Biochemical Conversion Processes

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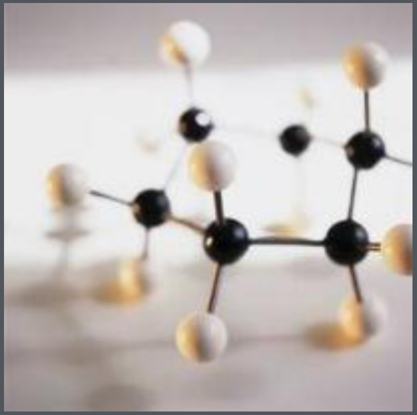


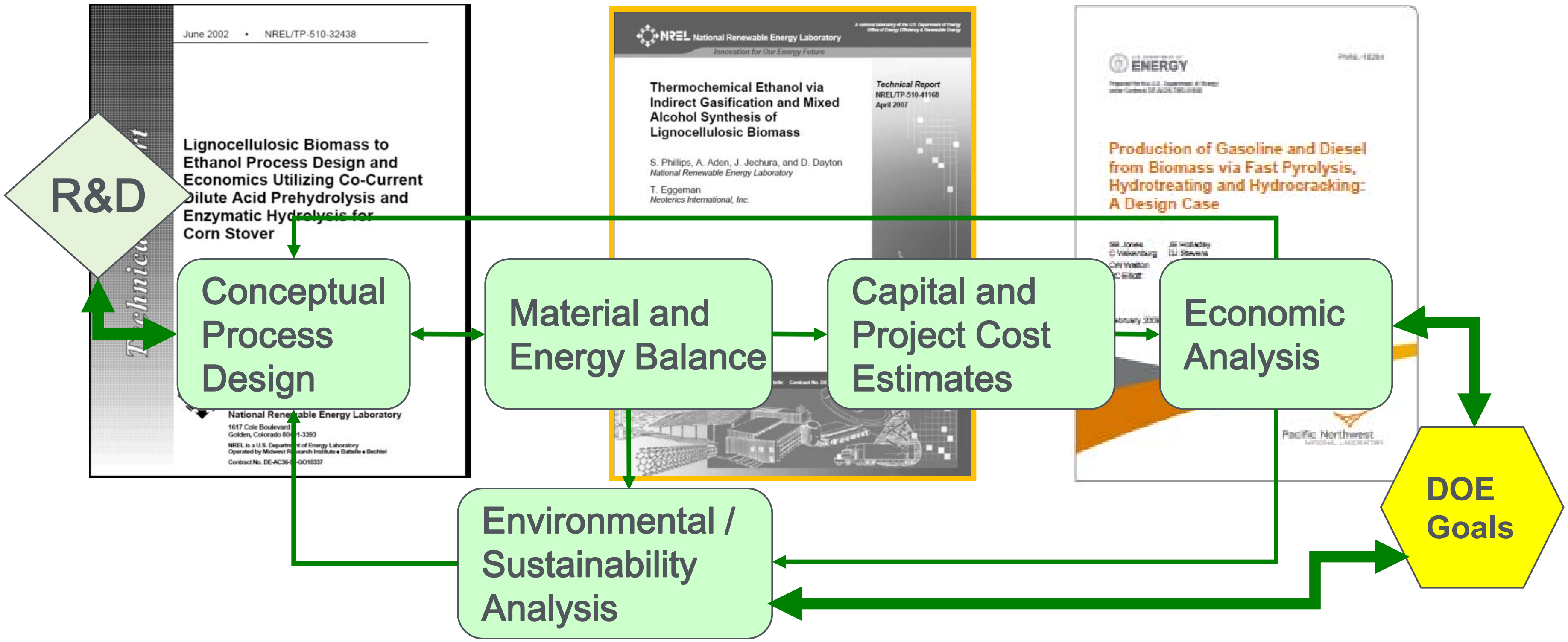
Advanced Bio-based Jet fuel Cost of Production Workshop

Mary Biddy (NREL)

November 27, 2012

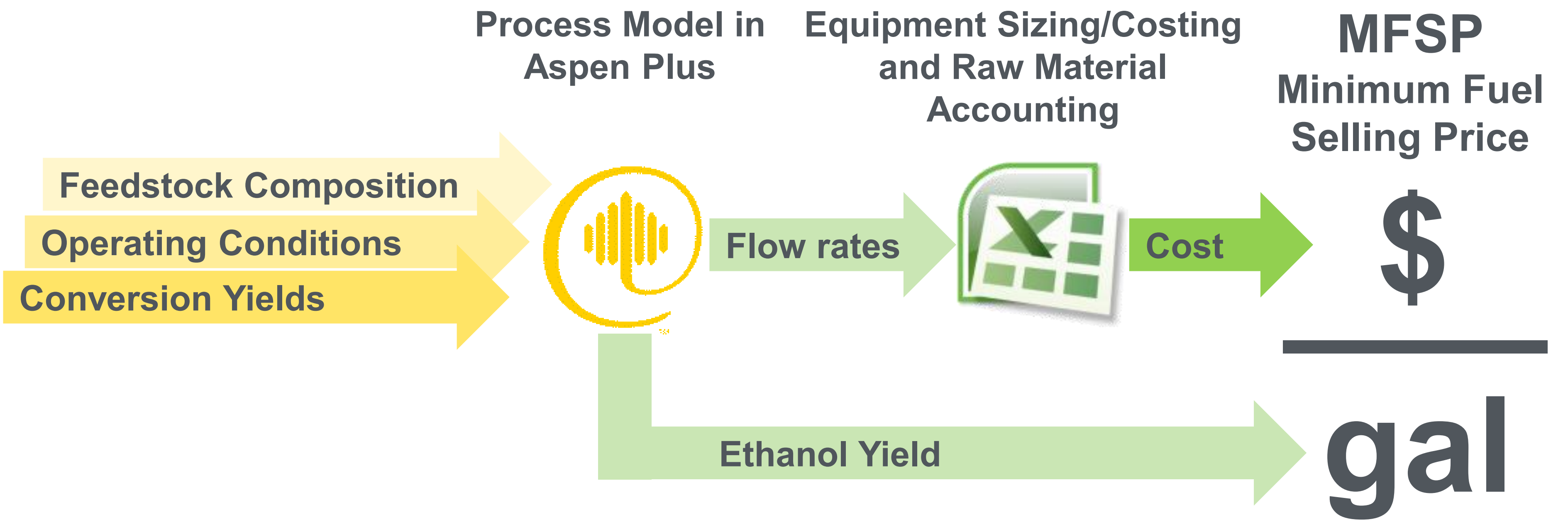
Overview

- Techno-Economic Analysis Approach
- Biochemical conversion to Ethanol
- Biochemical conversion to Advanced Hydrocarbons



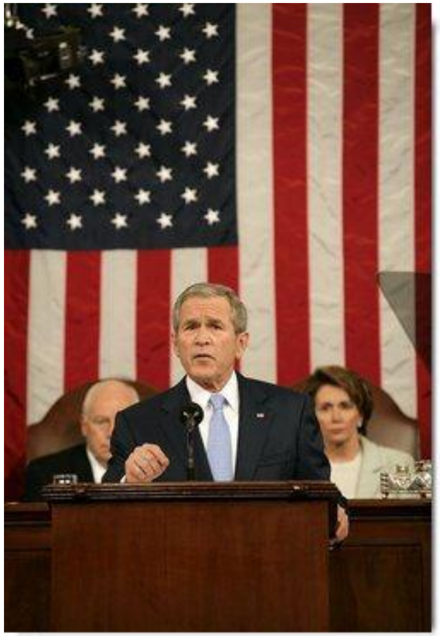
- Collaborate with engineering & construction firm to enhance credibility, quality
- Conceptual design reports are transparent, highly peer reviewed
- Iteration with researchers and experimentalists is crucial

Techno-Economic Analysis
Approach



- Modeling is rigorous and detailed with transparent assumptions
- Assumes *n*th-plant equipment costs
- Discounted cash-flow ROR calculation includes return on investment, equity payback, and taxes
- Determines the minimum selling price required for zero NPV

State of Technology Background



2006 State of the Union

"America is addicted to oil…the best way to break this addiction is through technology."

"Our goal is to make cellulosic ethanol practical and cost competitive within 6 years."

2007 State of the Union

"Reduce U.S. gasoline usage by 20% in 10 years – 75% from new fuels and 25% from vehicle efficiency"

"Mandatory fuel standard to require 35B gallons of renewable and alternative fuels by 2022."

State of Technology Background
Cost Targets Developed

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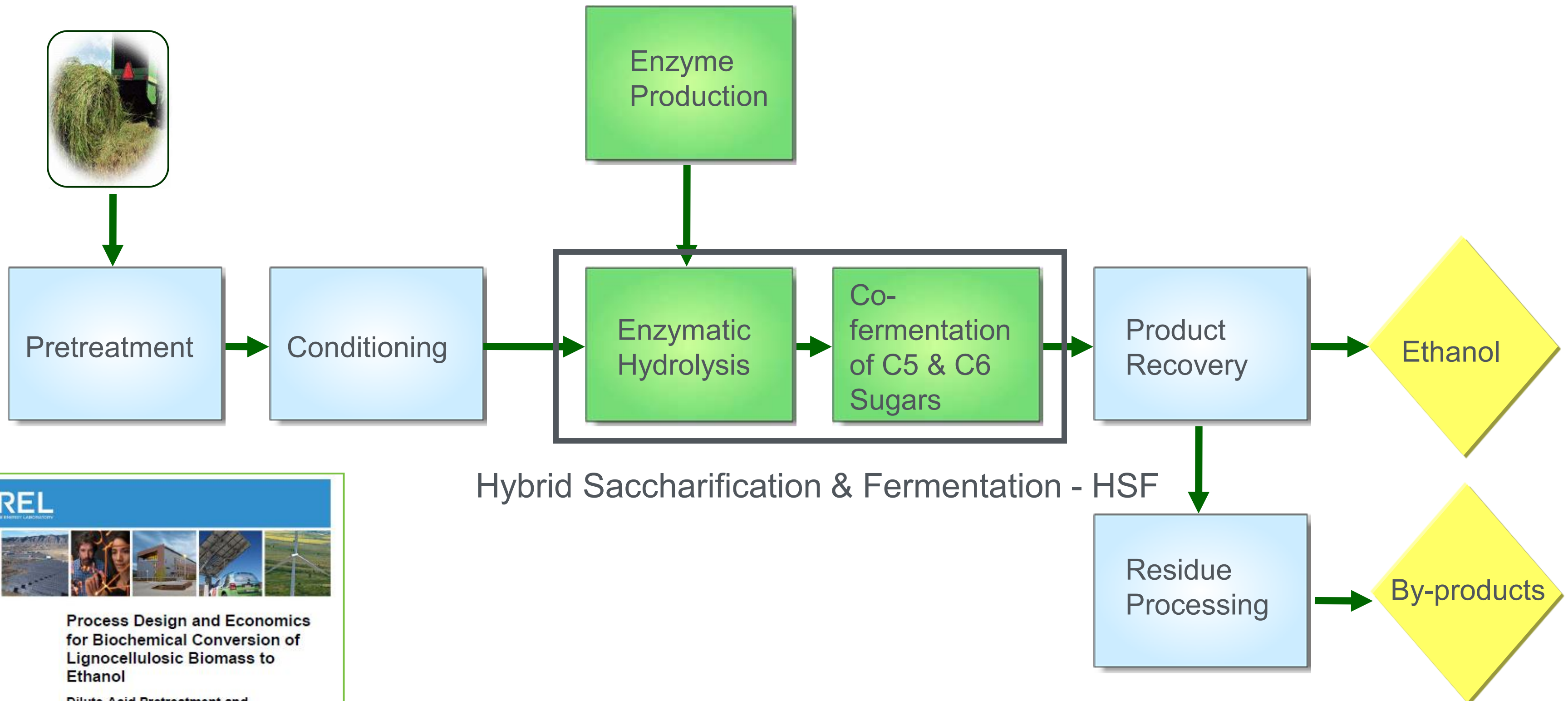
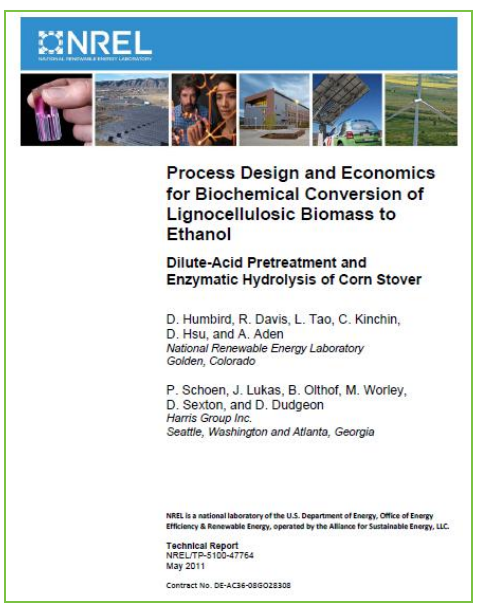
- **Original Design Reports updated to ~$2.00/gal target (2011 timeframe)**
  - *Total bottoms up approach with no end cost target in mind*
  - *Incorporation of state of the art knowledge on capital costs, financing assumptions, process design*
  - *Roughly equivalent to gasoline production at $110/BBL crude*

Organization	Oil Price Forecast in 2012 (2007$/barrel)	Ethanol Production Cost (2007$/gallon ethanol)
EIA, AEO2009, High Oil Price Case	116	2.06
EIA, AEO2009, Reference Case	95	1.76
EIA, AEO2009, Low Oil Price Case	51	1.04

State of Technology Background

2011 Design Report for Cellulosic Ethanol





NREL

Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol

Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover

D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, and A. Aden
National Renewable Energy Laboratory
Golden, Colorado

P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, and D. Dudgeon
Harris Group Inc.
Seattle, Washington and Atlanta, Georgia

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5100-47764
May 2011

Contract No. DE-AC36-08GO28308

- **Conceptual design of a 2,000 tonnes/day commercial plant – one possible tech package, not optimized**
- **NREL pilot plant based on this process**
- **Basis for connecting R&D targets to cost targets**
- **Has undergone rigorous peer review**
- **Basis for comparison against other technology options**

BC Conversion to Cellulosic Ethanol
Historic State of Technology

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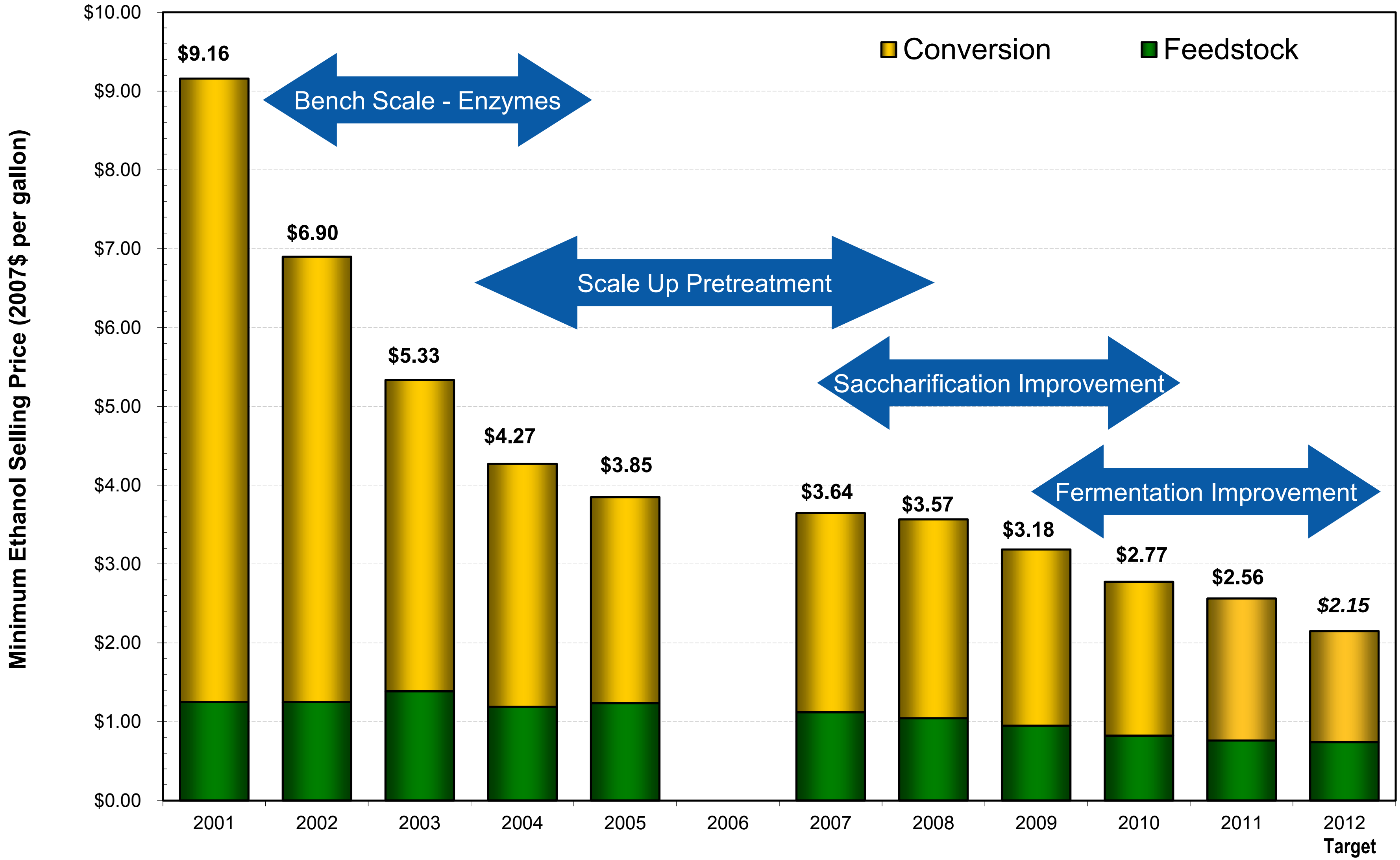

BC Conversion to Cellulosic Ethanol
Technical Target Table

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	2007	2008	2009	2010	2011 Targets	2011 Washed Solids	2011 Whole Slurry	2012 Targets
Minimum Ethanol Selling Price ($/gal)	**$3.64**	**$3.56**	**$3.19**	**$2.77**	**$2.62**	**$2.56**	**$2.37**	**$2.15**
Feedstock Contribution ($/gal)	$1.12	$1.04	$0.95	$0.82	$0.76	$0.76	$0.82	$0.74
Conversion Contribution ($/gal)	$2.52	$2.52	$2.24	$1.95	$1.86	$1.80	$1.55	$1.41
Yield (Gallon/dry ton)	69	70	73	75	78	78	71	79
Feedstock								
Feedstock Cost ($/dry ton)	$77.20	$72.90	$69.65	$61.30	$59.60	$59.60	$59.60	$58.50
Pretreatment								
Solids Loading (wt%)	30%	30%	30%	30%	30%	30%	30%	30%
Xylan to Xylose (including enzymatic)	75%	75%	84%	85%	88%	88%	78%	90%
Xylan to Degradation Products	13%	11%	6%	8%	5%	5%	6%	5%
Conditioning								
Ammonia Loading (mL per L Hydrolyzate)	50	50	38	23	25	25	25	25
Hydrolyzate solid-liquid separation	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Xylose Sugar Loss	2%	2%	2%	2%	1%	1%	1%	1%
Glucose Sugar Loss	1%	1%	1%	1%	1%	1%	1%	0%
Enzymes								
Enzyme Contribution ($/gal EtOH)	$0.39	$0.38	$0.36	$0.36	$0.36	$0.34	$0.38	$0.34
Enzymatic Hydrolysis & Fermentation								
Total Solids Loading (wt%)	20%	20%	20%	17.5%	20%	17.5%	17.5%	20%
Combined Saccharification & Fermentation Time (d)	7	7	7	5	5	5	5	5
Corn Steep Liquor Loading (wt%)	1%	1%	1%	1%	0.60%	0.25%	0.25%	0.25%
Overall Cellulose to Ethanol	86%	86%	84%	86%	86%	89%	80%	86%
Xylose to Ethanol	76%	80%	82%	79%	85%	85%	85%	85%
Arabinose to Ethanol	0%	0%	51%	68%	80%	47%	47%	85%

BC Conversion to Cellulosic Ethanol

Hemicellulose to Sugars (C_5)

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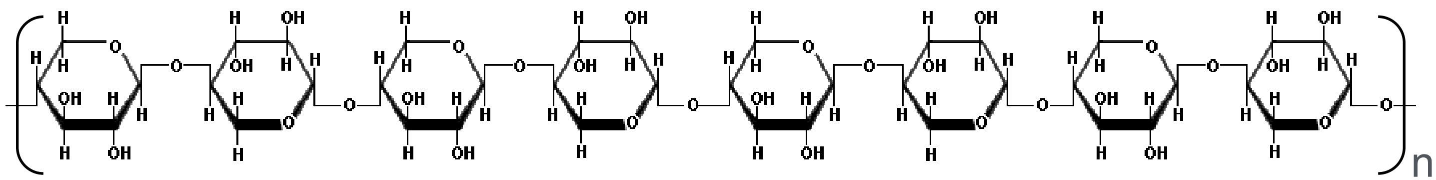
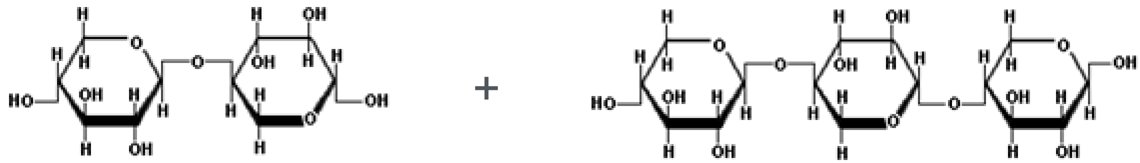
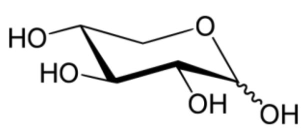
Xylan



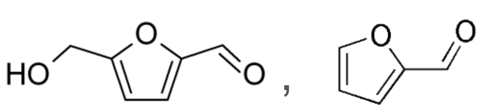
Oligomeric Xylose



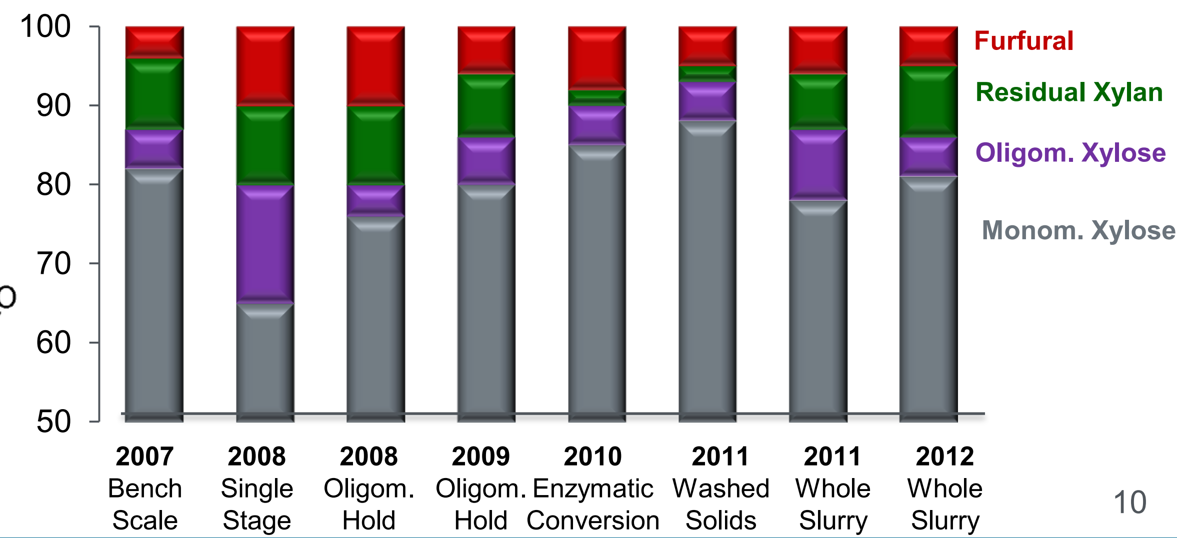
Monomeric Xylose



Degradation Products



Experimental Results from High-Solids Pretreatment



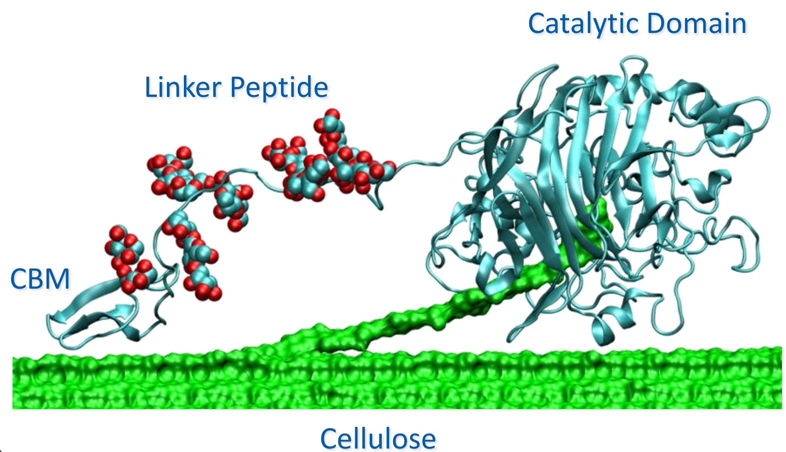
BC Conversion to Cellulosic Ethanol
Enzymatic Saccharification - Fundamentals

Molecular Structure
(experimentally verified)

X-ray crystallography
Structure diversity (genomics)
Homology modeling

Physical/Biochemistry
(physical experimentation)

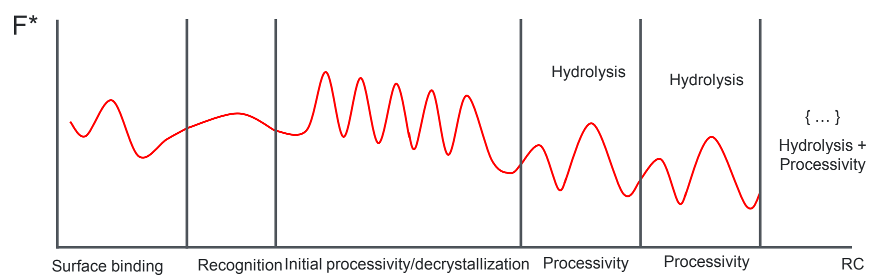
Protein purification
Physical/Chemical analyses
MS and spectro. analyses
Special and HTP activity testing



Numerical Models
(empirical experimentation)

Molecular dynamics
Multi-scale modeling (e.g. atomistic)
Detailed Sub-sets to the system
Force field determinations

Mechanistic Model
(systematic kinetics/thermodynamics)



BC Conversion to Cellulosic Ethanol
Enzymatic Saccharification

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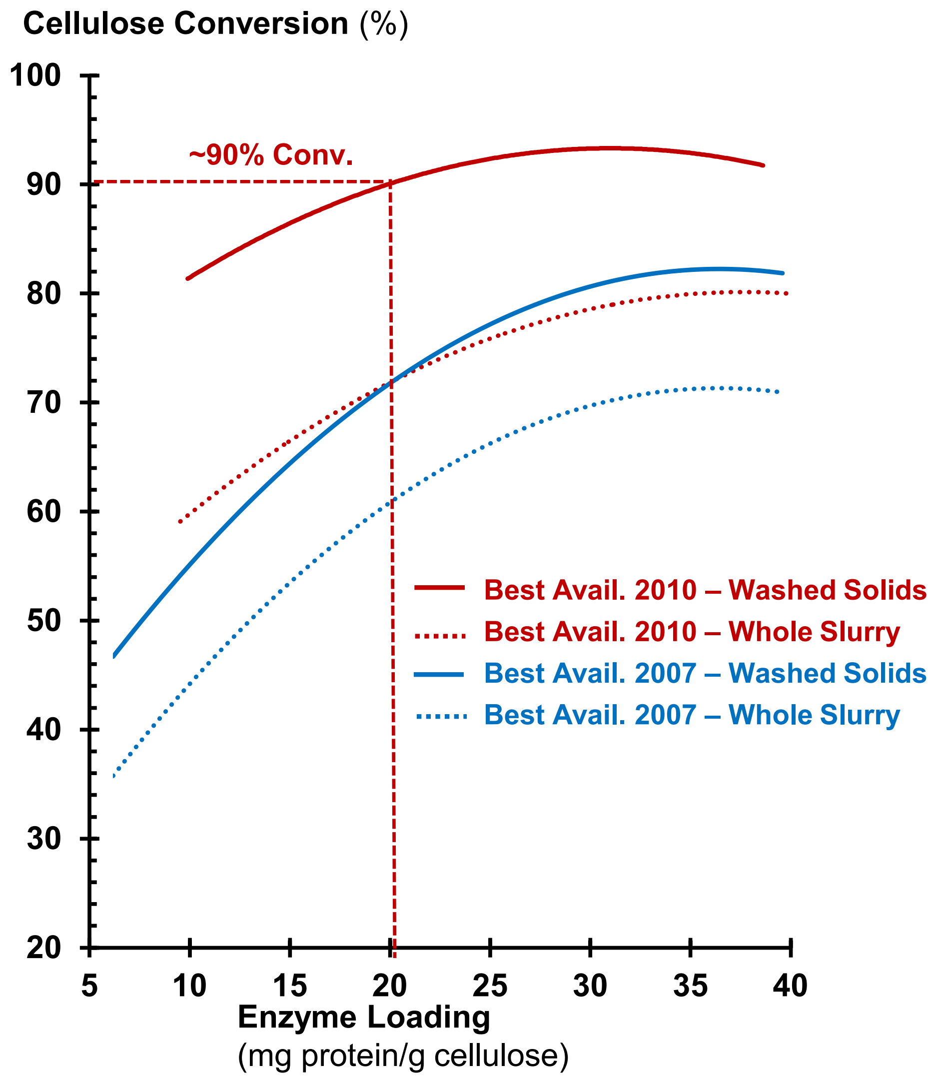


2010:

Commercial Enzyme Package 1 (40 mg/g)

- ~90% Cellulose to Glucose (Washed Solids)
- ~70% Cellulose to Glucose (Whole Slurry)

2011:

Commercial Enzyme Package 2 (40 mg/g)

- >90% Cellulose to Glucose (Washed Solids)
- >80% Cellulose to Glucose (Whole Slurry)

Commercial Enzyme Package 2 (20 mg/g)

- ~75% Cellulose to Glucose (Whole Slurry)

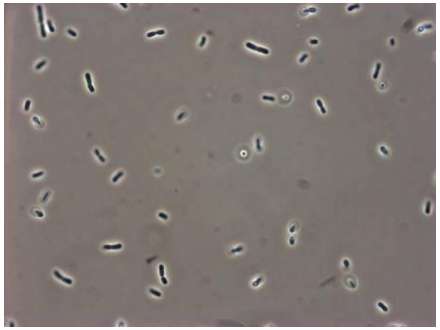
2012:

De-acetylation + Commercial Enzyme Package 2 (20 mg/g)

- ~78% Cellulose to Glucose (Whole Slurry)

BC Conversion to Cellulosic Ethanol
Strain Development

Microbial conversion of sugars to products



Development of *Zymomonas*

Introduced Xylose Utilization - 1994

Introduced Arabinose Utilization - 1995

Combined pentose utilization - 1997

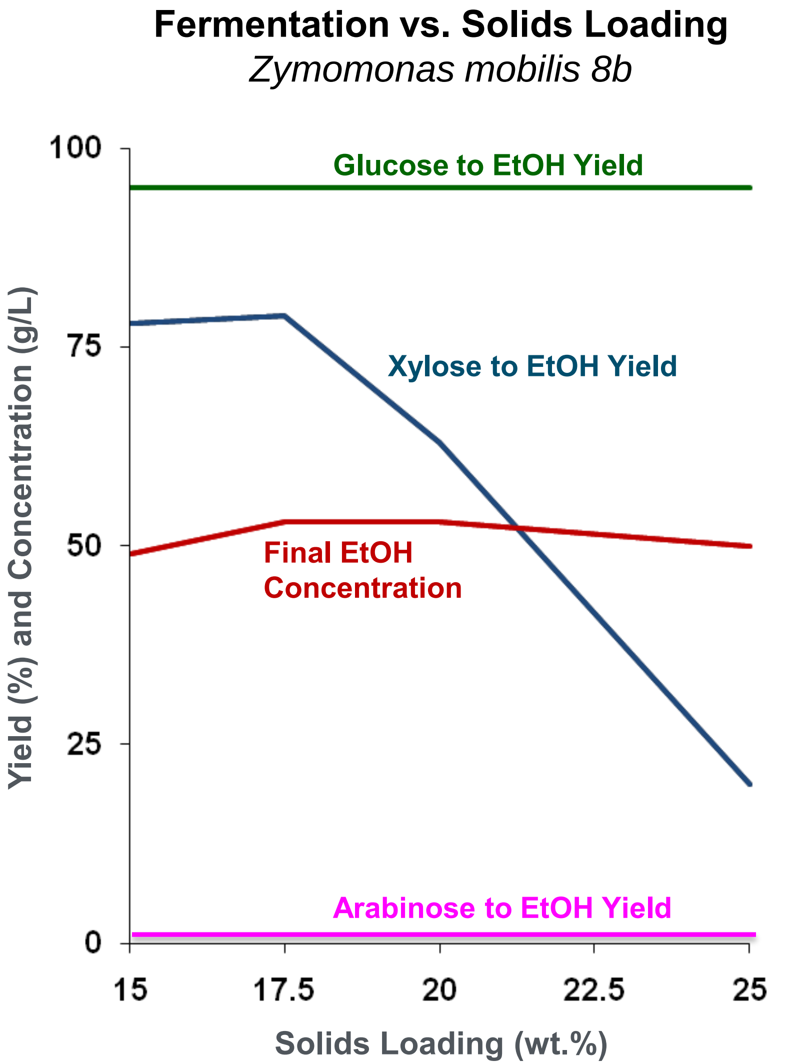
Stabilization by integration - 1999

Further Development in CRADA with DuPont 2002-2007

DOE Grants to Further Strain Development (2007-2011)

- Cargill
- Mascoma
- Purdue / ADM
- DuPont
- Verenium

BC Conversion to Cellulosic Ethanol
Fermentation - End Product Inhibition



(~100 g/L starting sugar concentration ~150 g/L)

2010:

Zymomonas mobilis 8b (NREL)

- ~95% Glucose to Ethanol
- ~79% Xylose to Ethanol
- No arabinose conversion demonstrated at NREL
- Ethanol titer ~50 g/L

2011:

Industrial Organism

- 95% Glucose to Ethanol
- 85% Xylose to Ethanol
- 47% Arabinose to Ethanol
- Ethanol titer ~ 55 g/L

2012:

De-Acetylation / Industrial Organism

- Decrease acetic acid and furfural dramatically
- 96-97% Glucose to Ethanol
- 93% Xylose to Ethanol
- 54% Arabinose to Ethanol
- Ethanol titer ~72 g/L

BC Conversion to Cellulosic Ethanol
Technical Target Table

	2011 Targets	2011 Washed Solids	2011 Whole Slurry	2012 Targets
Minimum Ethanol Selling Price ($/gal)	**$2.62**	**$2.56**	**$2.37**	**$2.15**
Feedstock Contribution ($/gal)	$0.76	$0.76	$0.82	$0.74
Conversion Contribution ($/gal)	$1.86	$1.80	$1.55	$1.41
Yield (Gallon/dry ton)	78	78	71	79
Feedstock				
Feedstock Cost ($/dry ton)	$59.60	$59.60	$59.60	$58.50
Pretreatment				
Solids Loading (wt%)	30%	30%	30%	30%
Xylan to Xylose (including enzymatic)	88%	88%	78%	90%
Xylan to Degradation Products	5%	5%	6%	5%
Conditioning				
Ammonia Loading (mL per L Hydrolyzate)	25	25	25	25
Hydrolyzate solid-liquid separation	Yes	Yes	No	No
Xylose Sugar Loss	1%	1%	1%	1%
Glucose Sugar Loss	1%	1%	1%	0%
Enzymes				
Enzyme Contribution ($/gal EtOH)	$0.36	$0.34	$0.38	$0.34
Enzymatic Hydrolysis & Fermentation				
Total Solids Loading (wt%)	20%	17.5%	17.5%	20%
Combined Saccharification & Fermentation Time (d)	5	5	5	5
Corn Steep Liquor Loading (wt%)	0.60%	0.25%	0.25%	0.25%
Overall Cellulose to Ethanol	86%	89%	80%	86%
Xylose to Ethanol	85%	85%	85%	85%
Arabinose to Ethanol	80%	47%	47%	85%

Keys to Hitting 2012 Targets

Pilot scale integrated testing was in place and ready

Whole slurry mode was necessary

- Solid/Liquid separation and washing too costly

Incorporation of de-acetylation

- Better fermentation (ethanol tolerance)
- Better digestibility (glucose yield) at lower enzyme loadings
- OPEX savings outweigh CAPEX costs
  - Lower acid usage
  - Lower ammonia usage
  - Lower wastewater treatment costs

BC Conversion to Cellulosic Ethanol
Summary

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2012 Cellulosic Ethanol Successful Demonstration

- Developed pretreatment/conditioning strategy (bench and pilot scale) capable of releasing >80% of the hemicellulosic sugars in whole slurry mode
- Reduced Enzyme Costs >20x and developed strategy for further reductions
- Developed Industrially Relevant Strains Capable of Converting C_5 and C_6 Cellulosic Sugars at total conversion yields >95% and tolerant of ethanol titers of ~72 g/L
- Built/adapted fully integrated pilot scale capability for 2012 demonstration
- Developed peer reviewed model for extrapolation to commercial scale
- Commercial demonstrations of similar design coming online (Poet, Abengoa)

Leveragability to Hydrocarbons

- Pretreatment and enzymatic saccharification technologies can make cellulosic sugars
- Compositional analysis techniques fully applicable
- Pilot/bench scale P/T, Saccharification and Fermentation equipment easily re-purposed
- Need some minor, relatively easy modifications for different downstream needs (e.g. separations, purification, hybrid techniques)

Hydrocarbon Pathways

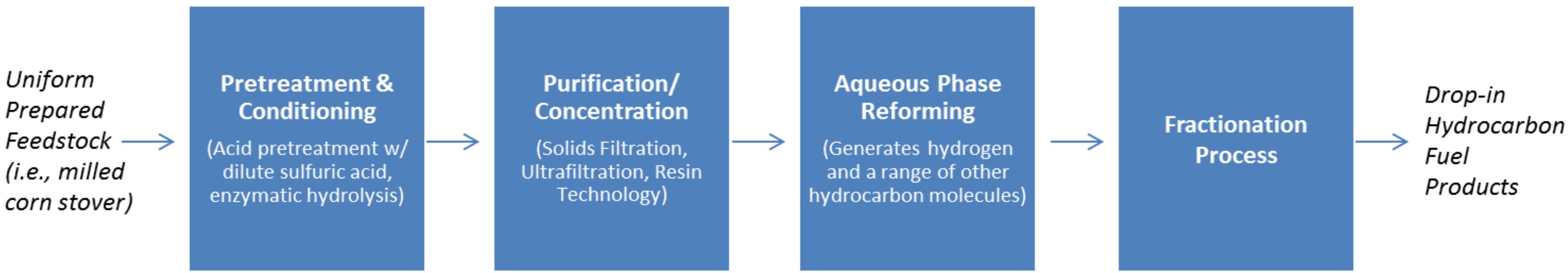
Fermentation of Sugars to Advanced Fuels

Uniform Prepared Feedstock (i.e., milled corn stover) → **Pretreatment & Conditioning** (Dilute sulfuric acid & Ammonia conditioning) → **Enzymatic Hydrolysis** (Enzymes, produced on-site, added to initiate reaction) → **Solids Separation** (Insoluble solids removed; dilute sugar stream concentrated via evaporation) → **Fermentation** (Anaerobic and Aerobic fermentative processes) → **Product Recovery and Purification** (Phase separation, centrifugation) → *Hydrocarbon intermediates or Fuel Products*

- Key research needs:
  - Maximize sugar production
  - Optimize process integration
  - Understand the need for hydrolyzate conditioning and effect of inhibitors
  - Maximize overall conversion yield to final products
  - Investigate routes to cost-effectively utilize entire biomass; Understand sustainability trade-offs

Hydrocarbon Pathways

Catalytic Conversion of Sugars to Advanced Fuels



- Key research needs:
  - Maximize sugar production
  - Optimize process integration
  - Understand the need for hydrolyzate conditioning and effect of inhibitors
  - Maximize overall conversion yield to final products
  - Investigate routes to cost-effectively utilize entire biomass; Understand sustainability trade-offs

Pathways to Jet Fuel

Direct from Ethanol

EERE is sponsoring research on producing jet-range hydrocarbons from minimally processed alcohols produced by fermentation or catalysis.

The example on this slide used a mixed alcohol feedstock (see table) which was fed into a catalytic reactor.

Compounds	Feed Concentration (wt%)
Methanol	0 to 2.5
Ethanol	8 to 28
C3+ Alcohols	1 to 3
Acetic Acid	4 to 14
C2+ Aldehydes	6 to 17
Ethyl Acetate	1 to 18
Water	41 to 60

Data from

Pacific Northwest NATIONAL LABORATORY

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Imperium Aviation Fuels

Pathways to Jet Fuel

Direct from Ethanol

- PNNL prepared samples for fuel property evaluation
- Off-site specification testing conducted by AFRL

- Possible jet fuel blend stock
- Large volume samples required for fit-for purpose testing

Specification Test	MIL-DTL-83133H Spec Requirement	PNNL-1	PNNL-2	FT-SPK	JP-8
Aromatics, vol %	≤25	1.9	2.2	0.0	18.8
Olefins, vol %		1.2	1.1	0.0	0.8
Heat of Combustion (measured), MJ/Kg	≥42.8	43.1	43.1	44.3	43.3
Distillation:					
IBP, °C		161	165	144	159
10% recovered, °C	≤205	165	171	167	182
20% recovered, °C		166	173	177	189
50% recovered, °C		171	183	206	208
90% recovered, °C		190	220	256	244
EP, °C	≤300	214	243	275	265
T90-T10, °C	*22*	25	49	89	62
Residue, % vol	≤1.5	1.1	1.1	1.5	1.3
Loss, % vol	≤1.5	1	0.8	0.9	0.8
Flash point, °C	≥38	44	48	45	51
Freeze Point, °C	≤-47	<-60	<-60	-51	-50
Density @ 15°C, kg/L	0.775 - 0.840 *(0.751 - 0.770)*	0.803	0.814	0.756	0.804

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Imperium Aviation Fuels