THERMODYNAMIC DRIVING FORCES FOR POST-GASIFICATION CARBON DEPOSITION

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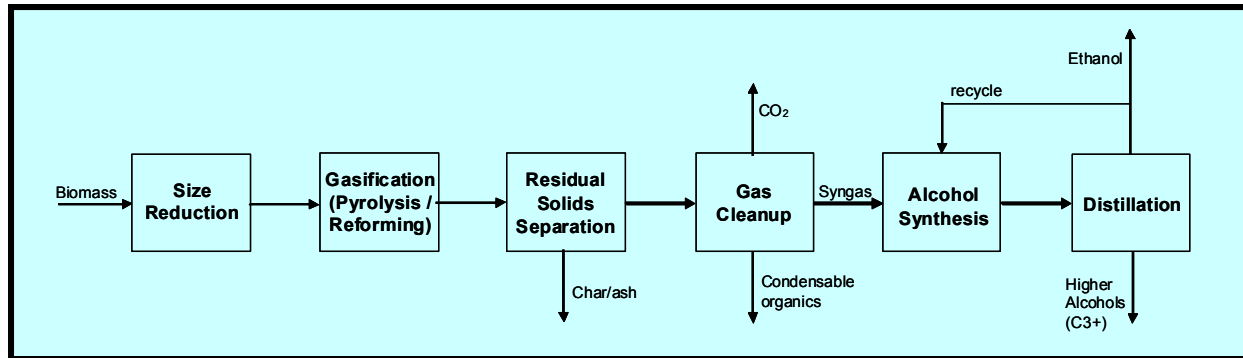
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Introduction / Problem Statement

Typical Biomass Gasification Process

Fuel production process shown

- Product stream from gasifier
  - T = 900-1100°C (1700-2000°F)
  - Need to cool for gas cleanup prior to downstream processing
  - May be able to recover heat as it cools
  - Stream is hot enough to react further
  - Possible solid formation and deposition as T drops
    - Tars: begin to condense at T < 400°C (750°F)
    - Solid carbon (soot)
  - Solid deposition can foul surfaces of downstream equipment

Economic viability of heat recovery depends on what T solid carbon formation and deposition occurs during cooldown for given system.

Reactions

Gas Phase Reactions Pertinent to Gasification Systems

Reaction	Name	$\Delta H°$ (kJ/mol)[*]	$\Delta G°$ (kJ/mol)[*]
$C + CO_2 = 2\ CO$	Boudouard	172	120
$C + H_2O = CO + H_2$	Water Gas	131	91
$C + 2\ H_2 = CH_4$	Methanation	- 75	- 51
$CO + H_2O = CO_2 + H_2$	Water Gas Shift	- 41	- 29
$CH_4 + H_2O = CO + 3\ H_2$	Steam Reforming	206	142
$CH_4 + CO_2 = 2\ CO + 2\ H_2$	Dry Reforming	247	171

* Standard values at 298 K

Objectives and Approach

Objective:

Find operating conditions at which solid carbon formation is thermodynamically disfavored during cooldown (post-gasifier, after char removal) $\longrightarrow$ temperature window where carbon formation is avoided.

Approach:

Use global equilibrium calculations for predicting:

- Temperature at which solid carbon first appears during cool-down (= T_{dep})

- Composition of product stream for given conditions

Kinetics need not be considered where solid carbon formation is not favored thermodynamically.

Approach

Global Equilibrium Calculations

- STANJAN solver used
- Approach minimizes Gibbs Free Energy of entire mixture (Method of Lagrange Multipliers)

Inputs:
- Temperature
- Pressure
- Atom fractions of C, H, O
- List of chemical species
  - Gas-phase {CH_4, CO, CO_2, H_2, H_2O}
  - C(S) [solid carbon – graphite]
- Thermodynamic properties of species in JANAF format

Outputs:
- Mole fractions of individual species
- Thermodynamic properties of mixture (ΔU, ΔH, ΔS)

- Also useful for predicting optimal gas-phase concentrations
  - CO, H_2 desired products; CH_4, CO_2 not desired

Approach

Operating Variables Explored:

- Pressure

- Steam/carbon (H_2O/C) mass ratio
  – Includes moisture in wood

- Amount of char formed in gasifier and removed prior to cool down (% char)

Base Case

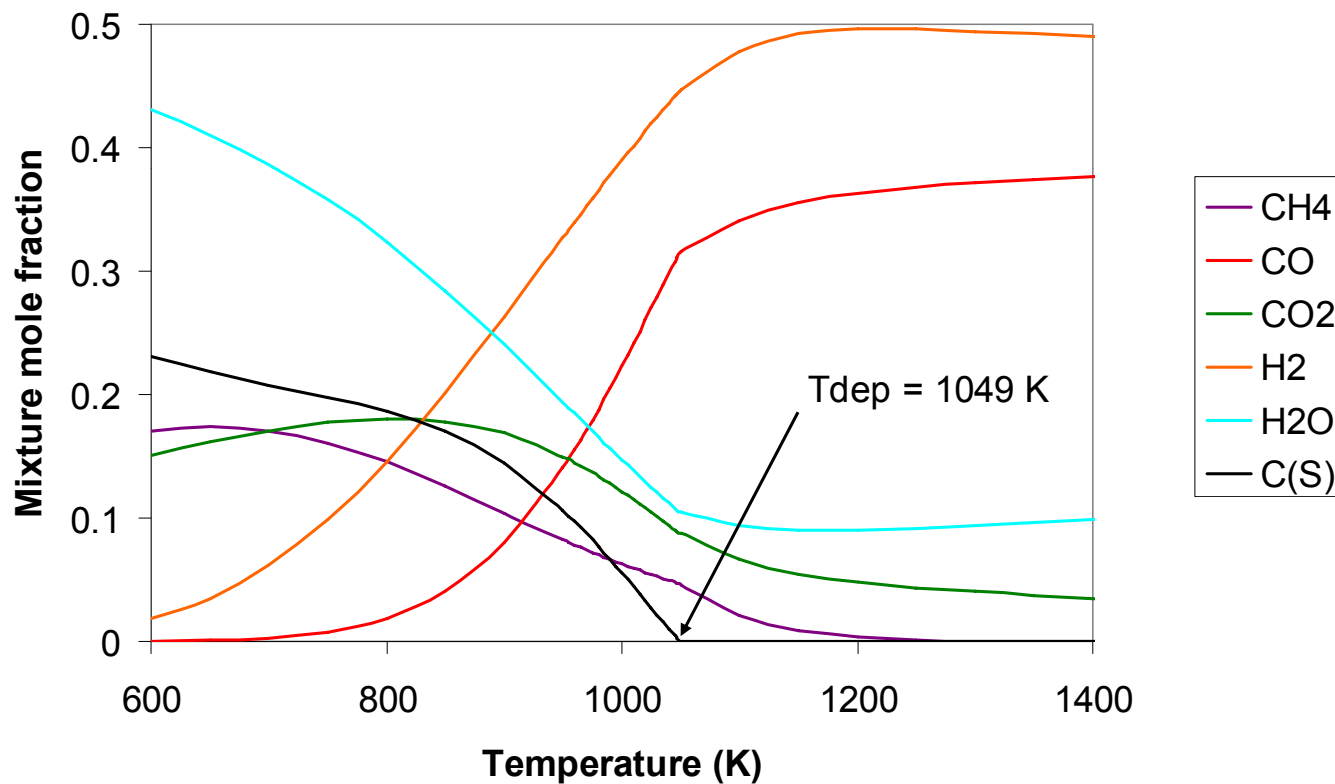## Base case conditions:

- **Typical gasifier operating conditions**
  - Pressure = 4 atm
  - H_2O/C mass ratio = 1.0
  - Char formed and removed (% char) = 5% of wood C

- **Wood properties**
  - Dry wood: 52% C, 6% H, 41% O by mass
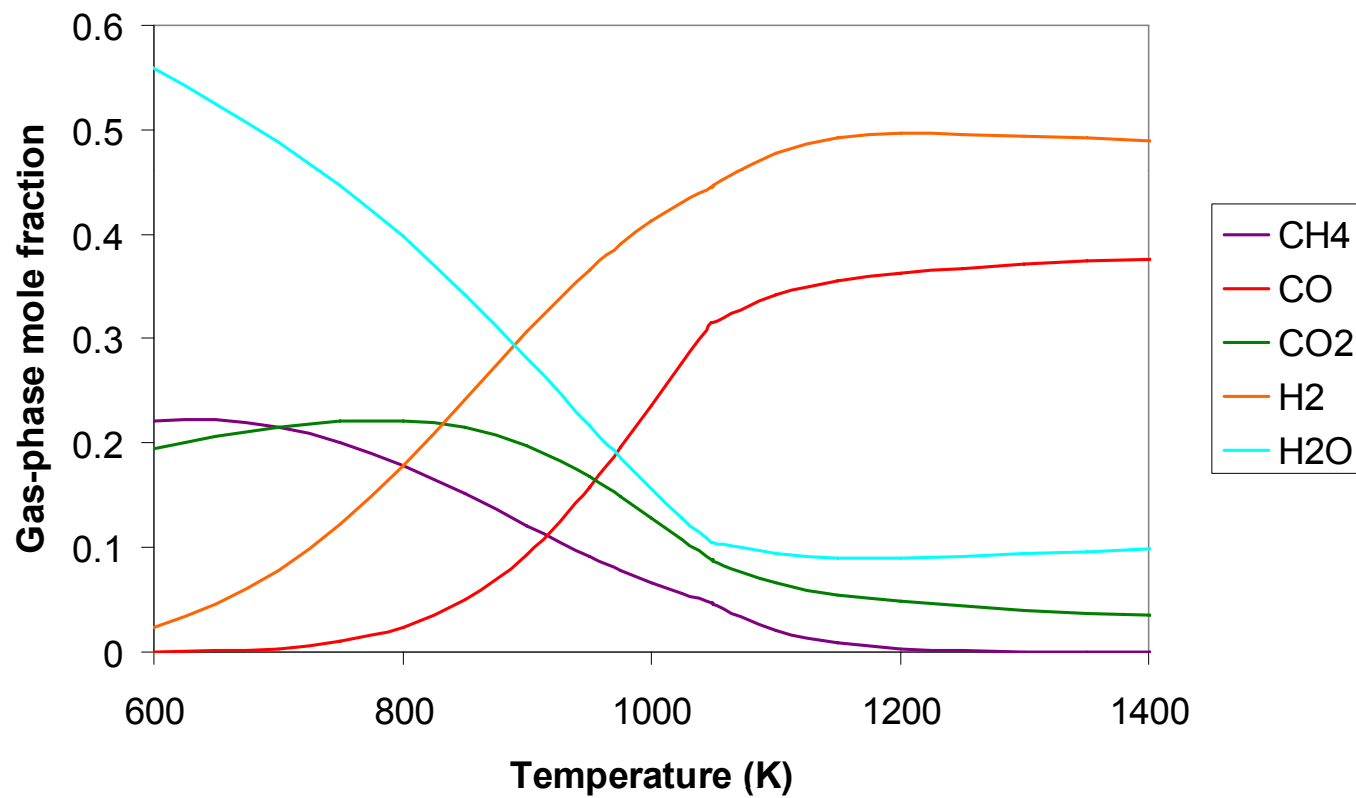 - Wood moisture = 25% by mass

Base Case

Mole fractions (for entire mixture)

H$_2$O/C = 1.0, 5% char, 4 atm
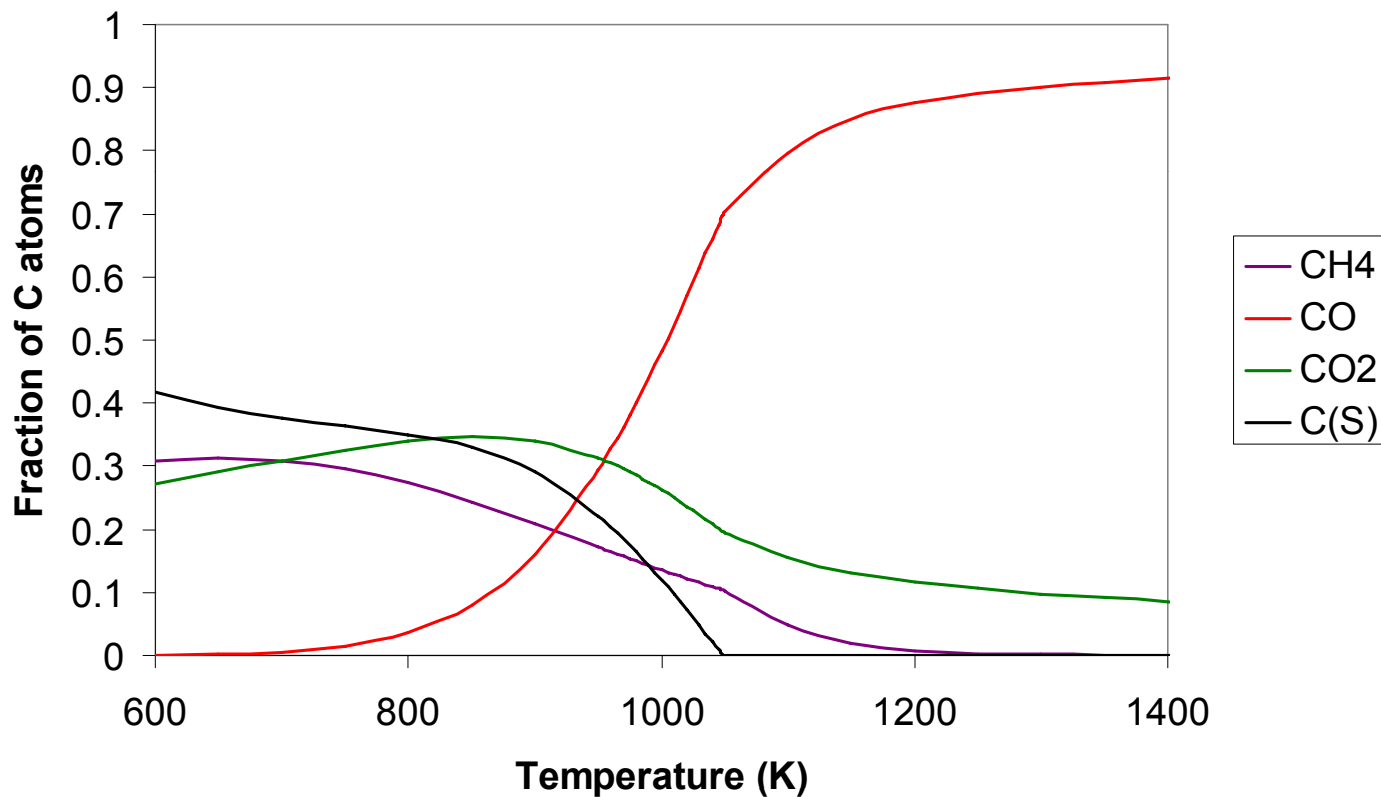
Base Case

Gas-phase mole fractions

H$_2$O/C = 1.0, 5% char, 4 atm

Base Case

Fraction of C as CH_4, CO, CO_2, and C(S)

H$_2$O/C = 1.0, 5% char, 4 atm

Carbon Deposition Temperature Values

Variation in T_{dep} (and atomic C/O ratio) with H_2O/C and % char [P = 4 atm]

T_{dep}(K) C/O ratio	$H_2O/C = 0.5$	$H_2O/C = 1.0$	$H_2O/C = 1.5$	$H_2O/C = 2.0$	$H_2O/C = 2.5$
1% char	* 1.071	1066 0.787	975 0.622	875 0.514	618 0.438
5% char	* 1.028	1049 0.755	958 0.597	830 0.494	578 0.421
10% char	1239 0.973	1028 0.716	934 0.566	711 0.468	539 0.399
15% char	1156 0.919	1006 0.675	901 0.534	621 0.442	505 0.376
20% char	1112 0.865	983 0.636	841 0.500	565 0.416	476 0.354
25% char	1078 0.811	956 0.596	705 0.468	522 0.390	455 0.332
30% char	1049 0.757	923 0.557	605 0.437	486 0.364	426 0.310

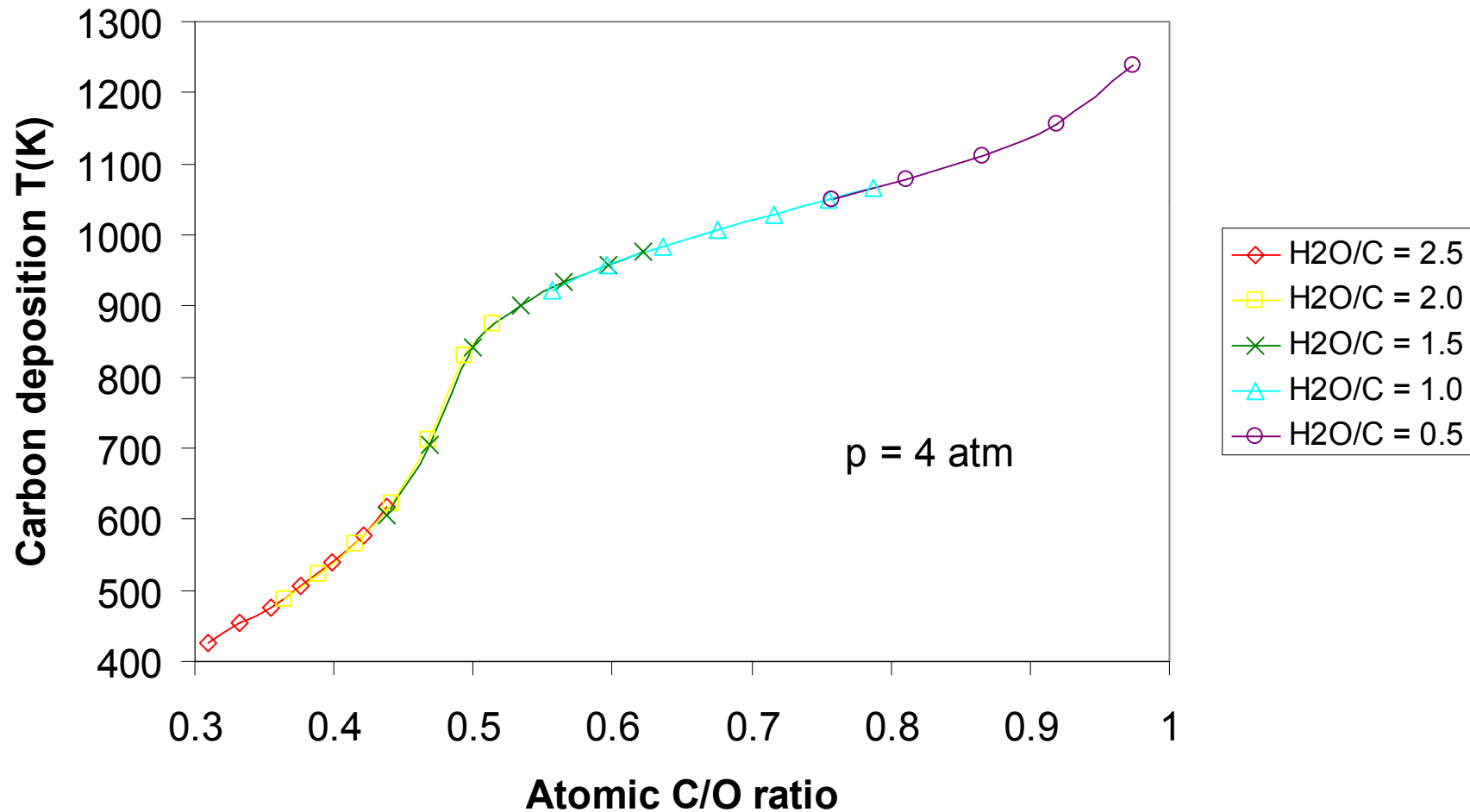Increasing heat recovery potential

Increasing heat recovery potential

* = solid carbon is predicted to form at all temperatures

☐ = base case for this study

Carbon Deposition Temperature Values

## Correlation between T_{dep} and atomic C/O ratio

Varying Pressure

Pressure variation results

- Higher pressure adversely affects C(S), gas-phase species:
  - T_{dep} increases
  - C(S) increases (at higher temperatures)
  - CO, H_2 decrease
  - CH_4, CO_2, H_2O increase

- However, reactor size decreases with increasing pressure, so there is a trade-off
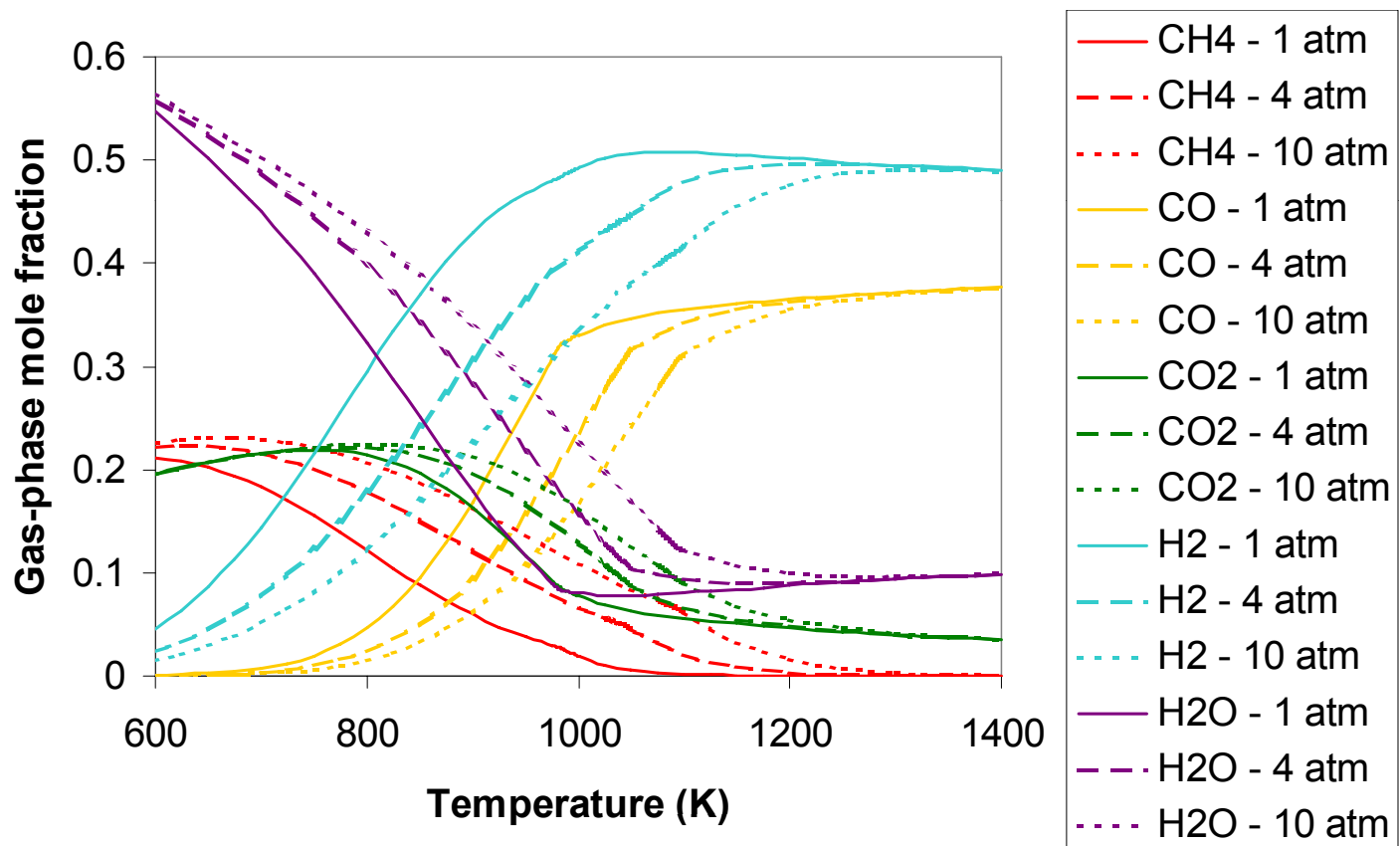
Varying Pressure

Solid carbon formation

Tdep is at C conversion = 0
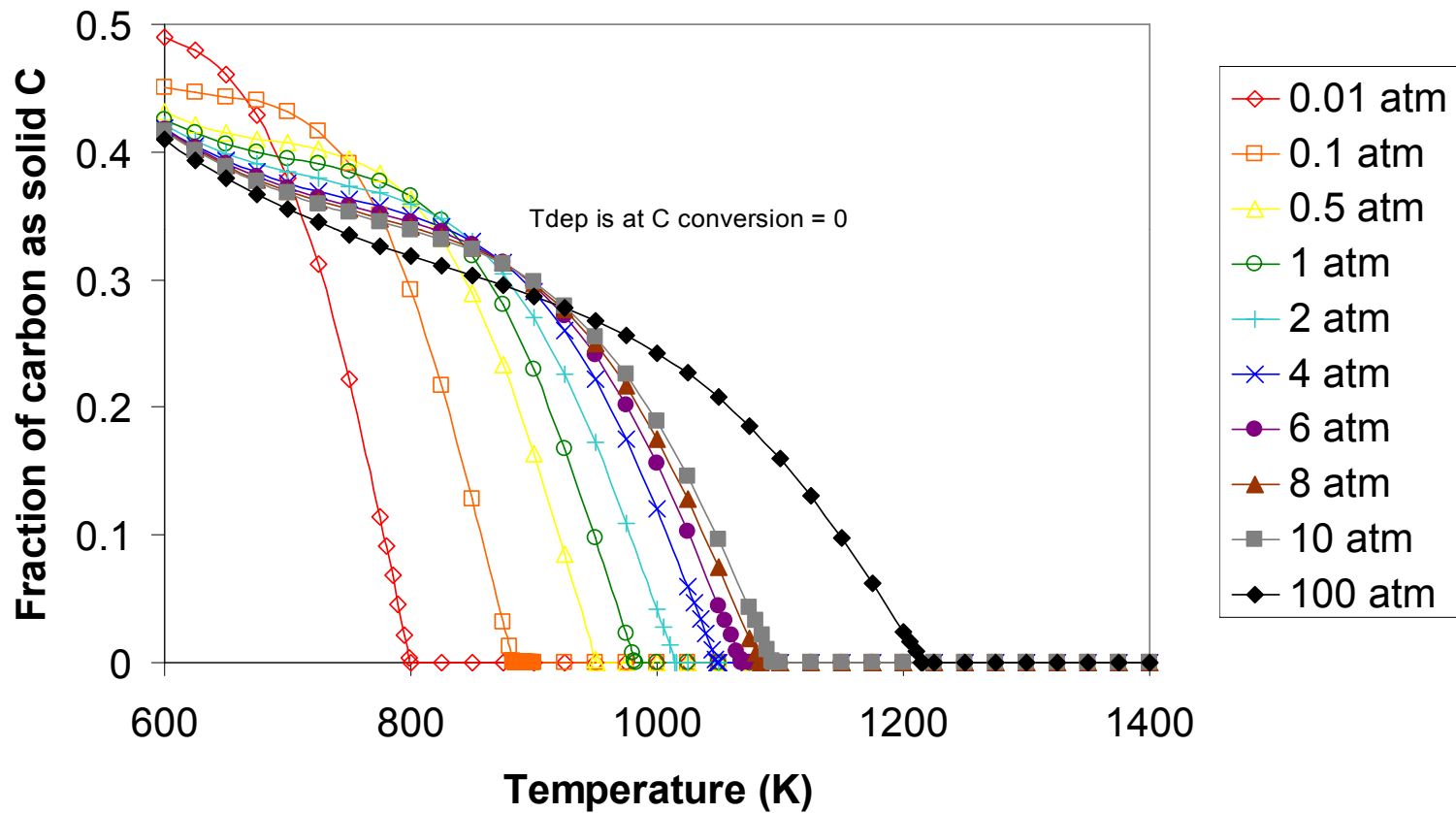
$H_2O/C = 1.0$, 5% char

Varying Pressure

Gas-phase mole fractions

H$_2$O/C = 1.0, 5% char

Varying Pressure

Fraction of C atoms as CH_4, CO, CO_2, $C(S)$

Legend:
- CH4 - 1 atm
- CH4 - 4 atm
- CH4 - 10 atm
- CO - 1 atm
- CO - 4 atm
- CO - 10 atm
- CO2 - 1 atm
- CO2 - 4 atm
- CO2 - 10 atm
- C(S) - 1 atm
- C(S) - 4 atm
- C(S) - 10 atm

X-axis: Temperature (K)
Y-axis: Fraction of C atoms
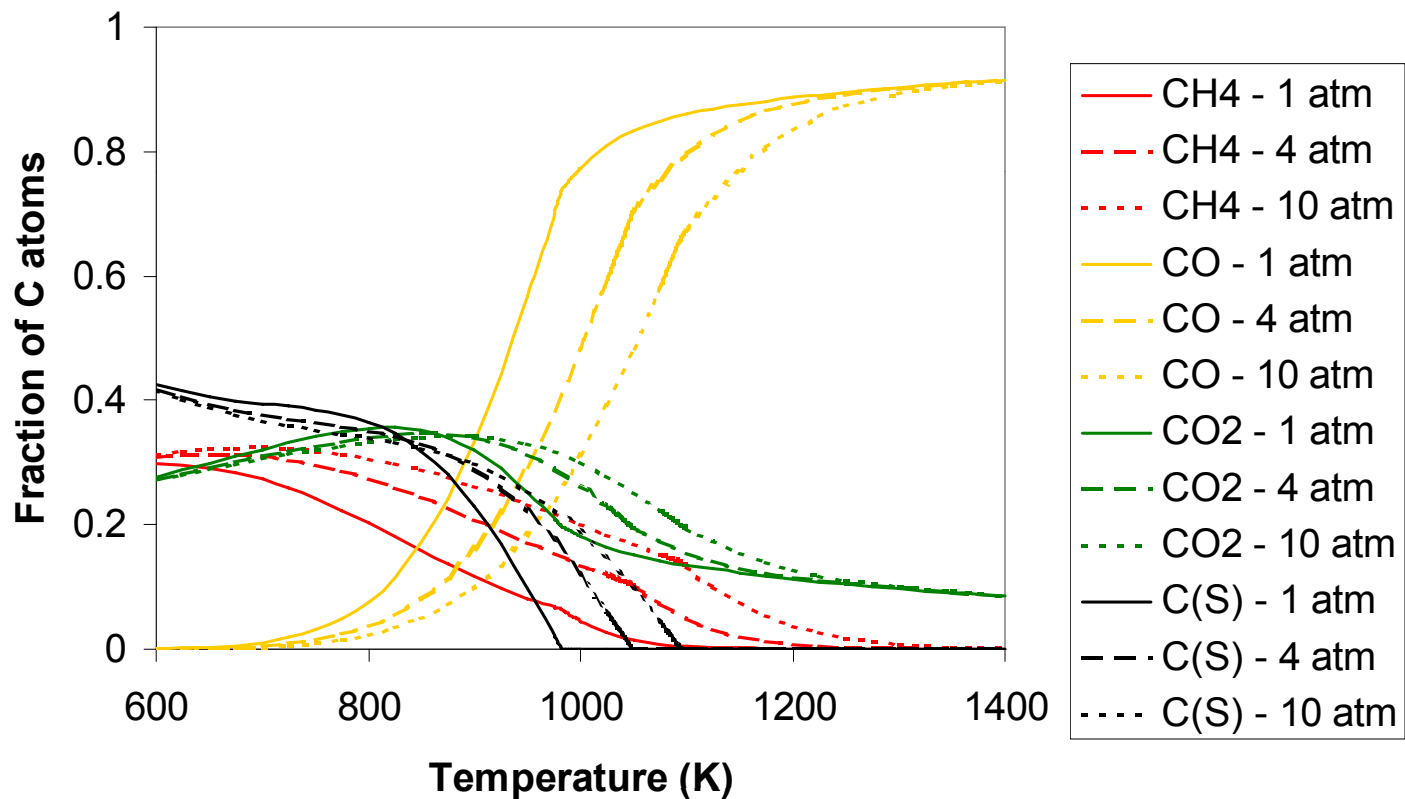
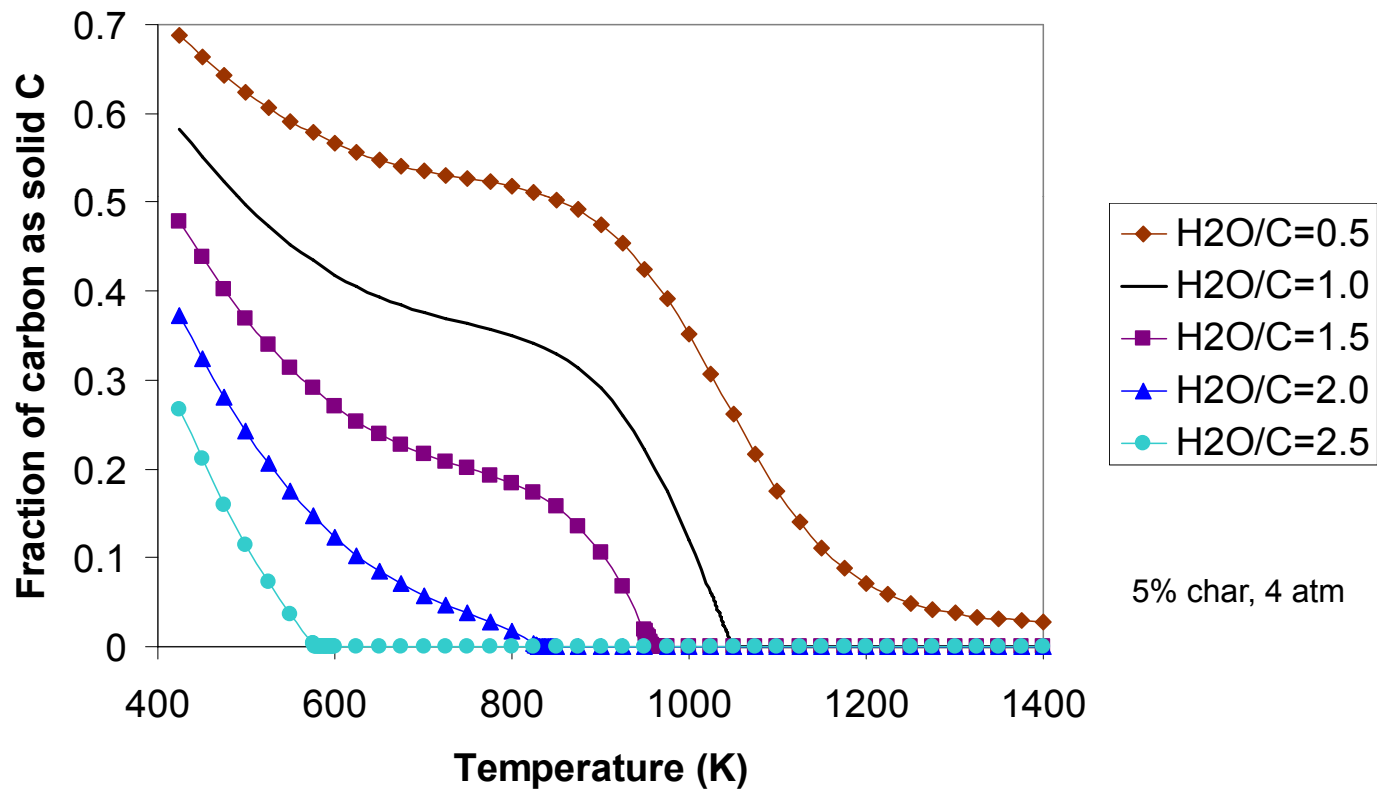$H_2O/C = 1.0$, 5% char

Varying H_2O/C ratio

H_2O/C ratio variation results

- Higher H_2O/C ratio (i.e., increasing steam) reduces carbon formation potential:
  - T_{dep} decreases
  - C(S) decreases
  - CO, CH_4, H_2 generally decrease
  - H_2O, CO_2 increase

- Examining fraction of C atoms distribution (instead of mole fraction) removes effects of dilution by steam

- Increased CO_2 quantities from Water Gas Shift reaction
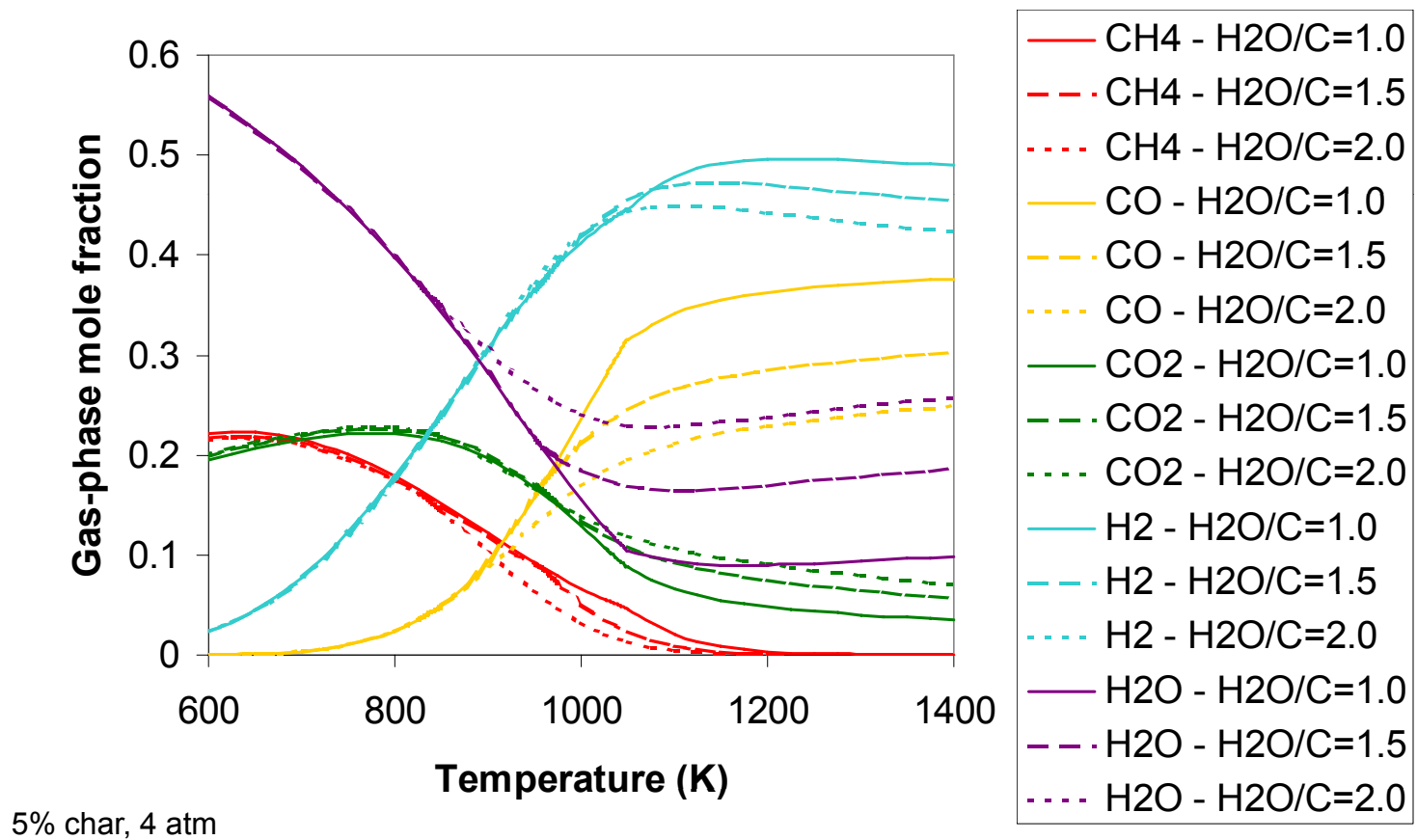
Varying H_2O/C ratio

Solid carbon formation

Plot of Fraction of carbon as solid C (y-axis, 0 to 0.7) versus Temperature (K) (x-axis, 400 to 1400) for curves: H2O/C=0.5, H2O/C=1.0, H2O/C=1.5, H2O/C=2.0, H2O/C=2.5. 5% char, 4 atm

Solid carbon formation and T_{dep} drop significantly with increasing steam

Varying H$_2$O/C ratio

Gas-phase mole fractions

5% char, 4 atm

Varying H$_2$O/C ratio

Fraction of C atoms as CH$_4$, CO, CO$_2$, C(S)
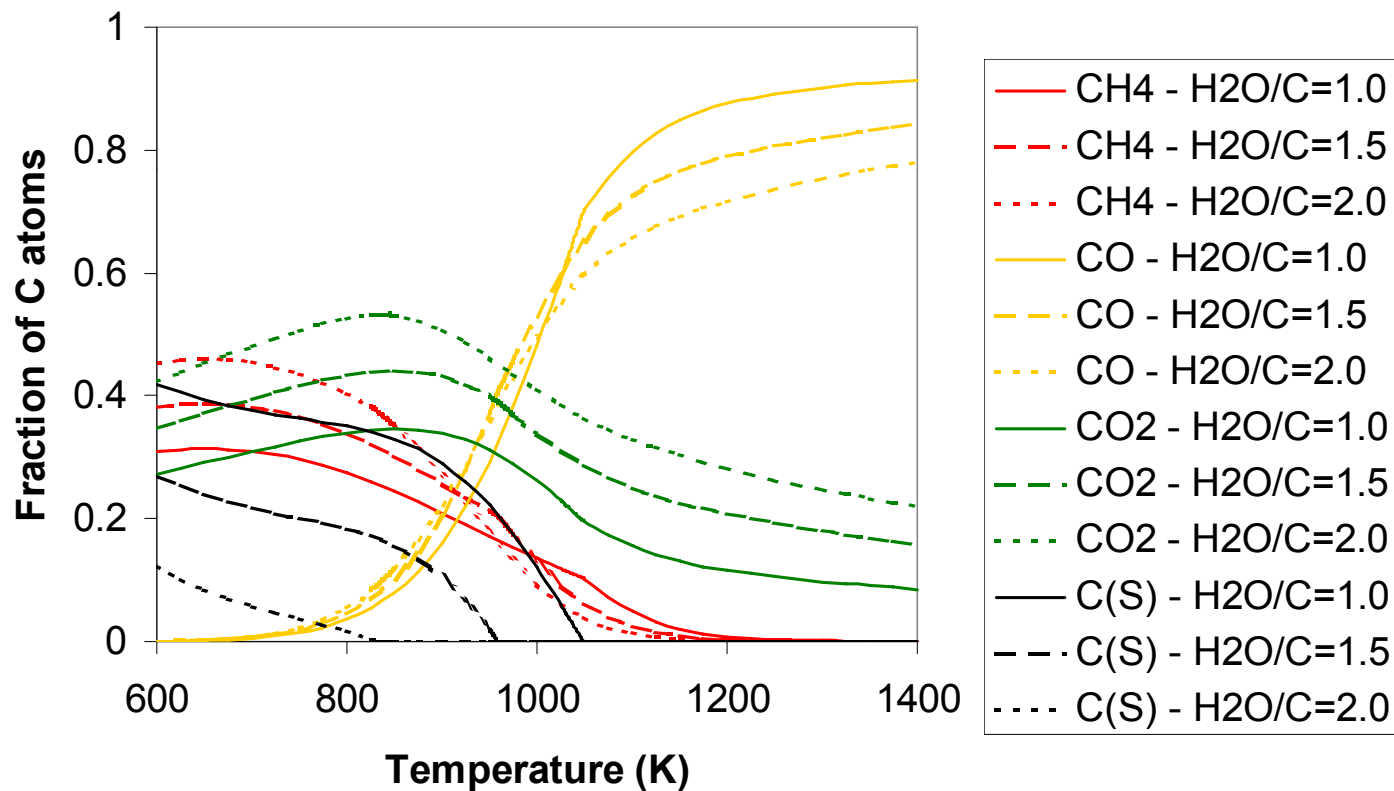

5% char, 4 atm

Varying % Char

% Char variation results

- Increasing amount of char formed and removed prior to cooldown decreases carbon in system:
  - T_{dep} decreases
  - C(S) decreases
  - CO, CH_4, H_2 decrease
  - CO_2, H_2O increase

- Difficult to manipulate % char directly

- As more char is formed and removed:
  - Less carbon enters post-gasifier cooldown
  - Comparing fraction of C distribution can be misleading since only post-char removal carbon quantity varies
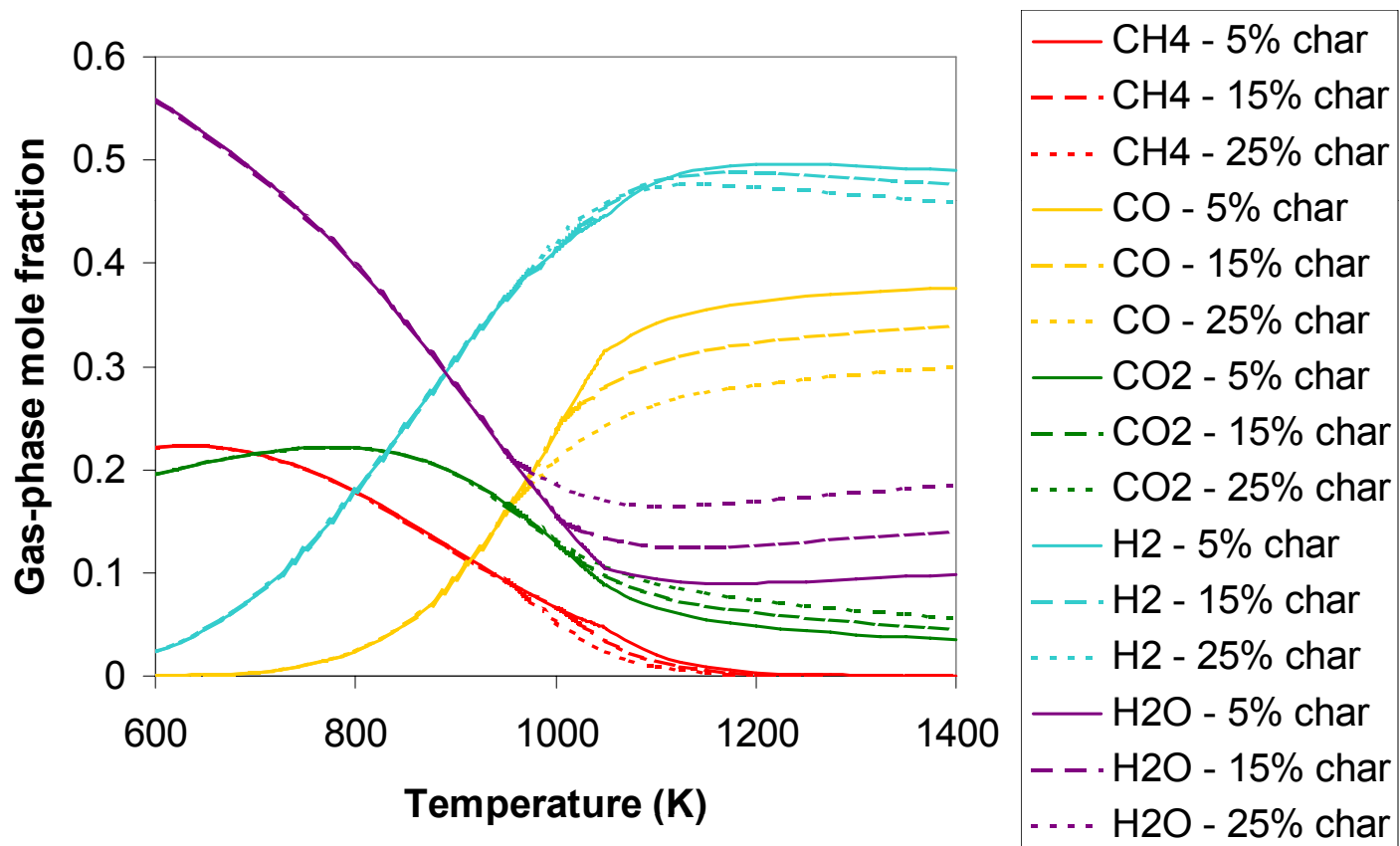
Varying % Char

Solid carbon formation
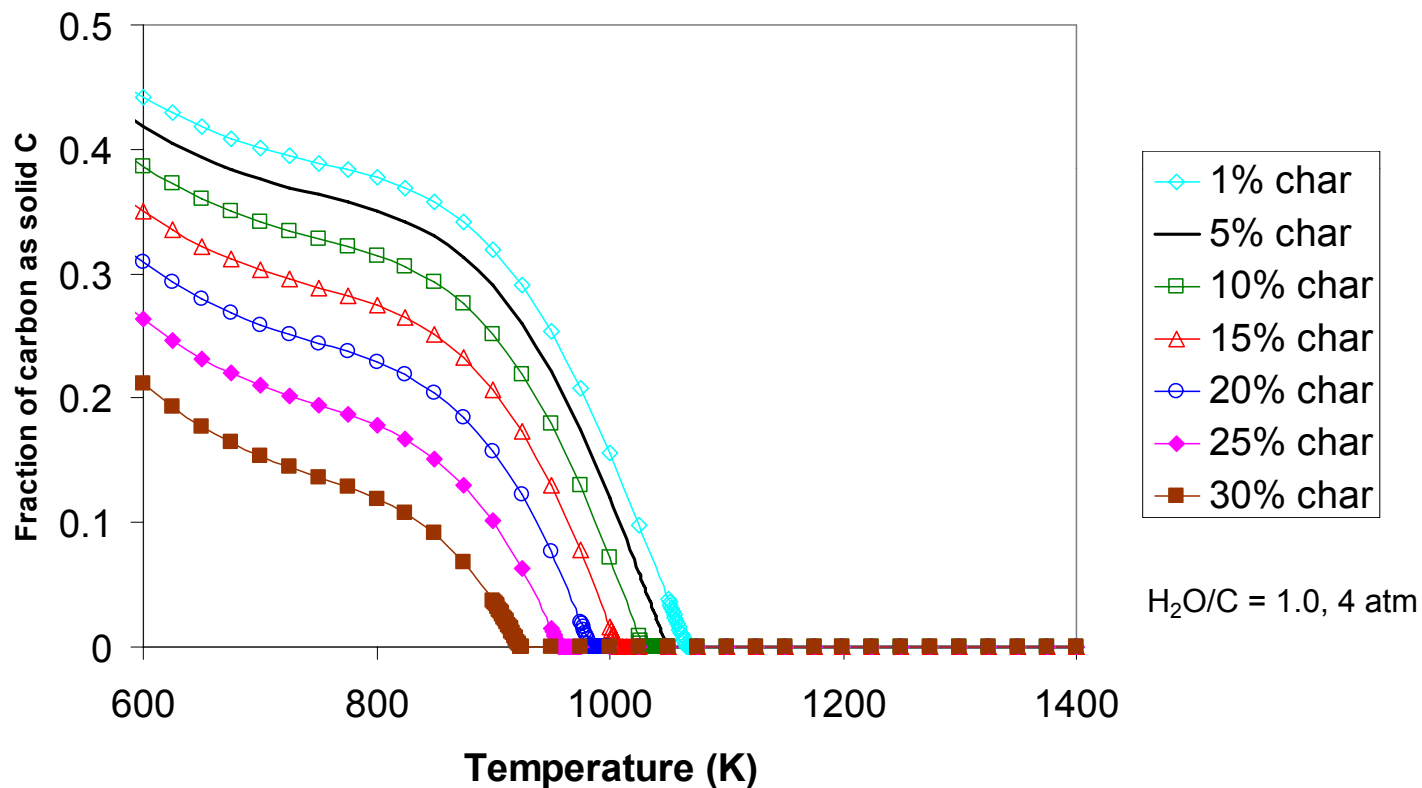
More char removed = less carbon in system = lower T$_{dep}$
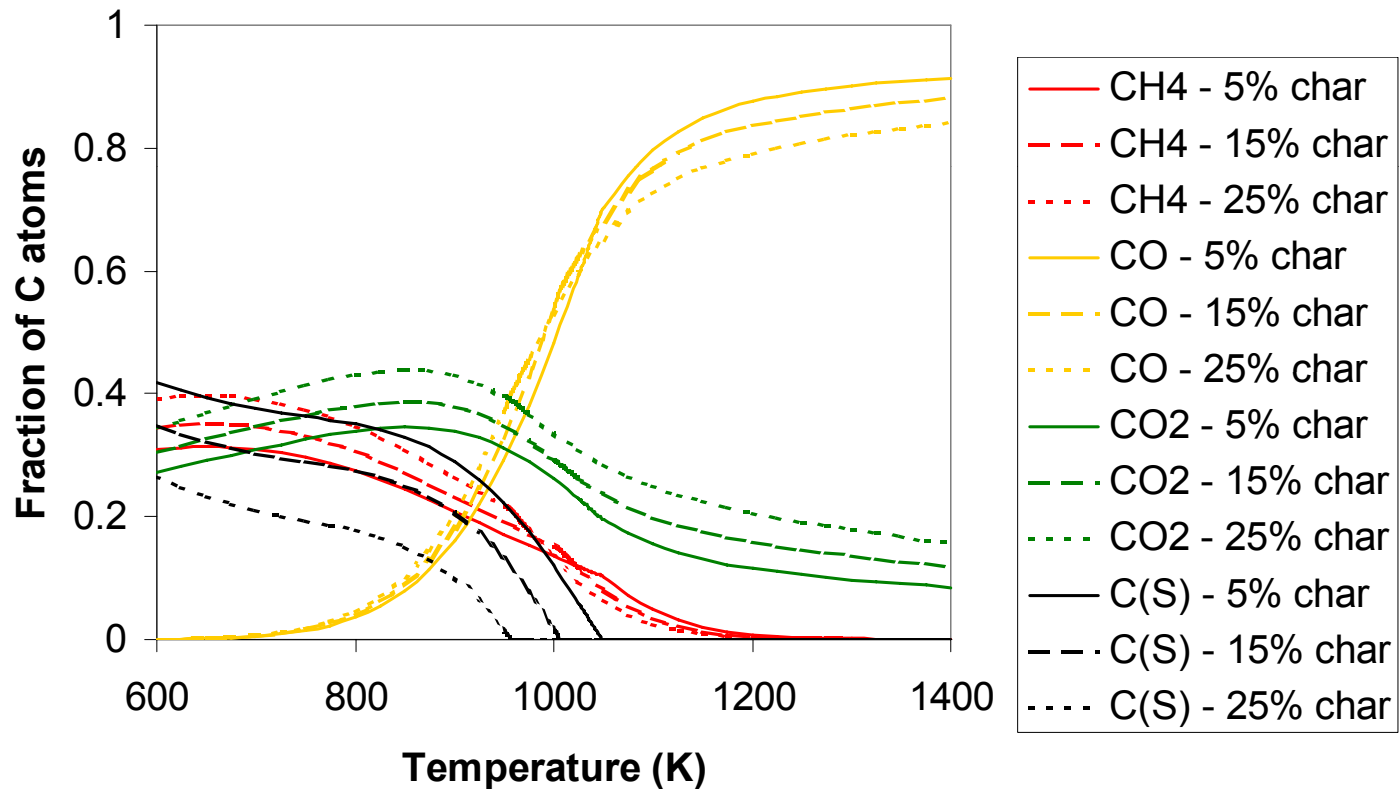
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Varying % Char

Gas-phase mole fractions

H$_2$O/C = 1.0, 4 atm

Varying % Char

Fraction of C atoms as CH$_4$, CO, CO$_2$, C(S)
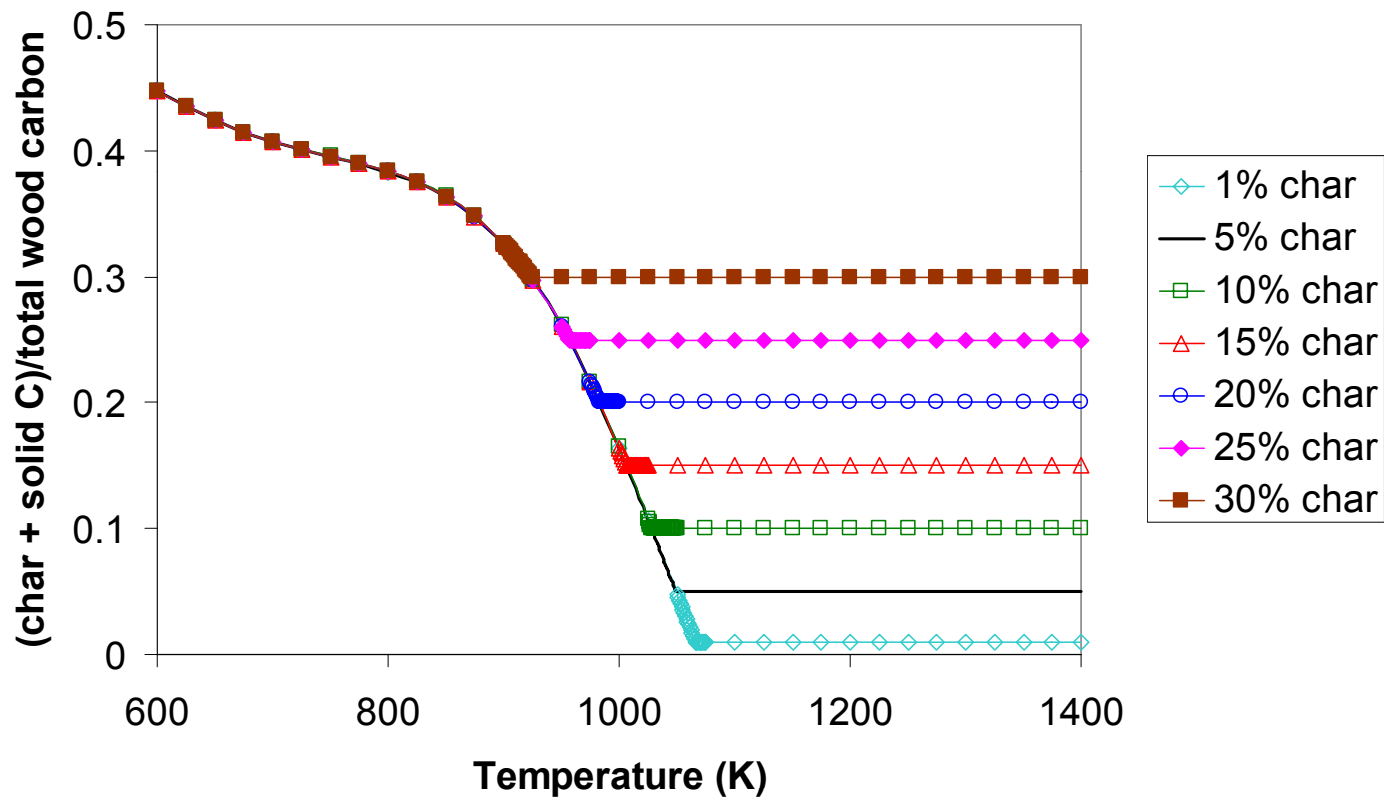

H$_2$O/C = 1.0, 4 atm

Varying % Char

% Char variation results (continued)

- Char formation itself is under kinetic control
  - Can be varied by changing gasifier conditions

- Total wood carbon lost as char plus (post-gasifier) solid carbon formation
  - Increases with increasing % char above T_{dep}
  - Trend in total wood C lost provides further evidence that char formation is under kinetic control

- Considering post-gasifier carbon-containing species as fraction of total wood carbon
  - Profiles of CH_4, CO, CO_2 similar to mole fraction profiles
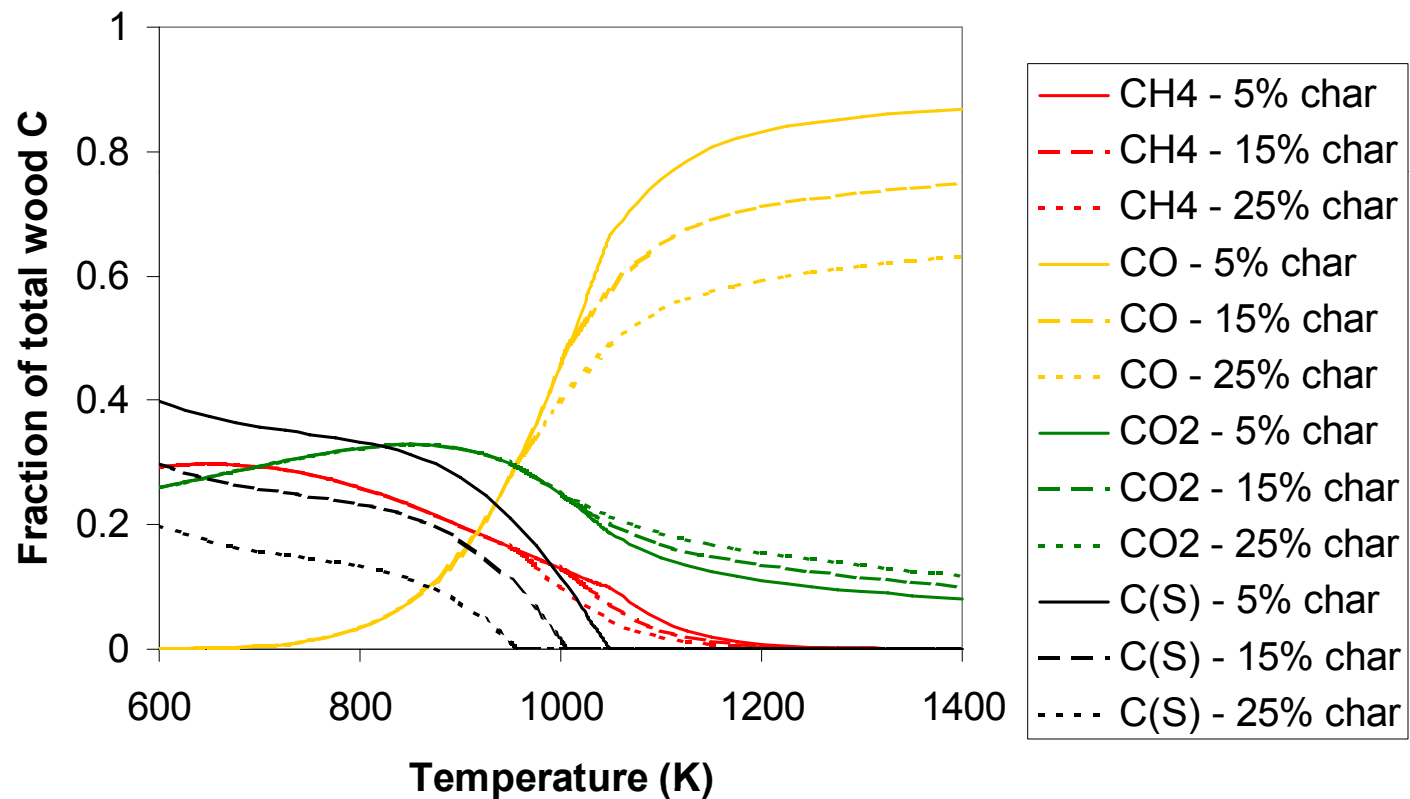
Varying % Char

Char + C(S) trends

H$_2$O/C = 1.0, 4 atm

Varying % Char

Fraction of total wood C atoms (yield) as CH_4, CO, CO_2, $C(S)$

$H_2O/C = 1.0$, 4 atm

Summary / Conclusions

Summary

- T_{dep} lowered by
  - Lowering pressure
  - Increasing H_2O/C ratio
  - Increasing % char formed and removed

- Low T_{dep} desired to increase temperature window for heat recovery

- Conditions which lower T_{dep} also lower $C(S)$

- However, these conditions also affect gas-phase concentrations....

Summary / Conclusions

Summary (continued)

- Desired products (CO, H_2) changed by conditions lowering T_{dep}:
  - Lower pressure *increases* CO, H_2
  - Increased H_2O/C *decreases* CO, H_2
  - Increasing % char also *decreases* CO, H_2
  - Effect on CO_2, H_2O opposite to that of CO, H_2

- CH_4 (not desired) also affected by conditions lowering T_{dep}:
  - Lower pressure *decreases* CH_4
  - Increased H_2O/C *decreases* CH_4 (at higher values of T)
  - Increasing % char also *decreases* CH_4

Summary / Conclusions

Conclusions

- Conditions found which optimize heat recovery without solid carbon formation during cooldown of post-gasifier stream

- Trade-offs exist between lowering T_{dep} and
  - Equilibrium gas-phase species distribution
  - Reactor size (= capital costs)

- Equilibrium calculations most valid at high T, long residence times

- Char formation in gasifier under kinetic control
  - Kinetics of post-gasifier solid carbon formation needed for further validation of approach