Review of Ethanol Production Process

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http://www.mrtexverett.com/Chemistry/isomerism/isomers.asp
Overview

• Introduction
• Simple Flow Chart
• Complex Flow Chart
• Our Unit Operations
• Cost Analysis
• Conclusion
• References

http://0.tqn.com/d/chemistry/1/7/1/d/ethanol.jpg
Introduction

- Ethanol has existed as a significant fuel for more than 100 years.
  - Model T
- Demand for ethanol increased during World War I as fuel needs increased.
- Ethanol is again gaining popularity as an alternative Automobile fuel.
- Objective: Produce enough 200 proof lab grade ethanol to supply the University Stores for one year.
Simple Flowchart Diagram

Feedstock

Pretreatment

Saccharification

Fermentation

Distillation

Molecular Sieve

Storage

Enzymes

Micro-organisms

Energy

Chemicals

Biomass

Water

Ethanol + Impurities

Chemicals

Energy

Water
12.5072 kg ground corn
31.0178 kg H₂O
1.77 g Alpha-amylase

sacchrifier
1) pH 6, (85° C)
2) pH 4.5, (55° C)

Trace amounts of sulfuric acid

5 -50L fermenters
(24° C)

50L of fermented beer

39.13 L Discarded slurry

60-2 Euro Still
60 L
(78° C)

10.87 L of 92% EtOH

Molecular sieve
3 bars, (140° C)

17.22 lb of 3A-EDG Ethanol Grade molecular sieves

.155089g Glucoamylase

1.5-50L fermenters
(24° C)

2 Packets of Alcotec 8 Super Turbo Yeast

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10.05 L of 190 proof Ethanol

3252.6 BTU

.8195 L water

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3252.6 BTU

.8195 L water

Complex Flowchart diagram
Feedstock Pretreatment

• Corn as a feedstock
  • Still the most economical
  • Readily available
  • Energy rich
    • 70-72% of kernel weight is starch (db)
Feedstock Pretreatment

- Corn Feedstock
  - Ground Corn
    - No. 30 screen
    - 0.5mm particle size
Feedstock Pretreatment

- **Mash Composition**
  - Consists of 75% water and 25% solids
  - Ground corn contains 13% moisture
  - Calculations:
    - \( C = 0.87s + 0.13m \)  \( \text{Eq. 1} \)
    - \( M = 0.25s + 0.75m \)  \( \text{Eq. 2} \)
    - \( W = 0.00s + 1.00m \)  \( \text{Eq. 3} \)
    - \( M = xC + yW \)  \( \text{Eq. 4} \)
  - Combine 1-4 and balance solid components:
    - \( 0.25s = x0.87s + y0.00s \)  \( \text{Eq. 5} \)
    - \( x = 0.287356 \)  \( \text{Eq. 6} \)
Feedstock Pretreatment

• Mash Composition Continued...
  • Again combine equations 1-4 and 6 and now balance moisture components:
    • \(0.75m = (0.287356)(0.13) + y(1.00)\) \hspace{1cm} Eq. 7
    • \(y = 0.712644\) \hspace{1cm} Eq. 8
  • We now can combine equations 4, 6, and 8 to get our relationship between the mash, corn and water:
    • \(M = (0.287356)C + (0.712644)W\) \hspace{1cm} Eq. 9
  • This equation shows that a mash with 25% solids is composed of 28.7% ground corn and 71.3% water.
Feedstock Pretreatment

- Mash Density.
  - The density of the mash is needed to calculate the mass needed to fill our 50L fermenters.
  - Mash density can be represented by:
    - \( \rho_M = x\rho_C + y\rho_W \)  
      
    - \( x \) and \( y \) are the same variables as from equation 9.
    - Solving for \( \rho_M \) we find:
      - \( \rho_M = 0.870499g/cm^3 \) or \( 870.499kg/m^3 \)  

Feedstock Pretreatment

• Mash Mass
  • We can now calculate mash mass needed using:
    • \( m_M = V\rho_M \quad \text{Eq. 12} \)
    • Volume is 50L or 0.05m\(^3\); solving for \( m_M \) we get:
      • \( m_M = 43.5249\text{kg} \quad \text{Eq. 13} \)
  • Using equation 9 we can find the mass of corn and water needed:
    • \( m_C = (43.5249\text{kg})(0.287356) = 12.5072\text{kg} = 12507.2\text{g} \quad \text{Eq. 14} \)
    • \( m_W = (43.52549\text{kg})(0.712644) = 31.0178\text{kg} = 31017.8\text{g} \quad \text{Eq. 15} \)

http://equalrightsforall.net/online_tutorial/web%2020p20/scales%20for%20inertia.gif
Feedstock Pretreatment

- **Enzyme Amounts**
  - Enzymes are needed to break the starch down into simple sugars.
  - Amylase is needed at a rate of 42.8 U/g corn solids.
  - Glucoamylase is needed at a rate of 0.6 U/g corn solids.
  - $m_a = \frac{m_c C_s a}{v_a}$  \text{Eq. 16}
  - Where $m_a$ is the mass of enzyme solution or powder needed.
  - $m_c$ is the mass of corn in the mash.
  - $C_s$ is the solid mass fraction in the corn.
  - $a$ is the units per gram of corn solids needed (U/g).
  - $v_a$ is the unit density of the enzyme solution (U/mg).
  - Solving this equation for the two enzymes gives:
    - $m_a=0.621g$  \text{Eq. 17}
    - $m_g=.0544g$  \text{Eq. 18}
Feedstock Pretreatment

- Processing Steps
  - Mix water and ground corn.
  - Add amylase, heat to 85°C, maintain pH of about 6, hold there and mix continuously for 90 minutes. This is called liquefaction.
  - Cool mash to 55°C, drop pH to 4.1±0.5, add glucoamylase, hold and mix for 2 hours. This is called saccharification.
  - Send mash to the fermenters.

http://3.bp.blogspot.com/-VVLZ/PSKTVl/AAAAAAAAAAU/_Wf_1B51uFW0/s1600/au-revoir.jpg
Fermentation Theoretical

- Alcotec 8 Super Turbo Yeast
  Greater yeast inoculum
  increased fermentation rate
- Claims to yield 20% ethanol by volume in 5 days.

- 50L Volume Fermenter
- Quantity: 5
- Must run continuously everyday.
Fermentation Unit

- From Pretreatment:
  - Mass of corn = 12.5072 kg

- Knowing the composition of corn:
  - Mass of starch = 0.595(12.5072) = 7.4418 kg

- Then with the addition of water to starch and an enzymatic reaction:
  - 1.1111 Glucose = Starch + 0.1111 Water
  - 7.441 starch + (0.1111)(7.441)water = 8.2669 kg = Mass of glucose

- Glucose breaks down to produce:
  - Glucose = 0.4589 Ethanol + 0.4641 CO2 + 0.05 other

- So we have:
  - 8.2669kg * 0.4589 = 3.7936 kg EthOH
  - 8.2669kg * 0.4641 = 3.83667 kg CO2
  - 8.2669kg * 0.05 = 0.413345 kg other waste
Fermentation Unit

• total mass – CO₂ mass = Mass of slurry
  43.5249kg - 3.83667kg = 39.6882kg = Mass of slurry
• % alcohol = mass of EthOH / mass of slurry
• 3.7936/39.6882 = .095585 = 9.56% Alcohol
• Mass Balance:
• IN: mash (from Pretreatment step) = 43.5749 kg
• OUT:
  • EthOH = 3.7936kg
  • CO₂ = 3.83667kg
  • All other wastes = 35.8946kg
Distillation

- Choosing a Still Size
  - \( \frac{3000 \text{L/year}}{365 \text{ days/year}} = 8.21 \text{ L/day} \)
  - \( 8.21 \text{ L/day} \times \left( \frac{1}{20\% \text{ ethanol in slurry}} \right) = 41.05 \text{ L of slurry/day} \)

- 50L or greater still will be large enough to reach our goal
Distillation Still

• Euro 60-2 dual element still
  • 60L capacity
  • 1L distillate per hour
  • 92% purity of ethanol
  • 2- 1500W heating elements

http://homdistiller.org/photos-sold.htm
Distillation Calculations

- **Time**
  - 50L slurry @ 20% EtOH = 10 L of EtOH
  - 10L of EtOH @ 92% purity = 10L / .92 = 10.87L distillate
  - 10.87L @ 1L/hour = 10.87 hours

- **Cost**
  - 2 x 1500 W = 3 kW
  - 3 kW x 10.87 hour = 32.61 kWh
  - @ 6.89 cents/kWh: 32.61 x $.0689 = $2.25 per batch

- **Mass Balance**
  - 50L = 50 kg
  - 50L in – 10.87L out = 39.13 L of slurry discarded after distillation

http://www.ratskey.com/images/time_money.jpg
Molecular Sieve

- Dehydration
- 3A-EDG Ethanol Grade
  - pore opening ~ 3 angstroms (0.3nm)
  - not absorbed 4.4 angstrom ethanol molecule
  - adsorb 2.8 angstrom water molecule
- Other parameters
  - bulk density = 47 lbs/cuft
  - equilibrium water capacity 21% wt
  - heat of adsorption = 1800 BTU/lb of $\text{H}_2\text{O}$
  - specific heat = 0.23 BTU/lb/ deg F

http://www.3angstrom.com/molecular_sieve.php
Molecular Sieve Dehydration Unit

- Vapor enters first column → water is adsorbed on the sieve → vapor continues through column → more water removed → dryer alcohol until fully dehydrated → vapors exit the column
- Once column reaches saturation limit → flow is diverted to second (dry) column → then first column is regenerated
- Recovery = 98%
- Purity = 99.5% dehydration alcohol as standard.
- Adsorption
  - 1.5-4 bar (20-60 psia)
  - 125-160°C (280-345°F)
- Water removal from the adsorbent
  - 0.1–0.5 bar (1.5-7 psia)

Molecular Sieve

- Dehydration unit has to run for ~ 4.34 minutes each day

\[
0.5 \text{ gpm} \times \frac{3.785 \text{ L}}{1 \text{ gal}} = 1.89 \text{ L/min} \times (x \text{ min}) = 8.21 \text{ L} \rightarrow x = 4.34 \text{ min}
\]

- Mass Balance: amount of distillate (10.87 L), feed purity (92%), final ethanol purity (99.5%), and water vapor (8%).
  - \(E = 0.92e + 0.08w\) = mass of inflow (distillate) (kg)
  - \(P = y(0.995e + 0.005w)\) = mass of ethanol product (kg)
  - \(W = x(1w)\) = mass of water vapor (kg)
  - Solving for \(y\): \(0.92e = y(0.995e) \rightarrow y = 0.9246\)
  - Solving for \(x\): \(0.08w = y(0.005w) + x(1w) \rightarrow x = 0.0754\)
  - \(E = 0.9246P + 0.0754W\).

- Mass of ethanol product = 10.05 kg
- Mass of water vapor = 0.8195 kg
Molecular Sieve

• Amount of molecular sieve needed:

\[
\frac{\text{Weight of water}}{\text{Weight of molecular sieve}} = 0.21 \quad \Rightarrow \quad \frac{0.8195 \, \text{kg} \times 9.81 \, \text{m/s}^2}{x} = 0.21
\]

\[\Rightarrow x = 38.28 \, N = 8.61 \, \text{lbs}\]

• Energy used by the molecular sieves = 3252.6 BTU
  • heat of adsorption (1800 BTU/lb of H₂O)
  • weight of the water vapor (1.807 lbs) in the molecular sieve dehydration unit
## Cost Analysis

### One Time Costs

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
<th>Unit Cost</th>
<th>Total Cost</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 L tank</td>
<td>1</td>
<td>$279.95</td>
<td>$279.95</td>
<td>Plasticmart.com 2011</td>
</tr>
<tr>
<td>Heating Element</td>
<td>4</td>
<td>$963.42</td>
<td>$3,853.68</td>
<td>Drillspot.com 2011</td>
</tr>
<tr>
<td>Agitator</td>
<td>1</td>
<td>$323.48</td>
<td>$323.48</td>
<td>Novatech-usa.com</td>
</tr>
<tr>
<td>Distillation Unit</td>
<td>1</td>
<td>$637.28</td>
<td>$637.28</td>
<td>Spirits 2011</td>
</tr>
<tr>
<td>Fermenter</td>
<td>5</td>
<td>$215.00</td>
<td>$1075.00</td>
<td>50L (13G) Variable Volume Fermenter 2011</td>
</tr>
<tr>
<td>Molecular sieve Dehydration Unit</td>
<td>1</td>
<td>$1,200.00 (assumption)</td>
<td>$1,200.00 (assumption)</td>
<td>Wintek 2010</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
<td></td>
<td></td>
<td><strong>$7369.39</strong></td>
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</table>

### Reoccurring Costs

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity per Batch</th>
<th>Unit Cost</th>
<th>Cost per Batch</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Corn</td>
<td>12.51 kg</td>
<td>$385/1000 kg</td>
<td>$4.82</td>
<td>Alibaba.com 2011</td>
</tr>
<tr>
<td>α-amylase</td>
<td>465718U</td>
<td>$288.50/50000000 U</td>
<td>$26.87</td>
<td>Sigma-Aldrich 2011</td>
</tr>
<tr>
<td>Glucoamylase</td>
<td>.054406g</td>
<td>$488.50/5g</td>
<td>$5.32</td>
<td>Sigma-Aldrich 2011</td>
</tr>
<tr>
<td>Distillation run</td>
<td>1 run</td>
<td>6.89 cents/kWh</td>
<td>$2.25</td>
<td>EIA 2011</td>
</tr>
<tr>
<td>Alcotec Super Turbo Yeast</td>
<td>2</td>
<td>$5.95</td>
<td>$11.90</td>
<td>Alcotec 2005</td>
</tr>
<tr>
<td>Molecular Sieve</td>
<td>17.22 lbs</td>
<td>$99.25/25 lbs</td>
<td>$68.36</td>
<td>3Angstrom 2009</td>
</tr>
<tr>
<td>Pretreatment Run</td>
<td>1 run</td>
<td>6.89 cents/kWh</td>
<td>$0.55</td>
<td>EIA 2011</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
<td></td>
<td></td>
<td><strong>$120.07</strong></td>
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</table>
Conclusion

- Ethanol is commonly used in many university and research labs.
- A variety of feedstocks and processes are available to make ethanol.
- The process outlined in this presentation demonstrates a method to make the necessary amount ethanol to supply the University Stores for one year.

http://i.treehugger.com/files/th_images/blue_ethanol_flame.jpg
Questions?