Combustion & Catalysis Laboratory

WTERT

Solid Carbon Conversion (Biomass & MSW) via CO_2

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Need refs and atom economy

Workshop on lignocellulosic biofuels using thermochemical conversion

June 14-15

Auburn University

Energy

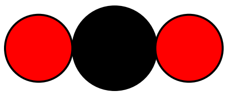
- Two-fold increase in energy consumption (*demand*)
  - From 472 exajoules to 791-1107 over next 40 years
- The world is sensitive to energy supply *(new paradigm)*
  - Security, Procurement → supply chain disruptions
- CO_2 atmospheric concentrations are rising *(environment)*
  - Prevent carbon dioxide emissions → sequester, create value

The Need

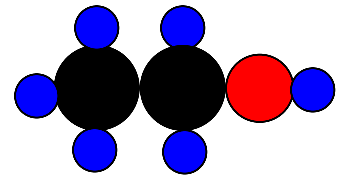
- Carbon neutral energy production
- Clean chemical production (e.g. H_2)
- Reduce the dependence on single feedstock
  - Indigenous source of fuel, distributed sources
- Power and chemicals produced must be economically attractive compared to current sources.

Working the Atom Economy

Energy conversion & Efficiency



C_xH_y
Biomass
MSW
Coal



Fuel (e.g. C_2H_5OH)

Biomass + ~~H_2O~~ → CO + H_2 η_{atom} =100%

Biomass + CO_2 → CO + H_2 η_{atom} =100%

- Energy and water savings

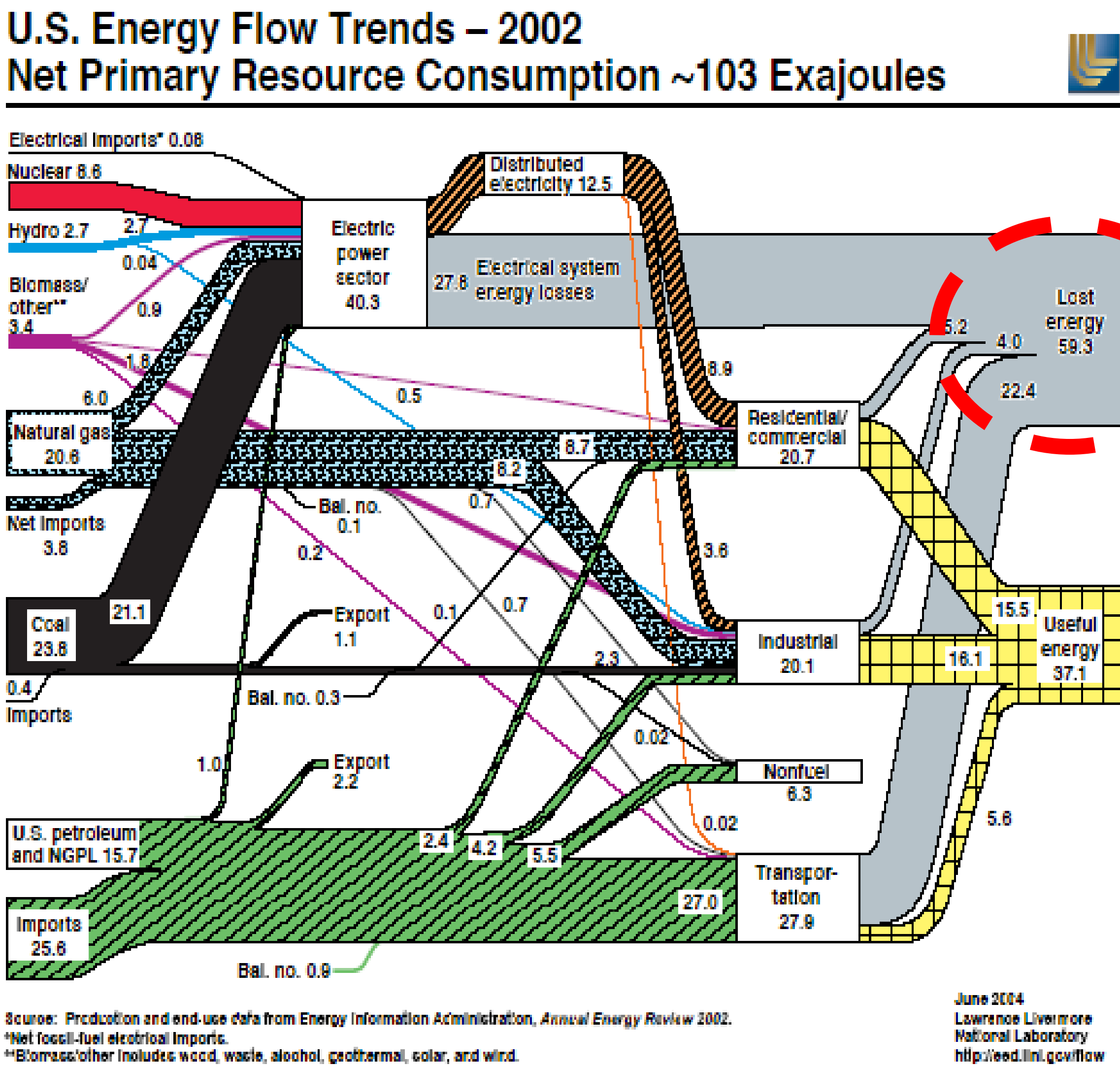
20% of 2008 total transportation energy demand incorporates CO_2

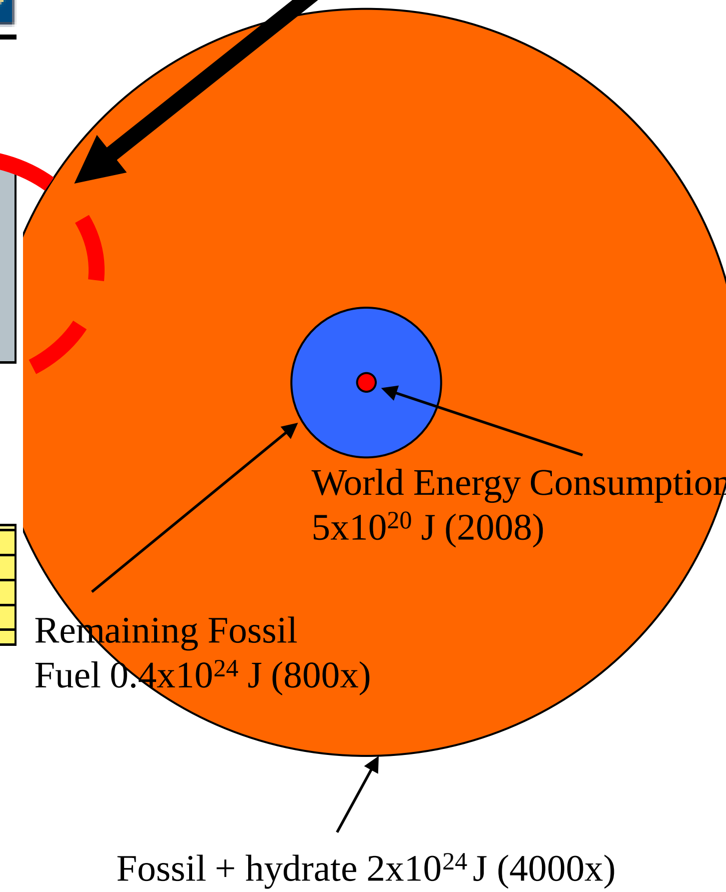
•Remove 308 million vehicles from the road

•Eliminate CO_2 emissions from 57 - 1000 MW coal-fired power plants.

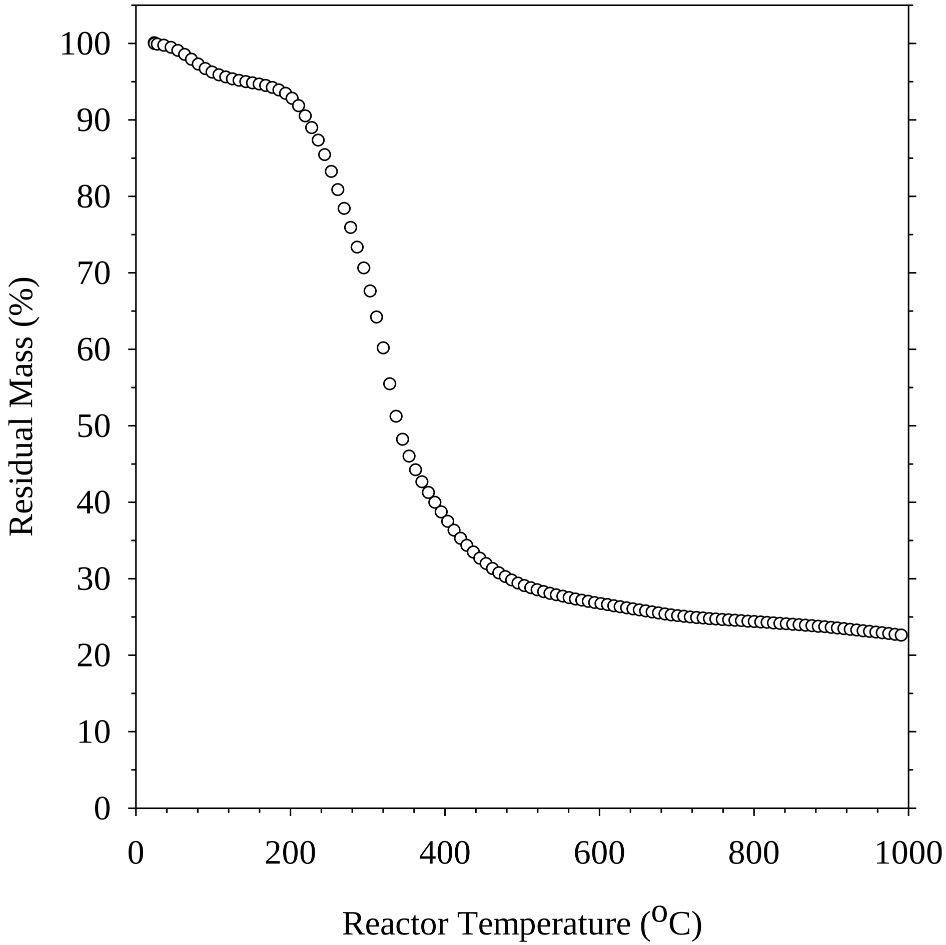
What is the Problem?

- *Energy sector is inefficient*
  - *~60% of energy is wasted!*





Conversion Problem

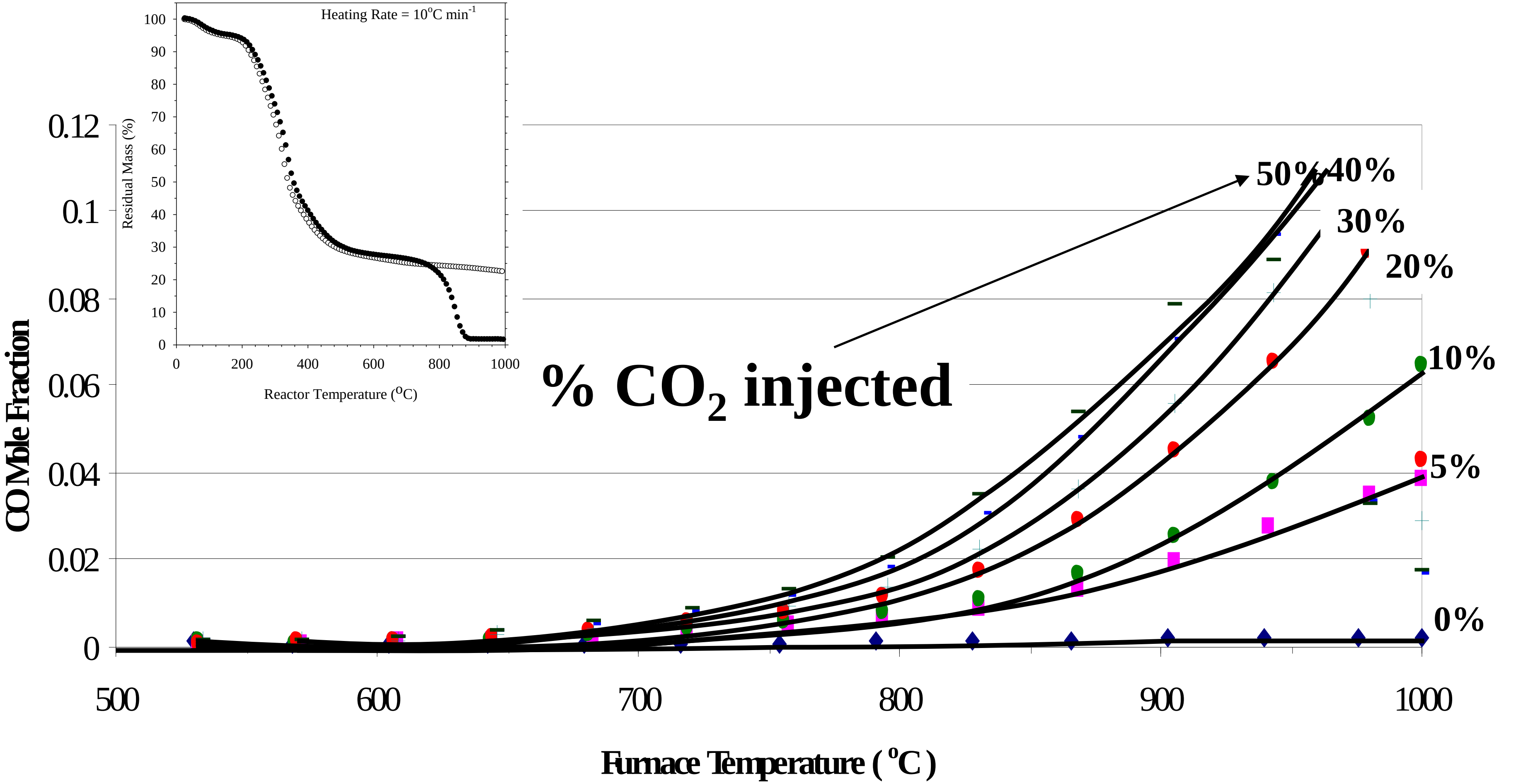


Determining and Understanding Reaction Mechanisms allows design of more efficient and selective processes and technologies.

Unprocessed residual

Completely processed to desired outcome

Enhanced Gasification



- *Enhanced CO production with CO_2*
- *Production begins to level off above 20% CO_2*

Butterman, H. C.; Castaldi, M. J., Environmental Engineering Science **2009**, 26, (4), 703-713

Value: CO_2 Enhanced Char Burnout

Walnut Shells: **0% CO_2**

Walnut Shells: **30% CO_2**

Douglas Fir: **0% CO_2**

Douglas Fir: **30% CO_2**

~20% biomass remaining

<2% remaining as inorganic ash

- Identical time on stream, reaction temperature profile, total flow rate
- ***Physical evidence of more efficient gasification with CO_2***

Observed for all samples tested

Butterman, H. C.; Castaldi, M.J, *Environ. Sci. Technol.*, **2009**, 43 (23), pp 9030–9037

Actual Biomass Steam vs CO_2 @ 1°C min^{-1}

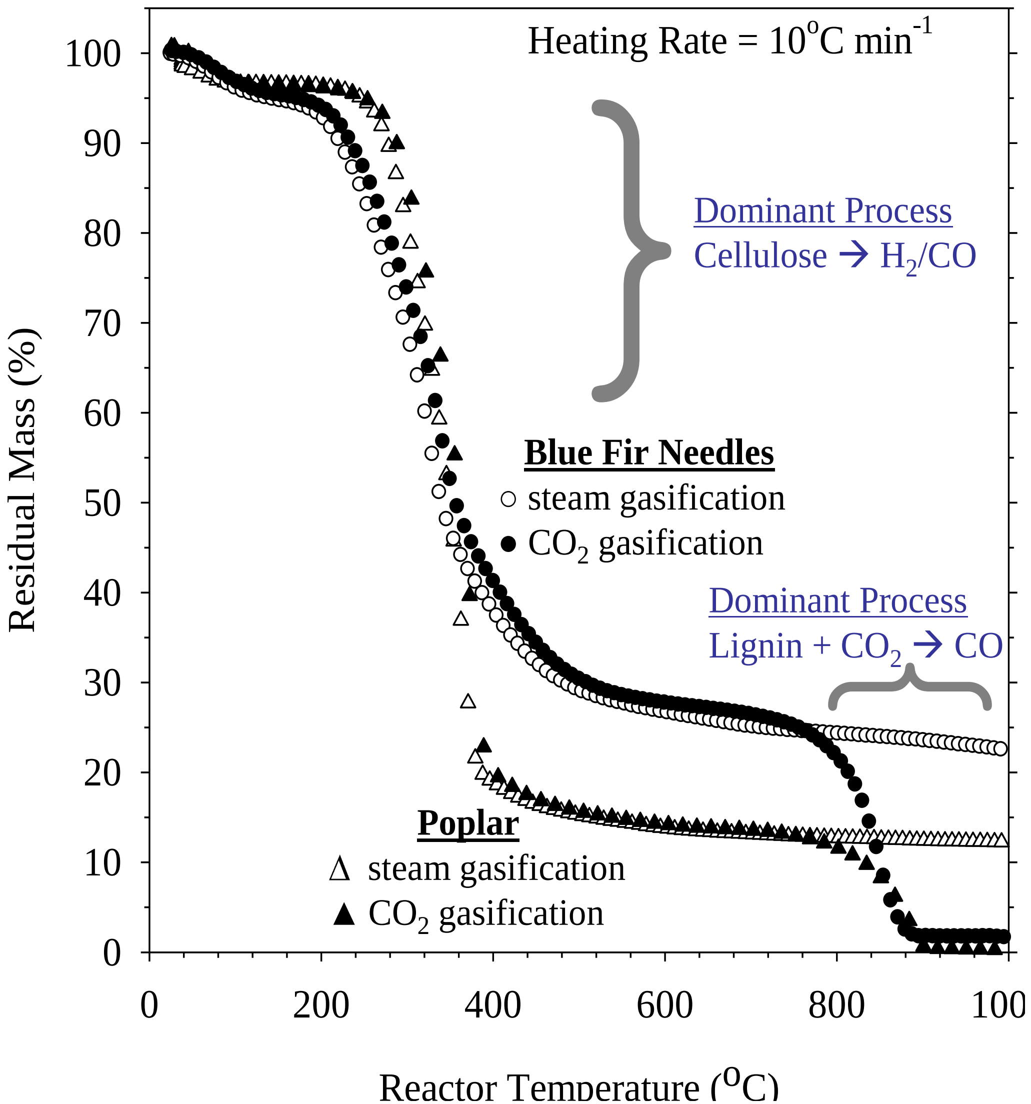
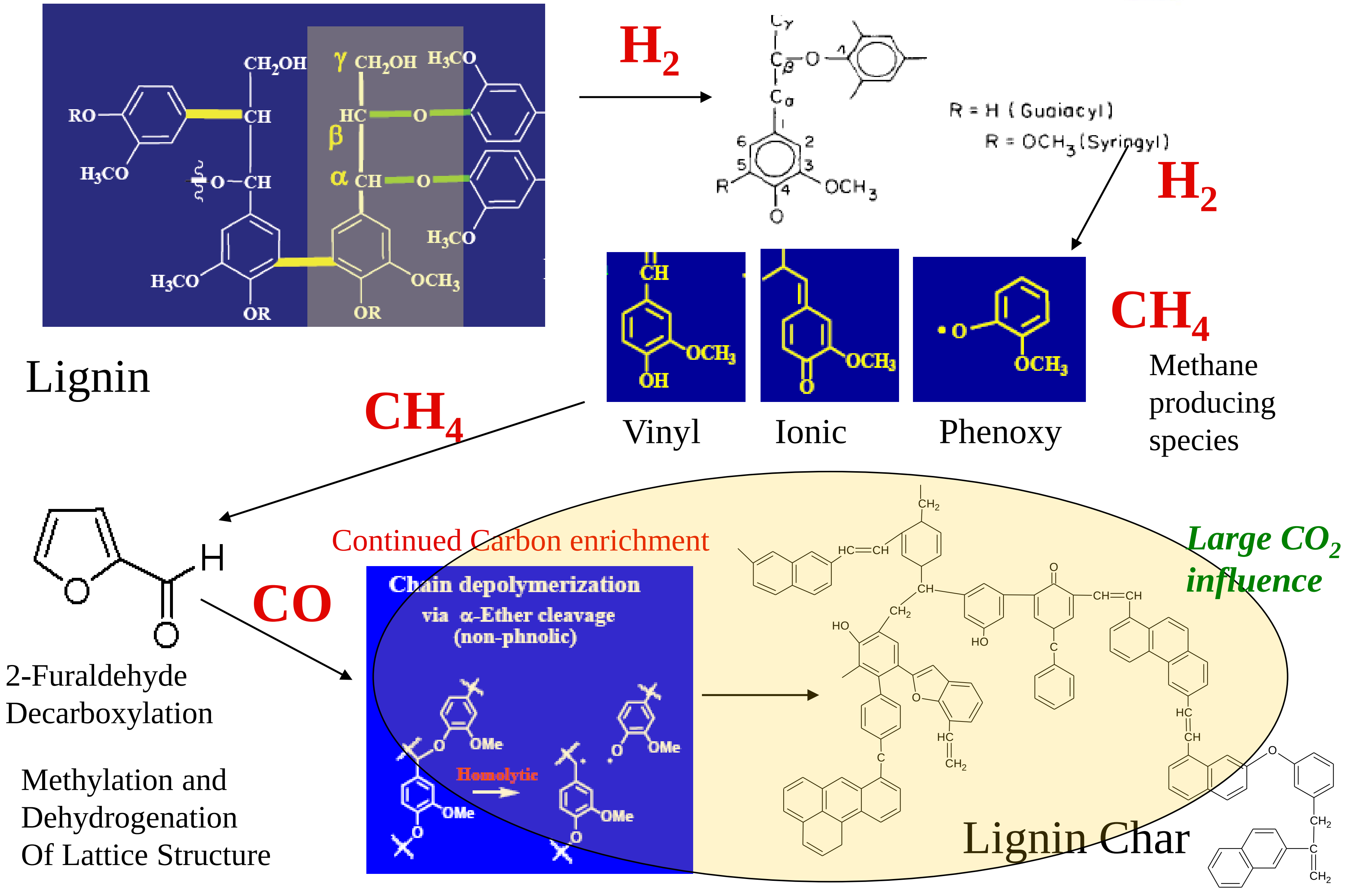


Figure 3B. Real Feedstock Decomposition Curve

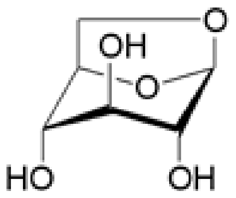
- low temperature pyrolysis behavior is similar for CO_2 & H_2O
- Blue Fir Needles, **higher lignin** begins pyrolytic degradation earlier (200°C) → slower rate of decay
- Poplar wood, **higher cellulose** begins pyrolytic degradation later (250°C) → faster decomposition rate
- Greatest difference between H_2O and CO_2 gasification after 900°C → < 2% ash remains using CO_2

Lignin Decomposition

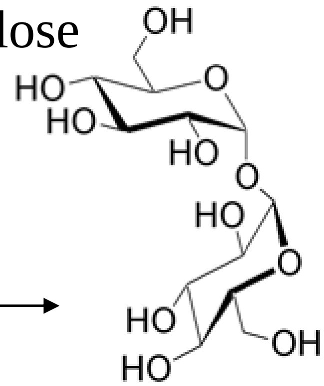


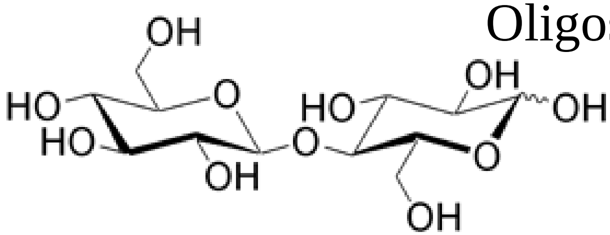
Cellulose Decomposition

Levoglucosan



Trehalose



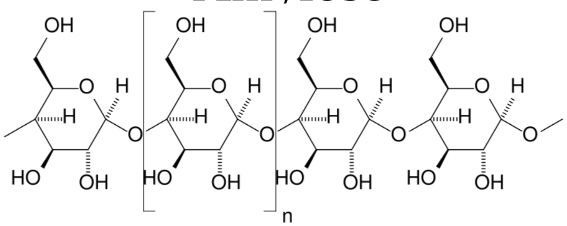


Cellobiose

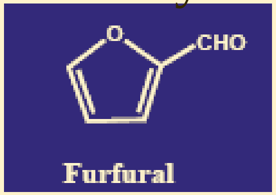
(Methanol soluble Oligosaccharides)

Dehydroxylation Polymerization

Amylose

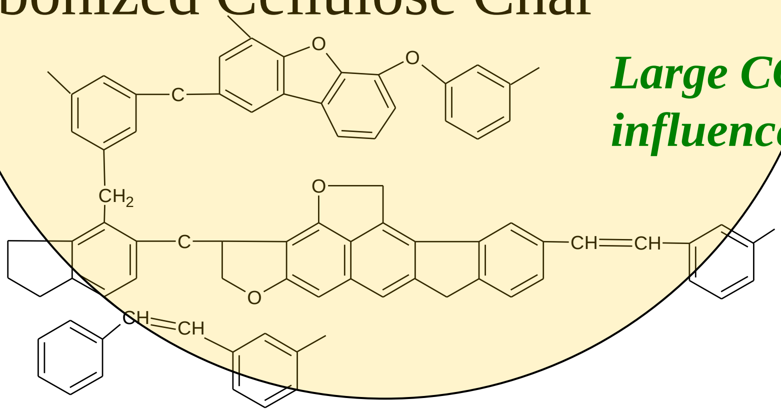


(Water soluble Polysaccharides and Furans and Carbonyls)



Furfural undergoes decarbonylation

Carbonized Cellulose Char



Large CO_2 influence

Devolatilization
No Char formation

Low MW Volatiles CO, CO_2, CH_4, H_2

Major Gasification Reactions

Low Temperature

Water Gas Shift

$CO + H_2O \leftrightharpoons CO_2 + H_2$

Methanation

$C + 2H_2 \leftrightharpoons CH_4$

$2CO + 2H_2 \leftrightharpoons CH_4 + CO_2$

$CO + 3H_2 \leftrightharpoons CH_4 + H_2O$

Steam Gasification

$C + H_2O \leftrightharpoons H_2 + CO$

High Temperature

Steam Gasification

$C + H_2O \leftrightharpoons H_2 + CO$

Boudouard

$C + CO_2 \leftrightharpoons 2CO$

Char Burnout: O (Biomass/Steam)

$C + ½O_2 \leftrightharpoons CO$

Reverse Water Gas Shift

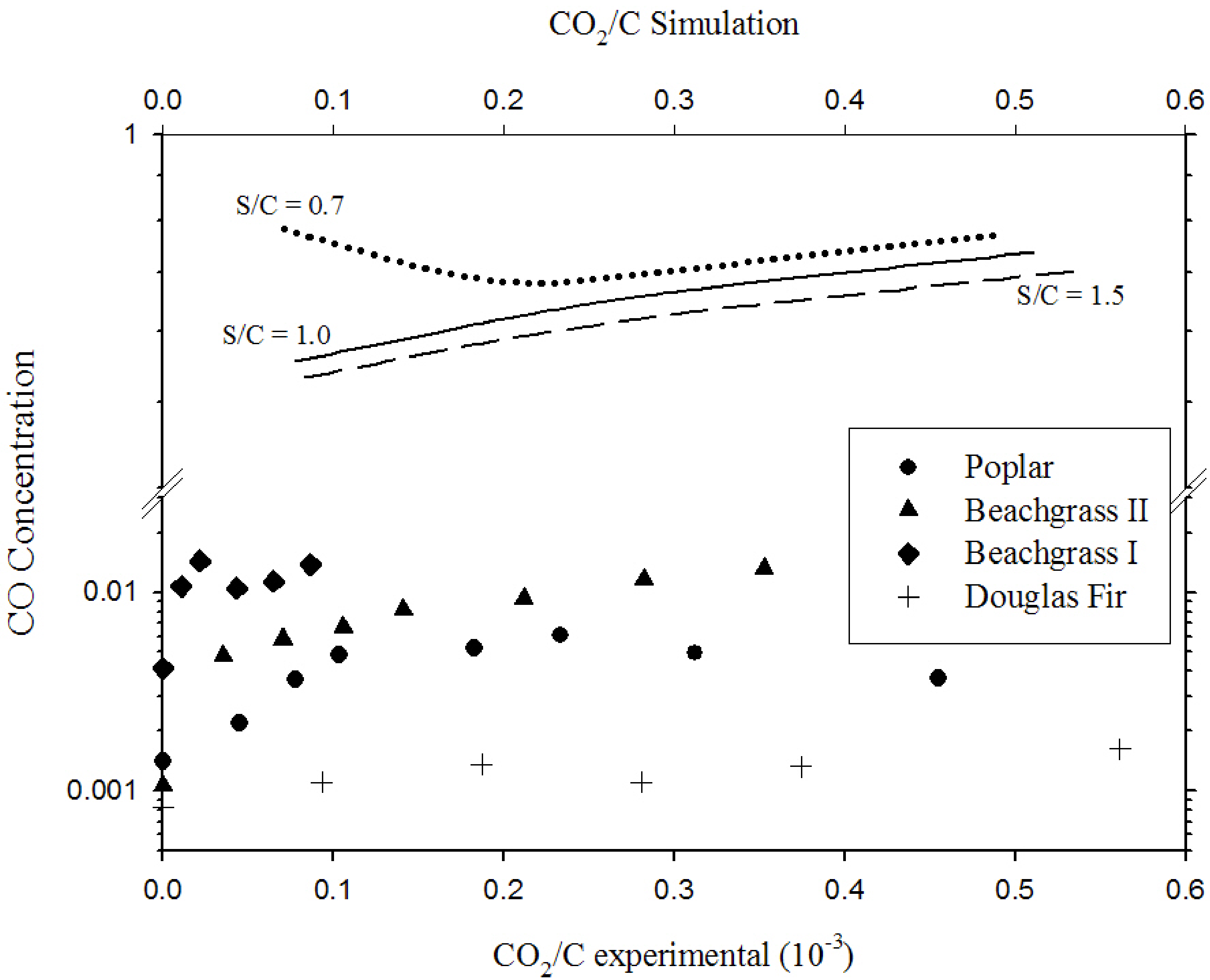
$CO_2 + H_2 \leftrightharpoons CO + H_2O$

Representative Kinetic Parameters CO_2 Pyrolysis (110-450°C)

Sample	A_o (sec^{-1} $K^{-½}$)	E_{ave} (kJ $mole^{-1}$)	n
Lignin (CO_2)	21.13	49.3	3
Lignin (N_2/H_2O)	316.89	47.8	3
Cellulose	1.40xE+18	219.0	1
Poplar	1.92xE+09	71.8	1
Douglas Fir	3.82xE+10	69.9	1
Pine	6.65xE+05	65.1	1
Maple	6.28xE+05	58.0	1
Oak	4.15xE+12	54.5	1
Spruce	2.89xE+10	54.3	1
A. Beachgrass	1.88xE+08	46.2	2
Maple Bark	1.41xE+03	42.9	2
Alfalfa	1.18xE+03	33.1	2
Blue Fir Needles	1.83xE+03	31.6	2
Green Pine Needles	47.24	27.6	2

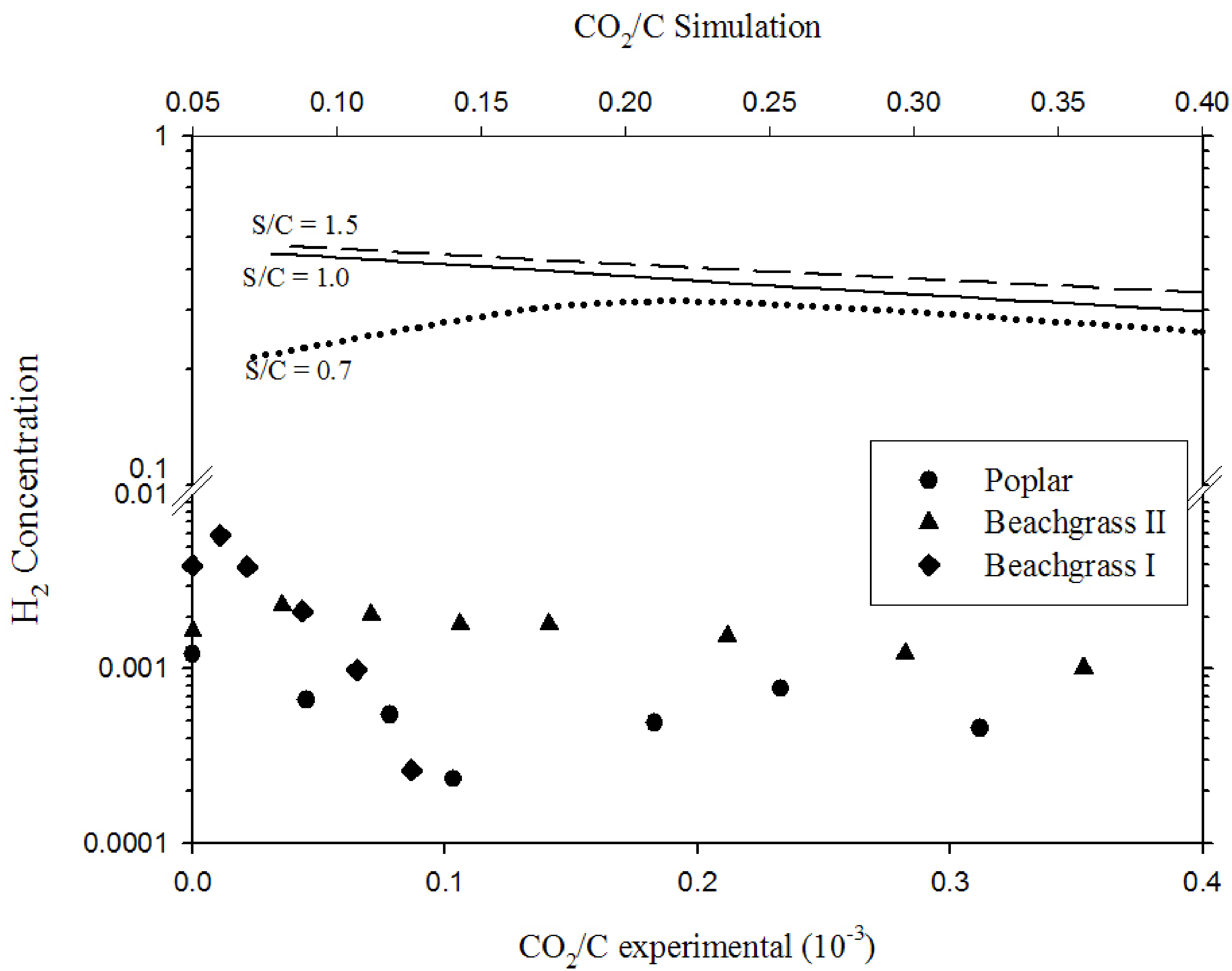
- **Cellulose** ↑ (Poplar – Spruce)
- **Lignin** ↑ (A. Beachgrass – Green Pine Needles)

CO Comparison



Butterman and Castaldi, Indus. & Eng, Chem. Res, (2007) ***47****, 8875-8886*

H_2 Comparison



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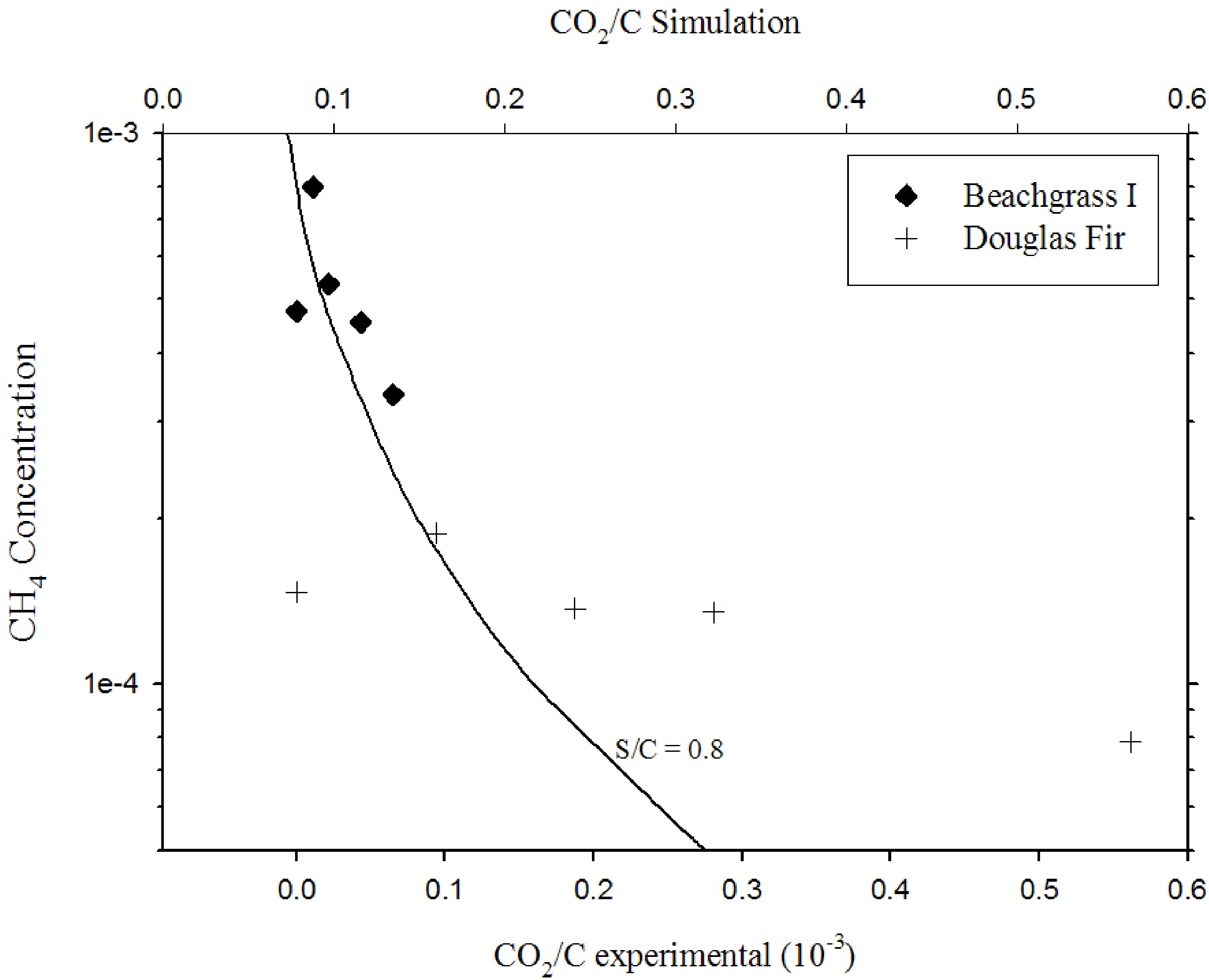
CH_4 Comparison



Butterman and Castaldi, Indus. & Eng, Chem. Res, (2007) ***47****, 8875-8886*

So What is happening? Why is CO_2 better?

Char Pore Development- Enhanced Char Burnout With CO_2

Lignin

0% CO_2 -H_2O/N_2

1°C/min, 22-860°C

Lignin

100% CO_2

1°C/min 22-860°C

Lignin

100% CO_2

1°C/min, 22-930°C

$$R = Ae^{\frac{-E_{act}}{RT}} \prod_i C_i^{\alpha}$$

Where;

$A = f$ (SA, V_{pore}, etc)

Butterman, H.C.; Castaldi, M.J.,*Env. Eng. Sci.*, **2010**, 27(7): 539-555

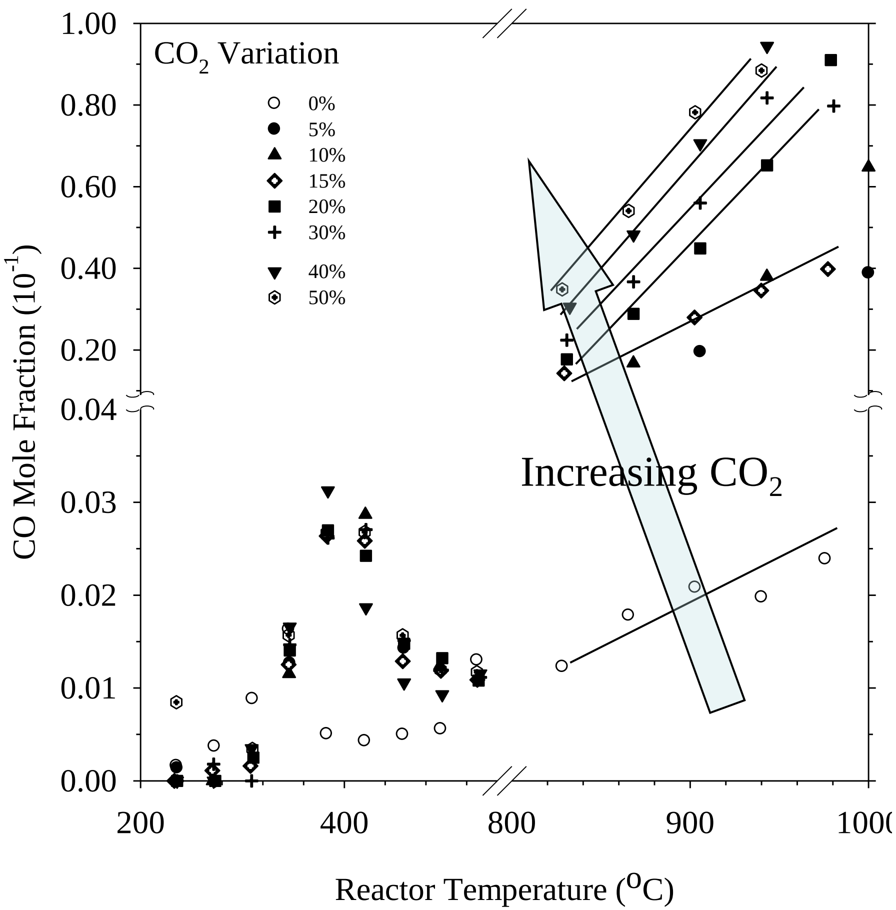
Physical Changes in Biomass during Gasification

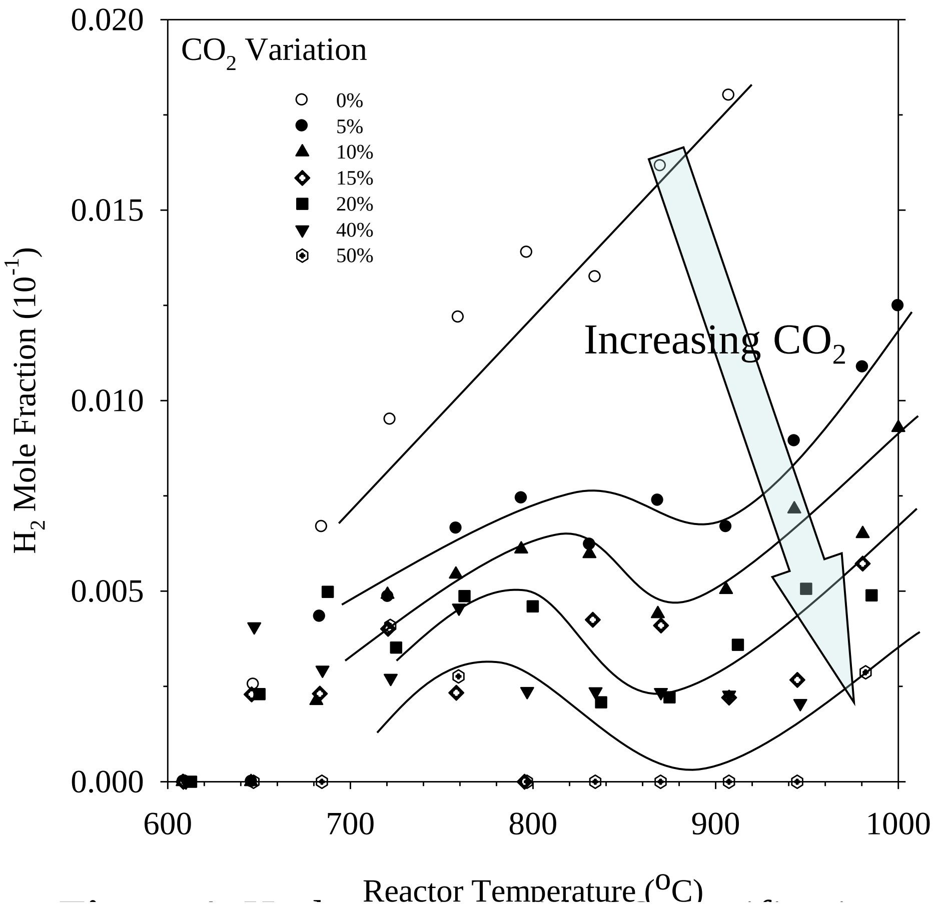
Removed - publication in preparation

Achieving high surface area: Why is sintering avoided with CO_2?

Removed - publication in preparation

CO_2 impact on gasification products



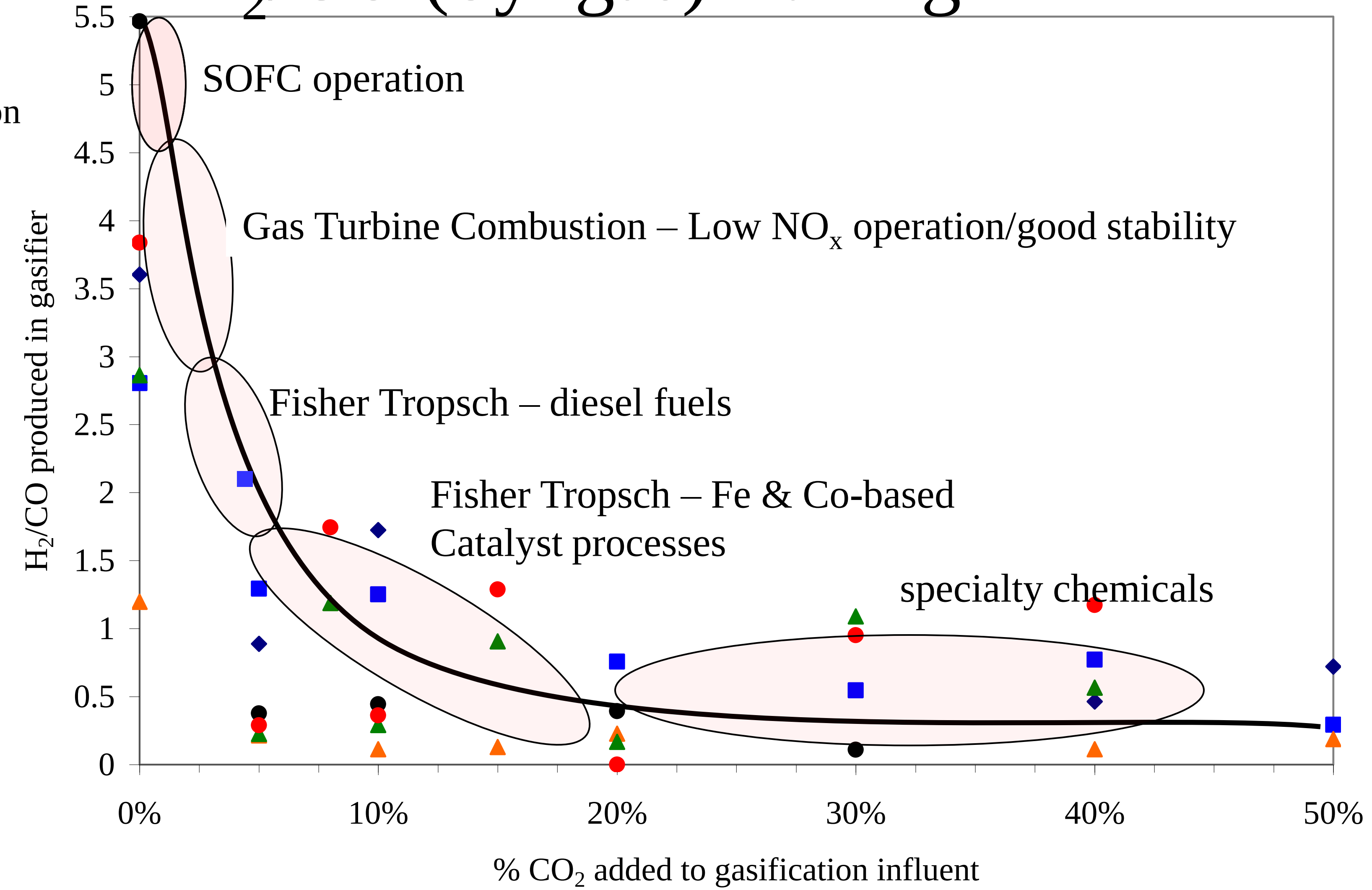


CO <u>increases</u> with CO_2

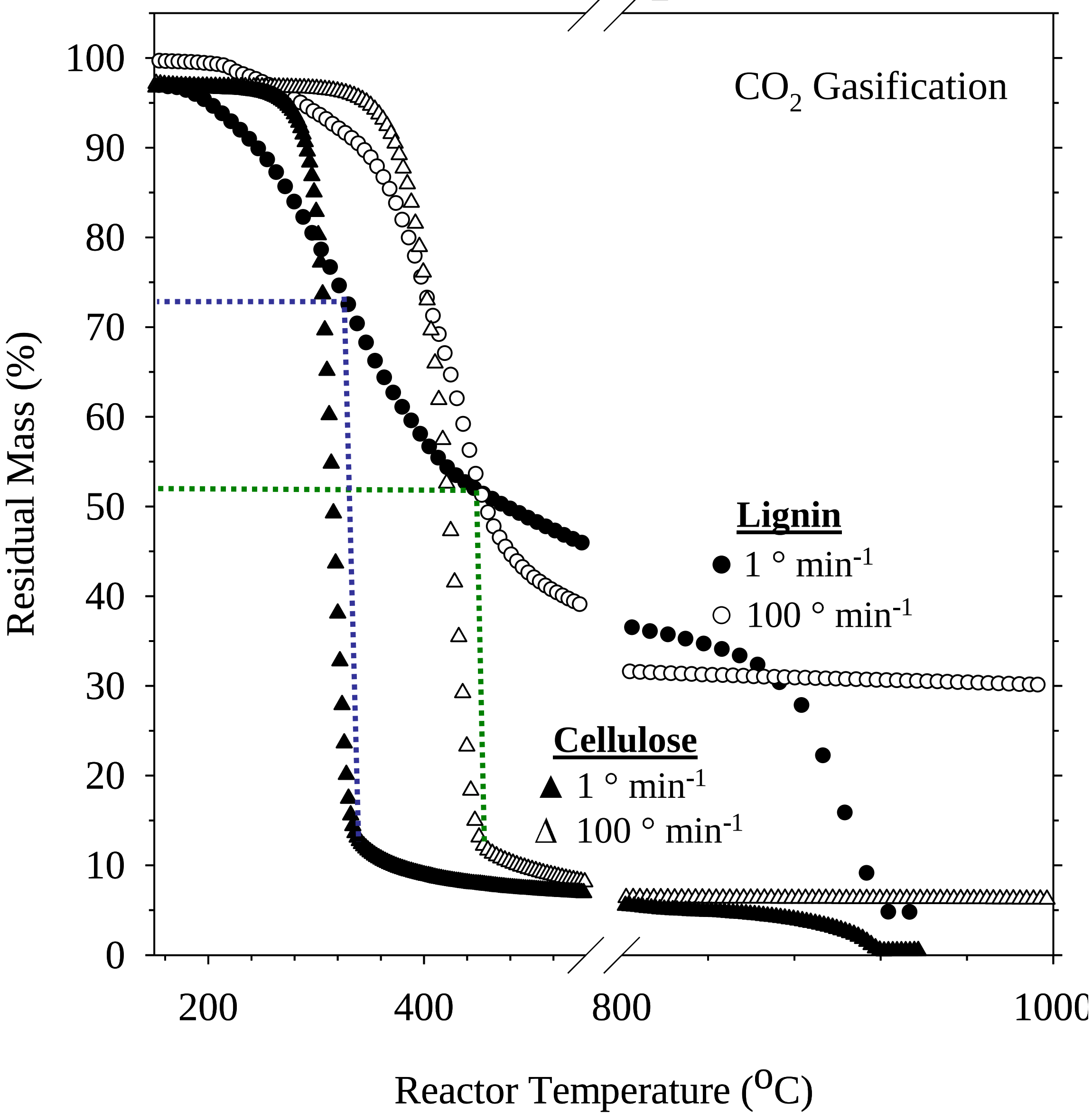
H_2 <u>decreases</u> with CO_2

H_2/CO (Syngas) Tuning

- Fuels
- Chemicals
- Combustion
- Fuel cells



Lignin & Cellulose w/ CO_2 @ 1 & 100°C min^{-1}



- Thermally process the cellulosic at low temperature
- Treat remaining lignin thermally and chemically via CO_2
- **Steam: ~40% of the lignin still unprocessed to volatiles by 930°C**
- **CO_2: 100% conversion by 930°C**
- Can optimize the percent of lignin in the pyrolytic char
- Thermal processing heating rate for steam gasification

Figure 3A: Lignin & Cellulose CO_2 gasification

Butterman, H.C.; Castaldi, M.J., *Env. Eng. Sci.*, **2010**, 27(7): 539-555

Oil Synthesis: Aromatic Adjustment

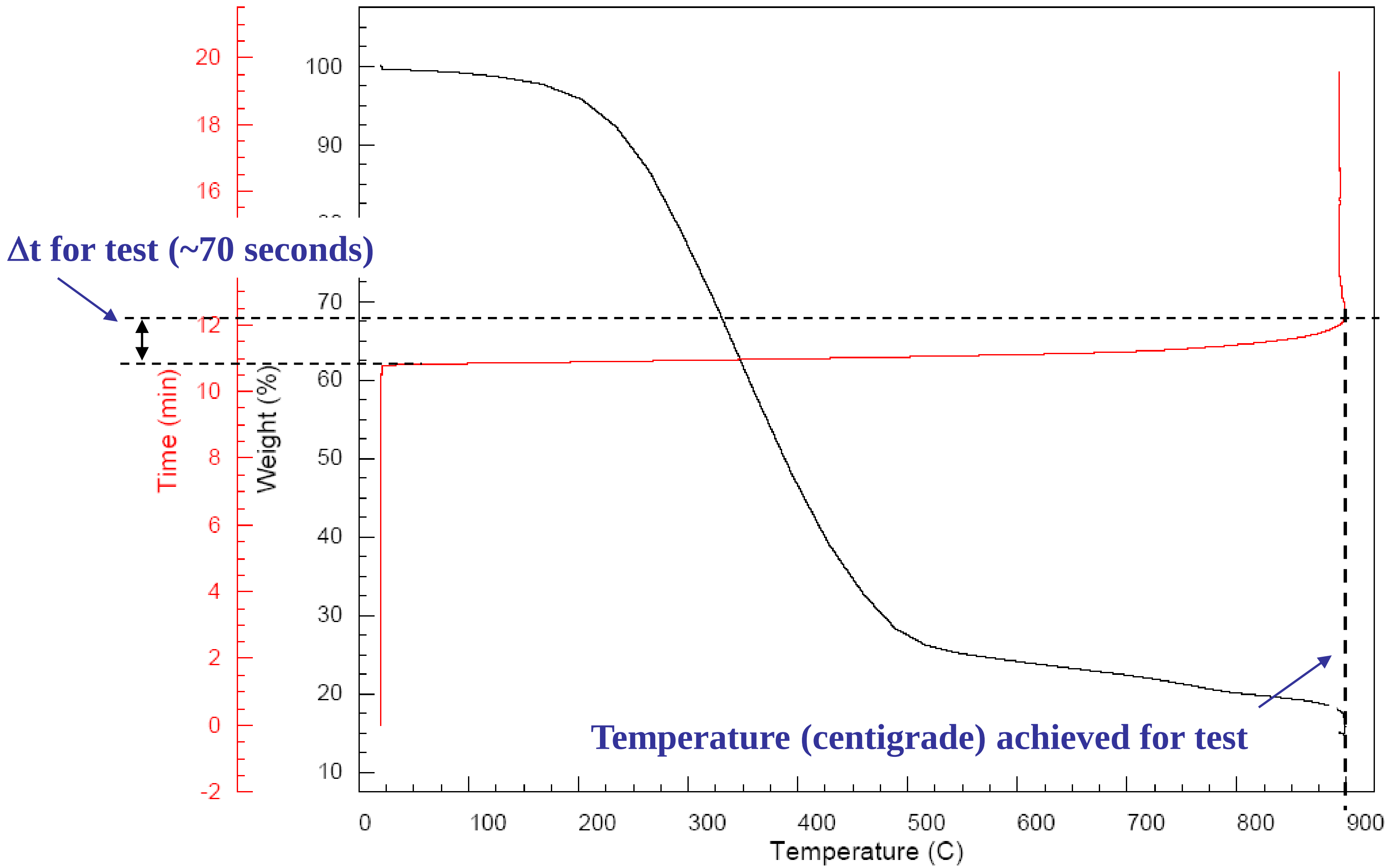
Removed - publication in preparation

Kwon, E., and Castaldi, M.J. (2008). *NAWTEC17*,Chantilly, VA, United States, May 18-20, 2009.

Ballistic Heating @ ~100°C min^{-1}

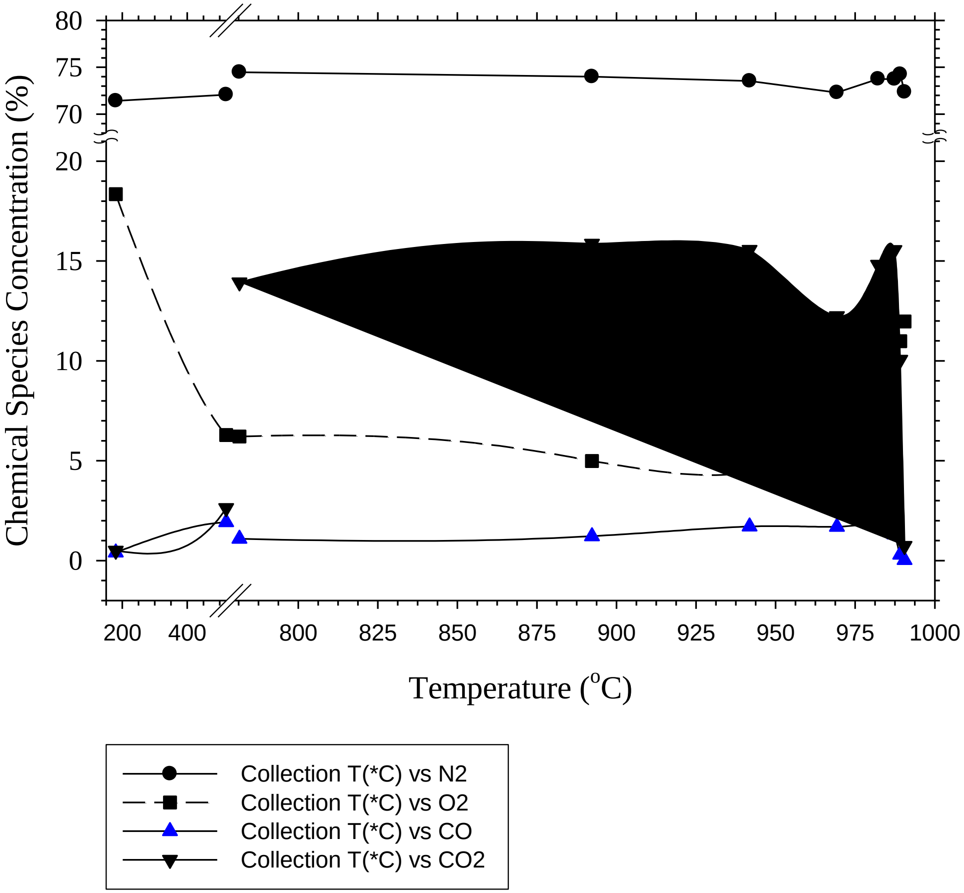
TGA

Mass Loss and Temperature continuously measured



Chemical Species with Ballistic Heating @ ~700°C min^{-1}

Major Species

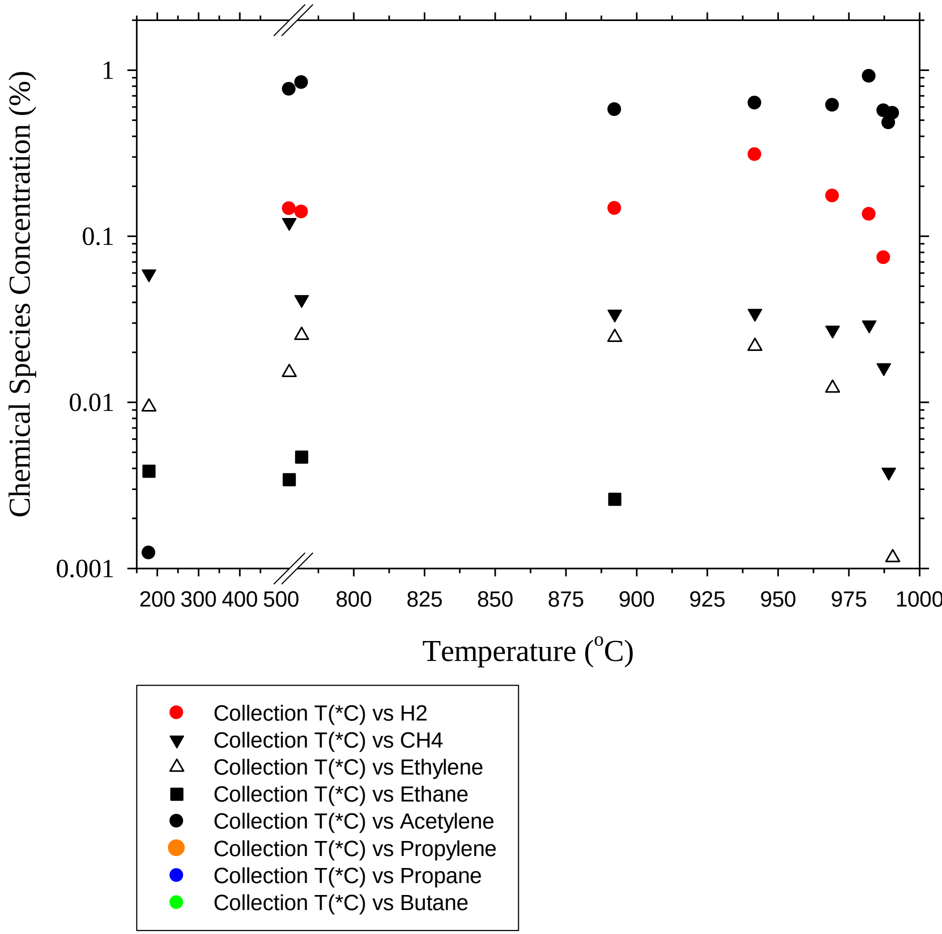


Online gas analysis capability

H_2: MW = 2 g gmol^{-1}

C_4's HC: MW = 58 g gmol^{-1}

Minor Species



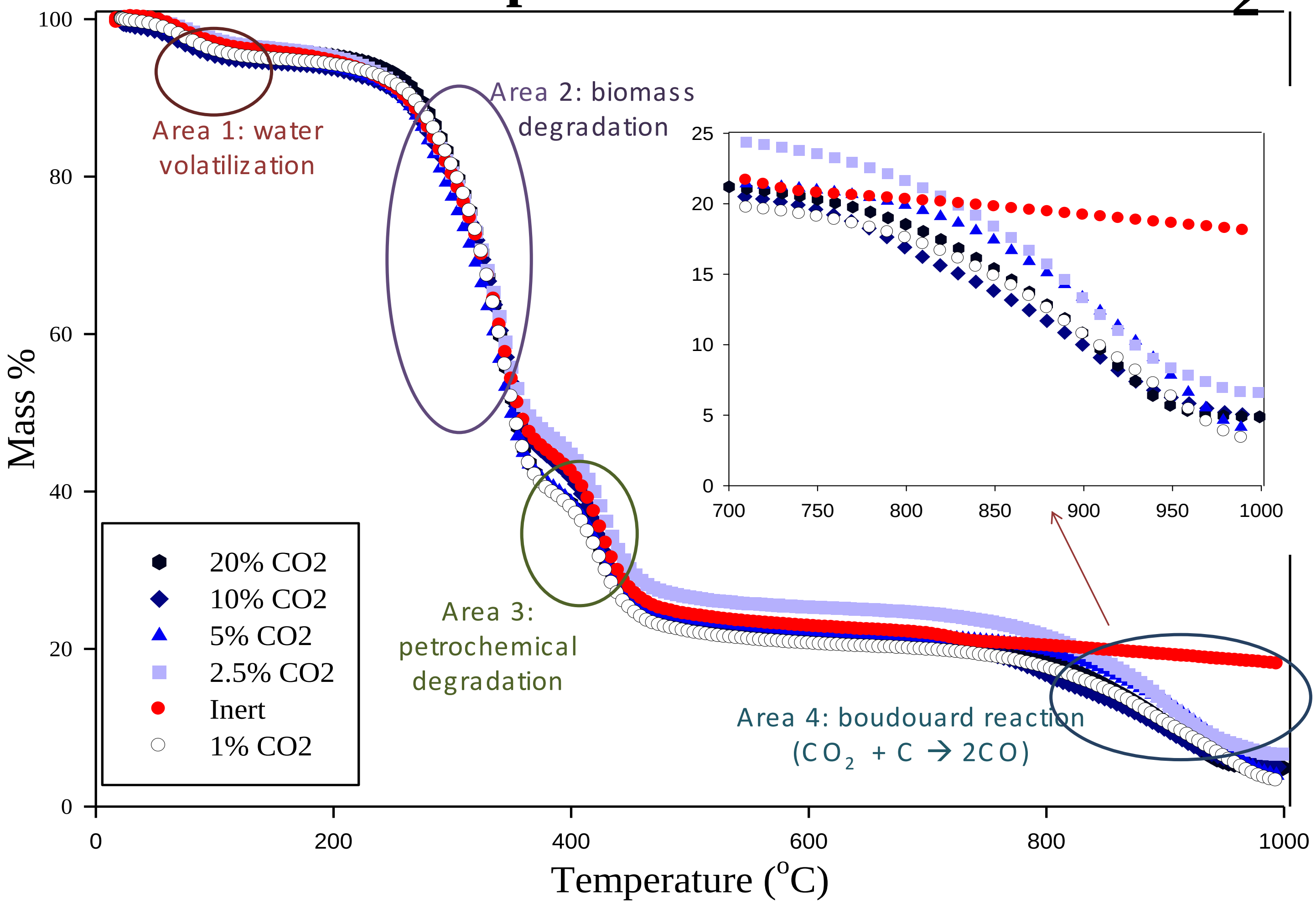
Higher Order Hydrocarbon Results

Removed - publication in preparation

- ***Trend toward dehydrogenation as temperature increases***
- ***Commensurate H_2 increase***

MSW DATA

Mass % vs Temp for Varius Amounts of CO_2



Kwon, E., and Castaldi, M.J. (2008). *NAWTEC17*,Chantilly, VA, United States, May 18-20, 2009.

Kwon, Eilhann; Castaldi, Marco J. *Environ. Sci. Technol.* **2009**, 43(15), 5996-6002.

CO_2 Impact on Coal

- **Decrease** in H_2 production with CO_2

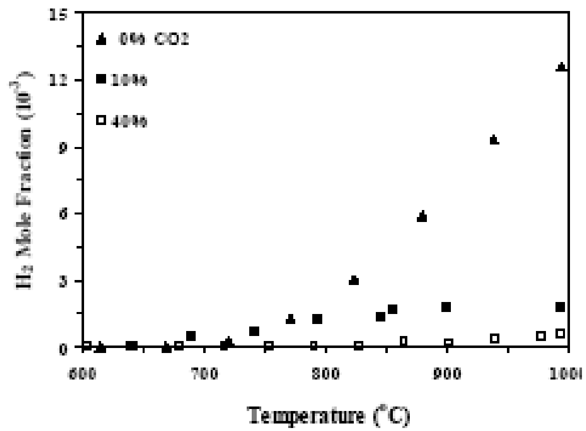


Figure 21. H_2 Evolution Depression from Montana coal using CO_2 (S/C = 10)

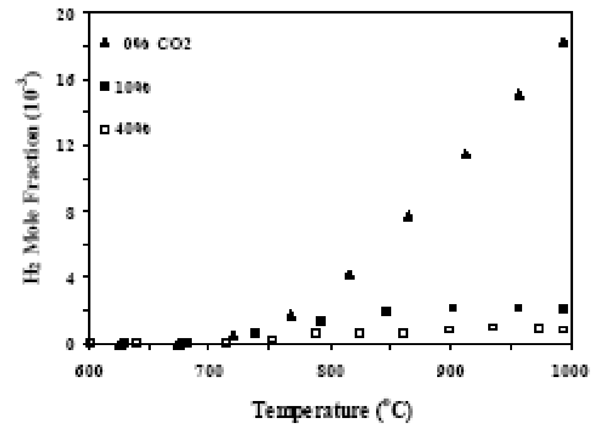


Figure 22. H_2 Evolution Depression from Wyoming coal using CO_2 (S/C = 9)

- **Increase** in CO production with CO_2

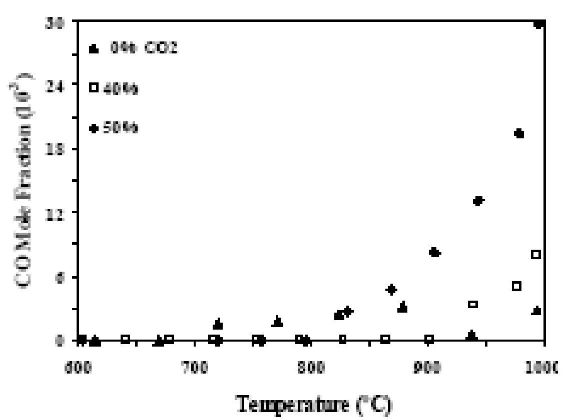


Figure 23.CO Evolution Enhancement from Montana coal using CO_2 (S/C = 10)

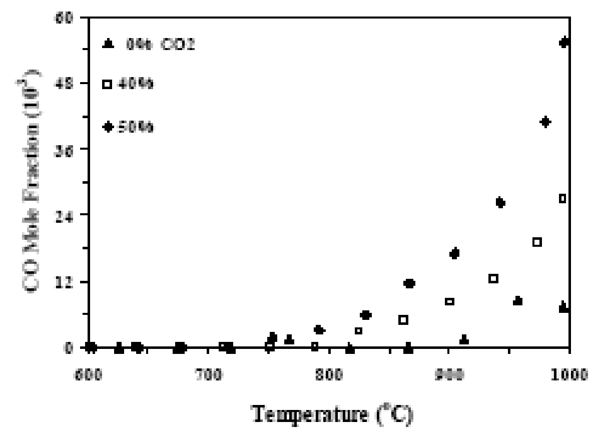
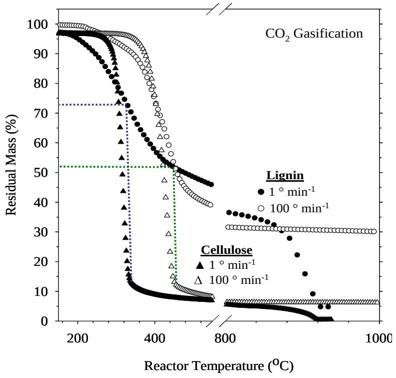


Figure 24.CO Evolution Enhancement from Wyoming coal using CO_2 (S/C = 9)

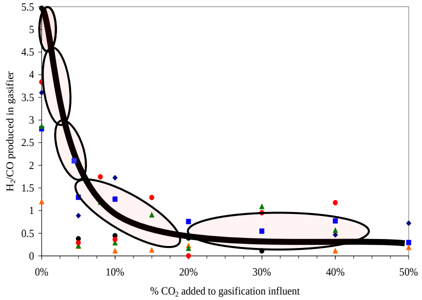
Conclusions

- Biomass, waste, coal – solid carbon fuels can be efficiently converted using CO_2 instead of steam



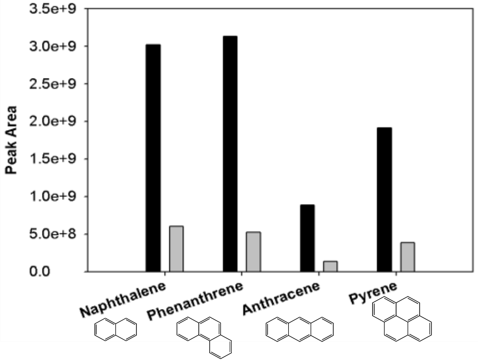
- CO_2 helps in thermal separation of lignin and cellulose

- CO_2 enhances CO production, suppresses H_2
  - Improved char burnout



- Modeling matches data

- Kinetic parameter estimation suggests reaction order 1.0 for cellulose and 3.0 for lignin



- Adjustment of aromatic content in liquid portion

Acknowledgments

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EPRI ELECTRIC POWER RESEARCH INSTITUTE

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