Lignocellulosic biomass to 2G liquid biofuels in the biorefinery

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Lignocellulosic biomass

Agricultural, forest residues wastes

Gasification (750 – 1200°C)

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

Depends: Use of air (gas HHV ~ 4-7 MJ/Nm³)
Use of H_2O (gas HHV ~ 15-20 MJ/Nm³)
Temperature, residence time, reactor type, feed technology, use of O_2 or H_2O

Gasification: $C + O_2 \rightarrow CO_2$ $\quad C + H_2O \rightarrow CO + H_2$
$C + CO_2 \rightarrow 2CO$ $\quad CO + H_2O \rightarrow CO_2 + H_2$
$C + 2H_2 \rightarrow CH_4$ $\quad 2H_2 + O_2 \rightarrow H_2O$

Pyrolysis: $C_mH_n \rightarrow n/4CH_4 + (m+n)/4C$
$C_mH_n + (4m-n)/2H_2 \rightarrow mCH_4$

Reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$
$C_mH_n + mH_2O \rightarrow mCO + (m-n/2)H_2$
$C_mH_n + mCO_2 \rightarrow 2mCO + n/2H_2$

5 kW_{th} pilot scale fluidized bed gasifier, AUTh, Greece

Char oxidation

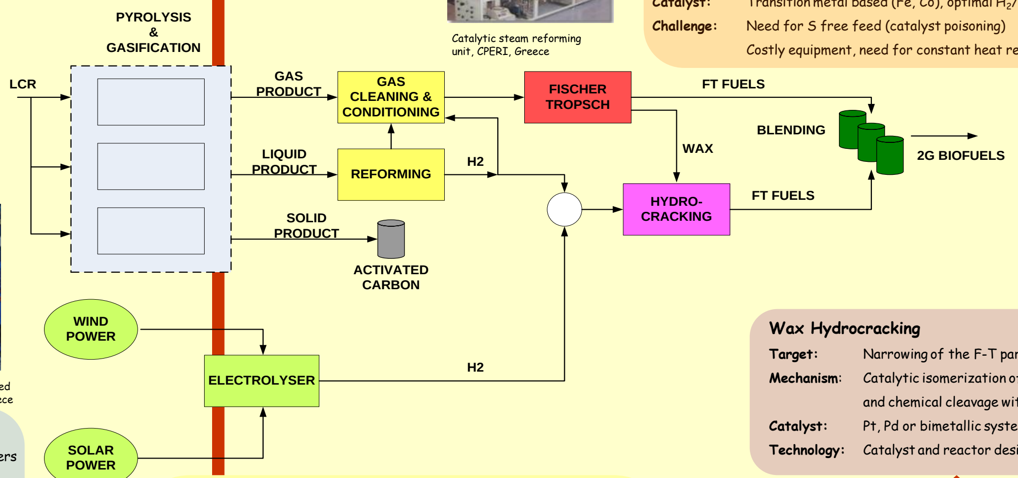
Syngas Cleaning

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/thermal cracking (tars) ~ catalysts, process conditions
Tar formation controlled by process conditions, gasifier type and catalyst
Cold cleaning → Secondary tar removal (gas filters, scrubbers)

Catalytic steam reforming unit, CPERI, Greece



Fischer-Tropsch Synthesis

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

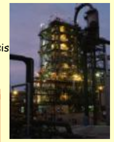
Yield: Mixture of linear paraffins
Feed composition, reactor design, residence time, catalyst

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



2G Liquid Biofuels

Hydrocracking unit
Source: www.cevron.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

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

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 (when H_2O is used for gasification)

Technology: Fluidized bed, catalyst regeneration
Spray feed at temperatures < 70°C

Heat requirements: Reforming 125 kg/mol oil
70-650°C heating (1/4 organics/water) → 319 kJ

Wind turbines

Solar panels

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

Water electrolysis in a PEM cell
Source:www.genhypem.u-psud.fr

Process Integration possibilities – Optimal Design

- Catalysts in the gasifier for tar cracking promotion
- Use of reformer gas in F-T synthesis (H_2/CO ~ 2)
- Energy management after syngas cooldown
- Wax hydrocracking products blending with F-T fuels
- Catalysts in the reformer for maximum H_2 production
- Use of reformer gas in hydrocracking (H_2/CO > 2)
- Recycle streams in F-T reactor, balance process conditions
- Exploitation of the heat from the F-T reactor

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