From biomass gasification to large scale liquid biofuels production

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SMARt CHP Biomass energy

Lignocellulosic biomass

Agricultural, forest residues

wastes

Pyrolysis (500-800°C)

Depends: Method, reactor type, particle size, process parameters

Low temperature + high residence times → solids

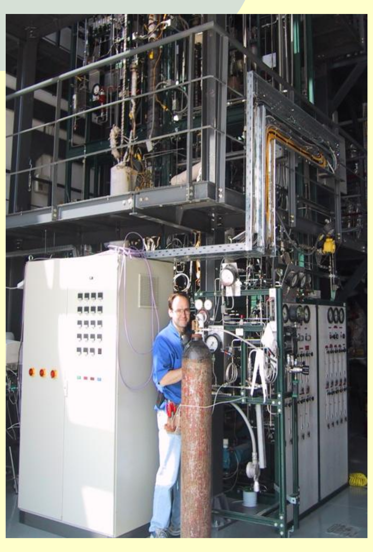
High temperature + low residence times → liquids

Yields: 60-80% w.t. yield bio-oil

High added value products

Catalysts: Zeolites / MCM with Ni, Al, Co, Mo, Fe, Cu

Challenges: Composition control, increased H_2, decreased polymerization rate, thermal control



Catalytic pyrolysis pilot unit, CPERI, Greece

Activated Carbons

High added value products

Applications: Gas & liquid cleanup

Feedstock: Sugarcane, fruit husks, kernels

Activated carbon

Gasification (750 – 1200°C)

Products: H_2, CO, CO_2, CH_4, C_nH_m, Tars, Solids

Use of air (gas HHV ~ 4-7 MJ/Nm^3)

Depends: Use of H_2O (gas HHV ~ 15-20 MJ/Nm^3)

Temperature, residence time, reactor type, feed technology, use of O_2 or H_2O

Gasification: $C + O_2 \rightarrow CO_2$ $C + H_2O \rightarrow CO + H_2$

$C + CO_2 \rightarrow 2CO$ $CO + H_2O \rightarrow CO_2 + H_2$

$C + 2H_2 \rightarrow CH_4$ $2H_2 + O_2 \rightarrow H_2O$

Pyrolysis: $C_mH_n \rightarrow n/4CH_4 + (m+n)/4C$

$C_mH_n + (4m-n)/2H_2 \rightarrow mCH_4$

Reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

$C_mH_n + mH_2O \rightarrow mCO + (m-n/2)H_2$

$C_mH_n + mCO_2 \rightarrow 2mCO + n/2H_2$

Char oxidation

5 kW$_{th}$ pilot scale fluidized bed gasifier, AUTh, Greece

Syngas Cleaning

Contents: particulates, sulphur and alkaline compounds, tars

Separation: Metal/ceramic filters (particulates)

filter selection, material, process conditions

Sorbents & membranes (S and alkalis)

sorbent selection, feed technology, fixed bed vessels

Tars: Steam reforming/ cracking (tars) ~ catalysts, process conditions

Tar formation controlled by process conditions, gasifier type and catalyst

Cold cleaning → Secondary tar removal

Bio-oil Reforming

Separation: Phenolic fraction → chemicals production

Hydrocarbonaceous fraction → energy production

Yield: Feedstock, composition, H/C fraction, residence time, catalyst

Lower temperature than methane reforming

70% conversion to H_2 at 600°C

Challenges: Uniform heat supply in catalytic bed

CO and CO_2 adjusting in the product

Operating parameters

Carbon disposition (gasification with H_2O)

Technology: Fluidized bed, catalyst regeneration

Spray feed at temperatures < 70°C

Heat needed: Reforming 125 kg/mol oil

70-650°C heating (1/4 organics/water) → 319 kJ

Catalytic steam reforming unit, CPERI, Greece

Hydrocracking unit
Source: www.cevron.com

Fischer-Tropsch Synthesis

Conditions: 150-300°C, elevated pressure (promote carbon chain growth)

Yield: Mixture of linear paraffins

Feed composition, reactor design, residence time, catalyst

Mechanism: $(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$, n the carbon chain length

Chain growth follows the ASF model $W_n/n = (1-a)^2a^{n-1}$

Catalyst: Transition metal based (Fe, Co), optimal H_2/CO ratio ~ 2

Challenge: Need for S free feed (catalyst poisoning)

Costly equipment, need for constant heat removal

Slurry reactor for Fischer-Tropsch synthesis
Source: www.sasol.com

Wax Hydrocracking

Target: Narrowing of the F-T paraffin distribution

Mechanism: Catalytic isomerization of the long carbon chains and chemical cleavage with H_2

Catalyst: Pt, Pd or bimetallic systems (e.g. Ni/Mo, Ni/W, Co/Mo)

Technology: Catalyst and reactor design

Liquid Biofuels

Wind turbines

Water Electrolysis

Electrolysis using RES (wind and/or solar power)

Technology: Electrolysis of water in a PEM

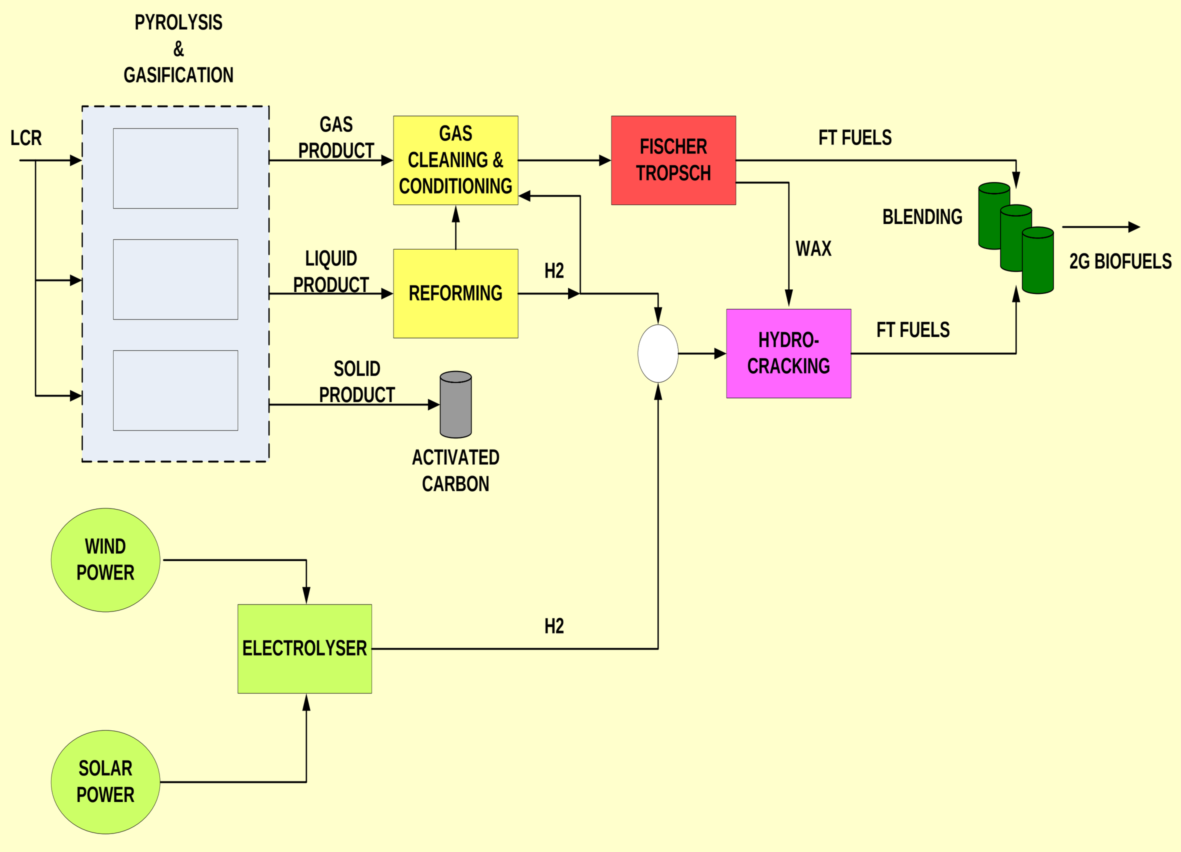
$H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Increased system efficiency and sustainability

Challenge: Detailed energy calculations

Key meteorological data required

Solar panels



Process Integration possibilities – Optimal Design

- Catalysts in the gasifier -> tar cracking
- Reformer gas in F-T synthesis (H_2/CO ~ 2)
- Energy management after syngas cooldown
- Hydrocracking products blending with F-T fuels
- Catalysts in the reformer->max H_2
- Reformer gas in hydrocracking (H_2/CO > 2)
- Recycle streams in F-T reactor
- Heat from the F-T reactor

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