PhaseOpt – Online tool for hydrocarbon dew point monitoring

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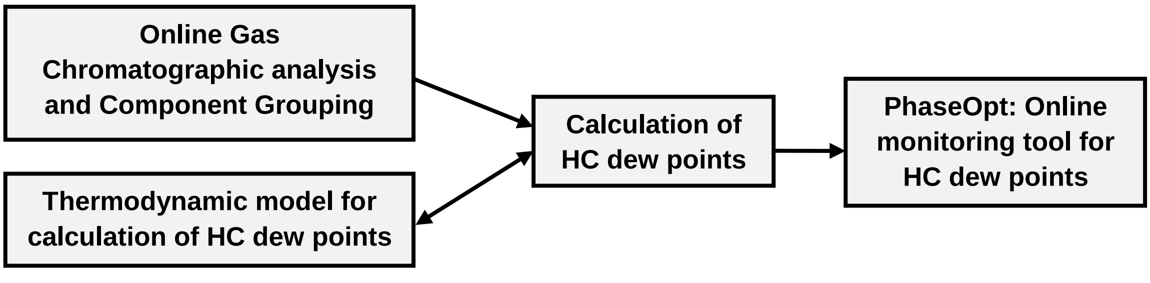
Abstract

The knowledge of the hydrocarbon dew point is of great importance for the oil & gas industry as it is one of the gas quality specifications used for ensuring safe transport of natural gas. The most used dew point specification for natural gas transported in the European pipeline system, is the cricondentherm specification used for sales gas (SG). On the Norwegian Continental Shelf, rich gas pipelines are commonly used to transport partly processed gas from offshore installations to onshore facilities in the dense phase region and thus, a cricondenbar specification has to be fulfilled.

The PhaseOpt technology is a tool for online monitoring of hydrocarbon dew point in rich gas pipelines. Accurate prediction of hydrocarbon dew point temperature and pressure is of great importance to obtain effective utilization of the natural gas pipelines and process plants without hydrocarbon liquid drop-out. Finally, given the deregulated European gas market and varying range of gas quality, a tool for reliable determination of the hydrocarbon dew point for pipeline gas is increasingly important.

The PhaseOpt technology is illustrated in the figure below and consists of:

- A sample system optimized to handle trace component analysis and traces of liquid glycol in the gas
- An online process GC-analyser providing extended compositional analysis with detailed composition up to C_{12}
- A reliable thermodynamic model for hydrocarbon (HC) dew point calculations with focus on cricondenbar
- Implementation of methods for online cricondenbar measurement into control system of pipelines and process plants



1 Introduction

Hydrocarbon dew point is one of the gas quality specifications used for ensuring safe transport of natural gas in Europe. Hydrocarbon condensates in natural gas pipelines represent risk of decreased regularity and pipeline integrity and can cause serious damages to machinery and equipment.

The most common dew point specification for natural gas transported in the European pipeline system, is the cricondentherm specification used for sales gas. On the Norwegian continental shelf, so called rich gas pipelines are also common. These pipelines transport partly processed gas, called rich gas, in the dense phase region at pressures higher than the cricondenbar. Accurate prediction of hydrocarbon dew point temperature and pressure is of great importance to obtain effective utilization of the natural gas pipelines and process plants without hydrocarbon liquid drop-out. Finally, given the deregulated European gas market and varying range of gas quality, a tool for reliable determination of the hydrocarbon dew point for pipeline gas is increasingly important.

1.1 Cricondenbar specification in rich gas pipelines and process plants

As illustrated in Figure 1 the cricondenbar pressure is defined as the highest pressure at which a liquid hydrocarbon phase can exist. Gas transport at pressures higher than the cricondenbar pressure ensures single phase flow without drop-out of any liquid hydrocarbons in the pipeline.

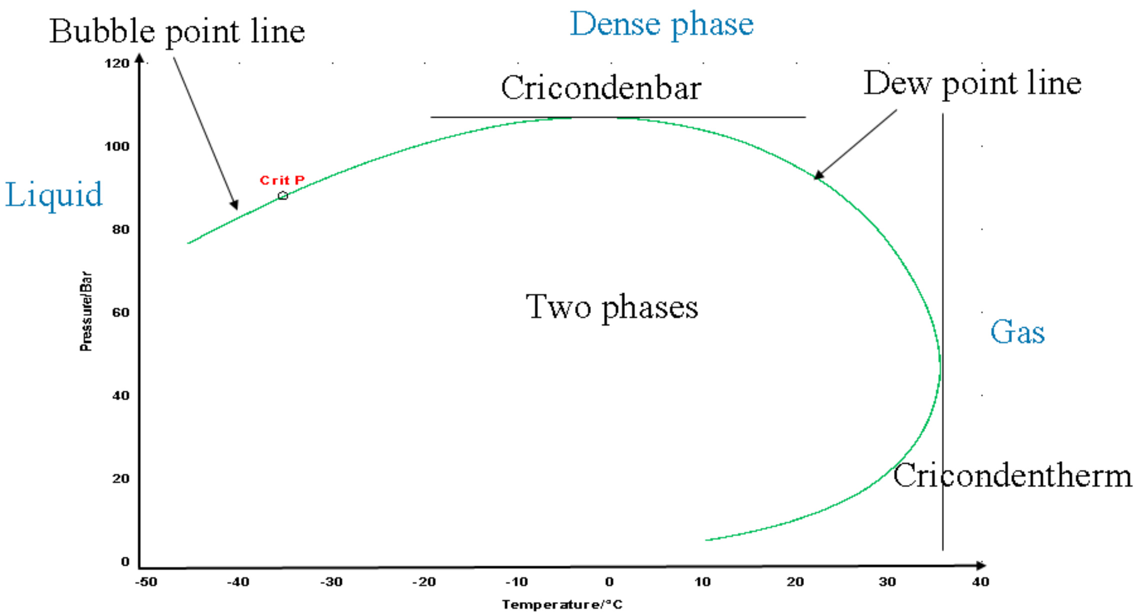


Figure 1: Phase behaviour of a typical natural gas

Figure 2 illustrates the Åsgard Transport pipeline which receives rich gas from various offshore producers like Åsgard, Kristin, etc, and delivers it to the Kårstø plant for final processing before reaching the market to Continental Europe. All offshore producers they have to fulfil a cricondenbar specification of maximum 105 barg in order to be allowed to deliver their gas to Åsgard Transport. The gas in Åsgard pipeline is transported in the dense phase at high pressures above the cricondenbar in order to avoid any liquid hydrocarbon phase in the system. In addition, the inlet pressure at the Kårstø plant has to be kept higher than the cricondenbar in order to ensure that this condition is met and hence ensure safe and stable operation.

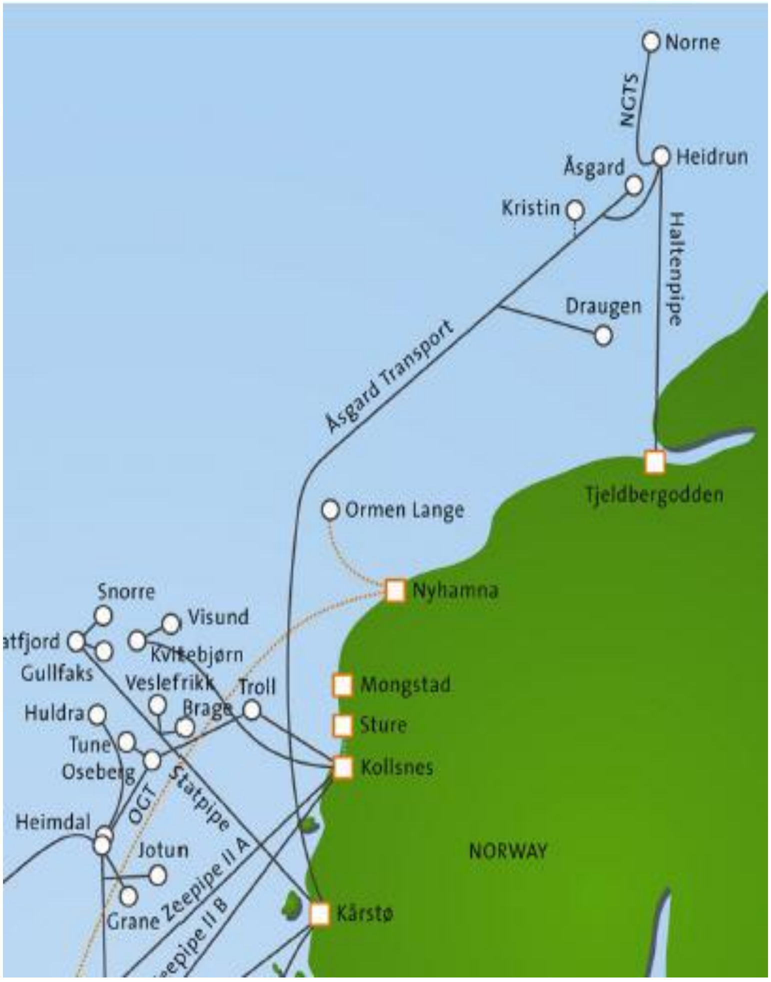


Figure 2: Åsgard Transport pipeline system and Kårstø gas processing plant

1.2 Business drivers for PhaseOpt technology

As various gas producers deliver gas to the Åsgard pipeline, the gas quality arriving at Kårstø can vary significantly. The offshore fields delivering gas to Åsgard transport are designed to deliver gas with a safety margin to the cricondenbar specification. Experiences have however shown that offshore producers often cannot meet the cricondenbar specification as per design and thus, process improvements and modifications are needed. Obviously, a tool for online monitoring of the cricondenbar specification to ensure gas quality would be very useful for offshore producers.

Moreover, the inlet facilities at Kårstø (Figure 2) involve water removal using adsorbents, H_2S and mercury removal using solid beds and other mechanical equipment (heat exchangers and turbo expanders). Liquid hydrocarbons will have a significant negative effect on the operation of these processes, and hence it is of high importance to prevent any liquid drop-out at the inlet facilities. As of today a relatively large operational pressure margin to the cricondenbar is necessary to secure safe operation of the inlet facilities. Also here a tool for online cricondenbar monitoring of the gas entering the Kårstø plant will be very useful. Such a tool will improve both regularity and the possibility to reduce safety margins for the pressure in the inlet facilities. This in turn could allow for increased capacity in Åsgard Transport due to increased difference between inlet and outlet pressure.

In conclusion, PhaseOpt technology comes exactly to serve these business needs, namely efficient operations in gas plants (offshore/onshore), optimise pipeline capacity and ensure gas quality of offshore producers, as also illustrated in Figure 3.

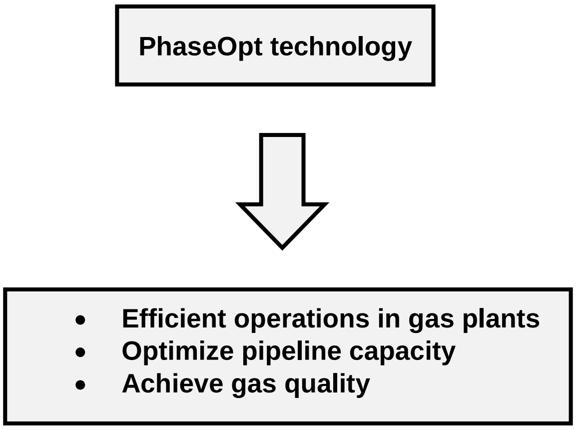


Figure 3: Business drivers for PhaseOpt technology

2 Description of PhaseOpt technology

The main technology elements in PhaseOpt are:

- A sample system optimized to handle trace component analysis and traces of liquid glycol in the gas
- An online process GC-analyser providing extended compositional analysis with detailed composition up to C_{12}
- A reliable thermodynamic model for hydrocarbon (HC) dew point calculations with focus on cricondenbar
- Implementation of methods for online cricondenbar measurement into control system of pipelines and process plants

The PhaseOpt technology is illustrated in Figure 4 below:

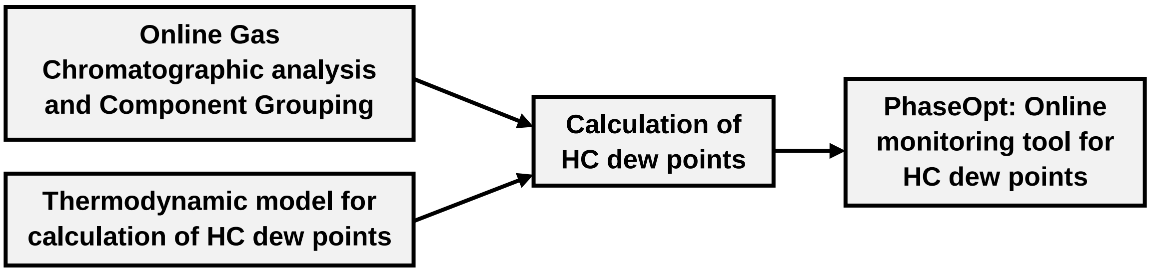


Figure 4: Illustration of PhaseOpt technology

2.1 Online Gas Chromatographic analysis (GC analysis)

Hydrocarbon dew point is highly influenced by the heavier hydrocarbons in the mixture (C_{6+} fraction). Therefore, the traditional "C6 plus" analysis provides insufficient data for a valid hydrocarbon dew point calculation. If suitable analytical sensitivity can be obtained, then the combination of extended on-line GC analysis with a subsequent calculation from a reliable model gives the possibility of on-line hydrocarbon dew point determination. The challenge with the GC analysis in PhaseOpt is to obtain detailed analysis of heavy components up to C_{12} while at the same time the analysis time is kept as short as possible.

Another challenge for the PhaseOpt GC was representative sampling at high pressures and handling of trace components such as glycols, water and heavy hydrocarbons in the sample. After a number of years with laboratory and field testing, we have gained valuable experience in developing methods to handle trace component analysis. These methods involve use of highly polished surfaces and use of silica treated materials to minimize adsorption of trace components and heavier hydrocarbons on the sample tubing.

Two Siemens Maxum II process gas chromatographs (GCs) are used in PhaseOpt. Gas from Åsgard Transport can be routed to both the two GCs via the sampling system.

The "PhaseOpt GCs" are equipped with 3 applications:

- Application 1 separates and quantifies the light end natural gas components: hydrocarbons from methane to n-pentane in addition to a C_{6+} composite peak (C_1-C_{6+}) with respect to boiling point, including carbon dioxide (CO_2) and nitrogen (N_2). For this separation, 4 separation columns are utilised with multiple thermo conductivity detectors (TCD).

- Application 2 separates and quantifies hydrogen sulphide (H_2S). A flame photometric detector (FPD) is utilised in this application (not in use for PhaseOpt).
- Application 3 separates and quantifies the heavy end natural gas components: hydrocarbons with higher boiling points than n-pentane (C_6-C_{12+}). For this two separation columns in series (8 m and 17 m respectively) with optional back flush of the first column, a flame ionisation detector (FID) is used.

Only data from application 1 and 3 are used for PhaseOpt. The analysis time for the two applications is three and nine minutes, respectively.

2.2 Thermodynamic model for calculation of cricondenbar (UMR-PRU)

For a number of years, we had focus on measuring dew points of export gas from our production fields in order to improve operations. Our experiences regarding measuring and modelling hydrocarbon dew points and how these were related to design and operation of process facilities were summarised in a previous paper [1]. As part of this work a large database with hydrocarbon dew point data of natural gases was prepared. The Statoil database with dew point data now contains data for approximately fifty natural gases from various fields where a detailed compositional analysis and the dew point curve up to the cricondenbar pressure has been experimentally established. This database has been important in developing the PhaseOpt thermodynamic model.

Statoil and Gassco have in cooperation with the Technical University of Athens (NTUA) developed a thermodynamic model capable of calculating dew points with higher accuracy than classical equation of states (EoS) such as the Soave Redlich-Kwong (SRK) and the Peng-Robinson (PR), most often used in the Oil & Gas industry. The new model is a predictive equation of state that combines the PR EoS with an original UNIFAC-type model for the excess Gibbs energy (G^E), through the universal mixing rules (UMR). The model is called UMR-PRU (Universal Mixing Rule – Peng Robinson UNIFAC) and it is the most accurate model for calculation of cricondenbar and hydrocarbon dew points we have tested until now [2, 3]. For simplicity, we will call the UMR-PRU model as "PhaseOpt model" in the rest of this work.

2.3 Component grouping from online GC to PhaseOpt model

Earlier studies indicated that detailed GC analysis up to C_9 with detailed PNA distribution in the C_7 to C_9 fractions together with analysis of total C_{10}, C_{11} and C_{12} fractions is sufficient for accurate calculation of cricondenbar and dew points of rich natural gases [1].

A complete separation of every individual hydrocarbon, heavier than n-hexane, will not be achievable on a process-GC for online analysis. Hence, most of the peaks eluting from application 3 of the GC column (C_6-C_{12} analysis) are so-called composite peaks, consisting of several compounds with similar retention times. When assigning names to these composite peaks, the chromatograms from Application 3 were compared to analysis performed with extended analysis from a laboratory GC with higher separation efficiency. Thus, in the C_7 fraction, all composite peaks consisting mainly of paraffinic (P), naphthenic (N) and aromatic peaks (A) are named C7P, C7N and C7A respectively. The same approach (PNA distribution) was used for the C_8 and C_9 fractions. Then each of the C7P, C7N, C7A groups are simulated as specific components in the UMR-PRU model. For example, C7P is simulated as n-C7, C7N as cyclo-C6, C7P as benzene, etc., as shown in Table 1. For the C_{10}-C_{12} fraction only the total C_{10}, C_{11} and C_{12} fraction is available from the GC and they are simulated as nC_{10}, nC_{11} and nC_{12}, respectively in the PhaseOpt model (Table 1).

Table 1: Component grouping from GC to PhaseOpt model

GC peaks	Group Name	PhaseOpt Component
nitrogen	N2	nitrogen
CO2	CO2	CO2
methane	C1	methane
ethane	C2	ethane
propane	C3	propane
i-butane	iC4	i-butane
n-butane	nC4	n-butane
i-pentane	iC5	i-pentane
n-pentane	nC5	n-pentane
2-M-C5, 2,3-DM-C4, cy-C5	2-M-C5	2-M-C5
3-M-C5	3-M-C5	3-M-C5
n-C6	n-C6	n-hexane
n-C7, 2-m-C6*	C7 (P)	n-heptane
cy-C6, m-cy-C5, C7-1-N*	C7 (N)	cy-hexane
benzene	C7 (A)	benzene
n-C8, C8-4-P*	C8 (P)	n-octane
e-cy-C5, Me-Cy-C6, C8-1-N, C8-2-N, C8-3-N, C8-5-N, C8-6-N, C8-7-N	C8 (N)	cy-heptane
Toluene	C8 (A)	toluene
n-C9, C9-3-P, C9-4-P, C9-5-P, C9-7-P, C9-11-P, C9-12-P	C9 (P)	n-nonane
e-cy-C6, C9-1-N, C9-2-N, C9-10-N, C9-13-N, C9-14-N, C9-15-N	C9 (N)	cy-octane
o-xylene, m-p-xylene, e-benzene	C9 (A)	m-xylene
all C10 peaks	C10	nC10
all C11 peaks	C11	nC11
All C12+	C12	nC12

3 Results from PhaseOpt qualification

Two field tests were done to evaluate and qualify the PhaseOpt technology. The first field test was done in June 2012 without the online GC available but with offline estimations of cricondenbar by PhaseOpt. The second field test was done in May 2013 with the online GC available and PhaseOpt fully operational. More information about the field tests can be seen in Table 2.

Table 2: Description of field tests done to qualify PhaseOpt

	Location	Time	Actions	Comments
Field test 1	Åsgard Transport	June 2012	• Manual dew point measurement in field • Sampling of gas on cylinders for laboratory GC analysis (Statoil and external laboratories) • Sampling of gas on cylinders for laboratory dew point measurements • Offline cricondenbar estimation using PhaseOpt technology	• Online PhaseOpt GC not available • Offline cricondenbar measurements
Field test 2	Åsgard Transport	May 2013	• Manual dew point measurement in field • Sampling of gas on cylinders for laboratory GC analysis (Statoil) • Sampling of gas on cylinders for laboratory dew point measurements • Online analysis of cricondenbar using PhaseOpt technology	• Online PhaseOpt GC available • PhaseOpt fully operational • Online cricondenbar measurements

3.1 Field Test 1

The first field test was done in June 2012 with gas from Åsgard Transport. The online PhaseOpt GC was not yet in operation and thus only offline cricondenbar estimations were available.

The following measurements were done during the first field test:

- Manual hydrocarbon dew point measurements in the field. A standard optical dew point instrument from Chandler Engineering, also called "Bureau of Mines" dew point analyser was used [4].
- Sampling of gas for laboratory GC analysis at Statoil and external laboratories. Details about the laboratory GC analysis can be found in a previous GPA paper [1]

- Sampling of gas on cylinders for laboratory dew point measurements. A standard optical dew point instrument from Chandler Engineering, also called “Bureau of Mines” dew point analyser, mounted into a temperature controlled chamber, as presented in a previous GPA paper [1].
- Offline cricondenbar estimation using PhaseOpt model

Measurements of dew points in the field proved to be difficult, as expected, due to a glycol film covering the mirror and the mirror had to be cleaned several times during the measurements. Field measurements require a well trained and experienced operator to manage to see the hydrocarbon dew point appearing behind the glycol film. In contrast, no problems with glycols were experienced in the dew point measurements done in the lab. Generally, it is less laborious to measure dew points in the lab due to better control of the experiment parameters such as the gas temperature and flow, the cooling rate, etc. For this reason, the measured cricondenbar in the lab will be used as our basis for all comparisons.

The comparisons between the measured and the estimated cricondenbar for the two samples taken during field test 1 are given in Table 3. For the first sample there is a very good agreement between the measured cricondenbar at the field and the one measured at the laboratory, with a deviation of only 0.2 bar. For the second sample the differences in the measured cricondenbar at the field and at the lab are higher (1.1 bar). When it comes to model predictions, the PhaseOpt model overpredicts the cricondenbar in both samples by 0.8 bar and 0.2 bar, respectively. The opposite happens for SRK which underpredicts the cricondenbar by 1.9 and 2.5 bar, respectively. In both cases the PhaseOpt model is superior to SRK when it comes to estimation of the cricondenbar pressure.

Table 3: Measured and estimated cricondenbar for two different samples from field test 1.

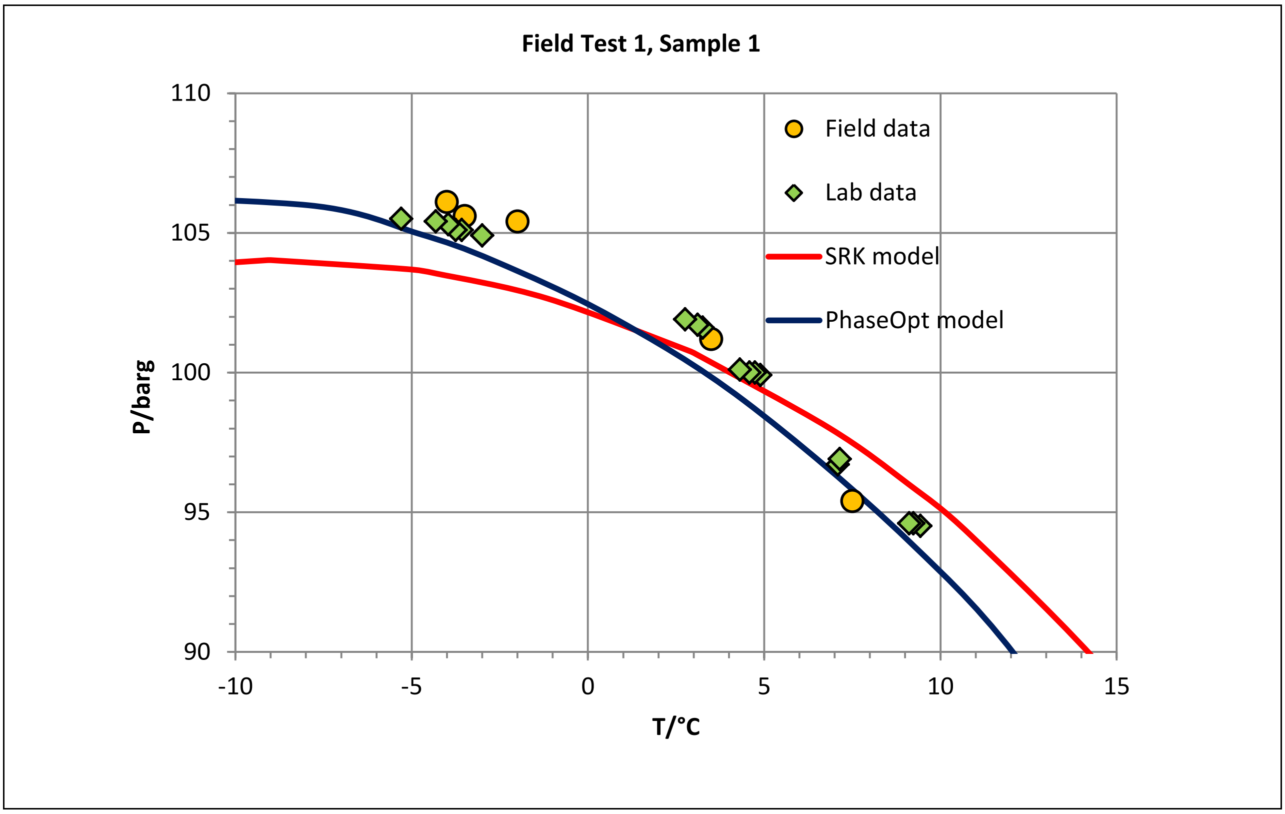
	Sample 1		**Sample 2**	
	Cricondenbar pressure	**Deviation (from lab measurement)**	**Cricondenbar pressure**	**Deviation (from lab measurement)**
	[barg]	**[bar]**	**[barg]**	**[bar]**
Lab measurement	105.9	-	101.8	-
Field measurement	106.1	+0.2	102.9	+1.1
SRK model	104.0	- 1.9	99.3	-2.5
PhaseOpt model	106.7	+0.8	102	+0.2

We can consider now another case where we are interested in the dew point pressure at a given temperature, let’s say at -5°C, which is close to the cricondenbar temperature measured in the lab. Such a case can be interesting for process plants where the gas is cooled to a certain temperature but the pressure should be kept above the dew point in order to avoid any liquid phase in the inlet facilities. The estimated dew point pressure at -5°C is shown in Table 4. Both SRK and PhaseOpt underpredict the dew point pressure. PhaseOpt underpredicts the pressure by 0.4 and 1.3 bar for sample 1 and 2, while SRK underpredicts the pressure by 1.7 and 2.5 bar, respectively. Also in this case the PhaseOpt model is superior to SRK when it comes to estimation of the dew point pressure at a given temperature.

Table 4: Measured and estimated dew point pressure at a certain temperature (-5°C) for two different samples from field test 1.

	Sample 1		**Sample 2**	
	Dew point pressure @ -5°C	**Deviation (from lab measurement)**	**Dew point pressure @ -5°C**	**Deviation (from lab measurement)**
	[barg]	**[bar]**	**[barg]**	**[bar]**
Lab measurement	105.4	-	101.3	-
SRK model	103.7	- 1.7	98.8	-2.5
PhaseOpt model	105.0	-0.4	100.0	-1.3

Figure 5 shows all measured and estimated dew points for Sample 1 and 2. The PhaseOpt model provides a clear improvement compared to the SRK model, when it comes to predicting the dew points at high pressures around the cricondenbar. PhaseOpt is also better than SRK in predicting the correct shape of the dew point line and it consistently underpredicts it. SRK fails to predict the correct shape of the dew point line. It underestimates the cricondenbar, while sometimes it overestimates the dew point pressure at higher temperatures (see Sample 1). This model behaviour is typical for real gas mixtures and is discussed in more details in our previous works [1, 3].



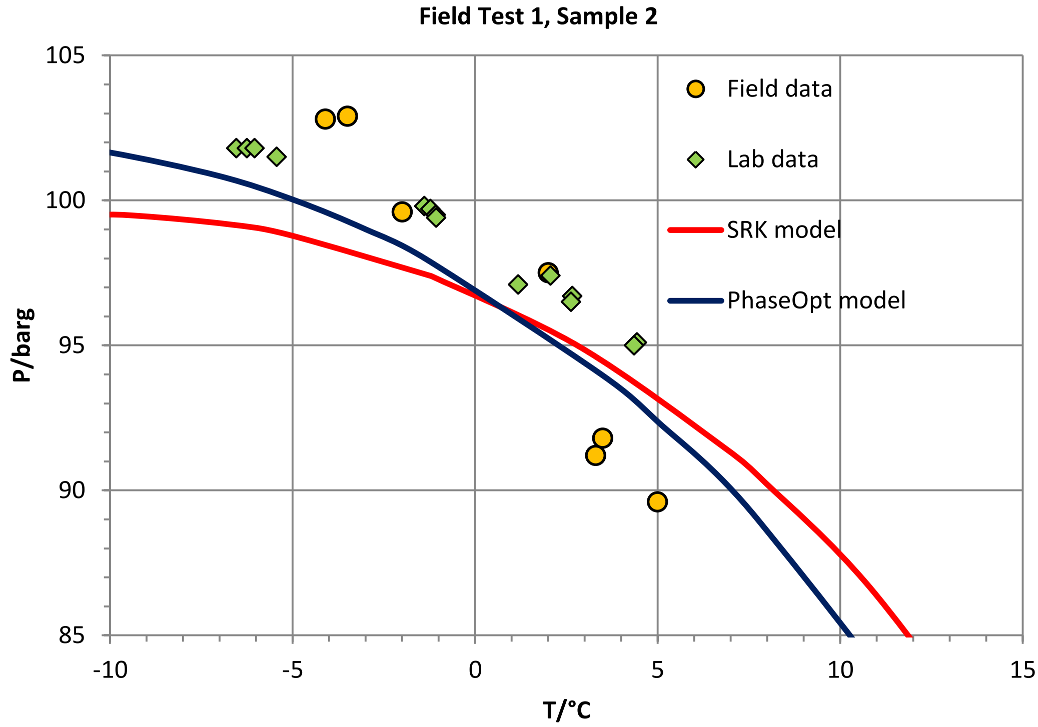


Figure 5: Measured and estimated dew points for two different samples from field test 1.

3.2 Field Test 2

The second field test was done in May 2013 with gas from Åsgard Transport. The online PhaseOpt GC was in operation and PhaseOpt was fully operational with online cricondenbar estimations.

The following measurements were done during the second test

- Manual hydrocarbon dew point measurements in the field. A standard optical dew point instrument from Chandler Engineering, also called “Bureau of Mines” dew point analyser was used [4].
- Sampling of gas for laboratory GC analysis at Statoil. Details about the laboratory GC analysis can be found in a previous GPA paper [1]
- Sampling of gas on cylinders for laboratory dew point measurements. A standard optical dew point instrument from Chandler Engineering, also called “Bureau of Mines” dew point analyser, mounted into a temperature controlled chamber, as presented in a previous GPA paper [1]
- Online cricondenbar estimation using PhaseOpt model

The same difficulties with measurements of dew points in the field were experienced in field test 2 as in the first test (see section 3.1). Thus, the measured cricondenbar in the lab will be used as the basis for our comparisons.

Figure 6 shows the PhaseOpt online cricondenbar measurements during the second test. The measured cricondenbar was quite stable and it varied between 101.1 barg to 101.4 barg.

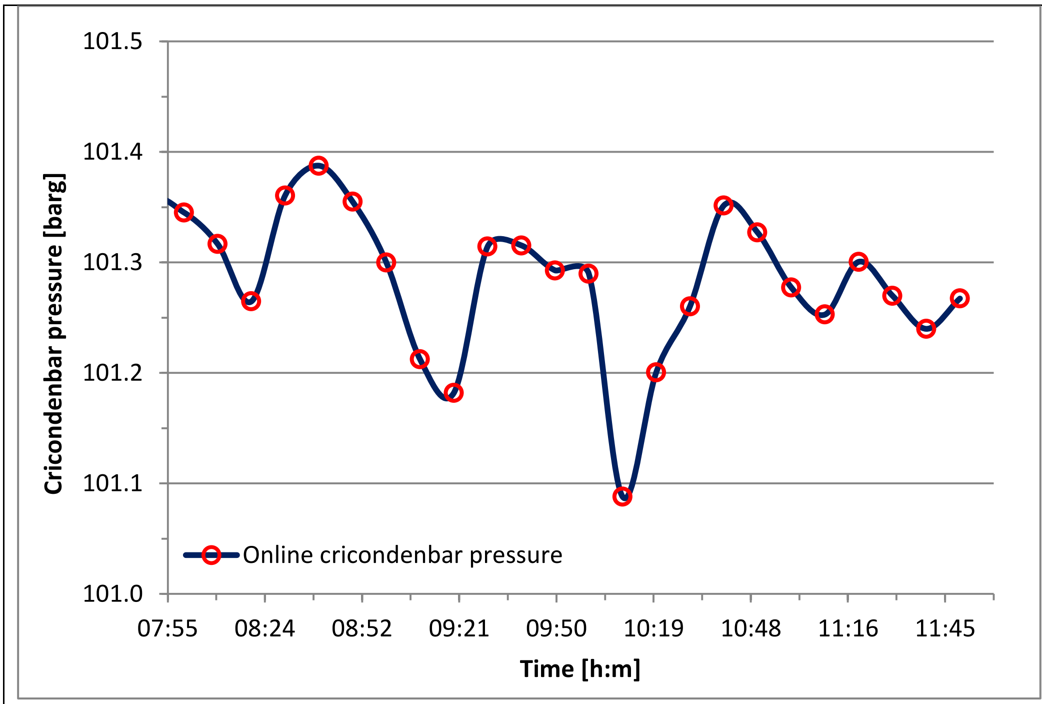


Figure 6: Online cricondenbar pressure estimation during field test 2

Figure 7 shows a comparison of the phase envelope of a gas sample taken during the test and the one calculated with PhaseOpt based on the online GC measurements during the same time period. The differences in the phase envelopes are only marginal and the effect on the cricondenbar area is about 0.2 bar. This verifies that the online PhaseOpt GC provides reliable compositional analyses.

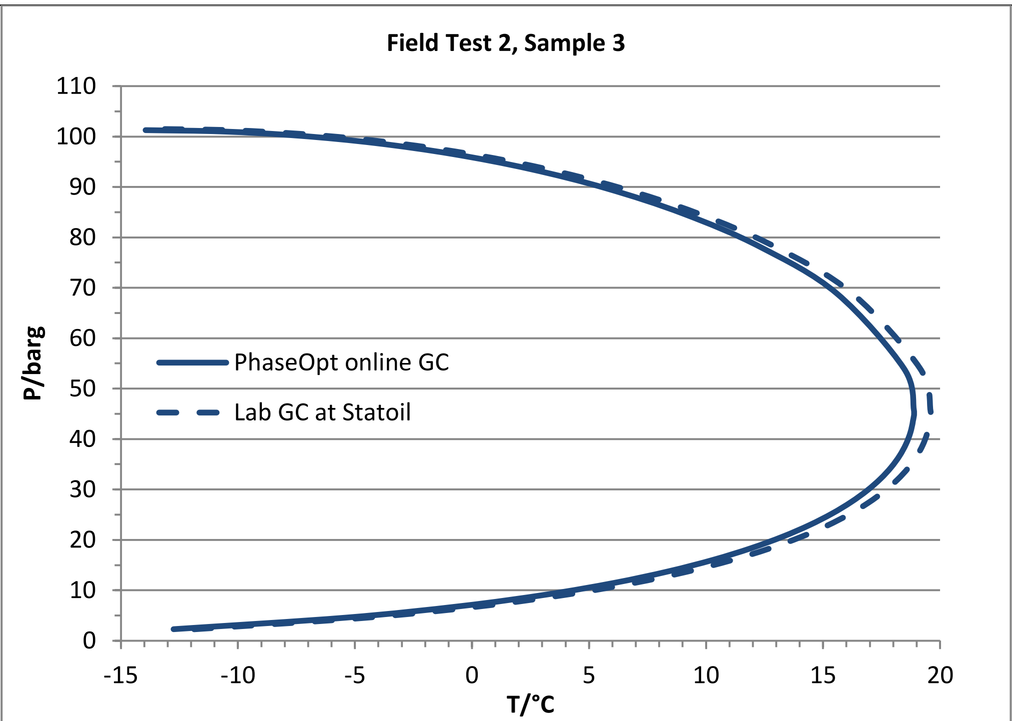


Figure 7: Phase envelope estimated with PhaseOpt model for Sample 3 analysed in Statoil laboratory and from online GC data for same period.

The comparison between the measured and the estimated cricondenbar for Sample 3 is given in Table 4. The agreement between the measured cricondenbar at the field and the one measured at the laboratory is very good with a deviation of only 0.2 bar. The PhaseOpt model underpredicts the cricondenbar by 1.2 bar, while SRK underpredicts the cricondenbar by 2.9 bar. Again, the PhaseOpt model is superior to SRK when it comes to estimation of the cricondenbar pressure.

Table 4 also shows the dew point pressure at a given temperature, at -7°C, which is close to the cricondenbar temperature measured in the lab. Both SRK and PhaseOpt underpredict the dew point pressure at this temperature. PhaseOpt underpredicts the pressure by 2.4 bar while SRK underpredicts the pressure by 3.3. Again the PhaseOpt model is superior to SRK when it comes to estimation of the dew point pressure at a given temperature.

Table 4: Measured and estimated cricondenbar and dew point pressure at a given temperature (-7°C) for sample 3 from field test 2.

	Sample 3		**Sample 3**	
	Cricondenbar pressure	**Deviation (from lab measurement)**	**Dew point pressure @ -7°C**	**Deviation (from lab measurement)**
	[barg]	**[bar]**	**[barg]**	**[bar]**
Lab measurement	102.5	-	102.4	-
Field measurement	102.7	+0.2	-	-
SRK model	99.6	- 2.9	99.1	-3.3
PhaseOpt model	101.3	-1.2	100.0	-2.4

Figure 8 shows all measured and estimated dew points for Sample 3. The first observation is that the difference between the field measurements and the lab measurements is higher than what we observed in the first field test. It is not clear why this happens. However, the measured cricondenbar pressure is almost the same (102.5 barg compared to 102.7 barg), while the deviation in the cricondenbar temperature is almost 4°C. Again, the PhaseOpt model provides a clear improvement compared to the SRK model, when it comes to predicting the dew points at pressures around the cricondenbar. PhaseOpt is also better than SRK in predicting the correct shape of the dew point.

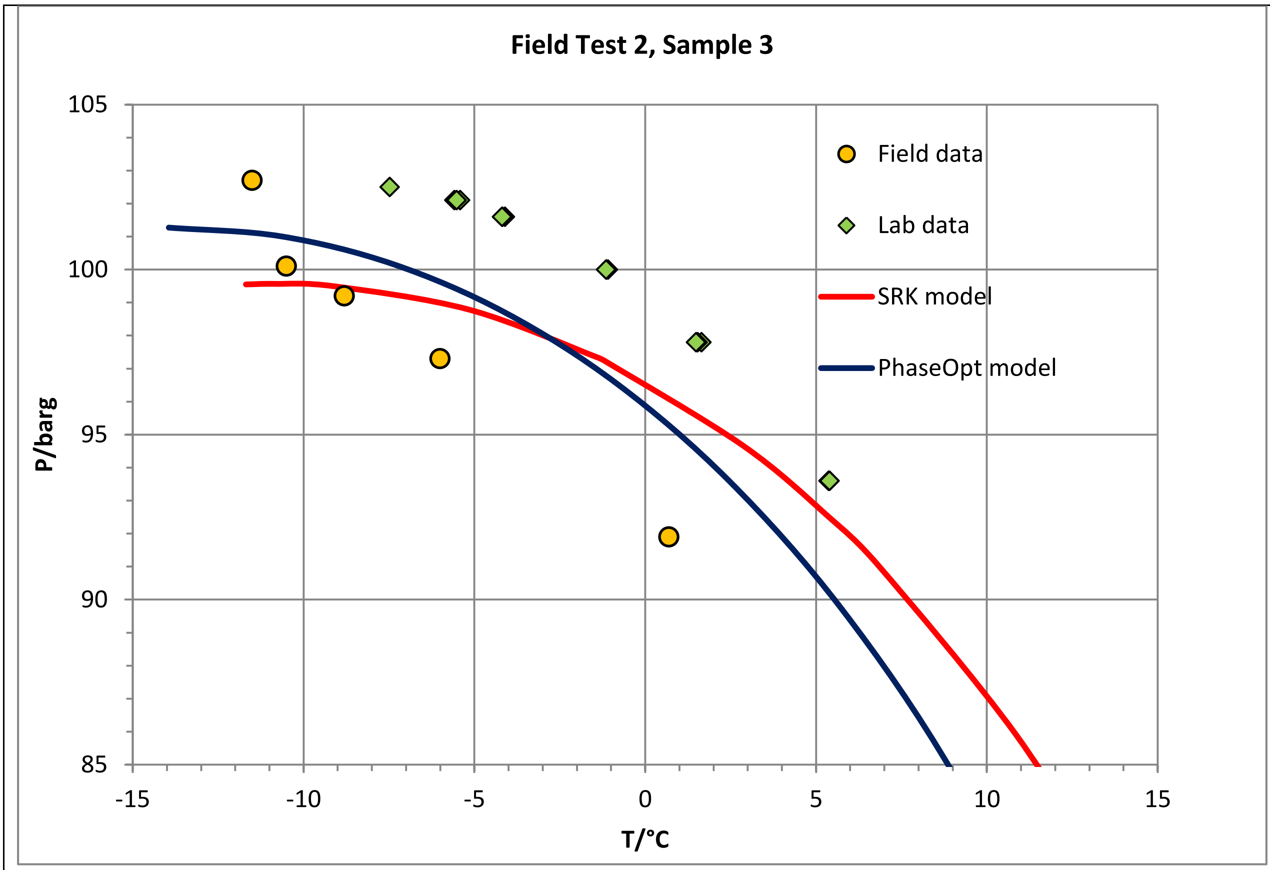


Figure 8: Measured and estimated dew points for sample 3 from field test 2.

4 Conclusions

The PhaseOpt technology is a tool for online monitoring of hydrocarbon dew point in rich gas pipelines. The main technology elements in PhaseOpt are:

- A sample system optimised to handle trace component analysis and traces of liquid glycol in the gas
- An online process GC-analyser providing extended compositional analysis with detailed composition up to C_{12}
- A reliable thermodynamic model for hydrocarbon dew point calculations with focus on the cricondenbar
- Implementation of methods for online cricondenbar measurement into control system of pipelines and process plants

The technology was tested during two field tests done in the period from June 2012 to May 2013 with real rich gas from Åsgard Transport pipeline. During field test 1 the PhaseOpt online GC analyser was not in operation and the dew points measured in field and laboratory were compared to calculated dew points based on the PhaseOpt model using laboratory GC analysis. During field test 2 the PhaseOpt online GC analyser was in operation and PhaseOpt was fully operational with online cricondenbar estimations.

The results from the two field test can be summarised as follows:

- Manual dew point measurements in the field are challenging. The glycols in the gas had a tendency to condense on the dew point mirror – and the hydrocarbon dew point was difficult to identify accurately.
- Dew point measurements in the lab were easier to perform and are considered to be more accurate than the field measurements. Therefore, the lab measurements were used as a basis for our comparisons.
- The maximum deviation between the cricondenbar pressure measured in the lab and in the field was 1.1 bar
- The maximum deviation between the cricondenbar pressure measured in the lab and the one estimated by PhaseOpt was 1.2 bar. The cricondenbar pressure was overpredicted in the first test, while it was underpredicted in the second test
- The maximum deviation between the cricondenbar pressure measured in the lab and the one estimated by SRK was 2.9 bar. The cricondenbar pressure was underpredicted in both tests.
- PhaseOpt manages to predict the correct shape of the dew point line even if it still underpredicts the dew point pressure at a given temperature.
- SRK fail to predict the correct shape of the dew point line and in some cases it overpredicts the dew point pressure at a given temperature.
- PhaseOpt model is superior to SRK in predicting both the cricondenbar pressure and the dew point pressure at a given temperature
- Since PhaseOpt consistently undepredicts the dew point pressure at a given temperature, a safety margin should be used to ensure safe use of the tool in industrial applications

Acknowledgements:

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5 References

1. B. Rusten, L. H. Gjertsen, E. Solbraa, T. Kirkerød, T. Haugum and S. Puntervold, "Determination of the phase envelope - crucial for process design and problem solving," GPA Annual Conference, Texas, 2008.

2. V. Louli, C. Boukouvalas, E. Voutsas, K. Magoulas and D. Tassios, Fluid Phase Equil. 261 (2007) 351-358.

3. V. Louli, G. Pappa, C. Boukouvalas, S. Skouras, E. Solbraa, K. O. Christensen and E. Voutsas, "Measurement and prediction of dew point curves of natural gas mixtures," *Fluid Phase Equilibria*, vol. 334, pp. 1-9, 2012.

4. Chandler Engineering, Bureau of Mines-Type Dew Point Tester, http://www.chandlereng.com/Products/LegacyProducts/dewpoint.aspx