Energy in Thermal Conversion

Nikolai DeMartini

The Forest Based Biorefinery, 3-7 May 2010

Introduction

- Many mass and energy balances around various ”scenarios” for the biorefinery
- All scenario’s have technical challenges and there are nth plant assumptions
- Energy, distribution of energy needs, reduction in carbon footpring all variables that should be considered

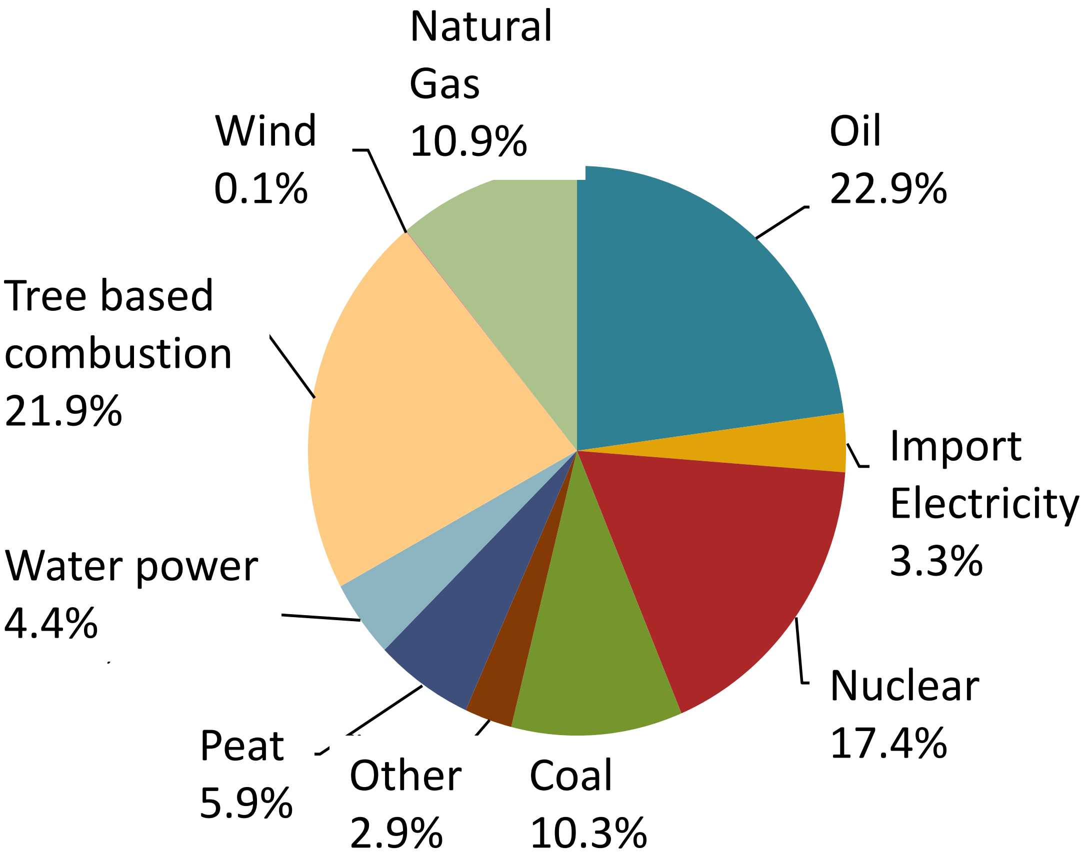
Overview

- Opportunities
- Energy use in Finland
- Energy distribution in pine & birch
- ”Minimum” value of lignin
- Example: energy use in BL gasification to liquid fuels
- Example: pyrolysis and catalytical hydrogenation of pyrolysis oil
- General comments on integration
- Well to wheel analysis

Opportunities in Energy

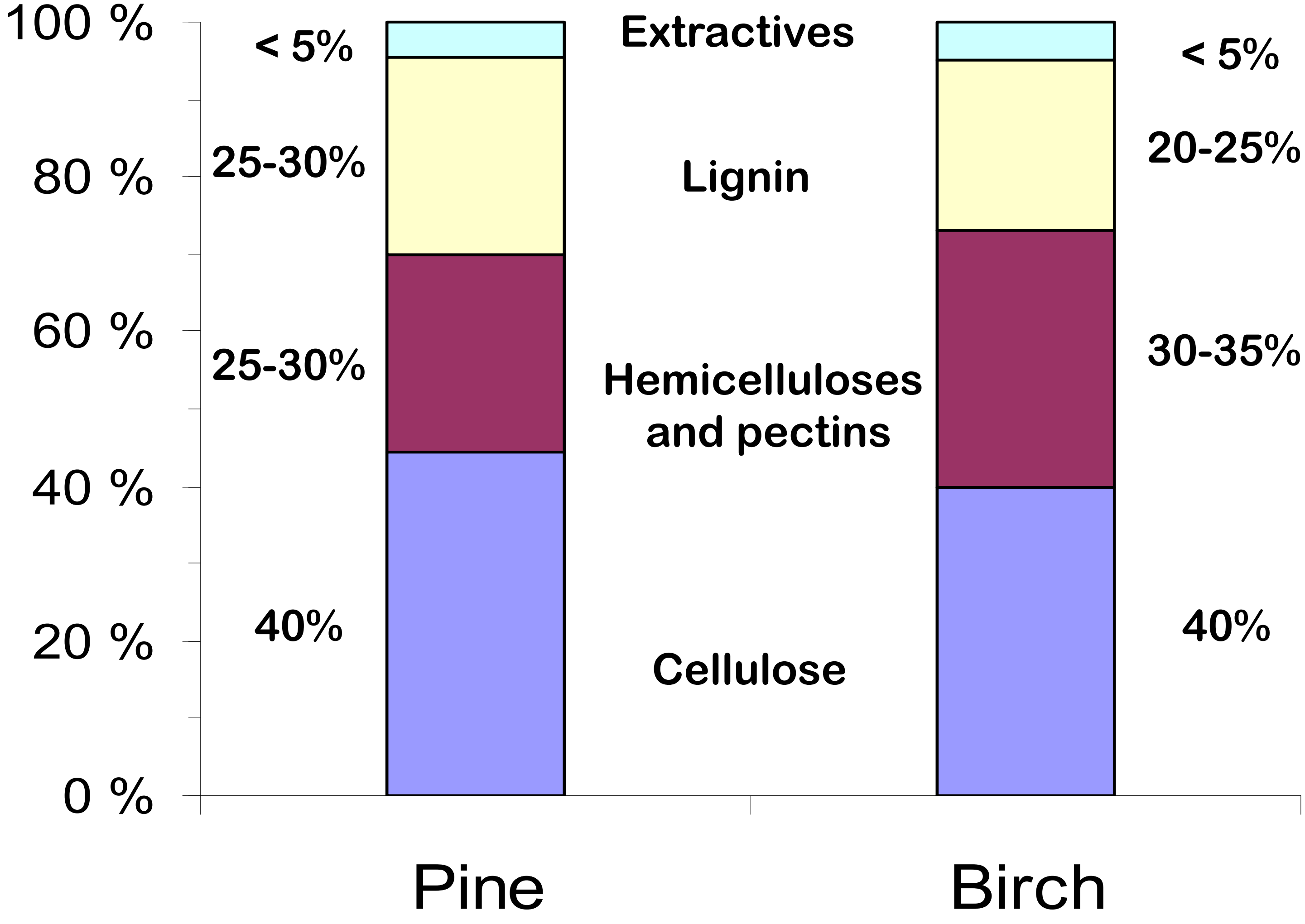
- Increasing world-wide energy demand
- Increasing pressure for reduced CO_2 emisisons
- ➢ Finland not only has the possibility to produce more bio-energy, but more importantly has the potential to export more of the technology to produce it
- ➢ Knowledge based economy
- ➢ This is a growth industry – existing technologies have not been proven/optimized for biomass
- ➢ Entrepreneurial opportunities

Energy Use in Finland 2008



- Total
  - 1.45×10^{18} J/y
- Chemical energy bound in tree growth in Finland
  - ~9×10^{17} J/y (100 Mm^3, 500 kg/m^3, 18 MJ/kg)

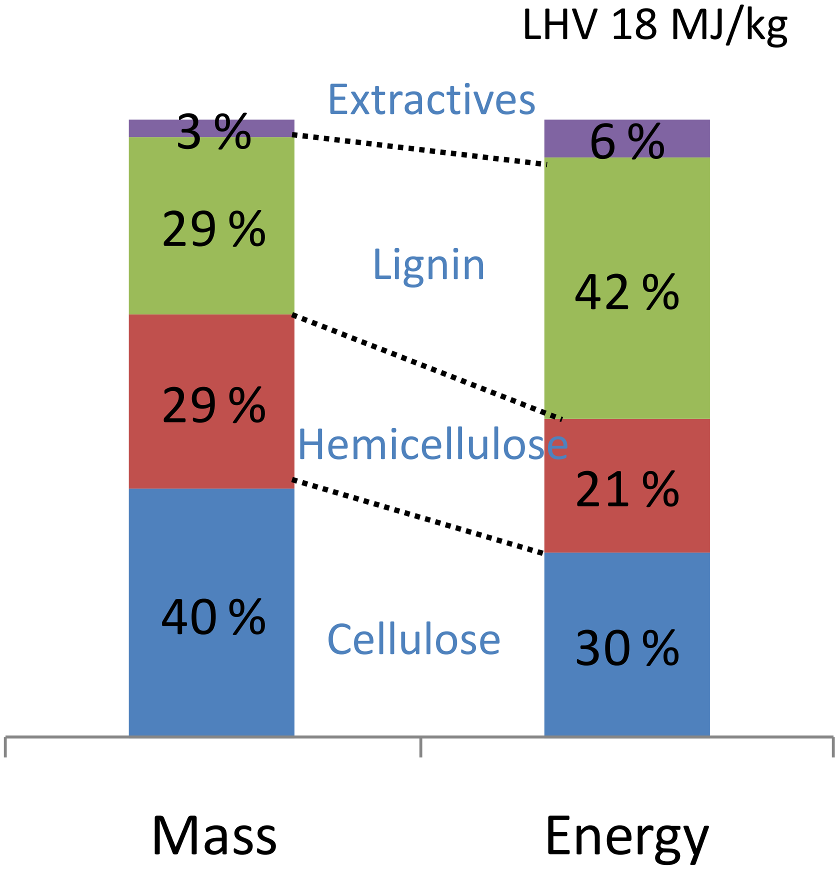
Chemical composition of pine (*Pinus sylvestris*) and birch (*Betula pendula*), % dry substance



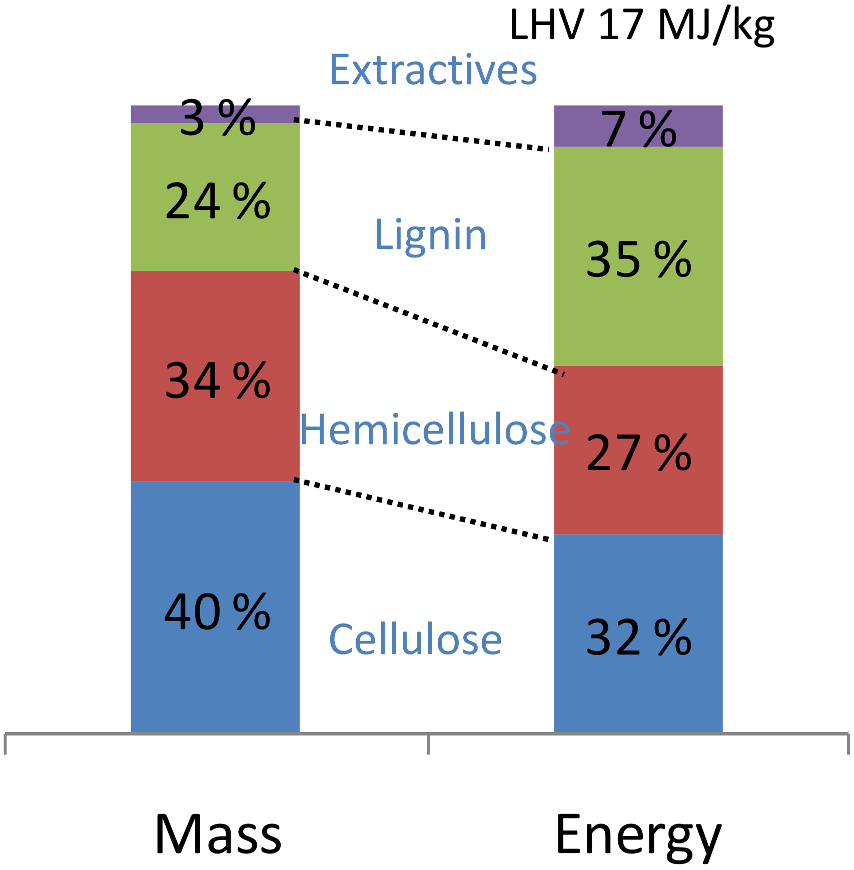
Approx. Lower Heating Values of Biomass Components

Component	**Heating Value (MJ/kg)**
Carbohydrates	13.6
Softwood lignin	26.9
Hardwood lignin	25.1
Resins, fatty acids	37.7

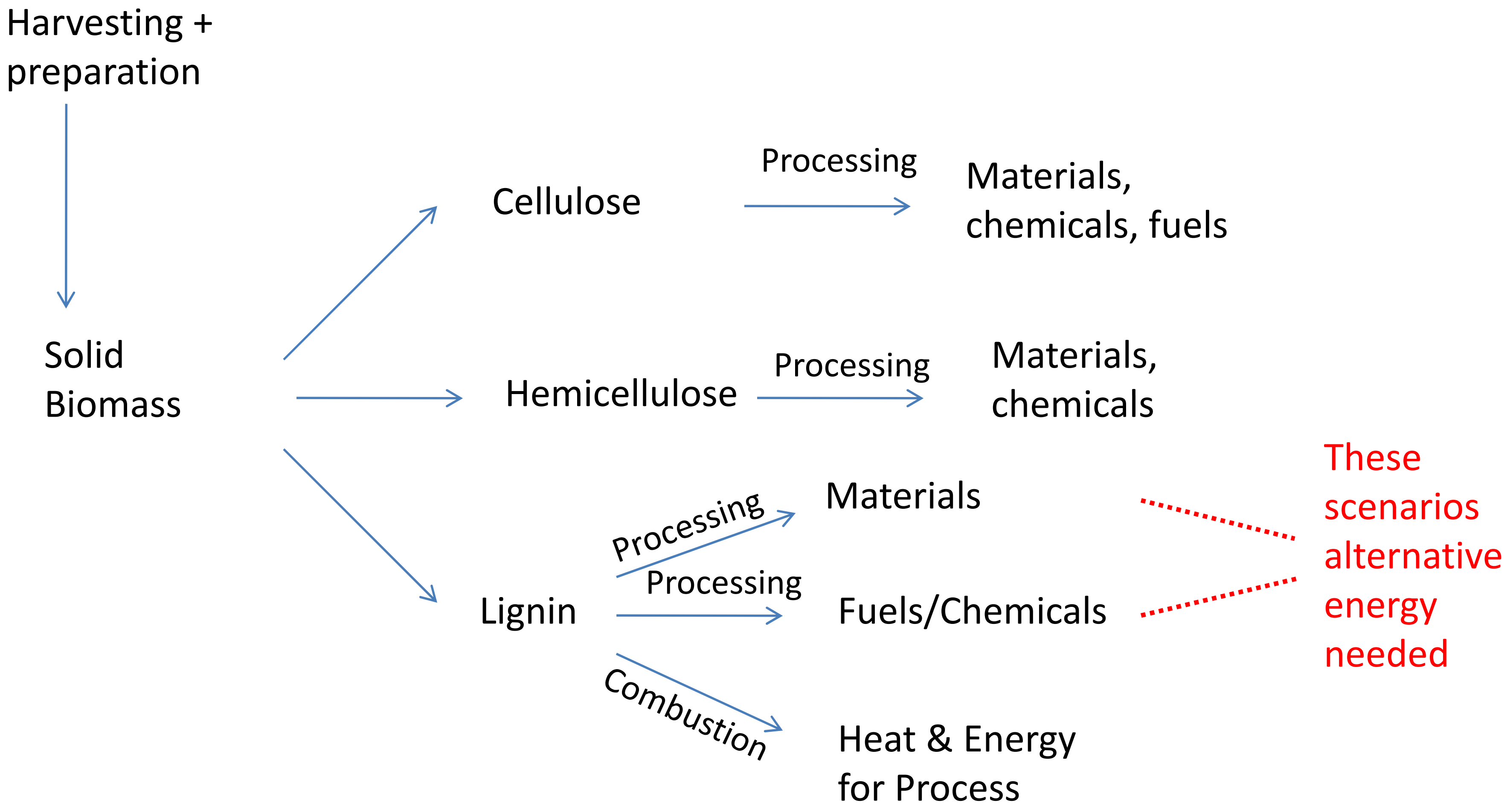
Pine


LHV 18 MJ/kg
Extractives
3 %
6 %
29 %
Lignin
42 %
29 %
Hemicellulose
21 %
40 %
Cellulose
30 %
Mass
Energy

Birch


LHV 17 MJ/kg
Extractives
3 %
7 %
24 %
Lignin
35 %
34 %
Hemicellulose
27 %
40 %
Cellulose
32 %
Mass
Energy

Fractionation followed by Conversion



Harvesting + preparation

Solid Biomass

Cellulose

Processing

Materials, chemicals, fuels

Hemicellulose

Processing

Materials, chemicals

Lignin

Processing

Materials

Processing

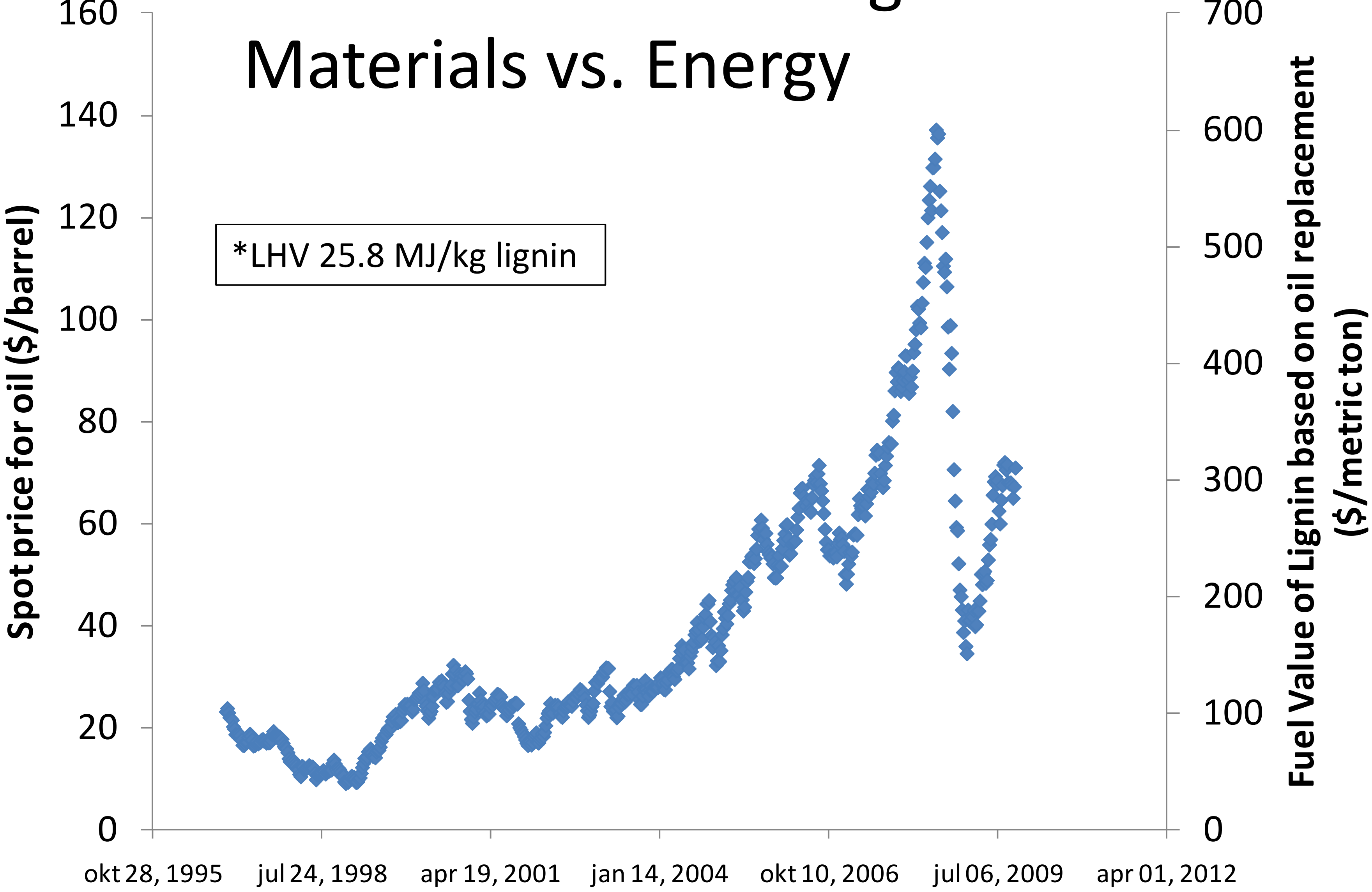
Fuels/Chemicals

Combustion

Heat & Energy for Process

These scenarios alternative energy needed

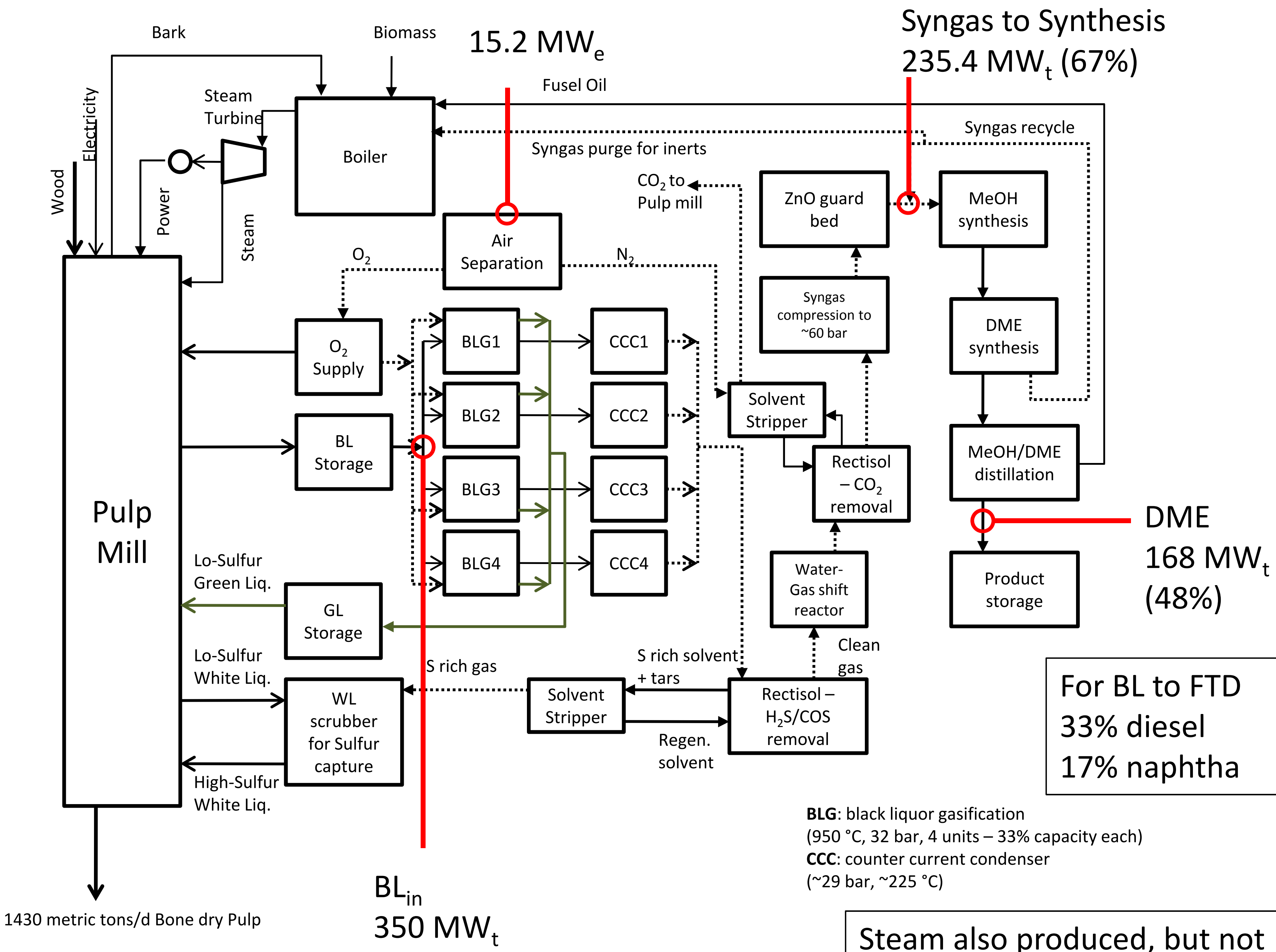
Minimum Value of Lignin – Materials vs. Energy



Lindgren, Karen. Potential lignin applications beyond energy 2nd Nordic Wood Biorefinery Conference. Helsinki, Finland Sept. 2-4, 2009.

Example – BL Gasification to Liquid Fuels

- Energy from BL used to supply the pulp mill with electricity and steam
- Modern stand alone pulp mill is capable of producing excess energy in the recovery boiler
- BLG to liquid fuels would result in an export of energy from the mill
- In future BLG to liquid fuels may make sense relative to biomass gasification in this sense – combust biomass in biomass boiler and gasify BL



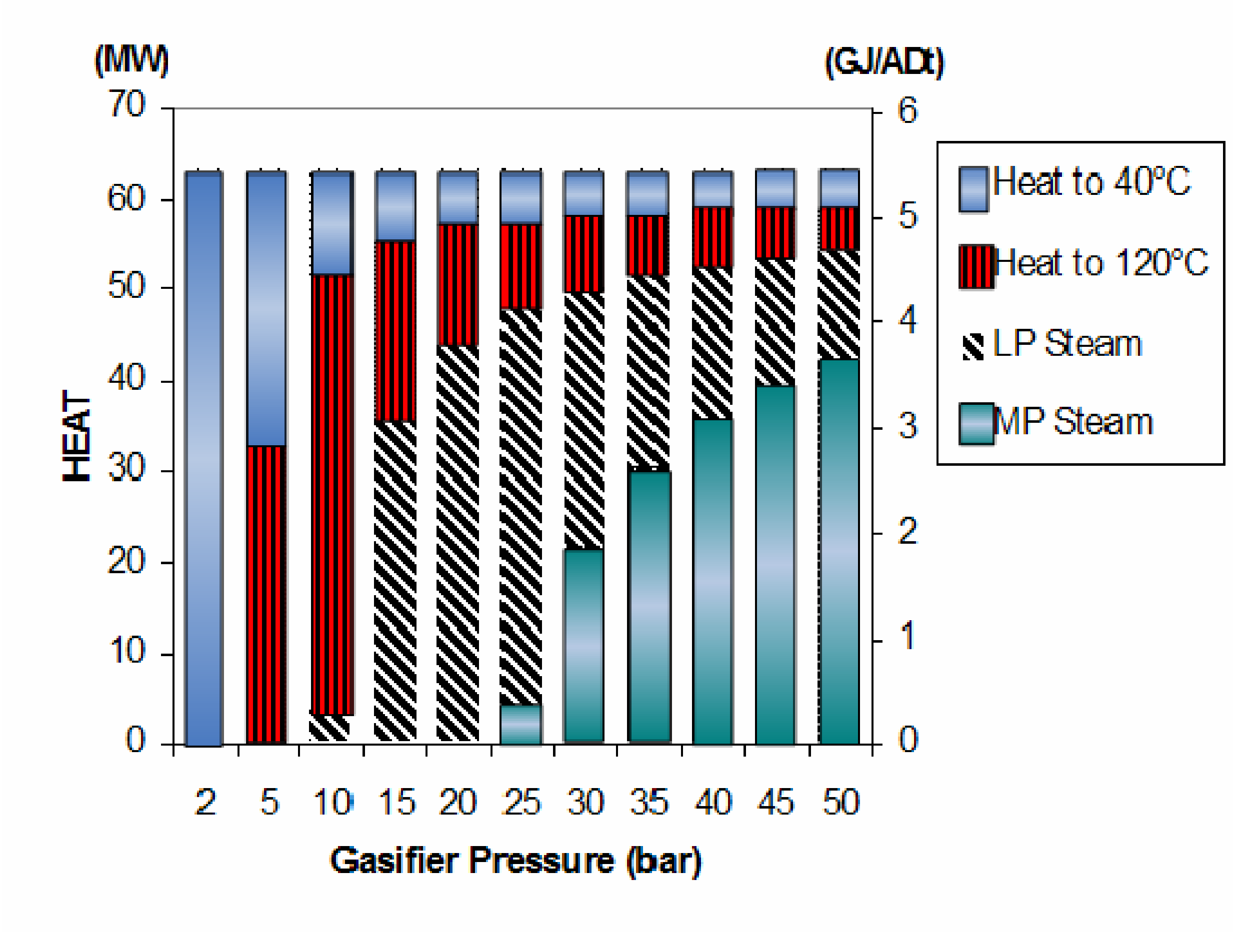
For BL to FTD
33% diesel
17% naphtha

BLG: black liquor gasification
(950 °C, 32 bar, 4 units – 33% capacity each)
CCC: counter current condenser
(~29 bar, ~225 °C)

Steam also produced, but not enough for mill w/o boiler

Ekbom, et al. (2003); Larson, et al., (2006)

Integration Example: Impact of Gasifier Pressure on Steam Production in Cooler



Scale for Finland

- If all of the BL in Finland was gasified, the analysis by Ekbom et al. (2003) estimates that ~50% of Finland's transportation fuels could be replaced (based on 1999 fuel consumption and 2000 BL production)
- Technology not yet proven
- Recovery boilers in Finland are relatively new

Economy of Scale

Feedstock to Liquid Transporation Fuels	Liquids Capacity (barrels/d diesel equiv.)	Capital Intensity ($/ barrel/d)
Petroleum refining	~150 000	15 000
Gas to liquid fuels	~100 000 to 150 000	25 000 to 50 000
Coal to liquid fuels	~100 000 to 150 000	50 000 to 70 000
BL/Biomass to liquid fuels	~1 000 to 7 000	60 000 to 150 000

Larson, E.D.; Consonni, S.; Katofsky, R.E.; Iisa, K.; Frederick, W.J. Jr. A cost-benefit assessment of gasification-based biorefining in the Kraft pulp and paper industry. Vol. 1: Main Report. Final Report DE-FC26-04NT42260, 21 Dec (2006), 152 pp.

BLGasification Combined Cycle

	Generation kWh/ADt	Consumption kWh/ADt	Sales kWh/Adt
New pulp mill w/ pressurized gasification			
High Temp	2100	1050	1050
Low Temp	2100	920	1180
New pulp mill w/ RB			
Conventional RB	1450	700	750
High power to heat RB	1700	730	970

Pulp Mill producing ~450 000 ADt/a → 70 Mwe gas turbine (GE6FA)
~1 600 000 ADt/a → 250 Mwe gas turbine (GE7FA)

Poor turndown so need natural gas to substitute for syngas when production drops

For gas valves on gas turbines (~500 °C is upper limit) so some gas cooling necessary

Na+K is manufacturer specific ~0.1 ppm in the syngas

Sulfur ~10-20 ppm depending on flue gas emissions control

Grigoray, M.Sc. LUT 2009; Vakkilainen et al. Pulp Pap Can, 2008

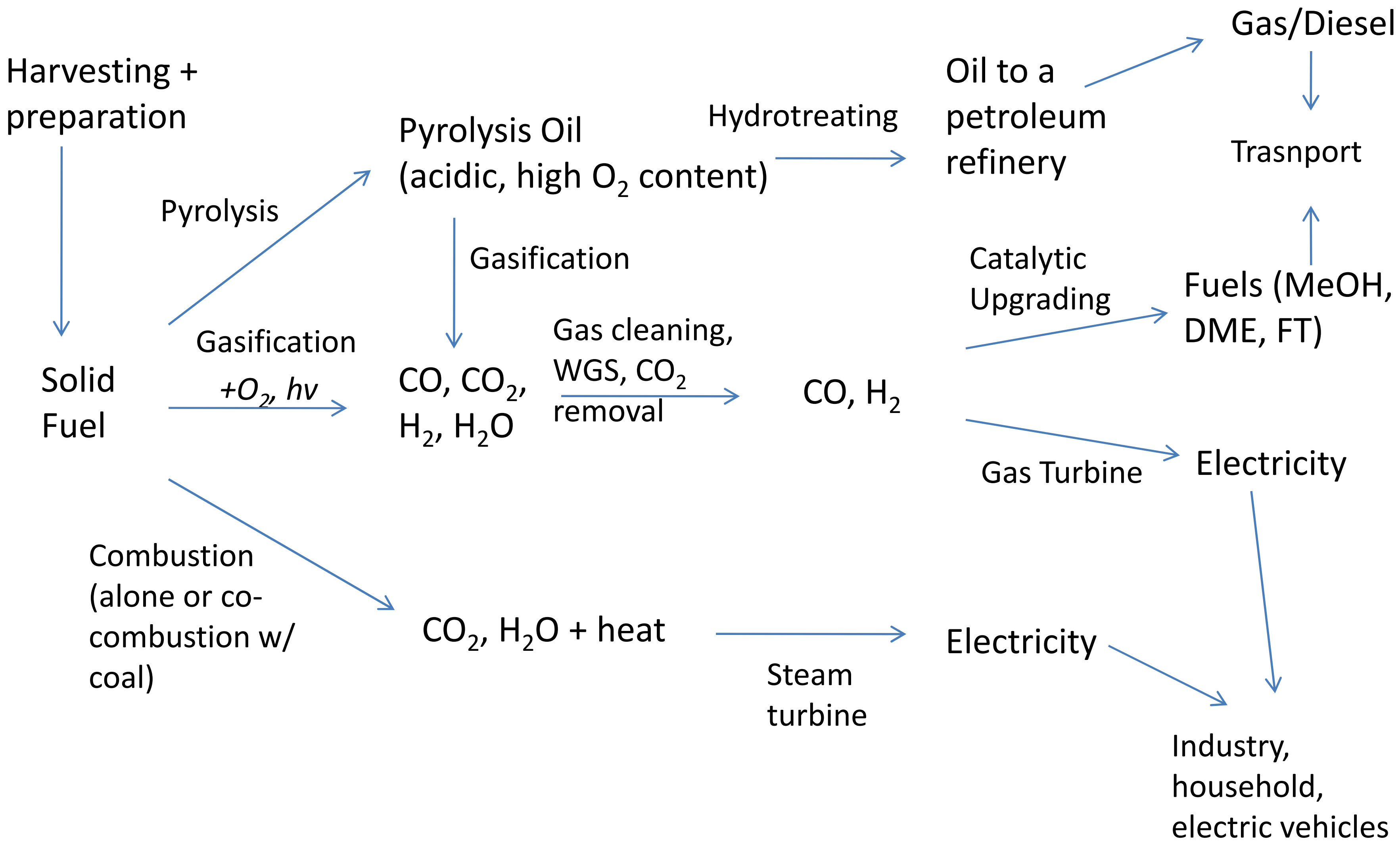
Black Liquor Gasification – Current Status

- MTRI steam reformer, 600 °C, 3 atm
  - Norampac, Trenton, ON, June 2003
  - 100 tds/day
  - This technology is no longer pursued
- Chemrec DP-1: 30 bar; 950 °C; O2-blown
  - Kappa Kraftliner in Piteå, Sweden (2005)
  - 20 tDS/24h (3 MWth)

Possible Mill Demonstration

- Domsjö Fabriker, Örnsköldsvik, Sweden
  - Sulfite biorefinery producing specialty cellulose, lignin (lignosulfonate), ethanol
  - Plan to gasify 1100 t dry solids/day sulfite liquor
  - Plan to use syngas to produce methanol (up to 450 tons/d) and/or dimethyl ether (DME) (up to 300 tons/d)
  - Decision on approval of a 70 M$ grant from the Swedish Energy Agency to be made by EU by the end of 2010

Thermal Conversion Routes w/o Fractionation



Harvesting + preparation

Solid Fuel

Pyrolysis

Pyrolysis Oil (acidic, high O_2 content)

Hydrotreating

Oil to a petroleum refinery

Gas/Diesel

Trasnport

Gasification

Gasification

$+O_2$, hv

CO, CO_2, H_2, H_2O

Gas cleaning, WGS, CO_2 removal

CO, H_2

Catalytic Upgrading

Fuels (MeOH, DME, FT)

Gas Turbine

Electricity

Combustion (alone or co-combustion w/ coal)

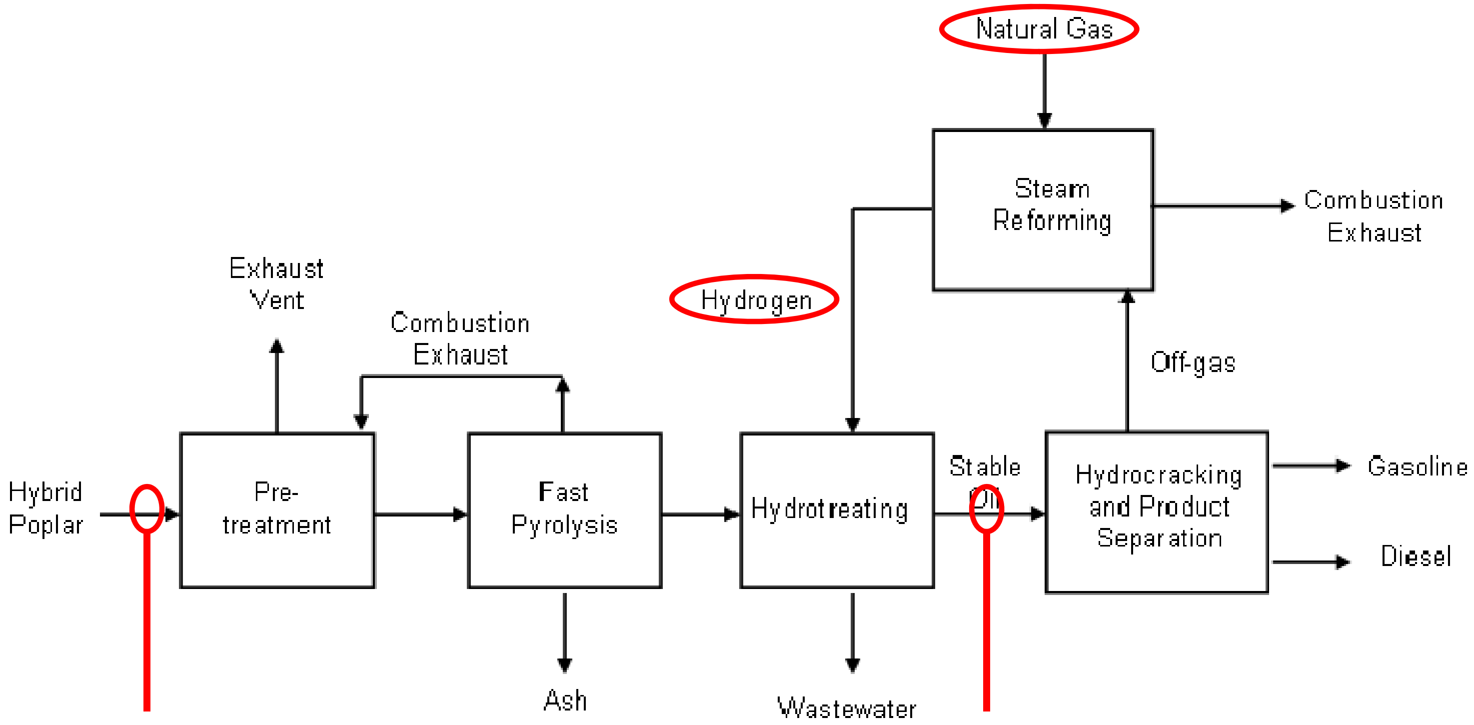
CO_2, H_2O + heat

Steam turbine

Electricity

Industry, household, electric vehicles

Example – Pyrolysis of Poplar



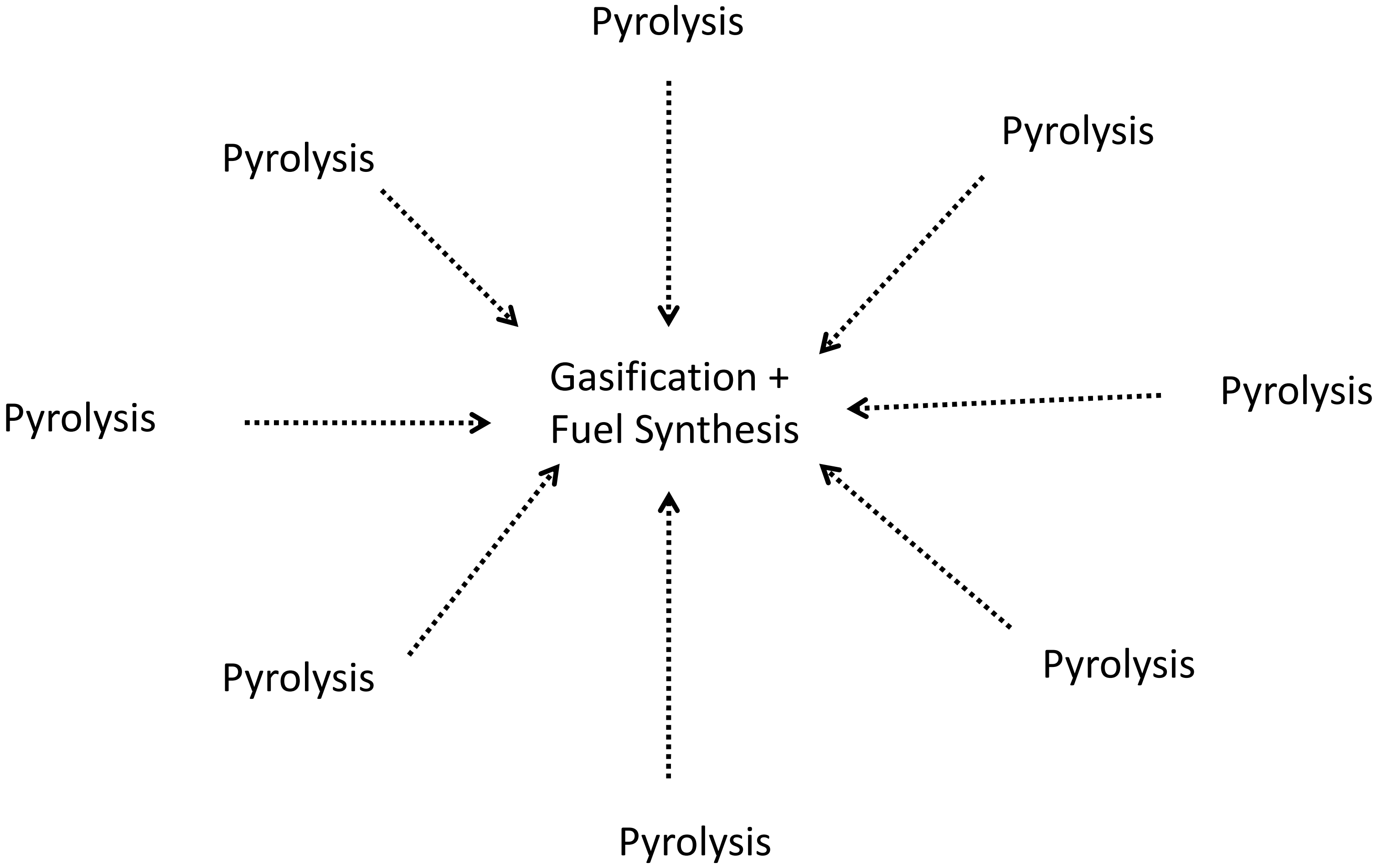
100% of Energy In

60% of Energy In

Jones, SB; Holladay, JE et al. Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case. PNNL DOE Contract DE-AC05 76RL 01830

BtL via pyrolysis + gasification

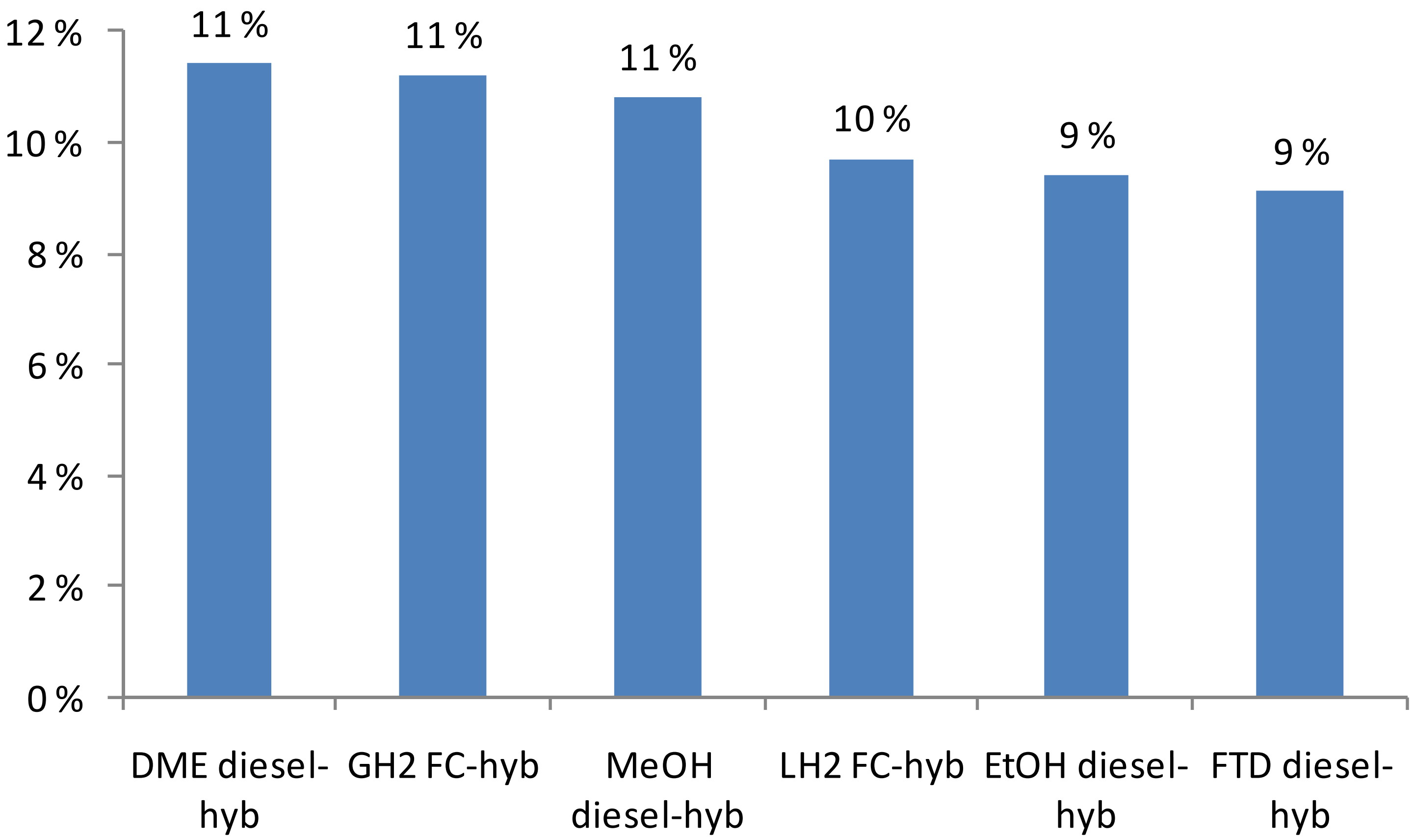
Advantage is transportation of biomass and larger scale of Gasification + Fischer-Tropsch



Integration

- Gasification to Liquid Fuels/Chemicals → user for steam produced from syngas cooling and catalytic processes
- Pyrolysis to liquid fuels → hydrogen source, refiner for bio-oil
- Integration improves the economy of the comparatively small scale

Well-to-Wheel Analysis



Ekbom, T.; Lindblom, M.; Berglin, N.; Ahlvik, P. *Technical and commercial feasibility study of black liquor gasification with methanol/DME production as motor fuels for automotive uses – BLGMF*. (ALTENER programme of the European Union, Contract No. 4.1030/Z/01-087/2001), (2003)
Ahlvik, P., Brandberg, Å., Hådell, O., Gustafsson, P., “Well-To Wheel Efficiency for alternative fuels from natural gas or biomass” Swedish National Road Administration, Vehicle Standards Division October 2001

Challenges

- Batteries & Fuel Cells
  - More environmentally benign batteries with adequate performance
  - Fuel cells that can handle more robust fuels
  - In long term could significantly alter electricity/fuels consumption
- Catalysis
  - Pyrolysis oil upgrading (both post or in-situ)
  - Pyrolysis + in-situ chemical processing
- Materials
  - High temperature corrosion (oxidizing and reducing gas atmospheres)
- Gas turbines
  - For lower heating value syngas
- Process Integration
  - Maximize heat integration & use of existing infrastructure
  - Process integration when proceeded by some fractionation
- Installation and maturation