

# Technoeconomic comparison of biofuels: ethanol, methanol, and gasoline from gasification of woody residues



**American Chemical  
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# Acknowledgements

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# Presentation Overview

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- Brief discussion on the three fuels evaluated
- Discussion of equivalent feedstock and front end processes
- For each fuel, discussion of back end processes
- Process comparisons of:
  - Efficiencies
  - Yields
  - Water usage
- Economic assumptions and results
- Conclusions

# Methanol, Ethanol, and Gasoline

## Methanol

- Intermediate to other fuels and chemicals

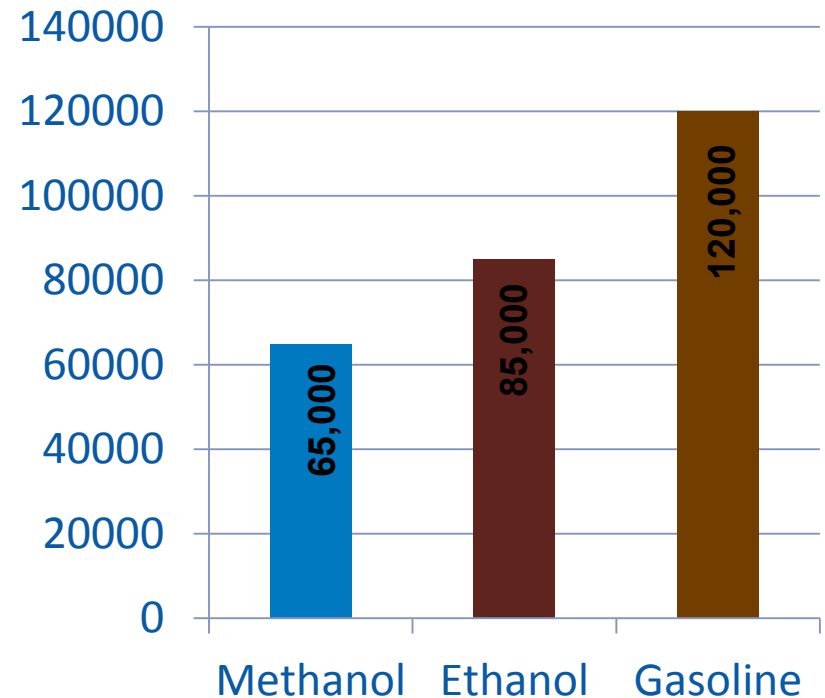
## Ethanol

- Well into American market with 10%-15% ethanol in much of the U.S. gasoline

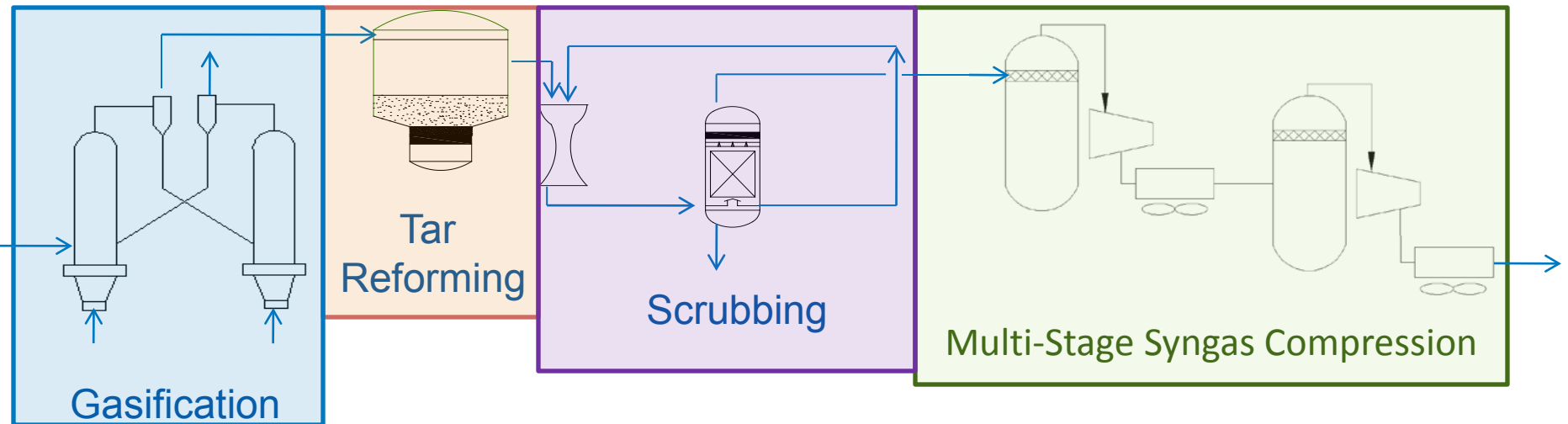
## Gasoline

- Today's primary fuel in the U.S. for lightweight vehicles

BTUs per Gallon



# Equivalent Front End Processes



Begin with equivalent:

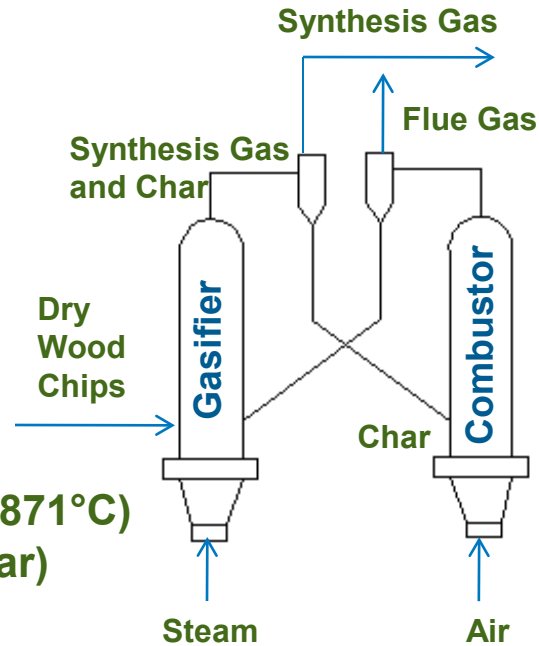
- Feedstock cost of \$61.57 per dry U.S. ton (\$67.87 per dry metric tonne) (includes capital and operating costs, and dry matter losses associated with feed delivery, drying, and handling)
- Plant size of 2,205 dry U.S. tons per day (2,000 dry metric tonnes per day) of woody residues

\* Feedstock cost is based on the 2011 Multi-Year Program Plan from the U.S. Department of Energy

# Gasification

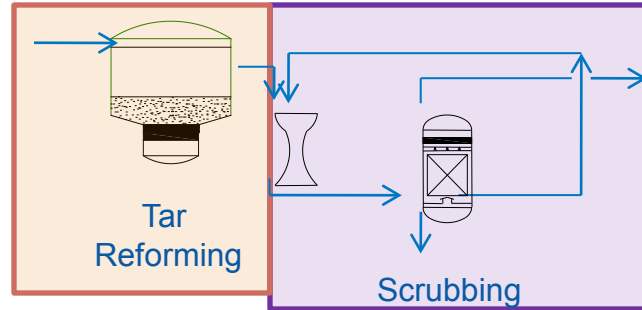
**Low-Pressure,  
Indirectly-Heated,  
Circulating, Fluidized  
Bed Gasifier**

**Temperature: 1,600°F (871°C)  
Pressure: 20 psi (1.4 bar)**



Syngas Composition	Mole Percent (wet)
H <sub>2</sub> (Hydrogen)	13.9
CO <sub>2</sub> (Carbon Dioxide)	7.1
CO (Carbon Monoxide)	23.7
H <sub>2</sub> O (Water)	43.6
CH <sub>4</sub> (Methane)	8.6
C <sub>2</sub> H <sub>2</sub> (Acetylene)	0.2
C <sub>2</sub> H <sub>4</sub> (Ethylene)	2.4
C <sub>2</sub> H <sub>6</sub> (Ethane)	0.1
C <sub>6</sub> H <sub>6</sub> (Benzene)	0.07
C <sub>10</sub> H <sub>8</sub> (Tar - Naphthalene)	0.1
NH <sub>3</sub> (Ammonia)	0.2
H <sub>2</sub> S (Hydrogen Sulfide)	0.04
H <sub>2</sub> :CO molar ratio	0.59
Gasifier Efficiency	72.8% HHV 72.4% LHV

# Syngas Cleanup



## Tar Reformer:

- Fluidized bed reactor
- Containing a nickel catalyst
- The hydrocarbons are converted to CO and H<sub>2</sub>

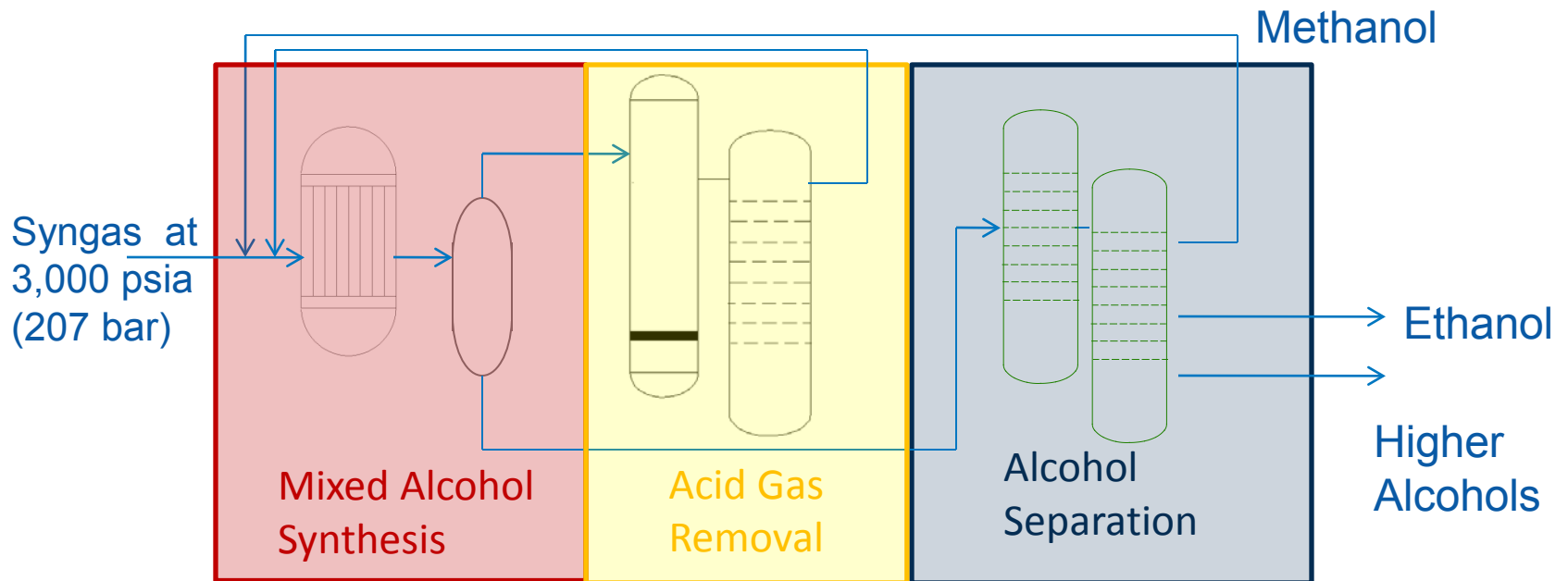
## Scrubbing:

- Venturi scrubber with a quench chamber
- Removes particulates, residual ammonia, and residual tars
- Prior to entering the quench, the syngas is cooled through heat exchange with the steam system from 1,600°F (871°C) to 140°F (60°C)

Compound	2012 Targets for Tar and Methane Conversion Reforming
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Methane (CH <sub>4</sub> )	80%
Ethane (C <sub>2</sub> H <sub>6</sub> )	99%
Ethylene (C <sub>2</sub> H <sub>4</sub> )	90%
Tars (C <sub>10+</sub> )	99.9%
Benzene (C <sub>6</sub> H <sub>6</sub> )	99%
Ammonia (NH <sub>3</sub> ) <sup>a</sup>	90%

# Ethanol – Back End Processes



## Mixed Alcohol Synthesis

- Within the reactor, this mix contacts a metal-sulfide catalyst (Dow's potassium-promoted cobalt molybdenum sulfide catalyst)

## Acid Gas Removal

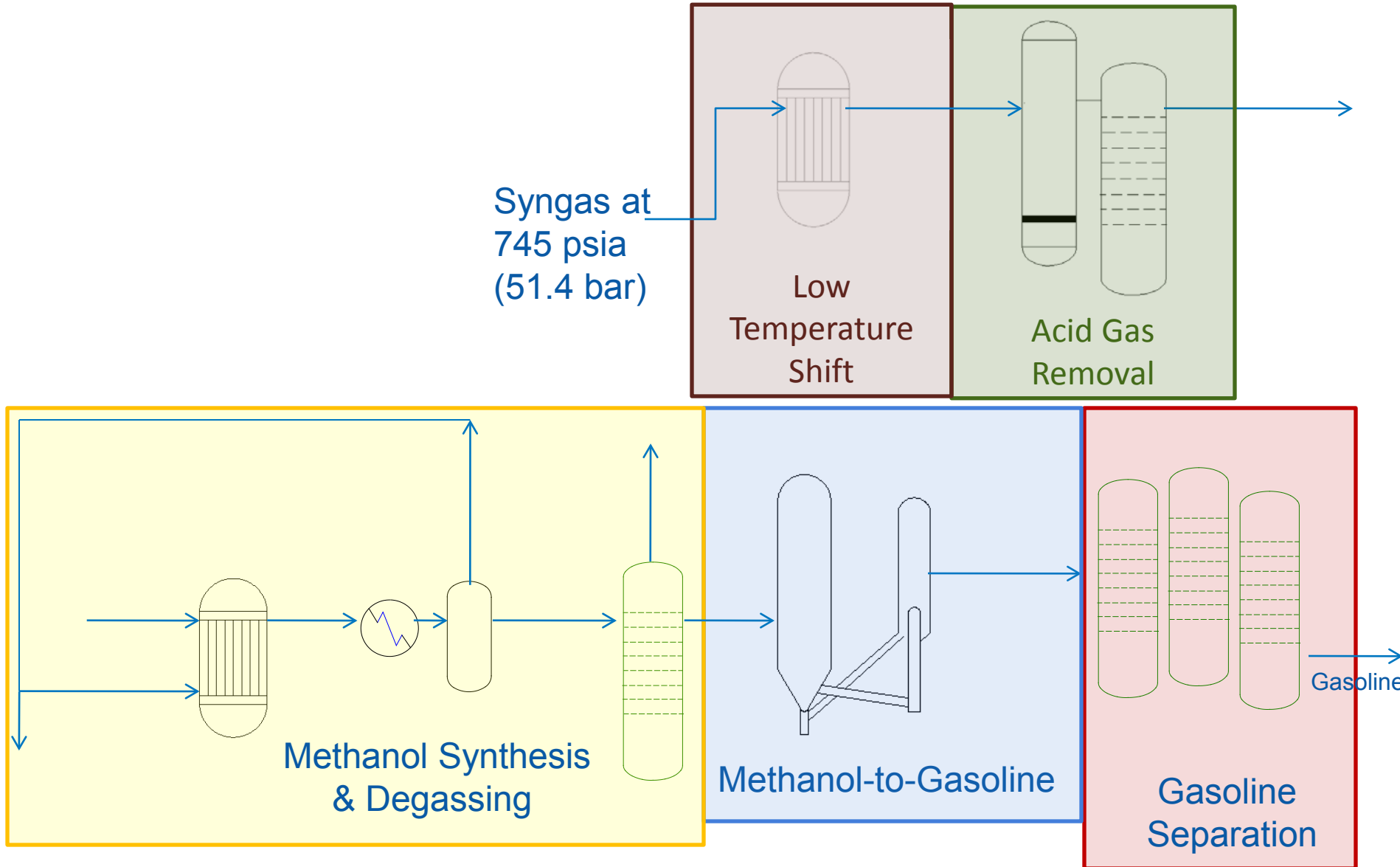
- Utilizes a physical solvent, dimethyl ethers of polyethylene glycol (DEPG) to remove nearly all of the  $H_2S$  and a portion of the  $CO_2$

## Alcohol Separation

- Molecular sieve removes water
- Two-step distillation for recovery of ethanol and higher alcohol products

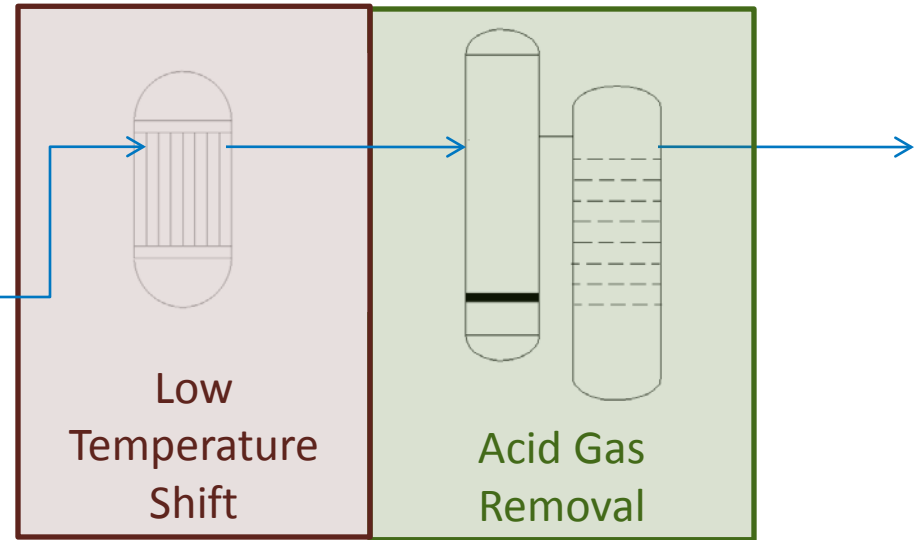


# Methanol and Gasoline Back End Processes



# Low Temperature Shift & Acid Gas Removal

Syngas at  
745 psia  
(51.4 bar)



## Low Temperature Shift

$H_2:CO$  ratio of 2.1 (mole basis)

A stoichiometric number of 1.75

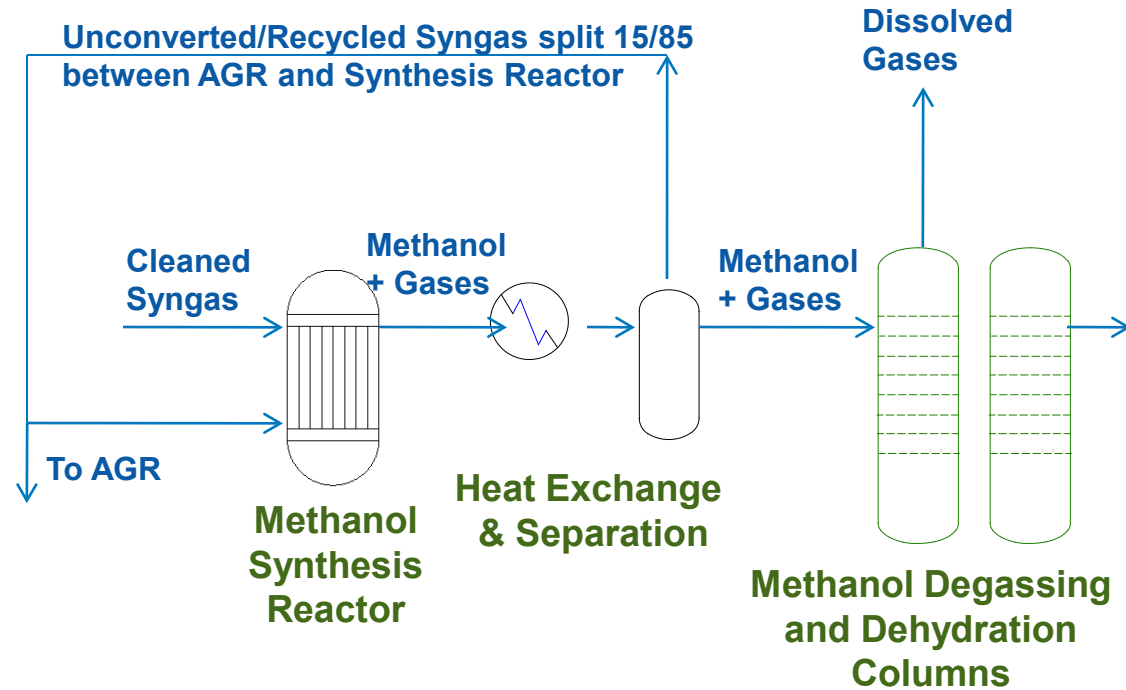
## Acid Gas Removal

Combined AGR and LOCAT systems  
remove the sulfur and  $CO_2$  to:

- 2.2 mol%  $CO_2$
- 0.06 ppm  $H_2S$

# Methanol Synthesis

- Fixed bed reactor containing a copper/zinc oxide/alumina catalyst
- Assumed conversion to 99% methanol
  - After 87 wt% of unconverted syngas is recycled to methanol synthesis reactor inlet
- Operating conditions
  - Temperature: 500°F (260°C)
  - Pressure: 735 psi (50.7 bar)

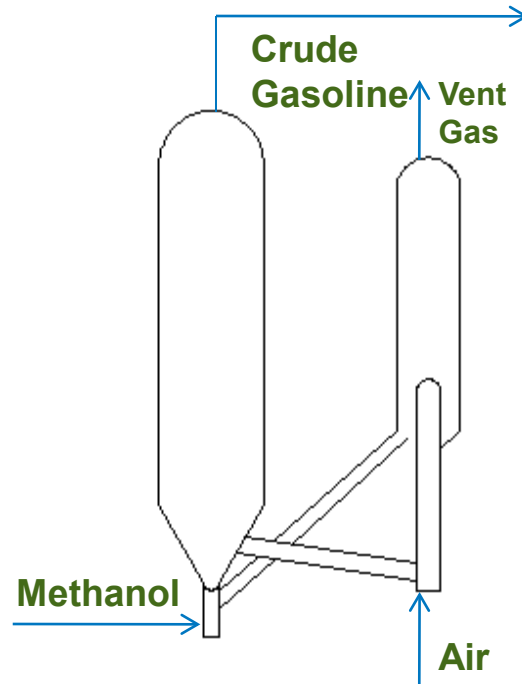


Temperature, °F (°C): 500 (260)  
 Pressure, psi (bar): 733 (50.5)

90 (32) 98 (37)  
 569 (39.2) 250 (17.2)

# Methanol-to-Gasoline Conversion

## Fluidized Bed Reactor



**Inlet Temp: 625°F (329°C)**  
**Exit Temp: 750°F (399°C)**  
**Pressure: 200 psi (13.8 bar)**

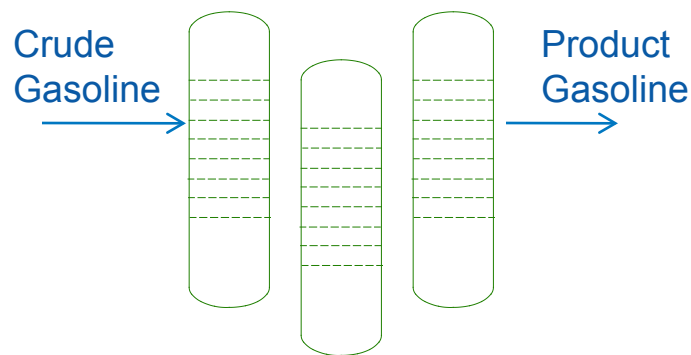
# Gasoline from MTG

<b>Temperature °C (°F)</b>	
Reactor Inlet	330 (625)
Reactor Outlet	400 (752)
<b>Pressure bar(psia)</b>	
Reactor Inlet	14.5 (210)
Reactor Outlet	12.8 (185)
<b>Yield, wt%</b>	
Hydrocarbons	44
Water	56
Total	100
<b>Gasoline Breakdown</b>	
Paraffins	58%
Olefins	20%
Aromatics	22%

<b>Crude Hydrocarbon Product, wt%</b>	
Light gas	2
Propane	5
Propylene	1
Isobutane	7
n-Butane	5
Butenes	1
C5+ Gasoline	79
Durene	<1
Total	100
<b>Finished Fuel Products, wt%</b>	
Gasoline	82
LPG	10
Fuel Gas	8
Total	100

# Gasoline Compositions

Gasoline Composition	(Mole Percent)
Butanes	16.2
Pentane	15.4
Pentene	2.3
Hexane	12.9
Hexene	1.9
Heptane	4.8
Heptene	3.2
Octane	1.4
Octene	3.6
Nonane	1.2
Nonene	1.3
Benzene	1.8
Toluene	1.6
Xylene	6.2
1,2,4 Trimethylbenzene	6.0
1,2,4,5 Tetramethylbenzene	0.4



Gasoline Composition	(Mole Percent)
Butanes	3.3
Pentane	22.0
Pentene	3.2
Hexane	18.4
Hexene	2.7
Heptane	6.8
Heptene	4.6
Octane	2.0
Octene	5.0
Nonane	1.8
Nonene	1.8
Benzene	2.6
Toluene	2.3
Xylene	8.8
1,2,4 Trimethylbenzene	8.7
1,2,4,5 Tetramethylbenzene	0.6

# Process Comparisons

Fuel (Co-Product)	Methanol	Ethanol (Mixed Alcohols)	Gasoline (LPG)	
Yield (gallons/dry U.S. ton feedstock)	130	84 (10)	61 (9)	
Production (million gallons annually)	100	65 (8)	47 (7)	
Energy Production (MMBtu/dry U.S. ton feedstock)	8.4	7.1	7.3	
Efficiencies	HHV	48.9	46.5	48.1
	LHV	45.8	44.9	48.0
Total Water Usage (gallons water/gallon fuel)	1.8	2.6	3.4	
Process Water Usage	1.0	1.2	2.2	
Utility Water Usage	0.8	1.4	1.2	

# Economic Assumptions

- Nth plant
- Equipment was sized and priced based on mass and energy data from Aspen Plus simulation
- Discounted cash flow rate of return completed
- Reference year of \$2007 U.S.
- 30 year plant life
- 10% internal rate of return
- 40% equity of total plant investment
- 8% loan rate on remaining 60% debt
- Co-products:
  - LPG from Gasoline Process – \$1.35/gallon (\$0.36/liter) co-product credit
  - Higher Alcohols from Ethanol Process – \$2.11/gallon (\$0.56/liter) co-product credit



# Economic Results & Comparison

	Methanol	Ethanol	Gasoline
Total Capital Investment (\$MM)	259	516	334
Capital Investment per Annual Gallon Gasoline Equivalent	4.7	12.1	7.1
PGP or Minimum Product Selling Price (\$/MMBtu, HHV basis)	18.42	24.10	22.66
(\$/gallon)	1.20	2.05	2.72

# Summary

	Methanol	Ethanol	Gasoline
Energy Content (Btu/gallon)	65,000	85,000	120,000
Efficiencies	HHV	46.5	48.1
	LHV	44.9	48.0
Yield (gallons/dry U.S. ton feedstock)	130	84 (10)	61 (9)
Production (million gallons annually)	100	65 (8)	47 (7)
Total Capital Investment (MM\$)	259	516	334
Plant Gate Price (\$/MMBtu)	18.42	24.10	22.66

- The energy basis PGP's are within the uncertainties inherent in technoeconomic analysis and thus should be considered as the same
- Specific advantages of gasoline fungibility, partnered with comparable process efficiencies and economics, warrant further research

# Supplemental Information

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# Capital Costs by Plant Section

	<b>Methanol</b>	<b>Ethanol</b>	<b>Gasoline</b>
Gasification	\$43,254,246	\$43,250,000	\$45,620,595
Syngas Cleanup and Compression	\$54,524,041	\$136,060,000	\$62,628,422
Alcohol Synthesis Reaction	\$7,320,586	\$41,420,000	\$10,289,705
Alcohol Separation	\$10,474,820	\$20,310,000	\$8,695,084
MTG Process			\$24,802,792
Steam System & Power Generation	\$23,469,623	\$46,110,000	\$29,562,825
Cooling Water & Other Utilities	\$9,770,000	\$9,620,000	\$9,980,000
Total Installed Equipment Cost (TIC)	\$148,813,413	\$296,780,000	\$191,579,578
Total Capital Investment (TCI)	259,380,000	516,390,000	333,680,000

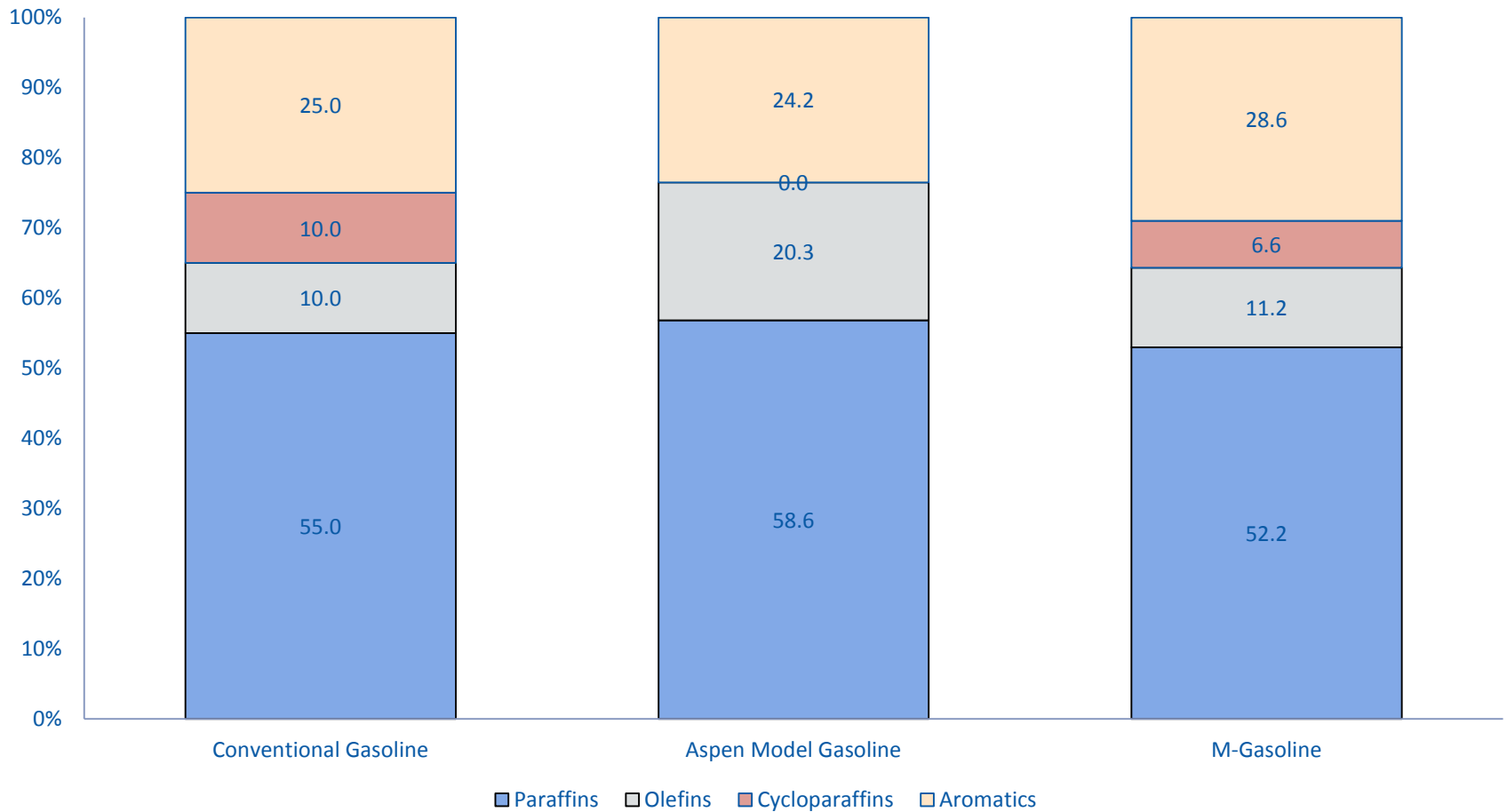
# Tar Reformer Conversions – 2012 Targets

Compound	2012 Targets for Tar and Methane Conversion Reforming
Methane (CH <sub>4</sub> )	80%
Ethane (C <sub>2</sub> H <sub>6</sub> )	99%
Ethylene (C <sub>2</sub> H <sub>4</sub> )	90%
Tars (C <sub>10+</sub> )	99.9%
Benzene (C <sub>6</sub> H <sub>6</sub> )	99%
Ammonia (NH <sub>3</sub> ) <sup>a</sup>	90%

# Acid Gas Removal Design Parameters

Acid Gas Removal Parameter	Value
Amine used	Monoethanolamine (MEA)
Amine concentration	35 wt%
Amine circ. rate	2,261.5 gpm (8,559.8 L/min)
Amine temp. @ absorber	110°F (43.3°C)
Absorber pressure	735 psia (50 atm)
Stripper condenser temperature	212°F (100°C)
Stripper reboiler temperature	230°F (110°C)
Stripper pressure	65 psia (4.4 atm)
Stripper reboiler duty	162 MMBtu/h (171 GJ/h)
Stripper condenser duty	108 MMBtu/h (114 GJ/h)
Amine cooler duty	54.3 MMBtu/h (57.3 GJ/h)
Heat duty per pound CO <sub>2</sub> removed	2,650 Btu/lb (6.19 MJ/kg)
CO <sub>2</sub> removed	61,170 lb/h (27,746 kg/h)

# Gasoline Comparison



# C5+ Breakdown for MTG Gasoline

	Weight %
PENTANE	14.6
PENTENE	2.1
HEXANE	14.6
HEXENE	2.1
HEPTANE	6.2
HEPTENE	4.2
OCTANE	2.1
OCTENE	5.2
NONANE	2.1
NONENE	2.1
BENZENE	1.8
TOLUENE	1.9
XYLENE	8.6
124TMB	9.5
1245TMB	0.7
ETHBENZ	0.8
Total	78.5



# MTG Reaction Conversions (in series)

1	2 METHANOL --> DME + H2O	1.00	13	3 DME --> HEXENE + 3 H2O	0.03
2	9 DME --> 2 124TMB + 9 H2O + 6 H2	0.10	14	2 DME --> BUTENE + 2 H2O	0.02
3	7 DME --> 2 TOLUENE + 7 H2O + 6 H2	0.02	15	DME --> C2H4 + H2O	0.01
4	4 DME --> ETHBENZ + 4 H2O + 3 H2	0.01	16	4 DME + H2 --> OCTANE + 4 H2O	0.04
5	4 DME --> XYLENE + 4 H2O + 3 H2	0.10	17	3 DME + H2 --> HEXANE + 3 H2O	0.26
6	5 DME --> 1245TMB + 5 H2O + 3 H2	0.01	18	2 DME + H2 --> N-C4H10 + 2 H2O	0.30
7	3 DME --> C6H6 + 3 H2O + 3 H2	0.03	19	DME + H2 --> C2H6 + H2O	0.02
8	9 DME --> 2 NONENE + 9 H2O	0.03	20	DME + 2 H2 --> 2 CH4 + H2O	0.03
9	7 DME --> 2 HEPTENE + 7 H2O	0.06	21	7 DME + 2 H2 --> 2 HEPTANE + 7 H2O	0.22
10	5 DME --> 2 PENTENE + 5 H2O	0.03	22	9 DME + 2 H2 --> 2 NONANE + 9 H2O	0.10
11	4 DME --> OCTENE + 4 H2O	0.08	23	5 DME + 2 H2 --> 2 PENTANE + 5 H2O	0.74
12	3 DME --> 2 C3H6 + 3 H2O	0.02	24	3 DME + 2 H2 --> 2 C3H8 + 3 H2O	1.00

# Process Comparisons (SI Units)

Fuel (Co-Product)	Methanol	Ethanol (Mixed Alcohols)	Gasoline (LPG)
Yield (liters/dry metric tonne feedstock)	542	351 (42)	255 (38)
Production (million liters annually)	379	246 (30)	178 (26)
Energy Production (GJ/dry metric tonne feedstock)	9.8	8.3	8.5
Efficiencies	HHV	48.9	46.5
	LHV	45.8	44.9
Total Water Usage (liters water/liter fuel)	1.8	2.6	3.4
Process Water Usage	1.0	1.2	2.2
Utility Water Usage	0.8	1.4	1.2

# Economic Results & Comparison (SI Units)

	Methanol	Ethanol	Gasoline
Total Capital Investment (\$MM)	259	516	334
Capital Investment per Annual Liter Gasoline Equivalent	1.2	3.2	1.9
PGP or Minimum Product Selling Price (\$/GJ, HHV basis)	17.45	22.84	21.48
(\$/liter)	0.32	0.54	0.72

# Summary (SI Units)

	Methanol	Ethanol	Gasoline
Energy Content (kJ/liter)	18,000	24,000	33,000
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Total Capital Investment (MM\$)	259	516	334
Plant Gate Price (\$/GJ)	17.45	22.84	21.48