

Impact of Pretreatment and Downstream Processing Technologies on Economics, Energy and Water Use in Cellulosic Ethanol Production

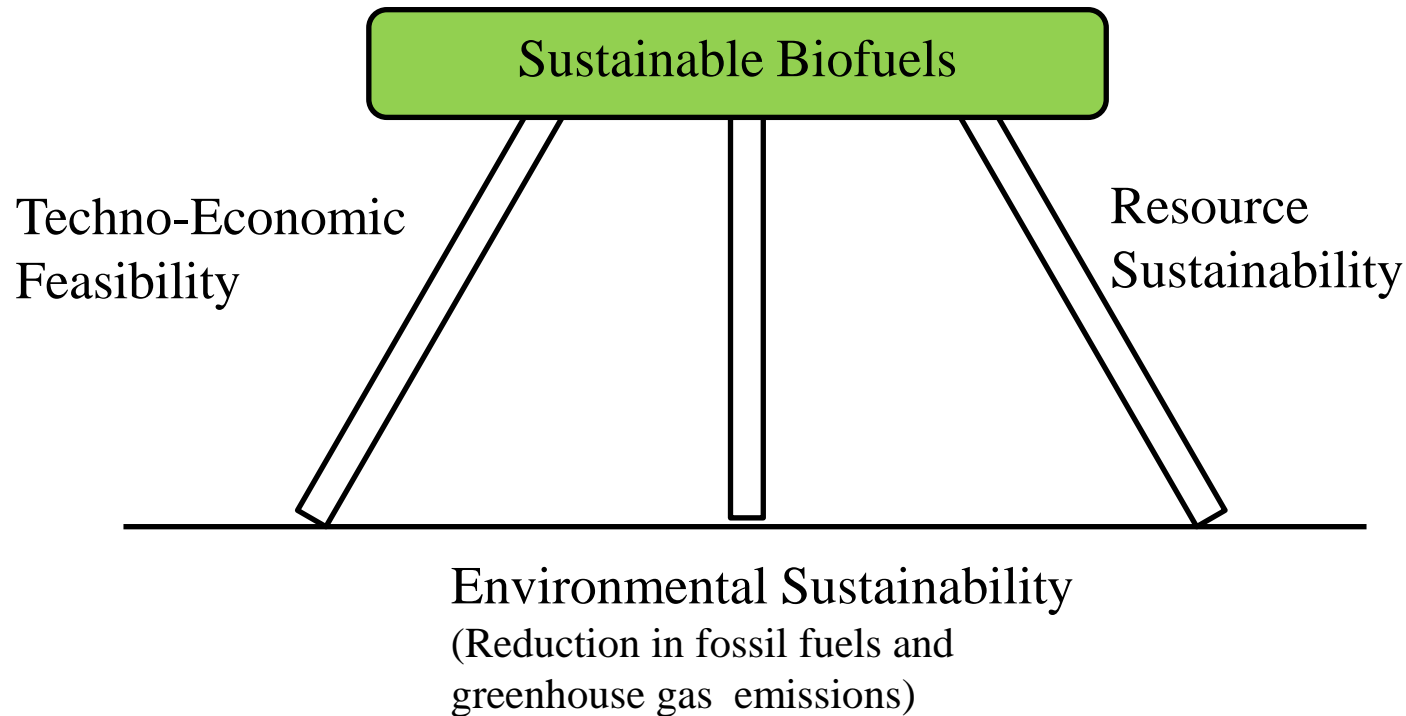
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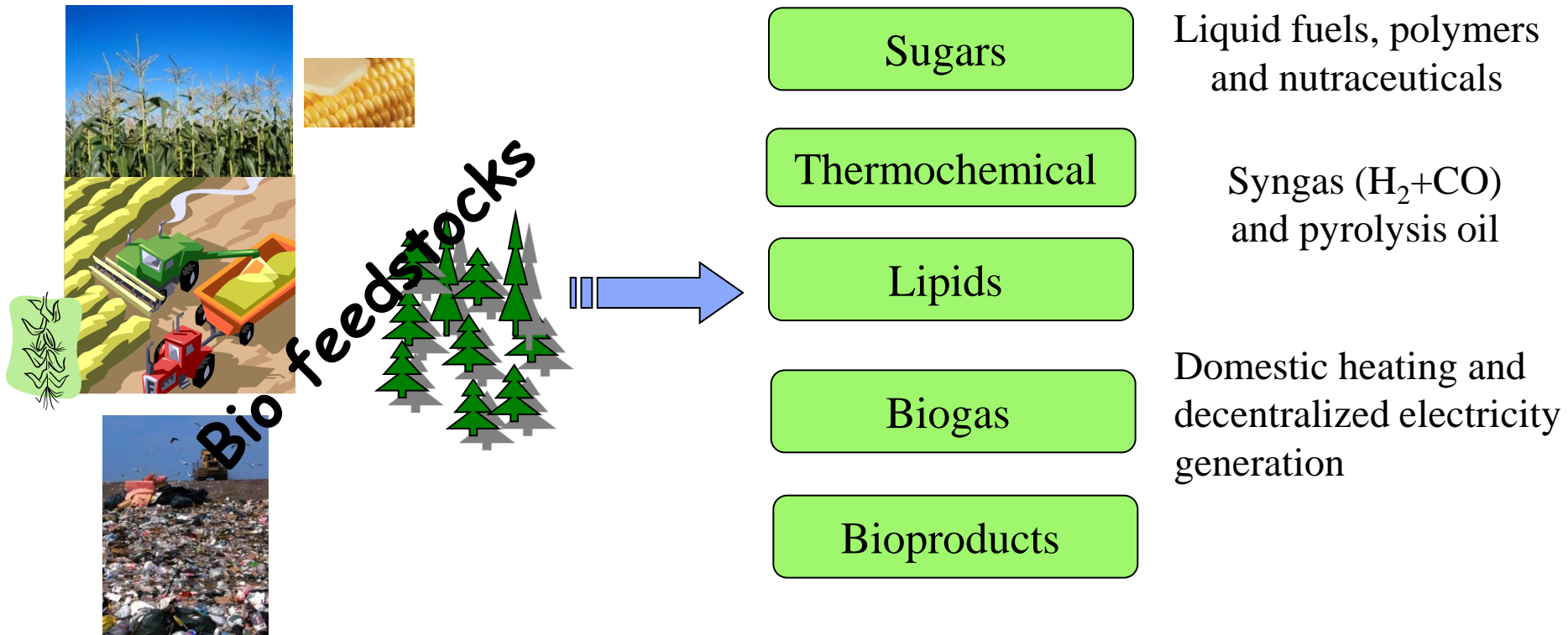
Three Important Criteria for Success of Biofuels

What are the environmental, economic and energy benefits of using this Biofuel?

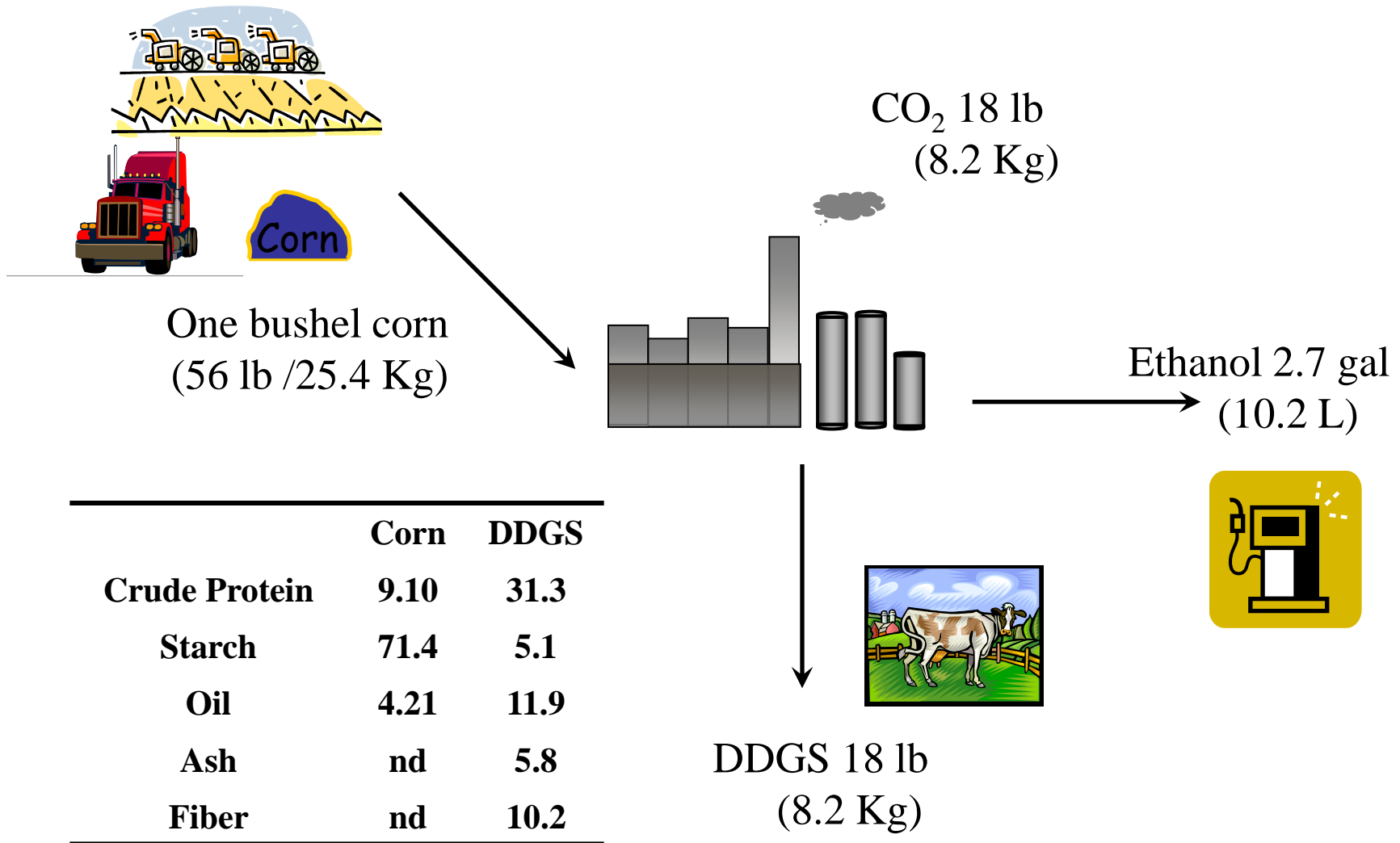


Technologies for Conversion of Bio-feedstock

Technologies for conversion of biomass can be divided into five platforms
(Biomass Program, DOE Classification)

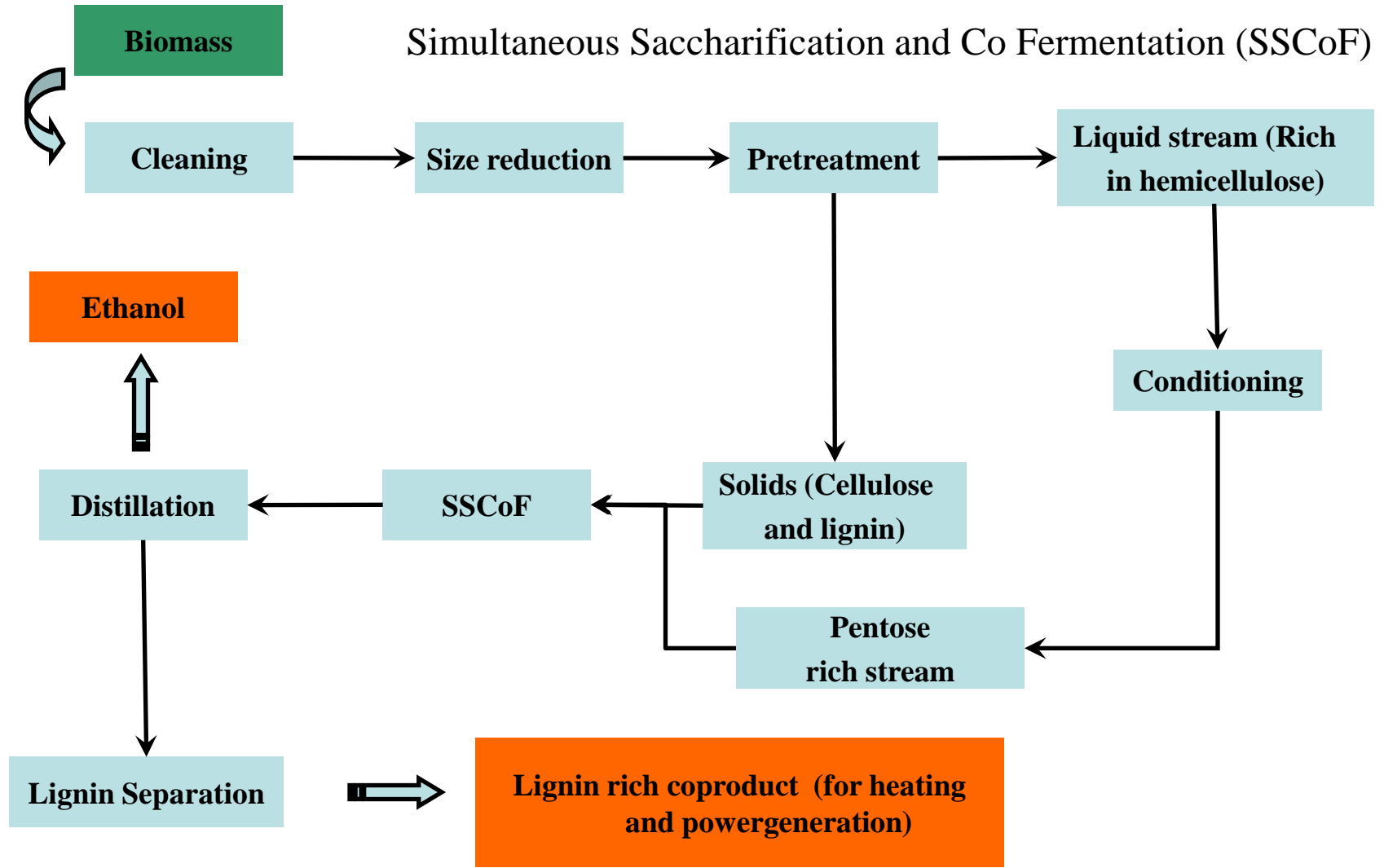


First Generation Biofuels: Dry Grind Corn Process



Ref: Belyea et al. 2004 and <http://www.ddgs.umn.edu/>

Second Generation Biofuels: Cellulosic Ethanol



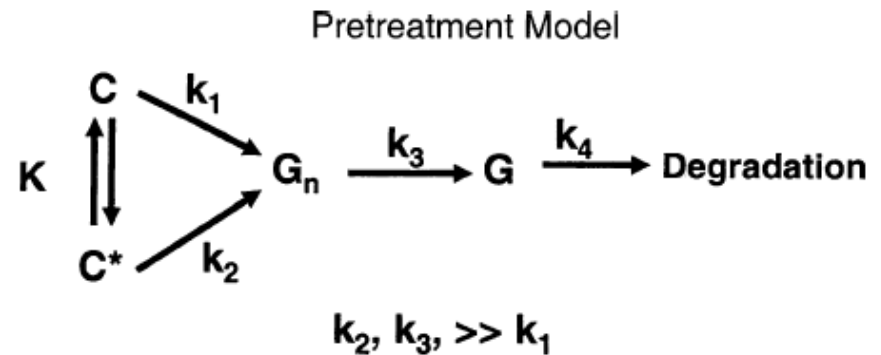
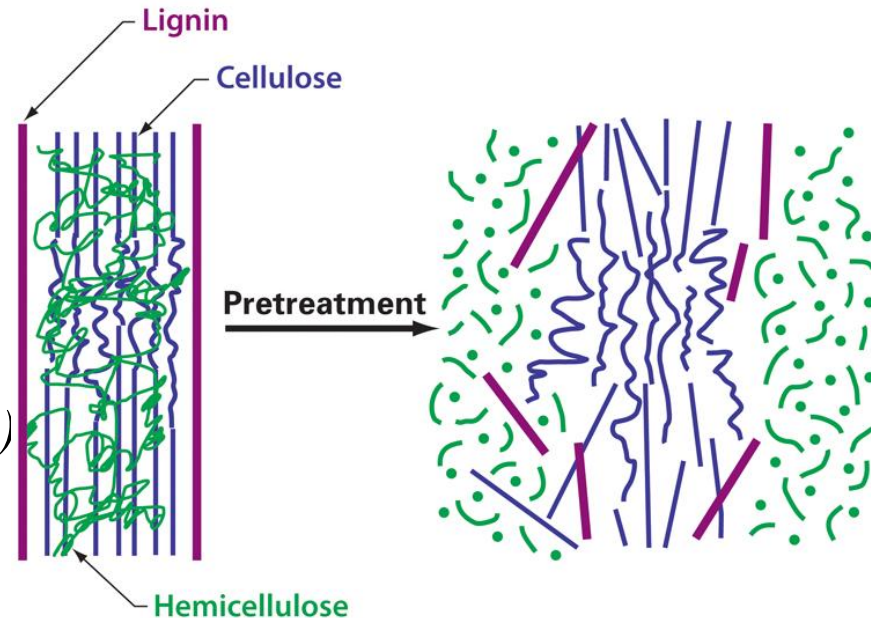
Pretreatment of Biomass

Physio-Chemical Methods

- *Steam Explosion*
- *Liquid Hot Water*
- *CO₂ Explosion*
- *Ammonia Fiber Explosion (AFEX)*

Chemical Methods

- *Acid Hydrolysis*
- *Alkali Hydrolysis*
- *Ozonolysis*
- *Organosolv Process*
- *Oxidative Delignification*

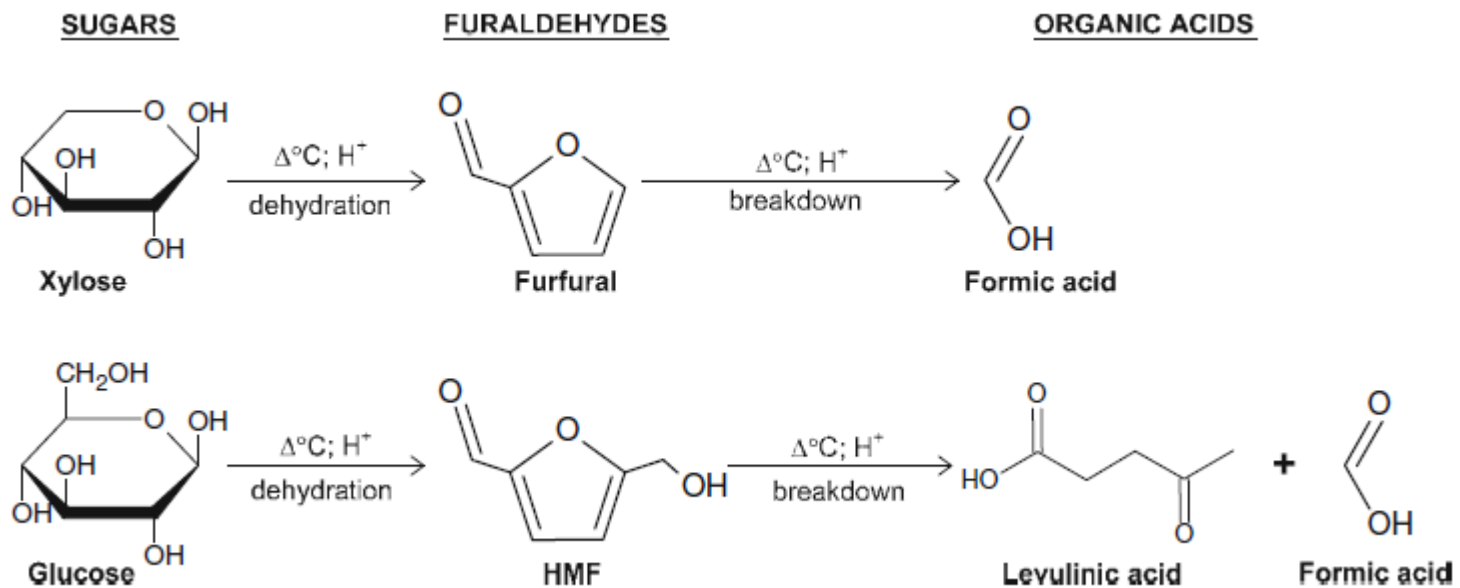


Ref: Sun and Cheng (2002)

Compounds Formed During Pretreatment Can Inhibit Fermentation

Inhibitors produced during pretreatment:

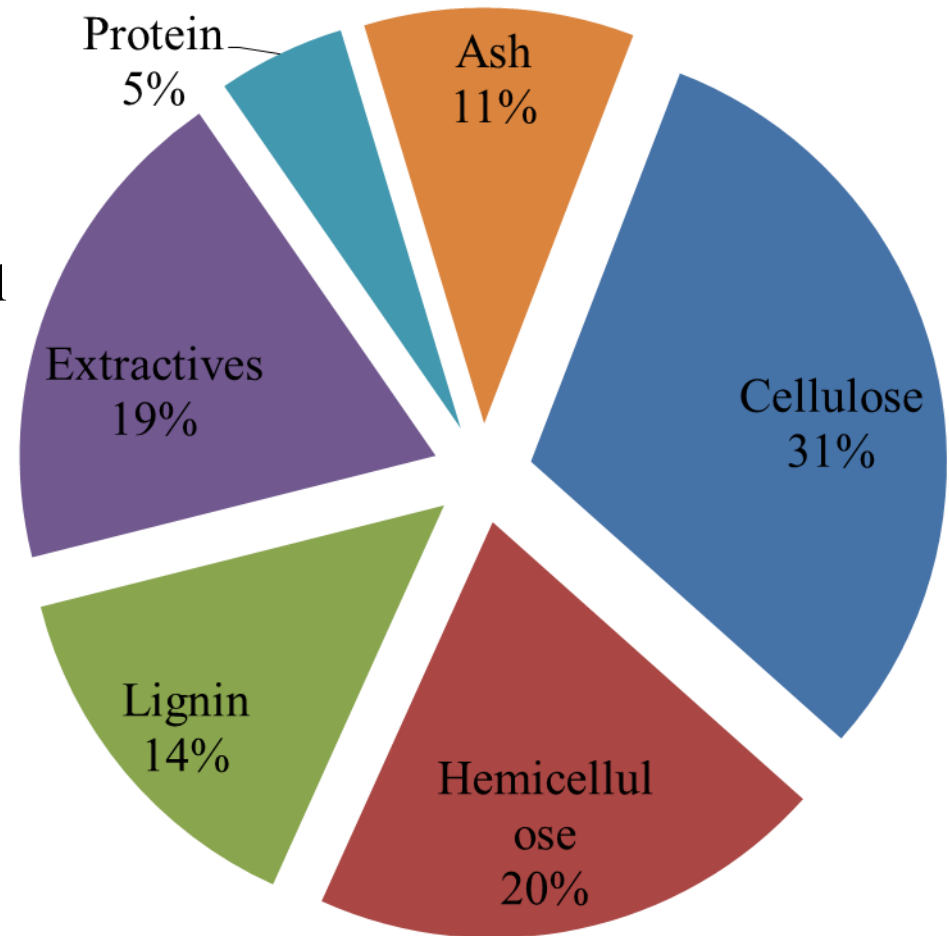
- Sugars: Hydroxy Methyl Furfural (HMF), Furfural
- Lignin: Cinnamaldehyde, p-hydroxybenzaldehyde and syringaldehyde
- Hemicellulose degradation products: acetate, formic, glucuronic and galacturonic acids)



Ref: Sanchez and Cardona (2008) Almeida et al. (2009)

Model Feedstock: Tall Fescue (*Festuca arundinacea* Schreb)

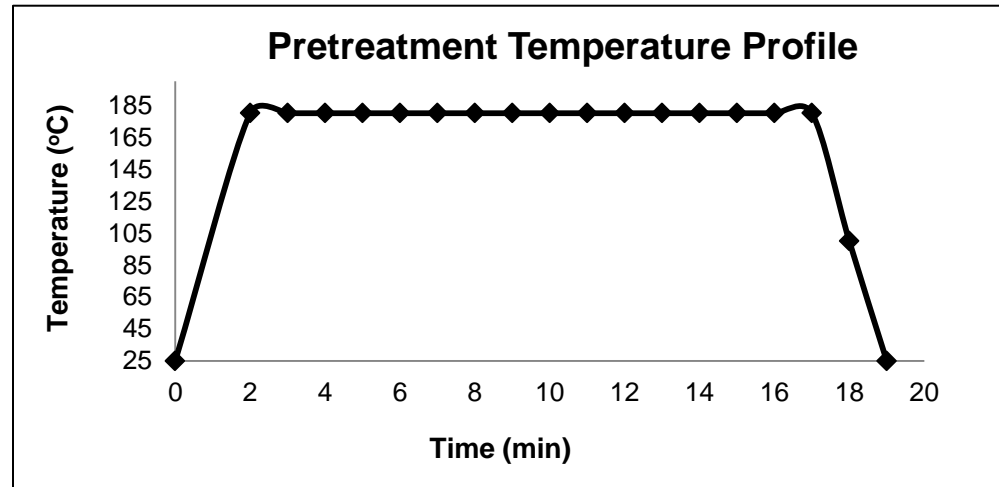
- Tall fescue grass is the largest fraction of the grass straw residues available for production of cellulosic ethanol in Oregon.



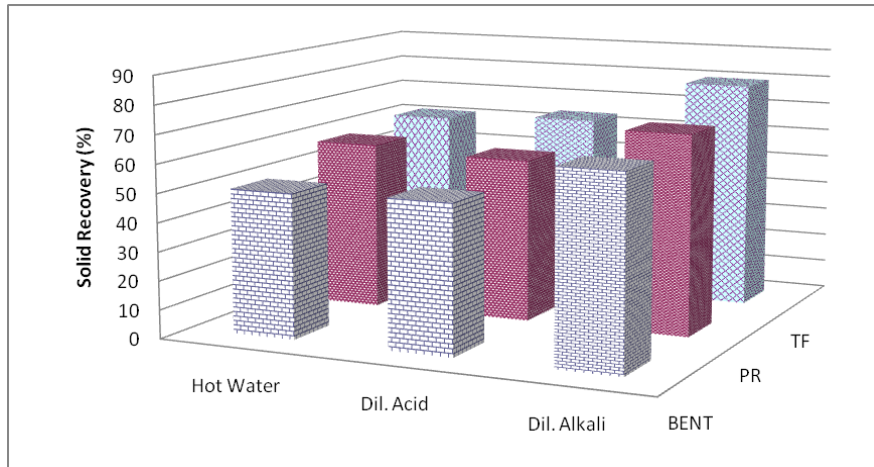
Ref: Graf and Koehler 2002, Banowetz et al 2008, Steiner et al 2006, Kumar and Murthy 2011

Pretreatment of Grass Straws

- Dilute Acid (1 % H_2SO_4 , 10 % solid loading at 180°C for 15 min.)
- Hot water (10 % solid loading at 180°C for 15 min.)
- Dilute Alkali (1 % $NaOH$, 10 % solid loading at 180°C for 15 min.)



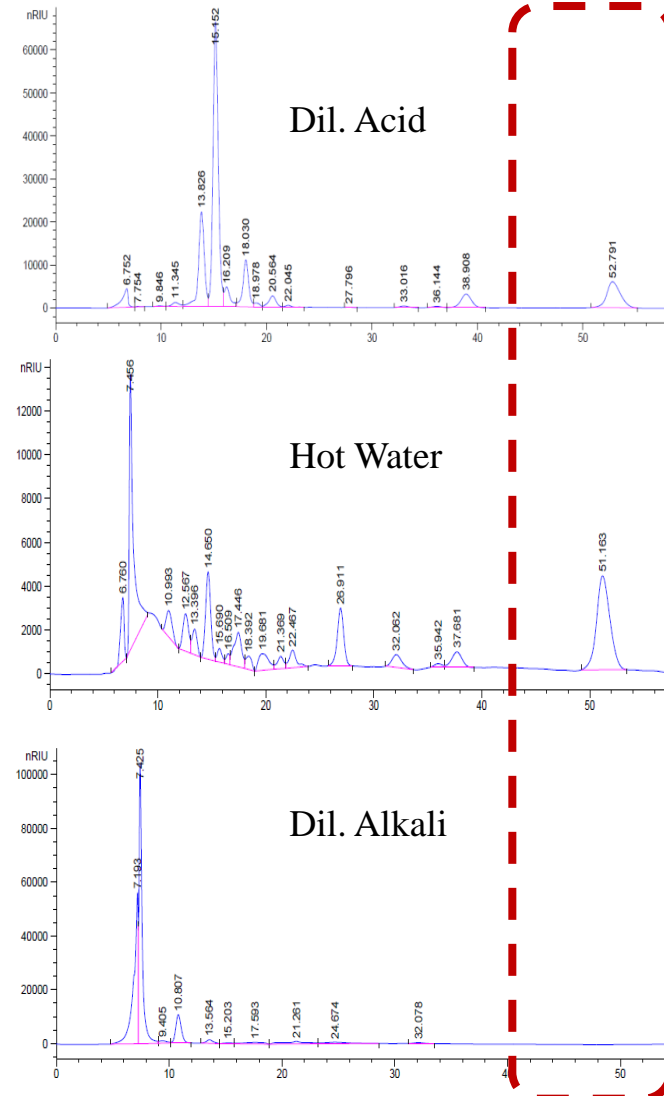
Pretreatment of Grass Straws



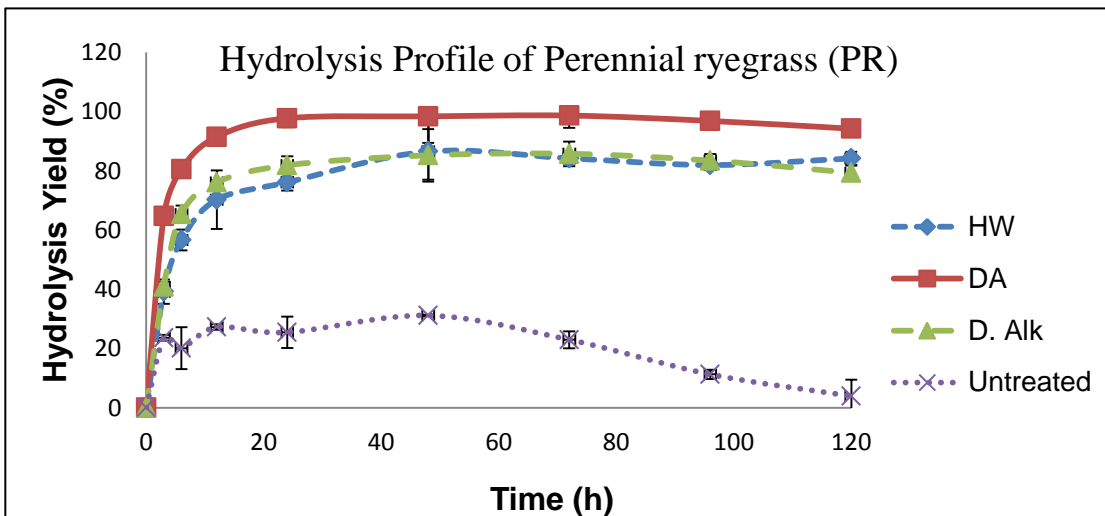
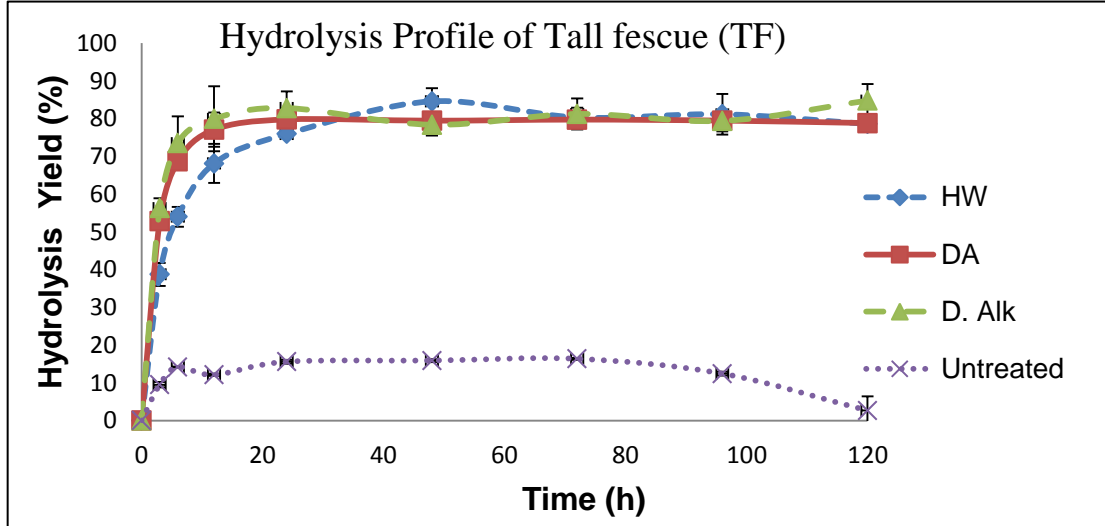
Solid recovery of grass straws after pretreatment

Sugars removed (% db) in the liquid after pretreatments

Pretreatment	Sample	Glucan	Xylan	Galactan	Arabinan
Dilute Acid	TF	13.04	60.26	8.55	55.07
	PR	19.53	58.48	22.59	61.59
Hot Water	TF	0.43	2.61	8.34	1.25
	PR	1.07	7.65	5.9	2.31
Dilute Alkali	TF	0.41	0.38	0.86	1.57
	PR	0.29	0.72	0	0.22



Enzymatic Hydrolysis of Pretreated Grass Straws



Potential Ethanol Yields

Potential Ethanol Yields from grass straws (L/ ton biomass)

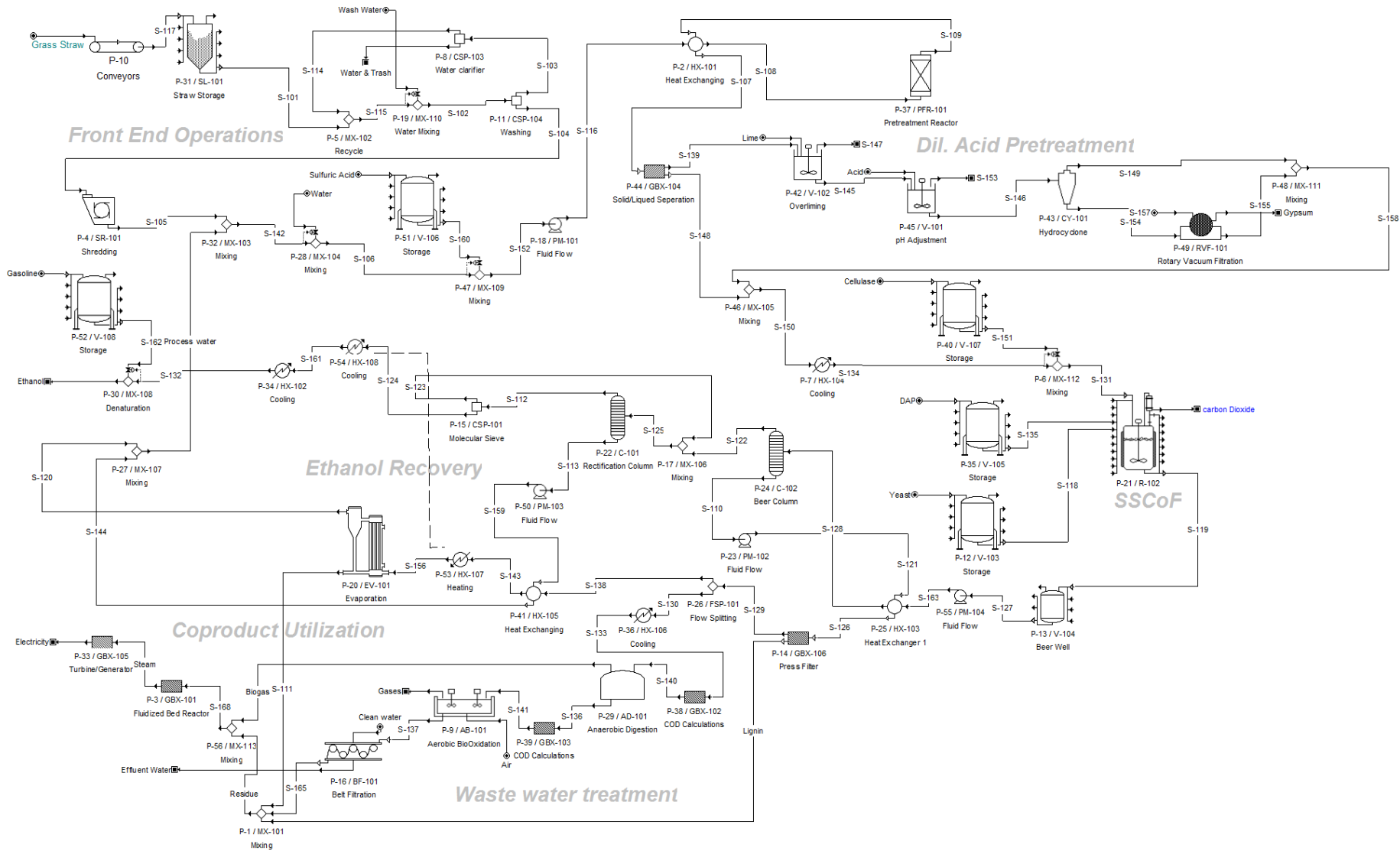
Grass	Estimated C6 Fermentation Yields				Maximum (C6+C5)
	Hot Water	Dil. Acid	Dil. Alkali	Maximum	
TF	173.74	184.63	187.52	220.16	360.57
PR	150.15	174.96	141.67	177.22	297.87
BENT	135.92	136.80	126.93	154.05	276.74

Process Model Development

Important assumptions for Techno-Economic analysis:

1. Plant capacity: 250,000 tons/year of biomass (from 92,000 Ha, i.e. 16.63 Km radius)
2. Pretreatment and hydrolysis data from laboratory experiments (100 mL scale)
3. Solids content fixed at 20% for dilute acid, dilute alkali and hot water and 30% for steam explosion pretreatment processes.
4. Fermentation efficiency: 95% hexose and 70% pentose sugars
5. Distillation efficiency: 99.9%
6. Cost of equipment based on earlier studies and built in models
7. Data for LCA obtained from OSU Extension, Farmers, GREET, US LCI and literature studies

Process Model Development: Dilute Acid Pretreatment



Techno-Economic Analysis: Overall Economics

Overall economics of the ethanol production plant with 250,000 tons/yr of biomass.

	Dil. acid	Dil. Alkali	Hot Water	Steam Exp.
Total Investment (Millions \$)	114.63	102.77	101.89	91.36
Operating Cost (Millions \$/yr)	50.06	52.70	48.10	45.83
Ethanol Revenue (Millions \$/yr)	65.41	65.21	65.07	58.64
Ethanol (Million L/yr)	59.66	59.47	59.36	53.53
Ethanol Unit Cost (\$/L)	0.840	0.885	0.811	0.856

Capital and Operating Costs Vary with Pretreatment Used

250,000 tons/year capacity	Dil. Acid	Dil. Alk.	Hot Water	Steam Ex.
Ethanol Unit Cost (\$/L(\$/gal))	0.84 (3.18)	0.89(3.35)	0.81(3.07)	0.86(3.24)
Direct Fixed Capital (\$)	106.37	94.68	94.24	84.26
Equipment Cost (\$/yr)	45.37	39.52	39.17	34.96
Raw Material Cost (\$/yr)	22.562	27.05	22.73	22.23
Effluent Water (Kg/yr)	207.37	208.63	206.76	128.43

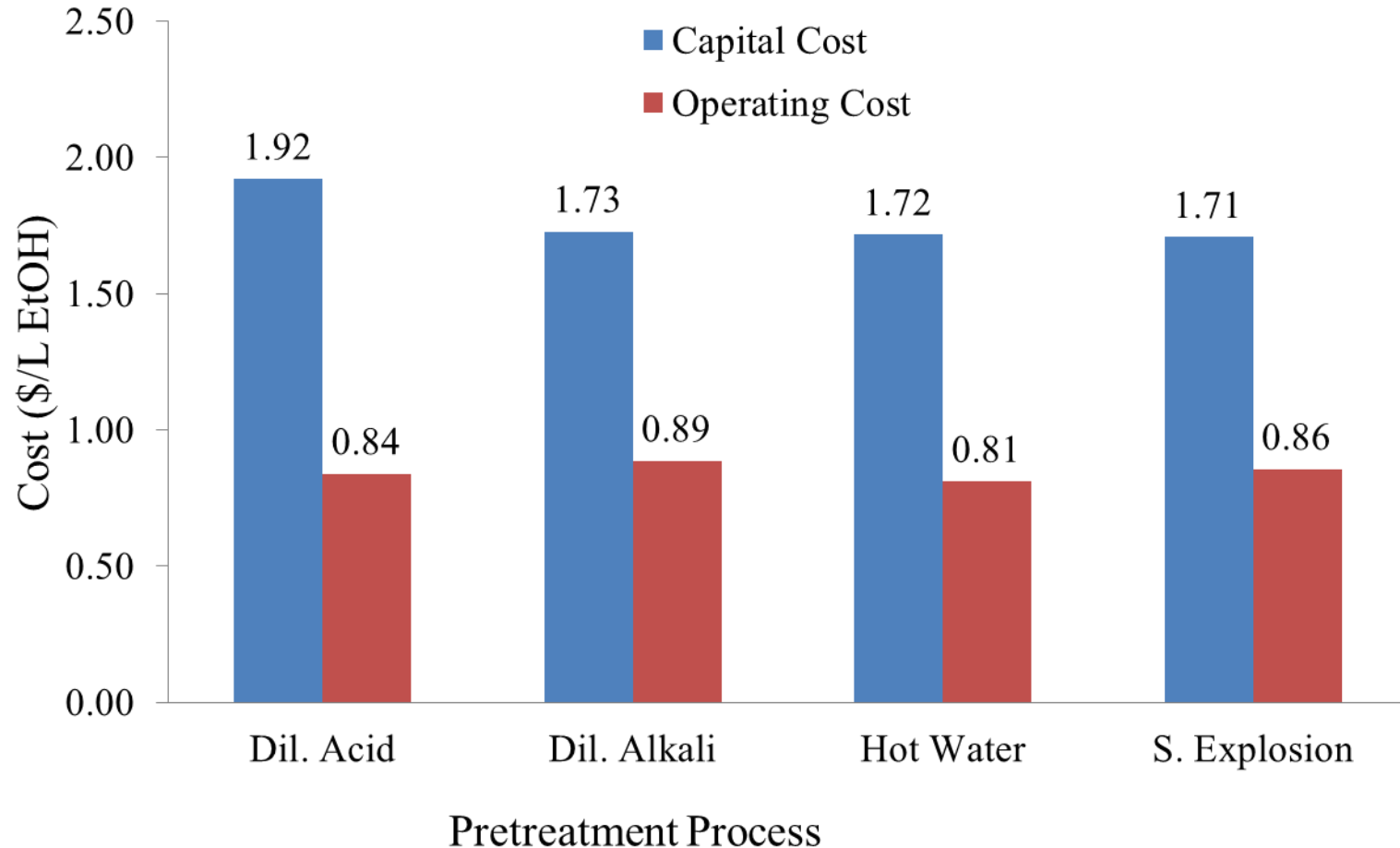
All numbers in millions.

Steam Demand and Electricity Production

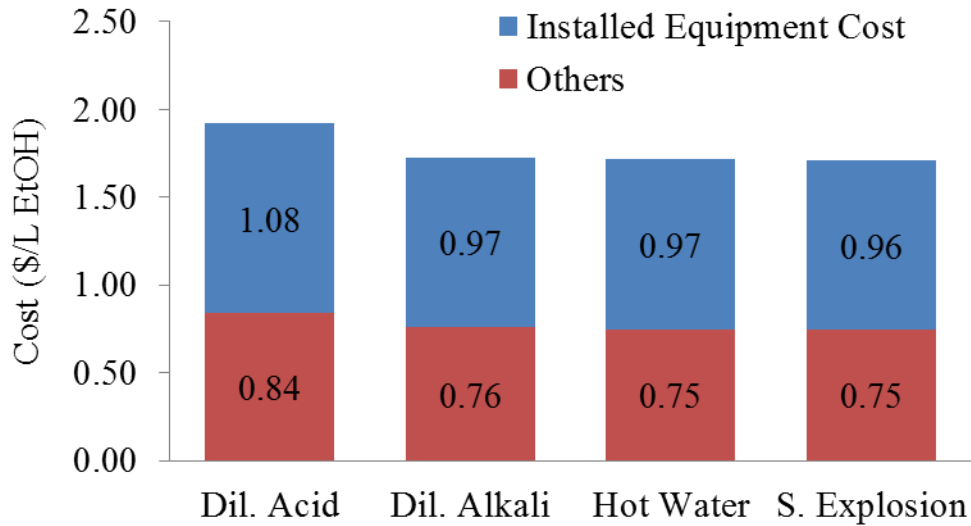
Pretreatment Process	Steam demand (kJ/L EtOH)	Lignin Energy (kJ/L EtOH)	Excess Lignin Energy (kJ/L EtOH)	Electricity Produced (kWh/L EtOH) ^a
Dil. Acid	19,010	28,232	9,223	0.769
Dil. Alkali	18,737	27,967	9,229	0.769
Hot Water	19,333	29,138	9,804	0.817
Steam Ex.	13,508	34,819	21,310	1.776

^aAssuming 30 % efficiency of lignin energy to electricity conversion

Techno-Economic Analysis: Cost Breakdown

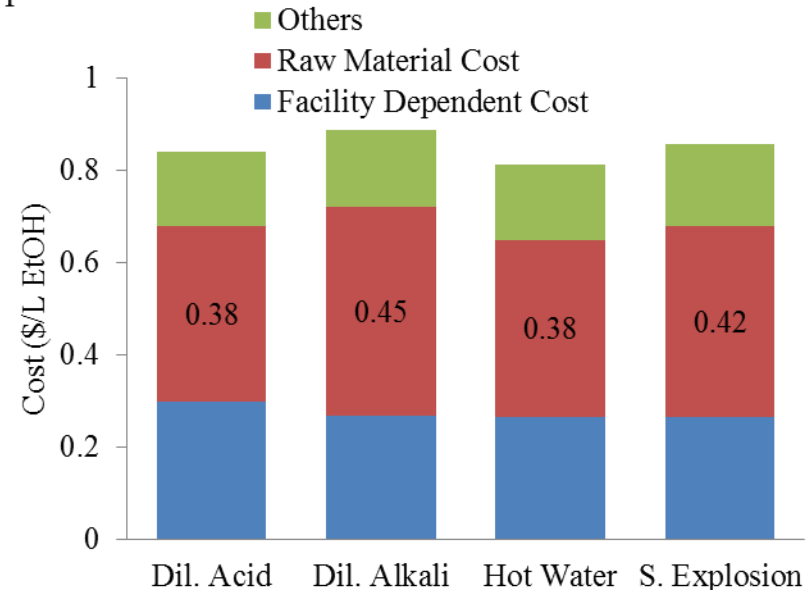


Techno-Economic Analysis: Cost Breakdown

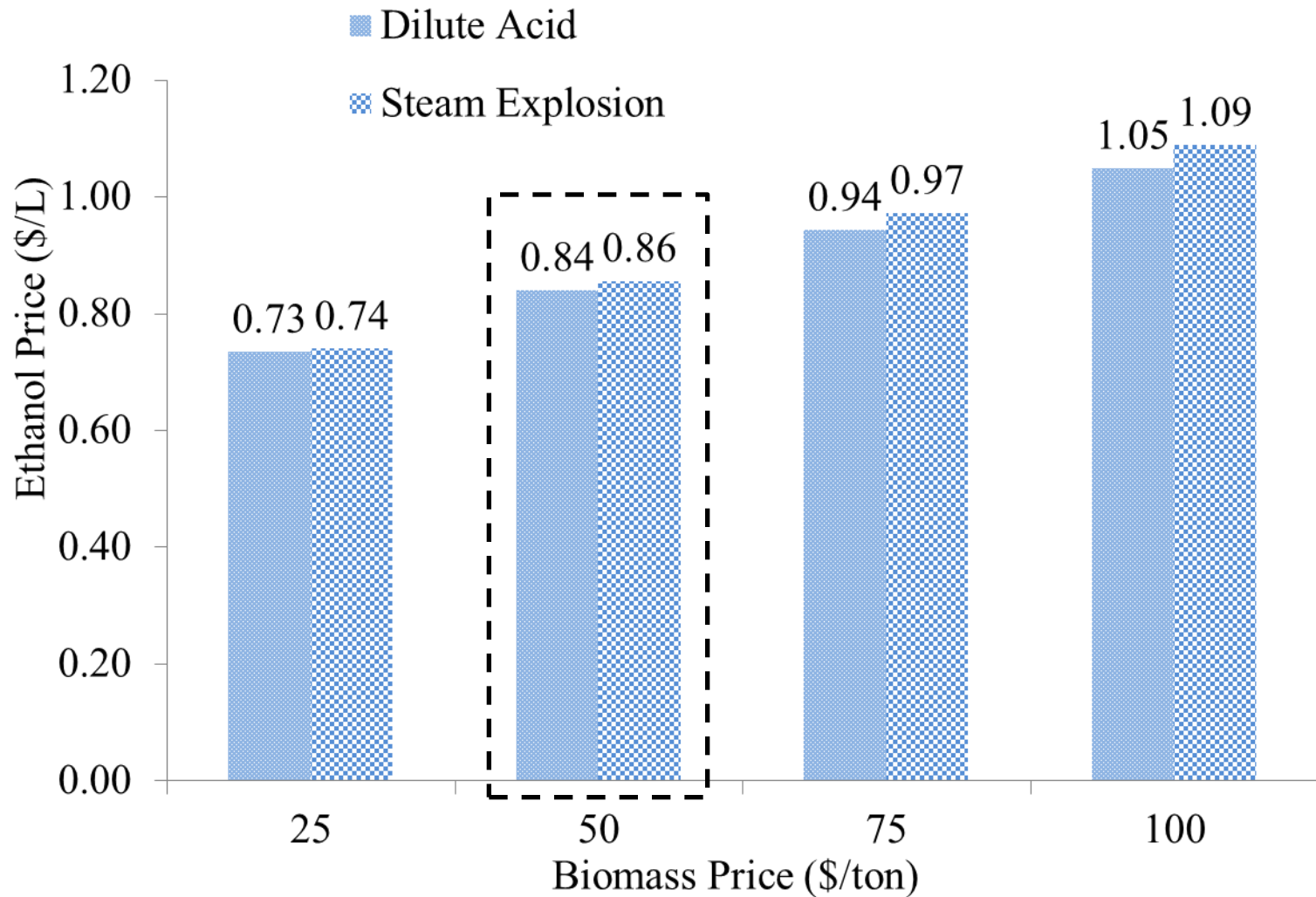


Capital Costs

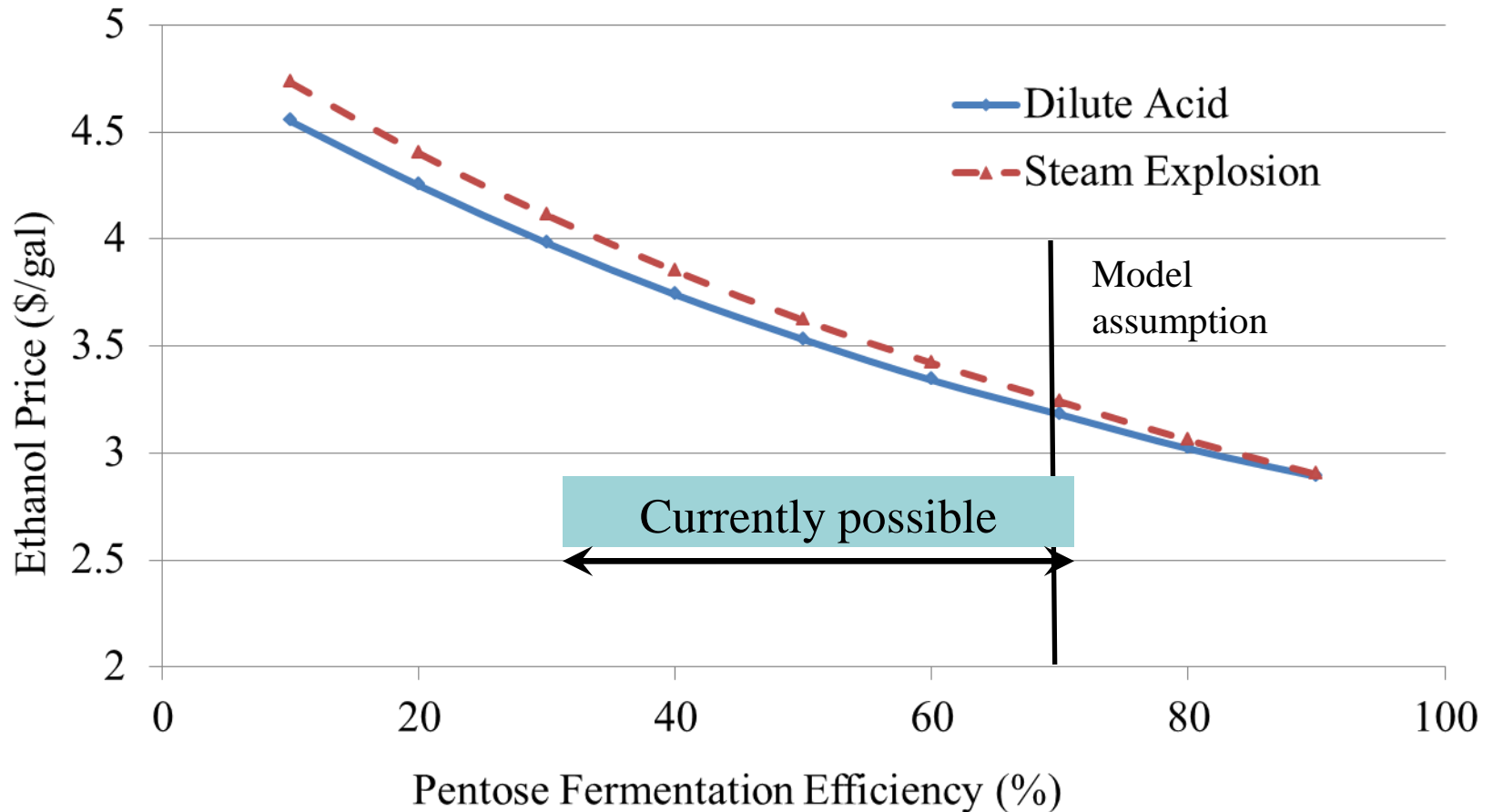
Operating Costs



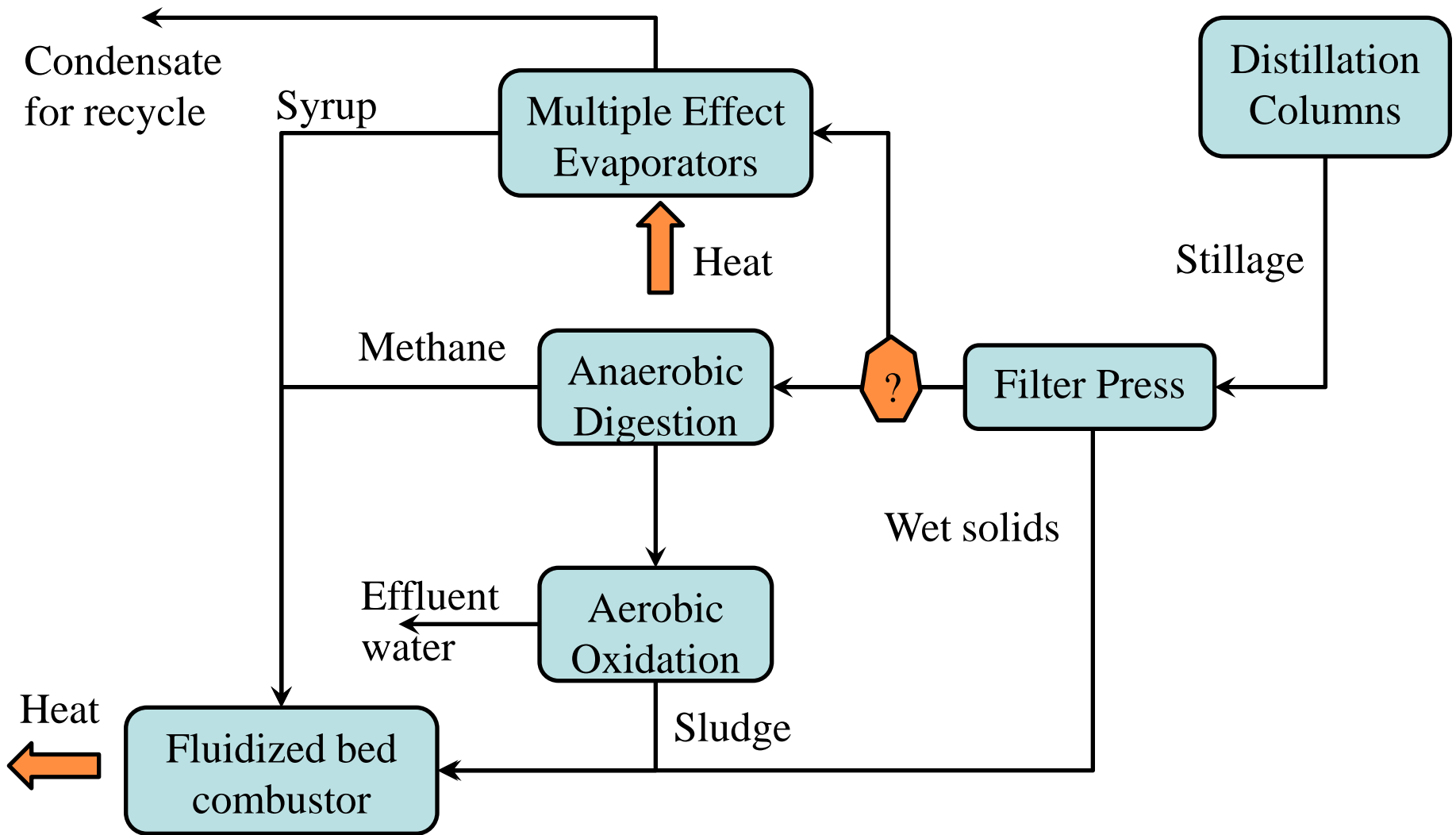
Ethanol Price is Affected Significantly by Feedstock Price



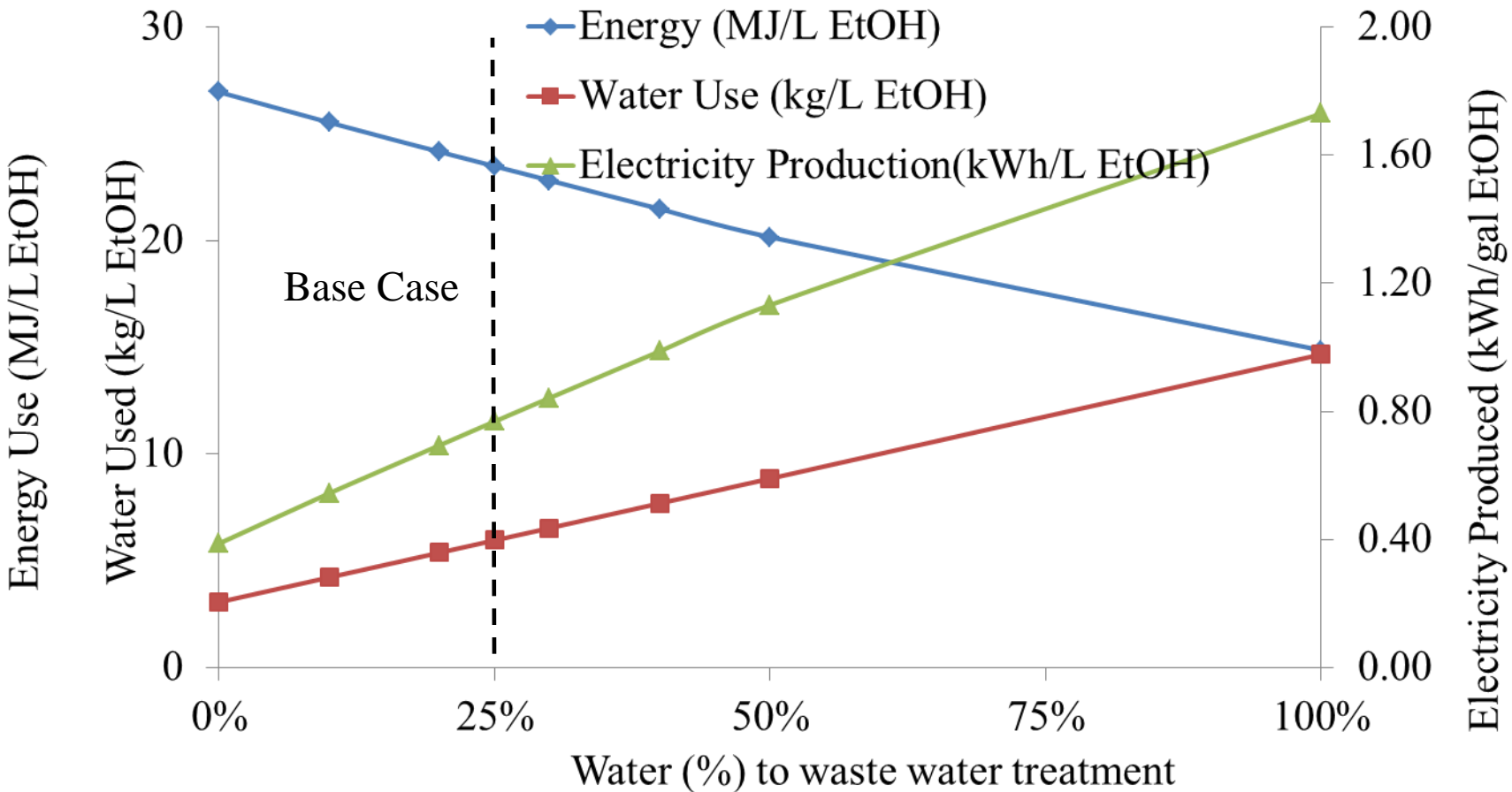
Pentose Fermentation Efficiency has a Impact on Ethanol Price



Capital Costs, Energy Use and Water Recycle are Interconnected

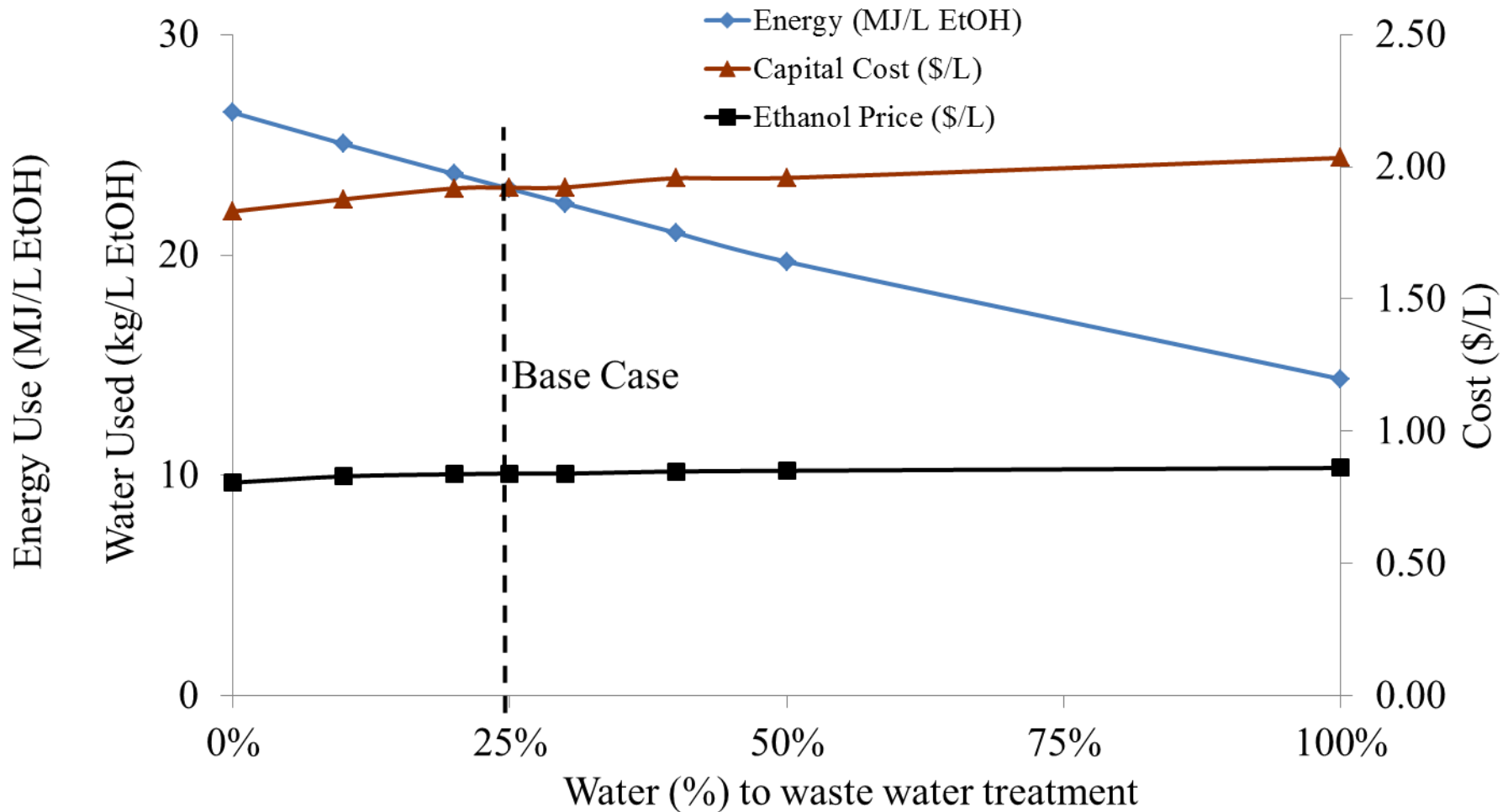


Energy Use and Water Use/Electricity Have a Strong Negative Correlation



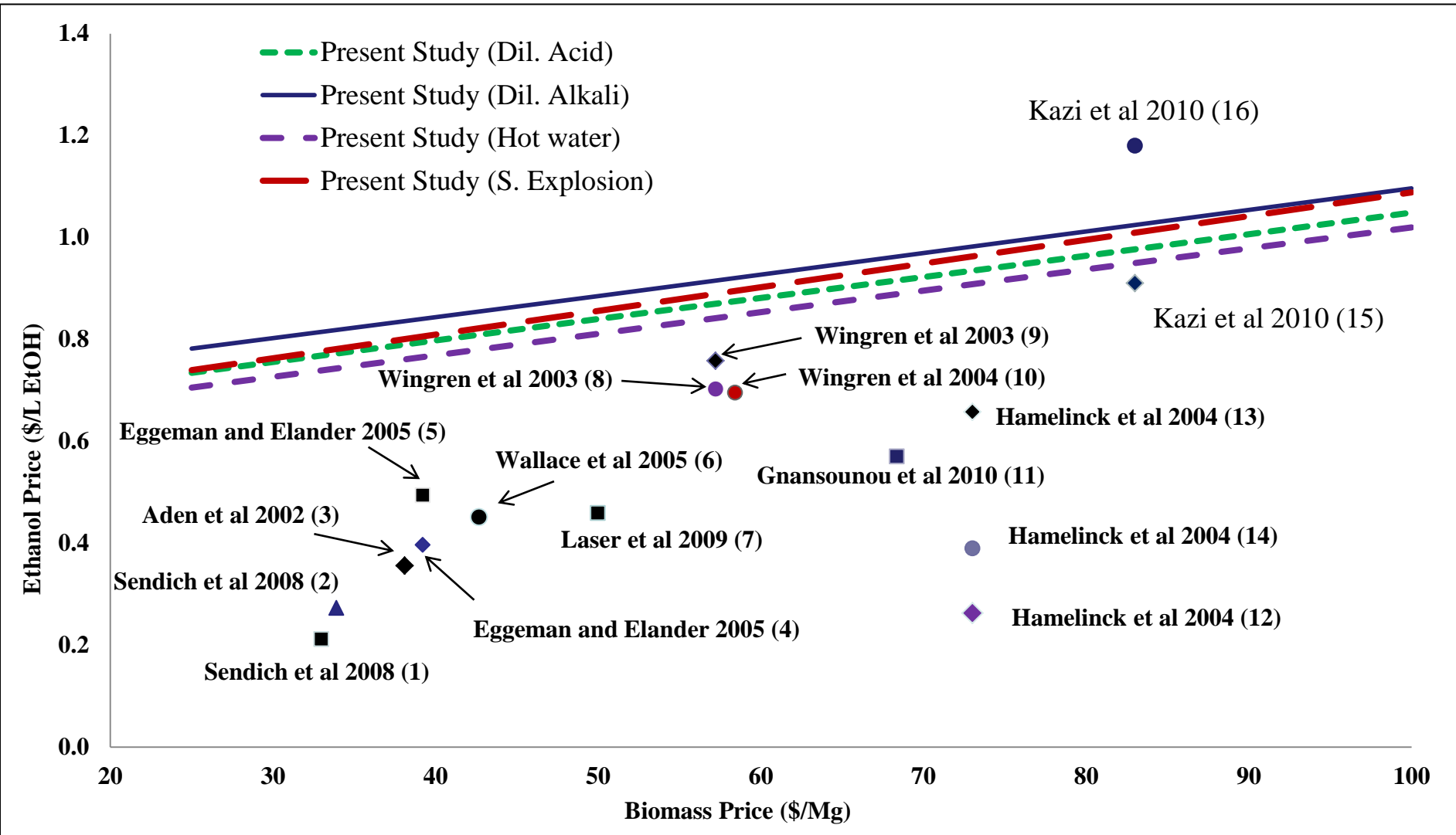
Dilute Acid Pretreatment Process Case

Energy Use and Capital/Ethanol Cost Have a Weak Negative Correlation



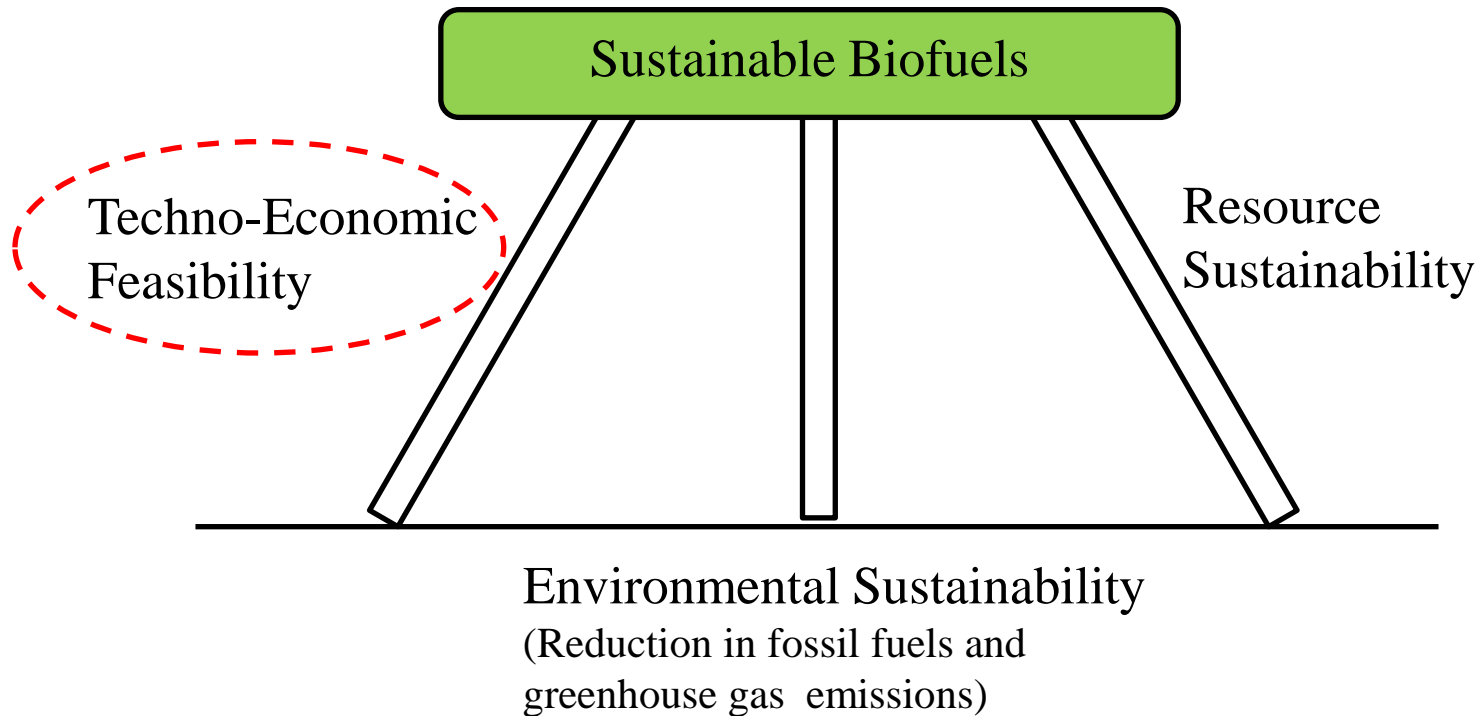
Dilute Acid Pretreatment Process Case

Comparison of Present Study to Extant Literature



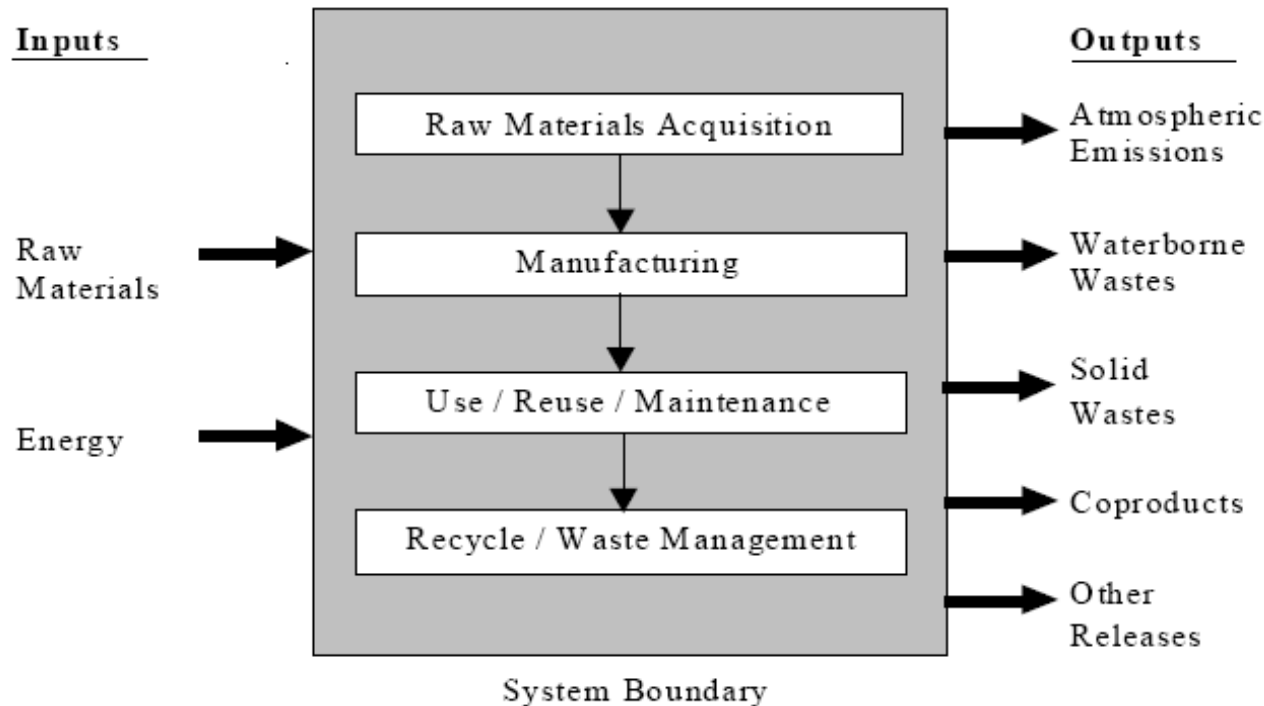
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What are the environmental, economic and energy benefits of using this Biofuel?



Life Cycle Analysis

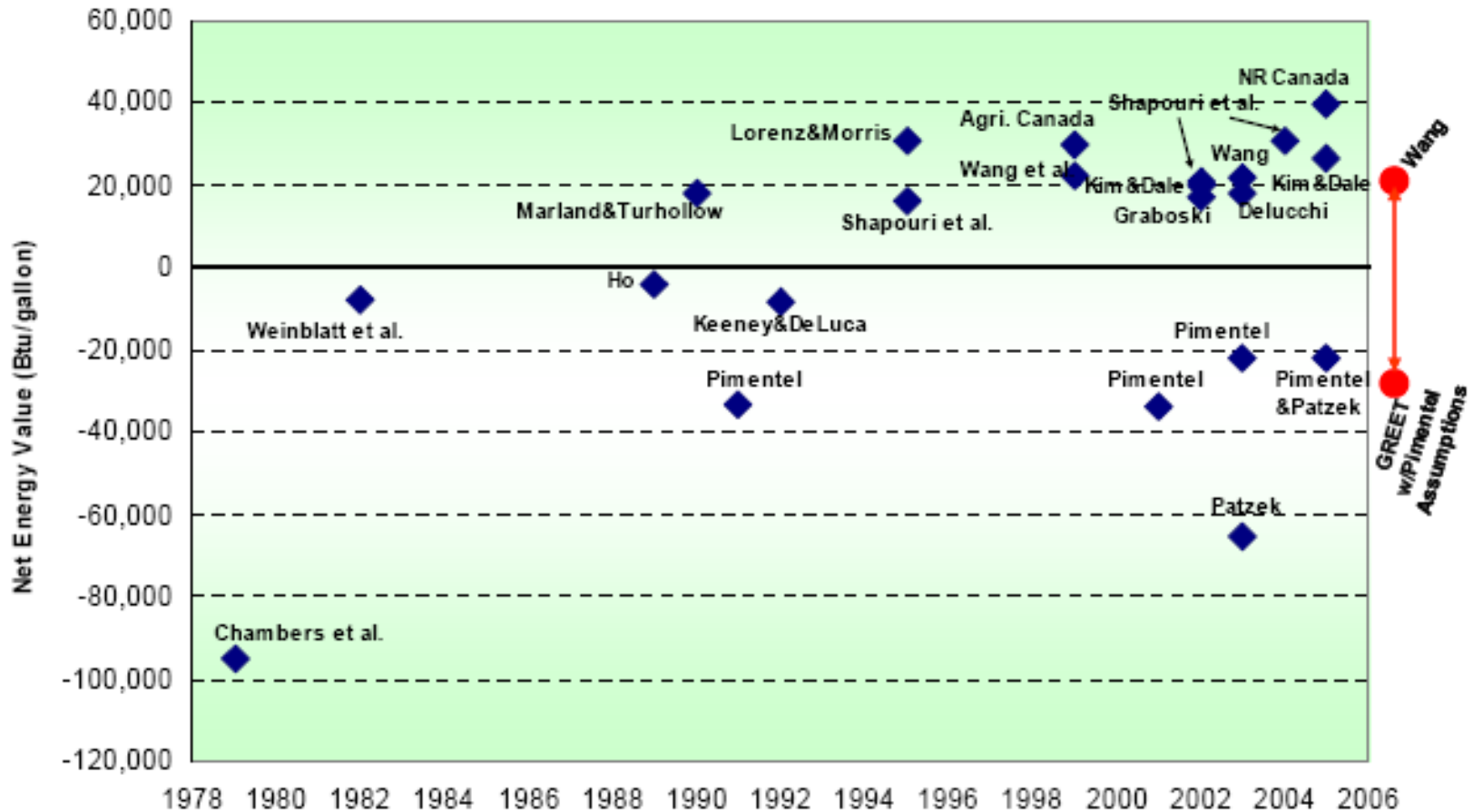
Life Cycle Analysis (LCA) is a tool to assess impact of products, processes and services on environment. All processes starting with the acquisition of raw materials, production, manufacturing and disposal are considered.



Ref: Life Cycle Analysis: Principles and Practice. EPA/600/R-06/060 (2006)

Results From Few Well to Pump LCA Studies for Corn Ethanol

Comparison of fuel ethanol energy balance from various studies

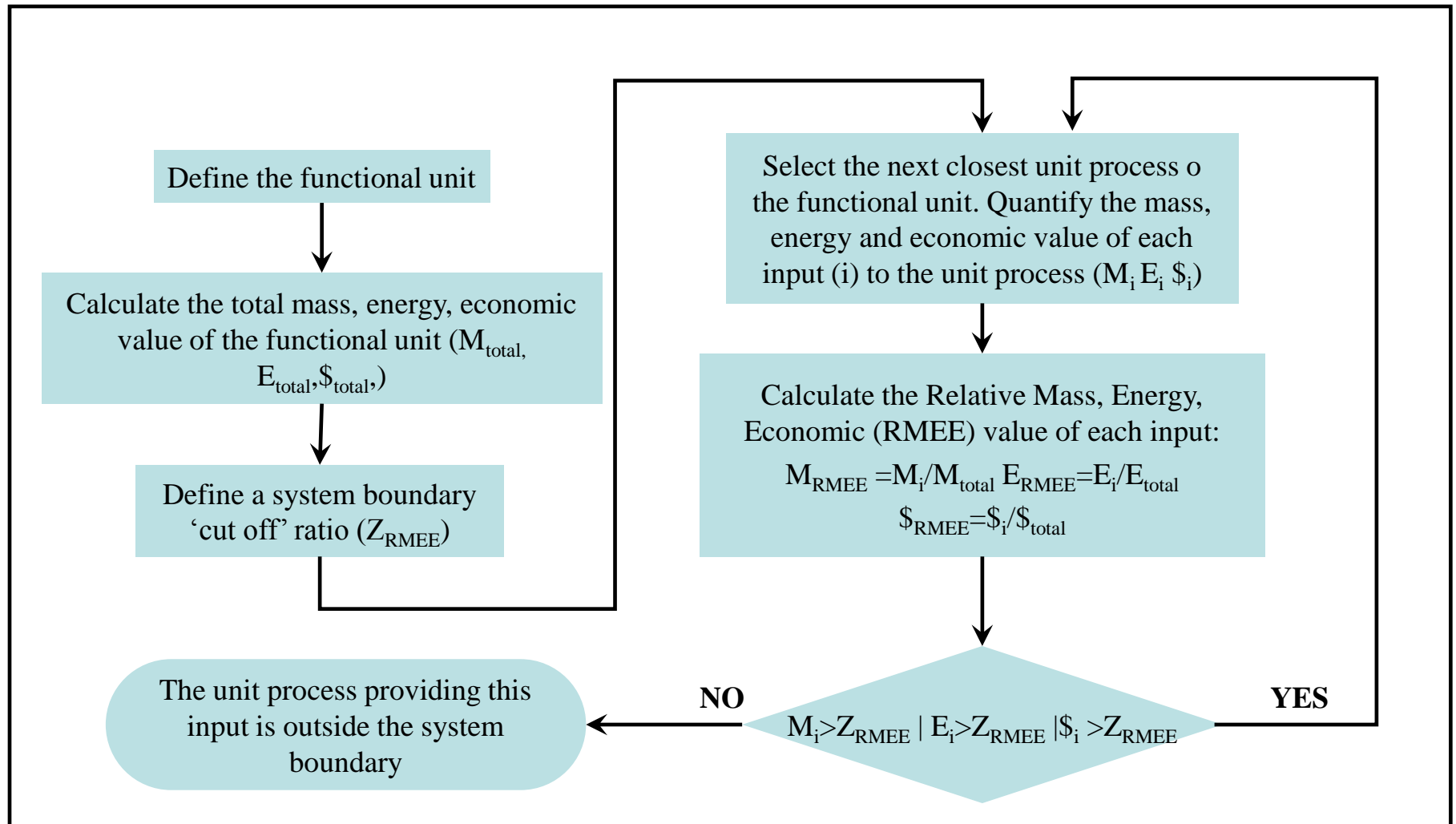


Ref: Wang, M. 2005. Updated energy and greenhouse gas emission results of fuel ethanol. Intl. Sympo. Alcohol Fuels.

Why Are The Results From Various LCA Analyses So Different?

- *System boundaries*
- *Data quality, accuracy*
 - *Age of data, sources of data, geographical context*
- *Allocation of coproducts*
 - *Mass, energy and displacement methods*
- *Nitrous oxide emissions*
 - *Varying fertilizer use for different crops*
- *Indirect land use change (ILUC)*
 - *Variation in ILUC among first, second and third generation fuels.*
- *Reported units*
 - *GHG emissions/MJ of fuel or GHG emissions/Ha of land?*

RMEE Method of LCA System Boundary Identification



RMEE Boundary

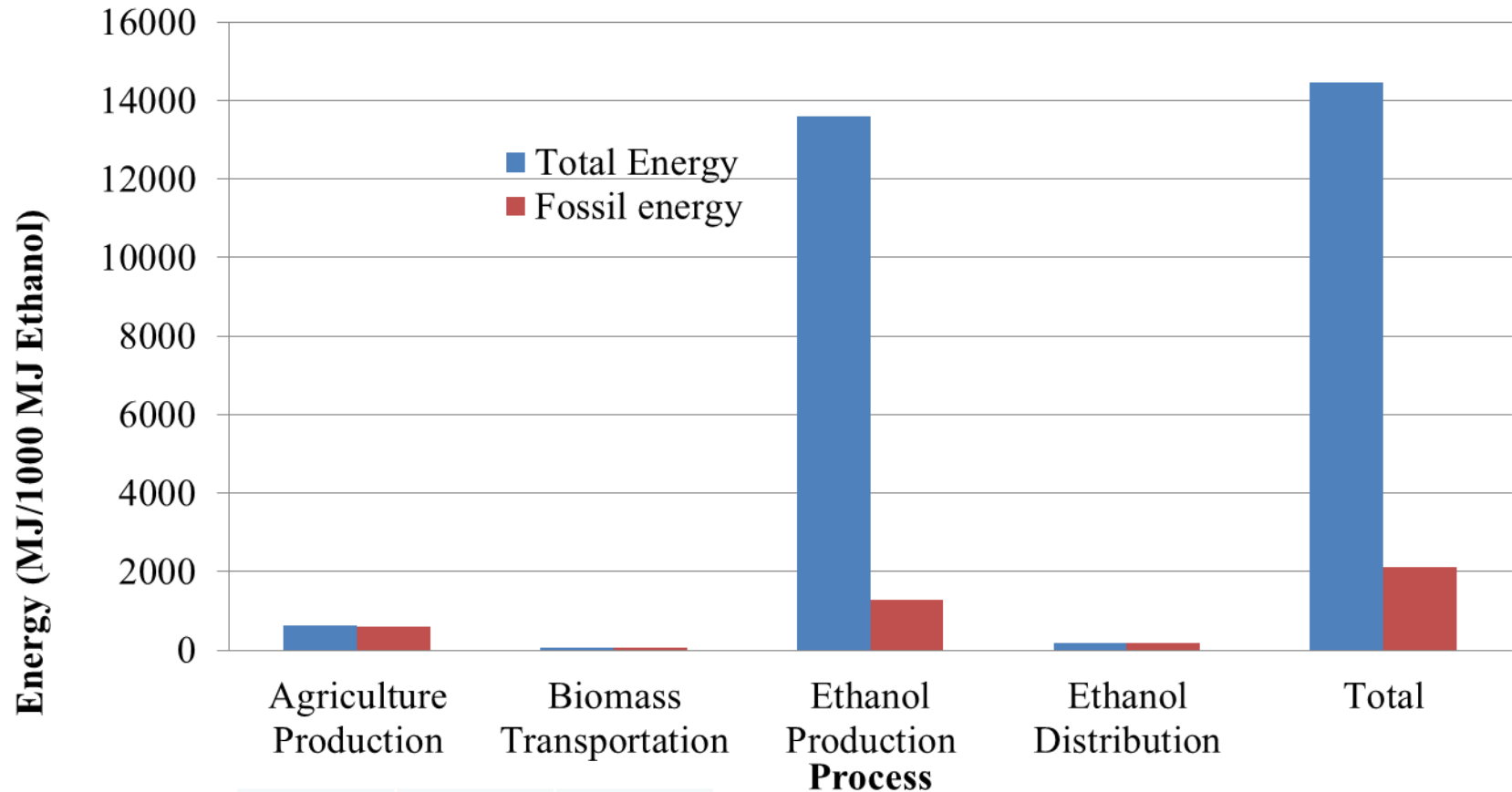
Functional unit: 10,000 MJ Energy (equivalent to \$322.85 or 371.03Kg ethanol)

	M_{total} (kg)	M_{ratio}	E_{total} (MJ)	E_{ratio}	$\$_{total}$ (\$)	$\$_{ratio}$
Inputs Biomass Transportation						
Diesel	1.227	0.003	52.531	0.005	1.112	0.003
Truck manufacturing and maintenance	small	~ 0	small	~ 0	small	~ 0
Inputs Grass Straw Production						
Agri. machinery Manufacturing	small	~ 0	small	~ 0	small	~ 0
Fertilizer - Nitrogen	53.352	0.144		0.000		
Fertilizer - P2O5	12.886	0.035		0.000		
Fertilizer - K2O	21.807	0.059		0.000		
Herbicide	2.288	0.006			24.262	0.075
Insecticides	0.765	0.002			14.890	0.046
Seeds	0.620	0.002			4.094	0.013
Diesel (Agri Machinery)	27.952	0.075	1196.234	0.120	36.186	0.112
Water	NA			NA		NA

LCA Results for Dilute Acid Pretreatment

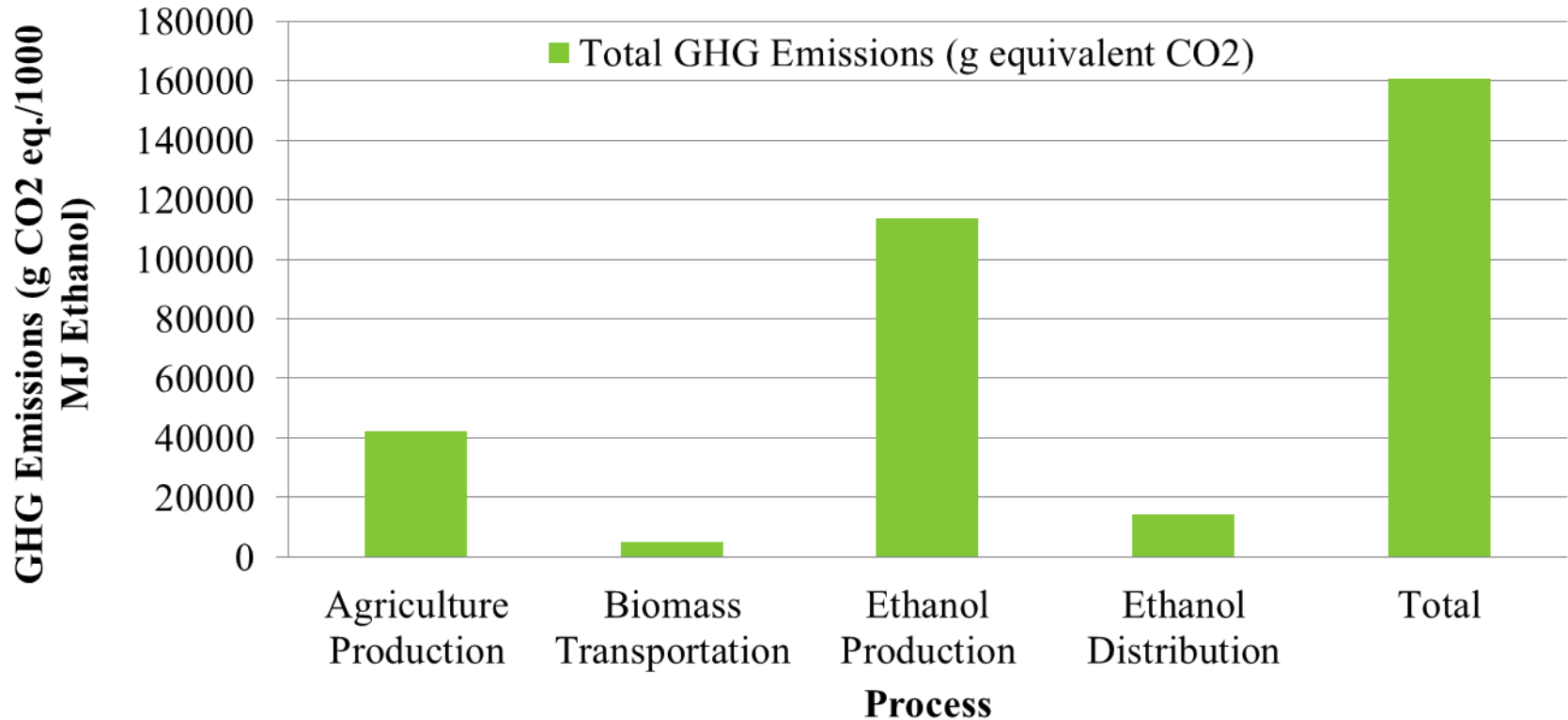
	Agriculture Production	Biomass Transportation	Ethanol Production	Ethanol Distribution	Total
Energy (Btu)					
Total Energy	592233.03	58892.51	12883421.28	169323.13	13534546.82
Fossil energy	577079.13	58707.03	1202622.23	168856.25	1838408.39
Water Use (kg)			2801.55		2801.55
Emissions (g)					
CO ₂	36316.77	4699.46	82173.40	13845.78	123189.62
CO	56.54	2.24	31.68	26.09	90.46
CH ₄	62.84	5.39	118.01	15.56	186.25
N ₂ O	13.29	0.11	1.08	0.32	14.49
NO _x	70.29	7.13	137.27	137.88	214.69
Total GHG Emissions (g equivalent CO ₂)	42018.92	4874.20	113766.98	14409.70	160660.10
Energy (MJ)					
Total Energy	624.84	62.135	13592.78	178.65	14458.40
Fossil energy	608.85	61.94	1268.84	178.15	2117.78
Total Energy (%)	4.32%	0.43%	94.01%	1.24%	100.00%
Fossil Energy (%)	28.75%	2.92%	59.91%	8.41%	100.00%
GHG (%)	26.15%	3.03%	70.81%	8.97%	100.00%

LCA Results for Dilute Acid Pretreatment



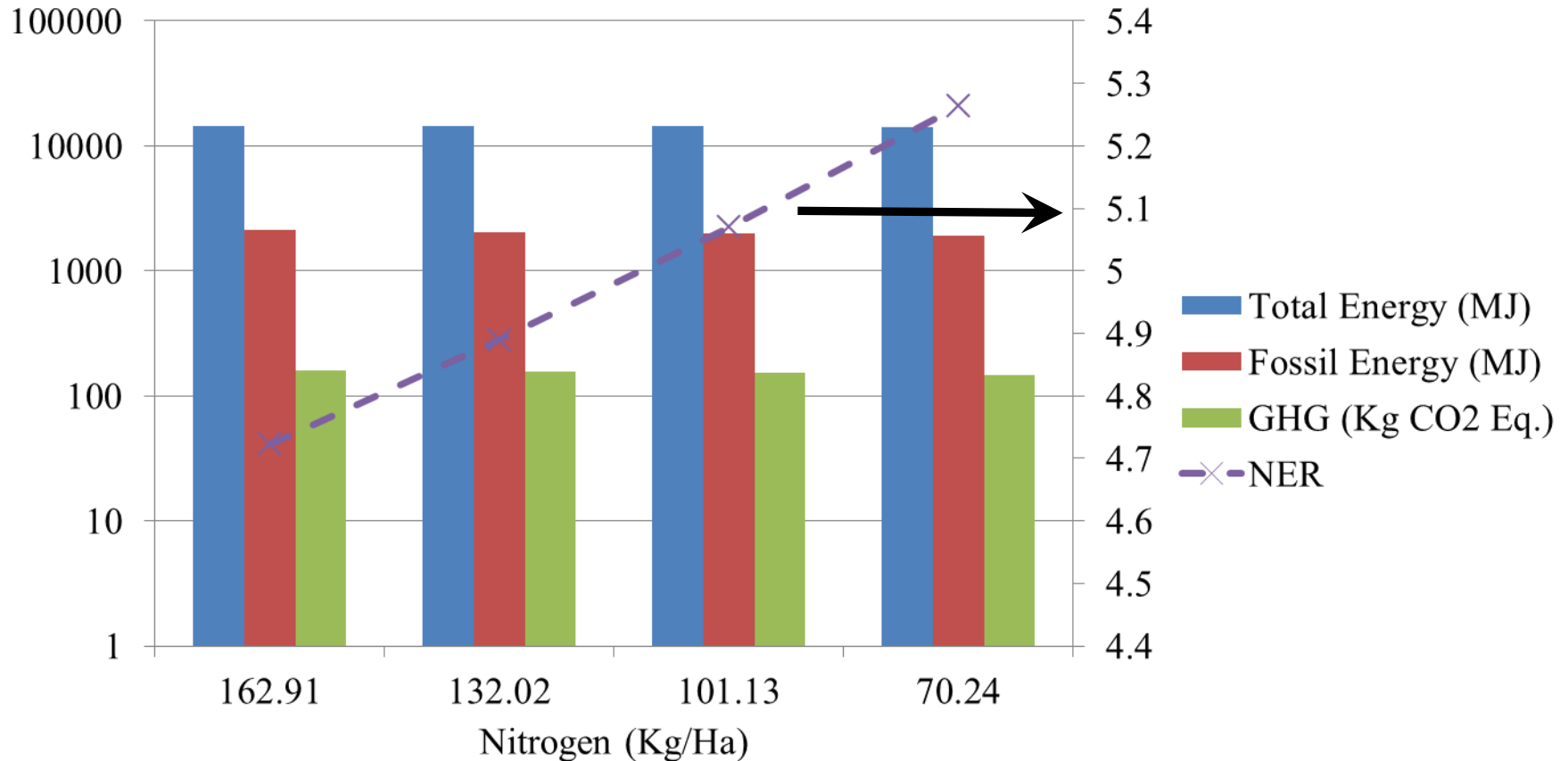
Net Energy Value	7882.22
Net Energy Ratio	4.72
% Net Energy	78.82%

LCA Results for Dilute Acid Pretreatment



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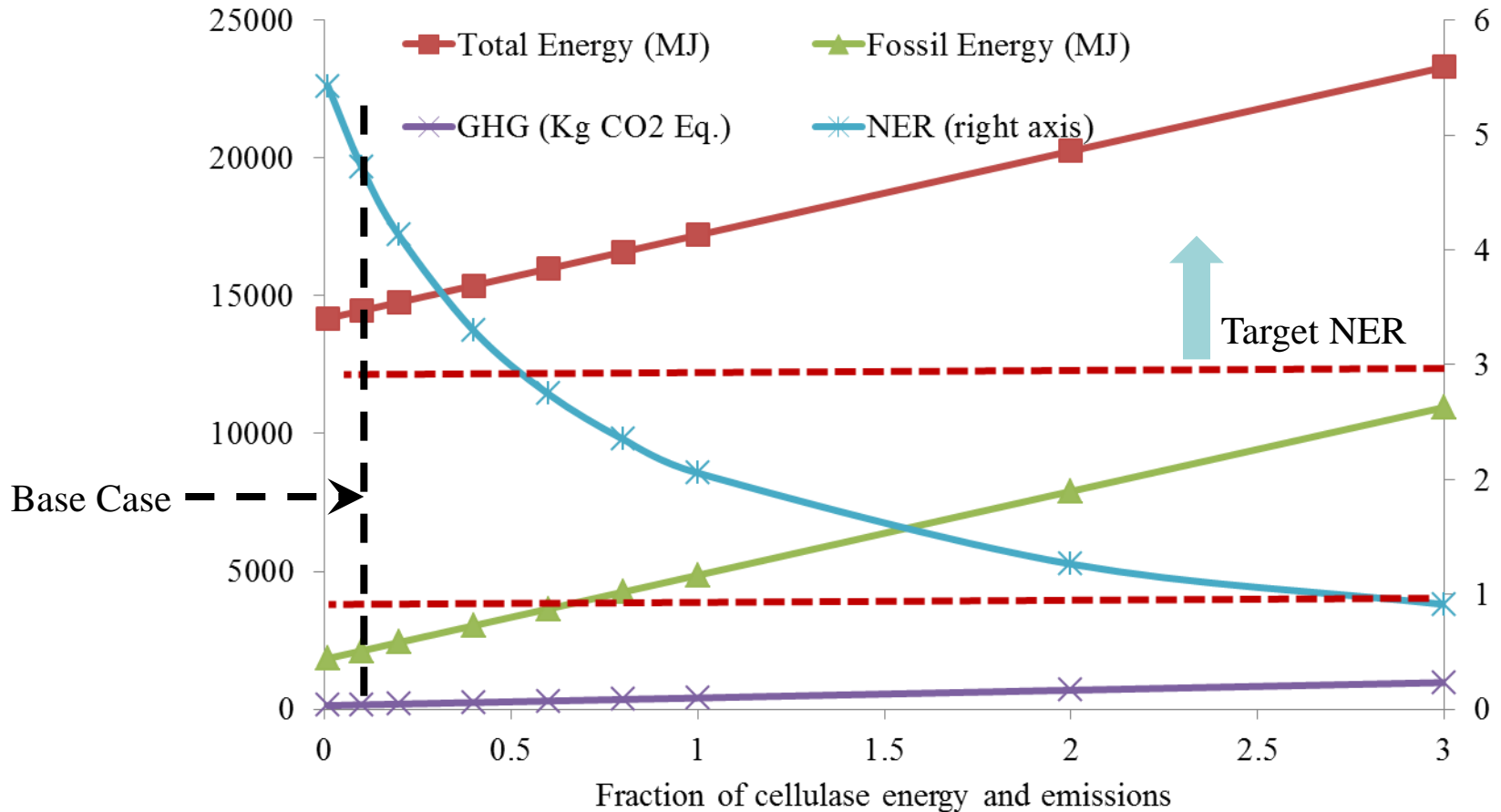
LCA Results Depend on Agricultural Inputs



LCA Results Depend on Process Inputs

(%)	Sulfuric Acid	Lime	NaOH	DAP	Cellulase	Steam	High Pressure Steam	Electricity	Co-Product	Total
Dilute Acid										
Energy	0.45	2.73	0.00	0.04	2.24	61.09	4.65	28.79	97.63	100.00
Fossil Energy	4.65	26.76	0.00	0.42	24.02	654.43	49.78	44.15	704.21	100.00
GHGs	4.30	25.01	0.00	0.35	24.46	0.00	0.00	45.89	1336.89	100.00
Dilute Alkali										
Energy	0.10	0.00	8.37	0.04	2.49	57.96	4.47	26.57	94.07	100.00
Fossil Energy	0.29	0.00	24.78	0.11	7.38	171.55	13.23	67.44	184.77	100.00
GHGs	0.66	0.00	62.26	0.23	18.68	0.00	0.00	18.16	884.66	100.00

LCA Results Depend on Enzyme Usage



Reference case (Fraction 1): 24.8 MJ/Kg, 2.264 Kg CO2 eq/Kg, 60 FPU/Kg

LCA Results Depend on Coproduct Allocation Strategy

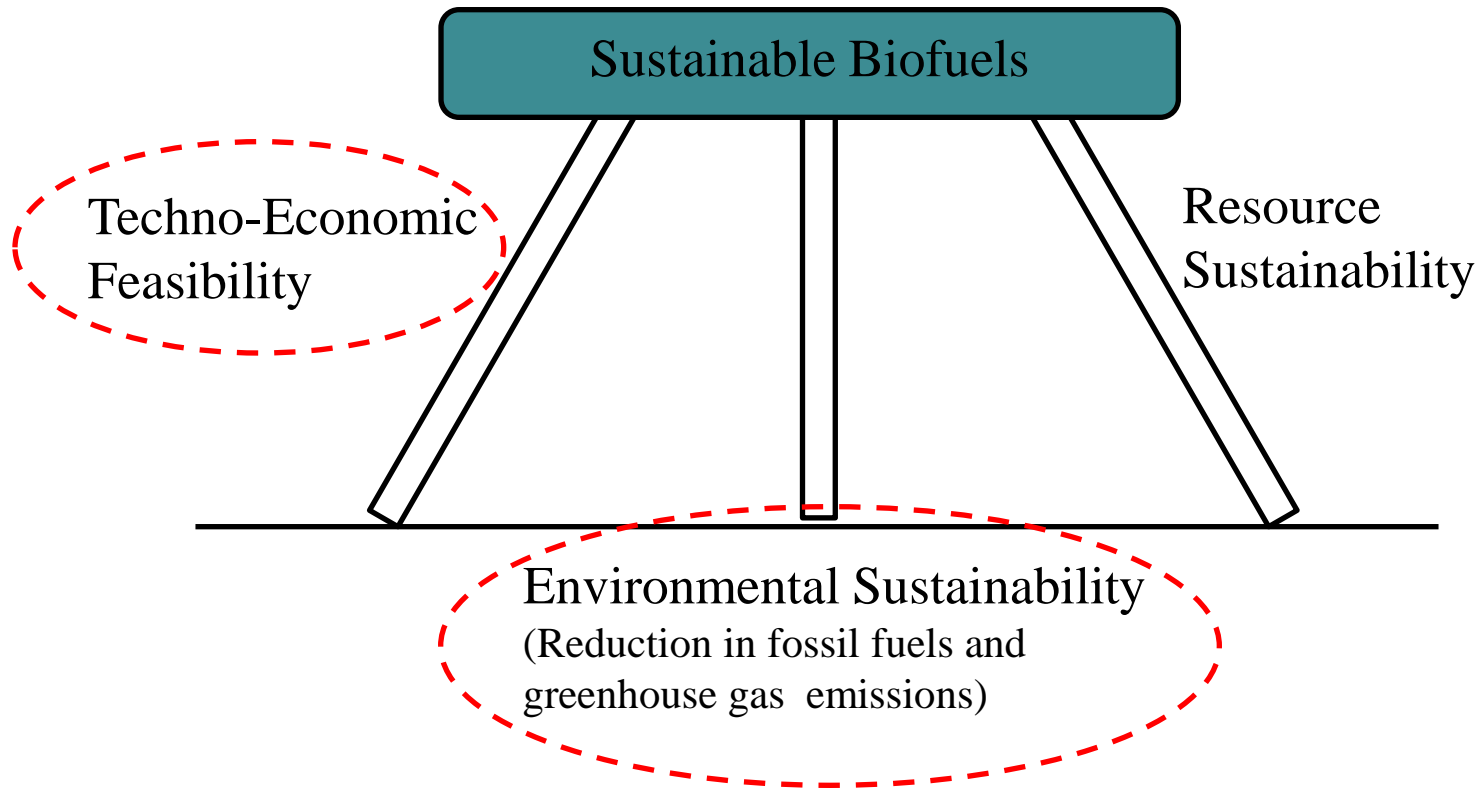
<i>Method</i>	<i>Dry Grind Plant</i>	<i>Wet Milling Plant</i>
Weight-based	51%	52%
Energy content-based	39%	43%
Market value-based	24%	30%
Energy use of individual processes	41%	36%
Displacement	20%	16%

Market value based allocation was used for Grass seed and Grass straw while displacement based allocation was used for electricity coproduced in the plant.

Ref: Wang, M. 2005. Updated energy and greenhouse gas emission results of fuel ethanol. Intl. Sympo. Alcohol Fuels.

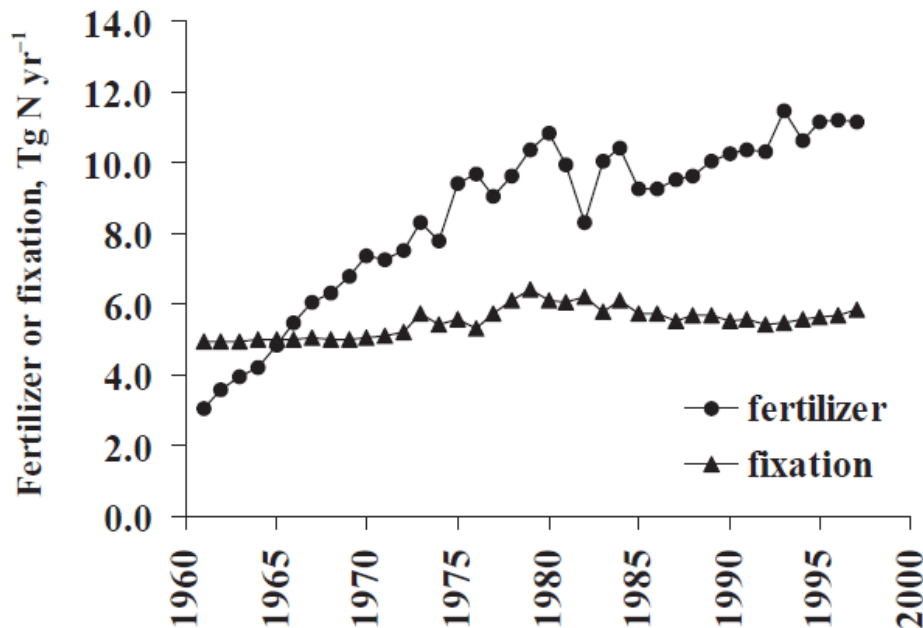
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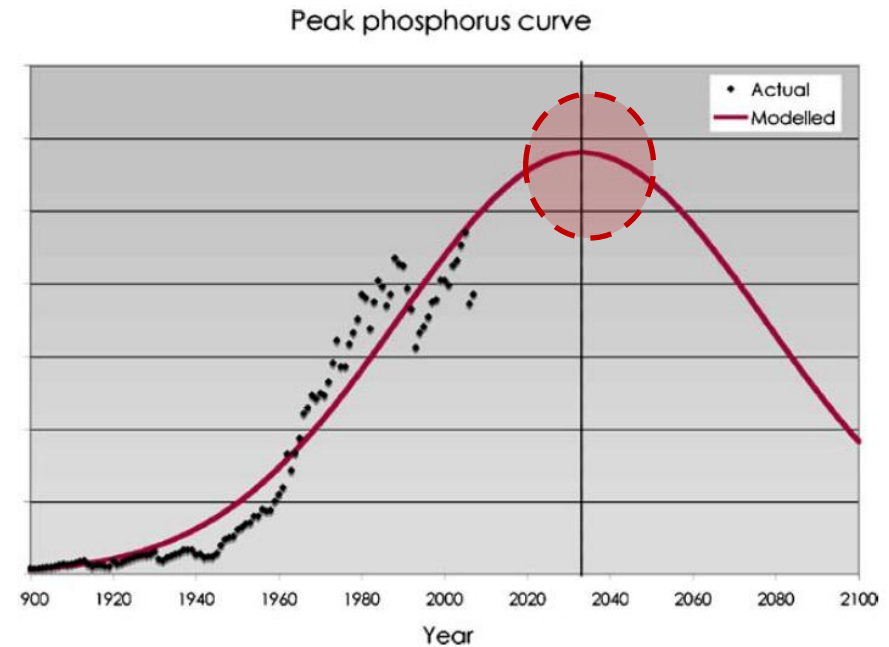


Nutrient Resource Limitations Could Limit Biofuel Production

Nitrogen supply and use

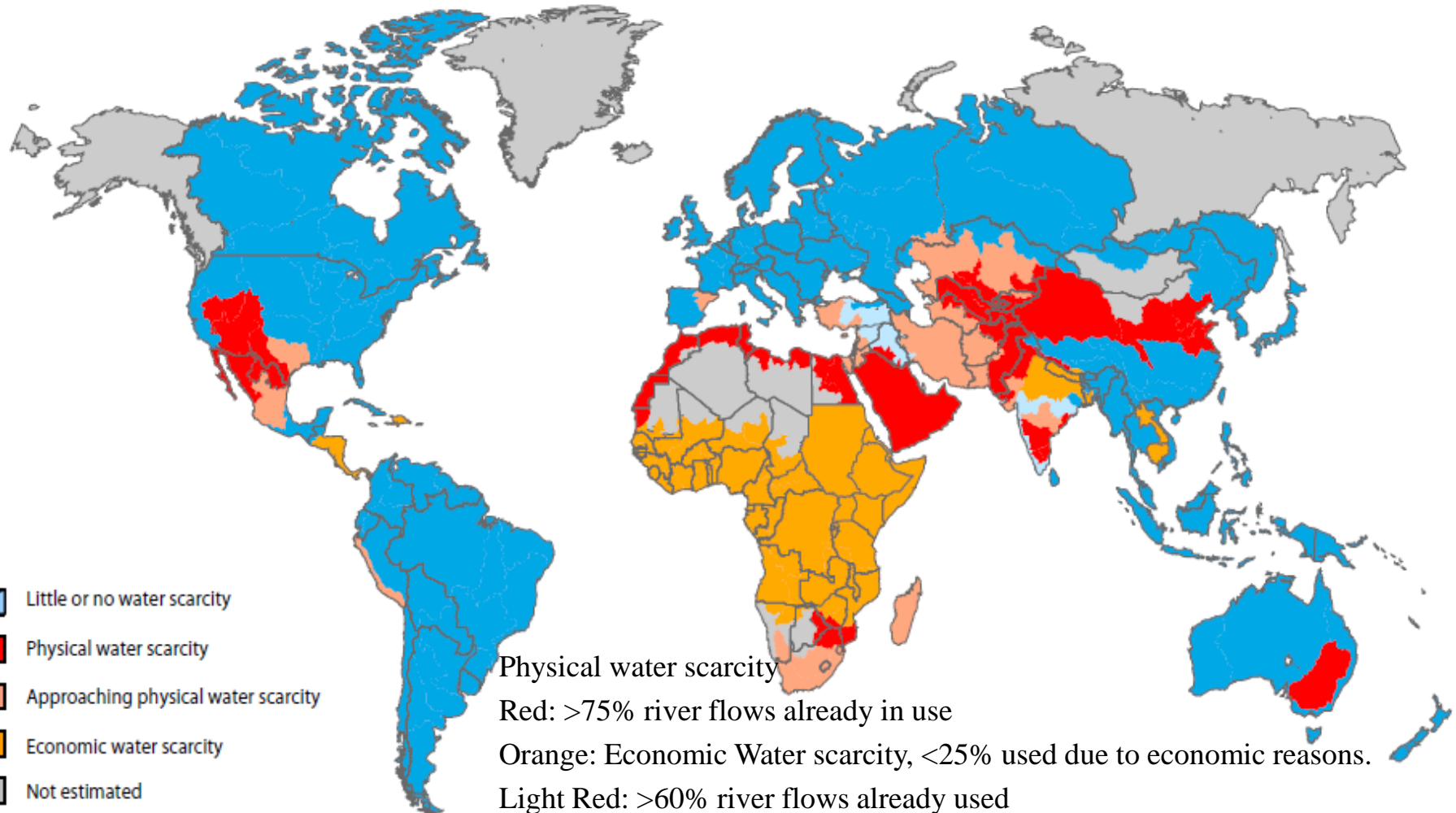


Peak phosphorous?



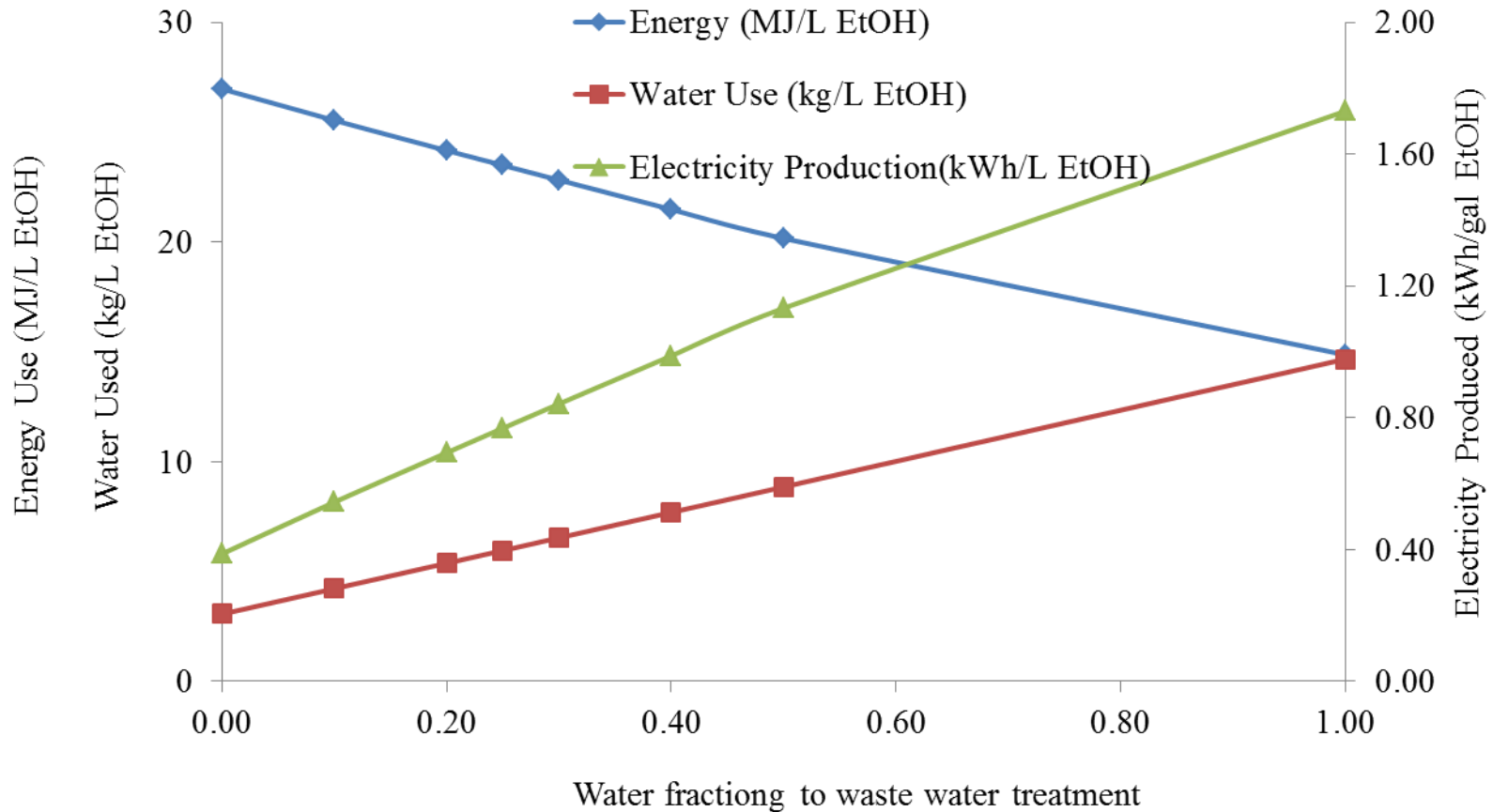
Ref: .Cordell et al. 2009. Global Env. Change. 19:292-305.

Resources: World Water Stress



Ref: .Comprehensive Assessment of Water Management in Agriculture, International Water Management Institute, 2006.

Impact of Technology on Water Use



Dilute Acid Pretreatment Process Case

EROEI and EROWI for Different Fuels

	Water usage (L/MJ)	EROWI (MJ/L)	EROEI (MJ/MJ)	Net EROWI
Nuclear Electric	1.162(0.145)	0.861(1.517)	10	0.775 (1.137)
Conv. Diesel	0.0035	285.3	5.01	228.4
Ethanol				
Sugarcane	38-156	0.026-0.0065	8.3	0.023-0.0057
Corn	73-346	0.014-0.0029	1.38	0.0039-0.00081
Lignocellulosic Crops				
Ethanol	11-171	0.091-0.0058	4.55	0.0071-0.0045

EROWI= Energy Return On Water Invested (MJ/L)

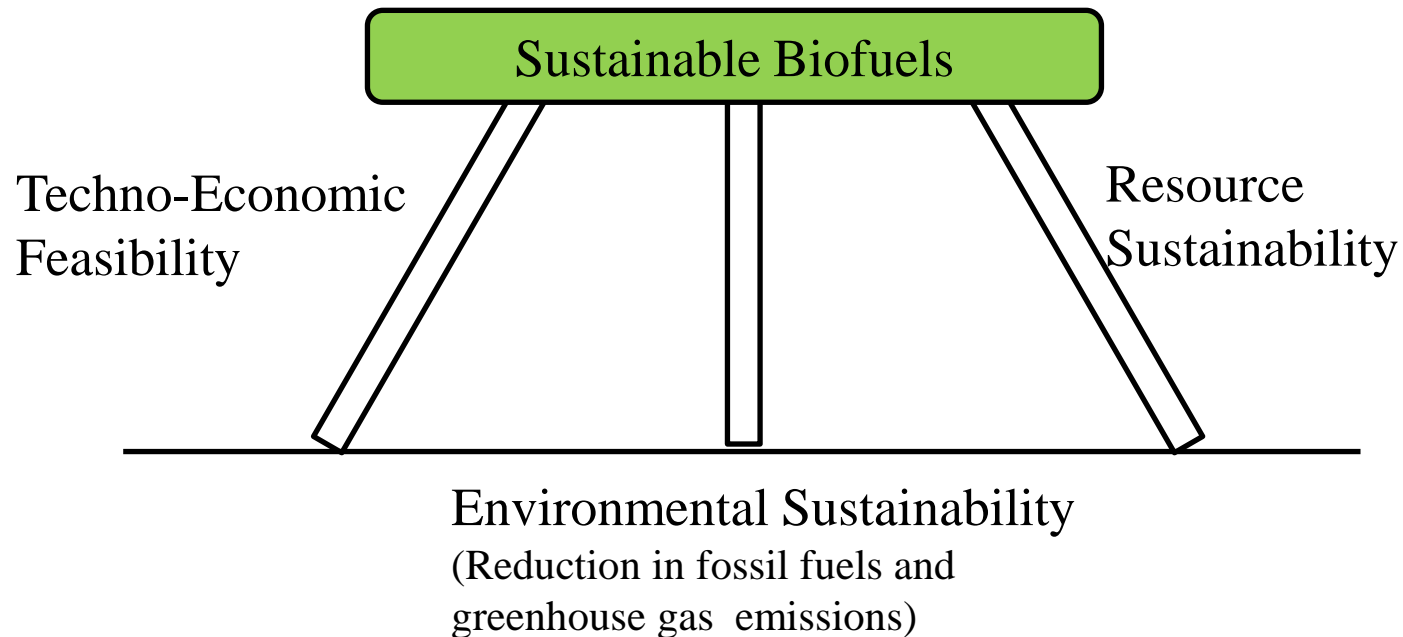
EROEI= Energy Return On Energy Invested (MJ/MJ)

Net EROWI = Net Energy Return on Water Invested (MJ/MJ) = EROWI/ ω

ω = EROEI/(EROEI-1), Amount of energy production needed for 1 unit of net energy.

Conclusions

1. Ethanol price and energy use were highly dependent on pretreatment and process conditions.
2. Significant ethanol cost reductions possible by increasing pentose fermentation efficiency, reducing biomass and enzyme costs.
3. The results demonstrated the importance of addressing the tradeoffs in capital costs, pretreatment and downstream processing technologies.



Sustainable Technologies Laboratory

Collaborators

- *Mr. Bill Rose*, Farmer and President of Rose Agri Seed.
- *Prof. Christine Kelly*, CBEE, Oregon State University
- *Prof. Michael Penner*, Food Science , Oregon State University.

Funding Support

- *US. Dept. of Transportation*
- *Western Sun Grant Center*
- *Oregon BEST*

Sustainable Technologies Laboratory

We do not inherit the Earth, we borrow it from our children-
Native American Proverb

Thank you

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