# Methanol Injection Rate for Natural Gas Hydrate Prevention – be careful what simulators tell you!

## Hydrates in Natural Gas Processing Facilities

The formation of hydrates in natural gas processing facilities and pipelines is a critical issue as hydrates can plug equipment, instruments, and restrict or interrupt the flow in pipelines. Generally, hydrates will form when the temperature is below the hydrate formation temperature, normally with "free" water present, depending on the gas composition and pressure.

### How Can Hydrates Be Prevented?

In general, hydrates can be prevented by:

1. Maintaining the system temperature above the hydrate formation temperature by using a heater and/or insulation.

2. Dehydration of the gas to prevent the condensation of a free water phase.

3. Injection of thermodynamic inhibitors to suppress the hydrate formation temperature in the free water phase.

Since heating or dehydration is often not practical or economically feasible, the injection of hydrate inhibitors is an effective method for preventing hydrate formation.

Methanol (MeOH) is widely used as an inhibitor in natural gas pipelines, particularly in cold climate facilities (e.g., Canadian environments). In these difficult environments, methanol injection is the most economical solution for preventing hydrate formation and is often the only option.

# Determination of Methanol Injection Rate

## The Challenge

The determination of methanol injection rate can be a very challenging task for engineers, mainly because of methanol partitioning: the injected MeOH may partition into three phases:

a. the aqueous phase
b. the vapor phase
c. the hydrocarbon phase.

The amount of MeOH to be injected must be sufficient to suppress hydrate formation in the aqueous phase, and also to replace methanol “losses” to the equilibrium vapor and hydrocarbon liquid phases.

In this article, we demonstrate how the GPSA manual and process simulators can be used to overcome these challenges and calculate the required methanol injection rate.  This information is crucial for safe pipeline operations.

## Methods to Determine the Injection Rate of Methanol

### 1. Manual Calculation per GPSA Engineering Data Book

**Steps**:

1. Determine the value of temperature suppression ‘d’ per design requirement.
2. The aqueous phase is where hydrate inhibition “occurs”. The inhibitor concentration in the aqueous phase can be calculated by Hammerschmidt’s equation or the Neilsen-Bucklin equation. Thus, the required MeOH in the aqueous phase is determined.
3. Once the required aqueous methanol concentration is fixed, it is necessary to establish the amount of methanol that is “lost” in the hydrocarbon liquid and gaseous hydrocarbon phases. By utilizing GPSA Fig 20-55 (GPSA 13th Edition SI), the MeOH losses in vapor phase can be determined.
4. Methanol losses to the hydrocarbon liquid phase are more difficult to predict. Solubility is a strong function of both the water phase and hydrocarbon phase compositions. By utilizing GPSA Fig 20-56 (GPSA 13th Edition SI), the MeOH loss to the hydrocarbon phase can be determined.
5. Total MeOH injection rate is the sum of the methanol in all three phases.

**Pros**: GPSA Engineering Data Book is widely available and the methods contained in it are accepted by industry for calculating MeOH injection rates and are field-proven.

**Cons**: Since the GPSA graphs (which are used to determine vapor and hydrocarbon losses) come from specific sources/experimental data, they only apply to a certain range of gas conditions or compositions.

2. **Process Simulators** (Aspentech HYSYS$^{TM}$)

A Process Simulator like HYSYS provides more rigorous calculations in regards to hydrate formation temperature (by using the HYSYS hydrate formation utility) and will automatically calculate the inhibitor distribution in different phases (by flash calculation/phase equilibrium).

Process Ecology has worked closely with HYSYS on several methanol partitioning studies through the years. It is crucial to choose an appropriate fluid property package (PP) to determine the methanol injection rate. Some commonly used property packages, like Peng-Robinson (PR) will largely overpredict MeOH requirement in the hydrocarbon phase.

In May 2015, Aspentech released HYSYS v8.8 with the addition of the Cubic-Plus-Association (CPA) fluid property package. The new CPA PP can more accurately model methanol phase behaviors, especially in the modelling of liquid-liquid equilibria (LLE) including the prediction of the partitioning of methanol between water and hydrocarbons in the hydrocarbon phase.

# Case study

Process Ecology was requested to determine the inhibitor requirement for a specified fluid defined by a client. The PFD of the system is shown below:

The results of the CPA package are promising, showing a marked improvement in methanol inhibitor predictions in particular when compared to alternative methods. For example, the amount of methanol required to suppress hydrate formation temperature in a specified fluid from 20 °C to 0 °C is as follows:

Using the CPA PP in HYSYS results in a MeOH injection rate that is much closer to the number calculated by GPSA, compared to the rate predicted by the Peng Robinson PP.

## Conclusions

In short, while process simulators like HYSYS bring significant benefits and convenience to operating and engineering companies, results must always be carefully evaluated and selection of the correct property package when performing calculations is essential.

For methanol injection rate calculations in HYSYS, we believe that the Peng Robinson property package vastly overpredicts the amount of methanol partitioned, or “lost” into the hydrocarbon liquid phase. We have demonstrated that the new CPA property package gives a much better prediction of required MeOH rates for hydrate suppression.

## References


1. Gas Processors Suppliers Association (GPSA) Engineering Data Book, 2012 SI unit,13th Edition
2. Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories. 2010. Georgios M. Kontogeorgis, Georgios K. Folas.


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