



**IHI E&C**



## Tackling the Issues with Pipeline Gas Contaminants for LNG Export Facilities

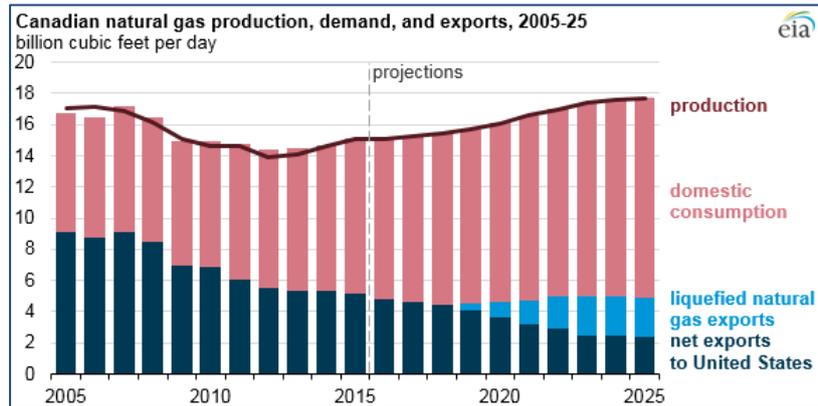
May 11, 2016

**CANADA**  
LNG  EXPORT  
CONFERENCE & EXHIBITION

*By: Kamal Shah, Eric Browning and Prabal Saxena*

## Background

British Columbia has significant natural gas resources. According to a recent U.S. Energy Information Administration based on Canada’s National Energy Board projections, Canadian natural gas production is expected to increase even though the net export to U.S. will reduce further from current levels (see chart below). The increase in natural gas production is a result of expected increase in domestic demand and Liquefied Natural Gas (LNG) export to Asia. The expected future major sources are Montney tight gas formation (accounting for almost 70% of the future gas production) and Horn River shale gas in British Columbia (see figure below).



**Source:** U.S. Energy Information Administration, April 2016 based on [Canada's National Energy Board, Canada's Energy Future 2016: Energy Supply and Demand Projections to 2040](#)



**Source:** Spectra Energy B.C. Pipeline Division, September 2015 <https://noms.wei-pipeline.com>

## Introduction

Feed to an LNG liquefaction unit must meet strict concentration requirements to ensure product quality and to prevent problems in the liquefaction unit itself. Table 1 below shows the range of Canadian pipeline gas quality specifications for natural gas supplied to LNG facilities and LNG export quality requirement.

CONTAMINANT	PIPELINE GAS QUALITY (TYPICAL SPECIFICATION / RANGES)	LIQUEFACTION OR LNG EXPORT REQUIREMENTS
Mercury	1-20 µg/Nm <sup>3</sup>	< 0.01 µg/Nm <sup>3</sup>
Carbon Dioxide	2 vol% max.	< 50 ppmv
Hydrogen Sulfide	6-23 mg/m <sup>3</sup> (4-16 ppmv)	< 4 ppmv
Total Sulfur	115 mg/m <sup>3</sup> max. (~ 80 ppmv)	< 30 ppmv
Mercaptans/Sulfides	Part of total sulfur spec.	
Water	65 mg/m <sup>3</sup> max. (4 lb/MMSCF)	< 1 ppmv
Oxygen	0.4 vol% max.	
Methanol	Approx. range: 5 - 100 ppmv	< 0.5 ppmv
Heavy Hydrocarbons (HHC)	-10°C Dew Point	C5+: <0.1 mole%; Benzene: < 1 ppmv

**Table 1: Pipeline Gas Quality Specifications & LNG Export Requirement**

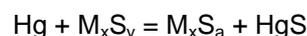
The typical pipeline gas quality specification range for various contaminants varies greatly compared to that of actual pipeline gas. Understanding the future field development and analysis of upstream gas processing facilities can help narrow the pipeline gas contaminant range. Establishing the appropriate design basis for the contaminants range expected in the pipeline feed gas to liquefaction will help in proper facility design. Discussed below are strategies for tackling common and less common contaminant issues in the feed gas.

### Lube Oil/ Condensates in the pipeline

Liquids are expected due to an upstream process upset or residues left during commissioning. These liquids if not removed could damage the Mercury Guard bed and may also cause upset in the amine unit. This issue is mitigated by the addition of an inlet separator with a good efficiency filter/coalescer downstream of it.

### Mercury

Little or no mercury is expected in pipeline gas (1-20 µg/Nm<sup>3</sup>) for a typical natural gas stream in North America). But a Mercury Removal Unit (MRU) provides cheap insurance against potential aluminum exchanger damage in the downstream Liquefaction area. Non-Regenerative metal sulfide adsorbents or sulfur-impregnated activated carbon beds are normally the two types of MRU's used to remove mercury from pipeline quality feed gas. The MRU can be placed either upstream of the Acid Gas Removal Unit (AGRU) or downstream of the Dehydration unit. Sulfur impregnated activated carbon beds are less effective at positions upstream of the Dehydration unit due to the risk of capillary condensation in the micropores of the carbon sub-structure<sup>1</sup>. For such applications, fixed bed metal sulfide beds are more advantageous. The reaction between mercury and metal sulfides (Puraspec)<sup>2</sup> is given below:



The suggested location of the MRU is just after the feed gas separator to fully protect all plant equipment. The placement of the MRU is critical to reduce the frequency of handling mercury-

contaminated process equipment during a plant turnaround. Most government agencies classify any equipment exposed to mercury as hazardous waste that needs to be disposed of properly according to local regulations<sup>3</sup>.

### **Carbon Dioxide**

Up to 2% by volume can be expected in the pipeline gas. With a desired concentration to Liquefaction of <50 ppmv. CO<sub>2</sub> is removed in the AGRU utilizing a chemical amine solvent such as a primary amine e.g. Diglycolamine (DGA), a secondary amine such as Diethanolamine (DEA) or a tertiary amine such as formulated Methyldiethanolamine (MDEA). DGA and formulated MDEA are the most widely used amines in LNG plants since very low concentrations (20-40 ppmv) can be achieved in the sweet gas which is very important for meeting the guaranteed product specifications. A combination of physical and chemical amines (such as Sulfinol) can also be used to achieve low CO<sub>2</sub> concentrations in a gas carrying large amounts of organic sulfur.

### **Water**

The maximum allowable amount of water in the pipeline gas is 65 mg/m<sup>3</sup> (4 lb/mmscf) but the gas becomes saturated with water as it exits the AGRU. This water is removed in the Dehydration unit, with the dry gas carrying <1 ppmv water before it enters the Liquefaction unit. Care must be taken to keep the pipeline gas temperature above its hydrate formation temperature until it enters the dehydration unit.

For LNG plants, the preferred method of water removal is by passing the wet gas through fixed beds containing molecular sieves. These beds can be regenerated using an open loop or a closed loop regeneration system.

Care must be taken to remove all the free liquids from the sweet gas from the AGRU before it enters the molecular sieves to avoid bed degradation. Hence, almost every plant employs a filter/coalescer upstream of the dehydration beds. The recommended liquid droplet removal size is 99.99% of droplets ≥ 0.3 microns<sup>4</sup>.

### **Hydrogen Sulfide/ Other Organic Sulfur Compounds such as COS, CS<sub>2</sub>**

Pipeline gas may contain 6-23 mg/m<sup>3</sup> (4-16 ppmv) H<sub>2</sub>S along with a maximum of 115 mg/m<sup>3</sup> (~80 ppmv) organic sulfur compounds such as COS and CS<sub>2</sub> etc. H<sub>2</sub>S is almost entirely removed in the amine unit. Removal of organic sulfur in the gas stream requires special attention in the selection of the amine. Targeted removal of COS can be achieved by using primary amine by adding an extra step for hydrolysis of COS to CO<sub>2</sub> and H<sub>2</sub>S. Sulfinol can also be used to remove organic sulfur.

Mole Sieve beds in the downstream dehydration unit can be sized to remove some of the sulfur compounds that escaped the AGRU. The Molecular Sieve vendor should be provided the correct treated gas characterization in order for the vendor to provide the correct mole sieve for the application.

H<sub>2</sub>S and other organic sulfur compounds removed in the AGRU and the downstream units are carried away by the acid/ off gas and can either be incinerated in a thermal oxidizer or a flare if the resultant SO<sub>x</sub> emissions are within the allowed emissions granted for the operating unit or they can be removed from the gas in a Sulfur Removal Unit (SRU) which is sometimes followed by a Tail Gas Treating Unit (TGTU) in order to decrease the SO<sub>x</sub> emissions. The use of a traditional Claus unit for converting H<sub>2</sub>S to elemental sulfur may not be feasible for some pipeline gas compositions due to very low H<sub>2</sub>S concentrations in the acid gas. In these cases, adsorbent beds utilizing a mix of metal oxides (Cu-Mn or Fe-Mn) can be used for selective removal of sulfur compounds from the acid gas. H<sub>2</sub>S in the acid gas can also be removed by the LO-CAT process which is a wet scrubbing, liquid redox system that uses a chelated iron solution to convert H<sub>2</sub>S to elemental sulfur.

## Mercaptans

Mercaptans originate from produced gas or associated gas. They are also added in the pipeline gas as odorant in order to detect potential gas leaks from the pipeline. These odorants are a mix of light as well as heavy mercaptans (such as methyl, ethyl, propyl and butyl mercaptans).

Mercaptans need to be removed from the natural gas just like H<sub>2</sub>S and organic sulfur compounds in order to meet the LNG product specification. A very small amount of mercaptans are removed in the amine unit if only chemical solvent is used. As per field observations, primary amine such as DGA removes ~25-30% of methyl mercaptans and ~5-10% of ethyl mercaptans depending on the temperature/pressure conditions. Most of the heavier mercaptans pass through the amine unit without being removed. Secondary and tertiary amines generally have a very small capacity for removal of mercaptans<sup>6</sup>. Sulfinol can therefore be utilized for selective removal of mercaptans. However, it should be noted that amine solutions containing physical amines will result in increased co-absorption of heavy hydrocarbons and aromatics. Remaining mercaptans can then be removed in the mole sieve beds and/or the HRU upstream of the liquefaction unit.

## Oxygen

As per data from various sources, oxygen concentration in pipeline gas can be anywhere from 10-20 ppmv up to 0.4% by volume.

Effects of oxygen in the gas processing facilities are well documented. Oxygen can cause severe corrosion in the piping systems and equipment resulting in shortening of equipment life thus increasing the facility downtime. Oxygen reacts with the amine solvent to form oxidative degradation products such as heat stable salts (HSS) and bicine which increase the corrosion in the amine unit as well as reducing the amine strength thus affecting its performance. High concentration of oxygen in the natural gas (>20 ppmv) also severely affects the downstream molecular sieves by reacting with hydrocarbons at elevated temperatures in the regeneration cycle forming water and CO<sub>2</sub> in an oxidation reaction or water and carbon deposition on the sieve as a result of a partial oxidation reaction. Formation of water prevents complete regeneration of the bed while carbon deposits decrease the sieve activity by reducing the number of active sites available for water adsorption. Additionally, higher concentrations of oxygen present safety concerns due to reaching flammability limits after further enrichment in certain process streams downstream such as the fuel gas system.

Mitigation options in the AGRU and in its process are listed below:

### Removal of Oxygen from Feed Gas

If the feed gas oxygen concentration exceeds 0.1 vol%, it is advisable to remove it from the gas before it enters AGRU. Commercially available technologies include catalytic oxidation which involves passing the hot stream of natural bed over a catalyst (such as palladium) to convert oxygen to carbon dioxide and water on reaction with methane. Reaction temperatures can go as high as 500°F - ~700°F<sup>8</sup>. The catalyst can be poisoned by natural gas containing high concentrations of sulfur compounds; hence the sulfur compounds need to be removed before the gas undergoes catalytic oxidation. Catalytic oxidation usually requires high capital expenditure due to the need for the extra equipment and piping to be rated for high temperature and pressure.

### Addition of Antioxidant in Amine Solutions + Amine Reclamation and Purging

Antioxidants can be added to the amine solution as an additive to reduce the formation of HSS and bicine. Additionally, build-up of HSS can be reversed by either thermal reclaiming (for DGA) or by an ion exchange process (for MDEA). Periodic purging of the amine solution and replacement with fresh amine also help to contain HSS build-up.

Mitigation options in the Dehydration unit are as follows:

Removing Oxygen from Regeneration Gas

Treating regeneration gas is a more economical alternative compared to feed gas since the regeneration gas flow rate is much smaller. Catalytic oxidation can be applied to the regeneration gas for oxygen removal with smaller additional investment since the regeneration gas heater can provide the heating requirement and the gas can be cooled in the regeneration gas cooler.

Use of Other Regeneration Sources

Nitrogen can be used in place of natural gas as the regeneration gas if its availability and purity is not an issue. However, the regeneration gas flow rate will be considerably higher for the same heating time and regeneration temperature as that for natural gas. Other low oxygen containing streams can also be considered for mole sieve regeneration.

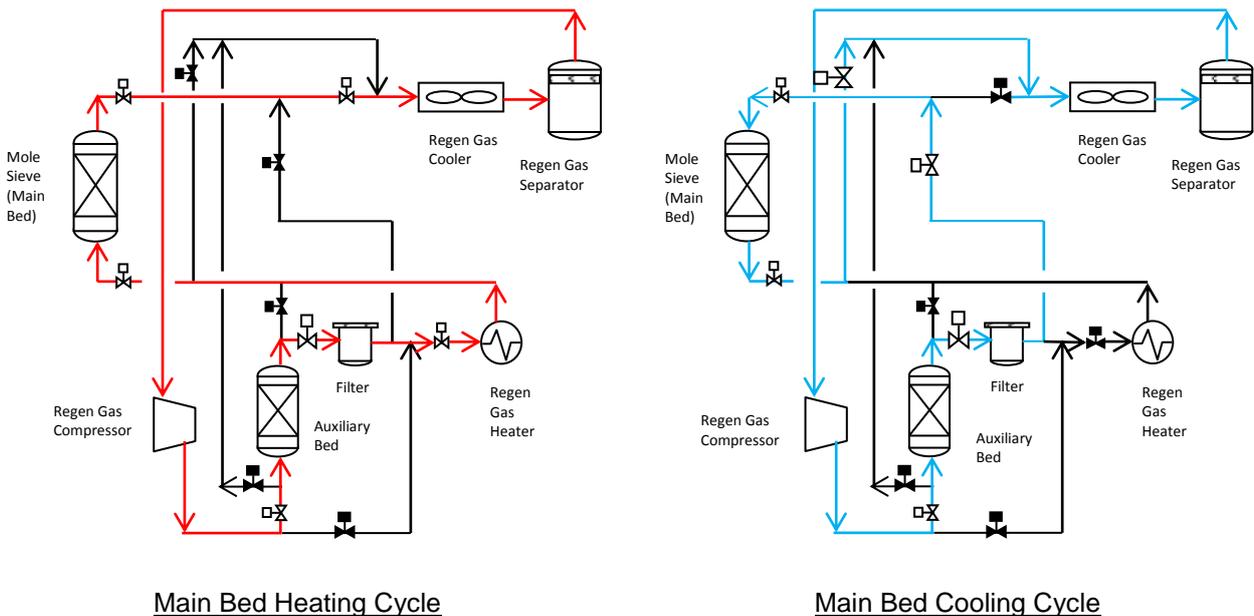
Closed Loop Regeneration System with Auxiliary Dryer

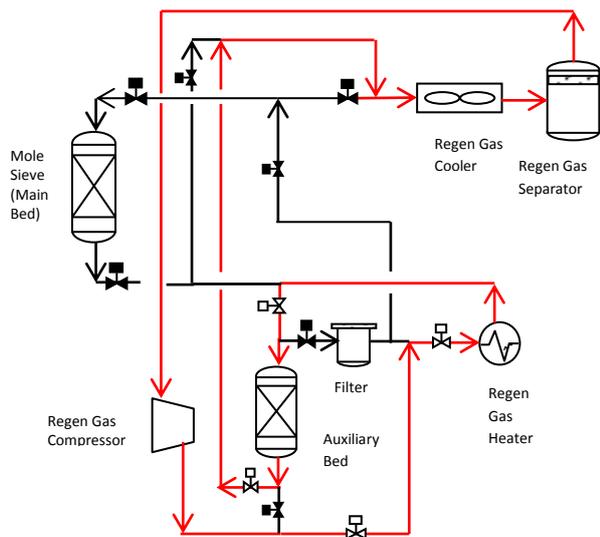
The oxygen-tolerant closed loop regeneration system employs an auxiliary molecular sieve bed in addition to the adsorption beds (main beds) ensuring that the regeneration gas going to the main bed is bone-dry. The auxiliary bed itself undergoes regeneration (heating and cooling) at the end of each regeneration cycle of the main bed. Hence, the main bed regeneration cycle is divided into four steps:

1. Main bed heating (auxiliary bed is in adsorption mode)
2. Main bed cooling (auxiliary bed is in adsorption mode)
3. Auxiliary bed heating (main bed on stand-by)
4. Auxiliary bed cooling (main bed on stand-by)

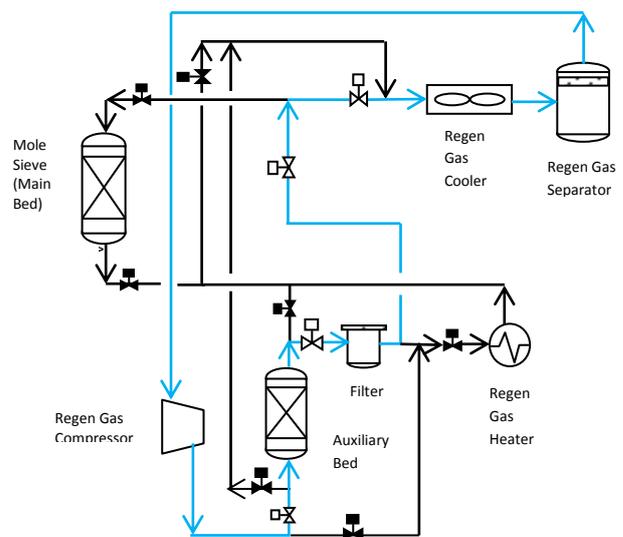
Closed loop regeneration system minimizes the exposure of the molecular sieve bed to oxygen and is a proven method that is used in several LNG facilities globally.

A schematic representation of the main and auxiliary bed heating and cooling cycles is shown below:





Auxiliary Bed Heating Cycle



Auxiliary Bed Cooling Cycle

According to industry experience, in many cases the oxygen report is either a sample error or a peak point which is not repeatable. Hence, proper sample analysis is extremely important while designing the system to mitigate the presence of oxygen.

### **Methanol**

Methanol is normally injected in the pipeline gas to prevent hydrate formation. Based on plant data from different sources, the amount of methanol added could range anywhere from 5-10 ppmv to ~100 ppmv. Maximum allowable methanol concentration in the gas entering the Cold Box/ Main Cryogenic Heat Exchanger (MCHE) is <0.5 ppmv since methanol has a potential of freezing at cryogenic temperatures. The presence of methanol in the feed gas going to the mole sieve beds also increases the chances of coking in the bed at high temperatures during the regeneration cycle.

Regardless of the methanol concentration in the gas at the inlet of the AGRU, it will gradually accumulate in the amine system since a part of the methanol boiled off from the Amine Regenerator returns back to the regenerator with the reflux stream due to its polar nature. Also, some methanol may not even be boiled away if the reboiler duty is not large enough. This build-up of methanol will hinder the further absorption of methanol as well as that of CO<sub>2</sub> and H<sub>2</sub>S in the absorber.

The Mole sieve beds in the dehydration unit can adsorb methanol but it will be displaced by water and eventually breakthrough if the bed is not sized to hold methanol. If the methanol breaks through from the mole sieve beds, it will go to the Liquefaction unit and cause freezing in the MCHE.

Effects of methanol can be mitigated by the employing one or a combination of the following measures:

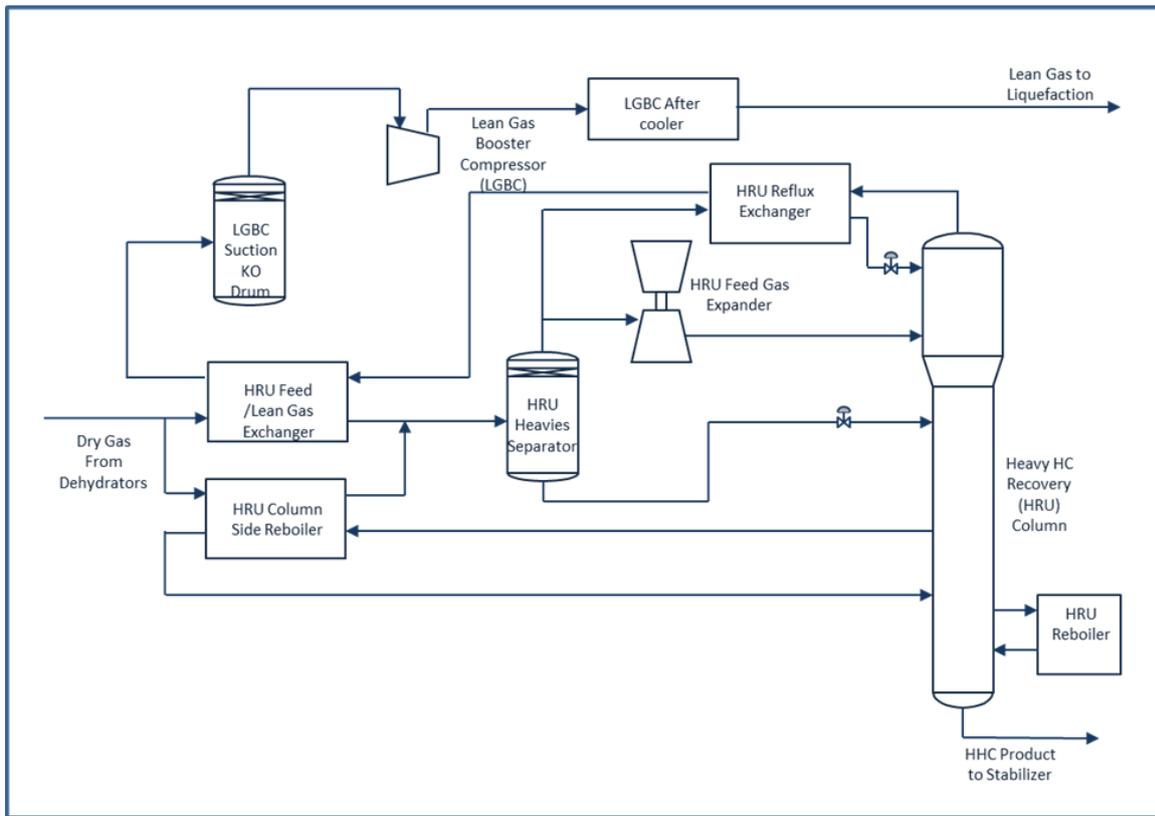
- Remove methanol completely from the feed gas by using water wash either upstream of the AGRU or on top of the acid gas absorber. Addition of a water wash upstream of the AGRU will prevent methanol build-up in the amine loop. It will also prevent potential fouling of the catalyst in the SRU catalyst<sup>5,7</sup> since the acid gas leaving the amine unit will be free of methanol. Spent water from the water wash will either need to be treated to remove the methanol before it can be reused or it will have to be discarded as waste.

- Monitor the concentration of methanol in the reflux going to the amine regenerator as well as the lean amine entering the Acid Gas Absorber and purge these streams as necessary. Increasing reboiler duty to strip out methanol from the amine regenerator will also help in maintaining low methanol concentrations in lean amine stream.
- Operating the Amine absorber at a higher pressure also slightly increases absorption of methanol in the amine solution.
- Design the mole sieve beds to adsorb methanol as well as water from the feed gas. However, this still does not help with the coking of the beds due to methanol presence during the regeneration cycle. The regeneration system can be designed for the regeneration gas carrying the methanol to return back to the AGRU to remove the methanol from the regeneration gas stream. This extra methanol shall be taken into account while assessing the methanol removal capability of the AGRU.
- Remove methanol in the Heavies Removal Unit (HRU) upstream of the liquefaction system.

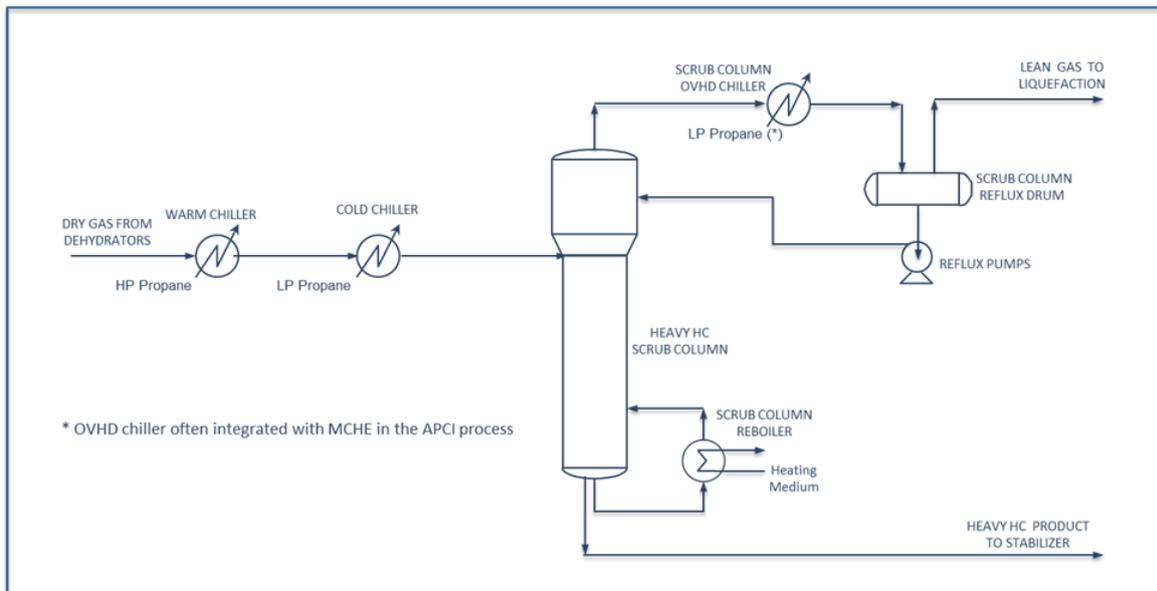
### Heavy Hydrocarbon (HHC) Removal

Pipeline specifications typically address hydrocarbon content in terms of hydrocarbon dew point. When designing an LNG Liquefaction plant it is very important to have a more detailed characterization of the feed gas. The specifications for C<sub>5</sub>+ components are generally based on avoiding any freezing in the downstream cryogenic section which could result in blockages and reduced capacity. Benzene for example freezes at 42°F<sup>9</sup>. Typical LNG Product Specifications require removal of C<sub>5</sub>+ to less than 0.1 mole% and Benzene to less than 1 ppmv. Therefore removal of benzene and similar compounds is particularly important to prevent plugging/fouling of the cryogenic equipment.

There are various methods that are well known to the industry for accomplishing heavies removal. Two of the more common methods are a Turboexpander Based NGL Recovery plant or a Scrub Column. Both processes use some type of refrigeration to condense and remove the heavies from the feed to the Liquefaction unit. The turboexpander based NGL Recovery plant as the name implies relies on using a turboexpander to generate refrigeration from isentropic pressure reduction of the feed gas. Such plants also employ significant heat exchange in the form of cold boxes to maximize the refrigeration gain from the turboexpander and remove the heavies in a Demethanizer column. A Scrub Column relies on the downstream liquefaction unit for its refrigeration. In this scheme a portion of the lean gas product from the scrub column is condensed and recycled back to the scrub column for use as a reflux to aid in heavy hydrocarbon removal. The feed to the scrub column is also typically refrigerated using a portion of the liquefaction refrigerant. Typical examples of both processes are shown in the figures below.



**Typical Turboexpander Based NGL Recovery Plant**



**Typical Scrub Column Based Process**

The above processes function well for typical natural gas compositions that contain relatively low amounts of benzene but also are accompanied by other hydrocarbons in the C<sub>3</sub>-C<sub>6</sub> range. A particular

situation to pay attention to is where the gas is relatively lean, with low amounts of  $C_{3+}$ , but still has benzene content higher than what is allowed in a feed to a liquefaction unit. Such a situation can occur for example when a portion of the gas traveling down a pipeline is sent to an LPG Extraction Plant. A portion of the gas is treated to remove  $C_{2+}$  and re-inject  $CH_4$  into the pipeline. The end result is that total quantities of  $C_{2+}$  in the pipeline can be reduced but benzene can remain in the untreated gas as well as from associated gas added elsewhere in the pipeline. Even ppm levels of benzene will be problematic in a liquefaction plant. It should be understood that this situation can develop over time; as more extraction plants come on line the gas will tend to become leaner and leaner.

Benzene has a relatively low solubility in liquid methane. The solubility increases with the presence of heavier alkanes<sup>12</sup>. Even at low temperatures a portion of the benzene may stay in the gas phase if only liquid methane is present. The result is that both a scrub column or turbo-expander type plant will have difficulty in removing sufficient amounts of benzene if the feed gas is too lean i.e. contains too little  $C_{3+}$ . For more typical lean gas cases a turbo-expander has greater flexibility than a scrub column. This is due to the ability to run the demethanizer column in a turbo-expander process at lower pressure which allows for easier separation of the heavy components. The downside is there will be additional expenses for the recompression of the treated gas, but this can often be justified by the increased efficiency of running the Liquefaction unit at a higher pressure. The turbo-expander process is also more flexible than a scrub column since the refrigeration is not integrated with liquefaction.

For more extreme cases IHI E&C has developed a proprietary process (Patent pending). This process is a variation on the turbo-expander process that can be used to remove traces of benzene from the leanest gas. It provides a simple, energy efficient alternative that can be operated with a wide range of pipeline feed gas compositions.

Chiyoda has also recently published a paper with several variations of the scrub column design incorporating an expander and recompression<sup>10</sup>. The process appears to be based in part on the APCI US patent 4,065,278. The addition of the expander and recompression is intended to increase the flexibility of a scrub column to allow it to more effectively deal with benzene removal from lean gas.

APCI has also suggested using adsorbents (temperature swing adsorption) to remove benzene and other heavy compounds if concentrations are low<sup>11</sup>.

## Conclusions

It is important to understand the source of the pipeline gas to narrow the pipeline gas contaminant range and establish a proper design basis. Detailed pipeline gas characterization during the conceptual development phase and understanding of future field gas processing is very important in establishing a good design basis. The presence of  $O_2$ , methanol and mercaptans can have significant impact on the pre-treatment design and appropriate risk mitigation should be considered. The possibilities of lean pipeline gas with traces of HHC, especially Benzene must be considered in the design.

It cannot be emphasized enough the importance of having a full range of compositions with all potential contaminants available during the early phases of engineering. With a full list of compounds and their realistic concentration levels it is possible to design a robust solution to any difficult concentration issue.

## REFERENCES

1. "Mercury Removal Processes – A Careful Evaluation of the Options for Removing Mercury from Natural Gas Plant Feed and Product Streams is a Prudent Exercise", N. Eckersley, D. Radtke, L. Rogers, S. Brennan.
2. Technical Bulletin: Puraspec – Purification Solutions for Gas Processing Industry
3. Technical Bulletin: UOP GB-562S Adsorbent.
4. "A Tale of Two Sieves", W. Qualls, J. Watkins, D. Radtke, Gastech 2011.
5. "Dealing with Methanol in an Amine Unit", Optimized Gas Treating, Inc., Volume 9, Issue 9, May 2015.
6. "Treating Difficult Feed Gases to LNG Plants", E. Bras, G. Zwet, J. Klinkenbijn, P. Clinton, Shell Global Solutions International B.V., Paper PS4-2.
7. "Adjusting Gas Treatment Strategies to Resolve Methanol Issues", D. O'Brien, L. Addington, Laurance Reid Gas Conditioning Conference, February 21-24, 2016.
8. Gas Processors Association, "GPA RR-201: Oxygen Removal in Natural Gas Systems", 2010.
9. GPSA Engineering Data Book
10. "Lean LNG Plants – Novel Heavy Hydrocarbon Removal Technologies for Efficient Liquefaction", Kameta, Masanori et al, LNG 18, 11-15 April 2016
11. "Lean Gas", Chen, Fei and Ott, Christopher M., LNG Industry, Jan/Feb 2013.
12. Kraemer Luks, Journal of Chem. Eng. Data, Vol 26, No.4, 1981

## ACKNOWLEDGEMENTS

We would like to thank UOP and Huntsman Chemicals for providing valuable data and information that went into putting together this paper.

## CONTACT INFORMATION

*Kamal Shah: Phone: 832-379-7874; Email: [kamal.shah@ihi-ec.com](mailto:kamal.shah@ihi-ec.com)*

*Eric Browning: Phone: 832-379-7718; Email: [eric.browning@ihi-ec.com](mailto:eric.browning@ihi-ec.com)*

*Prabal Saxena: Phone: 832-379-7865; Email: [prabal.saxena@ihi-ec.com](mailto:prabal.saxena@ihi-ec.com)*