The Effects of Increased Pressure on the Reaction Kinetics of Biomass Pyrolysis and Combustion

Charles Churchman, P.E.
Stephanie England, E.I.T.
International Applied Engineering, Inc.
Marietta, Georgia 30062
(770) 977-4248
Cgc@iaeinc.com
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Overview

- Purpose: Determine Effects of Increased Pressure on the reaction rates of Biomass Pyrolysis & Combustion
- Objective: Reduce the fixed capital costs for biofuels plants by increasing their operating pressures
- Advantages/Disadvantages of Increased Pressure Effects
- Combustion Reaction Kinetics vs. Pyrolysis Reaction Kinetics
- Unusual Biomass Characteristics which affect the study of pressure on combustion and pyrolysis kinetics
- The potential reduction in equipment sizes with currently known information
- Conclusions

Definitions

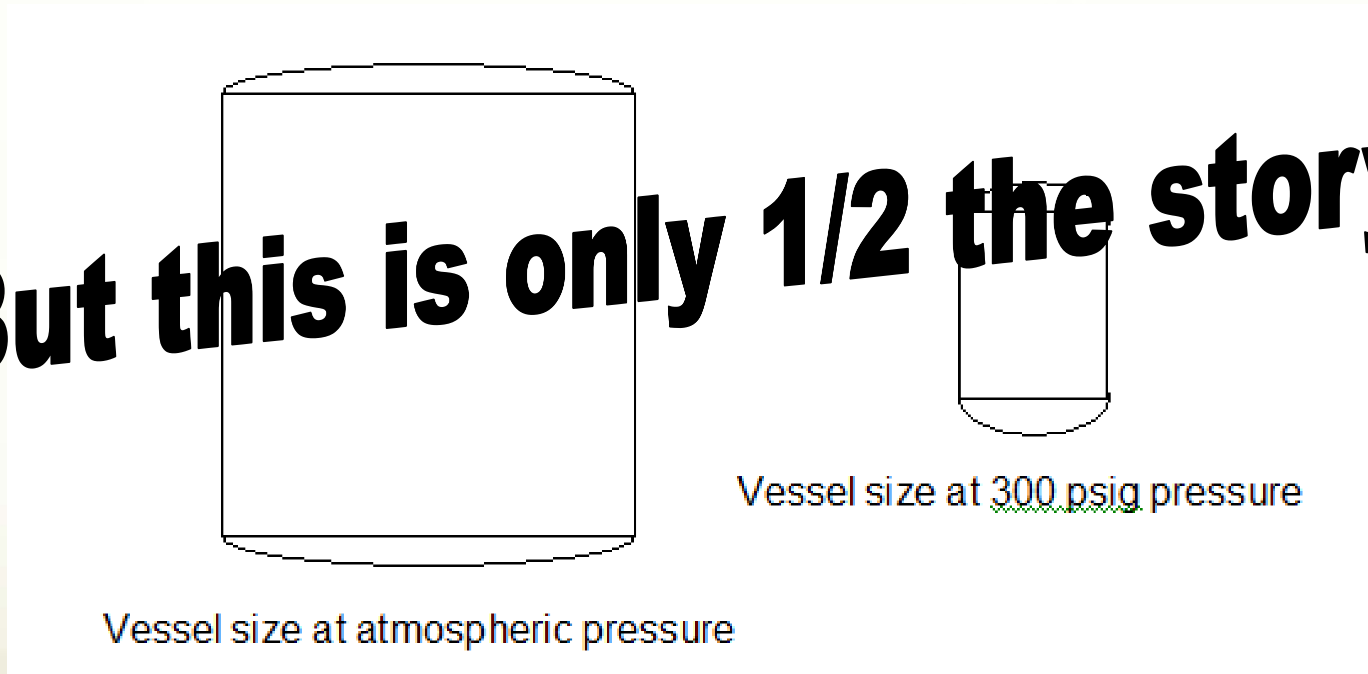
- *Combustion* – the reaction of oxygen with other materials, usually organic, with the evolution of light and heat, and the production of carbon dioxide and water.
- *Pyrolysis* – the decomposition of organic materials due to heating in the absence of oxygen
- *Kinetics* – the thermodynamic field which studies the rate of chemical reactions
- *Aspect ratio* – surface area to volume ratio of a particle undergoing combustion or pyrolysis
- *Char*- the 89-90% carbon structure left after evolution of lignins and other volatiles during pyrolysis; a series of ruptured and broken cellular tubes made up of the wood grain
- *Half life* – time it takes for ½ of a biomass sample to be combusted or pyrolyzed.

Objective

- Commercial plants should be able to produce drop-in replacement biofuels in a cost range around $ 60/bbl, assuming feedstock costs in the $ 30-50/dry ton range
- A common cost savings technique in the oil patch and chemical industries for gas-phase systems is to raise the pressure to reduce the size of vessels and piping.
  - Vessels and piping can run 30-40% of the fixed capital investment
  - Running at 10 x atmospheric pressure, at a straightforward ratio, the volumes required drop nearly by a factor of ten. (But wait – there's more!)
- **Reduce Fixed Capital Costs by at least 30%**

Pressurization Advantages

- High pressure → Equipment volume reduction



But this is only 1/2 the story....

Potentially Lower Capital Cost

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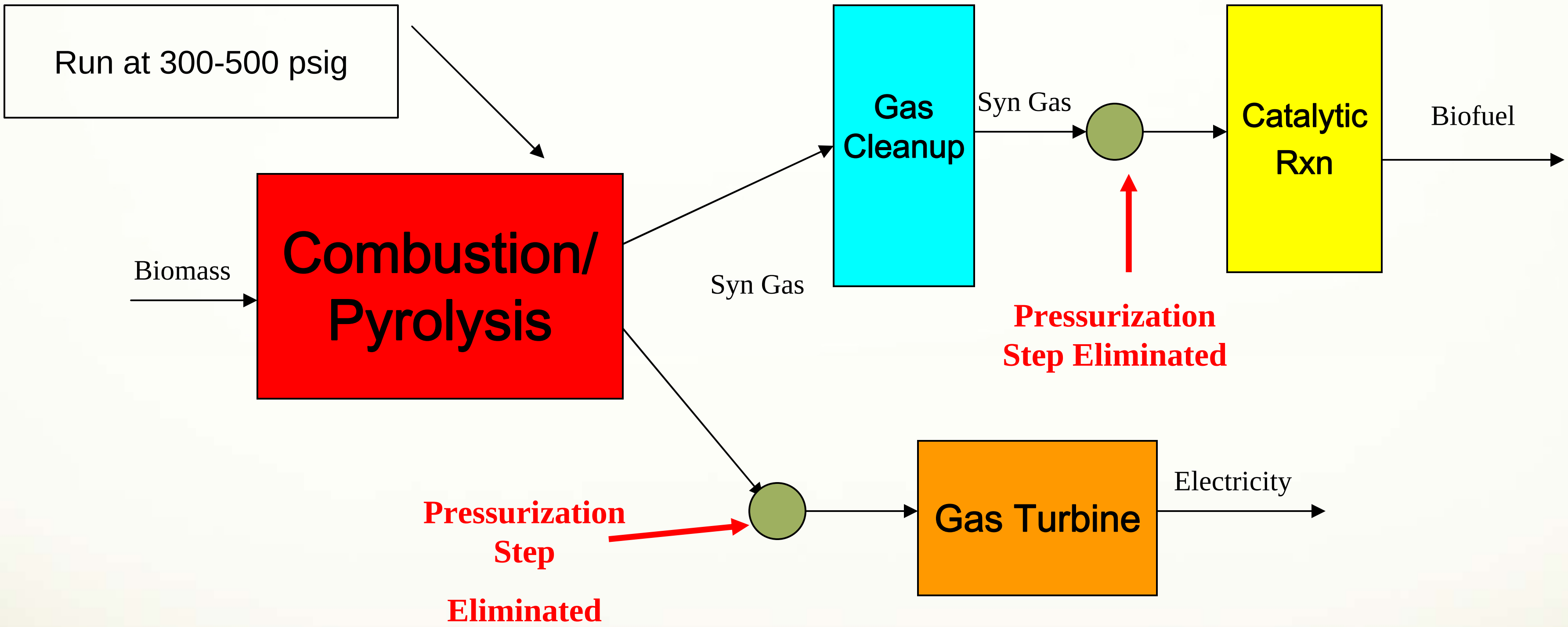
Increased Reaction Rates also Reduce Reactor Sizes

- Reactor sizing is a function of reaction rate, residence time, and approach to equilibrium. Pyrolysis reactions do not reach equilibrium quickly in the gas phase.
- At the same pressure, a faster reaction rate requires less residence time, and thus a smaller vessel.
- Thus, a faster reaction rate resulting from increased pressure has two multiplying factors to further reduce equipment sizes:
  - Higher pressure by volume reduction
  - Lower residence times by faster reaction rates
- The combination reduces the volume by MORE than the pressure ratio.

Another Pressurization Advantage



If combustion/pyrolysis is pressurized:

Eliminates Costly Downstream Compression Steps

Hydrogen impact on compression costs

- Biomass synfuels contain lots of hydrogen, anywhere from 15-50%.
- Hydrogen compressors are particularly expensive, due to the low density of hydrogen
- Hydrogen leakage from rotating equipment with seals can be a problem, and hydrogen flames are invisible in daylight
- The parasitic electrical load for compression is very high; it can run 10% of the produced electrical load.

Other Pressurization Advantages

- Smaller equipment sizes mean smaller surface areas for thermal heat losses
- Lower thermal heat losses yield higher internal reaction temperatures
- Higher reaction temperatures favor lower tar formation levels.
- Easier gas cleanup via larger allowable pressure drops in cyclones, filters and scrubbers
- Lower tar formation at higher pressures
- More effect latent heat recovery from water condensed from syngas

Pressurization Disadvantages

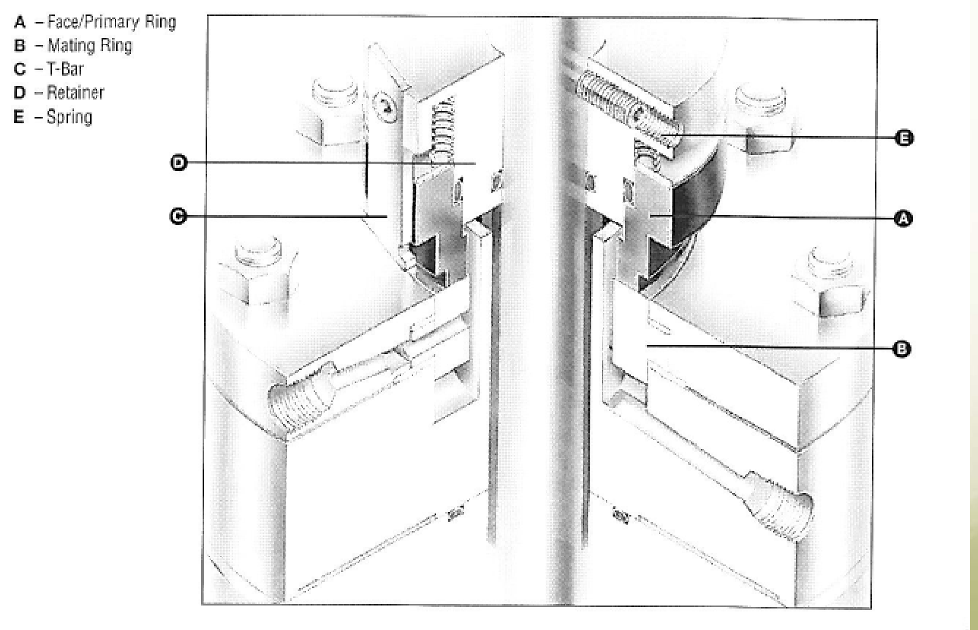
- Four main categories:
  - Mechanical Problems with equipment at elevated pressure
  - Less-than-linear reactivity increase due to pressure
  - Increased emissions
  - Possible increased methane concentrations in the syngas

Feed System Challenges

- Pyrolysis needs to remove the void space air between the biomass particles – backflush with nitrogen or steam needed.
- Nitrogen expensive, but steam has its problems:
  - Terpenes in biomass flash off with pressurized steam
  - Increased volatile losses w/increasing pressure
  - Environmental impacts for VOCs

Other Disadvantages

- Pressure sealing
  - High Maintenance
  - Expensive



John Crane Type 32 seal, good to 225 psig

Status of pyrolysis kinetics studies

- Not very much work has been done on the effects of pressure on pyrolysis kinetics
- Much more has been done on the effect of pressure on combustion kinetics
- A review of the effect of pressure on combustion kinetics can help understand what the potential impact is on pyrolysis kinetics
- More research and work on pyrolysis kinetics is warranted, and some of it will be starting soon.

New tools to study problem

- New Dimensionless numbers
  - Old tools included Reynolds number, Froude number,Prandlt number, Schmidt number
  - New tools include numbers which provide dimensionless correlations of the relative effects of heat transfer and reaction kinetics
  - Some of these are: Prater Number, Biot Number, Weisz Modulus, Thiele Modulus, and Effectiveness Factor
  - Newest CFD software combines particle gas phase fluid mechanics with reaction kinetics

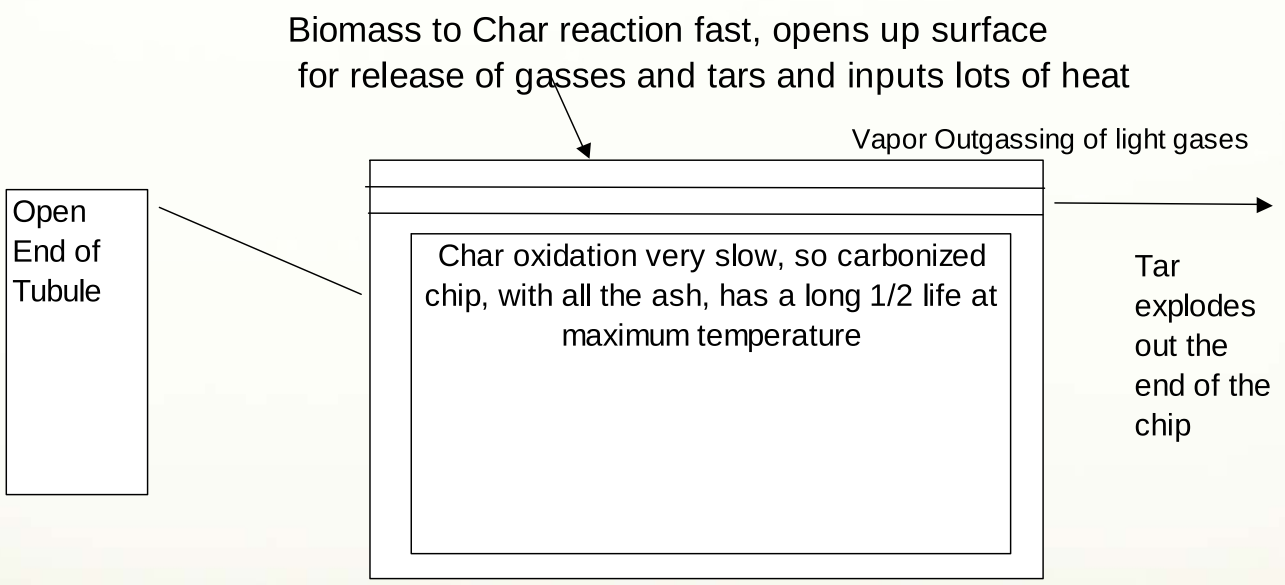
Biomass Characteristics

- Anisotropic
  - Affects combustion, pyrolysis and modeling parameters

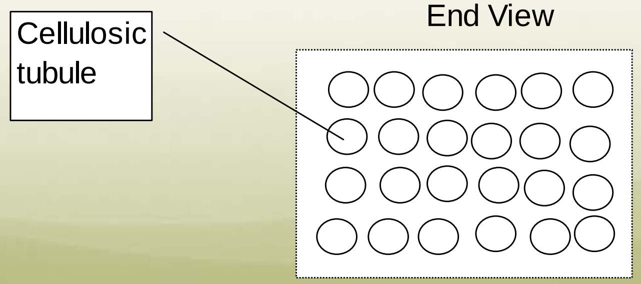
Wood Combustion Model

Wood Chip Undergoing Combustion

Side View of chip



End View



Fireside Chat

- This winter watch a fire in a fireplace for an education in combustion and pyrolysis kinetics.
- The orange flames in the fireplace are closer to pyrolysis temperatures than combustion temperatures. The cracking and popping are vapors exploding out of tubules.
- Watch a wood chip with an open end - when heated - releases a long yellow flame of tar-laden, yellow flame.
- Or get an oxy-acetylene torch, and just turn on the acetylene, then slowly turn on the oxygen.
- The smoky yellow flame will turn bright white, then get blue translucent as the incandescent carbon combusts.

Combustion Kinetics

Reaction	Reaction Rate Constant k (1/s)
biomass--> light gas	14,400
biomass--> tar	4,130,000
biomass--> char	738,000
char oxidation	301

Rate Limiting

From: Porteira et al, Combustion of Large Particles of Densified Wood, Energy & Fuels, Vol 21,No. 6, 2007, pg. 3157

Pressure Effects on Combustion

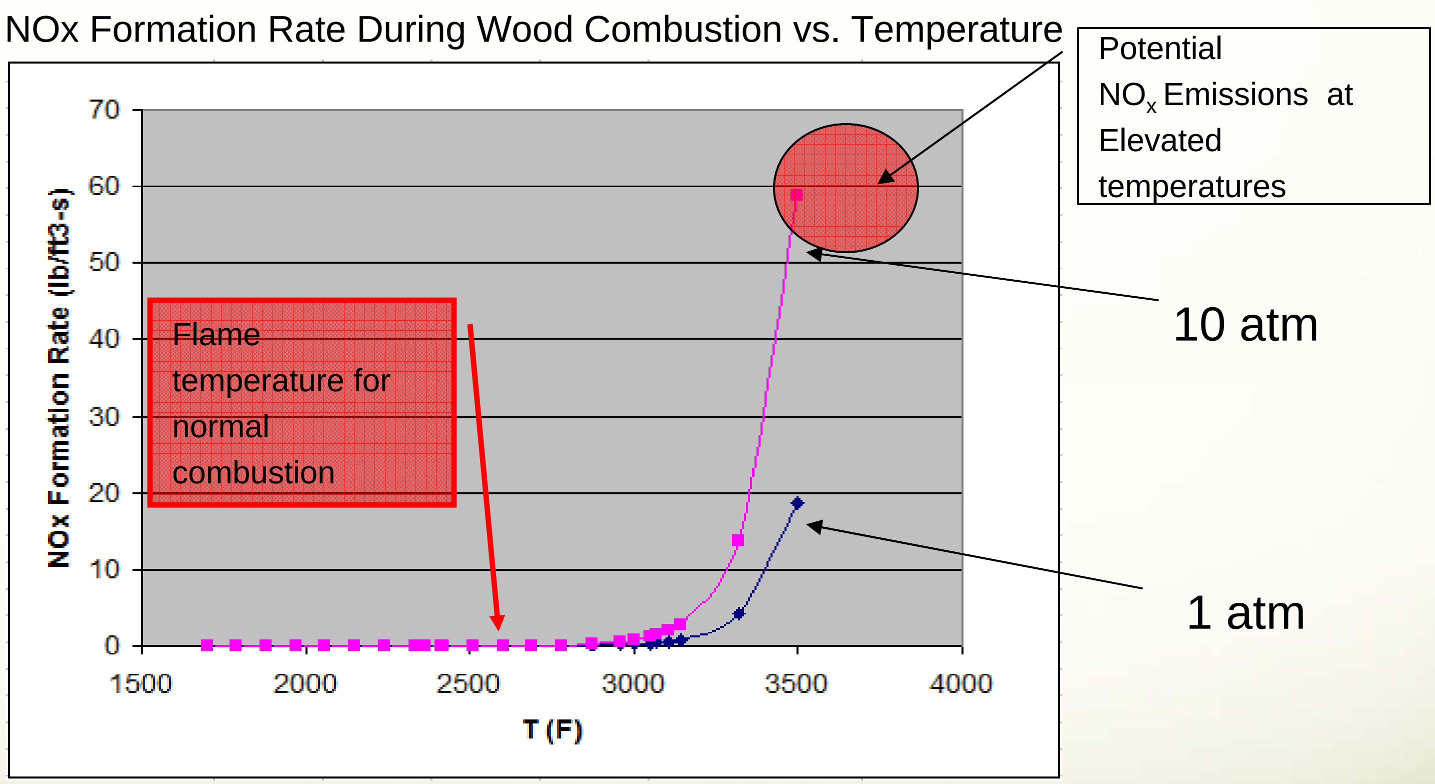
- IAE's empirical observations:

Pressure	Flame Temperature
1 atm	2500-2700 F
125-150 psig	3500-3700 F

- Results are expected
- Higher temperature indicates faster reaction rate

$$\dot{Q} = kT^4 \qquad r \propto P_{O_2}^{\ 0.5}$$

Pressure Effects on NOx formation rates



High pressure combustion may dramatically increase NOx formation

Pressure effect on combustion

- Published results indicate that the pressure effect on combustion kinetics is somewhat less than linear, and in some cases is close to the square root of the pressure:
- $$R = k(P_{O2})^{0.53\text{-}0.78}$$
  - Where:
    - R = reaction rate
    - K = constant
    - P_{O2}= partial pressure of oxygen

1992 Gravel Bed Combustion Study

$$m_{wood} = 0.95\ A_{bed} P^{0.72}\ T^{1.03}\ (air/fuel)^{-0.81} (100\text{-}\%moisture)^{0.46}$$

Where the units were:

M_{wood} = kg/hr

A_{bed} = square meters

P = atms

T = degrees Kelvin

Air = kg/hr

Fuel = kg/hr

Moisture = as-received basis

"Development of a gravel bed combustor for a solid fueled gas turbine", Ragland, et al, U of Wisconsin ME Dept., June 1992, DOE Contract No. DE-GF02-85E40735

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Pyrolysis kinetics versus combustion kinetics

- Pyrolysis occurs at much lower temperatures than combustion
  - Half Life of wood chips is much longer than in combustion, fractions of a second instead of milliseconds
  - Thermal driving force is lower, since the temperatures are lower
- More time to “distill” off the tars
- Gas phase reactions slower, less cracking of tars, and reactions do not reach equilibrium
- No free oxygen to accelerate char oxidation

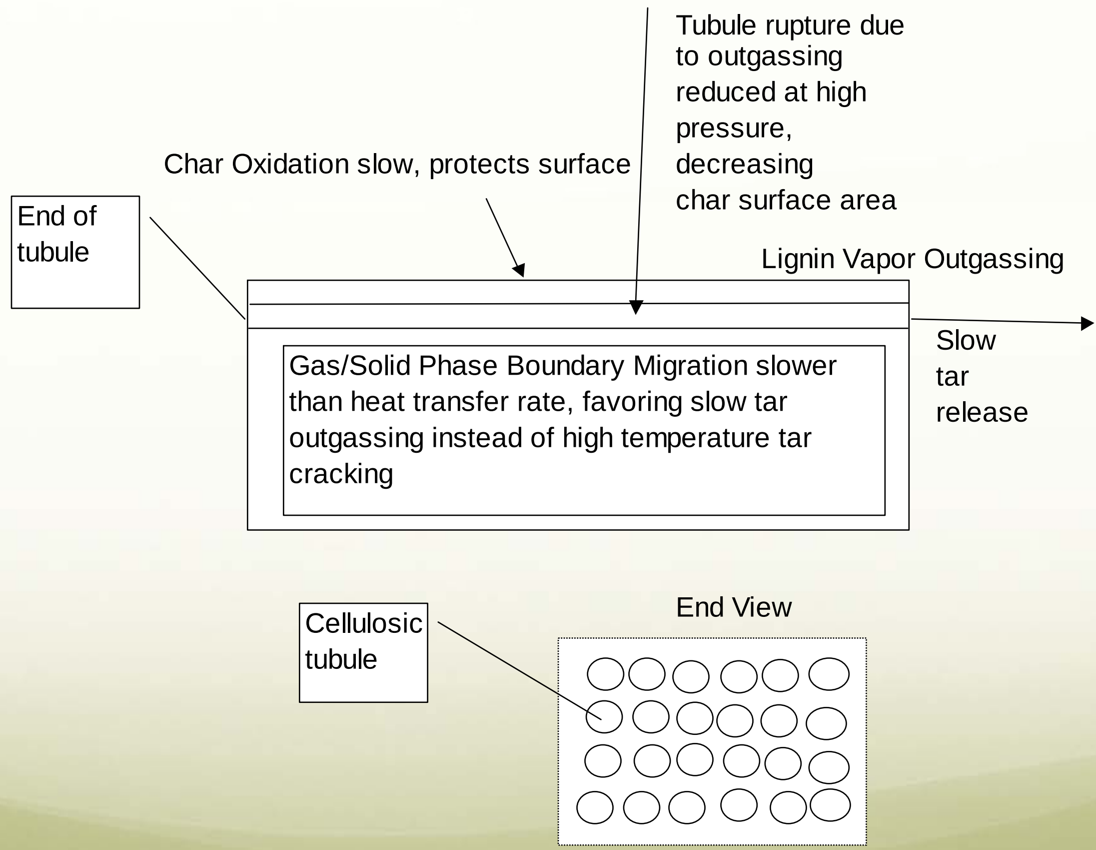
Pyrolysis versus combustion

- Reaction rates are slower
- More tars are formed in pyrolysis
- More carbon remains in the char in pyrolysis
- Pyrolysis equipment needs to be larger for the same throughput.
- NO_x emissions lower, since there is no free oxygen

Wood Pyrolysis Model

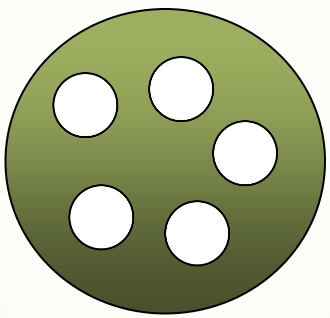
Wood Chip Undergoing Pyrolysis
at pressure

Side View



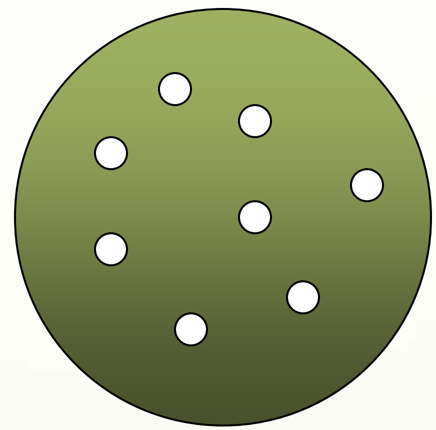
Pyrolysis Pressure Increase Disadvantages

Low Pressure Pyrolysis Char



High pore surface area(SA)
Smaller Particle

High Pressure Pyrolysis Char



Low pore SA: Gas diffusion
Larger particle: Conduction

High pressure pyrolysis ⇨ slower char reactivity

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Potential Equipment Volume Reduction Possible

Reactor: Assume operating pressure of 300 psia, versus 1 atm.

Volume reduction due to pressure change 95%

Assume reaction rate increase is $20^{0.6}$ = 6 x more!

Total volume change 20 x 6 = 120

1/120 = 0.8%. <u>Volume of the reactor < 1% that at 1 atm.</u>

Piping : diameter reduction due to volume decrease~ $(300/15)^{0.5}$= 4.5; assume pipe dia. req. ¼ the 1 atm. Case

Footprint Reduction: Unfortunately, as yet………..to be determined

Pyrolysis & Combustion Kinetics Theory

Pyrolysis Kinetics

- Not well understood area
  - Equilibrium unknown as a function of time; product gases not at equilibrium
  - Prediction of product gas composition and reactor sizing needs development
- Ongoing research on pressurized pyrolysis: Georgia Tech – pyrolysis research in operational 80 atm reactor funded by DOE(NREL).

Combustion Kinetics

- Some good data available, understanding of the full implications still have a fundamental problem with the measurement and prediction of kinetic rate equations at high pressure and temperature
- NO_x formation rates at high pressure problematic.

Conclusions

Pressurization Advantages:

- Eliminates downstream pressurization capital and operating costs(compressors)
- Huge Capital cost reduction with equipment size reduction due to pressure and faster kinetics
- Latent Heat recovery at higher temperatures

Disadvantages:

- Pressurized feed system
- Decreased char reactivity
- Not well understood effect on reaction rate
- Expensive pressure sealing, particularly with respect to hydrogen.

Conclusion: Benefits of pressurization still outweigh negative impacts; further research is still desperately needed