Fast Analysis of Syngas Using a Micro-Machined Gas Chromatograph System with a Thermal Conductivity Detector

Presented by Debbie Hutt
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Presentation Outline

- Introduction
- Syngas Composition
- Syngas Produced from Coal Gasification
  - Environmental Implications
  - Industry Example
- Syngas Produced from Natural Gas (Steam Methane Reforming)
  - Environmental Implications
  - Industry Example
- Gas Chromatography as an Analysis Option
- 3000 Micro GC Data and Repeatability
Introduction

- Syngas is an intermediate gas produced from:

1. Coal gasification, through pyrolysis to coke (destructive distillation), followed by:
   - $C + H_2O \rightarrow CO + H_2$
   - Combustion: $C + O_2 \rightarrow CO_2$
   - Gasification: $CO_2 + C \rightarrow 2CO$

2. Natural gas, through steam methane reforming (SMR)
   - SMR reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$
   - Recovery of additional hydrogen: $CO + H_2O \rightarrow CO_2 + H_2$

- Biomass can be either gasified or steam reformed
Syngas Composition

- Syngas contains:
  - Hydrogen (~50-70%)
  - CO (~25-50%)
  - CO₂ (~5-20%)
  - CH₄ (< 5%)
  - May also contain:
    - Nitrogen (~2-5%)
    - Ethane (C₂H₆, <1%)
    - Ethylene (C₂H₄, <1%)
    - Water (< 0.1%)
  - Possible “sour” components from gasification of coal:
    - H₂S (mid ppm, <1%)
    - COS (mid ppm, <1%)
Syngas Produced from Coal Gasification

- Industry example: Duke Energy Integrated Gasification Combined-Cycle (IGCC) Plant in Edwardsport, IN
- Driven by EPA standards for cleaner air
- Coal is converted to syngas, which is then introduced into turbines to produce electricity
  - More efficient than direct coal combustion
Coal Gasification Environmental Implications

- Provides 10x more electricity than a traditional energy plant with:
  - 70% lower sulfur dioxide, nitrogen oxides, and particulates
  - 30% less water consumption
  - Produces less solid waste

- The plant produces elemental sulfur and slag as byproducts, which can be sold for agricultural and constructional uses

- Displays a potential for carbon dioxide capture and storage
Coal Gasification – Duke Energy Plant

- GE Energy provides technology, such as gasification equipment, power generation and control equipment, and analytical services.
Syngas Produced from Natural Gas

- Steam methane reforming (SMR) is used to produce syngas from stranded (or associated) natural gas that would otherwise be wasted.

- Syngas can be converted, via the Fischer-Tropsch (FT) Process, to higher hydrocarbon synthetic fuels.

- Industry Example: Velocys, Inc. partnered with Oxford Catalysts, Plain City, OH.
SMR Environmental Implications

- Utilizes stranded (or associated) natural gas
  - Approximately 5 trillion cubic feet (TCF) of natural gas is not utilized each year worldwide
    - Equivalent of 500 million barrels of liquid fuel
  - The stranded gas can be:
    - Vented back into the atmosphere
      - Outlawed because methane has a global warming potential 21 times that of CO₂
    - Flared
      - Releases 200 million tons of CO₂ into the atmosphere
      - Banned in many countries
    - Re-injected into a reservoir
      - High cost
  - Converting stranded natural gas to liquid fuels is a greener option
SMR Environmental Implications

- Biomass can also be converted to liquid fuels
  - The US Department of Energy (DOE) estimates that there is enough domestic biomass to replace half of the petroleum-based distillate fuel demand in the US
  - Considered a renewable energy source
  - Sources of biomass include:
    - Municipal waste
    - Forest residues
    - Agriculture residues
    - Construction and demolition wasters
Natural Gas to Synthetic Liquid Fuels

- **Steps to produce synthetic fuels from natural gas:**
  1. Natural gas enters a SMR reactor to generate syngas
  2. Syngas is cooled, and water is removed
  3. Syngas composition is analyzed
  4. Syngas is fed to another reactor and passed over a catalyst to produce synthetic liquid fuels (FT Process)
Steam Methane Reforming

- Natural gas is mixed with steam and passed over a catalyst to break off hydrogen molecules to generate CO and H₂
  - Highly endothermic process
- Excess methane and hydrogen is burned in air to produce heat
Syngas Conversion to Synthetic Liquid Fuels

- Once through SMR, water and heat are removed from syngas
- Syngas is converted to liquid fuels by using the FT Process based on the following reaction:

\[ n\text{CO} + (2n + 1)\text{H}_2 \rightarrow C_n\text{H}_{2n+1} + \text{H}_2\text{O} \]

- The cooled gas reacts with a specially designed catalyst to create longer chain hydrocarbons such as:
  - Paraffin waxes
  - Diesel
  - Jet fuel
The Need for Precise Analysis

- **Requirements:**
  - Separation and quantification of individual syngas components at the percent level
  - A total un-normalized concentration (mole %) ranging from 97 to 103%
  - Analysis of results to optimize the system and maximize productivity
    - How much methane is being converted to H₂?
    - How much CO is being converted to CO₂?
  - Identification of possible byproducts
    - “Sour” components such as H₂S and COS
    - Ethylene, ethane, nitrogen
Gas Chromatography as an Analysis Option

- Gas chromatography (GC) technology provides separation and analysis capabilities for all syngas components

- GC software provides users with component composition information

- **Thermal conductivity detectors (TCD)** are universal detectors that provides required sensitivity with simple operation

- TCDs enhance the speed of analysis
  - Syngas monitoring requires close to real time analysis
  - A fast GC instrument like the 3000 Micro GC provides the necessary means
    - Runs are typically less than 2 minutes
Instrumentation

- INFICON 3000 Micro GC (MGC)
  - MEMS based TCDs and injectors

- 2-Channel Configuration
  - Each channel contains an injector, column, and TCD detector
  - Channel A: 10m Molsieve 5Å
    - Backflush injector to prevent column contamination and provide excellent precision
    - Argon carrier gas
  - Channel B: 8m PLOT Q (Polystyrenedivinylbenzene)
    - Fixed volume injector to provide excellent precision
    - Helium carrier gas

- 3000 Micro GC highlights:
  - Lightweight
  - Fast
  - Precise
Calibration Gas Standard - SMR

- Calibration gas was supplied by Velocys, Inc.
- Ten runs were conducted sequentially at the Velocys, Inc. facility in Plain City, OH

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>60.02</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.010</td>
</tr>
<tr>
<td>CH₄</td>
<td>5.800</td>
</tr>
<tr>
<td>CO</td>
<td>24.00</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.000</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>2.000</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1.000</td>
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3000 Micro GC Method Parameters
# Syngas Repeatability Channel A – 10 Runs

<table>
<thead>
<tr>
<th>Channel</th>
<th>Number of Analyte</th>
<th>Compound</th>
<th>Retention Time</th>
<th>Area % RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Hydrogen</td>
<td>43.90</td>
<td>0.179</td>
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<tr>
<td>1</td>
<td>2</td>
<td>Nitrogen</td>
<td>59.40</td>
<td>0.510</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Methane</td>
<td>73.78</td>
<td>0.245</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>CO</td>
<td>88.84</td>
<td>0.212</td>
</tr>
</tbody>
</table>
## Syngas Repeatability Channel B – 10 Runs

### Table 1: Analyte Retention Times and Area %RSD

<table>
<thead>
<tr>
<th>Channel</th>
<th>Number of Analyte</th>
<th>Compound</th>
<th>Retention Time</th>
<th>Area %RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5</td>
<td>CO$_2$</td>
<td>24.42</td>
<td>0.033</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Ethylene</td>
<td>29.60</td>
<td>0.063</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>Ethane</td>
<td>33.76</td>
<td>0.084</td>
</tr>
</tbody>
</table>
Syngas Repeatability – 10 Runs Overlaid
Calibration Gas Standard - Tail Gas Combustion

- The 3000 Micro GC can also analyze the tail gas stream for heat generating combustion

- Method parameters are identical to SMR

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>4.878</td>
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<tr>
<td>Oxygen</td>
<td>3.383</td>
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<tr>
<td>Nitrogen</td>
<td>83.652</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.476</td>
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<tr>
<td>CO</td>
<td>5.062</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.506</td>
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</table>
### Combustion Gas Repeatability Channel A – 4 Runs

<table>
<thead>
<tr>
<th>Channel</th>
<th>Number of Analyte</th>
<th>Compound</th>
<th>Retention Time</th>
<th>Area %RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Hydrogen</td>
<td>44.10</td>
<td>0.146</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>Oxygen</td>
<td>51.58</td>
<td>0.676</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Nitrogen</td>
<td>59.42</td>
<td>0.034</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>Methane</td>
<td>74.38</td>
<td>0.646</td>
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<tr>
<td>1</td>
<td>5</td>
<td>CO</td>
<td>91.24</td>
<td>0.589</td>
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</table>
## Combustion Gas Repeatability Channel B– 4 Runs

![Graph of TCD Channel B](image)

<table>
<thead>
<tr>
<th>Channel</th>
<th>Number of Analyte</th>
<th>Compound</th>
<th>Retention Time</th>
<th>Area % RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6</td>
<td>CO₂</td>
<td>24.76</td>
<td>0.233</td>
</tr>
</tbody>
</table>
Combustion Gas Repeatability – 4 Runs Overlaid
Conclusion

- Syngas is an intermediate gas in a series of reactions to generate power or fuel

- GC technology offers superior analysis for syngas

- Within 2 minutes, samples are separated and quantified to assist operators in maximizing the efficiency of their technology using the 3000 Micro GC
  - An RSD of less than 0.7% can be achieved for all syngas and combustion gas components
References

- **IGCC at a Glance.** 2011.  

- **Edwardsport Integrated Gasification Combined Cycle (IGCC) Station.** 2011.  


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Questions?