

Exploit the Benefits of Methanol

ALEJANDRO ESTEBAN, VICENTE HERNANDEZ, KEVIN LUNSFORD,
Bryan Research & Engineering, Inc,
Bryan, Texas

ABSTRACT

Methanol is probably one of the most versatile solvents in the natural gas processing industry. Historically, methanol was the first commercial organic physical solvent and has been used for hydrate inhibition, dehydration, gas sweetening and liquids recovery. Most of these applications involve low temperature where methanol's physical properties are advantageous compared with other solvents which exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress methanol's most significant disadvantage, high solvent loss.

Methanol has been extensively used as a hydrate inhibitor for conditions where the Hammerschmidt equation is applicable. Outside this range, predicting methanol's behavior is more complicated than the empirical correlations that are provided in industrial standard data books. In fact, the thermodynamic properties and phase equilibrium of mixtures of methanol, water and hydrocarbons are notoriously difficult to predict. Methanol shows both polar and non-polar characteristics. Consequently, these characteristics give methanol the unique ability to be used in an extensive range of applications. This paper will review some of these diverse applications: hydrate inhibition, gas dehydration, sweetening and liquids recovery.

Proceedings of 79th GPA Annual Convention. Atlanta, GA: Gas Processors Association, 2000:

[Bryan Research & Engineering, Inc.](#)

Visit our Engineering Resources page for more articles.

INTRODUCTION

As reported in Kohl and Nielsen [1], methanol is used to inhibit hydrate formation in natural gas, to remove acid gases, to dehydrate, and to recover heavy hydrocarbons. The ability to perform such a wide variety of the functions makes methanol probably one of the most versatile industrial solvents. Furthermore, methanol is relatively inexpensive and easy to produce. This makes methanol a very attractive alternative for gas processing applications.

METHANOL USE IN GAS PROCESSING

Hydrate inhibition

Methanol initially was used to inhibit the formation of hydrates. Hammerschmidt [2,3] authored two important papers in 1934 and in 1939 concerning the formation of hydrates and the corresponding procedure for coping with this problem. His later paper is the source of the widely used Hammerschmidt equation found in many gas processing handbooks as shown in equation (1).

$$\Delta T = 2335 X_1 / (MW_1 * (1 - X_1)) \quad (1)$$

Where ΔT is the depression of the gas hydrate point in °F, X_1 is the mass fraction of inhibitor in the aqueous phase, and MW_1 is the molecular weight of the inhibitor.

To use this equation, the hydrate formation temperature in the gas without the inhibitor being present must be known. Equation (1) can also be used with hydrate inhibitors such as ethylene glycol provided the appropriate constant is used. This equation gives engineers the ability to quantify the effects of inhibitor concentration on hydrate point suppression, making the design and operation of such facilities easy and predictable.

Recent studies from engineering data have made modifications to and limited the scope of applicability of the Hammerschmidt equation. Nielsen and Bucklin [4] give a theoretical basis for the development of equation (1) in the neighborhood of low methanol concentrations. They derived the Hammerschmidt equations using the freezing point depression of an ideal solution and truncated the higher order terms. This suggests that equation (1) is only valid at methanol concentrations up to 0.20 mass fraction. For higher methanol concentrations, Nielsen and Bucklin developed equation (2).

$$\Delta T = -129.6 \ln(X_{H_2O}) \quad (2)$$

where x_{H_2O} is the mole fraction of water in the aqueous phase. The authors claim that this equation is applicable to 90 wt% methanol, which gives the maximum hydrate suppression because methanol freezes at concentrations above 90 wt%. Nielsen and Bucklin also comment on how the first turboexpander plant in 1963 used methanol for hydrate suppression even though subsequent facilities tended to favor solid desiccants. Economic data presented by the authors show that methanol is a more cost effective water removal option.

From 1983 to 1987 the Gas Processors Association sponsored research to measure the hydrate points and corresponding effects of inhibitors such as methanol and glycol [5,6,7]. Based on this data, the Gas Processors and Suppliers Association (GPSA) Engineering Data Book [8] only recommends the Hammerschmidt equation up to 25 wt% methanol concentrations. The Nielsen-Bucklin equation is recommended only for methanol concentrations ranging from 25-50 wt%.

Maddox *et al.*[9] describe a graphical procedure which uses the activity coefficients of water in methanol and glycol. This technique is a trial and error approach which can be done by hand provided the activity coefficient figures are available. Better agreement between the measured data and the predictions have resulted from this technique; however, the GPSA only presents figures comparing the predictions using this method with the measured data. No recommended range of applicability is provided.

The most complete reference on hydrate formation thermodynamics and kinetics has been compiled by Dendy Sloan [10]. For engineering calculations, the CSMHYD computer program is provided with the text. This program gives estimates of hydrate formation temperatures and pressures along with the depression for methanol inhibition. This program can be used at methanol concentrations up to 60 wt%.

The interest in understanding hydrate formation and the effect of methanol on this process continues today. In 1999, Zuo and Zhang [11] report on hydrate formation in methanol solutions which also contain electrolytes. Other recent studies report on the rate of hydrate formation [12], and hydrate phase equilibrium in brine solutions [13].

The use of methanol as a hydrate inhibitor in processing facilities is well recorded. One of the most documented cases is the conversion of the Empress Gas Plant in Canada. In 1978, Nelson [14] describes the successful conversion from glycol to methanol. Hydrate inhibition was required in the feed to the lean oil absorption unit operating at -40°F and 600 psia since the feed gas was only partially dehydrated to about 4 lbs water/MMSCF. A methanol recovery facility was required since this gas plant is one of the world's largest, processing almost 2 billion SCFD. The paper also describes how methanol recovery by water washing the liquid propane stream was used. Furthermore, the conversion to methanol resulted in lower pressure drops in the inlet coolers and more stable operation. Methanol losses increased compared with glycol which increased solvent cost due to higher

losses. However, the power savings from recompression more than paid for the additional solvent.

Proposed modifications to the Empress Gas Plant in 1978 are reported by Nelson *et al.* [15]. To increase ethane recovery at the facility, a turboexpander facility was designed. Included in this paper is the gas inlet composition, and many of the operating parameters of the proposed design. This facility also addressed the problem of methanol absorption in a downstream amine sweetening unit and the partial recovery of the methanol in the condenser of the amine stripper.

In 1982, following the modifications, Nelson and Wolfe [16] describe some of the benefits and drawbacks of using methanol. Methanol yielded better heat transfer characteristics and lower pressure drop as compared with ethylene glycol. Methanol had lower operating and capital costs relative to a solid desiccant. Operational setbacks included the following. The deethanizer and depropanizer towers flooded when too much methanol was injected. Amine and caustic were carried over when the methanol concentration exceeded 1% in the lean solutions. The upper temperature is limited to -20°F otherwise methanol losses in the residue gas are excessive. The hydrocarbon liquid product becomes water saturated by the water wash to recover methanol. Flooding in the depropanizer column could be minimized by maintaining the solution concentration below 1 vol% methanol. The authors also described how anhydrous methanol can corrode plate-fin heat exchangers which are constructed with alloys containing greater than 5% magnesium. This problem can be minimized by only regenerating the methanol to 1 wt% water; the small amount of water is enough to maintain the protective aluminum oxide film. Methanol losses from the expander plant during stable operation were about 1.5 lb of methanol per MMSCFD of gas feed.

Reid and McLeod [17] discuss how methanol injection would be used more regularly with the discovery of gas sources in deep water and colder environments. They discussed how the Hammerschmidt equation and other heuristics such as 5 to 6 gal of methanol per MMSCF were only applicable with a gas stream from which the liquid hydrocarbons and free water were initially removed. Liquid hydrocarbon phases can support about 3 to 7 vol% methanol. Quantities of methanol injected for high pressure gas-condensate production might exceed 20 to 50 times that amount calculated by the simple equations because of the significant amount of free water and liquid hydrocarbon present. They also comment on how intermittent methanol injection was first used to remove hydrate buildup in heat exchangers and other simple process equipment. Methanol recovery was not a concern since the solvent was injected periodically. With continuous injection systems, economics often dictates that a recovery process be used.

Behrens, *et al.* [18] review the steps to choose the most suitable hydrate suppression system. They discuss both the hydrate prediction methods, and the effect of inhibitor concentration. Operating conditions, types of inhibitor and solid desiccants are also discussed.

Acid Gas and Sulfur Species Compound Removal, Rectisol®

Methanol was further exploited by Lurgi and Linde in the development of the Rectisol process. Although the common perception is that the Rectisol process uses only methanol as a solvent, Ranke and Mohr [19] discuss how toluene and mixtures of toluene and methanol are used to more selectively remove H_2S and slip CO_2 to the overhead product. Toluene has an additional advantage: COS is more soluble in toluene than in methanol. This review focuses on those Rectisol processes which use only methanol.

The Rectisol process was primarily developed to remove both CO_2 and H_2S along with other sulfur-containing species resulting from the partial oxidation of coal, oil, and heavy residue. The ability of methanol to absorb these unwanted components made it the natural solvent of choice. Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon components. Propane is more soluble in methanol than carbon dioxide. This behavior has limited the Rectisol process from being used further in the gas processing industry.

The process description of a coal to gas plant by Sasol is given by Hoogendoorn [20]. This paper provides some of the operating parameters of the absorber towers including the temperatures and pressures. The combined concentration of CO_2 and H_2S is reported to be lowered from about 30 mol% to less than 1 mol% (the inlet H_2S concentration from these partial oxidation feeds is usually less than 1 mol%). The process uses cold methanol at about -70°F along with three absorption towers: a pre-wash, a main wash where all of the H_2S along with a majority of the CO_2 is absorbed, and finally a fine wash where the remaining CO_2 is absorbed to the required

concentration. The main column has a temperature of -70°F whereas the fine wash has a temperature of -50°F . Ammonia absorption refrigeration maintains the main wash tower's cold temperature. Even with this cooling, the CO_2 heat of absorption increases the resulting rich temperature from the main absorber to -20°F .

Hoochgesand [21] provides a general overview of the Rectisol process and aspects of physical solvents as opposed to chemical solvents. Two versions of the Rectisol process are described: the two-stage and the once-through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of H_2S and CO_2 are about 1 and 5 vol%, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces a high sulfur feed for sulfur recovery. After shift conversion, the concentration of CO_2 increases to 35% and the total pressure is 750 psia. Methanol has a higher capacity than any other known system to absorb CO_2 at these partial pressures. Regeneration of the CO_2 loaded solvent is accomplished by flashing and nitrogen stripping. The once-through process is only applicable for high pressure partial oxidation products. The once-through process is also applicable when the H_2S to CO_2 content is unfavorable, in the neighborhood of 1:50.

Ranke [19] gives additional examples of different types of methanol wash diagrams. These include selective and non-selective flow diagrams. There is also limited process data for these flow sheets; however, utility demand is provided and can be used to estimate solvent flow rates and operating conditions. Staton [22] probably provides the most complete pilot plant data for the absorption of acid gas and regeneration steps of methanol. Data from several different pilot plant studies including regeneration by flashing and stripping with nitrogen are reported.

Dehydration, Liquids Recovery and Acid Gas Removal, IFPEXOL[®]

Recently, the Institute of the Francais Petrole (IFP) has developed a process using methanol which has the simultaneous capability to dehydrate, to remove acid gas, and to control hydrocarbon dew point. The initial United States Patents were issued in 1988 [23], and 1990 [24]. The IFPEXOL-1 is for water removal and hydrocarbon dew point control; the IFPEXOL-2 process is for acid gas removal.

The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low temperature separator (LTS).

That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that very simple discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the LTS to enhance the methanol recovery.

The IFPEXOL-2 process for acid gas removal is very similar to an amine type process except for the operating temperatures. The absorber operates below -20°F to minimize methanol losses, and the regenerator operates at about 90 psia. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process so excessive hydrocarbon absorption is not as great a problem. Also, Larue *et al.* [25] states water content of the regenerated solvent can be used to minimize hydrocarbon co-absorption.

The first commercial proven installation of IFPEXOL-1, a dehydration facility at Canada's East Gilby facility, is described by Larue *et al.* [25]. This process replaced a glycol injection facility. Patel [26] provides a discussion of the operating conditions after the conversion from glycol dehydration to IFPEXOL-1 process.

Holcek *et al.* [27], provide some general operating data for current operating facilities or recent proposals. Most notably, this paper provides the temperatures of the LTS; however, the gas composition and pressures are missing. The LTSs ranged from -60 to -31°F . For those facilities operating at cryogenic conditions, the methanol losses were about 2.0 U.S. gallons/MMSCF.

Minkinen *et al.* [28] describe an offshore platform designed for dehydration and liquids recovery. Methanol losses at this facility are about 2.0 U.S. gallons/MMSCF provided a water wash of the liquid hydrocarbon is used. This article is particularly noteworthy for the level of process detail which is provided concerning the design concept. Operating temperatures, pressures, total flow rates, molecular weights and methanol concentrations around the key process equipment are supplied. The inlet gas information includes molecular weight and percent of free condensate at the pressures and temperatures. The inlet gas composition is not given.

In 1998, Beaumont and Briery [29], describe the conversion from TEG dehydration to the IFPEXOL-1 process. Nociar and Bell [30] show how they used process simulation to minimize methanol losses in an IFPEXOL-1 process. They state that the Soave-Redlich-Kwong (SRK) and Peng Robinson equations of state were not accurate enough to predict the liquid hydrocarbon phase composition. The largest error was in overpredicting the methanol content in the hydrocarbon phase. A solution that they developed was to use different interaction parameters for the LTS. This modeling approach is limited to the temperature of the LTS for their particular facility and also probably their inlet gas composition; any extrapolation may be unreliable.

METHANOL Physical Properties and PHASE EQUILIBRIUM

Methanol has favorable physical properties relative to other solvents except for vapor pressure. Figure 1 compares the viscosity of methanol, water, glycols and amines as a function of temperature as calculated by PROSIM® [31]. The methanol viscosity is about one order of magnitude lower than other solvents, especially at colder temperatures. This lower viscosity decreases pumping costs and pressure drops in the exchangers. Benefits of methanol's low viscosity at low temperature are touted in the pressure drop improvement in the cold box of injection facilities and improved heat transfer. Nelson [14] reports almost 50% pressure drop improvement at the Empress gas plant with the switch from ethylene glycol to methanol. This decrease in pressure drop resulted in a compressor horse power savings that more than covered the cost of the methanol losses.

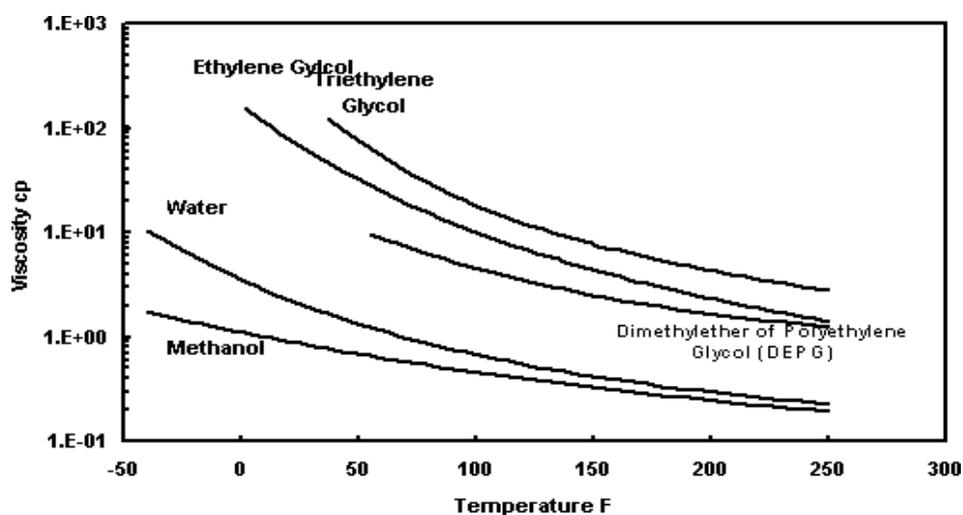


Figure 1. Comparison of Calculated Solvent Viscosity as a Function of Temperature

Methanol has a much lower surface tension relative to the other solvents as calculated by PROSIM, Figure 2. High surface tension tends to promote foaming problems in contactors. Methanol processes are probably not susceptible to foaming.

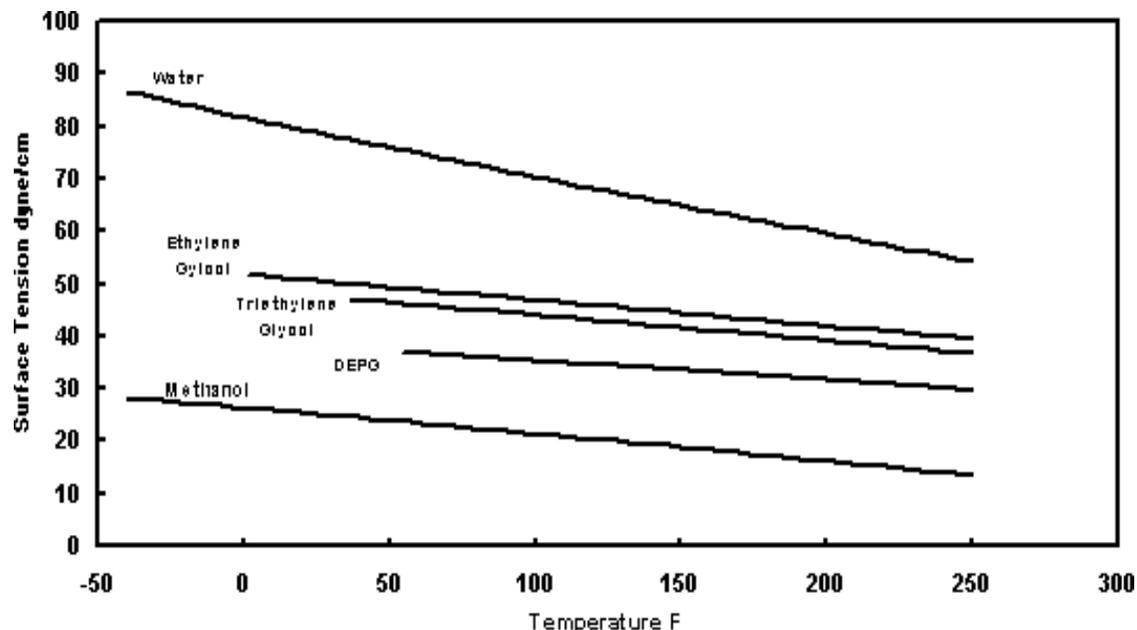


Figure 2. Comparison of Calculated Solvent Surface Tension as a Function of Temperature

The primary drawback of methanol is the high vapor pressure as calculated by PROSIM, Figure 3. The vapor pressure of methanol is several times greater than that of the glycols or amines. To minimize methanol losses and enhance water and acid gas absorption, the absorber or separator temperatures are usually less than -20°F.

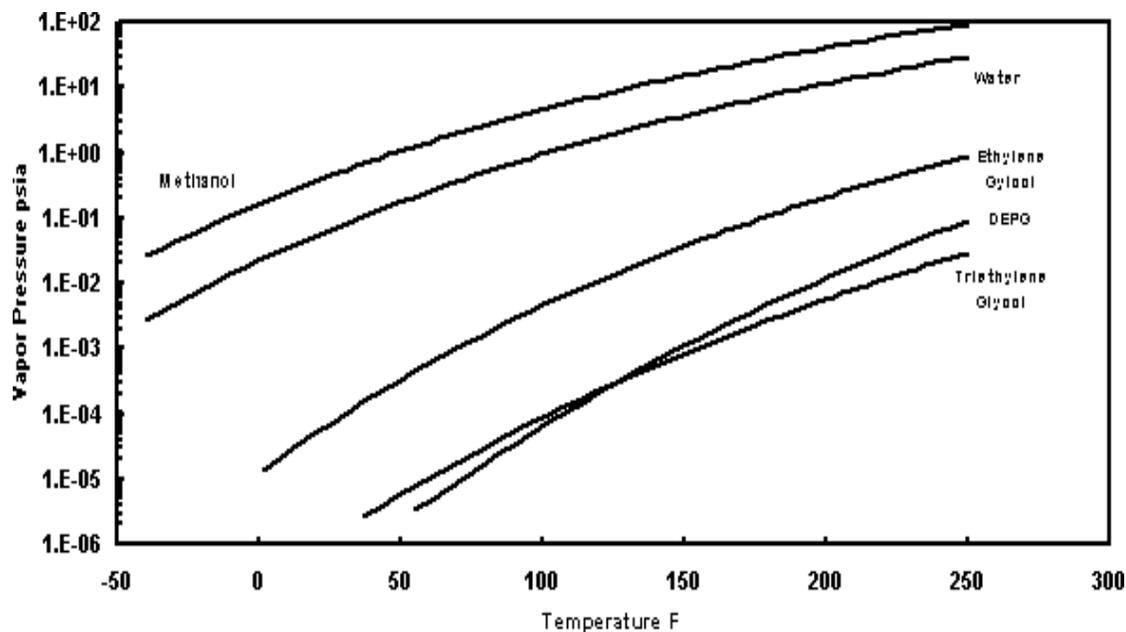


Figure 3. Comparison of Calculated Solvent Vapor Pressure as a Function of Temperature

The high vapor pressure of methanol may initially appear to be a significant drawback because of high solvent losses. However, the high vapor pressure also has significant advantages. Although often not considered, lack of thorough mixing of the gas and solvent can pose significant problems. Because of the high vapor pressure, methanol is completely mixed in the gas stream before the cold box. Glycols, because they do not completely vaporize, may require special nozzles and nozzle placement in the cold box to prevent freeze-up. Solvent carry-over to other downstream processes may also represent a significant problem. Since methanol is more volatile than glycols, amines, and other physical solvents including lean oil, methanol is usually rejected in the

regeneration step of these downstream processes. The stripper concentrates the methanol in the overhead condenser where it can be removed and further purified. Unfortunately, if glycols are carried over to amine units, the glycol becomes concentrated in the solution and potentially starts to degrade and possibly dilute the amine solution.

Two GPA research reports in 1988 [32] and 1995 [33] provide equilibrium data for methanol-water-hydrocarbon systems and systems containing acid gases. Lyddon *et al.* [34] show how the GPA data have led to the development of more accurate engineering calculations with the methanol system, especially in the area of methanol content in the liquid hydrocarbon phase. Prior to this published data, simulation models could have errors as high as one order of magnitude.

Predicting the phase behavior and equilibrium composition of methanol is extremely difficult. Two approaches for modeling hydrocarbon phase behavior are generally accepted, the equation of state and the activity coefficient model. For extrapolation purposes, whenever possible, the equation of state approach is usually favored because both temperature and pressure effects are taken into account. To account for highly polar materials like water and methanol, corrections to mixing rules and interaction parameters have been used successfully. The activity coefficient model approach or a Gibbs Excess Model is very effective for processes with limited temperature and pressure ranges. However, activity coefficient models are usually only valid at low pressure; predictions at high pressure may not be valid.

METHANOL PREDICTIONS AND PROCESS SIMULATION

The following examples and thermodynamic calculations have been performed with the process simulation program PROSIM. Another simulation program with similar capabilities could have been used. Predicting processes with methanol requires reliable methods for predicting hydrate formation temperatures and corresponding hydrate formation depression points with inhibitors, vapor-liquid-liquid equilibrium calculations, and the corresponding compositions in those phases. Over the years, Bryan Research & Engineering has done extensive work to develop mixing rules and techniques to predict methanol's behavior, especially in the three phase region. This work is primarily focused in the area of gas processing where some amount of water is present. With PROSIM, it is unnecessary for the engineer to perform additional work, such as modifying interactions and using different equations in different areas of the processing facility.

In the first comparison, PROSIM and the Hammerschmidt equation are compared to experimental hydrate formation temperature data. Figure 4 shows the methane system, Figure 5 shows the ethane system, and Figure 6 shows the propane system [5,6,7]. In all of the figures, the accuracy of the Hammerschmidt equation (dashed line) deteriorates above a methanol concentration of 25 wt%. The hydrate formation temperature predicted by the Hammerschmidt equation is too low for the methane and ethane systems and too high for the propane system. The predictions by PROSIM, shown in the solid line, more closely match the data especially at high methanol concentrations. At pressures above about 1000 psia, the PROSIM predictions tend to become conservative with regard to the hydrate formation temperature relative to the data. The simulator would predict more methanol than is necessary to achieve the actual hydrate formation temperature.

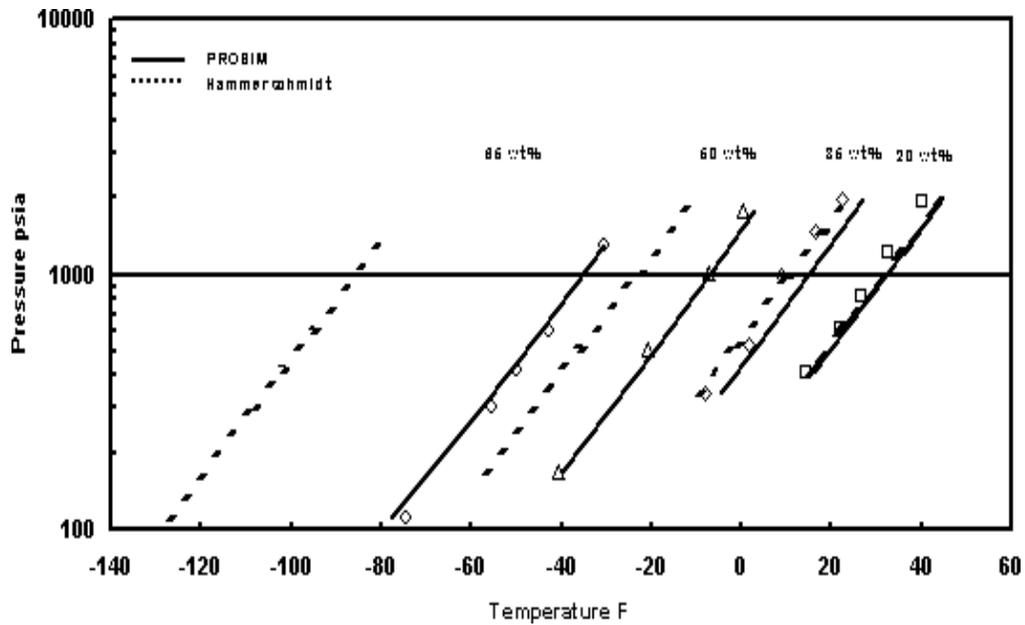


Figure 4. Comparison of Calculated Experimental Hydrate Formation Temperatures for the Methane System

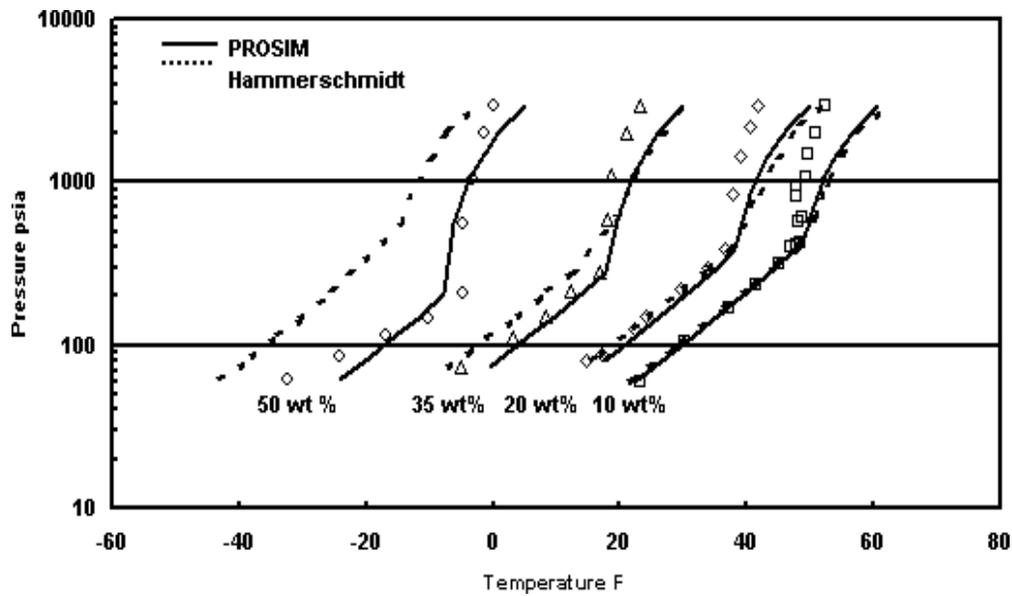


Figure 5. Comparison of Calculated Experimental Hydrate Formation Temperatures for the Ethane System

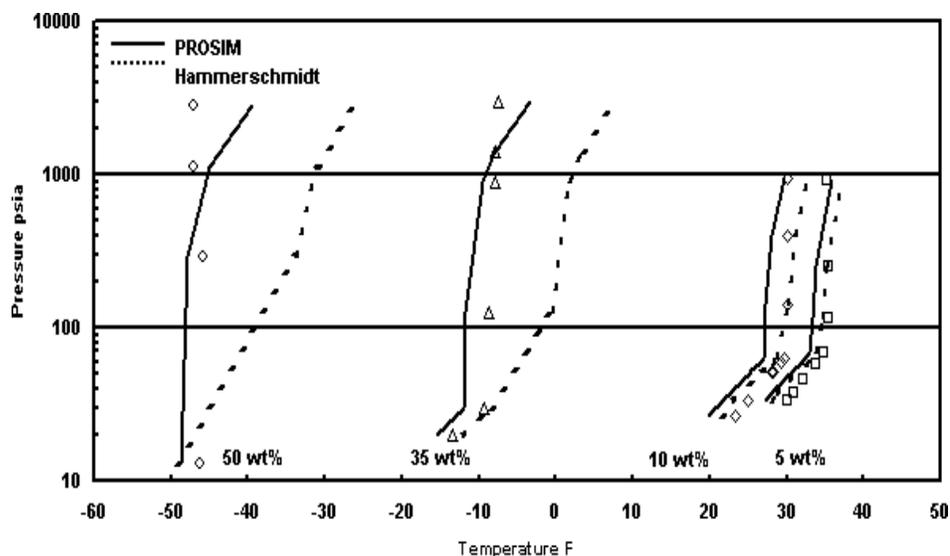


Figure 6. Comparison of Calculated Experimental Hydrate Formation

Temperatures for the Propane System

The second comparison is simulation results versus the vapor-liquid and vapor-liquid-liquid equilibrium measurements from the GPA Research Reports. Table I is a representative set of comparisons from the GPA Research Report 149 [33]. The temperature and pressure for the measurements are about 50°F and 1000 psia. The systems all include water, methanol and methane. The other components are hydrogen sulfide, carbon dioxide, propane, heptane, methylcyclohexane, and toluene. As used by Nociar and Bell [30], the Peng Robinson and SRK equations of state do not predict the three phase behavior of methanol accurately. Their model significantly over-predicted the amount of methanol in the hydrocarbon phase. In contrast, for the methanol concentration in the hydrocarbon phase in Table I, the agreement between the values predicted by PROSIM and measured data is quite favorable.

Table I.
Comparison of Vapor-Liquid-Liquid Equilibrium Composition with PROSIM Predictions^a

Condition	Components	Feed Mol frac.	Vapor		Organic		Aqueous	
			Data Mol frac.	PROSIM Mol frac.	Data Mol frac.	PROSIM Mol frac.	Data Mol frac.	PROSIM Mol frac.
53.8°F 1000 psia	Methane	0.1346	0.942	0.936	--	--	2.335e-3	2.164e-3
	H ₂ S	0.0139	5.731e-2	6.326e-2	--	--	6.841e-3	5.743e-3
	Methanol	0.1345	5.01e-4	5.29e-4	--	--	0.1564	0.1566
	Water	0.7170	3.13e-4	2.54e-4	--	--	0.8344	0.8355
51.8°F 1000 psia	Methane	0.1961	0.8991	0.9104	--	--	2.033e-3	2.065e-3
	CO ₂	0.0218	0.1000	0.08894	--	--	3.752e-3	3.570e-3
	Methanol	0.1235	4.39e-4	4.26e-4	--	--	0.1570	0.1569
	Water	0.6585	4.61e-4	2.33e-4	--	--	0.8373	0.8374
51.8°F 1004 psia	Methane	0.1800	0.9708	0.9721	0.2832	0.3163	2.786e-3	2.135e-3
	Propane	0.0156	0.02533	0.02429	0.1026	0.09964	0.66e-4	1.08e-4
	<i>n</i> -Heptane	0.0706	3.029e-3	2.939e-3	0.6123	0.5819	5.0e-6	4.0e-6
	Methanol	0.1160	5.26e-4	4.38e-4	1.621e-3	1.818e-3	0.1574	0.1595
	Water	0.6177	3.22e-4	2.20e-4	2.66e-4	3.25e-4	0.8398	0.8403

51.8°F 1004 psia	Methane	0.1543	0.9684	0.9674	0.2441	0.3030	2.671e-3	2.127e-3
	Propane	0.0222	0.02828	0.02906	0.1262	0.1175	0.64e-4	1.29e-4
	MCyC6 ^b	0.0938	2.47e-3	2.912e-3	0.6279	0.5772	1.3e-5	2.0e-5
	Methanol	0.1154	5.53e-4	4.40e-4	1.524e-3	2.092e-3	0.1574	0.1574
	Water	0.6142	3.14e-4	2.20e-4	2.07e-4	2.16e-4	0.8398	0.8403
51.8°F 1004 psia	Methane	0.1395	0.9556	0.9626	0.1574	0.1685	2.363e-3	2.155e-3
	Propane	0.0258	0.04164	0.03530	0.1285	0.1310	1.06e-4	1.61e-4
	Toluene	0.1150	1.704e-3	1.488e-3	0.7066	0.69278	2.01e-4	5.56e-4
	Methanol	0.1145	7.47e-4	4.40e-4	6.057e-3	6.795e-3	0.1574	0.1573
	Water	0.6052	3.34e-4	2.20e-4	1.354e-3	0.888e-3	0.8399	0.8398

^a Data from GPA Research Report 149 [33].

^b MCyC6 is for Methyl Cyclohexane

PROCESSING FACILITIES

Combining the versatility of methanol and the accuracy of calculations provided by new techniques for computing fluid phase equilibria, the ability to predict process facilities is further developed. Process calculations using methanol for hydrate suppression, acid gas removal, and dehydration and hydrocarbon liquids recovery are provided as illustrative examples. A comparison of the costs from various solvents as presented in Table II shows methanol is significantly less expensive than other solvents.

**Table II.
Solvent Costs**

Solvent	Cost / lb U.S. \$
Methanol	0.05
Ethylene Glycol	0.20-0.21
Diethylene Glycol	0.32-0.39
Triethylene Glycol	0.42-0.49
MEA	0.56
DEA	0.57
TEA	0.58

^a Source: the ChemEXPO Website
<http://www.chemexpo.com>

Example 1-Methanol Injection for Hydrate Suppression

The modifications of the Empress Gas plant are used as example process calculations. Table III gives the inlet gas composition and water content. Figure 7 shows the injection process for both methanol and glycol injection. Regardless of the downstream process (lean oil absorption or turbo expansion) the inlet process with the inhibitor is basically the same. The feed gas is injected with a certain amount of either glycol or methanol and cooled by the residue gas. Additional cooling is provided by propane refrigeration in the lean oil example and by ethane refrigeration in the case of turboexpansion. The chilled gas separates from the aqueous and hydrocarbon liquid phases in a three phase accumulator. The temperature of the accumulator for the lean oil is -40°F while the temperature for the turboexpansion is about -90°F. The aqueous phase containing a majority of the inhibitor is withdrawn and sent to the recovery process. The vapor and hydrocarbon phases are processed further to separate the methane from the heavier more valuable components. For the recovery process, the methanol product is recovered overhead as a liquid with a purity of about 99 mol%. The bottoms product is virtually pure water. This methanol recovery column operates at about 30 to 50 psia. With a glycol recovery process, the overhead is a vapor water product and the bottoms is the liquid glycol with a purity of about 80 wt% for ethylene glycol.

Table III.
Example 1 Inlet Composition and Conditions^a

Component	Mole %
Composition	
Nitrogen	1.90
Carbon Dioxide	0.50
Methane	91.46
Ethane	4.50
Propane	1.10
<i>i</i> -Butane	0.16
<i>n</i> -Butane	0.23
<i>i</i> -Pentane	0.06
<i>n</i> -Pentane	0.05
<i>n</i> -Hexane	0.03
Heptanes	0.01
Water Content	2.5 to 4 lb/MMscf
Conditions	
Temperature	65°F
Pressure	630 psia
Flow rate	1800 MMscfd

^a From Nelson *et al.* [15].

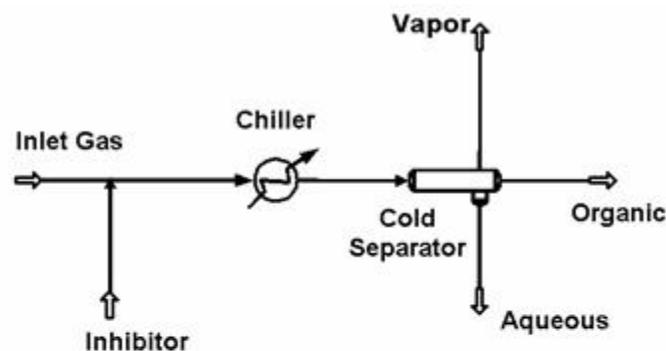


Figure 7. Hydrate Inhibitor Injection Flow Scheme

Table IV shows the calculated injection rate of ethyleneglycol and methanol to prevent hydrate formation at the corresponding LTS conditions of -40 and -90°F , respectively. The methanol is a more powerful inhibitor, only requiring about 1% of the mass flow rate relative to the ethylene glycol. However, the problem of methanol losses is also apparent. More than 99% of the glycol is recovered in the aqueous phase of the LTS while only two-thirds of the methanol is recovered. Furthermore, about one-third is potentially lost in the vapor. By contrast, when the LTS is operated at -90°F as with the turboexpander, the recovery of methanol in the aqueous phase is more

favorable. Losses to the vapor decrease but losses to the organic phase increase. This is primarily due to the increase in the amount of organic liquids produced at the colder temperature.

Table V shows the inhibitor concentration along with the recovery percent from the LTS. Reported values are compared with the PROSIM predictions where available. The predicted methanol concentrations in the aqueous phase are in very good agreement with the reported values, yet the reported recovery in the aqueous phase is roughly half of that predicted. It is unclear whether the recovery values reported for the LTS by Nelson [14] and Nelson and Wolfe [16] are actual measurements or estimated using the technique of Nielsen and Bucklin [16].

Table IV.
Example 1 Calculated Inhibitor Flow Rates from the LTS and Expander Exhaust

Technology	LTS			Inhibitor flow rate			Expander	
	Temp. °F	Injection lb/h	Vapor lb/h	Organic lb/h	Aqueous lb/h	Temp. °F	Vapor lb/h	Organic lb/h
Lean Oil								
Ethylene Glycol ^a	-40	8152	0.014	4.2e-3	8152	--	--	--
Methanol ^a	-40	1085	390	37	658	--	--	--
Turboexpansion								
Methanol ^b	-90	6102	28.23	61.44	6012	-130	1.45 ^c	53.32 ^c

^a Nelson [14]

^b Nelson and Wolfe [16]

^c Includes the injection of 100 gal/day or 26.53 lb/hr of methanol before the expander.

Table V.
Example 1 Comparison Between Reported and Calculated Inhibitor Concentration and Recovery from the LTS Aqueous Phase

Technology	Temp °F	Concentration		Recovery	
		Reported wt%	PROSIM wt%	Reported %	PROSIM %
Lean Oil					
Ethylene Glycol ^a	-40	--	78.08	--	99.99
Methanol ^a	-40	75-80	71.05	33	60.64
Turbo-expansion					
Methanol ^b	-90	80-90	86.27	>50	98.5
Methanol ^c	-90	90	86.27	44 ^c	98.5

^a From Nelson [14]

^b From Nelson and Wolfe [16]

^c From Nielsen and Bucklin [4]

Figures 8 and 9 show the methanol regeneration step and water-wash for both the lean oil and turboexpander, respectively. For both processes, a one to forty water to condensate ratio was specified. For the turboexpansion process, it is reported that all the methanol fed to the demethanizer is concentrated in the propane fraction. For the lean oil process, the authors do not report on the amount of methanol in the propane fraction and that which is left in the residue gas.

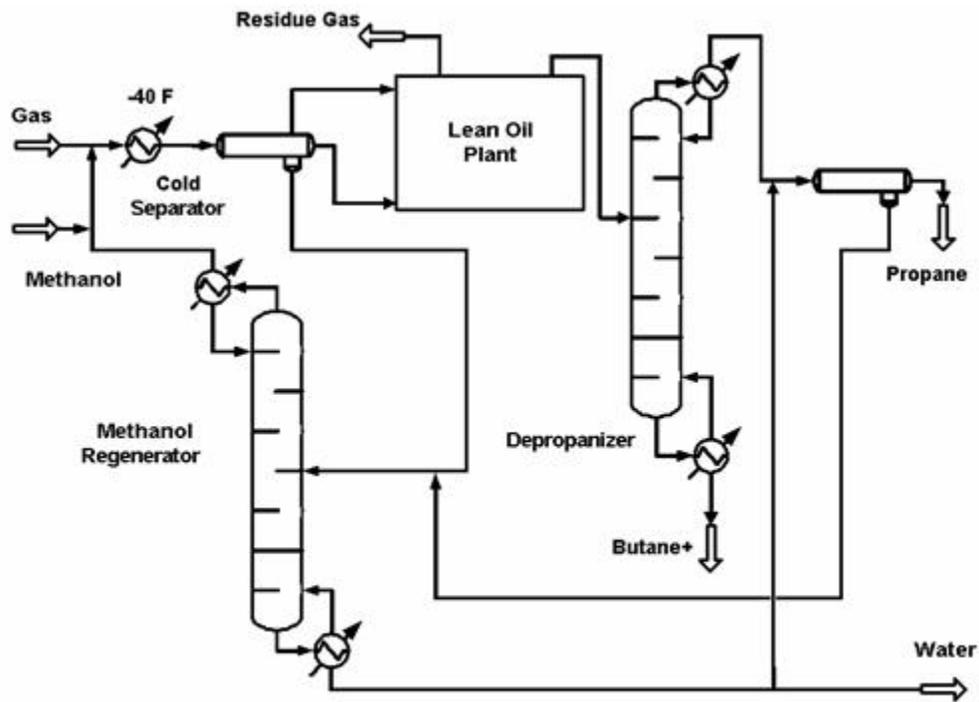


Figure 8. Methanol Recovery Process with Lean Oil Plant

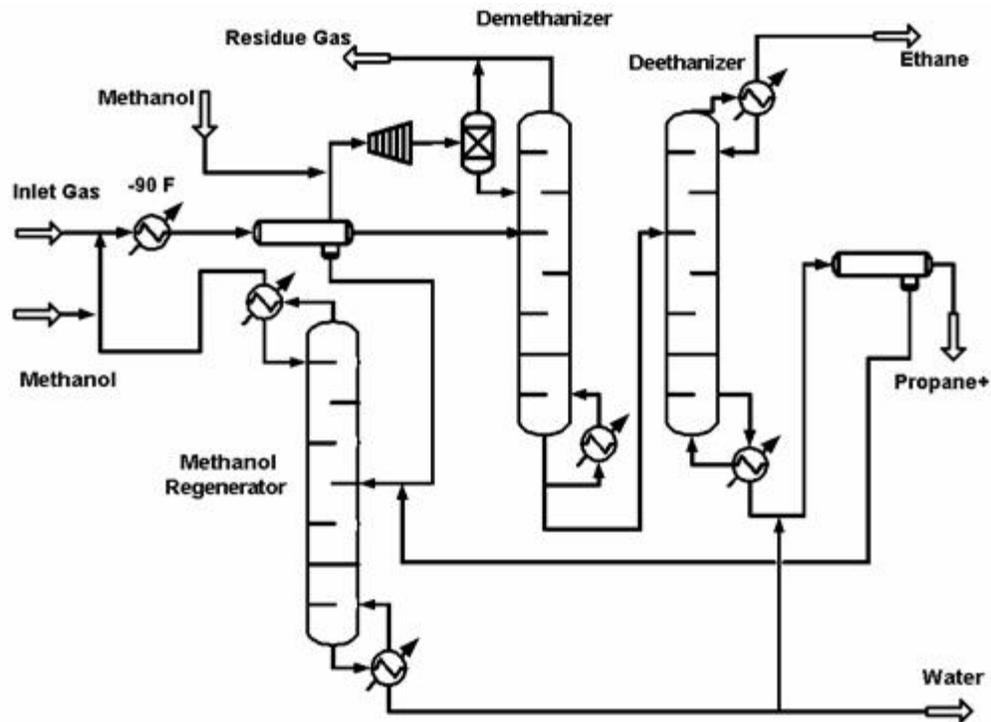


Figure 9. Methanol Recovery Process with Turboexpander Plant

Both lean oil and turboexpansion processes were modeled to determine the methanol loss. Some operating parameters were provided in the original articles, other specifications were obtained from general guidelines and

operating conditions of other similar lean oil and turboexpander processes. Table VI shows the overall inhibitor makeup for both the lean oil system and turbo expander plant. For the lean oil comparison, the calculated value of 2.76 lb/MMSCF is in good agreement with the reported 2.6 lb/MMSCF. As expected, the majority of methanol losses are accounted for in the residue gas. For the turboexpander plant, the calculated methanol makeup of 1.6 lb/MMSCF is also in good agreement with the reported value of 1.5 lb/MMSCF. In this case the residue gas and ethane product represent a majority of the methanol loss. The concentration of methanol in these streams is very small; which is probably why Nelson and Wolfe [16] make that statement that the methanol does not appear in these streams. However, the flow rate of the residue and ethane streams is so large compared with the liquids products that even at these low concentrations the methanol amounts represent a significant portion of the makeup.

**Table VI.
Example 1 Comparison Between
Reported and Calculated Solvent Makeup**

Technology	Solvent Makeup	
	Reported lb/MMSCF	PROSIM lb/MMSCF
Lean Oil		
Ethylene Glycol	--	0.02
Methanol ^a	2.6	2.76
Turbo-expansion		
Methanol ^b	1.5	1.63
Methanol ^c	3.18	1.63

^a Data from Nelson [14]

^b Data from Nelson and Wolfe [16]

^c Data from Nielson and Bucklin [4]

Example 2-Acid Gas Recovery with Cold Methanol

Figure 10 shows a non-selective methanol process for the removal of H₂S and CO₂ from a light synthesis gas stream [17]. Table VII gives the inlet composition used in the process model.

A comparison of the reported product flow rates and compositions with the calculated values from the PROSIM model are reported in Table VIII. Table IX shows the utilities as reported for electrical, steam and refrigeration. The electricity is assumed to be used for pumping and recompression, and the steam is assumed to regenerate the methanol and remove water. In the model, the refrigeration was set as a duty in the absorber on the stage above the inlet gas. This is the only external refrigeration in the facility.

Table VIII.
Example 2 Comparisons Between Reported and Calculated Compositions and Conditions^a

Component	Feed gas	Product		Tail Gas		Stripping Gas
	Mole %	Mole %	Mole %	Mole %	Mole %	Mole %
	Reported	Reported	PROSIM	Reported	PROSIM	Reported
H ₂	54.7	94.7	97.75	0.2	0.33	
N ₂	0.2	0.4	0.42	8.1	8.09	100
Ar-CO-CH ₄	2.8	4.5	4.40	0.4	0.57	
CO ₂	42.2	0.4	0.42	91.0	90.33	
H ₂ S-COS	0.1	0.5 ppm	0.99 ppm	0.3	0.2	
Flow rate (lbmole/hr)	22,073 ^b	12,727	12,691	10,184	10,240	380 ^b
Pressure (psia)	465 ^b	435	435 ^b	15.9	15.9 ^b	3 ^b
Temperature (° F)	77 ^c	--	6.3	--	54.1	90 ^c

^a From Ranke and Mohr [19]

^b Specified value in the simulation model.

^c Assumed value.

Table IX.
Example 2 Comparison Between Reported and Calculated Utilities^a

Utilities	Equipment	Reported	PROSIM
Electrical Energy (kW)	Recompression	--	151
	Semi-Lean Pump	--	658
	Lean Pump	--	331
	Total	1,100	1,140
Refrigeration (MMBtu/hr)	Absorber	20	20 ^b
Steam (MMBtu/hr)	Acid Gas Stripper	--	11.9
	Water Removal	--	2.8
	Total	13.7 ^c	14.7

^a From Mohr and Ranke [19].

^b Set parameter in the simulation.

^c Original reference gives a steam rate of 14,300 lbs/hr.

Example 3-Dehydration and Liquids Recovery with Methanol

Figure 11 shows a schematic of the process as described by Minkkinen and Jonchere [28]. This facility was processing gas from the West Harald offshore gas field located in the North Sea. The purpose of the facility was to produce a gas product with hydrocarbon and water dew points of 8°F at 580 psia as well as efficiently recover the liquid products. The incoming gas/condensate is first cooled followed by the removal of free condensate and

water. Of the vapor fraction, only 25% is used in the methanol stripping column, the remainder is bypassed. The stripping column is designed to recover the methanol and produce a water product in the bottoms with a methanol concentration of less than 100 ppm by weight.

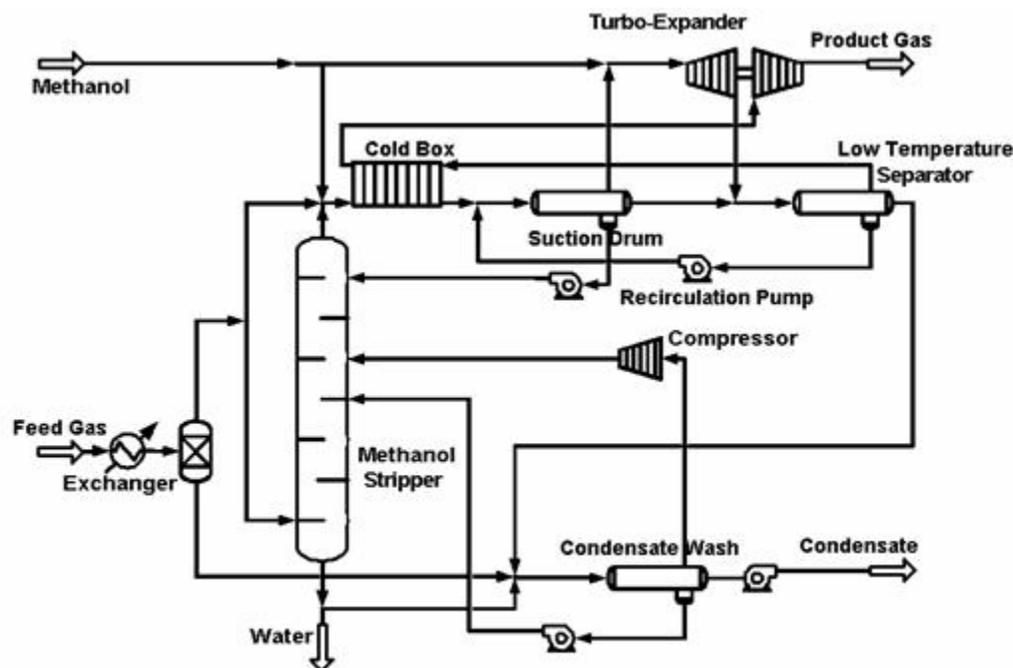


Figure 11. Dehydration and Hydrocarbon Liquids Recovery with Methanol

The overhead from the stripping column and the feed gas are mixed and methanol is injected before the cold section of the process. The injection rate is about 270 gal/day or 2.3 gal/MMSCF. The gas is cooled, flashed in a three phase separator, and expanded to 890 psia and about 0°F. This provides enough work to recompress the pipeline gas to 1045 psia. The aqueous phase is stripped in the methanol stripper and the hydrocarbon phase flows to the LTS. The pipeline gas from the LTS has a methanol molar concentration of about 200 ppm and a methanol to water ratio of about 5 to 1. The gas from the LTS is warmed to 100°F in the gas-gas exchanger and then recompressed. The heat transfer provides cooling for the gas entering the cold section of the process. The low temperature condensate has a methanol molar concentration of about 2000 ppm. The aqueous phase is recycled back to the expander suction scrubber.

To minimize methanol losses, the low temperature condensate is combined with the free condensate and is water-washed. The pressure of the three phase separator is not stated; however, the authors report the flow rate, molecular weight and methanol concentration of the vapor phase from the water wash. The concentration of methanol in the hydrocarbon phase is reported to be 140 ppm by mol and the aqueous phase has a methanol concentration of about 5 wt%. The wash water is recycled back to the methanol stripping column and introduced at the mid point, while the vapors are recompressed and also used as stripping gas.

A process simulation model is proposed; however, several assumptions were made in the initial set up due to the limited data reported. The authors report only a molecular weight of the incoming feed. Comparing data with Katz [35], a representative composition was assembled as shown in Table X. This composition yields a similar molecular weight and free condensate production at the inlet conditions.

Table X.
Example 3 Inlet Composition^a

Component	Mole %
Water	0.116
Carbon Dioxide	0.678

Methane		75.68
Ethane		13.13
Propane		4.395
<i>i</i> -Butane		0.6
<i>n</i> -Butane		0.7
<i>i</i> -Pentane		0.5
<i>n</i> -Pentane		0.5
<i>n</i> -Hexane		0.5
C7		0.4
C8		0.3
C9-C17	0.2 each	1.8
C18-C24	0.1 each	0.7

^a Minkkinen and Jonchere [28] and Katz *et al.*[35].

Table XI compares the PROSIM model with the reported values and the process conditions necessary to achieve the specified flow rates, molecular weights, and methanol concentration. The methanol molar concentrations predicted by PROSIM in the hydrocarbon phase from the LTS is only about 1000 ppm whereas the authors report a methanol concentration in excess of 2000 ppm. Furthermore, the water wash calculations do not show as much methanol removed as reported. The calculated methanol molar concentration is only 400 ppm relative to 140 ppm. These differences may be attributable to the assumed inlet composition.

Table XI.
Example 3 Comparisons to Reported and Calculated Operating Flow Rates, Molecular Weights, and Methanol Concentration^a

Description	Flow rate ^b		Molecular Weight		MeOH Concentration ppm		Temperature °F		Pressure Psia	
	Rep.	PROSIM	Rep.	PROSIM	Rep.	PROSIM	Rep.	PROSIM	Rep.	PROSIM
Gas										
Inlet	335	335 ^c	26.7	26.4	0	0 ^c	105	105 ^c	1365	1365 ^c
Cold Stripping	75.3	75.3 ^c	20.1	20.14	0	0 ^c	--	105	--	1365
Cold Process	323.0	323.1	20.2	20.23	810	374	--	113	--	1362
Warm	21.6	20.15	21.5	21.57	165	142	--	250	--	1370
Stripping Pipeline	304	302.3	19.2	19.28	200	150	--	125	1045	1065
Condensate										
Free	32010	32510	85.5	84.27	0	0 ^c	--	105	--	1365
Cold	11577	11915	36.0	34.46	2370	895	~ 0	1.5	890	890 ^c
Pipeline	33762	34930	97.9	91.97	140	433	--	64	--	1050
Water										
Stripper	--	50.5	--	18.02	< 100	69 ppm wt	--	105	--	1360
Bottom										
Condensate	--	6.6	--	18.35	~ 5 wt%	4.1 wt%	--	105	--	450
Wash										

^a From Minkkinen and Jonchere [28].

One final point, in the PROSIM model the simulator consistently warned about the temperatures being below the hydrate point for the initial cooling of the exchanger. This section of the process is at 1300 psia. At these high pressures, the simulator is conservative relative to the data as shown in Figures 4, 5, and 6.

CONCLUSIONS

For gas processing operations below -20°F , such as turboexpansion, methanol excels when compared to other physical solvents. Methanol is a more powerful hydrate inhibitor, has a lower viscosity and lower surface tension. The high vapor pressure which may initially appear to be a detriment is actually beneficial in many cases by allowing thorough mixing and easy recovery in downstream processes. For acid gas removal at cold temperatures, methanol offers the highest CO_2 absorption capacity relative to other solvents. Methanol has a high affinity for hydrocarbons as well as acid gas. This hydrocarbon loss problem can be mitigated with water washes and phase separation. Combining the processes of dehydration or inhibition, acid gas removal, heavy hydrocarbon recovery, along with simple and economical solvent recovery makes methanol a truly unique and powerful solvent. With the improvements to simulation programs to more accurately predict the behavior of methanol and recent process developments, engineers should have a better understanding of methanol and be more willing to exploit this versatile solvent.

REFERENCES CITED

1. Kohl A. and R. Nielsen, *Gas Purification*, 5th Ed., Gulf Publishing, 1997.
2. Hammerschmidt, E.G., "Formation of Gas Hydrates in Natural Gas Transmission Lines," *Industrial Engineering Chemistry*, Vol. 26, No. 8, 851-855, 1934.
3. Hammerschmidt, E.G. "Gas Hydrate Formations: A Further Study on Their Prevention and Elimination from Natural Gas Pipe Lines," *GAS*, 30-35, May 1939.
4. Nielsen, R.B. and R.W. Bucklin, "Why not use methanol for hydrate control?" *Hydrocarbon Processing*, Vol. 62, No.4, 71-78, April 1983.
5. Ng, H.-J. and D.B. Robinson, *Research Report 66 Equilibrium Phase Composition and Hydrating Conditions in Systems Containing Methanol, Light Hydrocarbons, Carbon Dioxide and Hydrogen Sulfide*, Gas Processors Association, Tulsa, Oklahoma, 1983.
6. Ng., H.-J. and D.B. Robinson, *Research Report 74 The Influence of Methanol on Hydrate Formation at Low Temperatures*, Gas Processors Association, Tulsa Oklahoma, 1984.
7. Ng., H.-J. and D.B. Robinson, *Research Report 106 The Influence of Methanol on Hydrate Formation and the Distribution of Glycol in Liquid-Liquid-Mixtures*, Gas Processors Association, Tulsa, Oklahoma, 1987.
8. Gas Processors Suppliers Association, *Engineering Data Book*, 11th Edition, Volume II, Section 20, "Dehydration," Gas Processors Association, Tulsa, Oklahoma, 1998.
9. Maddox, R.N., M. Moshfeghian, E. Lopez, C.H. Tu, A. Shariat, and A.J. Flynn, "Predicting Hydrate Temperature at High Inhibitor Concentration," *Proceedings of Laurance Reid Gas Conditioning Conference*, Norman, Oklahoma, 273-294, 1991.
10. Sloan, E. D., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York, 1990.
11. Zuo, J.Y. and D.D. Zhang, "Gas Hydrate Formation in Aqueous Solutions Containing Methanol and Electrolytes," *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, Oklahoma, 191-198, 1999.
12. Song, K.Y., G. Feneryrou, R. Martin, R. Kobayashi, *Research Report 161 Kinetics of Gas Hydrates with and without Inhibitors*, Gas Processors Association, Tulsa, Oklahoma, 1997.
13. Bishnoi, P.R. R.D Dholabhai, and K.H. Mahadev, *Research Report 156 Hydrate Phase Equilibria in Inhibited*

and Brine Systems, Gas Processors Association, Tulsa, Oklahoma, 1996.

14. Nelson, K., "Methanol Injection Cuts Costs," *Hydrocarbon Processing*, 161-163, September, 1973.
15. Nelson, K., F. Van Ginhoven, and J.D. Hammond, "Canadian Expander Plant Hikes Ethane Recovery," *Oil and Gas Journal*, 68-81, July 10, 1978.
16. Nelson, K. and L. Wolfe, "Methanol Injection and Recovery in a Large Turboexpander Plant," *Selected Proceedings of the Laurance Reid Gas Conditioning Conference 1951-1988*, Volume II, 681-691, 1993.
17. Reid, L.S. and W.R. McLeod, "Methanol Injection in High-Pressure Gas Condensate Production Systems," *Selected Proceedings of the Laurance Reid Gas Conditioning Conference 1951-1988*, Volume II, 656-662, 1993.
18. Behrens, S.D., K.K. Covington, and J.T. Collie III, "Selection of Hydrate Suppression Methods for Gas Streams," *Proceedings of the 78th GPA Annual Convention*, 46-52 Nashville Tennessee, 1998.
19. Ranke, G. and V.H. Mohr, "The Rectisol Wash New Developments in Acid Gas Removal from Synthesis Gas," in *Acid and Sour Gas Treating Processes*, S. A. Newman, Ed., 80-111, Gulf Publishing Company, Houston, Texas, 1985.
20. Hoogendoorn, J.C., and J.M. Salomon, "SASOL: World's Largest Oil-From-Coal Plant," *British Chemical Engineering*, 238-244, May, 1957.
21. Hoochgesand, G., "Rectisol and Purisol," *Industrial and Engineering Chemistry*, Vol 62, No 7, 37-43, July, 1970.
22. Staton, J.S., R.W. Rousseau, and J.K. Ferrell, "Regeneration of Physical Solvents in Conditioning Gases from Coal," in *Acid and Sour Gas Treating Processes*, S. A. Newman, Ed., 131-163, Gulf Publishing Company, Houston, Texas, 1985.
23. Rojey, A. and J. Larue, (Assigned to the Institut Francais du Petrole) "Integrated Process for the Treatment of a Methane-Containing Wet Gas in Order to Remove Water There From," U.S. Patent 4775395, October 4, 1988.
24. Rojey, A. A. Procci, and J. Larue, (Assigned to the Institut Francais du Petrole) "Process and Apparatus for Dehydration, Deacidification, and Separation of Condensate from a Natural Gas," U.S. Patent 4979966, December, 1990.
25. Larue, J., A.A. Minkkinen, and S. Patel, "IFPEXOL for Environmentally Sound Gas Processing," *Proceedings of the 71st GPA Annual Convention*, 20-28, Anaheim, California, 1992.
26. Patel, S. "IFPEXOL – A Year + Later," paper presented at Can Energy '94, Calgary, April 19-20, 1994.
27. Holcek, R.G., A. Minkkinen, and J. Larue, "The IFPEX-1 Process for Natural Gas Dehydration/Hydrate Inhibition, The North American Experience," *Proceedings of the Laurance Reid Gas Conditioning Conference*, 1-14, 1996.
28. Minkkinen, A. and J.P. Jonchere, "Methanol Simplifies Gas Processing," *Proceedings of the 76th GPA Annual Convention*, 227-233, San Antonio Texas, 1997.
29. Beaumont, M. and M. Brierly, "Replacement of Glycol Dehydration with IFPEXOL Technology – Design Concept and Operating Experience," *Proceedings of the 77th GPA Annual Convention*, 154-159, Dallas, Texas 1998.
30. Nociar, B. and K. Bell, "Control of Methanol Consumption in IFPEX-1 Units Based on AEC West's Sexsmith Gas Plant Operating Experience," *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman Oklahoma, 168-190, 1999.

31. Bryan Research & Engineering, Inc., BR&E Reference Manual, 1999, version 98.1.
32. Chen, C.J and H.-J. Ng, *Research Report 117 The Solubility of Methanol or Glycol in Water-Hydrocarbon Systems*, Gas Processors Association, Tulsa, Oklahoma, 1988.
33. Ng, H-J and C.-J. Chen, *Research Report 149 Vapor-Liquid and Vapor-Liquid-Liquid Equilibria for H₂S, CO₂, Selected Light Hydrocarbons and a Gas Condensate in Aqueous Methanol or Ethylene Glycol Solutions*, Gas Processors Association, Tulsa Oklahoma, 1995.
34. Lyddon, L.G. V.N. Hernandez-Valencia, M.W. Hlavinka, and J.A. Bullin "Applications and Benefits to the Gas Processing Industry of the GPA Research Program," *Proceedings of the 78th GPA Annual Convention*, 121-127, Nashville, Tennessee, 1999.
35. Katz, D.L., D. Cornell, J. A. Vary, R. Kobayashi, J.R. Elebaas, F. H. Poettmann, and C.F. Weinaug, *Handbook of Natural Gas Engineering*, McGraw-Hill, New York, New York, 1959.

copyright 2001 Bryan Research & Engineering, Inc.