

**IEA Bioenergy Agreement: 2007-2009**  
**Task 33: Thermal Gasification of Biomass**  
**Fall 2007 Meeting**  
**24 to 26, October 2007, ECN, Petten, Netherlands**

**Summary of Workshop (WS) on “Procedures/Guidelines for BMG synthesis gas characterisation”**

by

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**Programme:**

Characterization of Synthesis Gas for Conversion to Fuels and Chemicals– Poul Hojlund Nielsen, Haldor Topsoe, DK

Protocol for Synthesis Gas Characterization at NREL- Steve Deutch, NREL, USA

Synthesis gas Characterization at TUV-FICFB Demonstration BMG Plant at Güssing – Michael Fuchs, TUV, AT

Synthesis Gas Characterization for MeOH and SNG Production – Serge Biollaz, PSI, CH

Characterization of High-temperature Synthesis Gas –Hans Leibold, ITC, DE

Synthesis Gas Characterization for Minor and Trace Contaminants –Bill Farthing, GTI, USA

Synthesis Gas Characterization at VTT laboratories and test facilities. – Matti Reinikainen, VTT

Characterization of HCs in Synthesis Gas, Truls Liliedahl, KTH, SE

On-site/on-line Measurement of Synthesis Gas Properties, Berend Vreugdenhil, ECN

The WS was inaugurated by Mr. Jaap Kiel, Research Manager, ECN with an opening presentation on “Future of Biomass Energy in The Netherlands.” ECN hosted the WS

**Summary of Overview on Synthesis Gas Reactions:**

The presentation by Haldor Topsoe gave an overview about the different possible synthesis gas reactions and the known raw gas contaminants that poison the catalysts.

At present, industrial scale synthesis gas is produced primarily from natural gas or coal in different types of reformers or gasifiers. The type of fuel and reformer and the reformer operating conditions will influence the raw synthesis gas composition and especially the H<sub>2</sub>:CO ratio.

An overview of the gas composition of selected reformers and gasifiers is given in the following table:

**Table 1: Major Components of Synthesis Gas types from Selected Gasifiers and Reformers**

Synthesis Gas	Steam Ref	ATR	Dry Coal	Slurry	Biomass
H <sub>2</sub>	75%	66%	27%	36%	15-35%
CO	15%	27%	68%	47%	20-45%
CO <sub>2</sub>	8%	7%	3%	17%	12-25%
CH <sub>4</sub>	2%	-	-	- *)	0.4-16%

\*) E-Gas claims that they can go to high CH<sub>4</sub> (-7%)

There are several commercial synthesis gas processes. The most important are production of ammonia, hydrogen, and methanol.

Haldor Topsoe provides the following synthesis gas conversion processes:

- Ammonia
- Hydrogen

- Methanol
- Formaldehyde
- DME
- SNG
- TIGAS

In these, catalysts normally have useful lives of 2 – 5 years. The challenge for development of synthesis gas conversion with any new catalyst is the prevention of deactivation. Not only poisons, but also temperature distribution, hot spots, heating up rate, and pre-treatment / reduction can reduce the lifetime of a catalyst.

The most important poisons mentioned by Haldor Topsoe are:

- Sulphur compounds: causes deactivation of catalyst active centres
- Halogens: causes corrosion of catalysts
- Nitrogen compounds: causes amine formation (e.g. in methanol synthesis) and adds to smell to the product
- Tars: coat and cover catalysts by gum formation on the surface

The remainder of Workshop presentations gave an overview of the different gas cleaning methods and about the different analytical methods employed to characterise synthesis gas. An overview of the different analytical methods is given below:

In principle there are two different ways to analyse synthesis gas (GTI):

- Offline (Batch sampling) – *Take the sample to the lab* – i.e. collect a sample of gas in a bomb or series of impingers and deliver the sample to an analytical lab for subsequent analysis.
- On-line (Continuous sampling) – *Take the lab to the sample* – i.e. condition the synthesis gas stream so that it can be analyzed by laboratory instrumentation in real time. The need for on-line analyses of various industrial process gas streams is driving commercial development of advanced instruments. These improvements also include capabilities for unattended operation in potentially hazardous process areas with sample gas at elevated temperatures and pressures.

A short overview of different analytical techniques is given below (description from Wikipedia; <http://en.wikipedia.org>).

#### Ion chromatography (IC):

Ion exchange chromatography retains analyte molecules based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation exchange chromatography and anion exchange chromatography:

Cation exchange chromatography retains positively charged cations because the stationary phase displays a negatively charged functional group such as phosphoric acid

Anion exchange chromatography retains negatively charged anions using positively charged functional group such as a quaternary ammonium cation

#### NDIR:

Non-dispersive Infrared spectroscopy is the subset of spectroscopy that deals with the infrared (IR) region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify compounds or investigate sample composition. IR is a classical method to measure CO, CO<sub>2</sub> and CH<sub>4</sub> in gases.

#### FTIR:

Fourier transform infrared spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other types of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and electron spin resonance spectroscopy. There are several methods for measuring the temporal coherence of the light. The continuous wave Michelson or Fourier transform spectrometer is the most mature technology at this time.

#### Paramagnetism:

Paramagnetism is a form of magnetism which occurs only in the presence of an externally applied magnetic field. Paramagnetic materials are attracted to magnetic fields; hence they have a relative magnetic permeability greater than one (or, equivalently, a positive magnetic susceptibility). However, unlike ferromagnets which are also attracted to magnetic fields, paramagnets do not retain any magnetism in the absence of an externally applied magnetic field. Generally, oxygen is measured by instruments that are based on paramagnetism.

#### Thermal Conductivity:

Thermal conductivity is the property of a material that indicates its ability to conduct heat. Hydrogen is measured by thermal conductivity, but it has to take into account that CO and CO<sub>2</sub> have a big influence on the precision of measurement.

#### Gas Chromatography:

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex mixture. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their respective chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time or retention time. Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

A number of detectors are used in conjunction with gas chromatography. The most common are the flame ionization detector (FID) and the Thermal Conductivity Detector (TCD). Both are sensitive to a wide range of components and both work over a wide range of concentrations. While TCDs are essentially universal and can be used to detect any component other than the carrier gas (as long as their thermal conductivities of sample gaseous components are different from that of the carrier gas, at detector temperature), FIDs are sensitive primarily to hydrocarbons. In this regard, they are more sensitive than TCDs. However, an FID cannot detect water. Both detectors are also quite robust. Since TCD is non-destructive, it can be operated in-series before an FID, a destructive methodology, thus providing complementary detection of the same elutes.

Other detectors are sensitive only to specific types of substances, or work well only in narrower ranges of concentrations. They include:

- Discharge ionization detector (DID)
- Electron capture detector (ECD)
- Flame photometric detector (FPD)
- Pulsed flame photometric detector (PFPD)
- Hall electrolytic conductivity detector (EICD)
- Helium ionization detector (HID)
- Nitrogen phosphorus detector (NPD)
- Mass selective detector (MSD)
- Photo-ionization detector (PID)
- Pulsed discharge ionization detector (PDD)
- Sulphur chemiluminescence detector (SCD)

Some gas chromatographs are connected to a mass spectrometer which acts as the detector. The combination is known as GC-MS. Some GC-MS are connected to a Nuclear magnetic resonance (NMR) spectrometer which acts as a back up detector. This combination is known as GC-MS-NMR. Some GC-MS-NMRs are connected to Infrared spectra which act as an additional back up detector. This combination is known as GC-MS-NMR-IR. It must, however, be stressed this is very rare, as most standard or common analytical needs can be conducted with a GC-MS

The most commonly used detectors for chromatographs are described below:

**Sulfur Chemi-luminescence Detector (SCD):** This is based on the chemiluminescence produced from the reaction of sulfur monoxide with ozone. In such a detector, sulfur-containing molecules are converted to sulfur monoxide in a hydrogen flame. The flame converts approximately 0.4% of the sulfur molecules to sulfur monoxide and the system converts approximately 1 in 10<sup>9</sup> sulfur molecules into a photon that is detected by a photomultiplier tube. This efficiency allows for a detection limit of about 100 parts-per-trillion (pptv) with an electronic time constant of 6 seconds. Extensive laboratory experiments have shown that the SCD is free of interference effects from common atmospheric chemical species. A slight but measurable interference from hydrocarbons can be eliminated by adjusting the residence time of the flame in the burner housing.

**Flame Photometric Detector (FPD):** The elute from a GC column is fed into a hydrogen-rich flame and produces light emission. Optical filters are used to select the wavelength range of the emission which is characteristic of specific atoms (usually sulphur or phosphorus). The detector is a photomultiplier, and depending on the choice of optical filters. It can detect the S- and P-containing compounds down to 3 to 10 ppmv, but the detector is non-linear.

**Pulsed Flame Photometric Detector (PFPD):** This is a relatively new weapon in the arsenal of analytical chemist. Though it uses a flame like its namesake, the flame photometric detector, the PFPD is a significant improvement because it can provide better sensitivity and selectivity for sulphur and phosphorus compounds. The FPD was generally only used for selective detection of sulphur and phosphorus; however, the PFPD allows for selective detection of S and P primarily but also detects N, As, Sn, Se, Ge, Te, Sb, Br, Ga, In and Cu among others.

**Potoionization Detector (PID):** The selective determination of aromatic hydrocarbons or organo-heteroatom species is the job of the PID. This device uses ultraviolet light as a means of ionizing the elute as it exits from a GC column. The ions produced by this process are collected by electrodes. The current generated is therefore a measure of the elute concentration.

#### Detection Limits in Gas Chromatography:

The following appear to be conservative estimates of the detection limits (in parts-per-million by volume) that one might expect to find when sampling synthesis gas with a gas chromatograph:

- FID <1 ppm
- PID <0.1 ppm
- FPD <0.1 ppm (sulfur mode)
- SCD <0.01 ppm

These sensitivities should be readily attainable for compounds with molecular weights on the order of 50-200.

**Micro gaschromatograph ( $\mu$ GC):** A Micro gaschromatograph is an optimised GC, where the needed time for a selected analysis is very short in about 1-10 minutes, compared to a classical GC, which needs about 20-120 minutes for one set of analysis.

**Flame Ionisation Detector (FID):** The flame ionisation detector can not only be used in a GC, but also as stand alone unit to measure total amounts of hydrocarbons.

**Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES):** Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as ICP-OES, is a type of emission spectroscopy that uses plasma (e.g. inductively coupled plasma) to produce excited atoms that emit electromagnetic radiation at a wavelength characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. This technique is used primarily to detect metals.

**Ion mobility spectrometer (IMS):** This is a spectrometer capable of detecting and identifying very low concentrations of chemicals based upon the differential migration of gas phase ions through a homogeneous electric field. IMS devices come in a wide range of sizes (often tailored for a specific application) and are capable of operating under a broad range of conditions. Systems operated at atmospheric conditions, 1 atm or 760 Torr, employ elevated temperature (above 100° C) while lower pressure systems (1-20 Torr), do not require heating. Elevated temperature assists in removing ion clusters that may distort experimental measurements.

**Mass spectrometry (or informally, "mass-spec" and MS):** This is an analytical technique used to measure the mass-to-charge ratio of ions. It is most generally used to find the composition of a physical sample by generating a mass spectrum representing the masses of sample components. The mass spectrum is analyzed by a mass spectrometer. All mass spectrometers consist of three basic parts: an ion source, a mass analyzer, and a detector system. The various stages within a mass spectrometer include:

- Ionization of the sample
- Separating ions of differing masses
- Detecting the number of ions of each mass produced
- Collecting the data and generating the mass spectrum

The technique has several applications, including:

- Identification of unknown compounds by the mass of the compound molecules or their fragments
- Determining the isotopic composition of elements in a compound
- Determining the structure of a compound by observing its fragmentation
- Quantifying the amount of a compound in a sample using carefully designed methods (mass spectrometry is not inherently quantitative)
- Studying the fundamentals of gas phase ion chemistry (the chemistry of ions and neutral fragments in vacuum)
- Determining other physical, chemical, or even biological properties of compounds with a variety of other approaches

**Solid-phase adsorption (SPA):** This is a method to measure tars. About 100 ml of producer gas is passed through a disposable cartridge containing 500 mg of amino-phase (modified silica). After preparation, samples are analysed for individual compounds by GC.

**Ammonium Flow Injection Analyser (AMFIA):** This is an analyser developed by ECN for measuring ammonia in a liquid sample. It is developed by the atmospheric research group from ECN and it is also used for measuring ammonia concentrations in outside air by wet denuders.

**Flow Injection Analyser (FIA):** This is a well known liquid analysing technique where a liquid sample is injected into a liquid carrier stream and passes a detector sensitive to certain components. For example, at ECN to analyze -CN an UV detector is used.

A tabulation of different analytical methods and their analytical capabilities are given below:

**Table 2: Analytical Methods for Major Gaseous Components and Hydrocarbons**

	Research Organisation	Gas Composition (CO, CO <sub>2</sub> , CH <sub>4</sub> )	Gas Composition (H <sub>2</sub> )	Gas Composition (O <sub>2</sub> )	H <sub>2</sub> O	Hydrocarbons (C <sub>2</sub> -C <sub>6</sub> )	Tars (>C <sub>6</sub> )
Classical NDIR	Almost all	0-100%					
Classical Paramagnetic	Almost all			0-100%			
Classical Thermal Conductivity	Almost all		0-100%				
μGC	GTI	0-100%	0-100%	0-100%		0-100%	
μGC	NREL	0-100%	0-100%	0-100%		0-100%	
μGC	PSI	0-100%	0-100%	0-100%	?	0-100%	
μGC	ECN	0-100%	0-100%	0-100%		0-100%	Benz+Tol > 5 ppm
μGC	VTT	0-100%	0-100%	0-100%		0-100%	
CEN/TS 15439	ECN						1-1000000mg/Nm <sup>3</sup>
CEN/TS 15439	VTT						1-1000000mg/Nm <sup>3</sup>
FID	ITC					sum	
FTIR <sup>1,2</sup>	GTI	0-90%			0-90%	1 ppm-90% <sup>3</sup>	1 ppm-90% <sup>3</sup>
GC-FID <sup>1</sup>	GTI	> 1 ppm (CH <sub>4</sub> )				> 1 ppm	
GC-MS <sup>1</sup>	GTI					> 0.1 ppm	> 0.1 ppm
On-line MS	GTI	0-100%	0-100%	0-100%	0-100%	>1%	> 1%
On-line MS	NREL	0-100%	0-100%	0-100%		0.1-100%	0.1-100%
SPA	ECN, KTH						> 2.5 mg/ Nm <sup>3</sup>

Tar Dew Point	ECN				Dew point		Dew point
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**Table 3: Summary of Analytical Methods for Measuring Sulphur Compounds**

	Research Organisation	Total Sulphur	H <sub>2</sub> S	COS	Mercaptans	Thiophenes
μGC	GTI		> 10ppm	> 1ppm		
μGC	NREL		> 1ppm	> 1ppm		
μGC	ECN		> 1ppm	> 1ppm		
μGC	PSI		> 1ppm	> 1ppm		
μGC	VTT		> 1ppm	> 1ppm		
FTIR <sup>1</sup>	GTI			> 1 ppm		
GC-FPD <sup>1</sup>	GTI		> 100 ppb	> 100 ppb	> 100 ppb	> 100 ppb
GC-SCD <sup>1</sup>	GTI		> 10 ppb	> 10 ppb	> 10 ppb	> 10 ppb
GC-FTP	ECN		> 50ppb	> 50ppb	> 50 ppb	> 50 ppb
GC-SCD	PSI		>1ppm	>1ppm	>1 ppm	>1 ppm
IMS	FZK		> 1ppb			
Sampling in KOH / MEA and titration				> 0.1ppm		
Sampling in KOH and titration	FZK		> 0.1ppm			
Sampling in KOH and titration	TUV		> 0.1ppm		> 0.1 ppm	
Sampling in MeOH and GCMS	TUV					> 0.1ppm
SCD	PSI	>1ppm				

**Table 4: Analytical Methods for Measuring Halogens, Nitrogen compounds, and Metals**

	Research organisation	Halogens	HCl	NH3	HCN	Organic Nitrogen	Alkali Metals and Heavy Metals
FTIR <sup>1</sup>	GTI	> 1ppm		> 1ppm	> 1ppm		
ICP-OES	PSI						1ppb
IMS	FZK	> 1ppb					
Sampling in acid solution and AMFIA	ECN			> 50 ppb			
Sampling in acid solution and Kjeldahl Analysis	VTT			> 1ppm			
Sampling in H2O and IC	ECN		> 50 ppb				
Sampling in H2O and IC	FZK, TUV	1ppm					
Sampling in NaOH and FIA	ECN				> 50 ppb		

1. On-line sampling with gas dilution (by a factor of ~10) and maintenance of sample temperature at ~200°C. For sampling of cleaned synthesis gas, dilution is eliminated thus decreasing detection limit (by a factor of ~10) when needed.
2. Most analytical experience is at 185°C. Lower detection limits can be increased by an order of magnitude by removing water.
3. Specifically for benzene > 1ppm, toluene > 1ppm, ethylene > 5 ppm, and naphthalene > 1 ppm

**NEXT STEPS:**

The analytical techniques to measure major gas components, H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and other hydrocarbons are well established. However, the current plans to explore the use of biomass derived synthesis gas to produce fuels and chemicals, it is essential to measure with precision the quantity of sulphur, halogen, alkali, and nitrogen compounds contained in gaseous streams. Based on the proceedings from the WS, the next logical step could be to assemble a team of organizations to participate in a Round Robin test program to evaluate selected analytical methods to measure the contaminant compounds. The Round Robin test results should show the reliability of reproducing results and also to assess the need to develop standard analytical guidelines.