WTERT Research Update
Gasification of Biomass
Solid Carbon Conversion

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Waste-To-Energy Research and Technology Council

The Future

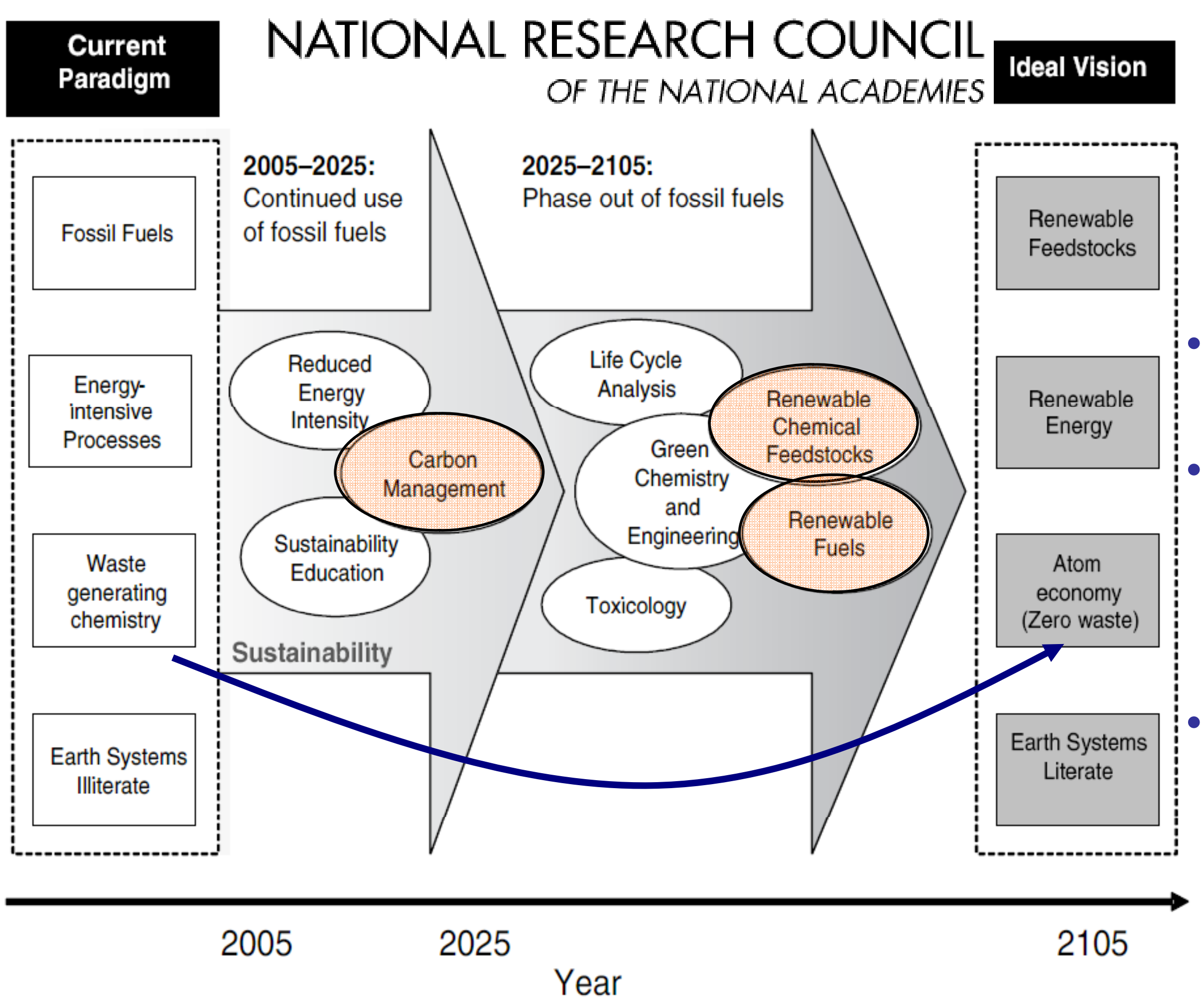

FIGURE ES-1 The Grand Challenges (ovals) for Sustainability (large arrows) that address the transition from current thinking to the ideal vision for the chemical industry over the next 100 years. See text for a more detailed description of figure and the Grand Challenges.

- Fossil Fuels will play smaller role
- Renewable / indigenous fuels will become more prominent
- Carbon management is here to stay

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The Need

- Carbon Neutral Energy Production
- Clean chemical (H_2) Production
- Zero emissions → more than CO_2 sequestration
- Reduce the dependence on single feedstock
  - Indigenous source of fuel, distributed sources
- Power and chemicals produced from waste/biomass must be economically attractive as compared to current sources.

Investment (wall Street)

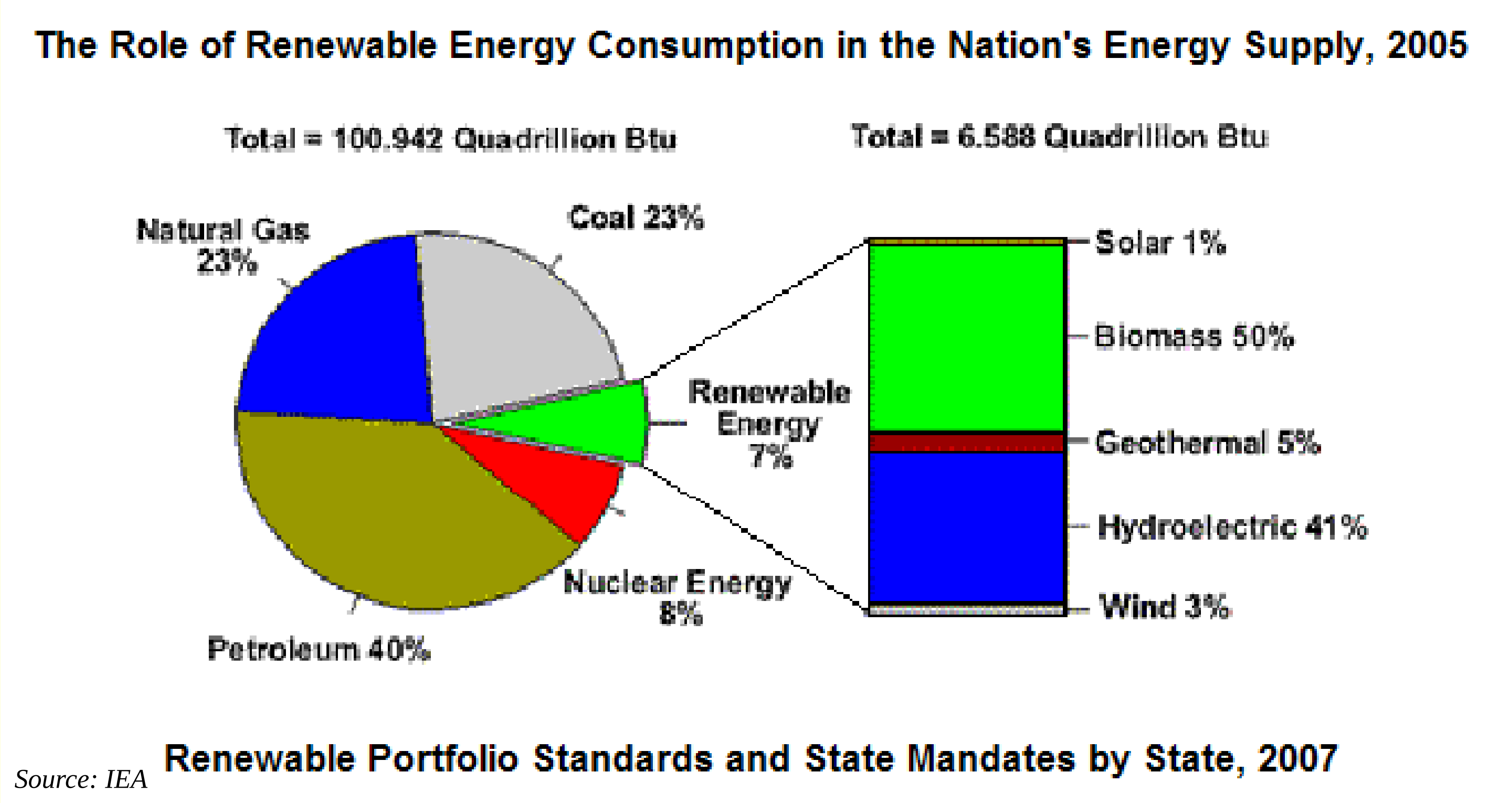
- Socially responsible investing
- Emissions control (CO_2)
- Eco-friendly business practices
- World Economic Forum
  - Businesses need to reduce the negative impact on the environment

"Many companies are now discovering that there my a be a strong correlation between 'doing good' and 'doing well'"

"The next turn of the market wheel may reward companies with strong free cash flow as well as innovative companies thinking green"

Alger Market Commentary March 31, 2007

Bioenergy

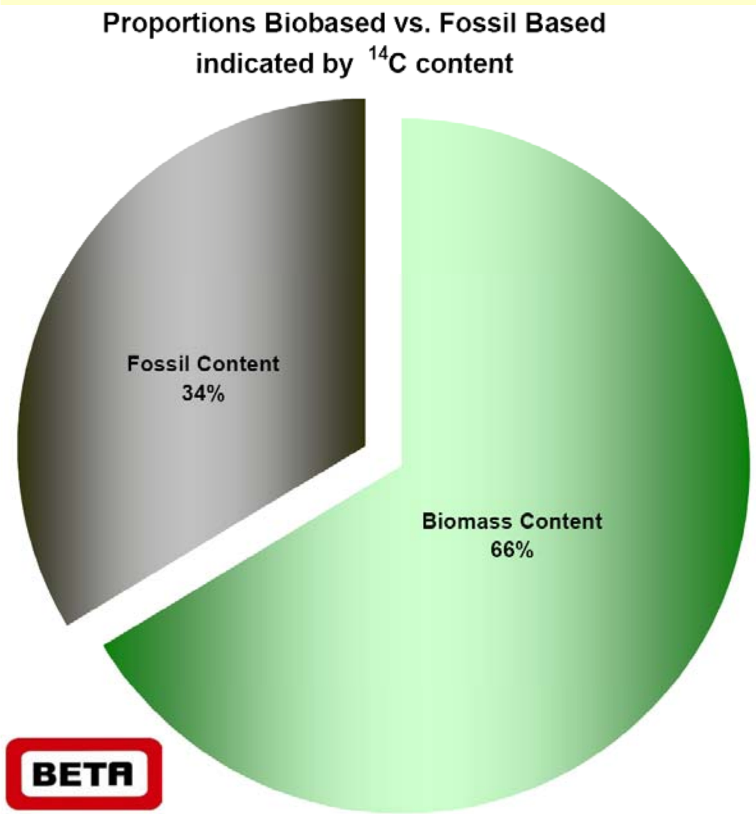


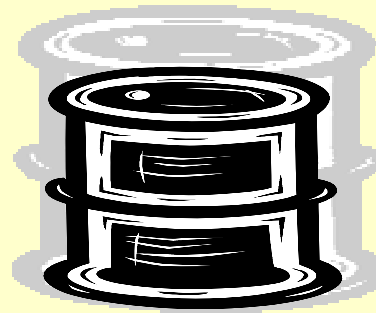
Source: IEA

Municipal Solid Waste (MSW)

- ~ 220 million tons of waste generated per year (U.S.)
- Landfills are filling up
- Disposal costs and energy costs are going up
- Greenhouse gas initiatives (RGGI, etc)

•Waste as fuel emits 2/3 less CO_2 than fossil fuel





Potential to replace ~ 20% of oil imports per year

Burning is good (WTE); instead of oil → use waste

- Gasification gives options
  - choice of products – Heat, fuels, chemicals

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Chemicals From Waste

- Military MISER program
  - Trash/Biomass/Solid hydrocarbons to fuels

- American Chemical Society (ACS)
  - Letters to the editor – "chemicals from waste"
    - C&EN April 2006

- Discover Magazine –
  - "DATA" Section : The Ultimate Garbage Disposal
    - How to turn trash into clean energy – Geoplasma Unit
      - 160 MW by 2009, St. Lucie County, Florida

- EnerChem/City of Edmonton - 2008

CO_2 & Waste / Biomass Enhanced gasification

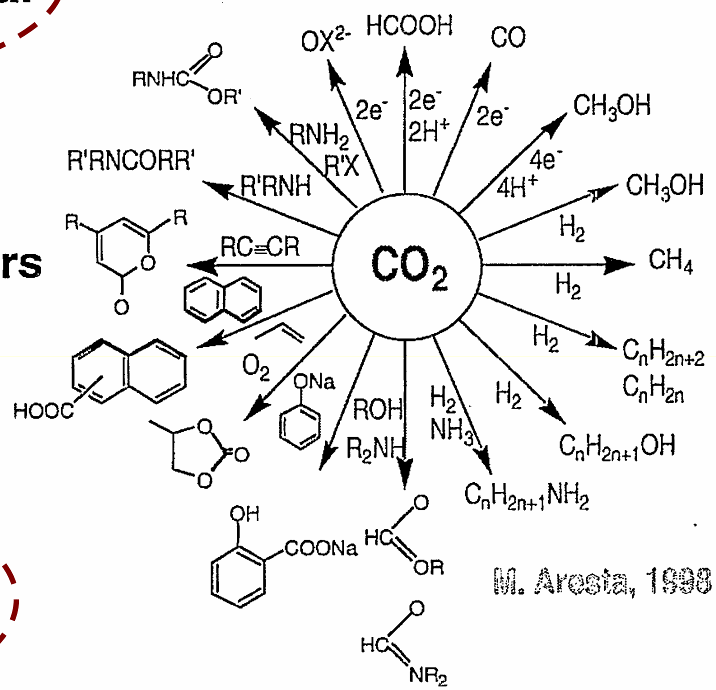
Intermediates or fine chemicals for the chemical industry

- -C(O)O- : Acids, esters, lactones
- -O-C(O)O- : Carbonates
- -NC(O)OR- : Carbamic esters
- -NCO : Isocyanates
- -N-C(O)-N : Ureas

Use as a solvent

Energy rich products

- CO, CH_3OH
- Hydrocarbons and their derivatives



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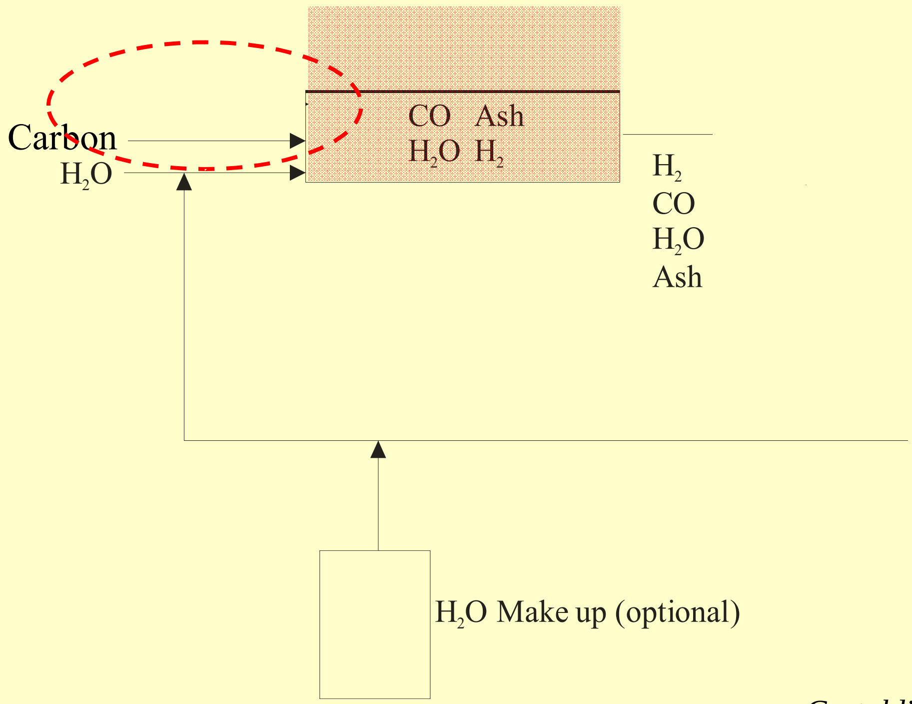
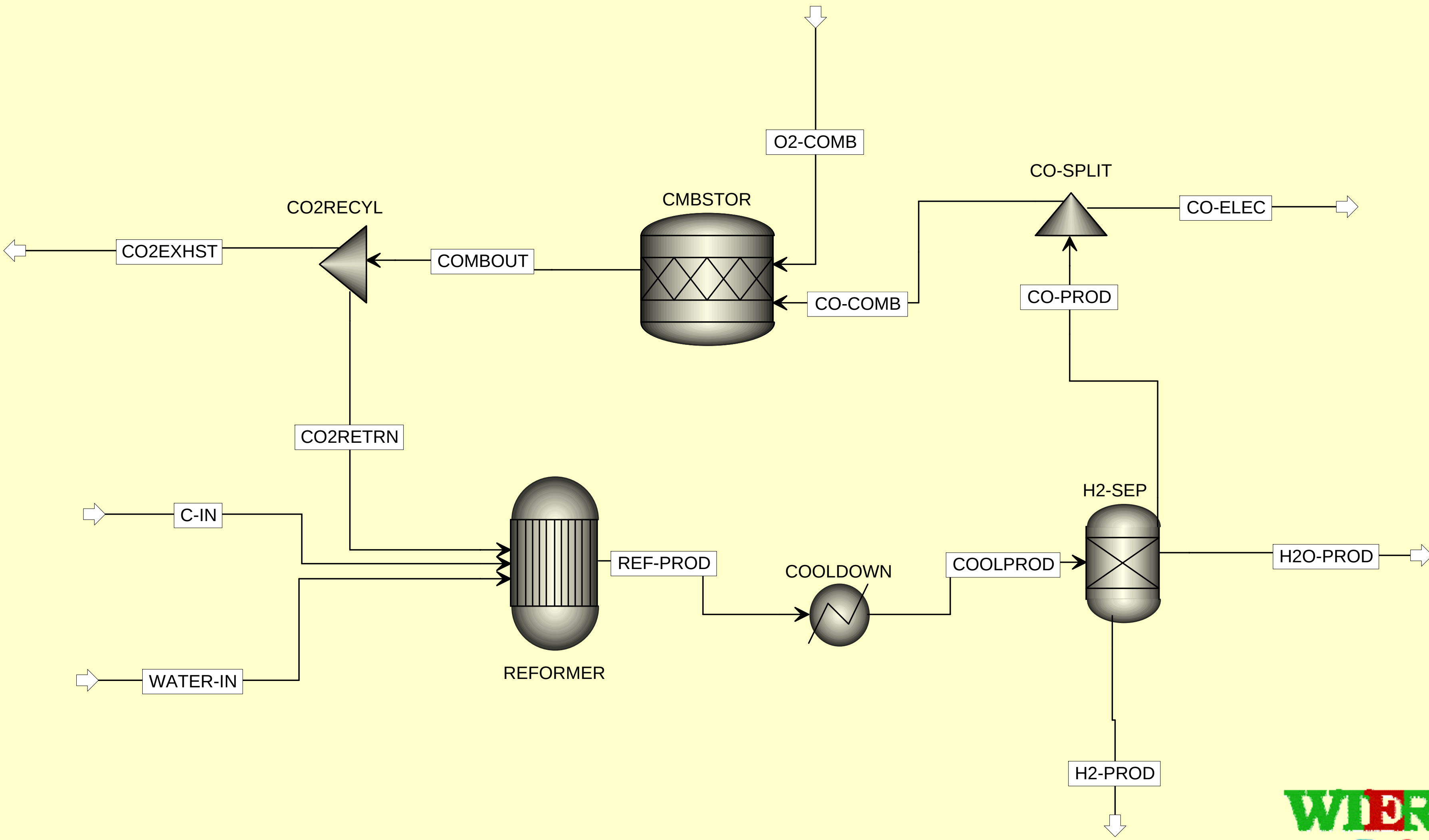
Catalytically Controlled Reaction Gasifier (CRG Process)



Castaldi MJ, Dooher JP. Int J Hydrogen Energy (2007), ***37****, 4170 - 4179*

CRG Aspen™ Simulation



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Baseline simulation results of energy balance and hydrogen generation for CRG process

Conventional Gasifier

H_2 → 0.7 kg/hr

CO_2 → ~ 15%

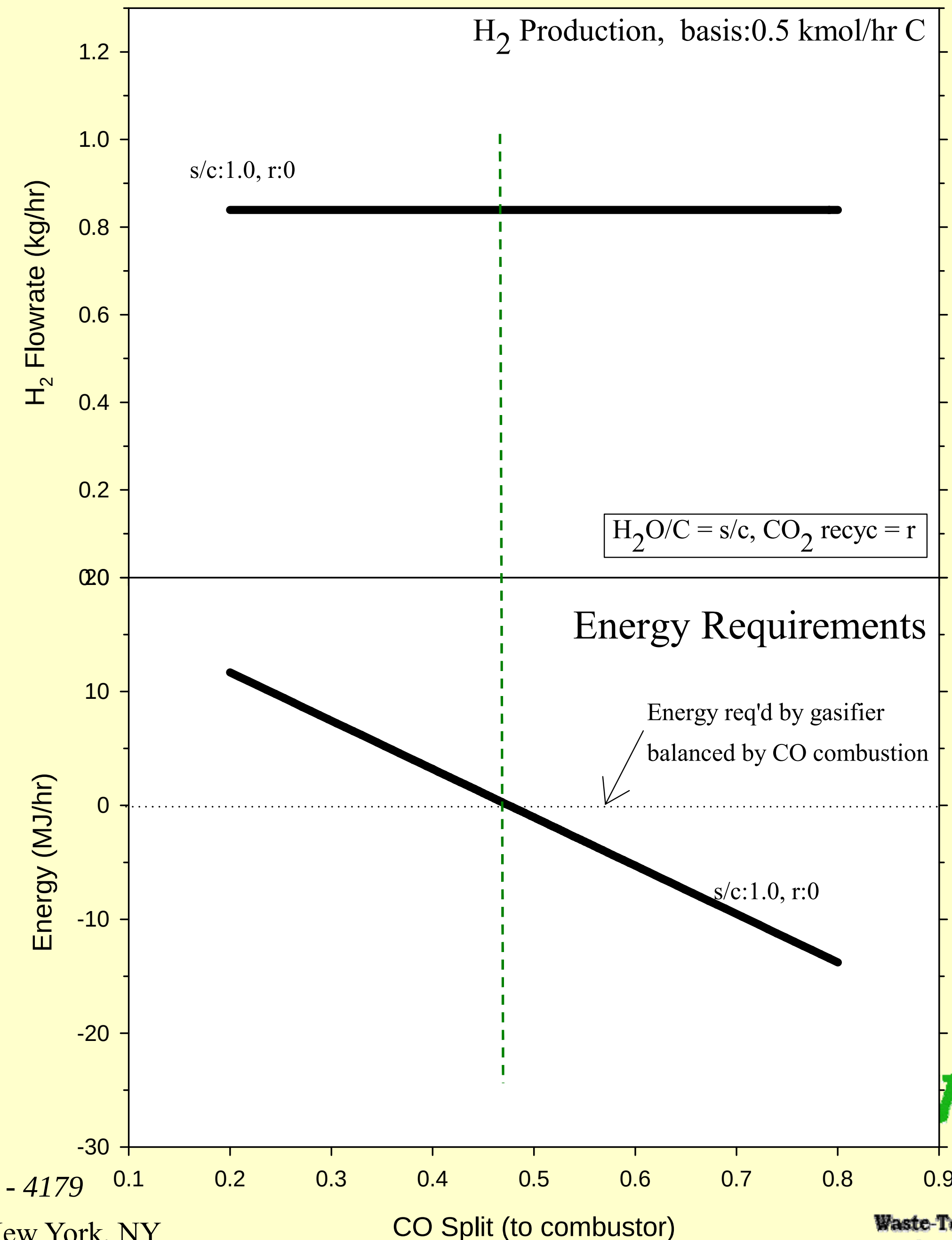
CRG Process

H_2 → 0.85 kg/hr

CO_2 → ~ 1.5%

e^- → ~13 kW/kmol C

CO Combustion → ~48%



*Castaldi MJ, Int J Hydrogen Energy (2007), **37**, 4170 - 4179*

Comparison of baseline and 25% CO_2 recycle to the reformer

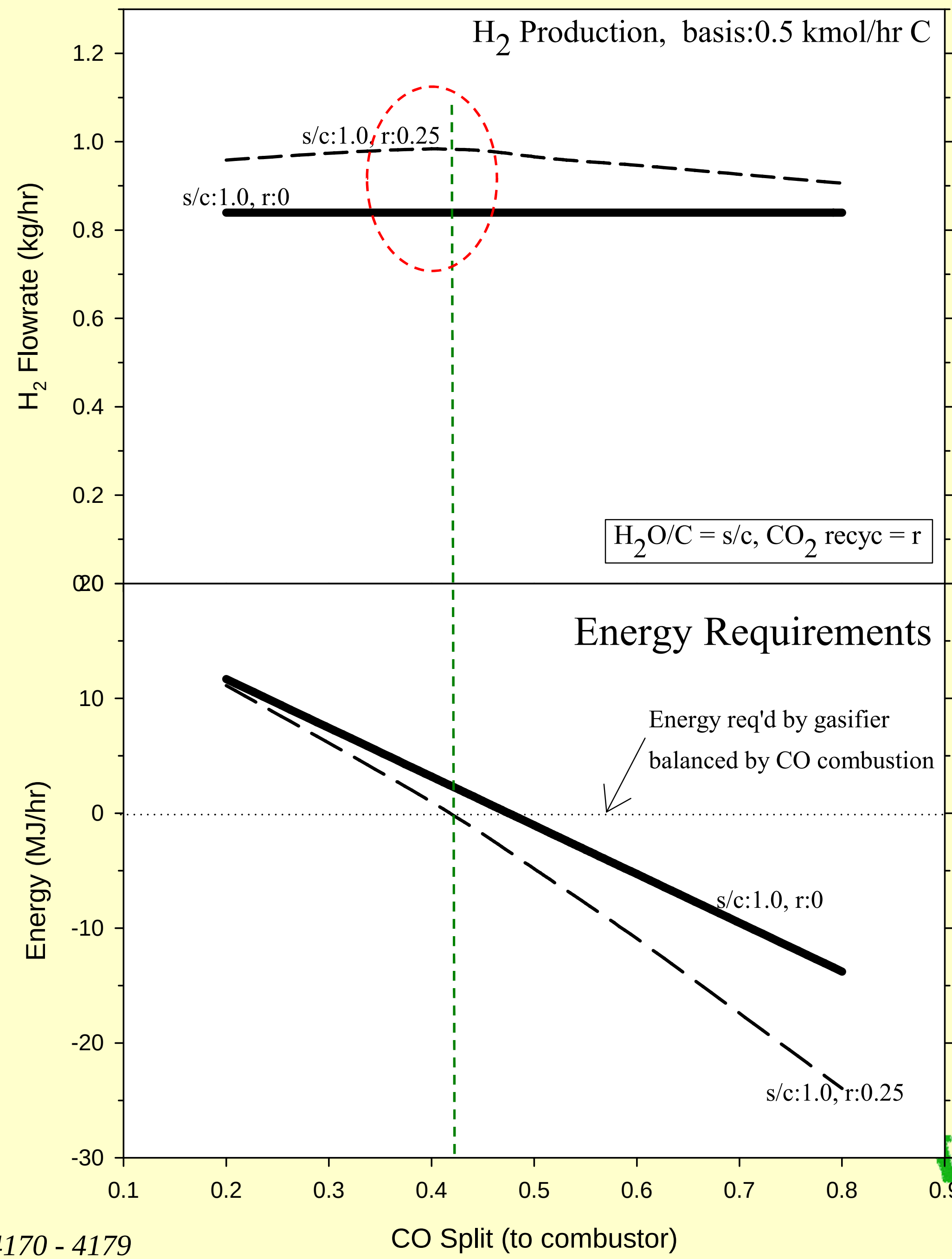
<u>CRG Process</u>

H_2 → 0.95 kg/hr

CO_2 → ~ 1.5%

e^- → ~13 kW/kmol C

CO Combustion → ~42%



*Castaldi MJ, Int J Hydrogen Energy (2007), **37**, 4170 - 4179*

Experimental Feedstock Tested

Biomass
Coal
Waste

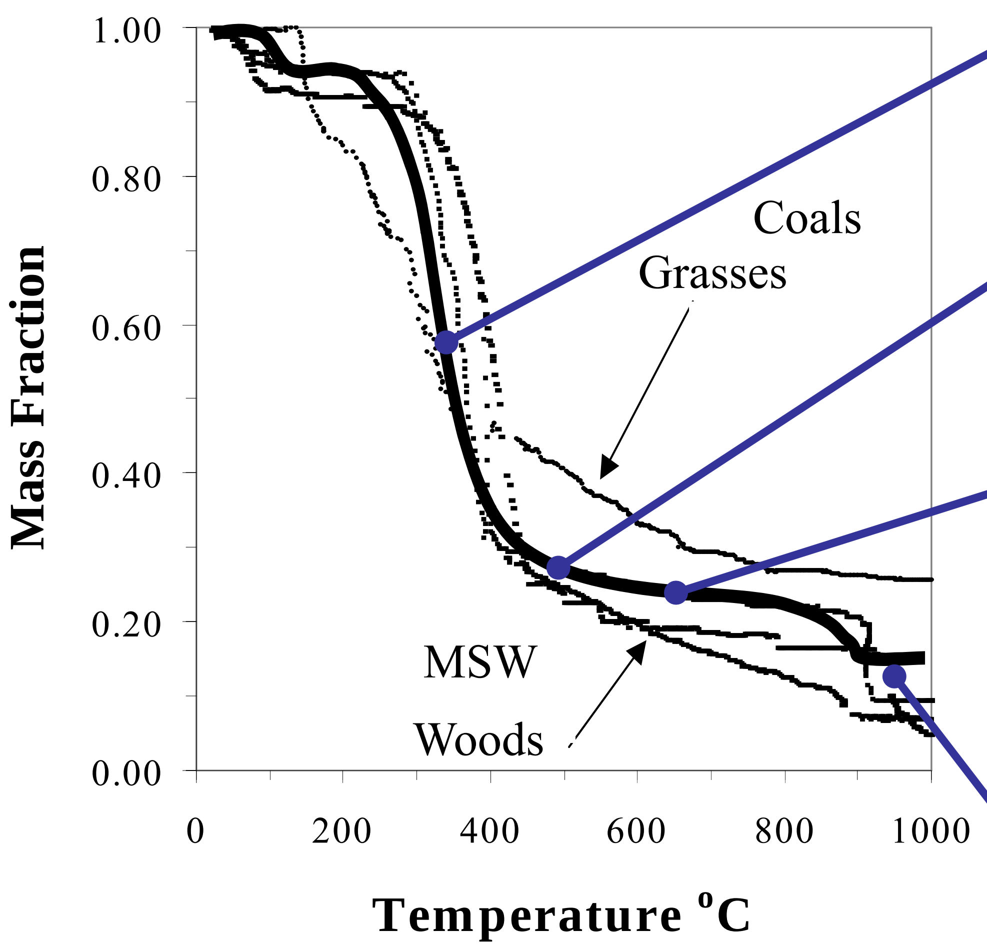
Biomass Fuel	Classification	Mass % Residue	HHV (calories/gram)	Cellulose	Hemicellulose	Lignin
Spruce	Softwood	0.338	4719	48	21	28
White Pine	Softwood	0.316	4781	42	21	26
Douglas Fir	Softwood	0.086	4769	41	24	28
Poplar	Hardwood	0.253	4699	41	21	24
Sugar Maple	Hardwood	0.240	4725	39	30	23
Red Oak	Hardwood	0.110	4782	40	25	26
Alfalfa	Grass	5.890	4338 (ECN)	30	14	14
Cordgrass	Grass	4.360	4448	43	33	16
Beachgrass	Grass	-	4329	45	31	12
Wheat Straw	Grass	-	4402 (ECN)	38	29	14
Maple Bark	Bark	4.760	4316	18	33	19
Blue Fir Needle	Needles	-	4278 (ECN)	38	24	31
Pine Needle	Needles	4.130	4350 (IIT)	43	22	38
Gr. Olive Pit	Shell/Pit	-	5165 (ECN)	-	-	-
Pecan Shell	Shell/Pit	-	4371 (SCERP)	38	23	29
Almond Shell	Shell/Pit	-	4553 (ECN)	-	-	-
Walnut Shell	Shell/Pit	-	4823 (BEF)	-	-	-
Peanut Shell	Shell/Pit	-	4732 (BEF)	36	19	30
Rice Hull	Hull/Husk	-	4575 (ECN)	6	-	25

Table 1. Furnace combustion mass % residue, HHV from calorimetry and databases, and structural composition

Coal Type	HHV (cal/gm)	Specific Gravity	%Ash	%Moisture	%C	%H	%O	%N	%Cl	%S
Wyoming	4690	1.26	5.43	29.59	49.22	3.41	11.02	0.77	0.01	0.31
Montana	5176	1.10	4.12	25.40	54.14	3.80	11.50	0.71	0.00	0.34

Table 2. Specifications of the sub-bituminous coals taken from the quality spec sheets of the Cordero-Rojo mine in Wyoming and the Spring Creek mine in Montana

Experimental Mass Decomposition Curve



- 250-400°C: Primary Reaction
  - Bulk mass loss
  - Devolatilization and pyrolysis
- 400-700°C: Secondary Reaction
  - Ligno-cellulosic gasification
- 700-900°C: Tertiary Reaction
  - Oxygen in feedstock & steam react with solid Carbon
  - Recycled CO_2 begins char burnout
- 950 - 1000°C Mass burnout complete
  - Higher residual correspond to lower lignin content

Butterman and Castaldi, Env. Eng. Sci (2007) ***22****, 31-44*

CO_2 Impact on Coal

- **Decrease** in H_2 production with CO_2
- **Increase** in CO production with CO_2

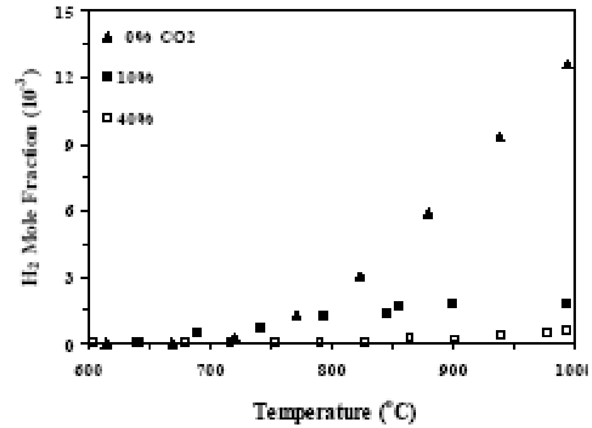


Figure 21. H_2 Evolution Depression from Montana coal using CO_2 (S/C = 10)

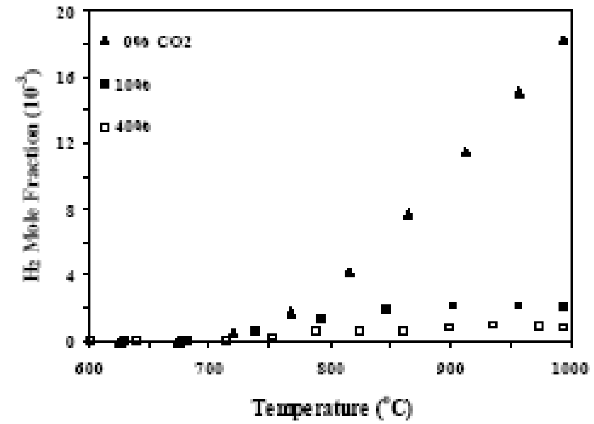


Figure 22. H_2 Evolution Depression from Wyoming coal using CO_2 (S/C = 9)

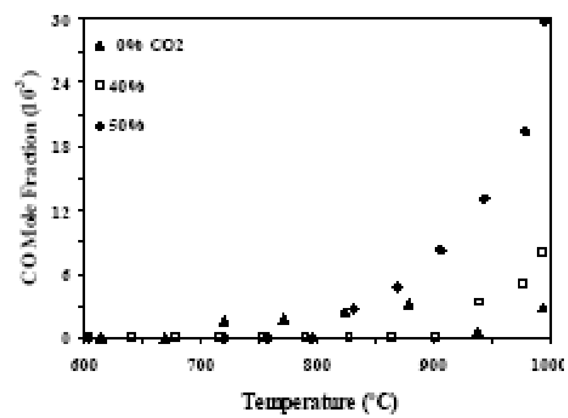


Figure 23.CO Evolution Enhancement from Montana coal using CO_2 (S/C = 10)

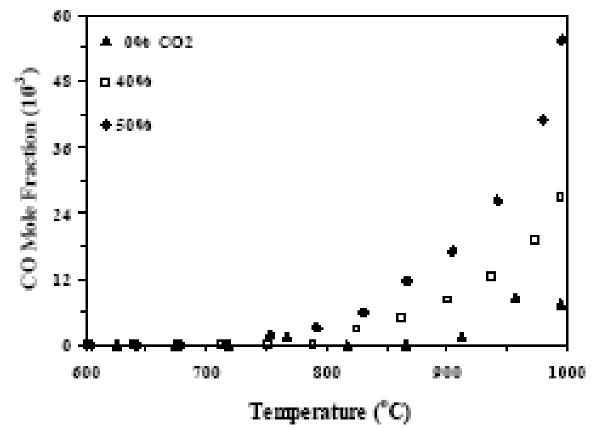
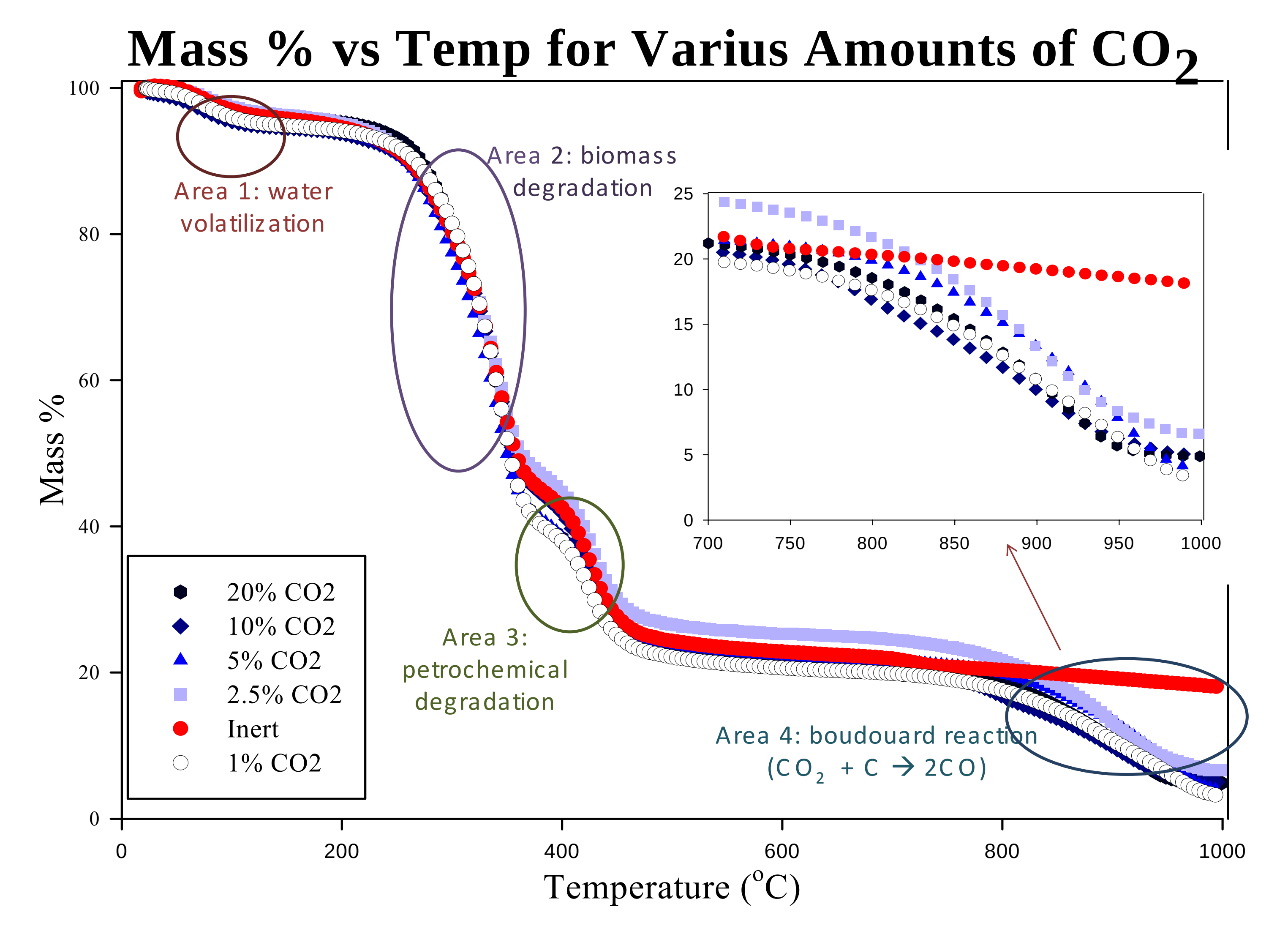


Figure 24.CO Evolution Enhancement from Wyoming coal using CO_2 (S/C = 9)

MSW DATA



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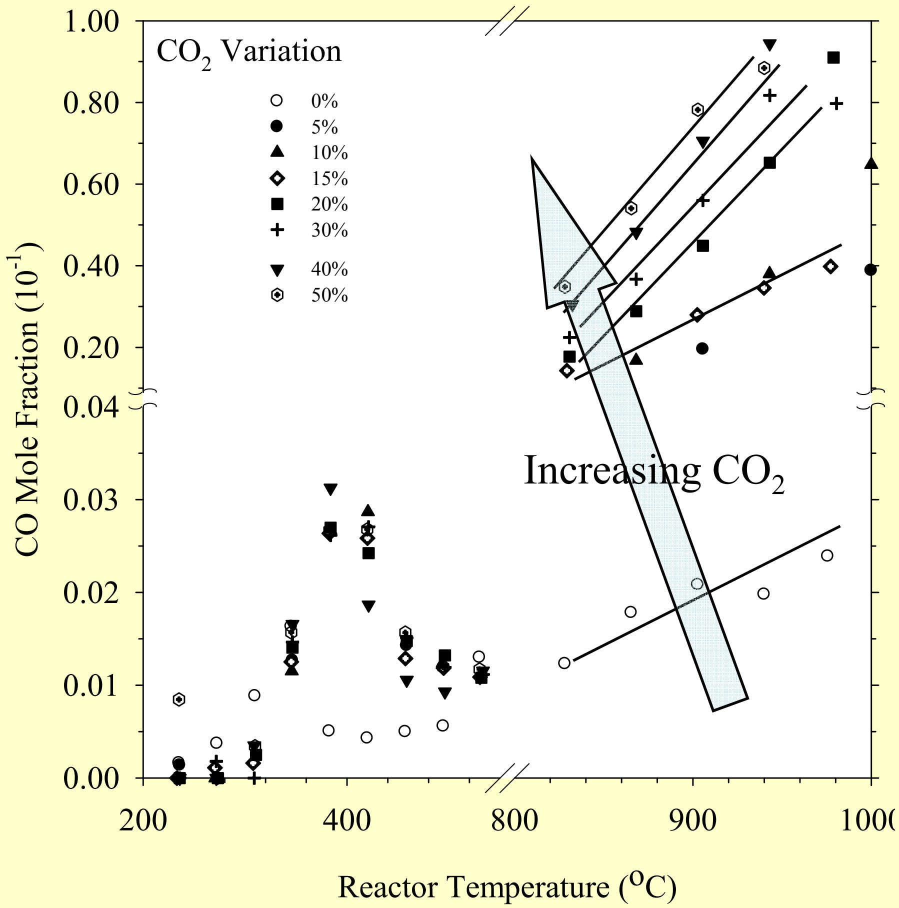
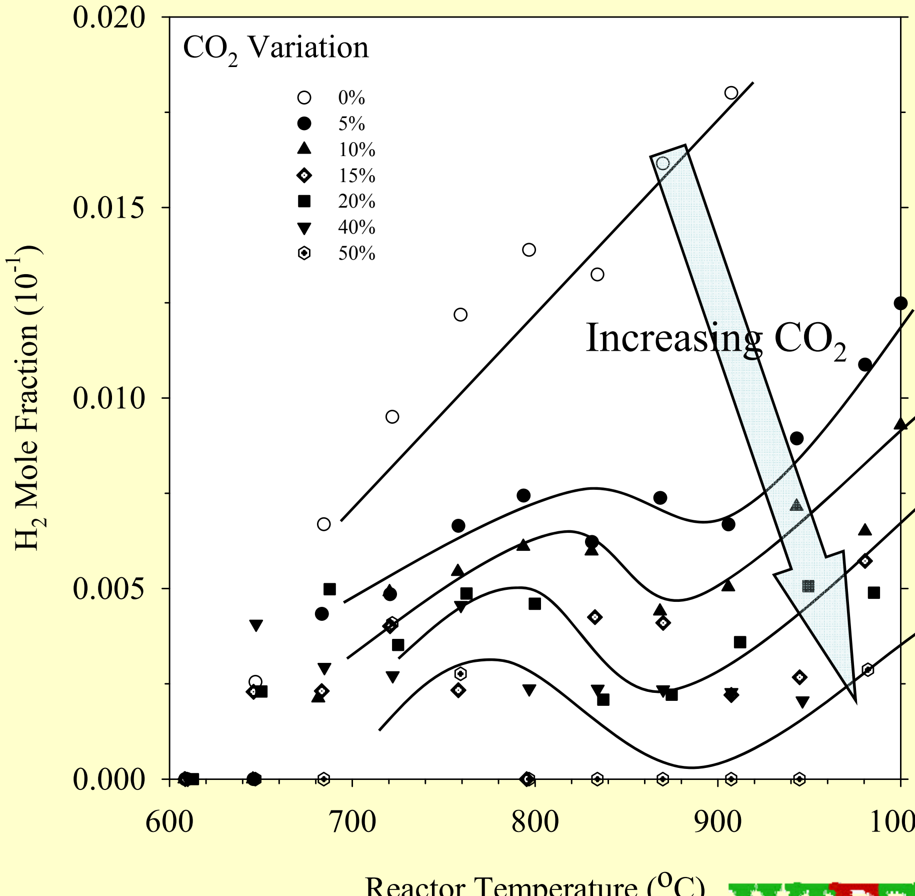
CO_2 impact on gasification products



CO increases with CO_2



H_2 decreases with CO_2

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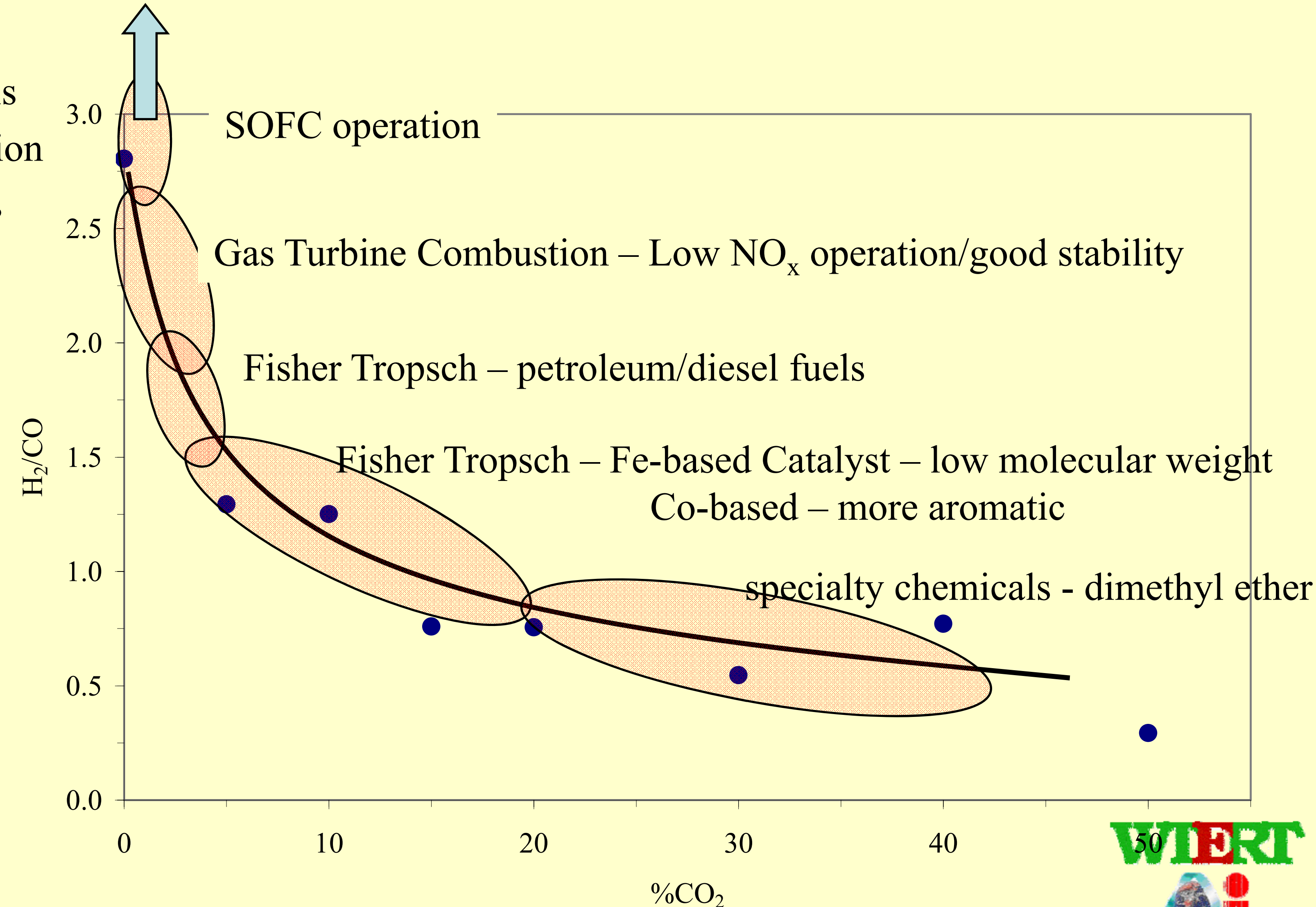
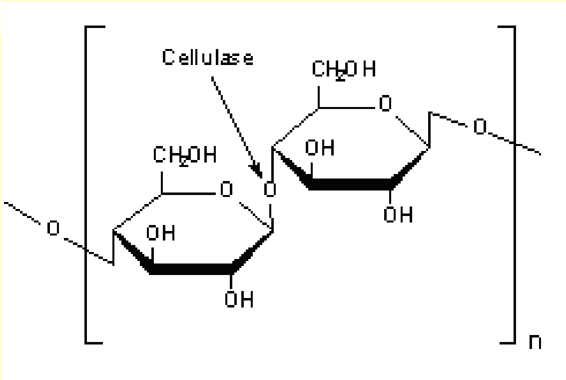
H_2/CO (Syngas) Tuning

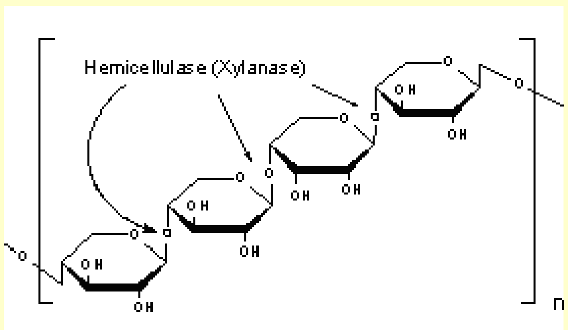
- Fuels
- Chemicals
- Combustion
- Fuel cells



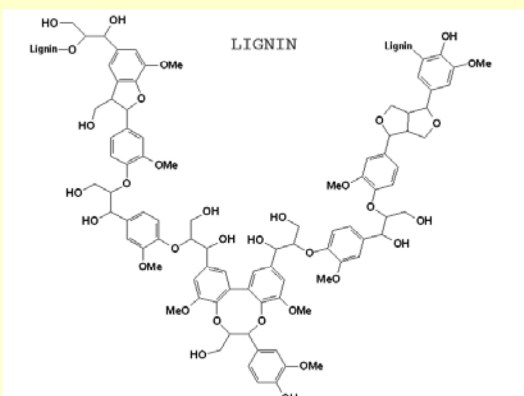
Structural Components of Biomass



Cellulose- the main structural component of biomass, linear crystalline polymer of glucose held together by β-glycosidic linkages strengthened by H-bonding between chains



Hemicellulose- short highly branched, less rigid and more easily hydrolyzed, amorphous polymer of 5 and 6-carbon sugars



Lignin- the structural component of biomass that strengthens the cell wall and cements the cells together, high MW, highly cross-linked aromatic

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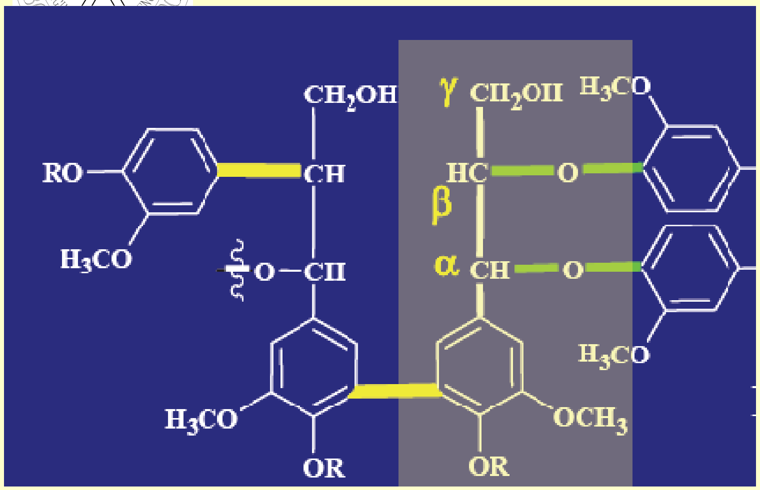
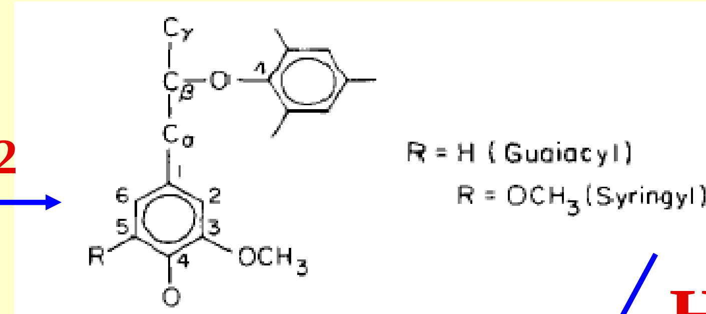
Lignin Decomposition

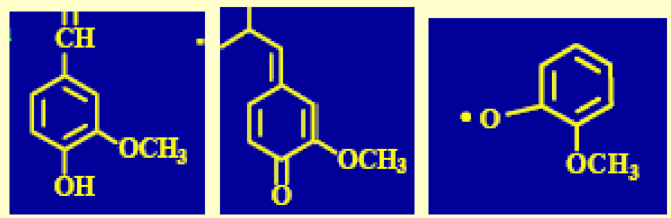


Lignin

H_2



H_2

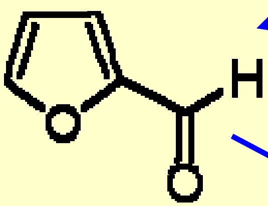


Vinyl Ionic Phenoxy

CH_4

Methane producing species

CH_4

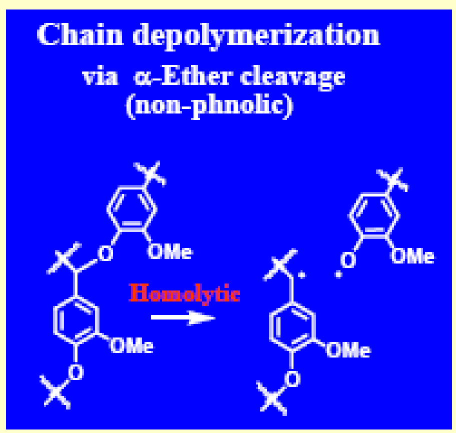


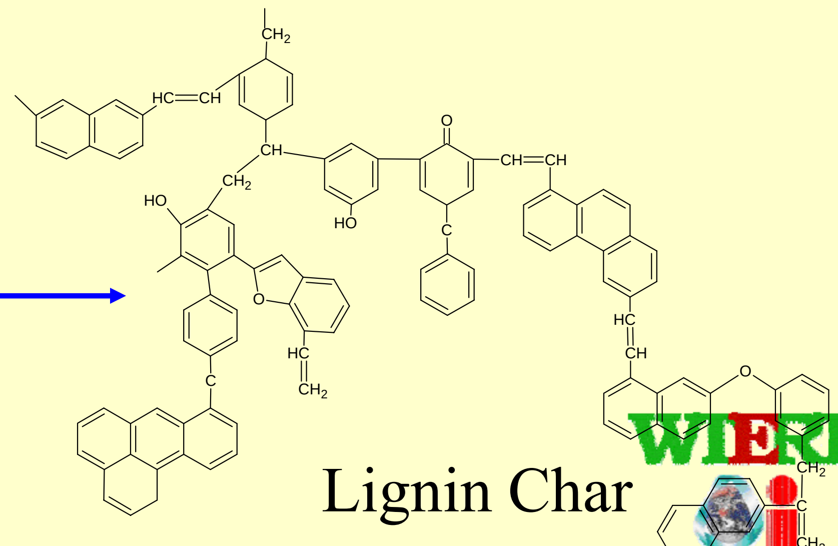
2-Furaldehyde Decarboxylation

Methylation and Dehydrogenation Of Lattice Structure

CO

Continued Carbon enrichment





Lignin Char

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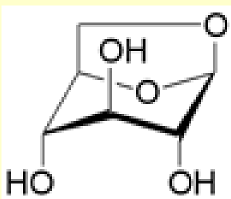
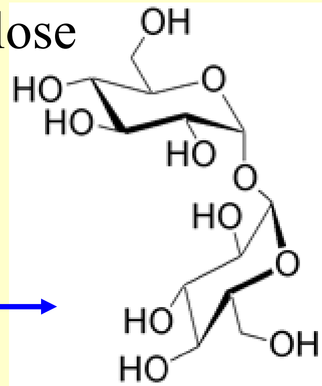
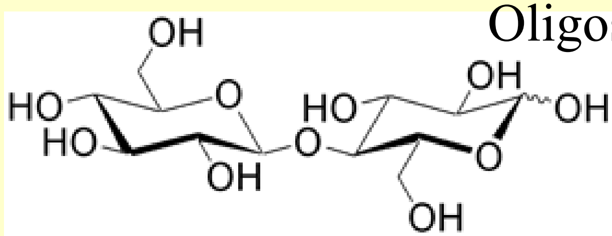
Cellulose Decomposition

Levoglucosan



Trehalose



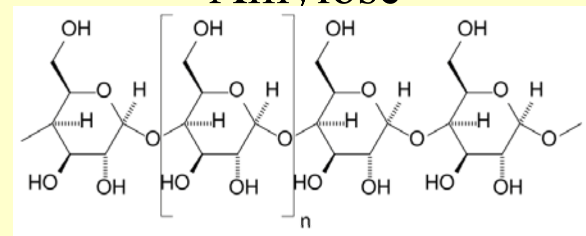


Cellobiose

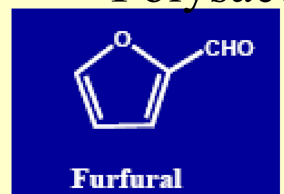
(Methanol soluble Oligosaccharides)

Dehydroxylation
Polymerization

Amylose



(Water soluble Polysaccharides and Furans and Carbonyls)

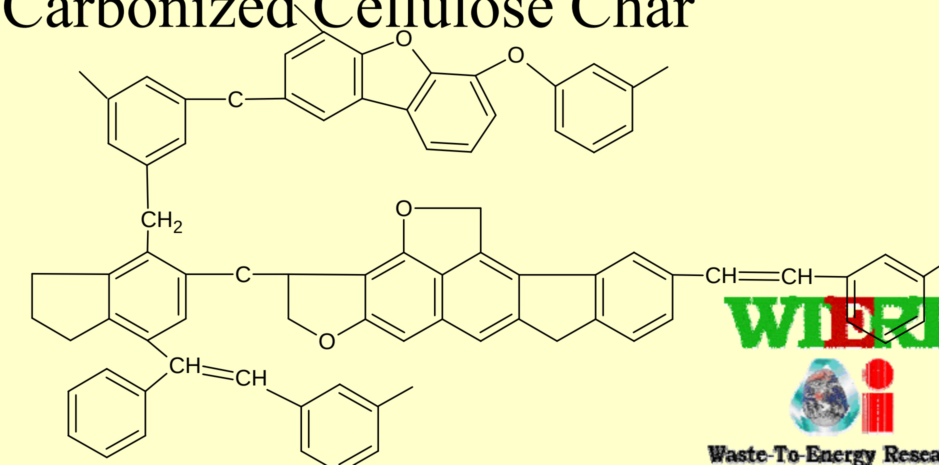


Furfural undergoes decarbonylation

Devolatilization
No Char formation

Low MW
Volatiles
CO, CO_2, CH_4, H_2

Carbonized Cellulose Char



Major Gasification Reactions

Low Temperature

Water Gas Shift

$CO + H_2O \rightarrow CO_2 + H_2$

Methanation

$C + 2H_2 \rightarrow CH_4$

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

$CO + 3H_2 \rightarrow CH_4 + H_2O$

Steam Gasification

$C + H_2O \rightarrow H_2 + CO$

High Temperature

Steam Gasification

$C + H_2O \rightarrow H_2 + CO$

Boudouard

$C + CO_2 \rightarrow 2CO$

Char Burnout: O (Biomass/Steam)

$C + \frac{1}{2}O_2 \rightarrow CO$

Reverse Water Gas Shift

$CO_2 + H_2 \rightarrow CO + H_2O$

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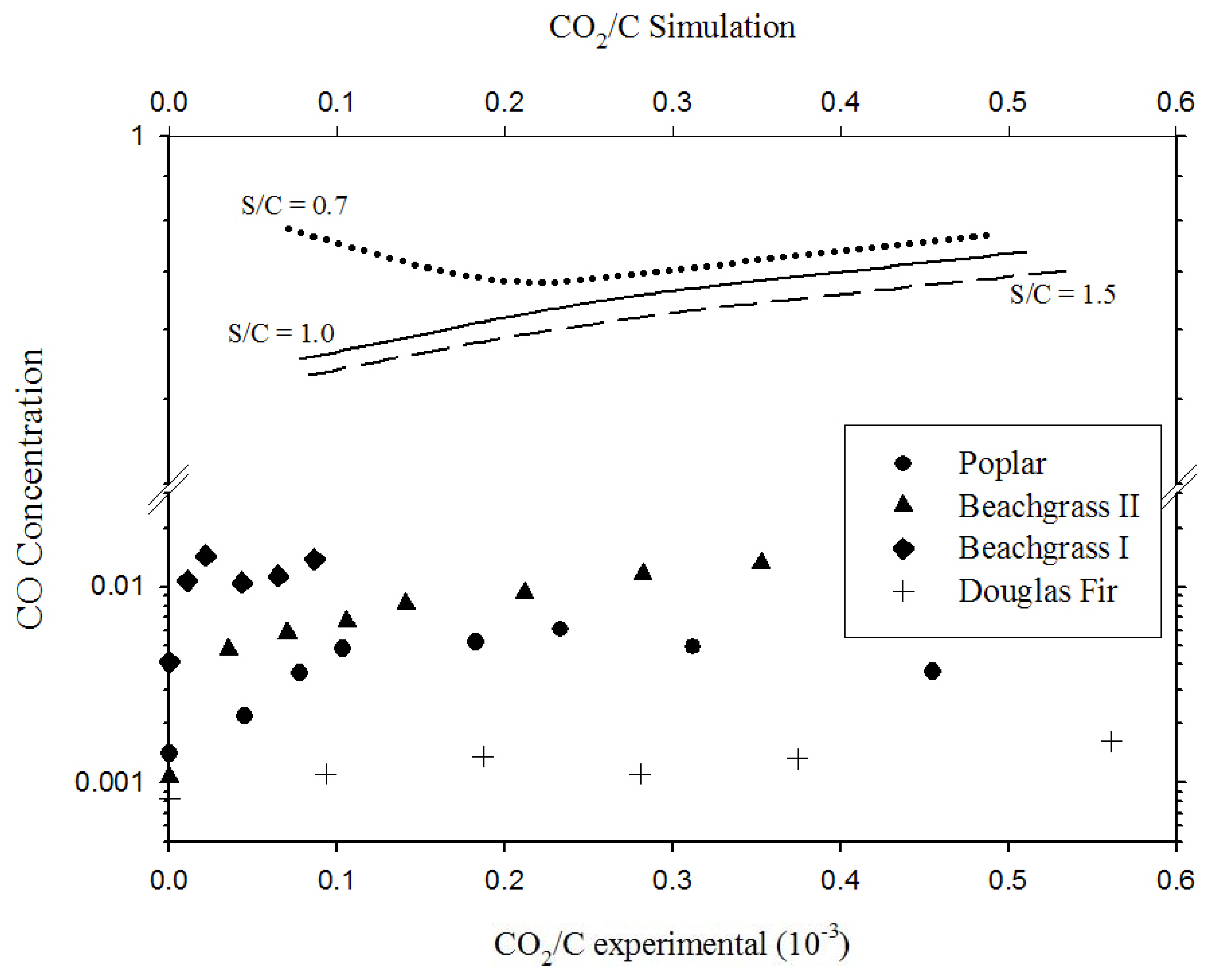
CO Comparison



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

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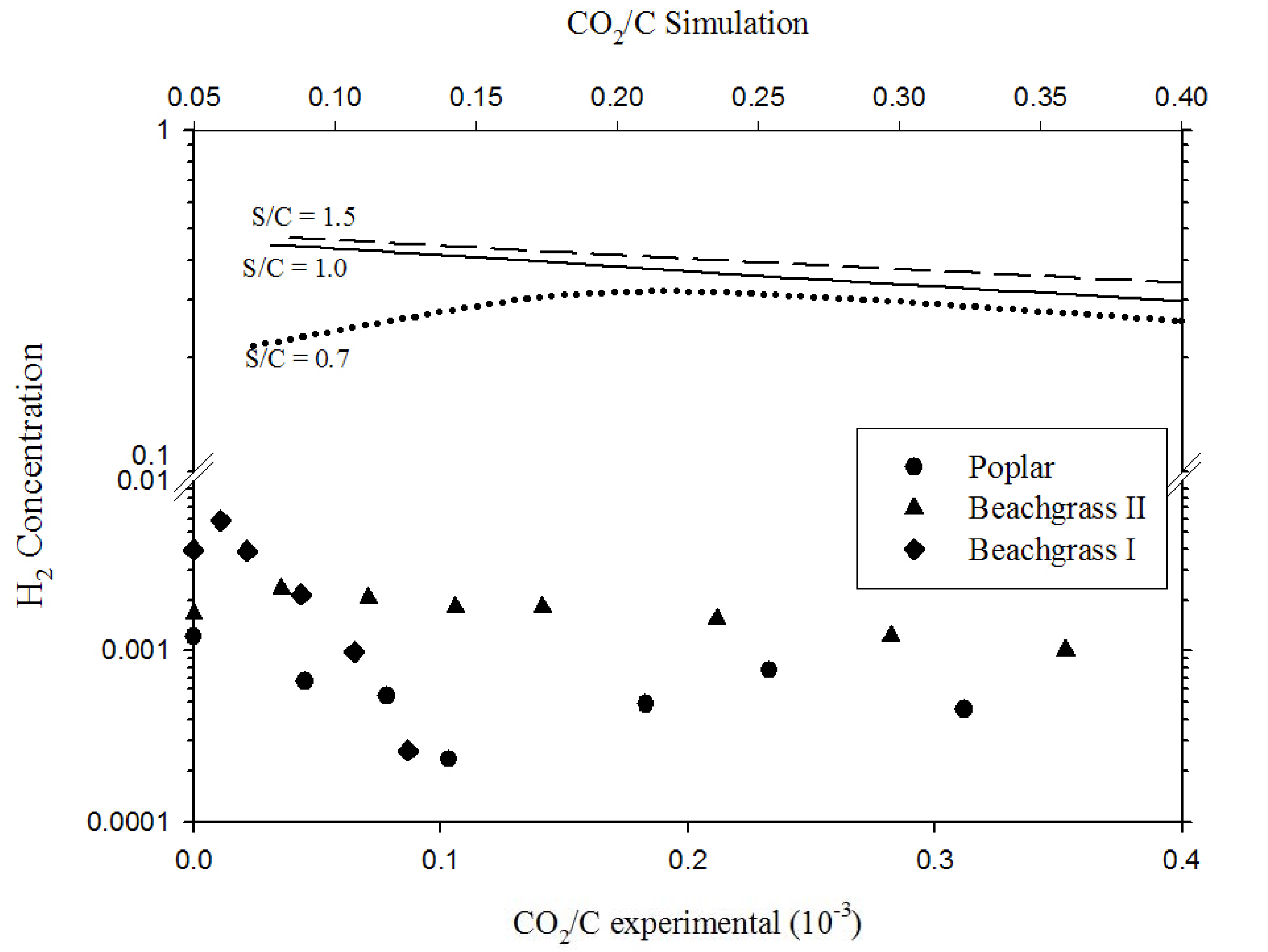
H_2 Comparison



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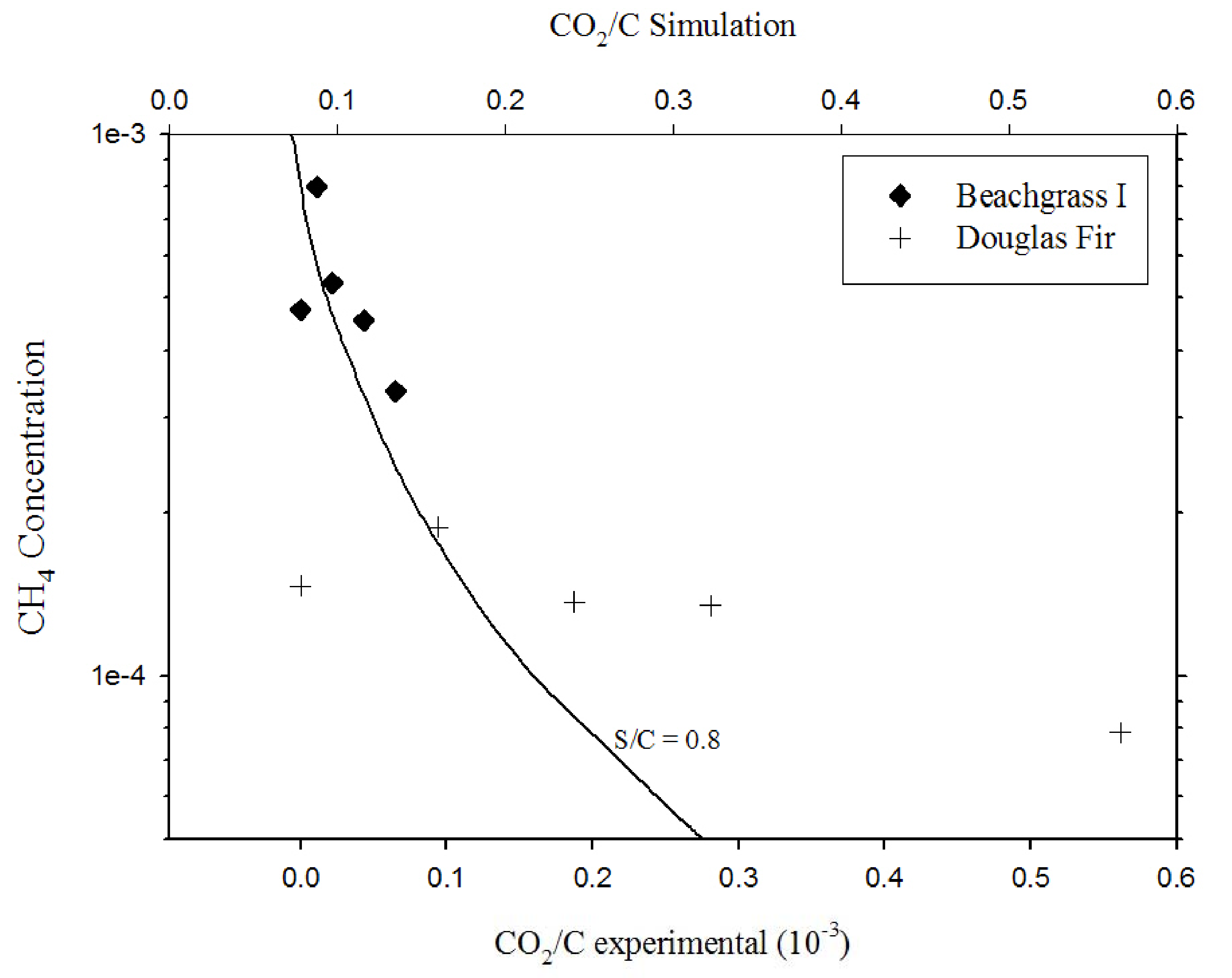
CH_4 Comparison



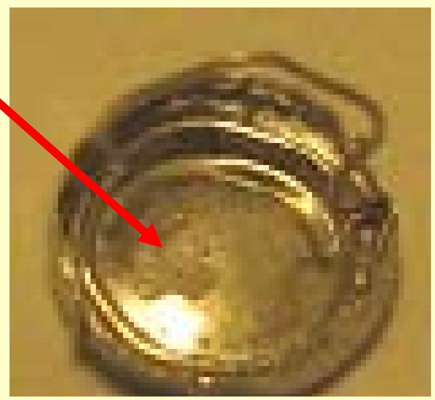
Butterman and Castaldi, Indus. & Eng, Chem. Res, (2007) 47, 8875-8886

Value: Enhanced Char Burnout With CO_2

Walnut Shells**: 0% CO_2**

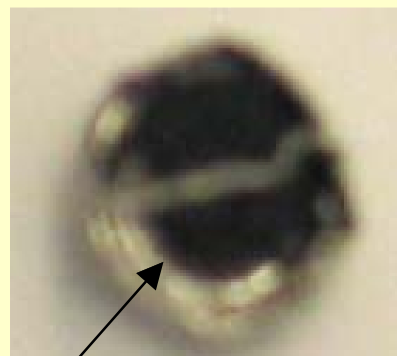
Walnut Shells: **30% CO_2**

Douglas Fir: **0% CO_2**



Douglas Fir: **30% CO_2**

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



Poplar: **0% CO_2**

Poplar: **34% CO_2**

- Observed for all samples tested

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

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Char Pore Development- Enhanced Char Burnout With CO_2

Lignin

0% CO_2-H_2O/N_2

1^{o}C/min,

22-860^{o}C

Lignin

100% CO_2

1^{o}C/min

22-860^{o}C

Lignin

100% CO_2

1^{o}C/min

22-930^{o}C

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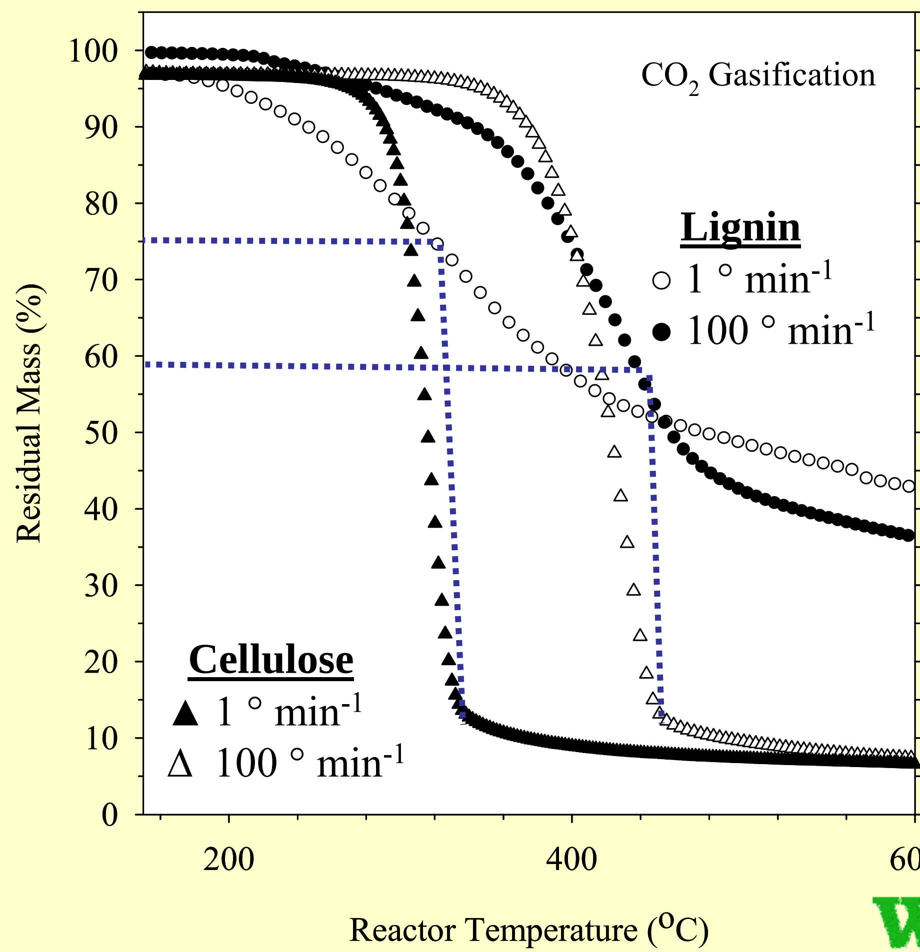
Cellulose/Lignin Separation

- Separation of lignin from cellulose, CO_2 processes lignin more efficiently than steam



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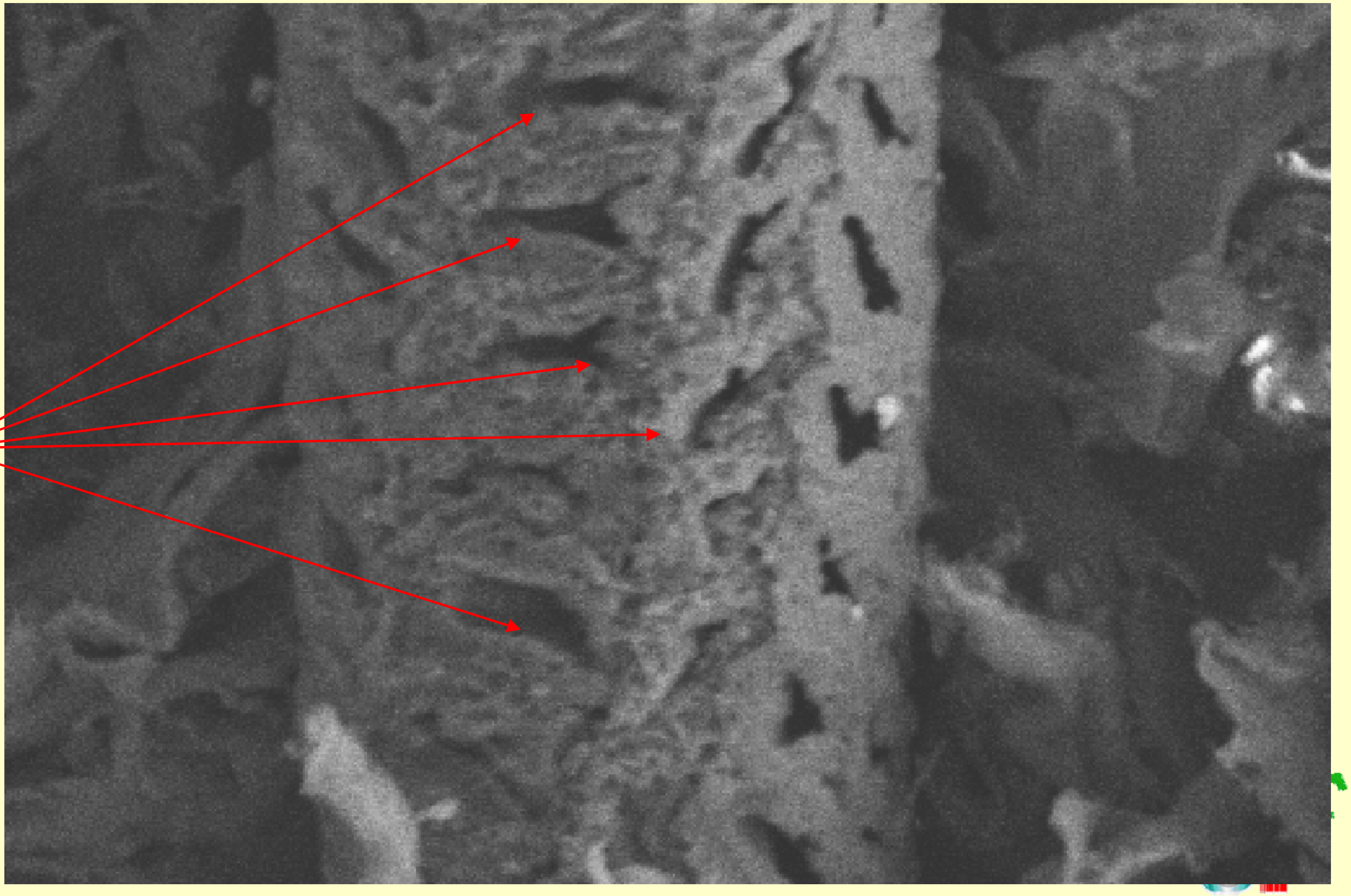
SEM - Douglas Fir Char Fiber Enhanced micropore structure during steam gasification

Increased porosity following thermal treatment



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Conclusions

- Data quantitatively matches Simulation

- CO_2 injection enhances CO production
  - T > 700^{o}C resulting in improved char burnout
  - Less residual ash, especially carbon

•CO production near 400^{o}C marks transition between the two thermal degradation regimes
  - 250-400^{o}C – Local maxima of CO production
  - T > 700^{o}C – Steady increase in CO

- H_2 production had two regions of abrupt production
  - 550-575^{o}C for herbaceous
  - 675-725^{o}C for woody feedstocks

- Coal and MSW follows trends of biomass

- CO_2 accesses the recalcitrant Char more effectively than steam

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Poster Session

Defining Sustainability

Many equate sustainability with no emissions, or minimized raw material usage, with considering the impacts at the boundaries – avoided emissions or decreased energy use

1. Sustainability is a path of continuous improvement, wherein the products and services required by society are delivered with progressively less negative impact upon the Earth – *IfS:AIChE*
2. Sustainability is an attempt to provide the best outcomes for the human and natural environments both now and into the indefinite future. - *Wikipedia*
3. Sustainable development as development that "**meets the needs of the present without compromising the ability of future generations to meet their own needs**". It relates to the continuity of economic, social, institutional and environmental aspects of human society, as well as the non-human environment - *Brundtland Commission*

Sustainability is not a way to raise taxes – NYC mayor, $8 to enter city by car during working hours

Currently

"The nature of environmental issues is changing from a regulatory to a resource focus" ***R. MacLean, Env. Protec. April 2003, P.12***

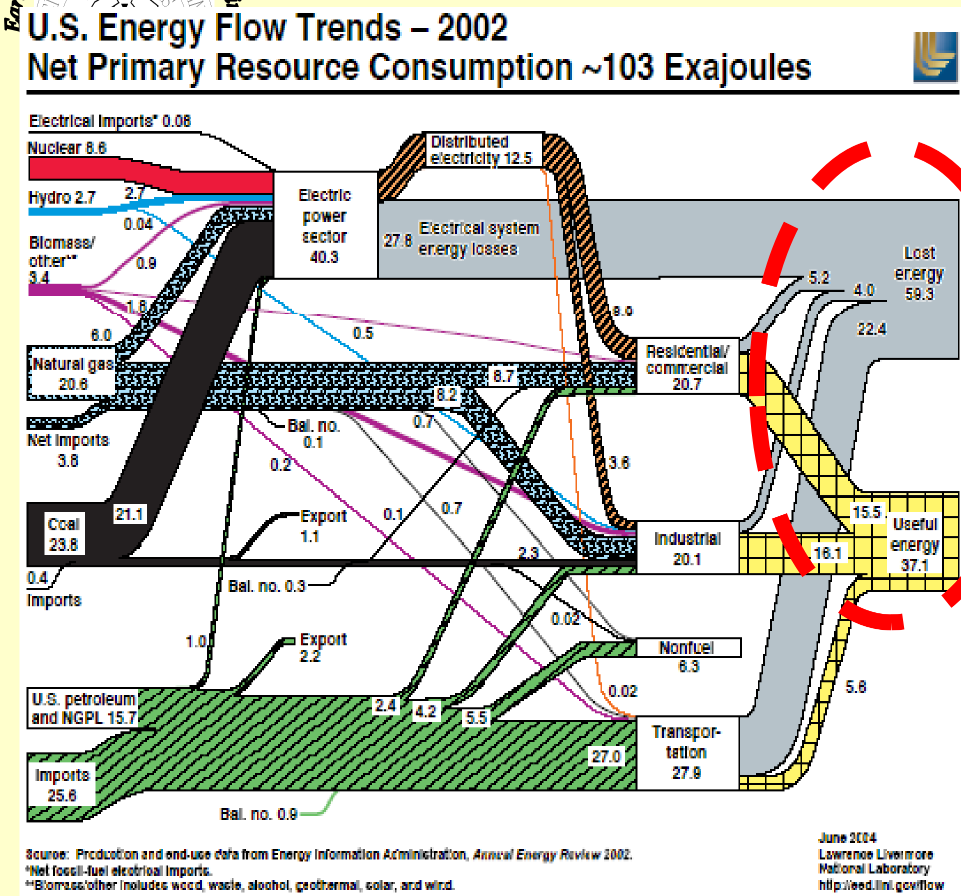
- **BP** → Re-staffing for environmental innovation
- **Walmart** → Supply chain vendors "20 chemicals of concern
- **Home Depot** → Eco-Label
- Carpet Recyclers profitable
- **GE** → wind power, clean water
- **NSF** → new directorate (EBW)
- **Venture Capital** → Niche energy/environment

- Education
  - Public Access to information
- Environment → resource utilization
  - Concentrators and Dilutors
- Climate change → economic issue

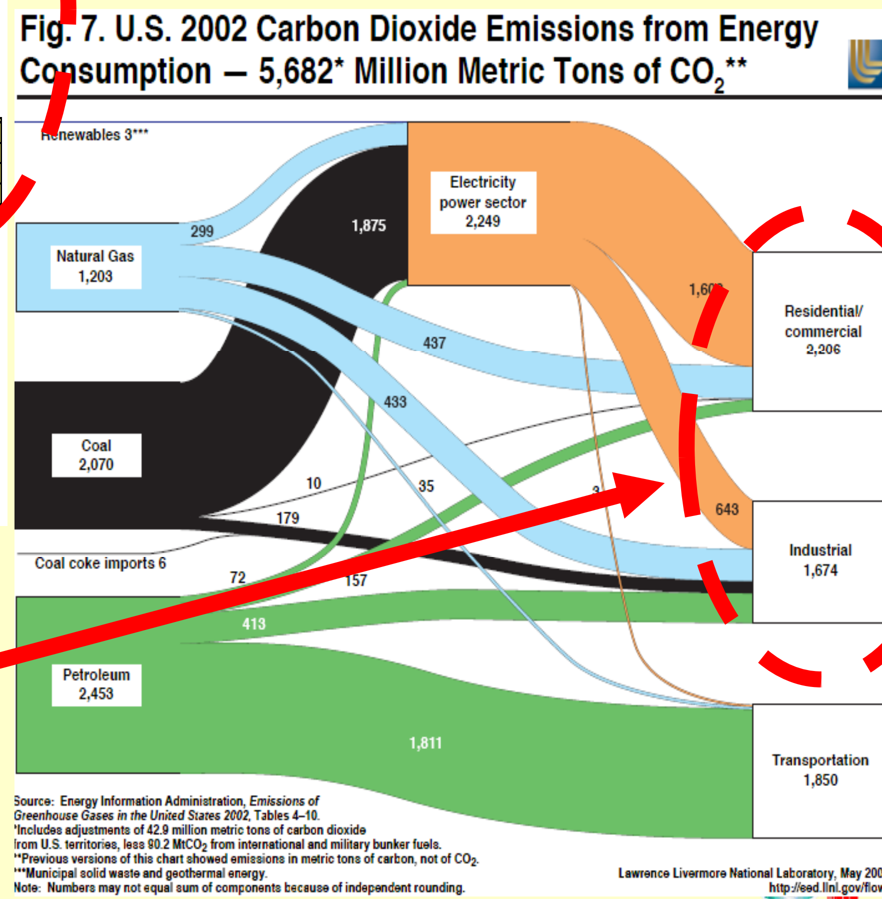
Alternative Energy

- The world is sensitive to energy supply *(new Paradigm)*
  - Security, Procurement → supply chain disruptions
- Two-fold increase in energy consumption (*demand*)
  - From 402 exajoules to 837-1041 over next 40 years.
- CO_2 atmospheric concentrations are rising *(environment)*
  - The need for separating carbon dioxide from the product gases and plant effluent in order to prevent it from entering the atmosphere.
  - Space constrained or preferred land use

Scale of the Issue



- ***Power / heat sectors are extremely inefficient***
  - ***~60% of energy is wasted!***
  - ***better power cycles and materials will help***
  - ***All fuels are needed!***



- ***Heat generation produces 2/3 of all CO_2 emissions***
- ***Better thermal conversion systems needed***
- ***Better Fuels needed!***

Energy from Waste

- ***WTE conserves fossil fuels by generating electricity. (Energy)***
  - 1 ton of waste combusted = 45 gallons of oil or 0.28 tons of coal
  - Most WTE facilities in U.S. process between 500 and 3,000 tons of waste per day
  - Electricity for 2.8 million homes
- **WTE facilities process 14% of the MSW in the United States. (Health)**
  - Trash-disposal needs about than 37 million people
- **WTE facilities meet some of the world's most stringent standards. (Environmental, local)**
  - Achieved compliance with new Clean Air Act pollution control standards in 2000
  - EPA data :dioxin emissions now account for less than 0.5% of dioxin emissions
- ***WTE facilities reduce greenhouse gas emissions. (Climate, global)***
  - EPA estimates :WTE facilities prevent 33 million metric tons of CO_2 per year avoided
- ***WTE facilities save real estate. (Land)***
  - They reduce the space required for landfills by about 90%
- ***WTE is compatible with recycling. (Resource Minimization)***
  - Communities served by WTE recycle 35% of their trash, compared to 30% for the general population.
  - Annually removes more than 700,000 tons of ferrous materials
  - Nearly 3 million tons of WTE ash is reused as landfill cover, roadbed, or building material.
- ***WTE facilities provide economic benefits*. (Economic)**
  - WTE is a $10 billion industry employs ~ 6,000 American workers annual wages ~ $400 million

Boundaries and interfaces of WTE cut across all sustainable fronts

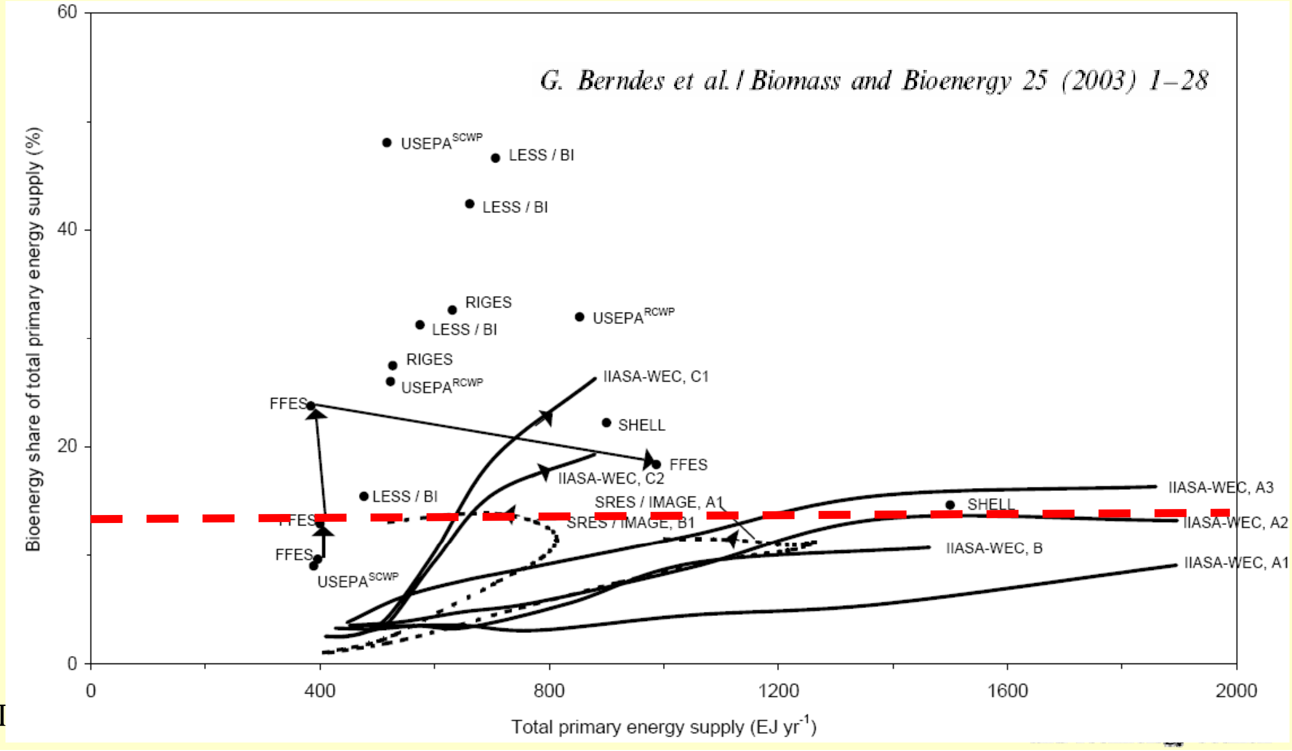
Waste-To-Energy Research and Technology Council

Bioenergy

- Sustainable carbon neutral power, heat and chemical feedstocks.
- Potential to provide ~ 15% of energy demand.
- Gasification
  - Lower PM, NO_x, and SO_2, than combustion
  - Steam addition – Increased concentration of H_2
  - CO_2 usage – enhanced char conversion and less residue for landfill.
  - Provides reagents (CO & H_2) for synthetic fuel/chemical production

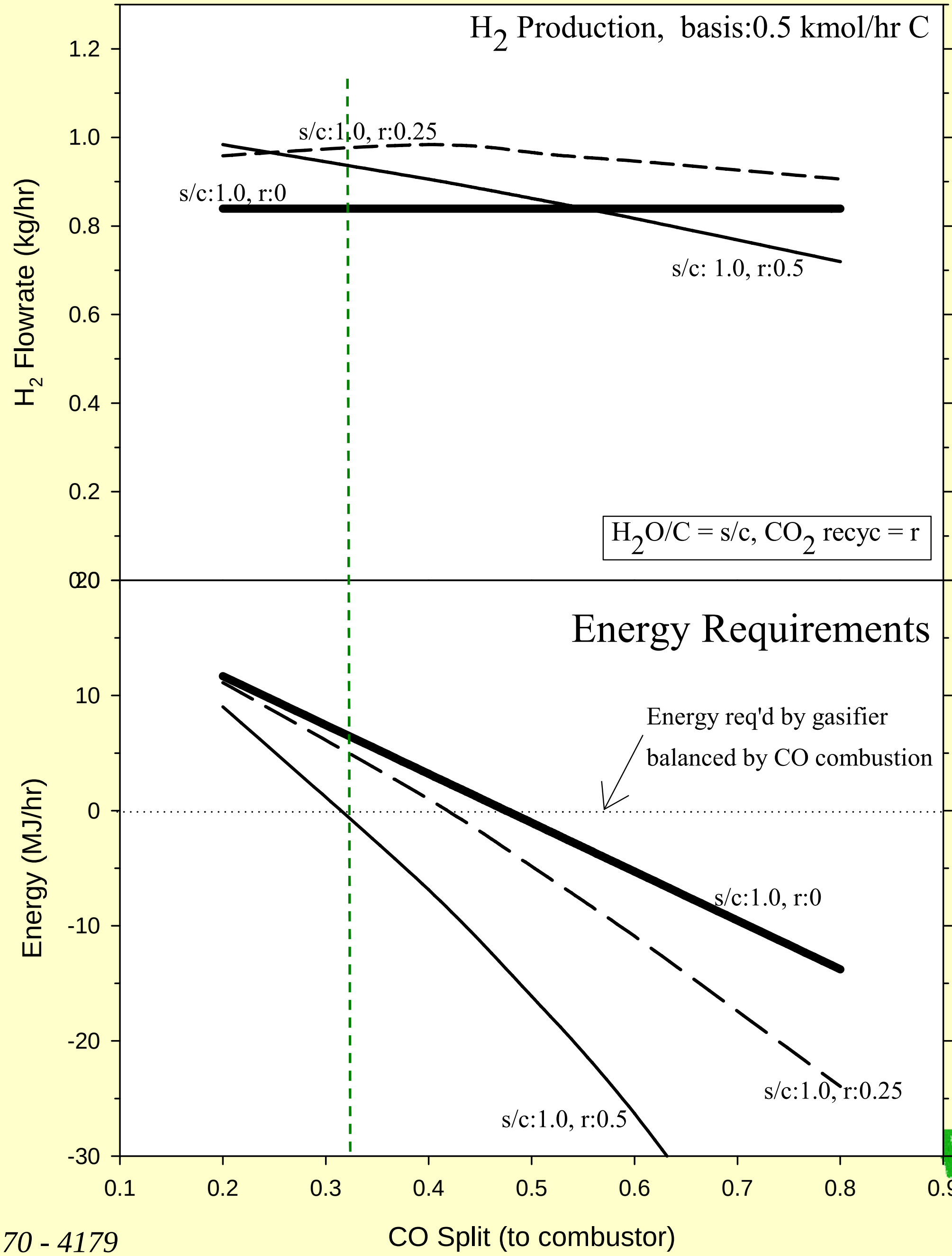
Estimations vary widely due to land availability and crop yields.

One piece of the alternative energy future technologies



CO_2 recycle comparison for steam to carbon ratio of 1.0.

Tradeoff: energy neutral vs H_2 production



*Castaldi MJ, Int J Hydrogen Energy (2007), **37**, 4170 - 4179*