

THERMODYNAMIC DRIVING FORCES FOR POST-GASIFICATION CARBON DEPOSITION

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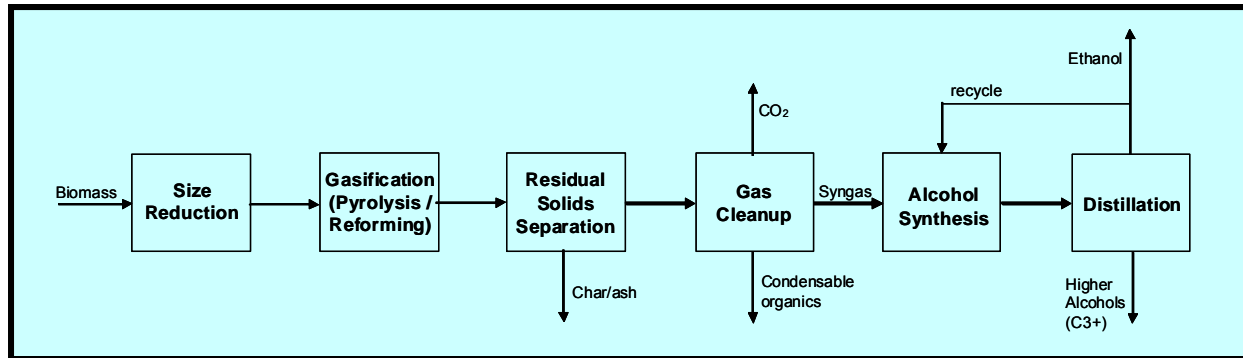


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Introduction / Problem Statement

Typical Biomass Gasification Process



Fuel production process shown

- Product stream from gasifier
 - $T = 900-1100^{\circ}\text{C}$ ($1700-2000^{\circ}\text{F}$)
 - 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 $T < 400^{\circ}\text{C}$ (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	ΔH° (kJ/mol)*	ΔG° (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) —————> 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 {CH₄, CO, CO₂, H₂, H₂O}
 - 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, H₂ desired products; CH₄, CO₂ 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)

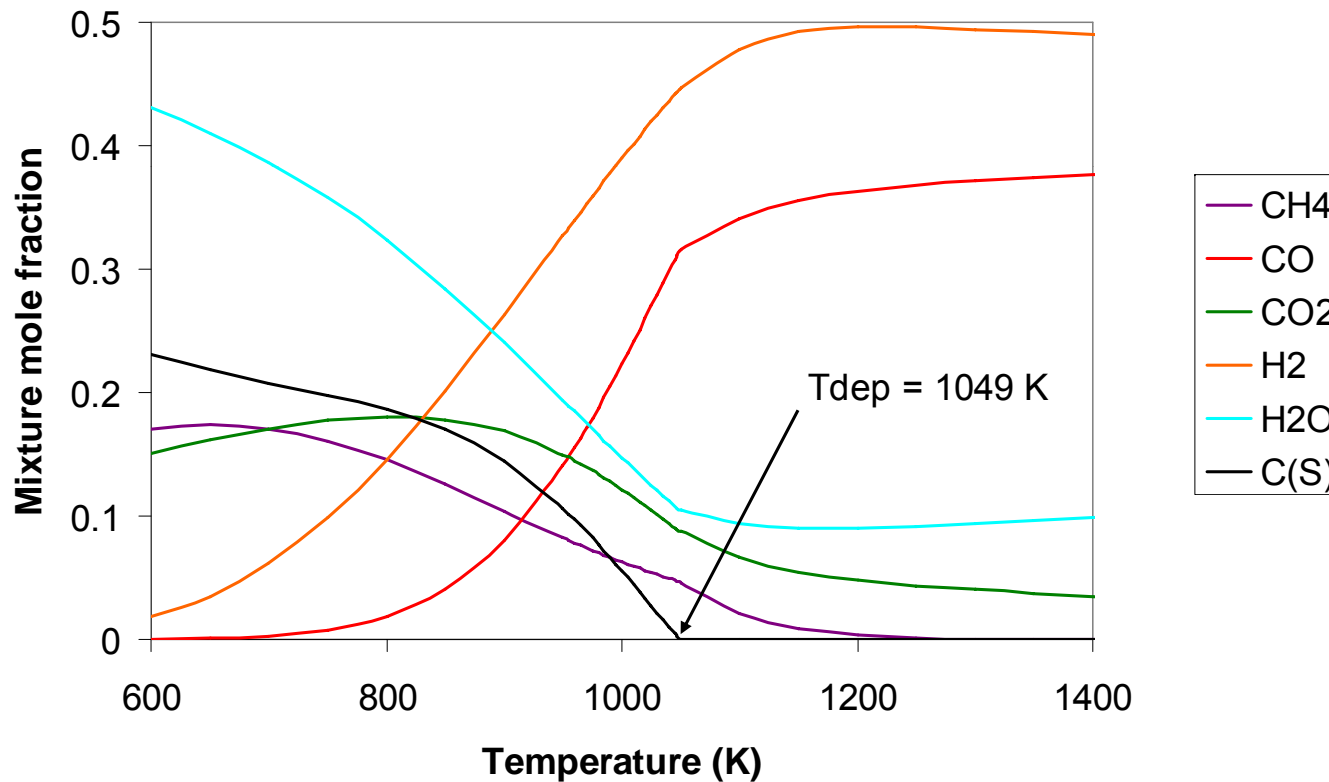
Base Case

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

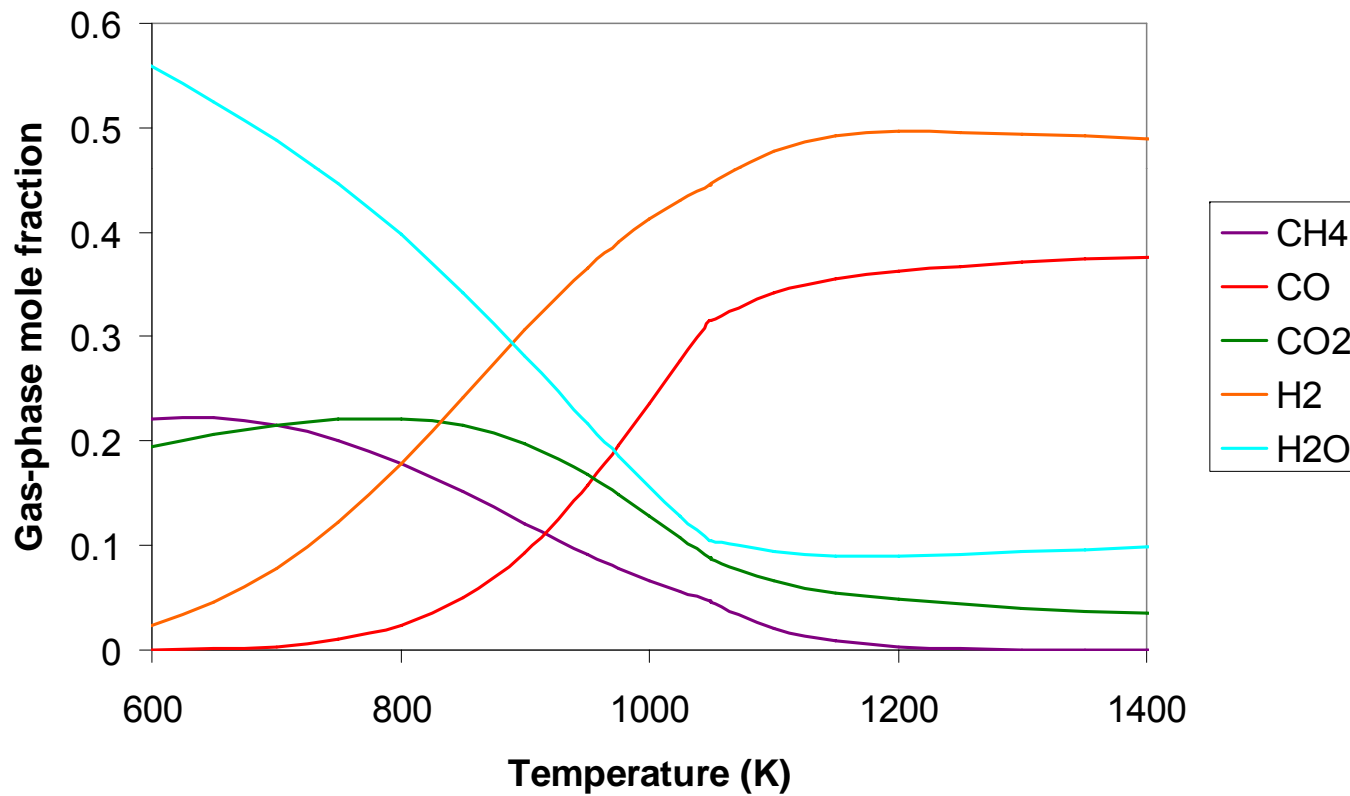
Mole fractions (for entire mixture)



H₂O/C = 1.0, 5% char, 4 atm

Base Case

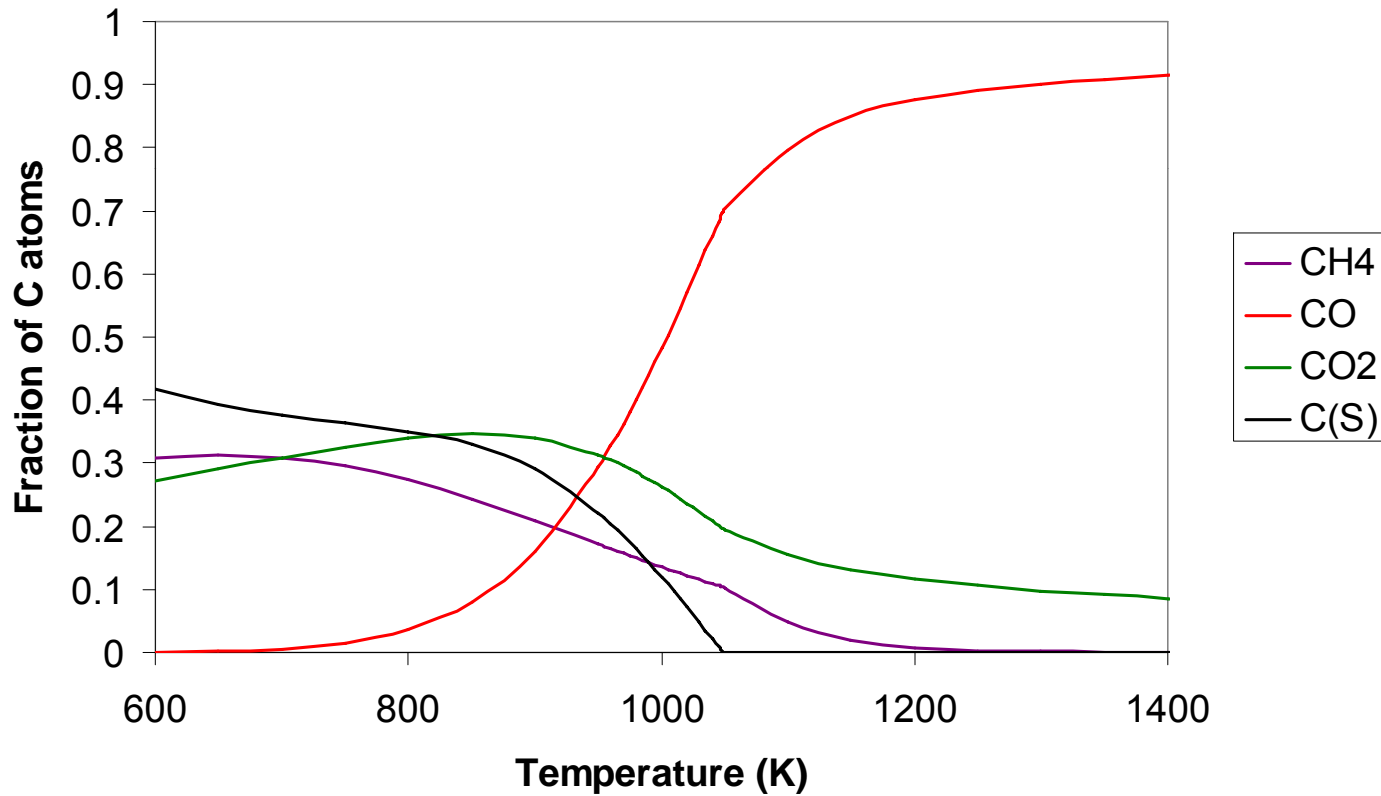
Gas-phase mole fractions



H₂O/C = 1.0, 5% char, 4 atm

Base Case

Fraction of C as CH₄, CO, CO₂, and C(S)



H₂O/C = 1.0, 5% char, 4 atm

Carbon Deposition Temperature Values

Variation in T_{dep} (and atomic C/O ratio) with $\text{H}_2\text{O}/\text{C}$ and % char
 [P = 4 atm]

T_{dep} (K) C/O ratio	$\text{H}_2\text{O}/\text{C} = 0.5$	$\text{H}_2\text{O}/\text{C} = 1.0$	$\text{H}_2\text{O}/\text{C} = 1.5$	$\text{H}_2\text{O}/\text{C} = 2.0$	$\text{H}_2\text{O}/\text{C} = 2.5$
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

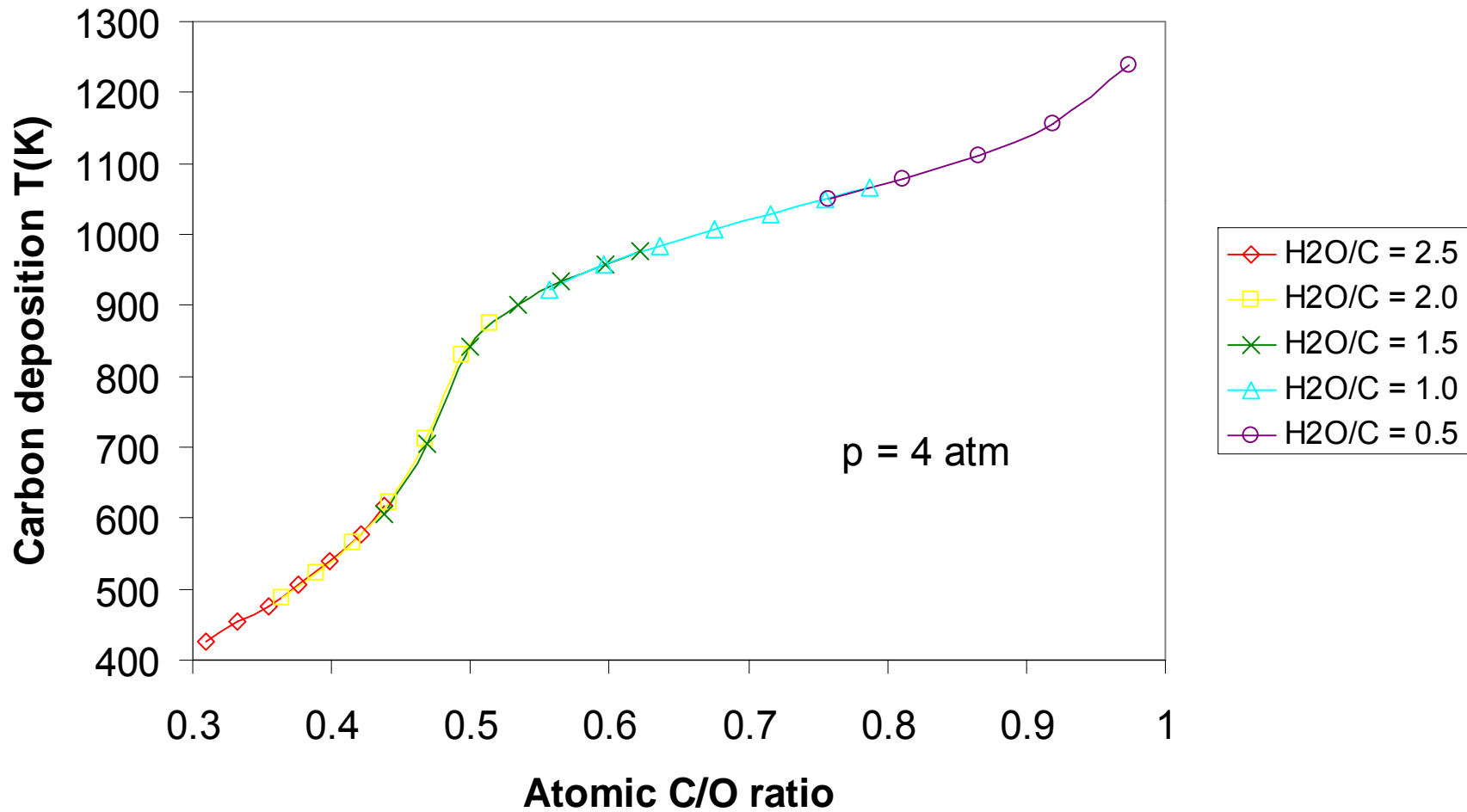
Increasing heat recovery potential

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



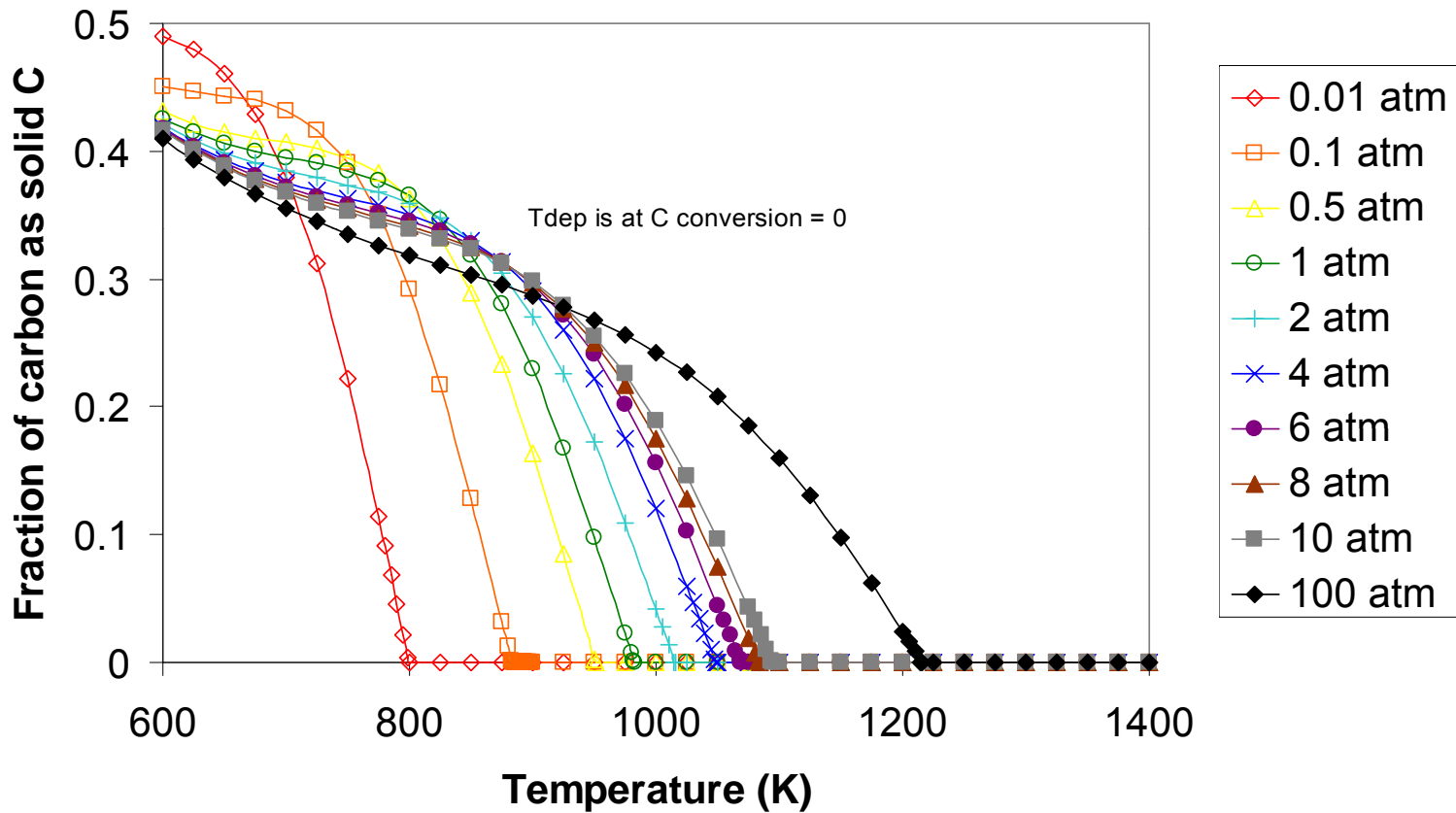
Varying Pressure

Pressure variation results

- Higher pressure adversely affects C(S), gas-phase species:
 - T_{dep} increases
 - C(S) increases (at higher temperatures)
 - CO, H₂ decrease
 - CH₄, CO₂, H₂O increase
- However, reactor size decreases with increasing pressure, so there is a trade-off

Varying Pressure

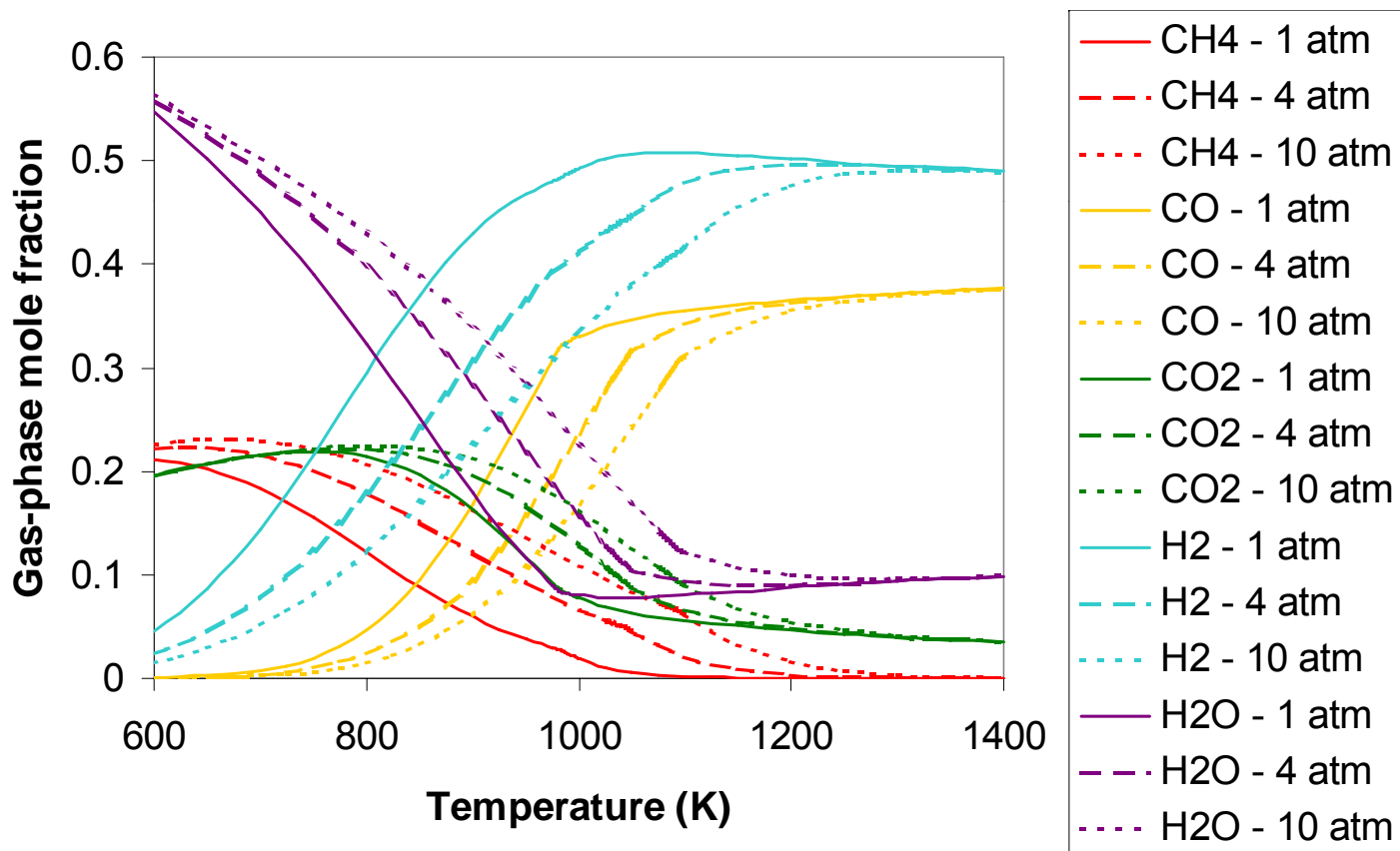
Solid carbon formation



H₂O/C = 1.0, 5% char

Varying Pressure

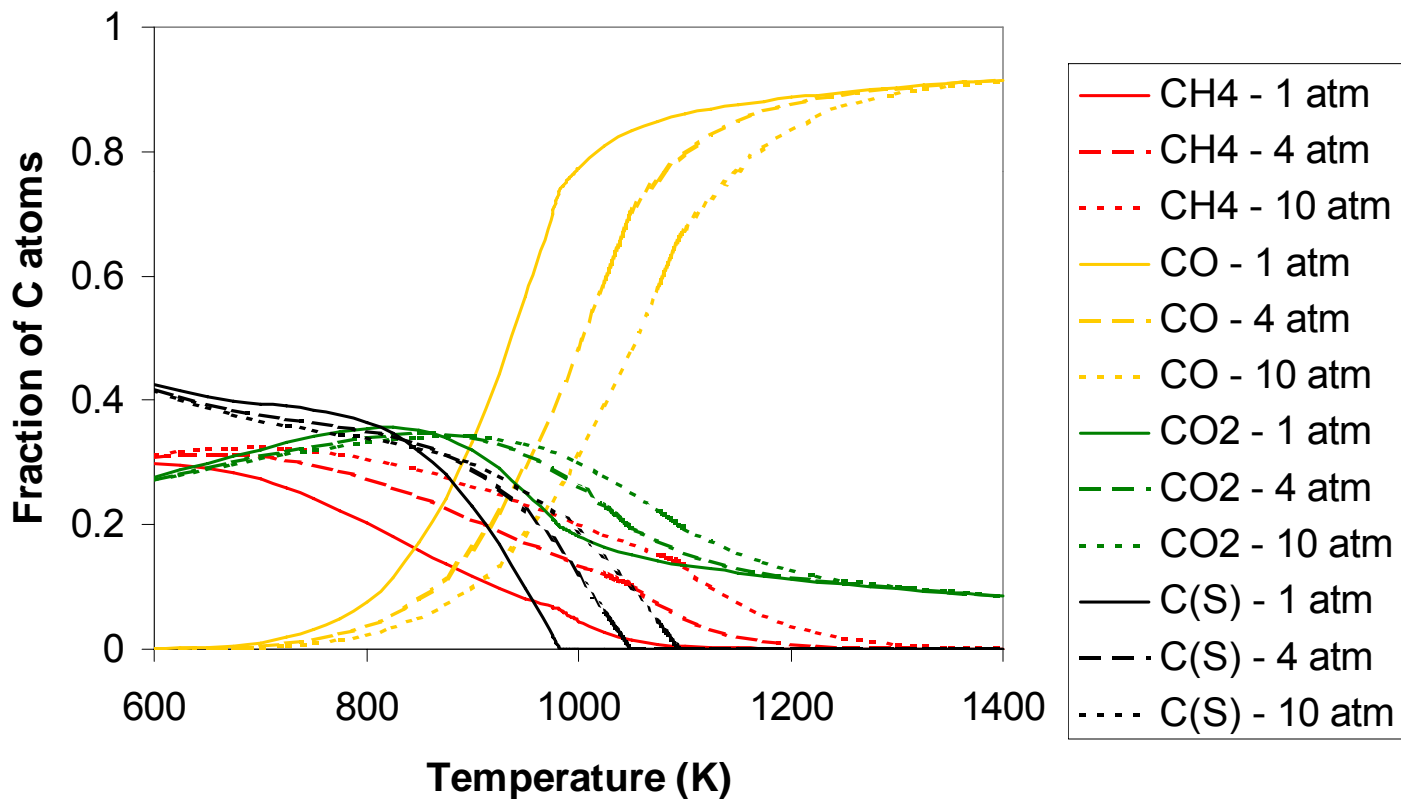
Gas-phase mole fractions



H₂O/C = 1.0, 5% char

Varying Pressure

Fraction of C atoms as CH₄, CO, CO₂, C(S)



H₂O/C = 1.0, 5% char

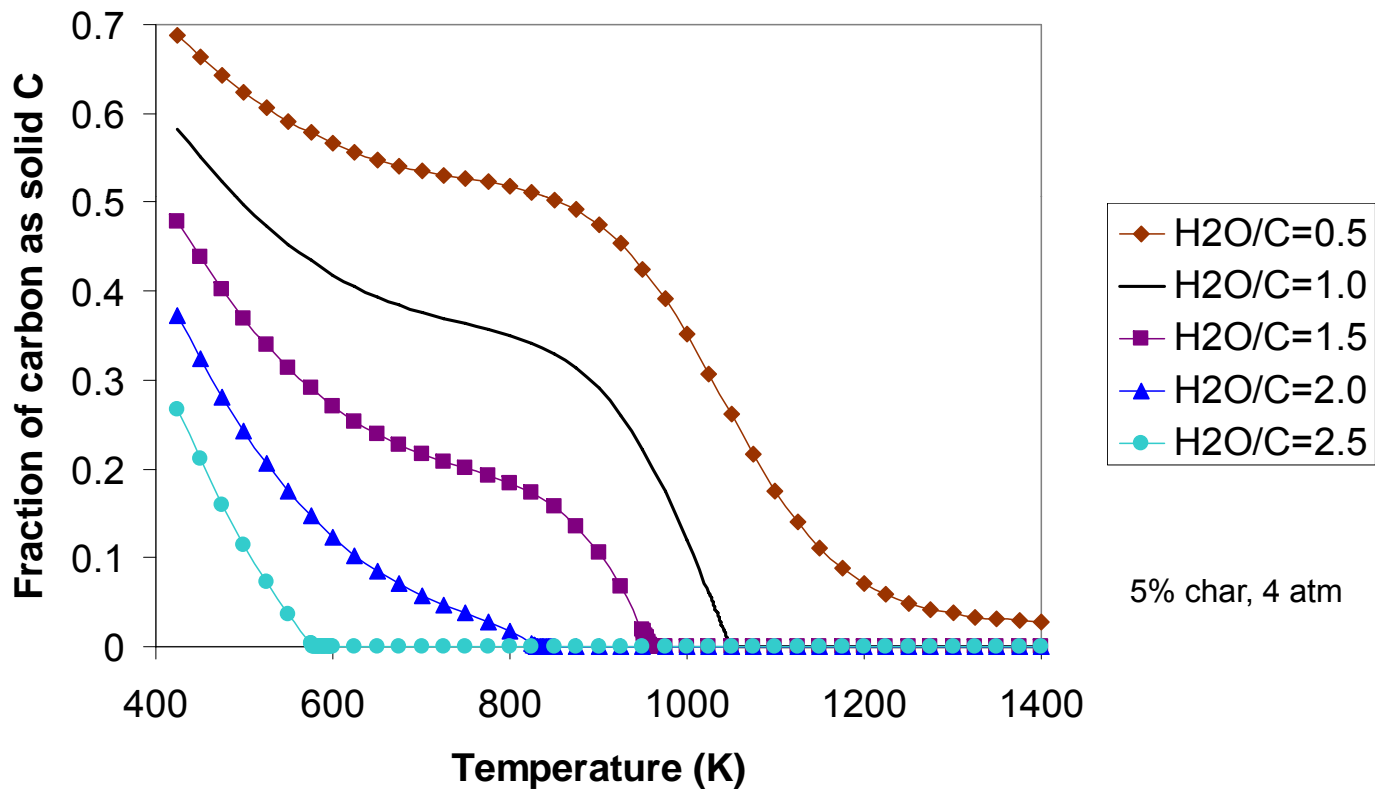
Varying H₂O/C ratio

H₂O/C ratio variation results

- Higher H₂O/C ratio (i.e., increasing steam) reduces carbon formation potential:
 - T_{dep} decreases
 - C(S) decreases
 - CO, CH₄, H₂ generally decrease
 - H₂O, CO₂ increase
- Examining fraction of C atoms distribution (instead of mole fraction) removes effects of dilution by steam
- Increased CO₂ quantities from Water Gas Shift reaction

Varying H₂O/C ratio

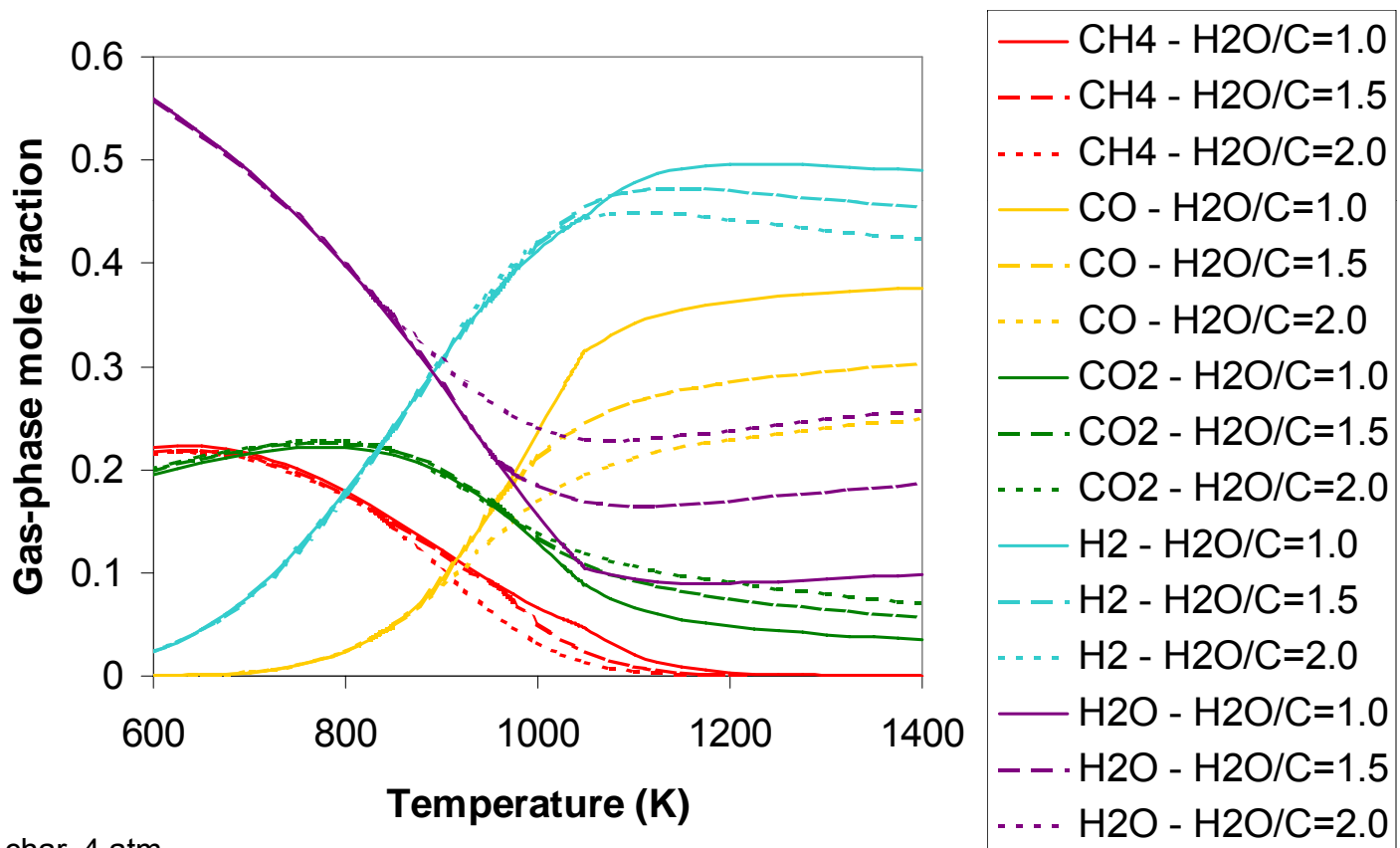
Solid carbon formation



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

Varying H₂O/C ratio

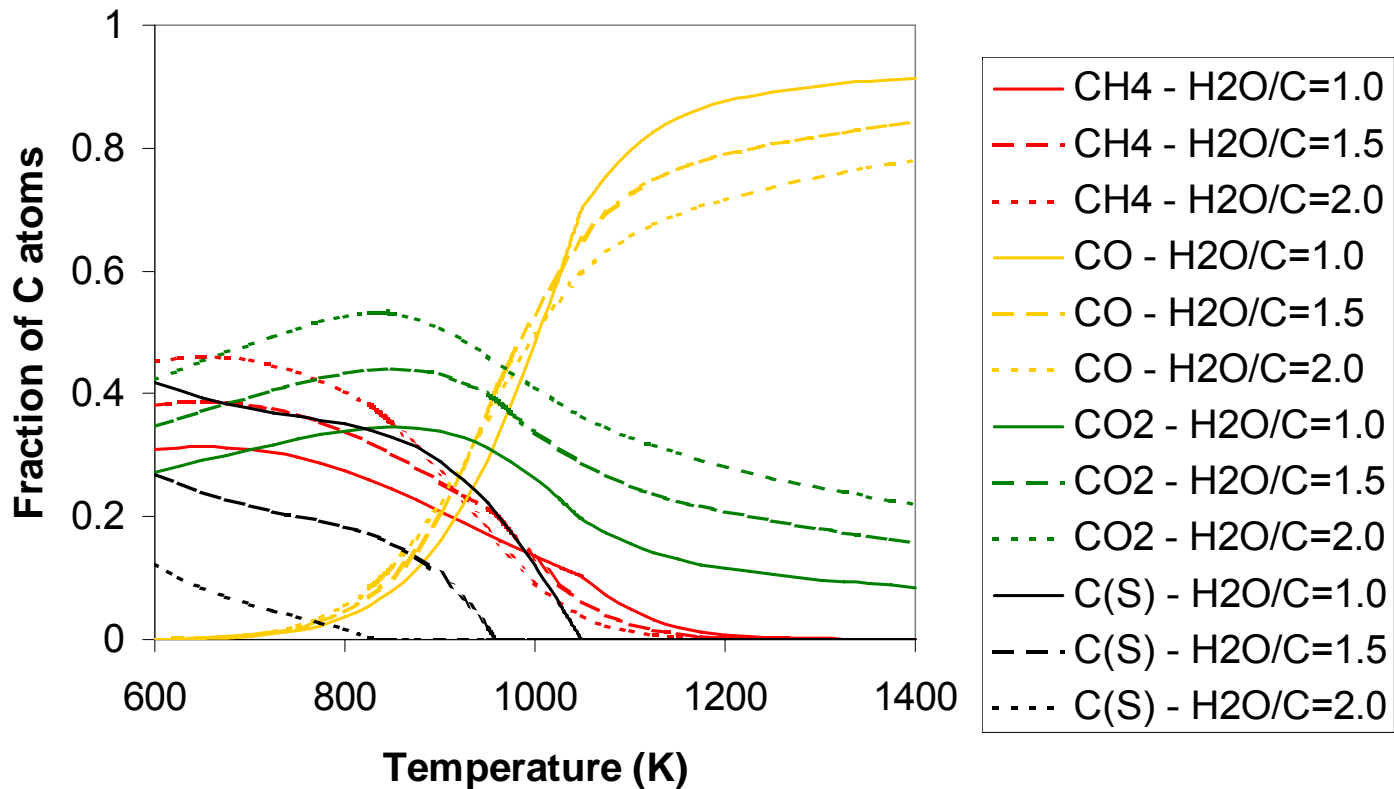
Gas-phase mole fractions



5% char, 4 atm

Varying H₂O/C ratio

Fraction of C atoms as CH₄, CO, CO₂, C(S)



5% char, 4 atm

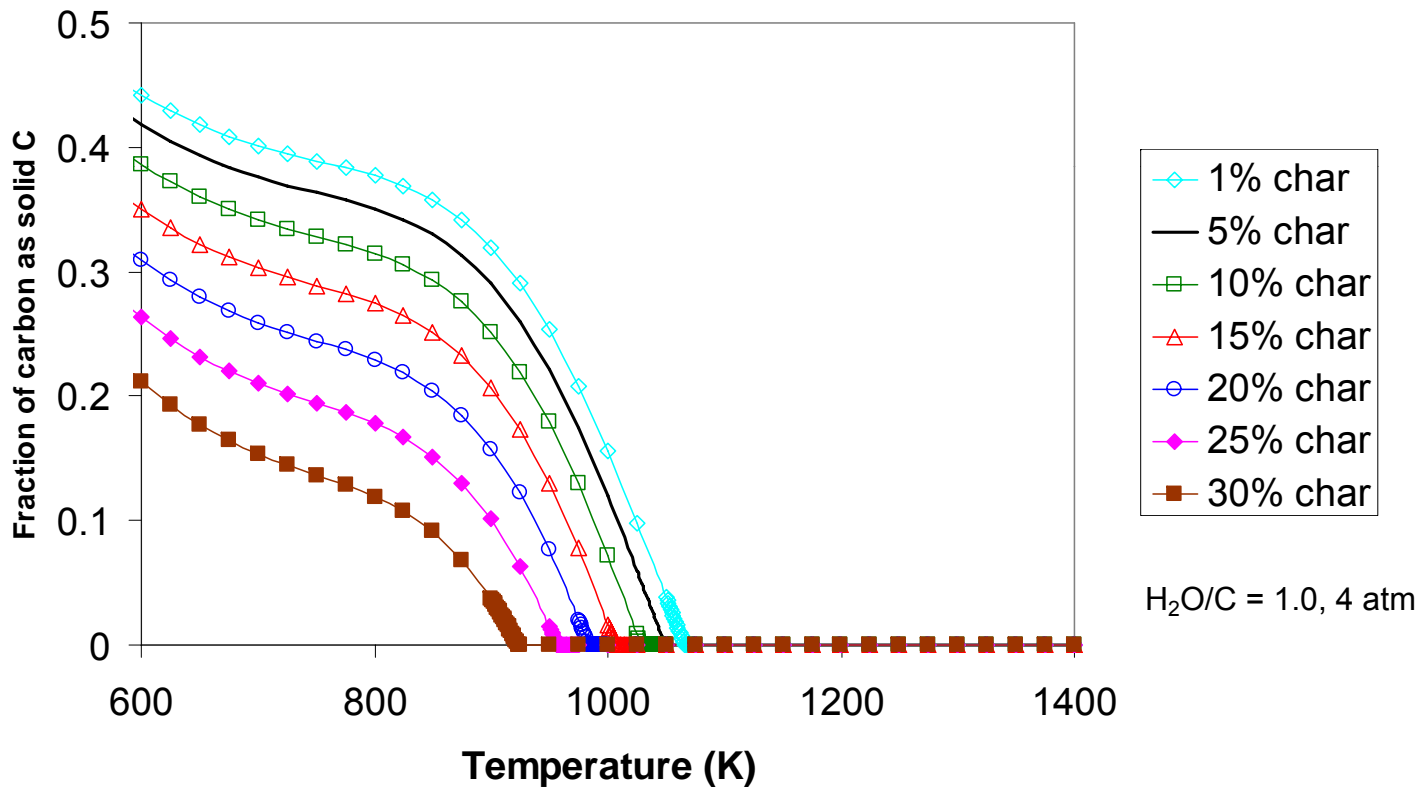
Varying % Char

% 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

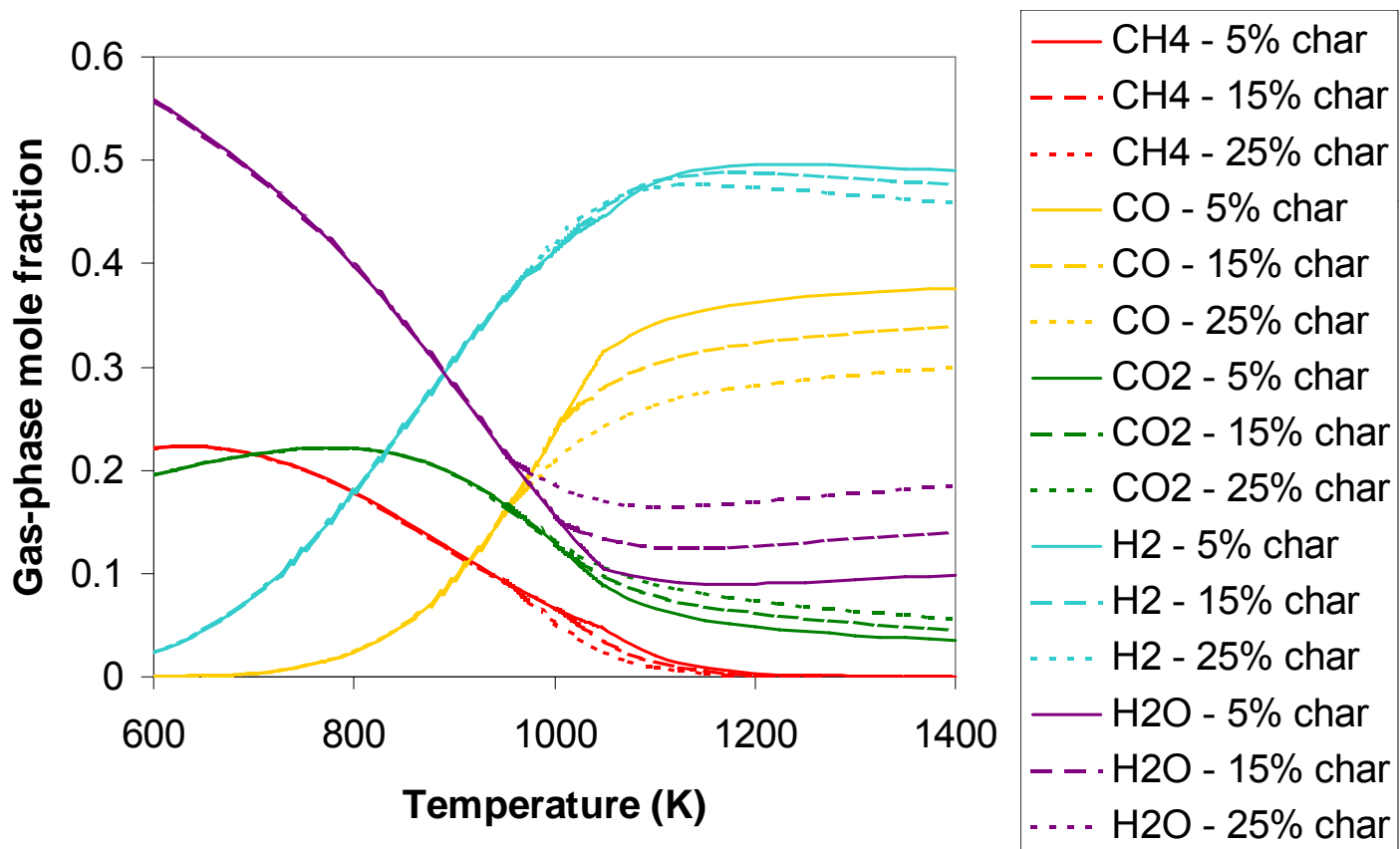
Solid carbon formation



More char removed = less carbon in system = lower T_{dep}

Varying % Char

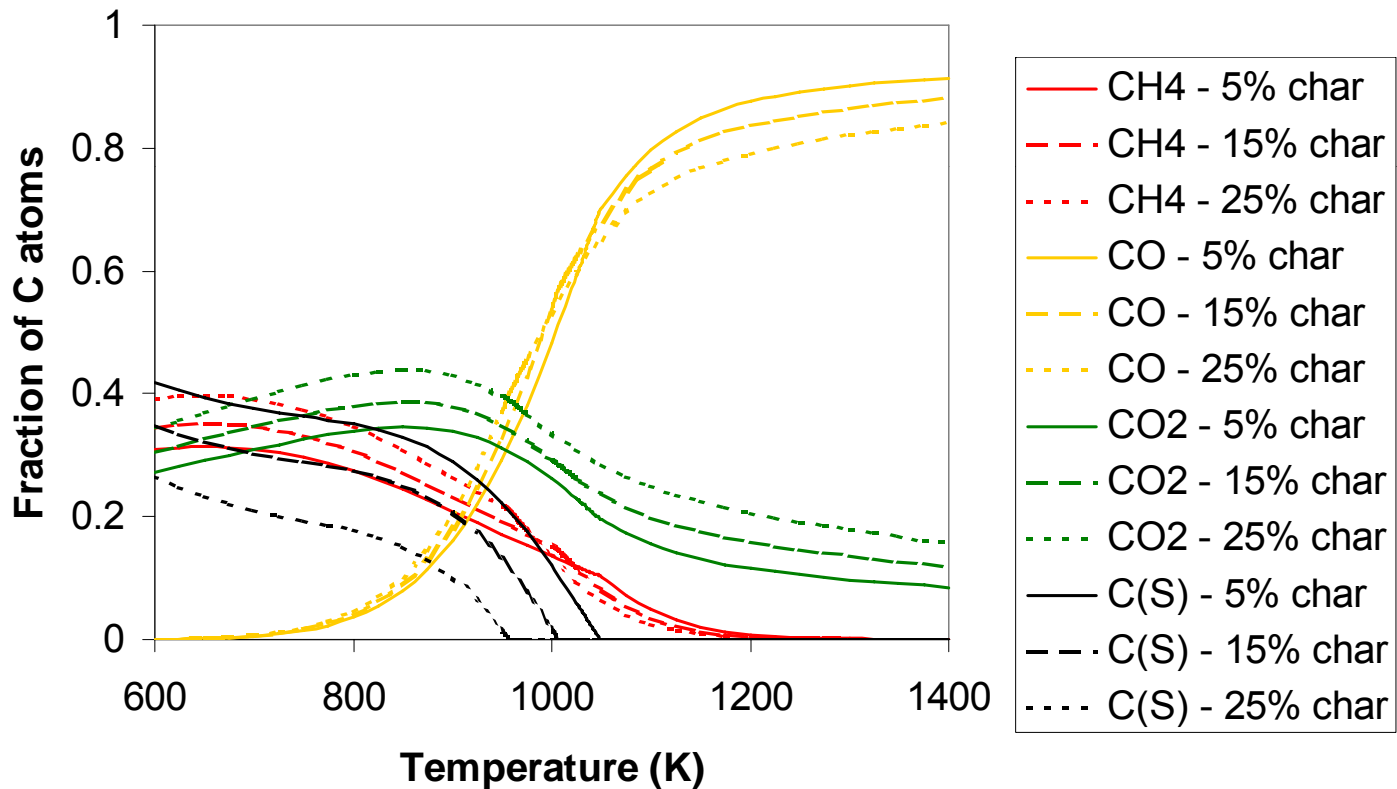
Gas-phase mole fractions



H₂O/C = 1.0, 4 atm

Varying % Char

Fraction of C atoms as CH₄, CO, CO₂, C(S)



H₂O/C = 1.0, 4 atm

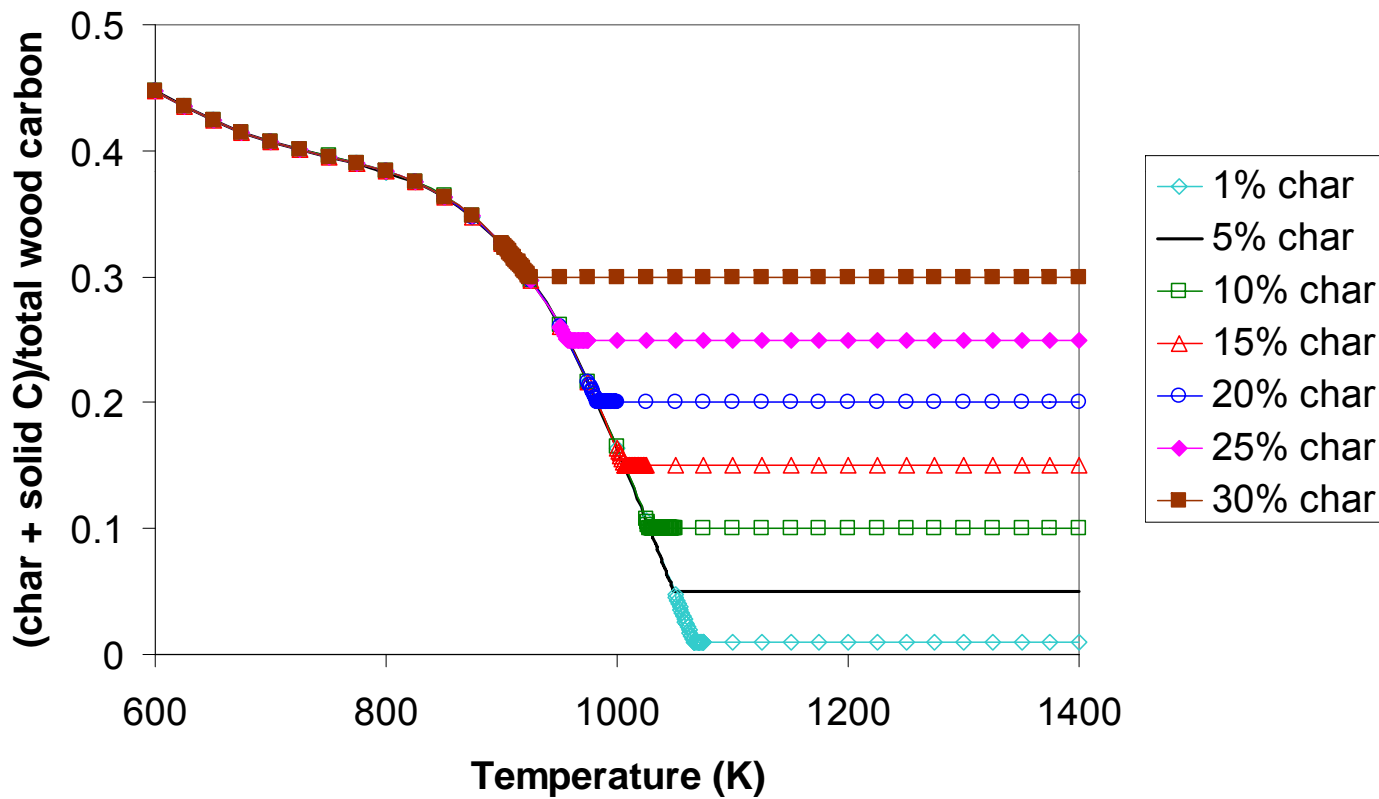
Varying % Char

% 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

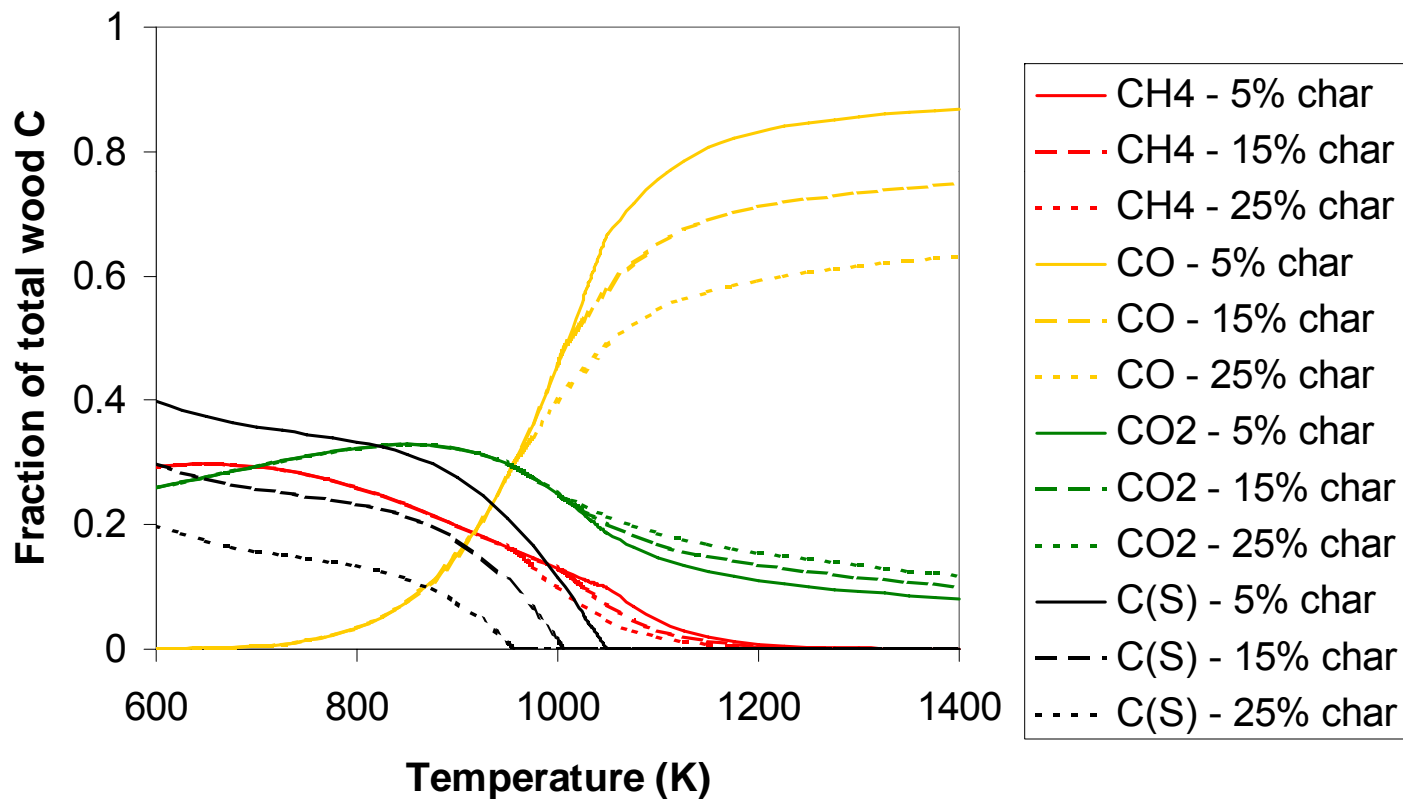
Char + C(S) trends



H₂O/C = 1.0, 4 atm

Varying % Char

Fraction of total wood C atoms (yield) as CH₄, CO, CO₂, C(S)



H₂O/C = 1.0, 4 atm

Summary / Conclusions

Summary

- T_{dep} lowered by
 - Lowering pressure
 - Increasing $\text{H}_2\text{O}/\text{C}$ ratio
 - Increasing % char formed and removed
- Low T_{dep} desired to increase temperature window for heat recovery
- Conditions which lower T_{dep} also lower $C(\text{S})$
- However, these conditions also affect gas-phase concentrations....

Summary / Conclusions

Summary (continued)

- Desired products (CO, H₂) changed by conditions lowering T_{dep}:
 - Lower pressure *increases* CO, H₂
 - Increased H₂O/C *decreases* CO, H₂
 - Increasing % char also *decreases* CO, H₂
 - Effect on CO₂, H₂O opposite to that of CO, H₂
- CH₄ (not desired) also affected by conditions lowering T_{dep}:
 - Lower pressure *decreases* CH₄
 - Increased H₂O/C *decreases* CH₄ (at higher values of T)
 - Increasing % char also *decreases* CH₄

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