EERC Energy & Environmental Research Center

EERC Technology – Putting Research into Practice

Biomass Conversion: Biorefining, Storage and Transportation

Presentation to
SBQ/ACS Biomass Conversion Workshop
May 30-31, 2007
Aguas do Lindoia, SP, Brazil

Prepared by Ed Olson, EERC

Biorefinery-Bioprocessing Concepts

- Higher alcohols from ethanol-methanol
- Lignocellulose pyrolysis
- Succinic acid biorefinery
- Biodiesel
- Biomass Gasification
- Ethyl levulinate
- Hydrocarbon fuels from sugar or vegetable oils

Perspectives

- Biorefining Processes
  - Serial vs Parallel Processing
- Constraints and opportunities for chemistry & engineering
  - Catalytic & Kinetic Principles
    - Selectivity – Oxidation and reduction
    - Enzyme expression and pathway blockage
  - Thermodynamics
    - Solubilities, affinities – where can we use phase transfer catalysis and solid phase extractions
    - Vapor pressures and heat transfer

Processes for Renewables

- Serial – one product and byproducts
  - Sugar beets to sucrose
  - Corn to ethanol (dry milling)
  - Soy to biodiesel
- Parallel – multiple products, feeds, simultaneous reactions, switching options
  - Cane to ethanol, sugar, sugar esters, power
  - Corn wet milling
  - Ethanol & methanol to higher alcohols
  - Glycerol conversions
  - Glucose to hydrocarbons
  - Cellulose conversions
  - Gasification, Pyrolysis, Wind power

Advantages of Parallel Processing

- Stable operation and workforce
- Avoids storage when market drops
- May lower transportation cost
- Share equipment

Convert serial to parallel?

Needs chemistry, market, and feedstock development

Corn wet milling

- Germ
- Fiber
- Oil
- Starch → Glucose → fermentation

Diacid polymer

Sorbitol
Gluconic acid

Ethanol
Lactic
Citric
Lysine
3HP
Isosorbide
Inositol

Corn wet milling

- Germ
- Fiber
- Oil → fatty acids + glycerol
  - **Metathesis**
  - **9-Decenoic acid**
- Starch → **Epoxy acid, decanol**

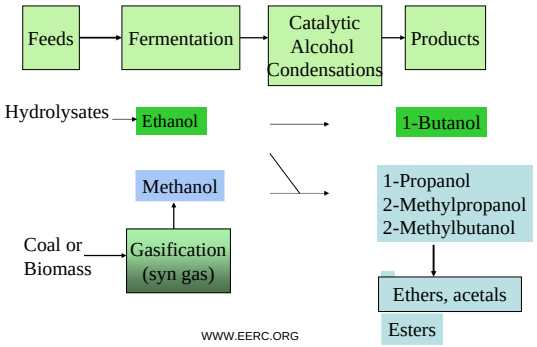
WWW.EERC.ORG

Hydrocarbon synthesis

- Glucose conversion directly to hydrocarbons
  - LS9 Petroleum Co.
  - Microbial
  - Avoids distillation
- Catalytic conversion of triglycerides

WWW.EERC.ORG

Higher Alcohols Biorefinery



WWW.EERC.ORG

Why Butanol?

- Fuel (spark engine) with higher energy density.
- Fuel with lower vapor pressure (facilitates storage).
- Less polar, less water take up (pipelinable).
- Convert to very high cetane diesel fuels.
- Chemical and polymer intermediates

WWW.EERC.ORG

Guerbet Reaction

- Multistep condensation of alcohols at >300°C
- Requires bifunctional catalyst
  - Dehydrogenation to aldehyde (H-transfer)
    $CH_3CH_2OH \rightarrow CH_3CHO$
  - Aldol condensation (Base)
    $2\ CH_3CHO \rightarrow CH_3CHOH\text{-}CH_2CHO$
  - Dehydration - Hydrogenation (H-transfer)
    $CH_3CHOH\text{-}CH_2CHO \rightarrow CH_3CH_2CH_2CH_2OH$
- Problems: Gas make, byproducts, catalyst decay
  - Requires high selectivity for alcohol products.

WWW.EERC.ORG

Ethanol Conversions

- $CH_3CH_2OH \rightarrow CH_3CH_2CH_2CH_2OH$
  (ETOH Conv = 47%)
- $CH_3CH_2OH + CH_3OH$ (excess) →
  $CH_3CH_2CH_2OH$ (1-propanol)
  $CH_3CH(CH_3)CH_2OH$
  (2-methyl-1-propanol)
  $CH_3CH_2CH(CH_3)CH_2OH$
  (2-methyl-1-butanol)
  (ETOH Conv = 70-100%)

WWW.EERC.ORG

Conclusions

- High conversions and yields at 360 C and ambient pressure.
  - 85% yield of isobutyl alcohol with fresh catalyst
  - 100% conversion of ethanol from M/E =7.2
- Low gas make from methanol (3%)
- Product selectivity can be varied by designing activated carbon.
- Catalysts degrade over time.
- Catalyst regeneration is possible.

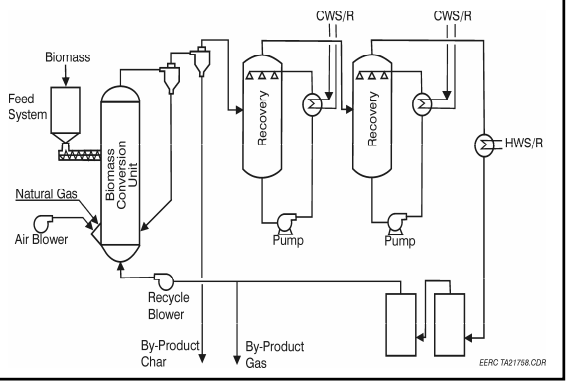
Fuel Characteristics of Mixed Alcohol (10%) Blends

- *Measured:*
  - Octane numbers
  - RVP
  - Water partitioning
- *Conclusions:*
- Mixed alcohols raise octane 1 unit, decrease Rvp 0.6 psi, partitioning to water 60%.
- Mixed esters raise octane 1.4 units, decrease Rvp 0.8 psi, partitioning to water 0%.

Ensyn-Red Arrow Model Fast Pyrolysis

- Minimize time in hot zone to prevent complete decomposition to gases.
  - RTP (Rapid thermal Processing) uses circulating hot sand to heat biomass particles.
  - RTP uses carrier gas to flush products from reactor.
- Fractionate products

Schematic for Ensyn's RTP™



Bio-oil Constituents

- Levoglucosan
- Furfural
- Tars from lignin
- Acids
- Aldehydes
- Flavor Components
- Resins
- Charcoal
- Gases

Amounts vary with biomass source and conditions

Biorefinery Research: New feedstocks for pyrolysis

Switch grass project conducted by Great Plains Institute

– Potential:
  - Convert prairie CRP land to grass production for fuel and chemicals

– Status:
  - Low production of anhydrosugars—wood may be much better feedstock
  - May be caused by potassium catalysis of decomposition

Biorefinery Research: Ethanol from Bio-oil?

- Separation and conversion of anhydrosugars to glucose is feasible.
- Difficult to purify sugars
  - Dehydration products, catechols
- Fermentation is severely inhibited by impurities.
- Need novel pyrolysis and/or condensation method to produce less contaminated sugars.

Pyrolysis R & D Needs

- New pyrolysis methods to optimize HA or anhydrosugars.
- Alternative method for HA production.
- Cost of production analysis for HA.
- Market evaluation for polyamines
  - Polymer flooding
  - Reservoir stabilization
- Polymer R & D: utilization and optimization of polymer properties.

Levulinic Acid

- Biofine production from waste cellulose
- DuPont conversions
  - Polymer intermediates (nylon, acrylates)
  - Solvents, surfacttants, ionic liquids
- EERC conversions
  - Direct formation of ethyl levulinate
  - Solvents, epoxy resins, plasticizers

Drivers for Biorefinery Research

- Better products
- Better processes: new catalysts, new equipment, new combinations
- Better compatability with storage and transportation
- Better economics, lower feed costs
- Environmentally sound
- Partnerships