National Renewable Energy Laboratory
Innovation for Our Energy Future
A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Distributed Reforming of Biomass Pyrolysis Oils

DOE Bio-Derived Liquids to Hydrogen Distributed Reforming Working Group Meeting

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Innovation / Overview

Biomass pyrolysis produces a liquid product, bio-oil, which contains a wide spectrum of components that can be efficiently, stored, and shipped, to a site for renewable hydrogen production and converted to H2 at moderate severity conditions (650°C).

Pyrolysis at 500°C:

$$CH_{1.46}O_{0.67} \rightarrow 0.71CH_{1.98}O_{0.76} + 0.21CH_{0.1}O_{0.15} + 0.08CH_{0.44}O_{1.23}$$

Biomass **Bio-oil (75%)** **Char (13%)** **Gas (12%)**

Catalytic Auto-thermal Reforming of Bio-Oil at 650°C:

$$0.71\ CH_{1.98}O_{0.76} + 0.31\ O_2 + 0.26\ H_2O \longrightarrow 0.71\ CO_2 + 0.96\ H_2$$

Key Performance Metrics

Catalytic Steam Reforming of Bio-oil:

Bio-oil (74 wt% $CH_{1.28}O_{0.41}$, 26 wt % H_2O) - 90 wt% of feed

CH_3OH - 10 wt% of feed

H_2O (2.5 mole ratio steam to carbon)

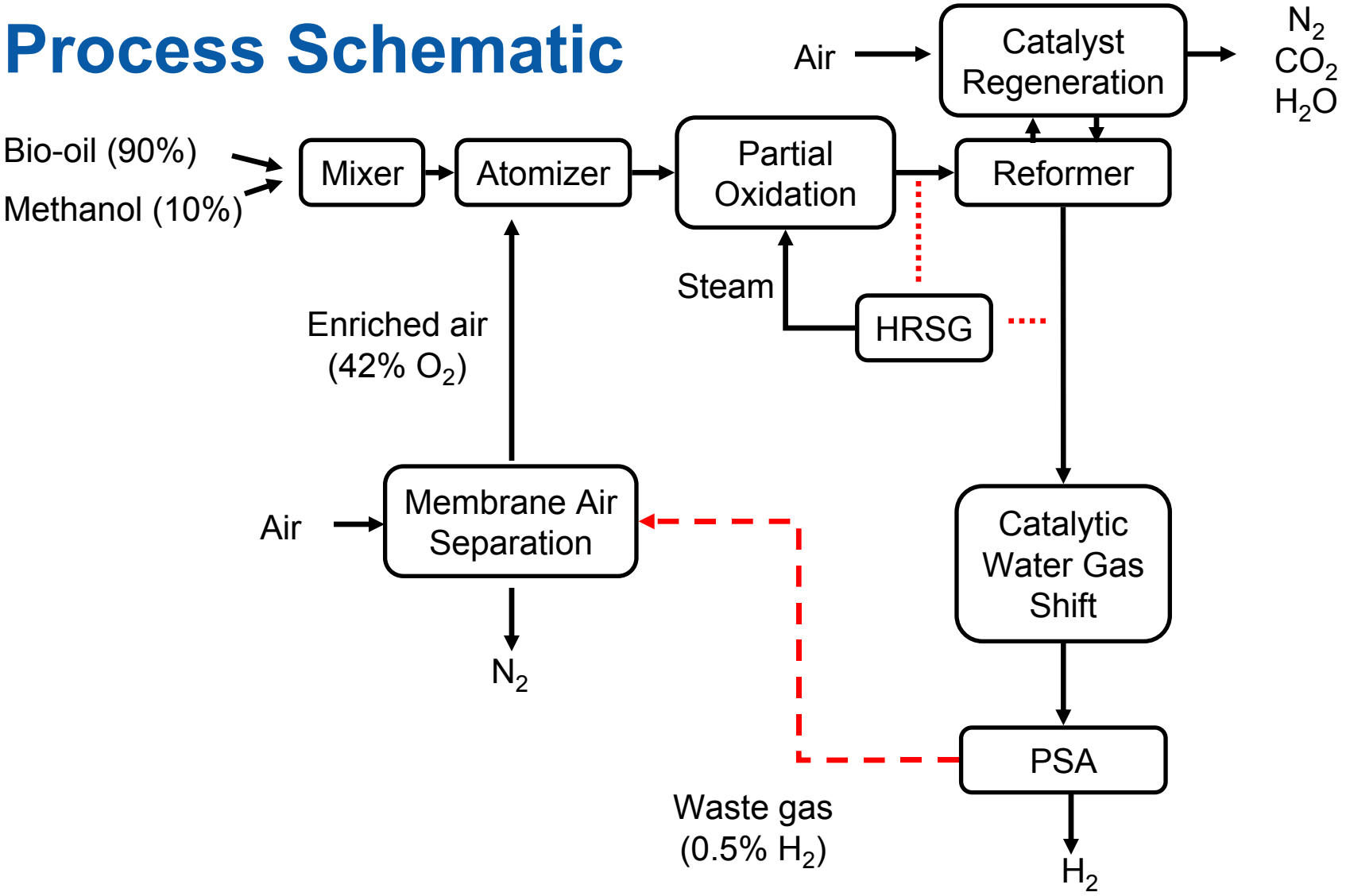
Overall Reaction;

$$CH_{2.18}O_{0.78} + 0.51O_2 + 1.66\ H_2O \rightarrow CO_2 + 1.47\ H_2O + 1.28\ H_2$$

Practical yield: 9.3 wt %

62% overall energy efficiency

Process Schematic



System Definition (1500 kg/day station used for H2A analysis)

Capital Costs

Bio-Oil Reforming H2A Analysis	Bio-Oil Case (Ethanol Case)
Bio-oil Storage Tank	$106,040
Reformer	$803,000
Shift Reactor, PSA, BOP	$1,031,781
Total Production Capital	**$1,940,821 ($1,422,384)**
H2 Compressor	$337,500
Storage subsystem	$1,073,625
Dispenser system	$80,640
Control and safety eq.	$22,320
Total Compression/Storage/Dispensing	**$1,514,085 ($1,607,492)**

Feed and Energy

Mass yield of biomass to bio-oil = 65.7%
Mass yield of bio-oil to hydrogen = 11.1%

Bio-oil

- LHV = 18 MJ/kg (Poplar LHV = 19.3 MJ/kg)
- sp. Grav. = 1.2 (Poplar sp. Grav. = 0.2)
- Usage = 9 kg/kg H2

Methanol

- LHV = 20.1 MJ/kg
- Usage = 0.1 kg/kg H2 (0.13 L/kg H2)

Electricity

- Usage = 2.92 kWh/kg H2

Other material input and output

Process water – 13.8 L/kg H2 based on 2.5 steam to carbon mole ratio

Rhodium Catalyst

- Price of Rhodium is approximately $6000/oz (Palladium is approx. $350/oz)
- 14.6 kg Rh catalyst needed = $193,600 initial investment
- $194,000 replacement costs every 5 years used in H2A analysis

Other operating costs – Used H2A forecourt assumptions

Catalyst Experimental Results

- Rhodium catalyst closest to equilibrium, but system did not include added water

	CH_3OH % conversion	CO wt. % C	CO_2 wt. % C	H_2 wt.% H	H_2O wt. % H
Equil.	100	69	24	80	13
Gas	49	39	7	13	38
Alumina	39	36	7	9	38
Pd	82	51	10	34	41
Pt	88	45	12	31	45
Rh	100	61	23	84	18
Ru	75	48	9	28	41

Status / Planned work

Bio-Oil Volatilization

- The experimental apparatus was improved and made larger to reduce the amount of oil hitting the wall and allow for independent introduction of water

Homogeneous Partial Oxidation of Bio-Oil

- Experiments were performed to characterize effects of varying O:C and S:C ratio on hydrogen yield, residual carbon, and formation of benzene
- Bench scale unit tests are proposed for FY 2008
  - Will allow larger flows, longer runs, and less methanol to be used
  - Better mass balances.
- Catalyst studies to begin working with University of Minnesota

Technical Challenges

Bio-Oil Volatilization

Management of residue

Oxidative Homogeneous Cracking

High Reactivity but Unexpected Aromatics

Catalyst System Design and Performance

Carbon Deposit Removal and Catalyst Regeneration Management

Process Energy Integration

Integrated Hydrogen Separation

Merit Review Questions

- *Scale up of ultrasonic nozzle atomization not well understood/explained.*
  - Will be further developed as part of bench scale design
- *Need to better quantify extent of sooting and degree to which it can be burned-off/cleaned*
  - Work is in progress
- *(Should) link work to thermochemical research in the Office of Biomass Programs at DOE to produce (bio)-products.*
  - Biomass Program is now examining pyrolysis
- *Good representation from national lab, academic and industrial partner, yet more collaboration with industry is needed.*
  - Colorado School of Mines
  - CRADA with Chevron.
  - University of Minnesota will be performing systematic catalyst study in FY08

Thank You

Questions?