# Producing Mixed Alcohols from Biomass

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## Goals

- Provide an economically feasible alternative to oil
- Provide a sustainable energy source
- Provide a use for municipal waste materials
- Provide a smaller "Carbon Footprint<sup>™</sup>" than oil production

#### • Dr. Mark T. Holtzapple

- Texas A&M University
- Developed MixAlco Process





- Mixalcs are a mixture of short chain alcohols such as; ethanol, butanol, propanol, pentanol an hexanol
- A mix of heavier alcohols can use existing technology









Mixed Alcohol Composition



#### How can Mixalcs be used?

- Mixalcs can be used as a "neat" fuel or blended in almost any proportion into gasoline
- Can even blend with heavier hydrocarbons to improve emissions

Fuel	Energy Content (BTU/gallon)				
Gasoline	125,000				
<b>Mixed Alcohols</b>	104,000				
Ethanol	84,300				

#### Where do mixalcs come from?

- Wide variety of feedstocks
  - Sweet Sorghum, Energy Cane
  - Municipal waste materials
  - Anything that decomposes!







#### Why are mixalcs so great?

- Renewable
- Cleaner than gasoline
- Higher energy content than ethanol
- Lower volatility than ethanol
- Lower heat of vaporization than ethanol



#### Carbon Footprint<sup>™</sup>

- Gasoline produces 19.4 lbCO<sub>2</sub>/gal

   This only includes combustion
- Mixalcs produce 14.6 lbCO<sub>2</sub>/gal
   This only includes combustion
- Gasoline produces 20% more energy
- ~17.5 lbCO<sub>2</sub>/gal

# **Business Plan**

# Strategy

- Start Slow Allow supply and demand to adapt
  - First sell mixalcs as addative
  - Then sell mixalcs as a substitute for gasoline
  - Finally expand at a rate agriculture can keep up with

# Logistics

- Ideal location: Agrarian rural location with plenty of livestock waste, access to oil infrastructure, and cheap real estate
- Western Kansas



# Logistics



Figure 11. Geographic Distribution of Cattle on Feed in Kansas, January 1, 1997 (2.22 million head)





# TCI

- 40 tonne unit was selected to do cost estimation
- Lang factors were used to scale the process to different capacities

Biomass Capacity	TCI
MT/h	\$
2	\$ 3,123,089
10	\$ 9,057,245
40	\$ 23,142,670
160	\$ 78,116,150
800	\$ 340,875,275



#### TCI

Equipment Costs for all sizes of Mixalc plants

						1.1					2		10
Code	Item	Qty	Unit Cost	Uni	t Cost(unce	Equipment Cost(r	Lang Factor	Exp 2&10	Exp 160&800	Inst	alled Cost	Ins	talled Cost
A-1	Biomass loader	1	50,000	\$	50,000	50,000	4.28	0.57	0.57	\$	38,800	\$	97,105
A-2	Lime screw conveyor	1	5,500	\$	5,500	5,500	4.28	0.56	0.56	\$	4,398	\$	10,831
A-3	Biomass/lime mixer	1	50,000	\$	50,000	50,000	4.28	0.57	0.57	\$	38,800	\$	97,105
A-4	Fermentor	4	537,474	\$	537,474	2,149,896	4.28	0.67	1.00	\$	1,236,435	\$	3,634,804
A-5	Saturator tank	1	20,000	\$	20,000	20,000	4.28	0.57	0.57	\$	15,520	\$	38,842
A-6	Air blower	1	3,000	\$	3,000	3,000	4.28	0.59	0.59	\$	2,193	\$	5,667
A-7	Carbon dioxide blower	1	4,000	\$	4,000	4,000	4.28	0.59	0.59	\$	2,923	\$	7,556
A-8	Circulating pump	4	18,000	\$	18,000	72,000	4.28	0.33	0.33	\$	114,666	\$	195,028
A-9	Heat exchanger	4	4,300	\$	4,300	17,200	4.28	0.50	0.50	\$	16,461	\$	36,808
B-1	Compressor	1	120,000	\$	120,000	120,000	5.04	0.79	0.79	\$	56,728	\$	202,295
B-2	Gas Turbine	1	280,000	\$	280,000	280,000	5.04	0.79	0.79	\$	132,366	\$	472,021
B-3	Steam Turbine	1	90,000	\$	90,000	90,000	5.04	0.79	0.79	\$	42,546	\$	151,721
B-4	Condenser	1	16,250	\$	16,250	16,250	5.04	0.60	0.60	\$	13,573	\$	35,649
B-5	Rankine Pump	1	1,330	\$	1,330	1,330	5.04	0.33	0.33	\$	2,494	\$	4,242
B-6	Heat Exchanger	1	75,000	\$	75,000	75,000	5.04	0.60	0.60	\$	62,643	\$	164,534
B-7	Evaporator	1	228,299	\$	228,299	228,299	5.04	0.75	1.00	\$	121,664	\$	406,808
B-8	Sensible Heat Exchanger 1	1	40,874	\$	40,874	40,874	5.04	1.00	1.00	\$	10,300	\$	51,501
B-9	Sensible Heat Exchanger 2	1	21,897	\$	21,897	21,897	5.04	1.00	1.00	\$	5,518	\$	27,590
B-10	Evaporator Pump	1	12,000	\$	12,000	12,000	5.04	0.33	0.33	\$	22,505	\$	38,276
B-11	Evaporator Turbine	1	12,000	\$	12,000	12,000	5.04	0.33	0.33	\$	22,505	\$	38,276
B-12	Lime Mixing Tank	1	9,000	\$	9,000	9,000	5.04	0.57	0.57	\$	8,224	\$	20,583
B-13	Solids Separator	1	40,000	\$	40,000	40,000	5.04	0.67	0.67	\$	27,089	\$	79,636
B-14	Lime Conveyor	1	10,000	\$	10,000	10,000	5.04	0.67	0.67	\$	6,772	\$	19,909
B-15	Noncondesible Stripper Column	1	14,000	\$	14,000	14,000	5.04	0.62	0.62	\$	11,013	\$	29,873
C-1	Reactive Distillation	1	42,000	\$	42,000	42,000	5.04	0.62	0.62	\$	33,040	\$	89,620
C-2	Reactive Distillation Reboiler	1	50,000	\$	50,000	50,000	5.04	0.62	0.62	\$	39,333	\$	106,690
C-3	Countercurrent Heat Exchanger	1	16,000	\$	16,000	16,000	5.04	0.62	0.62	\$	12,587	\$	34,141
C-4	Switching Distillation Column	1	46,000	\$	46,000	46,000	5.04	0.62	0.62	\$	36,187	\$	98,155
C-5	Reboiler Heat Exchanger 1	1	7,000	\$	7,000	7,000	5.04	0.62	0.62	\$	5,507	\$	14,937
C-6	Reboiler Heat Exchanger 2	1	7,000	\$	7,000	7,000	5.04	0.62	0.62	\$	5,507	\$	14,937
C-7	Reboiler Heat Exchanger 3	1	6,000	\$	6,000	6,000	5.04	0.62	1.00	\$	4,720	\$	12,803
C-8	Condenser	1	11,000	\$	11,000	11,000	5.04	0.62	0.62	\$	8,653	\$	23,472
C-9	Mixer	1	10,000	\$	10,000	10,000	5.04	0.69	0.69	\$	6,379	\$	19,365
C-10	Filter	1	100,000	\$	100,000	100,000	5.04	0.69	0.69	\$	63,785	\$	193,646
C-11	Filter Pump	1	6,000	\$	6,000	6,000	5.04	0.33	0.33	\$	11,252	\$	19,138
C-12	Evaporator	1	56,388	\$	56,388	56,388	5.04	0.75	1.00	\$	30,050	\$	100,478
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#### Numbers from Holtzapple

### Product Cost

- Product cost was heavily dependent on Raw Materials cost
- Biomass feedstock cost will be highly dependent on market conditions
- Used a 4% inflation rate to do future calculations
- Royalties to Holtzapple were assumed to be 3% of gross sales

Numbers from Holtzapple

#### Product Cost

Р	lant	Cost per rate or		
C	onsumptions	quantity		200
Plant Specifications				Calculated values, \$
Capacity, MT sorghum/h:	40			
Capacity, gal mixed alcohols/	45100000			
Fixed Capital Investment (FC	19671269			
Product Price \$/gal	2.00			
Raw Materials				
1 Sorghum	320000 MT/yr	\$40.00	USD/MT	\$12,800,000.00
2 Hydrogen	9,039,012 kg/yr	\$0.81	USD/kg	\$7,321,600.00
3 Lime	32000 MT/yr	\$44.00	USD/MT	\$1,408,000.00
4 Inhibitor	53,333 kg/yr	\$6.00	USD/kg	\$320,000.00
Labor (table 6-14)	8000 work-hr/year	\$173.75	USD/hr op	\$1,390,000
Utilities (table 6-14)				
Electricity	5.94E+05 kWh/yr	\$0.05	\$/kWh	\$31,467
790-kPa Steam	207680 MT/yr	\$6.00	\$/MT	\$1,246,080
Natural Gas	288320 GJ/yr	\$4.00	\$/GJ	\$1,153,280
Cooling Water	2.23E+07 m3/yr	\$0.05	\$/m3	\$1,004,400
Solid Fuel	-1.18E+06 GJ/yr	\$2.00	\$/GJ	(\$2,368,000
Maintenance and repairs	0.04 of FCI			786850.7
	of maintenance			
Operating supplies	0.15 and repairs			118027.61
Laboratory charges	0.15 of labor			\$208,500.00
Royalties (if not on lump-	of mixed alcohol			
sum basis)	0.03 sales			\$2,706,000.00
Depreciation - calculated				
separately below			Total variable production costs:	\$28,126,205.11
Taxes (property)	0.03 of FCI			590138.0
Financing (interest)	0 of FCI			
Insurance	0.007 of FCI			137698.88
Rent	0 of FCI			
			Fixed charges (without depreciation):	727836.95
			Plant overhead costs	\$2,308,323.3
			Administrative costs	\$208,500.00
			Distribution + marketing costs	\$577,080.84
			Research and Development	\$1,442,702.10
			Total general expenses	\$4,536,606.3
			Total product cost (w/o D) C:	\$33,390,648.3

Numbers from Holtzapple

# Profitability

- All processes can be profitable at reasonable mixalc prices
- Even if oil prices come down, mixalcs can be competitive

	Break even				
Mt/h	price for 8% ROI				
2	\$ 2.02				
10	\$ 1.09				
40	\$ 0.86				
160	\$ 0.80				
800	\$ 0.78				



# Profitability

Return on Investment	
ROI = profit/TCI = R-D-(R-dIf)*t	
ROI	19
Rate of Return based on discounted cash flow	
function = sumCF(1+i)^(n-k) + 0.15FCI + (TCI-FCI)-T	<sup>-</sup> CI(1+i)^10
function \$ 567,2	239,693.48
i	0.08
n	10
Net Present Worth	
$NPW = sum(CFk/((1+i)^k)+(CFn+Vs+Iw)/((1+i)^k)$	n)-TCI
i	0.08
NPW \$26	52,741,732
Pay Out Time	
POT = (FCI-0.15*FCI)+TCI*i*n/average cash flow	annually
Average Cash Flow \$4	13,247,008
i	0.08
РОТ 0.	814731856

# Profitability

	Mixalcs Produced	MixalcPrice	Annual sales	Production costs	Depreciation	Gross profit, GP	Net profit, Np
Year	Gallons/year	USD/gallon	(USD/year)	(USD/year)	(USD/year)	(USD/year)	(USD/year)
2007	45,100,000	2.00	\$90,200,000	\$33,390,648	\$1,672,058	\$55,137,294	\$35,839,241
2008	45,100,000	2.08	\$93,808,000	\$34,726,274	\$1,672,058	\$57,409,668	\$37,316,284
2009	45,100,000	2.16	\$97,560,320	\$36,115,325	\$1,672,058	\$59,772,937	\$38,852,409
2010	45,100,000	2.25	\$101,462,733	\$37,559,938	\$1,672,058	\$62,230,737	\$40,449,979
2011	45,100,000	2.34	\$105,521,242	\$39,062,336	\$1,672,058	\$64,786,848	\$42,111,451
2012	45,100,000	2.43	\$109,742,092	\$40,624,829	\$1,672,058	\$67,445,205	\$43,839,383
2013	45,100,000	2.53	\$114,131,775	\$42,249,822	\$1,672,058	\$70,209,895	\$45,636,432
2014	45,100,000	2.63	\$118,697,046	\$43,939,815	\$1,672,058	\$73,085,173	\$47,505,363
2015	45,100,000	2.74	\$123,444,928	\$45,697,408	\$1,672,058	\$76,075,463	\$49,449,051
2016	45,100,000	2.85	\$128,382,725	\$47,525,304	\$1,672,058	\$79,185,363	\$51,470,486

- An uncertainty of 30% was applied to all equipment prices, raw material prices, and product price
- @Risk was used to evaluate the variation in NPW at this uncertainty
- 30% uncertainty was chosen in order to cover all possible inaccuracies in pricing









- Agricultural prices will vary with demand
- This process and other biofuels processes will put huge demands on agricultural production
- The impact that the biofuels industry will have on the agricultural industry will affect prices and supply in the future

- Developed by Dr. Mark T. Holtzapple at Texas A&M University
- Converts biomass feedstocks into a mixture of light alcohols





From Holtzapple p.5

#### Advantages

- No enzymes
- No pure cultures
- Continuous
- Highly adaptable
- Has potential to recycle various waste products



#### **Pretreatment Fermentation**

- Feedstock of 80% sorghum foliage and 20% cattle manure
- Pretreat with lime, water, and methane inhibitor
- Pretreatment removes lignin
- Add bacteria such as marine mesophilic organisms
- Bacteria digests 80% of solid biomass<sup>1</sup>
- ~.5g of total acids per gram of feed<sup>1</sup>
- 4 piles each having the volume of 43,000m<sup>3</sup>

#### **Pretreatment Fermentation**





# Dewatering

- Vapor compression evaporation
- Introduce long chain acid to acidify broth
- Steam and lime used to remove noncondensable gases and calcium carbonate
- Water is evaporated to concentrate salt solution

#### Dewatering



From Holtzapple p.14



# Acid Springing

- Converts salts into acids
- Concentrated acids are blended with CO<sub>2</sub> and low molecular weight amines
- Removes calcium carbonate
- Calcium carbonate is recycled into pretreatment

# Acid Springing



From Holtzapple p.16



# Hydrogenation

- Converts acids to alcohols
- Concentrated acids are mixed with high molecular weight alcohols to form esters
- Esters are hydrogenated to form alcohol product

# Hydrogenation



# Summary

- Can be blended or used as a "neat" fuel
- Further study of biofuel industry impact on agriculture is needed
- Further study on yield of bacteria when digesting different biomass is needed

#### References

- Agbogbo, Frank K., & Holtzapple, Mark T. (2006). Fixed-bed fermentation of rice straw and chicken manure using a mixed culture of marine mesophilic microorganisms. *Bioresource Technology*, *98*, Retrieved February 16, 2007, from http://www.sciencedirect.com.
- 2. Holtzapple, Mark T. (2004). MixAlco Process: Biomass to Carboxylic Acids and Alcohols. Unpublished Manuscript. Viewed January 2007