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

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Presentation Outline

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- Syngas Composition
- Syngas Produced from Coal Gasification
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- Syngas Produced from Natural Gas (Steam Methane Reforming)
  - Environmental Implications
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- 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:** $CH_4 + H_2O \rightarrow CO + 3\ H_2$
     - **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%)
  - CO_2 (~5-20%)
  - CH_4 (< 5%)
  - May also contain:
    - Nitrogen (~2-5%)
    - Ethane (C_2H_6, <1%)
    - Ethylene (C_2H_6, <1%)
    - Water (< 0.1%)
  - Possible "sour" components from gasification of coal:
    - H_2S (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

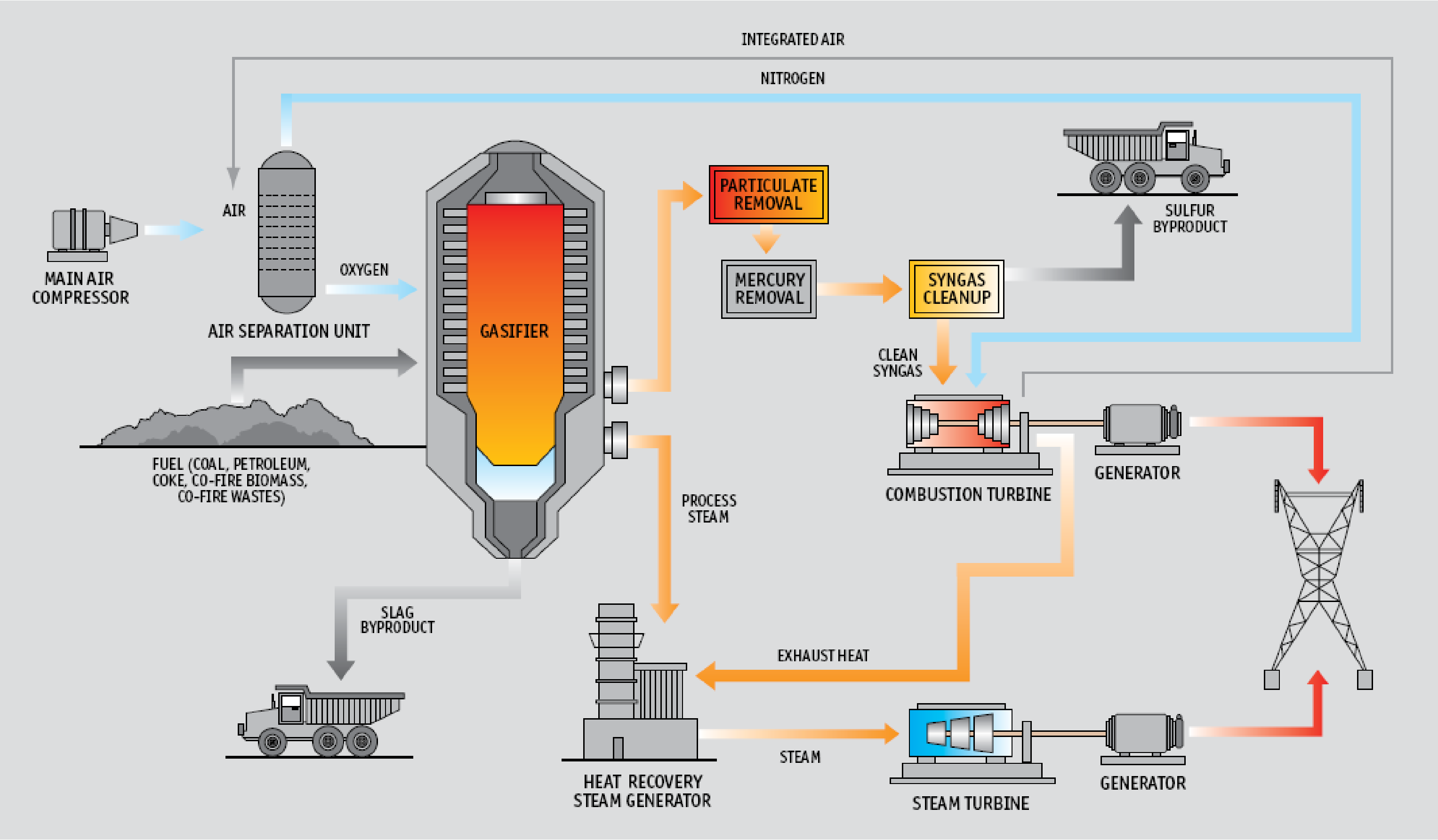
- The plant produces elemental sulfur and slag as byproducts, which can be sold for agricultural and constructional uses

- 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

GE Energy



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 CO_2
    - Flared
      - Releases 200 million tons of CO_2 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

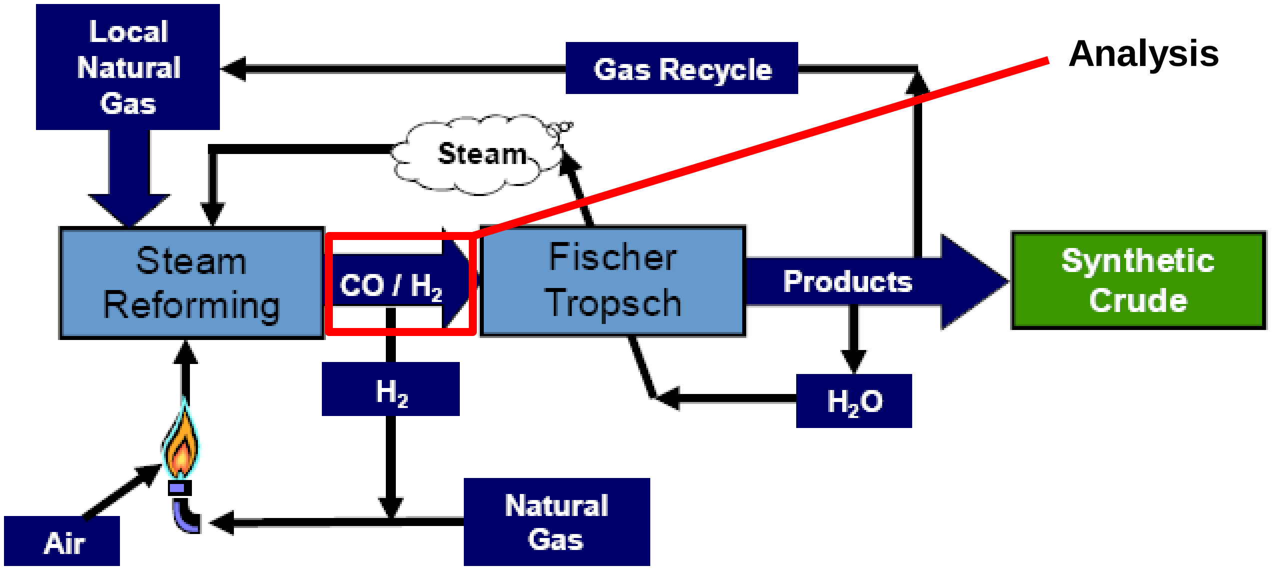
- **Biomass can also be converted to liquid fuels**
  - The US Department of Energy (DOE) estimates that there is enough domestic biomass to replace half of the petroleum-based distillate fuel demand in the US
  - Considered a renewable energy source
  - Sources of biomass include:
    - Municipal waste
    - 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 H_2
  - 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:

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+1} + H_2O$$

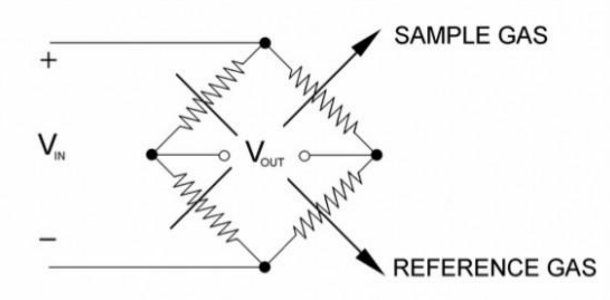
- The cooled gas reacts with a specially designed catalyst to create longer chain hydrocarbons such as:
  - Paraffin waxes
  - Diesel
  - Jet fuel

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 H_2?
    - How much CO is being converted to CO_2?
  - Identification of possible byproducts
    - “Sour” components such as H_2S 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

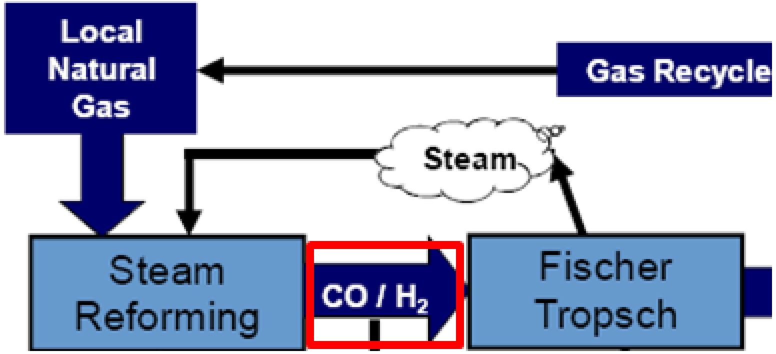
- INFICON 3000 Micro GC (MGC)
  - MEMS based TCDs and injectors

- 2-Channel Configuration
  - Each channel contains an injector, column, and TCD detector
  - Channel A: 10m Molsieve 5Ǻ
    - 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

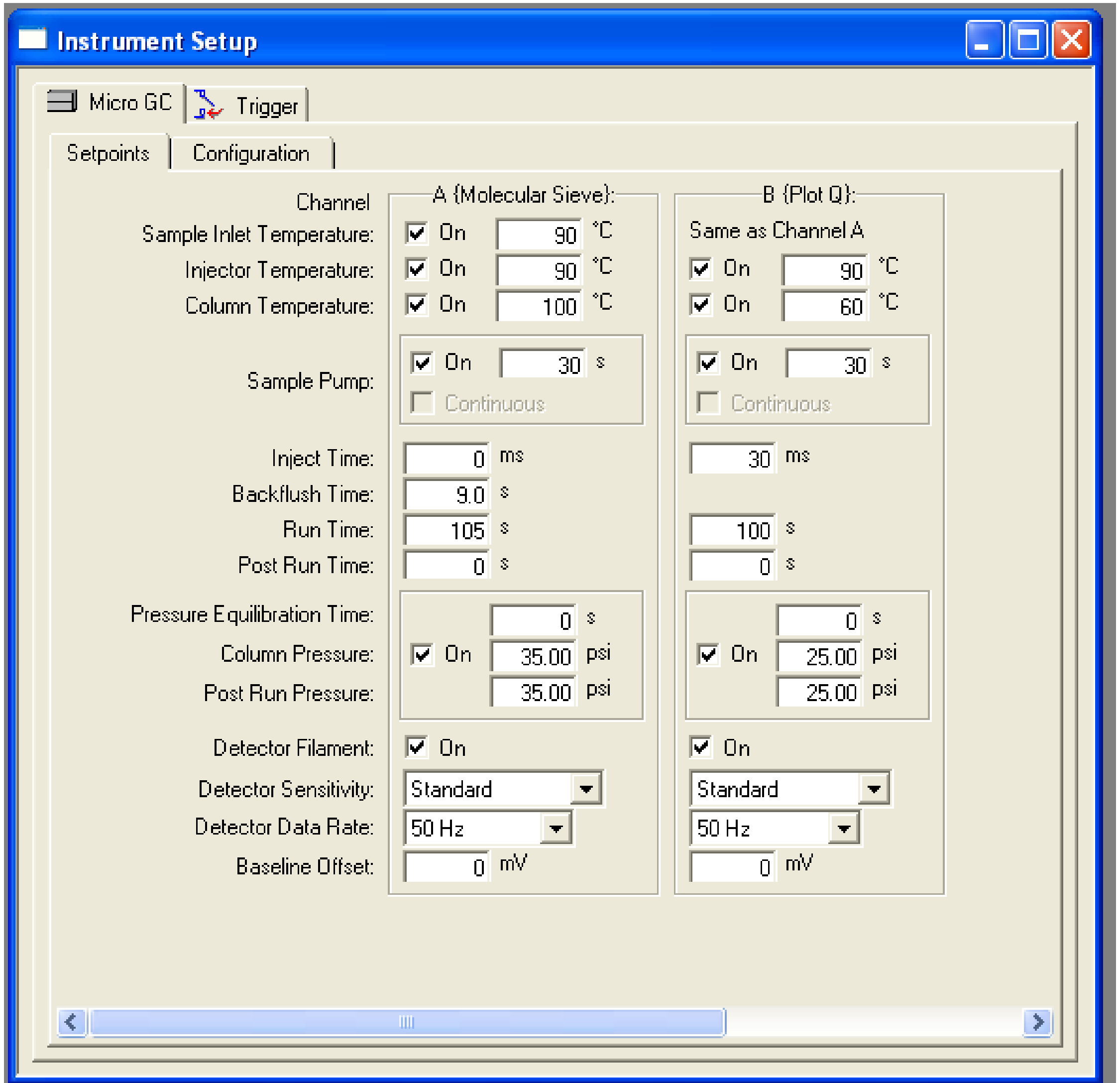
Calibration Gas Standard - SMR

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

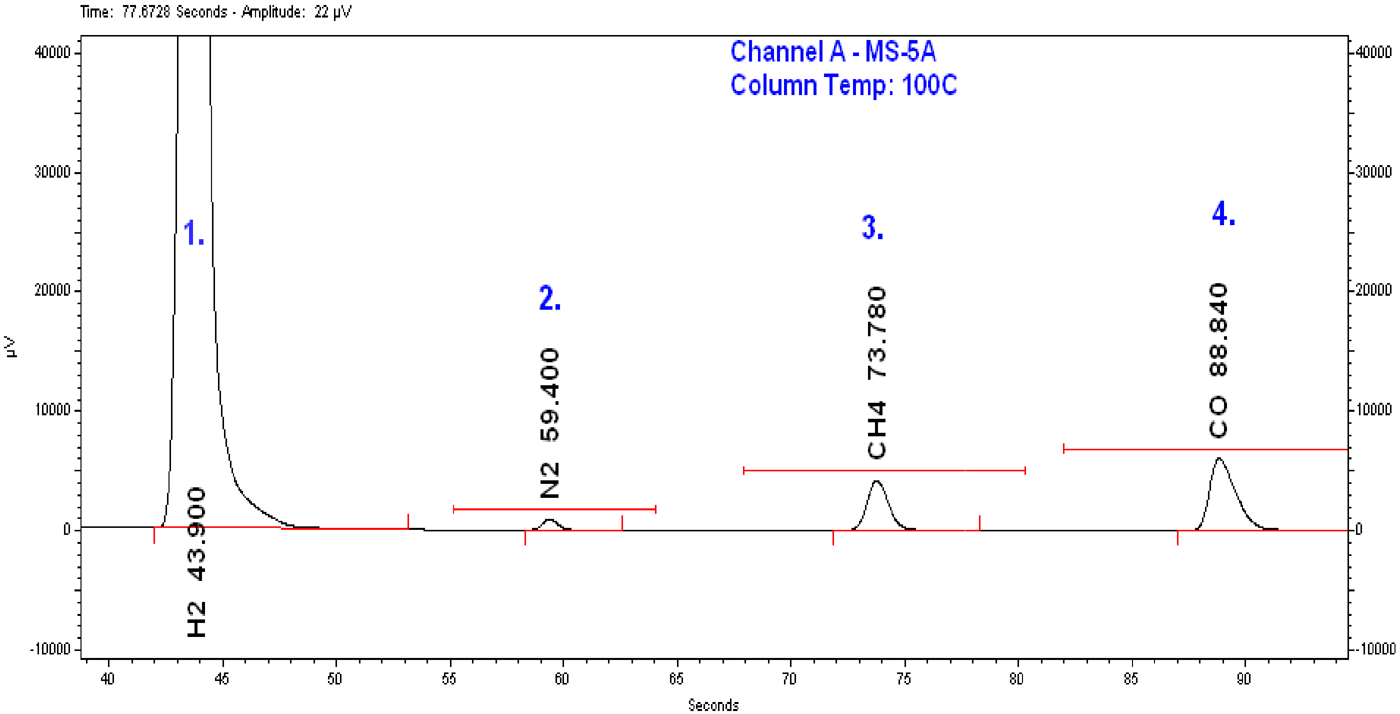


Component	Mol %
Hydrogen	60.02
Nitrogen	2.010
CH_4	5.800
CO	24.00
CO_2	5.000
C_2H_4	2.000
C_2H_6	1.000

3000 Micro GC Method Parameters

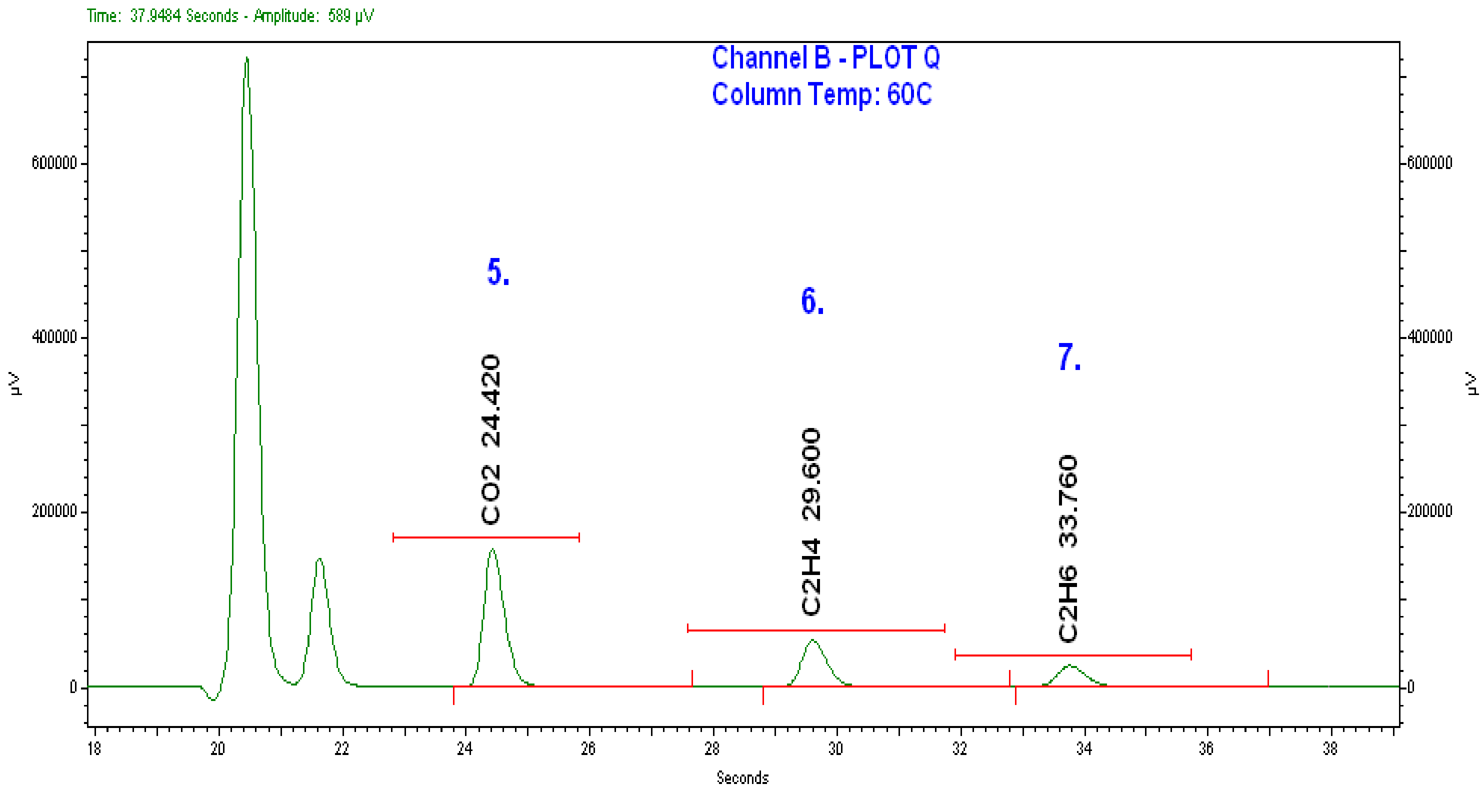


Syngas Repeatability Channel A – 10 Runs



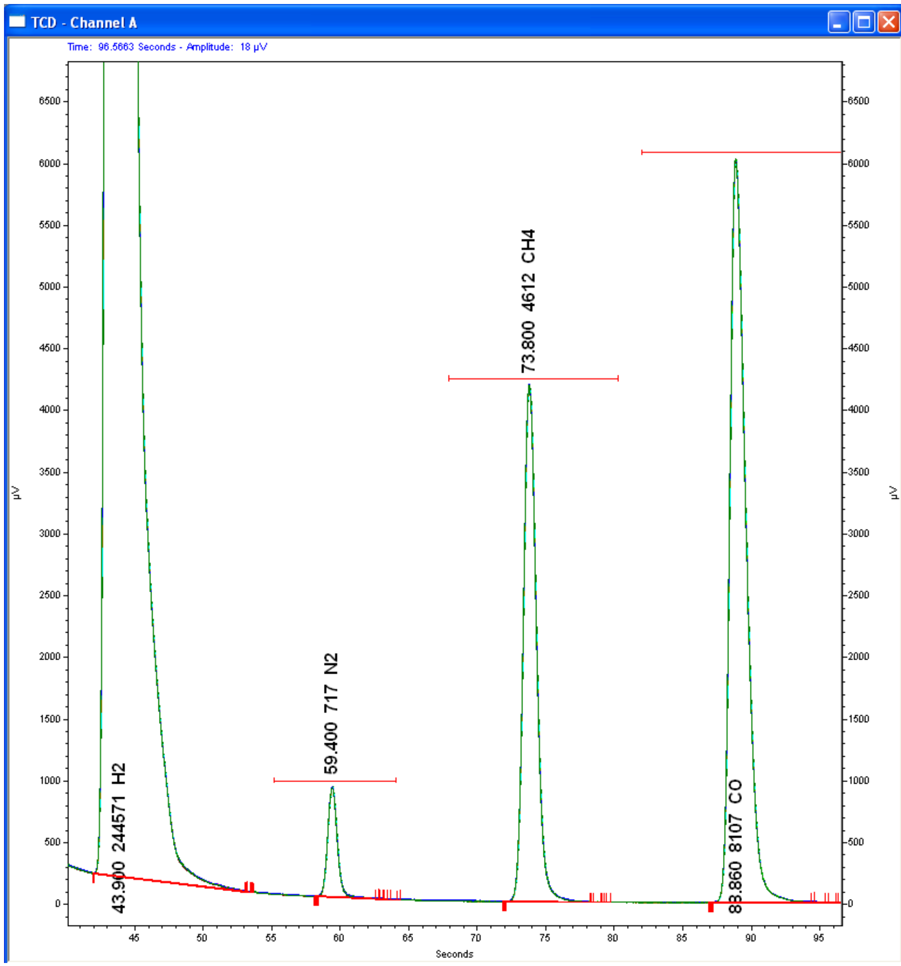
Channel	Number of Analyte	Compound	Retention Time	Area %RSD
1	1	Hydrogen	43.90	0.179
1	2	Nitrogen	59.40	0.510
1	3	Methane	73.78	0.245
1	4	CO	88.84	0.212

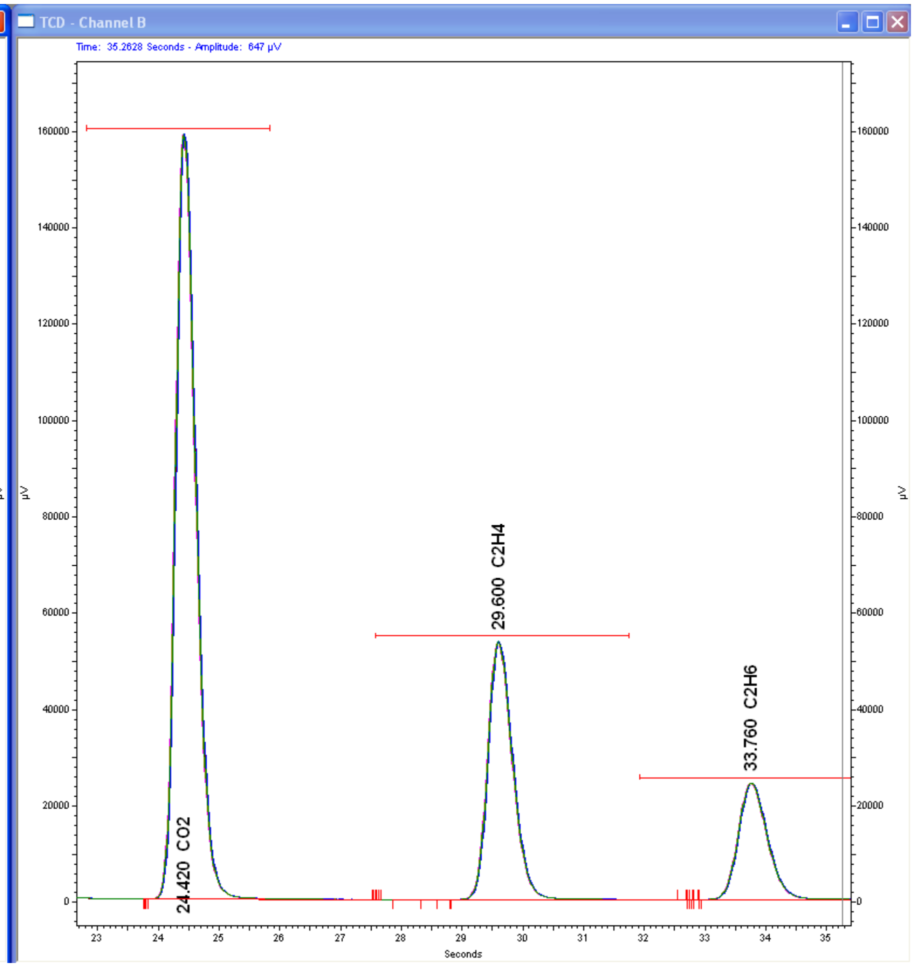
Syngas Repeatability Channel B – 10 Runs



Channel	Number of Analyte	Compound	Retention Time	Area %RSD
2	5	CO_2	24.42	0.033
2	6	Ethylene	29.60	0.063
2	7	Ethane	33.76	0.084

Syngas Repeatability – 10 Runs Overlaid



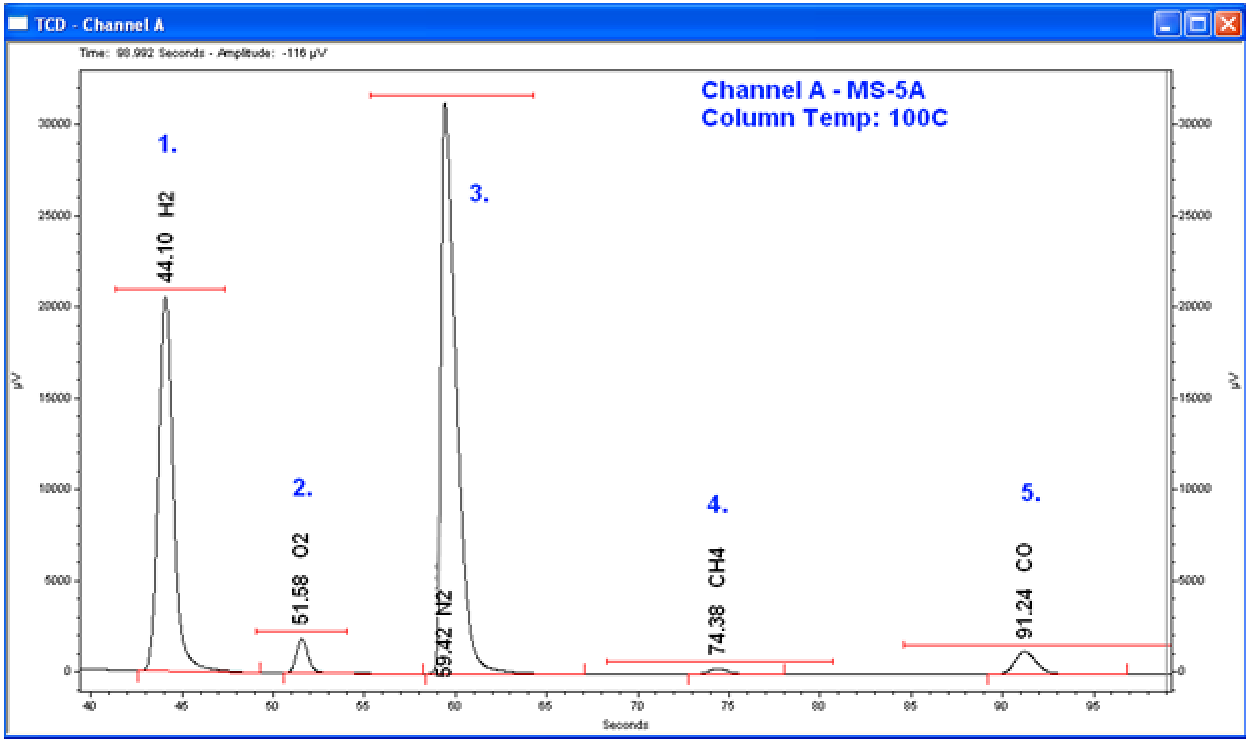


Calibration Gas Standard - Tail Gas Combustion

- **The 3000 Micro GC can also analyze the tail gas stream for heat generating combustion**
- **Method parameters are identical to SMR**

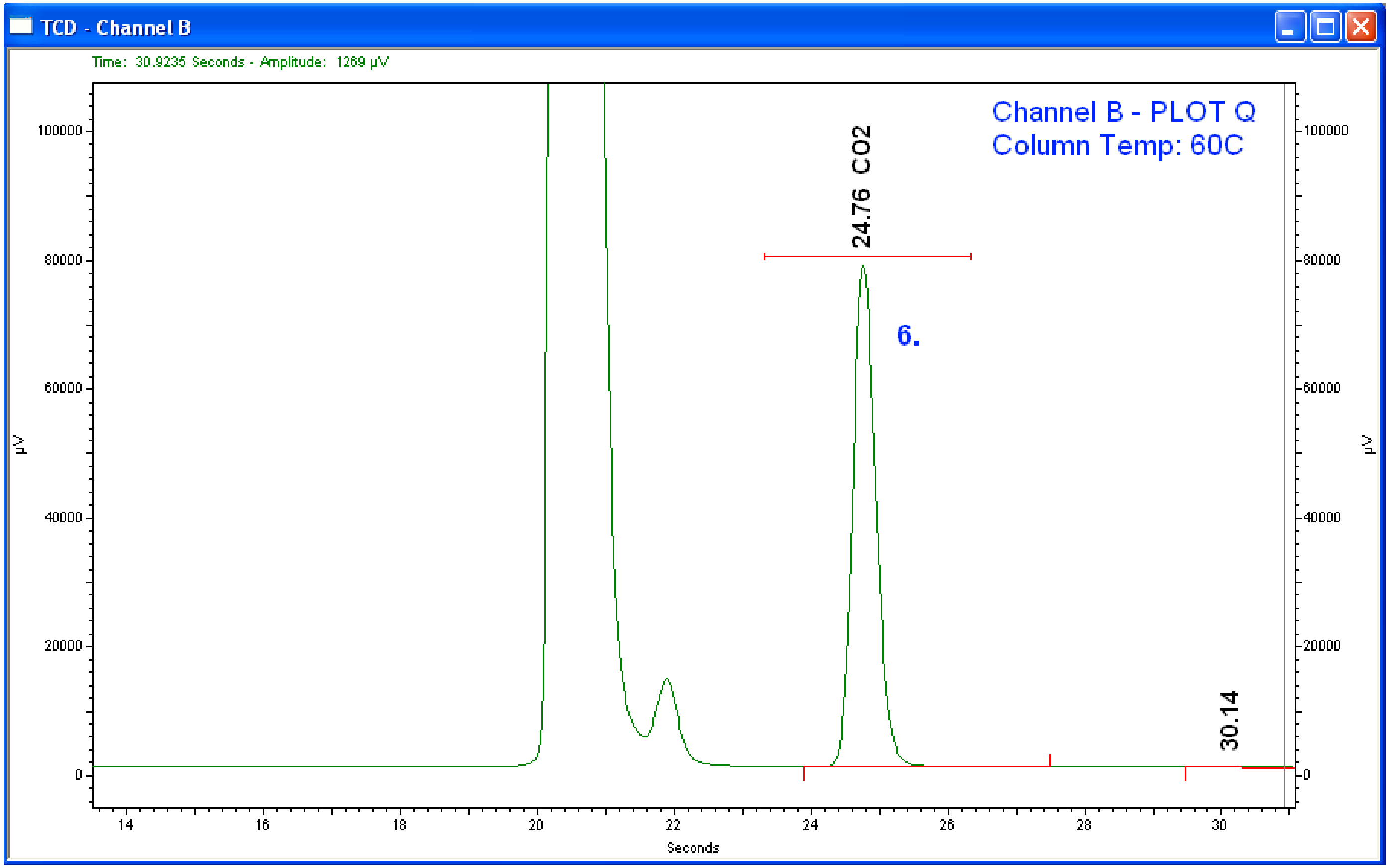
Component	Mol %
Hydrogen	4.878
Oxygen	3.383
Nitrogen	83.652
CH_4	0.476
CO	5.062
CO_2	2.506

Combustion Gas Repeatability Channel A– 4 Runs



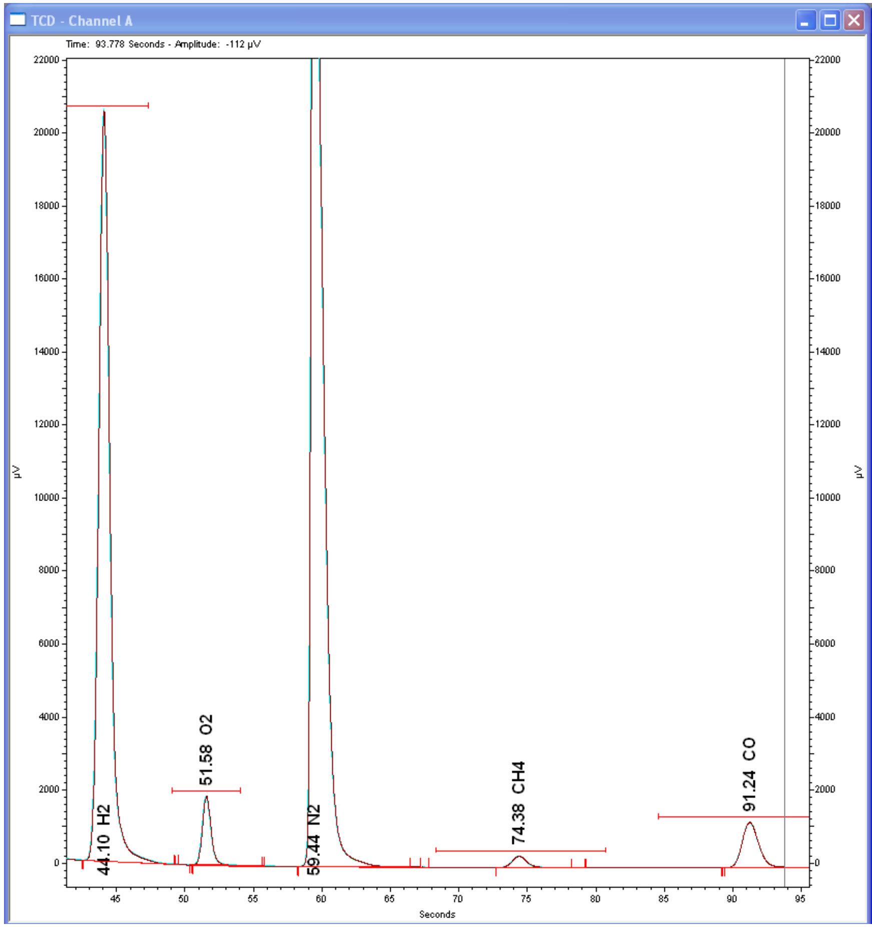
Channel	Number of Analyte	Compound	Retention Time	Area %RSD
1	1	Hydrogen	44.10	0.146
1	2	Oxygen	51.58	0.676
1	3	Nitrogen	59.42	0.034
1	4	Methane	74.38	0.646
1	5	CO	91.24	0.589

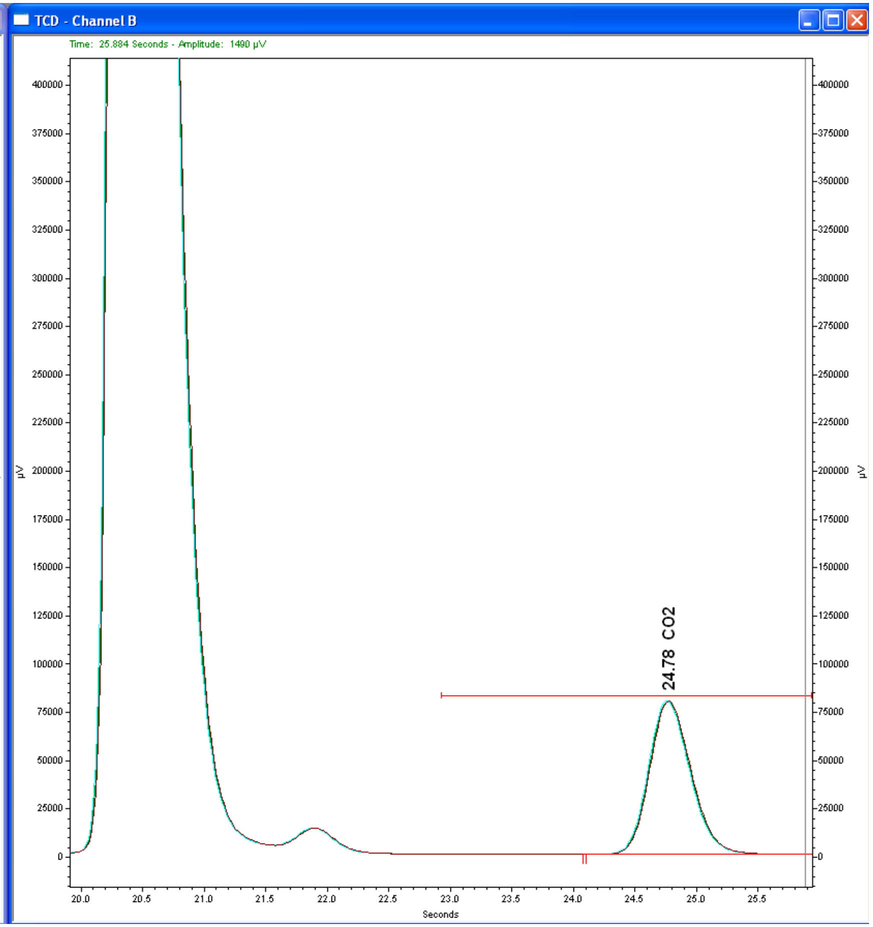
Combustion Gas Repeatability Channel B– 4 Runs



Channel	Number of Analyte	Compound	Retention Time	Area %RSD
2	6	CO_2	24.76	0.233

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, sample 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

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