

Syngas and Bio-Oil Upgrading

1st Brazil-U.S. Biofuels Short Course
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Outline

- Syngas Upgrading
 - Composition of syngas
 - Gas cleaning requirements
 - Contaminants in syngas and their elimination
 - Catalytic upgrading
- Bio-oil Upgrading
 - Why bio-oil is difficult to upgrade
 - Pathways to bio-oil conversion to transportation fuels
 - Description of bio-oil refining systems

Syngas

- Syngas consists of CO, H₂, CO₂, CH₄, and smaller quantities of higher hydrocarbons (the gas product from air-blown gasification contains as much as 50% molecular nitrogen and is known as producer gas)

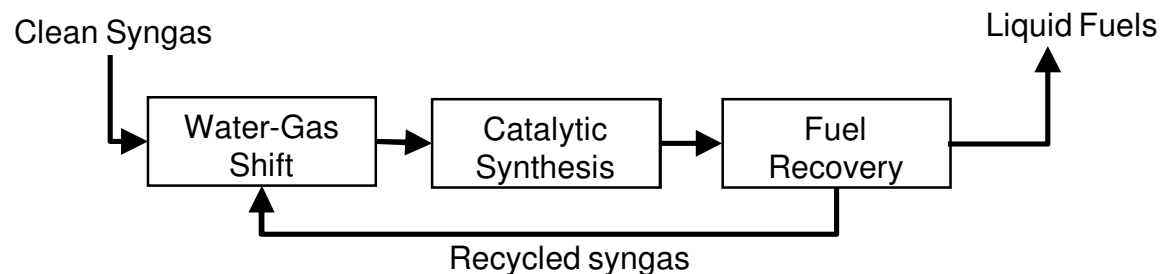
Composition of syngas (volume percent)					
Hydrogen	Carbon Monoxide	Carbon Dioxide	Methane	Nitrogen	HHV (MJ/m ³)
32	48	15	2	3	10.4

Pros and Cons of Syngas Upgrading

- Advantages (compared to biochemical platform)
 - Gasification tolerates relatively dirty biomass feedstock
 - Syngas is a uniform intermediate product
 - Proven method for “cracking the lignocellulosic nut”
 - Allows energy integration in biorefinery
- Disadvantages (compared to biochemical platform)
 - Gas cleaning technologies still under development
 - Synfuel processing occurs at high pressures
 - Economies of scale dictate large plant sizes

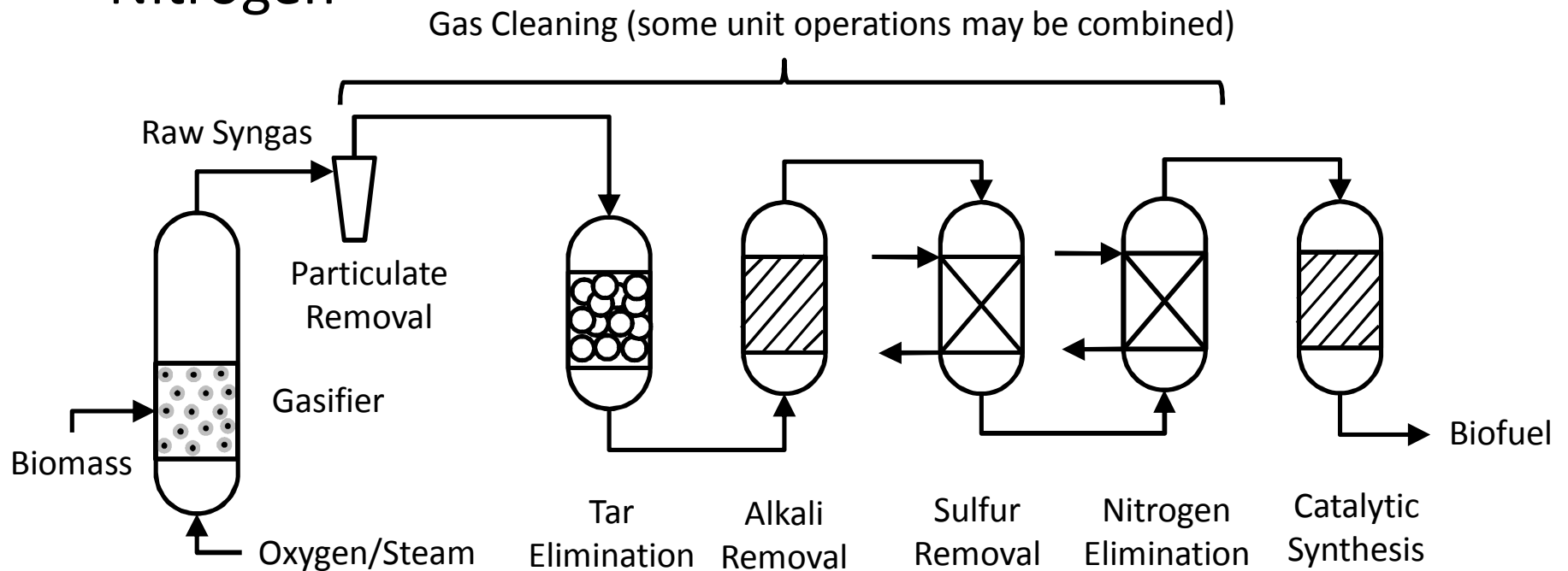


Fixed bed catalytic syngas reactor at Iowa State University



Contaminants found in Syngas

- Particulates
- Tar
- Alkali
- Sulfur
- Nitrogen



Particulate Removal

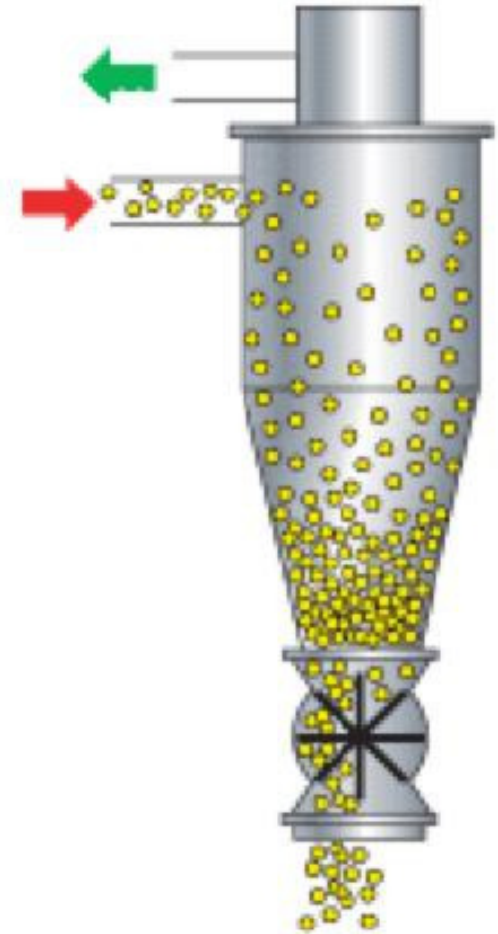
- Requirements vary
- Must be below
 - 50 mg/Nm³ for gas engines
 - 15 mg/Nm³ (>5 μm) for turbines
 - 0.02 mg/Nm³ for synthesis gas systems

Particulate Removal

- Primary Types
 - Cyclonic separators
 - Barrier filters
 - Electrostatic filters

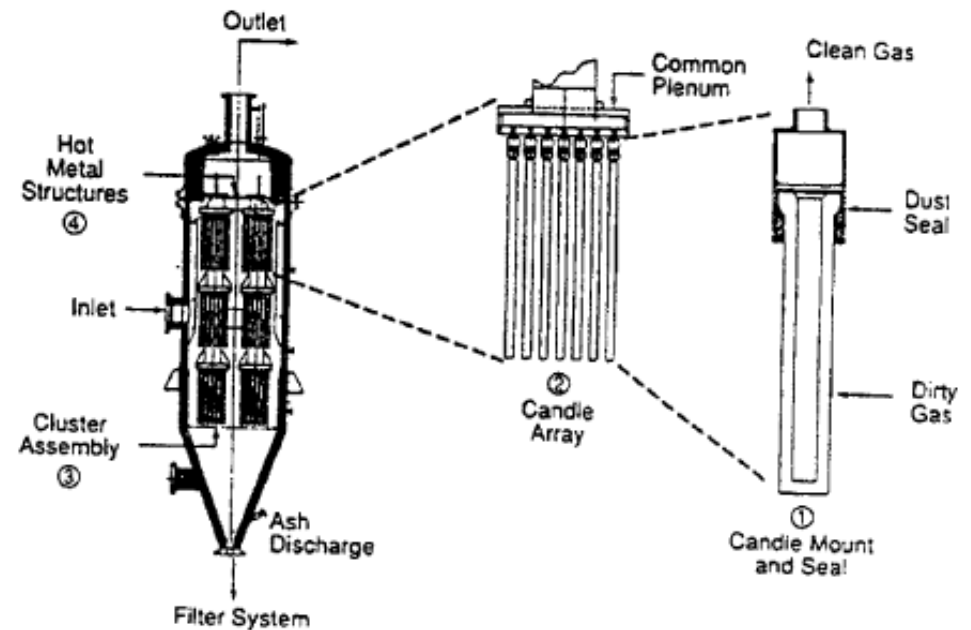
Cyclonic Separators

- Based on centrifugal removal of particles in fast-moving gas stream
- Low pressure drop compared to amount of PM removed
- Dry collection and disposal
- Temperature and pressure limitation are dependent on the materials of construction
- No moving parts, few maintenance requirements and low operating costs
- Compact design
- Low capital cost
- Not effective below about 10 microns



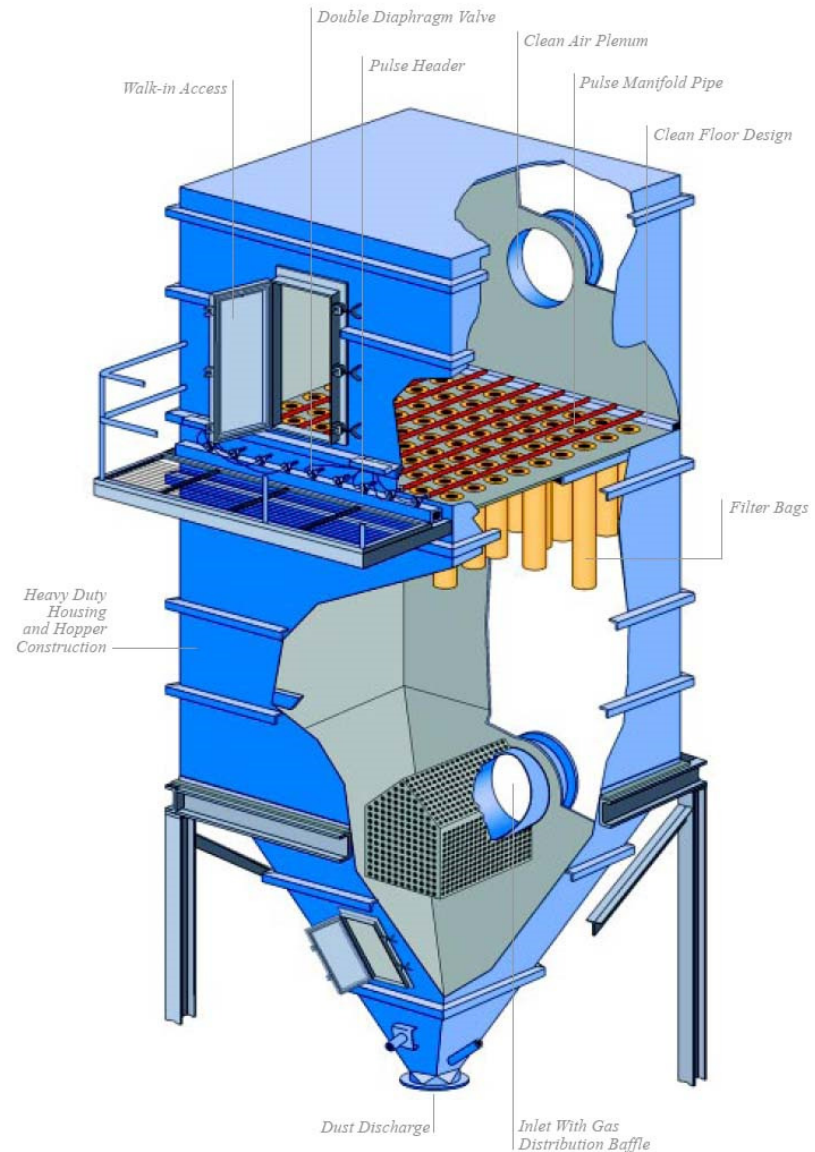
Barrier Filters

- Porous metal or ceramic materials that allow the gas to pass and hold back particles
- Removing particles with diameters of 0.5 to 100 μm
- Usually after a cyclonic filter



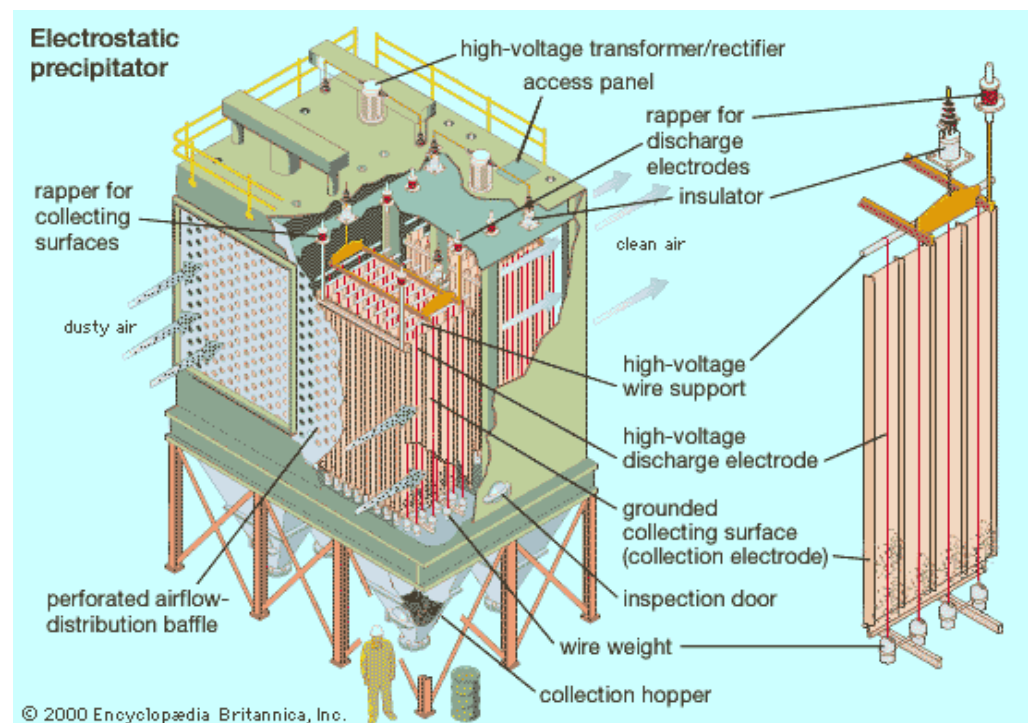
Bag Filters

- Woven material intercepts small particles by impingement
- Efficiency increases as the filter cake thickness increases
- Work well for small diameter, even sub-micron, particles
- Temperature limitations to about 400 C



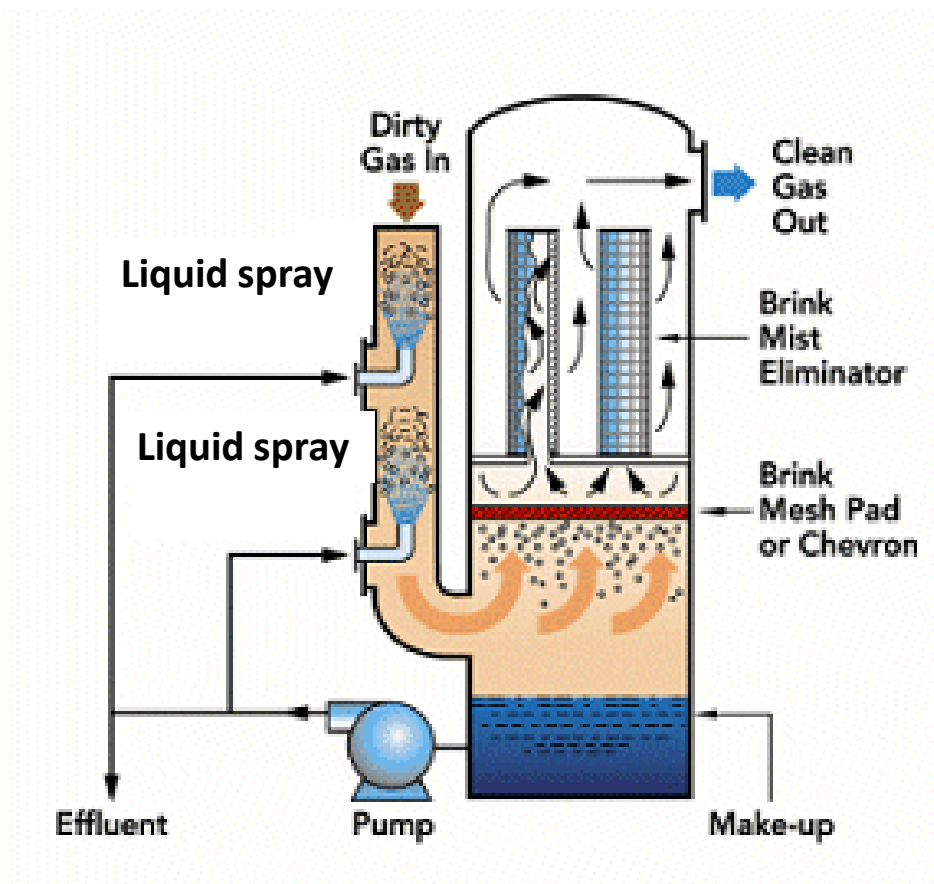
Electrostatic Filters

- Gas flows past high voltage electrode that imparts negative charges on the particles
- The gas then passes between positively charged plates that attracts the negatively charged particles
- Particles that accumulate on the positively charged plates are periodically removed by “rapping”



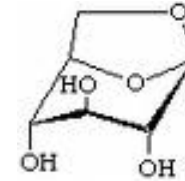
Wet Scrubbers/Oil Scrubbers

- Fine spray of water or oil washes particulate matter out of gas stream
- Mist eliminator prevents carry over of liquid droplets
- Also effective in removing tar and other contaminants
- Disadvantages:
 - Cools process stream
 - Produces wastewater problem



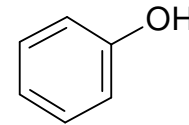
Tar

- Primary tar: released from pyrolyzing biomass (same oxygenated compounds as found in bio-oil)



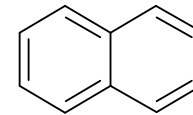
levoglucosan

- Secondary tar: decomposition to phenolics and olefins



phenol

- Alkyl tertiary tar: aromatic hydrocarbons



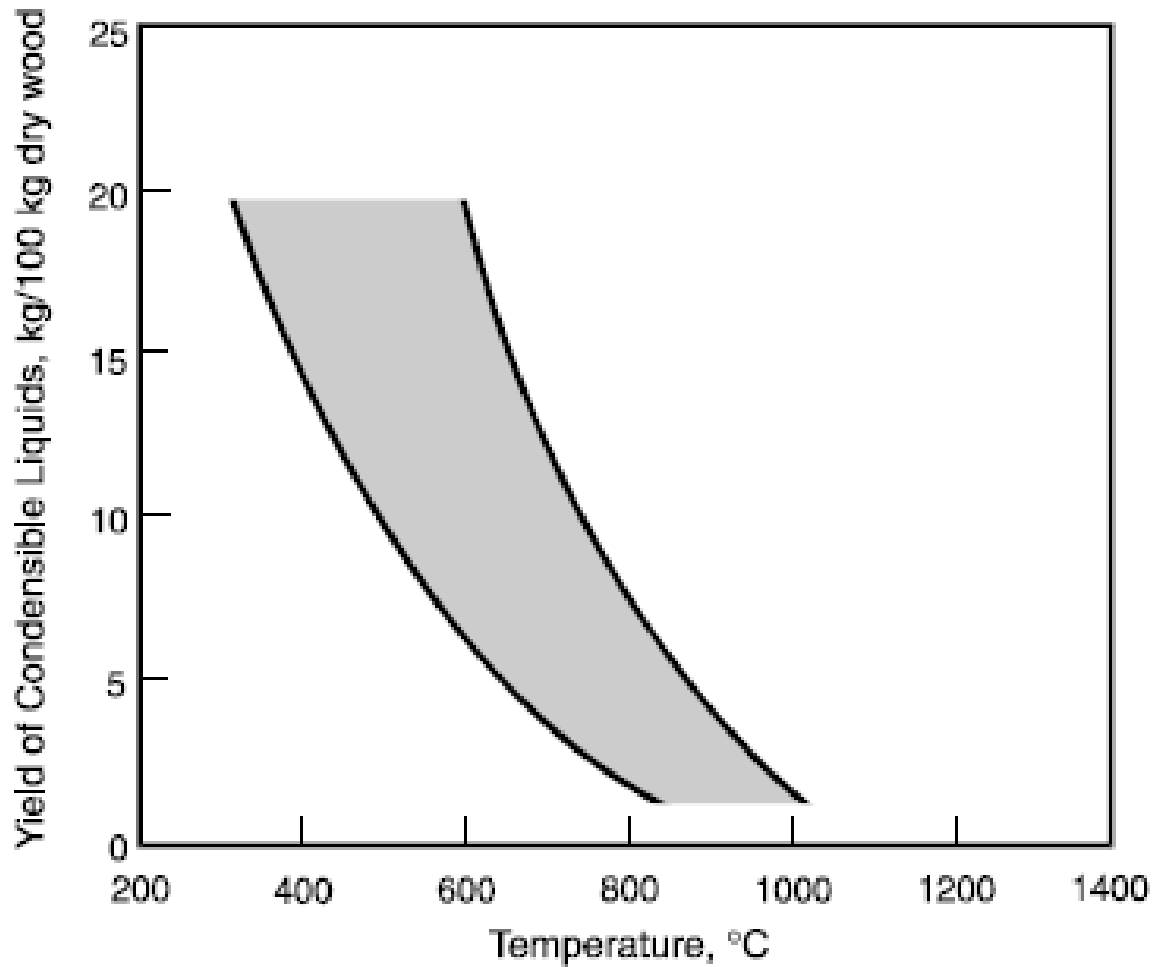
naphthalene

- Condensed tertiary tar (poly aromatic hydrocarbons)



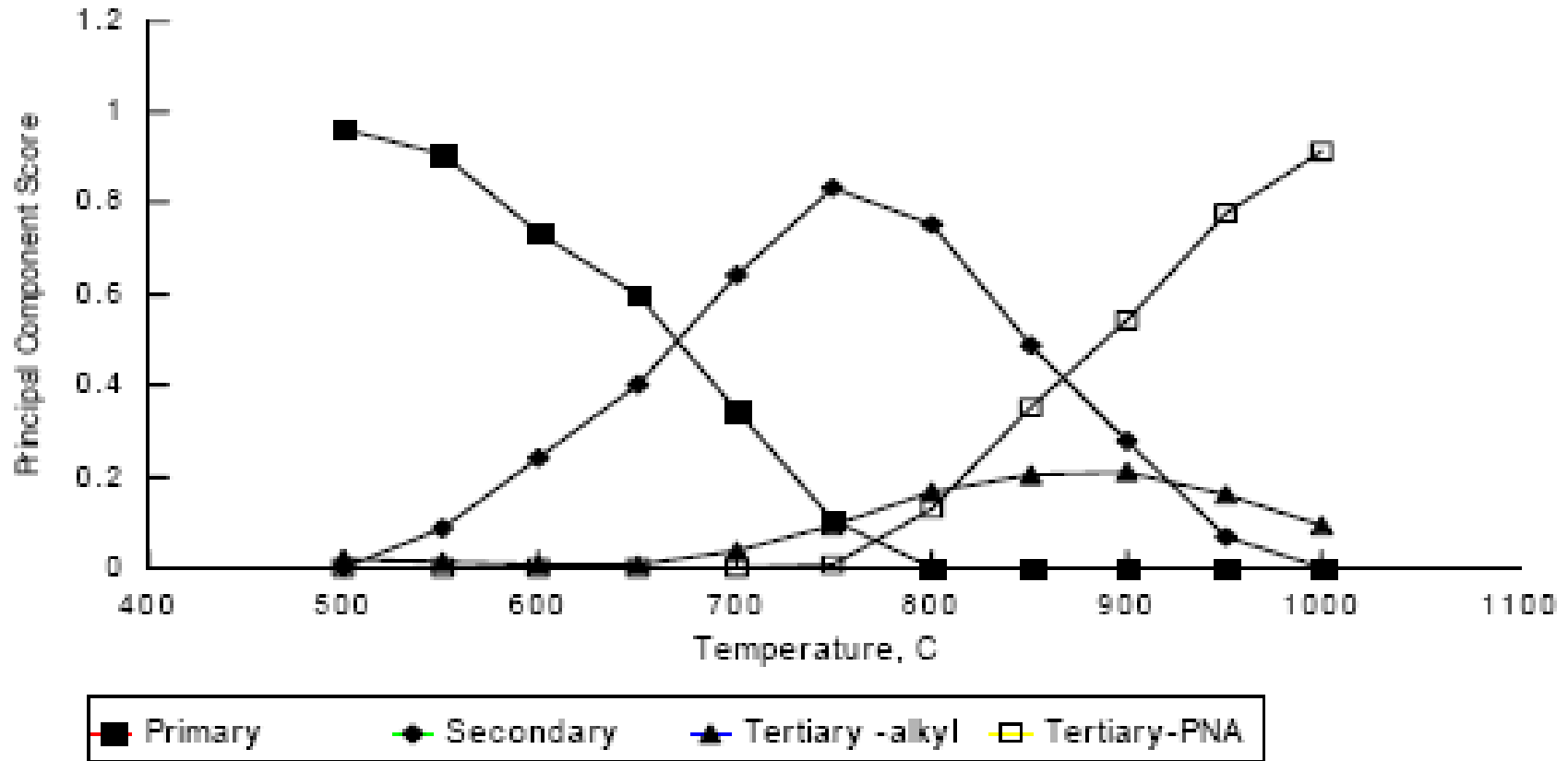
Milne, T. A.; Evans, R. J.; Abatzoglou, N. *Biomass Gasifier Tars: Their Nature, Formation and ConVersion; Report No. NREL/TP-570-25357*; National Renewable Energy Laboratory: Golden, CO,1998;
<http://www.osti.gov/bridge>.

Evolution of Tar



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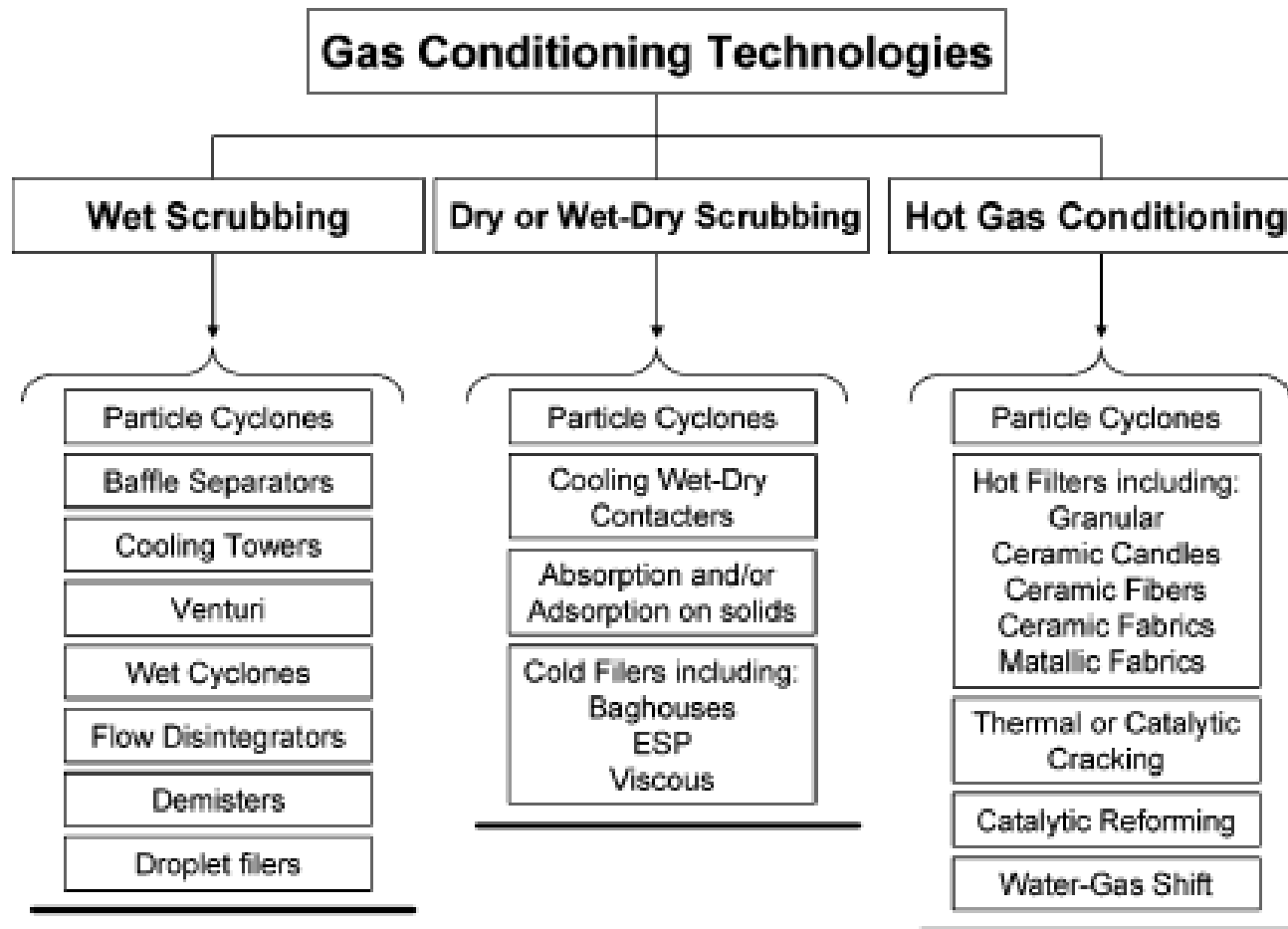
Tar Elimination

- Water or Oil Scrubbing
 - Integrated with particulate and ammonia removal
- Thermal Cracking
 - Tars decompose at sufficiently high temperature (typically 1000 °C or higher)
 - Refractory tars may be difficult to decompose
 - High temperatures encourage formation of carcinogenic polyaromatic hydrocarbons (PAH)
 - May require additional energy input to reach cracking temperature
- Catalytic Cracking

Catalytic Cracking

- Steam reforming process (800 - 900 °C)
 - $\text{Tar} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$
 - Enhances heating value of syngas
- Dolomites and nickel-based catalysts extensively studied
- Catalytic cracking system often includes guard bed of dolomite ahead of main reactor
- Tertiary tars are more “recalcitrant” to cracking
- Coking (deposition of carbon deposits on catalyst surfaces) is a common problem
- Catalysts readily poisoned by sulfur

Strategies for Tar Removal



Milne, T. A.; Evans, R. J.; Abatzoglou, N. *Biomass Gasifier Tars: Their Nature, Formation and ConVersion; Report No. NREL/TP-570-25357*; National Renewable Energy Laboratory: Golden, CO,1998; <http://www.osti.gov/bridge>.

Alkali

- Alkali (metals) in biomass include potassium and to a lesser extent sodium
- Alkali responsible for sticky ash deposits (ash fouling), corrosion, and catalyst poisoning
- Alkali exists as both solid and vapor (can vaporize at temperatures as low as 600°C)

Biomass feedstock	Alkali oxides (kg/GJ)	Fouling/ slagging probability
Yard waste	.50	Very high
Wood-Almond Shell mix	.40	Very high
Forest residuals	.22	Medium
Hybrid poplar	.17	Some
Red Oak	.09	Low

Miles, T. R., T.R. Miles Jr., L.L. Baxter, R.W. Bryers, B.M. Jenkins, and L.L. Oden, 1996a. Alkali Deposits found in Biomass Power Plants. Vol. I. NREL/TP-433-8142. National Renewable Energy Laboratory, Golden, Colorado.

Alkali Removal

- Conventional Approach
 - Gas stream cooled <600 °C to condense <5 μm particles of alkali salt
 - Use fine particulate filtration system to remove alkali particles
 - Energy inefficient
 - Corrosion can be a problem in filters
- Advanced approach
 - Alkali “getters” chemically adsorb alkali vapors
 - Fixed beds or pneumatically injected sprays of getters have been investigated
 - Inexpensive minerals like bauxite are preferred over regeneration
 - Chlorine can also be removed in this manner

Alkali	Measured concentration without bauxite filter, ppmw	Measured concentration with bauxite filter, ppmw
Na	28	0.07
K	11	0.58

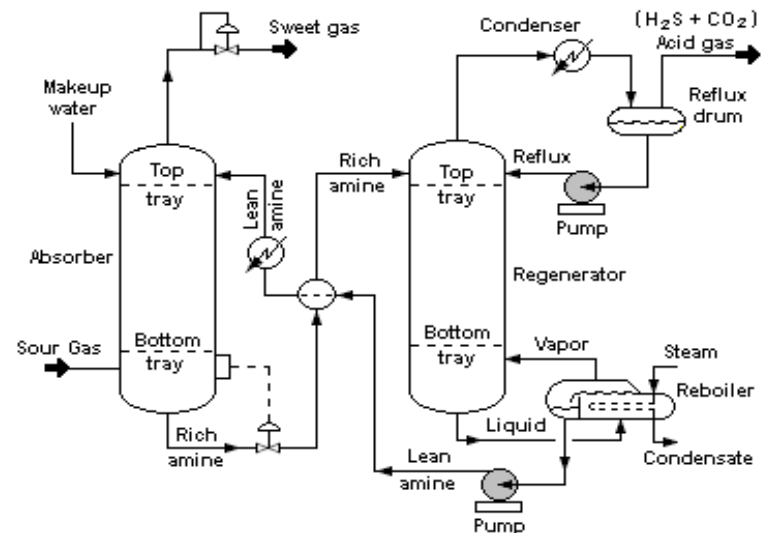
Turn, S.Q., C.M. Kinoshita, D.M. Ishimura, T.T. Hiraki, J. Zhou, and S.M. Masutani, 1999. An Experimental Investigation of Alkali Removal from Biomass Producer Gas using a Fixed Bed of Solid Sorbent. Proceedings of the Fourth Biomass Conference of the Americas, R.P. Overend and E. Chornet, eds. Elsevier Science, Oxford, United Kingdom. Pp. 934-946.

Sulfur

- Biomass typically contains <0.1 wt% sulfur for wood and <0.4 wt% for crop residues
 - Results in low levels (<100 ppm) of H₂S in syngas
- Sulfur poisons many catalysts requiring its removal to <1 ppm for fuel cells and <0.1 ppm for synfuels manufacture

Sulfur Capture

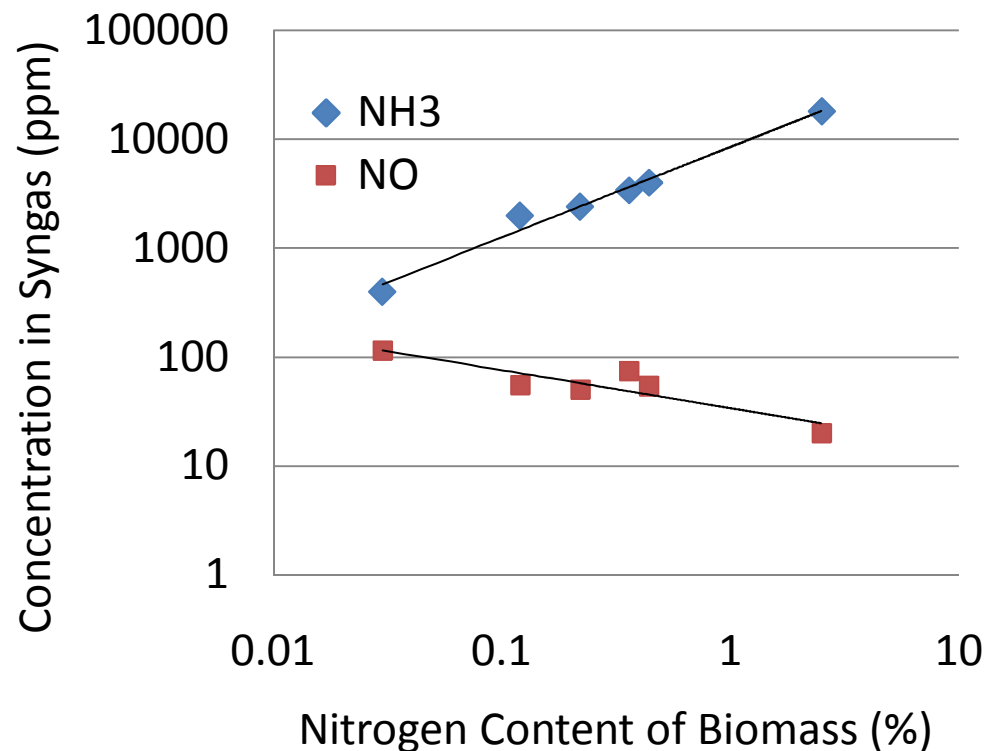
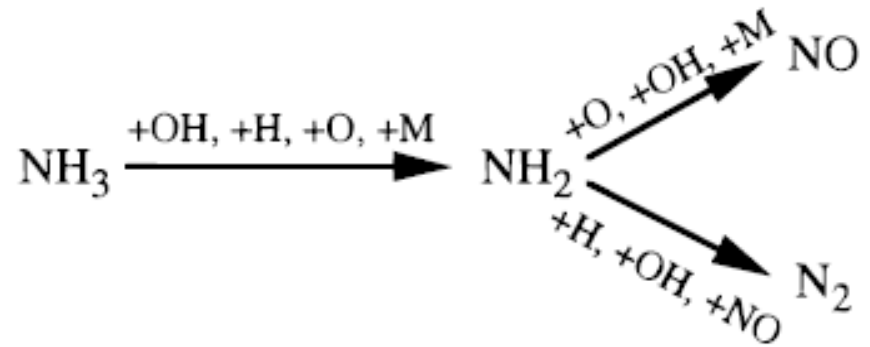
- Wet scrubbing
- Chemical gas treatments absorbs acid gases (both H_2S and CO_2) in a liquid followed by pressure let down or steam stripping to recover the acid gases
 - Selexol – proprietary solvent absorbs acid gases at 2.07 to 13.8 MPa
 - Rectisol - cold methanol ($-40\text{ }^\circ\text{C}$) absorbs acid gases at 2.76 to 6.89 MPa
 - Purisol - N-Methyl-2-Pyrrolidone is used to absorb acid gases
 - Amine Scrubbers – variety of amines absorb acid gases at $35 - 50\text{ }^\circ\text{C}$ with heat regeneration
- Solid sorbents
 - Metal oxides can reversibly adsorb H_2S at about $500 - 700\text{ }^\circ\text{C}$
 - These can be pelletized for fixed or moving beds or dispersed as fine powder into the syngas stream
 - Still under development



Amine Scrubber

Nitrogen

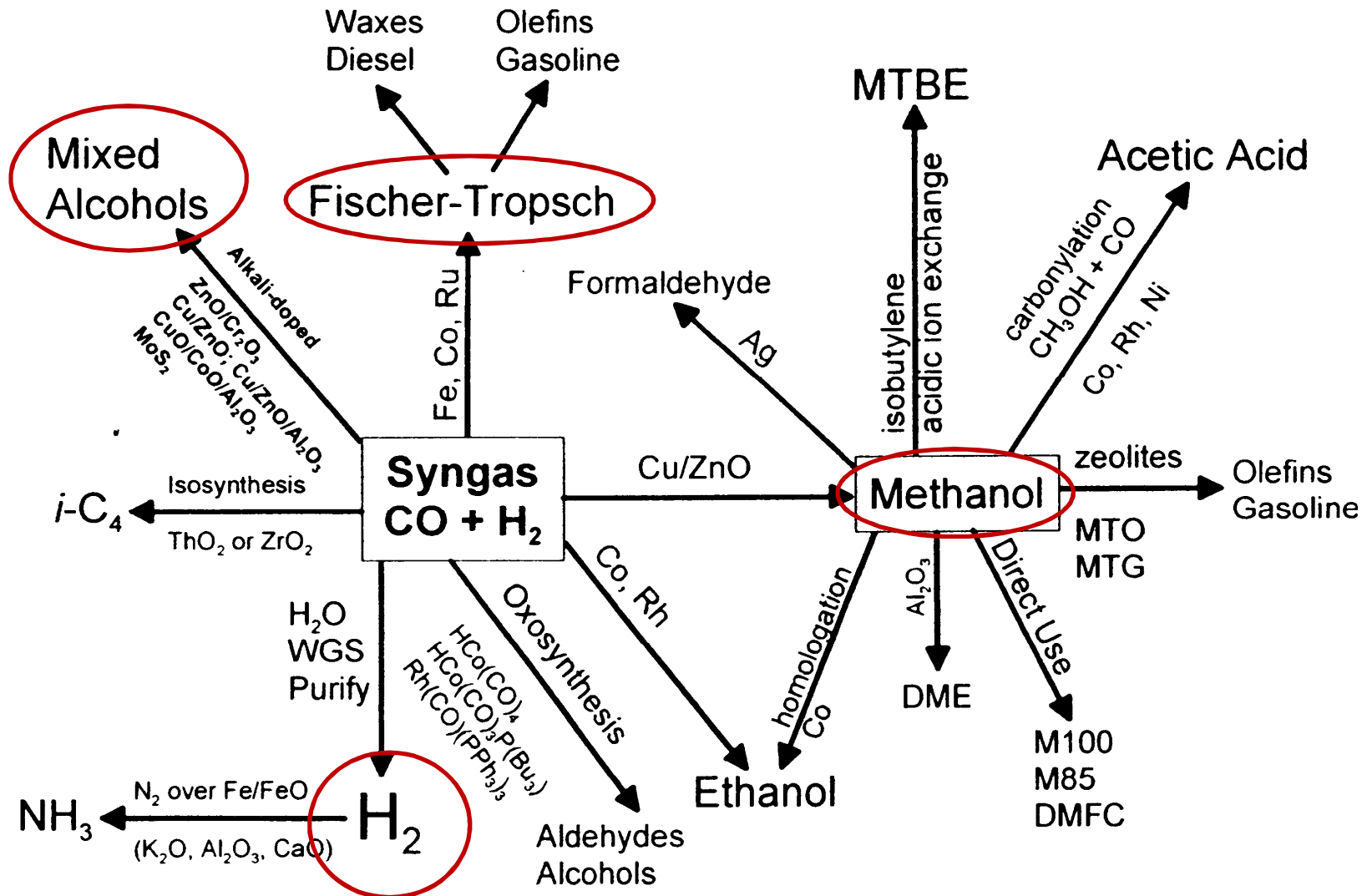
- Nitrogen absorbed in roots of plants as NO_3^- and NH_4^+
- Most converted to protein in leaves and young stems
- Gasification converts it to molecular nitrogen (N_2) or ammonia (NH_3) and smaller amounts of nitric oxide (NO)
- Amount of NH_3 and NO depend upon amount of nitrogen in biomass and processing conditions



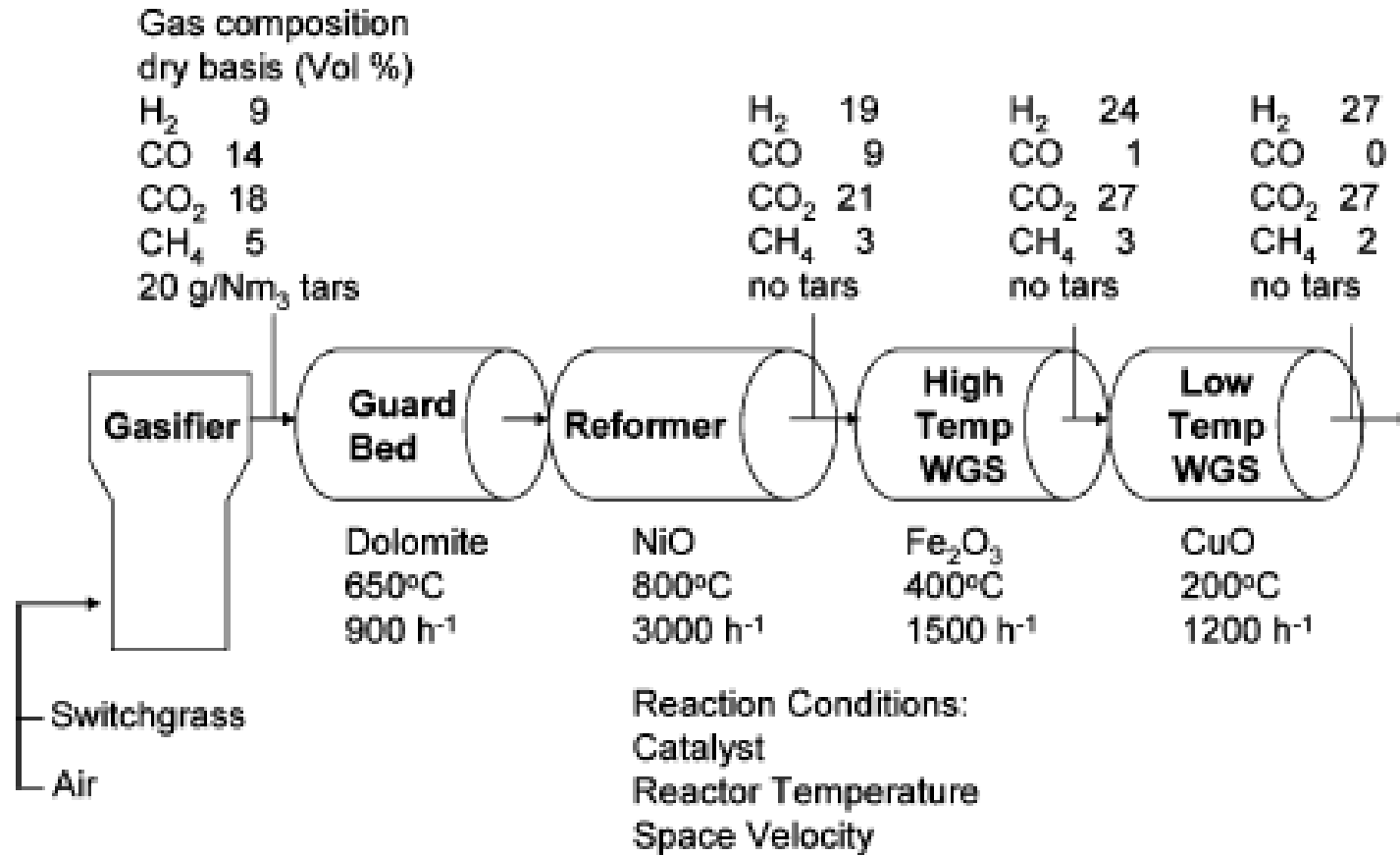
Nitrogen Elimination

- Ammonia removal: Wet scrubbing
 - Appropriate when syngas is cooled
 - Acidic aqueous solution readily removes ammonia
 - Energy inefficient
- Ammonia destruction: Catalytic reforming
 - Appropriate when syngas is not cooled
 - Reduction chemistry: $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$
 - Dolomite and nickel-based catalysts are effective at 800 °C while iron-based catalysts require temperatures of 900 °C
 - Can be accomplished during steam reforming of tar (same reactor)

Pathways to Syngas Products



Thermochemical Production of Hydrogen



Captures
sulfur, chlorine,
and tarry

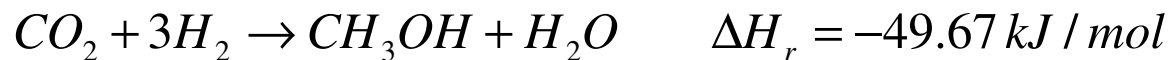


Catalysts for Hydrogen Production

- Steam Reforming
 - Converts methane, other light hydrocarbons, and tar to CO and H₂
 - Most steam reforming catalysts are 10-33 wt% NiO on a mineral support (alumina, cement, or magnesia)
- Water-gas shift
 - Increases hydrogen content of syngas while reducing carbon monoxide
 - $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
 - Used for both hydrogen production and adjusting H₂:CO ratio for catalytic synthesis
 - Thermodynamically favored at low temperatures, which requires multiple WS reactors to achieve high hydrogen yields
 - High temperature catalyst (iron oxide, chromium oxide basis)
 - Low temperature catalyst (copper oxide in mixture with zinc oxide)
- Promoter (potassium, lanthanum, ruthenium, and cerium)
 - Prevents coking of the reforming catalysts
 - Increases steam gasification of solid carbon which reduces coke formation

Methanol Synthesis

- A high temperature, high-pressure, exothermic, equilibrium limited synthesis reaction



- Theoretical stoichiometric ratio $(H_2 - CO_2)/(CO+CO_2) = 2$
- For kinetic reason and to control by-products, the ratio of higher than 2 is preferred
- Can achieve 99% conversion efficiency
- By-products of methanol production
 - CH_4 , DME, methyl formate, higher alcohols, and acetone
- Reaction is about 100 times slower when CO_2 is present

Methanol Reactors

- Cu/ZnO/Al₂O₃ operated at 220-275°C, 50-100 bar)
- Adiabatic reactors usually contain multiple catalyst beds separated by gas cooling devices (direct heat exchange/injection of cooled, fresh or recycled syngas)
- Isothermal reactors operate like a heat exchanger, continuously remove the heat of reaction



Mixed Alcohols

- Iron-based catalysts will convert syngas at 50 bar and 220-370°C to mixtures of alcohols (methanol, ethanol, 1-propanol, and 2-propanol)
- Selectivity to alcohols is over 95%, but production of pure ethanol is elusive
- Mixed alcohol synthesis has not been commercialized due to poor product selectivity and low syngas conversion.
- On a single pass, about 10% of syngas gets converted with most of the product composed of methanol.

Fisher-Tropsch Synthesis (FTS)

- Converts CO and H₂ mixtures to a wide range of paraffins (saturated hydrocarbons), olefins (unsaturated hydrocarbons), and oxygenated products (alcohols, aldehydes, ketones, acids and esters)
- Water is a by-product
- Utilizes transition metal catalysts (iron or cobalt)
- Reactions are strongly exothermic, requiring large amounts of heat removal from synthesis reactors

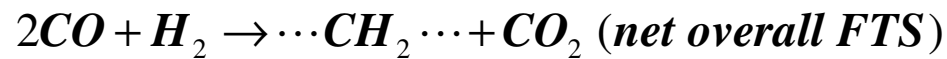
FTS Reactions

- Operating regime affects product distribution
 - low temperature (200-240°C) yields more waxes (which can be cracked to diesel fuel)
 - high temperature (300-350°C) yields more gasoline
- FTS reaction is usually kept under 400°C to minimize CH₄ production

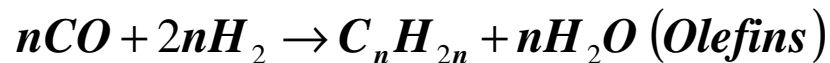
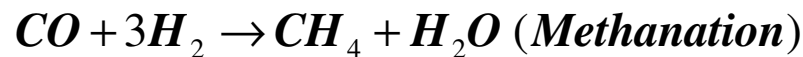
Chemistry behind FTS

- Basic reaction steps of FTS
 - Reactant (CO) adsorption on the catalyst surface
 - Chain initiation by CO dissociation followed by hydrogenation
 - Chain growth by insertion of additional CO molecules followed by hydrogenation
 - Chain termination
 - Product desorption from the catalyst surface

FTS reaction:



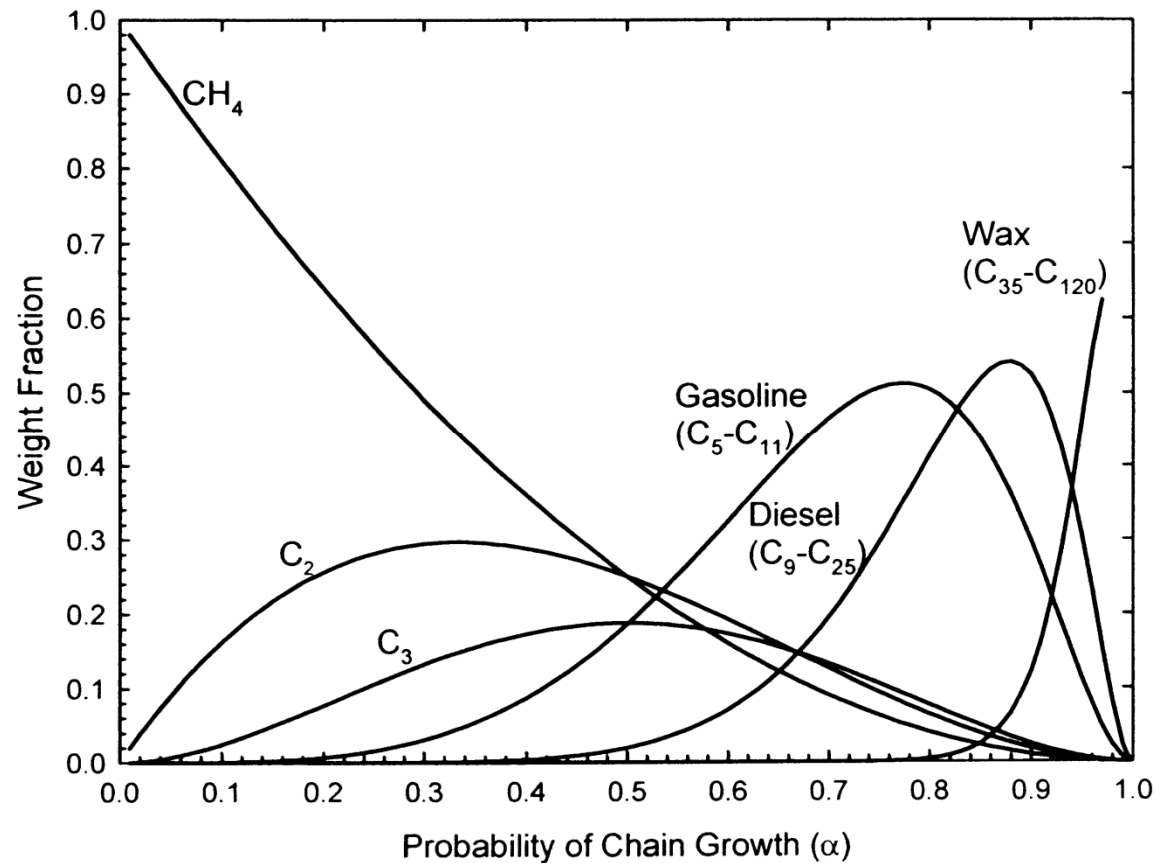
Synthesis reactions for specific FTS products:



Carbon deposition on the catalyst surface causes catalyst deactivation

- FTS is kinetically controlled
- Chain polymerization kinetics model
 - Anderson-Shulz-Flory (ASF) model

$$W_n = n(1-\alpha)^2 \alpha^{n-1}$$



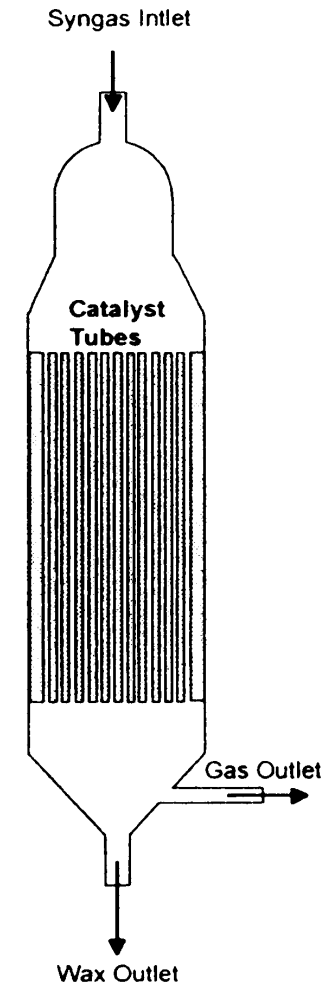
Catalysts

- In decreasing order of activity
 - Ru > Fe > Ni > Co > Rh > Pd > Pt

Ni	Methanation catalyst
Ru	Produces high molecular weight products at low temperature
Fe	Has water-gas shift activity and strong tendency to produce carbons (deposit on the surface and deactivates the catalyst)
Co	Improves carbon conversion to products Yields mainly straight chain hydrocarbons

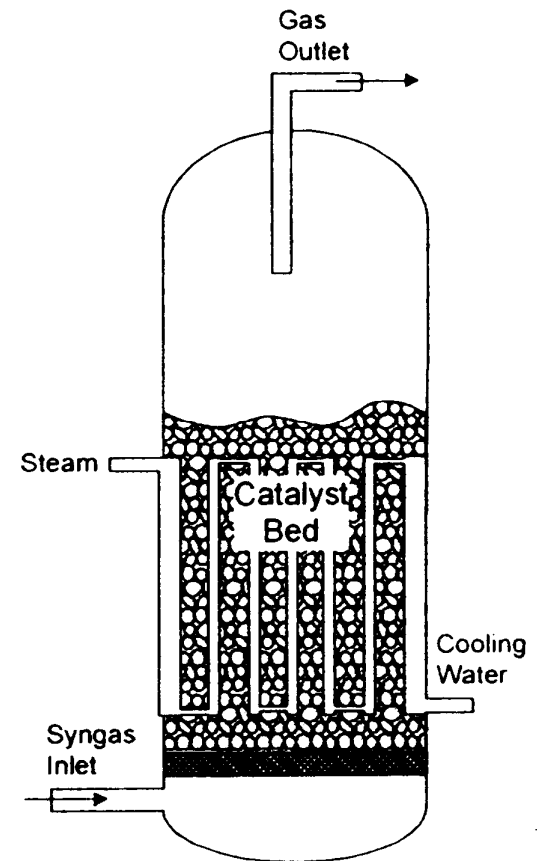
Fixed Bed Tubular Reactor

- 50% wax products
- Operate at 20-30 bar at 220-260°C
- Additional temperature control by high gas velocities and gas recycling
- Advantage
 - 70% conversion efficiency
 - Catalyst lifetime around 70-100 days
- Disadvantage
 - Catalyst removal is quite difficult



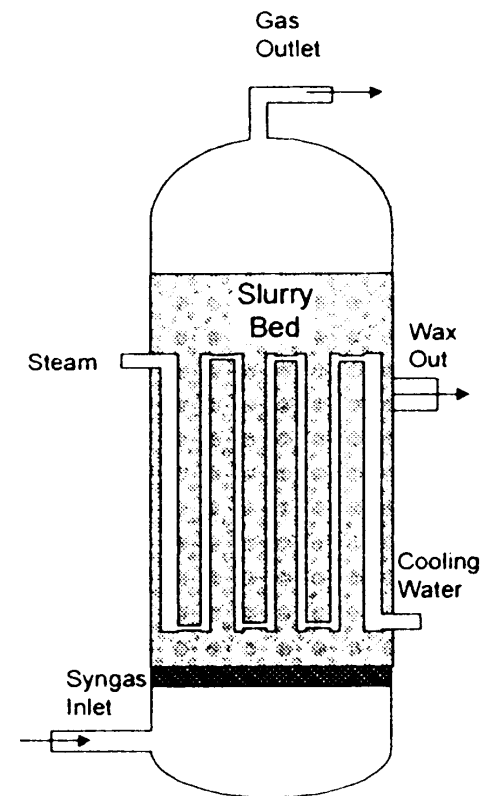
Fixed Fluidized Bed Reactor

- Replaced Sasol's circulating fluidized bed reactor
- Advantage
 - Have better thermal efficiency, a less severe temperature gradient, and a lower pressure drop than Synthol reactor
 - Lower operating cost
 - Greater flexibility in product distribution
 - Scale up option



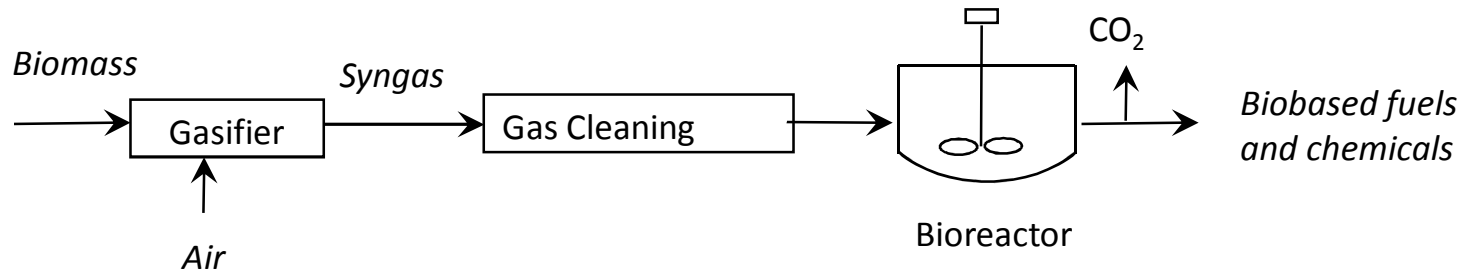
Low-Temperature Slurry Reactor

- Optimized high FT wax production with low methane production at low temperature
- Advantage
 - Better temperature control
 - Lower catalyst loading and attrition rates
 - Maintain higher average reaction temperature which lead to higher product conversion
 - 75% less expensive than complex tubular reactor
- Disadvantage
 - Difficult separation of catalyst from the FT waxes



Syngas Fermentation

- Traditional fermentations rely on carbohydrates as the source of carbon and energy in the growth of microbial biomass and the production of commercially valuable metabolites.
- Autotrophs use C_1 compounds as their sole source of carbon and hydrogen as their energy source
- Unicarbonotrophs use C_1 compounds as their sole source of both carbon and energy.
- Among suitable C_1 compounds are CO , CO_2 , and methanol (CH_3OH), all of which can be produced from thermochemical processing of biomass.
- Anaerobes offer the most energy efficient metabolic pathways: most of the chemical energy of the substrate appears in the products of fermentation.
- A number of microorganisms are able to utilize syngas for growth and production of hydrogen, alcohols, carboxylic acids, and esters.



Syngas Fermentation

- Advantages (compared to gasification biorefinery)
 - Biocatalysts tolerant to sulfur and chlorine contaminants
 - Flexibility in the pressures and CO/H₂ ratios employed
 - High selectivity in products produced
 - Genetic engineering can expand portfolio of products
- Disadvantages (compared to gasification biorefinery)
 - Low rates of gas-liquid exchange
 - Less developed technology



Brown, R. C. (2007) Hybrid thermochemical/biological processing, Applied Biochemistry and Biotechnology 137, 947-956.

Questions about Syngas Cleaning and Upgrading?

What makes syngas upgrading
inherently expensive?

Why do we worry about trace
contaminants in syngas?

Seems like wet scrubbers can eliminate most contaminants – why are alternatives to this simple technology sought ?

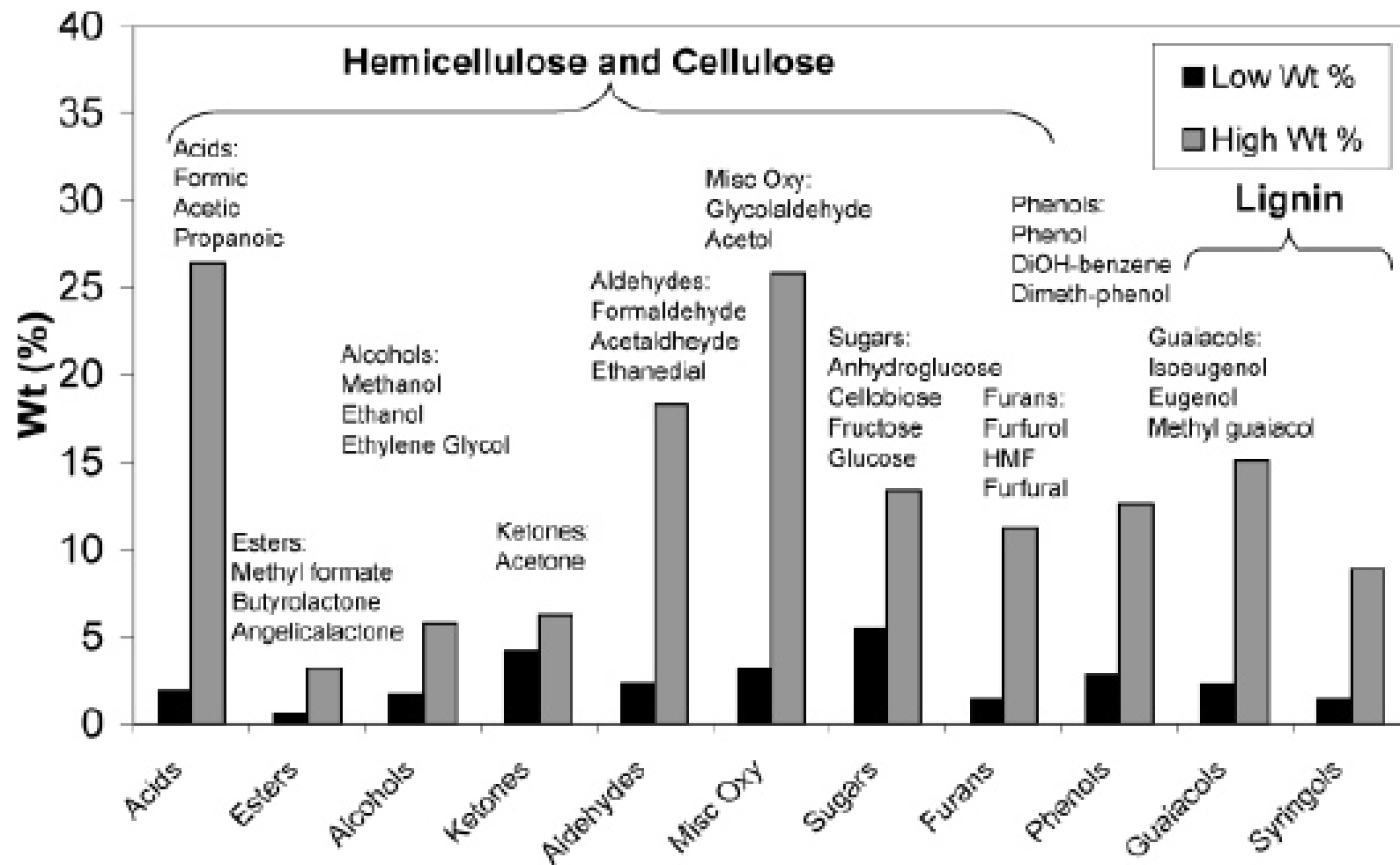
Can Fisher-Tropsch liquids supply
both gasoline and aviation fuel?

Bio-Oil Upgrading

Problems with Bio-Oil

- Low heating value
- Immiscible with hydrocarbon fuels
- Solids content
- High viscosity
- Incomplete volatility
- Chemical instability

What has to be upgraded in bio-oil?



Milne, T. A.; Agblevor, F.; Davis, M.; Deutch, S.; Johnson, D. In *Developments in Thermal Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie Academic and Professional: London, UK, 1997.

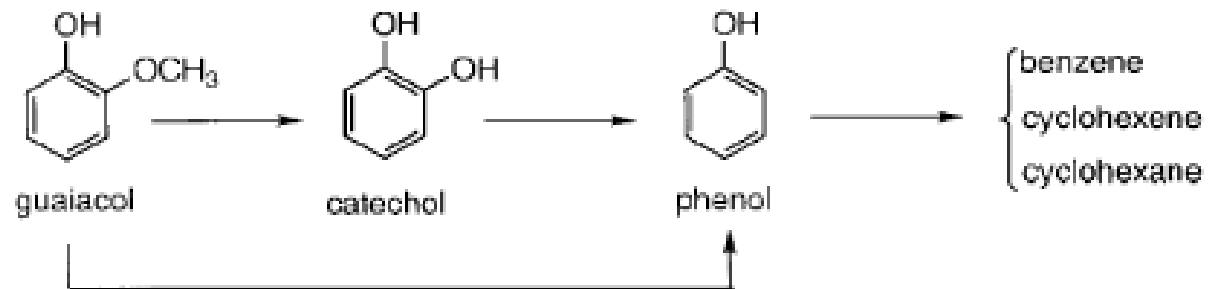
Pathways to Transportation Fuels

- Hydrodeoxygenation with hydrotreating catalysts
- Catalytic cracking over zeolites
- Steam reforming
- Gasification and catalytic upgrading of syngas
- Bio-oil fermentation

Hydrodeoxygenation (HDO)

- Catalysis-mediated removal of oxygen from bio-oil through reaction with hydrogen
 - Moderate temperatures (300 – 600 °C)
 - High partial pressures of hydrogen
 - Typically uses sulfided CoMo and NiMo-based catalysts similar to hydrotreating catalysts used to remove sulfur and nitrogen from petroleum
 - Water and saturated C-C bonds are formed

Model for
deoxygenating
lignin-derived
compounds



Hydrodeoxygenation (HDO)

- Advantages
 - High carbon efficiency
 - Technology compatible with existing petroleum hydrotreating technology
- Disadvantages
 - High hydrogen demand

Catalytic cracking over zeolites

- Zeolites: Crystalline microporous materials with well-defined pore sizes of 0.5-1.2 nm.
 - High surface areas in pores
 - Active (usually acidic) sites give them high catalytic activity
- Bio-oil upgrading over zeolite occurs at 350-500 °C at atmospheric pressure.
- Reactions include cracking, dehydration, deoxygenation, polymerization, and aromatization.

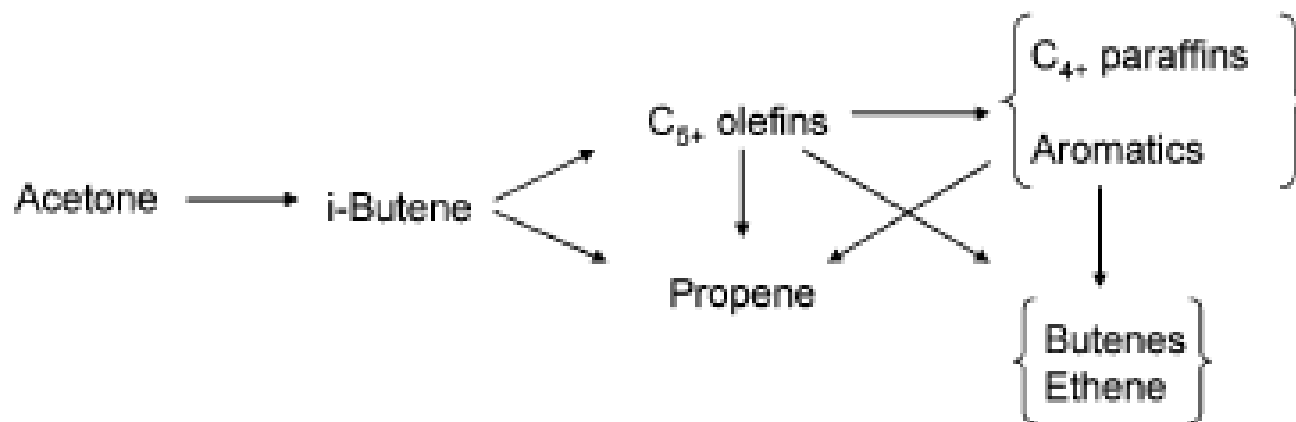
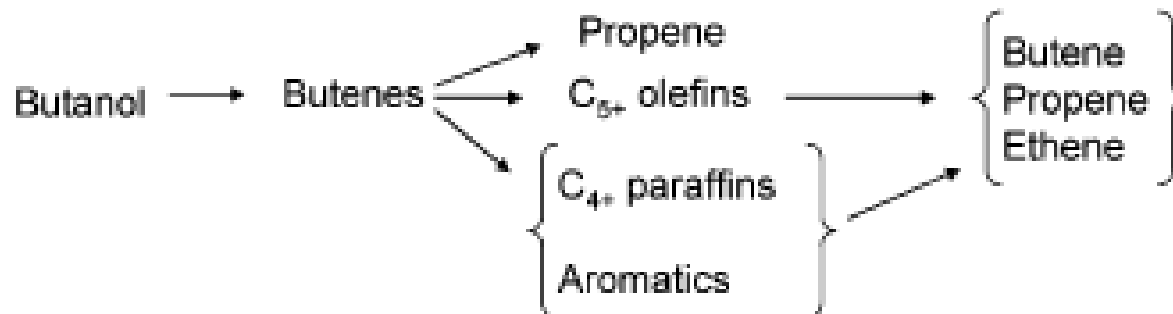


Bio-Oil Upgrading Results for Different Kinds of Zeolite Catalysts

	HZSM-5	silica–alumina (SiO ₂ –Al ₂ O ₃ ratio 0.14)	SAPO-5	SAPO-11	MgAPO-36
catalyst properties					
pore size (nm)	0.54	3.15	0.80	0.56	0.75
BET surface area (m ² /g)	329	321	330	205	196
acid area (cm ² /g) ^b	224.9		125.5	76.0	15.5
product yields (wt % of feed)					
organic liquid product	33.6	24.9	22.2	19.9	16.3
gas		6.1	10.3	12.2	10.1
coke + char ^c	20.5–30.2	40	30.0	25.5	38.7
tar ^d	0–4.1		9.5	11.9	10.1
aqueous fraction		25.0	24.2	26.3	23.1
composition organic liquid product (wt %)					
total hydrocarbons	86.7	45.6	51.0	56.8	51.6
aromatics	85.9 ^e	2.1	27.5	29.1	26.7
aliphatics	18.6	43.5	23.5	24.4	23.4

Source: Bakhshi and co-workers (1993, 1995, 1996)

Products of Zeolite Upgrading (Model Compounds)

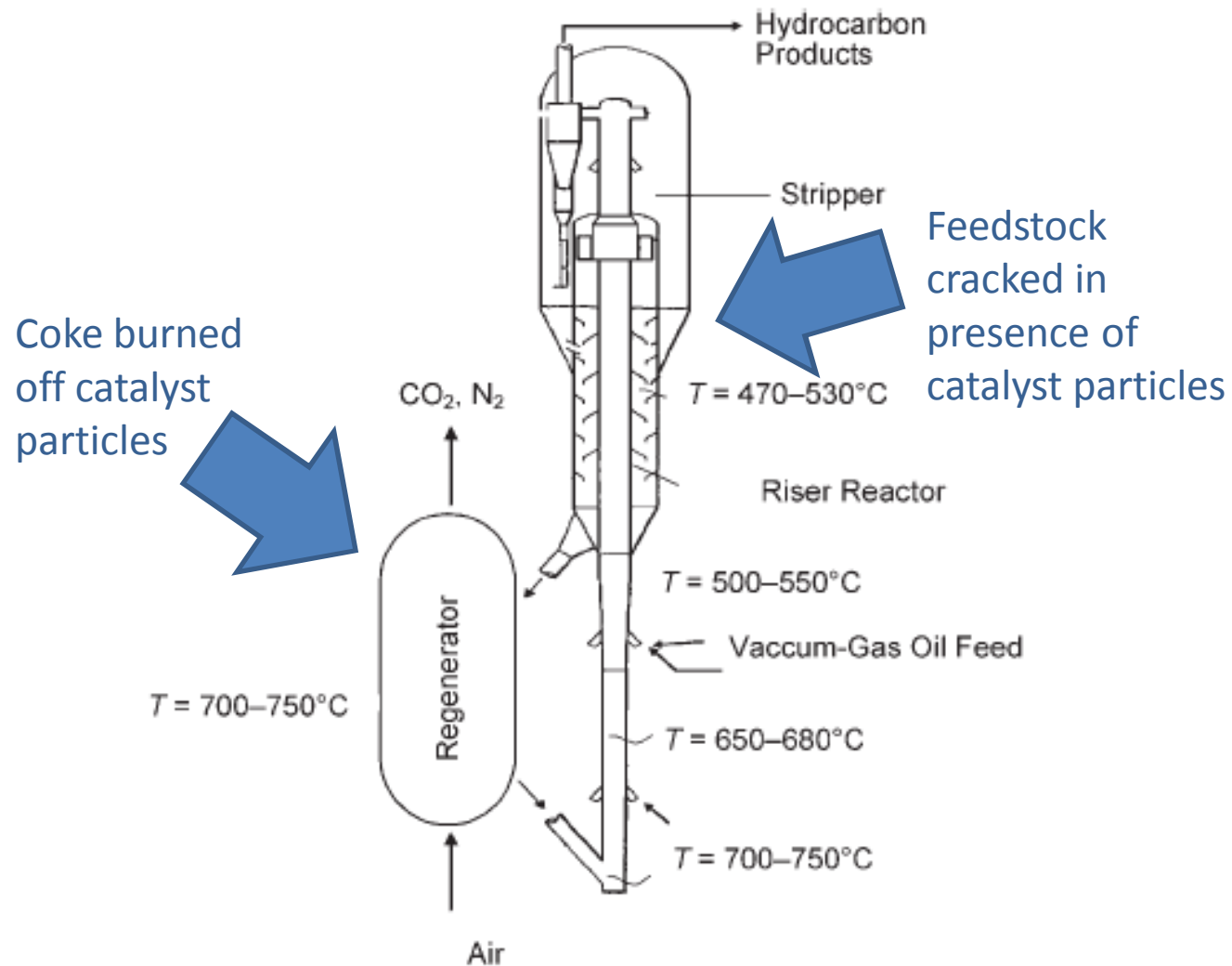


Gayubo et al. (2004) Ind. Eng. Chem. Res.

Catalytic cracking over zeolites

- Advantages
 - No hydrogen is used
 - Atmospheric operation is possible
- Disadvantages
 - Poor hydrocarbon yields
 - High coke yields

Fluidized Catalytic Cracker (FCC)



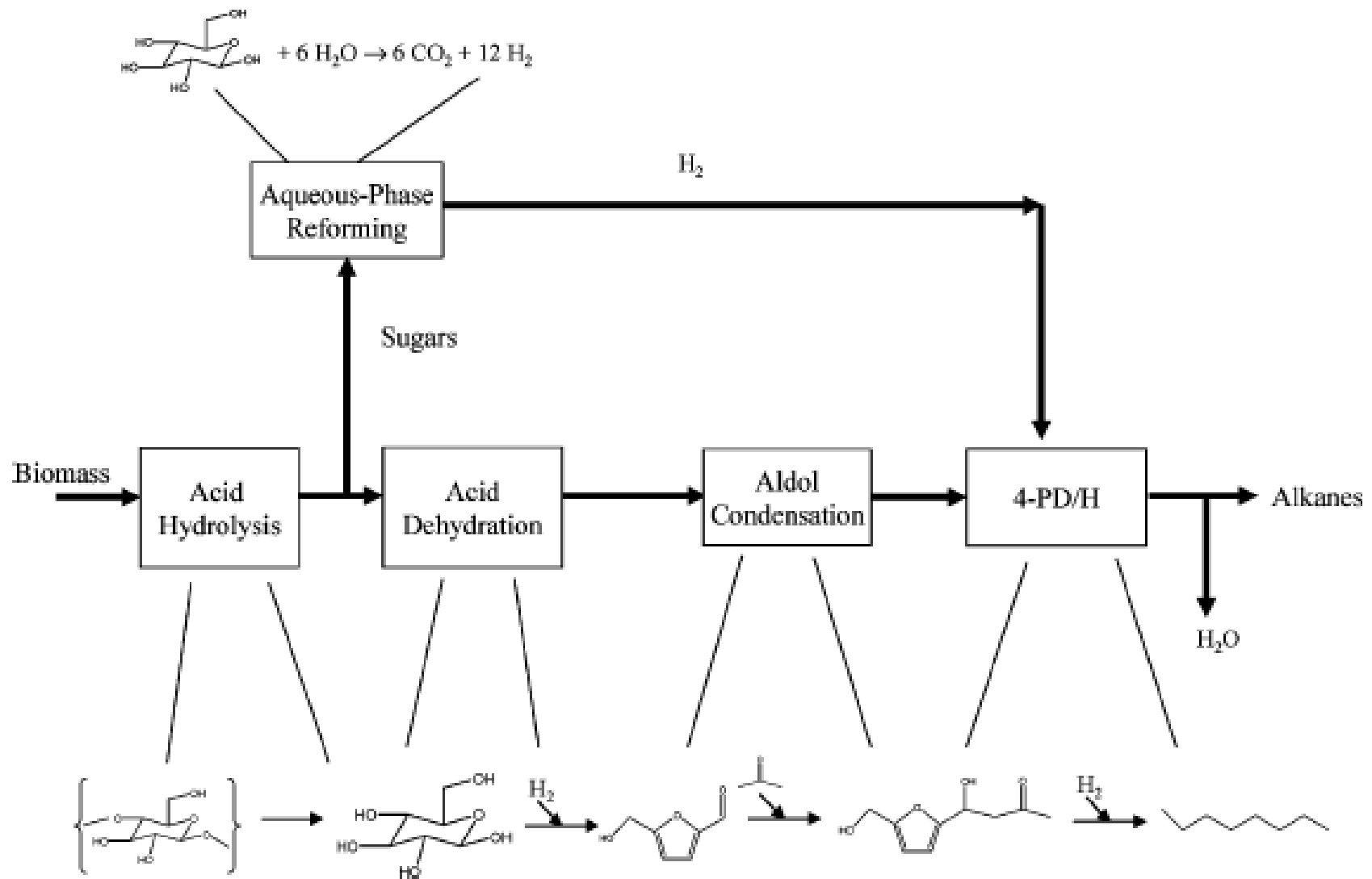
Steam Reforming

- Reaction of bio-oil with steam at 600 – 800 °C over Ni-based catalyst to produce hydrogen-rich syngas
- Important parameters
 - Temperature
 - Steam-to-carbon ratio
 - Catalyst-to-feed ratio
- Coking can be a major problem

Aqueous Phase Processing (APP)

- Furfural (from 5-carbon sugars) and 5-hydroxymethyl furfural (from 6-carbon sugars) are reacted in liquid water with heterogeneous (solid) catalyst at low temperatures (200 – 260 C) at 10-50 bar
- Originally developed to for aqueous phase reforming (APR) of carbohydrate into hydrogen
- Hydrocarbon formation is encouraged by addition of metal (Pt or Pd) and acid (SiO₂-Al₂O₃) sites to catalyze dehydration and hydrogenation reactions (ADP/H), respectively
- Hydrogen for ADP/H is provided by APR
- Bio-oil upgrading via APP is under development

Aqueous Phase Processing to Hydrocarbons

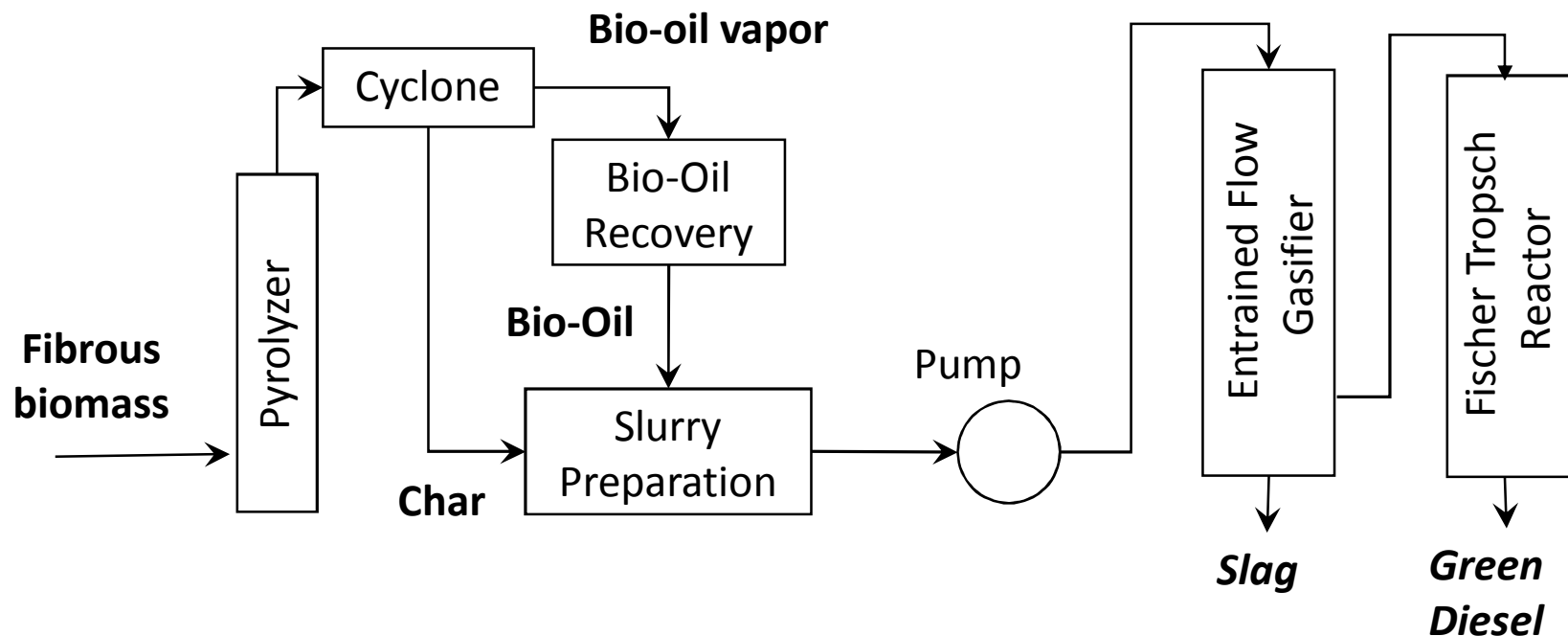


Aqueous Phase Processing to Hydrocarbons

- Advantages
 - Highly selective
 - Highly energy efficient
- Disadvantages
 - 5-hydroxymethyl furfural not efficiently produced from glucose
 - Hexane is major product, which is too volatile to be major fuel component
 - Has not been sufficiently developed to use real biomass feedstocks

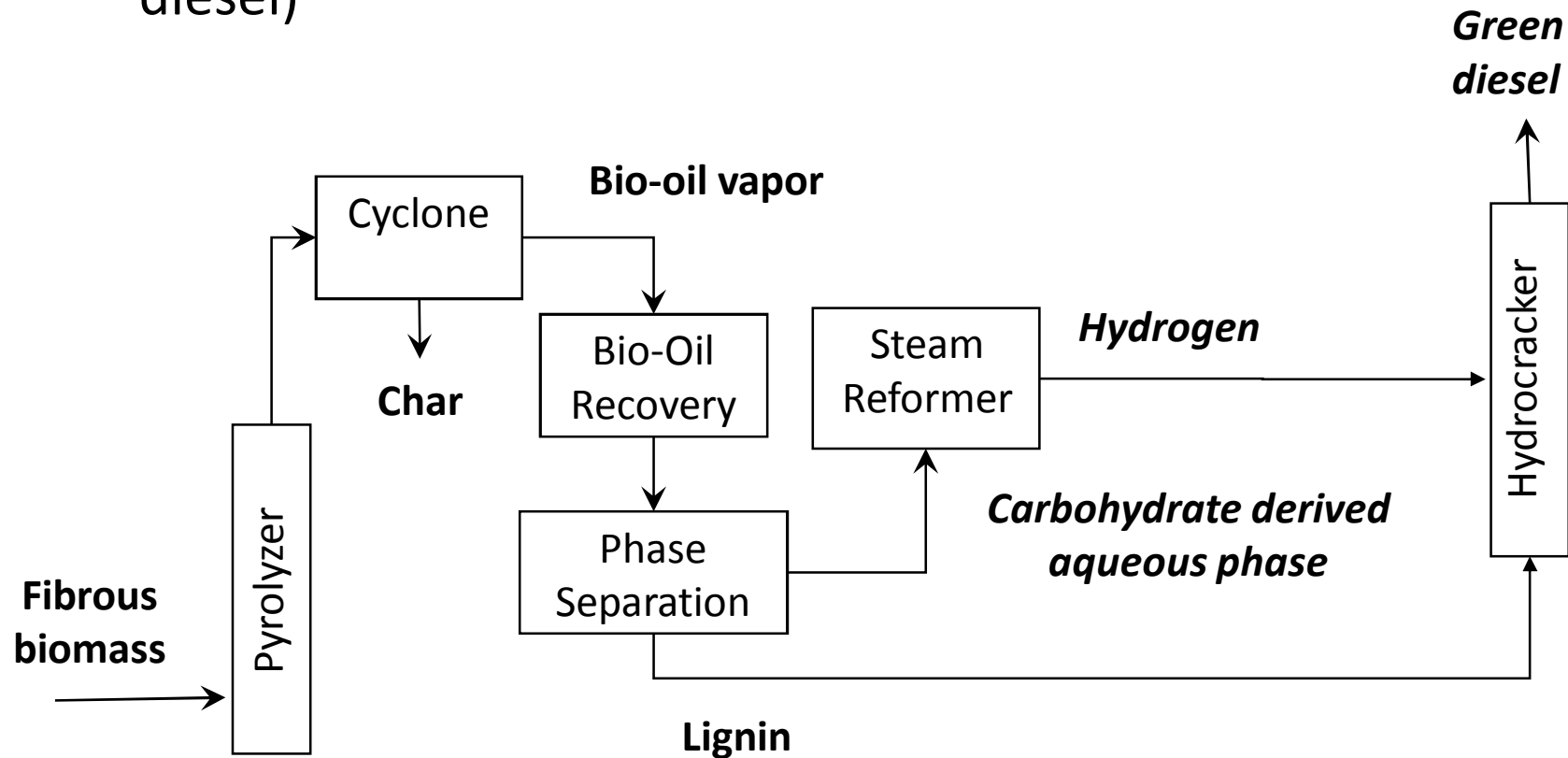
Bio-Oil Gasification

- Bio-oil and char slurried together to recover 90% of the original biomass energy
- Slurry transported to central processing site where it is gasified in an entrained flow gasifier to syngas
- Syngas is catalytic processed into green diesel (F-T liquids)

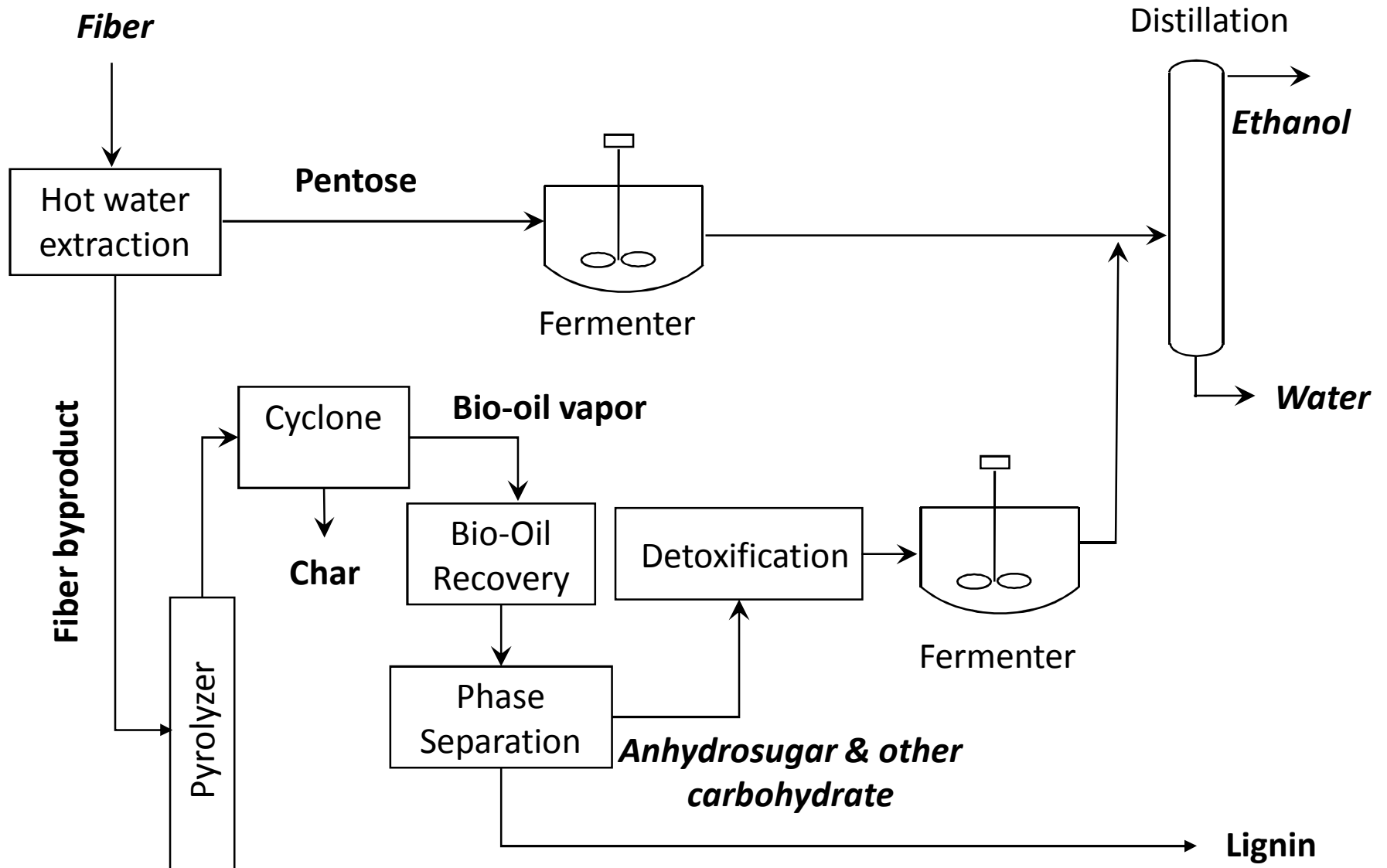


Bio-Oil Hydrocracking

- Directly converts biomass into liquid bio-oil (lignin, carbohydrate derivatives, and water) and char
- Bio-oil catalytically converted into hydrocarbon fuel (green diesel)



Bio-Oil Fermentation



Questions about Bio-Oil Upgrading?

Why does bio-oil need to be upgraded before it is used as transportation fuel?

How does hydrodeoxygenation
fundamentally different from
catalytic cracking?

If bio-oil and syngas are both “pyrolytic intermediates,” why would we consider gasifying bio-oil to produce biofuels?

What are some of the advantages of syngas fermentation compared to catalytic upgrading of syngas?