Biorenewable Fuels and Chemicals

Dennis J. Miller

Michigan State University

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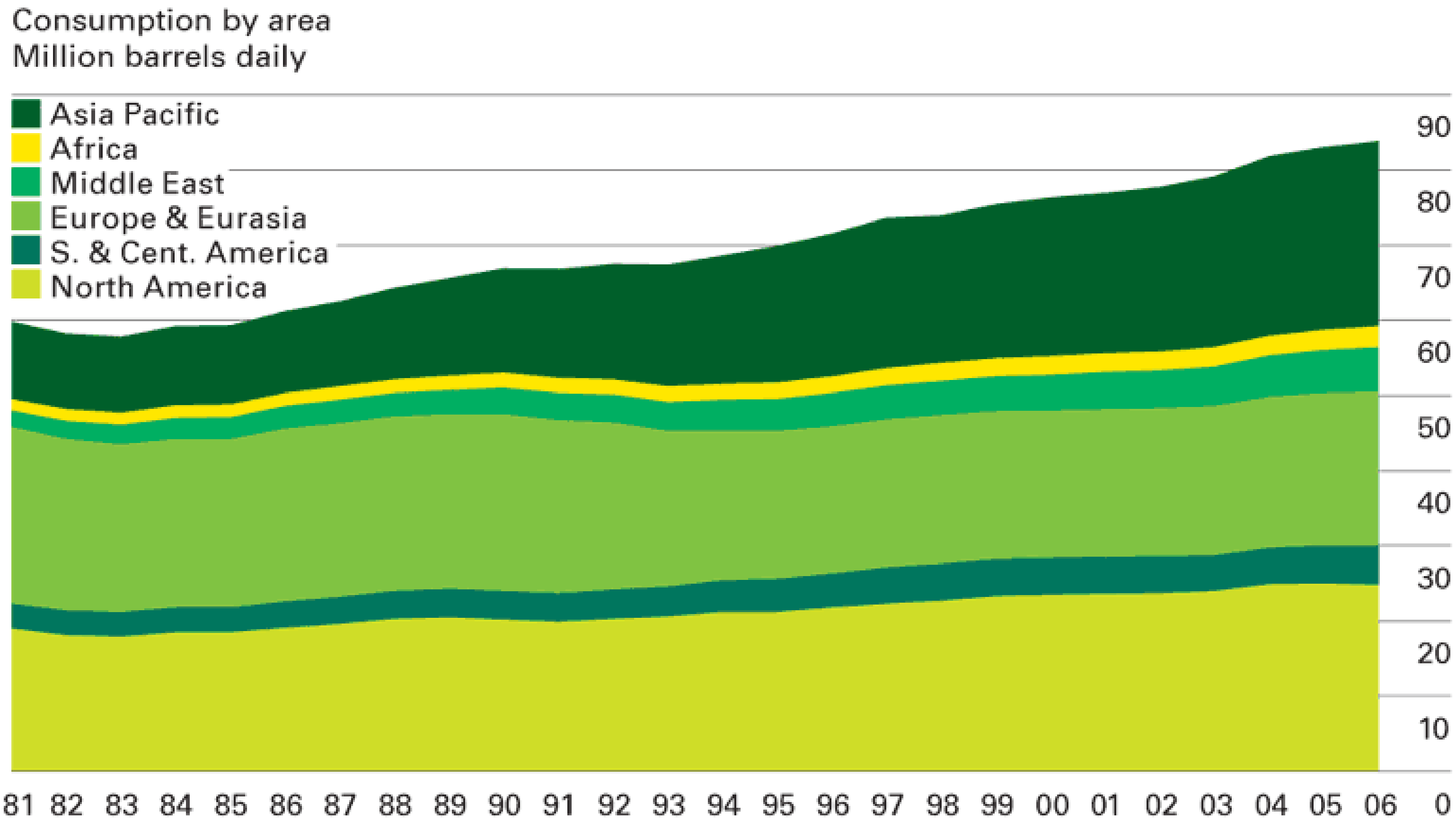
Oil consumption by region



World oil consumption rose by just under 650,000b/d in 2006, about half the 10-year average. OECD consumption fell by 400,000b/d, the biggest decline since 1983. Oil consumption growth was above average in China and oil-exporting countries.

www.bp.com

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The Emerging U.S. Bioeconomy

- Commercial ethanol production (6.5 B gal in 2007) approaching "blend barrier" – 8 billion gallons satisfies mandated fuel oxygenate demands
- 15 billion gallon "build-out" production for corn ethanol will occur in 3-5 years
- Demonstration-scale cellulosic ethanol production facilities in design stages (construction in 2009)
- Biodiesel production (~1.0 billion gallon capacity) limited to 15 – 20% of capacity by high raw material (plant oil) costs: $3.50 – $4.50/gallon (3/08)
- Small-scale entrepeneurial "niche" chemical manufacturers emerging and in some cases flourishing
- Major U.S. corporations actively engaged in biorenewable chemicals development, some initiating production (NatureWorks, DuPont, Dow, Cargill, ADM, Tate & Lyle, etc.)

Renewable Chemicals and Fuels for the U.S.

	Chemicals	Gasoline (Ethanol)	Diesel (Biodiesel)
Petroleum Equivalent (bbl/yr)	0.8×10^9	4×10^9	2×10^9
Biofuel equivalent (bbl/yr)		5.5×10^9	2×10^9
Required biomass acreage	90×10^6	450×10^6 (corn/cellulose) (500 g/a)	700×10^6 (oil crop) (120 g/a)
U.S. agricultural acreage		600×10^6	
TOTAL ACREAGE OF USA		$2,100 \times 10^6$	

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Corn Ethanol

U.S. corn production: 13.1 B bu (2007)

10.5 B bu (2006)

Ethanol (2007): 6.5 B gallons (2.5 B bu corn)

Energy balance

1.0 MJ fossil (coal*, CH_4*, oil) $\rightarrow$ 1.3 MJ ethanol

(30%, 55%, 15%)

(*Non-liquids) (Liquid)

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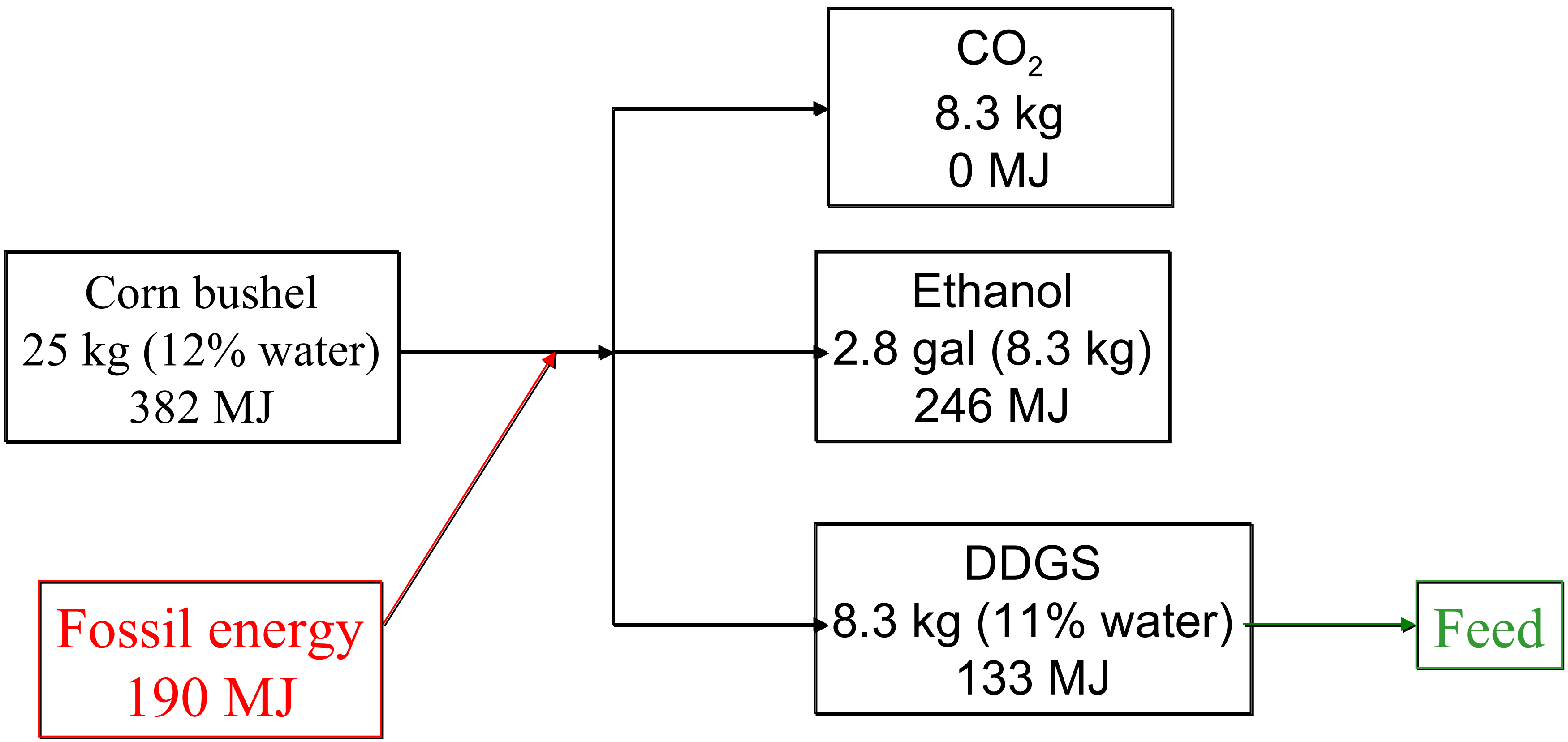
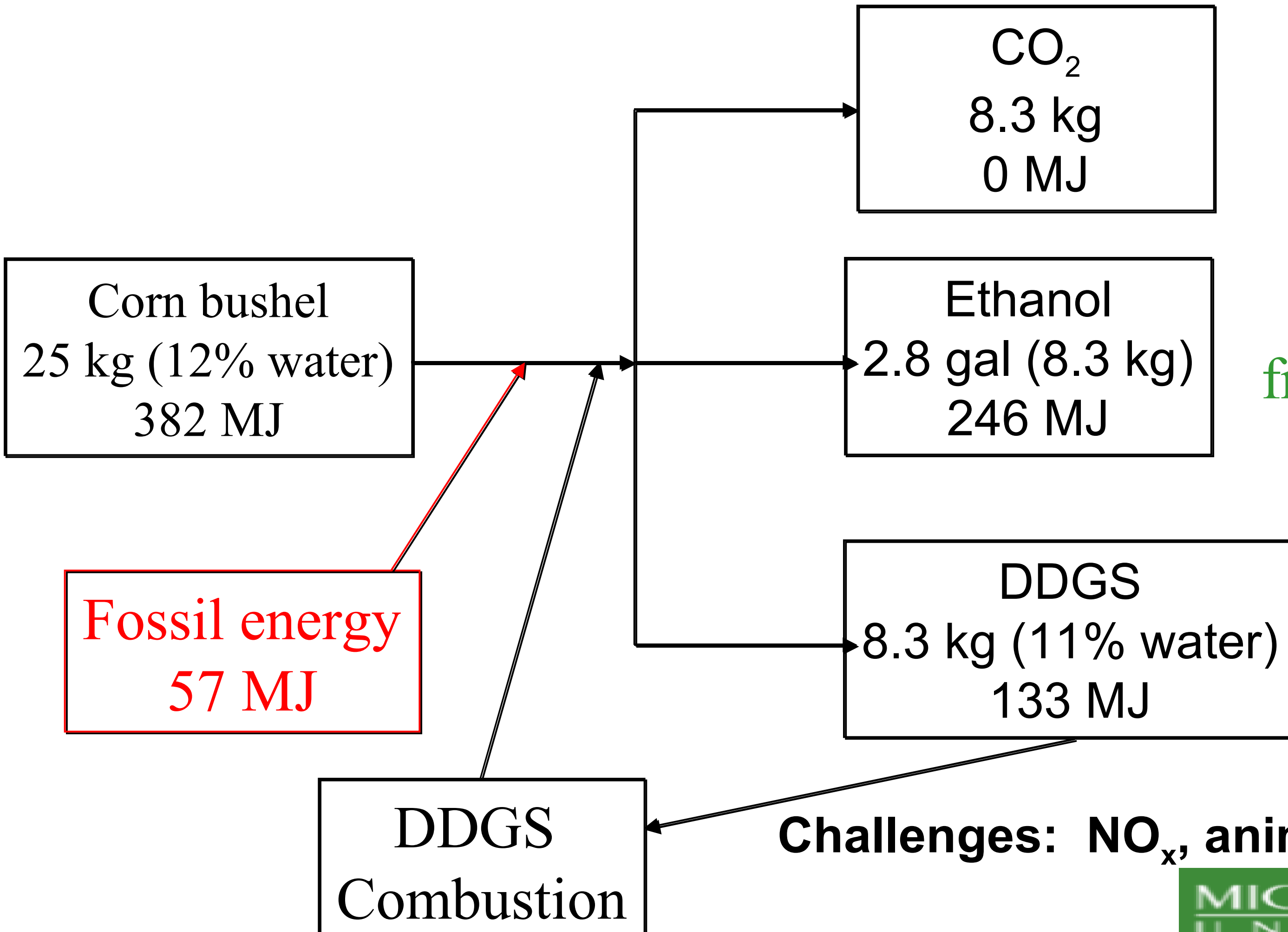
Corn Ethanol



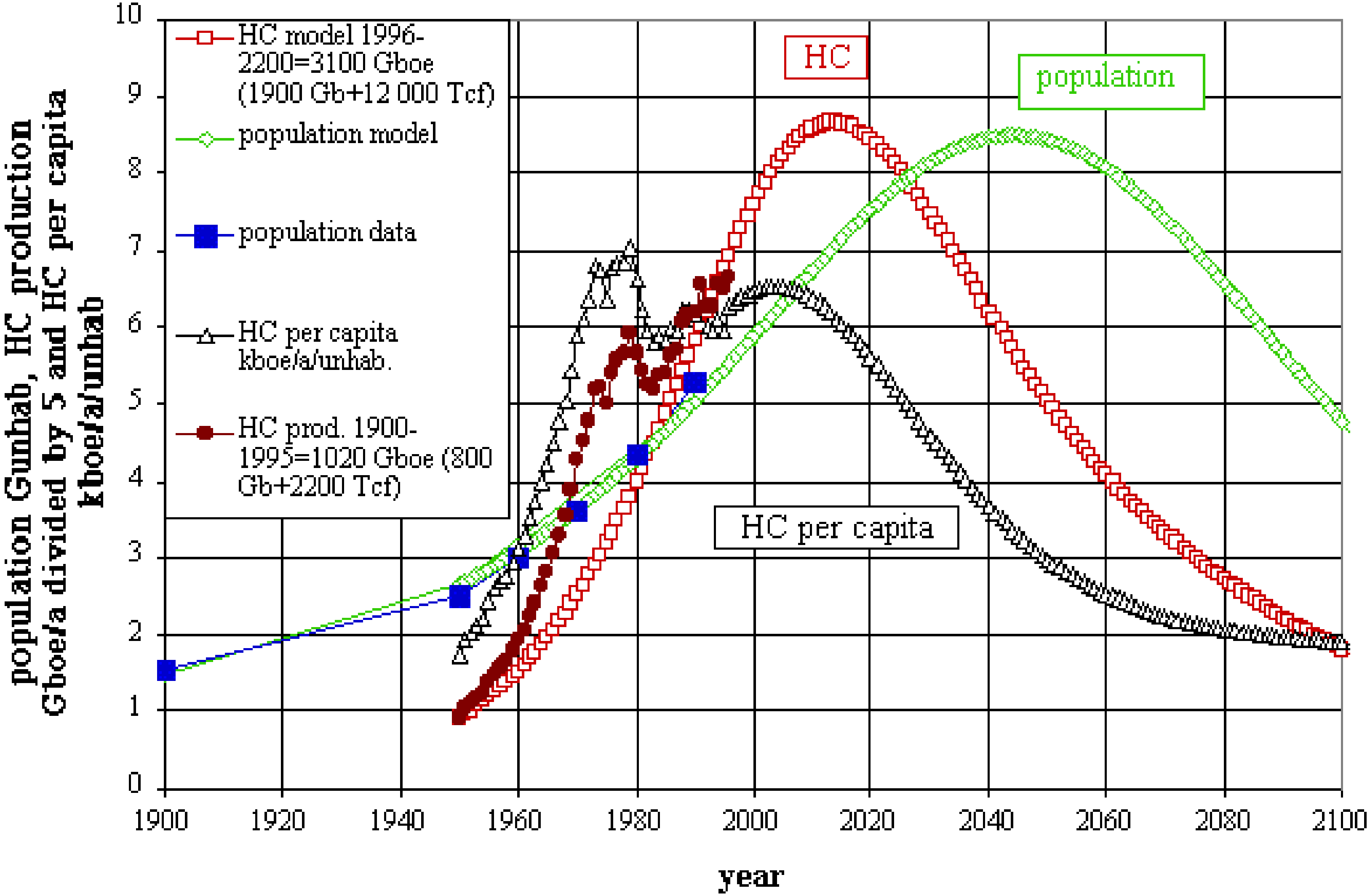
Enhancing the energy balance with DDGS combustion



Net energy from 1.3 to 4.3!

Challenges: NO_x, animal feed demand

Scenario of world's population and hydrocarbons (liquids+gas) production: 1900-2100



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The solution to petroleum independence and global warming

- Conservation
- Design efficiency
- Solar electricity
- Solar collection
- Solar passive
- Wind
- Tidal
- Geothermal
- Hydroelectric
- Nuclear
- Thermoelectronics
- Corn ethanol
- Cellulosic ethanol
- Biodiesel/biofuels
- Gasification
- Biogas
- Hydrogen/fuel cells

Biodiesel Profile

- ***Current production:***
  - **European production: ~1 billion gallons/yr**
  - **U.S. production: 150 million gallons/yr (2008)**
  - **U.S. production capacity: 1.0 billion gallons/yr**

- ***Economic evaluation[1] suggests required selling price***
  - **In 2006, $1.60 raw material costs (oil @ $0.20/lb)**
  - **In 2008, $4.00 raw material costs (oil @ $0.56/lb)**
  - **$0.90 processing costs**

- ***H.R. 4520, American Jobs Creation Act (passed 10/04), provides a $1.00/gallon tax credit for biodiesel production***

- [1]Zhang et al. *Bioresource Technology* **2003**, *89*, 1-16; *90*, 229-240.

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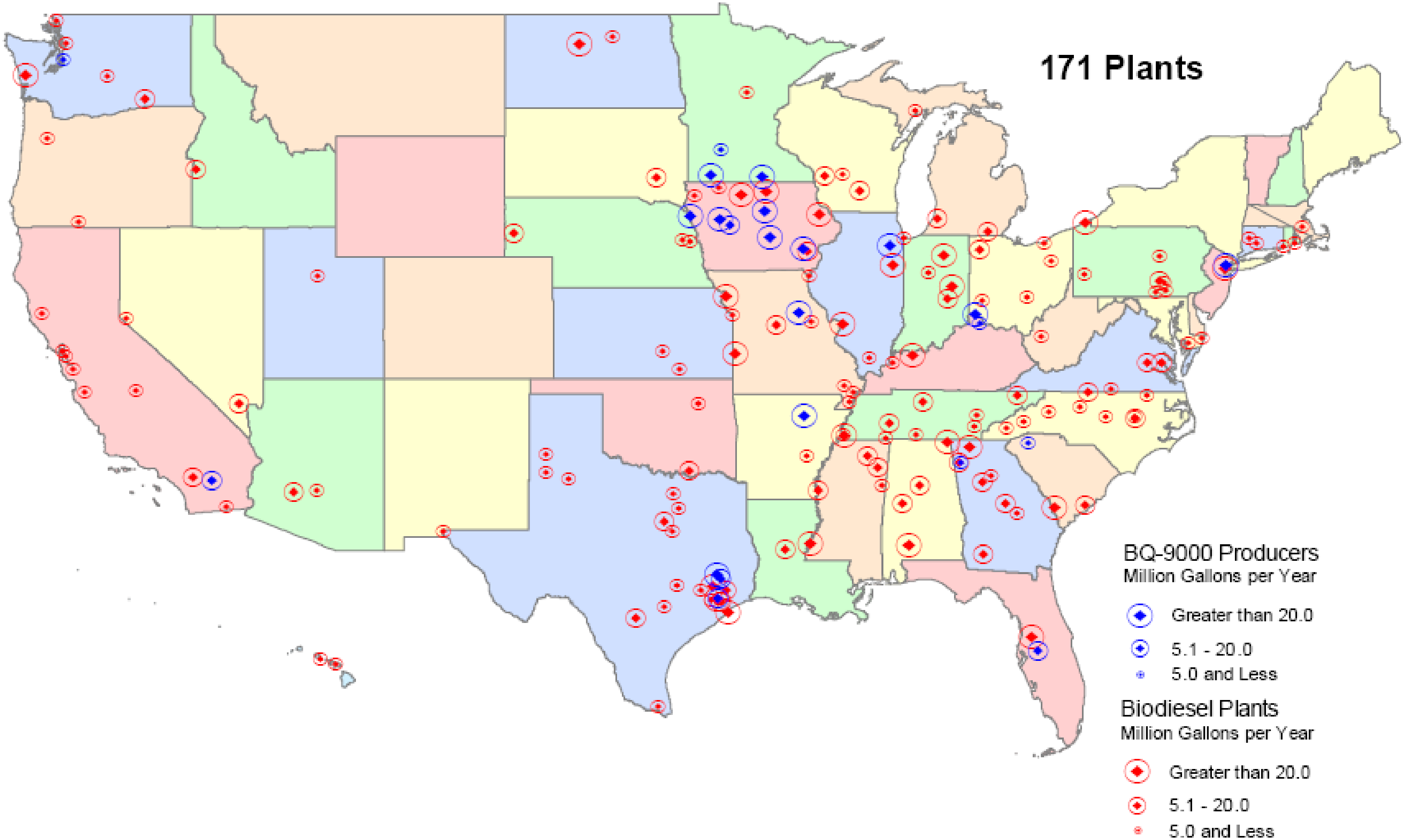
Commercial Biodiesel Production Plants (Jan. 25, 2008)



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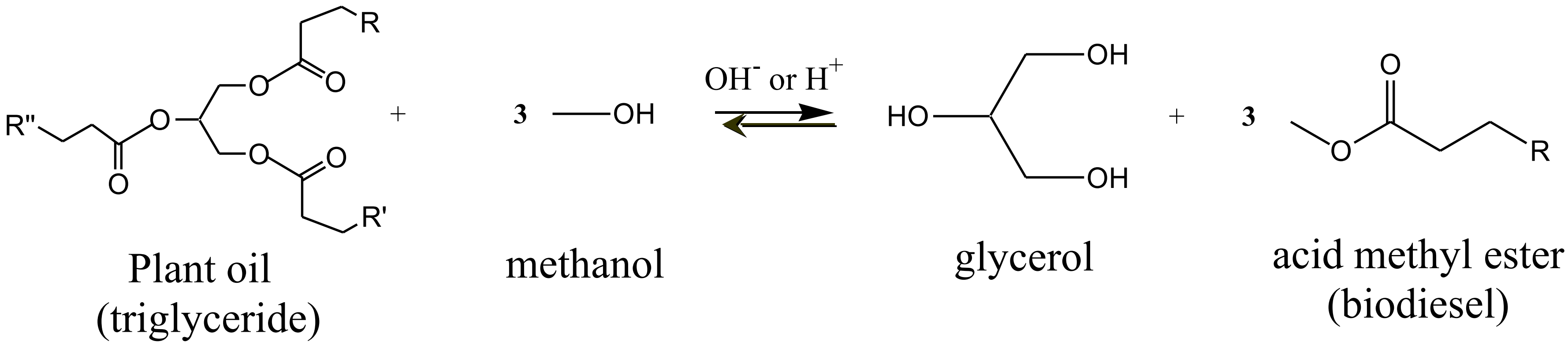
Biodiesel from oils via transesterification



- ***Plant oils include soy, rapeseed, canola, etc..***
- ***Waste cooking oils are minor potential source, are inexpensive, but contain water and free fatty acids that must be cleaned up.***
- ***Typical methanol:oil feed ratio of 6:1 gives >98% methyl ester yield***

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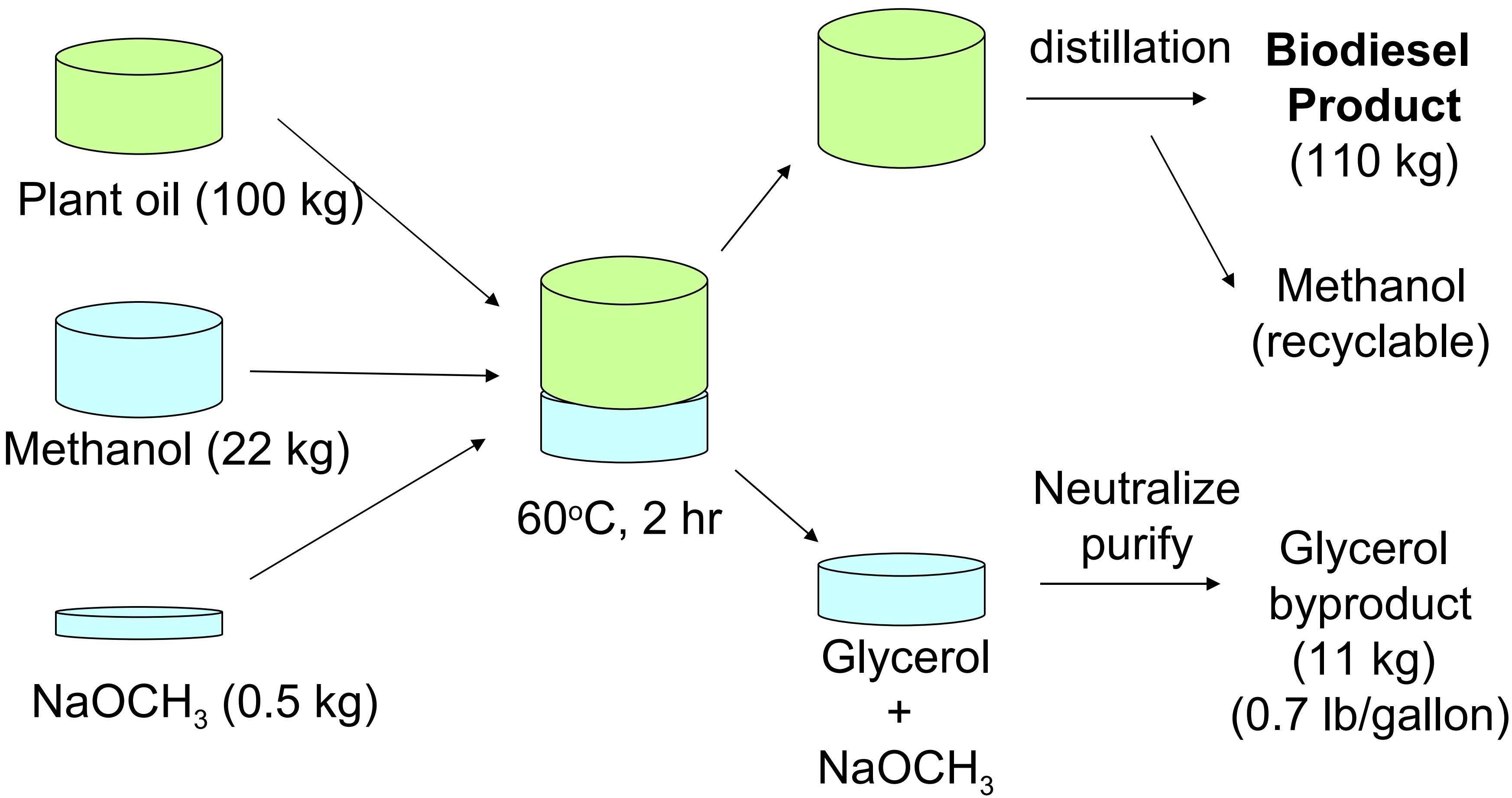
Current biodiesel production

(Batch production, labor and energy intensive)



ASTM International Specification

D6751: Standard Specification for Biodiesel Fuel

In 2002, ASTM International issued a standard specification for biodiesel fuel called D6751. This specification states that the only form of biodiesel that can be legally resold for commercial operations must meet ASTM specifications.

TABLE 1: Detailed Requirements for Biodiesel (B100)

Property	Test Method	Limits	Units
Flash point (closed cup)	D 93	130.0 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9–6.0	mm^2/s
Sulfated ash	D 874	0.020 max	% mass
Sulfur	D 5453	0.05 max	% mass
Copper strip corrosion	D 130	No. 3 max	N/A
Cetane number	D 613	47 min	N/A
*Cloud point	D 2500	Report to customer*	°C
Carbon residue	D 4530	0.050 max	% mass
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	% mass
Total glycerin	D 6584	0.240	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, atmospheric equiv. temp	D 1160	360 max	°C

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Oxidative Stability
A major issue in biodiesel viability

- *Unsaturated oils susceptible to oxidation*
  - Stability decreases by x10 w/ each additional double bond (C18:1 is 100x more stable than C18:3; saturated oils are stable)
  - Oxidative attack at double bond leads to peroxides, C-C bond cleavage and oligomer formation to give gums, sediments in fuel
  - Oxidation promoted by certain metals (Zn, Cu, etc..) and sunlight
- *Stability much increased by nitrogen blanketing of tanks*
- *Recommended B100 storage time 2-4 months, maximum of 6 months*
- *Antioxidants (natural or synthetic) greatly slow oxidation*

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MSU “Field to Wheels” Canola Project

200 Acres planted 07-08 in Eaton & Osceola Co.
(Photo early November 2007)

Advanced Biofuels

- Current biofuels are "one-dimensional"
  - Ethanol is single compound
  - Biodiesel is narrow range of compounds

- One-dimensional fuels have challenges in combustion and handling
  - Cold flow properties, oxidative stability, NO_x (biodiesel)
  - Vapor pressure, water uptake (ethanol)

- We seek heterogeneous biofuels with enhanced properties for <u>compression ignition engines</u>

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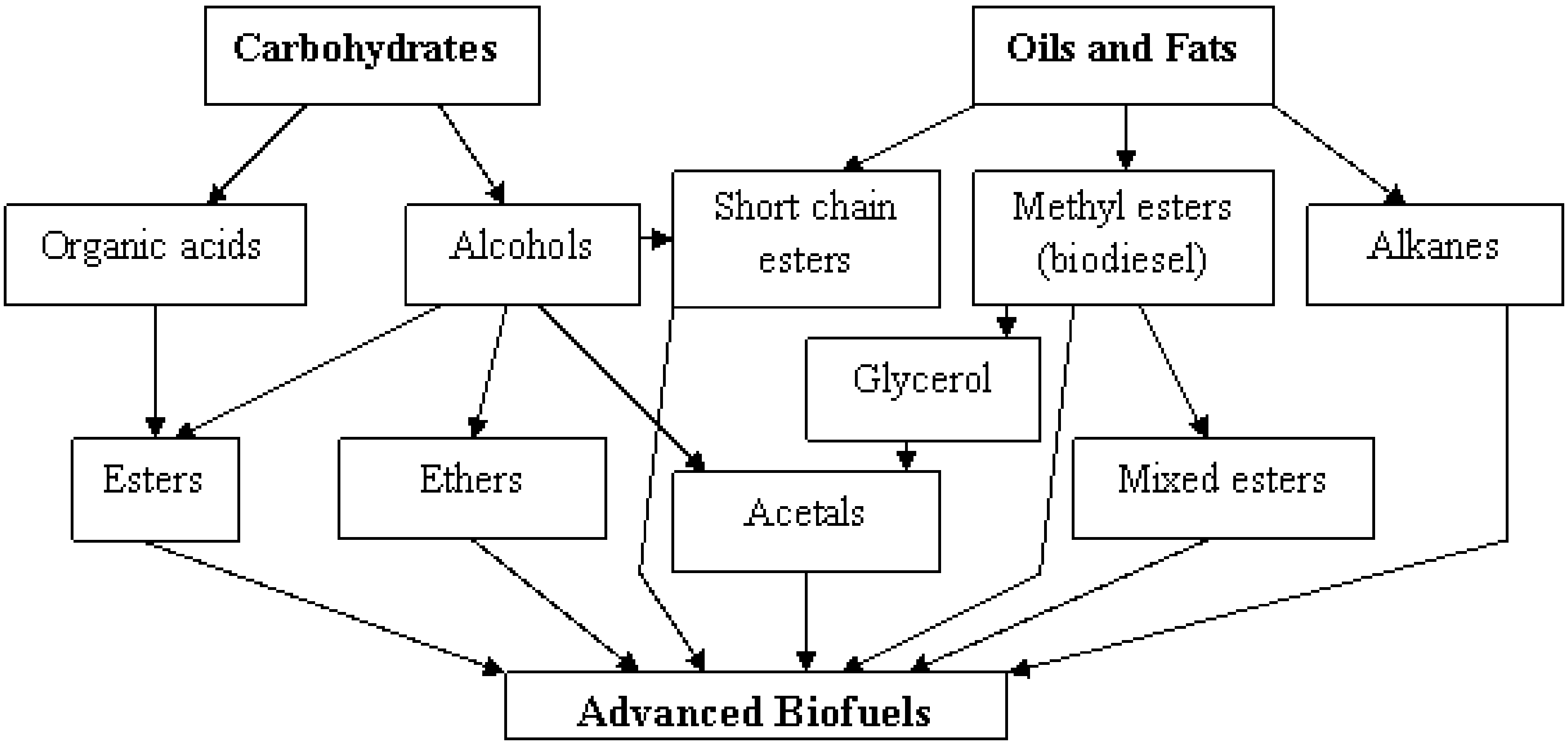
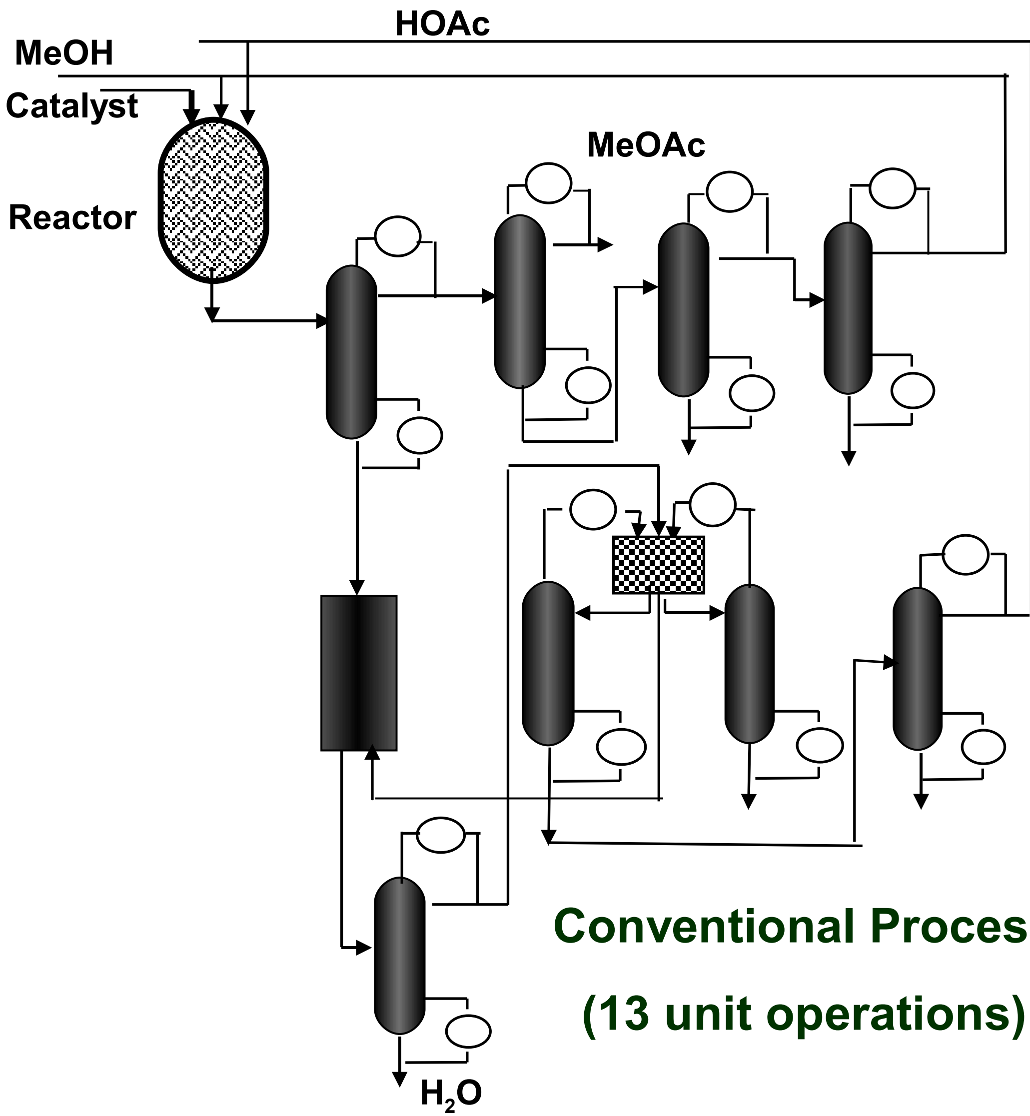
Biofuel blends for diesel engines – expanding the feedstock pool



Reactive Distillation – What is it?

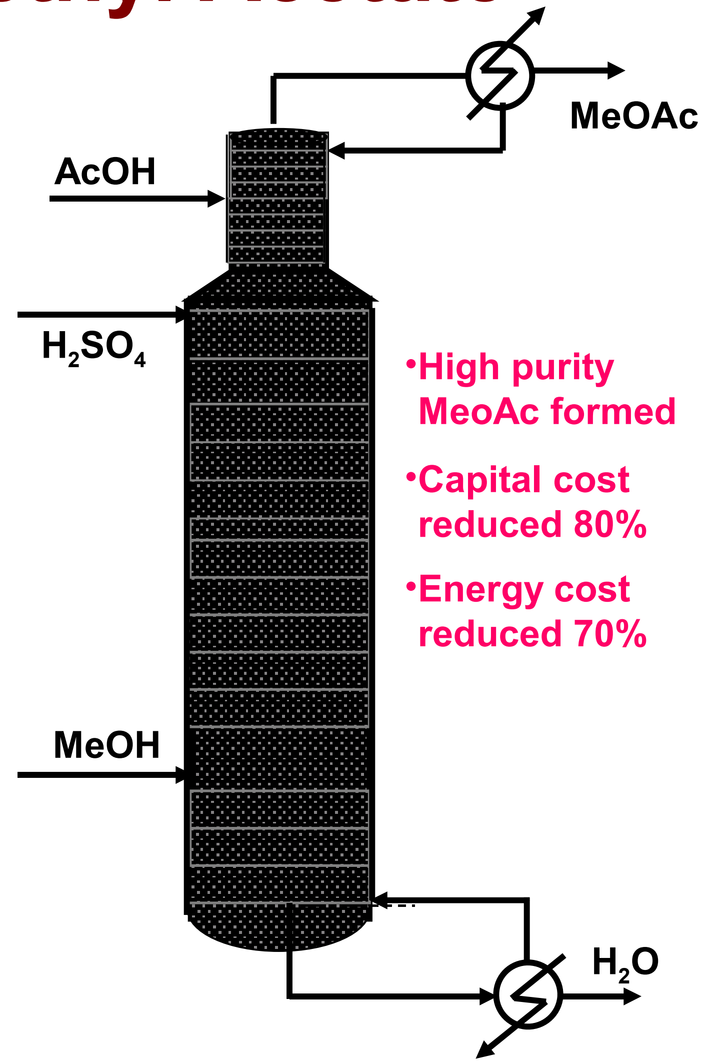
- Simultaneous reaction and separation in a single piece of process equipment
- Applicable to thermodynamically-limited reactions where one product is the most volatile component
- Process intensification results in lower energy and capital costs
- Each reaction system requires a unique approach for successful design and operation

A Classic Example: Methyl Acetate



Conventional Process

(13 unit operations)



- High purity MeoAc formed
- Capital cost reduced 80%
- Energy cost reduced 70%

Eastman Chemical Co
(Agreda *et al.*, 1990)

Reactive distillation facility

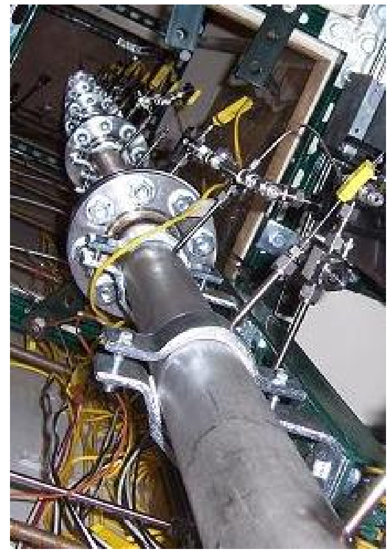
Michigan State University

Sulzer Katapak-S

- Facility includes two pilot-scale columns of height 6.0 m and diameter 0.05 m w/ full instrumentation and computer interfacing

- Columns packed with Sulzer Katapak-S structured packing

- Pilot-scale column simulation and commercial-scale design using AspenPlus process simulation software



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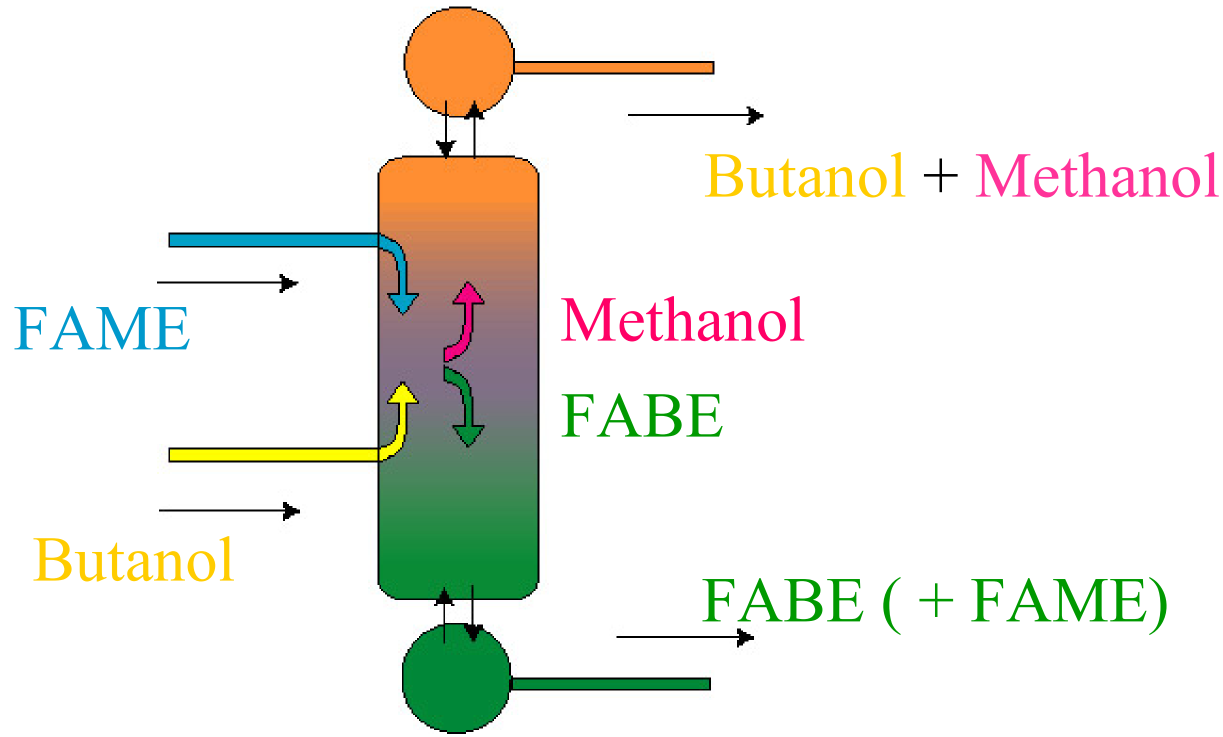
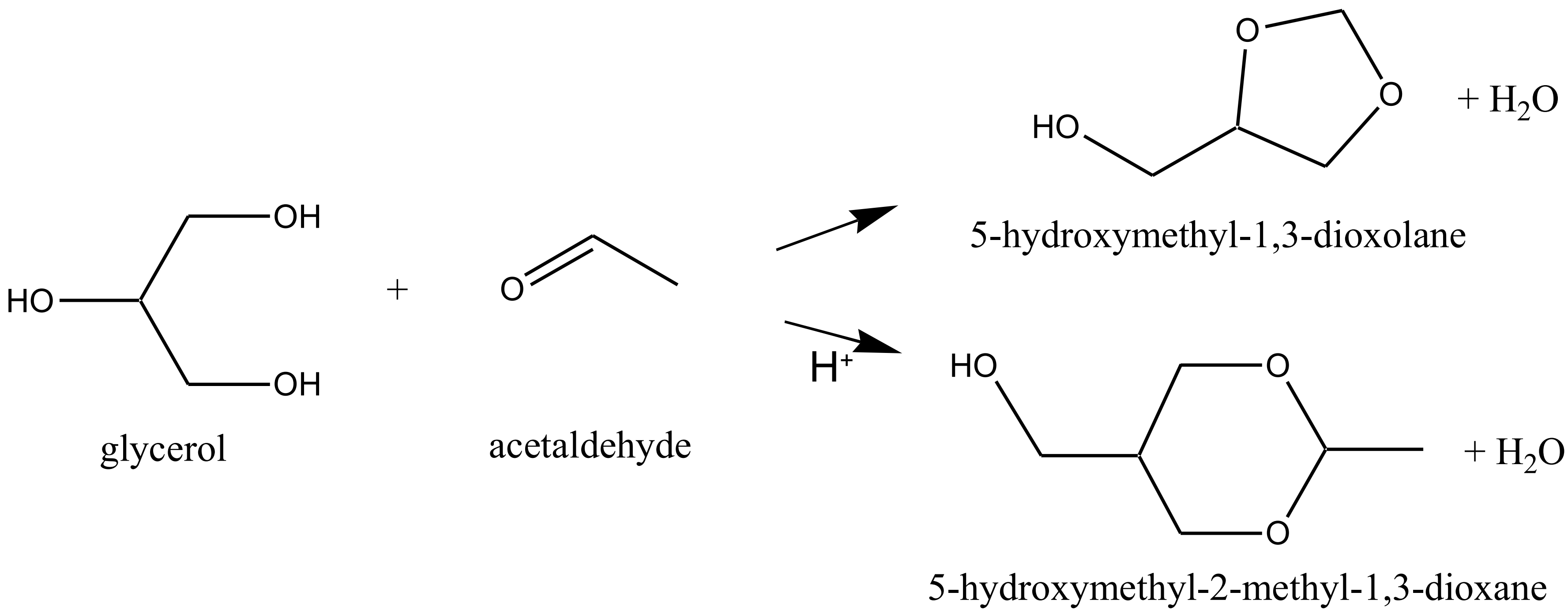
Transesterification via reactive distillation

FAME + Butanol = FABE + Methanol



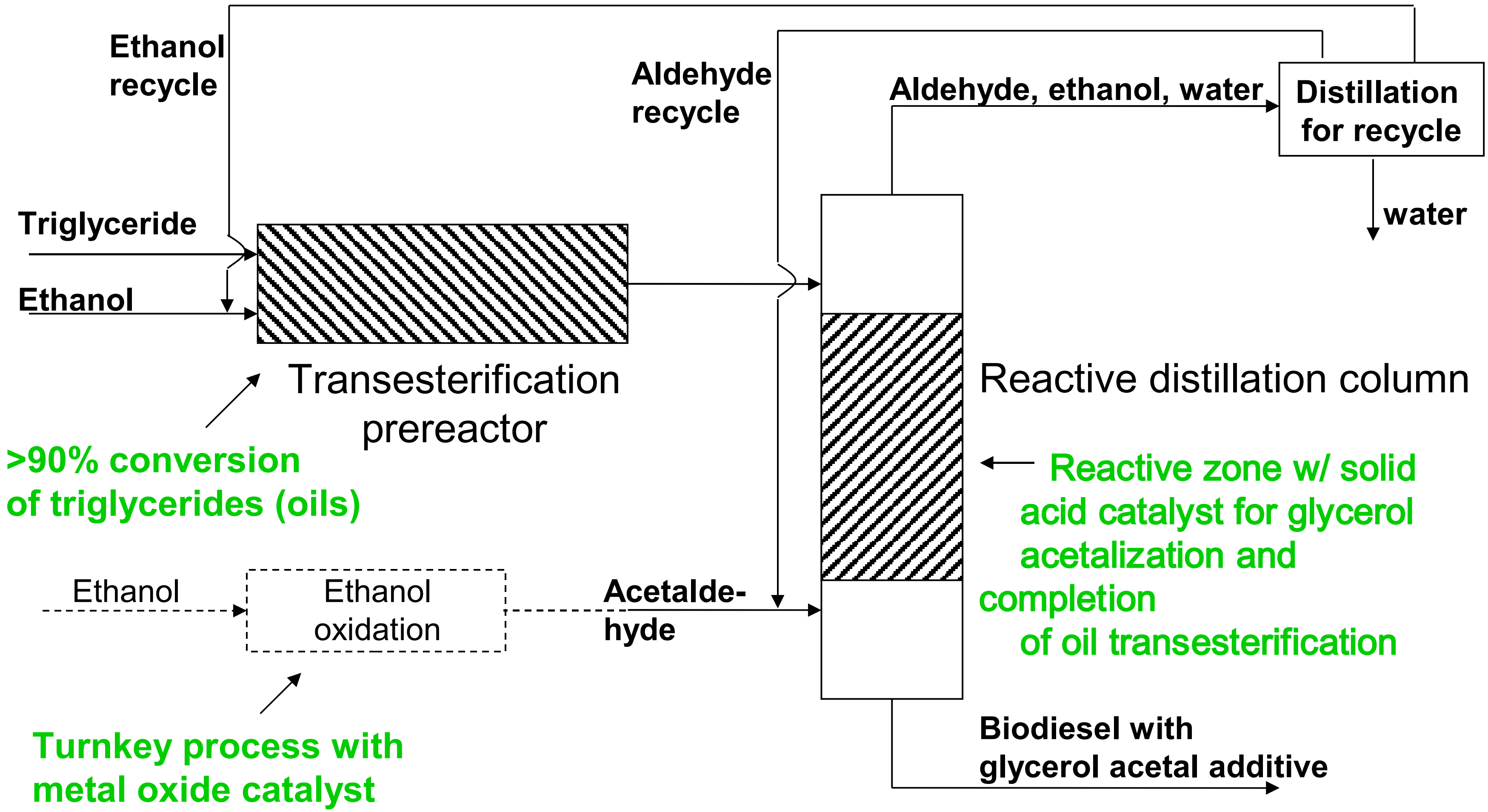
- Reaction catalyzed by cationic exchange resin or other solid acid catalyst
- Water-free reaction environment
- Output composition dictated by alcohol blend, residence time

Glycerol conversion to acetals

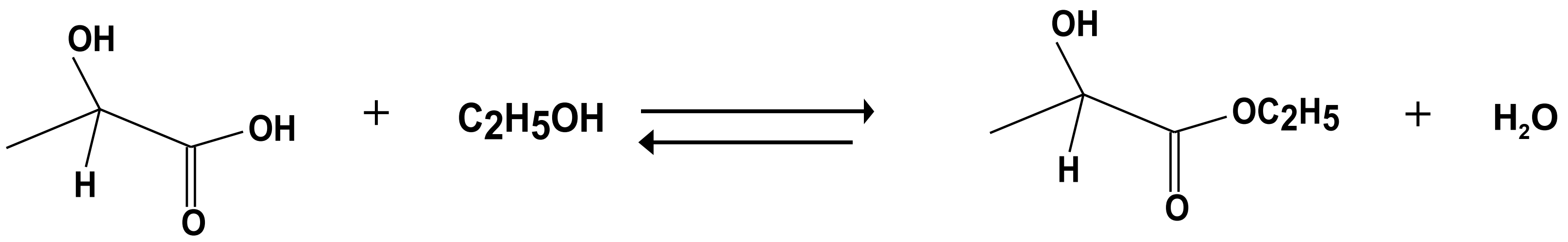


- ***Dioxane and dioxolane boiling points 180 – 200°C (in diesel range)***
- ***Reaction proceeds to >95% conversion w/ 2:1 excess acetaldehyde***
- ***Literature cites reduction in cloud/pour point w/ acetal addition to biodiesel***
- ***Literature cites reduced particulate emissions w/ acetal addition to petroleum diesel***
- ***Acetaldehyde can be produced inexpensively by ethanol oxidation***

Reactive distillation for simultaneous transesterification and glycerol acetalization



Ethyl Lactate: A prototypical bio-based commodity via reactive distillation



Lactic acid (L_1) **Ethanol (Et)** **Ethyl lactate (L_1E)** **Water**

- Ethyl lactate properties
  - Low volatility (low odor, little evaporative loss)
  - Stable to >150°C
  - Excellent solvent performance (use less, dissolve more)
  - Recoverable by distillation (b.p. 154°C)
  - Nontoxic, biodegradable, blendable, "green"
  - Minimal waste generation in production

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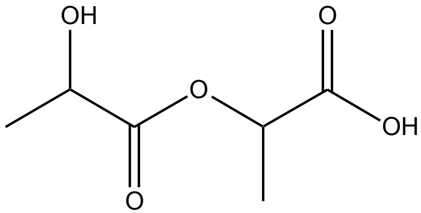
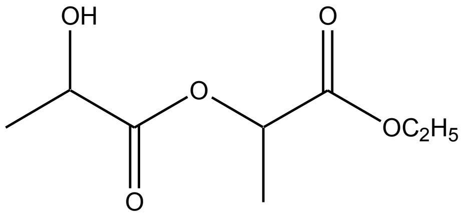
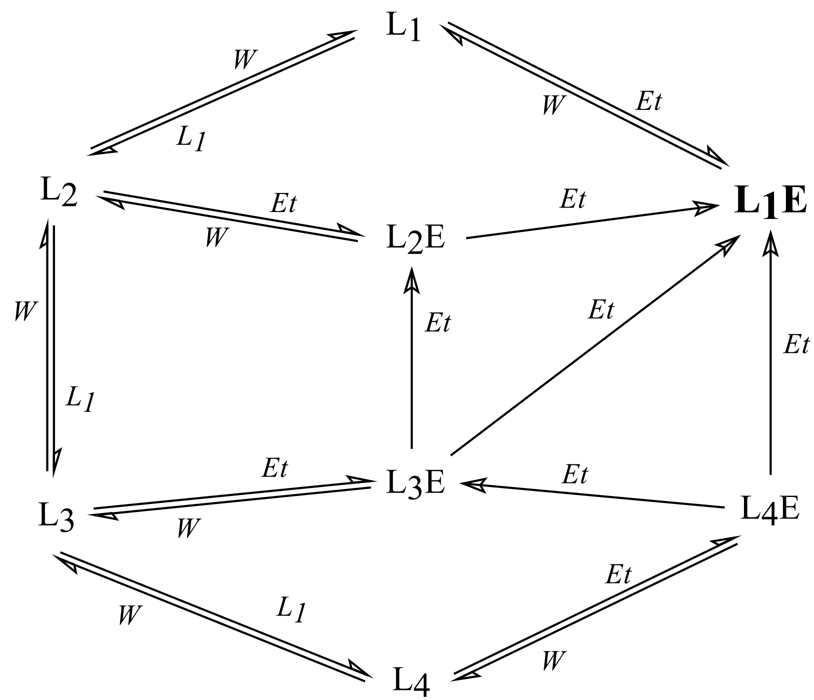
Reaction Network for Ethyl Lactate Esters



L_2



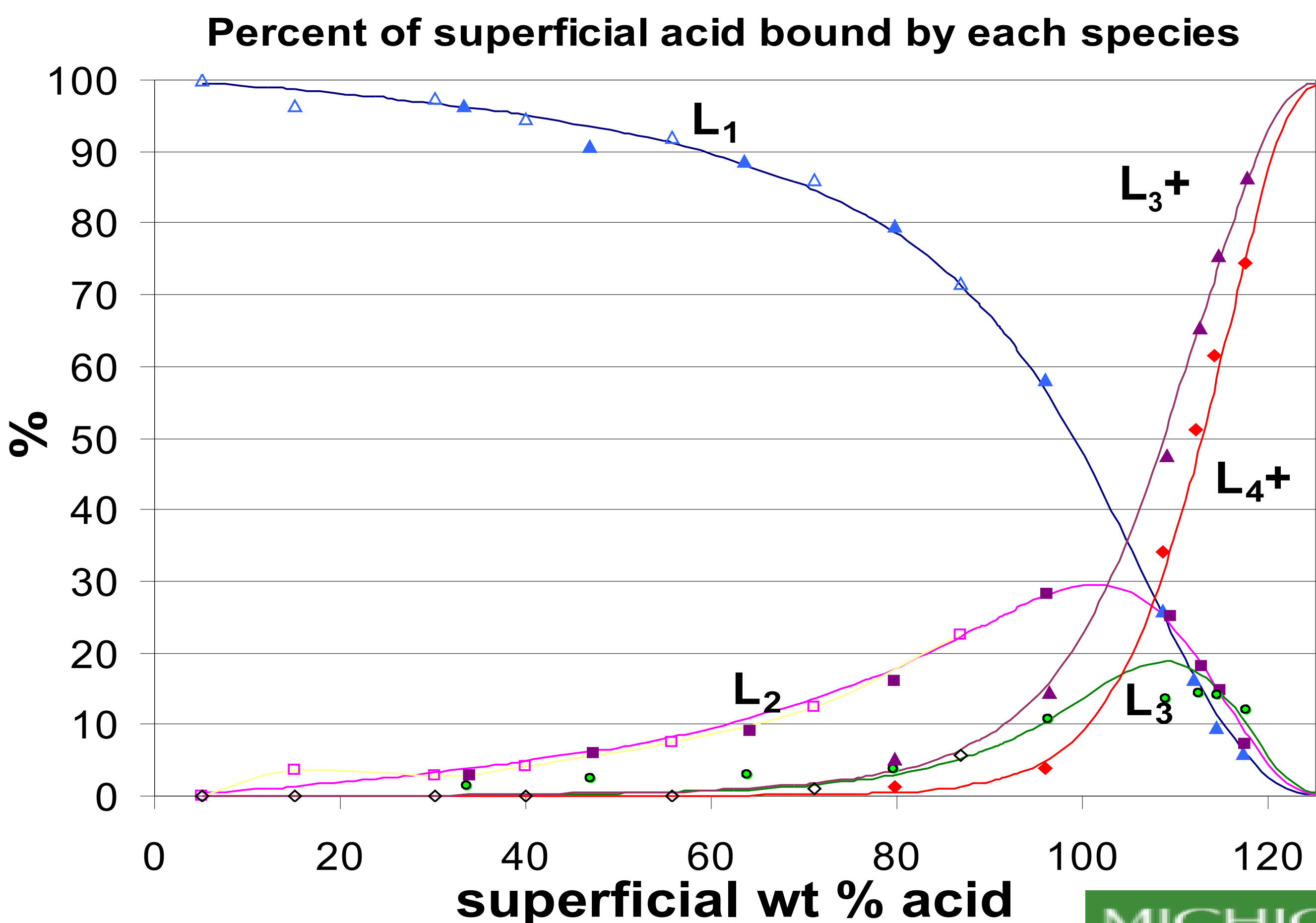
L_2E



Nominal lactic acid concentration (wt%)	Equilibrium oligomer distribution			
	L_1	L_2	L_3	L_4
20	20	-	-	-
50	42	8	-	-
88	58	22	6	2

Equilibrium Lactic Acid Oligomerization Comparison of Model with Experiment

(Activity-based series oligomerization model with K_n = 0.23)



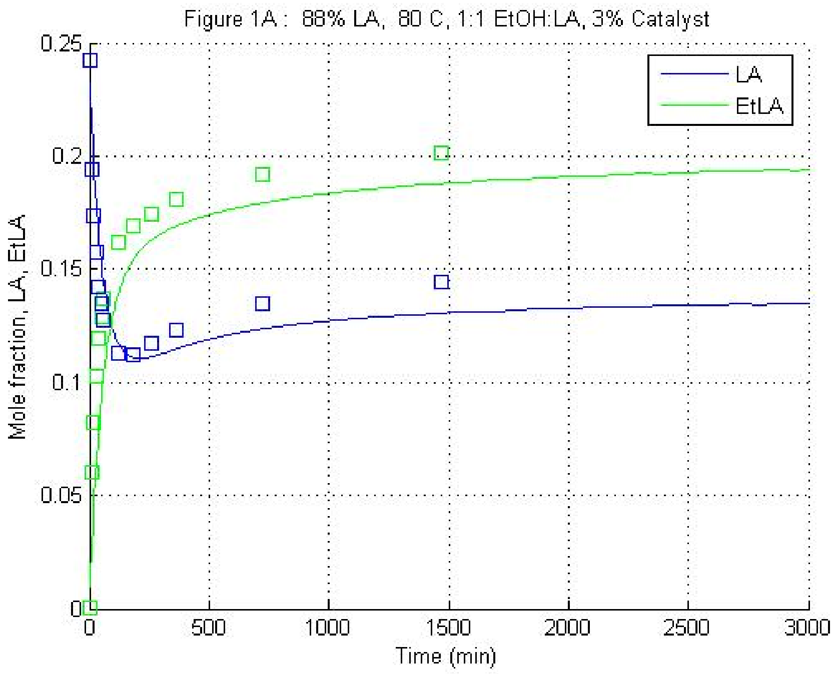
Kinetic model for lactate esterification

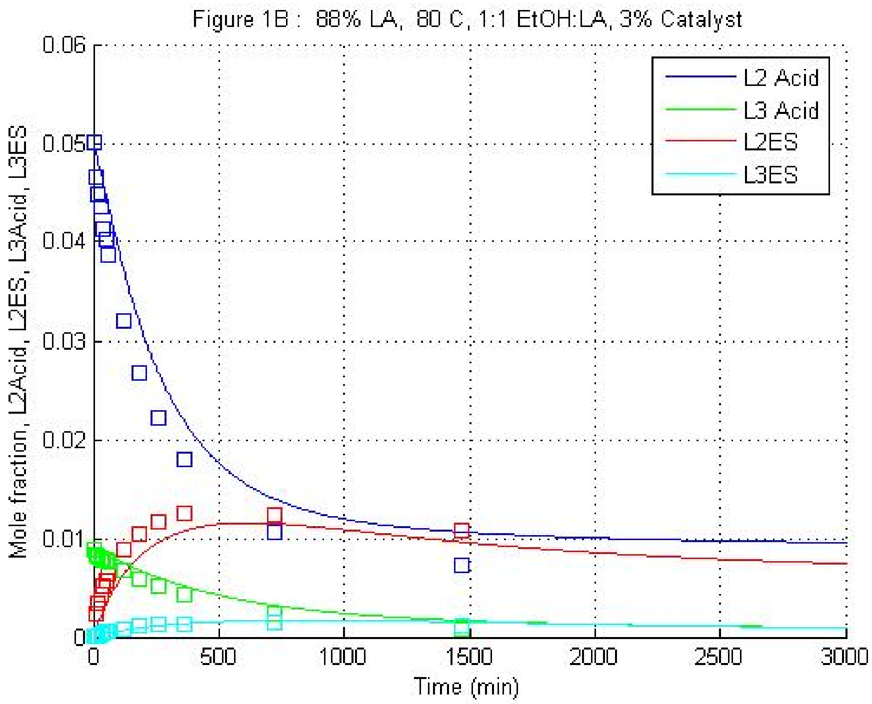
Power law activity model for esterification / hydrolysis

$$r_j = k_{f,j} a_{EtOH} a_j - k_r a_{H2O} a_k$$

Activity-based equilibrium model for lactic acid oligomerization

$$K_n = a_n a_{H2O} / a_{n-1} a_{L1} = 0.23$$





Ethyl lactate via reactive distillation

Lactic Acid + Ethanol = Ethyl lactate + Water

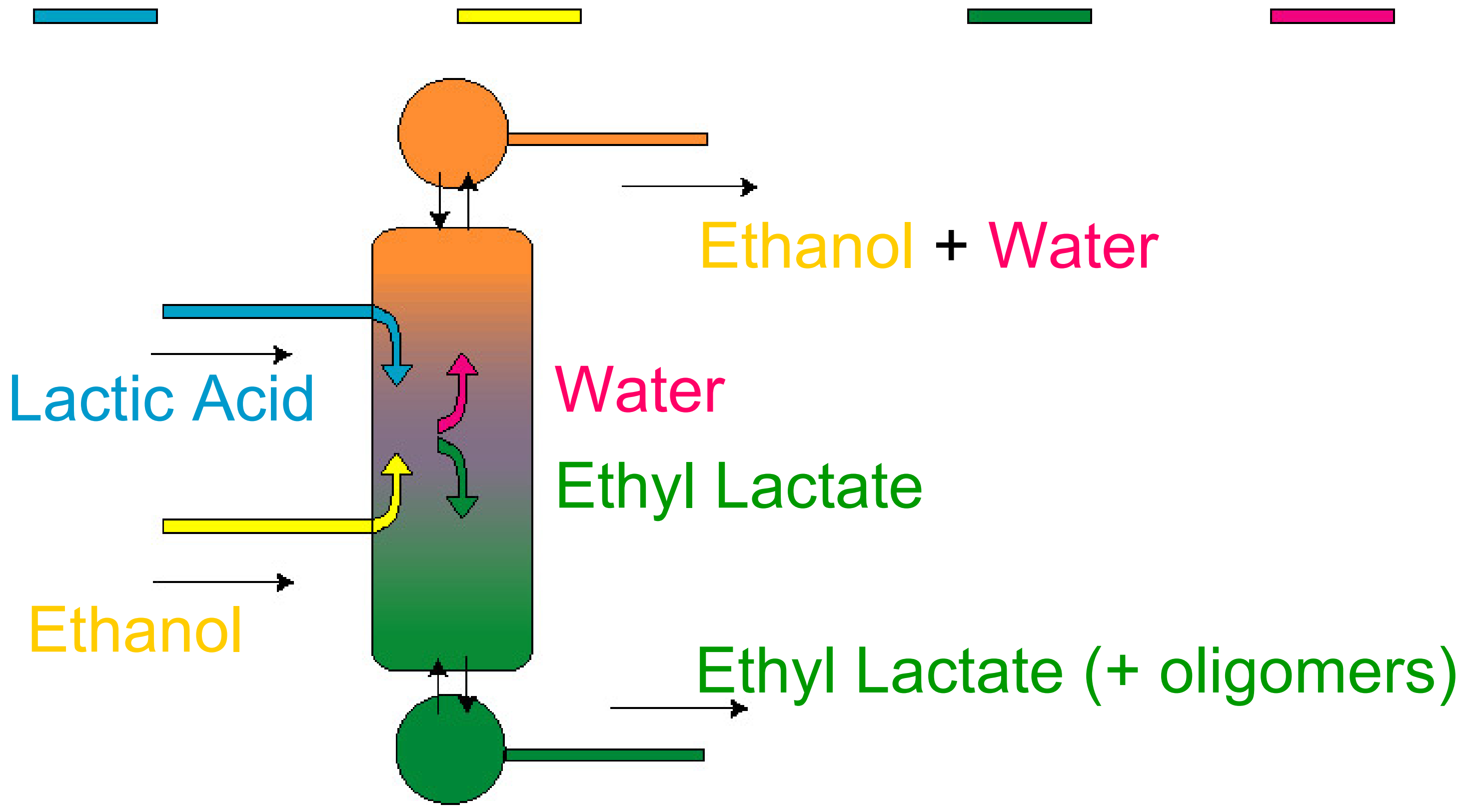


TABLE III. Pilot-scale results of ethyl lactate formation

Run	EtOH feed rate Mol/ min	H_2O feed rate Mol/ min	EtOH Feed temp. (°C)	EtOH: LA Molar ratio	Reflux ratio	% Acid Conv-ersion	L1E Yield (%)	Recov (%)	Bottom Product composition (wt%)						
									H_2O	EtOH	EtLa	L2ES	L3ES	LA	Higher Acids
9	0.345 100%	0.06	25	3.60	0.00	93.61	64.67	101.83	0.76	25.20	57	8.89	1.57	1.12	L2 – 2.41 L3 - 1.03 L4 – 0.379
10	0.345 100%	0.06	25	3.60	0.50	78.01	63.57	100.10	3.13	44.27	46	4.95	0.90	4.03	L2 – 3.49 L3 - 1.12 L4 – 0.34
11	0.36 95%	0.113	25	3.70	0.00	81.51	65.10	102.52	4.33	38.0	28	3.37	0.56	3.42	L2 – 1.55 L3 - 0.57 L4 – 0.16
12	0.36 95%	0.113	85 Vap	3.70	0.00	85.40	57.73	90.91	0.8	0.43	60	14.70	4.37	7.87	L2 – 5.96 L3 - 1.64 L4 – 0.78
13	0.36 100%	0.06	25	3.73	0.00	93.37	67.95	107.01	0.50	22.08	61	10.92	2.01	0.89	L2 – 1.19 L3 - 0.74 L4 – 0.30

Column operation optimal as reactive stripper (no reflux) with no water or ethanol in bottoms product

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Simulation of Commercial Scale Ethyl Lactate RD Column

FEED **(88% LA feed)**

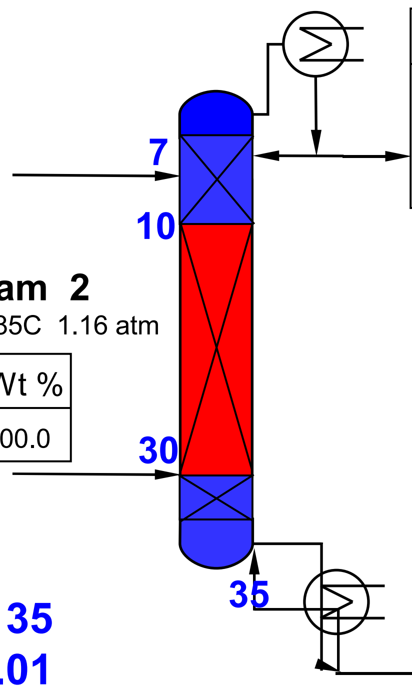
LA	**9.519**	**kmol/hr**
L2 Acid	**2.005**	**kmol/hr**
L3 Acid	**0.505**	**kmol/hr**
Water	**9.847**	**kmol/hr**
EtOH	**54.000**	**kmol/hr**

Feed Stream 1
Flow 21.87 kmol/hr 25C

	Wt %
LA	58.0
Water	14.0
L2 Acid	22.0
L3 Acid	8.0

Feed Stream 2
Flow 54.0 kmol/hr 85C 1.16 atm

	Wt %
EtOH	100.0



Stream 3
Flow 65.98 kmol/hr

	Wt %
EtOH	82.93
EtLA	0.13
Water	16.94

Stream 4
Flow 9.90 kmol/hr

	Wt %
LA	0.00
EtOH	0.30
EtLA	72.64
Water	0.13
L2ES	19.44
L3ES	6.11
L2 Acid	0.66

# Stages	**35**
Reflux ratio	**0.01**
Stage efficiency	**0.5**
Lactic acid conversion	**> 99%**

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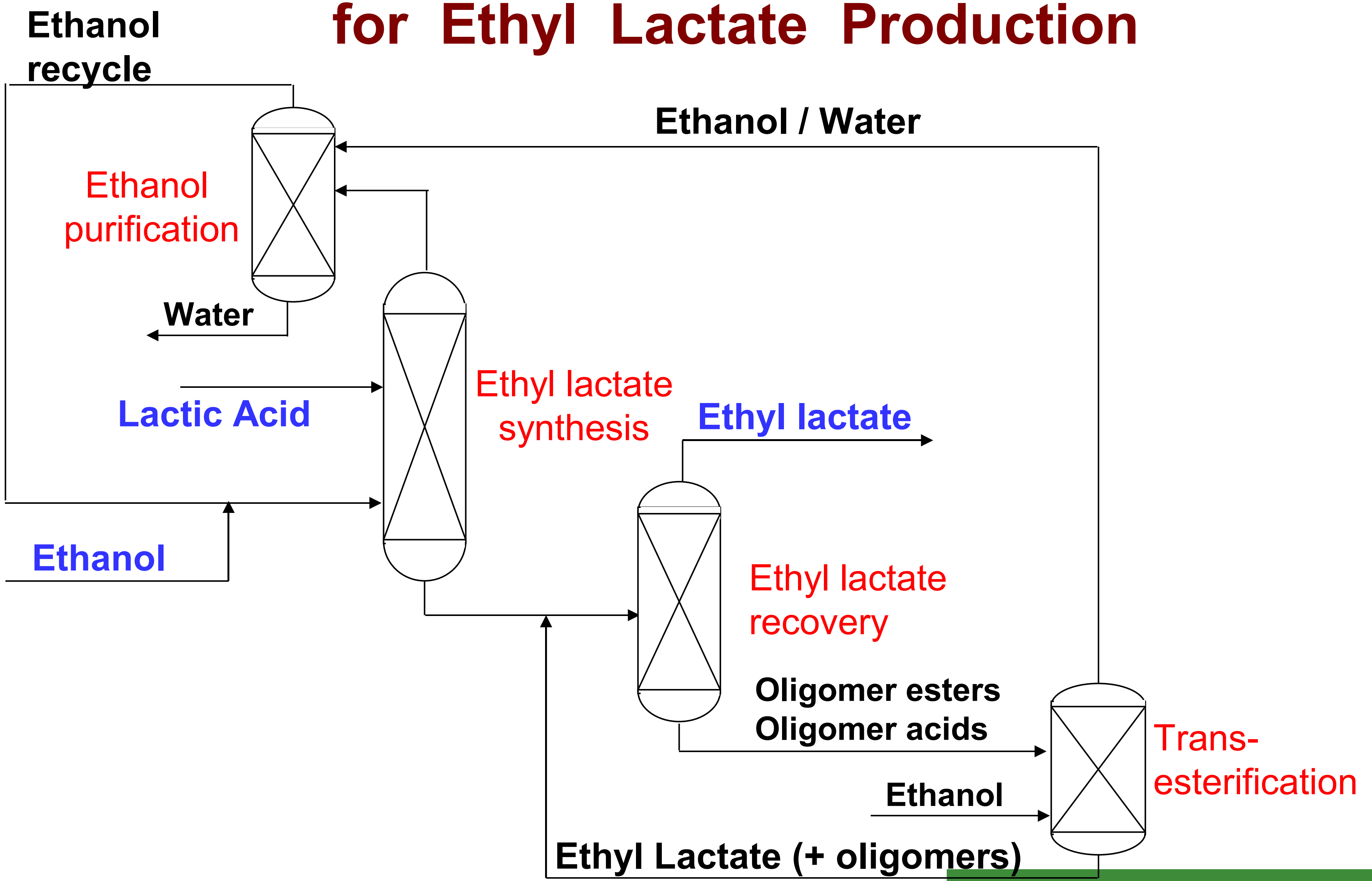
Process Concept for Ethyl Lactate Production



Summary of ethyl lactate economics
(Monsanto Envirochem/MCS, Inc.)

Basis: 25 MM lb/yr ethyl lactate production

Capital costs: $8 - 10 million

Ethyl lactate selling price (includes installed capital depreciation, taxes, 30 % ROI, labor, etc..) is heavily influenced by lactic acid feed cost

Lactic acid cost	Ethyl lactate
$0.25 /lb	$0.54 /lb
$0.50	$0.70
$0.80	$0.94

Current ethyl lactate market is 10 – 20 MM lb/yr
Current selling price $1.30 – 1.60 /lb

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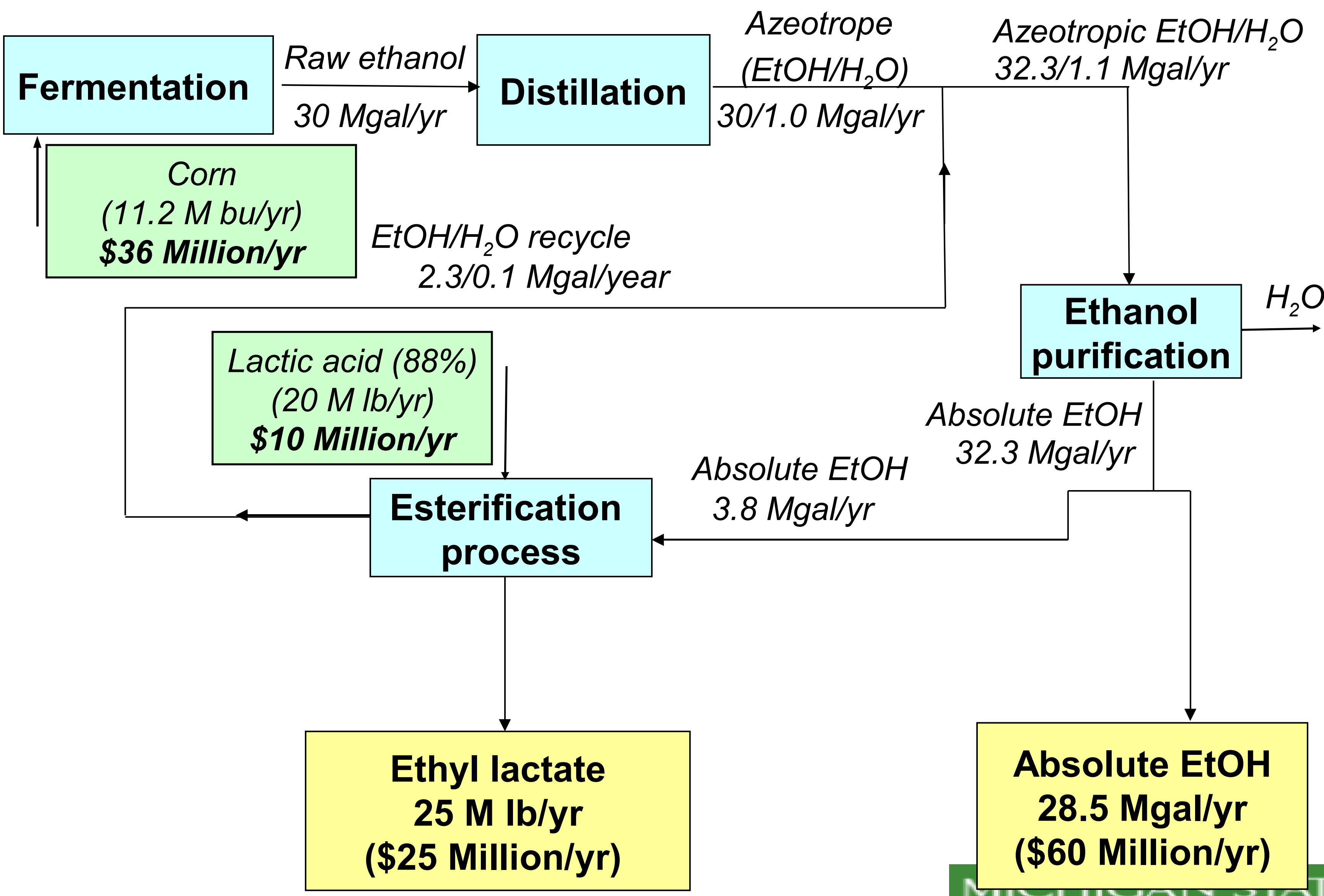
Integrated Ethyl Lactate / Ethanol Production



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Graduate Students

Dung Vu
Frank Jere
Mike Shafer
YuQing Chen
Sai Pappu
Yaoyan Xi
YuQing Chen
Xi Hong
Ketan Pimparkar
Alvaro Orjuela

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