Gasification & Liquid Fuel Synthesis
Topics

• Principles of gasification
  ▪ Gasification vs. combustion
• Gasifier & associated process configurations
• Products from syngas
  ▪ Fisher-Tropsch (FT) Synthesis
Thermochemical Conversions

- Pyrolysis
  - Thermal conversion (destruction) of organics in the absence of oxygen
  - In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product
  - Possibility of chemical and food byproducts
- Gasification
  - Thermal conversion of organic materials at elevated temperature and reducing conditions to produce primarily permanent gases, with char, water, & condensables as minor products
  - Primary categories are partial oxidation and indirect heating
Distinction between produced gas

- **Town Gas**
  - Gas produced from coal, about 50% hydrogen, 3%-6% carbon monoxide, & the rest mostly methane & carbon dioxide

- **Synthesis Gas (Syngas)**
  - Mixture of hydrogen & carbon monoxide

- **Synthetic Natural Gas (SNG)**
  - Mixture of mostly methane from syngas

- **Producer Gas**
  - Partial oxidation of coke with humidified air

- **Water Gas**
  - 50/50 mixture of hydrogen & carbon monoxide
Principles of Gasification

- **Low Btu Gas**
  - Feed: Steam, Air
  - Contaminants
  - Gasification
  - Purification: CO, H₂, N₂

- **Medium Btu Gas**
  - Feed: Steam, Oxygen
  - Contaminants
  - Gasification
  - Purification: CO, H₂

- **Medium Btu Gas**
  - Feed: Steam, Heat
  - Contaminants
  - Gasification
  - Purification: CO, H₂

- **High Btu Gas**
  - Feed: Hydrogen, Heat
  - Contaminants
  - Hydro-Gasification
  - Purification: CO, H₂, CH₄

- **SNG (Synthetic Natural Gas)**
  - Feed: Steam
  - Contaminants
  - Catalytic Gasification
  - Purification & Separation: CH₄

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**COLORADO SCHOOL OF MINES**
**EARTH ENERGY ENVIRONMENT**

6
Simplistic view of gasification
Stoichiometric Considerations

- Oxygen consumed (exothermic)
  - Hydro-gasification

  $$C + O_2 \rightarrow CO_2$$

  $$C + \frac{1}{2}O_2 \rightarrow CO$$

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

- Water-gas shift reaction

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

- Water-gas reactions (endothermic)
  - Methanation reaction

  $$C + H_2O \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2$$

- Bourdourd reaction (endothermic)

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

- Hydro-gasification

  $$C + 2H_2 \rightarrow CH_4$$

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

  $$C + CO_2 \rightarrow 2CO$$
Gasification vs. Combustion

Biomass Gasification: Fundamentals & Applications
Gasification vs. Combustion

Biomass Gasification: Fundamentals & Applications
Coal is not the only feedstock
Example Thermochemical Conversion

Personal communication Ryan Davis, NREL. November 2009.
Gasifier configurations – Counter-Current Moving Bed

Fig. 2. Diagram of a generic moving bed gasifier

Gasifier configurations – Fluidized Bed

Fig. 3. Diagram of a generic fluidized bed gasifier

Gasifier configurations – Entrained Flow

Fig. 4. Diagram of a generic entrained flow gasifier

Direct vs. Indirect Gasification

Figure 2. Low-pressure direct gasifier.

Figure 3. Indirect gasifier.

SilvaGas Indirect Gasifier

Gas Cleanup Technologies

- Particulate removal
  - Cyclones
  - Wet scrubbing
- Gas conditioning
  - Tar removal/destruction
  - CO$_2$ & H$_2$S removal
    - Solvent systems – amines, Selexol, ...
IGCC – Integrated Gasification Combined Cycle
Syngas Products

- Hydrogen
- Methanol and its derivatives (NH₃, DME, MTBE formaldehyde, acetic acid, MTG, MOGD, TIGAS)
- Fischer Tropsch Liquids
- Ethanol
- Mixed alcohols
- Olefins
- Oxosynthesis
- Isosynthesis
Fischer-Tropsch for Liquid Fuel Synthesis

- Set of reactions that “recreates” linear alkanes from syngas

\[(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\]

- Distribution of compounds well described by Anderson-Schulz-Flory distribution

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

where \(\alpha\) represents chain growth probability
Fischer-Tropsch for Liquid Fuel Synthesis

- Chain growth probability shifts from light products to wax
Fischer-Tropsch for Liquid Fuel Synthesis

• History
  ▪ Original process commercialized in Germany in 1936. Used by Germany & Japan during World War II to produce substitute fuels
  ▪ Sasol. Largest scale implementation series of plants operated by Sasol in South Africa. Required during time of apartheid.
  ▪ Shell Middle Distillate Synthesis. 12,000 barrels per day Shell facility converts natural gas into low-sulfur diesel fuels and food-grade wax in Bintulu, Malaysia.
  ▪ Ras Laffan, Qatar. Based on the Sasol technology, using cobalt catalysts at 230°C. Includes "Dolphin Gas Project" plant, converting natural gas to petroleum liquids at a rate of 140,000 barrels/day, with additional production of 120,000 barrels of oil equivalent in natural gas liquids and ethane. Was scheduled to commission in 2010.
  ▪ Rentech.
    • Demonstration F-T plant Commerce City, CO. Commercial scale facilities had been planned for Rialto, CA, & Natchez, MS.
    • Abandoned projects 2012. Sold technology in 2013.
  ▪ Three GTL facilities proposed in US: Lake Charles, LA (large scale); Karns City, PA; Ashtabula, OH
    • December 2013 Shell cancelled plans for another facility in LA because of high capital costs & market uncertainties for natural gas & liquid product prices
Fischer-Tropsch Process Considerations

• Catalyst types
  ▪ HTFT (High-Temperature Fischer-Tropsch)
    • Iron-based catalyst
    • 330°C-350°C
    • Used extensively by Sasol in their Coal-to-Liquid (CTL) plants
  ▪ LTFT (Low-Temperature Fischer-Tropsch)
    • cobalt based catalyst
    • 250°C or less
    • Shell’s integrated Gas-to-Liquid (GTL) plant in Bintulu, Malaysia.

• Product types
  ▪ Predominantly straight-chain alkanes. Lesser amounts of 1-alkenes & alcohols.
  ▪ Properties best for distillate fuels (jet, diesel) & wax
    • Low octane gasoline. Isomerization required
    • May hydrocrack was for increased fuel production
Fischer-Tropsch Reactor Types

“High quality diesel via the Fischer-Tropsch process – a review”
M.E. Dry, Journal of Chemical Technology & Biotechnology, v 77, pp 43-50

Figure 1. Multitubular fixed bed FT reactor.

Figure 2. Fluidized bed FT reactors. A is a circulating fluidized bed (CFB) reactor. B is an ebulating or fixed fluidized bed (FFB) reactor. C is a slurry-phase bubbling-bed reactor. Types A and B are two-phase systems (gas and solid catalyst) while C has three phases present, gas passing through a liquid in which the solid catalyst particles are suspended. Note the diagrams are not drawn to the same scale. The CFB reactors are about three times higher than the FFB or slurry reactors.
Fischer-Tropsch Chain Growth & Kinetics

Initiation:

\[ \text{CO} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]

Chain growth and termination:

- For Co:
  \[ \text{rate} = k \frac{p_{\text{H}_2} p_{\text{CO}}}{(1 + b p_{\text{CO}})^2} \]

- For Fe:
  \[ \text{rate} = k \frac{p_{\text{H}_2} p_{\text{CO}}}{p_{\text{CO}} + a p_{\text{H}_2\text{O}}} \]

- Water slows down rate for iron-based catalysts

Figure 5. FT stepwise growth process. Note that no specific chemical mechanism is implied in the sequence presented.

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Fischer-Tropsch – More Than Alkanes

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Fischer-Tropsch Process Considerations

http://www.eia.gov/todayinenergy/detail.cfm?id=15071
Production of Diesel

Figure 8. Flow scheme of an LTFT process for diesel fuel production.

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Production of Gasoline, Diesel, & Chemicals

Figure 7. Flow scheme of an HTFT process producing gasoline, diesel and chemicals.

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