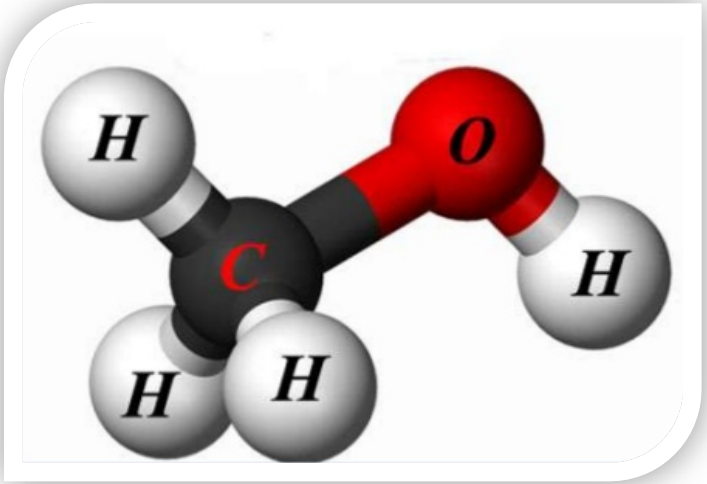
Analyzing for Methanol content using an online Gas Chromatograph



Methanol
“MeOH”

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Introduction

To avoid the capital cost/permitting implications associated with wellhead dehydration, methanol is a widely used thermodynamic inhibitor, which lowers the temperature of hydrate formation in wet gas systems. Ultimately, this wet gas is dehydrated and processed to meet sales gas specifications.

When the wet gas is processed in a hydrocarbon recovery plant, some or all of the methanol condenses into the Y-Grade NGL liquid product. End users that receive the NGL product are experiencing problems related to higher Methanol concentration. This high concentration is resulting in higher costs for the end users that are getting pushed back to the midstream processors in the form of fines.

Questions

- Why are producers increasing use of Methanol?
- Why are higher levels of Methanol a problem?
- What can processing plants do to effectively reduce Methanol?
- What options exist for measuring the content of Methanol in NGL?
- Why do we want to measure MeOH?

Properties of Methanol

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with formula CH_3OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colorless, flammable, liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol (drinking alcohol).

Methanol is a colorless liquid that boils at 64.96° C (148.93° F) and solidifies at -93.9° C (-137° F). It forms explosive mixtures with air and burns with a non-luminous flame. “Methanol is also a toxin and should not be ingested.”

***MeOH is miscible in both polar and non-polar molecules, meaning that MeOH that is injected in a wet gas stream will follow water & hydrocarbons.

http://www.methanol.org/

Many uses for Methanol (MeOH)

- Oxygenated Fuels - E85/M85
- Chemical feedstock
- Solvent
- Refrigerant
- Component of antifreeze
- Hydrogen carrier for fuel cell technology applications
- BioChem industry for extraction of bioactive compounds from plants
- Originally used in Oil & Gas industry for valve maintenance to remove water from seal pockets
- MeOH as Hydrate inhibitor

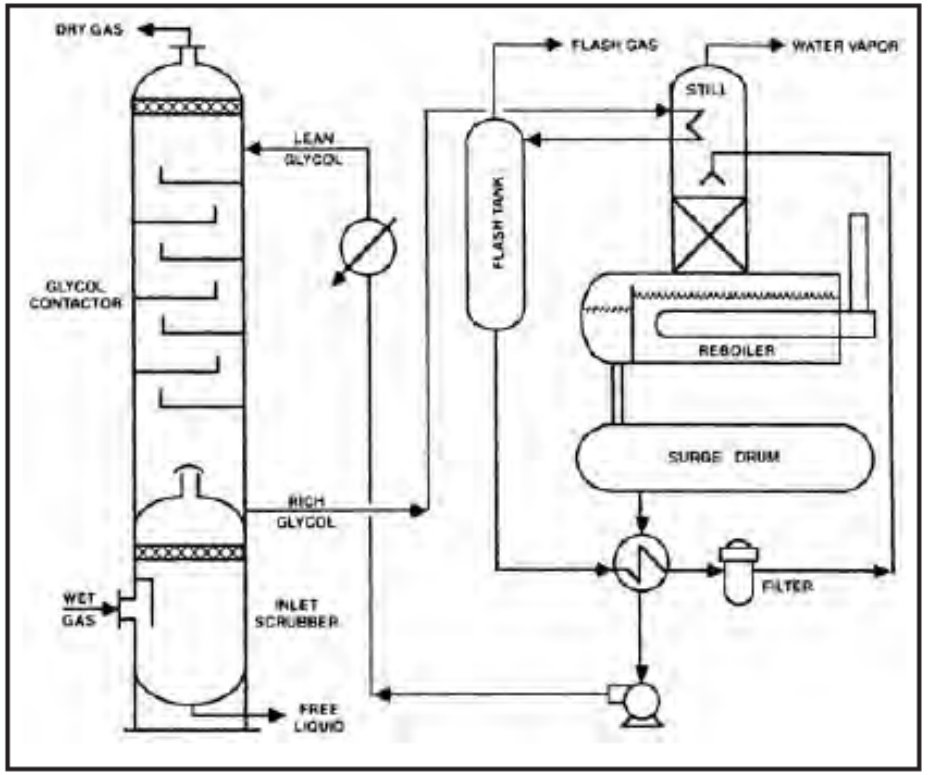
Hydrate Inhibitors

- Methanol and glycols are commonly used in the oil & gas industry as thermodynamic hydrate inhibitors.

Glycol is always preferred.

- Closed loop system is recovered and regenerated.
- Triethylene glycol (TEG) absorbs water only, easy to remove
- Ethylene glycol (EG) acts like antifreeze by decreasing freezing point, similar to MeOH

Example Process Flow Diagram for Glycol Dehydration Unit



GPSA Section 20

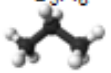
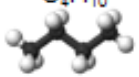
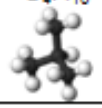
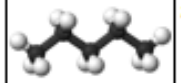
Why are producers increasing use of Methanol?

Glycol is always preferred but not always an option.

- Lower pressure of depleting wells increases water content. Reasons?
- Glycol dehydrator requires 150-250# wellhead pressure to operate efficiently.
- Can be more economical than installing wellhead dehydrators, MeOH as a raw chemical is more affordable than glycol.
- EPA Permitting/regulations make installing wellhead dehydrators less attractive.
- Corrosion inhibitors often include methanol. (H2S scavengers)
- Hydrates/freezing become a bigger issue in cold ambient conditions; so, we experience seasonal use of Methanol.
- In very cold applications (e.g. cryogenics), the viscosity of glycols is too high.

Why are higher levels of Methanol a problem?

- Expensive catalyst used by End Users is damaged by Methanol.

NGL Attribute Summary				eia
Natural Gas Liquid	**Chemical Formula**	**Applications**	**End Use Products**	**Primary Sectors**
Ethane	C_2H_6 	Ethylene for plastics production; petrochemical feedstock	Plastic bags; plastics; anti-freeze; detergent	Industrial
Propane	C_3H_8 	Residential and commercial heating; cooking fuel; petrochemical feedstock	Home heating; small stoves and barbeques; LPG	Industrial, Residential, Commercial
Butane	C_4H_{10} 	Petrochemical feedstock; blending with propane or gasoline	Synthetic rubber for tires; LPG; lighter fuel	Industrial, Transportation
Isobutane	C_4H_{10} 	Refinery feedstock; petrochemical feedstock	Alkylate for gasoline; aerosols; refrigerant	Industrial
Pentane	C_5H_{12} 	Natural gasoline; blowing agent for polystyrene foam	Gasoline; polystyrene; solvent	Transportation
Pentanes Plus*	Mix of C_5H_{12} and heavier	Blending with vehicle fuel; exported for bitumen production in oil sands	Gasoline; ethanol blends; oil sands production	Transportation

C indicates carbon, H indicates hydrogen; Ethane contains two carbon atoms and six hydrogen atoms
*Pentanes plus is also known as "natural gasoline." Contains pentane and heavier hydrocarbons.

Source: U.S. Energy Information Administration, Bentek Energy LLC.

Too much MeOH into a fractionator will reduce temp to an inoperable level, forcing a shutdown.

Industry has accepted 200 PPM (by weight) as off spec limit for Methanol in Y-Grade NGL.

GPA/API?

GPSA

Example Y-Grade Product Specification

	Specification Point	Test Method (Latest Issue)	Receipt	Delivery
			Specifications	
1.	**Composition** Carbon Dioxide Methane, Maximum Aromatics, Maximum Olefins, Maximum	Gas Chromatography MAPL Test No. 7 GPA 2177 Extended analysis MAPL Test No. 7A GPA 2186	 *(Note 1)* *(Note 2)* *10.00* *(Note 3)*	 *(Note 1)* *(Note 2)* *10.00* *(Note 3)*
2.	**Vapor Pressure** At 100°F, psig, Maximum	MAPL Test No. 1 ASTM D-1267	600	600
3.	**Corrosiveness** Copper Strip at 100°F	MAPL Test No. 9 ASTM D-1838	No. 1	No. 1
4.	**Volatile Sulfur** PPM by Weight, Maximum	MAPL Test No. 11 ASTM D-2784	1200	1200
5.	**Hydrogen Sulfide**	MAPL Test No. 12 ASTM D-2420	Pass	Pass
6.	**Distillation** End Point at 14.7, psia, °F, Maximum	MAPL Test No. 8 ASTM D-216	375	375 *(Note 4)*
7.	**Color** Saybolt Number, Minimum	MAPL Test No. 16 ASTM D-156	+27	+25 *(Note 4)*
8.	**Dryness** Free Water	MAPL Test No. 15 Inspection	None at 34°F	None
9.	**Product Temperature** Product containing 65 mole % or more Ethane, °F, Maximum Product containing less than 65 mole % Ethane, °F, Maximum		 90 110	 90 110

GPSA Section 2

Future #10:

200 PPMW MeOH??????

PPMV vs. PPMW?

Operational data

- MeOH is a bigger issue with lean inlet gas (2 – 3 GPM feed)
  - Less C2+ in Y-Grade NGL to dilute MeOH concentration
  - Example: 200 – 350 ppmv MeOH in inlet gas results in 2,000 ppmw MeOH (C2 Rejection) to 5,000 ppmw MeOH (C2 Recovery) in Y-Grade NGL product

- MeOH is less of an issue with gas dehydrated in wellhead facilities
  - Example: Inlet gas with wellhead dehydration was tested with 20 ppmv MeOH, while inlet gas without wellhead dehydration was tested with 200 – 350 ppmv MeOH

What can plants do to effectively reduce Methanol?

Once MeOH is in your product it is difficult to remove (because it's miscible in the hydrocarbon phase):

- Midstream processing companies are searching for options.
- Options include:
  - Specialty sieve on inlet gas or Y-Grade NGL (high capital/operating cost)
  - Amine treating on inlet gas or Y-Grade NGL (high capital/operating cost)
  - Oversized TEG unit on inlet gas (only feasible for small gas streams)
  - Water wash on Y-Grade NGL (requires downstream NGL dehydration)
  - Producers can switch to glycols for hydrate inhibition (higher operating cost)
- Methanol generally follows propane
  - Plants experience increase in Methanol concentration in their Y-Grade NGL product when operating in Ethane rejection.
- What do processors do with MeOH once it is removed????

What options exist for measuring the content of Methanol in NGL?

Analysis Method #1:

- Sampling for lab analysis
  - ➢ Inherent inconsistency in sample collection and handling
  - ➢ Spot vs. Composite (GPA guidelines)
  - ➢ Storage/Transport – Constant pressure cylinder (Shrinkage)
  - ➢ Cylinder material (Inert coated cylinder?)
  - ➢ Lab analyzers
  - ➢ Response time: Not fast enough to use for process optimization
  - ➢ Accuracy/Repeatability

What options exist for measuring the content of Methanol in NGL?

Analysis Method #2:

- Online analysis
- ➢ Quartz crystal cannot speciate water vs MeOH
- ➢ Differential spectroscopy: TDL – What makes this technology great at measuring H20, H2S, CO2 prevents it from seeing MeOH.
- ➢ Gas chromatograph – Column separation/backflush
- ➢ Response time: Real time for process optimization
- ➢ Accuracy/Repeatability

Gas Chromatograph

Use of Gas chromatograph is the most accepted method for analysis.

- Online GC provides real time data for process control.
- FID (0-5 ppm) vs TCD (5 ppm low level) Concentration level
  - Traditional approach is FID. It works but is maintenance intensive and expensive to operate as analyzer requires fuel for flame.
  - TCD is preferred to lower maintenance requirements and cost.

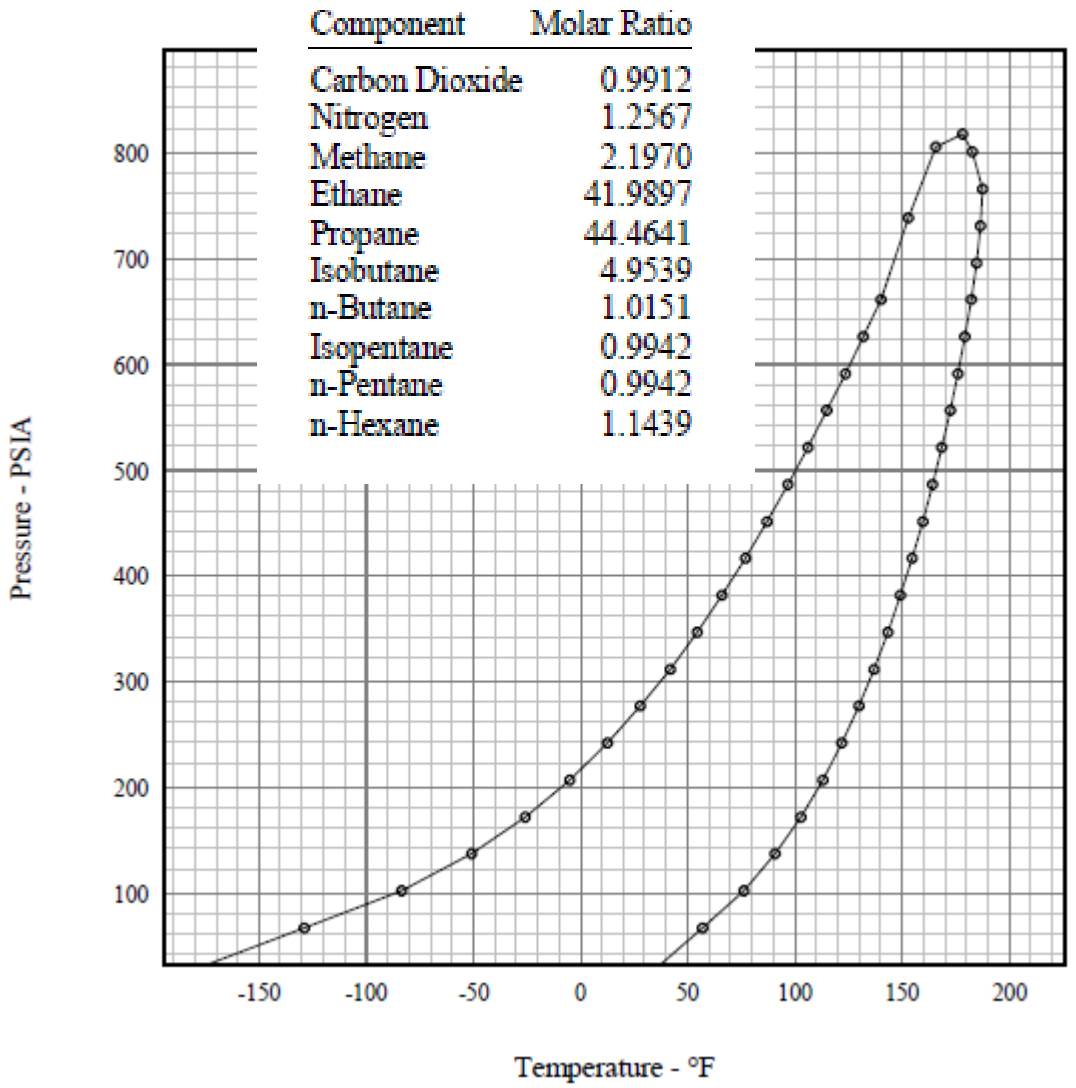
Gas Chromatograph

- There are many onshore and off shore installations for analyzers looking for MeOH in transmission type 90+% Methane streams.
- Easy application to provide analyzer with representative sample and not a difficult analysis.
- A TCD unit can provide C6+ BTU analysis with MeOH by using a 2 detector system.

Gas Chromatograph

- Most common to analyze for MeOH in Y-Grade liquid streams.
- Sample delivery and handling system is more complex.

Gas Chromatograph



- Examining the phase curve we can determine best approach.

1. Vaporize at the sample point and treat as a gas stream.
2. Transport as liquid and vaporize at the analyzer.
3. Transport as liquid and use liquid injection valve directly into the column set.

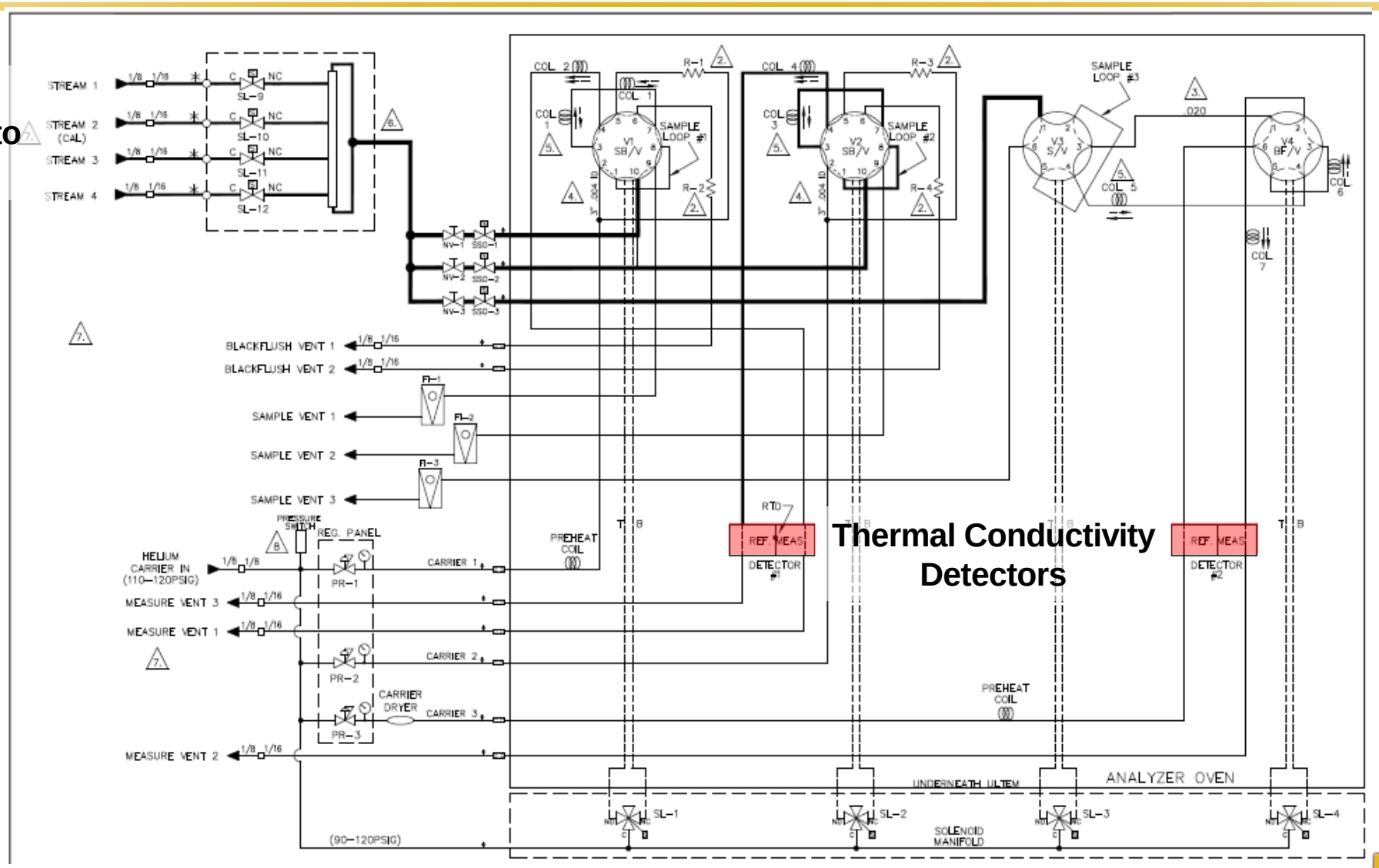
- Must use inert tubing to transport sample. (Teflon, electropolished, Sulfinert)
- Oxygen????

Gas Chromatograph

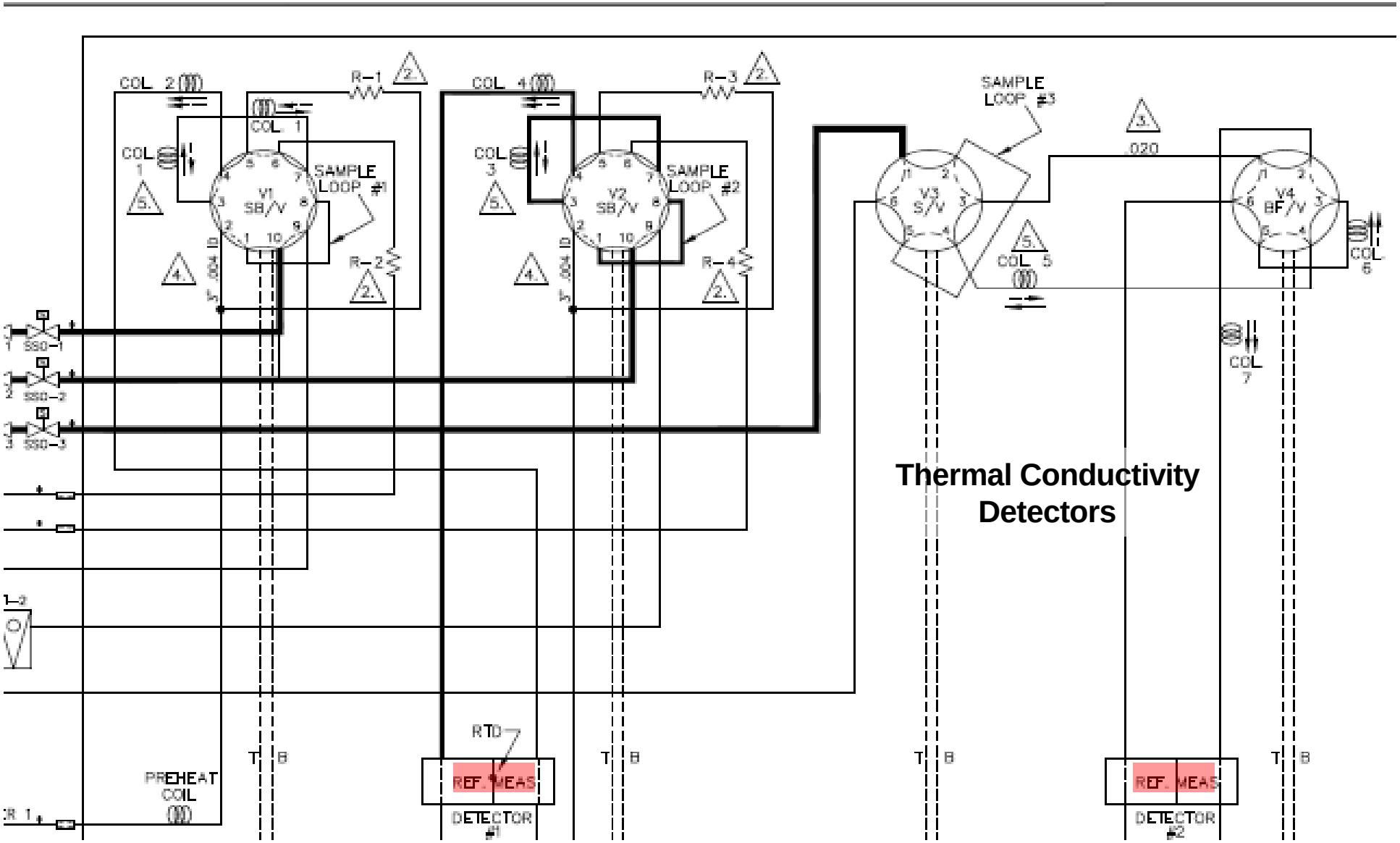
- All 3 methods result in a vapor being introduced into the columns so the components can be separated and identified.
- Once the sample is injected we can backflush all the heavy components and measure all the light hydrocarbons on Detector 1 and use a special column for picking out the MeOH.

Analytical Flow Path

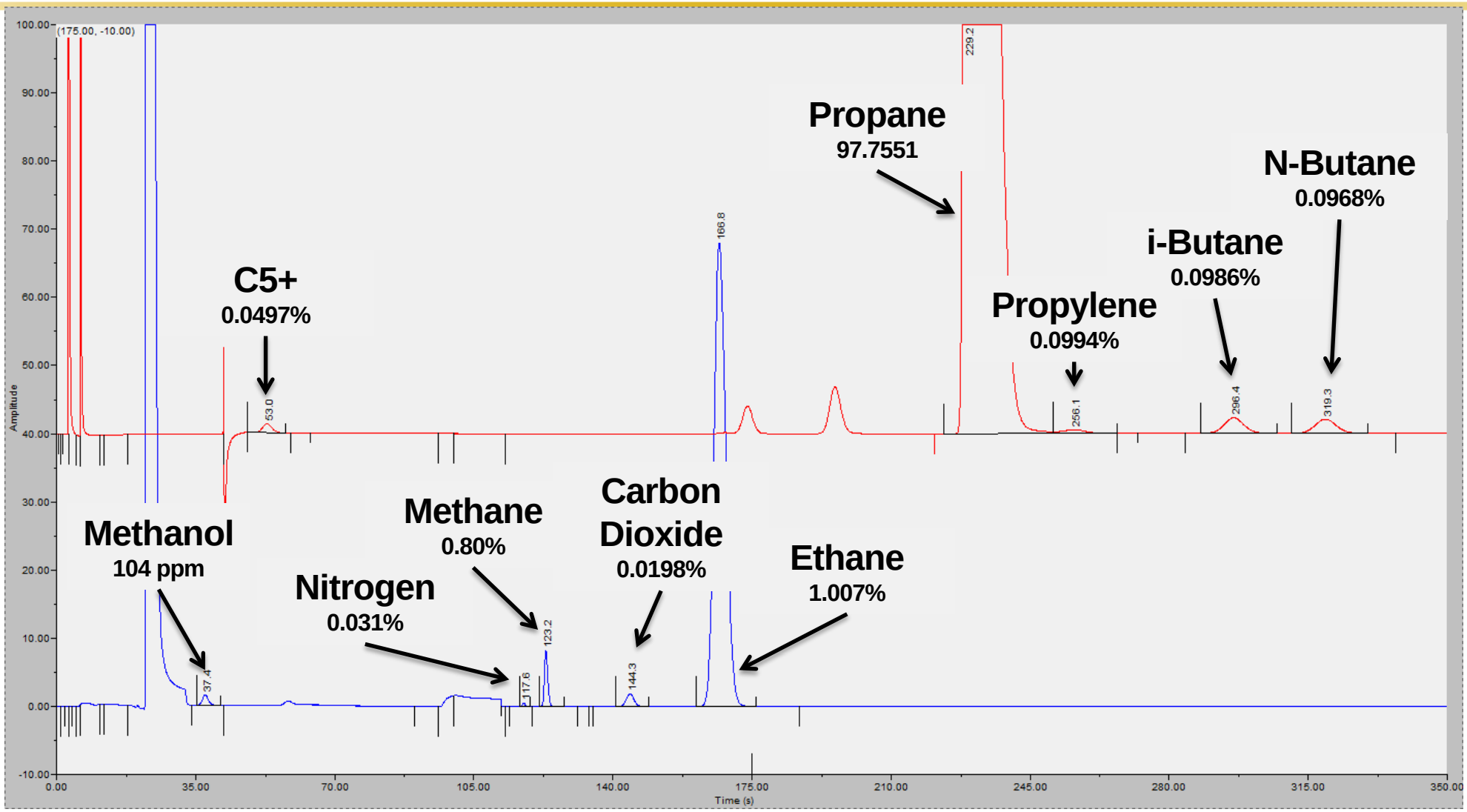
Vaporized Streams Into Oven



Analytical Flow Path



C3 Purity with Methanol



Business Results Achieved

- Plant operators can maximize efficiency of the removal process when they receive updated results every 5-8 minutes versus waiting for a lab analysis.
- Plant personnel are already familiar with operating and maintaining chromatographs as they are critical devices in all processing plants.
- In some cases, existing analyzers can be retrofitted in the field to add this new measurement, further increasing the savings benefit to the customer.
- The cost savings in potential reduced fines alone is approximately $1 per barrel. This is significant at 25,000 bpd processing plants.

Summary

- The industry is showing a need for monitoring the levels of MeOH present in EP Blends of NGL.
- There is much debate on the best way to provide an analysis that contract parties can agree upon.
- Midstream processing plants need a reliable method to monitor their removal processes.
- Online Gas Chromatograph provides the most repeatable analysis and the fastest response time.
- Questions?
- Feedback?

Where To Get More Information

- Very limited Web resources available for MeOH analysis.
  - http://www.eia.gov/
  - http://www.methanol.org/
- Customer interviews conducted to learn about source of the problem in Colorado, Wyoming, Ohio and West Virginia.
- Discussions with analysis technicians for gas transmission and gas processing facilities at residue/sales outlets and major NGL receipt points.
- Discussed analysis options with lab analysts, online field techs and analyzer factory applications engineers.