Experimental Determination of Pyrolysis Products from Carbon/Resin Ablative Materials

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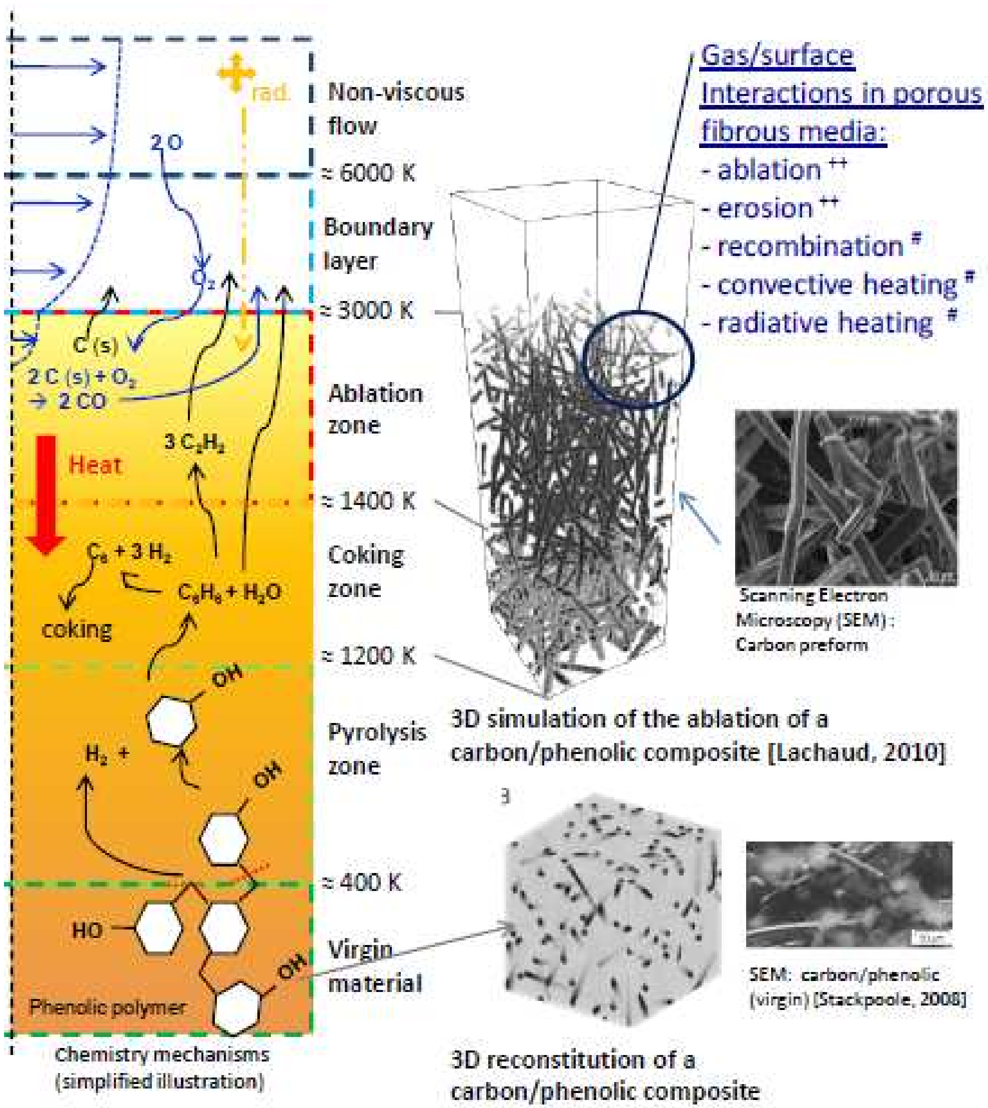
Detailed Pyrolysis Speciation and Production Rates Are Needed



Taken from Lachaud et al., 2012

- A class of low-density carbon/resin ablative materials has been developed, made of carbon fiber preform impregnated with phenolic resin

- The gas production rate from phenolic pyrolysis have an impact on the material response during ablation

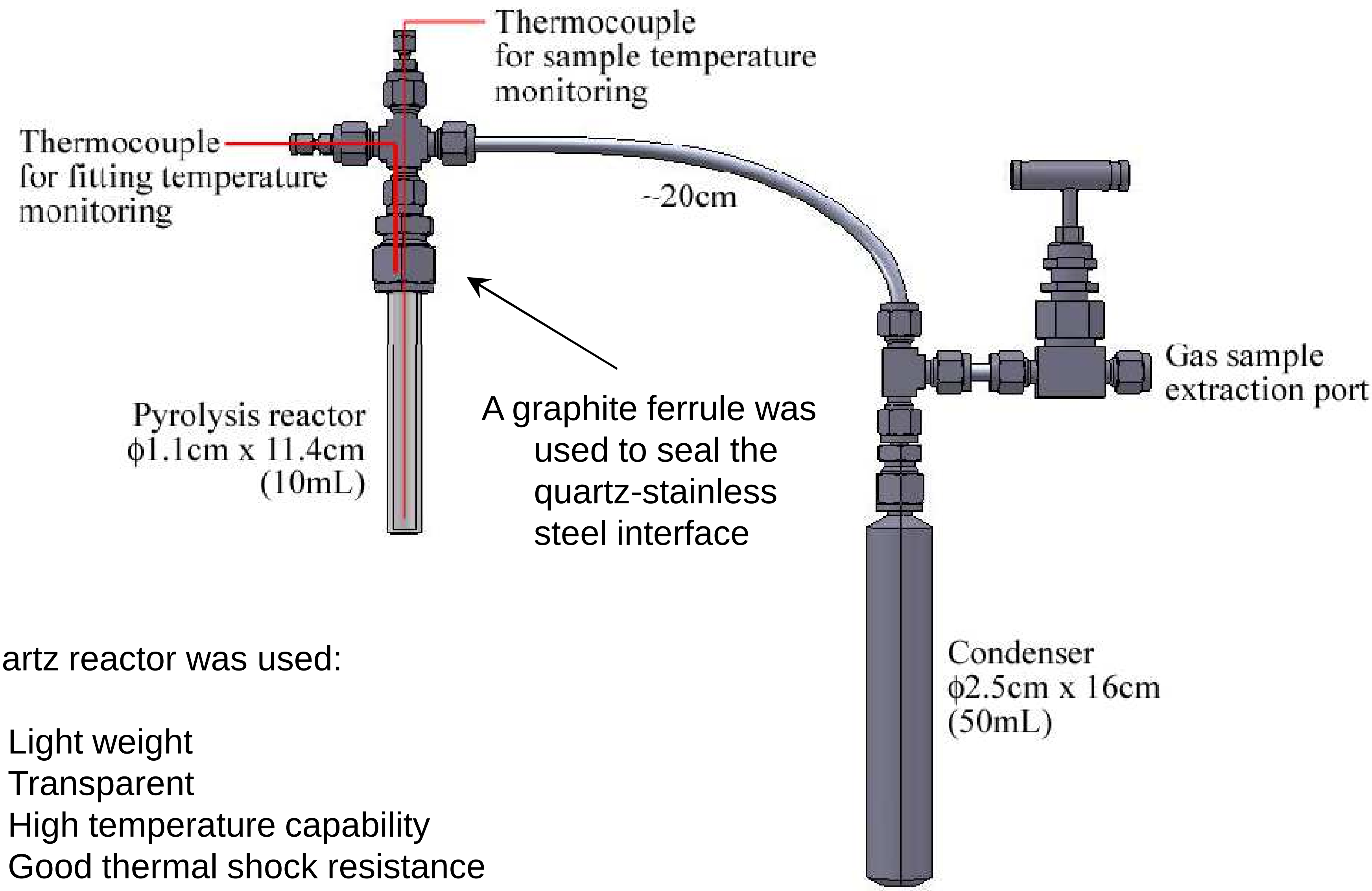
$$\Pi = -\partial_t(\epsilon_m \rho_m) = \epsilon_{mv}\rho_{mv}\sum_{j=1}^{N_p} F_j \partial_t(\xi_j)$$

$$\frac{\partial_t \xi_j}{(1-\xi_j)^{m_j}} = T^{n_j} \mathcal{A}_j \exp\left(-\frac{\mathcal{E}_j}{RT}\right)$$

Current Understanding of Phenolic Pyrolysis

- Current understanding of phenolic pyrolysis consists of three general steps:
  1) Crosslink of phenolic and formation of water, aromatics, and phenol derivatives from condensation reactions (550-800 K)
  2) Crosslink breaking and the production of permanent gases such as methane, carbon monoxide and carbon dioxide (700-1100 K)
  3) Charring and the formation of hydrogen gas (> 850 K)
- A five-step reaction mechanism describing this behavior is used in PATO
- **Quantitative** understanding of detailed chemical composition (speciation) of pyrolysis gases and rates of production of these species, which is critical to developing a more robust **finite-rate chemistry model**, is dated (Sykes, 1967)

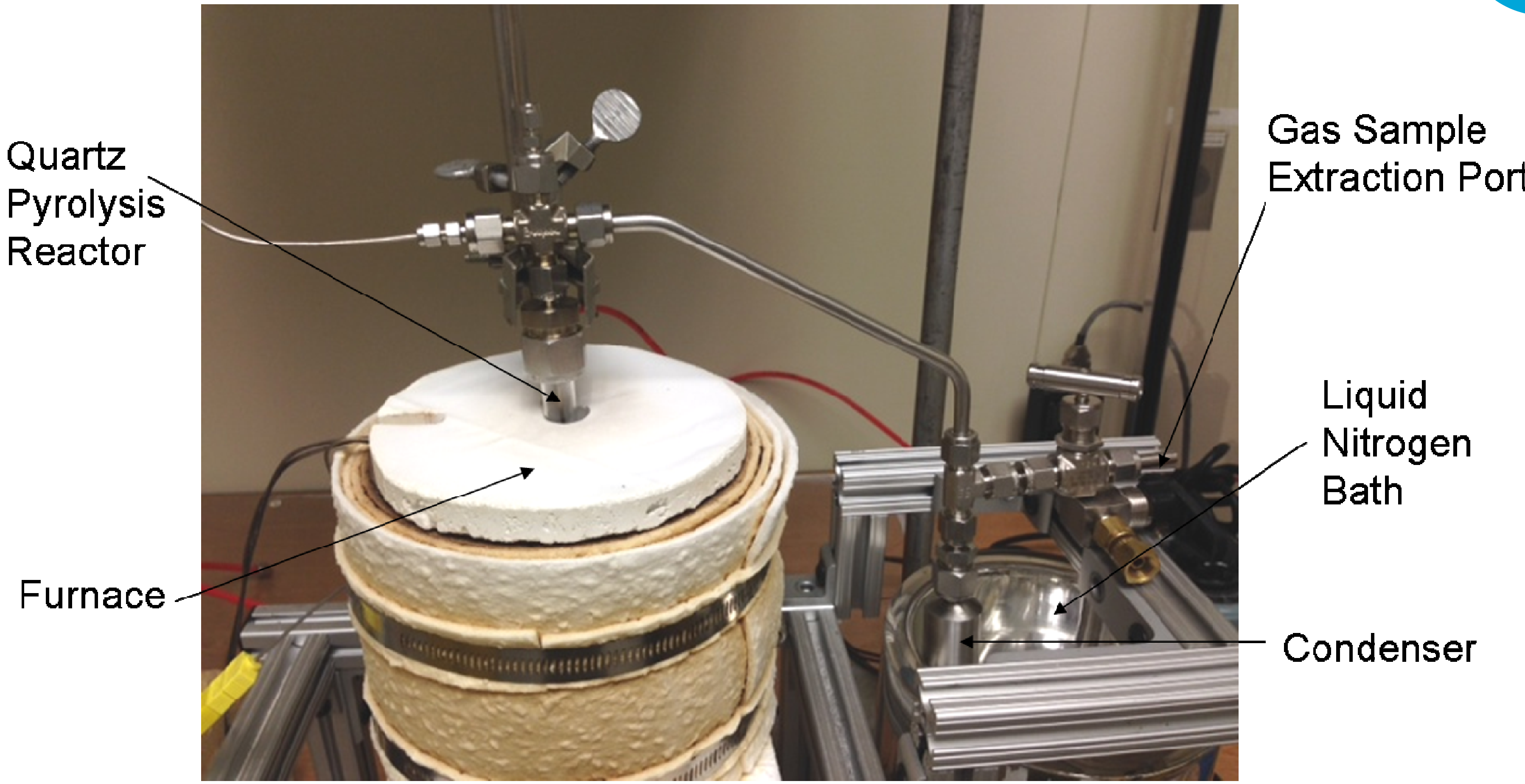
A Batch Reactor System Was Designed and Constructed



Quartz reactor was used:

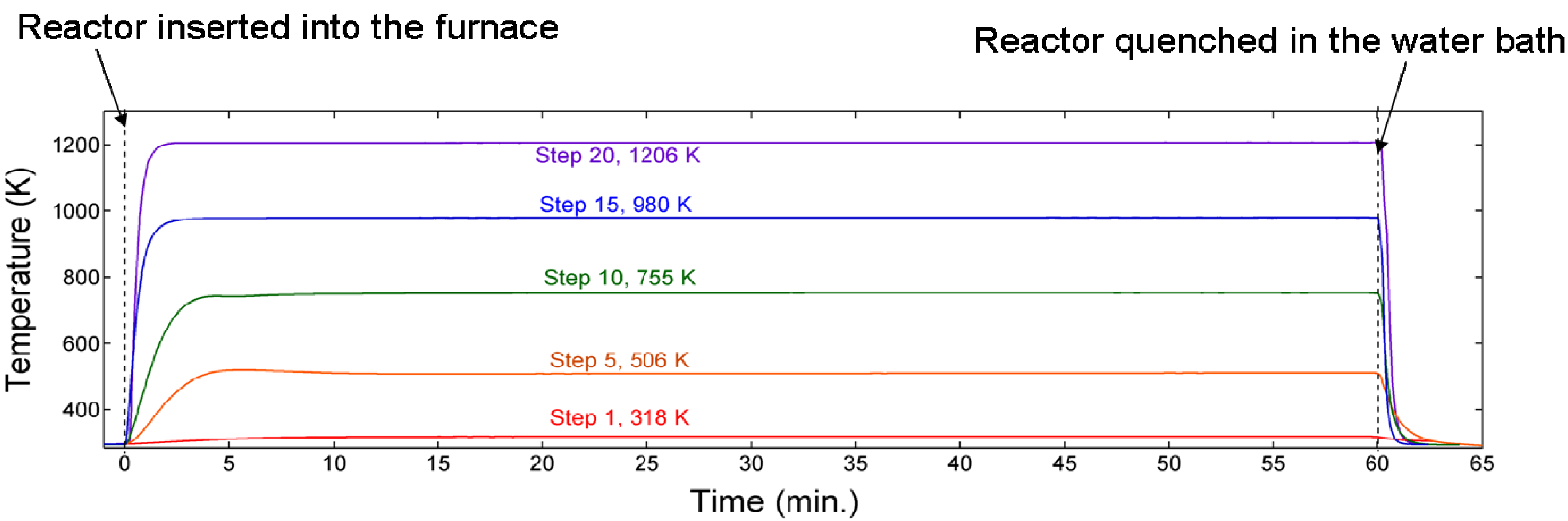
1) Light weight
2) Transparent
3) High temperature capability
4) Good thermal shock resistance

The Setup and the Configuration of the Reactor and the Furnace



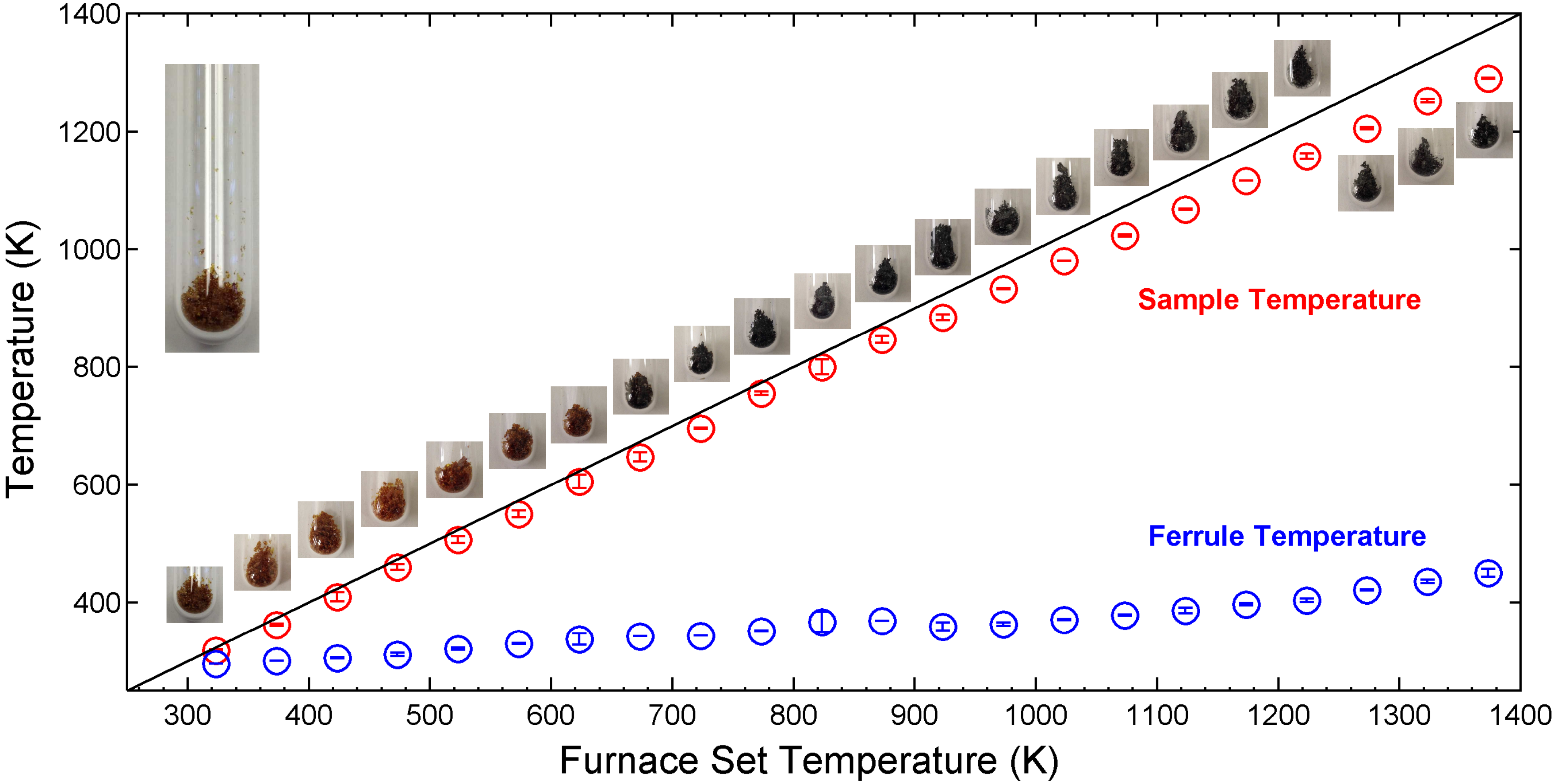
- The condenser was placed into the liquid nitrogen bath
- Only the reactor was placed into the furnace, allowing larger species with low volatility to condense and reducing system pressure

Experimental Procedure



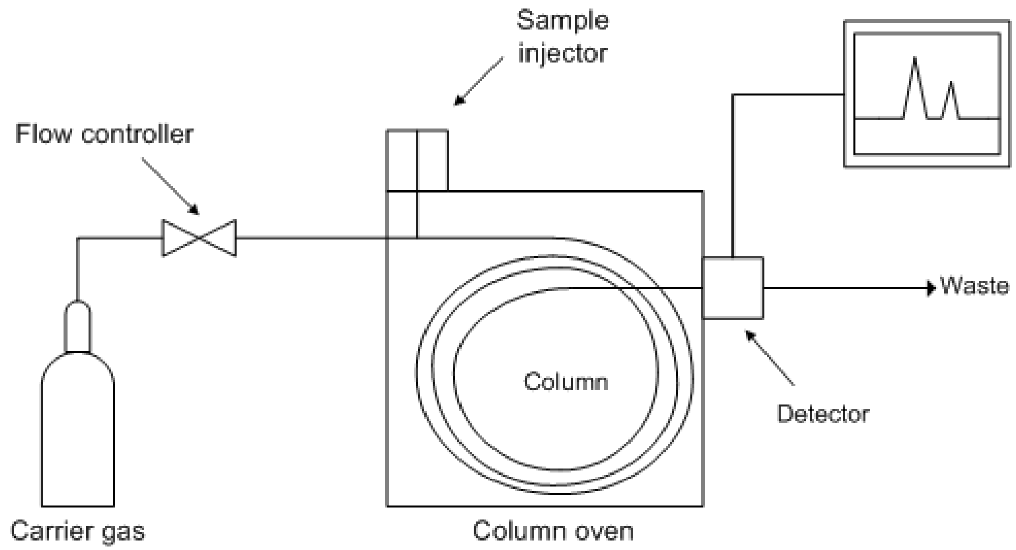
- 50 mg of cured phenolic sample were loaded in the reactor
- Quartz reactor tube was weighted by electronic balance before being attached to the assembly
- Furnace was preheated to the temperature of interest (first step was 323 K)
- Reactor assembly was pumped down to < 0.1 torr
- Reactor was inserted into the furnace; while condenser was inserted into the liquid nitrogen bath
- After 1 hour of reaction, reactor was quenched in a water bath to room temperature (< 300 K)
- Reactor pressure was measured, and an internal standard (C_5H_{12}, pentane) was added
- Gas phase products were analyzed with gas chromatography (GC)
- Quartz reactor was weighted for mass loss and preserved for the next run (step)
- Liquid phase products were extracted with solvent (dichrolomathane) and analyzed with GC
- The procedure was repeated with the preserved sample at a temperature 50 K higher

Sample and Ferrule Temperature



- Sample temperature increased linearly with furnace set temperature
- Ferrule temperature was no higher than 450 K, suggesting a large thermal gradient in the headspace of the reactor

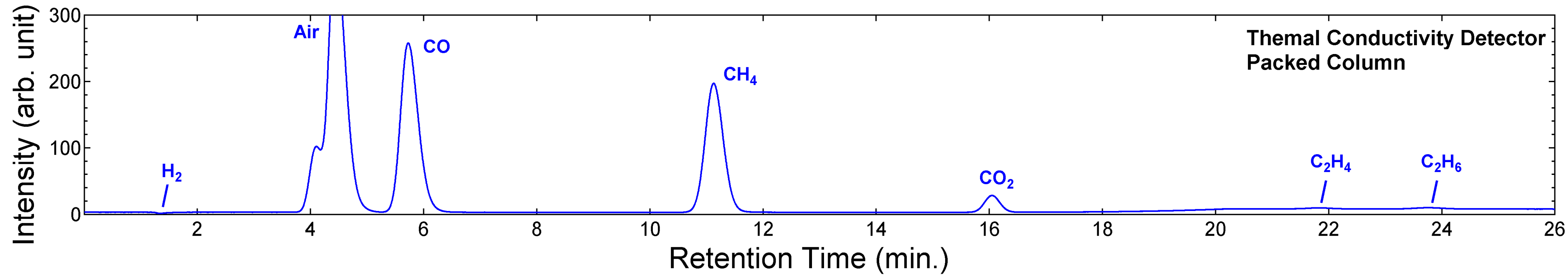
Chemical Species Were Identified and Quantified by Gas Chromatography

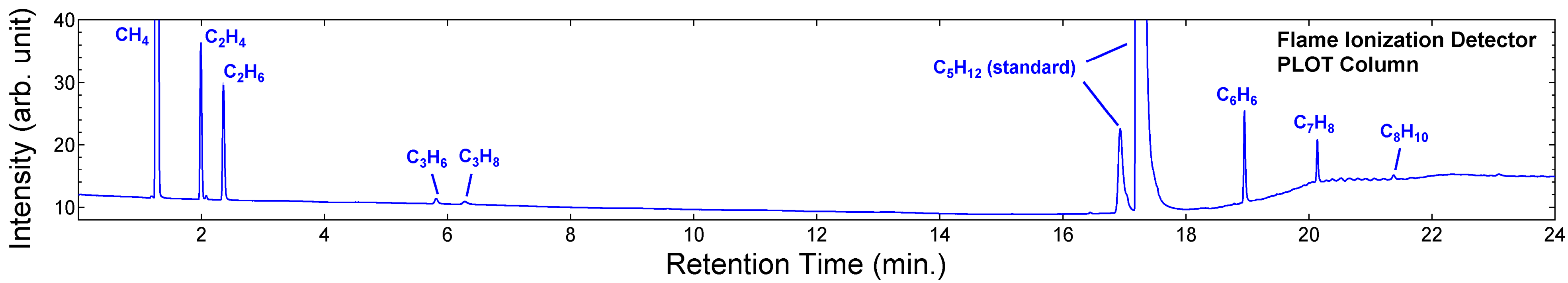


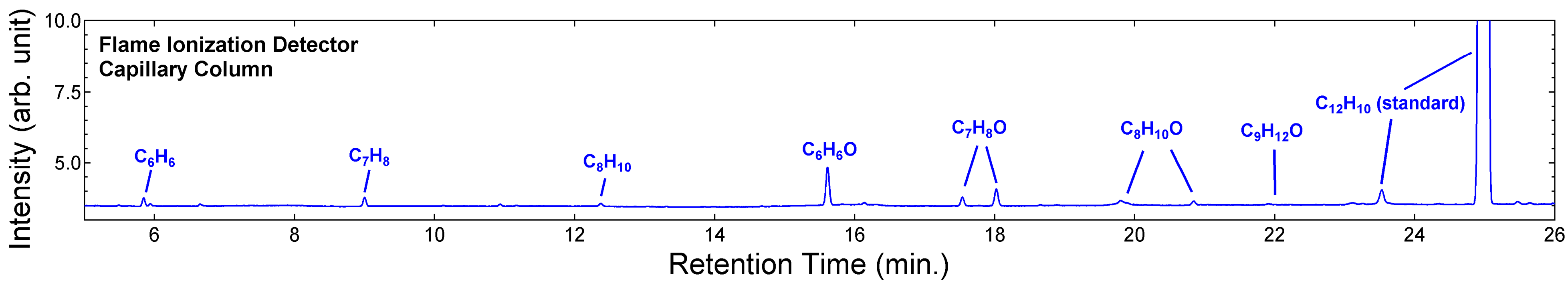
- A mixture of chemical species is injected into a heated inlet and carried by a carrier gas
- The compounds are separated by a column that is programmed to heat up with time:
  - Packed column: permanent gases
  - PLOT column: volatile vapors (< C_8)
  - Capillary column: non-volatile liquids (> C_6)
- Lighter species reach the detector earlier
- Different types of detectors can be used:
  - Flame ionization detector: hydrocarbons
  - Thermal conductivity detector: permanent gases
  - Mass spectrometer: mainly used for identification

Representative Chromatographs

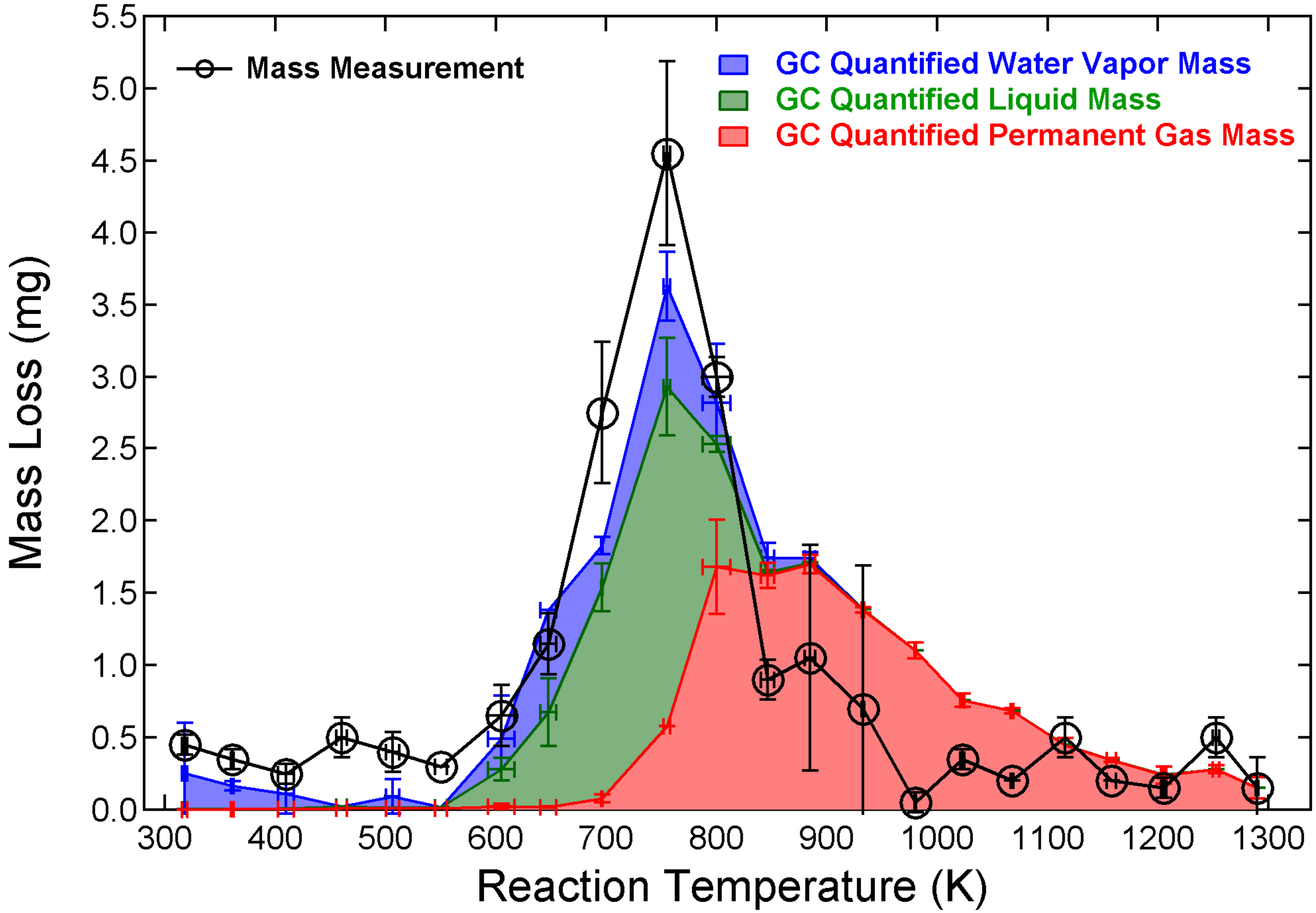
Reaction temperature ~ 850 K





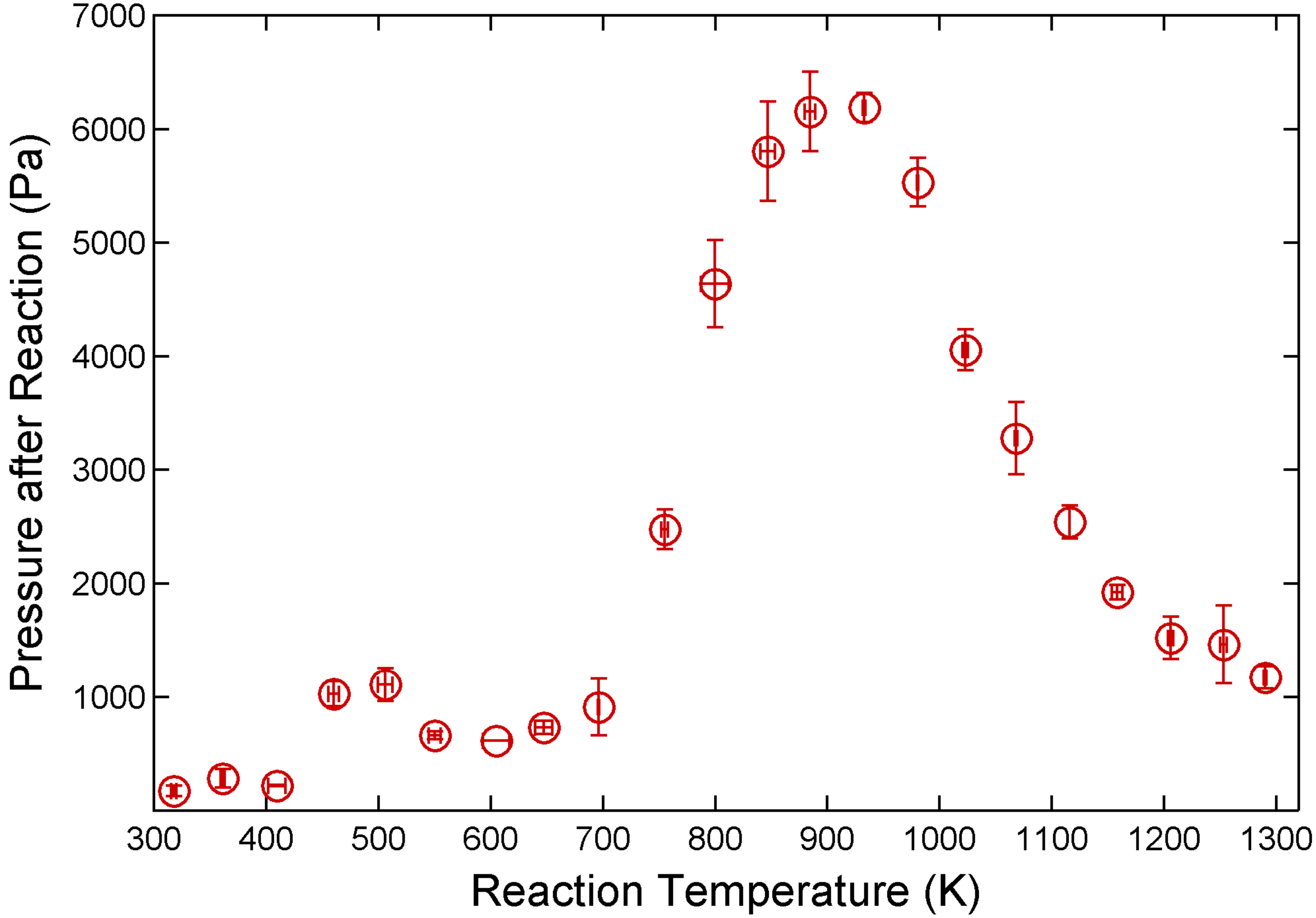


Mass Loss Was Measured by Electronic Balance and Quantified by GC



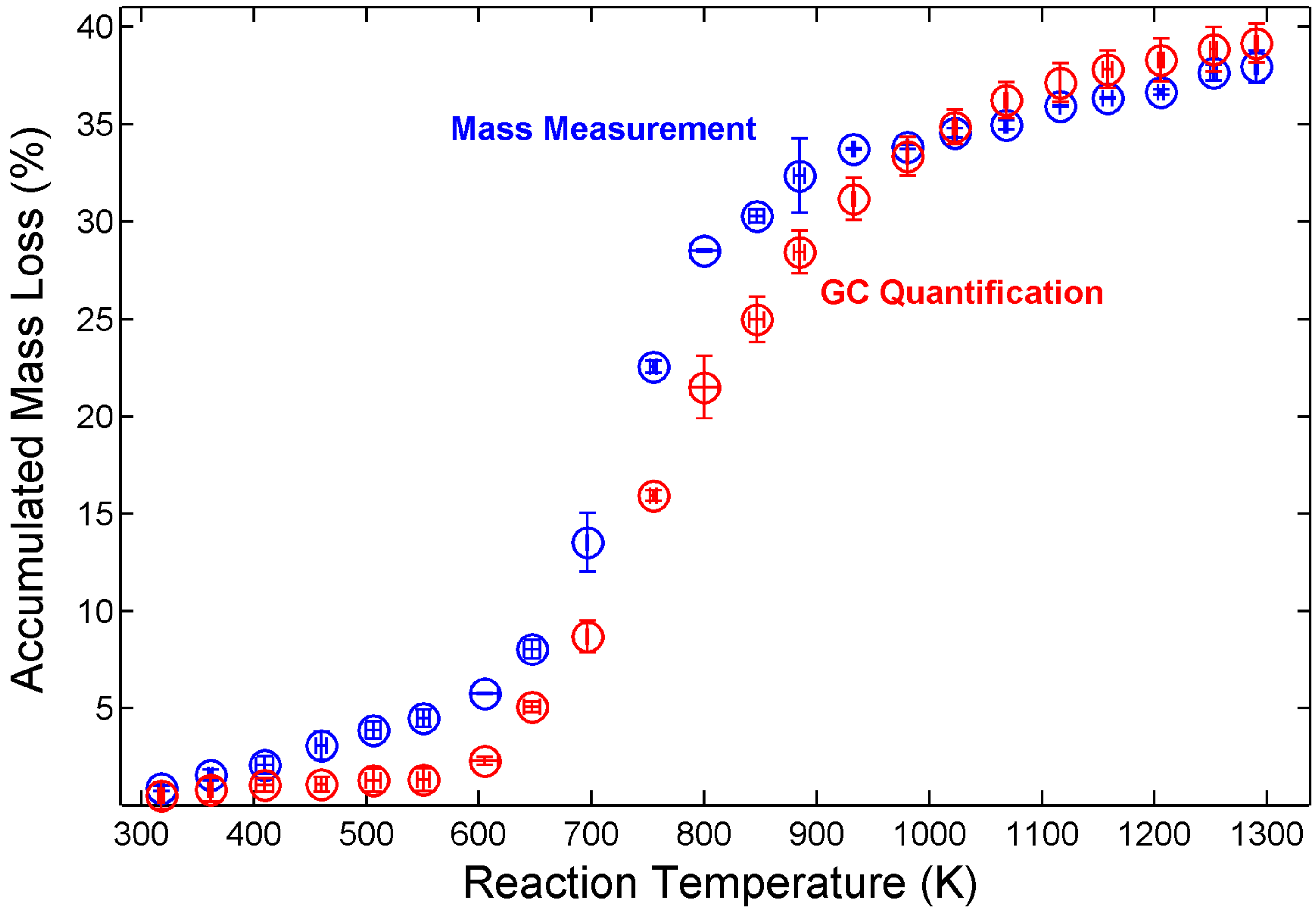
- Mass loss peaked at about 750 K
- Water dominated at low temperatures, and permanent gases dominated at higher temperatures

Reactor Pressure Measured after Each Step



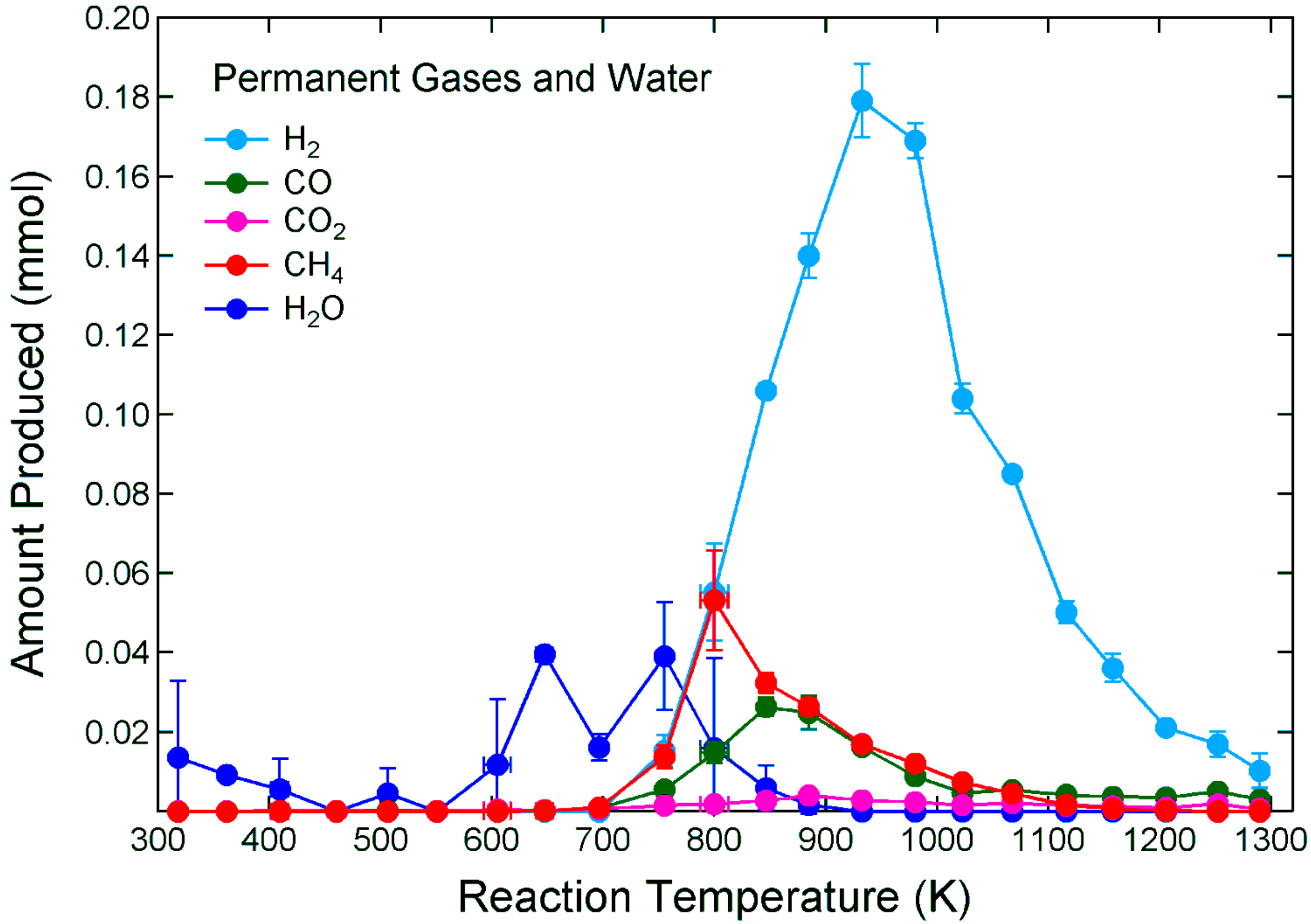
- Pressure peaked at about 900 K, higher than mass loss peak
- Pressure is more associated with molar loss rather than mass loss, suggesting lighter species were produced at higher temperatures

Accumulated Mass Loss Measured by Balance Agreed Well with GC Results



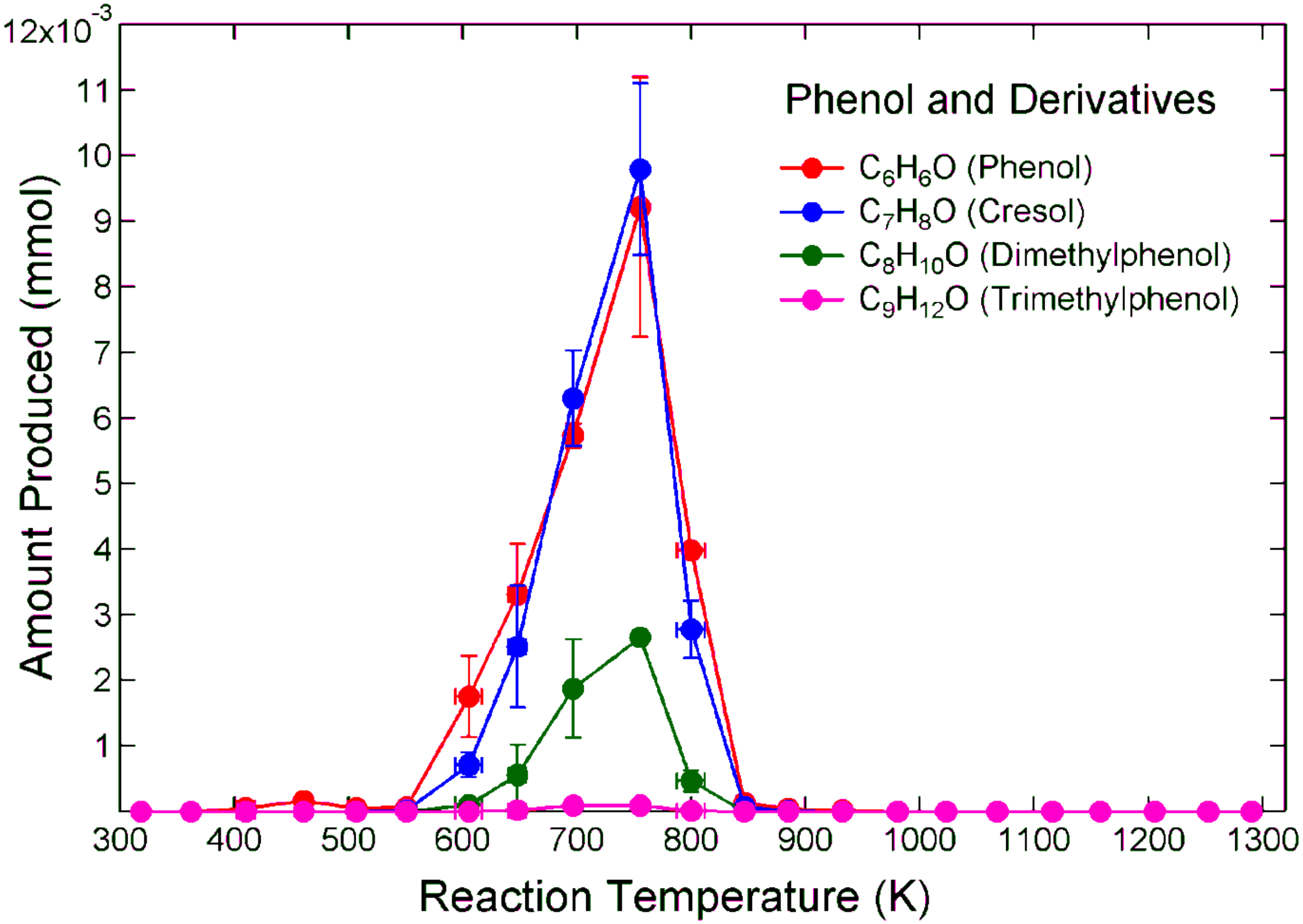
- GC quantification captured the trend and the amount of mass loss measured by the laboratory electronic balance
- Total mass loss reached about 40%

Speciation Results:
1) Permanent Gases and Water Vapor



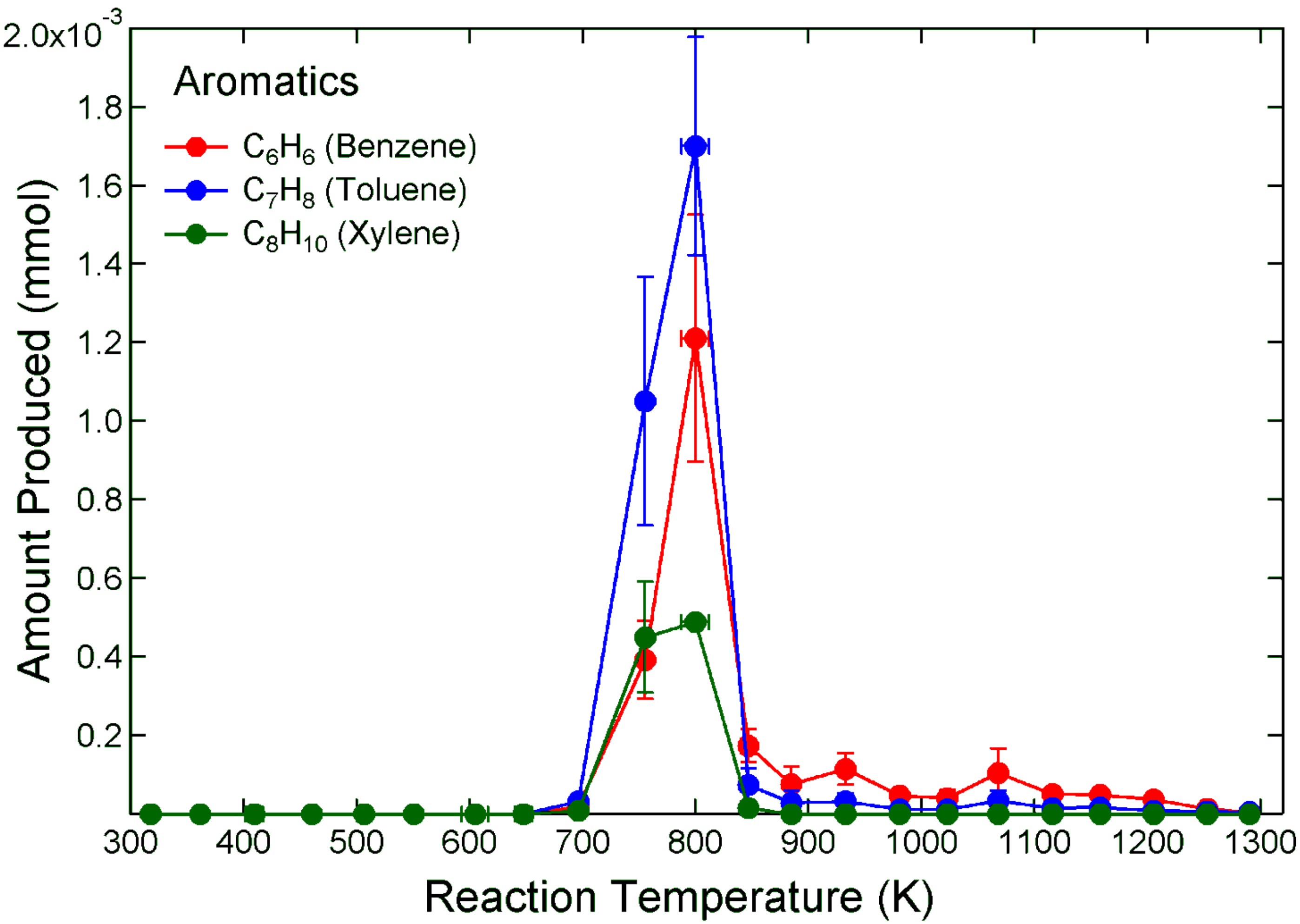
- Water vapor was produced at a temperature below 800 K
- Permanent gases were produced at a temperature higher than 700 K
- Hydrogen gas had the highest molar yields, followed by methane and carbon monoxide

Speciation Results:
2) Phenol and Derivatives



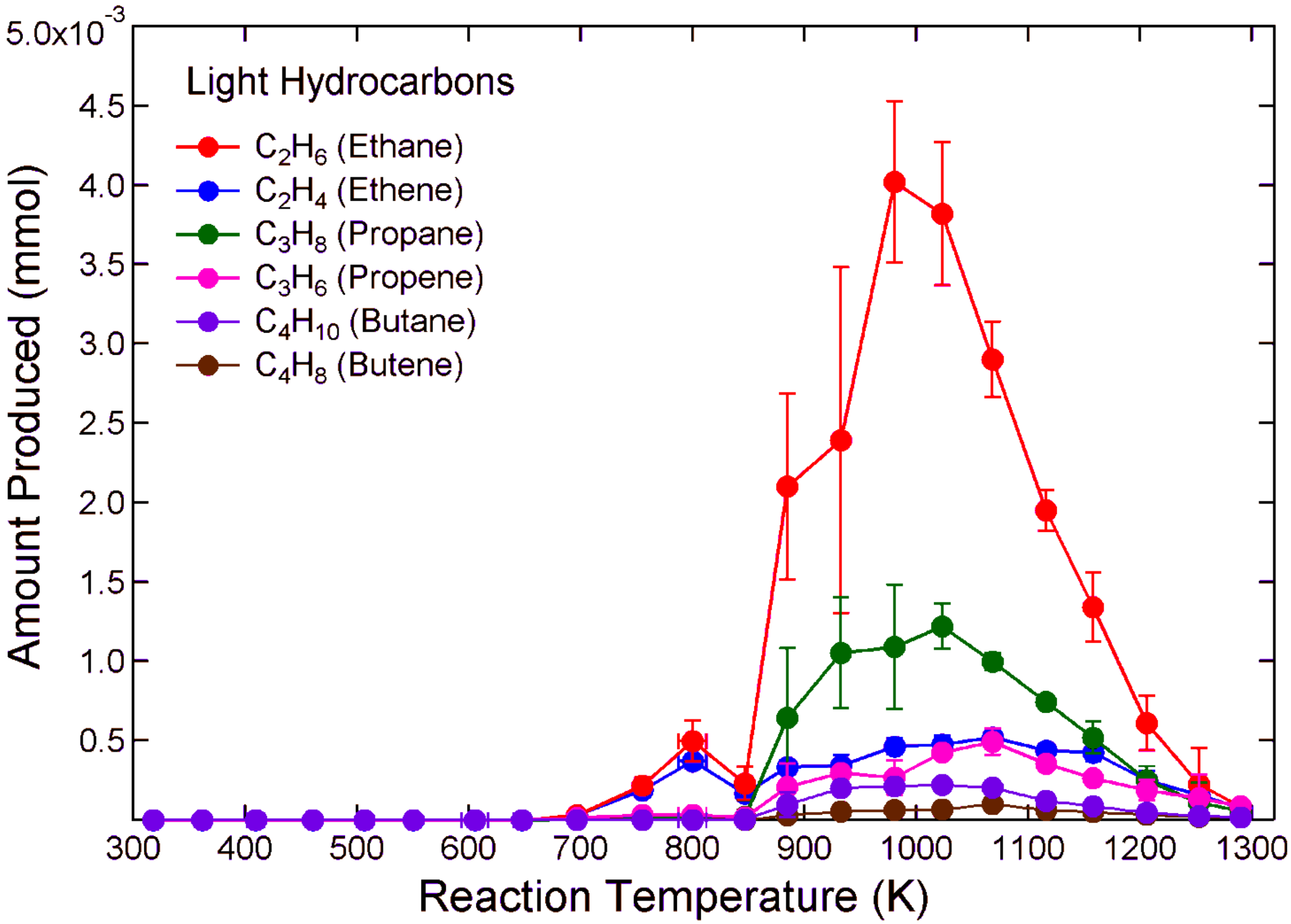
- Phenol, Cresol had higher yields than dimethylphenol and trimethylphenol
- Phenol and its derivatives were the most dominant liquid products and responsible for the peaked mass loss
- Production peaked at about 750 K

Speciation Results: 3) Aromatics



- Benzene, toluene, xylene (BTX) all peaked at about 800 K
- BTX had the lowest yields compared with other families of species

Speciation Results: 4) Hydrocarbons



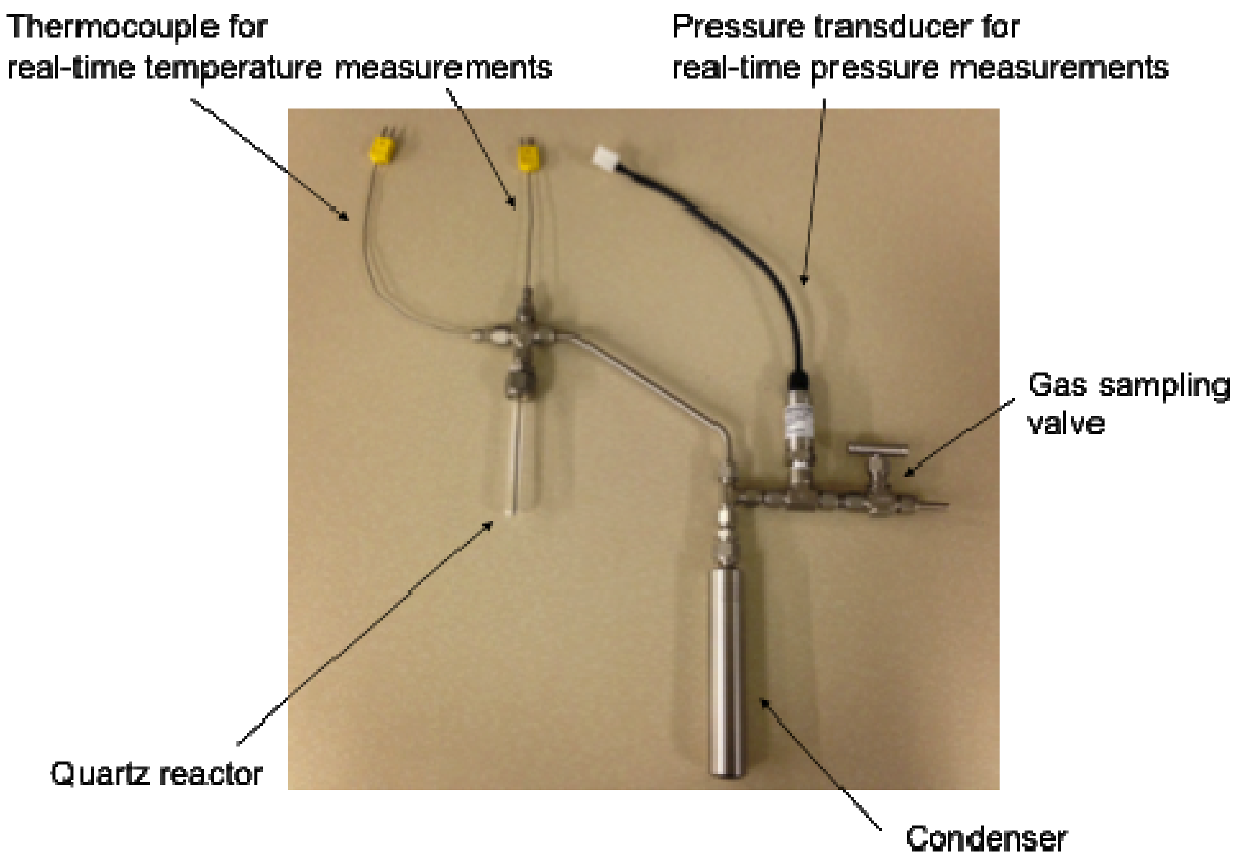
- Smaller alkanes, such as ethane, had higher yields than larger alkenes
- The overall yields of light hydrocarbons were much lower than permanent gases
- Production peaked at about 1000 K

Conclusions

- Batch pyrolysis of phenolic polymers was performed from room temperature up to 1300 K
- Chemical speciation was measured by gas chromatography:
  - Water was found to be only important below 800 K
  - Phenol and its derivatives were responsible for the peaked mass loss, and their yields peaked between 600 – 850 K
  - Minor molar yields of aromatic species were present between 750 – 850 K
  - Permanent gases were mostly produced between 700 – 1200 K
  - Yields of light hydrocarbons peaked at 1000 K
  - Lighter species were found to form at higher temperatures, consistent with the three-stage mechanism
- The molar production of these species will be used for the construction of a finite-rate chemistry model for phenolic pyrolysis

Ongoing and Future Work

- Two sets of pyrolysis experiments will be performed:
  - Pyrolysis of PICA
  - Pyrolysis of generic phenolic through carbon preform
- The time-dependent pressure will be recorded:



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