Iowa State University
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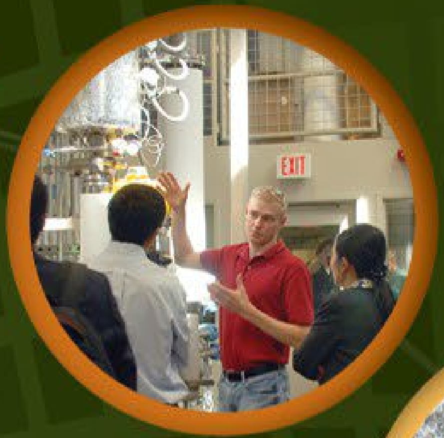

Selective Oxidation of Biochar During Autothermal Pyrolysis

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tcbiomass2022

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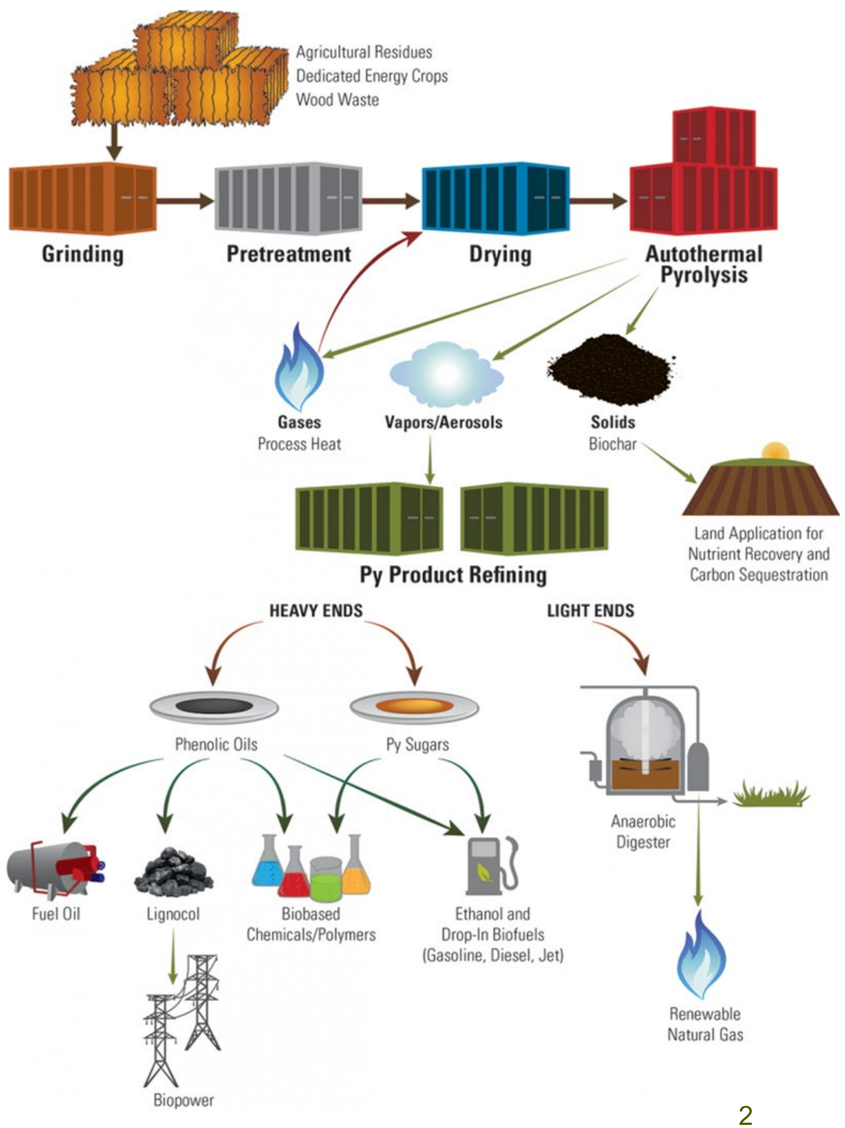
Vision for Biofuels and a Carbon Negative Economy

- The Bioeconomy Institute envisions a Carbon Negative economy through the pyrolysis of renewable resources for the production of biochar and renewable energy

- Optimize the production and recovery of pyrolytic sugars than can be upgraded to cellulosic fuels



Vision for Biofuels and a Carbon Negative Economy

- The Bioeconomy Institute envisions a Carbon Negative economy through the pyrolysis of renewable resources for the production of biochar and renewable energy

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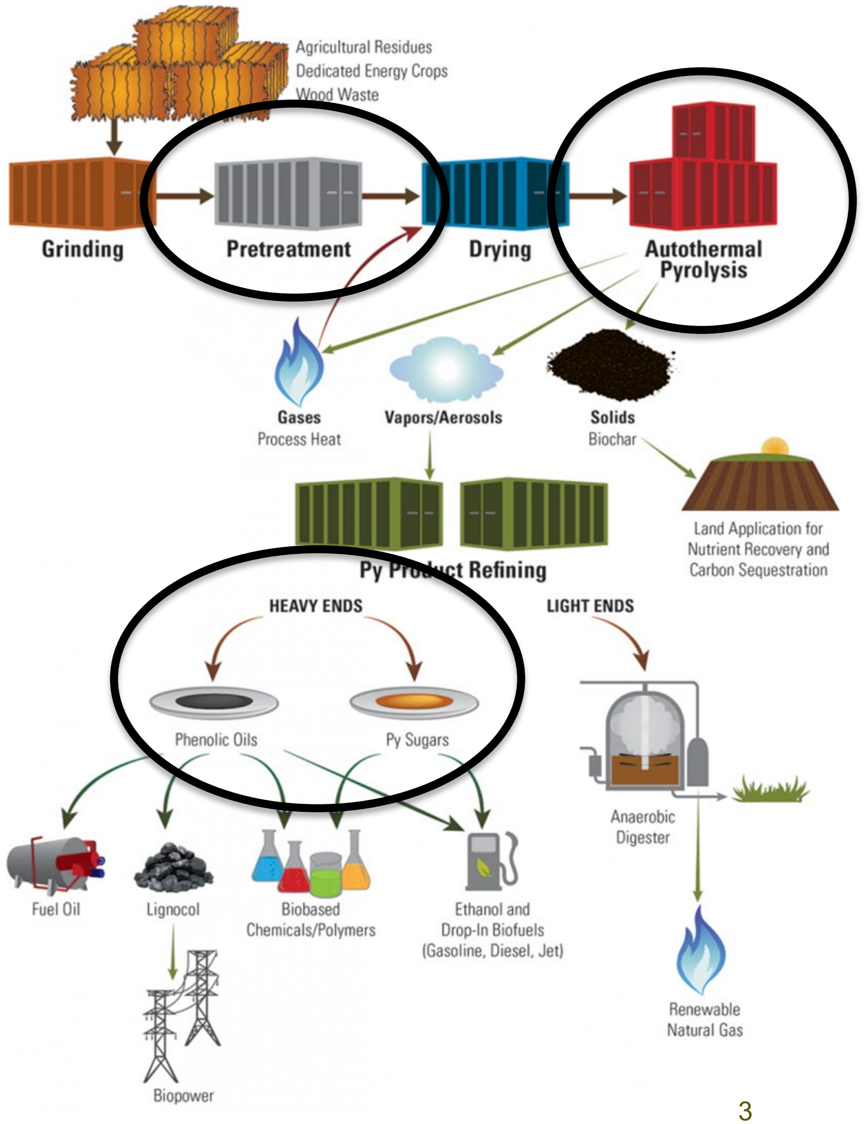
- **<u>This Discussion</u>:**

Autothermal Pyrolysis

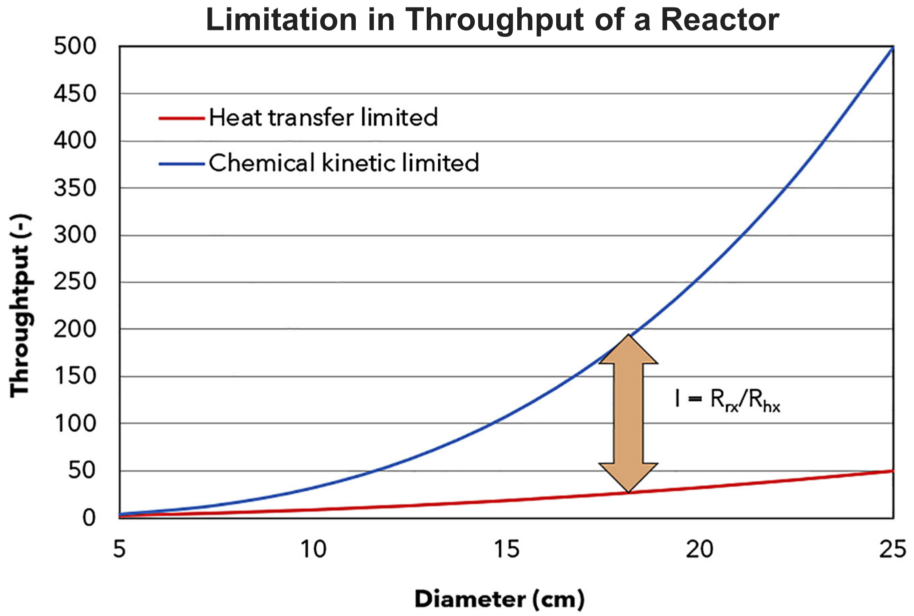
Biomass Pretreatment

Sugar Production and Recovery

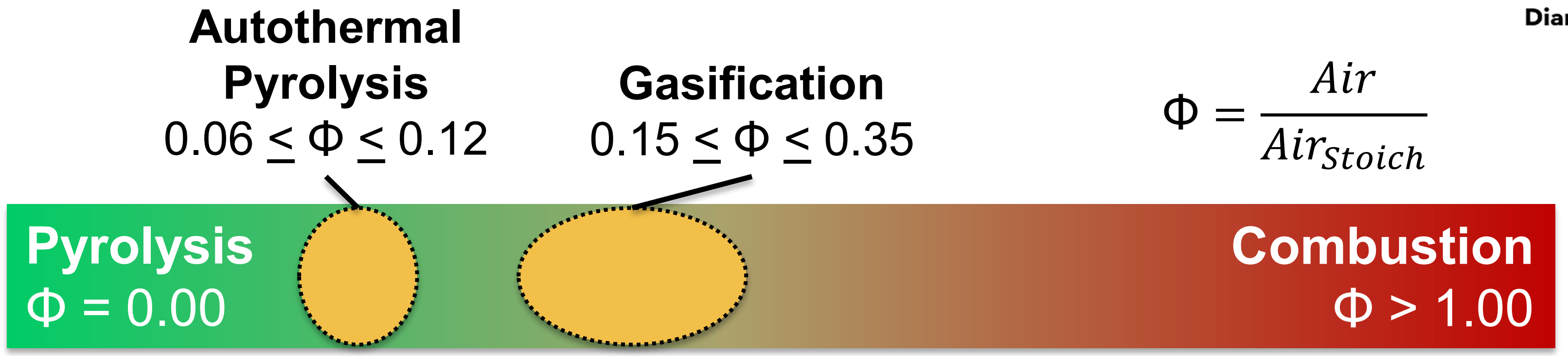


Autothermal Pyrolysis

- Conventional pyrolysis thermally decomposes organic compounds in the absence of oxygen to produce primarily liquids
  - Heat transfer limited process in overcoming endothermic reactions to provide enthalpy of pyrolysis (≈1 MJ/kg)



- Autothermal pyrolysis provides the energy for pyrolysis through partial oxidation of pyrolysis products within the reactor

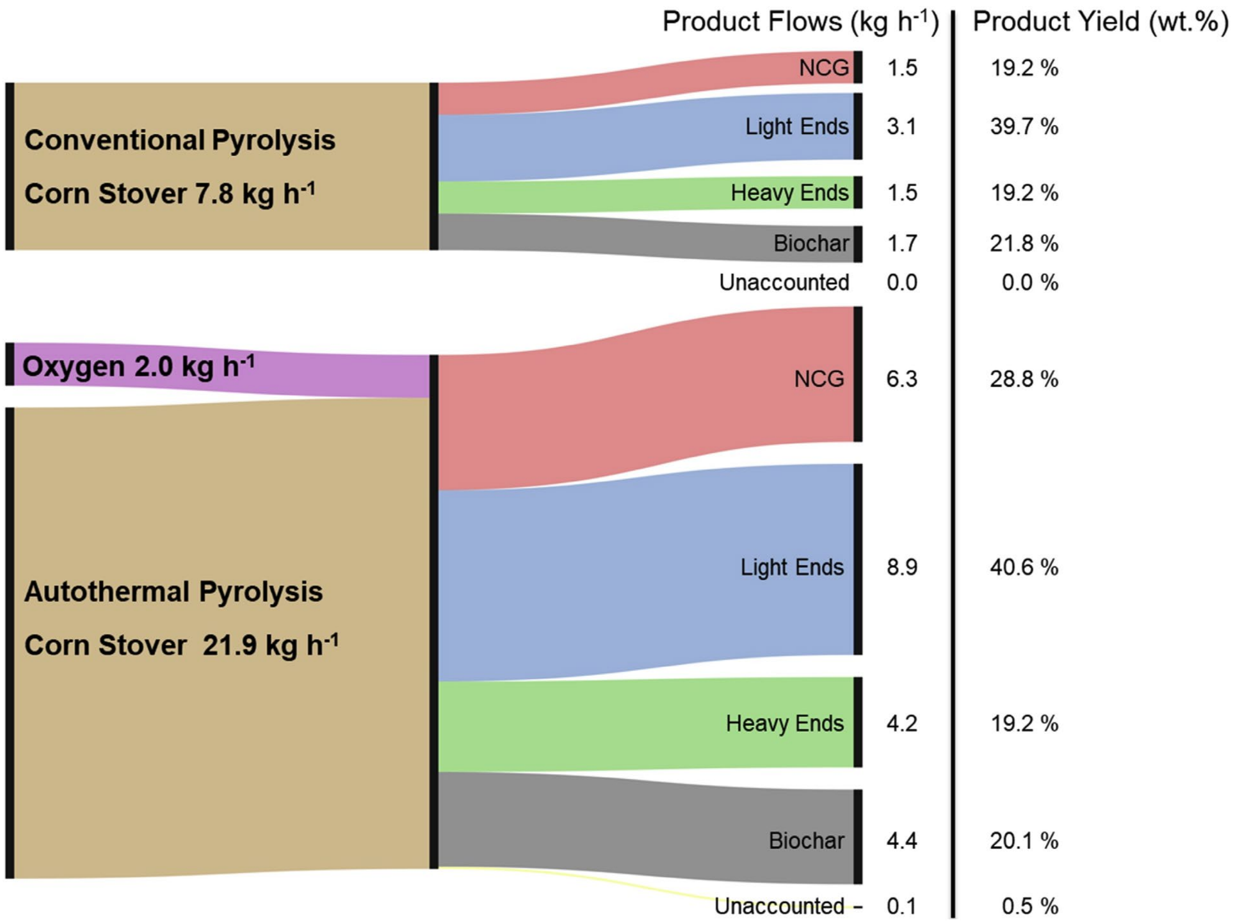


$$\Phi = \frac{Air}{Air_{Stoich}}$$

Reference: Brown, Robert C. Process intensification through directly coupled autothermal operation of chemical reactors. Joule 4.11 (2020): 2268-2289.

Three-fold Process Intensification using ATP

- Removal of heat transfer bottleneck through autothermal pyrolysis increases biomass throughput up to three-fold



<u>Autothermal Pyrolysis Advantages:</u>

- Process intensification
- Simplified reactor design
- Full-blown air fluidization
- Reduced capital costs

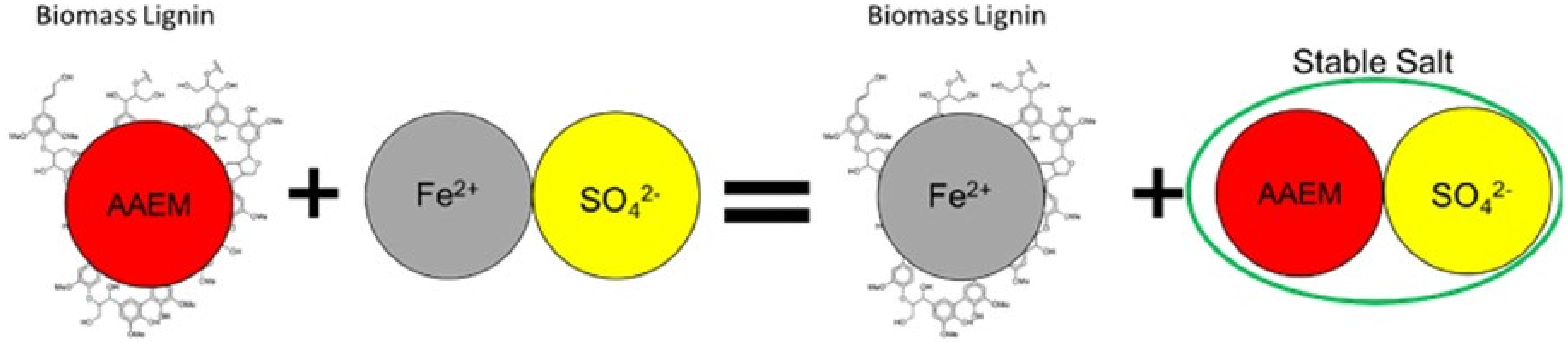
Reference: Polin, Joseph P., et al. Conventional and autothermal pyrolysis of corn stover: Overcoming the processing challenges of high-ash agricultural residues. Journal of Analytical and Applied Pyrolysis 143 (2019): 104679.

Enhanced Py Sugars with AAEM Passivation

- Passivation of alkali and alkaline earth metals (AAEM) with sulfuric acid pretreatment prevents fragmentation of pyranose and furanose rings
  - Increased sugar yields in an auger pyrolyzer at up to 250%
- Significant char agglomerations limit reactor operability
  - Passivation slows lignin decomposition resulting in melting

Char Agglomerations

- Developed ferrous sulfate pretreatment to enhance pyrolytic sugar formation and add a catalyst selective towards lignin depolymerization



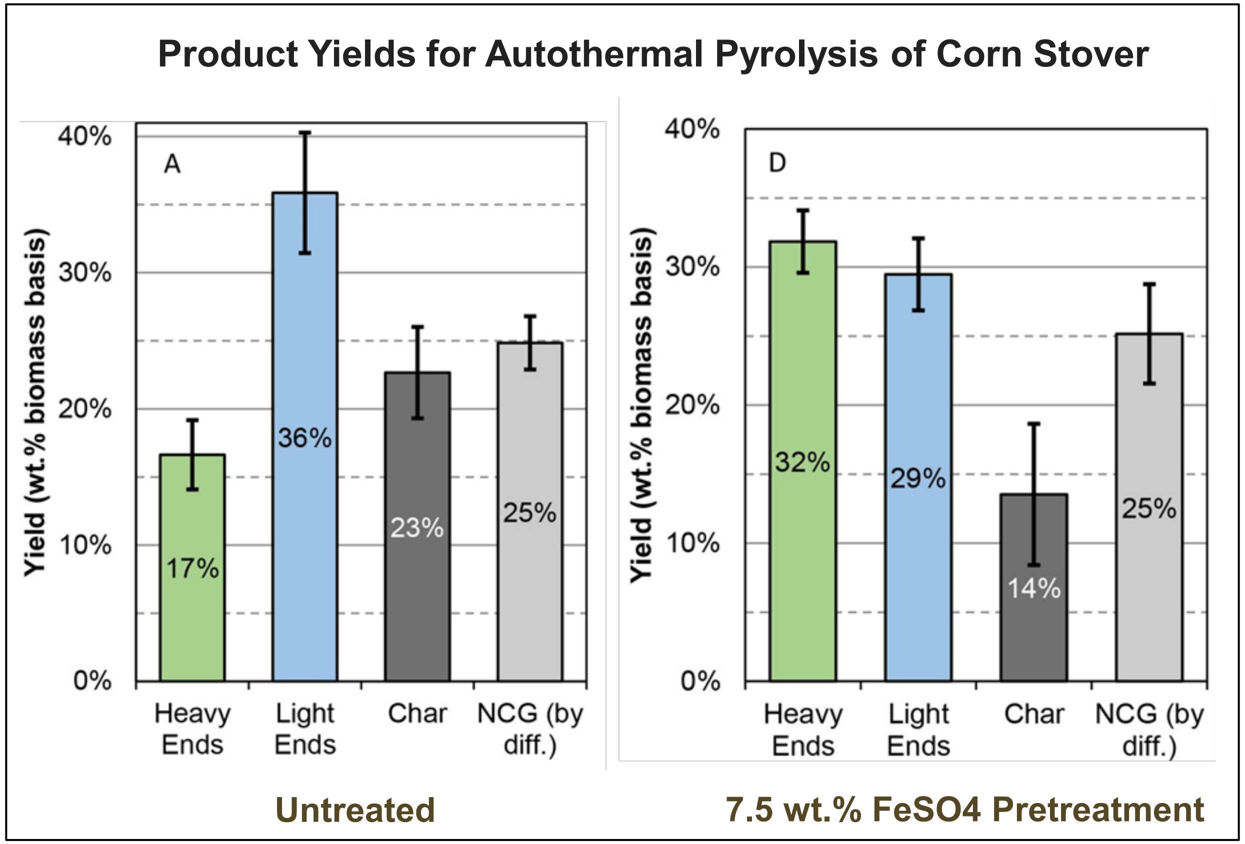
Reference: Dalluge, Dustin L., et al. Continuous production of sugars from pyrolysis of acid-infused lignocellulosic biomass. Green chemistry 16.9 (2014): 4144-4155.

Ferrous Pretreatment Enhanced Sugar Production

- Ferrous sulfate pretreatment allows for continuous operation of conventional pyrolysis with comparable yields to acid pretreatments

- Autothermal pyrolysis of ferrous sulfate pretreated corn stover achieved volumetric sugar production ≈2040 $gL^{-1}h^{-1}$
  - 32 times higher than conventional pyrolysis
  - 10 times higher than acid pretreatment

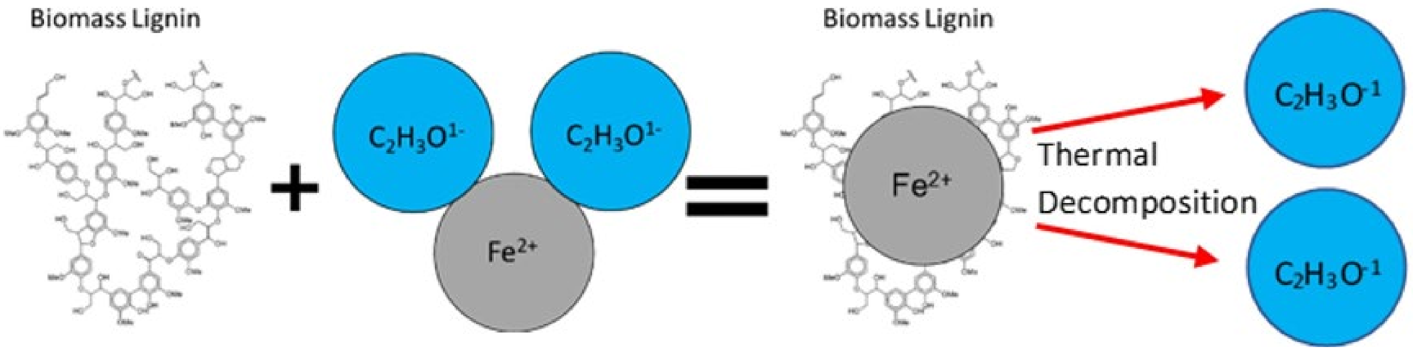
- Low ash feedstock (red oak) still produced agglomerations at increased biomass throughputs



Reference: S.A. Rollag, J.K. Lindstrom, R.C.R.C. Brown, Pretreatments for the continuous production of pyrolytic sugar from lignocellulosic biomass, Chem. Eng. J. 385 (2020) 123889.

Enhanced Oxygen Utilization with Iron Infused Char

- Increase the loading of catalytically active ferrous cations in low ash feedstocks by pretreating with a ferrous salt



- Combined ferrous pretreatment of red oak increased sugars 350% from 4.4 wt.% to 15.5 wt.% feedstock

- Preferential oxidation of iron-rich biochar
  - Reduced equivalence ratio
  - Increased CO_2 : CO production for energy efficiency

Combined Ferrous Pretreatment

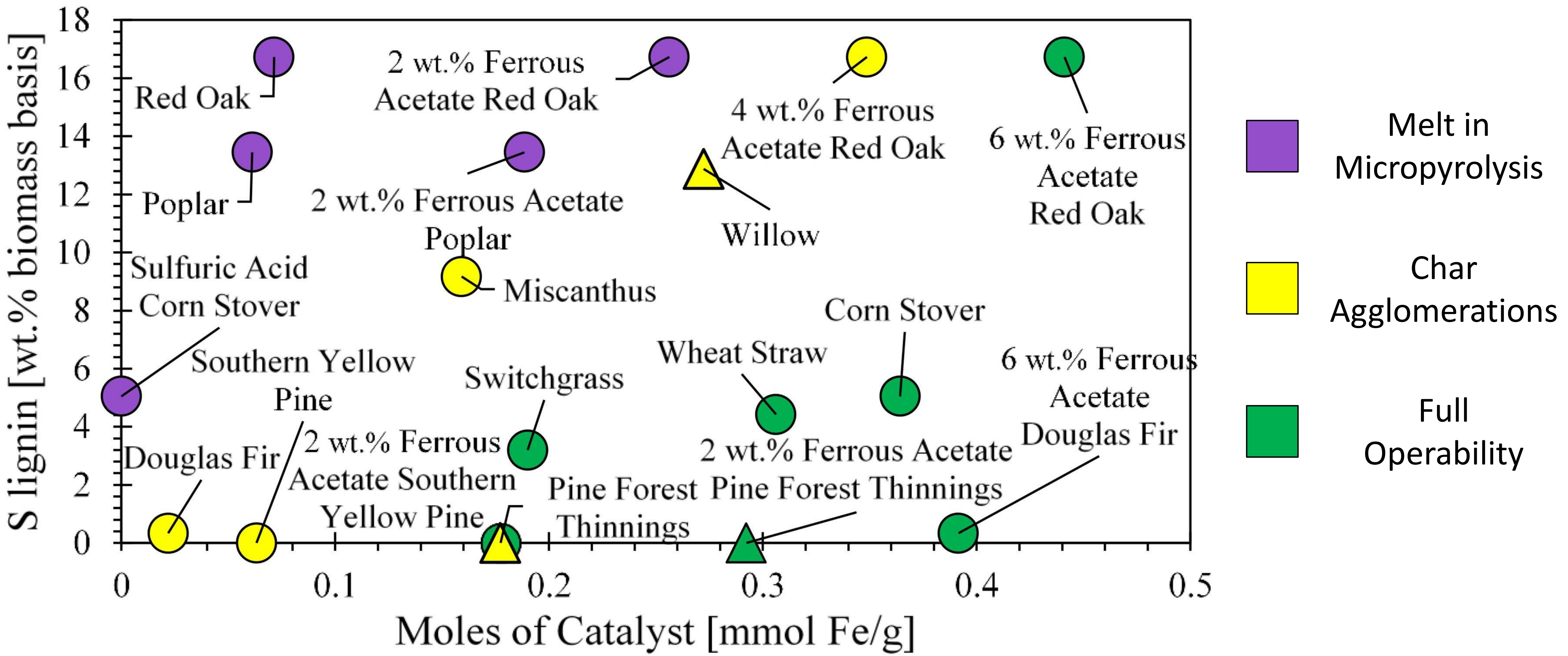
Heavy Ends
Sugars
Biomass Throughput

Light Ends
Char
Φ, Eq. Ratio

Reference: Rollag, Sean A., et al. The role of catalytic iron in enhancing volumetric sugar productivity during autothermal pyrolysis of woody biomass. Chemical Engineering Journal 427 (2022)

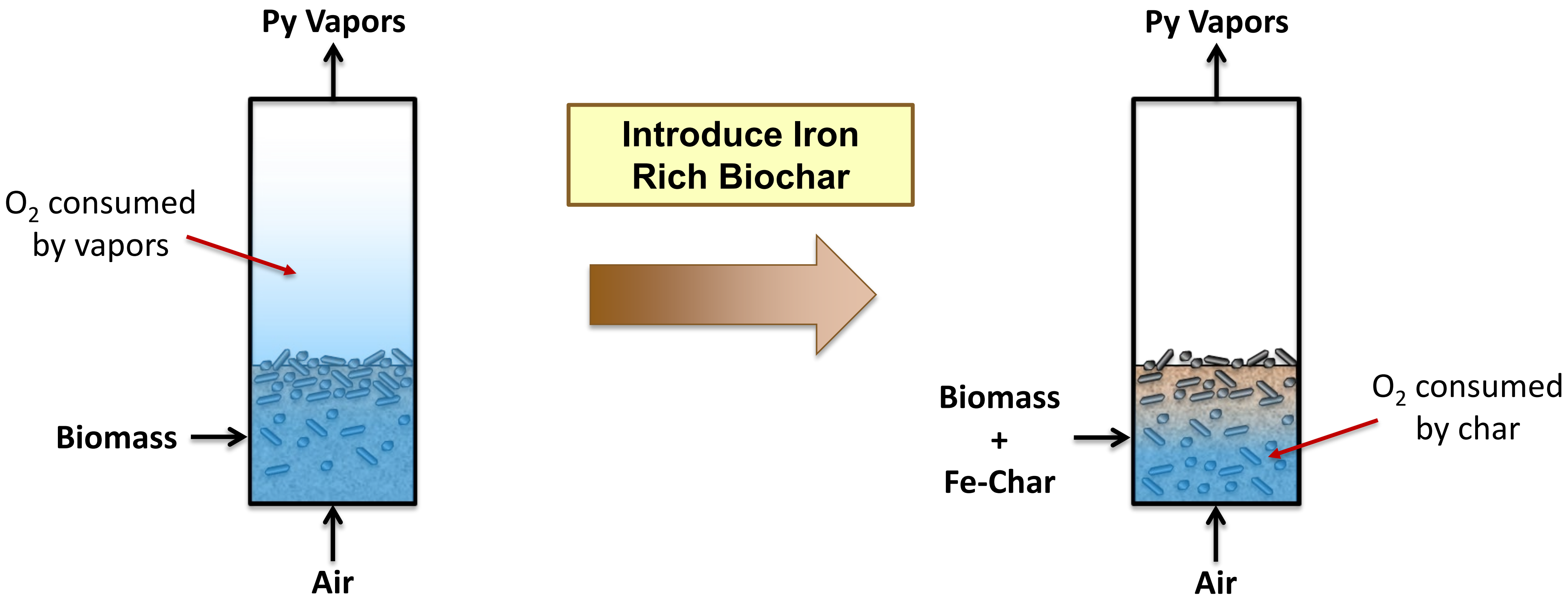
Ferrous Treatment Recipe to Continuous Operation

- Reactor operability depends on S-lignin content and catalyst loading



Proposed Selective Oxidation to Increase Py Sugars

- Introduce iron-rich char with biomass during autothermal pyrolysis to preferentially oxidize the char and provide the enthalpy of autothermal pyrolysis
- Minimize the oxidation of pyrolysis vapors to maximize sugar production



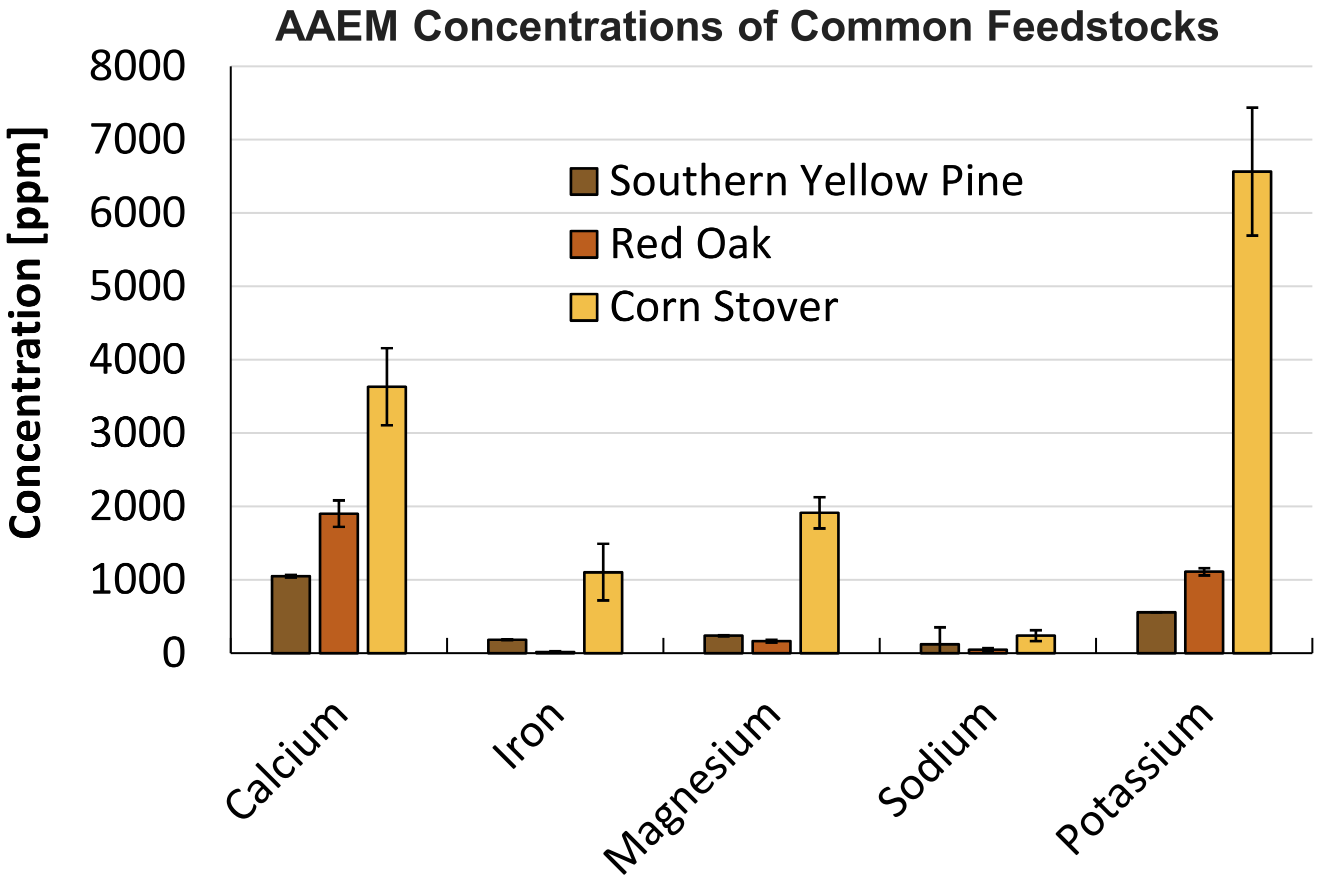
Southern Yellow Pine as Control Feedstock

- Southern yellow pine is low in ash content and S-lignin compared to other feedstocks

- Treat southern yellow pine with 2.0 wt.% Ferrous Acetate to produce ferrous-loaded char

- Co-feed 85 wt.% untreated southern yellow pine with 15 wt.% ferrous-char

- Autothermal conditions at 500^{o}C and 1 kg/hr



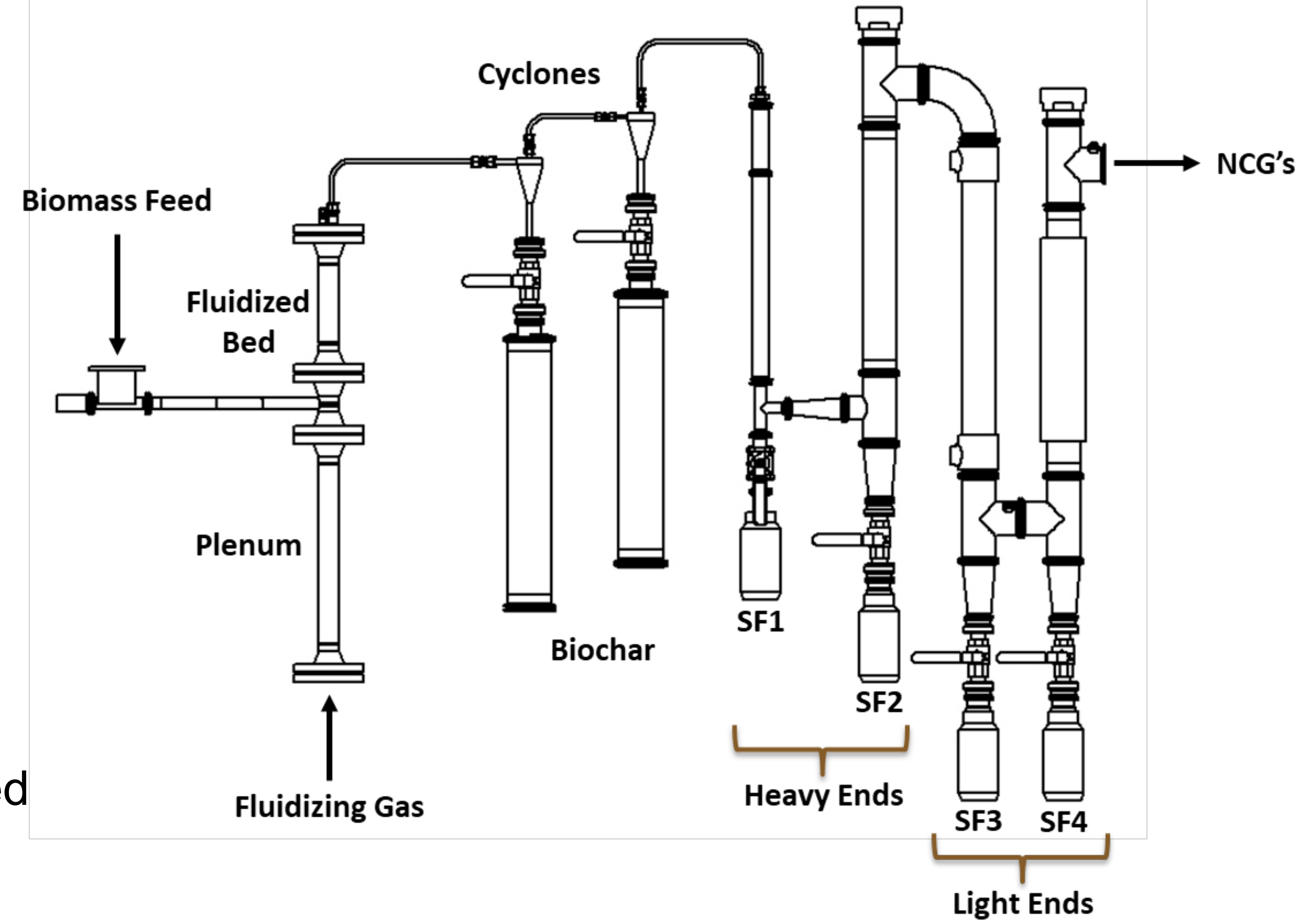
Continuous Production at the Laboratory Scale

Fluidized Bed Reactor:

- 3.81 cm (1.5 inches)
- Silica sand bed
- Conventional → N_2
- Autothermal → Air + N_2

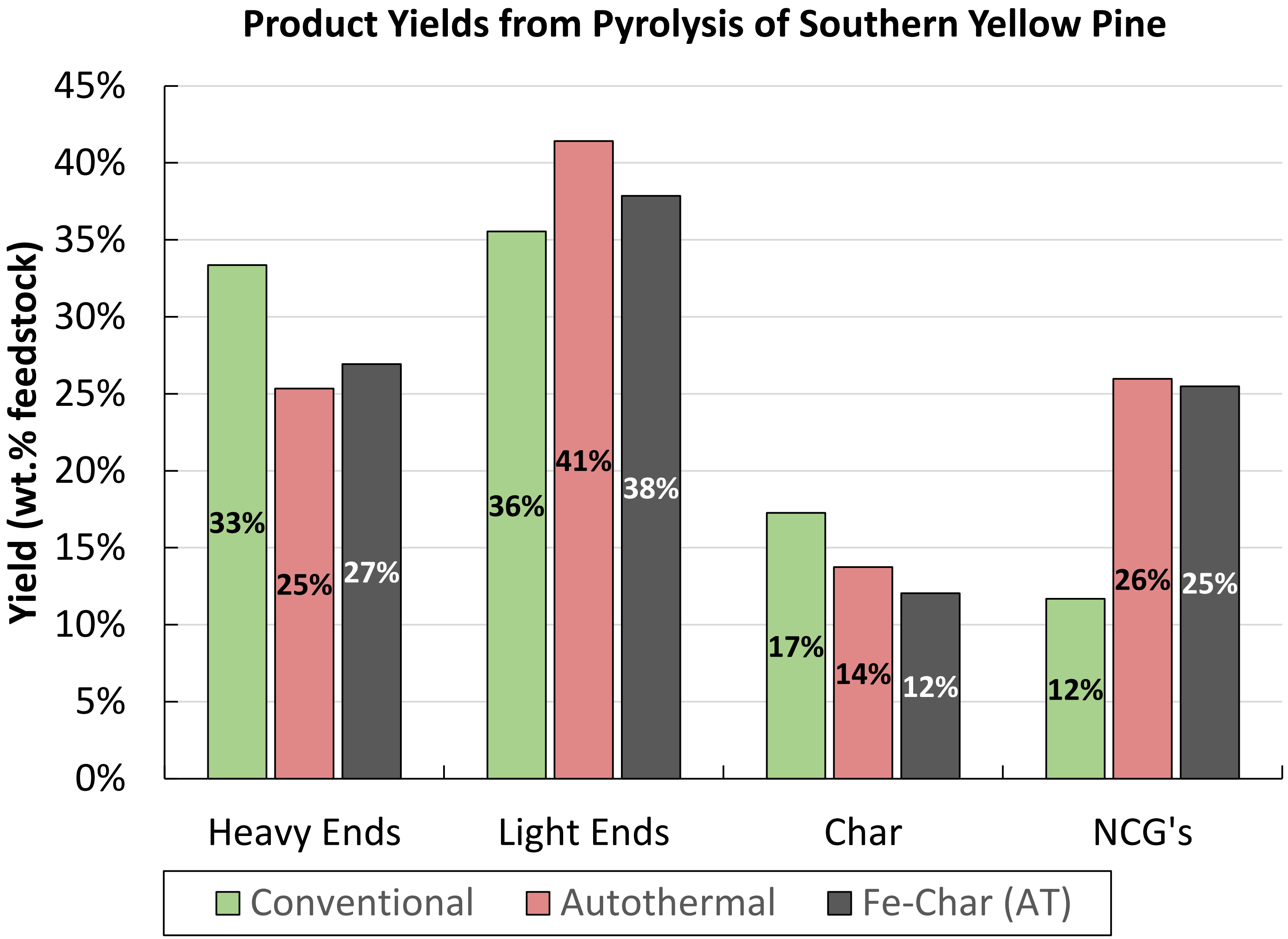
Collection System:

- Char removed via cyclones
- Hot condenser (SF1)
- Hot ESP (SF2)
- Cold Condenser (SF3)
- Cold ESP (SF4)
- Noncondensable gases quantified using micro-GC



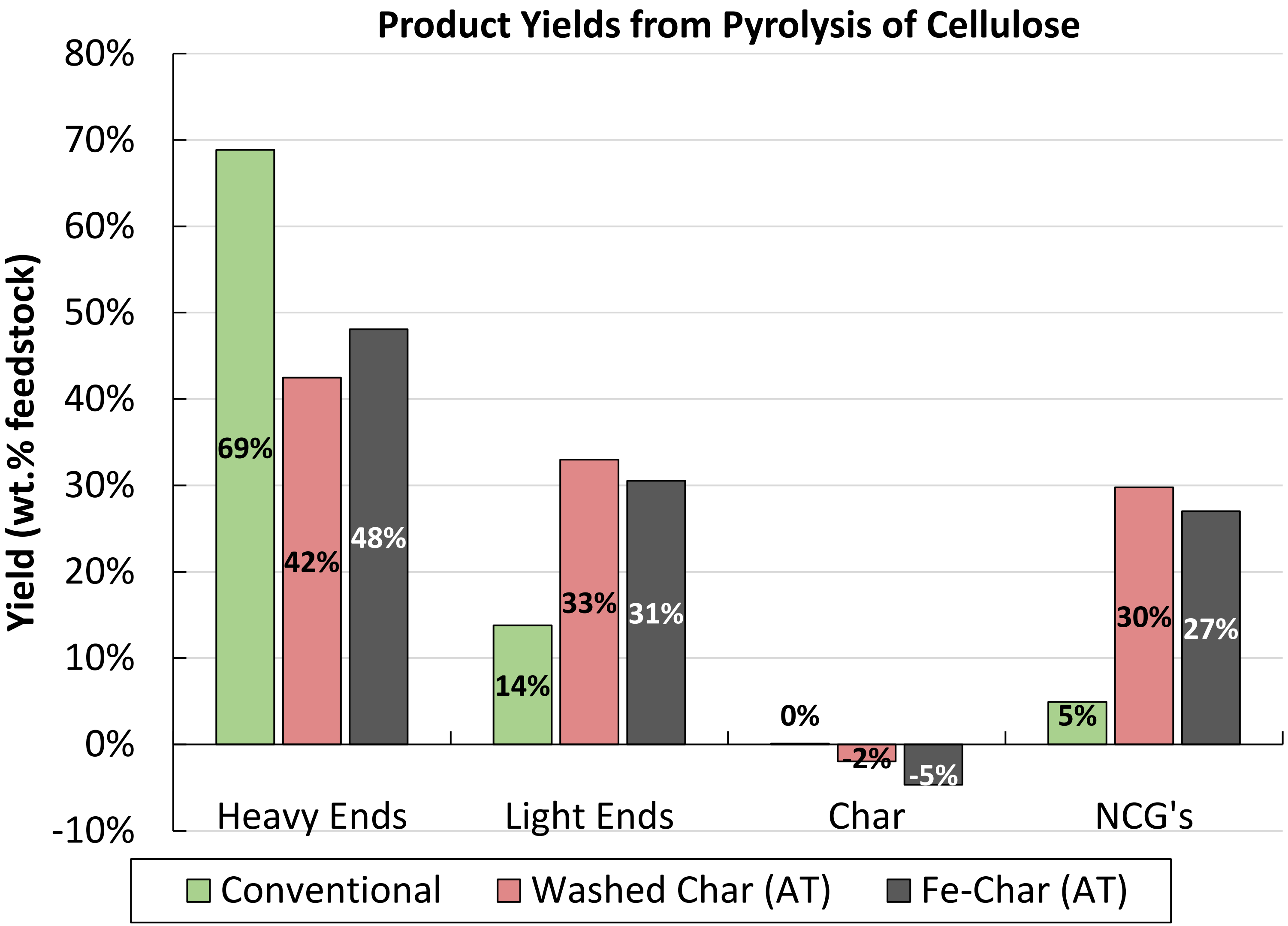
>20% Increase in Sugars with Ferrous Loaded Char

- Co-fed ferrous acetate char increased heavy ends and decreased light ends when compared to biomass only autothermal
- 22% increase in total sugars for autothermal:
  - Conventional = 7.2 wt.%
  - Autothermal = 5.4 wt.%
  - Fe-Char (AT) = 6.6 wt.%
- Decrease in char suggests improved char oxidation



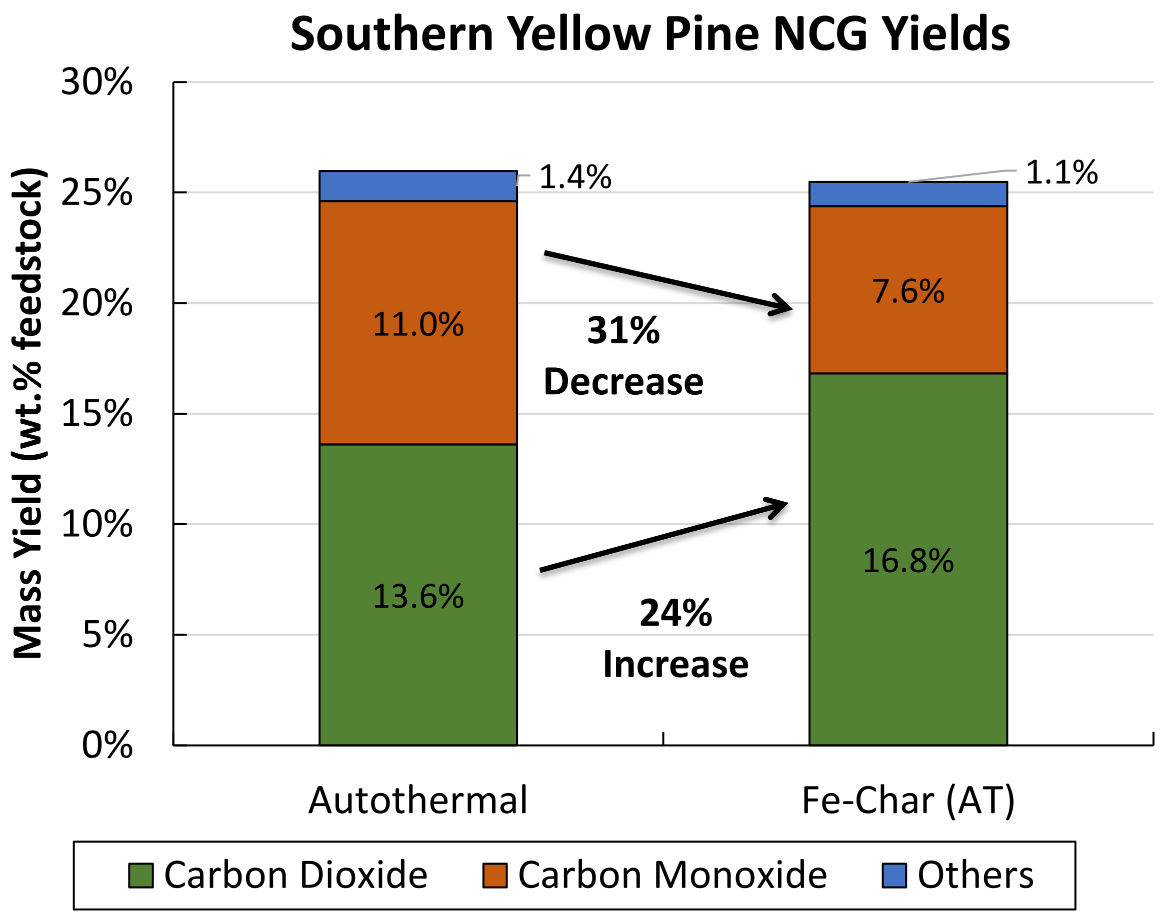
Cellulose co-fed with Char Supports Fe-Char Activity

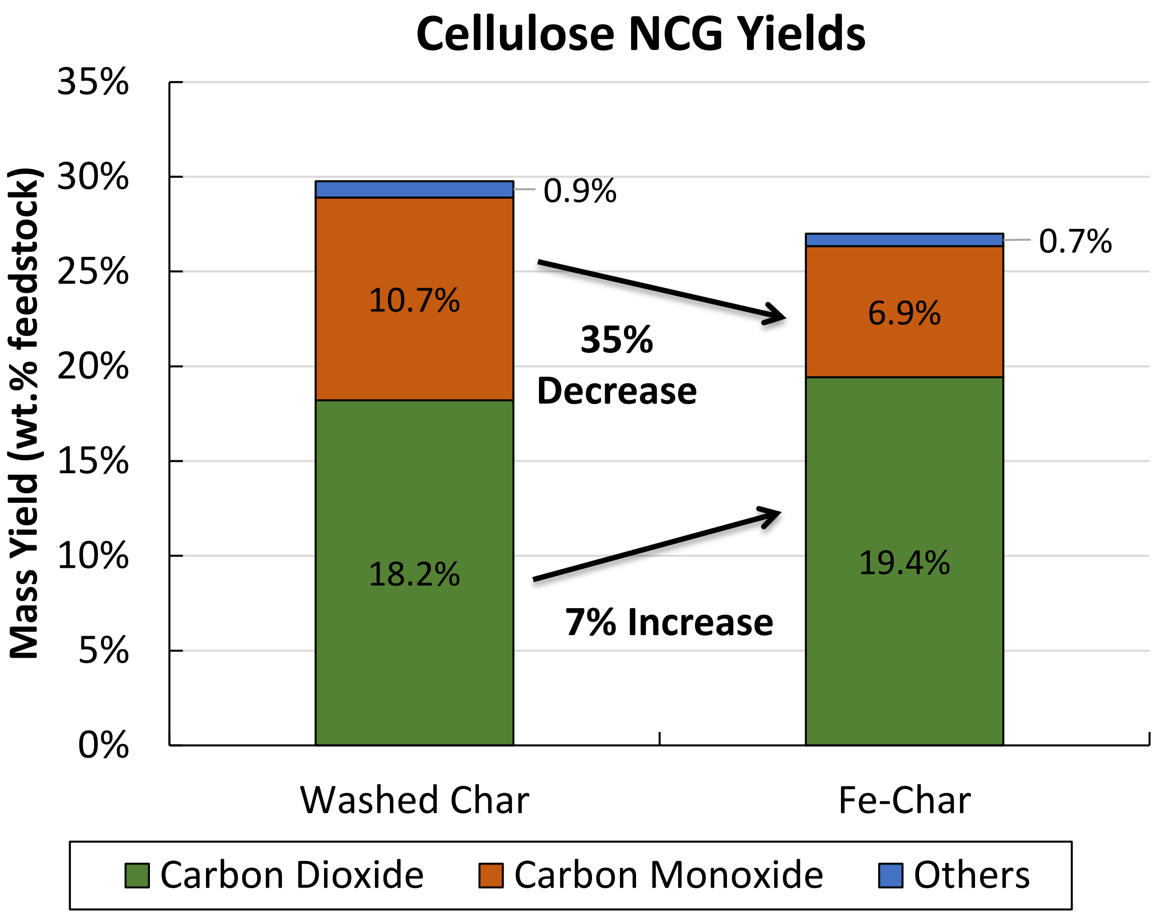
- Co-fed cellulose at 85 wt.% with 15 wt.% char
  - Washed 1M HCl char
  - Fe-loaded char
- Direct comparison of catalyst loading char shows improved recovery of sugars
- Total Sugars:
  - Conventional = 61.3 wt.%
  - Washed Char (AT) = 32.1 wt.%
  - Fe-Char (AT) = 36.2 wt.%



CO_2 Yield Supports Preferential Char Oxidation

- Ferrous loaded char boosted CO_2 : CO ratios → releases more energy for less carbon





Conclusions

- Ferrous pretreatments of biomass enhance pyrolytic sugar production during autothermal pyrolysis.
- Co-pyrolysis with ferrous loaded char and untreated biomass promoted oxidation of char and preserved sugar production.
- Preferential oxidation of ferrous loaded char yields predominately carbon dioxide thus releases more energy during autothermal pyrolysis.
- Co-feeding ferrous loaded char and biomass can selectively oxidize char to further enhance pyrolytic sugar production.

Acknowledgements

- Iowa State University's Bioeconomy Institute
  - Co-authors
  - Staff and students

- This research was funded in part by the US Department of Energy sponsored RAPID Institute.

- Be sure to catch our other talks/posters this week!
  - Demonstration Autothermal Pyrolyzer
  - Thermal-oxo degradation of plastics
  - Upcycling and pyrolysis of plastics

Questions?