of all chains doesn't set in until ~200ps (not shown)
- ◆ Water (H₂O) is the most dominant product of pyrolysis simulations. Other products found include H₂, C₂H₂, CO, C₂H₄, CO, CH₃OH

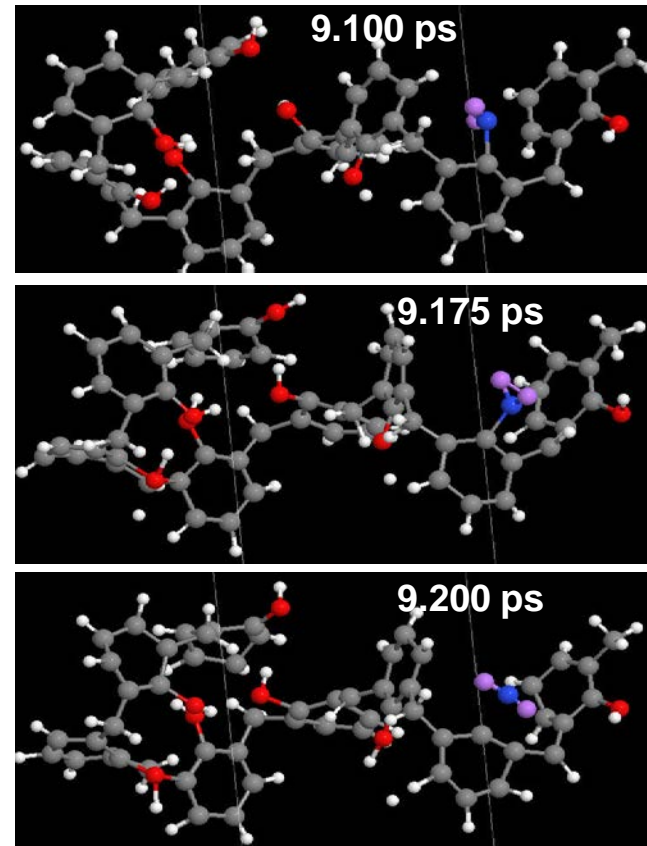
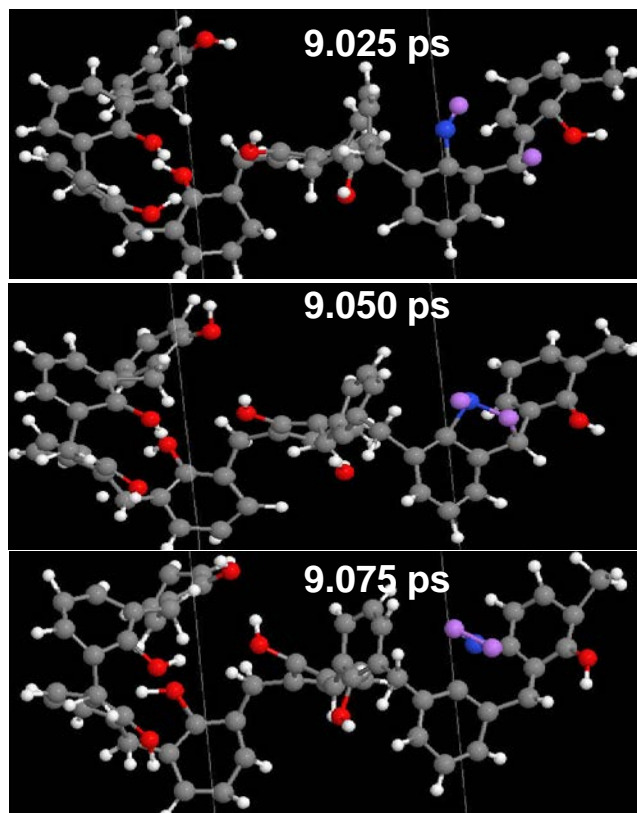


Dehydration Mechanism – Intrachain Reactions



C: Grey
H: White
O: Red

H₂O forming
atoms in blue
(O) & violet(H)



MD snapshots showing intrachain dehydration

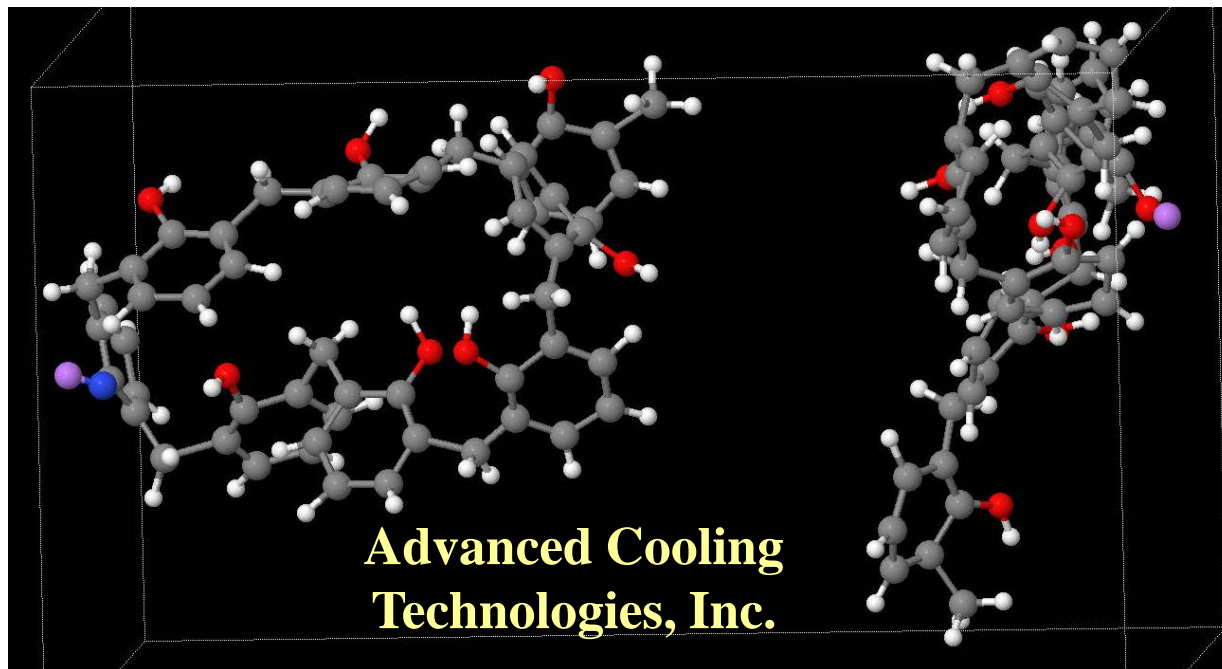
- ◆ Hydroxyl unit abstracts an H from its neighborhood
- ◆ H₂O unit breaks away from the chain



Dehydration Mechanism – Interchain Reactions



C: Grey
H: White
O: Red



Interchain atoms participating in H₂O formation

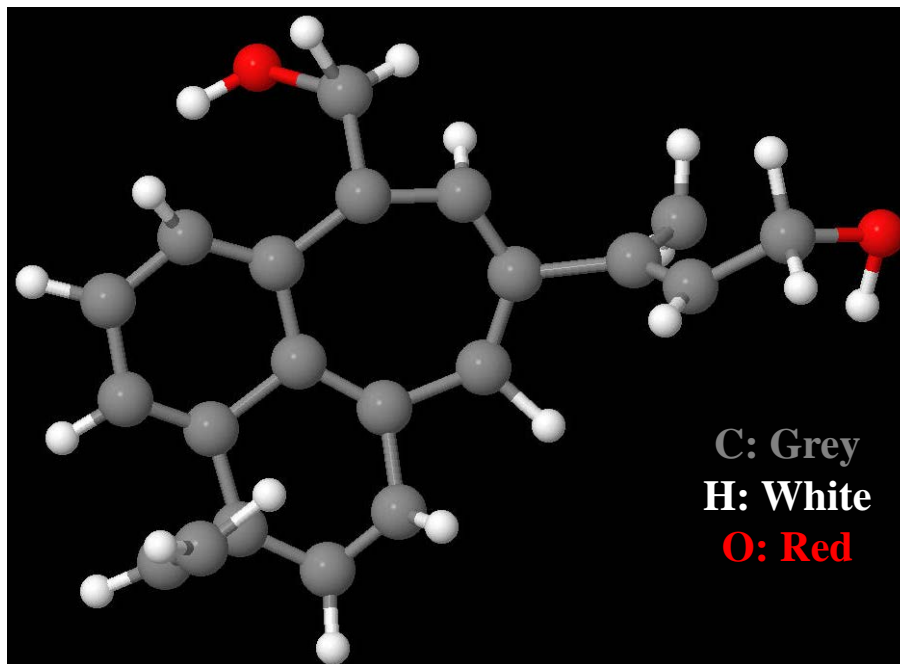
- ◆ The mechanisms for dehydration are:
 - -OH group and hydrogen from –CH₂– group
 - Between two –OH groups
 - Dissociated hydrogen and –OH group
 - H on a carbon ring and –OH group



Graphene Precursor Formation

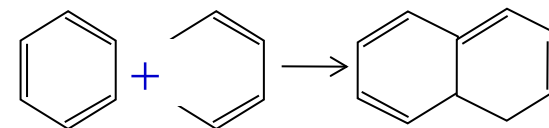


- ◆ At high temperatures ($\sim 3000\text{K}$), fused ring structures are observed



Fused rings obtained during NVT at 3250K after 40ps

Conventional Mechanism



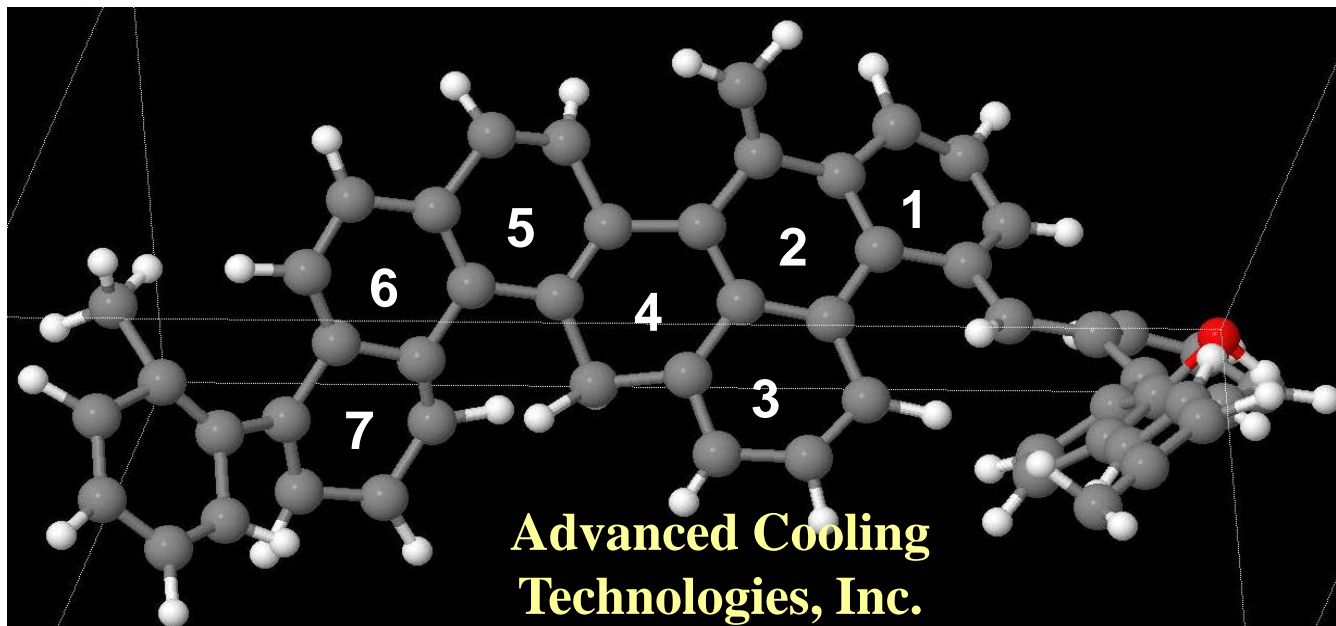
Fused rings are precursor for large graphene fragments



Char Precursor



- ◆ Fused-ring structures grow to yield precursor of char at low temperature



Char precursor observed after a long 12ns simulation at 1750K

Desai et.al., Polymer 52 (2011) 577

- ◆ Polymer chains (two) containing at least 7 fused rings were found.
- ☞ Essential to run simulations at low temperature to capture accurate physics



Accelerated Molecular Dynamics Simulations for Pyrolysis

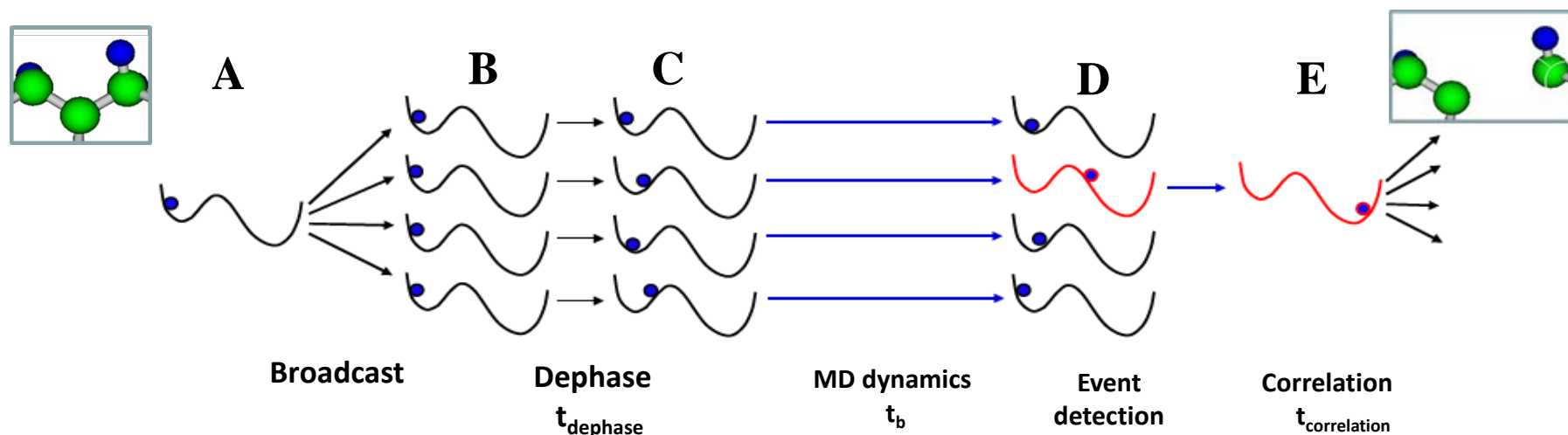
(at lower temperatures)

- ♦ *Accelerated Molecular dynamics (AMD)* can **extend the accessible timescale by orders of magnitude relative to MD**, while retaining full atomistic details.
 - Let the system (trajectories) evolve to find an appropriate way out of each state. But, coax it in doing so more quickly using statistical mechanics concepts .



- ♦ 3 types of AMD methods have been proposed:
 - * Hyperdynamics
 - * Parallel Replica dynamics (PRD)
 - * Temperature accelerated dynamics (TAD)
- ♦ Proposed by Arthur F. Voter, LANL
 - Phys. Rev. B, vol. 57 (22), 1998; Annu. Rev. Mater. Res. 2002, 32:321-46.
- ♦ Only one AMD study has been reported for reactive hydrocarbon systems
 - J. Chem. Phys., vol.121 (2), 2004.

- ♦ ACT developed an AMD framework for reactive systems using parallel replica dynamics.
 - Long term dynamics consisting of infrequent events between different states (activated process) can be modeled by following many replicas of the system in parallel.



- ♦ Only assumption is the system needs to obey first order kinetics, $p(t) = ke^{-kt}$
- ♦ Requires:
 - Event detection scheme
 - Account for correlated time

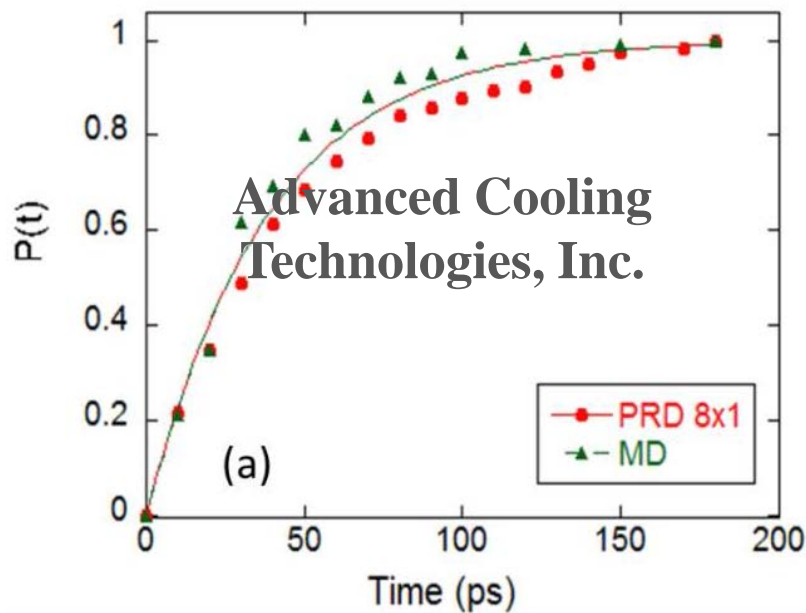
Time spend by system in a bonding state,
 $t_{\text{sum}} = \sum_i^M t_{\text{replica}}$ (time spent on all replicas)



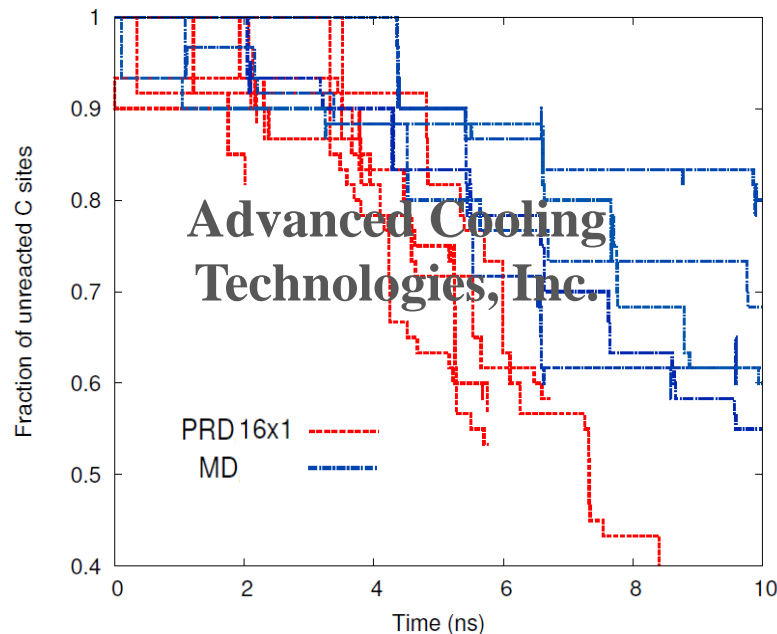
Comparison of AMD and MD Dynamics



- ◆ Using a polymer system as surrogate, the dynamics obtained from PRD simulations is compared with direct MD simulations



Probability distribution $P(t)$ for first bond break. For first order process $P(t) = 1 - e^{-kt}$.



Fraction of unreacted carbon sites obtained from 6 PRD runs (16x1) and 6 MD runs

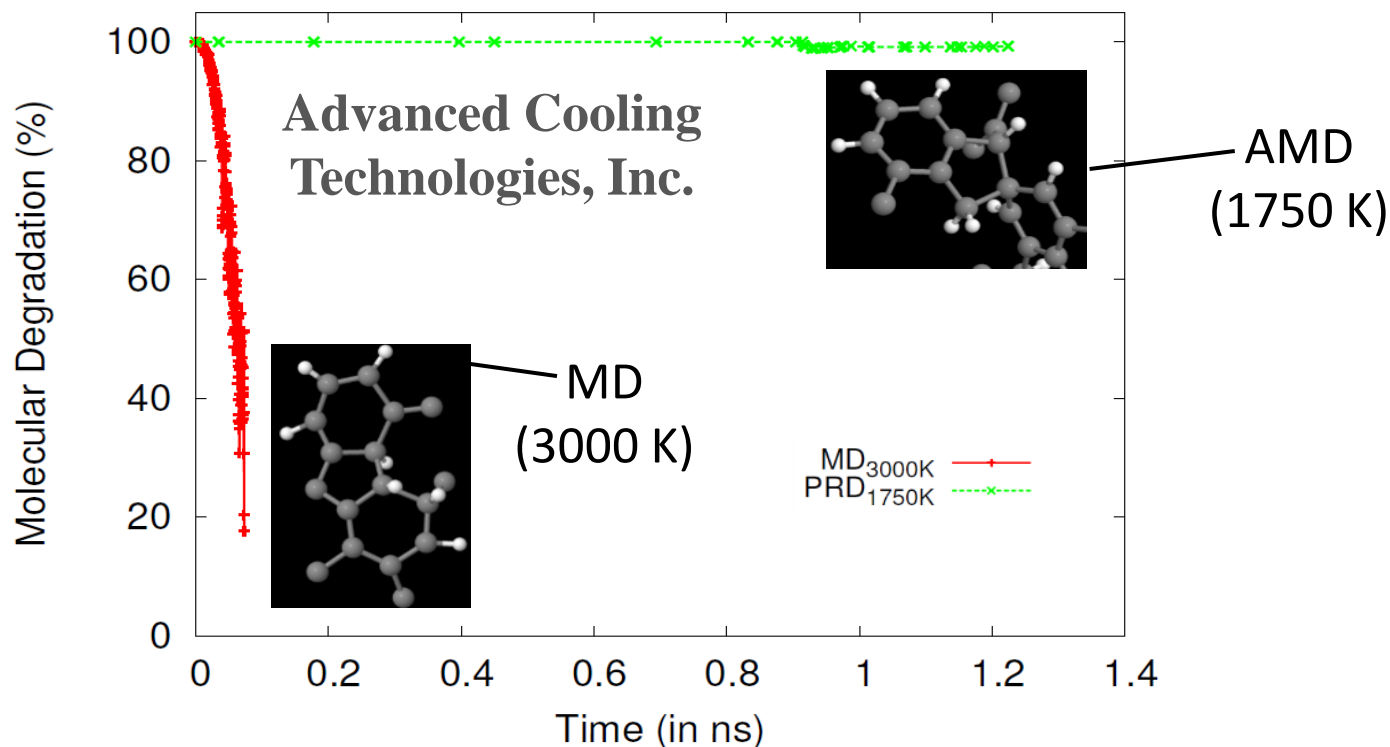
- ◆ Good agreement between PRD and direct MD for both reaction initiation and propagation.



ACT developed accelerated MD (AMD) method which allows simulation of pyrolysis reactions at significantly lower temperature than direct MD.

👉 Pyrolysis of PICA heat shield begins at 1000K.

AMD allows us to reach longer timescale



Molecular disintegration and structures observed during PRD simulation at 1750K in comparison to MD simulation at 3000K.



Summary



- ◆ Ablative materials are exposed to high temperatures ~ 2000 K, experimental prediction of reaction mechanisms during carbonization is difficult
- ◆ Reactive MD simulations were employed to capture high temperature pyrolysis behavior of EPDM, product formation and reaction pathways
- ◆ Reactive MD simulations were employed on phenolic resins to capture the initial stages of pyrolysis, pyrolysis products and reaction pathways (kinetic models)
- ◆ For the first time in the literature, formation of stable large graphitic precursors (7-fused rings) were captured
- ◆ Accelerated MD methodology relevant to chemically reactive systems has been developed
- ◆ Results indicate the potential of AMD in investigating low temperature reaction kinetics of 'char formation process'



Thank You



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